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A type IIa natural diamond was irradiated with 300 kV electrons at 16 and 87 K. Transmission electron microscopy and electron energy-loss spectroscopy were employed to investigate the phase stability of diamond under electron irradiation. At both temperatures, the diamond structure was found to be stable, and the formation of defect clusters was observed. The present results in comparison to previous work on ion implantation indicate that displacement cascade damage is a prerequisite for irradiation-induced phase transformation from diamond to amorphous carbon or graphite. The temperature dependence of the cluster size suggests that interstitials are thermally mobile above 50 K.

During ion implantation of diamond, it has been reported that diamond transforms to either amorphous carbon or graphite depending on the implantation temperature.[1-4] Silicon, which also has the diamond structure, is known to undergo a crystalline-to-amorphous transformation with heavy ion implantation,[5] but not with electrons.[6] In some intermetallic compounds, both ion and electron irradiation can induce such a phase transformation.[7,8] However, in the case of diamond, there has been no report to date regarding phase transformations induced by electron irradiation.

The characteristics of point defects in diamond produced by electron irradiation have been extensively investigated with optical absorption[9] and electron spin resonance (ESR) techniques.[10,11] However, the total electron dose for these studies may be too low, 10^{15}–10^{18} e^- cm^{-2}, to induce a structural transformation. In the present work, type IIa natural diamond was irradiated with 300 kV electrons in an electron microscope up to a dose of 7.2×10^{23} e^- cm^{-2} at temperatures of 16 and 87 K, and the structural change was examined by transmission electron microscopy (TEM) and electron energy-loss (EEL) spectroscopy. It was found that electron irradiation did not induce phase transformation but produced point defect clusters. Based on the temperature dependence of the cluster size and number density, the mobility of point defect is discussed.

A TEM sample was prepared in the following way. A thin wafer of type IIa natural diamond obtained from Dubbeldee Harris Corporation[12] was mounted on a Cu grid by using an epoxy. The wafer was ion-milled at room temperature with 4 kV Ar ions to obtain a thin area suitable for electron transparency. The sample was then irradiated in a Gatan cooling holder with 300 kV electrons in a Philips CM 30 electron microscope; use of liquid helium in the holder gave a specimen temperature of 16 K while use of liquid nitrogen gave a temperature of 87 K. Variation in the microstructure was examined *in situ* during electron irradiation by monitoring bright-field and dark-field images and selected area diffraction (SAD) patterns. EEL spectra were also taken before and after irradiation at 87 K with a Gatan parallel EEL spectrometer. For the microstructural study, irradiation was carried out in a thicker region to minimize surface effects on point defect mobility, while for EEL spectroscopy, thinner region near a hole edge was irradiated to minimize multiple scattering effects on EEL spectra.

The electron beam was focused to ~1 μm in diameter during irradiation. The electron flux averaged over the irradiated area was 5.6×10^{19} e^- cm^{-2} s^{-1}. The direction of the incident electron beam was a few degrees off from the [1$\bar{1}$0] zone axis towards the [110] direction. The displacement threshold energy in the [110] direction is 48 eV (Ref. 13) and the corresponding displacement cross section from Oen[14] is 2.5×10^{-24} cm^2. These values yield an estimated displacement rate of 1.4×10^{-4} dpa s^{-1}. It should be noted that the displacement rate is maximum at the beam center, and decreases rapidly away from the beam center due to the Gaussian intensity profile of the focused electron beam.

Beam heating effects are expected to be negligible due to the large thermal conductivity of diamond.[15] Using a model proposed by Fisher,[16] the temperature increment corresponding to the electron flux was estimated to be $\sim$0.01 K at a sample temperature of 16 K and even less at 87 K.

