Discussion of some “trap signatures” observed by admittance spectroscopy in CdTe thin-film solar cells

Jian V. Li, Steve W. Johnston, Xiaonan Li, David S. Albin, Timothy A. Gessert, and Dean H. Levi

Citation: Journal of Applied Physics 108, 064501 (2010); doi: 10.1063/1.3475373
View online: http://dx.doi.org/10.1063/1.3475373
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/108/6?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Impedance spectroscopy of thin-film CdTe/CdS solar cells under varied illumination

Hole current impedance and electron current enhancement by back-contact barriers in CdTe thin film solar cells
J. Appl. Phys. 100, 124505 (2006); 10.1063/1.2400799

Simulated admittance spectroscopy measurements of high concentration deep level defects in CdTe thin-film solar cells
J. Appl. Phys. 100, 033710 (2006); 10.1063/1.2220491

Nonlinear shunt paths in thin-film CdTe solar cells
J. Appl. Phys. 97, 054503 (2005); 10.1063/1.1856216

All-sputtered 14 % CdS/CdTe thin-film solar cell with ZnO : Al transparent conducting oxide
Discussion of some “trap signatures” observed by admittance spectroscopy in CdTe thin-film solar cells

Jian V. Li, Steve W. Johnston, Xiaonan Li, David S. Albin, Timothy A. Gessert, and Dean H. Levi
National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, Colorado 80401, USA

(Received 26 April 2010; accepted 8 July 2010; published online 16 September 2010)

Considerable ambiguity and controversy exist concerning the defect signatures (H1, H2, and H3) frequently observed in admittance spectroscopy of thin-film CdTe solar cells. We prove that the commonly labeled H1 defects, observed in all devices in this study, are actually due to the freeze-out of the majority carriers in the neutral CdTe absorber. This freeze-out is evident in the temperature dependencies of capacitance, carrier concentration, and depletion region width. Contrary to intuitive expectation, the activation energy of freeze-out is less than, not identical to, that of the conductivity. In some other cases, H2 or H3 are observed and attributed to the back-contact potential barrier, rather than to the carrier emission from the traps. We extract the back-contact barrier height from the activation energy of the saturation current determined from the temperature-dependent current-voltage curves using the back-to-back diode model. The back-contact barrier height agrees well with the H2 or H3 energy determined by admittance spectroscopy. We present a more comprehensive and realistic equivalent circuit that includes the admittances from both the back-contact and the neutral absorber. © 2010 American Institute of Physics. [doi:10.1063/1.3475373]

I. INTRODUCTION

Cadmium telluride (CdTe) is an important material for thin-film solar cells. The efficiency of CdTe thin-film solar cells is believed to be limited, in part, by defect-related recombination. There has been extensive research on defects in CdTe to identify their physicochemical origins (see Refs. 2 and 3 for theoretical and experimental reviews, respectively). The findings of defects vary as a result of differences in crystallinity, impurity, and device processing; therefore, the scope of this study is narrowed to p-type polycrystalline CdTe thin film only. The reported4–11 activation energies of majority-carrier traps in p-type polycrystalline CdTe generally fall within three ranges: 110–180 meV,4–6,8,11 220–370 meV,5,8–11 and 430–560 meV,4,6–11 which we label as H1, H2, and H3, respectively, following Seymour et al.5 Despite the significant data reported, major ambiguity and controversy remain concerning the origin of these defect signatures observed in capacitance spectroscopy. For example, although the H1 trap has generally4–6,8,11 been attributed to the $V_{\text{Cd}}^{2-} + \text{Cl}^{-}$ complex, it has also been hypothesized that it is due to $2\text{Cu}_{\text{Cd}}^{+} - \text{Te}^{2-}$ or to carrier freeze-out.11 Rather than pinpointing the chemical origin, this work attempts to clear some ambiguities concerning trap origin from the perspective of device physics.

Capacitance techniques—in particular, admittance spectroscopy—are the major tools for studying defects in thin-film solar cells.12 Admittance spectroscopy inspects the current response to an alternating current (ac) voltage modulation for carrier emission signified by transitions in the frequency and temperature dependence of the admittance. In an ideal single-junction device, it is possible to extract trap parameters such as activation energy, pre-exponential factor, and trap density of states. Other charge-storage and conduction phenomena such as dielectric relaxation and band discontinuity can—and inevitably will—show up as a signature by admittance spectroscopy as long as they also depend on frequency and temperature. Unfortunately, some of these false trap signatures are indistinguishable from those of real traps if one inspects only admittance spectroscopy data. This work employs coordinated experiments—namely, capacitance-voltage and current-voltage characterizations—to elucidate certain mechanisms common to practical CdTe thin-film solar cells, specifically those due to majority-carrier freeze-out and the presence of a second junction, to avoid possible misinterpretation of trap signatures.

