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A type IIa natural diamond was irradiated at room temperature with energetic electrons. The threshold energy for displacement of atoms from their lattice sites was determined for three principal crystallographic directions by observing the formation of defect clusters during irradiation in a transmission electron microscope. The displacement-threshold energies were found to be 37.5 ± 1.2 eV for the electron incident in the [100] direction, 45.0 ± 1.3 eV in the [111] direction, and 47.6 ± 1.3 eV in the [110] direction.

Recent progress in producing high-quality synthetic-diamond films has opened up the possibility of utilizing diamond as a component of a new class of semiconductor devices.[1] Ion-beam technology is expected to be employed extensively in conjunction with diamond films, as has been the case for conventional semiconductors. Generally, a crystalline structure and associated electrical properties are altered during processing with an energetic ion beam. In order to describe the response of a material to irradiation, the displacement threshold energy (hereafter denoted as T_d) has to be known. For diamonds, there have been contradictory reports on T_d, namely 35,[2] 55,[3] and 80 eV.[4] Since T_d can depend on the irradiation direction, this discrepancy may be due to the difference in the crystalline orientation with respect to the electron-beam direction. In this letter, we report T_d for three principal crystallographic directions, [100], [110], and [111], determined by the electron microscopy technique. Based on the obtained results, the previously reported results are critically discussed.

We employed thin wafers on type IIa natural diamond with a thickness of 180 μm. The wafers were thinned by ion milling with 5-keV Ar ions for electron transparency. The specimen was irradiated at room temperature in a Philips CM 30 electron microscope, and the formation of defect clusters was examined for various incident-electron energies changed by a 10 keV step. The electron beam was focused to about 1 μm in diameter during irradiation. A typical electron flux was in the range of $1.0\text{–}3.0 \times 10^{19}$ electrons $\text{cm}^{-2}\,\text{s}^{-1}$, depending on the accelerating voltage. A total electron dose for each irradiation experiment was about 3.5×10^{22} electrons cm^{-2}.

The following relation was used for the calculation of T_d.[5] When electrons collide with target atoms, the maximum recoil energy (T_m) is given as a function of a target mass (M) and the incident-electron energy (E),

$$T_m = \frac{2m}{M}\,\frac{(E + 2mc^2)E}{mc^2},$$

where m is an electron mass and c the velocity of light. If T_m is larger than the displacement-threshold energy, Frenkel pairs are produced, and subsequently, defect clusters form at a temperature where point defects are mobile. In general, T_d is defined as a T_m value corresponding to the minimum-incident energy to observe defect-cluster formation.

The electron-microscopy technique has provided values of T_d which are as reliable as those obtained by other carefully performed techniques. This is due to the following advantages of electron microscopy. Simple observation of cluster formation in the electron microscope eliminates possible analytical errors involved in a complicated theoretical-fitting procedure required in other techniques. Use of very thin samples (several tens of nanometer in thickness) minimizes multiple-scattering effects. The chance of secondary collision is also greatly reduced since the incident energy is just large enough to displace a target atom. Thus, the orientation dependence of T_d can be accurately and more easily determined with the electron-microscopy technique.

Figure 1 shows a typical result of electron irradiation along the [100] direction. At an incident energy of 170 keV [Fig. 1(a)], the formation of defect clusters is not observed in dark-field images after irradiation. Similar results are obtained after irradiation at 140, 150, and 160 keV. While at 180 keV [Fig. 1(b)], defect clusters form and are observed as white dots in a dark-field image. Irradiation at 190 keV is also found to produce defect clusters. These results indicate a T_d of 37.5 ± 1.2 eV in the [100] direction.

Similar experiments have been carried out in the [110] and [111] directions. The minimum incident energy for defect-cluster formation is found to be 210 and 220 keV in the [111] and [110] directions, respectively. The corresponding T_d is calculated to be 45.0 ± 1.3 and 47.6 ± 1.3 eV.

