Journal of Nuclear Materials 386–388 (2009) 1018–1022

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

High-temperature neutron irradiation effects on CVD-diamond, silicon and silicon carbide

Toyohiko Yano *, Takashi Sawabe, Katsumi Yoshida, Yoshiro Yamamoto [1]

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan

ARTICLE INFO

PACS:
28.52.Fa
61.80.Hg
61.82.Ms
61.82.Fk
78.30.Fs

ABSTRACT

Diamond films on single-crystal silicon and polycrystalline silicon carbide substrates were neutron-irradiated in JMTR up to a fluence of 8.1×10^{24} n/m^2 ($E > 0.1$ MeV) at 725 °C. Lattice parameter expanded 0.39%, 0.20–0.27%, 0.001%, in diamond, silicon carbide and silicon, respectively. Raman peaks of diamond at 1335 cm^{-1} was weakened and shifted 8 cm^{-1} after the irradiation, but after annealing up to 1500 °C relatively large peak at 1329 cm^{-1} and the peaks corresponding to disordered graphite were observed. Lattice parameter of diamond slightly decreased from the irradiation temperature and up to 1300 °C, but was not recovered completely after annealing at 1400 °C. Sp^2 clusters may be induced during irradiation and grow by annealing. The change in lattice parameter of silicon was negligible but broad scattering around 25° (2θ/CuKα) was observed, indicating the presence of amorphous region. Mobility of monovacancy at room temperature, different from those of diamond and silicon carbide, should be a cause of different irradiation response of silicon.

1. Introduction

In fusion reactors, many ceramics will be applied as structural and functional components to sustain the fusion plasma under very severe environments such as intense radiation, high temperature, high heat load, etc. [1–5]. In present experimental fusion facilities, radio-frequency heating of the plasma is a necessary support heating system. In that system, ceramic windows with very low $\tan\delta$ and very high heat-transfer properties are necessary. Diamond seems to be the best material for that window [6–8] and was actually applied to the JT-60 fusion experimental device in JAEA [9], due to its very high thermal conductivity in the order of >1000 W/m·K and low $\tan\delta$ in the order of $<1.3 \times 10^{-4}$ at 170 GHz before neutron irradiation [10]. It is well known that physical properties such as length, mechanical strength, thermal conductivity, $\tan\delta$ are greatly influenced by fast-neutron irradiation. Only a small number of reports on physical property change of CVD-diamond due to neutron irradiation have been published mainly by Heidinger et al. [11–13], except for the annealing behavior.

In the previous report of the present authors [14], the property changes of the CVD-diamond, single-crystal silicon and polycrystalline silicon carbide, all of them belong to the similar crystal structure, irradiated up to a fluence of 5.3×10^{24} n/m^2 (neutron energy: $E_n > 0.1$ MeV) at 380 °C in the Japan Materials Testing Reactor (JMTR) were clarified as follows. (1) Neutron irradiation induces graphite-like sp^2 clusters besides point defects in CVD diamond, which cannot recover after annealing up to 1500 °C. Due to the formation of sp^2 clusters, swelling of diamond is greater than that of silicon carbide. Lattice swelling was partially recovered by thermal annealing provided the annealing temperature is above the irradiation temperature. The recovering of the swelling increases with annealing temperature though it was not completed even at 1300 °C that was the highest experimented one. (2) Silicon carbide shows a response to neutron irradiation similar to diamond, but does not transform into other crystalline or non-crystalline forms. Therefore, most point defects, mainly interstitials and vacancies, were distributed throughout the original crystal and then they should annihilate after high temperature annealing up to 1400 °C by recombination. (3) Silicon was partly amorphized, and showed very slight expansion due to the irradiation.

In this study, we investigated the physical property change of CVD-diamond, single-crystal silicon and polycrystalline silicon carbide following neutron irradiation. Samples were irradiated in the same reactor to those in [14] but the irradiation temperature was 725 °C instead of 380 °C. Changes in the physical properties observed following irradiation are compared to those reported in [14] in order to find the role played by irradiation temperature.

