High dose carbon implantation in nickel

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The diffusion of ion-implanted carbon in single crystal and polycrystalline nickel has been investigated. 400 keV high dose ($8 \times 10^{17}$/cm$^2$) carbon ions were implanted into nickel samples, followed by annealing in flowing Ar gas at temperatures ranging from 300 to 1010°C. The diffusion of carbon atoms was studied using Rutherford backscattering spectrometry (RBS) and non-Rutherford proton elastic scattering combined with the channeling technique. In the case of single crystal nickel, segregation occurred at 400°C and significant carbon diffusion was observed at 600°C. After long-term annealing at 850°C/4 h plus 470°C/4 h, no measurable carbon remained in the implanted layer. For polycrystalline nickel, the segregation of the implanted carbon also occurred at 400°C. All of the implanted carbon was diffused out of the implanted layer at 650°C.

1. Introduction

Chemical vapor deposition (CVD) processes can produce crystalline diamond films only on single crystal diamond or c-BN substrates. The high cost and small size of single crystal diamond and c-BN almost exclude their possible large scale use as substrates. Recent reports [1–3] indicate that heteroepitaxial growth of single crystalline diamond on copper substrate is possible by implanting carbon ions into a heated copper substrate [1,2], or applying laser annealing after carbon implantation (room temperature implantation) [3]. Therefore these reports have attracted worldwide attention. However, the follow-up experiments in several laboratories failed to reproduce these results [4–8]. The ideas proposed in refs. [1–3] were also tested on nickel substrates [4]. The results were negative; no diamond was formed. Based on these reports, we became interested in studying the diffusion of implanted carbon in nickel. We report our preliminary study on the diffusion of deep-implanted carbon atoms in single- and polycrystalline nickel. Very little has been published on carbon implantation in nickel [9].

2. Experimental details

400 keV carbon ions, generated from a tandem accelerator at Texas Center for Superconductivity at the University of Houston, were implanted into nickel samples with doses of $8 \times 10^{17}$ C$^+$/cm$^2$. TRIM calculation [10] shows that the average range of 400 keV carbon ions in nickel is about 400 nm with straggling of 120 nm. Carbon beam current was limited to less than 0.9 μA. Beam spot is 5 mm in diameter. To limit the beam heating effect and to suppress possible diffusion of the carbon atoms during implantation, the nickel samples were mounted on a cold head which was cooled to liquid nitrogen temperature. The sample used was commercial high-purity single crystal nickel disc with (111) orientation and polycrystalline nickel foil. The quality of the single crystal nickel disc was not quite satisfactory since the channeling minimum yield near surface, $\chi_{\text{min}}$, is about 19%. The diffusion behavior of carbon atoms in such an imperfect single crystal will be different from that in perfect single crystal. Therefore the results obtained with such sample should only apply to those nickel crystals which have high density of defects. It is not easy to grow high quality nickel crystals. Most commercial nickel crystals are highly defective.

After carbon ion implantation, the nickel samples were annealed in flowing Ar gas in a furnace. The nickel foil sample was annealed sequentially in six temperature steps: 300, 400, 500, 550, 600 and 650°C. Each step took 30 min. The single crystal nickel sample was annealed in seven temperature steps: 300, 400, 500 and 600°C/30 min, 850°C/10 s, 1010°C/20 s and 800°C/4 h + 470°C/4 h. 2–2.5 MeV He ions RBS-channeling measurement and 1.5 MeV proton elastic scattering measurement were carried out after each annealing step to observe the movement of the implanted carbon atoms.

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3. Results and discussions

3.1. Carbon ion implantation in polycrystalline nickel foil

Fig. 1 shows the 2.5 MeV He ion RBS spectra for the nickel foil taken after each of the six annealing steps. A RBS spectrum for the as-implanted sample is included in fig. 1a for comparison. For clarification, instead of overlapping all the normalized spectra, the spectra for the annealed sample were moved up by adding 3750 counts to each channel of the spectrum. So, in fig. 1a, the vertical scale is only true for the spectrum of the as-implanted sample. It can be seen that each spectrum (except 650°C) has a dip centered at about 420 nm below the surface. This is due to the presence of a high concentration of implanted carbon atoms in this region which dilutes the nickel concentration, thus causing the number of the He ions backscattered from nickel to drop. Therefore, the center position and the shape of the dip reflect the carbon profile in nickel. Due to the insensitivity of the conventional He ion RBS measurement to light elements [11], the RBS signals of He ions backscattered from carbon atoms in the nickel sample are not visible. Proton elastic scattering is more sensitive to carbon because its scattering cross section is several times larger than the Rutherford cross section [12]. Thus, 1.5 MeV proton scattering measurements were carried out in this study to directly monitor the movement of the carbon in the nickel sample.

