Directed Vapor Deposition

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Doctor of Philosophy (Materials Science and Engineering)

by

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Approval Sheet

This Dissertation is submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Materials Science and Engineering

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Abstract

This dissertation describes the invention, design, construction, experimental evaluation and modeling of a new physical vapor deposition technique (U.S. Patent #5,534,314) for high rate, efficient deposition of refractory elements, alloys, and compounds onto flat or curved surfaces. The new Directed Vapor Deposition (DVD) technique examined in this dissertation was distinct from previous physical vapor deposition techniques because it used low vacuum electron beam (e-beam) evaporation in combination with a carrier gas stream to transport and vapor spray deposit metals, ceramics, and semiconducting materials. Because of the system's unique approach to vapor phase materials processing, detailed analyses of critical concepts (e.g. the e-beam accelerating voltage and power required for evaporation, the vacuum pumping capacity necessary to generate specific gas flow velocities exiting a nozzle) were used to reduce to practice a functioning materials synthesis tool. After construction, the ability to create low contamination films of pure metals, semiconducting materials, and compounds via this new method was demonstrated, and oxide deposition using an oxygen-doped gas stream in combination with a pure metal evaporant source was shown to be feasible. DVD vapor transport characteristics were experimentally investigated with deposition chamber pressure, carrier gas type, and e-beam power being identified as major processing parameters which affected vapor atom trajectories. The low vacuum carrier gas streams employed in DVD showed a dramatic ability to focus the vapor stream during transport to the substrate and thereby enhance material deposition rates and efficiencies significantly under certain process conditions. Conditions for maximum deposition efficiency onto flat substrates and continuous fibers were experimentally identified by varying chamber pressure, carrier gas velocity (Mach number), and e-beam power. Deposition efficiencies peaked at about 0.5 Torr when coating flat or fibrous substrates. Higher Mach numbers led to higher efficiencies below the efficiency peak, but above the peak this Mach number trend reversed. Increasing e-beam power decreased the magnitude of the deposition efficiency peak and shifted it to higher chamber pressures. Fiber coating experiments revealed a maximum deposition efficiency over twice the level expected for pure line-of-sight deposition, and scanning electron microscopy revealed that, for conditions of maximum efficiency, vapor was depositing simultaneously on the
The vapor transport and deposition trends appeared to result from vapor atom collisions with gas atoms in the carrier flow, collisions which affected vapor atom form (single atom or clusters), location in the flow, and interaction with the substrate (leading to line and non-line-of-sight coating). Atomic vapor transport in DVD was investigated using Direct Simulation Monte Carlo (DSMC) methods and biatomic collision theory (BCT). For atoms transported to a flat surface perpendicular to the vapor-laden carrier gas stream, the velocity vector during transport and impact location were calculated, making possible determination of adatom deposition efficiency, spatial distribution, impact energy, and incident angle with the substrate. Model results compared favorably with random walk predictions, independent experimental data of sputter atom energy loss, and low e-beam power experimental results. The model suggested that the atoms deposited in a DVD process had a low impact energy (< 0.1 eV) and a broad incident angular distribution with the substrate. The DSMC and BCT models were used to design an improved DVD system with significantly enhanced deposition efficiency.
Where a new invention promises to be useful, it ought to be tried.

Thomas Jefferson
Acknowledgments

I thank Professor Wadley for his support throughout this research program. I trust that the results of this project fulfill his hopes and expectations for the work. I am grateful to the Defense Advanced Research Projects Agency (W. Barker, Program Manager) and NASA (D. Brewer, Technical Program Monitor) for funding this research through NASA grant NAGW 1692. The assistance of Luke Hsiung, David Hill, and Andrew Ritenour during the equipment assembly phase of this project was critical. I enjoyed the discussions Andy and I had about Directed Vapor Deposition, and I am grateful for Andy’s enthusiastic efforts which completed the DVD computer interface. While I will receive much of the credit for turning ideas into reality on this project, I know that the deposition system ultimately functioned because of the efforts of Tommy Eanes who oversaw the installation of, or installed himself, most of the major system components. Tommy’s pleasant sense of humor kept my spirits up even when things appeared to be “Not so good!” Thanks to Richard Jaurich and Rainer Bartel for professionally and patiently working to install the electron beam gun. I greatly appreciate the time Subhas Desa, Eric Abrahamson, and Sarbajit Ghosal of SC Solutions (Santa Clara, CA) invested to review the details of the dissertation’s model. Their suggestions improved the work immensely. I sincerely appreciate the countless hours my friend Paul Cantonwine has given to listening as I thought out loud about the project - all the way from Minnesota to Virginia! I am grateful to my friend Beth Duckworth for her enthusiastic support during the last several years of this project. Her tremendous energy helped me reach the finish line. Thanks to Boris Starosta for putting his artistic abilities to work to illustrate many aspects of the project. Finally, as always, I want to express my loving appreciation to my parents and to God for their unwavering support as I toiled through the many years required to bring this endeavor to completion.

James Frederick Groves
Charlottesville, Virginia
April 1998
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List of Symbols

\(a\) \quad \text{Specific evaporation rate}

\(a_u\) \quad \text{Born radius (0.529 Å)}

\(A\) \quad \text{An individual atom}

\(A_2\) \quad \text{Two atom cluster}

\(A_3\) \quad \text{Three body cluster}

\(A_n\) \quad \text{Cluster containing } n \text{ atoms}

\(A_{n-1}\) \quad \text{Cluster containing } n-1 \text{ atoms}

\(A_{\text{pipe}}\) \quad \text{Area of the inlet flow tube}

\(b\) \quad \text{Impact parameter}

\(b_{\text{max}}\) \quad \text{Maximum range of interaction of atoms involved in a collision event}

\(B\) \quad \text{Beam energy}

\(B_0\) \quad \text{Initial beam energy}

\(c\) \quad \text{Speed}

\(\bar{c}\) \quad \text{Average speed}

\([\text{Cu}]\) \quad \text{Concentration of metal monomer}

\([\text{Cu}_2^*]\) \quad \text{Concentration of unstable dimers}

\(d\) \quad \text{Diameter}

\(d_s\) \quad \text{Local film thickness on a flat substrate}

\(d_{so}\) \quad \text{Maximum film thickness}

\(D\) \quad \text{Distance}

\(e\) \quad \text{Binary collision encounters}

\(e\) \quad \text{Charge on an electron}

\(E\) \quad \text{Kinetic energy}

\(f\) \quad \text{Velocity distribution function}

\(F\) \quad \text{External force}

\(h\) \quad \text{Thickness}
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<td>$U_{\text{ccm}}$</td>
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<tr>
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<td>$U_{\text{pipe}}$</td>
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<td>$V$</td>
<td>Volume</td>
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<td>$V$</td>
<td>Molar density of material</td>
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<td>$w$</td>
<td>Speed in third coordinate direction</td>
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<td>$\bar{w}$</td>
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<td>$\chi_{cutoff}$</td>
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<td>$\rho_o$</td>
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<tr>
<td>$\sigma_{ji}$</td>
<td>Viscous stress tensor</td>
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<tr>
<td>$\sigma(\chi)$</td>
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</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<td>---------</td>
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<td>Activity radius of a copper atom</td>
</tr>
<tr>
<td>$\sigma_{aCu2}$</td>
<td>Activity radius of an unstable dimer</td>
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<tr>
<td>$\sigma_d$</td>
<td>Directed momentum transfer cross-section</td>
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<tr>
<td>$\sigma_{rCu}$</td>
<td>Hard sphere radius of a copper atom</td>
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<td>$\sigma_{rCu}$</td>
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Chapter 1

Introduction

1.1 Vapor Phase Synthesis of Materials

Since Grove observed metal deposits sputtered from a glow discharge in 1852 [1] and Faraday experimented with metal wire explosion in an inert atmosphere five years later [2], researchers have synthesized a multitude of materials from the vapor phase, sought to understand the properties of those materials, and explored their scientific and technological applications. Film property research was limited until the 1940’s when vacuum technology improvements allowed clean films to be created with reproducible properties. Since then, engineers have realized that vapor phase created materials (i.e. materials created via physical vapor deposition (PVD) or chemical vapor deposition (CVD)) can meet the design requirements of countless products. In some cases a thin film meets the engineering need (e.g. an environmental [3] or wear resistant [4] coating). In other cases vapor phase processing represents the only method by which the desired material can be applied (e.g. optical gold coatings for lenses, mirrors, and cathode ray tubes [3] or aluminum and copper metallization layers which interconnect semiconductor devices [5]). In still other instances vapor phase synthesized films have unique properties and microstructures not
found in bulk processed materials (e.g. giant magnetoresistive (GMR) multilayers [6], thermal barrier coatings (TBC) [7], and functionally graded materials (FGM) [8, 9, 10]).

Since the 1940’s researchers have developed vapor creation methods to synthesize thin film materials (e.g. electron beam evaporation [11], diode and magnetron sputtering [12], CVD [12], reactive evaporation (RE)\(^1\) and activated reactive evaporation (ARE)\(^2\) [13, 14, 15], ion plating [16, 17], and ion-beam assisted deposition [18]). Even as these and other technologies are increasingly employed in manufacturing systems, new material demands press the scientific limits of vapor phase processing ability. Engineers and scientists repeatedly confront obstacles which hamper the attainment of processing goals. These obstacles include the high cost of vapor deposition, the material utilization efficiency limits associated with line-of-sight high vacuum coating, the difficulty of controlling deposit composition in thermal evaporation systems, and the slow material creation rates of sputtering systems. To overcome these and other processing hurdles, materials engineers reinvestigate material synthesis methods and search for new avenues to vapor phase material creation as they seek to uncover techniques affording greater processing capabilities (e.g., deposition of precise material compositions with unique microstructures).

Indeed, despite the impressive sophistication of today’s vapor phase processing, there appear to be numerous unexplored variations of the vapor phase materials synthesis techniques in use which could help create new products that depend upon their material properties for success. An historical perspective highlights the short length of time that vapor phase processing has had to evolve and suggests that with further exploration, vapor deposition technology can evolve to currently inconceivable levels of sophistication (Fig. 1.1).

---

1 reactive evaporation - evaporation in presence of a low partial pressure of reactive gas (e.g. oxygen or hydrogen).

2 activated reactive evaporation - similar to reactive evaporation except that one or more reactants is activated, i.e. ionized to form a plasma. This increases system reactivity.
Chapter 1. Introduction

1.2 Applications Motivating Vapor Phase Process Development

Two specific industries demanding enhanced physical vapor deposition (PVD) process technology are the aerospace and semiconductor device industries. Fig. 1.2 shows several products from these fields which engineers would like to produce using vapor phase synthesis techniques:

- Oxidation resistant bond coats and ceramic insulating layers onto turbine blades.
- Adhesion layers and via filling materials for semiconductor interconnects.
- SiO₂, polysilicon, and aluminum layers for thin film transistors.
- Oxides, alloys, and pure metals which comprise laminated multilayers.
- Metal and intermetallic alloys which envelope fibers used in continuous fiber reinforced composites.

Figure 1.1 Evolution of Materials Processing. This timeline illustrates how little historical time has been spent developing vapor phase processing compared to solid or liquid phase material synthesis. (Figure courtesy of D.M. Elzey.)
While innovative new PVD techniques could contribute to the synthesis of more products than those shown, this short list suggests the breadth of utility for new vapor phase film synthesis technology in these industries. Short descriptions of these industries’ needs provide further evidence of the motivation for enhanced vapor phase material synthesis.

The aerospace industry wants to use metal matrix composites (MMC’s) in higher temperature propulsion systems to increase aircraft speeds and engine power output [19, 20]. To make MMC’s economically competitive, industry experts estimate that tens of thousands of pounds of coated continuous ceramic fiber reinforcement must be produced yearly at a per pound cost comparable to that of current single crystal, superalloy turbine blades [21].

Figure 1.2 Engineering materials via PVD. The potential applications for enhanced PVD technologies are numerous.
The MMC’s produced from these coated fibers must also be microstructurally suitable for subsequent process steps (e.g. hot isostatic pressing) [20] and without fiber / matrix interface degradation due to excessive processing-induced stresses [22, 23] or reaction zone growth [24]. Storer [21] has indicated that current evaporation, sputtering, and CVD systems could lack the ability to create these advanced materials rapidly and economically enough to make continuous fiber reinforced MMC use a viable alternative. However, Storer has suggested that a high rate (> 10 µm/min), non-line-of-sight coating system could be economically viable [21].

Not only does the aerospace industry need an economic synthesis pathway for fabricating engine components such as compressor blades, blings (Rolls Royce), and fan frames (GE Aircraft Engines / Pratt & Whitney) [25, 26] but also it would like to apply a thermal barrier coating (TBC) to turbine blades used in engine hot sections. These TBC’s prevent blade oxidation at the high operating temperatures encountered and insulate the blades from the hot gas temperatures in the engine [7]. Many of the coatings envisioned for this application consist of highly engineered microstructures which require significant processing flexibility for their manufacture (e.g. composition and microstructure control). For these TBC’s, materials engineers want to produce porous microstructures of refractory (high melting point) metals and compounds [27, 28]. If a new PVD process can deposit material efficiently at different adatom energies, angles, and deposition rates, it may provide unparalleled process flexibility for the generation of useful, well-adhered, porous coatings.

In the semiconductor industry, the needs are different but equally demanding. For instance, dense metallic films often must be deposited onto engineered semiconductor devices containing precise doping concentrations in exact locations. Excessive substrate heating during processing can destroy the device by providing energy for implant diffu-
sion or for alloying between previously deposited metallization layers [5]. Studies suggest that use of a process which increases adatom kinetic energy could produce quality microstructures at reduced substrate temperatures [29 - 33].

In another electronic application, the ability to form polysilicon on a glass substrate maintained at a temperature below 600°C could replace the slow, expensive two-step deposit and anneal process currently used to produce thin film transistors [34]. Again, enhancement of adatom kinetic energy could hold the key to achieving this process capability.

An equally challenging manufacturing issue for the semiconductor industry is the filling of the small openings in the surface of a device “that connect the interconnect ‘wiring’ with the source, drain, and gate of the CMOS\(^1\) transistor, and those that connect one level of wiring with the underlying or overlaying level” [35]. As semiconductor designers make their devices smaller and smaller, the depth to width ratio of the device’s metal interconnect vias increases, from 1:1 in the 1980’s to 4:1 in the late 1990’s. As this ratio increases, the difficulty of filling these trenches completely with the desired metal also increases. The most technologically valuable via filling process of the late 1990’s and early 21st century will be able to fill these trenches with copper and other metal or metal compounds by means of line and non-line-of-sight techniques [35, 36].

### 1.3 Goals of the Dissertation

This dissertation’s work represents the first steps in the process of invention, discovery, and development of a new physical vapor deposition technology, termed Directed Vapor Deposition (DVD). This DVD technology has been envisioned most particularly as a method for depositing pure refractory (i.e. high melting point) elements, compounds, and

\(^1\) CMOS - complementary metal-oxide semiconductor
alloys rapidly and efficiently onto complex shapes. It is hoped that this research of PVD technology will lead to the introduction of a viable approach to vapor deposition into the mainstream of industrial vapor phase materials synthesis, particularly to meet the needs of the aerospace industry as it seeks to introduce continuous fiber reinforced (CFR) MMC’s into wide scale use. The work presented in this dissertation should allow many of the capabilities of this technology to be assessed for refractory material and also for other vapor phase material system applications such as those important to the semiconductor industry.

The next chapter of this dissertation reviews today’s state-of-the-art in vapor phase processing of refractory elements, compounds, and alloys. The analysis identifies reasons why it should be possible to enhance current refractory material PVD technology, in particular electron beam (e-beam) evaporation. Specifically, Chapter 2 will examine ways to modify standard e-beam system operating conditions to achieve enhanced refractory material processing. The invention of such a modified e-beam based PVD system is then described in Chapter 3. The design and reduction to practice of this new technology are presented in Chapter 4.

Chapter 5 experimentally investigates vapor transport in the Directed Vapor Deposition environment and seeks to develop an understanding of the effect of the system’s unique vapor transport means upon the vapor stream’s inherent characteristics. The work reported in Chapters 6 and 7 demonstrates the material processing capability of DVD by experimentally investigating the system’s ability to create films with low contamination levels, to synthesize amorphous and polycrystalline silicon on glass substrates, to create zirconia coatings via reactive deposition, and to deposit material efficiently onto flat and fibrous substrates. Chapters 6 and 7 generate numerous results which allow the vapor phase material synthesis utility of the technique to be assessed.
Chapter 8 uncovers modeling methodologies applicable to vapor transport in DVD and other similar technologies and uses those techniques to develop a model of interaction between evaporated atoms, background gas atoms in the chamber and the substrate. After model verification in Chapter 9, Chapter 10 uses the model to provide additional insight into the experimental deposition efficiency results and into the system’s general material synthesis behavior. In Chapter 11 the dissertation’s model is used to suggest a different system configuration which may facilitate more efficient materials synthesis for various vapor phase coating applications.

While the DVD system developed in this research may or may not become a pathway for the economic creation of tomorrow’s aerospace and electronic products, the knowledge generated through its study should contribute to the understanding of physical vapor deposition. Chapter 12 uses the results of the preceding chapters to assess the potential advantages of DVD, to identify those which appear to be attainable, and to suggest which material synthesis problems DVD might be well suited to attack. The overall organization of the dissertation is summarized in Fig. 1.3.
Figure 1.3  **Dissertation organization.** This dissertation contributes to science through development of new PVD technology, experimental and modeling analysis of that technology, and identification of its material synthesis utility.
Chapter 2

Background

As noted in section 1.3 of the previous chapter, the core motivation for this dissertation’s research has been a desire to discover an improved method for the deposition of refractory elements, compounds, and alloys rapidly, efficiently, and with little contamination. As the previous chapter also noted, Storer [21] has suggested that an economically feasible method for depositing such film structures onto complex shapes could be some type of non-line-of-sight coating technique. When attempting to identify a vapor deposition method which meets all of these requirements, the desired process capabilities do not appear to be available in one existing technology.

Sputtering deposits material slowly (~1 µm/min [12] versus 1 mm/min for e-beam systems [11]). Sputtering rates are generally low due to the difficulty of sustaining the intense plasma discharge density necessary for higher rate deposition [12]. Standard e-beam technology generates low deposition efficiencies (only line-of-sight deposition) when coating small cross-section substrates like continuous fibers to be used in metal matrix composites. Non-line-of-sight coating does not occur in e-beam systems because evaporation in these systems almost always occurs in high vacuum (pressures less than 10⁻¹ Pa / 10⁻³...
where material transfer occurs by collisionless, line-of-sight atomistic transport [11]. Resistive flash evaporators generally evaporate refractory materials slowly [12], and in these systems there is a risk of vapor stream contamination. Contact between a refractory evaporant source material (e.g. molybdenum) and an equally high melting point resistive heating target (e.g. tungsten) has a high probability of introducing both source material and heating target into the vapor stream. The apparent inability of any of these techniques to combine all of the desired processing abilities described in Chapter 1 has motivated thought about previously unconsidered material synthesis pathways.

This chapter examines the possibilities of modifying the desirable high rate electron beam evaporation tool so that it can perform uncontaminated line and non-line-of-sight material synthesis as efficiently as possible. In general, the process of vapor phase material synthesis consists of five steps:

1. Vapor creation.
2. Vapor transport.
3. Vapor adsorption onto the substrate.
5. Adatom movement by bulk diffusion through the growing film lattice to final positions.

Within the framework of these five steps, this chapter reviews the state-of-the-art of electron beam material synthesis and assesses its presently understood ability to synthesize engineering materials from the vapor phase.

---

1 133.3 Pa = 1 Torr, 1 atmosphere = 760 Torr = 101,300 Pa, space vacuum = 10^{-12} Torr
This examination of vapor phase material synthesis is generally limited to e-beam processing due to the complexity of the physical processes involved in producing vapor with an e-beam and due to the distinctly different manner in which other, less desirable, PVD techniques like sputtering produce their vapor (i.e. less desirable for the specific applications focussed upon in this research). This chapter examines current experimental and theoretical understanding of how to enhance an e-beam system’s vapor atom deposition distribution, efficiency, angle, energy, and form (monatomic or cluster). Finally, a brief examination of known relationships between processing parameters and final film microstructures at the end of this chapter illustrates why, if a new system can be invented, a uniquely configured e-beam system could provide vapor phase material processing engineers with an ability to synthesize unique engineering products by changing vapor transport, and thus vapor deposition, characteristics from those of a conventional e-beam PVD system.

2.1 Vapor Creation Using an Electron Beam Gun

When reliable vacuum pumping technology in the 1940’s first made it possible to achieve vacuums at or below the milliTorr range (~0.10 Pa), scientists made use of the resulting long electron mean free paths to generate electron beams that evaporated elements, alloys, and compounds for engineering material synthesis. Use of e-beams has been extensive over the ensuing years in part because of their ability to evaporate and deposit a large variety of materials rapidly, cleanly, and with a minimum consumption of energy [11].

2.1.1. Pure metal / metal alloy processing

E-beam systems have demonstrated an ability to evaporate and deposit not only easy to process pure elements like aluminum, zinc, gold, and silver but also more difficult to pro-
cess low vapor pressure elements like molybdenum, tungsten, and carbon, and highly reactive elements such as niobium, titanium, and tantalum [37]. E-beam systems evaporate and deposit all of these elements by cleanly bringing the heat source (electrons) directly into contact with the source material, often contained as a “skull” melt inside a water-cooled crucible (Fig. 2.1). A crucible is frequently used to contain the source material because it maintains solid source material (a “skull”) between the crucible wall and the molten evaporant pool, preventing vapor source contamination from the crucible.

Researchers have also demonstrated that alloys with a vapor pressure ratio as high as 1000:1 between their elements can be e-beam evaporated from a single crucible source and deposited with the correct chemical composition [38, 39]. This ability is crucial to the fabrication of materials for the MMC aerospace application described in Chapter 1 (e.g. deposition of Ti_xMo_(1-x), (Ti_2Al)_xNb_(1-x), or Ti-6wt%Al-4wt%V) [20, 21, 38, 39]. For alloys with elements having a greater vapor pressure ratio, lower melting point (and higher activity) material can be wire fed into a pool of the more refractory material [20] or separate element evaporation from adjacent crucible sources can be employed [11, 37]. When separate crucible evaporation is employed, alloys are created by mixing atomic fluxes as shown in Fig. 2.1.

E-beam processing of pure elements and alloys does present challenges to those attempting to control deposition characteristics precisely. During single crucible alloy processing, the initial vapor stream is rich in the more volatile component(s) of the feed-stock due to differences in evaporation rate for elements in the alloy. Langmuir [11] has provided a general relationship between an element’s evaporation rate, given as a mass flux, and its molecular weight, vapor pressure, and temperature:

\[ a \propto P_s \left( \frac{W}{T_v} \right)^{1/2} \] (2.1)
where \( a \) = Specific evaporation rate (kg/(m\(^2\) sec)),

\[
P_s = \text{Saturated vapor pressure at a temperature } T_v \text{ (Pa)} \[2],
\]

\[
W = \text{Molecular weight of the evaporant (kg/mol)}, \text{ and}
\]

\[
T_v = \text{Absolute temperature of the evaporant (K)}.
\]

Not only do elements initially leave the crucible at different rates due to differences in vapor pressure but also, for some length of time thereafter, the compositions of the melt pool and vapor stream continue to change until the compositions of the solid rod stock and the molten pool reach a stable equilibrium (i.e. until the rate at which vapor constituents A and B leave the molten pool equals the rate at which they are introduced from the solid) \[11, 12\]. Reaching this equilibrium state adds significantly to the processing cycle time.
(potentially hours), wastes valuable source material, and decreases system flexibility [11, 40]. While multiple crucible evaporation can sidestep this time dependent composition fluctuation, alloy processing from multiple crucibles in a high-vacuum e-beam system creates a stoichiometrically correct deposit only in that region above the crucibles where the vapor clouds of the neighboring crucibles intersect [11]. As a result, significant amounts of expensive vapor can be wasted (Fig. 2.1). Even in this region, small compositional differences exist as a result of variation in the vapor density distribution from the e-beam source and vapor collisions between species A and B which lead to different rates of interdiffusion [11]. Substrate translation is usually employed to reduce compositional gradations across the film surface.

In addition to vapor flux composition distributions which vary with time or position, all e-beam systems exhibit a vapor spatial density distribution which is nonuniform and dependent upon numerous process variables [39, 41]. It has been reported throughout the literature that atoms ejected from an e-beam target take on a distribution described by [12]:

\[ I(\theta) = I_o \cos^n \theta \]  

(2.2)

where \( I(\theta) \) = Vapor stream density in a direction \( \theta \) degrees from the normal to the vapor emitting surface,

\( I_o \) = Vapor stream density for \( \theta = 0 \), and

\( n \) = 2, 3, 4, or more.

While the vapor stream emerging from a planar surface element takes on a \( \cos \theta \) distribution (where \( n = 1 \)) [2], numerous authors note that e-beam vapor streams rarely exhibit this simple cosine vapor distribution for various reasons as described in Fig. 2.2 [11, 2, 42]. In addition to the influences shown in Fig. 2.2, e-beam vapor stream distributions also
depend upon the e-beam scanning cycle employed (rate and pattern) and the specific material evaporated [11, 38].

2.1.2. Compound processing

In addition to an ability to deposit pure elements and alloys, e-beam systems have demonstrated a reasonable ability to create material from compound sources. For compounds which are poor conductors of electricity and heat, some combination of reduced e-beam

Figure 2.2 Vapor distribution in an e-beam system. Several factors can combine to modify an e-beam evaporator’s vapor flux distribution [11].
power densities (below $2 \times 10^7$ W/m$^2$) [1], specialized e-beam scan patterns [1], and partially dense source materials (e.g. 60% dense yttria-stabilized zirconia for TBC applications [43]) are usually necessary to prevent source material cracking and generate a controlled vapor stream. When working with complex compound source materials like yttria-stabilized zirconia, vapor pressure problems can arise that are similar to those described for single crucible alloy evaporation.

A more common problem during compound evaporation is dissociation of the constituent elements, an event which precludes stoichiometrically correct film creation unless the lost elements are replaced during deposition [11]. While some compounds exhibit minimal dissociation with little of the gaseous element being removed by the process chamber vacuum pump [11, 15], most require introduction of additional reactive gas into the work chamber for useful RE or ARE deposition [2, 11, 15, 37, 44, 45]. RE allows compounds to reform during deposition by introducing reactive species into the processing chamber and raising the chamber pressure as high as 1 Pa (~10$^{-2}$ Torr). A primary drawback of RE for dense film synthesis is vapor atom thermalization\(^1\) leading to film porosity due to reduced adatom kinetic energy [11, 15]. Vapor atom thermalization during reactive evaporation has motivated development of ARE in which plasma-enhanced reactivity of the gas environment makes possible a decrease in reactive gas pressure, a corresponding reduction in gas/vapor collisions, and a minimization of vapor atom thermalization [11, 15].

2.1.3. Vacuum regime

E-beam material synthesis has occurred almost exclusively in chamber pressures below 10 Pa (~10$^{-1}$ Torr). However, recent material processing efforts by Eastman, Halpern, and

\(^1\) thermalization- a change in the velocity and energy of an atom towards the average velocity and energy of the surrounding gas as the result of momentum transferring atomic collisions.
Chapter 2. Background

others [46, 47] have demonstrated that useful vapor phase materials can be created at higher chamber pressures. Eastman et al. have used e-beam evaporation to create nanophase $\gamma$-Al$_2$O$_3$ clusters with a mean grain size of 2.5 nm in a 1 Torr (~$10^2$ Pa) oxygen rich environment while Halpern et al. have deposited resistively-evaporated gold by transporting vapor to a substrate in a helium gas jet at chamber pressures around 1 Torr.

Despite the work of Eastman and the development of RE and ARE processes for compound production which have utilized e-beam systems with chamber pressures up to 1 Pa (~$10^{-2}$ Torr), many researchers believe that e-beam film synthesis in reduced vacuum is not viable. This mindset has developed as a result of certain widely accepted “rules of e-beam processing.” The literature [11, 18, 37] generally states that e-beam vapor-phase processing must occur in high vacuum because:

- Operating an e-beam gun with pressures greater than $1\times10^{-2}$ Pa (~$10^{-4}$ Torr) in the electron generating workspace can result in dielectric breakdown of the reduced vacuum environment and high voltage arcing (i.e. shorting) between the negatively charged filament and nearby portions of the gun maintained at different electrical potentials. Thus, energy for source evaporation is instead transferred to the gun, potentially damaging it and preventing low vacuum e-beam processing [11].

- The tungsten filaments which generate electrons in many e-beam evaporation systems degrade rapidly in low vacuum or atmospheric pressure. Thus, if the vacuum in the filament workspace is poor, electron emission from the filament generates ions which bombard and erode the filament, preventing low vacuum processing [48].

- If the entire system’s pressure exceeds $1\times10^{-2}$ Pa, e-beam energy dissipation occurs via gas scattering in the gun and process chamber, and the energy is unavailable for material evaporation, making low vacuum e-beam processing unfeasible [11, 49].

- Conducting film synthesis in a low vacuum environment leads to vapor atom thermalization and poor quality deposit microstructures [11].
• Operating in high vacuum has often been considered necessary to avoid contamination [11, 50]. This belief has led to the development of long process cycles in which the chamber is evacuated below $10^{-2}$ Pa, the chamber and its internal fixtures are heated to “bake-out” contaminants prior to deposition, and deposition occurs at a pressure low enough to ensure few evaporant atoms react with contaminant particles. It has also produced processing rules stating that “for pure films a pressure/deposition rate ratio of $< 10^{-7}$ Torr/Å/sec [10^{-5} Pa/Å/sec] must be achieved” [51]. Although many researchers have deemed e-beam vapor phase material synthesis in reduced vacuum impractical [11, 12, 37], other researchers have demonstrated the feasibility of low vacuum / atmospheric e-beam material processing.

The need to weld thick steel plates for ships and submarines and a desire to use e-beams to induce chemical reactions has motivated research into methods of conducting e-beam material processing at pressures above $10^{-2}$ Pa, even in open atmosphere [11]. These applications have led to the development of e-beam guns employing either transparent thin foil windows or differentially pumped gun sections to decouple the high vacuum e-beam generating space from the low vacuum / atmospheric processing region [11, 52 - 56]. While 25 µm thick electron “transparent” windows of Ti or Al work in e-beam guns employing high accelerating voltages (i.e. > 30 kV) and low power densities, an open unimpeded path from filament to target is required for high current density welding systems [53]. During the 1960’s, systems with such electron pathways were perfected in which electrons could be generated in a $10^{-5}$ Pa workspace evacuated by one pump, passed through two separately pumped gun segments at $10^{-2}$ Pa and 1 Pa, and used to weld metal parts at atmospheric pressure. While these welders occasionally experienced filament erosion or high voltage breakdowns resulting from sudden pressure rises in the filament workspace (due to vapor bursts from the workpiece), they have demonstrated the feasibility of low vacuum / atmospheric material processing [11].
E-beam operation under reduced vacuum or atmospheric conditions has also been improved by maximizing beam propagation through the gas environment in the gun and processing chamber. Fundamental investigations of e-beam / gas interactions by Boedecker, et al., Arata, and others [11, 49, 57] have revealed that the most important factors affecting beam propagation are the beam path length through the increased pressure, the e-beam’s accelerating voltage, and the molecular weight of the gas through which the beam propagates. Thus, when processing material under low vacuum or atmospheric pressure, beam propagation can be maximized by passing the e-beam into the elevated pressure regime close to the target and by decreasing the scattering cross-section of the gas in the processing chamber (i.e. by using a high e-beam accelerating voltage and a low molecular weight gas in the processing chamber) [48, 49].

2.2 Vapor Transport

After atomistic vapor has been created with a PVD tool like an electron beam gun, vapor transport to the substrate occurs either as a result of the vapor creation process itself (e.g. thermal evaporation energy) or can be effected by various external means acting upon the individual vapor atoms (e.g. interaction with electric or magnetic fields or as the result of collisions with gas atoms in the chamber). Indeed, the particular method and process conditions used to generate the vapor stream have been shown to influence significantly the spatial distribution, angle of incidence, kinetic energy, deposition efficiency, and form (e.g. monatomic or multiatom clusters) of vapor atoms reaching a substrate. Process-induced modifications of these parameters critically affect film growth (section 2.3).
2.2.1. High vacuum vapor transport

Often, the inherent characteristics of a high vacuum e-beam vapor stream (e.g. deposition efficiency and spatial, angular, and energy distribution) do not coincide with the optimal vapor stream characteristics desired for an application.

2.2.1.1 Spatial distribution

As section 2.1.1. explained, the vapor distribution from an e-beam source can be described by equation (2.2) in which \( n = 2, 3, 4 \) or more. This diverging, nonuniform vapor distribution can cause material processing difficulties in some applications. For instance, when coating fibers, the vapor stream of e-beam systems (Fig. 2.3) leads to significant variation of the material deposition rate on neighboring fibers. The magnitude of this nonuniform coating (onto flat substrates) has been described using the following equation [11]:

\[
\frac{d_s}{d_{so}} = \frac{1}{\left[ 1 + \left( \frac{r_s}{h_v} \right)^2 \right]^{2(n+3)/2}}
\]  

(2.3)

where:  
\( d_s \) = Local film thickness on a flat substrate,  
\( d_{so} \) = Film thickness directly above vapor source,  
\( r_s \) = Distance from midpoint of substrate,  
\( h_v \) = Source to substrate separation distance, and  
\( n \) = Exponent as used in equation (2.2).

In the fiber coating application, nonuniform vapor deposition is generally undesirable and could result in improper fiber spacing in a consolidated composite material (Fig. 1.2).
For all substrate surfaces, the diverging vapor streams of Figs. 2.1 - 2.3 lead to variation in the angle of vapor deposition with lateral position and with source-to-substrate separation. When coating large substrates with variable surface topologies (e.g., trenches and vias on 200 - 300 mm semiconductor wafers), this leads to an angular deposition which can prevent proper coating of non-line-of-sight surfaces [58].

### 2.2.1.3 Kinetic energy

During a thermal material synthesis process like e-beam evaporation, as energy is introduced into a liquid, some fraction of the atoms in the melt gain enough vibrational kinetic
energy to overcome the intermolecular forces binding them to the liquid. Atoms leaving an e-beam melt generally have 0.1 - 0.2 eV of kinetic energy [59] and a tight energy distribution [60]. In the literature, the magnitude of the evaporation induced kinetic energy is generally related to the material’s vaporization temperature by the following Boltzmann temperature equation [11, 2, 61]:

\[ E = \frac{3}{2} k T_v = \frac{1}{2} m v^2 \]  \hspace{1cm} (2.4)

where \( E \) = Kinetic energy of the evaporated atoms (J), \( k \) = Boltzmann’s constant \((1.381 \times 10^{-23} \text{ J/K})\), and \( T_v \) = Vaporization temperature of the source (K).

Although it is not initially apparent why this relationship should be true, Maissel and Glang [2] have provided a semirigorous proof of equation (2.4). They explain that the speed \( c \) of any atom is comprised of three components \( u, v, \) and \( w \) perpendicular to each other. For an ensemble of atoms in a volume with different speeds, the mean square velocity of all \( N \) molecules is:

\[ \frac{-u^2}{u} = \frac{\sum\!u^\omega}{N} \]  \hspace{1cm} (2.5)

and the mean-square speed of those molecules is:

\[ \frac{-c^2}{c} = \frac{\sum\!c^\omega}{N} = \frac{-u^2 + v^2 + w^2}{N} \]  \hspace{1cm} (2.6)
Kennard [62] and Parker [63] have demonstrated that, within a volume $V$, molecules with a mass $m$ and a velocity $u$ exert a pressure:

$$P = \frac{N}{V} m u^2$$  \hspace{1cm} (2.7)$$
on a flat surface perpendicular to the direction of $u$. If the velocities in different directions are assumed to be uniformly distributed, then:

$$u^2 = \frac{1}{3}c^2$$  \hspace{1cm} (2.8)$$Substituting equation (2.7) into equation (2.8) yields:

$$P = \frac{N}{3V} mc^2$$  \hspace{1cm} (2.9)$$Given the Universal Gas Law, an expression for the relationship between gas temperature and velocity can now be written:

$$\frac{1}{3} mc^2 = kT$$  \hspace{1cm} (2.10)$$Multiplying equation (2.10) by $3/2$ gives an expression for kinetic energy and also equation (2.4).

More recently, Asano et al. [59] have demonstrated experimentally that actual atom velocities are frequently above the level suggested by the basic relation of equation (2.4). In a study of uranium, titanium, and copper mean atomic velocities, Asano et al. found that the mean velocity of each atom type exceeded the predicted thermal mean velocity. Uranium’s velocity was 2.1 times greater than predicted by equation (2.4) while titanium’s was 1.6 and copper’s 1.3. Interestingly, Asano et al. concluded that the increase in velocity was the result of electronic excited state energy to kinetic energy conversion during adiabatic
expansion away from the molten vapor source. (The exchange of excited state energy for kinetic energy has been demonstrated elsewhere during atomic collisions between alkali metals [64].) Asano et al. [59] explained that the increase in velocity was less substantial for copper due to its smaller number of possible excited states.

Whether the adatom energies in thermal evaporation systems are 0.2 eV or 1.3, 1.6, or 2.1 times that level, Thornton [65, 66, 67, 68] has experimentally demonstrated that substantially more energy per atom must be introduced into a growing vapor phase deposited material (> 0.5 eV) to generate dense microstructures at low substrate temperatures. Zhou et al. have used molecular dynamic modeling methods to illustrate this same requirement [31]. As section 2.2.2.3 will discuss, this energy requirement has led to the development of various methods of adatom energy enhancement so that useful films can be created for dense film applications.

2.2.1.4 Deposition efficiency

Frequently, applications require that vapor be deposited only in select locations (e.g., into the vias of semiconductor wafers and onto fibers for continuous fiber reinforced metal matrix composite creation). In their most basic configurations, high-vacuum e-beam (and sputtering) systems lack the ability to redirect their vapor stream after it leaves the source with a \( \cos^3\theta \) distribution. As a result, deposition into the deep trenches and vias which are a part of newer semiconductor devices is becoming increasingly difficult. Rossnagel et al. and Yang et al. have recently studied ways to tailor vapor stream angular distributions for the most efficient filling of electrical conduits on semiconductor devices [36, 54, 58, 69, 70]. The need to deposit materials efficiently in selected locations is also observed during line-of-sight fiber coating in high vacuum e-beam systems. Such systems often intersect little more than 5% of the total vapor stream (c.f. Fig. 2.3), allowing the rest of the highly refined, expensive matrix material to deposit uselessly onto the walls of the chamber.
2.2.2. Modification of vapor transport characteristics

Because the inherent characteristics of a high vacuum e-beam vapor stream sometimes do not generate desired material properties, researchers have developed ways to modify various aspects of the vapor stream [71].

2.2.2.1 Spatial distribution

Since the 1970’s, researchers have investigated ways to modify vapor distributions to produce a more uniform vapor stream and to enhance non-line-of-site coating. One of the more successful methods for varying the vapor stream distribution in e-beam systems has been to raise the background processing chamber pressure above $10^{-2}$ Pa ($\sim 10^{-4}$ Torr). Investigations by Beale and Grossklaus [44, 72] revealed that raising argon pressures to 0.1 Pa decreased the exponent for their $\cos^n\theta$ distribution from 8 to 5.5, indicating that higher chamber pressure led to a less focussed, more uniform coating. Interestingly, experimental investigations by Erikson et al. [73, 74] showed that, at argon pressures of $1\times10^{-4}$ Pa and higher, vapor focussing in their system became increasingly pronounced as chamber pressure rose (Fig. 2.4). While researchers generally agree that vapor distribution changes with varying gas pressure are the result of atomic collisions [11], the particular cause of vapor stream defocussing and then focussing with increasing chamber pressure has not been explained. In Erikson’s system, vapor atom clustering could have changed the effective mass of the vapor particles being scattered, decreasing their rate of lateral diffusion and increasing the focus of their final deposit. Alternatively, higher vapor pressures resulting from the elevated e-beam powers of Erikson’s study could have caused a more significant surface deformation of the source material and thereby generated a more focussed initial vapor stream (c.f. Fig. 2.2).
Another method investigated for vapor spatial density distribution variation has been substrate biasing. Erikson [73] reported that this did not change the distribution of vapor deposited from an ionized vapor cloud, and Krutenat [75] suggests that substrate biasing in combination with a plasma discharge between source and substrate led to “randomization” of the vapor stream and non-line-of-sight coating. The scattered depositions observed by Erikson and Krutenat are most probably the result of vapor/gas collisions between source and substrate with substrate biasing contributing little to vapor redirection. Although substrate biasing does not appear to affect vapor direction, Rossnagel et al. have shown that unbalanced magnetrons in sputtering systems are capable of affecting the distribution of vapor traveling from sputtering target to substrate [36, 54, 58, 70].

Figure 2.4 **Background gas pressure modifies vapor density distribution.** Results from Erikson’s study of medium vacuum e-beam deposition show an increase in vapor focus as argon chamber pressure is increased from 4 to 50 x 10^-5 Pa. (Evaporation rate = 32 g/min. Source-to-substrate distance = 32.4 cm) [73]
2.2.2.2 Angular distribution

In sputtering systems, researchers have changed the angular distribution of vapor through the use of collimators and unbalanced magnetrons. Collimation [76] places a physical filter between source and substrate to allow passage of only the fraction of atoms traveling nearly normal to the substrate. While collimation facilitates microelectronic trench and via filling, it is slow and inefficient [76]. Use of an unbalanced magnetron, which forces charged sputtered particles to travel along electromagnetic field lines, has proven more useful as a means for efficiently modifying vapor distributions [58, 61]. In sputtering systems, Rossnagel and others [70] have successfully used electrostatic collimation to manipulate the ionized vapor flux angular distribution for more efficient trench filling.

2.2.2.3 Kinetic energy

In sputtering, cathodic arc, and certain RE/ARE e-beam systems negative bias voltages of 50 - 300 V are frequently applied to substrates to increase the energy of the incident charged species [12, 16, 18, 77]. Mattox [16] and others [78] realized in electron beam systems that interaction of the e-beam with the gas in the chamber created an ionized plasma of vapor atoms and chamber gas atoms. By applying a negative electrical bias (~100 V) to the deposition substrate, both ionized gas and vapor atoms could be accelerated towards the substrate as part of an “ion plating” process, imparting kinetic energies of 10-10,000 eV to depositing atoms [16]. Kinetic energies of this magnitude lead to significant film densification, the removal of some atoms deposited via sputtering, and the introduction of disorder into the growing film unless significant substrate heating is permitted.

2.2.2.4 Deposition efficiency

Limited studies have shown that PVD processing with moderate background chamber pressures can lead to significant non-line-of-sight deposition and, for certain system configurations, an increase in deposition efficiency [44, 79]. For flat substrate coating studies,
Bunshah and colleagues [44] reported an overall decrease in deposition efficiency with increasing chamber pressure, but, for substrates with surfaces not in the line-of-sight of the source, they noted that non-line-of-sight coating efficiencies could be enhanced by:

- Changing the mass of the scattering gas introduced into the chamber. Bunshah noted that, for a given chamber pressure, the amount of non-line-of-sight coating increases as the mass of the scattering gas molecule approaches that of the evaporant.
- Increasing the pressure of the scattering gas in the chamber. Introducing gas into the chamber increased non-line-of-sight coating, and higher chamber pressures resulted in more non-line-of-sight coating.

Bunshah and colleagues offered no physical insight into the root cause of these trends except to say that they were dictated by simple momentum exchange principles between gas and vapor atoms.

In a study of deposition onto fibrous substrates from a metal vapor laden Jet Vapor DepositionTM inert gas stream, Hill [79] noted than the mass capture efficiency of the fibers was greater than the cross-sectional area occupied by the fibers. Hill attempted to explain his observations using a continuum-based vapor diffusion model designed to predict lateral diffusion of vapor atoms across carrier gas streamlines. While Hill only explored copper deposition in a helium chamber pressure of 4 Torr, he suggested that the magnitude of non-line-of-sight coating could be varied with changes to the carrier gas stream velocity (i.e. Mach number). Highest deposition efficiencies were reached at Mach numbers of 1.0 - 1.2 with decreasing deposition efficiency at higher and lower Mach numbers.

2.2.2.5 Evaporated material form

Material processing in medium or high vacuum with e-beam systems most often generates individual atoms of material which deposit on various substrates to form a multitude of important film products [11, 12, 37, 61]. While atomistic vapor is the most common mate-
rial form desired by those employing e-beam systems, some researchers have demonstrated that slight modifications to the PVD environment can lead to the formation of significant numbers of vapor clusters (agglomerations of atoms) [46, 50, 79-89]. As noted in Fig. 2.2, extremely high evaporation rates in conventional e-beam systems can lead to the formation of a virtual vapor source above the source material surface. In this region the density of vapor atoms is high enough to lead to vapor / vapor atom collisions, redistributing the vapor stream and in some cases leading to vapor cluster formation [11]. The results of Erikson [73] (section 2.2.2.1) also emphasize the important effects of clustering upon the material creation characteristics of a vapor deposition system.

Even when vapor densities are not extremely high, vapor atom cluster formation has been reported to be common in low vacuum processing environments [90, 91], suggesting that the background chamber gas plays a role in cluster formation. As Steinwandel and Hoeschele explain [92], the cluster nucleation process occurs via a series of steps in which individual atoms (A) and some other atomistic or molecular species (M) collide:

\[
A + A + M \leftrightarrow A_2 + M^* \quad (2.11)
\]

\[
A_2 + A + M \leftrightarrow A_3 + M^* \quad (2.12)
\]

\[
A_{n-1} + A + M \leftrightarrow A_n + M^* \quad (2.13)
\]

After the collision event the third species often becomes energized by the collision event (M*). Steinwandel and Hoeschele point out that “The reaction sequence [equations (2.11) - (2.13)] is frequently formulated without the three-body collision partner M. However, it should be noticed that three-body collisions are required due to the conservation laws of momentum, and energy for elementary reactions.” In the low vacuum environment, the third body will frequently be a background gas atom rather than a third vapor atom.
When attempting to describe cluster formation, numerous authors have taken a thermodynamic approach [86-88, 93-95] while others have pursued a kinetic activity explanation [96-100]. Study of the numerical results generated to date by both methods indicates that current kinetic models provide more reasonable predictions of experimental cluster formation results. Steinwandel and Hoeschele summarize [92]:

The classical [thermodynamic] theory of homogeneous nucleation is inadequate in order to describe the nucleation behavior of metal vapors at all degrees of supersaturation that could be realized experimentally. Nucleation appears to be a problem of elementary reaction kinetics in conjunction with a proper statistical thermodynamics formulation for stability criterions of small clusters.

The exact reaction kinetics and stability criterion appropriate to a particular system under study depend upon the characteristics of the system. For instance, as Smirnov and Strizhev note [100]: “The character of clustering is different for neutral and weakly ionized atomic beams. Ions of an atomic beam are nuclei of condensation, and the presence of charged atomic particles in an atomic beam is responsible for condensation of atoms.”

In a recent study of Jet Vapor Deposition™, a low vacuum vapor deposition technique, Hill [79] has calculated the probability of cluster formation for different processing conditions using a reaction kinetics approach and has used those results to delineate experimentally observed microstructures created during the coating of fibers. Hill calculated the importance of cluster formation by first determining the equilibrium concentration of unstable metal vapor dimer (i.e., prior to collision with a third body):

\[
[Cu_2^*] = \left[ \frac{Cu}{2} \right]^2 \frac{4}{3}\pi(\sigma_{aCu}^3 - \sigma_{rCu}^3)
\] (2.14)

where

\( [Cu_2^*] = \) Concentration of unstable dimers (dimers/m³),

\( [Cu] = \) Concentration of metal monomer (atoms/m³),
\[ \sigma_{aCu} = \text{Activity radius of a copper atom (m), and} \]
\[ \sigma_{rCu} = \text{Hard sphere radius of copper atom (m).} \]

Hill then indicated that the rate of stable dimer formation could be derived from:

\[ Z_{Cu_2-He} = [He][Cu_2^*]\pi \left( \frac{\sigma_{aCu_2} + \sigma_{rHe}}{2} \right)^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2} \]  \hspace{1cm} (2.15)

in which \( Z_{Cu_2-He} = \text{Volume collision frequency (collisions/m}^3/\text{sec)} \)
\( [He] = \text{Concentration of background gas (atoms/m}^3), \)
\( \sigma_{aCu_2} = \text{Activity radius for the unstable dimer (m),} \)
\( \sigma_{rHe} = \text{Hard sphere radius of a helium atom (m), and} \)
\( \mu = \text{Reduced mass of collision, defined as } 1/\mu = 1/\mu_{Cu} + 1/\mu_{He} \text{ (kg).} \)

Stable dimer formation then makes possible the formation of larger clusters (\( N + 1 \) atoms) at a rate given by [79]:

\[ Z_{Cu_N-Cu} = [Cu][Cu_N]\pi \left( \frac{\sigma_{aCu_N} + \sigma_{rCu}}{2} \right)^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2} \]  \hspace{1cm} (2.16)

Assuming a sticking coefficient of one, the growth rate of a \( N \)-mer will be the collision rate seen by an individual \( N \)-mer [79]:

\[ \frac{dN}{dt} = \frac{Z_{Cu_N-Cu}}{[Cu_N]} = [Cu]\pi \left( \frac{\sigma_{aCu_N} + \sigma_{aCu}}{2} \right)^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2} \]  \hspace{1cm} (2.17)

where \( 1/\mu = 1/\mu_{CuN} + 1/\mu_{Cu}. \)
Finally, for a given set of processing conditions and a time of flight (τ) for the metal atoms from source to substrate, Hill suggests that the average size of clusters ($N_{av}$) in a system is given by [79]:

$$N_{av} = \frac{1}{\tau} \int_{0}^{\tau} N(t) \, dt.$$  \hspace{1cm} (2.18)

While Hill has theoretically examined cluster formation rates, others like Dugdale [50] have experimentally explored how vapor phase nucleation of particle clusters affects film structure and has uncovered methods for avoiding cluster formation. Dugdale [50, 84] and others [46] have found that evaporation in low vacuum with an ambient temperature gas in the chamber can lead to homogeneous nucleation of vapor clusters and “the precipitation of powders which form friable and porous columnar structures” [50]. The parameters which determine when such structures appear include the evaporant material used, the evaporation rate, the specific ambient gas and pressure, the geometry of the system, and the temperature of the substrate [50]. Substrate heating alone does not eliminate the effects of vapor phase cluster nucleation upon microstructure. Further exploration by Dugdale [84] revealed however that the apparent effects of vapor phase cluster nucleation could be significantly reduced by heating the gas in the vacuum chamber as high as 600°C.

Dugdale [84] explained that chamber gas and vapor atom heating should theoretically decrease the vapor atom concentration, should increase the radius of a thermodynamically stable cluster [86], and should thus decrease the number of clusters which form. (The dependence of cluster formation rate upon temperature and vapor atom concentration has been examined in some detail elsewhere [86-88].) Dugdale concluded by reporting a reduction in cluster concentration as a result of heating the gas and vapor in his deposition chamber. This significantly changed film microstructure, from porous to dense columns.
While he did not suggest a physical explanation for the microstructural change, it is not difficult to envision that low energy cluster deposits form a porous material structure while individual atoms at a higher temperature create a denser microstructure (Fig. 2.5).

2.2.3. Jet Vapor Deposition™

During the 1980’s a new method was invented for creating films in a reduced vacuum and for manipulating vapor stream characteristics (i.e. distribution, energy, angle, efficiency, and form) during transport from source to substrate [47, 85]. Jet Vapor Deposition™ (JVD™) used a nozzle and gas jet to transport atoms or clusters of atoms to a substrate for deposition. This technique represents an extension of the technology of high pressure ratio molecular beam separators to a lower pressure ratio regime [101-110].

JVD™ often employs either a thermal evaporation source (a resistively heated wire) or another non-electron-beam heating source in combination with an inert gas jet to create
vapor atoms, to accelerate those atoms from their thermally induced velocities, to concentrate the vapor stream through a spray nozzle, and to deposit the adatoms onto a substrate in a low vacuum (~ $10^{-2}$ Pa) (Fig. 2.6) [9, 10, 12]. JVD\textsuperscript{TM} employs vapor atom collisions with a carrier gas flowing towards the nozzle exit to redirect the vapor and reshape the vapor’s density distribution. Using a pressure drop into the chamber to accelerate the entire flow, the JVD\textsuperscript{TM} method then makes use of the inertial momentum of the vapor atoms to create a focussed deposit since, for a critical range of pressures, many of the vapor atoms cannot be turned into the wall jet by atomic collisions with the carrier gas before contacting the substrate (Fig. 2.6).

Figure 2.6 Molecular beam deposition. Once vapor atoms are accelerated through a nozzle, they can either impinge upon the substrate or be deflected into the wall jet. The pressure ratios shown are representative of those employed in a JVD\textsuperscript{TM} system [12, 79].
Reported results from deposits created with molecular beam separators and JVD\textsuperscript{TM} processes suggest that they could have a unique ability to vary vapor atom spatial, angular, and energy distributions as well as deposition efficiencies and vapor atom forms [47, 80, 83, 101-112]. Though not reporting exact distribution information, JVD\textsuperscript{TM} results indicate that, by using a high molecular weight vapor atom / low molecular weight carrier gas combination (e.g. gold / helium), focussed, highly efficient, highly nonuniform deposits can be created on stationary substrates [47]. While reporting focussed, high deposition efficiencies for gold on flat substrates (95%), Halpern et al. [47] and others [113, 114] do not provide information on the exact vapor atom spatial, angular, or energy distributions during transport and deposition. Hill [79] does present limited fiber coating deposition distribution data for the JVD\textsuperscript{TM} process with basic continuum-based model explanations for the observed experimental results. In other modeling work related to the JVD\textsuperscript{TM} process, de la Mora et al. [115] and Marple et al. [104] use continuum fluid flow concepts such as Stokes number and drag coefficient to examine the influence of vapor cluster mass upon deposition efficiency. Little in-depth analysis appears to be available in the literature though for a complete assessment of the rapid material synthesis abilities of these low pressure molecular beam systems.

In addition to an ability to affect vapor atom deposition efficiency and distribution, molecular beam separators and the JVD\textsuperscript{TM} process could have the ability to increase adatom kinetic energy by passing the vapor through a nozzle. First order estimates of the maximum velocity attainable through use of a nozzle can be determined using one-dimensional equations for isentropic flow of a compressible fluid [116]. The important governing relationships between pressure, temperature, Mach number, and jet velocity are given by:

\[
\frac{P_o}{P_d} = \left[ 1 + \frac{\gamma-1}{2} M^2 \right]^{\gamma/(\gamma-1)}
\]  

\text{(2.19)}
and

\[ U = M \sqrt{\gamma R_s T} \]  

(2.20)

where

- \( P_o \) = Upstream pressure before the nozzle (Pa),
- \( P_d \) = Downstream pressure at the nozzle or in the chamber (Pa),
- \( \gamma \) = Ratio of specific heats (5/3 for helium and argon),
- \( M \) = Flow’s Mach number,
- \( U \) = Carrier gas stream speed (m/sec),
- \( T \) = Absolute temperature (K), and
- \( R_s \) = Specific gas constant (2077 J/(kg K) for helium, 208.1 J/(kg K) for argon).

2.2.4. Supersonic gas jet structure

While equations (2.19) and (2.20) give an upper bound to vapor atom velocity and kinetic energy exiting a molecular beam nozzle, multidimensional shock waves further downstream in low vacuum supersonic gas jets slow the carrier gas from supersonic velocities as the gas and vapor travel toward the substrate [117], making vapor atom velocity and position prediction with these one-dimensional equations impossible (Fig. 2.7). Two of the most important features of a supersonic nozzle expansion are the so-called zone of silence, where the gas flow accelerates to supersonic velocities, and a Mach disk, at which the gas flow rapidly decelerates to velocities below Mach 1 (Fig. 2.7). In addition to these structures, Adamson and Nicholls and others [117, 118] note that when a supersonic jet exits into a low vacuum (above a pressure of ~1 Pa), weak secondary shock structures can be present downstream of the sharply defined Mach disk.
Chapter 2. Background

The initial, expanding zone of silence is formed when the “high” pressure gas in the nozzle enters the chamber and expands in an attempt to match the lower background pressure found in the processing chamber. In many instances in which the background pressure is high enough to allow for a continuum description of atomic interaction, the nozzle exhaust overexpands, creating a lower pressure in the zone of silence than that found in the surrounding chamber. As a result, the background pressure forces the overexpanded barrel shock to narrow.

Figure 2.7 Structure of a continuum free-jet. The general structure of a continuum free-jet expansion has been well characterized [117-120]. The structure shown here is considered to be continuum-based since its existence requires a high enough density and collision frequency to allow for the definition of density and equilibrium temperature within the length scale of the apparatus [118].
At some point downstream, the compression waves surrounding the barrel shock coalesce to generate a diamond shock or a Mach disk shock if the pressure ratio \( P_d / P_a \) is significantly above the level necessary to generate supersonic flow (2.05 for helium and argon). Depending upon the pressure in the processing chamber, this expansion and contraction sequence can be repeated as the jet attempts to reach equilibrium with the surrounding gas. Subsequent shock waves beyond the initial Mach disk are of decreasing strength as viscous effects dissipate the jet’s energy [117]. While the zone of silence represents the primary region of supersonic flow, the repeated expansions of the jet downstream can create small additional regions of supersonic flow. The final major feature of the flow is the wall jet. Once the gas flow interacts with the substrate, the speed of the gas jet toward the substrate slows dramatically, a concave wall shock forms, and the gas is forced parallel to the substrate [120]. In sum, the idea of using a carrier gas stream to facilitate vapor deposition appears intriguing, but the technique is not well characterized or understood.

Interaction of the vapor atoms and carrier gas with the substrate undoubtedly decreases the adatom velocity component directed toward the substrate as the vapor atoms are redirected into the wall jet (c.f. Fig. 2.6). While the correlation between velocity and kinetic energy for vapor atoms of selected mass is simple \( E = \frac{1}{2} m v^2 \), little experimental or theoretical work has been done to determine the actual velocity of adatoms reaching the surface in a vapor deposition system utilizing a nozzle and gas jet.

2.2.5. Vapor transport modeling

Because of the development of low and medium vacuum technologies such as diode sputtering and JVD™, theoretical understanding of vapor transport for materials processing has become a point of focus in recent years. Numerous researchers have investigated vapor transport issues in these systems and have realized that modifications to initial
vapor stream characteristics result from collisions with gas atoms in the processing chamber which affect vapor deposition properties of the system (e.g. depositing atom energy, angle, and distribution) [121-137]. To understand the significance of vapor transport effects upon material deposition characteristics and to optimize the design of vapor deposition systems operating in medium or low vacuum, researchers have three primary avenues along which to investigate the phenomena: solution of the Navier-Stokes equations, solution of the Boltzmann equation, or direct physical simulation of the gas flow.

The Navier-Stokes equations [116] are a set of partial differential equations that represent the equations of motion governing a fluid continuum. While in actuality a fluid flow represents collision events between the individual atoms of a gas or liquid flow, under many conditions the Navier-Stokes equations allow the properties to be defined and solved for in a continuum (average) sense. One form of the Navier-Stokes equations is shown below in Einstein’s tensor notation [138]:

\[
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j} \rho u_j = 0 
\]

(2.21)

\[
\rho \frac{\partial u_i}{\partial t} + \rho u_j \frac{\partial u_i}{\partial x_j} = -\frac{\partial P}{\partial x_i} + \frac{\partial \sigma_{ji}}{\partial x_j}
\]

(2.22)

\[
\rho \frac{\partial H}{\partial t} + \rho u_j \frac{\partial H}{\partial x_j} = \frac{\partial P}{\partial t} + \frac{\partial}{\partial x_j} (\sigma_{ji} u_i - q_j)
\]

(2.23)

where

\( t \) = Time (sec),

\( x_i \) = Position (m),

\( u_i \) = Velocity (m/sec),

\( \rho \) = Density (g/cm\(^3\)).
\[ P = \text{Pressure (Pa)}, \]
\[ H = \text{Total enthalpy (kJ)}, \]
\[ \sigma_{ji} = \text{Viscous stress tensor (Pa), and} \]
\[ q = \text{Heat flux (W)}. \]

Whether or not it is appropriate to use the Navier-Stokes equations to analyze a fluid flow problem is determined through calculation of the dimensionless Knudsen number (Kn) of a flowfield [116]:

\[ (Kn) = \frac{\lambda}{L} \]

where \( \lambda \) = Mean free path (m), and
\( L \) = Characteristic dimension of the modeled geometry (e.g. source to substrate separation) (m).

As laid out by John [139] and Shames [140], a Knudsen number greater than 0.1 represents the transition to free molecular flow at which point a Boltzmann equation solution or discrete atom simulation must be employed rather than the continuum Navier-Stokes equations. To estimate the validity of continuum based computations, a quick calculation of \( \lambda \) can be made using the following equation [126, 141]:

\[ \lambda \equiv \frac{1}{\pi d^2 n} \]

where \( d \) = Gas atom hard-sphere diameter (m), and
\( n \) = Gas atom number density (atoms/m\(^3\)).
(The source of equation (2.25) will be explored extensively later in the dissertation - section 8.2.2.)

While several researchers have used the Navier-Stokes equations to examine vapor transport for materials synthesis [112, 125, 142] there are drawbacks to use of these equations. First, the continuum method does not provide information about individual atoms as desired for simulations of film growth [29-33]. Second, the Navier-Stokes equations which most commercial continuum codes employ often have difficulty capturing the phenomena associated with vapor transport at many of the rarefied processing pressures utilized [116, 139]. As Shames notes [140]:

The continuum breaks down when the mean free path of the molecules is of the same order of magnitude as the smallest significant length in the problem [e.g., nozzle diameter in a JVD™ system]. Under such circumstances we may no longer detect meaningful, gross manifestations of molecules. The action of each molecule or group of molecules is then of significance and must be treated accordingly.

In a slightly different explanation Bird [141] goes on to note that the Navier-Stokes equations can no longer be used once it becomes impossible to relate average values of appropriate molecular quantities such as shear stresses and heat fluxes to macroscopic quantities such as pressure, temperature, and velocity. According to Bird [141]:

More specifically, the transport terms in the Navier-Stokes equations of continuum gas dynamics fail when gradients of the macroscopic variables become so steep that their scale length is of the same order as the average distance travelled by the molecules between collisions, or mean free path.

An alternative to the use of the Navier-Stokes equations is solution of the older Boltzmann equation dating from 1872 which can be used to describe molecular behavior in a fluid
over a much wider range of Knudsen numbers, from Kn less than 0.001 to Kn greater than 100 [141]. The Boltzmann equation is shown below [143]:

\[
\frac{\partial f}{\partial t} + u_j \frac{\partial f}{\partial x_j} + F_j \frac{\partial f}{\partial u_j} = \frac{\partial f}{\partial t}
\]  

(2.26)

where

\( f \) = Velocity distribution function of a gas,

\( u \) = A single atom’s velocity function, and

\( F \) = Some external force acting upon the gas atom at time \( t \).

(The right side of the equation represents the change in the velocity-distribution function for the total gas with time as the result of binary collision encounters \( e \) at a fixed point. Chapman and Cowling [143] provide a thorough explanation of the origin of this equation.) The major drawback to using the Boltzmann equation for analysis of vapor transport has been the difficulty of obtaining solutions to the complex equation. A notable exception is the Chapman-Enskog solution of the Boltzmann equation for “a restricted set of problems in which the distribution function \( f \) is perturbed by a small amount from the equilibrium Maxwellian” distribution [141]. Solutions such as Chapman-Enskog will not always be valid in material processing systems where gas atom velocities are far from Maxwellian, e.g. supersonic gas expansion from a nozzle.

