ELSEVIER

Journal of Nuclear Materials 307–311 (2002) 1102–1106

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Physical property change of concurrently neutron-irradiated CVD-diamond, silicon and silicon carbide

T. Yano [a,*], Y. Yamamoto [a], T. Iseki [b]

[a] *Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan*
[b] *Department of Inorganic Materials, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

Abstract

Diamond films on single-crystal silicon or polycrystalline silicon carbide substrates were neutron irradiated up to a fluence of 5.3×10^{24} n/m^2 ($E_n > 0.1$ MeV) at 380 °C. After irradiation, changes in X-ray diffraction, Raman spectra and microstructure were observed. Some specimens were further annealed up to 1500 °C, and changes in these properties were measured. The lattice parameters expanded by 0.76%, 0.60% and 0.005% in diamond, silicon carbide and silicon, respectively. The Raman peak of diamond at 1335 cm^{-1} was weakened and shifted 30 cm^{-1} toward lower wave numbers and was asymmetric after irradiation, but after annealing up to 1500 °C a relatively large peak at 1331 cm^{-1} was observed. Raman peaks corresponding to sp^2 clusters were also observed after irradiation and post-irradiation annealing at 1500 °C. The lattice parameter of diamond started to decrease at around the irradiation temperature and linearly decreased up to 1200 °C, but not fully recovered after annealing at 1300 °C. Partial amorphization was observed only in irradiated Si.

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 to separate the vacuum chamber from the r.f. generator. Diamond seems to be the best material for that window and was actually applied to the JT-60 fusion experimental device in JAERI [6], due to its very high thermal conductivity in the order of >1000 W/m K and low $\tan\delta$ in the order of $<1.3 \times 10^{-3}$ before neutron irradiation [7]. It is well known that physical properties such as length, thermal conductivity and, $\tan\delta$ are greatly influenced by fast-neutron irradiation. A small number of reports on physical property changes of diamond have been published, particularly on the annealing behavior. Therefore, in this study, we investigated the physical property changes of CVD-diamond by fast-neutron irradiation. Single-crystal silicon and polycrystalline silicon carbide, both of which belong to the similar crystal structure with that of diamond, were concurrently irradiated, and changes in physical properties were compared to these of CVD-diamond.

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 10 μm and one surface of the substrates was coated. This diamond coating was polycrystalline and no special orientation was observed by X-ray diffraction (XRD). The substrates used were semiconductor-grade single-crystal silicon with the (1 1 1)

* Corresponding author. Tel.: +81-3 5734 3380; fax: +81-3 5734 2959.
E-mail address: tyano@nr.titech.ac.jp (T. Yano).

0022-3115/02/$ - see front matter
PII: S0022-3115(02)01113-3

plane parallel to the surface, and high thermal conductivity sintered polycrystalline SiC (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 the Japan Materials Testing Reactor up to a fluence of 5.3×10^{24} n/m^2 (neutron energy: $E_n > 0.1$ MeV) at 380 °C in a He encapsulated irradiation rig for 1065 h. After irradiation, changes in XRD pattern (Philips, PW-1700, Netherlands), Raman spectrum (Jobin Yvon, T6400, France) and microstructure (H-9000 transmission electron microscope, Hitachi Ltd., Japan) were observed. The lattice constant of diamond was measured at room temperature by the internal standard method using Si (NBS640, $a = 0.543088$ nm) on the (1 1 3) peak. That of SiC, diffraction angles of (2 0 3) and (2 1 9) were measured by the same method as diamond. The lattice constant of Si was measured using Pd ($a = 0.38898$ nm) as an internal standard, and (4 2 2), (5 1 1), (4 4 0), (5 3 1) and (6 2 0) peaks were measured. Raman spectra from the surface of specimens exited by an Ar-laser of 514.5 nm with beam diameter of about 1 mm was recorded at room temperature. The wave number was calibrated by an Hg peak at 1125 cm^{-1}, which came from room light. Some specimens were further isochronally annealed with each temperature up to 1500 °C for 1 h in vacuum, and changes in these properties were measured at room temperature.

3. Results

3.1. CVD-diamond

The lattice parameter expanded by 0.76% after neutron irradiation. The full-width at half-maximum of the (1 1 3) diffraction peak slightly increased to 0.32 (2θ deg., CuKα) from 0.21 before irradiation. The change in lattice parameter due to isochronal annealing of diamond is shown in Fig. 1. The lattice parameter of an unirradiated specimen was also measured. The result on the unirradiated specimen was not affected by annealing up to 1500 °C. That of the irradiated diamond did not change up to around 400 °C, which corresponded to the irradiation temperature. Above that temperature, the lattice parameter started to contract and decreased continuously up to around 1200 °C. At 1300 °C, it did not recover to the state of pre-irradiation, and still showed about 0.25% swelling.