* Corresponding author. Tel.: + 81 3 5734 3380; fax: + 81 5734 2959.
E-mail address: tyano@nr.titech.ac.jp (T. Yano).
[1] Present address: Japan Nuclear Fuel Limited, 4-108 Aza Okitsuke, Oaza Obuchi, Rokkasho-mura, Kamikita-gun, Aomori 039-3212, Japan.

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doi:10.1016/j.jnucmat.2008.12.203

2. Experimental procedures

Diamond films on single-crystal silicon or silicon carbide substrates were prepared by the CVD method (Sumitomo Electric Industries, Japan). The thickness of the coating was about 20 μm. This diamond coating was polycrystalline and no special orientation. The substrates used were semiconductor-grade single-crystal silicon with the (1 1 1) plane parallel to the surface, and high thermal conductivity sintered polycrystalline SiC (mainly 6H, Hitachi Ltd., SC 101 grade). The size of both substrates was 10 mm in diameter and 1 mm in thickness. These specimens were neutron-irradiated in JMTR up to a fluence of 8.1×10^{24} n/m^2 (neutron energy: $E_n > 0.1$ MeV) at 725 °C in a He encapsulated irradiation rig. After irradiation, changes in X-ray diffraction pattern (Philips, PW-1700, Netherlands), Raman spectrum (Jobin Yvon, T6400, France) and microstructure (H-9000 transmission electron microscope, Hitachi Ltd., Japan) were observed. Evaluation procedures were the same as mentioned elsewhere [14]. Property change of diamond mentioned below was obtained from CVD diamond on the SiC substrate, and those of SiC and Si were obtained from uncoated surface of SiC or Si substrates.

3. Results and discussion

3.1. CVD-diamond

The lattice parameter expanded by 0.39% after neutron irradiation at 725 °C, which was almost half of the case irradiated at 380 °C (0.76%). The full-width at half-maximum of the (1 1 3) diffraction peak slightly increased to 0.29° (2θ/Cu Kα) from 0.21° before irradiation, and mostly same as the case of the specimen irradiated at 380 °C (0.32). The lattice parameter of the unirradiated specimen (0.3568 nm) was almost same value (+0.03%) as that of the JCPDS 6-675 (0.3567 nm). This indicated the effect of coating, i.e., residual stress due to different swelling rates and also due to heat treatment during fabrication process, may be negligible, probably since the thickness of the coating was relatively large (~20 μm). The change in lattice parameter of diamond due to isochronal annealing is shown in Fig. 1. The lattice parameter change of the lower temperature irradiated specimen [14] and of an unirradiated specimen were also plotted. The lattice parameter of the present specimen irradiated at 725 °C was almost constant up to 800 °C and slightly decreased over that temperature up to 1200 °C. On the contrary, that of the specimen irradiated at lower temperature (380 °C) did not change up to around 400 °C, which corresponded to the irradiation temperature, and above that temperature the lattice parameter started to contract and decreased continuously up to around 1200 °C. It is interesting that the value after the annealing at 1300 °C of the present specimen and that of the lower temperature irradiated specimen was same. At 1400 °C, both specimen did not recover to the state of pre-irradiation, and still showed about 0.20% swelling.

Fig. 2 illustrates Raman spectra of the unirradiated specimen, as-irradiated specimen at 785 °C and annealed specimen at 1500 °C in the range from 1100 to 1700 cm^{-1}. The unirradiated specimen showed a single strong peak at 1335 cm^{-1}, which is a typical peak from diamond (sp^3), and a broad peak around 1520 cm^{-1}. After neutron irradiation, a relatively sharp and symmetric peak was observed at peak position of 1327 cm^{-1}, which is slightly shifted to lower wave number. Also broad peak at 1500 cm^{-1} was observed. After annealing at 1500 °C, a relatively sharp peak was observed at 1329 cm^{-1}, very close to the original position of the diamond peak. New peaks at 1390, 1410 and 1580 cm^{-1} were observed. These peaks did not develop in the as-