To attack problems of this type, researchers have turned to direct physical simulations of the gas flow in which computers are used to calculate the interaction of many thousands or even millions of representative atoms as they collide with one another or interact with boundaries in simulated physical space. Solutions for both steady and unsteady state problems are obtained by averaging over many small time steps. Some of the most recent vapor transport material processing modeling efforts of this type have been produced by Elsing, Knotek and others [121-124] in which vapor transport in diode sputtering has been
simulated. While providing a hint of the type of adatom deposition energy and angle information which can be produced by direct physical simulations of vapor transport, these initial efforts have been limited.

Proper theoretical description of the individual collision processes requires the use of interatomic potentials, energy dependent atomic cross-sections, and classical mechanics describing the collision of two bodies moving in three dimensions [58, 126-136, 144]. Elsing, Knotek, and others [121-124] have not employed any of these basic concepts in their models. In addition, their sputtering results assume that the gas atoms are stationary during collisions with energetic vapor atoms. Finally, they base their adatom energy and angular distribution conclusions upon the simulation of a limited number of atoms (~100), a number too small to eliminate statistical fluctuations from the results [137]. Simulation of just 100 atoms by Elsing and Knotek highlights one of the primary drawbacks to stochastic modeling of individual atom collisions, the computational expense of trying to track the many moles of atoms actually involved in vapor transport.

One of the more fully developed methods of direct physical simulation of thousands or millions of atoms in a gas flow is the Directed Simulation Monte Carlo (DSMC) method originally developed by G.A. Bird [141]. This method has been used extensively in recent years and has built a solid reputation as a modeling tool through comparisons of model results with independent laboratory experiments [120, 141, 148-151] for a number of engineering problems, including vapor transport [147, 148]. While providing reasonable accuracy, the DSMC method tries to minimize the computational expense of direct physical simulations by making certain approximations such as the use of variable hard sphere (VHS) and variable soft sphere (VSS) estimates of atomic dimensions rather than more accurate, but computationally expensive, estimates of energy dependent atomic cross-sections [141]. There are some indications that these estimates lead to discrepancies between
model and experiment [152, 153]. Bird [141] discusses that the problem with the VHS approximation is that “this scattering law is not realistic and that the cross-section is independent of the relative translational energy \( E = \frac{1}{2}m v^2 \) in the collision. Other than at extremely low temperatures, the effective cross-section of real molecules decreases as \( c_r \) [velocity] and \( E_t \) increase.” Bird also notes that even when the more sophisticated VSS model is invoked “the diameter varies in the same way as the VHS model, but the deflection angle is...” given somewhat more accurately.

In general though, use of the general DSMC method to model low vacuum vapor transport could provide a vital link between current understanding of vapor creation and general vapor deposition characteristics in this environment. Indeed it is probably the preferred method of simulation for studying the vapor transport problem due to its reliance upon a direct physical simulation of the problem, an approach valid at all mean free path lengths encountered in medium or low vacuum vapor transport. Reliance upon continuum methods could introduce severe uncertainty into results. The flow structure shown in Fig. 2.7 not only has significant changes in Mach number associated with various portions of the gas flow but also large changes in pressure and mean free path [110, 118]. While continuum equations could be valid in one portion of the flowfield, they could be quite inaccurate in others. Reliance upon DSMC methods, based on discrete particle concepts valid across the entire important range of Knudsen numbers, appears to be justified. Accurate prediction of deposition distributions, energies, impact angles, efficiencies, and forms with DSMC methods could provide accurate input to molecular dynamics and Monte Carlo simulations of vapor adsorption and diffusion on a substrate for the design of engineering structures [29-33].
2.3 Vapor Adsorption and Diffusion on a Substrate

The ultimate motivation for creating and transporting vapor to a substrate is the formation of useful engineering products from the vapor phase. Extensive research to date [12, 29-33, 61, 68, 154-182] has already provided great insight into what vapor creation and transport based processing parameters affect vapor phase material structural development. Although microstructure formation will not be a focal point of this dissertation’s research, the generation of desired, useful microstructure is ultimately the reason for developing a system which can manipulate vapor atom transport characteristics.

The desire to create films repeatedly and economically and to understand how the entire deposition process determines the film microstructure and properties has led researchers to explore film growth through experiments [12, 68, 154-173] and computer-aided modeling [29-33, 61, 174-183]. Much of this work has focussed upon understanding what determines the occurrence of point, linear, and planar defects during film nucleation and growth, the presence of chemical imperfections, and the formation of amorphous, polycrystalline, or single crystal deposits - all critical microstructural variables affecting the final physical properties of films in engineering applications. Many of the contributors to Bunshah’s book note [12] agree that the most important factors affecting vapor phase material growth are:

- Elemental composition of the depositing atoms [156],
- Film growth temperature [66, 155],
- Deposit thickness [65],
- Substrate material [1], cleanliness [183], crystallinity [1], and orientation [1, 61],
- Rate of deposition [66, 174],
- Kinetic energy of the atoms landing on the substrate [30, 179],
• Angle of incidence of the vapor atoms [76, 154], and
• Presence and nature of a surrounding gas phase [66, 159, 162, 163, 165, 169, 171-173].

As these parameters have been identified, efforts have focussed upon the development of processing roadmaps which can aid engineers as they design film synthesis equipment by showing the influence of the various parameters upon microstructure (e.g. Figs. 2.8 and 2.9). Both figures show how several of the factors listed above affect film microstructure.

![Figure 2.8 Thornton’s zone diagram.](image)

Experimental study of sputtering (e.g. Ti, Cr, Fe, Cu, Mo and Al) revealed repeatable microstructural trends - improving material quality with higher temperature and lower chamber gas pressure [66].

The underlying cause of a significant portion of the reported microstructure variation appears to be the directed energy of the adatoms. In Fig. 2.8, as chamber pressure increases, vapor atom thermalization becomes greater, and, as Zhou et al. [31] explain, adatoms depositing with lower energies and at normal incidence have a limited ability to...
move across the film surface to form a dense microstructure. Similarly, decreasing the substrate temperature makes less energy available to depositing adatoms. As a result, their ability to jump from one site on the surface to another is minimized, again leading to a more porous structure.

![Graph](image)

**Figure 2.9** Vacancy concentration as a function of adatom energy. Two dimensional molecular dynamics modeling, using an embedded atom method to describe interatomic interactions, reveals a lattice site vacancy concentration dependence upon incident Ni adatom energy; deposition rate = 10 nm/ns [31].

Both Figs. 2.8 and 2.9 highlight the dramatic changes which can be made to material structure as deposition parameters are varied. Experimental and modeling work to date has allowed many of the basic, important process-property relations to be uncovered and many significant vapor phase film processing technologies to be developed which can manipulate the important process parameters to create film products. While current technology based on this general understanding of deposition is capable of producing highly
engineered films, most researchers acknowledge that process capabilities must evolve and that process models of vapor creation, transport, and deposition, beyond the level of general film growth roadmaps, must be developed and employed during film synthesis to attain tomorrow’s more stringent specifications.

Indeed, some researchers believe vapor creation, transport, and deposition models will have to be incorporated into closed-loop, real-time process control systems (e.g. Intelligent Processing of Materials (IPM) [184, 185]) which utilize in-situ sensors throughout the process to ensure quality film creation. The work of Yang, Zhou, Johnson, and Wadley [29-33] to model deposition phenomenon represents an effort to move beyond general roadmaps and towards material design tools and eventually closed-loop control.

2.4 Summary

The preceding examination of electron beam film synthesis illustrates that e-beam systems have a strong ability to process a great number of elements, alloys, and compounds. At the same time, study of e-beam vapor deposition distributions, efficiencies, angles, and energies reveals that, for certain applications, an ability to chose the desired range of these parameters for different applications could enhance the attractiveness of electron beam systems to material processors.
Chapter 3

Invention of Directed Vapor Deposition

Having surveyed the state-of-the-art in electron beam processing and having reviewed various methods for the modification of e-beam material creation characteristics, it appeared that an opportunity did indeed exist for the enhancement of electron beam material synthesis characteristics. The desire was to develop a method which could deposit refractory elements, compounds, and alloys onto complex shapes by a rapid, efficient, and low contamination method capable of line and non-line-of-sight coating. The literature reviewed in Chapter 2, specifically section 2.2.2., indicated that non-line-of-sight could be achieved by synthesizing material from the vapor phase in low vacuum. However, deposition efficiencies in this environment were reported to be generally lower than in high vacuum systems. Still, the literature reviewed in section 2.2.3. suggested that improved vapor stream focus and deposition efficiency could be achieved by not only synthesizing vapor phase materials in a medium or low vacuum but also by using a carrier gas stream as a means of transporting vapor to the deposition surface.

Thus, in a departure from conventional electron beam (e-beam) evaporation methods [2, 11, 37] which create atomistic vapor in high vacuum \((10^{-6} \text{ - } 10^{-2} \text{ Pa} / 10^{-8} \text{ - } 10^{-4} \text{ Torr})\), a
new low vacuum e-beam based physical vapor deposition system, termed Directed Vapor Deposition (DVD), is proposed. This new method uses an e-beam in a low vacuum environment \(10^{-1} - 10^3 \text{ Pa} / 10^{-3} - 10 \text{ Torr}\) where a carrier gas stream can be utilized to entrain evaporants within that stream for efficient transport to and deposition on a substrate (Fig. 3.1) [186]. As conceived, the DVD system is the only e-beam system which seeks to capture evaporant in a reactive or inert carrier gas stream for transport to a surface (substrate) where deposition of either the pure vapor atoms or their reaction products, created in combination with carrier gas molecules, can occur [2, 11, 12, 13].

Figure 3.1 A preferred embodiment of Directed Vapor Deposition. In a Directed Vapor Deposition system, e-beam evaporant from a crucible is transported to a substrate in a carrier gas stream.
The Directed Vapor Deposition system represents an attempt to build upon the well documented material processing capabilities of electron beams [11] by placing e-beam evaporated material in a new environment, a medium or low vacuum gas stream. By introducing vapor into this flow, it could be possible to synthesize materials and microstructures from the vapor phase which have so far proven to be difficult to create via other methods. The subsequent work described in this dissertation focuses upon understanding the interaction of e-beam evaporant with a gas stream as a mechanism for creating engineered materials. Once this work has provided some initial insight into this interaction, it should be possible to focus future technology development of this type upon the areas of materials synthesis which hold greatest promise.

As noted in the Background chapter, the process of vapor phase material synthesis consists of five steps:

1. Creation of the vapor.
2. Transport of the vapor to the substrate.
3. Adsorption of the vapor onto the substrate.
4. Diffusion of the adatoms across the substrate surface.
5. Movement of the adatoms by bulk diffusion through the film lattice to their final positions.

While the DVD film synthesis method will follow these general process steps, there are several aspects of its specific approach to processing which could combine to present opportunities for economic, high quality materials synthesis not available with other processes. Thus, this new processing pathway, Directed Vapor Deposition, deserves to be investigated.
The intriguing, possible material processing features which could make DVD useful include the following.

- **DVD should entrain and focus vapor atoms in a carrier gas stream.** This feature could make it possible to change the distribution and angle of deposition for vapor atoms reaching the substrate. In applications where material is to be deposited over a small area (e.g. fiber coating for composite applications), DVD focussing of the vapor stream could greatly enhance material utilization efficiency, decrease production time, and lower final product cost. In applications where material is to be deposited onto uneven surfaces or surfaces with recessed regions (e.g. semiconductor via filling applications), changing the angle of the vapor stream could enhance surface coverage or feature filling [69, 76].

- **The lower portion of the DVD vacuum pressure regime is comparable to that found in diode sputtering systems.** As researchers [144, 188] have observed, the mean free path\(^1\) of the vapor atoms in this environment is short enough to result in significant vapor atom scattering and redirection in the processing chamber as a result of collisions with carrier gas atoms. Consequently, DVD should exhibit a similar high throwing power\(^2\) when compared to high vacuum deposition techniques [12, 50], leading to more efficient materials utilization, faster processing, and lower final product cost when depositing material onto curved or uneven surfaces.

- **For those material systems which are difficult to process in conventional e-beam or sputtering systems,** DVD’s use of a gas jet may facilitate mixing of vapor from different sources, allowing otherwise difficult to synthesize compounds and alloys to be fabricated rapidly. Material systems with widely different vapor pressures represent one area where DVD may provide important processing advantages (e.g. the addition of hafnium to nickel aluminide bond coat layers during TBC synthesis).

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\(^1\) **mean free path** - average distance between collisions with other atoms.

\(^2\) **throwing power** - ability to deposit vapor onto substrate surfaces that are not in the line-of-sight of the vapor source.
• If the carrier gas jet exits the flow tube (Fig. 3.1) with a high enough velocity, DVD atoms subsequently captured in the carrier gas stream should be accelerated. If acceleration occurs, the vapor atoms could impinge upon a substrate surface with 0.5 - 2 eV of kinetic energy. Such energy levels are comparable to the activation energy for surface diffusion [190]. Thus DVD adatoms could possess enough energy to increase their surface diffusion rates to low energy sites above levels observed with established thermal evaporation methods. Substrate bombardment by energetic carrier gas atoms might also aid in beneficial atomic rearrangement in a growing film [29 - 33]. While increasing adatom energy from thermal levels of 0.1 - 0.2 eV to enhanced energy levels of 0.2 - 2 eV, the DVD method should not raise energy levels to the point where substrate damage [191] or material sputtering can occur [16], as in ion plating.

• If DVD can enhance adatom kinetic energy, there will also exist an increased possibility of athermal atomic reconstruction at the growth surface as the result of impacting energetic vapor atoms moving across the substrate surface before settling in a preferred low energy surface site. Thus the DVD process could construct useful microstructures at reduced substrate temperatures, thereby reducing the importance of bulk diffusion. The ability to synthesize film products at reduced substrate temperatures could be critical to economic fabrication of numerous products (e.g., flat panel displays) (See section 1.2.).

• The creation of e-beam evaporant in a low or medium vacuum provides a natural environment for reactive deposition which combines elements normally in the vapor phase with those in the solid phase. Since DVD introduces gas into the processing chamber as part of its standard material synthesis routine, the DVD material synthesis environment will hopefully be able to produce not only pure materials but also compounds created via vapor / gas interaction during transport to the substrate. Compounds difficult to process in high vacuum could be more easily created in a reactive DVD carrier gas jet (e.g. yttria-stabilized ceria for thermal barrier coatings (TBCs)).
• The DVD process should take advantage of the high rate, energy efficient evaporation capability of electron beams [11]. Electron beam systems have demonstrated an ability to process a large array of pure metals, alloys, and compounds and to deposit material at rates as high as 1 mm/min over hundreds of square centimeters. In an industrial setting, high product throughput and economic power utilization can be keys to a process’ viability.

• The processing vacuum of DVD should be conducive to rapid batch or continuous material synthesis. While utilizing the well characterized electron-beam evaporation tool, DVD will operate this tool in a low vacuum environment, a distinct departure from conventional e-beam processing. As a result DVD will be able to employ high pumping capacity rotary piston pumps with mechanical boosters. These pumps are able to evacuate the synthesis chamber to process vacuum in less than two minutes, a significantly shorter time than the 20 minutes to 3 hours required by high vacuum diffusion or cryogenic pumps utilized in conventional, reactive evaporation (RE), or activated reactive evaporation (ARE) e-beam deposition systems [192, 193]. In an industrial setting, a decrease in product synthesis time directly correlates with a decrease in product cost.

In sum, should the DVD system conceived of in this chapter demonstrate an ability to create useful materials economically, it could become a valuable tool for the manufacture of products as varied as thermal barrier coatings for aircraft turbine blades, polycrystalline silicon deposits for thin film transistors, and metal matrix composites for high temperature structural applications.
Chapter 4

DVD System Design

In its most basic form (Fig. 3.1), the proposed Directed Vapor Deposition (DVD) system will consist of four primary components: a source of material to be evaporated, a means of creating an atomistic vapor from the source, a flow of carrier gas in which the atomistic vapor is transported through the processing chamber, and a substrate upon which the vapor deposits. As discussed in Chapters 1, 2, and 3, an electron beam gun was identified early in the technology development process as the desired source material evaporation tool because of its ability to vaporize refractory (i.e. high melting point) materials rapidly and cleanly. To create a basic but effective demonstration of the DVD concept, the design work described in this chapter seeks to integrate e-beam technology into a low vacuum processing environment where the vapor stream generated by the e-beam from a crucible can be captured in a carrier gas stream for transport to a chosen substrate. Central to this design approach is the thought that placing e-beam evaporant in a carrier gas stream might improve the vapor stream’s characteristics for specific applications (e.g., spatial, angular, and energy distribution as described in the Background chapter), making the technology an important vapor phase material synthesis tool. This chapter describes the trade-offs in specifications of the many DVD system components which will fit together to form the
DVD material synthesis tool. As the work of this chapter will demonstrate, detailed analysis of the basic idea laid out in Chapter 3 is required before the DVD concept can be reduced to practice in a functioning material processing system.

4.1 Electron Beam Gun

Although most electron beam gun technology has been developed to operate in systems in which both the gun and processing chamber are maintained at medium or high vacuum, the Background chapter (section 2.1.3.) noted that there exists no scientific barrier to employing an e-beam gun in a system which maintains a low vacuum in its processing chamber, as desired for the DVD system. To create such a system capable of processing refractory materials at high rates, numerous analyses must be made before a gun for the DVD system can be specified. The primary design issues for the gun include specification of the maximum power generation capability and the required e-beam accelerating voltage, selection of the beam generation mechanism, and choice of desired e-beam characteristics (e.g. beam diameter and scanning radius/rate).

4.1.1. Maximum e-beam gun power requirements

Specification of the maximum e-beam gun power capability for new (high or low vacuum) evaporation systems is challenging because of the uncertainty involved in determining the magnitude of the various e-beam energy losses between generation of the beam and generation of the vapor. The amount of e-beam energy actually available for material evaporation in a DVD system depends upon the energy losses which include those described in various references [11, 37] as well as additional energy sinks resulting from the low-vacuum DVD operating environment:
• Inside the gun due to some fraction of the beam impinging on various portions of the gun,
• In the gas and vapor cloud due to electron scattering collisions,
• From the evaporant material surface as a result of electron backscattering,
• Through conduction into the crucible containing the melt material,
• From the radiating molten evaporant surface, and
• Through convection caused by the gas jet blowing across the evaporant surface.

Schiller [11] and Storer [21] have indicated that, in a conventional high vacuum e-beam system employing a water-cooled crucible, the standard energy sinks listed above can lead to as little as 10% of the initial beam power actually being transformed into source material evaporation energy. Calculation of a necessary e-beam gun power capability for the DVD system assumed that even less of the initial beam power, as little as 3 - 3.5%, would actually contribute to material evaporation. This small number was selected for gun power calculations since energy losses in the DVD system should exceed those in a conventional e-beam system due to increased beam dissipation inside the gun and in the low vacuum environment and due to gas jet convection.

One of the materials of primary interest for fiber coating in the e-beam DVD system was titanium. An e-beam power calculation was undertaken to determine how powerful an e-beam gun would be required to deposit titanium in the DVD system. This calculation assumed that the temperature of the melt had to be raised to the material’s boiling point. In fact, studies have shown [11] that controlled e-beam evaporation typically occurs below the material’s boiling point at a source vaporization temperature ($T_v$) which induces an equilibrium vapor pressure of about 1 Pa. During calculation of the power requirement results of Table 4.1, determination of $\Delta H$ up to a vapor pressure of 1 Pa rather than the boiling point generally decreased the power required by about 10%. However, given the
uncertainties in power losses throughout the system, using the boiling point rather than the 1 Pa vapor pressure point was considered an acceptable safety factor.

Table 4.1: Thermophysical data
Calculation of power required to evaporate materials in the DVD system [194, 195].

<table>
<thead>
<tr>
<th>Elements</th>
<th>Al</th>
<th>Cu</th>
<th>Mo</th>
<th>Ni</th>
<th>Nb</th>
<th>Si</th>
<th>Ti</th>
<th>V</th>
<th>Y</th>
<th>Zr</th>
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</thead>
<tbody>
<tr>
<td>At. Wt. (g/mol)</td>
<td>27.0</td>
<td>63.6</td>
<td>95.9</td>
<td>58.7</td>
<td>92.9</td>
<td>28.1</td>
<td>47.9</td>
<td>50.9</td>
<td>88.9</td>
<td>91.2</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>2.70</td>
<td>8.96</td>
<td>10.2</td>
<td>8.90</td>
<td>8.57</td>
<td>2.33</td>
<td>4.54</td>
<td>6.11</td>
<td>4.47</td>
<td>6.51</td>
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<tr>
<td>$T_m$ (K)</td>
<td>933</td>
<td>1356</td>
<td>2893</td>
<td>1726</td>
<td>2740</td>
<td>1683</td>
<td>1940</td>
<td>2188</td>
<td>1803</td>
<td>2130</td>
</tr>
<tr>
<td>$T_b$ (K)</td>
<td>2793</td>
<td>2840</td>
<td>4880</td>
<td>3180</td>
<td>5010</td>
<td>2628</td>
<td>3560</td>
<td>3680</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>20.7</td>
<td>22.6</td>
<td>24.1</td>
<td>17.0</td>
<td>23.7</td>
<td>23.9</td>
<td>22.1</td>
<td>20.5</td>
<td>23.9</td>
<td>22.0</td>
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<tr>
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<td>12.3</td>
<td>5.6</td>
<td>1.2</td>
<td>29.5</td>
<td>4.0</td>
<td>2.5</td>
<td>10.0</td>
<td>10.8</td>
<td>7.55</td>
<td>11.6</td>
</tr>
<tr>
<td>c x 10$^{-5}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-4.1</td>
<td>-</td>
<td>0.8</td>
<td>0.3</td>
<td>-3.8</td>
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<tr>
<td>a</td>
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<td>29.7</td>
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<td>-</td>
<td>32.6</td>
<td>36.0</td>
<td>43.1</td>
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<td>b x 10$^3$</td>
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<td>4.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>c x 10$^{-5}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-9.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$L_f$ (kJ/mol)</td>
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<td>13.0</td>
<td>35.5</td>
<td>17.2</td>
<td>29.3</td>
<td>50.7</td>
<td>17.5</td>
<td>16.7</td>
<td>11.4</td>
<td>19.3</td>
</tr>
<tr>
<td>$L_e$ (kJ/mol)</td>
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<td>306</td>
<td>590</td>
<td>375</td>
<td>681</td>
<td>386</td>
<td>427</td>
<td>456</td>
<td>371</td>
<td>575</td>
</tr>
<tr>
<td>$\Delta H$ (kJ/mol)</td>
<td>372</td>
<td>350</td>
<td>744</td>
<td>498</td>
<td>659</td>
<td>475</td>
<td>550</td>
<td>575</td>
<td>508</td>
<td>661</td>
</tr>
<tr>
<td>Power (kW)</td>
<td>6.4</td>
<td>8.5</td>
<td>14</td>
<td>13</td>
<td>10</td>
<td>6.8</td>
<td>9.0</td>
<td>12</td>
<td>4.4</td>
<td>8.1</td>
</tr>
</tbody>
</table>

c$_p$ = Specific heat at constant pressure

$L_f$ = Latent heat of fusion

$L_e$ = Latent heat of evaporation

The e-beam gun power required to evaporate some material at a specified rate can be determined using the data of Table 4.1 and the following equation [11]:

$$W = \frac{r_e \Delta H}{V\varepsilon}$$  \hspace{1cm} (4.1)

where $W$ = Power required (W), $r_e$ = Evaporation rate (m$^3$/min), $\Delta H$ = latent heat of evaporation (kJ/mol), $c_p$ = specific heat (J/K mol), $L_f$ = latent heat of fusion (kJ/mol), $L_e$ = latent heat of evaporation (kJ/mol), $V$ = volume (m$^3$), $\varepsilon$ = evaporation rate (m$^3$/min), and $r_e$ = evaporation rate (m$^3$/min).
\[ \Delta H = \text{Enthalpy required to raise material from room temperature to evaporation temperature (kJ/mol)}, \]

\[ V = \text{Molar density of material (m}^3/\text{mol)}, \]

\[ \varepsilon = \text{Efficiency of energy utilization (3 - 3.5\%).} \]

For titanium deposition using DVD, the following material deposition parameters were specified based upon general industry specifications for the MMC application [20]. The gun should be capable of depositing material at a rate of 10 - 15 µm/min [21] onto 10 meters of 140 µm diameter, rotating fiber (e.g. SCS-6 SiC fibers rotating at 10 rpm) at 20% deposition efficiency. (All of these numbers factor into a determination of \( r_e \), the evaporation rate required in the system.) Calculation shows that about 9 kW of initial beam power would be required to evaporate titanium for the desired rate of coating. As a result of this calculation, a 10 kW gun was specified. For comparison, the power required to coat an identical substrate with other materials is shown at the bottom of Table 4.1.

### 4.1.2. Accelerating voltage selection

Although the calculations of the previous section produce a reasonable gun power specification, that specification is based on several assumptions: deposition efficiency (20%) and energy utilization efficiency (3 - 3.5%). Refining the deposition efficiency specification is difficult because a DVD system does not yet exist to coat fibers and determine the material utilization capabilities of the system. The energy utilization efficiency is also difficult to quantify without an actual system to analyze. However, to ensure that the gun can evaporate material at a rate greater than or equal to that which is desired, energy utilization efficiency can be maximized through the choice of an appropriate e-beam accelerating voltage which will minimize e-beam energy dissipation during travel from cathode to target. As noted in section 2.1.3., the actual beam power transmitted to the evaporation mater-
rial will be less than 10 kW due in part to beam energy dissipation as a result of atom / electron scattering interactions in the gun and chamber. The discussion in the Background section noted that increasing the accelerating voltage and thereby decreasing the scattering cross-section of the atoms in the chamber would increase beam propagation through the low vacuum. To ensure an ability to evaporate rapidly even high melting point materials (e.g. graphite, tungsten, and molybdenum), an accelerating voltage / carrier gas combination should be chosen which will transmit as much as possible of the beam’s initial energy to the source material.

The amount of electron beam scattering which occurs between the initial electron source and the final target depends upon the number of gas atom / electron interactions which occur (i.e. the gas pressure in the chamber), the range of the gas atom / electron interaction potential (Range increases with gas atom atomic number.), and the length of time over which the electron is acted upon by the interaction potential. This final element, length of time, is directly proportional to the velocity of the electrons in the beam where the velocity is determined by the accelerating voltage utilized in the gun (Higher accelerating voltages correspond to higher velocities.). Arata [49] has proposed equations, based upon experimental study, which describe electron-beam penetration through an inert gas with reasonable accuracy using a modified Bethe stopping power formula. (The Bethe range is considered to be the total distance that the beam’s electrons can travel through the gas before losing all of their energy [48].) The expression proposed by Arata [49] was:

\[ B = B_o \left(1 - \frac{h}{R_e}\right)^{1/2} \]  

(4.2)

where \( B \) = Beam voltage at distance \( h \) (m) from nozzle exit (kV),

\( B_o \) = Initial beam voltage (kV), and
\[ R_e = \text{Electron range (m)}. \]

\( R_e \) is a complicated function of the initial electron energy, the classic radius of an electron, and the temperature, density and atomic number of the gas in the chamber [49]. Equation (4.2) assumes that the gas density is constant along the e-beam path and that “above a certain fractional energy transfer, \( \varepsilon_1 \), the atomic electrons can be regarded as free, so that Moller’s cross section for scattering of free electrons by free electrons at rest in [sic.] Born approximation is applicable [196].” Moller’s cross-section is simply a description of the range of the interaction potential between the free electrons in the e-beam and free electrons at rest (i.e. around a gas atom nucleus).

Fig. 4.1 shows the predictions of Arata’s equation for an electron-beam propagating through various helium or argon pressures. Beam propagation through the lower atomic

Figure 4.1 **Electron beam propagation in low vacuum.** The distinctly different electron propagation distances (Bethe ranges) in helium and argon are illustrated for ambient temperature and various pressure conditions.
number helium is superior because of the shorter range electron / atom interaction potential in that system. While the propagation of electrons through helium is clearly better, Fig. 4.1 indicates that the use of low partial pressures of other inert (e.g., argon) or perhaps even reactive carrier gases (e.g. oxygen) is feasible should it offer some processing advantage. Given the results of Fig. 4.1, helium was chosen as the primary inert carrier gas in the DVD system, and the e-beam accelerating voltage was specified as 60 kV. This accelerating voltage level was selected to afford fairly efficient beam propagation while minimizing cost and x-ray problems associated with higher accelerating voltages [11].

4.1.3. Selection of an e-beam generation source

As Schiller et al. [11] explain in their book *Electron Beam Technology*, various types of electron generating cathodes are available for use in e-beam systems, including wire, strip-type, and solid cathodes. Filaments for e-beam systems are generally made out of tungsten, a tungsten-rhenium alloy, or lanthanum hexaboride (LaB₆). LaB₆ filaments generally require vacuums of at least 5x10⁻⁶ Torr (~5x10⁻⁴ Pa) or better to minimize reaction with the oxygen in air. This requirement makes LaB₆ an unlikely material for use in the DVD system where pressures in the beam generating space could reach 8x10⁻⁵ Torr. In addition, LaB₆ filaments usually generate just 10 - 100 µA of beam current [11]. Given that:

\[ W = IB \quad (4.3) \]

where \( I \) = Beam current (A) and \( B \) = Beam accelerating voltage (kV),

a LaB₆ system with a 60 kV accelerating voltage and 100 µA of beam current would generate at most 6 W of power rather than the required 9 kW! Thus, LaB₆ filaments, which
are often considered superior electron emission sources in electron microscopes, were
demed unacceptable in the DVD system due to the emission current requirements of the
DVD system and due to the vacuum requirements of a LaB$_6$ filament [11, 48].

For filaments made out of tungsten or a tungsten-rhenium alloy, strip-type and solid cath-
odes were easily eliminated from consideration. Strip-type filaments do not generate a
beam of electrons, as desired for the DVD application, but rather a planar-emitting sur-
face. Solid cathodes are generally used in much larger e-beam systems at the industrial
rather than research scale (i.e., systems generating 1.2 MW of power with a beam current
of 5 - 40 A, far more energy than is required for the system under design here). In consul-
tation with e-beam gun manufacturers [197], a small-area cathode in the form of a tung-
sten bolt cathode surrounded by a tungsten wire cathode inside of a Wehnelt cup was
selected to generate the beam electrons (Fig. 4.2). The Wehnelt cup serves to shape the ini-
tial beam generated from the bolt cathode by repelling the electrons and forcing them
down through the small hole in the electric field of the cup.

During operation, the tungsten wire cathode of this system is heated electrically by pass-
ing a current until it emits electrons via thermionic emission. These electrons bombard the
bolt cathode, heating it and leading to its own electron emission. Once the bolt cathode has
begun to emit electrons, electron bombardment from the wire cathode in combination with
direct electric current heating increases the bolt cathode temperature, increases its electron
current emission density, and results in a larger emitting surface than would be achieved
through bolt operation only [11]. During electron emission from the hot cathodes, a certain
fraction of the tungsten is vaporized. A portion of this tungsten is then ionized by the free
electrons in the system. This ionized tungsten subsequently bombards the bolt cathode
leading to its erosion, depositing tungsten vapor from the bolt onto the wire cathode and
Wehnelt cup, and necessitating bolt and wire cathode replacement every ten hours of oper-
4.1.4. **A modified e-beam deflection system was required**

In conventional e-beam gun systems, beam focussing and scanning are accomplished using electromagnets located within the body of the gun. Beam scanning is an integral feature of modern electron beam systems because it ensures rapid, uniform, controlled, atomistic evaporation from the largest possible target surface [11]. While beam focussing in a
Figure 4.3 Overall e-beam gun configuration for DVD. This system combines traditional e-beam gun elements (e.g. Wehnelt cup assembly, anode, and focussing coils) with newly developed components (e.g. pressure decoupling chamber, tungsten plug and aperture, and external beam scanning coils) to create a unique evaporation tool.

Low vacuum system can still occur inside the gun, scanning of the beam must be delayed until the beam passes through the foil window or gas flow limiting orifice separating the cathode filament from the processing chamber. This limitation of the conventional scanning system’s use in the DVD system is due to the addition of a specially-designed pressure decoupling attachment joining the gun to the processing chamber (Fig. 4.3). The
decoupling chamber provides an attachment for a medium vacuum pumping system which removes most of the gas entering the gun from the processing chamber and ensures that the gas pumping capacity of the high vacuum pump at the top of the gun is not exceeded when the cross-valve, separating the high vacuum portion of the gun from the rest of the system, is opened to provide an unimpeded beam path from cathode to target.

Gas flow from the chamber into the gun is restricted at the bottom of the decoupling attachment by a tungsten plug with a 2.5 mm diameter hole which allows beam passage into the processing chamber with minimal gas flow in the reverse direction. It is this small aperture which prevents normal e-beam scan coil operation. The standard coils of the conventional e-beam gun are still present in the DVD system. However, their work is limited to minor, constant beam deflections which ensure that the beam is always passing directly down the gun’s central axis and through the small aperture in the tungsten plug. The beam is able to pass through the 2.5 mm hole in the tungsten plug because the e-beam focus coils in the gun create a minimum beam diameter of 0.4 mm just at the point where the beam enters the process chamber.

To make possible scanning of the electron beam in the DVD system, a small set of scanning coils were designed and attached to the bottom of the gun as shown in Fig. 4.3. A custom, water-cooled x-y deflection coil system was built by Deuteron, Inc. (Sherborn, MA) and coupled with a two amp digital e-beam gun sweep supply, model XYC-10, supplied by The Eddy Co. (Apple Valley, CA) to deflect the beam across a 1.27 cm diameter evaporation target [194]. The selected digital sweep supply can store up to 99 scan patterns each with up to 89 dwell points across the target from which one pattern can be selected and scanned across the surface at 0.1 - 10 Hz (Fig. 4.4). The maximum sweep angle of the e-beam can be adjusted through the e-beam sweep supply by modifying the
4.1.5. Final e-beam gun configuration

A 10kW (maximum beam power)/60 kV (constant electron accelerating voltage) e-beam gun for the DVD system was designed and built in consultation with the Fraunhofer Institute for Electron Beam and Plasma Technology (F.E.P.) of Dresden, Germany (See Appendix A for detailed design drawings). The beam current of the F.E.P. high pressure evaporator (HPE) is adjustable in 1 mA increments from 1 to 170 mA. These current adjustments correspond to power increments of 60 W. The complete package delivered by F.E.P. included a power transformer, a computer control cabinet, and the e-beam gun itself.
The separate beam scanning system was subsequently attached to the bottom of the gun.

Figure 4.5 **The electron beam system delivered from Germany.** The three components of the electron beam evaporator delivered by F.E.P. of Dresden, Germany. (Photo courtesy of F.E.P.)

### 4.2 Processing Chamber

A second important component of the DVD system which had to be designed and built was the vacuum chamber inside of which e-beam processing was to be performed. The primary design issues for the chamber involved 1) constructing a chamber which did not permit x-ray escape from inside the chamber out into the laboratory and 2) configuring the chamber so that multiple evaporant sources could be used to coat flat or fiber substrates
sequentially or simultaneously. X-rays were primarily generated from electron beam interaction with the nozzle of the gun and with the evaporated source material. Although the initial system constructed for this dissertation research utilized only a single evaporant tool, provision was made in the design of the chamber to allow the option of adding two other vapor sources at a later date.

4.2.1. X-ray shielding for system user protection

The 60 kV accelerating voltage of the DVD system’s e-beam gun is capable of generating x-rays from the lightest elements up to the Kα1 x-ray of tungsten (energy = 59.32 KeV) [48, 198]. To protect individuals near the system during its operation, the walls of the processing chamber had to be designed to absorb these x-rays. Goldstein et al. [48] succinctly explain the basic mechanism of x-ray absorption:

“X-rays as photons of electromagnetic radiation can undergo the phenomenon of photoelectric absorption upon interacting with an atom. That is, the photon is absorbed and the energy is completely transferred to an orbital electron, which is ejected with a kinetic energy equal to the photon energy minus the binding energy (critical ionization energy) by which the electron is held to the atom. X rays can also be lost due to scattering.... Photoelectric absorption by electrons in a specific shell requires that the photon energy exceed the binding energy for that shell. When the photon energy is slightly greater than the binding energy, the probability for absorption is highest.”

Goldstein et al. [48] also provide an equation to describe the attenuation of x-rays passing through a material. They show that:

\[
\frac{I}{I_o} = \exp\left[-\left(\frac{\mu}{\rho}\right) \rho h\right]
\]

where \( I \) = X-ray intensity after passing through a material,
\[ I_o = \text{X-ray intensity before entering a material,} \]
\[ \mu/\rho = \text{Mass absorption coefficient of a material (m}^2/\text{kg),} \]
\[ \rho = \text{Material density (kg/m}^3\text{), and} \]
\[ h = \text{Distance penetrated by beam (m).} \]

The mass absorption coefficient for a material depends upon the element which generated the x-ray and the specific x-ray from that element which is being absorbed. Since the most energetic x-ray producible with a 60 kV accelerating voltage is a tungsten K\(\alpha_1\) x-ray and since most vacuum chambers are constructed of 304 stainless steel, an attempt was made to find a mass absorption coefficient for (K\(\alpha_1\))\text{W} in Fe. Despite extensive search of the literature, this data does not appear to be readily available [48, 198, 199].

Experiments at F.E.P. indicated that 4 mm of lead would be sufficient to cut emitted x-ray intensities by more than half and that 8 mm of lead would ensure operator safety. Examination of comparative x-ray attenuation data presented by Schiller et al. [11] indicated that for a 60 kV e-beam source, approximately 1.15 cm of steel would provide an equivalent amount of x-ray protection as 4 mm of lead. Thus, a safe chamber wall thickness was calculated to be 2.30 cm, and, after adding a small additional factor of safety, a stainless steel chamber wall thickness of 2.54 cm was specified.

In addition, viewing ports to permit direct observation of the evaporation process had to be covered with x-ray absorbing glass to protect observers of the process. The required glass thickness also had to be calculated. A search for x-ray absorbing glass found that Perkin-Elmer (Minneapolis, MN) manufactured x-ray shielding glass with a 25% lead content. Using the F.E.P. data for pure lead, 1.6 cm of this lead glass was deemed sufficient to absorb all generated x-rays. The glass was available in 0.64 cm thick pieces, and so three pieces were used to cover each window.
The processing chamber was manufactured by GNB Corporation (Hayward, CA), and once the DVD system was put into operation, x-ray emissions from the chamber were checked and monitored using a hand-held detector. While the detector did confirm that the chamber wall thickness and viewport glass specifications were sufficient to prevent x-ray emission from the system (i.e. no signal detected above background radiation), leaks were detected around the thin walls of the flange ports on the chamber, around the edge of the processing chamber door, through the exhaust flange leading to the processing chamber pump, and through the aluminum gate valve separating the medium vacuum pumping system from the gun. The flange port leaks and the medium vacuum pumping system leak were eliminated by wrapping them with lead tape. Future chamber designs should not have the flange ports extend from the side of the chamber. Instead they should be mounted flush with the thick chamber wall. All gate valves used on future systems should be made of stainless steel. Leaks around the door and through the large pump flange were eliminated by mounting additional stainless steel inside the chamber to absorb the x-rays. Improved chamber design at the outset, in consultation with F.E.P., could have eliminated x-ray leaks associated with the system.

4.2.2. The chamber could accommodate various sources and substrates

As initially envisioned, the DVD system should have the ability to employ several carrier gas streams either simultaneously or sequentially to deposit a variety of materials. Fig. 4.6 shows a setup using three jets where two use an inexpensive resistance heater to evaporate less reactive / low melting point metals just beyond their nozzle’s exit. Although only one source, an e-beam source, is installed as a part of this dissertation research, the vacuum chamber was constructed with three ports for vapor source insertion (See Appendix A for exact port positions.). This multisource configuration increases the number of materials
which could potentially be deposited via DVD. For example, in a conventional e-beam evaporation system, alloys containing elements with widely varying vapor pressures (e.g. Ti-Mg or Ti-Nb alloys) cannot be deposited stoichiometrically from a single evaporation source, and use of multiple crucible sources to accomplish the task can be quite inefficient (c.f. Fig. 2.1) [11]. In a DVD system, higher alloy materials utilization efficiency could be achieved by directing all of the vapor from separate sources towards a rotating substrate. These separate material sources could utilize different carrier gas jets and evaporation means (Fig. 4.6). (It is also conceivable that a single e-beam, scanned between the two or more material sources, could generate neighboring vapor streams which could be mixed and carried to the substrate by a single gas flow.)
Additionally, the design of the DVD system appears well suited for reactive compound deposition (Fig. 4.7). Use of the carrier gas jet as an integral part of the DVD material synthesis pathway makes reactive deposition a natural extension of pure metal vapor transport in an inert gas jet. Reactive elements can be introduced into the processing chamber as a portion of the primary carrier gas flow (See section 4.4.) or via another reactive gas injection system to reconstitute compounds decomposed during evaporation or to create new compounds with pure elements evaporated from the crucible. Such system flexibility considerably expands a DVD system’s material synthesis options (e.g., functionally graded materials). Heller describes in detail the means by which reactive gases can be introduced through an injection system as shown in Fig. 4.7 [200].

![Figure 4.7](image)

**Figure 4.7** Pathways for reactive material deposition in DVD. Reactive gases can be introduced before or after the metal vapor stream enters the carrier gas flow.

### 4.3 Crucible

A significant advantage of electron beam evaporation is the ability to bring the heating source, electrons, directly into contact with the source material to be evaporated. This avoids the need to conduct energy into the source material from hot, potentially reactive / contaminating crucibles or resistively heated wires. E-beam heating also allows enough
energy to be supplied to the source material for the evaporation of high melting point (refractory) materials. E-beam heating of the source usually results in the formation of a vapor-emitting molten pool which must be contained and controlled so that the molten top of the source does not run down the side of the feed rod like wax down a candle. This can be accomplished by placing the source material inside of a water-cooled crucible which cools the edge of the rod-stock sufficiently to contain the molten pool of evaporant inside a solid well of its own material, avoiding reactive contamination of the evaporant pool by the crucible.

A 1.27 cm diameter feed rod was chosen based on the known e-beam power and scanning coil deflection capabilities (section 4.1). In addition, the top of the crucible was carefully designed for use in the DVD system to minimize disruption of the carrier gas flow during operation (Fig. 4.8). The thickness of the crucible’s rodstock containing wall was mini-

Figure 4.8 **DVD’s unique crucible design.** The crucible design minimizes carrier gas stream interference from the vapor source while ensuring proper water cooling and rod stock containment.
mized and raised above the main portion of the water-cooled crucible so as to present a minimum cross-section to the gas flow. Sufficient cooling to this exposed crucible region was ensured by machining the entire center section of the crucible from one cylindrical piece of copper placed directly in contact with chilled cooling water. (For detailed crucible design drawings, see Appendix A.)

The DVD system crucible was constructed by Strohecker, Inc. (East Palestine, OH) to allow a 1.27 cm diameter rod of source material to be fed continuously up through the center of the water-cooled, copper crucible. An Aerotech, Inc (Pittsburgh, PA) computer-activated motor (model 140SMP) and multitasking motion controller (Unidex 100) was located outside the chamber and used to push the source material up to the top lip of the crucible. The motor’s rotary action was fed into the processing chamber using a Ferrofluidic, Inc. (Nashua, NH) model SS250CFCB rotary motion feedthrough. The rotary motion of the motor and feedthrough were converted to a translational motion via a rack and pinion gearing arrangement inside the chamber, directly beneath the source rod (Fig. 4.9).

4.4 Gas System

In the DVD system, the evaporated source material will be entrained in an inert or reactive gas flow and transported towards a substrate. One of the major concerns associated with low vacuum processing, which was noted in the Background section, is potential contamination of deposited films as a result of the gas in the chamber. To ensure that pure material films could be created using DVD technology, a gas introduction system was designed to minimize the concentration of carrier gas born contaminants in the system (Fig. 4.10). In addition to ensuring that gas introduced into the system was pure, the gas system had to be capable of regulating the rate of gas flow through the system and controlling the gas pressure ratio between the mixing and processing chambers.
To ensure uncontaminated deposits, high purity (99.999% pure) compressed gas cylinders of helium or argon were selected as the initial source of the carrier gas introduced into the system. While this gas purity level is reasonably good, many applications require that moisture and oxygen contamination levels be reduced to the level of parts per million or parts per billion to ensure quality material creation [5]. Thus, after leaving the gas bottles, further cleansing of the gas flow was undertaken. From the compressed gas cylinders, the carrier gas was conducted through stainless steel tubing and into a continuously operating purification (gettering) system to reduce oxygen and moisture levels below one part per billion.
billion and total impurity levels into the low parts per thousand million range. The Semi-Gas Systems (San Jose, CA) model L-2000 purifier utilizes beaded, porous, chemically stable organometallic polymers that irreversibly bind to a variety of vapor-phase impurities to produce a clean gas flow. At present a purification system has not been installed to remove moisture or other contaminants (e.g. carbon monoxide, carbon dioxide) from reactive carrier gases (e.g. oxygen).

Figure 4.10 A schematic showing the DVD system configuration. In the low vacuum DVD system, electron beam evaporated source material is transferred to a substrate by a directed gas flow entering the chamber through a nozzle.
Having established a means of gas purification, the rate of gas introduction into the system had to be precisely regulated so that repeatable experimental conditions could be established. To control gas flow rates, a parallel array of computer-activated mass flow control valves was inserted into the gas feed line of the DVD system. The mass flow control valves and their accompanying multigas controller were purchased from MKS, Inc. (Andover, MA) since this system allowed up to eight flow valves to be regulated through one controller. Although only two flow valves were initially installed, additional flow valves for other (reactive) gases or for second and third evaporation sources could be installed in parallel at a later time if needed.

The flow valves were calibrated for helium and argon and monitored by a model 647B MKS multigas controller. Mass flow rates were determined within the flow valves by measuring the heat required to maintain an elevated temperature profile along a laminar flow sensor tube built in parallel to the main laminar flow of gas through the valve. For a specific flow meter range and gas species, flow is proportional to the voltage necessary to maintain a constant temperature profile. The MKS sensing technique uses three heaters to create a known temperature profile along the sensor tube, and then maintains that profile during gas flow by means of an auto-balancing bridge circuit [201]. Argon and helium are sensed identically by the flow valves due to their similar thermal conduction properties, and thus combinations of the two gasses from a precisely mixed compressed gas cylinder can be passed through the flow valves and simultaneously regulated. The two valves installed for use with the e-beam evaporation source can control up to 10 standard liters per minute\(^1\) (slm) and 200 slm of gas flow respectively. While the 200 slm valve (model 1562A) is rated to control flows as low as 3 slm, its flow control at this level was found to fluctuate too much to provide constant experimental flow conditions, necessitating paral-

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\(^1\) standard liter - one liter of any gas at atmospheric pressure and room temperature.
Installation of the 10 slm valve (model 1259C) for use in low gas flow experiments. Installation of this second flow valve made possible the precise control of gas flows as low as 0.1 slm.

After purifying and regulating the gas flow through the DVD system, an additional mechanism had to be incorporated into the system design to allow variation of the pressure ratio between the mixing and processing chambers (Fig. 4.10). As explained in section 2.2.3., the ratio of gas pressures between the mixing chamber and the processing chamber controls the carrier gas jet velocity as it travels through the processing chamber and interacts with the substrate. An ability to change carrier gas velocity could correlate to changes in vapor transport and deposition characteristics affecting material property development. While fluid dynamics studies [116] have shown that the velocity in the throat of the nozzle can be at most sonic (Mach number, M = 1), the carrier gas accelerates to a higher Mach number and velocity, as predicted by equations (2.19) and (2.20), upon entering the processing chamber if flow at the throat is choked\(^1\). The maximum flow velocity attained depends upon the exact pressure ratio reached in the system.

In the DVD system (c.f. Fig. 4.10), two subsystem components were added to the gas flow system to make possible variation of the carrier gas velocity. To change the mixing chamber/processing chamber pressure ratio, either nozzles can be attached to the end of the gas flow tube leading from the mixing chamber into the processing chamber or a variable position throttle plate, located between the processing chamber and the main system vacuum pump, can be opened and closed. The nozzles allow the gas flow tube to be reduced from a maximum diameter of 2.2 cm. The mixing chamber / nozzle assembly was

---

\(^1\) choked flow - the type of fluid flow that occurs through a minimum area region (i.e. a nozzle) where the pressure ratio (mixing chamber / throat) is greater than or equal to that given by substituting M = 1 into equation (2.19).
designed by Hill [202], based upon design concepts presented in Fox and McDonald [116], and built by MDC (Hayward, CA). The nozzles designed for the system were straight orifice nozzles designed by Ratnaparkhi [203] as opposed to specially designed converging or converging / diverging nozzles. The variable position throttle plate was manufactured by GNB Corporation (Hayward, CA).

4.5 Vacuum Pumps

Critical to the proper operation of the DVD system are the vacuum pumps which maintain the proper vacuum levels in the e-beam gun and pull the carrier gas through the processing chamber at the necessary rates. Pumps for the high vacuum and medium vacuum portions of the e-beam gun were selected based upon pumping capacity specifications supplied by F.E.P. The chamber pumping capacity required to create a supersonic jet for a nozzle diameter up to 2.2 cm in chamber pressure between 1 Pa and 650 Pa (~0.01 - 5 Torr) was determined by Hill [202] using isentropic flow calculations (Appendix A).

In the DVD system constructed for this dissertation, the e-beam gun employs a differentially pumped gun column to generate an electron beam in a $10^{-8}$ Pa pressure zone evacuated by a Balzer (Hudson, NH) TPH330 double flow standard turbomolecular vacuum system in series with a Varian (Lexington, MA) SD300 roughing pump (total capacity = 22,200 l/min @ $10^{-7}$ Pa). Once created, the electron beam is transmitted with minimal energy loss down the gun column into a $10^{-4}$ Pa pressure region evacuated by an Edwards High Vacuum, Inc. (Poughkeepsie, NY) Model EH500 mechanical booster pumping package (a Roots type blower) in combination with an Edwards Model E2M80 (total capacity = 8500 l/min @ $10^{-4}$ Pa) direct drive, sliding vane type vacuum pump. Finally, the beam emerges into the evaporation chamber through the hole in the replaceable tungsten plug where experimental pressure conditions are maintained by a Stokes (Philadelphia, PA)
Model 1722 (total capacity = 30,000 l/min @ 10^{-2} Pa) blower package (a Model 412H11 rotary oil-sealed pump in combination with a Model 615-1 positive displacement, dry, high-vacuum booster).

4.6 Vacuum Gauges

Correct reporting of the vacuum pressures in the mixing and processing chambers of the DVD system is critical for assessing and controlling the vapor-phase material synthesis capabilities of the DVD system. These pressures and pressure ratios determine the Mach number and velocity throughout the carrier gas flow, process parameters likely to affect material property development. To ensure accurate pressure measurement in the mixing and process chambers, the three gauges mounted in this portion of the system were chosen to be gas independent capacitance manometer gauges which allow various process gases to be utilized during film synthesis without gauge recalibration. The two gauges on the mixing chamber and gas inlet tube are Leybold-Inficon (L.I.) model CDG100 vacuum gauges (East Syracuse, NY) while the gauge on the processing chamber is an Edwards High Vacuum, Inc. model 622AB. All three gauges can read pressures between 1 Pa and 10 KPa (~10^{-2} and 100 Torr). While the L.I. capacitance manometer gauges provide accurate readings at or near room temperature, the Edwards gauge guarantees accurate readings at gas temperatures up to 200° C (temperatures possibly generated by the DVD process and heater lamp warming of the gas).

In addition to the three gauges mounted on the mixing and process chambers, three more pressure measurement gauges mounted on the e-beam gun helped ensure proper gun operation by allowing pressures in the differentially pumped lower gun region and the high vacuum filament region to be monitored. E-beam gun specifications dictate that the vacuum level in the high vacuum portion of the system be better than 6.0 \times 10^{-4} Pa (~5 \times 10^{-6}
for proper bolt and wire cathode operation (section 2.1.3.). Pressure in this region is monitored using a L.I. thermocouple-type vacuum gauge (model TR901) in concert with a L.I. cold cathode vacuum gauge (model 850-610-G2). The dual gauge arrangement is required by the cold cathode gauge’s inability to operate at atmospheric pressure. Instead, it must be activated by the pressure reading of the thermocouple gauge after pressure in the high vacuum portion of the system drops below $1.9 \times 10^{-2}$ Pa ($\sim 10^{-4}$ Torr). The cold cathode gauge can read pressures as low as $1 \times 10^{-5}$ Pa ($\sim 10^{-7}$ Torr). Monitoring pressure in the gun is important to prevent damage to the gun or contamination of the filament as described in section 2.1.3. The two most likely reasons that the pressure in the high vacuum portion of the gun could be too high are that the cross-valve separating the high-vacuum region from the rest of the system has been opened before the processing chamber has been evacuated to processing pressure levels (0.001 - 5 Torr) and that the 2.5 mm hole in the tungsten plug at the bottom of the gun has been eroded and enlarged by excessive contact with the e-beam. Pressure in the medium vacuum portion of the gun is checked using another L.I. thermocouple gauge (model TR 901). The thermocouple gauge can read pressures as low as $1 \times 10^{-2}$ Pa. Readings from all six gauges were monitored by two L.I. digital readouts, models CM3 and CC3, capable of reading three gauges each and of being easily interfaced with a computerized data acquisition system.

### 4.7 Substrate Temperature Control System

As noted in Chapter 2, substrate temperature can be critical to the development of desired material properties. To provide flexibility in adjusting the temperature of the substrate, the DVD system was equipped with a temperature control system consisting of up to four Research, Inc. (Minneapolis, MN) heaters (model 5305-02) in combination with a power supply (model 609), an Omega (Stamford, CT) model CN76000 temperature controller,
and an Omega type J thermocouple. Each heater lamp has the rated ability of projecting 10 kW/linear meter onto a substrate 3.81 cm in front of the lamp. In a chamber without moving gas, these lamps could heat a substrate in excess of 1100°C. However, for gas flows between 1 and 20 slm, experiments in the flowing gas DVD system showed that properly tuned lamps could heat a flat metal substrate to just above 600°C.

4.8 Computer Control Methodology

The Directed Vapor Deposition system described in this dissertation represents a fairly sophisticated material synthesis tool comprised of numerous complicated subsystems. The individual monitoring and control of each subsystem was not deemed to be a safe or user-friendly mode of system operation. In addition, centralized computer control was identified as a way to facilitate data collection and minimize the number of consoles which had to be monitored, allowing the system operator to concentrate upon the experiment in progress. Development of a central operator/system interface was deemed critical to efficient system operation. Thus, every effort was made during system design to choose equipment (e.g. vacuum gauges, gas controllers, motor controllers, e-beam gun controller) which would make possible computer control of the DVD system.

Equipment manufacturers offered either serial or parallel interfaces for computer-based system monitoring and control. Both interfaces have strengths and weaknesses. Serial interfaces (e.g. RS-232, RS-485) can be hardware intensive since they must have a dedicated cable and interface unit installed in the control computer so that the computer knows from which device the signal is coming. If the control computer has a limited number of interface board “interrupts” available, the complexity of the system which can be controlled is limited. However, if sufficient hardware is available, serial connections can make possible rapid monitoring and control since the host computer does not have to
determine which device is transmitting data. It already knows which system component sends information to each dedicated serial board.

Parallel interfaces (e.g. IEEE-488.2 or GPIB) represent a more sophisticated communication interface since the IEEE standard specifies that all transmissions over its interface should include five bits of address information. This allows a total of thirty two ($2^5$) devices to communicate over one interface line and computer interface board (i.e. 1 computer plus 31 external devices). While this arrangement decreases the amount of hardware necessary for system interfacing, it limits control speed somewhat since address information must be sent with each signal and only one system component can send along the cable at any given time. Table 4.2 records the communications specification for each major piece of control equipment in the DVD system. For the current DVD system, the desired sampling rate was only about 1 sample / second, a rate sufficiently slow to make the IEEE-488 system configuration attractive.

### Table 4.2: Computer interface information for DVD system components

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Manufacturer</th>
<th>Model</th>
<th>Interface Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Beam Gun</td>
<td>F.E.P.</td>
<td>HPE 10/60</td>
<td>RS-232</td>
</tr>
<tr>
<td>Gas Flow Controllers</td>
<td>MKS</td>
<td>647B multigas controller</td>
<td>IEEE-488</td>
</tr>
<tr>
<td>Vacuum Gauges</td>
<td>Leybold Inficon, Edwards High Vacuum</td>
<td>CM3 or CC3 digital readout</td>
<td>IEEE-488</td>
</tr>
<tr>
<td>Source Feed Motor</td>
<td>Aerotech</td>
<td>Unidx 100 multitasking motion controller</td>
<td>IEEE-488</td>
</tr>
<tr>
<td>Heater Lamps / Thermocouple</td>
<td>Omega</td>
<td>CN76000 Temperature Controller</td>
<td>RS-485</td>
</tr>
</tbody>
</table>

In addition to the selection of hardware for computer / DVD system interfacing, a user / computer software interface also had to be selected. DVD system control was carried out
using National Instruments’ LabVIEW™ software version 3.0 running under MS Windows v.3.11 on a Gateway2000 486 CPU / 66MHz computer with 24 Mb of memory. LabVIEW™ allowed creation of a graphical user interface (GUI) from which the system operator can specify the file to which to save experimental run data, set gas flows, change e-beam powers, dictate motor actions, and observe real time graphs of pressure versus time data helpful in monitoring each experimental run (Fig. 4.11). Behind the GUI, Lab-

![Image of LabVIEW GUI](image)

**Figure 4.11** The graphical user interface developed for the DVD system. The LabVIEW™ front panel makes possible centralized DVD system monitoring, data acquisition, and open-loop control.

LabVIEW™ provided an object-oriented programming environment in which flow chart type
objects were connected by visual wires to form the necessary data acquisition and control algorithms rather than typing in traditional lines of computer code (Fig. 4.12).

Figure 4.12 **Object-oriented programming for the DVD computer interface.** This portion of the LabVIEW™ code monitors the user interface for changes in the desired gas flow through one of the mass flow controllers. If the user makes a change, the code sends the new value to the multigas controller which opens or closes the mass flow control valve to obtain the new flow level.

While the DVD system user can supply e-beam power setting information through the LabVIEW™ interface, the actual control of the e-beam gun occurs through an IBM PC compatible, 386 CPU computer and associated hardware dedicated to monitoring gun performance. Functions of this computer include ensuring that the cross-valve separating the high vacuum portion of the gun from the rest of the system is open, adjusting the power of the e-beam focussing electromagnets and executing a beam direction checking routine every time beam power is changed. The direction routine monitors the amount of current hitting the gun nozzle and anode and minimizes that current flow, thus ensuring that most
of the beam’s electrons are flowing out through the 2.5 mm hole in the bottom of the gun and into the processing chamber. If the nozzle or anode currents become excessive, the control computer automatically reduces the beam power to its lowest possible level while it attempts to correct the problem by varying the strength of the e-beam positioning coils. Once low nozzle and anode current readings are achieved (i.e. the beam is passing through the hole in the bottom of the gun), beam power is cycled back to the setting established through the LabVIEW™ front panel. The usual cause of a high anode current is an improperly assembled Wehnelt cup assembly. The most likely cause of an excessively high nozzle current is beam spreading caused by use of incorrect beam focussing currents (Fig. 4.3) or too high a chamber pressure. Once the strength of the electromagnetic field in the focussing coils is adjusted or the chamber pressure is reduced, beam spreading will diminish and the majority of the beam will pass through the opening in the bottom of the gun, allowing material synthesis to resume.

4.9 Concluding Remark

Having constructed the e-beam powered Directed Vapor Deposition system (Fig. 4.13), experiments could now be conducted and models of vapor transport developed to evaluate the system’s performance and to provide insight into how changes to the system’s process variables affected vapor transport in the system, particularly vapor adatom distribution, deposition efficiency, kinetic energy, and angle of incidence.
The assembled DVD system in the laboratory. This photograph shows the DVD system after all major components were assembled. To the right are the central control computers and hardware and the e-beam power supply. Behind the processing chamber and e-beam gun in the central portion of the picture are the vacuum pump for the lower portion of the gun (left) and the processing chamber vacuum pump (green).
Chapter 5

Experimental Investigation of Vapor Transport

5.1 Overview

As noted in previous chapters, the use of an electron beam gun in combination with a carrier gas stream sets Directed Vapor Deposition apart from other vapor phase materials processing systems. The experimental work described in this chapter seeks to establish the process boundaries of a first generation DVD system and to explore the basic vapor transport issues that define the boundaries and the system’s behavior within those boundaries. Fig. 5.1 shows the general geometric configuration for the DVD system used for all experiments described in this chapter. Three series of experiments were performed with this setup.

1. Without turning on the e-beam gun to evaporate material, either helium or argon gas was pumped through the system while nozzle diameters and throttle plate positions were changed. The resulting variation in pressure ratio between the mixing and processing chambers was measured to establish the carrier gas jet Mach number and velocity boundaries of the DVD system.
2. Without evaporating material, the electron beam was turned on and propagated through the carrier gas flow. This resulted in electronic excitation and possibly ionization of the gas stream that facilitated study of the structure of the gas stream.

3. The e-beam was used to evaporate copper which was then entrained in either an argon or helium gas flow. The green luminescence of the copper vapor atoms provided a convenient means of visualizing transport. This allowed the various processing parameters to be modified and the relationship between process parameters and vapor atom trajectories to be studied.

![Diagram of the DVD system configuration](image)

**Figure 5.1** The general DVD system configuration for all experiments described.

### 5.2 Accessible Processing Regime

Before utilizing the carrier gas flow to create films on flat or fibrous substrates, experiments were conducted to define the available carrier gas flow conditions for materials processing in this DVD system. Flow conditions were modified either by varying the amount
of gas pumped through the processing chamber per unit time or by changing the system’s upstream / downstream pressure ratio \(P_o/P_d\) (equation (2.19) and Fig. 5.1).

As noted in Chapter 4, the first generation DVD system allowed helium and / or argon carrier gas flow rates to be precisely varied between 0.1 slm and 200 slm by means of computer-controlled mass flow controllers. Initial evaporation experiments revealed that these upper and lower flow rate limits were not the defining boundaries of the DVD material processing environment. Instead, these boundaries were determined, at low gas flows (e.g. 0.1 - 1.0 slm of He), by an inability of the low density carrier gas jet to turn the vapor stream 90° towards the substrate as in Fig. 5.1, and, at high gas flows (e.g., 120 - 140 slm of helium or 15 - 30 slm of argon), by the maximum deposition chamber pressure rating of the e-beam gun.

To determine the carrier gas Mach number and velocity flow conditions available for materials processing in the DVD system, upstream and downstream pressure levels were recorded for different gas flow rates, nozzle diameters, and degrees of throttle plate closure. To determine the gas flow boundaries of the system, experiments were run with:

- Four different nozzle orifices (0.85, 1.27, 1.90, and 2.20 cm),
- Two different gas types (helium and argon), and
- A range of carrier gas fluxes (two to 200 slm).