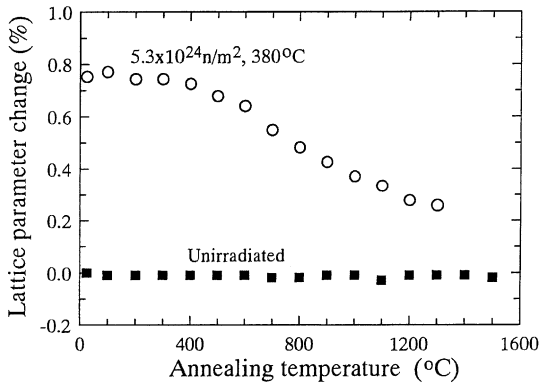

Fig. 1. Change in lattice parameter due to isochronal annealing of diamond.

Fig. 2 illustrates Raman spectra of the unirradiated specimen, as-irradiated specimen 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 broad and asymmetric peak with tailing on the lower frequency side was observed at peak position of 1305 cm^{-1}. Furthermore, a new broad peak at 1620 cm^{-1} occurred. After annealing at 1500 °C, a relatively sharp peak was observed at 1331 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-irradiated specimen.

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

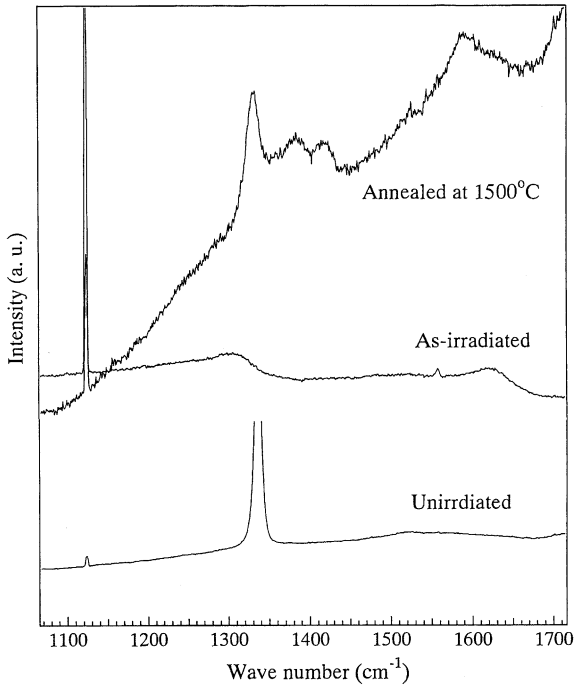

Fig. 2. Raman spectra in the range from 1100 to 1700 cm^{-1} of diamond, unirradiated, as-irradiated and annealed specimen at 1500 °C.

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.

3.2. Silicon

The lattice parameter of silicon was influenced by the neutron irradiation very slightly compared to those of diamond and silicon carbide. Only very little expansions of 0.005% were observed. The full-width at half-maximum of the (5 3 1) peak has not changed (about 0.13 (2θ deg., CuKα)). Another significant change in the XRD peaks was that of a broad peak at 17–27 (2θ deg., CuKα) with a maximum at 23 deg., as shown in Fig. 3. This peak was not observed before neutron irradiation. After annealing at 1000 °C, the intensity of this broad peak was weakened but it did not disappear completely.

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. After neutron irradiation, a new broad peak at around 480 cm^{-1} was observed.

Both by bright field images and high-resolution images using transmission electron microscopy, we could not detect any obvious changes in microstructure of silicon due to neutron irradiation, i.e., dislocation loops, black-dots like defects clusters or voids were not observed.

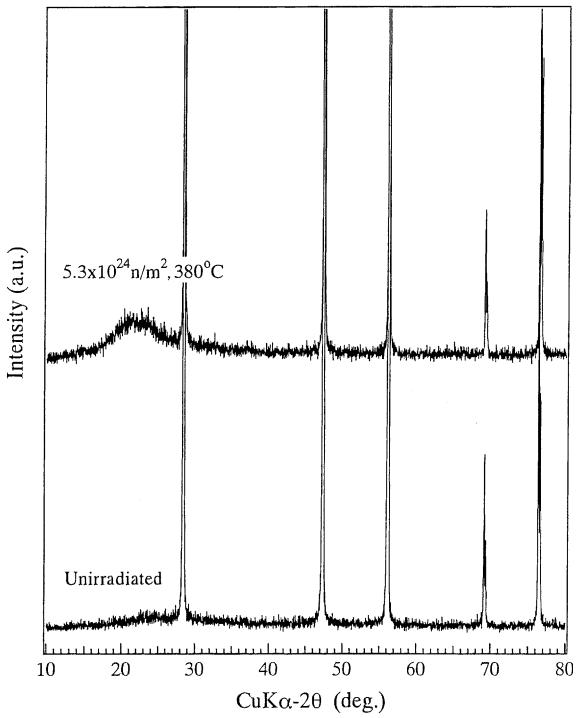

Fig. 3. XRD patterns of unirradiated and irradiated silicon.