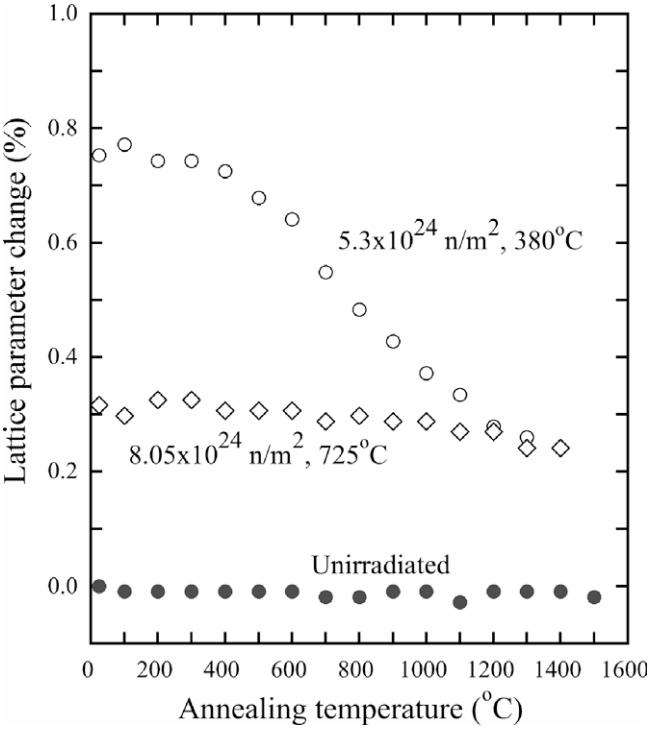

Fig. 1. Change in lattice parameter of diamond due to isochronal annealing for 1 h.

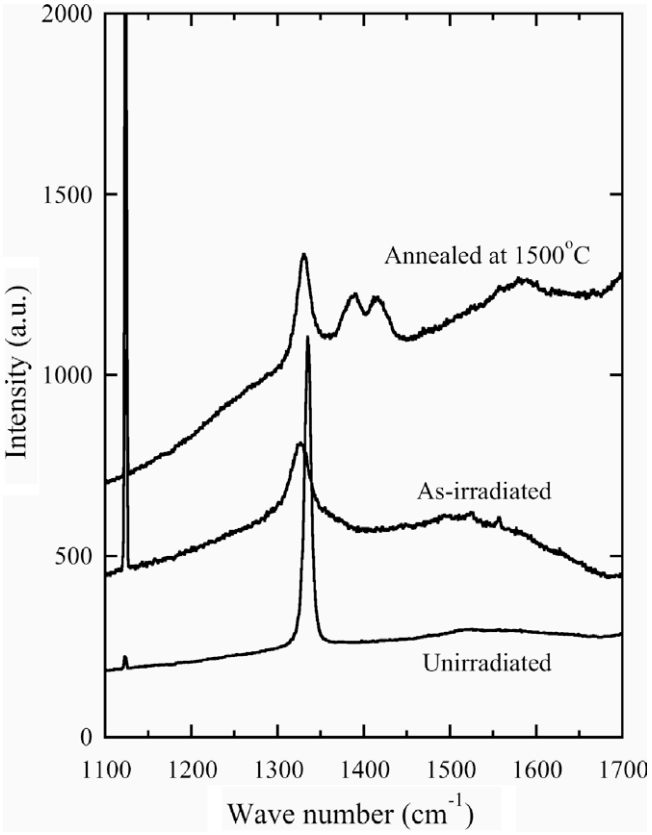

Fig. 2. Raman spectra of diamond in the range from 1100 to 1700 cm^{-1}. Unirradiated, as-irradiated to 8.05×10^{24} n/m^2 at 725 °C and post-irradiation-annealed specimen at 1500 °C for 1 h. The peak at 1125 cm^{-1} was Hg from room light.

irradiated specimen. These peaks were also observed for the specimen irradiated at 380 °C and annealed at 1500 °C.