The results of the carrier gas flow experiments are shown in Figs. 5.2 - 5.4. These figures highlight one of the boundaries for materials synthesis in the first generation DVD system, processing chamber upper pressure boundaries of 666 Pa for pure helium and of 133 Pa for pure argon. They also show that, for all pumping conditions attainable in the DVD system, the carrier gas flow entering the chamber reached supersonic velocity.
Because supersonic velocities are attained in the system, processing regimes, chamber pressures, and carrier gas fluxes are discussed in reference to Mach number to emphasize that all carrier gas expansions into the deposition chamber accelerate to supersonic velocities. Mach numbers listed throughout this chapter were calculated using the one-dimensional, isentropic flow relation of equation (2.19). While this relationship is only a one-dimensional approximation and is better suited for describing the Mach number associated with an optimal converging or converging/diverging nozzle [204], its use as a first level approximation is not unreasonable for the simple orifice-type nozzles employed here. Its use also provides a common scale against which to compare the gas flow results for differ-

**Figure 5.2** Available processing range (Mach number vs. chamber pressure). The shaded regions represent gas flow conditions available for material processing with the four nozzle diameters constructed for this dissertation. For a given nozzle diameter, the exact gas flow conditions in the system can be varied by changing the open/closed position of the “venetian blind” throttle plate.
ent nozzles, throttle plate positions, and gas flow rates. The velocity scale on the right side of Figs. 5.2 - 5.4 was calculated using equation (2.20) and represents the maximum carrier gas velocity which can be expected during processing. From these velocities, it is possible to compute a first approximation for the maximum energy which a vapor atom can attain in the carrier gas flow. For instance, using equation (2.4), if a copper atom is accelerated to 2000 m/sec, it will possess a kinetic energy of 1.32 eV.

Although Figs. 5.2 - 5.4 show gaps between the processing regimes accessible with the different nozzles constructed for this dissertation, these regions would certainly be available for materials processing with one or more nozzles of intermediate diameter. The

Figure 5.3 Available processing range (Mach number vs. carrier gas flux). Shaded regions to the left of the red dashed lines represent available processing conditions for each nozzle constructed for this dissertation when flowing pure helium through the system.
graphs also show that the available processing regimes of the different nozzles overlap at lower pressure processing conditions, affording an opportunity to explore the effect of nozzle diameter upon vapor transport and deposition.

Fig. 5.4 shows that the use of argon makes possible material processing at higher Mach numbers. However, while the attainable pressure ratio and Mach numbers are substantially higher for argon, equation (2.20) shows that the actual atomic velocities of the argon carrier gas jet in the processing chamber are in fact much lower. The flexibility to use the heavier but slower moving argon atoms alone or in combination with other carrier gases presents an additional degree of processing flexibility. Note that the portion of the shaded argon region actually available for materials processing in this first generation DVD sys-
tem is quite small. To enlarge this region, a higher accelerating voltage would need to be employed, to increase focussed beam penetration through the chamber gas prior to significant scattering. Experimentation indicated that deposition chamber pressures higher than about 133 Pa (1 Torr) led to an excessive gun nozzle current (See section 4.8.) which automatically shut down the gun. It also resulted in undesirable beam spreading in the chamber and contact of the beam with the scanning system. The gun manufacturer has indicated that a similar limit is reached when flowing helium through the processing chamber at a pressure of 666 Pa (5 Torr). Brief experimentation with helium suggested that the actual limit for this gas was somewhat higher than 666 Pa.

During actual evaporation runs, observation of the mixing and processing chamber pressures revealed a curious, repeatable effect. As a run progressed, the mixing chamber pressure (Fig. 5.1) slowly rose even though all other processing conditions were held constant, indicating that the carrier gas flow’s Mach number was slowly rising. Study of this effect revealed that its likely cause was heating of the nozzle. Using a thermocouple attached to the nozzle, a temperature rise to about 150°C was observed. The most likely cause of the heating was secondary electron bombardment of the nozzle due to backscattering from the surface of the rodstock [11]. It was hypothesized that bombardment of the nozzle led to heating and expansion of its stainless steel. The result of this expansion was a slight decrease in the diameter of the nozzle orifice and a greater pressure ratio between mixing chamber and deposition chamber. During certain extended runs this effect raised the system pressure ratio by as much as 10-20%. Constant pressure ratios could be achieved by adjusting the throttle plate position during the run, at the expense of a slight increase in the chamber pressure. The varying pressure ratio effect was secondary in nature since it affected all deposition runs only slightly, in the same manner, and could be controlled. In subsequent DVD designs, water cooling of the nozzle could minimize the effect.
Study of the carrier gas flow pressure ratios revealed that:

- All flows in the DVD system reached pressure ratios which accelerated the carrier gas to supersonic velocities.
- While argon can be used as a carrier gas, it generates a slower carrier gas velocity and can only be used in the current DVD system at chamber pressures up to 133 Pa (1 Torr) due to the larger electron scattering cross-section of argon.

### 5.3 Visual Observations of Gas Stream

When the DVD system e-beam was first turned on, it was apparent that electron beam interaction with a carrier gas jet led to luminescence in the optical spectrum as the result of excitation and ionization of the atoms in the carrier gas stream. This visible characteristic of the process provided a convenient means for study of the structure of the carrier gas stream. To record the effect of process parameter variation upon DVD carrier gas stream characteristics, photographs of the carrier gas flow were taken through the lead glass covered viewport on the front of the vacuum chamber using a 35 mm camera (with no special lenses or filters) and ASA 100 speed film. Conditions which were varied included the carrier gas flux (slm) and the carrier gas Mach number (again computed via equation (2.19)). For the gas flow visualizations a stationary e-beam (i.e. no scanning) was employed.

The results of section 5.2 demonstrated that for all DVD flow conditions, the gas exiting the flow tube and nozzle should accelerate to supersonic velocities. The shock wave structure of a supersonic free-jet\(^1\) expansion into low vacuum (Fig. 2.7) should be associated with this acceleration and subsequent deceleration [110, 112, 117, 118, 146]. This first

---

\(^1\) free-jet - A gas flow which has exited the confinement of a nozzle. If underexpanded (i.e. if the jet’s gas density is greater than the background pressure), jet expansion will occur “freely” until the background pressure in the nozzle exhaust region is matched.
series of experiments was designed to confirm the existence of this flow structure in the DVD system.

Initial visualization efforts were conducted with the crucible and substrate removed from the chamber. This allowed the unimpeded jet to be ionized by the e-beam and then travel without disruption to the far chamber wall. Initially the nozzle to e-beam separation was set at 3.5 cm (Fig. 5.5). For these experiments, the e-beam gun was turned on at 1.2 - 1.8 kW and passed through helium flows of 10 - 20 slm. Pressure ratios ($P_o/P_d$) corresponding to Mach 1.7 (1.27 cm diameter nozzle) and Mach 2.5 (0.85 cm diameter nozzle) conditions were established in the system. These tests did not reveal any of the structures noted in Fig. 2.7 even though a faint pink region of ionized helium gas flow was clearly visible.

Figure 5.5  **Initial system configuration for flow visualization.** Downstream from the e-beam, the initial DVD system configuration employed for carrier gas jet visualization (3.5 cm nozzle to beam separation) revealed only a faint pink region of ionized gas with no visible structure.
(Fig. 5.5), from the point of intersection of the e-beam and gas jet to the far wall of the processing chamber.

This puzzling result was resolved through additional study of the literature which emphasized that the structure of Fig. 2.7 should be present if the flow in the DVD system was actually supersonic. Scoles [118] indicated that the distance of the Mach disk from the end of the flow tube and nozzle could be calculated with reasonable accuracy given the nozzle diameter and pressure ratio (Mach number) utilized in the system:

\[
x_m = \frac{0.67 \cdot d \left( \frac{P_o}{P_d} \right)^{1/2}}{\gamma}
\]

where \( x_m \) = Mach disk distance from nozzle exit (m), and \( d \) = Nozzle diameter (m).

The literature also indicates that the diameters of the zone of silence and of the Mach disk should be ~0.75 \( x_m \) and ~0.50 \( x_m \), respectively [118]. (These dimensions are not as well defined as the Mach disk location, being more sensitive functions of the specific heat ratio \( \gamma \) and of \( P_o/P_d \) [118].) For the pressure ratios achievable in the DVD system, calculations indicated that for both the Mach 1.7 / 1.27 cm nozzle and Mach 2.5 / 0.85 cm nozzle flows of helium, the Mach disk should be located 2.3 cm downstream of the nozzle. Given the initial nozzle to e-beam separation of 3.5 cm, even if the primary zone of silence / Mach disk structure were present, it would not have been visible for either set of conditions since the ionization necessary for visualization occurred too far downstream.

To generate carrier gas flow ionization closer to the nozzle exit, a 2.2 cm long nozzle extender of inner diameter 2.2 cm was attached to the end of the flow tube. This decreased the nozzle to e-beam separation from 3.5 to 1.3 cm. Visualization experiments were again undertaken with a 1.27 cm diameter nozzle attached at the end of the nozzle extender. This
time argon rather than helium was used for the visualization study due to the greater brightness associated with its ionization (most probably the result of argon’s larger ionization cross-section). Note that, by employing argon rather than helium, both the Mach 1.7 and Mach 2.5 flows could be generated with the 1.27 cm diameter nozzle. The results of these visualization experiments at 50, 100, and 133.3 Pa for Mach 1.7 and Mach 2.5 flows are shown in Fig. 5.6.

For each set of conditions explored, the major flow structures of a supersonic free jet expansion (i.e. the zone of silence, the Mach disk, and the secondary “barrel” shocks [110, 112, 117, 118, 146]) were observed. While the zone of silence is just visible in the vicinity of the e-beam for the Mach 1.7 flow experiments, it is larger and more clearly visible in the Mach 2.5 flow runs as predicted in the literature. The sharp transition of the Mach disk is also dramatically evident. Estimates of the experimental separation between nozzle and Mach disk were made. They indicated a distance of 2.0 cm for the Mach 1.7 flows and 3.2 cm for the Mach 2.5 flows. These distances are within 10-15% of those predicted by equation (5.1). The agreement between the dimensions of the gas flow structure predicted in the literature and that observed in these experiments seems quite reasonable given the fact that equation (5.1) is a one-dimensional approximation best suited to an ideal expansion from a proper converging / diverging nozzle.

Adamson and Nicholls [117] explain that lower Mach numbers decrease the diameter of the zone of silence and the Mach disk. This trend is observed experimentally. To varying degrees, secondary barrel shocks are observed for all of the conditions explored. Interestingly, the persistence and width of the secondary shock structure varies with chamber pressure for a given Mach number. Higher chamber pressures lead to a broader and longer shock structure.

In general these studies confirm that:
Figure 5.6  **Gas flow structure.** Higher Mach numbers result in longer zones of silence. For one Mach number, higher pressures enlarge secondary shock structures.
• This first generation DVD system can generate supersonic flow. The dimensions of the supersonic flow structures in the DVD system agree with those predicted in the literature.

• For a given Mach number (pressure ratio) higher chamber pressures lead to greater persistence of the supersonic flow region.

The visible presence of these flow structures suggests that a vapor atom stream introduced into these flows may have a complex interaction with the flow structures and with substrates placed in the flows. To begin to understand these interactions, additional visualization experiments were undertaken in which crucible evaporation and substrates were added to the system configuration.

5.4 Gas Flow / Vapor Stream / Substrate Interactions

The visible characteristic of the DVD carrier gas and vapor streams provided a convenient way to study the mixing of the carrier gas stream with the vapor atoms leaving the crucible and the interaction of the combined stream with various substrates. To record the effect of process parameter variation upon DVD processing, photographs of carrier gas / vapor stream / substrate interaction were taken. Conditions which were varied included: carrier gas flux (slm), carrier gas Mach number (equation (2.19)), carrier gas type (argon vs. helium), and e-beam power (kW). E-beam scanning was employed during all evaporation visualization experiments. For all conditions investigated, the use of argon as the carrier gas instead of helium appeared to result in brighter luminescence of both the carrier gas and vapor atoms.
5.4.1. Carrier gas flux

The first set of full DVD system visualization experiments explored the effect upon vapor transport of varying carrier gas flux. While holding the carrier gas jet Mach number approximately constant, helium carrier gas jet fluxes were varied from 0.5 slm to 5.0 slm and then to 50 slm. While these gas flow conditions were transmitted through the chamber, copper was evaporated 3.5 cm downstream from the nozzle using 2.7 kW of e-beam power. The results of these experiments are shown in Fig. 5.7.

An increase in the carrier gas flux appears to lead to a more rapid entrainment of the vapor and a tendency for it to be transported along, rather than across, the flow’s streamlines. Figs. 5.7 b) and c) clearly show the ionized copper vapor stream being redirected by the carrier gas flow towards the substrate, albeit along distinctly different pathways. The presence of the vapor stream in Fig. 5.7 a) is much more difficult to discern. When the conditions for Fig. 5.7 a) were being established, the gas flow was reduced from about 3 slm to 0.5 slm. As this change occurred, the amount of visible copper vapor significantly decreased, indicating that vapor atom excitation probability is a function of gas pressure in the system [45]. It seems unlikely that less vapor was actually leaving the crucible as these low flow conditions were being established for at least three reasons:

- The beam power during the experiment was constant (2.7 kW). Therefore, over the entire gas flow range there was an essentially equal density of electrons available for metal vapor excitation and ionization.

- The literature [11] indicates that gas pressure above a crucible decreases the vaporization rate, indicating that the vaporization rate for the 0.5 slm conditions should be higher than for any of the other conditions observed even though its vapor is least visible.
Figure 5.7 **Vapor entrainment into carrier gas fluxes.** Increasing the helium or argon carrier gas flux by one or two orders of magnitude dramatically changes the trajectory of the copper atom stream. (E-beam power = 2.7 kW)
• Higher carrier gas fluxes convect significantly more heat away from the surface of the copper rodstock, decreasing evaporation rates. As a result, the evaporation rate for the 0.5 slm conditions should be higher than for any of the other conditions observed.

Even though the vapor stream was not clearly visible at 0.5 slm, the change in vapor atom trajectory was distinct as the gas flow decreased from 3 slm to 0.5 slm. As the gas flow decreased, the redirection angle of the vapor stream continually decreased and the vapor increasingly traveled up toward the bottom of the gun rather than toward the substrate positioned as in Fig. 5.1.

Observation of the vapor stream as the gas flow dropped toward 0.50 slm showed that the vapor distribution approached the \( \cos^n\theta \) vapor distribution normally observed directly above high vacuum e-beam heated vapor sources. As the gas flow was increased to 5.0 slm, interaction between the carrier gas flux and the vapor stream redirected the vapor in a broad swath towards the substrate. However, under these flow conditions much of the vapor stream appeared able to diffuse through or around the fast flow core of the carrier gas flux. This may be the result of the limited length of this fast flow region for a chamber pressure of 37.3 Pa (0.28 Torr). At much higher gas flows (50 slm), the vapor was confined to the bottom third of the extended fast flow region at 286 Pa (2.15 Torr) (Fig. 5.7 c)). This figure also reveals that under high gas flow conditions, a significant portion of the ionized vapor stream was redirected parallel to the substrate along with the carrier gas stream. This observation has troubling implications for high efficiency deposition onto flat substrates at elevated chamber pressures. In sum, for a constant Mach number, increases in chamber pressure lead to increased vapor transport along, as opposed to across, carrier gas flow lines.
5.4.2. *Mach number*

The next process variable investigated was Mach number, at constant gas flux (slm) and at constant chamber pressure (Pa / Torr). To avoid variations in carrier gas / vapor stream interaction due to changes in nozzle diameter, Mach number variations were confined to those possible with a single nozzle diameter of 1.27 cm. The crucible and copper rodstock were again positioned 3.5 cm downstream of the nozzle, and 2.7 kW of e-beam power were used for evaporation. Mach numbers were varied from 1.5 to 1.9. The results of these experiments for a constant 20 slm helium carrier gas flux are shown in Fig. 5.8. Note that while the carrier gas flux was held constant, an increase in Mach number led to a decrease in chamber pressure. Results for a constant helium chamber pressure of 93.3 Pa (0.70 Torr) are shown in Fig. 5.9. For this second set of experiments, a constant chamber pressure resulted in an increase in gas flow. The remarkable feature of all of these pictures is the lack of visible difference in the vapor stream trajectories. The pictures in Fig. 5.8 do show a slight broadening of the vapor stream with higher Mach number.

Each of these experiments revealed that a portion of the vapor stream was deflected parallel to the substrate (i.e., it is entrained in a wall jet), leading to deposition some distance from the carrier gas impact point with the substrate (or perhaps not at all). This phenomenon has important practical consequences for deposition distribution, efficiency, and material property development. As the vapor particles were turned into the wall jet, the component of their velocity vector carrying them towards the substrate decreased towards zero. It is therefore apparent that even if the entrained vapor contacts and sticks to the substrate, it does so at a greater incidence angle and with a lower energy. This fact is likely to affect the structure of the deposited film [29-33].

In summary, the range of Mach numbers available in the DVD system generate little change in the location of carrier gas / vapor stream contact with the substrate. It should be
Figure 5.8  **Constant carrier gas flux.** Variation of the carrier gas Mach number while holding its flux constant results in remarkably little copper vapor atom trajectory variation.

\[\begin{align*}
\text{a) } & \quad P = 161 \text{ Pa (1.21 Torr)} \\
& \quad \text{Mach Number} = 1.5 \\
& \quad \text{Carrier Gas Flux} = 20 \text{ slm} \\

\text{b) } & \quad P = 121 \text{ Pa (0.91 Torr)} \\
& \quad \text{Mach Number} = 1.7 \\
& \quad \text{Carrier Gas Flux} = 20 \text{ slm} \\

\text{c) } & \quad P = 93.3 \text{ Pa (0.70 Torr)} \\
& \quad \text{Mach Number} = 1.9 \\
& \quad \text{Carrier Gas Flux} = 20 \text{ slm}
\end{align*}\]
Figure 5.9  **Constant chamber pressure.** Variation of the carrier gas Mach number while holding the chamber pressure constant shows little copper vapor atom trajectory variation, like Fig. 5.8.

- **a)**
  - $P = 93.3 \text{ Pa (0.70 Torr)}$
  - Mach Number = 1.5
  - Carrier Gas Flux = 11.0 slm

- **b)**
  - $P = 93.3 \text{ Pa (0.70 Torr)}$
  - Mach Number = 1.7
  - Carrier Gas Flux = 13.6 slm

- **c)**
  - $P = 93.3 \text{ Pa (0.70 Torr)}$
  - Mach Number = 1.9
  - Carrier Gas Flux = 19.8 slm
noted that the minimal changes in vapor trajectories observed are for Mach number changes of only 15 - 20% in total magnitude. In contrast, the carrier gas flux variations recorded in Fig. 5.7 represent changes of two orders of magnitude. Thus a less dramatic vapor redirection effect can certainly be expected.

5.4.3. Carrier gas type / e-beam power

Although changing the carrier gas type from helium to argon modifies the carrier gas jet shock structure little [118], the difference in atomic mass of the two gasses and the different jet velocities generated by identical Mach numbers (Fig. 5.4) are likely to affect vapor atom trajectories during transport to the substrate. At the same time, examination of Fig. 5.7 shows the dramatic effect changing carrier gas fluxes has upon vapor trajectories. In principle a similar change in vapor atom trajectories might be observed if the vapor atom evaporation rate were significantly changed for a fixed set of carrier gas fluxes. To explore the effect of variations in the carrier gas type and vapor flux, two sets of visualization experiments were undertaken in which copper evaporation was performed using 2.1, 4.2, and 6.3 kW of beam power while flowing 25 slm of helium or 5 slm of argon into the system. The results of the experiments are shown in Figs. 5.10 and 5.11.

Both sets of pictures show similar trends. As the copper vapor flux increased (because of a higher e-beam power) the constant carrier gas stream was less and less able to direct the entire vapor stream towards the substrate. In addition, the overall vapor pathway became less focussed. This trend mirrors that recorded in Fig. 5.7 for decreasing gas flows. As the ratio of carrier gas atoms to vapor atoms increased at higher gas flows or lower vaporization rates, the vapor stream became more focussed. At 2.1 kW, both helium and argon flows rapidly turn the vapor stream almost immediately after it leaves the crucible. These same flows cannot turn the higher fluxes associated with 4.2 kW or 6.3 kW powers as rap-
Figure 5.10 **Effect of e-beam power variations in helium.** The redirection ability of a helium carrier gas flux diminishes as the copper vapor stream flux increases, even though all other conditions are constant.
Figure 5.11 Effect of e-beam power variations in argon. Despite a much lower carrier gas flux and chamber pressure, argon redirects the copper vapor stream in a similar manner to the helium flow of Fig. 5.10.
idly, despite the fast gas flow region clearly present all the way to the substrate in each of the argon deposition runs. The slight rise in chamber pressure for both sets of experiments results from an increased partial pressure of copper in the chamber at the higher e-beam powers. This variation of vapor atom trajectory with e-beam power has important implications for materials processing. Even though all other DVD parameters are held constant during a material synthesis run, changes in beam power lead to variations in the location of vapor impact on the substrate. As a result, it seems likely that the average energy and angle of vapor deposition will also change, potentially varying deposited film property development. Finally, note that 25 slm of helium are required to redirect the vapor stream along pathways similar to 5 slm of argon. While the argon atoms move slower than their helium counterparts, their vapor redirection abilities are much greater.

To summarize:

- For a given set of gas flow conditions, increasing the evaporation rate decreases vapor focus and increases the ability of the vapor stream to diffuse across or around carrier gas streamlines.
- For a given carrier gas Mach number and vapor atom composition, heavier (but slower) argon atoms redirect vapor atoms much more quickly than helium atoms do.

5.4.4. Carrier gas flux / vapor stream interaction with substrate / crucible

A final set of visualization experiments were undertaken to examine more closely the effect of interaction of the vapor containing jet with flat and fiber substrates and with the crucible. The substrate experiments specifically focussed upon gas flow rates above those studied in the previous subsections in an attempt to magnify subtle effects difficult to observe at lower gas fluxes. The results of these high gas flux experiments are shown in Figs. 5.12 a) and b). Both pictures reveal a similar wall shock structure previously observ-
Figure 5.12 *Flow interactions with substrates and crucible.* a) At elevated chamber pressures, a wall shock becomes visible directly in front of the substrate. Vapor entering this region is quickly redirected parallel to the substrate. b) A similar microwall shock is apparent in front of an array of SCS-6 fibers. c) Positioning of the crucible and rod stock too close to the carrier gas flux midline deflects the central jet stream, causing the entire flow structure to contact the substrate above its midpoint.
able only in Fig. 5.7 c), a bright region of luminescent gas and vapor directly in front of the substrate. Fig. 5.12 a) also shows that vapor entering this region is redirected parallel to the substrate and carried along the substrate surface in the wall jet. Careful observation of the wall jet during the experiment revealed that the vapor-laden wall jet separated from the substrate as its distance from the jet impact point increased. Vapor redirection caused by these wall shocks is likely to have significant implications for deposition efficiency and deposit material property development. The effect upon vapor transport of the microwall jet in front of the fibers is unclear. While the presence of these wall shocks at high gas fluxes does not prove their existence at lower gas flows, it seems reasonable to expect that the effect continues to affect vapor flow over some range of reduced fluxes for which ionization is insufficient to provide sufficient visualization of the effect.

Fig. 5.12 c) highlights the importance of keeping the crucible and source material below the fast flow region of the carrier gas jet. Jet interaction with the rodstock and crucible has deflected the combined stream at an elevated angle, leading to material deposition in a different substrate location, an undesirable inconsistency for high quality material synthesis.

In summary:

- Contact of the vapor-laden carrier gas jet with various types of substrates generates a brighter region of ionization, and perhaps a region of elevated pressure, which forces the vapor stream parallel to the substrate surface.

- Inserting the crucible into the primary carrier gas flow region changes the vapor atom trajectories for a given set of flow conditions.
5.5 Concluding Remarks

The results above have provided important insights into carrier gas / vapor atom / substrate interaction in the DVD process environment. The experimental flow visualizations indicate that the transport of evaporated material to a substrate is a sensitive function of the carrier gas atomic weight, carrier gas type (composition), vapor atom flux, and the deposition chamber pressure. As discussed in section 2.3, these variations have important consequences for a number of deposited film quality parameters.

The vapor transport process parameters uncovered in this chapter appear to affect DVD vapor deposition characteristics. However, although the results of this chapter allowed certain DVD material deposition trends to be postulated, further examination of DVD material synthesis appears necessary before definitive statements can be made. The next chapter provides initial insight into the utility of the DVD processing pathway for the deposition of high purity materials, the formation of polysilicon on glass at substrate temperatures below 600°C, and the synthesis of compounds via reactive deposition. The subsequent experimental chapter (Chapter 7) explores DVD material deposition through a series of deposition efficiency studies.
Chapter 6

Materials Synthesis Via Directed Vapor Deposition

6.1 Overview

Experimental work was undertaken to explore the ability of Directed Vapor Deposition to synthesize a variety of films in a low vacuum environment. Although extensive examination of specific material system applications will be left to future research, several sets of initial experiments were conducted to define the abilities of DVD to synthesize useful film structures. These investigations examined the ability of DVD:

- To deposit pure elements, without significant oxygen contamination from the carrier gas flow.
- To evaporate silicon for the creation of polysilicon films on glass substrates at substrate temperatures below 600°C.
- To deposit metal oxides reactively by evaporating pure metal sources and entraining oxygen in the carrier gas stream.

Fig. 6.1 shows the general geometric configuration of the DVD system for all experiments described in this chapter.
6.2 Contamination Study of Nonreactive Deposition

As noted in the Background chapter (section 2.1.3.), one of the major concerns in the scientific community regarding low vacuum vapor phase processing centers around the incorporation of contaminants into the deposited film from the gas in the chamber. To assess the ability of DVD to create clean, pure material deposits, copper (99.999% pure) and titanium (99.99% pure) obtained from ESPI (Ashland, OR) were separately deposited and the concentration of oxygen measured in each resulting film. For these studies, films approximately 80 µm thick were deposited in 30 minutes at a deposition rate of 2-3 µm/min. The substrate temperature was maintained at 200°C by substrate heaters. E-beam scanning was not employed for either deposition experiment. Instead, a fixed beam with a power of 1.5 kW was used throughout. A 10 slm purified helium gas flow was used to entrain vapor, and the processing chamber pressure was set at 95 Pa (~ 0.7 Torr) with a
mixing chamber pressure of 425 Pa (~ 3.2 Torr). These conditions resulted in deposition at a nominal Mach number of 1.58 through the 1.27 cm diameter nozzle.

In collaboration with P. Ratnaparkhi, the films were analyzed following deposition using Auger electron spectroscopy (AES) which has an oxygen detection limit of 0.1 atomic percent. After being introduced into the high vacuum Auger analysis chamber (P < 10^{-8} Torr), the samples were sputter cleaned insitu for a minimum of 45 minutes using a 3 keV argon beam to remove surface contaminants. Sputter rates were estimated to be about 400 nm/min for copper and about 200 nm/min for titanium. Once sputter cleaning had been completed, chemical analysis was immediately performed at electron beam energies of 3 and 5 keV.

Auger electron spectroscopy detects atomic composition close to the surface of a sample (within a few nanometers) through detection of a three electron process [205]. The initial incident electron, in this case an electron possessing 3 or 5 keV of kinetic energy, interacts with an atom near the sample surface and ejects an inner shell electron of that atom. Almost immediately the resulting inner electron shell hole of the atom is filled by an outer shell electron falling in to fill the gap. When the outer shell electron falls, it gives off energy, equal to the energy difference between its original shell and final shell positions. The energy released via this transition then either leaves the sample directly as an x-ray (the basis for x-ray photoelectron spectroscopy) or interacts with another outer shell electron which is subsequently ejected from the atom. The energy of this final ejected electron is what an AES system detects. The kinetic energy of the ejected Auger electron depends upon the specific element and intershell transition which generated it, allowing for electrons ejected from copper or titanium to be differentiated from those ejected from oxygen or carbon.
Chapter 6. Materials Synthesis Via Directed Vapor Deposition

An Auger scan obtained from this study shows the signal detected from a copper sample containing little oxygen contamination (Fig. 6.2). The auger analysis did not detect an oxygen signal which would have appeared at an energy of about 506 eV had more than 0.1 at. % of oxygen been present in the film. An extended Auger scan which focussed on the energy range around 506 eV and around the copper peaks allowed oxygen and carbon content of the copper films to be quantified at less than the detection limit of 0.1 at. % (equivalent to 1000 parts per millions (ppm)). For the titanium sample, auger analysis similarly indicated that oxygen incorporation into the titanium film during DVD processing was less than 1000 ppm [203]. The results of this section indicate that engineering films with low oxygen contamination levels can be created using Directed Vapor Deposition even though the technique operates at pressures above 10^{-3} Torr in the material synthesis chamber.

The analysis leaves unanswered the question of inert carrier gas incorporation into DVD films. Auger analysis cannot detect helium since helium has only two electrons. It seems unlikely though that neutral, inert helium would have any significant probability of bonding to the depositing film surface. However, the visualization studies of Chapter 4 suggest that there are excited and possibly ionized helium gas atoms in the chamber. The probability of these atoms binding to the film surface long enough to become incorporated into the film is not easily determined.

6.3 Study of Silicon Deposition

As a first attempt to investigate the ability of DVD technology to deposit a semiconducting material, a study of silicon deposition was undertaken. Silicon was deposited upon glass substrates to assess the quality and type (i.e. amorphous or polycrystalline) of microstructure created [206, 207]. For these experiments, a 5.08 cm diameter by 2.54 cm long, solid, phosphorous-doped (0.1 Ω-cm), single-crystal silicon ingot was used as the evapo-
The material was obtained from Virginia Semiconductor (Fredericksburg, VA). Due to the dimensions of the source material, it was not placed inside the crucible for evaporation. Instead it was set on a platform uncontained by any cooling apparatus.

Two runs were performed using helium as the carrier gas. The first run deposited silicon in a chamber maintained at 150 Pa (1.1 Torr) with a carrier gas Mach number of 1.5 (pressure ratio = 4.2) and a helium flow rate of 40 slm while the second run deposited material in a chamber pressure of 13 Pa (0.1 Torr) at a Mach number of 2.8 (pressure ratio = 26) and a helium flow rate of 5 slm. The 40 slm run made use of the 1.27 cm diameter nozzle to achieve its pressure conditions while the 5 slm run employed the 0.85 cm diameter noz-

Figure 6.2 An Auger electron spectroscopy scan of DVD deposited copper. This AES scan reveals little or no oxygen contamination in the deposited copper film.
zle. An unscanned electron beam with a power of 240 - 480 W was used to evaporate the silicon while stationary, unheated glass substrates were used to collect the deposit. The experimental system configuration was the same as shown previously in Fig. 7.1 for the deposition efficiency studies.

Initially, attempts were made to increase the e-beam power as a means of raising the silicon deposition rate. These attempts with an unscanned e-beam proved unsuccessful, with higher power runs leading to severe cracking of the silicon source material, highlighting the distinctly different evaporation behavior of a material like silicon when compared to a more thermally conductive material like copper. Study of thermal conductivity indicates that at 373.2 K copper has a thermal conductivity of 3.95 W/(cm K) while silicon has a conductivity of 1.08 W/(cm K) [208]. Since the silicon is unable to dissipate energy through heat conduction as rapidly as copper, it appears to disperse at least some of the e-beam’s energy via the formation of free surfaces (cracks) in the source material. At the time that these experiments were undertaken, the e-beam scanning system was not installed in the DVD system. Thus it was not immediately possible to develop a beam scan pattern with a high frequency scanning system to spread the e-beam power over the surface of the source material. Such an alteration should make possible higher rate evaporation and deposition of materials which are not as conductive as copper.

Optical transmission and reflection analysis of the deposited silicon films was undertaken by T. Globus to determine the silicon film form (amorphous or polycrystalline), the film thickness, and the average material deposition rate [209]. Measurements in the 0.6 - 2.4 μm energy wavelength range were made using a Cary 5E two-beam spectrophotometer. Film thicknesses were calculated from interference fringe patterns observed in the weak absorption portion of the visible spectrum. Deposition rates ranging from 20 to 440 nm/min were calculated. The highest rate was recorded from the 40 slm sample created
using 480 W of beam power. The thickest 3.1 μm film was deposited in 7 minutes over an area of approximately 6.45 cm². The optical transmission spectra from several films were used to calculate the thin film absorption spectrum shown in Fig. 6.3. The absorption spec-

![Graph showing optical absorption coefficient analysis of DVD deposited silicon.](image)

**Figure 6.3** Optical absorption coefficient analysis of DVD deposited silicon. The optical absorption coefficient as a function of photon energy for DVD silicon is distinctly different than that reported in the literature [210, 211] for hydrogenated amorphous silicon (a-Si, H) and crystalline silicon (c-Si).

The absorption edge for the DVD amorphous silicon (a-Si) thin films is shifted to lower energies relative to the PECVD hydrogenated amorphous silicon (i.e., a-Si, H in Fig. 6.3)
because the DVD material is not an $\alpha$-Si:H alloy. As a result, the photon energy absorption characteristics of the DVD material are quite similar to those of crystalline silicon for energies greater than 1.4 eV. This agreement of the DVD silicon results with the crystalline silicon, as opposed to the hydrogenated amorphous silicon absorption characteristics, does not necessarily indicate that polycrystalline silicon has been formed. Instead the similarity is generated by the dangling bonds in the DVD amorphous silicon which are not passivated (by hydrogen) and which lead to a large density of near bandgap edge states\(^1\).

Using the technique of Amer and Jackson [211], the concentration of these bandgap edge state defects was estimated to be \(10^{18} \text{ cm}^{-3}\). For comparison, the typical defect density in evaporated nonhydrogenated \(\alpha\)-Si is approximately \(10^{19} - 10^{20} \text{ cm}^{-3}\) [212]. While the defect density result suggests that the DVD deposit is different than a typical nonhydrogenated \(\alpha\)-Si film and the absorption spectrum shows it to be different than hydrogenated amorphous silicon, these results do not establish the crystallinity of the deposits.

Microstructural analysis of the films created by these deposition runs was performed by L. Hsiung to understand the form of these films further [213]. Analysis of the 3.1 µm thick, 40 slm sample revealed silicon atom clusters ranging from 20 to 300 nm in size and surrounded by microvoids. The material porosity was estimated to be 1.0%. Selected area diffraction (SAD) performed on this film indicated that it was completely amorphous. Similar analysis on the Mach 2.6 samples revealed several microcrystalline structures, suggesting that some crystalline nucleation can be achieved in the DVD system even at

\(^1\) Hydrogenated silicon experiments were not carried out due to concerns about the safety of flowing hydrogen through the DVD pumping systems. However, there is no technical barrier to conducting such experiments once safety concerns are properly addressed.
room temperature. This initial result is encouraging for the future deposition of low-temperature polycrystalline silicon.

Following the completion of this initial series of silicon deposition via e-beam DVD, a more extensive study was undertaken with Ritenour [214]. Ritenour’s study investigated the effect of substrate temperature, jet composition (argon and helium), and e-beam power upon amorphous and polycrystalline silicon formation. For deposition rates of 150 - 300 nm/min (e-beam power = 360 - 420 W), Ritenour observed a transition from amorphous to polycrystalline microstructure at a substrate temperature in the range of 475 - 515°C. The determination of crystallinity was made via a comparison of the optical absorption spectra for DVD silicon to that of crystalline silicon, similar to Fig. 6.3. For all silicon films deposited at temperatures above 300°C, a rough surface morphology considered unsuitable for electronic applications was observed via scanning electron microscopy. Amorphous silicon films deposited on a 70°C substrate at a higher deposition rate (e-beam power = 600 W) exhibited less surface roughness. For deposition runs performed under similar DVD process conditions, the addition of 5% argon to the jet was found to increase the film roughness. The details of Ritenour’s more detailed study, found in [214, 215], extend the findings of the initial silicon deposition study reported here. A portion of Ritenour’s results are summarized in Table 6.1. It certainly appears that under certain DVD process conditions it does appear that crystalline silicon depositing is feasible.

The results of this section indicate that while the microstructure of deposited silicon films needs to be improved through an elimination of internal porosity and a decrease in film surface roughness, Directed Vapor Deposition could have the ability to deposit polycrystalline silicon at temperatures compatible with the glass substrates used to create thin film transistors for use in devices such flat panel displays. If the DVD process can be modified
to improve deposited film quality, it could prove to be a useful tool for this industrial application.

Table 6.1: DVD deposition of silicon

<table>
<thead>
<tr>
<th>Substrate Temperature (°C)</th>
<th>E-beam Power (W)</th>
<th>Resulting Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>70¹</td>
<td>600²</td>
<td>Amorphous. Generally smooth morphology, repeated domed regions ~0.35 µm in diameter, no clear separation between adjoining domes. Film cracking evident. Optical appearance = grey.</td>
</tr>
<tr>
<td>325</td>
<td>480</td>
<td>Amorphous. Distinct columns ~0.25 µm in diameter, clear void spaces between columns, rough surface morphology. Optical appearance = grey.</td>
</tr>
<tr>
<td>425</td>
<td>360</td>
<td>Amorphous. Distinct columns ~0.25 µm in diameter, clear void spaces between columns, rough surface morphology. Optical appearance = grey.</td>
</tr>
<tr>
<td>475</td>
<td>420</td>
<td>Amorphous. Distinct columns ~0.25 µm in diameter, clear void spaces between columns, rough surface morphology. Optical appearance = grey.</td>
</tr>
<tr>
<td>515</td>
<td>420</td>
<td>Polycrystalline. Larger diameter columns ~0.33-0.50 µm in diameter, less obvious separation, continued rough surface morphology. Optical appearance = silver.</td>
</tr>
<tr>
<td>550</td>
<td>300</td>
<td>Polycrystalline. Larger diameter columns ~0.33-0.50 µm in diameter, less obvious separation, continued rough surface morphology. Optical appearance = silver.</td>
</tr>
</tbody>
</table>

¹ Condensation of the silicon vapor increased the substrate temperature from room temperature to 70° C.

² Deposition rate for this experiment exceeded the deposition rate used in other experiments.
6.4 Study of Reactive Deposition

While an ability to deposit pure metallic and semiconducting materials using Directed Vapor Deposition (DVD) is critical, another proposed area of DVD utility is the creation of compounds through the combination of solid materials with elements in the carrier gas flow. Since DVD introduces gas into the film synthesis chamber as part of normal processing, it appears to be a method well suited to the stoichiometrically-correct creation of compounds from either compound evaporant targets [216] or pure metal targets [200]. Research by others with conventional e-beam evaporators [11] has shown that during evaporation and deposition of compounds (e.g. zirconia for thermal barrier coatings), the stoichiometry of deposited films is frequently incorrect, most often the result of reactive element loss (e.g. oxygen) to the gas phase. To make up for this deficiency, process engineers have performed material deposition in a low pressure of the desired gaseous element (RE and ARE are described in the Introduction).

It should be possible to introduce reactive gas into the DVD carrier gas stream to ensure stoichiometrically-correct deposition from solid compound sources. Using the carrier gas jet of the DVD system it should also be possible to introduce all of the reactive elements into the system from the gas phase. If this approach proves successful, it will be possible to avoid the use of difficult to evaporate ceramic rods, which frequently crack in a manner similar to the silicon rods described above, and to evaporate instead from more controllable metal or alloy sources. To assess the ability of the Directed Vapor Deposition system to deposit material onto flat substrates following reaction between the vapor stream and a gas stream containing oxygen, a limited study was undertaken.

An initial experimental study of reactive DVD deposition was undertaken with Heller [200]. For this study of reactive deposition feasibility, deposition of zirconia (ZrO$_2$) was
investigated by evaporating pure zirconium metal from the water-cooled crucible and then introducing oxygen into the carrier gas/metal vapor flow downstream of the crucible via a separate gas injection subsystem as illustrated in Fig. 4.7. Ideally, reaction between the zirconium and oxygen should occur and lead to deposition of an oxide coating.

Only a few coatings were created using this system configuration and limited analysis of the samples was undertaken. Still, a marked change in the color of the excited vapor stream during deposition from a faint silver to a bright white was observed when oxygen was introduced into the system, suggesting that a reaction was occurring between the metal and oxygen. In addition, visual comparison of metallic zirconium deposits which were black or silver contrasted strongly with the white color of the reactively deposited material [200]. In subsequent studies of DVD reactive deposition in which a partial pressure of oxygen was introduced into the primary carrier gas flow, Hass et al. [217] have confirmed, via x-ray diffraction analysis, that DVD can deposit white zirconia films by evaporating pure zirconium into a reactive gas jet.

The oxide deposition tests performed with this system configuration quickly revealed that, while DVD appeared to have an ability to synthesize reactive films by evaporating pure materials into a reactive gas environment, the perpendicular injection of the oxygen stream into the carrier gas/vapor stream (the gas injection system shown to the right of the crucible in Fig. 4.7) significantly disrupted the flow of vapor toward the substrate. Rather than allowing the jet to continue to travel towards the substrate with oxygen added to the vapor-laden stream, the perpendicular orientation of the oxygen flow injection forced the inert gas/metal vapor stream from a horizontal into a generally vertical orientation well in front of the substrate, similar to the effect experiences as a result of jet interaction with the crucible (Fig. 5.12 c)). Although reaction and reasonable mixing appeared to be occurring, deposition rates were significantly reduced [200]. This disruption of the
primary gas and vapor flow was deemed unacceptable because of its apparent detrimental effect upon adatom deposition efficiency and energy. Since the DVD system also allows reactive gas elements to be added in precise quantities to the inert gas flow in the mixing chamber using the mass flow controllers (c.f. Fig. 4.10), it appears that the greatest success in DVD reactive deposition will occur when a reactive gas jet is passed through the nozzle and into the chamber for more predictable reactive deposition as Hass et al. have more recently done [217].

This section’s results show that DVD can use reactive deposition techniques to deposit compound films.

6.5 Concluding Remarks

The creation of uncontaminated films and compound films via reactive deposition has demonstrated an important ability of the Directed Vapor Deposition technique, selective incorporation of useful gas phase elements into film deposits. DVD’s demonstrated ability to deposit pure coatings of highly reactive titanium, combined with the method’s enhanced fiber coating material utilization efficiency, show that this vapor deposition technology should be considered as a method for creating continuous fiber reinforced MMCs. More research needs to be conducted before the utility of DVD reactive deposition or DVD polysilicon creation can be fully assessed. However, the initial results reported here suggest that with continued system development, DVD’s reactive deposition abilities could contribute to useful TBC synthesis [217], and DVD’s ability to deposit polysilicon at temperatures compatible with glass substrates could motivate system modifications which make possible electronic material synthesis via DVD.
Chapter 7

Experimental Investigations of Deposition Efficiency

7.1 Overview

In Chapter 5, flow visualization methods were coupled with fluid mechanics calculations to identify the characteristic features of DVD carrier gas/vapor atom flows. The numerous flow structures, vapor trajectories, and flow interactions with the substrate were all identified as a function of process conditions. These results illustrated the ability to change the vapor stream distribution during transport by adjusting the carrier gas jet. In Chapter 6, the ability of the system to deposit copper, titanium, silicon, and zirconia rapidly and with little contamination was demonstrated. Undoubtedly DVD can use the carrier gas stream concept to transport vapor to a substrate for deposition. However, some of the most important system requirements have not been examined - those related to source material utilization efficiency.

The investigations of this chapter examine deposition efficiency on both flat and fibrous substrates to:
• Determine if a DVD approach can increase the vapor deposition efficiency above the usual levels reported for conventional high vacuum e-beam systems,

• Identify the combination of process conditions that produces the highest deposition efficiencies,

• Develop a deeper insight into vapor transport and deposition during DVD processing, and

• Uncover the factors governing material structure development during DVD synthesis [29-33].

Fig. 7.1 shows the basic geometric configuration of the DVD system used for all the experiments reported in this chapter. The nozzle size, nozzle position relative to the crucible, substrate type, and e-beam gun distance from the crucible were all changed at various times during the experimental work. Most of these changes were undertaken to explore their effect upon DVD deposition characteristics although some were necessary to allow

Figure 7.1  The general dimensions of all deposition efficiency experiments.
upgrades of the system (e.g., the addition of e-beam scanning coils). The specific configuration employed for each set of experiments is noted when relevant to the experiments described below.

### 7.2 Deposition Efficiency Experimental Procedures

By establishing deposition efficiency trends it should be possible to gain important insight into DVD material synthesis. First, collection of deposition efficiency data should further understanding of DVD material synthesis by providing an initial link between the vapor transport characteristics recorded in the last chapter and important deposition parameters which affect film morphology development (e.g. deposition rate). Even if a high beam power is used to generate a high evaporation rate, DVD carrier gas flow conditions could be used to vary actual material deposition rates. Second, if specific process conditions can be identified under which DVD deposits material more efficiently than its conventional PVD counterparts, DVD could represent a faster and less expensive pathway for materials processing. Third, identification of process conditions which facilitate rapid, efficient deposition can reveal the best direction for future technology development.

For these studies, an average efficiency of deposition for each individual run was determined by weighing the evaporant source and deposition substrate before and after each deposition run. For all deposition runs the evaporant source was a 1.27 cm diameter rod of 99.9995% pure copper. Gettered (purified) helium carrier gas flows were conducted into the processing chamber through a 1.27 cm diameter orifice-type nozzle while using a precisely controlled e-beam power cycle for each test. E-beam scanning across the evaporant surface was employed only in selected experiments that are noted below. Experimental observation indicated that the e-beam power and scanning cycles used and the evaporant source position chosen led to consistent evaporant flux from the molten pool into the car-
rrier gas stream with limited evidence of molten metal droplet ejection during any of the runs.

Since the carrier gas stream flows are a sensitive function of many parameters (e.g. Mach number, chamber pressure, gas type) and since these structures affect vapor transport, it is important to understand how the various processing parameters influence deposition efficiency. The efficiency experiments therefore varied gas flow velocity (Mach number) and chamber pressure, e-beam power, and nozzle position relative to the crucible. Mach number variations were made by altering the relative mixing chamber/deposition chamber pressures through changes in the open/closed position of the throttle plate located in front of the chamber pump (See Fig. 4.10.). From the measured upstream/downstream pressures, Mach numbers were calculated using equation (2.19). These Mach numbers were varied between 1.45 and 1.95 with the upper and lower limits of the processing regime explored being dictated by the boundaries of the available process space shown in Fig. 5.2. While higher and lower Mach numbers could be reached with other nozzles, changing the nozzle diameter was identified as an additional variable worthy of study at another time. Chamber pressure variations were made by changing the number of standard liters per minute of gas entering the chamber using the computer-controlled mass flow controllers. Helium carrier gas fluxes ranged from 2.00 to 105.0 slm. Nozzle / crucible position changes were made by extending the gas flow tube.

7.3 Flat Substrate Results

For flat substrate coating experiments, the deposition substrate consisted of a 10.1 cm by 10.1 cm glass square positioned normal to the flow (See Fig. 7.1.). For all runs, care was taken to ensure that the vertical position of the substrate was consistent and that the middle of the glass plate was centered on the nozzle’s central axis. At the start of each run the flat
top of a copper evaporation rod was positioned approximately 0.5 mm above the top edge of the crucible. Upon melting, the flat top of this evaporation source formed a hemispherical molten pool. For the lower beam power experiments (e-beam powers below ~3.0 kW) this pool shape was maintained throughout the run. For higher power runs the surface of the molten pool flattened as evaporation progressed, and, for the majority of the run, the pool surface remained generally flat. During a deposition run, the copper rod was periodically raised in 1 mm increments using the computer-controlled motor drive to maintain the entire top of the rod at or slightly above the rim of the crucible.

7.3.1. Carrier gas flux / Mach number

The first set of flat substrate deposition efficiency experiments examined five different Mach numbers (1.45, 1.65, 1.75, 1.82, and 1.95). For each Mach number, seven to ten different gas flow rates were selected in the range of 2.00 to 105 slm. These flat substrate coating experiments did not employ e-beam scanning. For all runs, the beam power was initially set at 60W and then increased in 60W increments every 30 seconds until a beam power of 1200W was achieved. This beam power was maintained for ten minutes before being reduced immediately to 60W for thirty seconds and then shut off. The entire cycle took 20 minutes.

Fig. 7.2 shows the dependence of deposition efficiency upon chamber pressure for various Mach numbers. Collection of additional data at Mach 1.45 and Mach 1.95 for higher pressures than those shown was not possible because of limitations imposed by Mach number / pressure boundaries (See Fig. 5.2.) As the chamber pressure increased, the deposition efficiency rose quickly before reaching a maximum and then decreased gradually with increasing chamber pressure. To the left of the maximum deposition efficiencies, higher Mach numbers generally yielded higher deposition efficiencies. However, to the right of
Chapter 7. Experimental Investigations of Deposition Efficiency

Table 7.1 records the specific dependence of the deposition efficiency upon processing conditions.

The peak efficiency this trend was reversed, with lower Mach numbers generating higher deposition efficiencies. Table 7.1 reveals a peak efficiency at fairly low chamber pressures. As chamber pressure increases above the peak, efficiency decreases, most acutely for higher Mach number carrier gas flow conditions.

Table 7.1: Deposition efficiency of copper onto flat substrate
(no beam scanning, gun-to-crucible distance = 2.5 cm)

<table>
<thead>
<tr>
<th>Mach Number</th>
<th>Chamber Pressure (Pa/Torr)</th>
<th>Mass Evaporated (g)</th>
<th>Deposition Efficiency (%)</th>
<th>Gas Flow (slm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.45</td>
<td>26.7/0.20</td>
<td>2.063</td>
<td>16.3</td>
<td>2.00</td>
</tr>
<tr>
<td>1.45</td>
<td>46.6/0.35</td>
<td>2.610</td>
<td>34.0</td>
<td>3.95</td>
</tr>
</tbody>
</table>

Figure 7.2 Flat substrate deposition efficiency as a function of chamber pressure and Mach number. Efficiency results reveal a peak efficiency at fairly low chamber pressures. As chamber pressure increases above the peak, efficiency decreases, most acutely for higher Mach number carrier gas flow conditions.
Table 7.1: Deposition efficiency of copper onto flat substrate
(no beam scanning, gun-to-crucible distance = 2.5 cm)

<table>
<thead>
<tr>
<th>Mach Number</th>
<th>Chamber Pressure (Pa/Torr)</th>
<th>Mass Evaporated (g)</th>
<th>Deposition Efficiency (%)</th>
<th>Gas Flow (slm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.45</td>
<td>66.6/0.50</td>
<td>2.501</td>
<td>50.5</td>
<td>7.17</td>
</tr>
<tr>
<td>1.45</td>
<td>107/0.80</td>
<td>2.452</td>
<td>53.4</td>
<td>10.0</td>
</tr>
<tr>
<td>1.45</td>
<td>152/1.15</td>
<td>2.400</td>
<td>52.2</td>
<td>15.0</td>
</tr>
<tr>
<td>1.45</td>
<td>167/1.25</td>
<td>2.421</td>
<td>51.2</td>
<td>17.8</td>
</tr>
<tr>
<td>1.45</td>
<td>200/1.50</td>
<td>2.351</td>
<td>48.7</td>
<td>21.6</td>
</tr>
<tr>
<td>1.45</td>
<td>267/2.00</td>
<td>2.237</td>
<td>40.1</td>
<td>30.0</td>
</tr>
<tr>
<td>1.45</td>
<td>394/2.96</td>
<td>2.213</td>
<td>31.1</td>
<td>47.0</td>
</tr>
<tr>
<td>1.65</td>
<td>26.7/0.20</td>
<td>2.455</td>
<td>23.3</td>
<td>2.90</td>
</tr>
<tr>
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<td>46.6/0.35</td>
<td>2.268</td>
<td>46.0</td>
<td>6.05</td>
</tr>
<tr>
<td>1.65</td>
<td>82.6/0.62</td>
<td>2.386</td>
<td>49.6</td>
<td>10.0</td>
</tr>
<tr>
<td>1.65</td>
<td>113/0.85</td>
<td>2.522</td>
<td>46.6</td>
<td>15.0</td>
</tr>
<tr>
<td>1.65</td>
<td>167/1.25</td>
<td>2.353</td>
<td>39.9</td>
<td>23.8</td>
</tr>
<tr>
<td>1.65</td>
<td>197/1.48</td>
<td>2.292</td>
<td>34.2</td>
<td>30.0</td>
</tr>
<tr>
<td>1.65</td>
<td>267/2.00</td>
<td>2.365</td>
<td>28.2</td>
<td>41.6</td>
</tr>
<tr>
<td>1.65</td>
<td>372/2.79</td>
<td>2.098</td>
<td>20.0</td>
<td>60.0</td>
</tr>
<tr>
<td>1.65</td>
<td>466/3.50</td>
<td>2.159</td>
<td>21.0</td>
<td>77.0</td>
</tr>
<tr>
<td>1.65</td>
<td>542/4.07</td>
<td>1.852</td>
<td>18.5</td>
<td>90.0</td>
</tr>
<tr>
<td>1.75</td>
<td>26.7/0.20</td>
<td>2.685</td>
<td>26.9</td>
<td>3.50</td>
</tr>
<tr>
<td>1.75</td>
<td>46.6/0.35</td>
<td>2.324</td>
<td>45.6</td>
<td>7.20</td>
</tr>
<tr>
<td>1.75</td>
<td>72.0/0.54</td>
<td>2.222</td>
<td>49.6</td>
<td>10.0</td>
</tr>
<tr>
<td>1.75</td>
<td>100/0.75</td>
<td>2.624</td>
<td>46.6</td>
<td>15.0</td>
</tr>
<tr>
<td>1.75</td>
<td>167/1.25</td>
<td>2.430</td>
<td>31.8</td>
<td>30.0</td>
</tr>
<tr>
<td>1.75</td>
<td>247/1.85</td>
<td>2.418</td>
<td>20.6</td>
<td>45.0</td>
</tr>
<tr>
<td>1.75</td>
<td>322/2.42</td>
<td>1.947</td>
<td>16.0</td>
<td>60.0</td>
</tr>
<tr>
<td>1.75</td>
<td>466/3.50</td>
<td>1.946</td>
<td>11.5</td>
<td>90.0</td>
</tr>
<tr>
<td>1.82</td>
<td>26.7/0.20</td>
<td>2.419</td>
<td>34.3</td>
<td>4.00</td>
</tr>
<tr>
<td>1.82</td>
<td>46.6/0.35</td>
<td>2.605</td>
<td>45.8</td>
<td>8.15</td>
</tr>
<tr>
<td>1.82</td>
<td>65.3/0.49</td>
<td>2.591</td>
<td>49.0</td>
<td>10.0</td>
</tr>
<tr>
<td>1.82</td>
<td>88.0/0.66</td>
<td>2.568</td>
<td>46.6</td>
<td>15.0</td>
</tr>
<tr>
<td>1.82</td>
<td>156/1.17</td>
<td>2.304</td>
<td>31.1</td>
<td>30.0</td>
</tr>
</tbody>
</table>
Table 7.1: Deposition efficiency of copper onto flat substrate
(no beam scanning, gun-to-crucible distance = 2.5 cm)

<table>
<thead>
<tr>
<th>Mach Number</th>
<th>Chamber Pressure (Pa/Torr)</th>
<th>Mass Evaporated (g)</th>
<th>Deposition Efficiency (%)</th>
<th>Gas Flow (slm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.82</td>
<td>200/1.50</td>
<td>2.133</td>
<td>23.0</td>
<td>41.0</td>
</tr>
<tr>
<td>1.82</td>
<td>286/2.14</td>
<td>2.076</td>
<td>14.2</td>
<td>60.0</td>
</tr>
<tr>
<td>1.82</td>
<td>420/3.15</td>
<td>1.746</td>
<td>11.6</td>
<td>90.0</td>
</tr>
<tr>
<td>1.82</td>
<td>480/3.60</td>
<td>1.898</td>
<td>9.1</td>
<td>105.0</td>
</tr>
<tr>
<td>1.95</td>
<td>26.7/0.20</td>
<td>3.029</td>
<td>33.1</td>
<td>5.10</td>
</tr>
<tr>
<td>1.95</td>
<td>46.6/0.35</td>
<td>2.732</td>
<td>45.0</td>
<td>10.15</td>
</tr>
<tr>
<td>1.95</td>
<td>54.6/0.41</td>
<td>2.564</td>
<td>50.0</td>
<td>10.0</td>
</tr>
<tr>
<td>1.95</td>
<td>73.3/0.55</td>
<td>2.563</td>
<td>45.1</td>
<td>15.0</td>
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<td>1.95</td>
<td>129/0.97</td>
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<td>167/1.25</td>
<td>2.051</td>
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<tr>
<td>1.95</td>
<td>216/1.62</td>
<td>1.987</td>
<td>16.2</td>
<td>55.0</td>
</tr>
</tbody>
</table>

7.3.1.1 Vapor transport visualizations help explain efficiency results

The deposition efficiency variations with chamber pressure reported in Fig. 7.2 can be partially reconciled by comparing them with the flow visualizations of Fig. 5.7. Fig. 5.7 a) shows that when the carrier gas flux or Mach number is low, a significant portion of the vapor atoms diffuse completely across the main carrier gas flow and clearly can never reach the substrate. Indeed, for a Mach number / carrier gas flux combination close to zero, the vapor distribution must return to the $\cos^3\theta$ distribution observed in high vacuum e-beam systems. In such a case, a very small fraction of the flux would reach a substrate positioned as in these experiments.

As the carrier gas flux was increased in Fig. 5.7 b), the vapor diffuses into the center of the carrier gas jet, is transported to the substrate, contacts the substrate, and forms a deposit near the impact point of the jet on the substrate. Figs. 5.8 and 5.9 show that when the vapor is entrained in the jet center, it is likely to be directed towards the substrate for effi-
cient deposition rather than pass through the jet. However, once the carrier gas flux increases beyond a certain point (Fig. 5.7 c) and Fig. 5.11 a)), the vapor is confined to the bottom edge of the carrier gas jet, is slowed by the wall shock directly in front of the substrate, and is then deflected into the wall jet parallel to the substrate. Once in the wall jet some vapor atoms will diffuse towards the substrate surface and deposit, but a significant portion is also likely to be retained in the flow and transported out of the chamber, resulting in a decrease in average deposition efficiency as measured here.

The Mach number variation visualizations of Figs. 5.8 and 5.9 do not provide significant insight into the Mach number dependence of deposition efficiency as recorded in Fig. 7.2. Perhaps variation of the exact size and location of the secondary shock structure as recorded in Fig. 5.6 influences the probability that an entrained vapor atom reaches the substrate. To answer this type of question, more sophisticated (quantitative) studies of the principles of two component, rarefied fluid flow are certainly necessary.

### 7.3.1.2 A discussion of evaporation rate variations

The recorded variation in evaporated mass indicates that changes in flow conditions led to changes in evaporation rate. Due to the variation in beam power during the first half of each experiment, a constant evaporation rate was not computed, and a comparison of experimental evaporation rates with latent heat predictions was not made. Table 7.1 shows that higher gas flows generally resulted in decreased mass evaporation rates. This was a combined result of decreased beam power reaching the source rod (Fig. 4.1), increased cooling of the evaporant source as more gas was blown across its surface per unit time, and increased vapor atom backscattering to the molten surface as the chamber pressure increased [11]. However, several other factors could also have contributed to the evaporation rate variations.
First, the evaporation rate of the experiments appears to have been dependent upon the length of the rodstock used. General observation indicated that shorter rodstocks led to higher evaporation rates, probably the result of decreased heat conduction away from the molten evaporant pool. Second, visual observations of the evaporation process revealed significant differences in evaporation rates and resulting vapor atom trajectories as the result of variations in the vertical position of the rodstock. Elevating the rodstock too far above the crucible lip led to significant molten droplet ejection, preventing accurate measurement of vapor deposition efficiency. A slightly lower rodstock height led to formation of a hot hemispherical pool of copper not in contact with the crucible. Allowing the rodstock to sit too low in the crucible decreased evaporation rates by reducing the curvature of the surface of the rod stock and limiting the temperature of the rodstock surface. When the rod was lower in the crucible, water-cooling of the crucible played an enhanced role in determining the copper surface temperature and evaporation rate. In later experiments where e-beam scanning was employed, it was possible to raise the rod stock surface significantly above the lip of the crucible without generating significant molten droplet ejection. This arrangement appeared to decrease evaporation rates because of the increased surface area of the rod exposed to the cooling gas jet. A more definitive investigation of the relationship between evaporation rate and deposition efficiency is presented in section 7.3.2.

7.3.1.3 Deposited film appearance, adhesion depend on process conditions

Visual inspection of the flat substrate films produced during the visualization and coating efficiency studies revealed a distinct change in the appearance of the deposited films with process conditions as well as a change in the film’s adherence to the substrate as the gas flow increased from 0.5 to 50.0 slm. Copper films deposited with 0.5 slm and 5.0 slm of helium flow had a bright coppery appearance and adhered well to the substrate. (They
required vigorous scraping with a metal object to remove large flakes of the film.) Films produced with 50 slm of gas flow were generally black in color, powdery in form, and could be wiped from the substrate with a dry cloth, except for a region along the bottom third of the glass slide where the deposit transitioned to the more familiar, well adhering, coppery colored film (Fig. 7.3). The change did not appear to have resulted from significant differences in substrate temperature. For all runs, substrate heating resulted purely from adatom deposition, with temperatures, measured using a thermocouple, below 150°C.

Figure 7.3 **Two distinct regions of material deposit for high gas flows.** When vapor was deposited onto a substrate using high gas flows (forty five slm and above), resulting deposits exhibited two distinct regions, differing in location, color, and adhesion. The jet was perpendicular to the front of the substrate.
in all cases. Despite the common, low substrate temperature, changes in the film structure clearly occurred as the result of a change in carrier gas flux. The black appearance of the deposits could be the result of minimal light reflection from a rough cluster deposited surface (See Fig. 2.5.) generated by vapor phase nucleation of material clusters as observed by Dugdale [50, 84], described by Hill [79], and reviewed in the Background chapter. The probability of cluster formation during DVD vapor transport is examined in section 7.5.

Some deposits at higher gas flows (forty five slm and above) also showed regions in the center of the jet impingement location where little or no vapor was deposited. This clean center section was completely surrounded by a “halo” of black, sooty material. Apparently the pressure and Mach number of this center portion of the carrier gas jet was great enough to prevent vapor diffusion into it (Fig. 7.4).

7.3.1.4 A summary of initial deposition efficiency results

The experiments of section 7.3.1. show:

- Deposition efficiency is a significant function of chamber pressure and Mach number.
- As chamber pressure increases, deposition efficiency reached a peak near 70 Pa (~0.5 Torr). Further chamber pressure increases resulted in decreasing deposition efficiencies.
- Above the peak deposition efficiency near 70 Pa, lower Mach numbers lead to significantly higher deposition efficiencies for a given chamber pressure.
- Under some high chamber pressure conditions, vapor phase nucleation of clusters appears to have occurred and resulted in black, sooty, poorly adhering films.

The initial experiments raise several questions for further investigation:

- What is the effect of evaporation rate upon deposition efficiency?
Chapter 7. Experimental Investigations of Deposition Efficiency

• What is the effect of gas or vapor atom composition upon deposition efficiency?
• What is the effect of different nozzle diameters upon vapor transport and deposition?
• Are the black deposits observed at higher chamber pressure actually the result of vapor phase cluster formation?
• What impact does vapor phase nucleation of clusters have upon vapor transport, vapor deposition efficiency, and microstructure formation in a low vacuum deposition system like DVD?

Figure 7.4  **Formation of a deposition halo at high gas flows.** Under certain high carrier gas flux conditions, vapor is unable to diffuse into the center of the jet, resulting in a halo of deposit around the central jet impingement location.
7.3.2. E-beam power (evaporation rate effects)

Experiments were undertaken at different levels of scanned e-beam power (1.8, 2.4, 3.6, 3.9, and 5.4 kW) and a Mach number $M = 1.75$ to examine the effect of evaporation rate variation upon deposition efficiency. This set of experiments sought to determine if the peak in deposition efficiency shifted to higher chamber pressures as the e-beam power and therefore evaporation rate increased. A change in vapor atom trajectory with change in e-beam power was noted in Figs. 5.9 and 5.10, and this observed, reduced ability of the gas jet to redirect the vapor stream at higher beam powers suggested that such a trend might exist.

