High energy carbon ions implantation: An attempt to grow diamond inside copper

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1 MeV carbon ions were implanted into single-crystal copper which was then annealed in argon at temperatures ranging from 350 to 750 °C. Regrowth of the radiation-damaged copper was examined by RBS-channeling measurements. Carbon segregation occurred on annealing at 750 °C. Prolonged annealing at 750 °C caused blistering of the copper layer over the buried carbon. After removal of the blistered copper overlayer, the previously buried carbon layer was examined by Raman scattering, showing that graphite is the dominant phase.

This study is stimulated by recent reports[1,2] which indicate that the heteroepitaxial growth of single crystalline diamond on copper is possible by implanting carbon ions which will diffuse to the copper surface, into a heated copper substrate or by applying laser annealing after carbon implantation. However, so far, the results of these two reports can not be reproduced in other laboratories.[3–6] At normal temperature and atmospheric pressure, the nucleation of graphite is more favored than the nucleation of diamond because, under such conditions, graphite is the stable phase, whereas diamond is metastable.[7] Therefore, any carbon contamination on the copper surface will become the nucleation center for graphite. Carbon has a very low solubility in solid copper.[8] Therefore, deep inside copper, carbon contamination is negligible if the material is of high purity. Proper annealing may provide favorable thermodynamic conditions, mainly temperature and pressure, for the growth of diamond inside copper. We will discuss this point in more detail later in this letter.

With high energy, the implanted carbon will be buried deep inside the copper. Meanwhile, the near-surface region of the substrate overlying the implanted layer will not be damaged severely. When heat treatment is applied, this less damaged region will regrow inwards from the surface. The region which is below the implanted layer will regrow outwards. Such regrowth of copper is expected to be accompanied by the segregation of carbon in the regrown region due to the low solubility of carbon. The segregated carbon will be sandwiched by the regrown copper on both sides, which has a relatively good crystalline structure. It is interesting to find out which phase of the implanted carbon will be in such a sandwiched environment.

In this study, 1 MeV carbon ions generated from a 1.7 MeV tandem accelerator at the Texas Center for Superconductivity at the University of Houston were implanted into a single-crystal copper with ⟨100⟩ orientation. RBS-channeling measurements showed that the $\chi_{\min}$ value at the surface region was 4.7%, indicating that the copper sample had good crystalline quality. The total dose of the implantation was about 6.6×10^{17} at./cm^2. After carbon ion implantation, the copper sample was annealed in a furnace in an argon flow. The sample was annealed for 30 min at 350, 450, 550, 650, and 750 °C and RBS-channeling measurements with 3.5 MeV He ions were taken each time.

Figure 1 presents the 3.5 MeV He ion RBS-channeling spectra of the as-implanted copper sample. Three features of these spectra are worth noticing: (1) The random spectrum taken at the implanted area shows a deep dip around channel 182 which corresponds to a depth of 820 nm. This dip is due to the high concentration of implanted carbon buried in this region which dilutes the copper concentration, thus lowering the RBS counts from copper. Since the carbon is buried deep inside the copper crystal and also because the He ion RBS measurement is insensitive to the light elements,[9] the RBS signals from carbon cannot be seen in the He ion RBS spectrum. However, the existence of the buried carbon layer has been confirmed by 1.5 MeV proton non-Rutherford elastic scattering (spectrum not shown), which has a scattering cross section that is six to seven times the Rutherford cross section; (2) In the ⟨100⟩ aligned spectrum taken at the implanted area, the RBS counts from the region between the carbon buried layer and the surface are much lower than the random spectrum, indicating that relatively good crystalline structure has been retained after implantation. The $\chi_{\min}$ value near surface is about 20%. This will provide a good base for inward regrowth during subsequent annealing; (3) On the other hand, the region where the carbon is buried has been heavily damaged, as can be seen from the ⟨100⟩ aligned spectrum which shows that, in this region, the RBS counts have reached the random level (Fig. 1). Below the carbon buried layer, the copper is not damaged and has good crystalline quality. However, in the aligned spectrum of the implanted sample, the RBS counts corresponding to this part of the copper nearly reach the random level. This is mainly due to the high dechanneling of the He ions when transversing the carbon buried region which is heavily damaged.