Since the shape and the area of the dip in 300°C spectrum is essentially the same as the dip in the as-implanted spectrum, annealing at 300°C did not induce measurable diffusion of the carbon atoms in the nickel foil. The dip in the 400°C spectrum is narrower than the dip in the 300°C spectrum, but the area of these two dips are essentially the same, indicating that carbon segregation occurred at this temperature. Upon annealing at 600°C, the dip becomes much smaller, indicating that a significant portion of the carbon has diffused away from the implanted region. Further annealing at 650°C causes all of the carbon to diffuse away and the dip to disappear.

Details of the carbon diffusion are shown more clearly in fig. 1b, in which only the dip portions of the spectra are displayed. All six He ion RBS spectra are overlapped for comparison. Several features are worth noticing:

1) The dip in 400°C spectrum is narrower than the dip in 300°C spectrum, indicating carbon segregation was induced. Computer simulation with RUM code [13] shows that, after segregation, the maximum ratio of carbon/nickel in carbon buried region is about 50/50.

2) As the annealing temperature increases, more and more carbon atoms diffused away from the implanted region, which is indicated by the shrinking of the dip with the increased annealing temperature. The shrinking occurred only at the backside of the implanted region (around channel 190), which moves towards the surface of the nickel sample as the annealing temperature increases. The frontside (around channel 210) stays unchanged until the annealing temperature reached 650°C. A tentative explanation for this feature is given as follows: the carbon buried region is highly disordered. Therefore, carbon may diffuse faster in this region than in the grain boundaries of the rest of the sample when the temperature is below 650°C.
As soon as the carbon atoms diffuse to the front of the carbon buried region, further diffusion of carbon is governed by grain boundary diffusion, which is relatively slower at low temperatures. Therefore, part of the carbon will be stopped at the frontside. Thus, the shrinking of the dips appears only at backside. If this tentative explanation is incorrect, in other words, the grain boundary diffusion may be faster than the diffusion inside the carbon buried region. If this is the case, the carbon atoms near the frontside would diffuse through grain boundaries to the surface of the sample quicker than the carbon atoms from other part of the carbon buried region coming into the frontside region. In this case, the carbon concentration at the frontside region would reduce and the frontside would move inward. However, the He ions RBS spectra do not show such movement.

3) The tendency of the implanted carbon atoms to diffuse to the surface of the nickel is revealed by proton elastic scattering measurement. The spectra are presented in fig. 2 and are separated from each other using the same procedure as in fig. 1a. In the spectrum for the as-implanted sample, only one peak was observed, which is the signal of the protons backscattered from the buried carbon. Upon annealing at 400°C, a second peak appears at the position corresponding to the surface carbon, indicating that part of the buried carbon has diffused to the nickel surface. This surface carbon peak grows as the annealing temperature increases, and the buried carbon peak shrinks. The buried carbon peak disappeared after annealing at 650°C, indicating that all the carbon atoms (within the limit of the sensitivity of the measurement) has diffused from the implanted region. The total counts of the surface carbon peak in the 650°C spectrum is almost the same as that of the surface carbon peak in the 600°C spectrum. Therefore, 650°C annealing does not drive the rest of the buried carbon to the nickel surface, although the He ion RBS spectra (fig. 1) indicate that these carbon atoms have diffused away from the buried region. Where do the carbon atoms go? One possible explanation is that, instead of diffusing to the surfaces, they diffuse into the body of the nickel sample due to the change of the dominating diffusion mechanism from 600 to 650°C.

3.2 Carbon implantation in single crystal nickel

High dose, $8 \times 10^{17}$ C$^+$/cm$^2$, carbon ions were implanted into the single crystal nickel sample at liquid nitrogen temperature. Segregation of the implanted carbon was observed upon annealing at 400°C (see fig. 3, which shows that the dip of the 400°C spectrum is much narrower than the dip of the 300°C spectrum). The spectrum for the as-implanted sample is also included for comparison. It is essentially identical to the 300°C spectrum, indicating no appreciable diffusion occurred at 300°C annealing.