The as-synthesized, as-irradiated CVD-diamond and that after annealing at 1500 °C were observed by transmission electron microscopy. As-synthesized CVD-diamond contained a large number of stacking faults along the {1 1 1} planes. After neutron irradiation, no resolvable defects induced by neutron irradiation were observed except for black-dots defects. After annealing at 1500 °C, the microscopic feature has not changed significantly. No clear difference was observed for the specimens irradiated at different temperatures.

Primak et al. [15] reported that dilatation of diamond after irradiation of 1.8×10^{24} n/m^2 ($E_n > 75$ eV) at 30 °C was about 3.5 vol.%, and was not changed significantly (2.6%) after 1.1×10^{25} n/m^2 (fast neutron) at 270 °C. They also observed the gradual decrease without any steps in the lattice constant by thermal annealing up to 950 °C. Nikolaenko and Karpukhin reported about 3.8% volume increase after irradiation of 1.7×10^{24} n/m^2 ($E_n > 0.18$ MeV) at 500–600 °C [16], and 3.7% after 3×10^{24} n/m^2 ($E_n > 0.18$ MeV) at 60 °C [17]. Present result of the linear expansion of 0.39% is less than reported values mentioned above, regardless of volume expansion is nearly three times as much as corresponding linear expansion, but high irradiation temperature (785 °C) can explain it. The recovery behavior of lattice parameter from nearly irradiation temperature (Fig. 1) supported an early work by Primak et al. [15] and Pravdyuk et al. [18].

After neutron irradiation, the diamond Raman peak near 1327 cm^{-1} shifted 8 cm^{-1} to lower wave numbers. Khasawinah et al. observed resemble peak shift of this diamond peak for ^{10}B doped diamond after neutron irradiation in the order of 10^{24} n/m^2 ($E_n > 0.1$ MeV) [19]. Compare with the lower temperature irradiation case, the amount of shift and deformation of peak shape was small, indicating less damage. No clear peaks at around 1580–1620 cm^{-1} corresponding graphite sp^2 was observed, thus degree of broken sp^3 bonding is less significant at higher temperature irradiation. In the case of lower temperature irradiation, large shift and deformation of peak shape coupled with the presence of a characteristic peak at about 1600 cm^{-1} indicating presence of sp^2 cluster [19–21].

Due to the isochronal annealing, the lattice parameter slightly shrank from irradiation temperature with increasing annealing temperature, but did not recover until the pre-irradiation state after annealing at 1400 °C. The value after the annealing at 1400 °C of the present specimen and that of the lower temperature irradiated specimen was same. Primak et al. [15] showed that the lattice parameter did not recover completely by annealing up to 950 °C. The Raman spectrum of the present specimen after 1500 °C annealing indicates an increase in intensity of the diamond peak at almost the same shift (1329 cm^{-1}) as before irradiation. New peaks at 1390, 1410 and 1580 cm^{-1} were developed which were not observed before annealing. Both peaks at 1390 and 1580 cm^{-1} can be assigned to those of disordered graphite (sp^2 bonding), but the peak at 1410 cm^{-1} cannot be assigned. Therefore, sp^2 components should exist after annealing at 1500 °C, which correspond to the incomplete recovery of the lattice parameter.

3.2. Silicon

Only very little expansions of 0.001% were observed for the present higher irradiation temperature specimen, as mentioned by Chelyadinskii [22]. The full-width at half-maximum of the (5 3 1) peak has not changed (about 0.12°). Another significant change in the XRD peaks was that of a broad peak at 17–27° with a maximum at 23°, as shown in Fig. 3. This peak was not observed before neutron irradiation. This broad peak was slightly sharp in the case of higher temperature irradiated specimen. After annealing at 1000 °C, the intensity of this broad peak was weakened but it did not disappear completely. These features were common for higher and lower temperature irradiation.