Theoretically, Bauerlein[6] estimated T_d of diamond by using a displacement model proposed by Kohn[7] modified to include changes in electron energy states. In Table I, the calculated values[6] of T_d for diamond, Si, and Ge are listed together with the experimental T_d values[2–4,6] and dielectric constants[8] of each material. In the case of covalent materials, some fraction of the Coulomb-interaction energy may be added to the calculated values. In the past, the large T_d of 80 eV for diamond had been attributed to the smaller dielectric constant of diamond which gives rise to a larger Coulomb-interaction energy than that of Si and Ge.[9,10] However, the Coulomb-interaction energy is only inversely proportional to the dielectric constant and does not have a significant effect in Si and Ge. Therefore, the difference in

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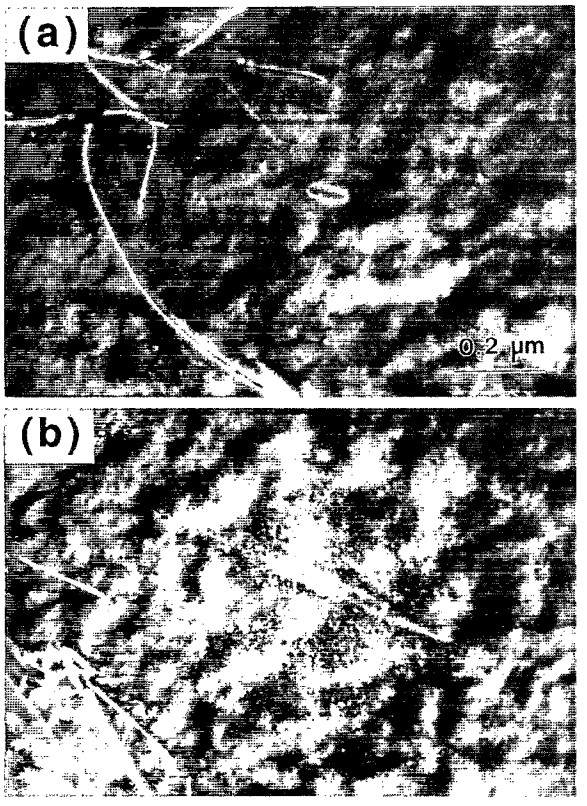

FIG. 1. Dark-field images after electron irradiation to a dose of 3.5×10^{22} electrons cm^{-2} at an incident energy of (a) 170 keV and (b) 180 keV. The electron beam is incident along the [100] direction.

T_d between diamond and other materials cannot be explained by the Coulomb interaction, and a T_d of 80 eV may not be the correct value as discussed in the following.

Clark, Kemmey, and Mitchell[4] have reported a T_d of 80 eV by analyzing the development of the optical-absorption peak at 2.0 eV and of resistivity during electron irradiation at various incident energies. However, there are several factors in their analysis that would lead to an overestimate of T_d. First, their specimen chamber had an aluminum window of 150 μm in thickness and the electron beam passed through the window before it reached the specimen. Apparently, the energy loss of the incident electrons in the Al foil was not taken into account. For an incident energy of 330 keV, corresponding to the T_d of 80 eV, the energy loss in the 150 μm Al foil is estimated to be 70 eV.[11] Had this been considered, T_d would have been determined to be 57 eV instead of 80 eV. Second, T_d was determined by using an improper irradiation-damage theory to fit to an experimental-damage rate curve measured at room temperature. It has been reported that one of the point-defect species in diamond, most likely interstitials, are mobile above 50 K.[12,13] Thus, at room temperature, recombination of Frenkel pairs is expected, and the number of remaining point defects should be smaller than the calculated value. The formation of defect clusters can also alter the point-defect population. However, these annealing effects were neglected in deriving their theoretical-damage rate curve. If the annealing effects had been considered, T_d would have been even smaller than 57 eV.

TABLE I. Calculated and experimental values of the displacement threshold energy (T_d) in eV and dielectric constants (ϵ) of diamond, Si, and Ge.

	T_d^{calc} (eV)		T_d^{exp} (eV)	ϵ
Diamond	24	35–80	37.5–47.6	5.7
Si	15	11–22		11.7–12.0
Ge	15	12–30		15.9–16.0
Reference	6	2–4, 6	This work	8

In contrast, Bourgoin and Massarani[2] obtained a T_d of 35 ± 5 eV by carrying out irradiation and a subsequent resistivity measurement at 15 and 12 K, respectively. At both temperatures, point defects are immobile[12,13] and the theoretical assumption, i.e., omission of annealing effects, is valid. Although they did not specify the irradiation direction, this value is in good agreement with our value in the [100] direction and not far from the values in the [110] and [111] directions. It is reasonable for their result to be in close agreement with our lowest T_d value because a much thicker sample was used in their experiment and multiple-scattering effects could lead to a predominance of displacements along a direction with the lowest T_d value.