Fig. 4 presents the channeling and random spectra taken after 500 and 600°C annealing. For clarification, the random spectra are moved up by adding 2000
counts to each channel. So the vertical scale is only true for the channeling spectra. The dip in the 500°C random spectrum is almost the same as the dip in the 400°C spectrum, showing no significant diffusion occurred at 500°C. Annealing at 600°C, however, caused a significant amount of carbon diffuse out of the buried region, as revealed by the reduced size of the dip in 600°C random spectrum as compared with that in the 500°C spectrum. The area of the dip reduced about 25%. In the region between the surface and the implanted layer, the counts of the 600°C channeling spectrum are lower than those of the 500°C channeling spectrum, indicating that a partial recovery of the damaged lattice occurs. The damage recovery in the implanted layer cannot be observed directly, because the counts of the 600°C spectrum in this layer are higher than those of 500°C spectrum (fig. 4). Since part of the carbon diffused away from this layer, the relative concentration of the nickel increased, and the RBS counts in 600°C channeling spectrum increased as compared with the counts in 500°C channeling spectrum. The carbon atoms which left implanted region did not preferentially diffuse to the nickel surface, as can be seen from the 1.5 MeV proton elastic scattering spectra shown in fig. 5. Although about 25% of the implanted carbon has left the implanted region after 600°C annealing (fig. 4), there is no measurable carbon peak at the nickel surface (fig. 5). The carbon atoms probably have diffused into the body of the sample. This is different from the carbon diffusion in polycrystalline nickel foil (see fig 2).

In order to promote the recovery of the damaged nickel lattice and to retain the carbon atoms in the implanted region, rapid thermal annealing at 850°C (10 s) was applied to the sample. Comparison was made between the He ion RBS random and channeling spectrum of the 600°C/30 min annealing and 850°C/10 s annealing, which indicates that no significant recovery of the damaged lattice occurred and few carbon atoms have diffused away after 850°C/10 s annealing. Therefore, a second rapid thermal annealing at 1010°C for 20 s was made. The random and channeling He ion RBS spectra both for 850°C/10 s and for 1010°C/20 s annealing are shown in fig. 6. The random spectrum taken after 1010°C/20 s annealing shows massive diffusion of the carbon atoms. Contrary to 600°C annealing, where the carbon did not diffuse preferentially to the surface, in the 1010°C/20 s annealing case, the carbon atoms diffuse towards the surface (see the random spectrum in fig. 6). In the channeling spectrum for 1010°C/20 s annealing, the dechanneling rate in carbon implanted region is still as high as those in 850°C/10 s annealing spectrum, indicating that high concentration extended defects still exist in this region.

Nickel carbide, Ni$_2$C, was reported to form when high dose carbon atoms are implanted into nickel [9]. Ni$_2$C is not stable [14]. The ranges of the decomposition temperature of Ni$_2$C reported in the literature are not in agreement with each other. Ref. [15] reported as above 700°C and ref. [16] reported as below 400°C. Considering the possibility of forming nickel...
4. Summary

High energy (400 keV) and high dose \(8 \times 10^{17} \text{ C}^+/\text{cm}^2\) carbon ions were implanted both into polycrystalline nickel foil and single crystal nickel.

In the case of the nickel foil, no significant carbon diffusion was observed up to 300°C annealing. At 400°C, carbon segregation occurred. From 500 to 600°C, carbon atoms started to diffuse preferentially to the nickel surface. The carbon diffusion in this temperature range may be governed by those grain boundaries located in the region between implanted layer and surface. Upon annealing at 650°C, the carbon diffused out of the implanted region without directional preference. There may be a change of the dominating diffusion mechanism from 600 to 650°C.

In the case of single crystal nickel, no measurable carbon diffusion was observed up to 300°C annealing; carbon segregation also occurred at 400°C as in nickel foil. Significant carbon diffusion occurred at 600°C. However, the carbon atoms did not preferentially diffuse to the nickel surface as they did in the nickel foil. Rapid thermal annealing at 850°C for 10 s did not induce significant carbon diffusion; however, rapid thermal annealing at 1010°C for 20 s drove the carbon atoms towards the nickel surface, which may indicate a change of the dominating diffusion mechanism from low (600°C) to high temperatures (1010°C). After long-term annealing (850°C for 4 h + 470°C for 4 h), all the carbon atoms left the implanted region. They may have diluted into the body of the nickel sample. Although less likely, they may also have been oxidized during the long-term annealing. The He ion RBS and proton elastic scattering measurements alone are not sufficient to decide conclusively where the carbon went. Since the single crystal nickel used in this study is highly defective, the diffusion behavior of carbon atoms in such sample will be different from that in a perfect crystal. The results obtained here should only apply to highly defective nickel crystals.

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References