Figure 1 shows the changes which occur in the bright-field image and diffraction pattern during irradiation at 16 K. The number at the corner of each micrograph indicates the electron dose in dpa. The unirradiated crystal contains dislocations such as are usually observed in type IIa diamond.[17] The diffraction pattern shows Kikuchi lines, indicated by a double arrow, adjacent to the 220 diffraction spot. After irradiation to 0.21 dpa, fine black spots are observed around the electron beam center and the dislocation image is significantly disturbed. The corresponding SAD pattern from the irradiated area shows that the Kikuchi lines have disappeared and that 111 diffraction spots on the neighboring Laue zone have appeared. These observations indicate that the irradiated region contains a large number of defect clusters and that the strain arising from cluster formation locally buckles the sample. Further irradiation to a dose of 0.84 dpa simply expands the area con-

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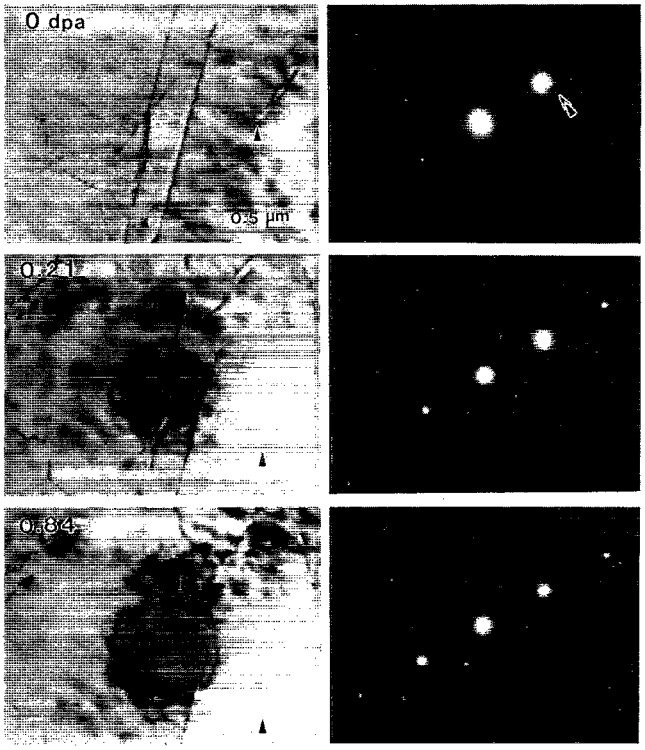

FIG. 1. Changes in bright-field images and selected area diffraction patterns during electron irradiation at 16 K. The number at the upper left-hand side of each micrograph indicates the electron dose in dpa. Arrows in micrographs are to indicate the same position of the sample.

taining defect clusters. The SAD pattern shows no sign of amorphous phase formation. After annealing the sample at 295 K for 15 h, the microstructure remained the same, indicating that the clusters formed at 16 K are stable at room temperature.

Figures 2 (a) and 2(b) show dark-field images of irradiated areas at 16 and 87 K, respectively, to a dose of 0.21 dpa. The formation of defect clusters is seen in both images. The clusters formed at 87 K appear to be much larger in size (5–10 nm in diameter) and smaller in number density than those formed at 16 K (less than 5 nm in diameter). This indicates that thermally activated migration of point defects is involved in cluster formation by increasing irradiation temperature from 16 to 87 K.

EEL spectra taken before and after irradiation to 1.8 dpa at 87 K are shown in Figs. 3(a) and 3(b), respectively. There is no noticeable difference in the spectrum shape near the carbon K-edge region, indicating retention of long range crystalline order of the diamond structure after irradiation. It should also be noted that the spectra do not show the so-called π^* peak near 284 eV that is due to electron excitation from the $1s$ to $2p$ antibonding (π^*) state and is characteristic of both amorphous carbon and graphite, but not of diamond.[18]

The present results show that the diamond structure is stable under electron irradiation at 16 and 87 K. This is in contrast to the results obtained by ion implantation, which show transformation to amorphous carbon or graphite,[1–4] and indicates that displacement cascade damage is a prerequisite for irradiation-induced structural transformation in diamond.

Frenkel pairs are found to be mobile under electron irradiation even at 16 K, as evidenced by the formation of defect clusters. To date the mobility and configuration of point defects in electron irradiated diamond are not well known. Vacancies are reported to be immobile up to 1123 K, based on the thermal stability of the "GR1" optical absorption center, which is thought to be a vacancy center.[19] On the other hand, the mobility of interstitials has been controversial. Both conductivity measurements[20] and ESR studies[10,11] of electron-irradiated diamond, respectively at 15 and 12 K, revealed the first recovery stage at ~50 K and the second stage at ~260 K upon isochronal annealing up to room temperature. Massarani and Bourgoin[20] proposed that the first stage is due to charge redistribution and the second to the interstitial migration resulting in recombination of interstitial-vacancy pairs. Flint and Lomer,[11] on the other hand, proposed from the ESR study that the first stage involves migration of either interstitials or impurities forming interstitial-impurity complexes.