For these experiments, beam power was raised in 300 W increments every 20 seconds until the desired setpoint was reached. That setpoint power level was then maintained for the duration of each 20 minute experiment. Prior to conducting these experiments, the e-beam gun was raised to accommodate the e-beam scanning coils at the bottom of the gun. This system modification increased the separation between the gun and crucible from 2.50 cm to 8.80 cm. The increased beam propagation distance in the chamber relative to the original flat substrate deposition study of section 7.3.1. resulted in greater e-beam energy losses in the chamber gas (c.f. Fig. 4.1). Because of the introduction of beam scanning and a different gun to source distance, the results generated in this section come from a distinctly different system than that explored in the previous section. While the trends observed in this section and the last should apply to both system configurations, the exact deposition efficiency results can be compared only if the effect of system reconfiguration is considered.

The results of the beam power experimental runs are recorded in Fig. 7.5 and Table 7.2. While the results from the 2.4, 3.6, 3.9, and 5.4 kW runs revealed a consistent trend, the results from the 1.8 kW experiments were deemed inconclusive (despite conducting multi-
ple runs at each chamber pressure setting), and thus not included in Fig. 7.5 (See section 7.3.2.1. for an examination of the 1.8 kW results.). Three distinct trends can be observed in the four sets of graphed data in Fig. 7.5. First, as the beam power increases, the peak of the deposition efficiency curve moves to higher pressures. Second, as the beam power increases, the maximum deposition efficiency of the peak decreases. Third, as the beam power increases, the deposition efficiency curve broadens, forming a less distinct peak.

The first trend can be explained quite readily in light of the visualizations of Figs. 5.9 and 5.10. Higher beam powers clearly allow the vapor stream to diffuse through and around...
the primary (fast flow) portion of the gas flow for a given set of carrier gas flow conditions. Thus at low flows and high beam powers, the vast majority of the vapor stream
passes through the gas jet and over the top of the flat substrate. Only as the gas flow is increased does this higher density vapor flux get redirected towards the substrate by the carrier gas flow.

The second and third trends appear to result from the competition between the positive redirection of the higher density carrier gas flow and the negative redirection of the higher density wall jet. Once there is enough carrier gas momentum to redirect the high density vapor flux towards the substrate, there is also enough carrier gas present to direct the vapor into the wall jet before it has a chance to contact the substrate. Therefore even at peak efficiency, the deposition efficiencies of all high power deposition runs are lower than their low power / lower gas flow counterparts because of the influence of the wall jet.

7.3.2.1 Low beam power experiments generate inconsistent results

The scatter in efficiency results at the low evaporation rates generated by 1.8 kW of scanned e-beam power appears to have been caused in large part by the difficulty of maintaining a constant, repeatable evaporation rate between runs conducted under identical gas flow conditions. Study of the results indicates that in addition to the factors mentioned in section 7.3.1.2 which affect evaporation rate (e.g., rod length and position in crucible), the precise manner in which the molten rod first comes into contact with the water cooled crucible and the area over which the rod and crucible are in continued contact significantly affect heat transfer to the water-cooled crucible and thus evaporation rate for low beam power experiments. Despite the fact that a consistent rod stock length was employed for these 1.8 kW experiments, significant variation in evaporation rate and deposition efficiency was observed for a common e-beam power setting.
7.3.2.2 Visual inspection of films revealed chamber pressure and beam power effects

The substrates removed from the chamber at the end of each run revealed changes in the film appearance with process conditions. As observed previously, chamber pressure increases changed the deposited films from well-adhered copper-colored films to sooty, black films. This trend was most pronounced at high beam powers where the entire inside of the chamber was black following a deposition run. This observation suggests that higher carrier gas pressures and higher copper vapor pressures both contribute to a change in deposited vapor appearance. Although not confirmed experimentally, it seems possible that this change in appearance is the result of vapor atom clustering during the deposition run spurred on by higher gas and vapor atom concentrations. (Clustering in the DVD system will be examined in more detail in section 7.5.)

7.3.2.3 A summary of evaporation rate results

The primary results of this dissertation section are:

- As e-beam power is increased, the deposition efficiency peak moves to higher chamber pressures and carrier gas flows for a given Mach number.
- As e-beam power is increased, the deposition efficiencies decrease for all conditions as a result of the enhanced influence of the wall jet at the chamber pressures under study.
- As e-beam power is increased, the deposition efficiency peak broadens.
- Changes in deposited film appearance occur as the result of chamber pressure and evaporation rate variations.

This section does not answer the following question: If the change in film appearance is the result of vapor atom clustering, what effect does this have upon the observed deposition efficiency trends?
7.3.3. Crucible to nozzle separation effects

An additional set of flat substrate deposition experiments was undertaken to observe what, if any, difference crucible position relative to the end of the nozzle made upon deposition efficiency. While the crucible itself was not moved, a nozzle extender was attached to the end of the carrier gas flow tube and then the 1.27 cm nozzle attached to the end of this extension. As a result, the distance from the end of the nozzle to the center of the evaporant source was decreased from 3.50 cm to 1.30 cm (c.f. Fig. 7.1). The nozzle to crucible separation could not be reduced further due to the physical dimensions of the nozzle and crucible. These tests examined whether making the initial evaporant atom position just below the zone of silence, close to the high velocity Mach disk observed in Fig. 5.6, would lead to more efficient vapor entrainment in the center of the carrier gas stream and higher deposition efficiencies.

For these runs, the gun to crucible separation was 8.80 cm and the scanned e-beam power was increased 300 W every 30 seconds until a total beam power of 2.1 kW was reached. This setting was maintained for 15 minutes before being reduced to 60 W for 30 seconds and then turned off. Each experiment lasted for a total of 19 minutes. Using the raised gun position and the scanning coils, experiments were run with and without the nozzle extender for Mach 1.65 conditions at gas flow conditions ranging from 2.5 to 90 slm.

Fig. 7.6 compares deposition efficiency results for Mach 1.65 runs employing the nozzle extender with a new set of Mach 1.65 data taken without the nozzle extender. The new set of data without a nozzle extender was generated to ensure that deposition efficiency variations were the result of the nozzle extender and not the new gun position or e-beam scanning. Table 7.3 records the numerical results for the newly generated data.
The deposition efficiency results show that use of the nozzle extender appears to have improved deposition efficiency moderately over deposition runs conducted without a nozzle extender. These results illustrate that the configuration of the crucible in relation to the supersonic flow structure of the carrier gas jet can significantly influence the deposition characteristics of the Directed Vapor Deposition process. The precise reason for the deposition efficiency increase is unclear. However, by introducing the vapor into the gas flow earlier, the vapor atoms may have more opportunity to diffuse into the center of the jet before encountering the substrate and wall jet. Thus, when they begin to turn into the wall jet, their trajectories carry them closer to the substrate, allowing more of them to come into contact with the substrate before completely making the turn and being swept away into the process chamber.

Figure 7.6 Crucible to nozzle separation effects upon deposition efficiency. The nozzle extender generated some improvement in deposition efficiency.
7.3.3.1 Initial vapor distribution effects upon deposition efficiency

It is of interest to note the difference in deposition efficiency between a previous series of experiments (section 7.3.1.) and this series. Fig. 7.7 shows the deposition efficiency results for the raised gun configuration with beam scanning (Fig. 7.6) in comparison with results obtained earlier with a smaller gun-to-crucible separation and without beam scanning (Fig. 7.2). Study of the deposition efficiency results in light of the different system configurations suggests that the shift in maximum deposition efficiency to higher pressure is the result of more beam power reaching the evaporant source. The shift of the peak to higher efficiencies appears to result from a tighter focus of the initial vapor stream.

First, the shorter gun to crucible distance in the original experiments allowed more of the original beam power to reach the vapor source, leading to higher evaporation rates for the section 7.3.1. data (Table 7.1 versus 7.3). As shown in Fig. 7.5, higher beam powers shift the peak efficiency to higher chamber pressures. Second, the fixed e-beam employed in

### Table 7.3: Deposition efficiency of copper onto flat substrate

(beam scanning, gun-to-crucible distance = 8.8 cm)

<table>
<thead>
<tr>
<th>Mach Number</th>
<th>Chamber Pressure (Pa/Torr)</th>
<th>Mass Evaporated (g)</th>
<th>Deposition Efficiency (%)</th>
<th>Gas Flow (slm)</th>
<th>Nozzle Extender</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.65</td>
<td>21.3/0.16</td>
<td>1.090</td>
<td>33.2</td>
<td>2.50</td>
<td>Yes</td>
</tr>
<tr>
<td>1.65</td>
<td>42.6/0.32</td>
<td>1.560</td>
<td>47.2</td>
<td>5.00</td>
<td>Yes</td>
</tr>
<tr>
<td>1.65</td>
<td>72.0/0.54</td>
<td>0.608</td>
<td>44.4</td>
<td>10.0</td>
<td>Yes</td>
</tr>
<tr>
<td>1.65</td>
<td>149/1.12</td>
<td>0.464</td>
<td>28.3</td>
<td>22.0</td>
<td>Yes</td>
</tr>
<tr>
<td>1.65</td>
<td>272/2.04</td>
<td>0.298</td>
<td>19.0</td>
<td>45.0</td>
<td>Yes</td>
</tr>
<tr>
<td>1.65</td>
<td>530/3.98</td>
<td>0.138</td>
<td>15.0</td>
<td>90.0</td>
<td>Yes</td>
</tr>
<tr>
<td>1.65</td>
<td>21.3/0.16</td>
<td>0.432</td>
<td>25.1</td>
<td>2.50</td>
<td>No</td>
</tr>
<tr>
<td>1.65</td>
<td>42.6/0.32</td>
<td>0.644</td>
<td>39.5</td>
<td>5.00</td>
<td>No</td>
</tr>
<tr>
<td>1.65</td>
<td>72.0/0.54</td>
<td>0.630</td>
<td>40.2</td>
<td>10.0</td>
<td>No</td>
</tr>
<tr>
<td>1.65</td>
<td>149/1.12</td>
<td>0.538</td>
<td>25.4</td>
<td>22.0</td>
<td>No</td>
</tr>
<tr>
<td>1.65</td>
<td>272/2.04</td>
<td>0.283</td>
<td>12.4</td>
<td>45.0</td>
<td>No</td>
</tr>
<tr>
<td>1.65</td>
<td>530/3.98</td>
<td>0.123</td>
<td>12.2</td>
<td>90.0</td>
<td>No</td>
</tr>
</tbody>
</table>

7.3.3.1 Initial vapor distribution effects upon deposition efficiency
the section 7.3.1. experiments led to significant evaporation from only the top of the molten vapor source hemisphere and thus more of the vapor being ejected vertically up into the primary helium jet flow. Consequently, fewer atoms started along trajectories which carried them outside the primary helium flow where they could quickly be carried away from the substrate. As a result, the narrower initial vapor velocity vector distribution (i.e. a point source with a more focussed \( \cos^\theta \) distribution) led to more efficient vapor entrainment in the jet under many conditions and more efficient deposition. In conclusion, these experiments raise an additional question for future investigation, what is the optimal rela-
tionship between nozzle diameter and evaporation surface diameter which leads to maximum vapor entrainment and deposition efficiency?

7.3.3.2 Summary of nozzle position experiments

The primary results of section 7.3.3. are:

- Changing the nozzle to crucible separation from 3.50 cm to 1.30 cm leads to a modest increase in deposition efficiency for a given set of processing conditions.
- Deposition efficiency depends not only upon carrier gas flow conditions but also upon the spatial relation between nozzle, crucible, and substrate.
- Deposition efficiency in the DVD system is a function of the initial vapor stream’s focus. Injecting a higher percentage of the vapor into the core of the carrier gas stream increases deposition efficiency.

7.4 Fiber Substrates

In the flat substrate coating experiments, the presence of the substrate appears to have had a significant influence upon deposition efficiency, with the wall shock and wall jet leading to decreased deposition efficiency at chamber pressures above some peak. To determine if fiber coating deposition efficiency trends were similar to those observed for flat substrates and to investigate the effect of the observed microwall jet (Fig. 5.12 b)) upon efficiency, fiber coating studies were conducted using test conditions similar to those employed for the flat substrates.

An array of 142 μm diameter SCS-6 fibers (supplied by Textron Specialty Materials, Lowell, MA) was set up in a square aluminum frame with an inside edge dimension of 5.08 cm. 25 colinear fibers were mounted vertically with a nominal center-to-center fiber spacing of 2 mm. During each run, the fiber frame itself was covered with aluminum foil to
ensure that metal deposition on it was not included in the weight change measurements. For the fiber spacing used, 7.1% of the cross-sectional area of the frame interior was occupied by fibers. Thus, if a uniform flux were incident upon the fibers and deposition occurred only on surfaces that were “insight” of the flux, the average deposition efficiency would be 7.1%.

The gun to crucible distance for this set of experiments was 7.1 cm. The increased beam propagation distance in the chamber relative to the original flat substrate deposition study (7.10 vs. 2.50 cm) resulted in greater e-beam energy losses (c.f. Fig. 4.1), and so, to obtain a fiber experiment vapor flux rate generally comparable to that of the original flat substrate coating work (section 7.3.1.), a modified e-beam heating cycle was used. For these experiments, no scanning of the e-beam was performed across the feed rod surface. Once the fixed-position e-beam was initially turned on at 60W, the e-beam power was increased in increments of 60W every 20 seconds until a beam power of 1500W was achieved (after 8 minutes). This beam power was maintained for 11.5 minutes before being reduced to 60W for thirty seconds and then shut off. Each deposition run lasted a total of 20 minutes. The original nozzle to crucible spacing of 3.50 cm was utilized for all fiber coating experiments.

7.4.1. Fiber coating deposition efficiency trends mirror flat substrate results

The observed chamber pressure / Mach number / deposition efficiency trends were similar to those recorded for flat substrate coating. Fig. 7.8 plots the relationship between Mach number, chamber pressure, and relative fiber coating efficiency (compared to that achieved by a purely line-of-sight deposition process). In the experimental configuration the small diameter fibers occupied 7.1% of the cross-sectional area through which the carrier gas stream passed. It should be noted that the deposition efficiency measured in this
study is an average value over the entire surface area of the fibers. As a result, maximum deposition rates reached 50 - 100 µm per minute in certain portions of the fiber array while falling to 1 - 2 µm per minute in other regions.

As with flat substrate coating, low chamber pressures (low carrier gas fluxes) did not entrain the vapor and transport it towards the fiber array, resulting in low deposition efficiencies. Instead, the main vapor stream crossed the primary carrier gas flow and passed between the gun and the top of the fiber array. Still, larger Mach numbers resulted in higher deposition efficiencies at low chamber pressures as seen in the flat substrate experiments. Once the carrier gas flow was increased so that the vapor passed through the

Figure 7.8 Material utilization efficiency during DVD fiber coating. For many experimental conditions, deposition efficiencies were above line-of-sight levels. The relative average efficiency of 1.0 represents the coating expected for pure line-of-sight coating, illustrated in the top right portion of the figure.
frame, deposition efficiencies increased dramatically. Increasing carrier gas flows again led to a peak in deposition efficiency (at about 70 Pa) followed by a significant decrease as chamber pressure was raised. This trend suggests that the presence of the observed microwall jet (Fig. 5.12b) could result in vapor atom redirection around the fibers, much as the larger wall shock and wall jet deflected vapor away from the flat substrates. Table 7.4 lists deposition efficiency results for the fiber coating study with two experiments being used to generate each data point.

Table 7.4: Deposition efficiency of copper onto stationary fibers  
(no beam scanning, gun-to-crucible distance = 7.1 cm)

<table>
<thead>
<tr>
<th>Mach Number</th>
<th>Chamber Pressure (Pa/Torr)</th>
<th>Mass Evaporated (g)</th>
<th>Deposition Efficiency (%)</th>
<th>Gas Flow (slm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>33.3/0.25</td>
<td>2.224</td>
<td>8.81</td>
<td>2.85</td>
</tr>
<tr>
<td>1.50</td>
<td>66.6/0.50</td>
<td>1.837</td>
<td>15.0</td>
<td>7.05</td>
</tr>
<tr>
<td>1.50</td>
<td>133/1.00</td>
<td>1.921</td>
<td>13.4</td>
<td>13.2</td>
</tr>
<tr>
<td>1.50</td>
<td>267/2.00</td>
<td>1.500</td>
<td>11.3</td>
<td>31.0</td>
</tr>
<tr>
<td>1.50</td>
<td>400/3.00</td>
<td>1.100</td>
<td>10.3</td>
<td>51.0</td>
</tr>
<tr>
<td>1.50</td>
<td>533/4.00</td>
<td>0.831</td>
<td>8.06</td>
<td>70.0</td>
</tr>
<tr>
<td>1.65</td>
<td>13.3/0.10</td>
<td>2.411</td>
<td>1.28</td>
<td>1.12</td>
</tr>
<tr>
<td>1.65</td>
<td>33.3/0.25</td>
<td>2.054</td>
<td>10.5</td>
<td>3.83</td>
</tr>
<tr>
<td>1.65</td>
<td>66.6/0.50</td>
<td>2.440</td>
<td>13.2</td>
<td>9.50</td>
</tr>
<tr>
<td>1.65</td>
<td>133/1.00</td>
<td>1.866</td>
<td>11.4</td>
<td>19.0</td>
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<td>1.65</td>
<td>267/2.00</td>
<td>1.856</td>
<td>10.3</td>
<td>41.0</td>
</tr>
<tr>
<td>1.65</td>
<td>400/3.00</td>
<td>1.372</td>
<td>8.89</td>
<td>65.0</td>
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<tr>
<td>1.65</td>
<td>533/4.00</td>
<td>0.747</td>
<td>6.29</td>
<td>89.0</td>
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<tr>
<td>1.80</td>
<td>13.3/0.10</td>
<td>2.199</td>
<td>2.09</td>
<td>1.50</td>
</tr>
<tr>
<td>1.80</td>
<td>33.3/0.25</td>
<td>2.811</td>
<td>10.2</td>
<td>5.30</td>
</tr>
<tr>
<td>1.80</td>
<td>66.6/0.50</td>
<td>2.638</td>
<td>12.2</td>
<td>9.80</td>
</tr>
<tr>
<td>1.80</td>
<td>133/1.00</td>
<td>2.058</td>
<td>10.2</td>
<td>24.0</td>
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<td>1.80</td>
<td>267/2.00</td>
<td>1.799</td>
<td>8.45</td>
<td>53.8</td>
</tr>
</tbody>
</table>
7.4.2. Non line-of-sight deposition enhances deposition efficiency

The fiber coating experiments revealed a peak deposition efficiency over twice the 7.1% expected for line-of-sight deposition. Scanning electron microscopy (Fig. 7.9) of these samples revealed that, for conditions of maximum efficiency, vapor deposited not only on the surface of the fiber facing the incoming vapor but also on the fiber’s sides and its back. The backside fiber coating phenomenon appeared to be a manifestation of atomic scattering from the flow as it passes the fiber, a phenomenon observed and discussed previously by Hill in experiments with JVD [79]. The deposited coating also appeared to exhibit a columnar growth morphology.

### Table 7.4: Deposition efficiency of copper onto stationary fibers
(no beam scanning, gun-to-crucible distance = 7.1 cm)

<table>
<thead>
<tr>
<th>Mach Number</th>
<th>Chamber Pressure (Pa/Torr)</th>
<th>Mass Evaporated (g)</th>
<th>Deposition Efficiency (%)</th>
<th>Gas Flow (slm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.80</td>
<td>400/3.00</td>
<td>0.652</td>
<td>6.13</td>
<td>83.0</td>
</tr>
<tr>
<td>1.80</td>
<td>533/4.00</td>
<td>0.372</td>
<td>5.11</td>
<td>112.0</td>
</tr>
<tr>
<td>1.95</td>
<td>13.3/0.10</td>
<td>2.195</td>
<td>3.32</td>
<td>2.00</td>
</tr>
<tr>
<td>1.95</td>
<td>33.3/0.25</td>
<td>2.435</td>
<td>11.3</td>
<td>6.90</td>
</tr>
<tr>
<td>1.95</td>
<td>66.6/0.50</td>
<td>2.064</td>
<td>10.6</td>
<td>12.0</td>
</tr>
<tr>
<td>1.95</td>
<td>133/1.00</td>
<td>1.398</td>
<td>8.23</td>
<td>31.0</td>
</tr>
<tr>
<td>1.95</td>
<td>267/2.00</td>
<td>0.703</td>
<td>6.97</td>
<td>67.0</td>
</tr>
</tbody>
</table>

7.4.3. Inspection of coated fiber characteristics

Examination of the arrays of fibers coated in different experiments revealed that vapor deposition across the front surface of the fiber array was highly nonuniform - much more so than observed during flat substrate coating. The non-uniform flux generally resulted in fibers at the center of the array having significantly thicker coatings than those at the sides.
In the center portion of the array where coating was thickest, the deposit on the front face of the fibers did not generate a circularly symmetric thickness profile as seen in traditional e-beam systems (c.f. Fig. 2.3). Instead, the evaporant stream was elongated in the horizontal direction (Fig. 7.10). The horizontal broadening of the vapor stream appeared to be the result of vapor initially intersecting the bottom of the fast flow region of the carrier gas stream and not being able to diffuse easily into this region. As a result the vapor stream flattened horizontally.

In addition to significant deposition nonuniformity, macroscopic deposition structure variations with processing conditions were observed that were similar to those recorded for flat substrate coating. Although no active substrate heating was undertaken, lower chamber pressure runs again resulted in shiny, well adhered films while higher chamber pres-
Chapter 7. Experimental Investigations of Deposition Efficiency

7.4.4. Summary of fiber coating study

The results of this section demonstrate that:

- When compared to a conventional high vacuum e-beam system, DVD can deposit vapor onto fibers much more efficiently.

Figure 7.10 Vapor density distribution during transport. The DVD vapor stream often appeared to be flattened in the horizontal direction during fiber coating experiments utilizing an unscanned e-beam.

Pressures resulted in a generally darker, more powdery deposit. Certain intermediate pressure deposition runs showed both shiny, well adhered coatings near the center of the fiber array and powdery deposits towards the edges of the array. Often the change from one structure to the other along an individual fiber was sudden, suggesting that the exact location of the vapor in the carrier gas flow had a dramatic effect upon depositing film structure.

Figure 7.10 Vapor density distribution during transport. The DVD vapor stream often appeared to be flattened in the horizontal direction during fiber coating experiments utilizing an unscanned e-beam.

Pressures resulted in a generally darker, more powdery deposit. Certain intermediate pressure deposition runs showed both shiny, well adhered coatings near the center of the fiber array and powdery deposits towards the edges of the array. Often the change from one structure to the other along an individual fiber was sudden, suggesting that the exact location of the vapor in the carrier gas flow had a dramatic effect upon depositing film structure.
• The structure of the deposited coating depends upon processing conditions and upon vapor location relative to the centerline of the carrier gas jet.

• As observed for flat substrate coating, deposition efficiency is a significant function of chamber pressure and Mach number.

• As observed for flat substrate coating, after reaching a peak deposition efficiency, increasing chamber pressures result in decreased deposition efficiencies.

• As observed for flat substrate coating, above the peak deposition efficiency, lower Mach numbers lead to higher deposition efficiencies for a given chamber pressure.

These experiments raise several questions for future investigation:

• How does vapor deposition distribution vary with changes in processing conditions, including e-beam power and vapor atom and gas atom type?

• What is the effect upon deposition efficiency of changing the e-beam power, the vapor atom type or the carrier gas type?

7.5 Clustering

Several of the previous sections have suggested that vapor phase nucleation of material could be occurring and contributing to variations in deposition efficiency and deposited material appearance. To understand possible vapor atom clustering effects during flat substrate vapor deposition, a low evaporation rate experiment was undertaken with 1200 W of scanned e-beam power, a 1.27 cm nozzle, a gas flow of 45 slm, a chamber pressure of 2.0 Torr, and a flow Mach number of 1.75. As shown in Fig. 7.3, the resulting deposit consisted of two distinct regions, a black sooty material easily wiped from the surface of the center of the glass slide and a more difficult to remove copper colored region along the bottom of the slide. It has been hypothesized that these two distinct regions are the result of copper cluster deposition and copper vapor atom deposition respectively (Fig. 7.11).
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Using the method of Hill presented in the Background chapter and in more detail in [79], calculations were performed, using equations (2.14) - (2.18), to provide a sense of the importance of clustering under different DVD processing conditions. For these calculations the copper evaporation rates were assumed to vary from about 40 - 400 mg/min, rates comparable to those observed experimentally. The partial pressures of atomic copper

Figure 7.11 Scenarios to explain the effect of clustering upon deposit appearance. The experimentally observed vapor deposits containing two distinct regions of deposition are probably generated by a combination of cluster formation directly above the crucible and during vapor transport in the carrier gas jet.

Using the method of Hill presented in the Background chapter and in more detail in [79], calculations were performed, using equations (2.14) - (2.18), to provide a sense of the importance of clustering under different DVD processing conditions. For these calculations the copper evaporation rates were assumed to vary from about 40 - 400 mg/min, rates comparable to those observed experimentally. The partial pressures of atomic copper
generated by these evaporation rates were assumed to remain constant from source to substrate even though some of the copper might be consumed by cluster formation. Evaporation was assumed to occur in a gas temperature of 270K and the transport time from source to substrate was estimated to be 100 µsec.

7.5.1. **Clustering probabilities for various process conditions**

The results of the clustering probability calculations are shown in Table 7.5. These calculations assumed an average jet velocity of 600 m/sec during vapor transport over the 6 cm distance from source to substrate. To determine reasonable copper concentrations for these calculations, the copper was assumed to be contained within about a 3 cm diameter cylindrical volume during transport. Given these assumptions, the copper partial pressures listed in Table 7.5 correspond to evaporation rates of 20 - 200 mg/min, rates comparable to those generated during evaporation experiments. Appendix B contains an example of the Mathematica implemented numerical integration solution for average cluster size during transport (equation (2.18)).

The cluster size estimated by this solution is highly sensitive to the transport time. For instance, for the lowest copper concentration computed (3.33x10^{18} atoms/m³), changing the transport time to 500 µsec increases the average cluster size to 5.5 atoms. Increasing the transport time to 1 msec increases it to 100 atoms. For higher copper concentrations, increased transport times resulted in rapid cluster growth, a clustering avalanche, once critical nuclei had been formed. In the real system this rapid increase would be dampened by a decrease in single copper atom concentration. The stiff relationship between transport time and cluster size provides an indication for why distinct changes are observed in the appearance of films deposited onto neighboring portions of a fiber. The carrier gas jet velocity varies with position (Fig. 5.6). Most atoms captured in the jet’s fast flow region
may reach the fiber as individual atoms in 100 $\mu$sec while atoms captured in the jet’s periphery might not reach the fiber for 500 $\mu$sec or 1 msec.

**Table 7.5: Variation of clustering probability with process conditions**

<table>
<thead>
<tr>
<th>Time of flight (100 $\mu$s)</th>
<th>[Cu] (atoms/m$^3$)</th>
<th>[He] (atoms/m$^3$)</th>
<th>Percentage of Cu forming dimers</th>
<th>Average cluster size (atoms)</th>
<th>Percentage of Cu atoms in clusters</th>
</tr>
</thead>
<tbody>
<tr>
<td>3x10$^{18}$ (A)</td>
<td>2.4x10$^{19}$ (D)</td>
<td>2.75x10$^{-6}%$</td>
<td>2.4</td>
<td>6.6x10$^{-6}%$</td>
<td></td>
</tr>
<tr>
<td>3x10$^{18}$</td>
<td>2.4x10$^{20}$</td>
<td>2.75x10$^{-5}%$</td>
<td>2.4</td>
<td>6.6x10$^{-5}%$</td>
<td></td>
</tr>
<tr>
<td>3x10$^{18}$</td>
<td>2.4x10$^{21}$ (E)</td>
<td>2.75x10$^{-4}%$</td>
<td>2.4</td>
<td>6.6x10$^{-4}%$</td>
<td></td>
</tr>
<tr>
<td>3x10$^{18}$</td>
<td>2.4x10$^{22}$</td>
<td>2.75x10$^{-3}%$</td>
<td>2.4</td>
<td>6.6x10$^{-3}%$</td>
<td></td>
</tr>
<tr>
<td>3x10$^{18}$</td>
<td>2.4x10$^{23}$ (F)</td>
<td>0.028%</td>
<td>2.4</td>
<td>0.066%</td>
<td></td>
</tr>
<tr>
<td>1x10$^{19}$ (B)</td>
<td>2.4x10$^{19}$</td>
<td>9.2x10$^{-6}%$</td>
<td>3.5</td>
<td>3.2x10$^{-5}%$</td>
<td></td>
</tr>
<tr>
<td>1x10$^{19}$</td>
<td>2.4x10$^{20}$</td>
<td>9.2x10$^{-5}%$</td>
<td>3.5</td>
<td>3.2x10$^{-4}%$</td>
<td></td>
</tr>
<tr>
<td>1x10$^{19}$</td>
<td>2.4x10$^{21}$</td>
<td>9.2x10$^{-4}%$</td>
<td>3.5</td>
<td>3.2x10$^{-3}%$</td>
<td></td>
</tr>
<tr>
<td>1x10$^{19}$</td>
<td>2.4x10$^{22}$</td>
<td>9.2x10$^{-3}%$</td>
<td>3.5</td>
<td>3.2x10$^{-3}%$</td>
<td></td>
</tr>
<tr>
<td>1x10$^{19}$</td>
<td>2.4x10$^{22}$</td>
<td>9.2x10$^{-3}%$</td>
<td>3.5</td>
<td>3.2x10$^{-3}%$</td>
<td></td>
</tr>
<tr>
<td>3x10$^{19}$ (C)</td>
<td>2.4x10$^{19}$</td>
<td>3.0x10$^{-5}%$</td>
<td>100</td>
<td>0.003%</td>
<td></td>
</tr>
<tr>
<td>3x10$^{19}$</td>
<td>2.4x10$^{20}$</td>
<td>3.0x10$^{-4}%$</td>
<td>100</td>
<td>0.03%</td>
<td></td>
</tr>
<tr>
<td>3x10$^{19}$</td>
<td>2.4x10$^{21}$</td>
<td>3.0x10$^{-3}%$</td>
<td>100</td>
<td>0.3%</td>
<td></td>
</tr>
<tr>
<td>3x10$^{19}$</td>
<td>2.4x10$^{22}$</td>
<td>0.030%</td>
<td>100</td>
<td>3.0%</td>
<td></td>
</tr>
<tr>
<td>3x10$^{19}$</td>
<td>2.4x10$^{22}$</td>
<td>0.30%</td>
<td>100</td>
<td>30%</td>
<td></td>
</tr>
</tbody>
</table>

(A) Cu partial pressure = 0.01 Pa (~10$^{-4}$ Torr)  
(B) Cu partial pressure = 0.03 Pa (~4x10$^{-4}$ Torr)  
(C) Cu partial pressure = 0.13 Pa (~10$^{-3}$ Torr)  
(D) He partial pressure = 0.1 Pa (~7.5x10$^{-4}$ Torr)  
(E) He partial pressure = 10 Pa (~0.075 Torr)  
(F) He partial pressure = 1000 Pa (~7.5 Torr)

Illustrated via a general process parameter map (Fig. 7.12), the results of these calculations emphasize two points. First, for a constant evaporation rate, increasing the carrier gas pressure in the system increases the number of vapor atoms which combine into stable clusters. Second, at a constant carrier gas introduction rate, increasing the vapor atom concentration can also increase the number of vapor atoms contained within clusters.
These results agree with experimental observations. The effect of increased chamber pressure was reported in section 7.3.1.3. The sooty deposits created as chamber pressures were raised above about 200 Pa (1.5 Torr) are likely the result of vapor atom cluster deposition. The copper colored deposits at the bottom of the substrates (See Fig. 7.3.) are probably the result of individual atom deposition. The vapor atom clusters probably began forming prior to entrainment of the vapor in the main carrier gas flow during their short residence

Figure 7.12 **Cluster probability as a function of process conditions.** The probability of cluster formation rises with an increase in either mass evaporation rate or carrier gas pressure. Increasing either process parameter raises the probability of three body collisions necessary for cluster formation.
time above the crucible (c.f. Fig. 2.2), especially at the higher experimentally explored evaporation rates. Significantly more clustering occurred during the longer vapor transport time to the substrate (Fig. 7.11). As a result of cluster formation, the increased mass of the vapor atom clusters would allow them to diffuse further through the center of the carrier gas jet (even to pass over the top of the substrate under certain conditions) and would allow them to diffuse through the wall jet more easily for deposition at a higher point on the substrate than that reachable by individual vapor atoms.

The effect of increased vapor atom concentrations was reported in section 7.3.2.2. The significant blackening of the deposition chamber walls during high rate evaporation was probably the result of clustering induced by increased vapor atom concentrations. To state definitively that clustering induced the black deposits on the chamber walls and on various substrates, additional experimental characterization is needed.

7.5.2. Ionization effects upon cluster formation probability

As noted in the Background chapter, in addition to homogeneous cluster nucleation, the literature indicates that clustering occurs even more readily when a portion of the vapor flux is ionized, with ions representing a fertile source of heterogeneous nucleation sites. Clearly, operation of the e-beam in a low vacuum environment leads to optical excitation of gas and vapor atoms. Given the 60 kV accelerating voltage of the electron beam gun, it seems reasonable to believe that some ionization of the vapor-laden carrier gas stream is also occurring. Consideration of this phenomenon suggests an additional reason for why clustering is observed more frequently during elevated pressure DVD deposition runs.

Experimental observation of DVD revealed that higher chamber pressures led to increased visibility of the carrier gas and vapor streams. Even if the power setting of the e-beam gun was unchanged, increasing the carrier gas pressure in the chamber increased the visibility
of the vapor stream. This is hypothesized to occur because of an increased number of collision events between the original electron beam and carrier gas atoms in the chamber. As a result of these collisions, more secondary electrons and x-rays were generated in the chamber. These energetic entities then excited and ionized more of the carrier gas and vapor atoms with an increased concentration of both types of ions providing more sites for heterogeneous nucleation. At present there does not appear to be a clear understanding of the magnitude of nucleation enhancement induced by the presence of ions in a system [90-100]. As Seto et al. note in their 1997 article [95], “Although this phenomenon [ion-induced nucleation] has been studied since Wilson’s work [in 1889], very little precise quantitative information is available to critically evaluate and refine existing theories.”

7.6 Summary

The experimental results presented demonstrate the complexity of the Directed Vapor Deposition process. Clearly many factors determine if and when vapor atoms will reach the substrate for deposition. Some of the more important factors uncovered while conducting the research for this chapter include the effect of e-beam scanning, e-beam power, the size and position of the evaporant source rod, the carrier gas flux density, and the Mach number of the carrier gas flux. In addition, changes in the composition of the carrier gas and evaporant material can also be expected to affect vapor transport and deposition.

Throughout this chapter, numerous references were made to the difficulty of generating repeatable, measurable experimental conditions. These problems highlight the lack of readily available process sensors to control DVD and underscore the fact that empirical determination of optimum processing conditions for a multifaceted process like DVD could take years or prove to be impossible due to the difficulty of understanding the interrelation between process variables. To obtain additional understanding of the physical
phenomenon at work, development of an experimentally verified model-based description of the process appears justified. An initial theoretical description of the DVD vapor transport and deposition process will be developed in Chapter 8, tested in Chapter 9, and used in Chapter 10 to provide insight into several of the experimental variables identified here.
Chapter 8

Vapor Transport Model Development

The deposition efficiency and spatial thickness distribution of films created by Directed Vapor Deposition synthesis have been shown to be sensitive functions of the flow conditions in the system. To explore the origins of the effects reported in Chapters 5 and 7, a detailed model for vapor transport in the low vacuum gas jets encountered in DVD has been developed using a Monte Carlo (i.e. stochastic) method (Fig. 8.1). The goal of this work was to build a high fidelity model of the deposition process so that the role of the many process parameters could be assessed and understood. The approach began by applying the Direct Simulation Monte Carlo (DSMC) method of G. A. Bird [141] to calculate the velocity, pressure, and temperature field data for the carrier gas flow throughout the modeled region. As described in section 2.2.5., the DSMC technique seeks to predict the position and momentum of all particles in the fluid system by conducting a direct physical simulation of the fluid problem, rather than solving the possibly valid Navier-Stokes equations or the complex, but certainly applicable, Boltzmann equation. By tracking binary collisions between a subset of representative atoms for the system, the DSMC method replicates the behavior of the much larger number of atoms actually involved in the flowfield.
Chapter 8. Vapor Transport Model Development

The output fields of the DSMC model are then used as the inputs to a biatomic collision theory (BCT) based model developed in this chapter to calculate the mean free path and velocity vector of individual vapor atoms contained in a carrier gas flow. By analyzing vapor atom trajectories with the BCT approach it is possible to calculate the vapor atom deposition efficiency, the spatial distribution of the film thickness, the impacting atom energy, and the impact angle of vapor atoms contacting the substrate. When combined with emerging microstructure models [29 - 33], these vapor transport model results help account for the experimental observations of a strong microstructure dependence upon

Figure 8.1 Vapor transport modeling of DVD. The modeling of this dissertation utilizes a Direct Simulation Monte Carlo (DSMC) code, shown here in a two dimensional axisymmetric configuration, to generate information about the carrier gas in the system. DSMC code outputs become the inputs to a bimolecular collision theory (BCT) model which determines vapor atom deposition information.

The output fields of the DSMC model are then used as the inputs to a biatomic collision theory (BCT) based model developed in this chapter to calculate the mean free path and velocity vector of individual vapor atoms contained in a carrier gas flow. By analyzing vapor atom trajectories with the BCT approach it is possible to calculate the vapor atom deposition efficiency, the spatial distribution of the film thickness, the impacting atom energy, and the impact angle of vapor atoms contacting the substrate. When combined with emerging microstructure models [29 - 33], these vapor transport model results help account for the experimental observations of a strong microstructure dependence upon
processing conditions [233]. The modeling approach is later used (Chapter 10) to drive design of an improved (second generation) DVD system.

### 8.1 Direct Simulation Monte Carlo (DSMC) Modeling of the Flowfield

#### 8.1.1. Selection of discrete atom modeling method

As discussed at some length in Chapter 2 (section 2.2.5.), carrier gas flowfield properties can be analyzed using a continuum (Navier-Stokes equations) approach, a molecular (Boltzmann equation) approach, or a direct discrete atom simulation. The correct selection is determined by the “degree of rarefaction” of the gas and the ease with which the applicable equations can be solved [141]. For moderately dense gases, the mean free path between atomic collisions is small compared with the size of physical objects in the system, continuum methods are valid approaches for the calculation of the flowfield, and solution of the Navier-Stokes equations can be accomplished using any number of commercially available CFD codes (e.g. Flow-3D from AEA-CFDS, Inc. [142]). At low gas densities atoms have much longer mean free paths and, as these distances approach the size of objects encountered by a flow, the continuum method breaks down. In this limit, flowfield properties can be obtained through an analysis of atomic collisions (i.e. either by solving the Boltzmann equation or by directly simulating the atomic collision problem [141].)

To determine the most appropriate modeling methodology for analysis of vapor transport during DVD, Knudsen numbers (equation (2.24)) were computed for the process conditions encountered in the experimental chapters of this dissertation. The decision was made to estimate Knudsen number at the nozzle throat for the selected conditions, using the noz-
The nozzle diameter as the characteristic length substituted into equation (2.24). The numbers used for and the results of the calculations are shown in Table 8.1.

<table>
<thead>
<tr>
<th>Mach Number</th>
<th>Gas Temperature (K)</th>
<th>Chamber Pressure (Pa/Torr)</th>
<th>Nozzle Diameter (cm)</th>
<th>Knudsen Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.45</td>
<td>300</td>
<td>27/0.2</td>
<td>1.27</td>
<td>0.01</td>
</tr>
<tr>
<td>1.95</td>
<td>300</td>
<td>540/4.0</td>
<td>1.27</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

These numbers indicate that conditions at the nozzle throat can be modeled using any of the three methods listed above since only Knudsen numbers greater than about 0.1 preclude use of the Navier-Stokes equations. Still, as demonstrated in Chapter 4, the conditions in the DVD gas jet change rapidly as the gas travels through the processing chamber. For supersonic flow conditions, as soon as the carrier gas jet enters the chamber, it expands, and the pressure and temperature in the center of the jet decrease substantially, perhaps leading to free molecular flow (Kn > 0.1) in portions of the modeled volume where continuum techniques will not produce valid results. As Bird notes [234], “A Knudsen number of 0.1 has traditionally been quoted as the boundary between the continuum and transition regimes, but the characteristic dimension of complex flow fields may be specified in many different ways and the use of an ‘overall Knudsen number’ may be misleading.”

Because of uncertainties about the validity of the Navier-Stokes equations throughout the entire modeled volume and because of the difficulty of solving the Boltzmann equation, a discrete particle simulation method (e.g. DSMC) was chosen to simulate the carrier gas flow. Choice of this method for the initial carrier gas simulation also makes it easy to link the DSMC outputs in as the BCT model inputs for the vapor atom tracking portion of the DVD model. This choice of the DSMC method also makes possible modeling of any con-
ditions where the local Knudsen number reaches or surpasses the continuum limit of 0.1, (e.g. \( M = 1.45, \) chamber pressure = 6.6 Pa / 0.05 Torr), with the same code used for smaller Knudsen numbers. Finally, since the discrete atom DSMC method utilizes the same general solution techniques as those employed by the BCT model described in section 8.2, use of DSMC will facilitate the eventual integration of the two models into a comprehensive two (or more) component vapor transport model.

The validity of employing the Direct Simulation Monte Carlo method to model nozzle exhaust flows in low vacuum has been established in recent years by Boyd and others [149, 150, 151], where its primary use has been to understand the interaction of satellite rocket nozzle exhaust plumes with satellite components like solar arrays. The DSMC code used for this modeling work was obtained from Bird’s recent book [141] and modified to the particular geometry and flow conditions of the DVD problem. The primary drawback to using the DSMC approach with Bird’s code, designed to run on a single processor, is the significant length of time required to simulate high pressure process conditions. Use of a parallelized DSMC code could minimize this limitation [239]. Fig. 8.2 shows the computational sequence employed by Bird’s DSMC code for flowfield data generation.

### 8.1.2. Adaptation of DSMC code to DVD

Modeling the carrier gas flow with the DSMC code (Appendix C) required the generation of a grid of points at which the pressure \( (P_c) \), velocity \( (U_c) \), and temperature \( (T_c) \) of the carrier gas flow were recorded. The length and radial dimensions of the gridded region were based upon the DVD processing space employed for the experimental studies (Fig. 8.3), but, to simplify the modeling process, geometric asymmetries such as the crucible and scanning system were removed from the modeling configuration. This allowed a two-dimensional axisymmetric flow volume to be modeled using a rectangular mesh with a
Figure 8.2  A flowchart summary of Bird’s DSMC code. The computational sequence of G. A. Bird’s Direct Simulation Monte Carlo code for modeling a two-dimensional axisymmetric flowfield.

line of symmetry about the flow’s central (z) axis (Fig. 8.4). For all simulations, the spacing between adjacent gridpoints followed Bird’s stipulation that cell dimensions, in flow
Figure 8.3 An overlay of the DSMC modeling grid onto the experimental setup. The locations of the primary DVD components used for the experimental deposition efficiency study define the relative positions of the nozzle, substrate, and crucible source for modeling.

Figure 8.4 Specifications for the DSMC modeling grid. The basic DSMC grid configuration utilized for DVD calculations (10 cm long, 5 cm radial width).
regions with large macroscopic gradients, should be approximately one third the local
mean free path, and time steps over which molecular motion and collisions are uncoupled
conformed to Bird’s suggestion that they be much less than the local mean collision time
[141]. A greater density of gridpoints was placed along the main carrier gas flow line to
capture the significant changes in pressure, velocity, and temperature when the flow accel-
erates out of the nozzle before slowing as it “senses” the substrate’s presence and changes
direction parallel to the substrate surface (e.g. Fig. 5.12 a)).

Unless noted otherwise, all simulations employed a nozzle radius of approximately 6.35
mm. One-dimensional isentropic\(^1\) flow calculations of a compressible\(^2\) fluid [116, 139]
were used to determine the initial carrier gas pressure, velocity, and temperature at the
nozzle exit since, as the gas passes from the mixing chamber into the nozzle, all three of
these gas properties change. The magnitude of their change is dependent upon the fluid’s
ratio of specific heats and the Mach number of the flow. The validity of employing isen-
tropic theory to establish initial conditions at the nozzle has been well established [150].
Fluid dynamics research has shown that for transonic (\(M = 1\)) or supersonic flow (\(M > 1\)),
the velocity, pressure, and temperature conditions at the exit of the nozzle (i.e. the smallest
cross-section through which carrier gas flows) always correspond to “choked” or Mach
1.0 conditions. This allows equations (2.19) and (2.20) to be used in combination with the
following one-dimensional, isentropic flow equation to calculate the necessary input
information [116, 139]:

\[
\frac{T_o}{T_d} = 1 + \frac{\gamma - 1}{2} M^2. \tag{8.1}
\]

In this equation:

\(^1\) isentropic - entropy changes to not occur in the flow.
\(^2\) compressible - density variations within the flow are nonnegligible.
\[ T_o = \text{Upstream temperature (K) and} \]
\[ T_d = \text{Downstream temperature (K).} \]

Thus, if the upstream (mixing chamber) temperature and pressure are 293 K and 667 Pa (5 Torr) respectively, equations (2.19), (2.20), and (8.1) indicate that the model inputs for the nozzle throat should be 220 K, 325 Pa (2.44 Torr), and 873 m/sec if a helium carrier gas is used. While these three equations can be used to predict the carrier gas pressure, velocity, and temperature at the throat and at some distance downstream, they do not describe the change in these properties accurately throughout the two-dimensional axisymmetric free-jet\(^1\) expansion present in the DVD process. Thus the downstream flowfield’s pressure, velocity, and temperature values must be determined using the DSMC code, with the one-dimensional isentropic flow values setting only the initial conditions at the nozzle throat.

For DSMC modeling of the DVD flowfield, Bird provides a large number of parameters which can be set to adapt his code to the particular problem under study. Within the main cells shown in Fig. 8.4, Bird’s code allows subcells to be specified. The specification of these subcells helps to ensure that, when representative collision pairs are selected (Fig. 8.2), atoms as close to one another as possible are chosen for interaction. This helps to ensure that accurate results are generated by the code even if sharp velocity gradients exist across a single cell (e.g. in the vicinity of a Mach disk shock).

Bird’s code also provides for the specification of radial weighting factors when conducting axisymmetric simulations such as the DVD simulations described here. Bird [141] explains that “The most severe practical problem associated with DSMC calculations for axially symmetric flows is the small fraction of the molecules that are located near to the axis. For example, if there are 50 equally spaced cells in the radial direction in uniform

\(^1\) free jet - a gas flow expansion unconstrained by a diverging nozzle.
flow, the sample size in the outermost cell will be 100 times greater than that in the cell at the axis.” Radial weighting factors ensure that molecules located far from the axis of symmetry represent more real molecules than ones near the axis.

For atomic interaction with the substrate boundary, Bird’s code allows the form of the interaction to be specified as either specular or diffuse. If specular reflection is stipulated then atoms contacting the substrate undergo a perfectly elastic reflection. For diffuse reflection the velocities of the reflected atoms are distributed in accordance with a Maxwellian distribution based upon the local gas temperature.

Finally, as noted in Chapter 2, Bird’s DSMC model does not attempt to calculate an energy dependent cross-section for each collision event. Instead his DSMC code employs a variable hard sphere (VHS) or variable soft sphere (VSS) approximation [141]. Associated with these approximations are several inputs which factor into the determination of atomic radius. Table 5.1 summarizes the user-configurable parameters just described and their settings for the DVD simulations in this chapter, including the variables associated with VHS and VSS specification. An in-depth explanation of each variable can be obtained from [141]. The boundary conditions employed for all DVD simulations were a nozzle, a symmetry axis (along the jet centerline), a substrate, and a low vacuum stream along the other flowfield boundaries (~ 5 m/sec in the positive z direction of Fig. 8.1). The low vacuum stream was designed to simulate the pull of the vacuum pump across the chamber. It also allowed the chamber pressure to be defined in accordance with the experimentally measured chamber pressures of Chapter 4 rather than as a pure vacuum.

The simulated flow conditions were designed to allow reproduction of the experimental deposition efficiency results and thus utilized pure helium as the carrier gas for all simulations. The relevant gas parameters were obtained from [141]. In each simulation, the helium carrier gas velocity at the nozzle throat was set to 872 m/sec and the temperature to
220°K (based upon equations (2.19), (2.20), and (8.1)). Eight background chamber pressures were simulated - 1.33, 4.00, 6.66, 13.3, 26.7, 53.3, 93.3, and 187 Pa (0.01 - 1.40 Torr) - to parallel the experimental results of Chapter 5. For each chamber pressure, three Mach numbers were simulated - Mach 1.45, 1.75, and 1.95. While the total number of atoms simulated was held generally constant (~1,000,000), the number of atoms per cell decreased as the background chamber pressure increased. The effect which this might have on the accuracy of results was of concern. Bird’s most recent publication suggests that each cell should contain a minimum of ten to twenty atoms per cell [234]. Examination of the simulated conditions showed that to meet this criterion, the number of atoms simulated for the 187 Pa conditions had to be increased to more than 2 million to provide a reasonable level of accuracy. Higher chamber pressures were not simulated due to the extreme computational expense of higher pressure runs. Carrier gas flowfield simulations performed with 2,000,000 atoms at 167 Pa required 7-10 days of dedicated computational time on an IBM J40 system. (There were no other users of the system while these calcula-

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform cell width in x direction</td>
<td>Yes</td>
</tr>
<tr>
<td>Uniform cell width in y direction</td>
<td>No</td>
</tr>
<tr>
<td>Ratio of cell width at outer y boundary to that at the inner y boundary</td>
<td>3</td>
</tr>
<tr>
<td>Number of subcells in x and y directions</td>
<td>2</td>
</tr>
<tr>
<td>Weighting factor</td>
<td>Yes</td>
</tr>
<tr>
<td>Weighting factor reference radius</td>
<td>0.004</td>
</tr>
<tr>
<td>Diffusely reflecting substrate</td>
<td>Yes</td>
</tr>
<tr>
<td>Substrate circumferential velocity</td>
<td>0 m/sec</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>300 K</td>
</tr>
<tr>
<td>Carrier gas reference diameter (He)</td>
<td>2.33x10^{-10} m</td>
</tr>
<tr>
<td>Carrier gas data reference temperature</td>
<td>273 K</td>
</tr>
<tr>
<td>Carrier gas molecular mass</td>
<td>6.65x10^{-27} kg</td>
</tr>
<tr>
<td>Viscosity temperature power law</td>
<td>0.66</td>
</tr>
<tr>
<td>Reciprocal of the variable soft sphere scattering parameter</td>
<td>1</td>
</tr>
</tbody>
</table>
tions were being performed!) Based on Bird’s criterion of ten to twenty atoms per cell, at least 3-4 million atoms should be simulated at a chamber pressure of 333 Pa. It is estimated that each run would then have required 3-4 weeks of uninterrupted, dedicated computational time just to obtain the flowfield. Atom tracking would then have required perhaps 1-2 weeks of additional multiprocessor computational time if eight or more J40 processors could be dedicated to the effort. These calculations were not attempted.

8.2 Biatomic Collision Theory (BCT) Modeling of Vapor Transport

Modeling the transport of vapor atoms in the flow of a rarefied transonic jet was performed using a stochastic biatomic collision theory (BCT) model which employs many of the same general binary elastic collision concepts as the DSMC method just described. While the DSMC from Bird allowed the overall gas flowfield characteristics to be determined, the BCT code allowed individual atoms to be tracked through a flowing background gas from vapor source to deposition substrate with the trajectories of the individual atoms being determined by binary collisions. Written in fortran 77 (Appendix D), the compiled code follows vapor atoms one at a time from the crucible source to the substrate or out of the modeled volume (c.f. Fig. 8.1). During vapor atom transport modeling, vapor atom collisions with individual carrier gas atoms were simulated at intervals determined from mean free path calculations, with each collision event being treated as an elastic, momentum transferring event which changes the velocity vector of the vapor atom. The flow chart of Fig. 8.5 lays out the computational sequence of the BCT model and lists the outputs of the model which simulated a neutral, monoelemental, monatomic carrier gas interacting with a neutral, monoelemental, monatomic vapor atom. To allow comparison between modeling results and the experimental work of Chapter 4, copper was used as the vapor atom for all DVD simulations.
8.2.1. Initial conditions

The inputs for the BCT model are listed in Table 8.3. The source material temperature during evaporation ($T_v$) and the exponent (n) for the equation describing the vapor distribu-
tion as it leaves the crucible (equation (2.2)) were used at the beginning of the model calculations to determine the initial magnitude and direction of the vapor atom’s velocity vector. As described in Chapter 2, studies have shown [11] that controlled e-beam evaporation typically generates evaporant atoms with 0.1 - 0.2 eV of kinetic energy at a source vaporization temperature \( T_v \) which would lead to an equilibrium vapor pressure of 1 Pa. Using readily available empirical data of vapor pressure versus vaporization temperature for the elements [2, 11], a reasonable value of \( T_v \) for the chosen vapor atom was selected as an input to the model (e.g., for a vapor pressure of 1 Pa, \( T_v \)\textsubscript{Cu} = 1550 K). The initial kinetic energy of each vapor atom was then calculated using the Boltzmann temperature equation and the standard kinetic energy equation (equation (2.4)). For copper, the evaporant surface temperature of 1550 K resulted in an initial vapor atom kinetic energy of 0.2 eV, corresponding to a speed of 777 m/sec.

Having computed the magnitude of the initial vapor atom velocity, the direction of the vapor atom leaving the crucible also had to be determined. As noted in Chapter 2, the density of vapor atoms leaving a high-vacuum e-beam evaporant surface can be described generally by equation (2.2). For the DVD simulations described, the exponent \((n)\) in equation (2.2) was chosen as five based upon experimental measurement of the vapor distribution leaving a crucible in a high vacuum e-beam system (Appendix E)\(^1\). In the newly developed BCT model, the vapor atom’s initial direction of travel was selected by generat-

---

**Table 8.3: Required inputs for bimolecular collision theory model**

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>Vapor Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>Atomic Number</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>( r, z ) location of DSMC code grid points (Fig. 8.1)</td>
<td>Source material temperature ((T_v)) at which equilibrium vapor pressure = 1 Pa</td>
</tr>
<tr>
<td>( U_c, P_c, T_c ) at DSMC code grid points</td>
<td>Exponent (n) for the vapor distribution (see equation (2.2))</td>
</tr>
</tbody>
</table>
ing two random numbers which were used to select the angles $\theta$ and $\alpha$ (Fig. 8.6). While

![Diagram showing the calculation of the initial vapor atom trajectory.](image)

Figure 8.6 **Calculation of the initial vapor atom trajectory.** Given the magnitude of the initial vapor atom velocity ($U_{vi}$), selection of $\theta$ and $\alpha$ allows the vapor atom velocity vector ($U_{vi}$) to be described.

the probability density function (PDF) for $\alpha$ was equally weighted across the range 0 to $2\pi$, the PDF for $\theta$ was weighted in accordance with the variation of $I/I_0$ in equation (2.2) across the range 0 to $\pi/2$. Schiller et al. [11] provided the actual PDF (equation (2.3)) which was used to generate the vapor atom distribution (Fig. 8.7).

Having computed the initial magnitude and direction of the vapor atom velocity vector, the vapor atom was released into the flowfield for calculation of its subsequent trajectory resulting from carrier gas / vapor atom collisions. The center of the vapor atom source was placed 3.5 cm from the nozzle towards the substrate and 6.4 mm below the modeled volume centerline with the crucible oriented as shown in Fig. 8.1. The radius of the source

---

1 Research by others shows that this simple equation precisely predicts the vapor distribution density at low and moderate e-beam evaporation rates (e.g. from 5 - 10 kW systems), for $\theta$ between 0 and $\pi/6$, while slightly overpredicting the density for angles between $\pi/6$ and $\pi/2$ [11].
was chosen as 3.175 mm and vapor atoms had an equal probability of leaving any point on
the target surface to simulate evaporation using a fixed e-beam for evaporation.

8.2.2. Distance between collisions

Once the vapor atom was released, it traveled along its constant velocity vector until col-
liding with a carrier gas atom. McDaniel [126] and Bird [141] have both shown that the
point at which such a collision occurs can be determined from a calculation of the atom’s

Figure 8.7 Spatial distribution of deposited vapor. Variation of the exponent n in
equation (2.3) allows the vapor distribution deposited onto a flat substrate to
be rapidly modified.
mean free path ($\lambda$), and, for an atom traveling in a gas whose velocity distribution follows a Maxwell-Boltzmann distribution:

$$\lambda = \frac{RT_c}{\sqrt{2}P_cN_A\sigma_d}$$  \hspace{1cm} (8.2)

where $R = \text{Universal gas constant (8.3145 J/(mol K))}$,

$T_c = \text{Average carrier gas temperature along vapor atom’s path of travel (K)}$,

$P_c = \text{Average carrier gas pressure along vapor atom’s path of travel (Pa)}$,

$N_A = \text{Avogadro’s number (6.0221x10}^{23}\text{ atoms/mol)}$, and

$\sigma_d = \text{Directed momentum transfer cross-section for the specific gas/vapor combination.}$

Note that equation (8.2) is a more detailed expression of equation (2.25) in which the density ($n$) is now expressed using the Universal Gas Law and in which the atomic hard-sphere area ($\pi d^2$) is expressed more precisely by the directed momentum transfer cross-section ($\sigma_d$). While equation (8.2) provides the mean free path, the distance between collisions actually varies in the real system. This variation is typically described using a Poisson distribution [188, 145]:

$$P_{\text{collision}} = \frac{1}{\lambda} e^{-x/\lambda} dx$$  \hspace{1cm} (8.3)

to generate the probability of a collision occurring between $x$ and $x + dx$. Equation (8.3) was employed in the BCT model to distribute the free path.

Of the variables included in equation (8.2), $\sigma_d$ is the most challenging to determine. While $T_c$ and $P_c$ were obtained directly from the output of the DSMC code, the directed momentum transfer cross-section ($\sigma_d$) had to be computed using classical two-body collision con-
cepts wherein the final calculated cross-section depended upon the relative kinetic energy of the two atom’s involved in a scattering event (E), the impact parameter\(^1\) (b), the center of mass scattering angle (\(\chi\)), and the angular differential cross-section (\(\sigma(\chi)\)). Massey [127] notes the applicability of these classical concepts to the two-atom collision event under study here:

Because of the relatively large masses of gas atoms, these collisions [elastic collisions between gas atoms with energies in the thermal or near-thermal range] are nearly classical. Thus the wavelength of relative motion is short compared with the range of interaction between the atoms, with the exception of only helium atoms at low temperatures [\(\sim 1 - 5\,^0\text{K}\)]. Apart from this exception, the viscosity and diffusion coefficients of gases may be calculated by classical mechanics, provided the atomic interactions are known.

8.2.3. Calculation of the directed momentum transfer cross-section (\(\sigma_d\))

Massey and Burhop and others [128, 129, 130] show that the directed momentum transfer cross-section of equation (8.2) is defined by:

\[
\sigma_d = 2\pi \int_0^\pi (1 - \cos \chi) \sigma(\chi) \sin \chi \, d\chi
\]  

(8.4)

where \(\chi\) = Deflection angle for either atom in center of mass reference frame and \(\sigma(\chi)\) = Angular differential cross-section.

The angular differential cross-section employed in equation (8.4) is given by [131, 187]:

\[
\sigma(\chi) = \frac{b}{\sin \chi} \left| \frac{db}{d\chi} \right|
\]  

(8.5)

\(^1\) impact parameter - the closest approach that would be achieved by two atoms if their interatomic potentials were not allowed to induce repulsion or attraction.
where both $\chi$ and $b$ are functions of the energy of the atomic interaction event ($E$). Substitution of (8.5) into (8.4) yields:

$$
\sigma_d = 2\pi \int_0^{b_{max}} (1 - \cos \chi) b db
$$

(8.6)

where $b_{max}$ is the maximum range of interaction (i.e. maximum effective radius) of atoms involved in collision event.

In equation (8.6) $\chi$ is a function of $b$ and of the energy ($E$) of the specific collision event, making exact solution of $\sigma_d$ difficult for the dynamic problem under consideration here (i.e., Each collision has a unique energy associated with it, creating a unique functional dependence of $\chi$ upon $b$.) The energy of a collision event is determined by computing the relative velocity of the two atoms ($U_r$) and a “reduced” mass ($m_r$) of a single particle interacting with an interatomic potential field (Fig. 8.8). The kinetic energy of the collision event ($E$) is thus given by equation (2.4). In this equation, the mass is a “reduced” mass:

$$
m_r = \frac{m_v m_c}{m_v + m_c}
$$

(8.7)

where $m_v = \text{Vapor atom mass}$ and $m_c = \text{Carrier gas atom mass}$.

The relative velocity is:

$$
\hat{U}_r = \hat{U}_v - \hat{U}_c,
$$

(8.8)

where $U_v = \text{Vapor atom velocity vector before collision}$ and $U_c = \text{Carrier gas atom velocity vector before collision}$. 
Fig. 8.8 illustrates the functional relationship between $b$ and $\chi$ for the universal potential [136] and for various values of $E$. To simplify solution of equation (8.6), Somekh [188] suggests that a straight-line approximation be made (the dashed lines of Fig. 8.8) in which:

$$\chi(b) = \frac{d\chi}{db} b + \pi \tag{8.9}$$

where $\frac{d\chi}{db} = \text{Constant slope}$. 

**Figure 8.8  Impact parameter / deflection angle vs. energy of collision event.** The range of impact parameters over which a significant interatomic collision induced deflection takes place is dependent upon the relative kinetic energy of the particles being deflected.
Given this approximation, equation (8.4) can be solved to yield:

\[
\sigma_d = \pi (b_{\text{max}})^2 + 2\pi \left[ \left( \frac{db}{d\chi} \right)^2 \cos \left( \frac{db}{d\chi} b_{\text{max}} \right) + \left( \frac{db}{d\chi} b_{\text{max}} \right) \sin \left( \frac{db}{d\chi} b_{\text{max}} \right) - \left( \frac{db}{d\chi} \right)^2 \right]. \quad (8.10)
\]

Despite the reasonable ease with which this equation can be obtained, study of Fig. 8.8 shows that the straight-line approximation which it represents severely underestimates the actual distance over which an atom’s interatomic potential acts for the low energy interaction events of interest here. Johnson has suggested that \(\sigma_d\) can be approximated as follows:

\[
\sigma_d \equiv \pi (b_{\text{max}})^2 \quad (8.11)
\]

if \(b_{\text{max}}\) can be reasonably determined for each collision event [189]. The next section will propose a method for calculating such an estimate of \(b_{\text{max}}\) which will then allow the distance between collisions in the modeled system to be calculated using the approximation of equation (8.11).