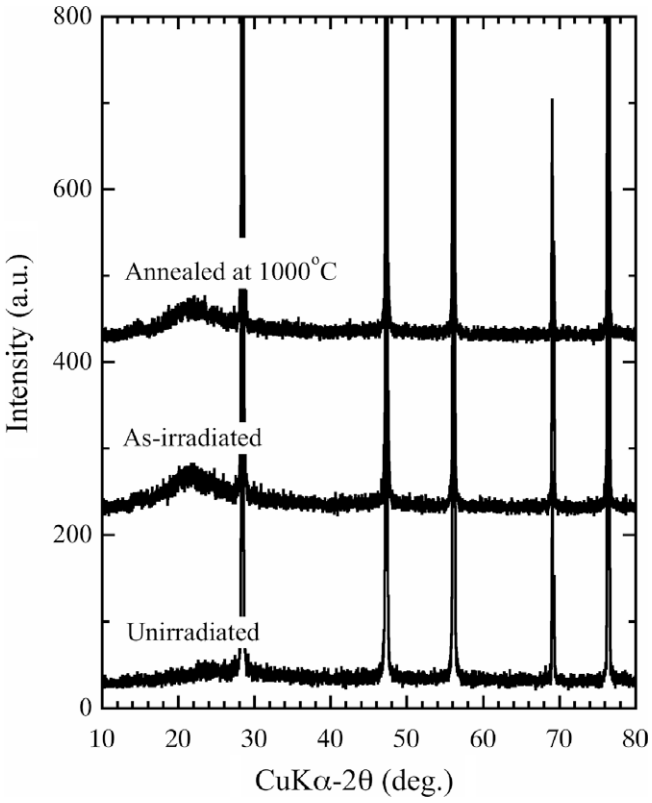

Fig. 3. X-ray diffraction patterns of silicon, unirradiated and as-irradiated to 8.05×10^{24} n/m^2 at 725 °C and post-irradiation-annealed at 1000 °C for 1 h.

Raman spectra of the unirradiated and irradiated silicon are shown in Fig. 4. At 521 cm^{-1}, a strong peak was observed commonly in the unirradiated and irradiated specimens, that is attributed for crystalline Si. After neutron irradiation, a new broad peak at around 480 cm^{-1}, attributed for amorphous silicon [23], was observed both for higher and lower temperature specimens.

Both by bright field images and high-resolution images using transmission electron microscopy, we could not detect any obvious change in microstructure of silicon due to neutron irradiation, i.e., dislocation loops, black dots like defects clusters or voids were not observed. Oshima et al. [24] reported damage structure of neutron-induced defects in silicon by weak-beam TEM observation, and indicated these were vacancy type.

3.3. Silicon carbide

The lattice parameter of silicon carbide measured on uncoated surface after 785 °C irradiation expanded by 0.20% along the *a*-axis and 0.27% along the *c*-axis, which was smaller in the case of 380 °C irradiation, 0.58% along the *a*-axis and 0.60% along the *c*-axis. The change of the present specimen was not isotropic. Full-width at half-maximum of the (2 1 9) peak increased to 0.31° (2θ/CuKα) by the irradiation, compared to unirradiated and irradiated specimen at the lower temperature, 0.18° and 0.20°, respectively. Only black dots like contrasts were observed by lower magnification electron microscopy, but at high-resolution observation the modification of crystalline lattice were observed, as reported elsewhere [25]. The *a*- and *c*-axis lattice parameters of the present SiC started to decrease from about 1000 °C, and continuously contracted by isochronal annealing up to about 1400 °C. After annealing at