II. EXPERIMENT

The thin-film CdTe solar cells were fabricated with nominally the same procedure as described in Ref. 13. First, a layer of transparent conductive oxide was grown on the glass substrate. Then, a layer of CdS was grown using chemical-bath deposition, followed by the growth of the CdTe thin film (~8 μm) with close-spaced sublimation. Nominally identical Cl treatment was applied to all the samples. Up to this point, all samples were fabricated identically; the difference is in the next two processing steps that form the back contact. The standard procedure calls for an etching step in nitric-phosphoric acid, followed by applying a graphite paste back-contact layer containing Cu. To vary the electrically active CdTe film thickness, we used three different conditions: (1) with Cu after nitric-phosphoric acid, labeled Cu/NP, (2) without Cu after nitric-phosphoric acid,
FIG. 1. The differential capacitance spectra for all the three types of devices and the raw capacitance data taken at 2 kHz from the Cu/NP device plotted against temperature (a) and the Arrhenius plots (b) for the “trap signatures” observed by admittance spectroscopy. Three groups, labeled H1, H2, and H3, are clearly identifiable, the parameters of which are consistent with previous reports.

labeled X/NP, and (3) neither Cu nor nitric-phosphoric etch, labeled X/X. Except for the back-contact formation process, all devices are nominally identical.

We conducted the admittance spectroscopy measurement using an Agilent 4194A impedance analyzer. The direct current bias of the device was fixed at zero unless otherwise mentioned. The ac modulation amplitude was 35 mVrms. We swept the frequency from 1 kHz to 1 MHz and varied the temperature from 350 to 70 K.

III. RESULTS

Figure 1(a) shows the differential capacitance spectra from all three types of devices and the raw capacitance for the Cu/NP device, all plotted against the temperature. The negative peaks in the differential capacitance spectrum correspond to the step transition points in the capacitance-temperature curve [e.g., see data from the Cu/NP device in Fig. 1(a)]. The Arrhenius plots (peak frequencies in the differential capacitance spectrum plotted against inverse temperature) are used to extract the activation energies: H1 (181 ± 15 meV) and H3 (494 ± 9 meV) in the X/NP device; H1 (134 ± 3 meV), H2 (332 ± 36 meV), and H3 (504 ± 41 meV) in the Cu/NP device; and H1 (114 ± 5 meV) plus a deeper trap (177 ± 23 meV) in the X/X device. All the trap parameters compare well with previous reports (e.g., Table I of Seymour et al.), except for those of the deeper trap signature in the X/X device.

However, when we look carefully at the temperature dependencies of the capacitance, as well as those of the hole concentration and depletion width (data taken from the X/NP device are shown in Fig. 2 as an example), it becomes clear that H1 corresponds to the majority-carrier freeze-out effect. The C(T) curve measured at 2 kHz exhibits a sharp drop as temperature decreases below 100 K. This step transition is usually used to identify H1. At the same time, W jumps from 3.6 to 5.8 μm, with the latter number corresponding to the effective thickness of CdTe thin film after NP etching. The carrier concentration N0L measured by the standard capacitance-voltage method and contributed by both shallow and deep levels, exhibits a sharp increase by more than one order of magnitude, which is a tell-tale sign that the entire CdTe thin film is depleted at this frequency. After the temperature drops below the freeze-out temperature, the depletion region effectively extends from CdS, across the entire CdTe film, to the high-conductivity material [Te (Ref. 14) in the case of the X/NP device] at the back contact or at the bottom of the grain boundary created by NP etching. The bottom of the grain boundary could extend a few microns deep from the back contact and accounts for the difference between the original CdTe film thickness (∼8 μm) and the measured depletion width after freeze-out (e.g., 5.8 μm in the case of the X/NP device). Although the transition temperature and the high-conductivity material near the back contact [graphite paste and Cu5Te (Ref. 13) for X/X and Cu/NP devices, respectively] vary, the same freeze-out phenomenon is consistently seen for all three type of devices. Incidentally, one of the earliest CdTe defect study by Isett11 considered the freeze-out effect but did not provide experimental evidence. Earlier, Lang et al.15 also looked at freeze-out in amorphous silicon devices.