### 8.2.4. Determination of the range of atomic interaction \((b_{\text{max}})\)

To make vapor transport calculations possible, researchers have suggested various cutoff values for \(b_{\text{max}}\), near the intersection of the straight-line approximation with the x-axis (Fig. 8.8). For instance, Somekh [188] has proposed that the selected value of \(b_{\text{max}}\) should correspond to 1.1 times the value of \(b\) defined by the intersection of the straight line approximation with the x-axis of Fig. 8.8. The BCT model employed a different approach in which \(b_{\text{max}}\) was chosen to represent the impact parameter corresponding to a chosen minimum “cutoff” deflection angle (e.g., 0.01 radians). The \(b_{\text{max}}\) chosen through this method is greater than that proposed by Somekh [188] and others [129]. To solve for the
\( b_{\text{max}} \) corresponding to a “cutoff” deflection angle, the relationship between \( \chi, b, \) and \( E \) used to generate Fig. 8.8 must be evaluated [129, 131, 133]:

\[
\chi = \pi - 2 \int_{r_{\text{min}}}^{\infty} \frac{b}{r^2} \left[ 1 - \left( \frac{b}{r} \right)^2 - \frac{V(r)}{E} \right]^{1/2} dr
\]  

(8.12)

where

- \( r = \) Distance between the atoms,
- \( r_{\text{min}} = \) Distance of closest interatomic approach, and
- \( V(r) = \) Interatomic potential.

Robinson [129] and Johnson [131] note that integration of equation (8.12) is difficult due to the infinite upper limit and the singularity of the integrand at the point of closest approach \( r_{\text{min}} \). Except for the limited cases in which an analytical solution is possible (e.g. for a Coulomb interaction potential), both authors suggest the use of quadrature schemes to solve for the deflection angle, with Johnson proposing a simple quadrature in which [135]:

\[
\chi(b) \approx \pi \left[ 1 - \frac{1}{m} \sum_{i=1}^{m} g(x_i) \right]
\]  

(8.13)

where

\[
g(x_i) \equiv \frac{b}{r_{\text{min}}} \left[ \frac{1 - x_i^2}{1 - \left( \frac{b}{r_{\text{min}}} \right)^2 x_i^2 - \frac{V(r_{\text{min}})}{E} x_i^2} \right]^{1/2}
\]  

(8.14)
and

\[ x_i = \cos \left[ \frac{(2i - 1)\pi}{4m} \right] \] (8.15)

with \( m \) being the number of terms used in the calculation\(^1\). (\( m \) was chosen as 10 for these calculations. This estimation was found to introduce errors of a few percent into the calculations.)

For the BCT model of DVD vapor transport, the universal potential of Ziegler et al. [136] was chosen to describe the interaction of the carrier gas and vapor atoms:

\[ V(r) = \frac{Z_A Z_B e^2}{r} \Phi \left( \frac{r}{a_u} \right) \] (8.16)

where

- \( Z_A \) = Atomic number of carrier gas,
- \( Z_b \) = Atomic number of vapor atom,
- \( e \) = Charge on an electron (1 eV),
- \( a_u \) = Born radius (0.529 Å), and

\[ \Phi \left( \frac{r}{a_u} \right) = 0.1818 e^{-3.2(r/a_u)} + 0.5099 e^{-0.9423(r/a_u)} + 0.2802 e^{-0.4029(r/a_u)} + 0.02817 e^{-0.2016(r/a_u)} \]

In the expression for \( \Phi \), \( r \) and \( a_u \) are both expressed in terms of angstroms. This purely repulsive potential represents the curve fitting results of theoretically generated potentials to laboratory data for randomly chosen atom pair interactions. Comparison with previously proposed potentials (e.g. Moliere, Lenz-Jensen, and C-Kr) shows that the universal potential produces better agreement between theory and experiment (standard deviation =

\(^1\) Calculation of \( \chi(b) \) could also be accomplished, perhaps more quickly, using a so-called Magic Formula (e.g. the Biersack-Haggmark scattering Magic Formula) [136].
5%) when interaction event energies are greater than a few eV [136]. The use of the universal potential in low energy collision events between species like helium and copper (e.g., total collision energy < 1 eV as most often encountered in the DVD system) is somewhat less appropriate due to a need to include precise orbital calculations at these energy levels [136, 218, 219]. Still, Ziegler, et al. [136] note that “the universal potential is valid for noble gas scattering to potential energies well below 1 eV,” and the current lack of interaction potential data for low energy collisions between species such as helium and copper suggests that use of the universal potential for DVD modeling is a reasonable approach at this time [220, 221].

The solution of equation (8.12) for a specific value of $\chi_{\text{cutoff}}$ must be done in an iterative manner by choosing a value of $b$ for a given $E$, finding $r_{\text{min}}$, and then computing $\chi$. Using a standard bisection solution routine [222], $b$ is then increased or decreased from its initial value until $b_{\text{max}}$ is determined for the desired cutoff angle $\chi$. Fig. 8.9 shows the relationship between $b_{\text{max}}$ and $E$ for three different cutoff values of $\chi$. Because of the log-linear relationship between $E$ and $b_{\text{max}}$ for a given value of $\chi$, once $\chi_{\text{cutoff}}$ is chosen, the specific functional relationship can be determined and the simple function placed inside the BCT code to compute $b_{\text{max}}$.

During the solution of equation (8.12), $r_{\text{min}}$ is also computed iteratively. Robinson and others [129, 133] point out that $r_{\text{min}}$ is the zero of the radicand in equation (8.12). Thus, the same bisection routine employed to find $b_{\text{max}}$ can be used to compute $r_{\text{min}}$, given upper and lower bounds on its possible magnitude (e.g., 0 and 15 Å).

Determination of $b_{\text{max}}$ allows $\sigma_d$ and in turn $\lambda$, the mean free path, for any given collision event energy ($E$) to be calculated. Fig. 8.10 summarizes the steps involved in computing the directed momentum transfer cross-section and thus the vapor atom’s mean free path. As the flowchart of Fig. 8.5 notes, if the vapor atom has not left the modeled region or hit
Figure 8.9 **Log-linear fits for** $\chi_{\text{cutoff}}$. For copper-helium interactions, the data points represent solution of equation (8.12) while the lines represent the log-linear curve fits noted above each line.

---

**Compute vapor atom mean free path**

- Compute relative velocity of atoms, $U_r$.
- Compute reduced mass, $m_r$, of single particle interacting with a potential field.
- Compute energy, $E(U_r, m_r)$, of collision event.
- Determine maximum range of atomic interaction, $b_{\text{max}}(E)$, as per Fig. 8.9.
- Compute the directed momentum transfer cross-section using equation (8.11).
- Compute the mean free path using equation (8.2).

Figure 8.10 **Summary of steps required to determine atomic mean free path** $\lambda$. 
the substrate after traversing one mean free path, the change in the magnitude and direction of the vapor atom velocity vector resulting from a collision must now be calculated.

8.2.5. Collision event

Landau and Lifshitz [133] succinctly describe how to solve for the energy and momentum transfer during an elastic two body collision in three dimensions, with the two atoms involved in the collision event changing velocity vector (magnitude and direction) as the result of the interaction. The velocity vectors of the two atoms prior to the collision event \((\mathbf{U}_c, \mathbf{U}_v)\), the mass of the atoms \((m_c, m_v)\), and the form of the interaction potential \(V(r)\) represent the three critical inputs to the calculation. For this BCT model, the average carrier gas velocity vector \((\mathbf{U}_c)\) provided by the DSMC code for the directions \(r, \theta,\) and \(z\) was modified to generate more realistic vapor velocity vectors following a collision. The carrier gas atoms in the actual flow possessed a distribution of velocities approximately described by an ellipsoidal drifting Maxwellian (normal) distribution [118]:

\[
\phi = n \left( \frac{m_c}{2 \pi k T_c} \right)^{3/2} \exp \left( -m_c \left( \frac{(U_{\|} - U_c)^2}{2kT_c} - U_{\perp}^2 \right) \right)
\]  

(8.17)

where \(\phi\) =Magnitude of the normal distribution for a given value of \(U_c\),

\(n\) = Carrier gas atom number density \((\text{atoms/m}^3)\)

\(U_{\|}\) = Carrier gas velocity parallel to primary flow, and

\(U_{\perp}\) = Carrier gas velocity perpendicular to primary flow.
Note that equation (8.17) is a modification of the more commonly used Maxwell-Boltzmann equation used to describe a distribution of atomic velocities in a gas at thermal equilibrium [223]:

\[
\phi = 4\pi \left( \frac{m_c}{2\pi k T_c} \right)^{3/2} \nu^2 \exp\left( \frac{-m_c \nu^2}{2k T_c} \right)
\]

(8.18)

where \( \nu \) is the molecular speed (m/sec).

Equation (8.17) is designed to take into account the fact that there is a directional flow of gas in the DVD system, and therefore it was used to distribute the velocity vector of the carrier gas atom involved in each collision from the average DSMC value. For simulations of DVD, carrier gas atom velocities were distributed using the inflection points of the bell shaped curve (\( \phi \)) as the standard deviation (\( \zeta \)) [224]:

\[
\zeta = \pm \left[ U_{ll} - \left( \frac{k T_c}{m_c} \right)^{1/2} \right].
\]

(8.19)

As is traditionally done in the literature when computing the results of an elastic collision event, the initial velocity vectors of the two atoms involved were converted from their laboratory reference frame to vectors in the center-of-mass (CM) reference frame, allowing calculation of the momentum and energy change resulting from the collision:

\[
\hat{U}_{vcm} = \frac{m_v \hat{U}_r}{m_v + m_c}
\]

(8.20)

\[
\hat{U}_{ccm} = \frac{-m_v \hat{U}_r}{m_v + m_c}
\]

(8.21)

where \( U_{vcm} = \) Velocity of vapor atom in CM system prior to collision,
\( U_{ccm} = \) Velocity of carrier gas atom in CM system prior to collision, 
\( m_v = \) Vapor atom mass, and 
\( m_c = \) Carrier gas atom mass.

In this reference frame, the center of mass is at rest (Fig. 8.11). \( U_{vcm}, U_{ccm}, \) and the center of mass are all contained within one plane, and the momenta of the two particles are equal in magnitude, opposite in direction. Because the momenta of the two particles are equal in magnitude, the angle of deflection (\( \chi \)) of the particles in the CM system will also be equal. Landau and Lifshitz note that in the CM system an elastic collision simply rotates the two atoms through an angle \( \chi \) (change in velocity direction) but does not change their speed.

Figure 8.11 Parameters factoring into a collision calculation. If the velocity and position vectors of colliding atoms are written in a center of mass coordinate system, then the relation between the atoms, collision event (b) impact parameter, and resulting angle of deflection (\( \chi \)) can be succinctly illustrated. Here the positions of two colliding atoms are shown at snapshots in time throughout the collision event.
(velocity magnitude). If the collision were to occur between two hard spheres \textit{with no interatomic potential active between them}, then \(b\) would equal 0, \(\chi\) would equal \(\pi\), and the direction of the two particles would be exactly reversed in the CM system after the collision. However in a system where interatomic potentials are active, a collision occurs whenever the two particles are in the vicinity of one another, resulting in some generally smaller deflection (less than or equal to \(\pi\) and greater than \(\chi_{\text{cutoff}}\) as noted in section 8.2.4.).

In such an event, an atom which was moving along a direction \(q\) (unit vector) prior to the collision will be moving along a direction \(n_o\) (unit vector) after the collision (Fig. 8.12).

![Figure 8.12 Determination of the post-collision velocity vector.](image)

To compute the overall change in vapor atom speed and direction following a collision, the change in direction of the vapor atom in the CM reference frame from \(q\) to \(n_o\) must first be determined. Then the atom’s new velocity vector in the CM system (unchanged in magnitude) can be added to the velocity vector of the center of mass to establish the vapor atom’s new velocity (speed and direction) in its original laboratory frame of reference.
Landau and Lifshitz [133] state that the velocity vector for the vapor atom after a collision is given by:

\[
\vec{U}_v = \frac{m_v \hat{U}_v}{m_c + m_v} + \frac{m_v \hat{U}_v + m_c \hat{U}_c}{m_c + m_v}
\]  

(8.22)

where the first term represents the vapor atom’s new CM velocity vector and the second term represents the velocity of the center of mass.

Determination of \(n_o\) involves computing the proportion of the post-collision vapor atom CM velocity vector which lies in the original vapor atom CM velocity vector direction (\(q\)) and the proportion which lies perpendicular to that original direction, along \(s\). The only requirement for \(s\) (unit vector) is that it be in the plane perpendicular to \(q\). Although \(s\) has three components of its vector which must be determined (e.g. \(a_i + b_j + c_k\)), only two governing relationships can be specified about \(s\) since it is not an explicit vector but rather any vector confined to the plane perpendicular to \(q\). First, \(s\) is perpendicular to \(q\). Therefore the dot product \(q \cdot s\) will equal zero. Second, since \(s\) is a unit vector, the sum of the squares of its three components will equal one. Substituting the solution of the first equation (for \(a_i\)) into the second equation leads to a second order polynomial (for \(b_j\)) in terms of the third component (\(c_k\)) of \(s\) and the three components of \(q\). Since the three components of \(q\) are known, a quadratic equation can be set up to solve for \(b_j\) in terms of \(c_k\). \(s\) can now be solved for explicitly by selecting \(c_k\) subject to two restrictions. First, \(c_k\) must be from -1 to 1 since \(s\) is a unit vector. Second, the \(c_k\) component randomly chosen between -1 and 1 must create a real number as a part of the root of the quadratic equation for \(b_j\). If the \(c_k\) randomly selected between -1 and 1 does not produce a real number, another value for \(c_k\) can be randomly chosen from -1 to 1. This process can be repeated until a valid \(c_k\) (and thus \(s\)) is produced.
To complete the calculation, the magnitude of $b$, in the $s$ direction, can be randomly chosen between 0 and $b_{\text{max}}$, and then the CM deflection angle $\chi$ can be calculated by the sequence of steps described in section 8.2.4. Once equation (8.22) has been solved, the computational sequence shown in Fig. 8.5 can be repeated until the vapor atom contacts the substrate or crosses one of the other modeling volume boundaries. Fig. 8.13 summarizes the steps involved in computing the change in the vapor atom velocity vector as a result of the collision.

**Figure 8.13 Steps to compute new vapor atom velocity vector after a collision.**

### 8.3 Summary

Having described the design of the vapor transport model developed as a portion of this research program, the accuracy of the method will be assessed in Chapter 9 before being used to study Directed Vapor Deposition in Chapters 10 and 11. Most calculations for this modeling work were performed on either a 16 node IBM SP2 computer system or two 8 CPU IBM J40 computer systems. Both types of systems are RS6000 class, Unix-based
machines. While the DSMC code was not designed to operate in parallel, it was possible to run the BCT model in a simple parallel mode because it simulated one vapor atom in the carrier gas field at a time. Thus several BCT simulations could be run simultaneously on separate processors using different random number seeds to ensure that the data set generated by each parallel run was unique.
Chapter 9

Vapor Transport Model Verification

Having constructed a vapor transport model for the study of Directed Vapor Deposition, model verification studies were undertaken to assess the ability of the model to replicate different well characterized results presented in the literature. These studies examined the ability of Bird’s two dimensional axisymmetric DSMC model to reproduce the carrier gas jet structure observed in Fig. 5.6. They also explored the ability of the BCT model to predict the distance between atomic collisions in a system for a given pressure (i.e. to estimate the mean free path correctly), the random walk motion of an individual argon atom in an argon gas volume at thermal equilibrium, and the energy loss for sputtered atoms traveling from sputtering target to deposition surface through various pressures of argon.

9.1 Verification of DSMC Results

To validate the flowfield results produced by the DSMC code, a simulation was run to reproduce the gas jet structure recorded in Fig. 5.6 a). To replicate this experimentally observed result, the DSMC code was configured to use argon as the carrier gas entering a chamber pressure of 50 Pa (0.375 Torr) with a nominal Mach number of 1.70 (mixing
chamber/process chamber pressure ratio = 5.40). The model’s results are shown in comparison with the experimentally recorded flowfield structure (Fig. 9.1).

![Figure 9.1](image)

**Figure 9.1 Comparison of flowfield simulation with experimental result.** Comparison of DSMC output with experimental visualization demonstrates reasonable reproduction of actual flow structures. (Conditions: gas type = argon, chamber pressure = 50 Pa (0.375 Torr), pressure ratio = 5.40)

The comparison of model and experiment shows reasonable agreement between the two. Specifically, the location of the zone of silence, Mach disk, and secondary barrel shocks observed experimentally are replicated by the model. Note however that the model does not show the fast flow region narrowing as quickly as is observed experimentally. Conceivably, the ionization/excitation phenomenon which makes the flowfield visible experi-
mentally is not producing a profile of Mach number but rather of some other process variable like temperature or pressure. However, visualization of these two system variables with the DSMC code did not lead to a closer fit between experiment and model; the width of the core flow region remained essentially the same for all variables.

Another distinct result of the modeling is that, for the given pressure ratio, portions of the gas flow reach substantially higher Mach numbers than is suggested through the use of equation (2.4). This latter point probably highlights the limited validity of the one dimensional isentropic flow equations rather than a problem with the DSMC code.

An additional comparison between model and experiment was performed to replicate the flow structure of Fig. 5.6 d) for argon at a chamber pressure of 50 Pa and a pressure ratio of 16.7 (nominal M = 2.5). These results did not show the same level of agreement between model and experiment. The model predicted the Mach disk to be significantly further downstream than actually observed. This overprediction of the length of the zone of silence by the DSMC method has also been reported elsewhere by Boyd et al. [150]. In their study, Boyd et al. suggest that the discrepancy could be the result of selecting incorrect boundary or inlet conditions for the DSMC modeled regime. The discrepancy could also be the result of VHS and VSS approximations as discussed in section 2.2.5. Although the discrepancy is of concern, its effect upon the conditions simulated in Chapter 10 should be minimal since the simulated Mach numbers of 1.45, 1.75, and 1.95 are near the pressure ratio regime where good agreement has been demonstrated (Fig. 9.1).

9.2 BCT Model Verification

The validity of the BCT code was assessed through a set of model verification simulations. As highlighted in the flowchart of Fig. 8.5, model accuracy depends most impor-
tantly upon correct calculation of the vapor atom velocity vector following a collision event where assessment of the validity of the velocity vector involves verification of both its direction and magnitude. None of the BCT model verification tests described in this section relied upon the DSMC code. Rather than use a flowing gas field as an input, these verification studies employed just sixteen gridpoints to describe the temperature, pressure, and size of a cylindrical volume filled with argon gas at thermal equilibrium.

9.2.1. Random walk

Having demonstrated the ability of the BCT model to predict the distance between atomic collisions correctly, a study was undertaken to investigate whether or not the BCT model correctly computed the angle of deflection of the atoms involved in each collision event. For this purpose the model was configured to simulate the “random walk” of a thermalized argon atom in a volume of argon at equilibrium.

Random walk theory has been the subject of numerous books and articles and has been used throughout science to describe various processes such as surface diffusion of an atom (Fig. 9.2) and vapor phase diffusion in an equilibrium gas [225-227]. For the classic, pure

Figure 9.2  **Random walk on an atomic surface.** During surface diffusion, an atom on the surface of a crystal has an equal probability of jumping to any of the neighboring sites. This leads to random walk of the atom.

random walk problem of atomic surface diffusion on a perfect lattice, the atom illustrated
in Fig. 9.2 has an equal probability of jumping in any of four directions. Since it is equally probable that the atom will travel in any of the four directions for any jump, on average, there will be no net motion in any one direction. However, as time passes, the probability increases that the atom will be found some distance from its starting point. If a large number of atoms are simulated, after \( n \) jumps of a constant length \( l \), the average straight line distance an atom has moved from its starting point will be \( D = n\sqrt{l} \) [61]. (Note: This is not the total distance the atom has traveled, which would be \( D = nl \).)

When applied to atomic diffusion in the vapor phase, random walk theory must account for subtle but important distinctions from the surface diffusion example. The most important difference is that vapor phase diffusion is not a pure random walk problem. In the surface diffusion example, the atom had an equal probability of jumping to any of the neighboring surface sites. In the vapor transport problem, such an equal probability would mean that, following a collision event, the atom being tracked has an equal probability of leaving a collision point in any direction. This is not the case for vapor phase diffusion because the velocity of the tracked atom coming into the collision event biases its future direction of travel. Chapman and Cowling summarize the effect of this bias [143]:

> After a collision with another molecule the velocity of a given molecule will, on the average, still retain a component in the direction of its original motion. This phenomenon is known as the persistence of velocities after collision. As a consequence, the average distance traversed by a molecule in the direction of its velocity at a given instant, before (on the average) it loses its component motion in that direction, is somewhat greater than its (Tait) mean free path.

Fig. 9.3 illustrates a single “jump” for the case of vapor phase diffusion. Surprisingly, an analytical solution describing the magnitude of this forward bias does not appear in the literature to date [228]. Thus, simulation of vapor phase random walk will provide only a
Figure 9.3  **Persistent random walk during vapor phase diffusion.** Persistence of the velocity of the atom being tracked results in a probability density function for the angle of scattering which is not uniform over all angles but rather a function of the velocity of the atom being tracked. A forward bias exists even though the atom with which it collides has an equal probability of entering the collision from any direction and on average has the same velocity magnitude as the tracked atom.

A general measure of the BCT code’s validity. Rather than describing the distance traveled by \( D = n \sqrt{l} \), it should be possible to describe the distance by \( D = n \sqrt[3]{\lambda_e} \) where the effective mean free path \( \lambda_e \) is slightly greater than the actual, measured value of \( \lambda \) (as Chapman and Cowling have explained). Thus a plot of distance from the starting point versus number of collision events should show that \( D = n \sqrt[3]{\lambda} \) slightly underpredicts the distance traveled by a consistently small amount (\( \sqrt[3]{\lambda_e} / \sqrt[3]{\lambda} \)).

It should also be noted that random walk theories of vapor phase transport employ hard spheres with no interatomic potentials active between them. (The model is capable of sim-
ulating random walk in a system employing interatomic potentials and could be used as a tool for developing a simple random walk expression in this system similar to \( D = n \sqrt{\lambda} \).

Fig. 9.4 shows the results of a hard sphere simulation of vapor phase random walk in which no interatomic potential is active. The figure compares this prediction with than of pure random walk as described \( D = n \sqrt{\lambda} \).

Figure 9.4 **Pure vs. persistent random walk.** The BCT simulation of random walk for an argon atom in thermal equilibrium with a chamber full of argon shows the expected forward bias which makes the atom travel slightly further than predicted by pure random walk theory.

The results plotted in Fig. 9.4 represent the average distance traveled by 1000 argon atoms from their starting point as a result of 1 to 10,000 collisions with background argon atoms (i.e., the straight-line distance from start point to finish point). Each of the 1000 atoms was tracked individually with the average distance traveled per mean free path step computed after all atoms had been simulated. The average mean free path for all diffusion during the
simulation was 5.18 mm, and this value of $\lambda$ was used to compute the pure random walk line shown in Fig. 9.4. The “distance traveled” results generated by the BCT model predict that the vapor atom will travel 11.5 - 13.5% further each mean free path step than predicted by pure random walk theory (i.e. $\lambda_e/\lambda = 1.115 - 1.135$). While there is no vapor phase random walk theory against which to compare this result, the bias generated by the BCT model is consistent over all 10,000 steps, and it represents a bias in the direction predicted by Chapman and Cowling. Thus, it appears that the model reasonably predicts the direction of the vapor atom after a collision.

9.2.2. Atomic energy loss

To investigate whether or not the BCT model correctly transfers energy between two colliding atoms, the model was configured to simulate a sputtering system in which high energy copper atoms departing a sputtering target travel through an argon gas atmosphere. During their traverse of the sputtering chamber, the energetic copper atoms collide with argon gas atoms (in thermal equilibrium at 350K), leading to a reduction in copper atom kinetic energy. Sputtered atom energy was measured at fixed distances from the target (2.50 and 5.00 cm) for different chamber pressures ($10^{-6}$ - 100 Pa) to reveal the dependence of kinetic energy loss upon chamber pressure. To assess the validity of the BCT model’s results, the energy loss results produced by the model were compared with the models of others [229, 230] and with one of the few sets of experimental data available in the literature for sputtered atom energy loss versus argon chamber pressure and distance [231].

The initial copper atom kinetic energy distribution leaving a sputtering target is substantially different than that of atoms leaving an e-beam evaporant source [60]. A sputtered atom energy distribution based upon study of the literature [232] was incorporated into the
BCT model to facilitate more accurate simulation of sputtering (Fig. 9.5). Interatomic potentials were employed for these simulations with $\chi_{\text{cutoff}} = 0.01$ radians. To allow comparison with the results reported in the literature, the average energy of the sputtered atoms as they left the sputtering target was 5.1 eV.\(^1\) Atoms were allowed to leave from a target 5.08 cm in diameter which was centered above the round 10.00 cm diameter substrate surface. During calculation of the momentum transfer during a collision event, equation (8.17), used to distribute gas atom velocities in the flowing carrier jet, was replaced with the more common Maxwell-Boltzmann distribution (equation (8.18)) used to describe atom velocities in a thermal equilibrium gas [223].

\(^1\) The authors of the experimental data suggest that the average starting energy of their copper atoms was much higher, ~13 eV. This seems unreasonable given the reported accelerating voltage of their system, 410 V [231], and the sputtered atom energy distribution generated by other similar sputtering systems [232].

Figure 9.5 **Energy distribution of atoms leaving a sputtering target.** While most atoms leaving the target have energies less than 10 eV, a number of atoms have energies well above this level, creating a high energy tail on the energy distribution.
The results of these simulations are plotted in Figs. 9.6 and 9.7 while the actual numerical results are recorded in Tables 9.1 and 9.2. Note that for each set of conditions investigated, a minimum of 10,000 atoms had to reach the measurement distance to create a valid simulation. Study of various data set sizes between 100 and 20,000 atoms indicated that results averaged from 10,000 atoms reaching the 10.0 cm diameter substrate represented well converged solutions. While the results in Figs. 9.6 and 9.7 do not exactly reproduce the experimental data of Ball, et al. [231], they do represent a closer fit to the experimental data than previous modeling efforts by Westwood [229] and Meyer, et al. [230].

Figure 9.6  **Energy loss at 2.5 cm.** The results of the BCT model for a target to substrate distance of 2.5 cm show better agreement with experimental results than the modeling efforts of Westwood [229] or Meyer, et al. [230].
The fit of the BCT data to the experimental results becomes more encouraging when the findings of Ball, et al. are examined more closely. Ball et al. suggest that, at low argon chamber pressures, their experimental method underestimates the actual energy of the sputtered atoms in part because of their assumption that the sputtered copper atoms have a Maxwell-Boltzmann energy distribution just after leaving the sputtering target [231]. Given this acknowledged error, the energy predictions of the BCT model could be quite close to the actual sputtered atom energies for chamber pressures below a few Pascals.

Figure 9.7 Energy loss at 5.0 cm. When compared to the experimental data of Ball, et al. [231], the BCT model underpredicts sputtered atom energy loss at low chamber pressures and overpredicts it at higher pressures for a target to substrate distance of 5.0 cm.
At higher chamber pressures the BCT model predicts complete vapor atom thermalization before it is observed experimentally. The exact cause of this discrepancy is unclear but could result from the presence of argon ions in the actual sputtering system with smaller scattering cross-sections, from the sputtered atoms in the experimental setup having a different initial energy distribution than that used (e.g. a longer, more significant high energy...
tail), or from the use of an interatomic potential in the BCT model which incorrectly predicts the dependence of scattering angle (and thus energy loss) upon interatomic separation. For some portion of the distance between sputter target and deposition substrate, argon ions in the actual sputtering system would be under the influence of the electric field which accelerates them into the target to generate copper atoms for film creation. As a result, their velocities cannot be described by the thermal equilibrium Maxwell-Boltzmann distribution, taken at 350 K. Instead, their higher velocities decrease their cross-section, increase the distance between collisions with copper atoms, and lead to a persistence of copper atom energy at higher chamber pressure. Despite these discrepancies, the BCT results presented in Figs. 9.6 and 9.7 suggest that the model predicts energy transfer during collisions with reasonable accuracy given the limitations of the equations upon which it is based.

Finally it should be noted that the experimental data reported by Ball et al. does not completely agree with their assertion that the argon gas temperature in their chamber was 350 K. Serway et al. [223] note that, given a Maxwell-Boltzmann argon velocity distribution, the average velocity of atoms in the system is given by:

\[
\begin{align*}
\varv_{\text{avg}} &= \sqrt{\frac{8kT}{\pi m}}
\end{align*}
\]  

(9.1)

Calculations based on this equation show that for argon atoms at 350 K, copper atoms will have approximately 0.061 eV of energy once they have been completely thermalized. This energy level is represented as a dashed line in Figs. 9.6 and 9.7. This energy level is above the energy level reported for certain experimental measurements. To place the line below the lowest experimental data would suggest that the gas temperature in the chamber was as low as 230 K. This seems too cold, suggesting that either the Maxwell-Boltzmann dis-
tribution does not exactly predict the velocity distribution of the argon or that the experimental data results are not completely correct.

9.3 Summary

The results of this chapter show reasonable agreement between independent experiments and DSMC/BCT vapor transport model results, and they demonstrate an ability of the model to replicate expected trends. Thus, with some degree of confidence the model can now be applied to a study of Directed Vapor Deposition deposition results reported in Chapter 7. The goal of Chapter 10 is to use the vapor transport model to provide additional insight into Directed Vapor Deposition’s low vacuum material synthesis behavior.
Chapter 10

Vapor Transport Modeling of DVD

Having developed a reasonable level of confidence that the vapor transport model captures the correct trends for vapor atom direction of travel and energy exchange, the model can now be used to simulate Directed Vapor Deposition to provide additional insight into DVD material synthesis, to answer such tantalizing questions as:

- Can the model replicate experimentally observed vapor transport and deposition trends?
- Can DVD deposit atoms at enhanced energy levels?
- Can DVD vary the angle of adatom deposition?
- Can DVD create deposits more focused than those generated by conventional e-beam systems?

DVD modeling runs were undertaken at three different Mach numbers (1.45, 1.75, and 1.95) and eight different chamber pressures (1.333, 4.000, 6.665, 13.33, 26.66, 53.32, 93.31, and 186.6 Pa). For these computations the helium flowfield was simulated first using Bird’s DSMC code (Appendix C). The number of grid points in the r and z direction for each simulation are shown in Table 10.1. Then individual copper vapor atoms were
Chapter 10. Vapor Transport Modeling of DVD

introduced into the flow one at a time and followed from the vapor source to the substrate or to the edge of the modeled flowfield volume using the BCT code of Chapter 8 (Appendix D). The center of the vapor source was located at \( x = 0.0 \text{ cm}, \ y = -0.635 \text{ cm}, \) and \( z = 3.5 \text{ cm} \) given an origin at the center of the nozzle throat. (See Fig. 7.10 for \( x, y, \) and \( z \) orientation.) For atoms contacting the substrate, a sticking coefficient of one was assumed, and the atom’s velocity vector and position at the time of impact were recorded.

In this chapter the DSMC + BCT model is used to examine DVD vapor transport (atom energy, angle, and location during travel) and to generate deposition efficiency, energy, angle, and distribution information for atoms landing on a flat, 10 cm diameter circular substrate. Where possible transport and deposition data has been compared to the experimental results of Chapters 5 and 7. In areas where experimental data was less readily available, the results of the model have been used to extend understanding of DVD.

### 10.1 Vapor Transport Predictions

Table 10.1: Number of grid points used for each chamber pressure

<table>
<thead>
<tr>
<th>Chamber Pressure (Pa / Torr)</th>
<th>Grid points in radial direction</th>
<th>Grid points along axis of symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33 / 0.01</td>
<td>13</td>
<td>26</td>
</tr>
<tr>
<td>4.00 / 0.03</td>
<td>13</td>
<td>26</td>
</tr>
<tr>
<td>6.67 / 0.05</td>
<td>13</td>
<td>26</td>
</tr>
<tr>
<td>13.3 / 0.1</td>
<td>26</td>
<td>51</td>
</tr>
<tr>
<td>26.7 / 0.2</td>
<td>51</td>
<td>101</td>
</tr>
<tr>
<td>53.3 / 0.4</td>
<td>101</td>
<td>201</td>
</tr>
<tr>
<td>93.3 / 0.7</td>
<td>176</td>
<td>351</td>
</tr>
<tr>
<td>187 / 1.4</td>
<td>351</td>
<td>701</td>
</tr>
</tbody>
</table>

To investigate model predictions of vapor transport, a set of illustrative figures was created in which ten atomic trajectories from crucible source to substrate were superimposed
upon the helium carrier gas flowfield Mach number (Figs. 10.1 - 10.3). The figures represent a two dimensional vertical slice through the cylindrical modeled volume (c.f. Fig. 8.1), and, although the vapor emitting surface is shown in these figures, it was not included as a geometric entity in the actual simulations.

![Figure 10.1](image)

**Figure 10.1** Vapor atom transport at low chamber pressure. For a background chamber pressure of 1.33 Pa (0.01 Torr) and a nominal Mach number of 1.75 (based on equation (2.19)), the model suggests that vapor atoms will receive only minimal direction toward the substrate.

Study of Figs. 10.1 - 10.3 show a vapor redirection trend similar to that observed experimentally (c.f. Fig. 5.7). At low chamber pressure the vapor atoms are kept away from the nozzle by the fast flow region of the carrier gas stream, but outside of this region the atoms either move in fairly straight paths affected little by the low density chamber gas or show
Characteristics of random walk in a flowing background gas. At this chamber pressure (1.33 Pa), the calculated copper mean free path was 450 - 650 µm. At higher chamber pressures (Figs. 10.2 and 10.3), the vapor stream redirection towards the substrate is predicted to be much more pronounced, until the vapor reaches the vicinity of the substrate. Once the vapor atoms near the substrate they begin to wander and to travel parallel to the substrate, under the influence of the wall jet (evident in Fig. 10.3). At the intermediate chamber pressure visualized, most of the vapor atoms appear to deposit on the bottom half of the substrate although one moves vertically upward across the mid-point of the substrate while another is carried out of the modeled volume by the carrier gas. At the highest
simulated chamber pressure, the wall jet effect appears strong enough to keep many of the atoms away from the substrate even though the carrier gas carries all the atoms quite close to the substrate. For the intermediate and high pressure conditions visualized, the mean free paths of the vapor atoms were 30-60 µm (13.3 Pa) and 2-4 µm (186.6 Pa).

Figure 10.3 **Vapor atom transport at high chamber pressure.** This illustration of a 186.6 Pa (1.40 Torr) Mach 1.75 simulation shows that, while higher chamber pressure extends the fast flow region and carries vapor atoms closer to the substrate than seen in Fig. 10.2, the more prominent wall jet present at these pressure levels prevents much of the vapor from contacting the substrate.

10.1.1. Model predicts redirection at lower pressures than experiments

While the theoretically predicted vapor redirection trend is similar to experimental observations (See section 5.4.1.), the simulations show the vapor atoms being redirected toward
Chapter 10. Vapor Transport Modeling of DVD

10.1.2. Dissipation of jet’s fast flow limits vapor direction to substrate

Further study of Figs. 10.1 - 10.3 leads to a second interesting observation. During discussion of the experimental efficiency results (Chapter 7), low deposition efficiency at low chamber pressure was attributed solely to the fact that the vapor stream was diffusing through a low density high velocity carrier gas stream and passing over the top of the substrate. While this certainly contributes to the observed experimental trend, the model suggests an additional factor. At lower chamber pressures, the fast flow region of the gas stream dissipates before reaching the substrate (Fig. 5.6 a) and Fig. 10.1). As a result, at the lowest simulated chamber pressures (Fig. 10.1) the vapor atoms are never entrained in a fast flowing carrier gas stream for transport toward the substrate. Instead, they receive some minimal direction away from the nozzle while generally wandering across and even-
tually leaving the modeled volume above the volume’s centerline. As the chamber pressure increases, the fast flow region lengthens toward the substrate (Fig. 5.6 b) and c) and Figs. 10.2 and 10.3). Thus, at intermediate chamber pressures, vapor atoms entrained in this region are carried close enough to the substrate to make contact with the substrate before being carried out of the modeled volume. At still higher chamber pressures the vapor atoms are carried even closer to the substrate by the fast flow region, but many are prevented from contacting the substrate by the increased presence of a wall jet (Fig. 5.12 a) and Fig. 10.3).

10.1.3. Adatom kinetic energies are below initial evaporation energies

To provide additional insight into DVD and a sense of the change in vapor atom kinetic energy during travel to the substrate, Fig. 10.4 shows the average kinetic energy for twenty vapor atoms reaching the substrate as they traveled from vapor source to substrate for each of the three vapor transport conditions visualized in Figs. 10.1 - 10.3. To generate the average vapor atom energies, the energy of the atoms was sampled at 1 mm intervals during transport from source to substrate.

For each simulation, an interesting and distinctly different energy profile was observed. In the case of the 1.33 Pa simulation, an initial rapid energy loss led to low energy vapor transport all the way to the substrate at approximately thermal levels ($E_{\text{thermal}} = 0.05$ eV given $T_{\text{He}} = 275$ K). The cause of this low energy deposit is evident in Fig. 10.1 where, as noted in section 10.1.1., the low chamber pressure simulations indicate that the high velocity portion of the gas jet dissipates before the carrier gas flow even reaches the crucible. As a result, after a few collisions the vapor atoms are experiencing slightly directed diffusive random walk of the vapor atoms toward the substrate at low energy.
For the intermediate chamber pressure visualization (13.3 Pa), a distinctly different energy profile was observed. Collisions with vapor atoms dissipated the initial kinetic energy of the vapor atoms perpendicular to the carrier gas flow. Continued collisions with the fast flow region of the carrier jet then led to energy gain directed toward the substrate, the initial hump in the energy curve (4 to 6 cm from nozzle). This energy increase was short lived as the gas jet slowed and then began to encounter the substrate. The effect of the wall jet upon vapor atom energy was observed as a temporary kinetic energy increase just in front of the substrate (8.5 to 9.5 cm from nozzle) as the vapor atoms were accelerated parallel to the flat deposition surface (Figs. 10.2 and 10.3). Finally gas/vapor collisions in the

Figure 10.4 **Vapor atom energy during transport.** The presence of the flowing carrier gas in the process chamber has a significant effect upon vapor atom energies, leading to low energy deposition for all conditions visualized.
stagnant boundary layer directly in front of the substrate led to low energy deposition at energy magnitudes only slightly above background gas thermal levels and well below the deposition energies of high vacuum e-beam systems (approximately 0.2 eV).

For the highest chamber pressure simulation (186.6 Pa), the vapor atoms experienced a different energy variation. The longer, denser fast flow region at this pressure level was able to double the initial vapor atom energy. However, as the velocity of the carrier gas decreased, the velocity and energy of the vapor atoms dropped as well. A slight, temporary rise in vapor atom energy in the vicinity of one of the secondary shock structures was observed (6.5 to 8 cm from nozzle). Then, very close to the substrate a substantial increase in vapor atom energy occurred (>0.2 eV) as the vapor atoms were turned and accelerated into the wall jet. However, once the vapor atoms diffused through this jet and into the stagnation region directly in front of the substrate, the vapor atom energies rapidly dropped back toward local thermal levels as the result of multiple collisions with low velocity carrier gas atoms (mean free path approximately 2-4 µm).

10.1.4. Adatom angle of incidence determined by gas near the substrate

Fig. 10.5 shows the relationship between adatom position and average angle relative to the substrate normal for the Mach 1.75 simulations visualized in Figs. 10.1 - 10.3. The figure reveals that for all visualized conditions the depositing vapor atoms were turned towards the substrate shortly after leaving the crucible. For the lowest chamber pressure visualization the vapor was on average at a 30-40° angle at it traveled toward the substrate. For the higher pressure runs the influence of the carrier gas flow upon the vapor atoms was much more pronounced, leading to transport nearly normal to the substrate until the fast flow region dissipates. The graph suggests that the more persistent fast flow region of the 186.6 Pa simulation kept the vapor perpendicular longer, but both conditions deposited vapor at
a 35-45° angle due to the influence of the wall jet. It should be noted that a conventional e-beam system with an initial \( \cos^5\theta \) vapor distribution positioned 6.5 cm from the substrate will deposit atoms at an average angle of 20-21°.

10.1.5. Flowfield temperature and pressure

Visualization of the carrier gas temperature and pressure profiles throughout the modeled volume produced little remarkable new information. The temperature and pressure profiles for the 13.33 Pa / Mach 1.75 simulation are shown in Fig. 10.6 and 10.7. Study of visualizations for all of the simulations showed that the flowfield temperature profile in each case closely mirrored the Mach number profiles. The exact temperature values of the
flowfield depended upon the conditions simulated. The pressure profile in each simulation showed a rapid pressure drop as the gas expanded out of the nozzle. No other discernible feature was evident for any simulated conditions except at elevated chamber pressures where a region of elevated pressure, the wall shock of Fig. 5.12 a), was clearly observed in front of the point where the carrier gas flow impinged upon the substrate.

Figure 10.6 **Flowfield temperature profile at intermediate chamber pressure.** The temperature profile for the 13.33 Pa (0.10 Torr) and Mach 1.75 simulation mirrors the Mach number variation of Fig. 10.2.
10.2 Vapor Deposition Predictions

10.2.1. Model predicted deposition efficiency trends

Fig. 10.8 shows graphically how the model predicts the deposition efficiency should change with Mach number and chamber pressure. The model’s deposition efficiency trends are quite similar to the experimental results of Fig. 7.2. An initial increase in chamber pressure resulted in a rise in deposition efficiency to a maximum before a decrease in deposition efficiency was observed with further increases in chamber pressure. For a given chamber pressure the experimentally observed relationship between Mach number
Chapter 10. Vapor Transport Modeling of DVD

and deposition efficiency is generally replicated here. Below the peak efficiency, higher Mach numbers lead to higher deposition efficiencies. Above the peak this trend slowly reverses as the pressure is systematically increased. The average numerical results generated by each of these simulations are shown in Table 10.2.

The deposition efficiency results of Fig. 10.8 and Table 10.2 are easily interpreted in terms of Figs. 10.1 - 10.3. At low chamber pressures, diffusive atom wandering leads to low deposition efficiencies because many vapor atoms are not directed to the substrate by the
carrier gas stream’s rapidly dissipating fast flow region. At intermediate pressures the fast flow region of the carrier gas jet transports the vapor to the vicinity of the substrate where the atoms are able to penetrate the moderate wall jet for deposition. At higher chamber pressures the denser wall jet prevents the vapor atoms from reaching the substrate.
10.2.2. Vapor concentration effects

The deposition efficiency peak shown in Fig. 10.8 for all three Mach numbers is greater in magnitude and occurs at a lower pressure than that recorded for any of the experimental results of Figs. 7.2 or 7.5. Examination of Fig. 10.9 shows that the results predicted by the model are consistent with the experimental data from Chapter 7. Clearly the number of atoms leaving the crucible per unit time and interacting with the gas flow influences the material deposition behavior of the DVD system. While the model appears to capture vapor transport and deposition characteristics of the system reasonably well at low flow, it also misses the important vapor flux effect completely.

10.2.3. Predicted efficiencies

In addition to DVD deposition efficiency comparisons between model and different experimental conditions, it is important to compare DVD material utilization efficiency to that of a traditional e-beam system in which the source to substrate distance and substrate diameter are the same (10.0 cm for both). Using equation (2.2) with an exponent of 5, it is possible to determine quickly that a traditional e-beam system would deposit 73% of its evaporant on a flat substrate for a similar system configuration in which the substrate was positioned above the vapor source (e.g. Fig. 2.1). This deposition efficiency is higher than that obtained for any of the DVD flat substrate processing conditions simulated or experimentally explored (59% maximum)! While Figs. 5.7 - 5.12, Fig. 10.2, and Fig. 10.3 appear to show significant vapor focusing under many conditions, wall effects apparently prevent important quantities of vapor from depositing on the substrate.
Figure 10.9 **Effect of dilute limit approximation upon modeling results.** While the model predicts the deposition efficiency trends, comparison with experiment (data from Fig. 7.5) reveals how evaporation rate influences DVD deposition characteristics. (All data shown is for a nominal Mach number = 1.75.)

10.2.4. **Deposition energy distributions change little with process conditions**

Perhaps the most interesting information revealed by the model is embodied in the adatom energy information of Table 10.2 and Fig. 10.4. When the DVD system was first designed and built, it was thought that the supersonic gas jet blowing over the surface of the e-beam crucible would accelerate the vapor atoms toward the substrate, increasing their energy into the 1 - 2 eV range. Then, despite a reduction in carrier gas velocity as the helium atoms encounter the substrate, the inertia of the vapor atoms would carry them on to the
substrate for deposition at energies near this elevated level. The model suggests that this is not in fact the case for any of the conditions experimentally explored and replicated herein with the model. The results of Table 10.2 confirm the limited energy data of Fig. 10.4 by revealing that DVD deposits atoms with less than half their initial energy under all conditions simulated.

Fig. 10.10 shows several typical energy distributions for DVD adatom deposition. While a few atoms reach the substrate with more than 0.2 eV of energy, the vast majority have significantly less energy. The validity of these model predictions of adatom energy is supported by the experimental observations of others in which much of the microstructure created using the present DVD system has consisted of low energy Zone 1 or Zone T structures (Fig. 2.8 a)) [214, 217, 233]. Higher energy structures have been created only when significant substrate heating was performed during deposition. The insensitivity of these deposition energy distributions to process conditions appears to result from the fact that the velocity of the vapor atoms during deposition is dominated by wall effects, not the jet’s initial or maximum velocity.

10.2.5. Deposition angle distributions

Fig. 10.11 shows the distribution of adatom deposition angle for several processing conditions. Interestingly the graph shows that, while Fig. 10.5 and Table 10.2 show an average angle of deposition between 32 and 39°, a significant number of atoms deposit from every angle (i.e. the angular distribution is quite scattered) for all deposition conditions. Jet impingement on the substrate slows both the helium and copper atoms and begins to turn the vapor atoms parallel to the substrate prior to contact with the surface. Although the vapor atoms generally flow into the low velocity wall jet and then away from the substrate, their motion in the wall jet and most especially in the stagnation region just in front
of the substrate is much less predictable than during fast flow carrier gas jet entrainment. This unpredictability leads to a wide distribution of vapor atom deposition angles. Also, noted in section 10.1.4., the lack of angular variability between process conditions appears to result primarily from the dominant effect of the background carrier gas in the vicinity of the substrate.

10.2.6. Deposition distribution

Examination of the average vertical position of vapor deposition recorded in Table 10.2 shows that as the chamber pressure increases, the average location of vapor atom deposition moves down the substrate. This trend is consistent with the experimentally observed vapor transport trend (See the discussion of section 5.4.1.) and appears to result from
decreased vapor atom diffusion across the modeled volume at increased chamber pressure, especially as the fast flow region of the carrier gas jet lengthens (Figs. 10.1, 10.2, and 10.3). The average horizontal position for all the deposited material was just 118 μm from the vertical centerline of the modeled volume, a result which provides further confirmation that the model correctly tracks atoms in the flowfield (i.e. There should be no horizontal deposition bias since the flowfield is axially-symmetric and the starting point for the vapor atoms is at a horizontal position of x = 0.0 cm.). Given the fact that some of the datasets showed a slight negative offset and some a slight positive offset from the vertical centerline, the average horizontal position including direction of offset was -52 μm.

Figure 10.11  **Distributions of impact angle for various conditions.** Neither the average angle of deposition (Table 10.2) nor the angle of deposition distribution changes significantly with chamber pressure.
Fig. 10.12 shows the average position of deposition moving down the substrate with increased chamber pressure. It also reveals distinctly different deposition distributions. At low pressure, the vapor has passed across the horizontal centerline of the substrate for deposition near the top of the substrate across a broad area. At intermediate pressures, the vapor interaction with the fast flow region of the gas stream generates a low density deposit region in the center of the substrate where little or no material deposition occurs. This vapor distribution is similar to that observed experimentally and described in section 7.3.1.3. for high gas flows and elevated chamber pressures. At the model’s highest visualized chamber pressure (Fig. 10.12 c)), the vapor begins to show a significant focus on the bottom portion of the substrate.

In addition to the overall deposition profiles of Fig. 10.12, a horizontal slice of data through the peak point of deposition was taken for the three visualized conditions. These results are plotted in Fig. 10.13 in comparison with the expected vapor distribution for a conventional high vacuum e-beam system with a \( \cos^5 \theta \) vapor distribution located 6.5 cm from the substrate. These results suggest that while DVD cannot deposit material as efficiently as a conventional system, it can focus the vapor it does deposit onto the substrate.

**10.3 Summary**

Clearly the results of this chapter present a mixed picture of DVD utility. While the system can deposit material at low energies useful for applications like thermal barrier coatings [217], it cannot create such deposits more efficiently then conventional e-beam systems with similar configurations. Furthermore, despite wide variation in process conditions (e.g. chamber pressures varying by two orders of magnitude from 1.33 - 187 Pa) the current configuration of the system has not demonstrated an ability to alter adatom energy, angle, or efficiency over wide, useful ranges. These deposition parameters appear insensi-
Figure 10.12  **Simulated vapor distributions.** a) 1.333 Pa, b) 6.665 Pa, and c) 13.33 Pa (M = 1.75). These reveal variations of the thickness profiles.
Figure 10.13  **Line scans across simulated thickness profiles.** Simulations indicate that the DVD system can generate a vapor deposit more focused than that produced by a high vacuum e-beam evaporator.

tive to process parameter variation given the current DVD system configuration. DVD simulations do indicate that the method has some ability to focus vapor onto a substrate.

Since the original system configuration was based solely on general concepts of vapor transport in a gas flow, it seems reasonable to employ the more sophisticated vapor transport model developed in this dissertation to explore whether or not the system can be reconfigured to make better use of the energy of the carrier gas flow. System reconfiguration might allow Directed Vapor Deposition to generate higher efficiency, higher energy deposits in addition to the low energy deposits it can currently create. The following chapter will use the model to explore possible ways to improve the processing ability of DVD.
Chapter 11

DVD System Development

Having developed insight into Directed Vapor Deposition through the work of Chapters 5 - 10, this chapter looks beyond the current system configuration and focuses upon additional work which could increase system utility for material synthesis and provide further insight into how DVD process parameter variation influences deposited material characteristics. In particular this chapter recommends system reconfigurations, additional experiments, and model enhancements. Portions of this discussion employ the DSMC + BCT model of Chapters 8 - 10 to support recommendations for additional work. While the model has limitations, its results have demonstrated an ability to capture general vapor transport phenomena at work in the DVD system. Thus, it should be possible to use the model to make important recommendations for system development.
11.1 Reconfiguration of the Gun, Vapor Source, and Carrier Gas Flow

11.1.1. Justification for system reconfiguration

The experimental and modeling results presented in Chapters 5 - 10 indicate that DVD film synthesis modifies the vapor stream focus, angle and energy of deposition, and deposition efficiency from that of other physical vapor deposition systems. While modifying these parameters, often in useful ways [217], it does not appear that the initial DVD system configuration possesses the full range of process flexibility initially envisioned. Examination of DVD results presented in the previous chapters reveals that an important limitation upon flexibility results from a system configuration which uses the gas jet to redirect the vapor stream 90° after it leaves the crucible source (c.f. Fig. 4.10).

Turning the vapor stream limits the ability of the system to operate at low gas flow rates or high evaporation rates, as demonstrated experimentally in the visualizations of Chapter 5. Under low gas flow or high evaporation rate conditions, vapor travels up towards the e-beam gun and over the top of the substrate. If the carrier gas flux is increased to provide enhanced vapor redirection to the substrate, deposition efficiency decreases as the magnitude of the wall jet grows as demonstrated clearly in Chapters 5, 7, and 10. Because so many carrier gas atoms are needed to turn the vapor towards the substrate, for all chamber pressures simulated in Chapter 10 the energy and direction of the vapor atoms is determined by carrier gas atoms in their immediate vicinity. Thus, for conditions at which significant numbers of atoms are directed to the substrate, the heavier vapor atoms cannot use their inertia to “punch through” the surrounding carrier gas near the substrate and reach the substrate for high efficiency and possibly high energy, low angle deposition.

Fig. 11.1 shows a suggested system reconfiguration which could improve the usability of the DVD technology at reduced gas flows and extremely high evaporation rates and
should facilitate vapor atom punch through. The primary change required for this system redesign is the repositioning of the electron beam gun at an angle (30-40°) to the evaporant surface. Such a configuration would allow the system to use the vapor atoms’ initial thermally induced velocity to start the atoms toward the substrate. The accelerating supersonic gas jet can then contribute to this initial directed velocity to achieve enhanced DVD. This system modification allows the carrier gas stream to focus and accelerate the vapor flow rather than expend valuable energy redirecting the vapor stream. The result will be a

Figure 11.1 A reconfigured DVD system. Shown here reactively depositing a TBC top coat layer this system would more efficiently use the carrier gas, focussing the vapor without having to turn it 90° towards the substrate (c.f. Fig. 4.10.).
more efficient DVD system which uses significantly less carrier gas; note the reduced pressures in the mixing and processing chambers compared to Fig. 4.10.

As a result of the system reconfiguration the carrier gas stream would no longer need to turn the vapor stream 90°, and thus the total carrier gas flux could be decreased. This decrease in gas flux should facilitate more efficient, more directed, and under certain conditions perhaps more energetic vapor deposition through an increase in vapor atom mean free path and minimization of the wall jet present in higher gas flow processing conditions. This new configuration should also decrease the carrier gas/vapor atom ratio, minimizing possible film contamination problems due to carrier gas impurity incorporation. Finally, this configuration, with its decreased carrier gas flow, should decrease problems associated with vapor phase nucleation of material clusters through minimization of atomic backscattering by carrier gas atoms between the vapor source and deposition substrate (See the discussion of Dugdale’s research in Chapter 2 and the clustering calculations of Chapter 7.).

11.1.2. Model-based analysis of system reconfiguration

In the reconfigured DVD system, the diameter of the carrier gas nozzle will be somewhat larger than in the current system (e.g. 2.20 cm instead of 1.27 cm) to accommodate the source material, crucible, and gas flow within the throat of the nozzle while also allowing the scanned e-beam to reach each of the separate crucible sources (Fig. 11.1). As noted in equation (5.1), this larger diameter (d) nozzle should have an advantageous effect upon the gas flow characteristics of the system. Equation (5.1) shows that the distance of the Mach disk from the nozzle (x_m) increases proportionally with the nozzle diameter. As the nozzle diameter increases, the length of the supersonic flow region increases, bringing high velocity carrier gas and vapor atoms closer to the substrate and decreasing the distance the
energetic vapor atoms must travel through low velocity carrier gas before depositing efficiently onto the substrate.

Central to optimum deposition in this reconfigured system is the vertical position and diameter of the crucible within the nozzle. To investigate this issue properly a new DSMC code by G.A. Bird (compiled by Bird for use under DOS on a personal computer) was obtained [235] which made possible simulation of more sophisticated two dimensional axisymmetric geometries than those which could be examined using the code employed in Chapters 9 and 10. Fig. 11.2 shows the grid developed to examine gas flow around the crucible located inside the mixing chamber, through the nozzle orifice, and out into the deposition chamber. The vertical left boundary of the mixing chamber was defined as a specified flow boundary condition while the other mixing chamber boundaries were defined as solid surfaces. The processing chamber boundaries other than the substrate (10 cm in diameter) were defined as stream boundaries, identical to the same boundaries in the previous model.

To examine the vapor deposition characteristics of this system reconfiguration, a set of calculations was run in which the chamber pressure was defined to be 1.33 Pa and the upstream pressure at the model boundary inside the mixing chamber was defined as 16.1 Pa. For this simulation the nozzle diameter was 2.20 cm and the evaporation surface of the crucible was positioned 0.75 cm down inside the nozzle lip. The crucible was configured to allow evaporation from four neighboring source pools each 3.175 mm in diameter (Fig. 11.3), an arrangement designed to facilitate mixing of adjacent vapor streams containing materials with significantly different vapor pressures (e.g. yttria-stabilized ceria). For this simulation, evaporation occurred from an individual source pool centered at \( x = 0.0 \) cm, \( y = 0.47625 \) cm.
The simulation results in Fig. 11.4 and Table 11.1 highlight the enhanced deposition efficiency of this system reconfiguration compared to an identically configured conventional e-beam source operating under high vacuum. Study of the results of these two simulations indicate that the primary advantage of this basic reconfiguration is a significant increase in deposition efficiency over that of the original DVD system configuration (c.f. Table 10.1) and over that of a conventional e-beam system. The simulation results indicate that the energy of deposition would still be below thermal levels, and the angle of adatom deposition would still be much greater than in a conventional e-beam system.
Figure 11.3 Close-up of reconfigured system. In the reconfigured system, a sophisticated high speed (50-100 kHz) e-beam scanning system can allow precise amounts of power to be delivered to neighboring source pools [236] for precise composition control of the resulting vapor stream, shown here depositing an advanced TBC top coat layer.

Study of the vapor atom trajectories in Fig. 11.4 shows that their trajectories quickly become less directed as soon as the fast flow region of the carrier gas stream dissipates. Lack of direction over the final few centimeters of travel to the substrate appears to be the primary reason why deposition efficiency in this reconfigured system is not 100%. To bring the fast flow region of the carrier gas stream closer to the substrate, any one of three design parameters could be modified. First, the substrate could be moved closer to the nozzle opening. Second, the nozzle opening could be enlarged, extending the length of the
supersonic flow regime (equation (5.1)). Third, the pressure ratio from inside the mixing chamber to the processing chamber could be increased, lengthening the supersonic flow regime (equation (5.1)). Each of these options has drawbacks.

Moving the substrate closer to the nozzle limits the diameter of the substrate that can be coated in the DVD system. The scanned e-beam which emanates from the gun exit located

Figure 11.4 **Simulation of vapor transport in the reconfigured system.** Placing the vapor source inside the mixing chamber leads to less vapor atom wandering during transport, until the fast flow region of the carrier gas jet dissipates.

<table>
<thead>
<tr>
<th>Mach Number</th>
<th>Chamber Pressure (Pa/Torr)</th>
<th>Atoms Simulated</th>
<th>Deposition Efficiency (%)</th>
<th>Average Deposition Energy (eV)</th>
<th>Average Deposition Angle (degrees)</th>
<th>Average Vertical Position (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.30</td>
<td>1.333/0.01</td>
<td>12,000</td>
<td>83.61</td>
<td>0.0626</td>
<td>36.12</td>
<td>0.00279</td>
</tr>
<tr>
<td>Conventional</td>
<td>16,000</td>
<td>66.53</td>
<td></td>
<td>0.2092</td>
<td>17.59</td>
<td>0.00240</td>
</tr>
</tbody>
</table>

supersonic flow regime (equation (5.1)). Each of these options has drawbacks.

Moving the substrate closer to the nozzle limits the diameter of the substrate that can be coated in the DVD system. The scanned e-beam which emanates from the gun exit located
20 cm above the crucible surface [236] must be able to pass by the edge of the substrate. Given a 10 cm diameter substrate and a 30° inclination on the gun, the nozzle to substrate distance can be no less than 8 cm. Both enlarging the nozzle opening and increasing the Mach number of the carrier gas stream require a larger pumping capacity. For the nozzle opening and Mach number shown in Fig. 11.4, the pumping capacity required in this system configuration at $10^{-2}$ Torr (~1 Pa) is already about 50% larger than that employed in the current DVD system (See Appendix A for pumping capacity equations and calculations.). Although larger pumping systems are available, the size, weight, and cost of such systems make them an unattractive way to improve DVD deposition characteristics.

### 11.2 Substrate Bias

The model simulations presented in Chapters 10 and 11 indicate that while a reconfigured DVD system can significantly enhance deposition efficiency, adatom energies are still quite low and adatom angles quite high compared to a conventional e-beam system. Certainly the simulations in Chapters 10 and 11 have not explored all processing conditions reachable in the DVD system, and while further work with the model may reveal an ability to deposit atoms with average energies of 0.2 eV and higher, it does not appear that the carrier gas flow alone will succeed in generating higher adatom energies or lower adatom angles.

Additional acceleration could in certain applications be generated through the application of an electrical bias voltage to the substrate. As seen in the experimental photographs of Chapter 4, use of a gas jet in combination with a vapor flux leads to excitation and probably ionization of both species. By placing a bias voltage on the substrate (as low as -10 V up to -200 V) it should be possible to accelerate vapor ions for energetic film growth.
Another means by which additional energy could be imparted to the growing film is through the use of an ion beam source. Use of an ion beam source in chamber pressures above about 15 Pa (~0.10 Torr) is impractical due to the short mean free path of the ions. However, as noted in Fig. 11.1, the reconfigured DVD system may have an optimal chamber pressure range below this limit, making use of traditional ion beam sources feasible. The combination of a reconfigured DVD system operating at lower pressure with an ion beam surface modification tool might allow DVD to synthesize high quality polycrystalline silicon films with improved surface morphologies which could be used in thin film transistor applications (See section 6.3.).

11.3 Experimental Work

In addition to the continued model-based development of the system just described, more in-depth experimental research needs to be undertaken to reveal the film growth characteristics of DVD. Study of DVD films using analysis tools such as SEM, TEM, XRD, FIB, XPS, AES, AFM, and STM should facilitate understanding of the relationship between processing conditions and film growth characteristics. In addition to the experimental knowledge produced by such study, the experimental results will provide a basis of comparison for evaluating the validity of results generated by molecular dynamics and Monte Carlo models of film growth [29 - 33].

To ensure that experiments are being conducted repeatably under desired conditions, it is important that sensor technology be incorporated into the DVD system. As suggested in Chapter 5, important sensors for DVD synthesis monitoring include a melt pool temperature sensor, a vapor composition and velocity sensor, and a film temperature and thickness sensor. As these sensor technologies are added to the system, the basic LabVIEW™ interface currently in use on the DVD control computer will need to be upgraded to present and
store the additional data during an experiment. This type of sensor and data collection development will move the DVD system towards closed loop control and begin to make IPM system control a real possibility in the future. As suggested in Chapter 2, this type of system development could be the key to producing useful vapor phase materials via DVD.

With or without adoption of the system design changes recommended in section 11.1, the design of the nozzle employed in the DVD system can be improved to generate a more efficient flow of carrier gas into the system. Fig. 11.5 illustrates how a properly designed converging nozzle can lead to smoother gas flow as it expands into the processing chamber. The DSMC modeling concepts employed to study gas jet expansion into the processing chamber could also be employed to investigate the effect of nozzle geometry upon gas and vapor transport. It seems reasonable to expect that modifying the current orifice type nozzle could lead to more efficient vapor transport to the substrate.

Figure 11.5 Nozzle geometry can affect gas focus.
11.4 Model Development

The vapor transport model developed as a portion of this dissertation clearly demonstrates the utility of the Direct Simulation Monte Carlo and bimolecular collision theory methodologies as a means for gaining a deeper understanding of Directed Vapor Deposition. As noted in Chapter 8, the current model of DVD is capable of modeling vapor transport only in the diffuse limit (i.e., at low vapor fluxes). One of the main reasons for developing an innovative low vacuum e-beam material processing system has been the desire to achieve controlled, high rate material evaporation. This desire is also one of the motivating factors behind the system redesign proposed in section 11.1. To create a modeling tool which is capable of more precisely predicting DVD system behavior at high evaporation rates, the current model must be significantly revised.

While the new model would still use the same collision concepts employed in Bird’s DSMC code and the newly developed BCT code, it would have several distinct differences. It should be able to:

- Simulate vapor atom and carrier gas flows simultaneously,
- Simulate three-body collisions and the formation of multiatom clusters,
- Simulate ions as well as neutrals,
- Perform two-dimensional, two-dimensional axisymmetric, and full three-dimensional simulations of DVD, and
- Perform calculations using a parallel computer processing system.