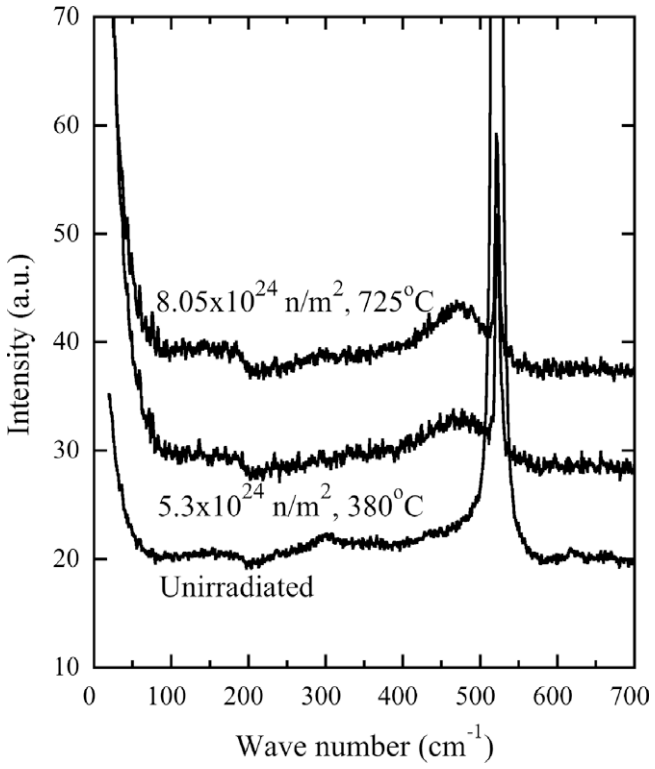

Fig. 4. Raman spectra of silicon in the range from 50 to 700 cm^{-1}. Unirradiated, irradiated to 8.05 × 10^{24} n/m^2 at 725 °C and irradiated to 5.3 × 10^{24} n/m^2 at 380 °C.

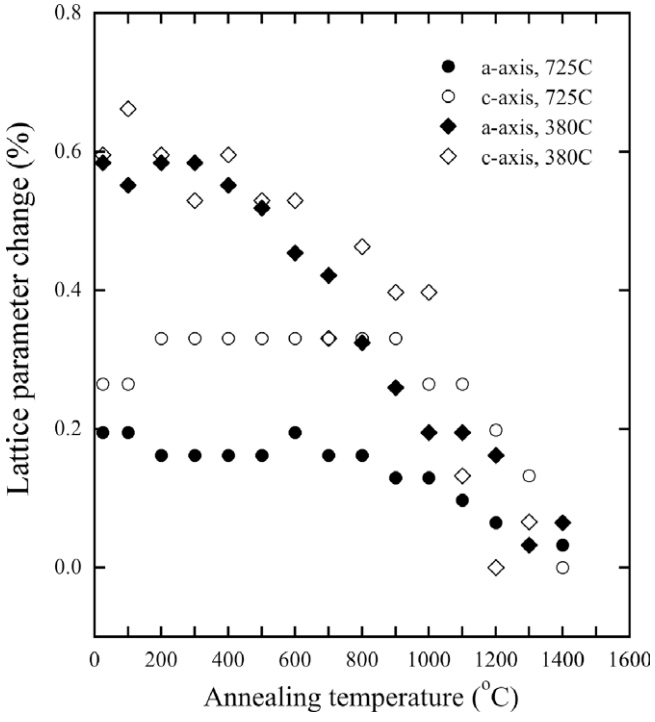

Fig. 5. Change in lattice parameter of silicon carbide irradiated to 8.05 × 10^{24} n/m^2 at 725 °C and irradiated to 5.3 × 10^{24} n/m^2 at 380 °C due to isochronal annealing for 1 h.

1400 °C, these values were fully recovered to the pre-irradiation values, and anisotropy was diminished, as shown in Fig. 5.

3.4. Comparison of three materials

Diamond, silicon and silicon carbide belong to a very similar crystal structure based on the diamond structure. Their atomic bonding nature has predominantly covalent character. Silicon and SiC are semiconductors, whereas diamond is basically an insulator. The melting point of Si (1414 °C) is much lower than that of silicon carbide (2830 °C) and diamond (>3000 °C). The reported displacement energies of diamond (80 eV) and SiC (45–90 eV) are higher than that of silicon (11–22 eV) [26].