Prins, Derry, and Sellschop[3] have reported a T_d of 55 eV by analyzing volume expansion measured during 170 keV fluorine ion implantation at room temperature. Vacancy accumulation was attributed to volume expansion and the vacancy volume was assumed to be the same as the atomic volume. Annealing effects were included in their analysis. However, the relaxation volume of vacancies in most metals is known to be in a range between 20% and 50%.[14] If the relaxation volume of diamond falls in this range, it would be too large to be neglected in the calculation. Prins and co-workers[14] properly suggested that if lattice relaxation around vacancies is considered, T_d can be smaller than 55 eV. We then reanalyzed their results by including lattice relaxation and found that T_d decreases to 35 and 48 eV, respectively, when the vacancy volume decreases by 35% and 10% of the atomic volume. These T_d values, obtained by including the volume relaxation, are more realistic than 55 eV, and agree better with the present results.

Finally, we consider the orientation dependence of T_d. It was found that the [100] direction has the lowest T_d value. This appears to be in contrast to the theoretical prediction that the [111] is the easiest displacement direction in materials with the diamond structure.[7] Previous reports on the T_d have shown that the orientation dependence cannot be interpreted in a straightforward way and is related to the incident-electron energy and irradiation temperature. For example, in Ge,[15,16] orientation dependence was clearly observed at 78 K at an intermediate incident energy between 370 and 920 keV: the displacement rate was larger in the [111] direction than the [100] and [110] directions. At an incident energy smaller or larger than this range, the orientation dependence van-

ished. Increasing the irradiation temperature from 78 to 269 K at an intermediate incident energy was also found to reduce the orientation dependence.[15]

The complicated orientation dependence of the displacement rate can be interpreted as follows. Among many displacement mechanisms, the replacement-collision sequence is most sensitive to the crystallographic direction of incoming projectiles, and is known to occur most easily in the close-packed direction[17] and allows interstitials to form away from vacancies. The orientation dependence at an intermediate incident energy can be attributed to this sequence. When the incident energy is too large, the recoil energy may exceed the focusing energy, and displacement occurs in random directions. A temperature increase also defocuses the replacement-collision sequence due to enhanced atomic vibration and reduces the orientation dependence. At a small incident energy near the threshold, primary knock-on atoms may not have a sufficient energy to propagate the replacement collision far enough to produce stable interstitials. In this case, the recombination volume plays an important role for the stability of point defects. The recombination volume generally has a shape extended in the close-packed direction[18,19] which makes the survival of atoms displaced in this direction with a small kinetic energy more difficult due to a greater probability of spontaneous recombination. This tendency may be stronger in the diamond structure because of the rigid tetrahedral bonding in the close-packed direction.

Potential calculations[9] for various interstitial configurations revealed that the ⟨100⟩ split interstitials are the most stable compared with ⟨110⟩ and ⟨111⟩ split interstitials and substitutional interstitials at tetrahedral and hexagonal sites. Since the atomic column in the ⟨100⟩ direction has a relatively small channel, assisted focusing may occur in this direction and form the ⟨100⟩ split interstitials at the end of a replacement-collision sequence. This process may occur most easily if the recombination volume in the ⟨111⟩ direction is much greater than that in the ⟨100⟩ direction.

Therefore, the theoretical prediction of the easiest displacement direction may be valid at an intermediate incident energy at low temperature where the replacement-collision sequence predominates the displacement mechanism. However, it is not necessarily the case near the threshold energy or at relatively large incident energies. Particularly near T_d, the easiest displacement direction may be different from the close-packed direction due to the extended shape of the recombination volume, and be determined by stability of the interstitial configuration.

In summary, we have determined the displacement-threshold energy of type IIa natural diamond in three principal crystallographic directions by examining the formation of defect clusters using transmission-electron microscopy. T_d was found to be 37.5 ± 1.2 eV in the [100] direction, 45.0 ± 1.3 eV in the [111] direction, and 47.6 ± 1.3 eV in the [110] direction. These values agree well with the single value reported by Bourgoin and Massarani.[2] The discrepancy with the values reported by other authors was discussed. Careful re-analysis of their results shows closer agreement with the present work.

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