Implementation of the first three items listed above should eliminate a significant portion of the discrepancies currently observed between model and experiment. In the current model, the momentum of a flux of vapor atoms leaving the crucible does not in any way modify the flow of the carrier gas since the model simulates only a single vapor atom at a
time, after the carrier gas flowfield properties have been established. While this model configuration provides some insight, the visualizations of Chapter 5 (Figs. 5.10 and 5.11) and the experimental data of Chapter 7 (shown in Figs. 7.5 and 10.9) clearly demonstrate that increasing the vapor atom flux from the crucible changes the general trajectory of that flux even though the carrier gas flow conditions are held constant. Certainly this change is the result of an increase in the vapor atom momentum flux leaving the crucible, and accounting for it could yield significantly different vapor deposition distribution, energy, angle, and efficiency data, data which agrees more closely with that observed experimentally. Implementation of this model improvement should be fairly straightforward, requiring only an investment of additional time to configure the DSMC code to allow two sources of atoms. Indeed it appears possible to obtain an improved simulation code from other research institutions [237].

Configuring the DSMC method to account for three body collisions, ions, and the formation of multiatom clusters represents a more challenging endeavor. The enhanced model will need to determine the probability of cluster formation for local conditions in the flow (homogeneous and ion-induced nucleation) and then track clusters which form until they reach the substrate or leave the modeled region. Accurately predicting cluster formation and cluster/gas atom, cluster/vapor atom, and cluster/cluster interaction during transport will require knowledge of the interaction potentials for the clusters. Given the lack of precise gas atom/vapor atom interatomic potentials available today, it seems unlikely that precise cluster/single atom or cluster/cluster interaction potentials currently exist that can be confidently relied upon to predict collision events in the several eV energy range experienced in the DVD system. Thus, to resolve this model discrepancy properly will require a significant amount of experimental and theoretical research.
Developing an ability to predict ion formation in the DVD system and then tracking the effect of those ions upon the system behavior represents a significant modeling development effort, especially if a substrate bias is introduced into the problem. Some guidance can be obtained from the direct simulation investigation of ionized flow undertaken by Carlson and Hassan [238]. Ion interatomic potentials will be needed to describe ion interaction with neutral gas and vapor atoms and vapor atom clusters. It will also be necessary to incorporate an additional step into the DSMC computation scheme, a substep within the main time step during which the ions are acted upon by the applied fields. As with the previous two model improvements, this model upgrade will have a computational expense associated with it.

To model DVD vapor transport most efficiently, each two dimensional, two dimensional axisymmetric, and three dimensional vapor transport code should be designed to run in a parallel computing environment. Development of these parallel codes will require an understanding of how to divide up the computational problem most effectively. Boyd [239] provides suggestions for how best to break down the vapor transport problem for study in a parallel computing environment. The code should be parallelized to run simultaneously on all eight processors of the University of Virginia’s IBM RS6000 J40 and J50 computers [239]. Parallelization of the code is essential due to the numerical complexity of the integrated model. The new model will not only need to simulate carrier gas/carrier gas atom collisions but also carrier gas/vapor atom and vapor atom/vapor atom collisions. If multiple gases and multiple vapor materials are included as in Fig. 11.3 the model will require even more computational power. Depending upon the complexity of the new model it may eventually be possible to incorporate three-body collisions rather than just bimolecular collisions into simulations. Such a model would allow vapor phase nucleation of clusters to be studied and its effect upon film synthesis to be understood, perhaps allow-
ing the observations of Erikson [73] described in Chapter 2 to be explained as well as some of the discrepancies observed between experiment and model in Chapters 7 and 10.

11.5 Concluding Remarks

Although nearly six years have been spent designing and building a DVD system and exploring its material processing characteristics, real development of the technology has just begun. The analysis presented in this chapter represents an attempt to show how the scientific insight generated in this dissertation can be used to modify the technology and to make useful vapor-phase film products via a more flexible material synthesis platform. While the initial DVD system was built based upon a knowledge of general vapor deposition concepts, future DVD development can proceed with knowledge of actual system characteristics as presented in this dissertation. The modeling results presented in this chapter are intended only to highlight the system behavior trends affecting film creation in the DVD system. Certainly the current vapor transport model is not capable of exactly describing the behavior of a DVD system employing multiple crucibles for simultaneous evaporation. However, the distinct differences between original system deposition characteristics and reconfigured system deposition characteristics predicted by the model almost certainly reveal the correct trends in system behavior and thereby point out the direction for future system development.
Chapter 12

Discussion

As noted at the outset of the Introduction chapter, this dissertation has recorded the invention and initial experimental and theoretical investigation of a new physical vapor deposition technology - Directed Vapor Deposition. Prior to the commencement of this project in 1992, the concepts behind Directed Vapor Deposition technology were untested and in many cases not yet clearly defined. The work of this dissertation has refined and developed those initial ideas and reduced them to practice as a functioning materials synthesis system. The preceding chapters not only describe the synthesis tool design pathway from concept to functioning system but also they present a significant volume of experimental and theoretical information which allows an initial assessment of DVD’s utility to be made. In Chapter 3, a long list of possible material processing features of DVD was presented. In light of the work presented in this dissertation those suggested advantages of DVD can now be reviewed and the ability of the technology to deliver those advantages can be assessed.
12.1 Focus, Efficiency, and Angular Distribution

The first point of Chapter 3 stated that DVD should be able to entrain and focus vapor atoms in a carrier gas stream for efficient deposition at selectable angles. Under certain conditions, the technology has demonstrated its ability to deliver some of this advantage. As clearly demonstrated in Fig. 5.12 b) the technology is capable of focused deposition on substrates like fibers, and Fig. 7.8 shows that deposition on such substrates is more efficient than conventional high vacuum e-beam processing. These results certainly suggest that DVD could make a contribution to industrial coating of continuous fibers for metal matrix composite applications.

When coating flat substrates, it is not quite so clear that DVD is a superior processing pathway. Fig. 10.13, which compares model predictions of DVD film thickness profiles with conventional e-beam vapor deposition profiles, indicates that DVD can increase vapor deposition focus. However, Figs. 5.12 a) and 7.2 illustrate that, while focussed, the efficiency of this deposition is far less than desired. Indeed much of the vapor which reaches the vicinity of the substrate is carried away from possible deposition by the wall jet (c.f. Fig. 10.3), leading to deposition efficiencies below the level of conventional e-beam systems. The vapor transport model for DVD does provide insight into how the deposition efficiency of this technology could be improved to exceed that of conventional techniques through reconfiguration of the system.

The model also suggests that DVD does not afford materials engineers with the ability to vary deposition angle or angular distributions (Table 10.1 and Fig. 10.11). In all cases examined, the angular distributions are broad, with an average deposition angle greater than 30° from the normal. As noted in the dissertation Introduction, it was thought that if DVD could deposit material at angles less than 10° from the normal, it might prove useful...
for microelectronic via filling. Although via filling has not been specifically examined either experimentally or theoretically, the work of this dissertation allows an assessment of the technology’s applicability to be made. Specifically, study of Fig. 10.5 does not reveal any conditions under which the average vapor atom angle is even close to 10° in the vicinity of the substrate. Thus it does not appear that DVD technology is well-suited for the microelectronics via filling application.

12.2 Non-line-of-sight Coating

The second point raised in Chapter 3 suggested that DVD could have an ability to deposit vapor onto substrate surfaces not in the line-of-sight of the vapor source. Fig. 7.9 clearly shows that DVD has this ability. The desire to coat metal matrix composite continuous fiber reinforcement quickly and efficiently represented the primary motivating application for Directed Vapor Deposition development. At the inception of the project it was hoped that DVD would be able to surpass the capabilities of conventional sputtering or e-beam systems and offer a viable high rate, high efficiency material synthesis alternative. The experimental results of Chapter 7 show that DVD can more than double vapor deposition efficiency onto fiber reinforcement while rapidly coating fibers from a focussed vapor stream.

SEM study of the metal coated fibers reveals that the cause of the increased efficiency is vapor deposition on portions of the fiber surface not in the line of sight of the primary vapor flux. Recent use of DSMC simulation programs produced by Bird [235] confirms the suggestions of Hill [79] that the non line-of-sight coating is the result of vapor atom collisions with gas atoms, collisions which redirect vapor atoms into contact with the top, bottom, and back side of the fiber. This ability of DVD to more than double line-of-sight
deposition efficiencies through use of its focussed gas jet should appeal strongly to companies interested in decreasing fiber coating costs.

One major concern regarding DVD deposition onto fibers has to be the low energy of deposition which creates porous, columnar microstructures (Figs. 2.8 and 7.9). McCullough et al. [20] have demonstrated that such structures allow significant oxygen incorporation into deposited films, leading to the formation of unacceptably brittle microstructures. Some additional means of producing a dense microstructure via DVD could be required before the method can be seriously considered for this application (e.g. Dugdale’s heating of the chamber gas [50, 84] or activation of the vapor stream as demonstrated by various individuals at F.E.P. [240-243]).

For industrial coaters of fiber, the visualization work of Chapter 5 and the modeling work of Chapters 10 and 11 indicate that the current DVD system configuration may be the preferred setup for the fiber coating application. Figs. 5.12 and 10.2 show that using the gas jet to bend the vapor stream $90^\circ$ towards the substrate not only creates an environment in which non-line-of-sight coating can occur but also it leads to much more significant vapor focusing than is evident in the simulations of the reconfigured system (Fig. 11.4). The original DVD system design presents a narrow region through which rotated fibers can be horizontally passed for uniform, high rate ($50 - 100 \mu$m/min.), high efficiency vapor deposition. These results suggest that it may be possible to accomplish industrially acceptable high rate fiber coating using a fairly small, low-cost e-beam gun system, perhaps even a system the size of the experimental setup developed for this project.
12.3 Vapor Stream Mixing

The third point of Chapter 3 suggested that DVD’s use of a gas jet could facilitate mixing of vapor atoms from adjacent sources. This concept was not experimentally explored in this dissertation and the limitations of the model preclude theoretical examination of the issue. To assess more fully the ability of DVD to coat fibers in an industrial setting, research should be conducted which will demonstrate the technology’s ability to deposit the correct alloy compositions desired for the metal matrix composite fiber application (e.g., Ti-6wt%Al-4wt%V) [20]. Single crucible evaporation of this alloy system using DVD will almost certainly experience the same stoichiometry problems observed with conventional e-beam systems [11]. However, use of two in-line vapor targets and the gas jet could quite conceivably overcome this troublesome problem by mixing the two vapor plumes for efficient, compositionally correct deposition (Fig 11.1). Incorporation of a high rate scanning system into the current DVD configuration would allow the beam power to be precisely split between the two targets for stoichiometrically-correct evaporation [236]. Additional research will need to be conducted to investigate the deposition rate around fibers for different elements, since as noted in the Background chapter, the non-line-of-sight coating efficiency of low vacuum systems is a function of the mass of the chamber gas and the vapor atoms. No data currently exists which explains how to obtain a stoichiometrically correct Ti-6-4 deposit in a DVD system.

12.4 Enhanced Energy Deposition

Point four of Chapter 3 suggested that DVD could possess an ability to deposit atoms onto substrates with energies above their initial 0.2 eV thermal levels. The modeling work of Chapters 8 - 11 strongly suggests that the supersonic carrier gas stream cannot achieve this
goal for the system configurations examined. Fig. 9.6 shows that the model is capable of predicting with reasonable accuracy the vapor atom energy changes as the result of collisions with a background gas, and Fig. 10.4 suggests that for some DVD flow conditions the vapor atoms are temporarily accelerated to energies above thermal limits. However, it appears reasonable to believe that these model results are correct when they predict that the temporarily high energy levels are not sustained, most often because of the wall jet which rapidly slows vapor atoms prior to contact with the substrate. Since the system does not demonstrate an ability to enhance depositing atom energy, there is no reason to believe that point five, an increased possibility of athermal atomic reconstruction at the growth surface, will be satisfied either.

Figure 12.1 **Multicrucible vapor stream mixing in DVD.** Stoichiometrically-correct deposition using this DVD system configuration could be much faster and more efficient than that achieved in a conventional multicrucible e-beam evaporation system (c.f. Fig. 2.1).
Even when the system is reconfigured as in Chapter 11, it is not possible to generate flow conditions which deposit vapor atoms with 1 - 2 eV. To accelerate the vapor atoms in a DVD system it certainly appears that some other mechanism must be employed to generate high energy deposits. Substrate biasing designed to pull in the ionized vapor atoms appears to be a logical system enhancement which might achieve this goal.

Despite deposition energies well below initial thermal levels, research by Hass et al. [217] suggests that there are important applications like the thermal barrier coating of aircraft engine turbine blades for which DVD could be an ideal deposition tool. The TBC application requires high rate, efficient deposition of low energy columnar microstructures (Fig. 2.8 a) composed of refractory alloys and compounds with elements having significantly different vapor pressures. Although a significant amount of development work needs to occur before DVD might be adopted by industry for the TBC application, this seems to be a second promising application area for the technology.

### 12.5 Rapid, Continuous Processing of Pure Materials and Compounds

The final three points of Chapter 3 propose that DVD could be capable of rapid, continuous processing of pure materials and compounds. The experimental work of Chapter 6 and the subsequent efforts of Hass et al. [217] encouragingly indicate that DVD can deposit both pure materials and compounds from its low vacuum environment. The major problem with the system configuration visualized in Chapter 5 is the variability of vapor stream location with e-beam power and thus material evaporation rate. Industrial systems are almost certainly going to have to be configured to eliminate this variability. There is some reason to believe that the system reconfiguration proposed in Chapter 11 will largely diminish the problem since vapor atom travel to the substrate will not depend upon significant numbers of carrier gas/vapor atom collisions for 90° redirection. Since the model
cannot examine transport effects resulting from a change in vapor atom flux density, the level of deposition distribution variation with changes in density cannot be examined.

Although continuous processing was not attempted in the research DVD system constructed, there appears to be little to suggest why continuous batch processing (e.g. individual turbine blades) through load-locks or continuous material feed (e.g. continuous fiber) through differentially pumped material introduction chambers should not be possible [186]. If industry decides to develop the technology, these issues should be resolved quickly.

### 12.6 Other Applications

In this dissertation, exploration of DVD’s ability to manufacture films useful for other applications has been limited. However, DVD’s ability to create films using reactive deposition techniques and the ability to create polycrystalline silicon at temperatures compatible with glass substrates (Chapter 6) suggests that, with further development, DVD might be applied to the microelectronics application area (e.g. thin film transistor silicon substrates). The major drawback at present for the use of DVD in the microelectronics industry appears to be the system’s inability to produce fully dense film coatings. While Chapter 11 suggests ways in which a system reconfiguration could create higher energy deposits by substrate biasing or ion bombardment, there is no experimental evidence available demonstrating that such a DVD system produces a fully dense film. Since DVD already generates many excited and ionized vapor atoms, it is appealing to consider using this feature of the system for some film creation benefit. Use of DVD for the synthesis of microelectronic materials could require a lower accelerating voltage to minimize harmful x-ray generation. Conveniently, use of a lower accelerating voltage appears feasible in a system configured according to the ideas presented in section 11.1 in which chamber pres-
sures are in the milliTorr (1 Pa) range. The lower processing chamber pressures of this system are compatible with lower accelerating voltages (equation (4.2) and Fig. 4.1) and with ion bombardment systems should such additional tools prove necessary.

12.7 Other System Configurations

The experimental work of Chapters 5 - 7 demonstrates that, for applications other than fiber coating, the current DVD system configuration has several important design flaws. The most important of these is the variation in material deposition characteristics with changes in e-beam power (Figs. 5.10 and 5.11). Industry almost certainly will demand that the process provide a more consistent processing environment, not one which requires increasing amounts of carrier gas to bend the vapor stream towards the substrate as the e-beam gun power is raised while simultaneously decreasing material utilization efficiency.

The modeling results of Chapter 11 suggest that it could be possible to reconfigure the DVD system in a manner which will yield more consistent results. However, before industry will adopt DVD in such a configuration, the capabilities of a reconfigured system must be demonstrated in the lab or a more sophisticated model must be developed which is capable of simulating the effect of various vapor atom flux densities upon DVD deposition characteristics.

12.8 Summary

A great deal of effort has already been invested in the development of Directed Vapor Deposition. However, as suggested in this chapter, a great deal more work must be done before industry will be convinced that the technology represents a well-understood tool capable of creating products with desired microstructures and properties.
Chapter 13

Conclusions

A novel materials processing pathway, Directed Vapor Deposition, has been designed, constructed, demonstrated to work, and experimentally explored as a method for creating thick and thin film materials from the vapor phase in a distinctly different manner than possible with existing physical vapor deposition systems [142, 186, 206, 207, 215, 244, 245]. Its method of vapor transport has also been modeled. The configuration of the DVD system explored in this dissertation employed an electron beam gun to evaporate material in a low vacuum environment. An inert gas jet was then used to capture that vapor stream and transport it to a substrate for deposition. The system was created with the idea that it might be able to deposit a more focussed vapor stream onto flat and fibrous substrates with higher efficiencies and adatom energies than possible using existing thermal evaporation sources. In addition the system was initially envisioned as a highly flexible material synthesis tool for depositing material at varying adatom energies, angles, and distributions.

The two part model employed in this dissertation utilized the Direct Simulation Monte Carlo method developed by G. A. Bird to simulate the carrier gas flow directed at the sub-
strate and then employed fundamental bimolecular collision theory concepts to follow vapor atoms in the carrier gas flow from source to substrate. Vapor atoms were tracked through the system until they left the modeled volume or contacted the substrate. For atoms contacting the substrate, their velocity and position vectors were recorded. This information allowed adatom deposition efficiency, energy, angle, and distribution information to be tabulated for various processing conditions, providing additional material synthesis insight not available through the experimental work.

The experimental and modeling work of the dissertation showed that for certain specific applications the technology may represent a more attractive material synthesis pathway than existing vapor deposition techniques. DVD demonstrated an ability to create focussed efficient deposits onto selected substrate forms (e.g. fibers) where the gas scattering characteristics of the technology can be put to advantageous use, coating surfaces in and out of the line of sight of the vapor stream. The research of this dissertation also suggests DVD could prove useful in applications where elements from the gas phase need to be reacted and combined with elements which are normally liquids or solids at room temperature (e.g. thermal barrier coatings). Finally the modeling work of this dissertation suggests that there exists room for improvement of DVD technology through system reconfiguration and addition of other processing subsystems (e.g. substrate biasing or ion beam substrate modification tools).

### 13.1 Specific Conclusions

As a result of the work conducted for this dissertation, many specific conclusions can be drawn:
Experimental:

- A free jet expansion from a sharp-edged orifice does create a region of supersonic carrier gas flow inside the processing chamber.

- The carrier gas velocity (Mach number), deposition chamber pressure, and e-beam power are three of the most important processing parameters affecting the efficiency and distribution of deposited material in a DVD system.

- While Mach number, chamber pressure, and e-beam power are of primary importance, many other factors influence vapor deposition. Other important factors include vapor atom composition, carrier gas atom composition, length of source material rod and crucible temperature.

- For both flat substrate and fiber coating experiments, deposition efficiency initially rises, goes through a maximum and then decreases as the deposition chamber pressure increases.

- For both flat substrate and fiber coating experiments, the deposition efficiency increases with increasing Mach number at a fixed deposition chamber pressure (below the pressure at which peak efficiency is observed).

- For both flat substrate and fiber coating experiments, the deposition efficiency increases with decreasing Mach number at a fixed deposition chamber pressure (above the pressure at which peak efficiency is observed).

- For the experimental configurations examined, the position of the vapor source relative to the nozzle and substrate has some small effect upon deposition efficiency. Placing the crucible closer to the nozzle lip increases deposition efficiency.

- Under selected carrier gas velocity and chamber pressure conditions, Directed Vapor Deposition can deposit vapor onto fibers at twice the efficiency of traditional, high vacuum, line-of-sight vapor deposition systems.
• The dependence of deposition upon a large number of process variables highlights the importance of incorporating sensors into the DVD system to monitor the critical issues of vapor source surface temperature, vapor composition and velocity, and film growth rate and surface temperature.

• DVD can deposit compounds created via reaction between pure metals and gas phase elements.

*Modeling:*

• The DSMC plus BCT model developed in this dissertation can be used to model diode sputter deposition of materials. Compared to the theoretical predictions of other researchers reported in the literature, this model more accurately predicts energy loss between target and substrate resulting from vapor atom / background gas atom collisions.

• Vapor deposits created in the current DVD system are low energy deposits with a wide angular distribution of deposit.

• Variation of carrier gas flow Mach number and chamber pressure generates deposition efficiency trends which mirror those observed experimentally.

• While the current DVD system does not generally deposit vapor more efficiently than traditional e-beam systems for the same source to substrate distance, it can create deposits which are significantly more focussed than those systems under selected process conditions.

• The DVD system can be redesigned to provide vapor deposition efficiency above the level observed in the current DVD system and above the level achievable in conventional e-beam systems.
• To produce an accurate picture of vapor transport during Directed Vapor Deposition additional model development must be undertaken in which a flux of atoms is allowed to interact with the carrier gas stream. The single vapor atom approach employed in this dissertation allows accurate simulation of vapor transport only in the diffuse limit.

• Using the carrier gas stream to redirect the vapor atoms 90° toward the substrate is quite inefficient, wasting significant amounts of carrier gas and inefficiently depositing vapor onto a substrate. Much greater deposition efficiency can be achieved by using the carrier gas only to focus and accelerate the vapor stream.

13.2 Final Thought

As noted in the Introduction to this dissertation, the specific system examined for this research project might or might not become a desirable method for industrial application. However, by studying this method several application areas have been identified for the technology and better understanding of low vacuum materials synthesis has been generated. As Chapter 11 demonstrates, continued efforts to understand the system should lead to incremental improvements in the technology, ultimately resulting in the development of a well understood process technology with desirable characteristics for the synthesis of highly engineered materials in strategically selected applications.
References


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Appendix A - DVD Specifications

The following pages contain engineering drawings of the e-beam gun, the processing chamber, and the water-cooled crucible as provided by the various manufacturing companies. Clearly the schematic illustrations do not provide all of the design details necessary to reconstruct the DVD system. However, these diagrams, in combination with the system description of Chapter 4, should provide sufficient information to allow critical evaluation of the design of the first generation DVD system. These diagrams should also represent a reasonable departure point for someone interested in further developing DVD technology.

A.1 E-beam Gun Design Drawings

Figure A.1 Wehnelt cup assembly which generates the e-beam.
Figure A.2 **Overview drawing of traditional components of DVD e-beam gun.** The pressure decoupling system unique to the DVD system is not shown.
Figure A.3  Beam Generating Assembly, top portion of DVD e-beam gun.
Figure A.4  Beam Guidance System, center section of DVD e-beam gun.
Figure A.5  **Pressure Decoupling Chamber, bottom section of DVD e-beam gun.**
Figure A.6  Stainless steel processing chamber with 2.54 cm thick walls.

Note: These drawings incorrectly indicate that the hinged door assembly is opposite the wall containing the two angled vapor source introduction ports. The final design actually placed the door opposite the wall containing the chamber pump port.
A.3 Water-Cooled Crucible Design Drawings

Figure A.7 Specially designed DVD water-cooled crucible.
A.4 Processing Chamber Pumping Capacity Design Calculations

Note: The description and calculations in this section were generated by D. Hill and are included here to provide a more complete description of the design of the original Directed Vapor Deposition system. Simulation of the reconfigured DVD system in Chapter 10 suggests that the calculations of this subsection may not be entirely correct. The Chapter 10 simulations suggest that the required pumping capacity does not go through a maximum at Mach 1.0 as shown in Fig. A.9 below. Instead the required pumping capacity appears to continue to increase as the Mach number is increased. Equations A.2 and A.3 were used to calculate required pumping capacity in Chapter 10.

During the design of the original DVD system, the following equations describing carrier gas flow through the DVD processing chamber were used. They employ the flow’s desired Mach number at the tube exit, the stagnation temperature of the carrier gas (helium), and the inside diameter of the inlet flow tube to determine required pumping capacity. This analysis assumed that the inlet flow tube was smooth and not excessively long (< 2 m). Thus, friction and heat transfer through the pipe wall were assumed to be negligible. Fig. A.8 shows the assumed geometry of the modeled system.

Important flow geometry features assumed in the analysis included:

1. The inside diameter of the settling chamber was at least five times that of the flow tube, ensuring nearly zero velocity and stagnation conditions in the chamber.

2. The diameter of the chamber pump inlet was at least three times the diameter of the inlet flow tube, ensuring that the at-pump gas velocity is extremely low.

3. The inlet flow tube was straight.

The controlling variables for pumping capacity are Mach number (at the pipe exit), stagnation temperature (in the settling chamber), and pipe diameter. Equations (2.19), (2.20),
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and (8.1) were used in conjunction with the following equation to compute the necessary pumping capacity.

\[
\frac{\rho_o}{\rho} = \left[1 + \frac{\gamma - 1}{2} M^2\right]^{\frac{1}{\gamma - 1}}.
\]  \tag{A.1}

where \( \rho_o = \) Settling chamber gas density and 

\( \rho = \) Downstream gas density (e.g. in the inlet flow tube).

The necessary chamber pumping capacity \( \dot{U}_{pump} \) was computed from the following equation:

\[
\dot{U}_{pump} = \dot{U}_{pipe} \frac{p_{pipe}}{p_{pump}}
\]  \tag{A.2}

where 

\[
\dot{U}_{pipe} = A_{pipe} U_{pipe}
\]  \tag{A.3}

with \( A_{pipe} = \) Area of the inlet flow tube and

Figure A.8 **Estimation of chamber pumping requirements.** Isentropic flow calculations provide a means for estimating the chamber vacuum pumping capacity required in the DVD system.
$U_{\text{pipe}}$ = Velocity of the carrier gas through the inlet flow tube.

The calculated required pumping capacity for the original DVD processing chamber pump system is shown in Fig. A.9.

Figure A.9 **Achievable gas flow velocity for various pumping configurations.** The results of the isentropic flow calculations show the pumping capacity required to achieve supersonic carrier gas flows in the original DVD system under typical processing conditions.
Appendix B - Clustering Calculations

The following code segment illustrates the method of solution for the vapor atom cluster size data shown in Table 7.5. The code numerically integrates equation (2.18).

\[
\begin{align*}
CCu &= 3.33 \times 10^{18}; \text{ Concentration of Copper (atoms/m}^3) > \\
kBz &= 1.3807 \times 10^{-23}; \text{ Boltzmann’s constant } > \\
TK &= 270; \text{ Temperature } > \\
Mass &= 1.06 \times 10^{-25}; \text{ Copper atom mass } > \\
tau &= 0.0001; \text{ Time step (sec) } > \\
\text{sol} &= \text{NDSolve}\{y'[x] == CCu \pi (2.9 \times 10^{-10} y[x] + 3.9 \times 10^{-10})^2 \sqrt{(1 + y[x])8kBzTK/(\pi y[x] Mass)}}, y[0] == 2.} \text{, } \{x, 0, \tau\}
\text{Plot[Evaluate[y[x]/.sol],\{x, 0, \tau\};}
\text{\{y -> InterpolatingFunction[{{0, 0.0001}},<>\}}]
\end{align*}
\]

Figure B.1 Cluster size as a function of time. Evaluation of equation (2.18) for a copper concentration of $3.33 \times 10^{18}$ atoms/m$^3$ yields this vapor atom cluster size prediction as a function of time.
* DSMC2A.FOR
*
* PROGRAM DSMC2A
*
*--axially symmetric steady flow program (axis at y=0, y is radius)
*--x is in the axial direction, z is in the circumferential direction
*--the flowfield is a rectangular region in the x-y plane
*--radial weighting factors may be employed
*--the cells and sub-cells are rectangular
*--the cell spacing may be a geometric progression in each direction
*--each of the four boundaries may be either
*--a uniform stream,
*--a plane of symmetry (only for boundaries normal to the axis)
*--a vacuum, or
*--the axis
*--there may be one or two one-sided surfaces
*--they must lie along a cell boundary
*--they may lie along a flow boundary
*--they may be back-to-back to form one double-sided surface
*--the surface reflection may be diffuse, specular,
*--or follow the Cercignani-Lampis-Lord (CLL) model
*--the surface may be moving in the circumferential direction
*--(the CLL model cannot be used with circumferential velocities)
*--there may be one uniform jet
*--this must lie along a cell boundary
*
*--SI units are used throughout
*
*-------------------------DESCRIPTION OF DATA---------------------------
*
*--PARAMETER variables must be consistent with data in subroutine DATA2A
*
*--IWF 0,1 for no weighting factors, or factors proportional to radius
*--RWF the reference radius below which the weighting factors are unity
*--required only for IWF=1, very small values are not recommended
*
*--NCX the number of cells in the x direction (cell columns)
*--NCY the number of cells in the y direction (cell rows)
*--(MNC must be equal to or greater than NCX*NCY)
*
*--NSCX the number of sub-cells per cell in the x direction
*--NSCY the number of sub-cells per cell in the y direction
*--(MNSC must be at least MNC*NSCX*NSCY)
*
*--IFCX set to 0 or 1 for uniform or non-uniform cell widths in x dim.
*--if IFCX=1, set CWRX as the ratio of the cell width at the outer x
*--boundary to that at the inner x boundary (default 0)
*--IFCY and CWRY similar to IFCX and CWRX for the y direction
*
*--IIS 0 if there is no stream, 1 if there is a uniform stream
*--ISG 0 if there is a stream and the initial state is a vacuum, or
*--1 if the initial state is a uniform stream, or
*
*--if part of the rectangular region is excluded from the flow, set
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*--LFLX if positive no flow below where LFLY condition is also satisfied
*-- if negative no flow above where LFLY condition is also satisfied
*--LFLY if positive no flow below where LFLX condition is also satisfied
*-- if negative no flow above where LFLX condition is also satisfied
*--for example, if LFLX=3 and LFLY=-2, there is no stream in the corner
*--below cell column 3 and above cell row 2
*--if no flow is excluded, LFLX,Y are automatically set to 0
*
*--FTMP the stream temperature if IIS=1, or a temperature characteristic
*--of the flow otherwise (if FTMP is not set for IIS= 0, the
*--default value of 273 is used to set the initial value of CCG(1)
*
*--FND the initial number density for IIS=1
*--or need not be set for IIS=0
*
*--VFX the stream velocity in the x direction
*--need not be set for IIS=0
*
*--FSP(L) the fraction (by number) of species L in the initial stream
*--a value is required for each species, but need not be set for IIS=0
*
*--FNUM the number of real mols. represented by each simulated molecule
*
*--DTM the time step over which the motion and collisions are uncoupled
*
*--the following data is required for each boundary
*--K=1 for the lower value of x
*--K=2 for the higher value of x
*--K=3 for the lower value of y
*--if a boundary is on the axis, it must be boundary 3
*--K=4 for the higher value of y
*
*--CB(K) the coordinate of the boundary (x for K=1 or 2, y for K=3 or 4)
*
*--IB(K) the type code of the boundary
*--1 for stream, 2 for plane of symmetry, 3 for vacuum, 4 for axis
*
*--ISURF(K) with K=1, 2 for the two surfaces
*--0 if there is no surface
*--1 if the surface normal is in the positive y direction
*--2 if the surface normal is in the negative y direction
*--3 if the surface normal is in the positive x direction
*--4 if the surface normal is in the negative x direction
*
*--the following surface data is required if ISURF(K) > 0
*
*--LIMS(K,L) with K as before, and the surface lies along the
*--lower boundary of the cell row or column given by L=1
*--one edge of the surface is at the lower edge of the row or column
*--given by L=2, and the other is at the upper edge of the row or
*--column given by L=3
*
*--WSURF(K) the circumferential velocity of the surface
*--applies only to surfaces parallel to the axis and
*--these surfaces must be diffusely reflecting
*--TSURF(K) the temperature of the surface
*--if TSURF is negative, the reflection is specular
*--if TSURF is positive, the following must also be specified:
*--ALPI(K) should be -1. for diffuse reflection, or between 0 and 1
*--for the rotational energy accommodation coefficient for CLL model
*--ALPN(K) the normal momentum accommodation coeff. in the CLL model
*--ALPT(K) the tangential momentum accommodation coeff. in the CLL model
*----(if ALPI is not set explicitly, it is set to default value of -1.)
*--end of surface data
*--IJET 0 if there is no jet, or
*----1 if the jet is in the positive y direction
*----2 if the jet is in the negative y direction
*----3 if the jet is in the positive x direction
*----4 if the jet is in the negative x direction
*--end if IJET > 0, the following data is required
*--LIMJ(L) the jet efflux plane lies along the
*----lower boundary of the cell row or column given by L=1
*----one edge of the plane is at the lower edge of the row or column
*----given by L=2, and the other is at the upper edge of the row or
*----column given by L=3
*--TMPJ the jet temperature
*--FNDJ the number density of the jet
*--FVJ the jet velocity
*--FSPJ(L) the fraction (by number) of species L in the jet
*----a value is required for each species
*--end of jet data
*--ISPD (required only for gas mixtures) set to 0 if the diameter,
*----viscosity exponent, and VSS scattering parameter for the
*----cross-collisions are to be set to the mean values, or
*----set to 1 if these quantities are to be set as data
*--the following data must be repeated for each species (L=1 to MNSP)
*--SP(1,L) the reference diameter
*--SP(2,L) the reference temperature
*--SP(3,L) the viscosity temperature power law
*--SP(4,L) the reciprocal of the VSS scattering parameter (1. for VHS)
*--SP(5,L) the molecular mass
*--ISP(L) the collision sampling group in which the species lies
*----this must be LE.MNSC (not required if MNSG=1)
*--ISPR(1,L) the number of rotational degrees of freedom
*--ISPR(2,L) 0, 1 for constant, polynomial rotational relaxation number
*--ISPR(3,L) 0, 1 for common or collision partner species dependent
*----rotational relaxation rate
*--SPR(1,L,K) the constant value, or constant in the polynomial for Zr
*----in a collision of species L with species K
*--the following two items are required only if ISPR(2,L)=1
*--SPR(2,L,K) the coefficient of temperature in the polynomial
*--SPR(3,L,K) the coefficient of temperature squared in the polynomial
*--end of data for the individual species
*--the following data on the cross-collisions is required only if ISPD=1
*--then only for L,NE.M, but L,M data must be repeated for M.L
Appendix C - Flowfield Modeling Code

*--SPM(1,L,M) the reference diameter for species L-M collisions
*--SPM(2,L,M) the reference temperature for species L-M collisions
*--SPM(3,L,M) the viscosity temperature power law for species L-M colls.
*--SPM(4,L,M) the reciprocal of the VSS scattering parameter
*--end of species data
*
*--NIS the number of DTM time steps between samplings
*--NSP the number of samples between prints
*--NPS the number of prints to the assumed start of steady flow
*--NPT the number of prints to STOP
*------------------------------------------
* PARAMETER (MNM=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304,&
& MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)
*--MNMR 1 if all molecules are monatomic, MNM otherwise
*--MNMS 1 if there is only one species, MNM for a gas mixture
*--MBC the maximum number of cell divisions along any entry boundary
*--MNB the maximum number of molecules in the duplication delay buffer
*--other variables as defined in DSMC2.FOR
*
* DOUBLE PRECISION COL(MNSP,MNSP),MOVT,NCOL,SELT,SEPT,CS(9,MNC,MNSP)
*--CS(8 the sample (unweighted) number
*--CS(9,1 the square of the sample (all species)
*--other variables as defined in DSMC0.FOR, but all values are weighted
* DOUBLE PRECISION CSR(MNC,MNSP)
*--CSR(M,L) the sum of the rotational energy of species L in cell M
* DOUBLE PRECISION CSS(9,MNSE,MNSP)
*--CSS(N,M,L) sampled info. on the molecules striking the boundaries
*----M is the code number of the element; L is the species
*----N=1 the weighted number sum
*----N=2 the sum of the normal momentum of the incident molecules
*----N=3 the sum of the normal momentum for the reflected molecules
*----N=4 the sum of the incident tangential momentum
*----N=5 the sum of the incident translational energy
*----N=6 the sum of the reflected translational energy
*----N=7 the sum of the incident rotational energy
*----N=8 the sum of the reflected rotational energy
*----N=9 the sum of the reflected tangential momentum
*
* COMMON /MOLS2 / NM,PP(2,MNM),PV(3,MNM),IPL(MNM),IPS(MNMS),IR(MNM)
*--variables as defined in DSMC0.FOR except that PP( is two-dimensional
* COMMON /MOLSR / PR(MNMR)
*--PR(M) is the rotational energy of molecule M
*
* COMMON /MOLD  / NMB,PPB(2,MNB),PVB(3,MNB),PRB(MNB),IPLB(MNB),&
& IPSB(MNB),IRB(MNB)
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*--NMB the number of molecules in the duplication delay buffer
*--PPB etc. the molecule properties in the buffer

* COMMON /CELL2 / CC(MNC),CG(6,MNC),IC(2,MNC,MNSG),ISC(MNSC),
& CGG(2,MNC,MNSG,MNSG),IACG(2,MNSC,MNSG),IG(2,MNSG),
& NCX,NCY,IFCX,IFCY,CWRX,CWRY,APX,RPX,APY,RPY
* 
*--IFCX,IFCY 0,1 for uniform, geometric progression for cell width
*--CWRX, CWRY the ratio of cell width, height at higher valued boundary
*----to that at the lower valued boundary
*--other variables as defined in DSMC0.FOR except that
*----CG(4,5,6 for y correspond to CG(1,2,3 for x
* 
* COMMON /GAS / SP(5,MNSP),SPM(6,MNSP,MNSP),ISP(MNSP)
* 
*--variables as defined in DSMC0.FOR
* 
* COMMON /GASR / SPR(3,MNSP,MNSP),ISPR(3,MNSP),CT(MNC)
* 
*--variables as defined in DSMC0R.FOR
* 
* COMMON /SAMP2A/ COL,NCOL,MOVT,SELT,SEPT,CS,TIME,NPR,NSMP,FND,FTMP,
& TIMFSP(MNSP),ISP,DVF
* 
*--VFX stream velocity component in X direction
*--other variables as defined in DSMC0.FOR
* 
* COMMON /SAMP2 / CSR
* 
* COMMON /SAMP3 / CSS
* 
* COMMON /COMP / FNUM,DTM,NIS,NSP,NPS,NPT
* 
*--variables as defined in DSMC0.FOR
* 
* COMMON /GEOM2A/ NSCX,NSCY,CB(4),IB(4),ISURF(2),LIMS(2,3),IIS,ISG,
& TSURF(2),IJET,LIMJ(3),TMPJ,FNDJ,FVJ,FSPJ(MNSP),
& AMEJ(MNSP,MBC),AMRJ(MNSP,MBC),AMEI(MNSP,MBC),AMRI(MNSP,MBC),
& AMR(4,MNPSP,MBC),CW,FW,CH,FH,WJ,LPLX,LPLY,ALP(2),
& ALPN(2),ALPT(2),JWF,RWF,WSURF(2)
* 
*--IIS 0, 1 if the initial flow is a vacuum, uniform stream
*--NSCX,NSCY the number of sub-cells per cell in x,y directions
*--CB(N) the location of the boundary
*----N=1,2 for lower, higher value of x
*----N=3,4 for lower, higher value of y
*--IB(N) N=1 to 4 as above, the type code for the boundary
*--ISURF(K) 0 for no surface, otherwise direction of normal to surface K
*--LIMS(K,3) defines the location of the surface
*--TSURF(K) the temperature of the surface (negative for specular refl.)
*--WSURF(K) the circumferential velocity of the surface
*--IJET 0 for no jet, otherwise the jet direction
*--LIMJ(K) defines the location of the jet
*--TMPJ the jet temperature
*--FNDJ the number density of the jet
*--FVJ the jet velocity
*--FSPJ(L) the fraction of species L in the jet
*--AMEE(N,L,K) number of molecules of species L that enter element K of
*----side N each DTM
*--AMRI(N,L,K) the remainder associated with AME
*--AMEJ(L,K) number of molecules of species L that enter el. K of jet
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*--AMRJ(L,K) the remainder associated with AMEJ
*--CW the cell width for uniform cells
*--FW the flow width
*--ALPI(K) the accommodation coefficient for rotational energy for CLL
*----model this should be negative if the reflection is to be diffuse
*--ALPN(K) the CLL accommodation coefficient for normal momentum
*--ALPT(K) the CLL accommodation coefficient for tangential momentum
*--IWF 0,1 for no weighting factors, factors proportional to radius
*--RWF the reference radius for weighting factors
*----if IWF=1, a simulated molecule at radius r represents r*FNUM/RWF
*------real molecules

COMMON /CONST / PI,SPI,BOLTZ

*--variables as defined in DSMC0.FOR

WRITE (*,*) ' INPUT 0,1 FOR CONTINUING,NEW CALCULATION:- '
C     READ (*,*) NQL
WRITE (*,*) ' INPUT 0,1 FOR CONTINUING,NEW SAMPLE:- '
C     READ (*,*) NQLS

NQL = 1
NQLS = 1

IF (NQL.EQ.1) THEN
CALL INIT2A
ELSE
WRITE (*,*) ' READ THE RESTART FILE'
OPEN (4,FILE='/bigtmp/DSMC2A5.RES',STATUS='OLD',FORM='UNFORMATTED')
READ (4) ALPI,ALPN,ALPT,APX,APY,FND,AME,AMEJ,AMR,AMRJ,BOLTZ,CB,
& CC,CCG,CG,CH,COL,CS,CSR,CSS,CT,CW,CWRX,CWRY,DTM,FND,J,
& FNUN,FSPJ,FTMP,FVJ,FH,FW,IB,IC,IFCX,IFCY,IJS,IDENT,IP,,
& IPL,IPS,IPB,IR,ISC,ISCG,ISG,ISP,ISR,ISURF,IFW,
& LFLX,LFLY,LIMJ,LMIS,MONT,NCOL,NCX,NCY,NIS,NMB,NPS,
& NSCG,NSCY,NSMP,NPR,NPT,NSP,PLP,PPB,PRB,PRP,PV,PRX,
& RPY,RWF,SELT,SEPT,SP,SPM,SPR,TIME,TIMI,TMPJ,TSURF,
& VFX,WI,WSURF
CLOSE (4)
END IF

IF (NQLS.EQ.1) CALL SAMPI2A

100 NPR=NPR+1
IF (NPR.LE.NPS) CALL SAMPI2A

DO 200 JJJ=1,NSP
DO 150 III=1,NIS
TIME=TIME+DTM
WRITE (*,99001) III,JJJ,NIS,NSP,NM
99001     FORMAT (' DSMC2A:- Move',2I5,' of',2I5,' Mols',I14,
& ' Colls')
CALL MOVE2A
CALL INDEXM
* CALL COLLMR
*
150   CONTINUE
* CALL SAMPLE2A
*
200   CONTINUE
*
C WRITE (*,*) ' WRITING RESTART AND OUTPUT FILES, NPR, OF, NPT
C OPEN (4,FILE='/bigtmp/DSMC2A5.RES',FORM='UNFORMATTED')
C WRITE (4) ALPI,ALPN,ALPT,APX,APY,FND,AME,AMEJ,AMRJ,BOLTZ,CB,
C & CC,CCG,CG,CH,COL,CS,CSR,CSS,CT,CW,CWRX,CWRY,DTM,FNDJ,
C & FNUM,FSPJ,FTMP,FVJ,FW,FB,IC,IFCX,IFCY,IS,ISPR,ISEXT,ISURF,
C & IJET,IPR,IRB,ISC,ISCG,ISP,ISPJ,ISRFD,ISRURF,JWF,
C & LFLX,LFLY,LIMJ,LIMS,MOVT,NCOL,NCX,NCY,NIS,NSC,NSG,NSM,
C & NSN,NSM,NSP,NPR,NPT,NS,PP,PPB,PR,PRB,PV,PV,B,RPX,
C & RPY,RWF,SELT,SEPT,SP,SPJ,SPM,SPR,TIMI,TIMJ,TMPJ,TSURF,
C & VFX,VJ,W,WSURF
C CLOSE (4)
*
CALL OUT2A
*
IF (NPR.LT.NPT) GO TO 100
STOP
END
* INIT2A.FOR
*
SUBROUTINE INIT2A
*
PARAMETER (MNM=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304,
& MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)
*
DOUBLE PRECISION COL(MNSP,MNSP),MOVT,NCOL,SELT,SEPT,CS(9,MNC,MNSP)
DOUBLE PRECISION CSR(MNC,MNSP)
*
COMMON /MOLS2 / NM,PP(2,MNM),PV(3,MNM),IPL(MNM),IPS(MNMS),IR(MNM)
COMMON /MOLSR / PR(MNMR)
COMMON /MOLD / NMB,PPB(2,MNB),PVB(3,MNB),PRB(MNB),IPLB(MNB),
& IPSB(MNB),IRB(MNB)
COMMON /CELL2 / CC(MNC),CG(6,MNC),IC(2,MNC,MNSG),ISC(MNMS),
& CCG(2,MNC,MNSG,MNSG),ISCG(2,MNSC,MNSG),ISG(2,MNSG),
& NCX,NCY,IFCX,IFCY,CWRX,CWRY,APX,APB,APR,APR
COMMON /GAS / SP(5,MNSP),SPM(6,MNSP,MNSP),ISP(MNSP)
COMMON /GASR / SP(3,MNSP,MNSP),ISPR(3,MNSP),CT(MNC)
COMMON /SAMP2A/ COL,NCOL,MOVT,SELT,SEPT,CS,TIMI,NPR,NSMP,FND,FTMP,
& TIMJ,FSP(MNSP),ISP,FVD
COMMON /SAMP / CSR
COMMON /COMP / FNUM,DTM,NIS,NSP,NPS,NPT
COMMON /GEOM2A/ NSCX,NSCY,CB(4),IB(4),ISURF(2),LIMS(2,3),JIS,ISG,
& TSURF(2),IJET,LIMJ(3),TMPJ,FNDJ,FVJ,FSPJ(MNSP),
& AMEJ(MNSP,MBC),AMRI(MNSP,MBC),AME(4,MNSP,MBC),
& AMR(4,MNSP,MBC),CW,FW,CH,FB,IC,LFLX,LFLY,ALPI(2),
& ALPN(2),ALPT(2),JWF,RWF,WSURF(2)
COMMON /CONST / PL,PLPI,BOLTZ
*
*--set constants
* Pi=3.141592654
SPI=SQRT(Pi)
Appendix C - Flowfield Modeling Code

BOLTZ=1.380622E-23
*
*--set data variables to default values that they retain if the data
*----does not reset them to specific values
IWFe=0.
FNd=0.
FTMP=273.
VFX=0.
IFCX=0.
IFCY=0.
LFLX=0.
LFLY=0.
ALPi(1)=-1.
ALPi(2)=-1.
WSURF(1)=0.
WSURF(2)=0.
NMB=0.
DO 100 N=1,4
IB(N)=3
DO 50 L=1,MNSP
ISPl(L)=1
FSP(L)=0.
DO 20 K=1,MBC
AME(N,L,K)=0.
AMR(N,L,K)=RF(0)
20        CONTINUE
50      CONTINUE
100   CONTINUE
DO 200 L=1,MNSP
DO 150 K=1,MBC
AMEJ(L,K)=0.
AMRJ(L,K)=RF(0)
150     CONTINUE
200   CONTINUE
*
CALL DATA2A
*
*--set additional data on the gas
*
IF (MNSP.EQ.1) ISPD=0
DO 300 N=1,MNSP
DO 250 M=1,MNSP
IF ((ISPR(3,N).EQ.0).AND.(M.NE.N)) THEN
SPR(1,N,M)=SPR(1,N,N)
SPR(2,N,M)=SPR(2,N,N)
SPR(3,N,M)=SPR(3,N,N)
END IF
IF ((ISPD.EQ.0).OR.(N.EQ.M)) THEN
SPM(1,N,M)=0.25*PI*(SP(1,N)+SP(1,M))**2
*--the collision cross section is assumed to be given by eqn (1.35)
SPM(2,N,M)=0.5*(SP(2,N)+SP(2,M))
SPM(3,N,M)=0.5*(SP(3,N)+SP(3,M))
SPM(4,N,M)=0.5*(SP(4,N)+SP(4,M))
*--mean values are used for ISPD=0
ELSE
SPM(1,N,M)=PI*SPM(1,N,M)**2
*--the cross-collision diameter is converted to the cross-section
END IF
SPM(5,N,M)=SP(5,N)/(SP(5,N)+SP(5,M))**2
SPM(6,N,M)=GAM(2.5-SPM(3,N,M))
Appendix C - Flowfield Modeling Code

250 CONTINUE
300 CONTINUE
*
*-- initialise variables
*
TIME=0.
NM=0
NPR=0
NCOL=0
MOVT=0.
SELT=0.
SEPT=0.
*
DO 400 M=1,MNSP
  DO 350 N=1,MNSP
    COL(M,N)=0.
  350 CONTINUE
400 CONTINUE
*
FW=CB(2)-CB(1)
FH=CB(4)-CB(3)
CG(1,1)=CB(1)
IF (IFCX.EQ.0) THEN
  CW=FW/NCX
  RPX=CWRX**(1./(NCX-1.))
  APX=(1.-RPX)/(1.-RPX**NCX)
END IF
CG(4,1)=CB(3)
IF (IFCY.EQ.0) THEN
  CH=FH/NCY
  RPY=CWRY**(1./(NCY-1.))
  APY=(1.-RPY)/(1.-RPY**NCY)
END IF
DO 500 MY=1,NCY
  DO 450 MX=1,NCX
    M=(MY-1)*NCX+MX
    CT(M)=FTMP
    IF (MX.EQ.1) CG(1,M)=CG(1,1)
    IF (MX.GT.1) CG(1,M)=CG(2,M-1)
    IF (IFCX.EQ.0) THEN
      CG(2,M)=CG(1,M)+CW
      ELSE
      CG(2,M)=CG(1,M)+FW*APX*RPX**(MX-1)
    END IF
    CG(3,M)=CG(2,M)-CG(1,M)
    IF (MY.EQ.1) CG(4,M)=CG(4,1)
    IF (MY.GT.1.AND.MX.EQ.1) CG(4,M)=CG(5,M-1)
    IF (MY.GT.1.AND.MX.GT.1) CG(4,M)=CG(4,M-1)
    IF (IFCY.EQ.0) THEN
*-- the macroscopic temperature is set to the freestream temperature
*-- set the x coordinates
  IF (MX.EQ.1) CG(1,M)=CG(1,1)
  IF (MX.GT.1) CG(1,M)=CG(2,M-1)
  IF (IFCX.EQ.0) THEN
      CG(2,M)=CG(1,M)+CW
  ELSE
      CG(2,M)=CG(1,M)+FW*APX*RPX**(MX-1)
  END IF
  CG(3,M)=CG(2,M)-CG(1,M)
*-- set the y coordinates
  IF (MY.EQ.1) CG(4,M)=CG(4,1)
  IF (MY.GT.1.AND.MX.EQ.1) CG(4,M)=CG(5,M-1)
  IF (MY.GT.1.AND.MX.GT.1) CG(4,M)=CG(4,M-1)
  IF (IFCY.EQ.0) THEN

\( CG(5,M) = CG(4,M) + CH \)
ELSE
\( CG(5,M) = CG(4,M) + FH * APY * RPY^{* (MY - 1)} \)
END IF
\( CG(6,M) = CG(5,M) - CG(4,M) \)
\( CC(M) = \pi * CG(3,M) (CG(5,M)^2 - CG(4,M)^2) \)
DO 410 L=1,MNSG
DO 400 K=1,MNSG
\( CCG(2,M,L,K) = RF(0) \)
\( CCG(1,M,L,K) = SPM(1,1,1) * 300. * \sqrt{FTMP / 300.} \)
410 CONTINUE
420 CONTINUE
*--the maximum value of the (rel. speed)*(cross-section) is set to a
*--reasonable, but low, initial value and will be increased as necessary
450 CONTINUE
500 CONTINUE
IF (IFCX.EQ.1) THEN
\( APX = (1. - RPX) / APX \)
\( RPX = \log(RPX) \)
*--APX and RPX are now the convenient terms in eqn (12.1)
END IF
IF (IFCY.EQ.1) THEN
\( APY = (1. - RPY) / APY \)
\( RPY = \log(RPY) \)
*--APY and RPY are now the convenient terms in eqn (12.1)
END IF
*
*--set sub-cells
*
DO 600 N=1,MNC
DO 550 M=1,NSCY
DO 520 K=1,NSCX
\( L = (N-1) * NSCX * NSCY + (M-1) * NSCX + K \)
\( ISC(L) = N \)
520 CONTINUE
550 CONTINUE
600 CONTINUE
*
IF (IIS.GT.0.AND.ISG.GT.0) THEN
*--if IIS=1 generate initial gas with temperature FTMP
*
DO 650 L=1,MNSP
\( REM = 0 \)
IF (IIS.EQ.1) VMP=\( \sqrt{2 * BOLTZ * FTMP / SP(5,L)} \)
*--VMP is the most probable speed in species L, see eqns (4.1) and (4.7)
DO 620 N=1,MNC
\( IPROB = 1 \)
IF (IWF.EQ.0) THEN
\( WMIN = 1. \)
ELSE
\( WMIN = CG(4,N) / RWF \)
IF (WMIN.LT.1.) WMIN=1.
END IF
*--WMIN is the minimum weighting factor in the cell
IF (LFLX.NE.0) THEN
\( NY = (N-1) / NCX + 1 \)
\( NX = N - (NY - 1) * NCX \)
*--NX and NY are the cell column and row
IF ((LFLX.GT.0.AND.LFLY.GT.0).AND.
& (NX.LT.LFLX.AND.NY.LT.LFLY)) IPROB=0
IF ((LFLX.GT.0.AND.LFLY.LT.0).AND.}
& (NX.LT.LFLX.AND.NY.GT.-LFLY)) IPROB=0
IF ((LFLX.LT.0.AND.LFLY.GT.0).AND.
& (NX.GT.-LFLX.AND.NY.LT.LFLY)) IPROB=0
& (NX.GT.-LFLX.AND.NY.GT.-LFLY)) IPROB=0
END IF
IF (IPROB.EQ.1) THEN
A=FND*CC(N)*FSP(L)/(FNUM*WMIN)+REM
*--A is the number of simulated molecules of species L in cell N to
*--simulate the required concentrations at a total number density of FND
IF (N.LT.MNC) THEN
MM=A
REM=(A-MM)
*--the remainder REM is carried forward to the next cell
ELSE
MM=NINT(A)
END IF
IF (MM.GT.0) THEN
DO 604 M=1,MM
IF (NM.LT.MNM) THEN
*--round-off error could have taken NM to MNM+1
NM=NM+1
IF (MNSP.GT.1) IPS(NM)=L
PP(1,NM)=CG(1,N)+RF(0)*(CG(2,N)-CG(1,N))
NCOLM=(PP(1,NM)-CG(1,N))*NSCX-.001)/CG(3,N)+1
*--set the random radius from the distribution of eqn (C6)
PP(2,NM)=SQRT(CG(4,N)**2+RF(0)*(CG(5,N)**2-CG(4,N)**
& 2))
IF (IWF.EQ.1) THEN
WF=PP(2,NM)/RWF
IF (WF.LT.1.) WF=1.
IF (WMIN/WF.LT.RF(0)) THEN
NM=NM-1
GO TO 604
*--above takes account of the weighting factor variation in the cell
END IF
END IF
IR(NM)=NM
NROW=(PP(2,NM)-CG(4,N))*(NSCY-.001)/CG(6,N)+1
IPL(NM)=(N-1)*NSCX*NSCY+(NROW-1)*NSCX+NCOLM
*--species, position, and sub-cell number have been set
DO 602 K=1,3
CALL RVELC(PV(K,NM),A,VMP)
602          CONTINUE
PV(1,NM)=PV(1,NM)+VFX
*--velocity components have been set
*--set the rotational energy
IF (ISPR(1,L).GT.0) CALL SROT(PR(NM),FTMP,ISPR(1,L))
END IF
604        CONTINUE
END IF
END IF
620       CONTINUE
650     CONTINUE
*
WRITE (*,99001) NM
99001   FORMAT (',I8,' MOLECULES')
END IF
IF (IIS.GT.0) THEN
*--calculate the number of molecules that enter at each time step
DO 700 N=1,4
IF (IB(N).EQ.1) THEN
*--across the four sides of the simulated region
DO 660 L=1,MNSP
VMP=SQRT(2.*BOLTZ*FTMP/SP(5,L))
*--VMP is the most probable speed in species L, see eqns (4.1) and (4.7)
IF (N.LT.3) NCS=NCY
IF (N.GT.2) NCS=NCX
DO 655 NC=1,NCS
IF (N.EQ.1) SC=VFX/VMP
IF (N.EQ.2) SC=-VFX/VMP
IF (N.EQ.3) SC=0.
IF (N.EQ.4) SC=0.
*--SC is the inward directed speed ratio
IF (ABS(SC).LT.10.1) A=(EXP(-SC*SC)+SPI*SC*(1.+ERF(SC)))/(2.*SPI)
IF (SC.GT.10.) A=SC
IF (SC.LT.-10.) A=0.
*--A is the non-dimensional flux of eqn (4.22)
IF (N.EQ.1.OR.N.EQ.2) THEN
MC=(NC-1)*NCX+1
AME(N,L,NC)=FND*FSP(L)*A*VMP*DTM*PI*(CG(5,MC)**2-CG(4,MC)**2)/FNUM
ELSE
IF (N.EQ.3) AME(N,L,NC)=FND*FSP(L)*A*VMP*DTM*2.*PI*CG(3,NC)*CB(3)/FNUM
IF (N.EQ.4) AME(N,L,NC)=FND*FSP(L)*A*VMP*DTM*2.*PI*CG(3,NC)*CB(4)/FNUM
END IF
655 CONTINUE
660 CONTINUE
END IF
*--now calculate the number that enter in jet
IF (IJET.GT.0) THEN
*--molecules enter from a jet
DO 720 L=1,MNSP
VMP=SQRT(2.*BOLTZ*TMPJ/SP(5,L))
*--VMP is the most probable speed in species L, see eqns (4.1) and (4.7)
SC=FVJ/VMP
*--SC is the inward directed speed ratio
IF (ABS(SC).LT.10.1) A=(EXP(-SC*SC)+SPI*SC*(1.+ERF(SC)))/(2.*SPI)
IF (SC.GT.10.) A=SC
IF (SC.LT.-10.) A=0.
*--A is the non-dimensional flux of eqn (4.22)
NCS=LIMJ(3)-LIMJ(2)+1
DO 750 NC=1,NCS
NCL=NC+LIMJ(2)-1
IF (IJET.EQ.1.OR.IJET.EQ.2) THEN
WJ=2.*PI*CG(3,NCL)
ELSE
MC=(NCL-1)*NCX+1
WJ=PI*(CG(5,MC)**2-CG(4,MC)**2)
END IF
AMEJ(L,NC)=FNDJ*FSPJ(L)*A*VMP*DTM*WJ/FNUM
720 CONTINUE
750  CONTINUE
      END IF
      RETURN
   END
*
* SUBROUTINE MOVE2A
*
*--the NM molecules are moved over the time interval DTM
*
PARAMETER (MNM=2000000, MNMR=1, MNC=1326, MNSC=5304,
               &   MNSP=1, MNSG=1, MNSE=26, MBC=51, MNB=200)
*
DOUBLE PRECISION COL(MNSP,MNSP), MOVT, NCOL, SELT, SEPT, CS(9, MNC, MNSP)
DOUBLE PRECISION CSS(9, MNSE, MNSP)
*
COMMON /MOLS2/ NM, PP(2,MNM), PV(3, MNM), JPL(MNM), IPS(MNMS), IR(MNM)
COMMON /MOLSR/ PR(MNMR)
COMMON /CELL2/ CC(MNC), CG(6, MNC), IC(2, MNC, MNSG), ISC(MNSC),
               &   CCG(2, MNC, MNSG, MNSG), ISCG(2, MNSC, MNSG), IJG(2, MNSG),
               &   NCX, NCY, IFCX, IFCY, CWRX, CWRY, APX, APY, RPY
COMMON /GAS/ SP(5, MNSP), SPM(6, MNSP, MNSP), ISP(MNSP)
COMMON /GASR/ SPR(3, MNSP, MNSP), ISPR(3, MNSP), CT(MNC)
COMMON /SAMP2A/ COL, NCOL, MOVT, SELT, SEPT, CS, TIME, NPR, NSMP, FND, FTMP,
               &   TIMLFSP(MNSP), ISPD, VFX
COMMON /SAMPS/ CSS
COMMON /COMP/ FNUM, DTM, NIS, NSP, NPS, NPT
COMMON /GEOM2A/ NSCX, NSCY, CB(4), JB(4), ISURF(2), LIMS(2, 3), IJS, ISG,
               &   TSURF(2), IJET, LIMJ(3), TMPJ, FNDJ, FVJ, FSPJ(MNSP),
               &   AMEJ(MNSP, MBC), AMRJ(MNSP, MBC), AME(4, MNSP, MBC),
               &   AMR(4, MNSP, MBC), CW, FW, CH, WJ, LFLX, LFLY, ALPI(2),
               &   ALPN(2), ALPT(2), IWF, RWF, WSURF(2)
*
IFT=-1
*--a negative IFT indicates that molecules have not entered at this step
N=0
100  N=N+1
    IF (N.LE.NM) THEN
      IF (IR(N), LT, 0) GO TO 100
*--a duplicated molecule that has already moved has a negative IR
      IF (IFT, LT, 0) AT=DTM
      IF (IFT, GT, 0) AT=RF(0)*DTM
*--the time step is a random fraction of DTM for entering molecules
150  MOVT=MOTV+1
    MSC=IPL(N)
    IF (MSC, LE, 0, OR, MSC, GT, MNSC) CALL REMOVE(N)
    MC=ISC(MSC)
*--MC is the initial cell number
    XI=PP(1, N)
    IF ((XI, LT, 0.0001, *CG(3, 1), LT, CB(1)), OR,
       &   (XI, 0.0001, *CG(3, MNC), GT, CB(2))) THEN
       WRITE (*, *) ' MOL ', N, ' X COORD OUTSIDE FLOW ', XI
       CALL REMOVE(N)
    GO TO 100
    END IF
    YI=PP(2, N)
    IF ((YI, LT, 0.0001, *CG(6, 1), LT, CB(3)), OR,
       &   (YI, 0.0001, *CG(6, MNC), GT, CB(4))) THEN
       WRITE (*, *) ' MOL ', N, ' Y COORD OUTSIDE FLOW ', YI
       CALL REMOVE(N)
Appendix C - Flowfield Modeling Code

GO TO 100
END IF
DX=PV(1,N)*AT
DY=PV(2,N)*AT
DZ=PV(3,N)*AT
X=XI+DX
YD=YI+DY
Y=SQR(YD*YD+DZ*DZ)
DO 200 KS=1,2
*
--check the surfaces
IF (ISURF(KS).GT.0) THEN
IF (ISURF(KS).EQ.1.OR.ISURF(KS).EQ.2) THEN
L1=LIMS(KS,1)
ELSE
YS=CB(4)
L1=L1-1
END IF
IF ((ISURF(KS).EQ.1.AND.(YI.GT.YS.AND.YD.LT.YS)).OR.
 & (ISURF(KS).EQ.2.AND.(YI.LT.YS.AND.Y.GT.YS))) THEN
A=DY**2+DZ**2
B=YI*DY/A
C=B*B-(YI*YI-YS*YS)/A
IF (C.GT.0.) THEN
C=SQRT(C)
S1=-B+C
S2=-B-C
*--S1 and S2 are the trajectory fractions to the intersection points
*--the mol. collides with the cyl. if there is a value between 0 and 1
IF (S2.LT.1.) THEN
IF (S1.LT.0.) THEN
S=S1
ELSE
S=2.
ELSE IF (S1.LT.S2) THEN
S=S1
ELSE
S=S2
END IF
ELSE IF (S1.LT.S2) THEN
S=S1
ELSE
S=S2
END IF
ELSE
S=2.
*--setting S to 2 indicates that there is no intersection
END IF
*--S is the least positive solution
IF (S.LT.1.) THEN
XC=XI+S*DX
IF (XC.LE.CB(1).AND.IB(1).EQ.2) THEN
XC=2.*CB(1)-XC
PV(1,N)=-PV(1,N)
END IF
IF (XC.LE.CB(2).AND.IB(2).EQ.2) THEN
XC=2.*CB(2)-XC
PV(1,N)=-PV(1,N)
END IF
L2=LIMS(KS,2)
L3=LIMS(KS,3)
XSU=CG(1,L2)
XSD=CG(2,L3)
IF (XC.GT.XSU.AND.XC.LT.XSD) THEN
Appendix C - Flowfield Modeling Code