The activation energy determined from the freeze-out transition by the conventional admittance spectroscopy has been interpreted15 as identical to the activation energy of the conductivity. We show below that this is not strictly true. Instead, the activation energy of freeze-out is less than that of the conductivity. The inflection frequency in the differential capacitance spectrum that characterizes the freeze-out transition at zero-bias assumes the following expression:16
\[ \omega_p = \frac{C_g \sigma}{C_d \varepsilon} = \frac{W \sigma}{\varepsilon} = \sqrt{\frac{2V_{bi}}{q\varepsilon^2 N_n^{1/2}}} \, , \]

where the depletion capacitance \( C_d = \varepsilon / W \), the geometrical capacitance \( C_g = \varepsilon / t \), and the depletion width \( W = \sqrt{2(\varepsilon / q) N_n} V_{bi} \), \( \varepsilon \) is the permittivity, \( q \) is the electron charge, \( N_n \) is the hole density, \( V_{bi} \) is the built-in voltage, and \( \sigma \) is the conductivity of the CdTe thin film. Neglecting the slow-varying parameters with respect to temperature, one sees that \( \omega_p \propto \sigma \sqrt{N_n} \propto \sigma / e^{(E_F-E_V)/kT} \), where \( E_F \) is the Fermi energy and \( E_V \) is the valence band edge. Therefore, \( E_p = E_v - (E_F-E_V)/2 \), where \( E_p \) is the activation energy of the conductivity for that temperature range. The activation energies of freeze-out and conductivity differ by half the Fermi energy. Alternatively, since \( \sigma = q \mu N_n \), where \( \mu \) is the hole mobility, another expression of the inflection frequency is \( \omega_p \propto \mu \sqrt{N_n} \propto \mu e^{(E_F-E_V)/kT} \). That is, \( E_p = E_v + (E_F-E_V)/2 \), where \( E_v \) is the activation energy of hole mobility for that temperature range, if applicable. There have been reports\(^{17-19}\) of decreasing hole mobility with decreasing temperature in single-crystal CdTe. Both Ottaviani \textit{et al.}\(^{17}\) and Suzuki \textit{et al.}\(^{19}\) conjectured a trap-limited mechanism with an activation energy of 0.14 eV. It is possible that the hole mobility in this study may obey similar thermal activation mechanism. An independent investigation of the mechanisms dominating the temperature dependence of mobility is necessary for accurate determination of \( E_F \), although it is beyond the scope of this study.

**IV. DISCUSSIONS**

We now look at the effect due to a back-contact potential barrier. According to Niemegeers \textit{et al.}\(^{20}\) and Eisenbarth \textit{et al.}\(^{21}\) the back-contact barrier introduces a characteristic frequency that is proportional to the conductance of the back-contact \( G_c \)

\[ \omega_c = \frac{G_c + G_d}{C_c + C_d} \, , \]

where \( G_c \) and \( C_c \) are the conductance and capacitance due to the back contact, respectively. \( G_c \) is usually much larger than \( G_d \). In the thermionic emission regime, \( G_c \) is proportional to the saturation current density: \( G_c = \frac{dJ}{dV(V=0)} = qJ_0/kT = A^* q/kT \exp(-q\phi_B/kT) \), where \( A^* \) is the effective Richardson constant.\(^{22}\) This characteristic frequency is observed in the admittance spectroscopy experiment and can be confused as a trap signature whose activation energy is just the barrier height of the back contact. Unlike the freeze-out phenomenon, there is no simple and direct experiment to prove that the back contact is producing “trap” signatures in admittance spectroscopy measurements. Eisenbarth \textit{et al.}\(^{21}\) resorted to theoretical simulation for indirect evidence that the “trap” signatures they observed were indeed due to the back-contact potential barrier. In this work, we seek experimental support from the temperature dependence of the current-voltage characteristics measured by a semiconductor parameter analyzer HP4140B.