The lattice parameter expanded to relatively large values of 0.39% and 0.20–0.27% in diamond and silicon carbide, respectively, compared with a very small value of 0.001% in silicon. Pravdyuk et al.[18] remarked that swelling of diamond exceeded that of SiC after the same neutron fluence of the order of 10^{24} n/m^2 at 100–200 °C. The present result on swelling also indicated the same feature whereas the irradiation temperature was higher than in the early study. One of the reasons of the very small lattice expansion in silicon can be attributed to the estimation that the relative volume change per interstitial ($\Delta\Omega_i = +0.55$) in silicon is only slightly in excess of that of a vacancy ($\Delta\Omega_v = -0.50$) [27]. From Raman spectroscopy and X-ray diffraction, an amorphization of the crystal was clearly observed only in silicon as broad peaks at 17–27° by XRD and by Raman peaks at 480 cm^{-1}, which was assigned to an amorphous phase [28,29]. In silicon, an amorphous phase is formed as a result of neutron irradiation over a fluence of 10^{25} n/m^2 [29] besides vacancy clusters [30]. This result was supported by the molecular dynamic simulation by Diaz de la Rubia et al. [31] induced by 3–5 keV displacement cascades in silicon carbide and silicon, where amorphization took place only in silicon, otherwise the disordered region retains the basic crystal structure in SiC. As a reason of a larger expansion of diamond than that of silicon carbide, we can attribute a diamond graphite transition induced in diamond. The atomic volume of graphite (0.0088 nm^3) is much greater than that of diamond (0.0057 nm^3), therefore homogeneous nucleation of small sp^2 clusters may induce lattice expansion [32]. A further basic difference during irradiation is the vacancy mobility. The mobility of interstitials is high in all three materials, but that of vacancies is low except for in silicon. High mobility of monovacancies and divacancies in silicon at less than room temperature or a few hundreds °C, respectively, is reported [33]. Large differences in radiation response in silicon from those in diamond and silicon carbide are basically corresponding to the differences in mobility or stability of defects and thus the remaining defects in the crystals despite of similar geometric structures.

4. Conclusions

CVD-diamond on single-crystal silicon or polycrystalline silicon carbide substrates were neutron-irradiated up to a fluence of 8.1 × 10^{24} n/m^2 (E_n > 0.1 MeV) at 785 °C. Changes in XRD patterns, Raman spectra and microstructure were observed after irradiation and post-irradiation annealing, and compared with the results on the specimens irradiated to 5.3 × 10^{24} n/m^2 at 380 °C.

(1) Neutron irradiation induced no clear graphite-like sp^2 clusters besides point defects in CVD diamond at 785 °C. Sp^2 clusters probably nucleated during irradiation, and grow and could not recover after annealing up to 1500 °C. Due to the nucleation of these clusters, swelling of diamond may be greater than that of silicon carbide. Lattice swelling decreased from around the irradiation temperature, but recovery was not completed due to the presence of sp^2 clusters.

(2) Silicon was partly amorphized independent of irradiation temperature. The very small expansion was explained by the small difference in relative volume change per interstitial and that of a vacancy despite of the small displacement energy. Furthermore, the mobility of monovacancies at room temperature, different from that of diamond and silicon carbide, should be a cause of irradiation response.
(3) Silicon carbide did not transform into other crystalline or non-crystalline form. Therefore, most point-like defects were distributed throughout the crystal and then they annihilate during annealing up to 1400 °C by pair recombination.

Acknowledgements

We would like to thank Prof. Kakihana of Tohoku University for assistance in Raman spectroscopy and useful discussions. The work was partly supported by the Grant-in-Aid for Scientific Research from The Japan Society for Promotion of Science. The irradiation experiment was kindly supported by the staff of the O-arai branch, Institute of Materials, Tohoku University.

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