*--molecule collides with surface at XC
  IF (IFCX.EQ.0) THEN
    MC=(XC-CB(1))/CW+0.99999
  ELSE
    XD=(XC-CB(1))/FW+1.E-6
    MC=1.+((LOG(1.-XD*APX))/RPX
  END IF
  *--the cell number is calculated from eqn (12.1)
  IF (MC.LT.1) MC=1
  IF (MC.GT.NCX) MC=NCX
  MCS=MC-(L2-1)
  IF (ISURF(KS).EQ.1) MC=MC+(L1-1)*NCX
  IF (ISURF(KS).EQ.2) MC=MC+(L1-2)*NCX
  *--MC is the cell number for the reflected molecule
  IF (KS.EQ.2) MCS=MCS+LIMS(1,3)-LIMS(1,2)+1
  *--MCS is the code number of the surface element
  AT=AT*(X-XC)/DX
  CALL AIFR(YI,DY*S,DZ*S,YS,PV(2,N),PV(3,N))
  CALL REFLECT2A(N,KS,MCS,XC,YS,MC)
  IF (IWF.EQ.1) THEN
    IF (YI.GT.RWF.OR.YS.GT.RWF) THEN
      WFI=YI/RWF
      IF (WFI.LT.1.) WFI=1.
      WF=YS/RWF
      IF (WF.LT.1.) WF=1.
      CALL WEIGHT(N,WFI,WF)
    END IF
  END IF
  GO TO 150
  END IF
  END IF
  END IF
  IF (ISURF(KS).EQ.3.OR.ISURF(KS).EQ.4) THEN
    L1=LIMS(KS,1)
    IF (L1.LE.NCX) THEN
      XS=CG(1,L1)
    ELSE
      XS=CB(2)
    END IF
    L1=L1-1
    IF ((ISURF(KS).EQ.3.AND.(XI.GT.XS.AND.X.LT.XS)).OR.
      (ISURF(KS).EQ.4.AND.(XI.LT.XS.AND.X.GT.XS))) THEN
      YCD=YI/(XS-XI)*DY/DX
      ZC=(XS-XI)*DZ/DX
      YC=SQRT(YCD**2+ZC**2)
      L2=LIMS(KS,2)
      L3=LIMS(KS,3)
      YSU=CG(4,(L2-1)*NCX+1)
      YSD=CG(5,(L3-1)*NCX+1)
      IF (YC.GT.YSU.AND.YC.LT.YSD) THEN
        *--molecule collides with surface at YC
        IF (IFCY.EQ.0) THEN
          MC=(YC-CB(3))/CH+0.99999
        ELSE
          YD=(YC-CB(3))/FH+1.E-6
          MC=1.+((LOG(1.-YD*APY))/RPY
        END IF
        *--the cell number is calculated from eqn (12.1)
        IF (MC.LT.1) MC=1
        IF (MC.GT.NCY) MC=NCY
      END IF
    END IF
Appendix C - Flowfield Modeling Code

MCS = MC - (L2 - 1)
IF (ISURF(KS).EQ.3) MC = (MC - 1) * NCX + L1
IF (ISURF(KS).EQ.4) MC = (MC - 1) * NCX + L1 - 1

*--MC is the cell number for the reflected molecule
IF (KS.EQ.2) MCS = MCS + LIMS(1,3) - LIMS(1,2) + 1

*--MCS is the code number of the surface element

AT = AT * (X - XS) / DX
A1 = AT * (XS - XI) / DX
CALL AIFR(YI, PV(2,N)*A1, PV(3,N)*A1, YC, PV(2,N), PV(3,N))
CALL REFLECT2A(N, KS, MCS, XS, YC, MC)

IF (IWF.EQ.1) THEN
  IF (YI.GT.RWF.OR.YC.GT.RWF) THEN
    WFI = YI / RWF
    IF (WFI.LT.1.) WFI = 1.
    WF = YC / RWF
    IF (WF.LT.1.) WF = 1.
    CALL WEIGHT(N, WFI, WF)
  END IF
END IF
GO TO 150
END IF
END IF
END IF
END IF
END IF

200 CONTINUE
CALL AIFR(YD,Y, PV(2,N), PV(3,N))
IF (X.LT.CB(1).OR.X.GT.CB(2)) THEN
  IF (X.LT.CB(1)) K = 1
  IF (X.GT.CB(2)) K = 2
  *--intersection with boundary K
  IF (IB(K).EQ.2) THEN
    *--specular reflection from the boundary (eqn (11.7))
    X = 2.*CB(K) - X
    PV(1,N) = -PV(1,N)
  ELSE
    *--molecule leaves flow
    CALL REMOVE(N)
    GO TO 100
  END IF
END IF
IF (Y.LT.CB(3).OR.Y.GT.CB(4)) THEN
  IF (Y.LT.CB(3)) K = 3
  IF (Y.GT.CB(4)) K = 4
  *--intersection with boundary K
  IF (IB(K).EQ.2) THEN
    *--specular reflection from the boundary is not allowed
    WRITE (*,*)
    & ' CURVED BOUNDARIES CANNOT BE A PLANE OF SYMMETRY'
    STOP
  ELSE
    *--molecule leaves flow
    CALL REMOVE(N)
    GO TO 100
  END IF
END IF
END IF

* IF (X.LT.CG(1,MC).OR.X.GT.CG(2,MC).OR.Y.LT.CG(4,MC).OR.
& Y.GT.CG(5,MC)) THEN
  *--the molecule has moved from the initial cell
  IF (IFCX.EQ.0) THEN
    MCX = (X-CB(1))/CW + 0.99999
  END IF
END IF
ELSE
XD=(X-CB(1))/FW+1.E-6
MCX=1.+(LOG(1.-XD*APX))/RPX
*--the cell number is calculated from eqn (12.1)
END IF
IF (MCX.LT.1) MCX=1
IF (MCX.GT.NCX) MCX=NCX
*--MCX is the new cell column (note avoidance of round-off error)
IF (IFCY.EQ.0) THEN
YC=(Y-CB(3))/FH+0.99999
ELSE
YD=(Y-CB(3))/FH+1.E-6
MCY=1.+(LOG(1.-YD*APY))/RPY
*--the cell number is calculated from eqn (12.1)
END IF
IF (MCY.LT.1) MCY=1
IF (MCY.GT.NCY) MCY=NCY
*--MCY is the new cell row (note avoidance of round-off error)
MC=(MCY-1)*NCX+MCX
END IF
MSCX=((X-CG(1,MC))/CG(3,MC))*(NSCX-.001)+1
MSCY=((Y-CG(4,MC))/CG(6,MC))*(NSCY-.001)+1
MSC=(MSCY-1)*NSCX+MSCX+NSCX*NSCY*(MC-1)
*--MSC is the new sub-cell number
IF (MSC.LT.1) MSC=1
IF (MSC.GT.MNSC) MSC=MNSC
IPL(N)=MSC
PP(1,N)=X
PP(2,N)=Y
IF (IWF.EQ.1) THEN
IF (YI.GT.RWF.OR.Y.GT.RWF) THEN
WFI=YI/RWF
IF (WFI.LT.1.) WFI=1.
WF=Y/RWF
IF (WF.LT.1.) WF=1.
CALL WEIGHT(N,WFI,WF)
END IF
END IF
GO TO 100
ELSE IF (IFT.LT.0) THEN
IFT=1
*--new molecules enter
CALL ENTER2A
N=N-1
GO TO 100
END IF
RETURN
END
*   ENTER2A.FOR
*
SUBROUTINE ENTER2A
*
*--new molecules enter at boundaries
*
PARAMETER (MNM=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304,
&  MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)
*
DOUBLE PRECISION COL(MNSP,MNSP),MOVT,NCOL,SELT,SEPT,CS(9,MNC,MNSP)
*
COMMON /MOLS2 / NM,PP(2,MNM),PV(3,MNM),IPL(MNM),IPS(MNMS),IR(MNM)
COMMON /MOLSR / PR(MNMR)
Appendix C - Flowfield Modeling Code

DO 100 N=1,4
*--consider each boundary in turn
   IF (IB(N).EQ.1) THEN
      IF (N.LT.3) NCS=NCY
      IF (N.GT.2) NCS=NCX
      DO 20 NC=1,NCS
         IF (IWF.EQ.0) THEN
            WMIN=1.
         ELSE IF (N.LT.3) THEN
            MC=(NC-1)*NCX+1
            WMIN=CG(4,MC)/RWF
            IF (WMIN.LT.1.) WMIN=1.
         ELSE
            WMIN=CB(N)/RWF
            IF (WMIN.LT.1.) WMIN=1.
         END IF
         IF (LFLX.NE.0) THEN
            *--bypass entry into the excluded region of the flow
            IF (N.EQ.1.OR.N.EQ.2) THEN
               IF (ABS(VFX).GT.1.E-6) THEN
                  IF (N.EQ.1) SC=VFX/VMP
               END IF
            END IF
         END IF
         DO 10 L=1,MNSP
            *--consider each species in turn
            VMP=SQRT(2.*BOLTZ*FTMP/SP(5,L))
            A=AME(N,L,NC)/WMIN+AMR(N,L,NC)
            M=A
            AMR(N,L,NC)=A-M
            *--M molecules enter, remainder has been reset
            IF (M.GT.0) THEN
               IF (N.EQ.1.OR.N.EQ.2) THEN
                  IF (ABS(VFX).GT.1.E-6) THEN
                     IF (N.EQ.1) SC=VFX/VMP
                  END IF
               END IF
            END IF
         END DO 10
   END IF
   DO 100 L=1,MNSP
*--consider each species in turn
   VMP=SQRT(2.*BOLTZ*FTMP/SP(5,L))
   A=AME(N,L,NC)/WMIN+AMR(N,L,NC)
   M=A
   AMR(N,L,NC)=A-M
*--M molecules enter, remainder has been reset
   IF (M.GT.0) THEN
      IF (N.EQ.1.OR.N.EQ.2) THEN
         IF (ABS(VFX).GT.1.E-6) THEN
            IF (N.EQ.1) SC=VFX/VMP
         END IF
      END IF
   END IF
END DO 100
IF (N.EQ.2) SC=-VFX/VMP 
END IF 
END IF 
FS1=SC+SQRT(SC*SC+2.) 
FS2=0.5*(1.+SC*(2.*SC-FS1)) 
* the above constants are required for the entering distn. of eqn (12.5) 
DO 4 K=1,M 
C WRITE(*,*) NM 
IF (NM.LT.MNM) THEN 
NM=NM+1 
*--NM is now the number of the new molecule 
IF (N.LT.3.AND.ABS(VFX).GT.1.E-6) THEN 
QA=3. 
IF (SC.LT.-3.) QA=ABS(SC)+1. 
2 
U=-QA+2.*QA*RF(0) 
*--U is a potential normalised thermal velocity component 
UN=U+SC 
*--UN is a potential inward velocity component 
IF (UN.LT.0.) GO TO 2 
A=(2.*UN/FS1)*EXP(FS2-U*U) 
IF (A.LT.RF(0)) GO TO 2 
*--the inward normalised vel. component has been selected (eqn (12.5)) 
IF (N.EQ.1) PV(1,NM)=UN*VMP 
IF (N.EQ.2) PV(1,NM)=-UN*VMP 
IF (N.EQ.3) PV(1,NM)=UN*VMP 
IF (N.EQ.4) PV(1,NM)=-UN*VMP 
ELSE 
IF (N.EQ.1) PV(1,NM)=SQRT(-LOG(RF(0)))*VMP 
IF (N.EQ.2) PV(1,NM)=-SQRT(-LOG(RF(0)))*VMP 
IF (N.EQ.3) PV(2,NM)=SQRT(-LOG(RF(0)))*VMP 
IF (N.EQ.4) PV(2,NM)=SQRT(-LOG(RF(0)))*VMP 
*--for a stationary external gas, use eqn (12.5) 
END IF 
IF (N.LT.3) CALL RVELC(PV(2,NM),PV(3,NM),VMP) 
IF (N.GT.2) THEN 
CALL RVELC(PV(1,NM),PV(3,NM),VMP) 
P(1,NM)=PV(1,NM)+VFX 
END IF 
*--a single call of RVELC generates the two normal velocity components 
IF (ISPR(1,L).GT.0) CALL SROT(PR(NM),FTMP,ISPR(1,L)) 
IF (N.EQ.1) PP(1,NM)=CB(1)+0.001*CG(3,1) 
IF (N.EQ.2) PP(1,NM)=CB(2)-0.001*CG(3,MNC) 
IF (N.EQ.3) PP(2,NM)=CB(3)+0.001*CG(6,1) 
IF (N.EQ.4) PP(2,NM)=CG(6,MNC) 
*--the molecule is moved just off the boundary 
IF (MNSP.GT.1) IPS(NM)=L 
IF (N.LT.3) THEN 
IF (N.EQ.1) MC=(NC-1)*NCX+1 
IF (N.EQ.2) MC=NCX 
PP(2,NM)=SQRT(CG(4,MC)**2+RF(0)*(CG(5,MC)**2 CG(4, & MC)**2)) 
*--this case employs eqn (C6) for the selection of radius 
END IF 
IF (N.GT.2) THEN 
IF (N.EQ.3) MC=NC 
IF (N.EQ.4) MC=(NCY-1)*NCX+NC 
PP(1,NM)=CG(1,MC)+RF(0)*CG(3,MC) 
END IF 
IR(NM)=NM 
IF (IWF.EQ.1) THEN 
WF=PP(2,NM)/RWF
IF (WF.LT.1.) WF=1.
IF (WMIN/WF.LT.RF(0)) THEN
   NM=NM-1
GO TO 4
*--above takes account of the weighting factor variation in the cell
END IF
END IF
MSCX=((PP(1,NM)-CG(1,MC))/CG(3,MC))*(NSCX-.001)+1
MSCY=((PP(2,NM)-CG(4,MC))/CG(6,MC))*(NSCY-.001)+1
MSC=(MSCY-1)*NSCX+MSCX+NSCY*(MC-1)
*--MSC is the new sub-cell number
IF (MSC.LT.1) MSC=1
IF (MSC.GT.MNSC) MSC=MNSC
ELSE
   WRITE (*,*)
   &' WARNING: EXCESS MOLECULE LIMIT - RESTART WITH AN INCREASED FNUM'
END IF
4              CONTINUE
END IF
10        CONTINUE
20        CONTINUE
END IF
100   CONTINUE
*--now the jet molecules
IF (IJET.GT.0) THEN
   NCS=LIMJ(3)-LIMJ(2)+1
   DO 150 NC=1,NCS
   DO 120 L=1,MNSP
   *--consider each species in turn
   VMP=SQRT(2.*BOLTZ*TMPJ/SP(5,L))
   NCL=NC+LIMJ(2)-1
   IF (IWF.EQ.1) THEN
      WMIN=CG(4,NCL)/RWF
      IF (WMIN.LT.1.) WMIN=1.
   ELSE
      WMIN=1.
   END IF
   A=AMEJ(L,NC)/WMIN+AMRJ(L,NC)
   M=A
   AMRJ(L,NC)=A-M
*--M molecules enter, remainder has been reset
   IF (M.GT.0) THEN
      IF (ABS(FVJ).GT.1.E-6) SC=FVJ/VMP
      FS1=SC+SQRT(SC*SC+2.)
      FS2=0.5*(1.+SC*(2.*SC-SC*SC))
      * the above constants are required for the entering distn. of eqn (12.5)
      DO 105 K=1,M
         IF (NM.LT.MNM) THEN
            NM=NM+1
         END IF
         QA=3.
         IF (SC.LT.-3.) QA=ABS(SC)+1.
         102                U=-QA+2.*QA*RF(0)
         *--U is a potential normalised thermal velocity component
      UN=U+SC
*--UN is a potential inward velocity component
      IF (UN.LT.0.) GO TO 102
      A=(2.*UN/FS1)*EXP(FS2-U*U)
      IF (A.LT.RF(0)) GO TO 102
      *--end
      END IF
      END IF
   END IF
   END IF
   END IF
150         CONTINUE
END IF

Appendix C - Flowfield Modeling Code 306
 Appendix C - Flowfield Modeling Code 307

*--the inward normalised vel. component has been selected (eqn (12.5))

IF (IJET.EQ.1) PV(2,NM)=UN*VMP
IF (IJET.EQ.2) PV(2,NM)=-UN*VMP
IF (IJET.EQ.3) PV(1,NM)=UN*VMP
IF (IJET.EQ.4) PV(1,NM)=-UN*VMP
ELSE
IF (IJET.EQ.1) PV(2,NM)=SQRT(-LOG(RF(0)))*VMP
IF (IJET.EQ.2) PV(2,NM)=-SQRT(-LOG(RF(0)))*VMP
IF (IJET.EQ.3) PV(1,NM)=SQRT(-LOG(RF(0)))*VMP
IF (IJET.EQ.4) PV(1,NM)=-SQRT(-LOG(RF(0)))*VMP

*--for a stationary external gas, use eqn (12.3)

END IF

IF (IJET.LT.3) CALL RVELC(PV(1,NM),PV(3,NM),VMP)
IF (IJET.GT.2) CALL RVELC(PV(2,NM),PV(3,NM),VMP)

*--a single call of RVELC generates the two normal velocity components

IF (ISPR(1,L).GT.0) CALL SROT(PR(NM),TMPJ,ISPR(1,L))

IF (IJET.LT.3) THEN
MC=(LIMJ(1)-1)*NCX+LIMJ(2)-1+NC
YJ=CG(4,MC)
IF (IJET.EQ.2) MC=MC-NCX
END IF

IF (IJET.GT.2) THEN
MC=LIMJ(1)+(LIMJ(2)-1)*NCX+(NC-1)*NCX
XJ=CG(1,MC)
IF (IJET.EQ.4) MC=MC-1
END IF

IF (IJET.EQ.1) PP(2,NM)=YJ+0.001*CG(6,MC)
IF (IJET.EQ.2) PP(2,NM)=YJ-0.001*CG(6,MC)
IF (IJET.EQ.3) PP(1,NM)=XJ+0.001*CG(3,MC)
IF (IJET.EQ.4) PP(1,NM)=XJ-0.001*CG(3,MC)

*--the molecule is moved just off the boundary

IF (MNSP.GT.1) IPS(NM)=L
IR(NM)=NM
IF (IJET.LT.3) PP(1,NM)=CG(1,MC)+RF(0)*CG(3,MC)
IF (IJET.GT.2) PP(2,NM)
&=SQRT(CG(4,MC)**2+RF(0)*(CG(5,MC)**2-CG(4,MC)**2))
IF (IWF.EQ.1) THEN
WF=PP(2,NM)/RWF
IF (WF.LT.1.) WF=1.
IF (WMIN/WF.LT.RF(0)) THEN
NM=NM-1
GO TO 105

*--above takes account of the weighting factor variation in the cell

END IF

END IF

MSCX=((PP(1,NM)-CG(1,MC))/CG(3,MC))*(NSCX-.001)+1
MSCY=((PP(2,NM)-CG(4,MC))/CG(6,MC))*(NSCY-.001)+1
MSC=(MSCY-1)*NSCX+MSCX+NSCX*NSCY*(MC-1)

*--MSC is the new sub-cell number

IF (MSC.LT.1) MSC=1
IF (MSC.GT.MNSC) MSC=MNSC
IPL(NM)=MSC
ELSE
WRITE (*,*)
&WARNING: EXCESS MOLECULE LIMIT - RESTART WITH AN INCREASED FNUM'
END IF

105 CONTINUE
END IF
120 CONTINUE
END IF
* REFLECT2A.FOR
SUBROUTINE REFLECT2A(N,KS,K,XC,YC,MC)

*--reflection of molecule N from surface KS, element K,
*----location XC,YC, cell MC
*
PARAMETER (MNM=2000000, MNMR=1, MNMS=1, MNC=1326, MNSC=5304,
& MNSP=1, MNSG=1, MNSE=26, MBC=51, MNB=200)
*
DOUBLE PRECISION COL(MNNSP,MNNSP), MOVT, NCOL, SELT, SEPT, CS(9,MNC,MNNSP)
DOUBLE PRECISION CSS(9,MNSE,MNNSP)
*
COMMON /MOLS2 / NM, PP(2,MNM), PV(3,MNM), IPL(MNM), IPS(MNMS), IR(MNM)
COMMON /MOLSR / PR(MNMR)
COMMON /CELL2 / CC(MNC), CG(6,MNC), IC(2,MNC,MNNSG), ISC(MNSC),
& NCX,NCY, JFCX, JFCY, CWRX, CWRY, APX, APY, RPX, RPY
COMMON /GAS / SP(5,MNNSP), SPM(6,MNNSP, MNNSP), ISP(MNNSP)
COMMON /GASR / SPR(3,MNNSP, MNNSP), SPR(3,MNNSP), CT(MNC)
COMMON /SAMP2A/ COL, NCOL, MOVT, SELT, SEPT, CS, TIME, NPR, NSMP, FND, FTEMP,
& TMLFSP(MNNSP), ISPD, VFX
COMMOM /SAMPS /CSS
COMMON /COMP / FNUM, DTM, NIS, NSP, NPT
COMMON /GEOM2A/ NSCX, NSCY, CB(4), JB(4), ISURF(2), IMS(2,3), IIS, JIS,
& TSURF(2), JET, LIMJ(3), TMPJ, FNDJ, FVPJ(MNNSP),
& AME(JMNSP, MBC), AMRJ(MNNSP, MBC), AME(JMNSP, MBC),
& AMR(JMNSP, MBC), CW, FW, CH, FH, WJ, LFLX, LFLY, ALPI(2),
& ALPN(2), ALPT(2), JWF, RWF, WSURF(2)
COMMON /CONST / PI, SPI, BOLTZ
*
IF (IWF.EQ.1 .AND. YC .GT. RWF) THEN
WF=YC/RWF
ELSE
WF=1.
END IF
IF (MNNSP,GT.1) THEN
L=IPS(N)
ELSE
L=1
END IF
*
--sample the surface properties due to the incident molecules
CSS(1,K,L)=CSS(1,K,L)+WF
IF (ISURF(KS),EQ.1) THEN
CSS(2,K,L)=CSS(2,K,L)-SP(5,L)*WF*PV(2,N)
CSS(4,K,L)=CSS(4,K,L)+SP(5,L)*WF*PV(1,N)
END IF
IF (ISURF(KS),EQ.2) THEN
CSS(2,K,L)=CSS(2,K,L)+SP(5,L)*WF*PV(2,N)
CSS(4,K,L)=CSS(4,K,L)+SP(5,L)*WF*PV(1,N)
END IF
IF (ISURF(KS),EQ.3) THEN
CSS(2,K,L)=CSS(2,K,L)-SP(5,L)*WF*PV(1,N)
CSS(4,K,L)=CSS(4,K,L)+SP(5,L)*WF*PV(2,N)
END IF
IF (ISURF(KS),EQ.4) THEN
CSS(2,K,L)=CSS(2,K,L)+SP(5,L)*WF*PV(1,N)
CSS(4,K,L)=CSS(4,K,L)+SP(5,L)*WF*PV(2,N)
END IF
CSS(5,K,L)=CSS(5,K,L)+0.5*SP(5,L)
& $(\sqrt{PV(1,N)^2+PV(2,N)^2+PV(3,N)^2})$

*IF (MNMR.GT.1) CSS(7,K,L)=CSS(7,K,L)+PR(N)*

*IF (TSURF(KS).LT.0.) THEN

*--specular reflection

*IF (ISURF(KS).EQ.1.OR.ISURF(KS).EQ.2) PV(2,N)=-PV(2,N)

IF (ISURF(KS).EQ.3.OR.ISURF(KS).EQ.4) PV(1,N)=-PV(1,N)
ELSE IF (ALPI(KS).LT.0.) THEN

*--diffuse reflection

VMP=$\sqrt{2.*BOLTZ*TSURF(KS)/SP(5,L)}$

*--VMP is the most probable speed in species L, see eqns (4.1) and (4.7)

*IF (ISURF(KS).EQ.1) THEN
PV(2,N)=$\sqrt{-\log(RF(0))}$*VMP
CALL RVELC(PV(1,N),PV(3,N),VMP)
PV(3,N)=PV(3,N)+WSURF(KS)
END IF

*IF (ISURF(KS).EQ.2) THEN
PV(1,N)=$\sqrt{-\log(RF(0))}$*VMP
CALL RVELC(PV(2,N),PV(3,N),VMP)
PV(3,N)=PV(3,N)+WSURF(KS)
END IF

*IF (ISURF(KS).EQ.3) THEN
PV(1,N)=$\sqrt{-\log(RF(0))}$*VMP
CALL RVELC(PV(2,N),PV(3,N),VMP)
END IF

*IF (ISURF(KS).EQ.4) THEN
PV(1,N)=$\sqrt{-\log(RF(0))}$*VMP
CALL RVELC(PV(2,N),PV(3,N),VMP)
END IF

*--the normal velocity component has been generated

*--a single call of RVELC generates the two tangential vel. components

*IF (ISPR(1,L).GT.0) CALL SROT(PR(N),TSURF(KS),ISPR(1,L))
ELSE IF (ALPI(KS).GE.0) THEN

*--Cercignani-Lampis-Lord reflection model

VMP=$\sqrt{2.*BOLTZ*TSURF(KS)/SP(5,L)}$

*--VMP is the most probable speed in species L, see eqns (4.1) and (4.7)

*IF (ISURF(KS).EQ.1.OR.ISURF(KS).EQ.2) THEN

IF (ISURF(KS).EQ.1) VNI=-PV(2,N)/VMP
IF (ISURF(KS).EQ.2) VNI=PV(2,N)/VMP
UPI=PV(1,N)/VMP
END IF

IF (ISURF(KS).EQ.3.OR.ISURF(KS).EQ.4) THEN

IF (ISURF(KS).EQ.3) VNI=-PV(1,N)/VMP
IF (ISURF(KS).EQ.4) VNI=PV(1,N)/VMP
UPI=PV(2,N)/VMP
END IF

WE=PV(1,N)/VMP
ANG=ATAN2(WPI,UPI)
VPI=$\sqrt{UPI*UPI+WPI*WPI}$

*--VNI is the normalized incident normal vel. component (always +ve)

*--VPI is the normalized incident tangential vel. comp. in int. plane

*--ANG is the angle between the interaction plane and the x or y axis

*--first the normal component

ALPHAN=ALPN(KS)
R=$\sqrt{-ALPHAN*\log(RF(0))}$
TH=2.*PI*RF(0)
UM=$\sqrt{R^2-ALPHAN}$

VN=$\sqrt{R^2+UM^2+2.*R*UM*\cos(TH)}$

*--VN is the normalized magnitude of the reflected normal vel. comp.

*----from eqns (14.3)
*--then the tangential component
ALPHAT = ALPT(KS)*(2. - ALPT(KS))
R = SQRT(-ALPHAT*LOG(RF(0)))
TH = 2.*PI*RF(0)
UM = SQRT(1.-ALPHAT)*VPI
VP = UM + R*COS(TH)
WP = R*SIN(TH)

*--VP, WP are the normalized reflected tangential vel. components in and
*----normal to the interaction plane, from eqn(14.4) and (14.5)
IF (ISURF(KS).EQ.1.OR.ISURF(KS).EQ.2) THEN
    IF (ISURF(KS).EQ.1) PV(2,N)=VN*VMP
    IF (ISURF(KS).EQ.2) PV(2,N)=-VN*VMP
    PV(1,N)=(VP*COS(ANG)-WP*SIN(ANG))*VMP
    END IF
IF (ISURF(KS).EQ.3.OR.ISURF(KS).EQ.4) THEN
    IF (ISURF(KS).EQ.3) PV(1,N)=VN*VMP
    IF (ISURF(KS).EQ.4) PV(1,N)=-VN*VMP
    PV(2,N)=(VP*COS(ANG)-WP*SIN(ANG))*VMP
    END IF
PV(3,N)=(VP*SIN(ANG)+WP*COS(ANG))*VMP
IF (ISPR(1,L).GT.0) THEN
*--set rotational energy by analogy with normal vel. component
ALPHAI = ALPI(KS)
OM = SQRT(PR(N)*(1.-ALPHAI)/(BOLTZ*TSURF(KS)))
IF (ISPR(1,L).EQ.2) THEN
    R = SQRT(-ALPHAI*LOG(RF(0)))
    CTH = 2.*RF(0)-1.
    END IF
PR(N)=BOLTZ*TSURF(KS)*(R*R+OM*OM+2.*R*OM*CTH)
END IF
END IF
IF (ISURF(KS).EQ.1) THEN
    PP(1,N)=XC
    PP(2,N)=YC+0.001*CG(6,MC)
    END IF
IF (ISURF(KS).EQ.2) THEN
    PP(1,N)=XC
    PP(2,N)=YC-0.001*CG(6,MC)
    END IF
IF (ISURF(KS).EQ.3) THEN
    PP(1,N)=XC+0.001*CG(3,MC)
    PP(2,N)=YC
    END IF
IF (ISURF(KS).EQ.4) THEN
    PP(1,N)=XC-0.001*CG(3,MC)
    PP(2,N)=YC
    END IF
IPL(N)=(MC-1)*NSCX*NSCY+1
*--sample the surface properties due to the reflected molecules
IF (ISURF(KS).EQ.1) CSS(3,K,L)=CSS(3,K,L)+SP(5,L)*WF*PV(2,N)
IF (ISURF(KS).EQ.2) CSS(3,K,L)=CSS(3,K,L)+SP(5,L)*WF*PV(2,N)
IF (ISURF(KS).EQ.3) CSS(3,K,L)=CSS(3,K,L)+SP(5,L)*WF*PV(1,N)
IF (ISURF(KS).EQ.4) CSS(3,K,L)=CSS(3,K,L)+SP(5,L)*WF*PV(1,N)

*--for polyatomic case, apply acceptance-rejection based on eqn (14.6)
10  X=4.*RF(0)
    A=2.7182818*X*X*EXP(-X*X)
    IF (A.LT.RF(0)) GO TO 10
    R=SQRT(ALPHAI)*X
    CTH=2.*RF(0)-1.
    END IF
PR(N)=BOLTZ*TSURF(KS)*(R*R+OM*OM+2.*R*OM*CTH)
END IF
END IF
END IF
END IF
IF (ISURF(KS).EQ.1) THEN
    PP(1,N)=XC
    PP(2,N)=YC+0.001*CG(6,MC)
    END IF
IF (ISURF(KS).EQ.2) THEN
    PP(1,N)=XC
    PP(2,N)=YC-0.001*CG(6,MC)
    END IF
IF (ISURF(KS).EQ.3) THEN
    PP(1,N)=XC+0.001*CG(3,MC)
    PP(2,N)=YC
    END IF
IF (ISURF(KS).EQ.4) THEN
    PP(1,N)=XC-0.001*CG(3,MC)
    PP(2,N)=YC
    END IF
IPL(N)=(MC-1)*NSCX*NSCY+1
IF (ISURF(KS).EQ.1) CSS(9,K,L)=CSS(9,K,L)-SP(5,L)*WF*PV(1,N)
IF (ISURF(KS).EQ.2) CSS(9,K,L)=CSS(9,K,L)-SP(5,L)*WF*PV(1,N)
IF (ISURF(KS).EQ.3) CSS(9,K,L)=CSS(9,K,L)-SP(5,L)*WF*PV(2,N)
IF (ISURF(KS).EQ.4) CSS(9,K,L)=CSS(9,K,L)-SP(5,L)*WF*PV(2,N)
CSS(6,K,L)=CSS(6,K,L)-0.5*SP(5,L)*WF*(PV(1,N)**2+PV(2,N)**2+PV(3,N)**2)
IF (MNMR.GT.1) CSS(8,K,L)=CSS(8,K,L)-PR(N)
RETURN
END

SUBROUTINE REMOVE(N)

PARAMETER (MNM=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304, &
          MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)

COMMON /MOLS2 / NM,PP(2,MNM),PV(3,MNM),IPL(MNM),IPS(MNMS),IR(MNM)
COMMON /MOLSR / PR(MNMR)
COMMON /MOLD  / NMB,PPB(2,MNB),PVB(3,MNB),PRB(MNB),IPLB(MNB), &
          IPSB(MNB),IRB(MNB)

PP(1,N)=PP(1,NM)
PP(2,N)=PP(2,NM)
DO 100 M=1,3
PV(M,N)=PV(M,NM)
100   CONTINUE
IF (MNMR.GT.1) PR(N)=PR(NM)
IPL(N)=IPL(NM)
IF (MNSP.GT.1) IPS(N)=IPS(NM)
NM=NM-1
N=N-1
RETURN
END

SUBROUTINE WEIGHT(N,WFI,WF)

PARAMETER (MNM=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304, &
          MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)

COMMON /MOLS2 / NM,PP(2,MNM),PV(3,MNM),IPL(MNM),IPS(MNMS),IR(MNM)
COMMON /MOLSR / PR(MNMR)
COMMON /MOLD  / NMB,PPB(2,MNB),PVB(3,MNB),PRB(MNB),IPLB(MNB), &
          IPSB(MNB),IRB(MNB)

A=WFI/WF
LL=0
100   IF (A.LT.1.) THEN
    IF (RF(0).LT.A) LL=LL+1
    IF (LL.EQ.0) CALL REMOVE(N)
    LL=LL-1
    IF (LL.LE.0) THEN
      DO 120 J=1,LL
      IF (NM.LT.NM) THEN
        NTM=NMB+1
      ELSE IF (NM.GE.NM) THEN
        NTM=RF(0)*(NMB-.01)+1
      END IF
      IF (NM.LT.NM) THEN
        NM=NM+1
      ELSE IF (NM.GE.NM) THEN
        NM=NM-1
      END IF
      IF (RF(0).LT.A) LL=LL+1
    END IF
    CALL REMOVE(N)
  END IF
120   CONTINUE
RETURN
END

*--a random molecule is read from the duplication delay file
NMB=NMB-1
NM=NM+1
DO 102 M=1,2
   PP(M,NM)=PPB(M,NTM)
102      CONTINUE
DO 104 M=1,3
   PV(M,NM)=PVB(M,NTM)
104      CONTINUE
IF (MNMR.GT.1) PR(NM)=PRB(NTM)
      IPL(NM)=IPLB(NTM)
IF (MNSP.GT.1) IPS(NM)=IPSB(NTM)
      IR(NM)=IRB(NTM)
END IF
*--a negative IR(NM) flags a duplicated molecule that has already moved
IF (NMB.LT.MNB) NMB=NMB+1
DO 105 M=1,2
   PPB(M,NTM)=PP(M,N)
105      CONTINUE
DO 110 M=1,3
   PVB(M,NTM)=PV(M,N)
110      CONTINUE
IF (MNMR.GT.1) PRB(NTM)=PR(N)
      IPLB(NTM)=IPL(N)
IF (MNSP.GT.1) IPSB(NTM)=IPS(N)
      IRB(NTM)=IR(N)
END IF
120    CONTINUE
END IF
RETURN
ELSE
   LL=LL+1
   A=A-1.
   GO TO 100
END IF
END
*   SAMPI2A.FOR
* SUBROUTINE SAMPI2A
* *--initialises all the sampling variables
* * PARAMETER (MN=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304,
* & MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)
* DOUBLE PRECISION COL(MNSP,MNSP),MOVT,NCOL,SELT,SEPT,CS(9,MNC,MNSP)
* DOUBLE PRECISION CSR(MNC,MNSP)
* DOUBLE PRECISION CSS(9,MNSE,MNSP)
* COMMON /SAMP2A/ COL,NCOL,MOVT,SELT,SEPT,CS(9,MNC,MNSP)
* & TIML,FSP(MNSP),ISP,NIS,NSP,NPT
COMMON /SAMPR / CSR
COMMON /SAMPS / CSS
COMMON /COMP  / FNUM,DTM,NIS,NSP,NPS,NPT
* NSMP=0
   TIMI=TIME
   DO 200 L=1,MNSP
   DO 50 N=1,MNC
      CS(1,N,L)=1.E-6
   DO 20 M=2,9
      CS(M,N,L)=0.
20      CONTINUE
CSR(N,L)=0.

Appendix C - Flowfield Modeling Code

50 CONTINUE
DO 100 N=1,MNSE
CSS(1,N,L)=1.E-6
DO 60 M=2,9
CSS(M,N,L)=0.
60 CONTINUE
100 CONTINUE
200 CONTINUE
RETURN
END

SAMPLE2A.FOR

SUBROUTINE SAMPLE2A

*--sample the molecules in the flow.
*
PARAMETER (MNM=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304,
&MNSE=26,MBC=51,MNB=200)
*
DOUBLE PRECISION COL(MNSP,MNSP),MOVT,NCOL,SELT,SEPT,CS(9,MNC,MNSP)
DOUBLE PRECISION CSR(MNC,MNSP)
*
COMMON /MOLS2 / NM,PP(2,MNM),PV(3,MNM),IPL(MNM),IPS(MNMS),IR(MNM)
COMMON /MOLSR / PR(MNMR)
COMMON /CELL2 / CC(MNC),CG(6,MNC),IC(2,MNC,MNSG),ISC(MNSC),
&CCG(2,MNC),MNSG,MNSG),ISCG(2,MNC,MNSG),ISG(2,MNC),
&NCX,NCY,IFCX,IFCY,CWRX,CWRY,APX,RPX,APY,RPY
COMMON /SAMP2A/ COL,NCOL,MOVT,SELT,SEPT,CS,TIME,NPR,NSMP,FND,FTMP,
&TIML,FSP(MNSP),ISPD,VFX
COMMON /SAMPR / CSR
COMMON /GEOM2A/ NSCX,NSCY,CB(4),IB(4),ISURF(2),LIMS(2,3),IIS,ISG,
&TSURF(2),IJE,TIMJ(3),TMPJ,FNJ,FSPJ(MNSP),
&AMEJ(MNSP,MBC),AMRJ(MNSP,MBC),AME(4,MNSP,MBC),
&AMR(4,MNSP,MBC),CW,FW,CH,FW,W1,LFLX,LFLY,ALP(2),
&ALPN(2),ALPT(2),IWF,RFW,WSURF(2)
COMMON /COMP / FNUM,DTM,NIS,NSP,NPS,NPT
*
NSMP=NSMP+1
DO 100 NN=1,MNSG
DO 50 N=1,MNC
L=IC(2,N,NN)
CS(9,N,1)=CS(9,N,1)+L*L
IF (L.GT.0) THEN
DO 10 J=1,L
K=IC(1,N,NN)+J
M=IR(K)
IF (IWF.EQ.1.AND.PP(2,M).GT.RWF) THEN
WF=PP(2,M)/RWF
ELSE
WF=1.
END IF
IF (MNSP.GT.1) THEN
I=IPS(M)
ELSE
I=1
END IF
CS(1,N,I)=CS(1,N,I)+WF
CS(8,N,I)=CS(8,N,I)+1.
DO 5 LL=1,3
CS(LL+1,N,I)=CS(LL+1,N,I)+PV(LL,M)*WF
CS(LL+4,N,I)=CS(LL+4,N,I)+PV(LL,M)**2*WF
50 CONTINUE
100 CONTINUE
RETURN
END
Appendix C - Flowfield Modeling Code

CONTINUE
IF (MNMR.GT.1) CSR(N,I)=CSR(N,I)+PR(M)
CONTINUE
END IF
CONTINUE
RETURN
END

SUBROUTINE OUT2A

*--output a progressive set of results to file DSMC2A.OUT.

PARAMETER (MNM=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304,
&           MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)

DOUBLE PRECISION COL(MNSP,MNSP),MOVT,NCOL,SELT,SEPT,CS(9,MNC,MNSP)
DOUBLE PRECISION CSR(MNC,MNSP)
DOUBLE PRECISION CSS(9,MNSE,MNSP)

COMMON /MOLS2 / NM,PP(2,MNM),PV(3,MNM),IPL(MNM),IPS(MNMS),IR(MNM)
COMMON /MOLSR / PR(MNMR)
COMMON /CELL2 / CC(MNC),CG(6,MNC),IC(2,MNC,MNSG),ISC(MNSC),
&              CCG(2,MNC,MNSG,MNSG),ISCG(2,MNSC,MNSG),IG(2,MNSG),
&              NCX,NCY,IFCX,IFCY,CWRX,CWRY,APX,RPX,APY,RPY
COMMON /GAS / SP(5,MNSP),SPM(6,MNSP,MNSP),ISP(MNSP)
COMMON /GASR / SPR(3,MNSP,MNSP),ISPR(3,MNSP),CT(MNC)
COMMON /SAMP2A/ COL,NCOL,MOVT,SELT,SEPT,CS,TIME,NPR,NSMP,FND,FTMP,
&                TIMI,FSP(MNSP),ISPD,VFX
COMMON /SAMPR / CSR
COMMON /SAMPS / CSS
COMMON /GEOM2A/ NSCX,NSCY,CB(4),IB(4),ISURF(2),LIMS(2,3),IIS,ISG,
&              TSURF(2),IET,JET,LIMJ(3),TMPJ,FNDJ,FSPJ(MNSP),
&              AME(MNSP,MBC),AMRI(MNSP,MBC),AME(4,MNSP,MBC),
&              AMR(4,MNSP,MBC),CW,FW,CH,W1,L1X,FLY,ALP(2),
&              ALPN(2,ALP(2),JW,RF,WSURF(2)
COMMON /COMP / FNUM,DTM,NIS,NSP,NPT
COMMON /CONST / PI,SPI,BOLTZ

DOUBLE PRECISION VEL(3),SMU(3),SVEL(3,MNC),SN,SM,SMCC,SRDF,SRE,TT,
&                 TROT,DBOLTZ,SS(9)
DBOLTZ=BOLTZ

OPEN (4,File='DSMC2A.OUT',Form='FORMATTED')
OPEN (4268,File='VEL1.OUT')
OPEN (4269,File='pvtflow')

WRITE (4,*) ' FLOW SAMPLED FROM TIME ',TIMI,' TO TIME ',TIME
WRITE (4,*) ' COLLISIONS:'
WRITE (4,*) ' TOTAL NUMBER OF SAMPLES ',NSMP
WRITE (4,*) NM,' MOLECULES'
WRITE (4,*) MOVT,' TOTAL MOLECULAR MOVES'
IF (NCOL.GT.0) THEN
  WRITE (4,* Int(SELT), ' SELECTIONS ',INT(NCOL),
                ' MEAN COLLISION SEPARATION ',
                REAL(SEPT/NCOL)
ELSE
  WRITE (4,* ' NO SELECTIONS' )
ENDIF
C WRITE (4,*)
DO 100 KS=1,2
  IF (ISURF(KS).GT.0) THEN
    WRITE (4,*) ' SURFACE ',KS
    WRITE (4,*)
    NEL=LIMS(KS,3)-LIMS(KS,2)+1
    IF (KS.EQ.1) THEN
      NEL1=1
      NEL2=NEL
    ELSE
      NEL1=LIMS(1,3)-LIMS(1,2)+2
      NEL2=NEL1+NEL-1
    END IF
    A=FNUM/(TIME-TIMI)
    WRITE (4,*)
    &' X COORD     Y COORD    SAMPLE    FRACTION SPECIES 1   FRACTION SPECIES 2....'
    DO 20 K=NEL1,NEL2
      IF (ISURF(KS).LT.3) THEN
        IF (LIMS(KS,1).LE.NCY) THEN
          NC=(LIMS(KS,1)-1)*NCX+1
          Y=CG(4,NC)
        ELSE
          Y=CB(4)
        END IF
        NC=LIMS(KS,2)+K-NEL1
        X=0.5*(CG(1,NC)+CG(2,NC))
      ELSE
        Y=CB(4)
      END IF
      IF (ISURF(KS).GT.2) THEN
        IF (LIMS(KS,1).LE.NCX) THEN
          X=CG(1,LIMS(KS,1))
        ELSE
          X=CB(2)
        END IF
        NC=(LIMS(KS,2)+K-NEL1-1)*NCX+1
        Y=0.5*(CG(4,NC)+CG(5,NC))
      END IF
      SS(1)=0.
      DO 10 L=1,MNSP
        SS(1)=SS(1)+CSS(1,K,L)
      10 CONTINUE
      WRITE (4,99002) X,Y,SS(1),(CSS(1,K,L)/SS(1),L=1,MNSP)
    99002 FORMAT (2F12.5,F12.1,6F12.6)
    20 CONTINUE
  END IF
C WRITE (4,*)
C &' X COORD Y COORD SAMPLE FRACTION SPECIES 1 FRACTION SPECIES 2....'
DO 20 K=NEL1,NEL2
  IF (ISURF(KS).LT.3) THEN
    IF (LIMS(KS,1).LE.NCY) THEN
      NC=(LIMS(KS,1)-1)*NCX+1
      Y=CG(4,NC)
    ELSE
      Y=CB(4)
    END IF
    NC=LIMS(KS,2)+K-NEL1
    X=0.5*(CG(1,NC)+CG(2,NC))
    AR=2.*PI*CG(3,NC)
  END IF
  IF (ISURF(KS).GT.2) THEN
    IF (LIMS(KS,1).LE.NCX) THEN
      X=CG(1,LIMS(KS,1))
    ELSE
      X=CB(2)
    END IF
    NC=(LIMS(KS,2)+K-NEL1-1)*NCX+1
    Y=0.5*(CG(4,NC)+CG(5,NC))
    END IF
    SS(1)=0.
    DO 10 L=1,MNSP
      SS(1)=SS(1)+CSS(1,K,L)
    10 CONTINUE
    WRITE (4,99002) X,Y,SS(1),(CSS(1,K,L)/SS(1),L=1,MNSP)
  99002 FORMAT (2F12.5,F12.1,6F12.6)
  20 CONTINUE
* C WRITE (4,*)
C &' X COORD Y COORD NUM FLUX INC PRESS REFL PRESS INC HS TR REFH SH STR INC TR EN REFL TR EN INC ROT EN REFL ROT EN C & NET HEAT FLUX'
DO 60 K=NEL1,NEL2
  IF (ISURF(KS).LT.3) THEN
    IF (LIMS(KS,1).LE.NCY) THEN
      NC=(LIMS(KS,1)-1)*NCX+1
      Y=CG(4,NC)
    ELSE
      Y=CB(4)
    END IF
    NC=LIMS(KS,2)+K-NEL1
    X=0.5*(CG(1,NC)+CG(2,NC))
    AR=2.*PI*CG(3,NC)
  END IF
  IF (ISURF(KS).GT.2) THEN
    IF (LIMS(KS,1).LE.NCX) THEN
      X=CG(1,LIMS(KS,1))
    ELSE
      X=CB(2)
    END IF
    NC=(LIMS(KS,2)+K-NEL1-1)*NCX+1
    Y=0.5*(CG(4,NC)+CG(5,NC))
    END IF
    SS(1)=0.
    DO 10 L=1,MNSP
      SS(1)=SS(1)+CSS(1,K,L)
    10 CONTINUE
    WRITE (4,99002) X,Y,SS(1),(CSS(1,K,L)/SS(1),L=1,MNSP)
  99002 FORMAT (2F12.5,F12.1,6F12.6)
  60 CONTINUE

IF (ISURF(KS), GT, 2) THEN
  IF (LIMS(KS, 1), LE, NCX) THEN
    X = CG(1, LIMS(KS, 1))
  ELSE
    X = CB(2)
  END IF
  NC = (LIMS(KS, 2) + K - NEL1 - 1) * NCX + 1
  Y = 0.5 * (CG(4, NC) + CG(5, NC))
  AR = PI * (CG(5, NC) ** 2 - CG(4, NC) ** 2)
END IF
DO 30 N = 1, 9
  SS(N) = 0.
  DO 25 L = 1, MNSP
    SS(N) = SS(N) + CSS(N, K, L)
  25 CONTINUE
  DO 40 N = 1, 9
    SS(N) = SS(N) * A / AR
  40 CONTINUE
  WRITE (4, 99003) X, Y, (SS(N), N = 1, 4), SS(9), SS(5), SS(6), SS(7),
               SS(8), SS(5) + SS(6) + SS(7) + SS(8)
C99003 FORMAT (14E12.5)
END IF
100 CONTINUE
*
C   WRITE (4, *) ' FLOWFIELD PROPERTIES '
C   WRITE (4, *) 'SAMPLES'
C   WRITE (4, *)
C   & ' CELL MEAN SQ. FL SAMPLE SP 1 SAMPLE SP 2 ETC '
DO 200 N = 1, MNC
  SS(1) = 0.000001
  DO 150 L = 1, MNSP
    SS(1) = SS(1) + CS(8, N, L) / FLOAT(NSMP)
  150 CONTINUE
  FLM = (CS(9, N, 1) / FLOAT(NSMP) - SS(1) * SS(1)) / SS(1)
200 CONTINUE
C99004 FORMAT (' ', I6, E12.4, 5I9)
*
C   WRITE (4, *) ' FLOWFIELD PROPERTIES '
C   WRITE (4, *)
C   & ' CELL X COORD Y COORD DENSITY TR TEMP ROT TEMP OVT '
C   &EMP U V W '
*--first the mixture properties
DO 400 N = 1, MNC
  A = FNUM/(CC(N) * NSMP)
  SN = 0.
  SM = 0.
  DO 250 K = 1, 3
    SMU(K) = 0.
  250 CONTINUE
  SMCC = 0.
  SRE = 0.
  SRDF = 0.
  DO 300 L = 1, MNSP
    SN = SN + CS(1, N, L)
  300 CONTINUE
*--SN is the number sum
SM = SM + SP(5, L) * CS(1, N, L)
*--SM is the sum of molecular masses
DO 260 K = 1, 3
  SMU(K) = SMU(K) + SP(5, L) * CS(K + 1, N, L)
260 CONTINUE
Appendix C - Flowfield Modeling Code

*--SMU(1 to 3) are the sum of mu, mv, mw
260 CONTINUE
   SMCC=SMCC+(CS(5,N,L)+CS(6,N,L)+CS(7,N,L))*SP(5,L)
*--SMCC is the sum of m(u**2+v**2+w**2)
   SRE=SRE+CSR(N,L)
*--SRE is the sum of rotational energy
   SRDF=SRDF+ISPR(1,L)*CS(1,N,L)
*--SRDF is the sum of the rotational degrees of freedom
   SUU=SUU+SP(5,L)*CS(5,N,L)
*--SUU is the sum of m*u*u
300 CONTINUE
   DENN=SN*A
*--DENN is the number density, see eqn (1.34)
   DEN=DENN*SM/SN
*--DEN is the density, see eqn (1.42)
   DO 350 K=1,3
      VEL(K)=SMU(K)/SM
   SVEL(K,N)=VEL(K)
350      CONTINUE
*--VEL and SVEL are the stream velocity components, see eqn (1.43)
   UU=VEL(1)**2+VEL(2)**2+VEL(3)**2
   TT=(SMCC-SM*UU)/(3.D00*DBOLTZ*SN)
*--TT is the translational temperature, see eqn (1.51)
   IF (SRDF.TG.1.E-6) TROT=(2.D00/DBOLTZ)*SRE/SRDF
*--TROT is the rotational temperature, see eqn (11.11)
   TEMP=(3.D00*TT+(SRDF/SN)*TROT)/(3.+SRDF/SN)
*--TEMP is the overall temperature, see eqn (11.12)
   CT(N)=TEMP
   XC=0.5*(CG(1,N)+CG(2,N))
   YC=0.5*(CG(4,N)+CG(5,N))
*--XC,YC are the x,y coordinates of the midpoint of the cell
C WRITE (4,99005) N,XC,YC,DEN,TT,TROT,TEMP,VEL(1),VEL(2),VEL(3)
C WRITE (4,99005) N,XC,YC,DEN,TT,TROT,TEMP,VEL(1),VEL(2),VEL(3)
C WRITE (4,99005) N,XC,YC,DEN,TT,TROT,TEMP,VEL(1),VEL(2),VEL(3)
C WRITE (4,99005) N,XC,YC,DEN,TT,TROT,TEMP,VEL(1),VEL(2),VEL(3)
400 CONTINUE
* C WRITE (4,*)
   DO 500 L=1,MNSP
*--now the properties of the separate species
C WRITE (4,*) ' SPECIES ',L
C WRITE (4,*)
C & CELL X COORD Y COORD N DENS DENSITY TTX TTY
C & T TZ TR TEMP ROT TEMP TEMP U DIF VEL V DIF VEL
C & W DIF VEL '
   DO 450 N=1,MNC
      A=FNUM/(CC(N)*NSMP)
      DENN=CS(1,N,L)*A
*--DENN is the partial number density
      DEN=SP(5,L)*DENN
*--DEN is the partial density, see eqn (1.13)
   DO 420 K=1,3
      VEL(K)=CS(K+1,N,L)/CS(1,N,L)
*--VEL defines the average velocity of the species L molecules
420 CONTINUE
   UU=VEL(1)**2+VEL(2)**2+VEL(3)**2
   TTX=(SP(5,L)/DBOLTZ)*(CS(5,N,L)/CS(1,N,L)-VEL(1)**2)
   TTY=(SP(5,L)/DBOLTZ)*(CS(6,N,L)/CS(1,N,L)-VEL(2)**2)
   TTZ=(SP(5,L)/DBOLTZ)*(CS(7,N,L)/CS(1,N,L)-VEL(3)**2)
*--the component temperatures are based on eqn (1.30)
   TT=(SP(5,L)/(3.D00*DBOLTZ))
& *((CS(5,N,L)+CS(6,N,L)+CS(7,N,L))/CS(1,N,L)-UU)
*--TT is the translational temperature, see eqn (1.29)
IF (ISPR(1,L).GT.0) THEN
   TROT=2.D00*CSR(N,L)/(ISPR(1,L)*DBOLTZ*CS(1,N,L))
ELSE
   TROT=0.
END IF
*--TROT is the rotational temperature, see eqn (11.10)
TEMP=(3.D00*TT+ISPR(1,L)*TROT)/(3.+ISPR(1,L))
DO 440 K=1,3
   VEL(K)=VEL(K)-SVEL(K,N)
*--VEL now defines the diffusion velocity of species L, see eqn (1.45)
440 CONTINUE
XC=0.5*(CG(1,N)+CG(2,N))
YC=0.5*(CG(4,N)+CG(5,N))
WRITE (4,99006) N,XC,YC,DENN,DEN,TTX,TTY,TTZ,TT,TROT,TEMP,
&                    VEL(1),VEL(2),VEL(3)
C99006 FORMAT (' ',I5,2F9.4,1P,2E12.4,0P,9F10.4)
450 CONTINUE
500 CONTINUE
*
CLOSE (4)
CLOSE (4268)
CLOSE (4269)
* RETURN
END
* SROT.FOR
* SUBROUTINE SROT(PR,TEMP,IDF)
*--selects a typical equilibrium value of the rotational energy PR at
*----the temperature TEMP in a gas with IDF rotl. deg. of f.
* COMMON /CONST / PI,SPI,BOLTZ
IF (IDF.EQ.2) THEN
   PR=-LOG(RF(0))*BOLTZ*TEMP
*--for 2 degrees of freedom, the sampling is directly from eqn (11.22)
ELSE
   A=0.5*IDF-1.
   50 ERM=RF(0)*10.
*--the cut-off internal energy is 10 kT
   B=((ERM/A)**A)*EXP(A-ERM)
   IF (B.LT.RF(0)) GO TO 50
   PR=ERM*BOLTZ*TEMP
END IF
RETURN
END
* SROT.FOR
* FUNCTION ERF(S)
*--calculates the error function of S
* B=ABS(S)
   IF (B.GT.4.) THEN
      D=1.
   ELSE

C=EXP(-B*B)
T=1/(1+0.3275911*B)
D=1-.254829592*T+0.284496736*T*T+1.421413741*T*T*T-
& 1.453152027*T*T*T*T+1.061405429*T*T*T*T*T)*C
END IF
IF (S.LT.0.) D=-D
ERF=D
RETURN
END

* INDEXM.FOR
*
SUBROUTINE INDEXM
*
--the NM molecule numbers are arranged in order of the molecule groups
--and, within the groups, in order of the cells and, within the cells,
--in order of the sub-cells
*
PARAMETER (MNM=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304,
& MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)
*
COMMON /MOLS2 / NM,PP(2,MNM),PV(3,MNM),IPL(MNM),IPS(MNMS),IR(MNM)
COMMON /CELL2 / CC(MNC),CG(6,MNC),IC(2,MNC,MNSG),ISC(MNSC),
& CCG(2,MNC,MNSG,MNSG),ISCG(2,MNSC,MNSG),IG(2,MNSG),
& NCX,NCY,IFCX,IFCY,CWRX,CWRY,APX,RPX,APY,RPY
COMMON /GAS / SP(5,MNSP),SPM(6,MNSP,MNSP),ISP(MNSP)
*
DO 200 MM=1,MNSG
IG(2,MM)=0
DO 50 NN=1,MNC
IC(2,NN,MM)=0
50      CONTINUE
DO 100 NN=1,MNSC
ISCG(2,NN,MM)=0
100     CONTINUE
200   CONTINUE
DO 300 N=1,NM
IF (MNSP.GT.1) THEN
  LS=IPS(N)
ELSE
  LS=1
END IF
MG=ISP(LS)
IG(2,MG)=IG(2,MG)+1
MSC=IPL(N)
ISCG(2,MSC,MG)=ISCG(2,MSC,MG)+1
MC=ISC(MSC)
IC(2,MC,MG)=IC(2,MC,MG)+1
300   CONTINUE
*
*--number in molecule groups in the cells and sub-cells have been counte
M=0
DO 400 L=1,MNSG
  IG(1,L)=M
ELSE
  LS=1
END IF
MG=ISP(LS)
IG(2,MG)=IG(2,MG)+1
MSC=IPL(N)
ISCG(2,MSC,MG)=ISCG(2,MSC,MG)+1
MC=ISC(MSC)
IC(2,MC,MG)=IC(2,MC,MG)+1
400   CONTINUE
DO 600 L=1,MNSG
  M=IG(1,L)
DO 450 N=1,MNC
  IC(1,N,L)=M
  M=M+IC(2,N,L)
450   CONTINUE
*--the (start address -1) has been set for the cells
M=IG(1,L)
DO 500 N=1,MNSC
   ISCG(1,N,L)=M
   M=M+ISCG(2,N,L)
   ISCG(2,N,L)=0
500     CONTINUE
600   CONTINUE
*--the (start address -1) has been set for the sub-cells
DO 700 N=1,NM
   IF (MNSP.GT.1) THEN
      LS=IPS(N)
   ELSE
      LS=1
   END IF
   MG=ISP(LS)
   MSC=IPL(N)
   ISCG(2,MSC,MG)=ISCG(2,MSC,MG)+1
   K=ISCG(1,MSC,MG)+ISCG(2,MSC,MG)
   IR(K)=N
700   CONTINUE
RETURN
*   SELECT2A.FOR
*  SELECT2A
*--selects a potential collision pair and calculates the product of the
*--collision cross-section and relative speed
*--collision cross-section and relative speed
* PARAMETER (MNM=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304,
  & MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)
* COMMON /MOLS2 / NM,PP(2,MNM),PV(3,MNM),IPL(MNM),IPS(MNMS),IR(MNM)
* COMMON /CELL2 / CC(MNC),CG(6,MNC),IC(2,MNC,MNSG),ISC(MNSC),
  & CCG(2,MNC,MNSG,MNSG),ISCG(2,MNSC,MNSG),IG(2,MNSG),
  & NCX,NCY,IFCX,IFCY,CWRX,CWRY,APX,RPX,APY,RPY
* COMMON /GAS   / SP(5,MNSP),SPM(6,MNSP,MNSP),ISP(MNSP)
* COMMON /CONST / PI,SPI,BOLTZ
* COMMON /ELAST / VRC(3),VRR,VR,L,M,LS,MS,CVR,MM,NN,N
* K=INT(RF(0)*(IC(2,N,NN)-0.001))+(IC(1,N,NN)+1
  L=IR(K)
*--the first molecule L has been chosen at random from group NN in cell
  NATT=0
100   NATT=NATT+1
   MSC=IPL(L)
   IF ((NN.EQ.MM.AND.ISCG(2,MSC,MM).EQ.1).OR.
   & (NN.NE.MM.AND.ISCG(2,MSC,MM).EQ.0)) THEN
      NST=1
      NSG=1
   ELSE
      INC=NSG*NST
      NSG=-NSG
      NST=NST+1
      MSC=MSC+INC
      IF (MSC.LT.1.OR.MSC.GT.MNSC) GO TO 150
      IF (ISC(MSC).NE.N.OR.ISCG(2,MSC,MM).LT.1) GO TO 150
      END IF
*--the second molecule M is now chosen at random from the group MM
Appendix C - Flowfield Modeling Code

*--molecules that are in the sub-cell MSC
K=INT(RF(0)*(ISCG(2,MSC,MM)-0.001))+ISCG(1,MSC,MM)+1
M=IR(K)
IF (L.EQ.M) GO TO 100
*--choose a new second molecule if the first is again chosen
*
   DO 200 K=1,3
      VRC(K)=PV(K,L)-PV(K,M)
   CONTINUE
*--VRC(1 to 3) are the components of the relative velocity
VRR=VRC(1)**2+VRC(2)**2+VRC(3)**2
IF (VRR.LT.1.E-6) THEN
*--attempted collision between identical molecules, this is due to
*----duplication so choose another as long as there is no infinite loop
IF (NATT.LT.10) GO TO 100
VRR=1.E-6
END IF
VR=SQR(T(VRR))
*--VR is the relative speed
IF (MNSP.GT.1) THEN
   LS=IPS(L)
   MS=IPS(M)
ELSE
   LS=1
   MS=1
END IF
CVR=VR*SPM(1,LS,MS)*((2.*BOLTZ*SPM(2,LS,MS)/(SPM(5,LS,MS)*VRR))**(SPM(3,LS,MS)-0.5))/SPM(6,LS,MS)
*--the collision cross-section is based on eqn (4.63)
RETURN
END
*   ELASTIC.FOR
*
SUBROUTINE ELASTIC
*
*--generate the post-collision velocity components.
*
PARAMETER (MNM=2000000,MNMR=1,MNMS=1,MNC=1326,MNSC=5304,
&   MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)
*
COMMON /MOLS2 / NM,PP(2,MNM),PV(3,MNM),IPL(MNM),IPS(MNMS),IR(MNM)
COMMON /GAS   / SP(5,MNSP),SPM(6,MNSP,MNSP),ISP(MNSP)
COMMON /CONST / PI,SPI,BOLTZ
COMMON /ELAST / VRC(3),VRR,VR,L,M,LS,MS,CVR,MM,NN,N
*
DIMENSION VRCP(3),VCCM(3)
*--VRCP(3) are the post-collision components of the relative velocity
*--VCCM(3) are the components of the centre of mass velocity
*
RML=SPM(5,LS,MS)/SP(5,MS)
RMM=SPM(5,LS,MS)/SP(5,LS)
DO 100 K=1,3
   VCCM(K)=RML*PV(K,L)+RMM*PV(K,M)
100 CONTINUE
*--VCCM defines the components of the centre-of-mass velocity, eqn (2.1)
IF (ABS(SPM(4,LS,MS)-1.).LT.1.E-3) THEN
*--use the VHS logic
   B=2.*RF(0)-1.
   A=SQR(T(1.-B*B))
   VRCP(1)=B*VR
C = 2. * PI * RF(0)

*-- C is a random azimuth angle
VRCP(2) = A * COS(C) * VR
VRCP(3) = A * SIN(C) * VR
ELSE

*-- use the VSS logic
B = 2. * (RF(0)**SPM(4, LS, MS)) - 1.