RBS-channeling measurements show that significant regrowth of the radiation-damaged copper occurred on annealing at 450 °C (spectrum not shown). Annealing at 650 °C results in substantial recovery in the region between

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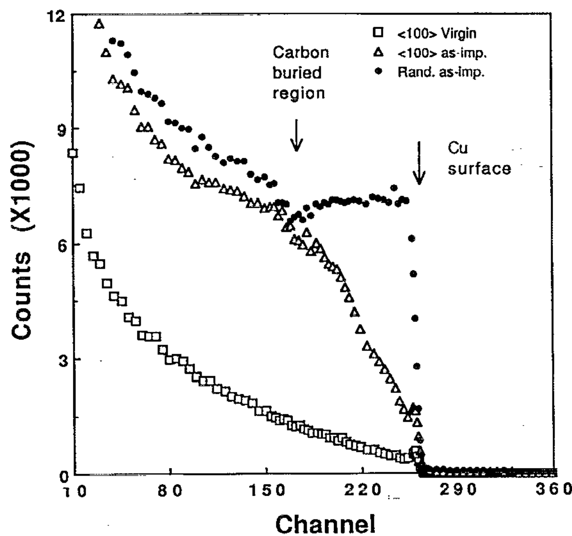

FIG. 1. 3.5 MeV He ions RBS-channeling random and ⟨100⟩ aligned spectra of the as-implanted single-crystal copper sample. The dip in the copper random spectrum is due to the high concentration of buried carbon. As a comparison, the ⟨100⟩ aligned spectrum taken at the unimplanted area is also presented.

the buried carbon layer and the surface (Fig. 2). In the ⟨100⟩ aligned spectrum (Fig. 2), the RBS counts of the copper corresponding to this region has dropped to very close to that of the unimplanted area, and the χ_{min} value of the near-surface region recovers from 20% to 4.9%. Meanwhile, the RBS counts corresponding to the buried carbon region are lower than that of the random spectrum, indicating partial recovery in this region even though it contains a high concentration of carbon. Nevertheless, the 650 °C annealing did not stimulate appreciable diffusion of the buried carbon, since the shape as well as the position of

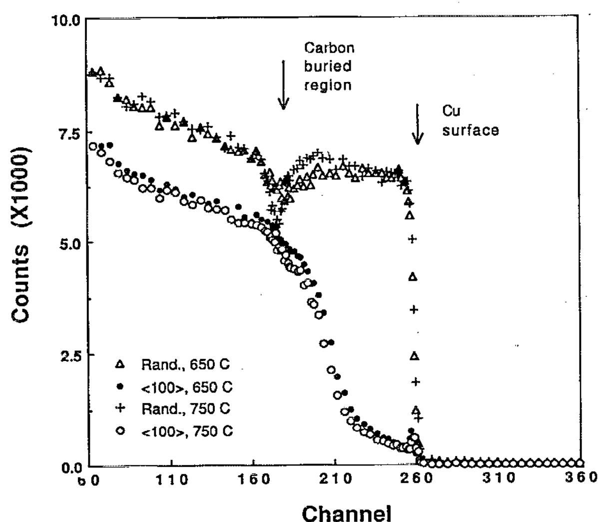

FIG. 2. 3.5 MeV He ions RBS-channeling random and ⟨100⟩ aligned spectra for annealing at 650 and 750 °C, respectively. The carbon segregation occurred on annealing at 750 °C, as shown by the narrowing of the dip in the random spectrum of 750 °C as compared with that of the 650 °C annealing.