We use the back-to-back diode model to extract a back-contact barrier height to compare with the activation energy determined from admittance spectroscopy. This method was first developed by Stollwerck and Sites.\(^{23}\) Essentially, one looks for the rollover feature on the current-voltage curve at a specific temperature [Fig. 3(a)] where it drops off from the projected current level of the forward-biased main diode (n\textsuperscript{+}-CdS/p-CdTe in this case) due to the current-limiting effect by the reverse-biased back contact. The intercept point of the prerollover and postrollover slopes provides a good approximation of the saturation current density of the back contact at that temperature \( J_0 = A^* T^2 \exp(-q\phi_B/kT) \). The Arrhenius plot of \( J_0(T)/T^2 \) then yields the barrier height of the back contact \( \phi_B \), assuming a thermionic emission mechanism. Data presented in Fig. 3(b) show that the back-contact barrier height determined using from the current-voltage data for the X/NP sample is 552 ± 10 meV. This is in good agreement with the activation energy (494 ± 9 meV) of the H3 trap determined by admittance spectroscopy [Eq. (2)] in the same device, after taking into account \((E_F-E_V)/2\), which characterizes the activation energy of the \( C_c + C_d \) term. The effective Richardson coefficient of the Schottky contact, assuming the thermionic emission model, is 90 A/cm\textsuperscript{2}/K\textsuperscript{2}. This yields an effective hole mass of 0.8 times the free-electron mass, which is close to expectation and justifies the use of the thermionic emission model. The barrier height of 552 meV is also consistent with valence-band discontinuity at the Te/CdTe interface determined by photoelectron spectroscopy.\(^{24}\) We are, therefore, confident that the H3 observed in our X/NP sample is actually due to the back contact and its activation energy to the barrier height.
The back-contact barrier height extracted from the X/X device is 223 ± 17 meV, which agrees with the activation energy 177 ± 23 meV of H2 extracted from the admittance spectroscopy and provides additional support to the conjecture above. The effective Richardson coefficient of the X/X device is much lower than the ideal Schottky contact under the thermionic emission model. A thick layer of native oxide is known to exist at the unetched CdTe surface of the X/X device; therefore, it is not surprising to see the failure of the ideal thermionic emission model. Instead, a tunneling model or a more detailed metal-insulator-semiconductor model should be used to explain the current-voltage characteristics. The Cu/NP device exhibits a back-contact barrier height of 267 ± 13 meV, probably benefiting from the formation of CuTe alloy for lowering the barrier height. Still, a tunneling mechanism must be adopted to explain the low saturation current. It is worth noting that \( J_0 \) for the back contact in the Cu/NP sample is noticeably higher than that of the X/X sample, although the barrier heights are comparable, which is desirable for suppressing the back-contact influence to the device performance. The barrier height of the Cu/NP device does not match very well the activation energies of either H2 or H3. We notice that the admittance spectroscopy data for the Cu/NP sample shows a broad feature (H3) with activation \(~0.5\) eV that is most likely due to Cu-related deep levels. These trap signatures outweigh the H2 feature, which could be due to the back-barrier height, and make its energy (332 ± 36 meV) unreliable to extract.

To include the influence from both the back contact and the neutral absorber, we present the more comprehensive and realistic equivalent circuit for CdTe thin-film solar cells in Fig. 4. It consists of three complex admittance connected in series: \( C_d \) from the depletion region, \( C_b \) and \( G_b \) from the neutral region, and \( C_c \) and \( G_c \) from the back contact. Here, \( C_b = \varepsilon / (t - W) \) and \( G_b = \sigma (t - W) \). The conductance of the depletion region is omitted because it does not meaningfully affect the overall admittance. The complete formulation of admittance and its frequency and temperature dependency are rather intensive algebraically. We instead identify two practical scenarios that are tractable by simple analysis. In the first scenario, the frequency is sufficiently high (or temperature sufficiently low) that the neutral CdTe region is in the freeze-out regime, and we can then effectively neglect the back contact. In the second scenario, the frequency is sufficiently lower than the freeze-out frequency, so the capacitance of the neutral CdTe region can then be effectively neglected; the remaining conductance is counted as part of the total series resistance. In these two respective scenarios, we identified features in admittance spectroscopy measurements that could be mistaken as trap signatures from H1, and H2 or H3.

V. CONCLUSIONS

To conclude, we used capacitance-voltage profiling to prove that the so-called H1 trap signature seen by admittance spectroscopy in all the CdTe thin-film solar cells in this study is actually due to majority-carrier freeze-out in the neutral CdTe absorber. The freeze-out activation energy extracted by traditional admittance spectroscopy differs from that of the conductivity and indeed consists of the thermal activation of holes and their mobility. We also applied the back-to-back diode model to extract the saturation current of the back-contact junction from the temperature-dependent current-voltage curves and derive the back-contact barrier height from the activation energy of the saturation current, which agrees well with the activation energy of some of the H2 or H3 signatures from admittance spectroscopy. Thin-film CdTe materials have low intrinsic doping and are difficult to form ohmic contacts with; thus, the freeze-out and back-contact effects are expected to be somewhat ubiquitous to devices fabricated in both laboratory and industry. We, therefore, suggest pursuing a defect study on CdTe thin-film solar cells by capacitance techniques to use the coordinated characterizations described here, to rule out the possibility of misidentifying related false-trap signatures. To that effect, the more realistic equivalent circuit we present here, which consists of three complex admittances connected in series, includes both the back-contact and neutral-absorber effects and may prove a practical and accurate tool for such study.

ACKNOWLEDGMENTS

The authors are grateful for insightful discussions with Dr. Yanfa Yan at the National Renewable Energy Laboratory, Dr. Jennifer Heath at Linfield College, and Dr. Oleg Sulima at GE Global Research. This research is supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308.

---

8. V. Komine, V. Viswanathan, B. Tetal, D. L. Morel, and C. S. Ferekides, Proceedings of the 29th IEEE Photovoltaics Specialists Conference, New...