*-- B is the cosine of the deflection angle for the VSS model, eqn (11.8)
A = SQRT(1. - B**2)
OC = COS(C)
SC = SIN(C)
D = SQRT(VRC(2)**2 + VRC(3)**2)
IF (D > 1.E-6) THEN

VRCP(1) = B * VRC(1) + A * SC * D
VRCP(2) = B * VRC(2) + A * (VR * VRC(3) * OC - VRC(1) * VRC(2) * SC) / D
VRCP(3) = B * VRC(3) - A * (VR * VRC(2) * OC + VRC(1) * VRC(3) * SC) / D
ELSE

VRCP(1) = B * VRC(1)
VRCP(2) = A * OC * VRC(1)
VRCP(3) = A * SC * VRC(1)
END IF

*-- the post-collision relative velocity components are based on eqn (2.22)
END IF

*-- VRCP(1 to 3) are the components of the post-collision relative vel.
DO 200 K = 1, 3
PV(K, L) = VCCM(K) + VRCP(K) * RMM
PV(K, M) = VCCM(K) - VRCP(K) * RML
200 CONTINUE
RETURN
END

* RVELC.FOR

* SUBROUTINE RVELC(U, V, VMP)

*-- generates two random velocity components U and V in an equilibrium gas
*-- with most probable speed VMP (based on eqns (C10) and (C12))

* A = SQRT(-LOG(RF(0)))
B = 6.283185308 * RF(0)
U = A * SIN(B) * VMP
V = A * COS(B) * VMP
RETURN
END

* GAM.FOR

* FUNCTION GAM(X)

*-- calculates the Gamma function of X.

A = 1.
Y = X
IF (Y LT 1.) THEN
A = A / Y
ELSE
50 Y = Y - 1
IF (Y GE 1.) THEN
A = A * Y
GO TO 50
END IF
END IF
GAM = A*(1 - 0.5748646*Y + 0.9512363*Y**2 - 0.6998588*Y**3 +
              0.4245549*Y**4 - 0.1010678*Y**5)
RETURN
END
* COLLMR.FOR
*
SUBROUTINE COLLMR
*
--calculates collisions appropriate to DTM in a gas mixture
*
PARAMETER (MNM=2000000, MNMR=1, MNMS=1, MNC=1326, MNSC=5304,
&  MNSP=1, MNSG=51, MNB=200)
*
DOUBLE PRECISION COL(MNSP,MNSP), MOV'T, NCOL, SELT, SEPT, CS(9,MNC,MNSP)
DOUBLE PRECISION CSR(MNC,MNSP)
*
COMMON /MOLS2 / NM, PP(2,MNM), PV(3,MNM), IPL(MNM), IPS(MNMS), IR(MNM)
COMMON /MOLSR / PR(MNMR)
COMMON /CELL2 / CC(MNC), CG(6,MNC), JCC(2,MNC), ISC(MNSC),
&  NCX, NCY, ICX, IFCY, CWRX, CWRY, APX, APY, APY, PRCY,
COMMON /GAS / SP(5,MNSP), SPM(6,MNSP), ISP(MNMR)
COMMON /GASR / SPR(3,MNSP), ISPR(3,MNSP), JCC(2,MNC)
COMMON /GEOM2A/ NSCX, NSCY, CB(4), IB(4), TSURF(3), LSURF(3), IJS, IJSG,
&  TSURF(2), TSURF(3), LIMJ(3), FNDJ, FVJ, FSPJ(MNSP),
&  AMEJ(MNSP, MBC), AMRJ(MNSP, MBC), AMEJ(MNSP, MBC),
&  AMRJ(MNSP, MBC), CW, FW, CH, FH, WI, FLX, LFLY, ALP(2),
&  ALP(2), ALPT(2), 1WF, RWF, WSURF(2)
COMMON /SAMP2A/ COL, NCOL, MOV'T, SELT, SEPT, CS, TIME, NPR, NSMP, FND, FTMP,
&  TML, FSP(MNSP), ISP, VFX
COMMON /SAMPR / CSR
COMMON /COMP / FNUM, DTM, NIS, NSP, NPS, NPT
COMMON /CONST / PI, SPI, BOLTZ
*
*--VRC(3) are the pre-collision components of the relative velocity
*
DO 100 N = 1, MNC
*
DO 20 MM = 1, MNSG
*
DO 30 K = 1, MNSP
*
SN = 0.
*
IF (ISP(K) .EQ. MM) SN = SN + CS(1,N,K)
*
10 CONTINUE
*
IF (SN .LT. 1) THEN
*
AVN = SN / FLOAT(NSMP)
ELSE
*
AVN = IC(2,N,MM)
*
END IF
*
*--AVN is the average number of group MM molecules in the cell
*--ASEL is the number of pairs to be selected
*--ASEL .LT. 1.0, then
*--if there are insufficient molecules to calculate collisions,
ELSE
CVM=CCG(1,N,NN,MM)
SELT=SELT+NSEL
DO 12 ISEL=1,NSEL
*                 CALL SELECT2A
*                 IF (CVR.GT.CVM) CVM=CVR
*                 IF (RF(0).LT.CVR/CCG(1,N,NN,MM)) THEN
*                 THE collision is accepted with the probability of eqn (11.6)
*                 NCOL=NCOL+1
                   SEPT=SEPT+
&                   SQRT((PP(1,L)-PP(1,M))**2+(PP(2,L)-PP(2,M))**2)
                   COL(LS,MS)=COL(LS,MS)+1.D00
                   COL(MS,LS)=COL(MS,LS)+1.D00
*                 IF (ISPR(1,LS).GT.0.OR.ISPR(1,MS).GT.0) CALL INELR
*                 CALL ELASTIC
                  END IF
12              CONTINUE
                  CCG(1,N,NN,MM)=CVM
                  END IF
                  END IF
20        CONTINUE
50      CONTINUE
100   CONTINUE
RETURN
END
*   INELR.FOR
*   SUBROUTINE INELR
*   adjustment of rotational energy in a collision
*   PARAMETER (MNMR=2000000,MNMS=1,MNMC=1326,MNSC=5304,
&           MNSP=1,MNSG=1,MNSE=26,MBC=51,MNB=200)
*   COMMON /MOLSR / PR(MNMR)
   COMMON /GAS   / SP(5,MNSP),SPM(6,MNSP,MNSP),ISP(MNSP)
   COMMON /GASR  / SPR(3,MNSP,MNSP),ISPR(3,MNSP),CT(MNC)
   COMMON /ELAST / VRC(3),VRR,VR,L,M,LS,MS,CVR,MM,NN,N
*   DIMENSION IR(2)
*   IR is the indicator for the rotational redistribution
*   ETI=0.5*SPM(5,LS,MS)*VRR
*   ETI is the initial translational energy
*   ECI=0.
*   ECI is the initial energy in the active rotational modes
*   ECF=0.
*   ECF is the final energy in these modes
*   ECC=ETI
*   ECC is the energy to be divided
*   XIB=2.5-SPM(3,LS,MS)
*   XIB is th number of modes in the redistribution
*   IRT=0
*--IRT is 0.1 if no, any redistribution is made
DO 100 NSP=1,2
*--consider the molecules in turn
IF (NSP.EQ.1) THEN
  K=L
  KS=LS
  JS=MS
ELSE
  K=M
  KS=MS
  JS=LS
END IF
IR(NSP)=0
IF (ISPR(1,KS).GT.0) THEN
  IF (ISPR(2,KS).EQ.0) THEN
    ATK=1./SPR(1,KS,JS)
  ELSE
    ATK=1./(SPR(1,KS,JS)+SPR(2,KS,JS)*CT(N)+SPR(3,KS,JS)**2)
  END IF
*--ATK is the probability that rotation is redistributed to molecule L
IF (ATK.GT.RF(0)) THEN
  IRT=1
  IR(NSP)=1
  IF (MNMR.GT.1) THEN
    ECC=ECC+PR(K)
    ECI=ECI+PR(K)
  END IF
  XIB=XIB+0.5*ISPR(1,KS)
END IF
END IF
100 CONTINUE
*--apply the general Larsen-Borgnakke distribution function
IF (IRT.EQ.1) THEN
  DO 150 NSP=1,2
  IF (IR(NSP).EQ.1) THEN
    IF (NSP.EQ.1) THEN
      K=L
      KS=LS
    ELSE
      K=M
      KS=MS
    END IF
    XIB=XIB-0.5*ISPR(1,KS)
    IF (ISPR(1,KS).EQ.2) THEN
      ERM=1.-RF(0)**(1./XIB)
    ELSE
      XIA=0.5*ISPR(1,KS)
      CALL LBS(XIA-1.,XIB-1.,ERM)
    END IF
    IF (MNMR.GT.1) THEN
      PR(K)=ERM*ECC
      ECC=ECC-PR(K)
    END IF
  END IF
  END IF
150 CONTINUE
ETF=ETI+ECI-ECF
*--ETF is the post-collision translational energy
*--adjust VR and, for the VSS model, VRC for the change in energy
   
   \[ A = \sqrt{2 \times \frac{\text{ETF}}{\text{SPM}(5,LS,MS)}} \]
   
   \[ \text{IF} \left( \left| \text{SPM}(4,LS,MS) - 1. \right| < 1 \times 10^{-3} \right) \text{ THEN} \]
   
   \[ VR = A \]
   
   ELSE
   
   DO 160 K=1,3
   
   \[ \text{VRC}(K) = \text{VRC}(K) \times A / VR \]
   
   160 CONTINUE
   
   \[ VR = A \]
   
   END IF
   
   END IF
   
   RETURN
   
   END
   
*   LBS.FOR
   
*   SUBROUTINE LBS(XMA,XMB,ERM)
   
*--selects a Larsen-Borgnakke energy ratio using eqn (11.9)

100 \[ \text{ERM} = \text{RF}(0) \]

IF (XMA.LT.1.E-6.OR.XMB.LT.1.E-6) THEN

IF (XMA.LT.1.E-6.AND.XMB.LT.1.E-6) RETURN

IF (XMA.LT.1.E-6) \[ P = (1 - \text{ERM})^*XMB \]

ELSE

\[ P = ((XMA+XMB)*\text{ERM}/XMA)^*XMA \times ((XMA+XMB)*(1-\text{ERM})/XMB)^*XMB \]

END IF

IF (P.LT.RF(0)) GO TO 100

RETURN

END
   
*   AIFR.FOR
   
*   SUBROUTINE AIFR(YI,DY,DZ,Y,V,W)
   
*--calculates the new radius and realigns the velocity components in

*----the axially symmetric flow

\[ \text{DR} = \text{DZ} \]

\[ \text{VR} = \text{W} \]

\[ \text{A} = \text{YI} + \text{DY} \]

\[ \text{Y} = \sqrt{\text{A}^2 + \text{DR}^2} \]

\[ \text{S} = \text{DR} / \text{Y} \]

\[ \text{C} = \text{A} / \text{Y} \]

\[ \text{B} = \text{V} \]

\[ \text{V} = \text{B}^*\text{C} + \text{VR}^*\text{S} \]

\[ \text{W} = -\text{B}^*\text{S} + \text{VR}^*\text{C} \]

RETURN

END
   
*   RF.FOR
   
*   FUNCTION RF(IDUM)
   
*--generates a uniformly distributed random fraction between 0 and 1

*----IDUM will generally be 0, but negative values may be used to

*-----re-initialize the seed

SAVE MA,INEXT,INEXTP
PARAMETER (MBIG=1000000000,MSEED=161803398,MZ=0,FAC=1.E-9)
DIMENSION MA(55)
DATA IFF/0/

IF (IDUM.LT.0.OR.IFF.EQ.0) THEN

IFF = 1

MJ = MSEED-IABS(IDUM)

MJ = MOD(MJ,MBIG)

MA(55) = MJ

MK = 1

DO 50 I = 1,54
II = MOD(21*I,55)
MA(II) = MK
MK = MJ-MK
IF (MK.LT.MZ) MK = MK+MBIG
MJ = MA(II)
50    CONTINUE
DO 100 K=1,4
   DO 60 I=1,55
      MA(I) = MA(I) - MA(1+MOD(I+30,55))
      IF (MA(I).LT.MZ) MA(I) = MA(I) + MBIG
   60    CONTINUE
100   CONTINUE
INEXT=0
INEXTP=31
END IF
200   INEXT=INEXT+1
   IF (INEXT.EQ.56) INEXT=1
   INEXTP=INEXTP+1
   IF (INEXTP.EQ.56) INEXTP=1
   MJ = MA(INEXT)-MA(INEXTP)
   IF (MJ.LT.MZ) MJ = MJ + MBIG
   MA(INEXT)=MJ
   RF=MJ*FAC
   IF (RF.GT.1.E-8.AND.RF.LT.0.99999999) RETURN
   GO TO 200
END

* DATA2A.FOR
* SUBROUTINE DATA2A
*
*--defines the data for a particular run of DSMC2A.FOR.
*
PARAMETER (MNM=2000000, MNMR=1, MNMS=1, MNC=1326, MNSC=5304, 
&       MNSP=1, MNSG=1, MNSE=26, MBC=51, MNB=200)
*
DOUBLE PRECISION COL(MNSP,MNSP), MOVT, NCOL, SELT, SEPT, CS(9,MNC,MNSP)
*
COMMON /GAS   / SP(5,MNSP), SPM(6,MNSP,MNSP), ISP(MNSP)
COMMON /GASR  / SPR(3,MNSP,MNSP), ISPR(3,MNSP), CT(MNC)
COMMON /CELL2 / CC(MNC), CG(6,MNC), IC(2,MNC,MNSG), ISC(MNSC),
&       CCG(2,MNC,MNSG,MNSG), ISCG(2,MNSC,MNSG), IG(2,MNSG),
&       NCX,NCY,IFCX,IFCY,CWRX,CWRY,APX,RPX,APY,RPY
COMMON /SAMP2A/ COL, NCOL, MOVT, SELT, SEPT, CS, TIME, NPR, NSMP, FND, FTMP,
&       TIMLFS2P(MNSP), ISPD, VFX
COMMON /COMP  / FNUM, DTM, NIS, NBP, NPS, NPT
COMMON /GEOM2A/ NSCX, NSCY, CB(4), IB(4), ISURF(2), LIMS(2,3), IIS, ISG,
&       TSURF(2), JET, LIMJ(3), TMPJ, FNDJ, FSPJ(MNSP),
&       AMEJ(MNSP,MBC), AMRJ(MNSP,MBC), AME(4,MNSP,MBC),
&       AMR(4,MNSP,MBC), CW, FW, CH, FW, W1, LFLX, LFLY, ALP(2),
&       ALP(2), ALPT(2), IWF, RWF, WSURF(2)
*
*--set data (must be consistent with PARAMETER variables)
*
IWF=1
RWF=0.004
NCX=51
NCY=26
NSCX=2
NSCY=2
IFCX=0
IFCY=1
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CWRY=3
IIS=1
ISG=1
LFLX=-50
LFLY=26
FTMP=273.
FND=1.605E21
VFX=5.
ESP(1)=1.
FNUM=.200E12
DTM=1.E-6
CB(1)=0.00
CB(2)=0.102
CB(3)=0.00
CB(4)=0.051
IB(1)=1
IB(2)=1
IB(3)=4
IB(4)=1
ISURF(1)=4
LIMS(1,1)=51
LIMS(1,2)=1
LIMS(1,3)=25
TSURF(1)=300.
WSURF(1)=0.
ALPI(1)=1.
ISURF(2)=1
LIMS(2,1)=26
LIMS(2,2)=51
LIMS(2,3)=51
TSURF(2)=300.
WSURF(2)=0.
ALPI(2)=1.
IJET=3
LIMJ(1)=1
LIMJ(2)=1
LIMJ(3)=6
TMPJ=220
FNDJ=4.04E21
FVI=872
FSPI(1)=1
SP(1,1)=2.33E-10
SP(2,1)=273.
SP(3,1)=0.66
SP(4,1)=1.0
SP(5,1)=6.65E-27
ISPR(1,1)=0
SPR(1,1,1)=1.
ISPR(2,1)=0
NIS=2
NSP=10
NPS=20
NPT=40
*
RETURN
END
Appendix D - Atom Tracking Code

PROGRAM trace

C Version 1.43
C This file compiled with command:
C f77 output.f -bmaxdata:300000000 -o output
C This code is designed to perform three tasks: 1) simulate
C random walk of an Ar atom in thermal equilibrium with Ar,
C 2) To follow vapor atoms in a sputtering systems from source
C to substrate and observe the energy loss of the sputtered atoms
C with distance from the target, 3) To follow vapor atoms in the
C DVD system from source to substrate, recording their energy, location
C and angle of deposition.
C The model allows the position and energy perpendicular to the substrate
C to be recorded for a vapor atom as it travel from source to substrate.

***** VARIABLE DECLARATIONS *****
DOUBLE PRECISION A, Alpha, AD(500), AE, AP, AT
DOUBLE PRECISION AX, bmax, BN, BD, C, CCS
DOUBLE PRECISION data(2000,2000,7), Dist
DOUBLE PRECISION E, Eff, FM, VM, AvgVel, Focus
DOUBLE PRECISION FMA, FMVz, AvgSputter, Num(4)
DOUBLE PRECISION initial(3),MagVel, MaxVz
DOUBLE PRECISION PT(5), profile(250,250,3)
DOUBLE PRECISION Poisson, Posit, RN, time1, time2
DOUBLE PRECISION RV, SR, Stdev, TD, TE, TotalVel
DOUBLE PRECISION Theta, Timer, Timez, TTheta, TV, VMag
DOUBLE PRECISION trajec(50000,6), vapor(6), VD(500)
DOUBLE PRECISION vaporposit(3), VelDev, CountVel
DOUBLE PRECISION SUB, x, Therm(3), Target
DOUBLE PRECISION path1, path2, start(3), D2(22000)
DOUBLE PRECISION TR, ThermVel, Total, Avgtime, TotalTime
DOUBLE PRECISION Random(3), vel(4)
DOUBLE PRECISION vcx, vcy, a1, b1, c1
INTEGER Jump, GPR, GPZ
INTEGER Counter, I, J, M, P, Q
INTEGER R, Trip, Z, Jumps, Za, Zb
LOGICAL Loop, Vertical
LOGICAL AtomTrack, Sputter, RandomWalk, DVD, Scatter

***** CONSTANT DECLARATION *****
C AN - Avogadro's number [atoms/mol]
C Rcon - Universal gas constant [J/(mol K)]
C Boltz - Boltzmann's constant [J/K]
C NA - Number of atoms
C eV - Conversion factor from eV to J
C NBXY - # of bins in x/y directions for spatial distribution profile
C NB - # of bins in x/y directions for angle & velocity distribution output
C Pi - The number Pi.
PARAMETER (AN=6.0221E23,Rcon=8.3145,Boltz=1.3807E-23,
NA=1,eV=1.602E-19,NBXY=13,NB=15,Pi=3.14159265359)

***** SIMULATION CONFIGURATION *****
C All user configurable parameters are located in this simulation
configuration section. Changes further down in the code can have unpredictable effects upon the operation of the code, and the validity of such changes will need to be verified by the user.

The program requires an input file to be provided. The file contains grid point locations, and chamber gas (fluid) velocity, pressure, and temperature information. GPZ and GPR need to be set according to the size of grid used for the particular simulation. For \( z \) and \( r \) orientation see Groves dissertation.

GPZ - # of gridpts in Z dir. (from DSMC grid info)
GPR - # of gridpts in R dir. (from DSMC grid info)

GPZ = 32
GPR = 28

Set AtomTrack to TRUE if you want to record the trajectories of the first 10 atoms leaving the vapor source. Tracking more atoms creates a very large data file!

AtomTrack = .TRUE.

If you are using the model to simulate random walk, set RandomWalk to TRUE, otherwise FALSE.
RandomWalk = .FALSE.

If you are using the model to simulate sputtering, set Sputter to TRUE, otherwise FALSE.
Sputter = .FALSE.

If you are using the model to simulate the DVD process with a gas jet, set DVD to TRUE, otherwise FALSE.
DVD = .TRUE.

The following three IF THEN statements configure the code to simulate the process chosen above - Random Walk, Sputtering, or DVD.

FM - Fluid mass in processing chamber [kg/atom]
VM - Mass of vapor atom being tracked [kg/atom]
Za - Atomic number of fluid
Zb - Atomic number of vapor
bmax - Atomic diameter for random walk [Angstroms]
EVA - Kinetic energy of vapor atom leaving crucible [eV]
EnergyDev - Standard deviation used to calculate initial vapor atom starting energy distribution [eV]
TS - Number of timesteps into which each mean free path is broken down.
Vertical - Determines vapor source orientation. TRUE = vertical (+y), FALSE = horizontal (+x)

Target - Target radius (m)

IF (RandomWalk) THEN

Fluid = argon
Vapor = argon
FM = 6.64E-26
VM = 6.64E-26
Za = 18
Zb = 18

The value for bmax comes from G. A. Bird Appendix A.
bmax = 4.17
EVA = 0.03878
EnergyDev = 0.000
TS = 1
n = 1.0
Jumps = 10000
Vertical = .TRUE.
Target = 0.003175
ENDIF

IF (Sputter) THEN
C   Fluid = argon
C   Vapor = copper
FM = 6.64E-26
VM = 1.06E-25
Za = 18
Zb = 29
EnergyDev = 0.000
TS = 1
n = 1.0
AvgSputter = 5.100
Jumps = 100000
Vertical = .FALSE.
Target = 0.025400
ENDIF

IF (DVD) THEN
C   Fluid = helium
C   Vapor = copper
FM = 6.65E-27
VM = 1.06E-25
Za = 2
Zb = 29
EVA = 0.2000
EnergyDev = 0.01
TS = 1
n = 5.0
C Atoms which don't hit the substrate after 50000
C collisions are thrown away (i.e. We assume they
C will never hit the substrate.).
Jumps = 20000
Vertical = .FALSE.
Target = 0.003175
ENDIF

C ***** INITIALIZATION OF ATOM TRACKING VARIABLES *****
C REQUIRED FILE (to run this program) = pvtflow (output of DSMC code).
C Includes z, r position, x, y, z velocity, P, T at each grid point.

C The following three lines define the crucible position (in meters)
start(1) =  000.000000
start(2) =  000.000000
start(3) =  000.025400

C The following lines initialize the random number generator.
RN = -0.01
x = RAN3(RN)

C************************ All User Configurable Parameters Above This Line ************************
C Read the carrier gas flow field properties in from DSMC file.
C data(Z,R,1) = overall fluid z position (m)
C data(Z,R,2) = overall fluid r position
Appendix D - Atom Tracking Code

C data(Z,R,3) = overall fluid x velocity (m/sec)
C data(Z,R,4) = overall fluid y velocity
C data(Z,R,5) = overall fluid z velocity
C data(Z,R,6) = overall fluid pressure (Pa)
C For randomwalk and DVD pressure is read in as kg/m^3.
C data(Z,R,7) = overall fluid temperature (K)

OPEN(1, FILE='pvtflow')
DO 250 R=1,GPR,1
DO 200 Z=1,GPZ,1
READ(1,*)data(Z,R,1),data(Z,R,2),data(Z,R,3),
$ data(Z,R,4),data(Z,R,5),data(Z,R,6),data(Z,R,7)
IF (.NOT. Sputter) data(Z,R,6) =
$ data(Z,R,6)*Rcon*data(Z,R,7)/(AN*FM)
200 CONTINUE
250 CONTINUE

C Determine substrate radius (SR). Since modeled region is axisymmetric,
C substrate region will be round. This line assumes the substrate radius
C is one gridpoint less than the diameter of the modeled regime.
SR = data(GPZ,GPR-1,2)
MaxVz = 0.0

C atompath is an output file of this program which will contain x, y,
C and z position of each vapor atom which hits the substrate.
C It also contains x, y, z components of velocity of
C vapor atom at instant it hits substrate.
OPEN(2, FILE='atompath')
WRITE(2,*) 'x position   y position   z position   x velocity   y
$ velocity   z velocity'
C Prepare to record position, energy of vapor atom as it travels
C to the substrate.
IF (AtomTrack) OPEN(4268, FILE='atomtrack')
IF (AtomTrack) OPEN(4269, FILE='nrgtrack')
IF (AtomTrack) OPEN(4270, FILE='angltrck')

C ***** Start of Main Loop *****
DO 390 I=1,NA,1
C Initial vapor(1), (2), and (3) are x, y, and z position
C of vapor source. Atoms are ejected from this point into flow
C field for modeling purposes.
C vapor(1) = vapor atom x position (m)
C vapor(2) = vapor atom y position
C vapor(3) = vapor atom z position
C vapor(4) = vapor atom x velocity (m/sec)
C vapor(5) = vapor atom y velocity
C vapor(6) = vapor atom z velocity
C
C Initial vapor atom location (x,y,z).
Alpha = RAN3(RN)*2*Pi
Random(1) = RAN3(RN)
IF (Vertical) THEN
  vapor(1) = start(1) + Random(1)*Target*Cos(Alpha)
  vapor(2) = start(2)
  vapor(3) = start(3) + Random(1)*Target*Sin(Alpha)
ELSE
  vapor(1) = start(1) + Random(1)*Target*Cos(Alpha)
  vapor(2) = start(2) + Random(1)*Target*Sin(Alpha)
  vapor(3) = start(3)
ENDIF

C
Appendix D - Atom Tracking Code

initial(1) = vapor(1)
initial(2) = vapor(2)
initial(3) = vapor(3)

IF (AtomTrack .AND. I .LE. 10) WRITE(4268,*) ' '
IF (AtomTrack .AND. I .LE. 10) WRITE(4269,*) ' '
IF (AtomTrack .AND. I .LE. 10) WRITE(4270,*) ' '

C Determine the total velocity (TV) and velocity standard deviation
C (VelDev) of the atom leaving the crucible.
C E = 1/2 m v^2 rearranged with eV to J conversion.
IF (Sputter) THEN
  E = AvgSputter*1.0789*(-LOG(RAN3(RN)))**0.80
  TV = SQRT(2.0*E*eV/VM)
ELSE
  TV = SQRT(2*EVA*eV/VM)
  VelDev = SQRT(2*EnergyDev*eV/VM)
  x = RANDN(RN)
  TV = TV + x*VelDev
ENDIF

C The total velocity is now broken down
C into its three components.
C Theta is as shown in Groves dissertation Fig. 5.4
C See equation 3.50 of Schiller for equation used to create
C Theta equation.
Theta = ATAN(SQRT(((RAN3(RN))**(-2.0/(n+3.0)))-1))
IF (Vertical) THEN
  vapor(5) = TV*Cos(Theta)
ELSE
  vapor(6) = TV*Cos(Theta)
ENDIF

C Remaining velocity (RV)
RV = SIN(Theta)**TV

C Alpha is as shown in Groves dissertation Fig. 5.5
Alpha = RAN3(RN)*2*Pi
vapor(4) = Sin(Alpha)*RV

C For vertically oriented source
IF (Vertical) THEN
  vapor(6) = Cos(Alpha)*RV
ELSE
  vapor(5) = Cos(Alpha)*RV
ENDIF

Loop = .TRUE.
Trip = 0
Jump = 0

8 FORMAT (1X,A28,1X,F11.5,1X,A6)

***** LOOP FOR TRACKING ATOM THROUGH FLOW *****
C PT(1) = local fluid x velocity (m/sec)
C PT(2) = local fluid y velocity
C PT(3) = local fluid z velocity
C PT(4) = local fluid pressure (Pa)
C PT(5) = local fluid temperature (K)
C While vapor atom has not intersected boundary, DO (to line 380).
   IF (Loop) THEN
   C Keep initial vapor atom position
   vaporposit(1) = vapor(1)
   vaporposit(2) = vapor(2)
   vaporposit(3) = vapor(3)

   IF (AtomTrack .AND. I .LE. 10) THEN
   WRITE(4268,*) vapor(1), vapor(2), vapor(3)
   VMag = SQRT(vapor(4)**2 + vapor(5)**2 + vapor(6)**2)
   WRITE(4269,*) vapor(3),(0.5*VM*VMag**2)/eV
   WRITE(4270,*) vapor(3),ABS(ATAN(SQRT(vapor(4)**2 +
   vapor(5)**2)/vapor(6))*180/Pi)
   ENDIF

305 Num(1) = 5.0
       Num(2) = RAN3(RN)*Num(1)
       Num(3) = Exp(-Num(2))
       Num(4) = Exp(-1.0)
       IF (Num(3)/Num(4) .LT. RAN3(RN)) GOTO 305
       Poisson = Num(2)

   C This loop (line 310) finds avg. mean free path for
   C vapor along its path of travel, sampling carrier gas
   C conditions TS times along way.
   J = 1
   TotalTime = 0.0

310 IF (J .LE. TS) THEN
   CALL TimeOfFlight(data,PT,vapor,time1,RN,Poisson,
   FM,VM,RandomWalk,Sputter,DVD,J,Za,Zb,bmax)
   time1 = time1/TS
   vapor(1) = vapor(1) + vapor(4)*time1
   vapor(2) = vapor(2) + vapor(5)*time1
   vapor(3) = vapor(3) + vapor(6)*time1
   CALL InOrOut(vapor,vaporposit,data,Loop,J,TS,GPR,GPZ)
   IF (Loop) CALL TimeOfFlight(data,PT,vapor,time2,RN,Poisson,
   FM,VM,RandomWalk,Sputter,DVD,J,Za,Zb,bmax)
   time2 = time2/TS
   Avgtime = (time1 + time2)/2.0
   vapor(1) = vapor(1) - vapor(4)*time1 + vapor(4)*Avgtime
   vapor(2) = vapor(2) - vapor(5)*time1 + vapor(5)*Avgtime
   vapor(3) = vapor(3) - vapor(6)*time1 + vapor(6)*Avgtime
   IF (.NOT. Loop .OR. Z .EQ. 0) J = TS
   CALL InOrOut(vapor,vaporposit,data,Loop,TS,GPR,GPZ)
   TotalTime = TotalTime + AvgTime
   J = J + 1
   GOTO 310
ENDIF
C If vapor atom has not crossed a boundary after traveling 1 avg.
C MFP as determined in previous loop, next loop (line 320) calculates
C velocity of vapor atom after collision with a carrier gas atom.
C First, carrier gas velocity from DSMC code is statistically modified
C to a Maxwell-Boltzmann (normal) type distribution. Velocity
C standard deviation
C equation taken from "Atomic and Molecular Beam Methods"
Appendix D - Atom Tracking Code

320 IF (Loop) THEN
325 IF (RandomWalk .OR. Sputter) THEN
330 vel(1) = 2.24*ThermVel
vel(2) = RAN3(RN)*vel(1)
vel(3) = 4*Pi*((FM/(2*Pi*Boltz*PT(5)))**1.5)*(vel(2)**2)*
       Exp((-FM*vel(2)**2)/(2*Boltz*PT(5)))
vel(4) = 4*Pi*((FM/(2*Pi*Boltz*PT(5)))**1.5)*(ThermVel**2)*
       Exp((-FM*ThermVel**2)/(2*Boltz*PT(5)))
IF (vel(3)/vel(4) .LT. RAN3(RN)) GOTO 330
AvgVel = (CountVel*AvgVel + vel(2))/(CountVel + 1.0)
CountVel = CountVel + 1.0
Write(*,*) AvgVel
WRITE(*,*) ' ' 
334 CONTINUE
ENDIF
C ENDIF ^ goes with IF on line 325.
335 IF (DVD) THEN
C Standard deviation expression comes from second derivative
C of expression used for velocity distribution (Scoles p. 27).
C StndDev = zeros of second deriv.
C IF (ABS(PT(3)) .GE. ABS(PT(2)))
   $ StndDev = ABS(PT(3) - SQRT(-1/(2*C)))
C IF (ABS(PT(3)) .LT. ABS(PT(2)))
   $ StndDev = ABS(PT(2) - SQRT(-1/(2*C)))
DO 340 M = 1,3,1
   PT(M) = vel(2)*Random(M)/TR
   IF (RAN3(RN) .LT. 0.5) PT(M) = -PT(M)
340      CONTINUE
C ENDIF ^ goes with IF on line 335.
C Calculate new vapor atom velocity / direction after collision.
vapor(1) = vaporposit(1)
vapor(2) = vaporposit(2)
vapor(3) = vaporposit(3)
Scatter = .TRUE.
CALL NewVelVector(vapor,PT,TotalTime,RN,CCS,vapor,FM,VM,RandomWalk,Sputter,DVD,Za,Zb,bmax,Scatter)

ENDIF

C ENDIF ^ goes with IF statement on line 320.
Jump = Jump + 1

350 IF (RandomWalk) THEN

C path1 is a measure of how far the atom has traveled since the last collision.
path1 = SQRT((vaporposit(1) - vapor(1))**2 +
(vaporposit(2) - vapor(2))**2 +
(vaporposit(3) - vapor(3))**2)

C path2 is a measure of how far the atom has traveled since time 0.
path2 = SQRT((initial(1) - vapor(1))**2 +
(initial(2) - vapor(2))**2 +
(initial(3) - vapor(3))**2)

D2(Jump) = ((I - 1)*D2(Jump) + path1)/I
D2(Jump+Jumps) = ((I - 1)*D2(Jump+Jumps) + path2)/I
ENDIF

C ENDIF ^ goes with IF on line 350.
IF (Jump .GE. Jumps) Loop = .FALSE.
GOTO 300

380 ENDIF

C ***** END OF LOOP FOR TRACKING ATOM THROUGH FLOW *****

C Next code segment calculates position of vapor atom impact
C onto substrate. First have to calculate if atom makes it to
C substrate or flies out of modeled region.
MagVel = dmax1(dSQRT(vapor(4)**2 + vapor(5)**2),1.d-20)
vcx = vapor(4)/MagVel
vcy = vapor(5)/MagVel
a1 = vcx**2 + vcy**2
b1 = 2*(vapor(1)*vcx + vapor(2)*vcy)
c1 = vapor(1)**2 + vapor(2)**2 - SR**2
Dist = (-b1 + dSQRT(b1**2 - 4*a1*c1))/(2*a1)
IF (a1 .LT. 1.d-20) Dist = SR
Timer = Dist/MagVel
SUB = data(GPZ-1,1,1)
Timez = (SUB - vapor(3))/vapor(6)
C If Timez is less than Timer vapor atom will hit substrate.
IF (Timer .GT. Timez .AND. Timez .GT. 0) THEN
TIME = Timez
Loop = .TRUE.
C Calculate location of vapor atom impact.
vapor(1) = vapor(1) + vapor(4)*TIME
vapor(2) = vapor(2) + vapor(5)*TIME
vapor(3) = vapor(3) + vapor(6)*TIME
ELSE
TIME = Timer
Loop = .FALSE.
ENDIF

10000 FORMAT (1X,F9.6,3X,F9.6,3X,F9.6,3X,F10.3,3X,F10.3,3X,F10.3)

385 IF (Sputter .OR. DVD) THEN

C Counter keeps track of how many vapor atoms reach substrate. This
C is useful later for reading data back in for number crunching and
C for determining efficiency.
Counter = Counter + 1
TotalVel = SQRT(vapor(4)**2 + vapor(5)**2 + vapor(6)**2)
IF (TotalVel.GT. MaxVz) MaxVz = TotalVel

IF (AtomTrack .AND. I .LE. 10) THEN
  WRITE(4268,*) vapor(1),vapor(2),vapor(3)
  VMag = SQRT(vapor(4)**2 + vapor(5)**2 + vapor(6)**2)
  WRITE(4269,*) vapor(3),(0.5*VM*VMag**2)/eV
  WRITE(4270,*) vapor(3),ABS(ATAN(SQRT(vapor(4)**2 + vapor(5)**2)/vapor(6))*180/Pi)
ENDIF
ENDIF
ENDIF

C ENDIF ^ goes with IF on line 385.
PRINT *,I
390 CONTINUE
C ***** END OF MAIN LOOP *****
CLOSE(2)

C ***** Preparation of Output Data *****
C Randomwalk records atom position for r.w. verification
IF (RandomWalk) THEN
  OPEN (1008, FILE='randomwalk')
  DO 395 M=1,Jumps,1
      Total = Total + D2(M)
  WRITE(1008,*) M,D2(M+Jumps)
  395   CONTINUE
  WRITE(1008,*) 'Mean Free Path = ',Total/Jumps
  CLOSE(1008)
ENDIF

397 IF (Sputter .OR. DVD) THEN
  TD = Counter
  Eff = TD/NA
  OPEN(2, FILE='atompath')
  C Read back in x, y, and z location and vx, vy, and vz of vapor atom impact onto substrate.
  READ(2,*')
  DO 400 M=1,Counter,1
     READ(2,*')traject(M,1),traject(M,2),traject(M,3),
     traject(M,4),traject(M,5),traject(M,6)
  400 CONTINUE
  C Write x, y location of deposited atoms.
  450 FORMAT (F9.6,3X,F9.6)
  OPEN(3, FILE='distrib')
  DO 500 M=1,Counter,1
     WRITE(3,450)traject(M,1),traject(M,2)
  500 CONTINUE
  C Calculate the average kinetic energy (AE) of atom hitting substrate.
  TE = 0
  DO 900 M=1,Counter,1
     TV = SQRT(traject(M,4)**2 + traject(M,5)**2 +
     traject(M,6)**2)
     TE = TE + (0.5*VM*TV**2)/eV
     AP = AP + traject(M,2)
     AX = AX + traject(M,1)
     Focus = Focus + SQRT(traject(M,1)**2 + traject(M,2)**2)
  900 CONTINUE
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AE = TE/Counter
AP = AP/Counter
AX = AX/Counter
Focus = Focus/Counter

C Count atoms hitting surface with energies in a range to create an energy density plot.
FMVz = MaxVz/NB DO 1000 M=1,Counter,1
BN = INT(traject(M,6)/FMVz) + 1 VD(BN) = VD(BN) + 1 1000 CONTINUE

1050 FORMAT (F8.6,3X,F6.1) OPEN(5, FILE='veldistr') WRITE(5,1050) 0.0,0 DO 1100 M=1,NB,1 WRITE(5,1050)(0.5*VM*(FMVz*M - FMVz/2)**2)/eV,VD(M) 1100 CONTINUE

C Fraction of the maximum angle (FMA) C Count atoms hitting substrate with angles in a range to create an angle density plot.
FMA = 90./NB DO 1200 M=1,Counter,1
TV = SQRT(traject(M,4)**2 + traject(M,5)**2 + traject(M,6)**2)
Theta = ACOS(traject(M,6)/TV)
TTheta = TTheta + Theta Theta = 180.*Theta/Pi BN = INT(Theta/FMA) + 1 AD(BN) = AD(BN) + 1 1200 CONTINUE

AT = 180.*TTheta/(Counter*Pi)

1250 FORMAT (F5.2,3X,F6.1) OPEN(6, FILE='angldist') WRITE(6,1250) 0.0,0 DO 1300 M=1,NB,1 WRITE(6,1250) FMA*M - FMA/2,AD(M) 1300 CONTINUE CLOSE(6)

OPEN(7, FILE='avgout') WRITE(7,*) 'Energy of atoms leaving crucible = ',EVA,' eV.' WRITE(7,*) 'Deposition Efficiency = ',Eff*100, '%.' WRITE(7,*) 'The average adatom energy = ',AE,' eV.' WRITE(7,*) 'The average angle of impact = ',AT,' degrees.' WRITE(7,*) 'The average vertical position = ',AP,' meters.' WRITE(7,*) 'The average horizontal position = ',AX,' meters.' WRITE(7,*) 'The average atom offset from substrate center = ',Focus,' meters.' $

C Create square 3-D surface plot of deposition onto center of circular substrate.
OPEN(8, FILE='square3d') A = 2*SR*SIN(Pi/4)
BD = A/NBXY DO 1380 M = 1,NBXY,1
DO 1360 P = 1,NBXY,1 profile(M,P,1) = -A/2 + M*BD - BD/2
profile(M,P,2) = - A/2 + P*BD - BD/2
DO 1340 Q = 1,Counter,1
   IF (traject(Q,2) .LE. -A/2 + P*BD .AND.
$   traject(Q,2) .GT. -A/2 + (P-1)*BD .AND.
$   traject(Q,1) .LE. - A/2 + M*BD .AND.
$   traject(Q,1) .GT. - A/2 + (M-1)*BD)
$   profile(M,P,3) = profile(M,P,3) + 1.
1340 CONTINUE
1350 FORMAT (F8.6,3X,F8.6,3X,F9.4)
WRITE(8,1350)profile(M,P,1),profile(M,P,2),profile(M,P,3)
1360 CONTINUE
1380 CONTINUE
END

C ***** SUBROUTINES AND FUNCTIONS *****

SUBROUTINE TimeOfFlight(data,PT,vapor,time,RN,Poisson, $FM,VM,Random,Sputter,DVD,J,Za,Zb,bmax)
DOUBLE PRECISION data(2000,2000,7),PT(5),vapor(6),time,FM,VM
DOUBLE PRECISION RTP(2),Distz,DistR,T1,T2,T3,T4,Poisson
DOUBLE PRECISION Alpha,AMFP,RelVel,dummy(6),CCS,bmax
DOUBLE PRECISION Radial_Position, TempVel
INTEGER J,L,R,Z,RN,Za,Zb
LOGICAL Random, Sputter, DVD, Scatter
PARAMETER(AN=6.0221E23,Rcon=8.3145)

C This subroutine is the heart of the determination of the vapor atom mean free path. It determines where the atom is in the modeled regime, determines what the gas fluid conditions are at that location, and uses that information to determine how far the vapor atom will travel before colliding with a fluid gas atom.

C Change x and y coords to r position, set z = z. Find vapor atom position in axisymmetric flow field r, z space. Understanding this may require some thought!

RTP(1) = vapor(3)
RTP(2) = SQRT(vapor(1)**2 + vapor(2)**2)

C Find closest z, r flowfield grid point just to left and just below current vapor atom position.
Z = 0
R = 0
1400 IF (data(Z+1,1,1) .LE. RTP(1)) THEN
   Z = Z + 1
   GOTO 1400
ENDIF
1500 IF (data(1,R+1,2) .LE. RTP(2)) THEN
   R = R + 1
   GOTO 1500
ENDIF

C Determine carrier gas velocity, pressure, and temperature at current vapor atom location by interpolating data from four nearest grid points. Note: Gridpoints are located at the center point of the DSMC cells.
Distz = (RTP(1) - data(Z,R+1,1))/
       (data(Z+1,R+1,1) - data(Z,R+1,1))
\begin{verbatim}
Distr = (RTP(2) - data(Z+1,R,2))/(data(Z+1,R+1,2) - data(Z+1,R,2))
S
T1 = (1 - Distr)*(1 - Distz)
T2 = (1 - Distr)*Distz
T3 = Distr*(1 - Distz)
T4 = Distr*Distz

DO 1600 L = 1,5,1
PT(L) = T1*data(Z,R,L+2) + T2*data(Z+1,R,L+2) +
T3*data(Z,R+1,L+2) + T4*data(Z+1,R+1,L+2)
S
1600    CONTINUE

IF (R .EQ. 0 .AND. Z .GT. 0) THEN
DO 1610 L = 1,5,1
PT(L) = (1 - Distz)*data(Z,1,L+2) + Distz*data(Z+1,1,L+2)
1610    CONTINUE
ENDIF

IF (Z .EQ. 0 .AND. R .GT. 0) THEN
DO 1620 L = 1,5,1
PT(L) = (1 - Distr)*data(1,R,L+2) + Distr*data(1,R+1,L+2)
1620    CONTINUE
ENDIF

IF (Z .EQ. 0 .AND. R .EQ. 0) THEN
DO 1630 L = 1,5,1
PT(L) = data(1,1,L+2)
1630    CONTINUE
ENDIF

C The following section distributes x and y velocity
C components from original r, z, theta = 0 flow plane to
C actual plane in which vapor atom currently lies.

Radial_Position = SQRT(vapor(1)**2 + vapor(2)**2)
Alpha = ACOS(vapor(1)/Radial_Position)
IF (vapor(2) .LT. 0.0) Alpha = -Alpha
C Alpha varies between -Pi and + Pi.

TempVel = SIN(Alpha)*PT(1) + COS(Alpha)*PT(2)
PT(2) = -COS(Alpha)*PT(1) + SIN(Alpha)*PT(2)
C
PT(1) = TempVel
C
PT(1) = COS(Alpha)*PT(2)
PT(2) = SIN(Alpha)*PT(2)
C
C Determine cross section for directed momentum transfer (CCS)
C based on local fluid / vapor atom conditions.
Scatter = .FALSE.
CALL NewVelVector(vapor,PT,time,RN,CCS,dummy,FM,VM,
$ Random,Sputter,DVD,Za,Zb,bmax,Scatter)
C
C Calculate vapor atom’s avg. mean free path (AMFP) based on carrier
gas conditions along travel path and CCS. Form of equation from:
AMFP = Poisson*Rcon*PT(5)/(SQRT(2.0)*PT(4)*AN*CCS)
C
We must include fluid velocities to get correct time between collisions as
atom moves in flowfield. (Think about this!) The procedure records new atom
position and then checks to make sure atom has not crossed out of modeling
region. If it has crossed substrate boundary, vapor atom position is reset
\end{verbatim}
C to its last position so later portion of code can calculate IF vapor atom impacts substrate.

$$ \text{RelVel} = \sqrt{(vapor(4) - PT(1))^2 + (vapor(5) - PT(2))^2 + (vapor(6) - PT(3))^2} $$

C Time must be calculated to determine new vapor atom position at collision
time based upon current vapor atom velocity vector.
time = AMFP/RelVel
END

SUBROUTINE InOrOut(vapor,vaporposit,data,Loop,J,TS,GPR,GPZ)
DOUBLE PRECISION vapor(6),vaporposit(3),data(2000,2000,7)
INTEGER J, TS, GPR, GPZ
LOGICAL Loop
C This subroutine checks to ensure the vapor atom has not left the
C modeled region.
IF (SQRT(vapor(1)**2 + vapor(2)**2) >
   data(GPZ,GPR,2)) THEN
  vapor(1) = vaporposit(1)
  vapor(2) = vaporposit(2)
  vapor(3) = vaporposit(3)
  Loop = .FALSE.
  J = TS
ENDIF
IF (vapor(3) > data(GPZ-1,GPR,1)) THEN
  vapor(1) = vaporposit(1)
  vapor(2) = vaporposit(2)
  vapor(3) = vaporposit(3)
  Loop = .FALSE.
  J = TS
ENDIF
IF (vapor(3) < 0.0) THEN
  vapor(1) = vaporposit(1)
  vapor(2) = vaporposit(2)
  vapor(3) = vaporposit(3)
  Loop = .FALSE.
  J = TS
ENDIF
END

SUBROUTINE NewVelVector(vapor,PT,time,RN,CCS,Tvapor,
DOUBLE PRECISION vapor(6), PT(5), b, bmax
DOUBLE PRECISION Chi, E, time, LabMag
DOUBLE PRECISION T vapor(6), CCS, RM
DOUBLE PRECISION ipvapor(3), ipPT(3), TVV
DOUBLE PRECISION vrel(3), Tvrel, Lab(3)
DOUBLE PRECISION FM, VM, PositVec(3), VelVec(3)
DOUBLE PRECISION Magvec, Kvec, Ivec, Jvec
DOUBLE PRECISION NI, NJ, NK, Quad(3), RI, RJ, RK
DOUBLE PRECISION MagR, RIvec, RJvec, RKvec, Root
DOUBLE PRECISION RMag, QMag, QIvec, QJvec, QKvec, PV(3)
DOUBLE PRECISION Evapor, Efluid, EnergyBefore, EnergyAfter
DOUBLE PRECISION MoBefore(4),MoAfter(4)
INTEGER D, Za, Zb, RN
LOGICAL RandomWalk, Sputter, DVD, Scatter
PARAMETER (Pi = 3.14159265359, eV = 1.602E-19)
This subroutine is used to determine the vapor atom collision cross-section critical for MFP calculation. It also figures the new velocity vector and speed of the vapor atom after a collision.

See Groves dissertation (Chapter 8) for explanation of following lines which yield new vapor atom velocity vector following collision. Based on Landau and Lifshitz pp.44-45.

Evapor = 0.5*VM*(vapor(4)**2 + vapor(5)**2 + vapor(6)**2)
Efluid = 0.5*FM*(PT(1)**2 + PT(2)**2 + PT(3)**2)
EnergyBefore = Evapor + Efluid
MoBefore(1) = VM*vapor(4) + FM*PT(1)
MoBefore(2) = VM*vapor(5) + FM*PT(2)
MoBefore(3) = VM*vapor(6) + FM*PT(3)
MoBefore(4) = dSQRT(MoBefore(1)**2 + MoBefore(2)**2 + MoBefore(3)**2)

RM = VM*FM/(VM + FM)

vrel(1) = vapor(4) - PT(1)
vrel(2) = vapor(5) - PT(2)
vrel(3) = vapor(6) - PT(3)
Tvrel = SQRT(vrel(1)**2 + vrel(2)**2 + vrel(3)**2)
E = 0.5*RM*Tvrel**2/eV

The following line should be uncommented only if you want to explore diffusion with atoms that have interatomic potentials rather than the elastic sphere assumption made for the basic random walk problem currently simulated. Most basic random walk theory work assumes that collisions are occurring between hard elastic spheres.

bmax for Ar-Ar collisions
IF (RandomWalk) bmax = 5.30 - 1.31*Log10(E)
bmax for Cu-Ar collisions
IF (Sputter) bmax = 5.31 - 1.24*Log10(E)
bmax for Cu-He collisions
IF (DVD) bmax = 7.60 - 1.50*Log10(E)
CCS comes from Groves dissertation Chapter 8.
CCS = Pi*(bmax**2)*1E-20

Solve for vel. magnitude using Conservation of Energy, Momentum.

For the actual collision event choose an impact parameter.
b = bmax*RAN3(RN)
CALL RminNChi(Chi,b,E,Za,Zb)
IF (RandomWalk) Chi = 0.0

Location of vapor atom collision
Tvapor(1) = vapor(1) + vapor(4)*time
Tvapor(2) = vapor(2) + vapor(5)*time
Tvapor(3) = vapor(3) + vapor(6)*time

Atom velocities in CM system
DO 1695 D = 1,3,1
ipvapor(D) = FM*vrel(D)/(FM + VM)
ipPT(D) = -VM*vrel(D)/(FM + VM)
1695 CONTINUE

Velocity vector of center of mass
Lab(1) = (VM*vapor(4) + FM*PT(1))/(FM + VM)
Lab(2) = (VM*vapor(5) + FM*PT(2))/(FM + VM)
Lab(3) = (VM*vapor(6) + FM*PT(3))/(FM + VM)

C

LabMag = SQRT(Lab(1)**2 + Lab(2)**2 + Lab(3)**2)

$\quad TVV = SQRT(ipvapor(1)**2 + ipvapor(2)**2 + ipvapor(3)**2)$

C

Unit vector of center of mass velocity vector
C

RI = ipvapor(2)*NK - NJ*ipvapor(3)
RJ = ipvapor(3)*NI - NK*ipvapor(1)
RK = ipvapor(1)*NJ - NI*ipvapor(2)

C

MagR = SQRT(RI**2 + RJ**2 + RK**2)

C Unit vector in vapor atom direction after collision
C

RIvec = RI/MagR
RJvec = RJ/MagR
RKvec = RK/MagR

1697

RIvec = RAN3(RN)

IF (RAN3(RN) .LT. 0.5) RIvec = -RIvec

Quad(1) = 1 + ipvapor(2)**2/ipvapor(3)**2
Quad(2) = 2*ipvapor(1)*ipvapor(2)*RIvec/

$\quad ipvapor(3)**2$

Quad(3) = RIvec**2 + (ipvapor(1)*RIvec/

$\quad ipvapor(3))**2 - 1$

Root = Quad(2)**2 - 4*Quad(1)*Quad(3)

IF (Root .LT. 0.0) GOTO 1697

IF (RAN3(RN) .LT. 0.5) THEN

RJvec = (-Quad(2) + dSQRT(Root))/(2*Quad(1))
ELSE

RJvec = (-Quad(2) - dSQRT(Root))/(2*Quad(1))
ENDIF

RKvec = -(ipvapor(1)*RIvec + ipvapor(2)*RJvec)/

$\quad ipvapor(3)$

C

WRITE(*,*) 'ip',ipvapor(1),ipvapor(2),ipvapor(3)
C

WRITE(*,*) 'quad',Quad(1),Quad(2),Quad(3)
C

WRITE(*,*) 'root',Quad(2)**2 - 4*Quad(1)*Quad(3)
C

WRITE(*,*) 'Rvec',RIvec, RJvec, RKvec
C

WRITE(*,*) dSQRT(RIvec**2 + RJvec**2 + RKvec**2)
C

WRITE(*,*) RIvec*ipvapor(1) + RJvec*ipvapor(2) +

$\quad RKvec*ipvapor(3)$

C

PAUSE

QMag = TVV*COS(Chi)
IF (RandomWalk) QMag = -QMag
RMag = TVV*SIN(Chi)

C

Unit vector in vapor atom direction before collision
C

QIvec = ipvapor(1)/TVV
QJvec = ipvapor(2)/TVV
QKvec = ipvapor(3)/TVV

Ivec = QMag*QIvec + RMag*RIvec
Jvec = QMag*QJvec + RMag*RJvec
Kvec = QMag*QKvec + RMag*RKvec

Magvec = SQRT(Ivec**2 + Jvec**2 + Kvec**2)
Ivec = Ivec/Magvec
Jvec = Jvec/Magvec
Kvec = Kvec/Magvec

Tvapor(4) = FM*Tvrel*Ivec/(FM + VM)
Tvapor(5) = FM*Tvrel*Jvec/(FM + VM)
Tvapor(6) = FM*Tvrel*Kvec/(FM + VM)

PV(1) = -VM*Tvrel*Ivec/(FM + VM) + Lab(1)
PV(2) = -VM*Tvrel*Jvec/(FM + VM) + Lab(2)
PV(3) = -VM*Tvrel*Kvec/(FM + VM) + Lab(3)

Tvapor(4) = Tvapor(4) + Lab(1)
Tvapor(5) = Tvapor(5) + Lab(2)
Tvapor(6) = Tvapor(6) + Lab(3)

Evapor = 0.5*VM*(Tvapor(4)**2 + Tvapor(5)**2 + Tvapor(6)**2) +
Efluid = 0.5*FM*(PV(1)**2 + PV(2)**2 + PV(3)**2)
EnergyAfter = Evapor + Efluid
MoAfter(1) = VM*Tvapor(4) + FM*PV(1)
MoAfter(2) = VM*Tvapor(5) + FM*PV(2)
MoAfter(3) = VM*Tvapor(6) + FM*PV(3)
MoAfter(4) = dSQRT(MoAfter(1)**2 +
&D MoAfter(2)**2 + MoAfter(3)**2)

WRITE(*,*) 'A',EnergyAfter/eV,MoAfter(4)
PAUSE

ENDIF  
C ENDIF ^ goes with IF on line 1690
END

SUBROUTINE RminNChi(Chi,b,E,Za,Zb)
DOUBLE PRECISION b, Chi, DR, E, F, FMID, G
DOUBLE PRECISION Gtemp, PTL, RMID, Rmin, TG, x
INTEGER H, Za, Zb
PARAMETER(TOP = 15.0D0,BOTTOM = 0.5D0,ACC=0.0001,
$ HMax = 40, Pi = 3.14159265359, eVeV = 1, M = 10)

FMID = FUNC(TOP,b,E,Za,Zb)
F = FUNC(BOTTOM,b,E,Za,Zb)

IF (F .LT. 0.0) THEN
Rmin = BOTTOM
DR = TOP - BOTTOM
ELSE
Rmin = TOP
DR = BOTTOM - TOP
ENDIF
DO 1700 H = 1,HMAX,1
  DR = DR*0.5
  RMID = RMIN + DR
  FMID = FUNC(RMID,b,E,Za,Zb)

  IF (FMID .LE. 0.0) Rmin = RMID
  IF (ABS(DR) .LT. ACC .OR. FMID .EQ. 0.0) GO TO 1800

1700    CONTINUE
C Use quadrature scheme to solve for center of mass (CM) deflection function
C for a reduced-mass particle.  See Johnson, 1990, p. 69.
C TG is just the total G summed below.
1800    TG = 0.0
  DO 1900 H = 1,M
    x = COS((2*H - 1)*Pi/(4*M))
    PTL = Za*Zb*(eVeV**2)*Phi(Rmin/x,Za,Zb)/(Rmin/x)
  C IF included below b/c very occasionally the denominator goes slightly
  C negative.  Code is correct, just numerical rounding
  C errors I believe. Error occurs once every 1000 - 4000 atoms.
    G = (b/Rmin)*SQRT((1-x**2)/(1-(b*x/Rmin)**2 - PTL/E))
    Gtemp = (1-x**2)/(1-(b*x/Rmin)**2 - PTL/E)
    IF (Gtemp .LT. 0.0) G = 0.0
    TG = TG + G
  1900    CONTINUE
  Chi = Pi*(1 - TG/M)
END
FUNCTION Phi(S,Za,Zb)
  DOUBLE PRECISION S, au
  INTEGER Za, Zb
  PARAMETER(ao = 0.529)
  C    ao = 0.529 Angstroms - the Bohr radius
  C
  au = 0.8854*ao/(Za**0.23 + Zb**0.23)
  Phi = 0.1818*EXP(-3.2*S/au) + 0.5099*EXP(-0.9423*S/au) +
    0.2802*EXP(-0.4029*S/au) + 0.02817*EXP(-0.2016*S/au)
END
FUNCTION FUNC(S,b,E,Za,Zb)
  DOUBLE PRECISION b,E,S,PTL
  INTEGER Za, Zb
  PARAMETER(eVeV = 1)
  C    Interatomic potential (PTL) is Universal Potential of Ziegler
  C
  PTL = Za*Zb*(eVeV**2)*Phi(S,Za,Zb)/S
  C  For FUNC see Robinson p.187, L&L p.49.
  C
  FUNC = (b/S)**2 + 2*PTL/E - 1
END
FUNCTION RANDN(RN)
C The function RANDN() returns a normally distributed pseudo-random
C number with zero mean and unit variance. The program uses the
C uniformly distributed random numbers of the interval (0,1), already
C generated, to create the Gaussian distribution.
C The algorithm uses the ratio of uniforms method of A. J. Kinderman
C and J. F. Monahan augmented with quadratic bounding curves.
The function was obtained from http://www.netlib.org/toms/712

DATA V5,V6,V7,V8 / 0.449871, -0.386595, 0.19600, 0.25472/
DATA R1,R2/ 0.27597, 0.27846/
DOUBLE PRECISION RN
REAL V1,V2,V3,V4,V9

C Generate P = (V1,V2) uniform in rectangle enclosing acceptance region

2000 V1 = RAN3(RN)
V2 = RAN3(RN)
V2 = 1.7156*(V2 - 0.5)

C Evaluate the quadratic form

V3 = V1 - V5
V4 = ABS(V2) - V6
V9 = V3**2 + V4*(V7*V4 - V8*V3)

C Accept P if inside inner ellipse
IF (V9 .LT. R1) GO TO 2100

C Reject P if outside outer ellipse
IF (V9 .GT. R2) GO TO 2000

C Reject P if outside acceptance region
IF (V2**2 .GT. -4.0*ALOG(V1)*V1**2) GO TO 2000

C Return ratio of P's coordinates as the normal deviate.

2100 RANDN = V2/V1
END

FUNCTION RAN3(IDUM)
C Returns a uniform random deviate between 0.0 and 1.0. Set IDUM to any
C negative value to initialize or reinitialize a sequence.
PARAMETER (MBIG=1000000000,MSEED=161803398,MZ=0,FAC=1./MBIG)
C According to Knuth, any large MBIG, and any smaller (but still large) MSEED
C can be substituted for the above values.
C The value used in MA below is special and should not be modified.
DIMENSION MA(55)
DATA IFF /0/

2150 IF (IDUM .LT. 0 .OR. IFF .EQ. 0) THEN
IFF = 1
MJ = MSEED - IABS(IDUM)
MJ = MOD(MJ,MBIG)
MA(55) = MJ
MK = 1
DO 2200 I=1,54,1
II = MOD(21*I,55)
MA(II) = MK
MK = MJ - MK
IF (MK .LT. MZ) MK = MK + MBIG
MJ = MA(II)
2200 CONTINUE
DO 2400 K = 1,4,1
DO 2300 I = 1,55,1
MA(I) = MA(I) - MA(1 + MOD(I + 30,55))
IF (MA(I) .LT. MZ) MA(I) = MA(I) + MBIG
2300 CONTINUE
2400 CONTINUE
INEXT = 0
INEXTP = 31
IDUM = 1
ENDIF
INEXT = INEXT + 1
IF (INEXT .EQ. 56) INEXT = 1
INEXTP = INEXTP + 1
IF (INEXTP .EQ. 56) INEXTP = 1
MJ = MA(INEXT) - MA(INEXTP)
IF (MJ .LT. MZ) MJ = MJ + MBIG
MA(INEXT) = MJ
IF (MJ*FAC .GT. 1.0) GOTO 2150
IF (MJ*FAC .LT. 0.0) GOTO 2150
RAN3 = MJ*FAC
RETURN
END
Appendix E - E-beam Vapor Distribution

During a visit to 3M Corporation’s Metal Matrix Composites Program Division (Eden Prairie, MN), thickness profile measurements were taken of a high-vacuum e-beam source’s Ti-6(wt%)Al-4(wt%)V vapor density distribution. Evaporant was produced in a high vacuum chamber (pressure ~1x10^{-5} Torr) by a 90° 25 kW/25 kV e-gun (Leybold-Heraeus). The deposits were made on a plate parallel to the evaporant surface and 33 cm above it. The 4.92 cm diameter vapor source, contained in a water-cooled crucible, was scanned by a 0.635 mm diameter beam to a radius of 1.90 cm. Table E.1 shows deposit thickness data taken from the substrate. Fig. E.1 and E.2 show the deposit thickness profile across the plate. Note that the deposit is not completely symmetric about the point taken to be directly above the center of the evaporant (data point 33).

Given the deposit’s lack of symmetry and the narrow width of the plate, only data points with y = 5.1 cm were used to determine the dependence of deposit thickness upon position. To find the exponent of equation (2.2) Schiller [11] gives an equation (equation (2.3)) for relative film thickness d_s/d_{so} on a plane parallel to a vapor emitting source as a function of r_s/h_v and the exponent n. Analysis of data points with x ≤ 14.0 cm revealed that their interpolation function most closely fit a distribution with n = 4.5. Similar analysis of data points with x ≥ 14.0 cm revealed a close fit to the distribution with n = 5.0.
### Table E.1: Deposited vapor thickness versus location

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<tr>
<th>point</th>
<th>x (m)</th>
<th>y (m)</th>
<th>thickness (m)</th>
<th>point</th>
<th>x (m)</th>
<th>y (m)</th>
<th>thickness (m)</th>
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<td>0.000</td>
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<td>0.074</td>
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<td>0.099</td>
<td>0.0076</td>
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Figure E.1  **Distribution of Ti-6-4 on substrate located directly above evaporant.**

Figure E.2  **Ti-6-4 distribution on substrate directly above evaporant.**