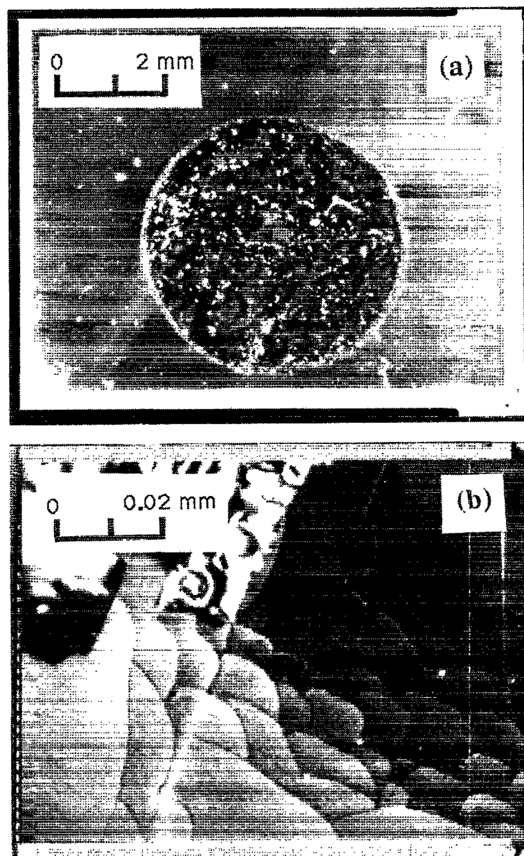

FIG. 3. Optical microphoto taken from the carbon-implanted area after annealing at 750 °C: (a) with the blistered copper layer; (b) after removal of the blistered copper layer.

the dip in the random spectrum after 650 °C annealing is nearly the same as that of as-implanted random spectrum (see Fig. 1). Another interesting feature in Fig. 2 is that the dechanneling in the ⟨100⟩ aligned spectra is very high, indicating a high concentration of secondary defects and/or a high internal stress. The nature of the defects are not known at this stage.

After 650 °C annealing, the sample was put back into the furnace and annealed at 750 °C for 30 min. The spectra after this annealing are also shown in Fig. 2. The regrowth front is pushed further inwards. The important message revealed by the RBS-channeling measurement is that carbon segregation occurs at this temperature, as evidenced by the narrowing of the dip in the random spectrum. It is easy to notice that, from the 650 °C annealing to the 750 °C annealing, the area of the dip essentially did not change. Thus, we conclude that no measurable carbon has diffused away from the implanted layer.

In order to promote further regrowth of the buried carbon region, the sample was annealed again at 750 °C for 60 min. After annealing, it was found that the whole implanted area had blistered (Fig. 3). Although the structure of the copper layer overlying the buried carbon layer had undergone such a dramatic change, the carbon still stayed where it was. The position of the dip in the RBS random spectrum (not shown) did not change essentially.

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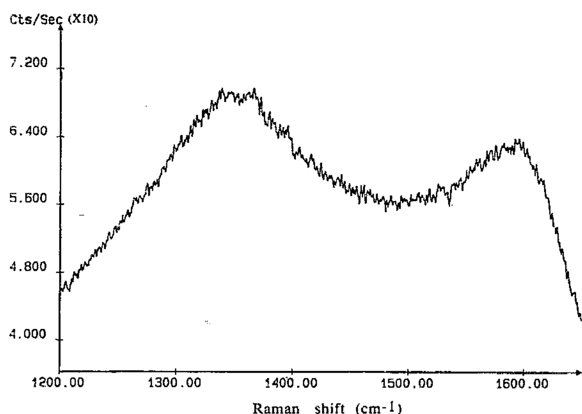

FIG. 4. Raman spectrum taken at carbon-implanted area after the removal of the blistered copper layer. Two Raman bands appear at 1350 and 1600 cm^{-1}, indicating the presence of the graphite phase (Ref. 10).

To identify the phase of the buried carbon, the blistered copper layer was lifted off with scotch tape. Figure 3 is an optical microphoto of the implanted area after lift-off. It shows that the defects are distributed all over the implanted area. However, micro-Raman scattering shows two bands at 1350 and 1600 cm^{-1}, respectively, which are the characteristics of the graphite phase[10] (Fig. 4).