Our observation clearly indicates that migration of point defects occurs far below the second recovery stage, thus ruling out the model by Massarani and Bourgoin. The present results in conjunction with reexamination of the ESR and conductivity data lead to the following conclu-

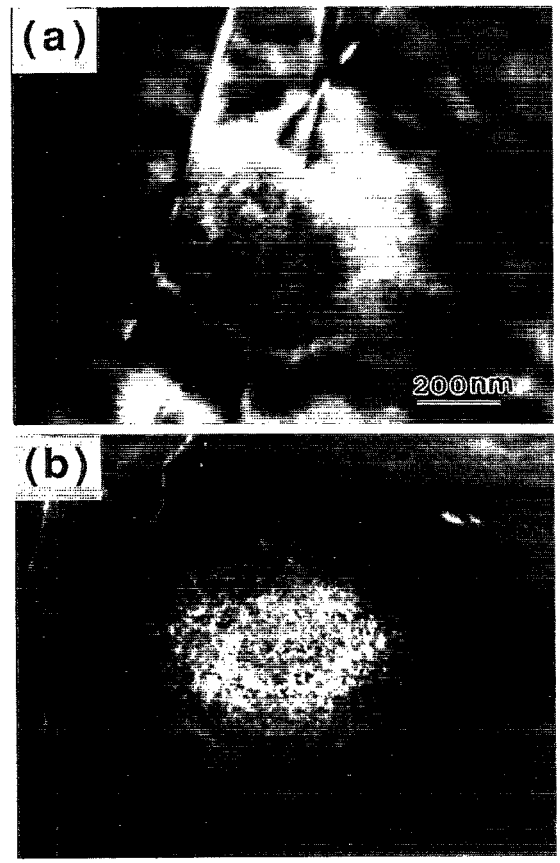

FIG. 2. Dark-field images ($g = 111$) showing cluster formation after irradiation to 0.21 dpa at (a) 16 K and (b) 87 K.

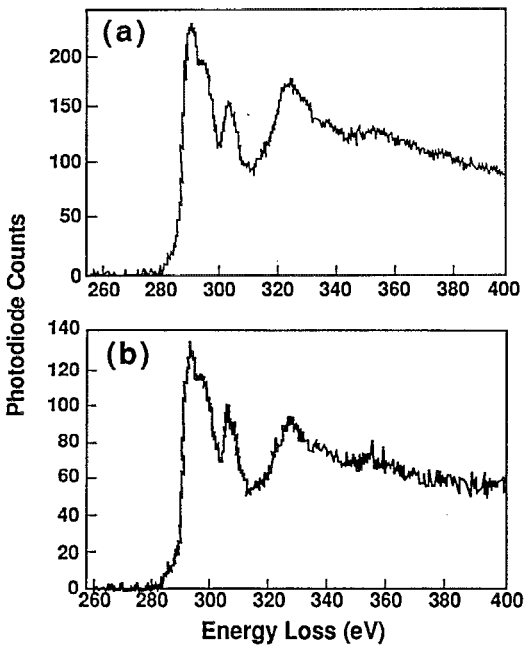

FIG. 3. Electron energy-loss spectra at 87 K; (a) before electron irradiation, and (b) after irradiation to a dose of 1.8 dpa.

sion: interstitials become thermally mobile near 50 K, so that the defect clusters observed at 16 K are due to a thermal migration of interstitials caused by ionization-enhanced diffusion.[21] This conclusion is based on the following facts: the conductivity data showed a temperature-independent region below 50 K and a notably temperature-dependent region above 50 K. The peak intensity of the ESR spectra also changed as the sample was annealed at temperatures above 50 K. These previous results suggest that either component of Frenkel pairs, most likely interstitials, become thermally mobile only above 50 K. Further work is underway to identify the type of defect clusters unambiguously and determine the activation energy for interstitial migration.

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