Although this preliminary effort to obtain the diamond phase by deep carbon implantation in copper is not successful, it is probably still worthwhile to further test this approach, Liu *et al.*[11] has demonstrated that a thick amorphous diamond layer caused by high dose carbon implantation in diamond will homoepitaxially regrow upon appropriate annealing. The definition of the "amorphous diamond" was explained by Liu *et al.* as the diamond which is heavily damaged but still retains a large fraction of the diamond bondings. The regrowth starts from the crystal-amorphous interface all the way down to about 53 nm below the surface. Only this top 53 nm layer has transformed into graphite. The difference in the transformations was attributed by Liu *et al.* to the difference in the pressures experienced by the deep amorphous diamond layer and the surface amorphous diamond layer. Graphitization results in volume expansion which causes higher pressure if the graphitization occurs in the deeper region; thus graphitization in the deeper region is prevented. Near the surface, the pressure is not high, thus graphitization results. For the deep implantation of carbon in copper, the problem we face is heteroepitaxial regrowth. It is well documented that the noble gases, such as Kr, Xe, and Ar, implanted into metals, such as copper, nickel, and aluminum, will form solid bubbles (crystallites) epitaxial with the host metals.[12–16] The pressures on these solid bubbles are estimated from the measurements to be a few tens of kbars. In the case of deep implantation of carbon in copper, the pressure on the segregated carbon is not known. However, it is probably reasonable to infer from the noble gas cases that the pressure on the segregated carbon may be on the same order of magnitude, i.e., a few tens of kbars. If this is the case, then, considering the Berman–Simon diamond-graphite equilibrium curve,[17] the few tens of kbar could be favorable for the formation of the diamond phase at temperatures of a few hundred degrees.

Our study shows that the diffusion of carbon is slower than the regrowth of copper below 750 °C. Therefore, proper selection of the substrate temperature for the implantation may reduce the stress, promote copper regrowth, and meanwhile, not stimulate the diffusion of the carbon. The pressure on the carbon is expected to depend on the size of the precipitates. The lower implantation dose may be more favorable.

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[1] J. F. Prins and H. L. Gaither, *Proceedings of the 2nd International Conference of New Diamond Science and Technology*, edited by R. Messier, J. T. Glass, J. E. Butler, and R. Roy (Materials Research Society, Pittsburgh, 1991), p. 561.
[2] J. Narayan, V. P. Godbole, and C. W. White, Science **252**, 416 (1991).
[3] S.-T. Lee, S. Chen, G. Braunstein, X. Feng, I. Bello, and W. M. Lau, Appl. Phys. Lett. **59**, 785 (1991).
[4] S.-T. Lee, S. Chen, J. Agostineli, G. Braunstein, L. J. Huang, and W. M. Lau, Appl. Phys. Lett. **60**, 2213 (1992).
[5] S. P. Withrow, D. M. Hembree, Jr., C. W. White, R. A. Zhur, J. W. MaCamy, and S. J. Pennycook, J. Appl. Phys. (to be published).
[6] N. R. Parikh (private communications, 1991).
[7] J. Wilks and E. Wilks, *Properties and Applications of Diamond* (Butterworth–Heinemann, Oxford, 1991).
[8] M. B. Bever and C. F. Floe, *Solubility of Carbon in Molten Copper*, (AIME Tech., 1945), p. 1802.
[9] W. K. Chu, J. W. Mayer, and M.-A. Nicolet, *Backscattering Spectrometry* (Academic, Orlando, FL, 1978).
[10] W. L. Johnson III, in *Microbeam Analysis*, edited by A. D. Romig, Jr. and W. F. Chamber (San Francisco Press, San Francisco, 1986), p. 26.
[11] B. Liu, G. S. Sandhu, N. R. Parikh, M. L. Swanson, and W. K. Chu, Nucl. Instrum. Methods B **45**, 420 (1990).
[12] H. H. Andersen, J. Bohr, A. Johanson, L. Sarholt-Kristensen, and V. Surganov, Phys. Rev. Lett. **59**, 1589 (1987).
[13] Elichi Yagi, Nucl. Instrum. Methods B **39**, 68 (1989).
[14] S. E. Donnelly and C. J. Rossouw, Nucl. Instrum. Methods B **13**, 485 (1986).
[15] C. Templier, H. Garem, J. P. Riviere, and J. Dolafond, Nucl. Instrum. Methods B **18**, 24 (1986).
[16] J. H. Evans and D. J. Mazey, J. Phys. **15**, 1 (1985).
[17] R. Berman, in *Physical Properties of Diamond*, edited by R. Berman (Clarendon, Oxford, 1965), p. 371.

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