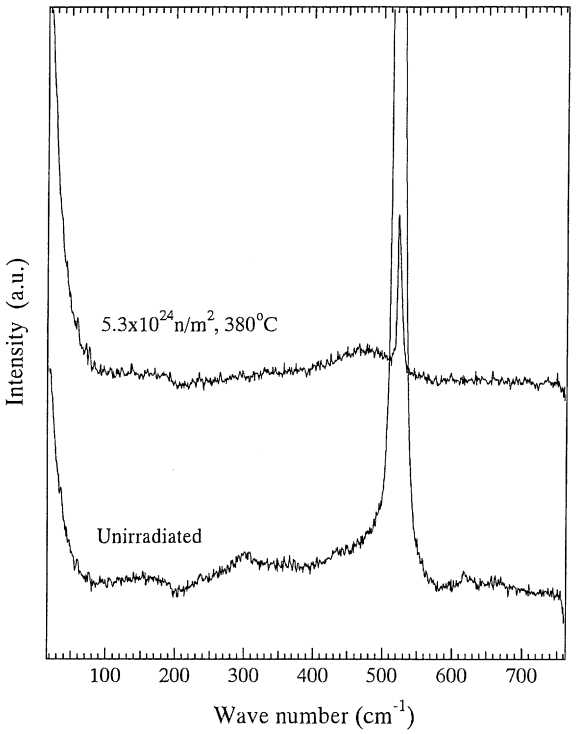

Fig. 4. Raman spectra of unirradiated and irradiated silicon.

3.3. Silicon carbide

The present silicon carbide consisted mainly of hexagonal 6H polytype. The lattice parameter of silicon carbide expanded by 0.58% along the *a*-axis and 0.60% along the *c*-axis. The change was nearly isotropic. Full-width at half-maximum of the (2 1 9) peak has not changed by irradiation. Only black-dots like contrasts were observed by electron microscopy. The *a*- and *c*-axis lattice parameters started to decrease from about 400 °C, and continuously contracted by isochronal annealing up to about 1400 °C. After annealing at 1400 °C, these values were fully recovered to the pre-irradiation values.

4. Discussion

4.1. Irradiation effects on CVD-diamond

Primak et al. [8] 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) at 270 °C. They also observed the gradual decrease without any steps in the

lattice constant by thermal annealing up to 950 °C. Nikoraenko 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 [9], and 3.7% after 3×10^{24} n/m^2 ($E_n > 0.18$ MeV) at 60 °C [10]. Present results of the linear expansion of 0.76% mostly coincides with reported values mentioned above. The recovery behavior from rough irradiation temperature as shown in Fig. 1 supported an early work by Pravdyuk et al. [11]. It was also reported that diamond will be amorphized (loss of (3 3 1) X-ray peak) after neutron irradiation over the fluence of 4×10^{25} n/m^2 at 477 °C, corresponding to a volume swelling of 3.4% at 327 °C [12]. The irradiation condition of the present specimen is not in excess of both the neutron fluence and volume swelling, so that it does not amorphize, as supported by XRD observation.

After neutron irradiation, the diamond Raman peak near 1333 cm^{-1} shifted 30 cm^{-1} to lower wave numbers and was asymmetric. Khasawinah et al. observed the resembling peak shift and broadening 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) [13]. The shift observed in this study was larger compared with their result, and cannot be interpreted only by irradiation induced stress [13]. Then it should be attributed partly to crystalline size effects, so-called nano-sized diamond containing sp^2 cluster with a characteristic peak at about 1600 cm^{-1} [13–15]. A decrease in intensity and broadening of the diamond (sp^3) 1333 cm^{-1} Raman peak, and corresponding increase in thermal resistivity of single-crystal diamond were reported by Morrelli et al. [16]. Within their experimental conditions (fluence $<4.5 \times 10^{22}$ n/m^2), no evidence of sp^2 bonds was observed (1360 and 1580 cm^{-1}), except for 1620 cm^{-1}, the same as the present study. From microstructure observations and change in XRD profiles, coupled with Raman spectra, it is reasonable to conclude that neutron irradiation induces small sp^2 clusters besides vacancies and interstitials in the present CVD-diamond. It is not clear whether defect clusters observed by TEM correspond to sp^2 clusters detected by Raman spectroscopy.

Due to the isochronal annealing, the lattice parameter shrank from irradiation temperature almost linearly with increasing annealing temperature, but did not recover until the pre-irradiation state after annealing at 1300 °C. Primak et al. [8] 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 (1331 cm^{-1}) as before irradiation. New peaks at 1390, 1410 and 1580 cm^{-1} were developed instead of the peak at 1620 cm^{-1} 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. Khasawinah et al. mentioned that nano-phase diamond, which includes sp^2 bond, induced by neutron irradiation could be recovered by annealing at 1000 °C for 8 h [13]. This is a contradictory result from the present study.

4.2. Comparison of three materials

Diamond and silicon belong to the same diamond-type crystal structure, and silicon carbide has also 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 Debye temperature of Si (645 K) is also much lower than those of diamond (2230 K) and β-silicon carbide (1270 K) [17,18]. The reported displacement energies of diamond (80 eV) and SiC (45–90 eV) are higher than that of silicon (11–22 eV) [19].

The lattice parameter expanded to relatively large values of 0.76% and 0.60% in diamond and silicon carbide, respectively, compared with a very small value of 0.005% in silicon, as mentioned by Chelyadinskii [20]. Pravdyuk et al. [11] 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 ($\Delta i/\Omega = +0.55$) in silicon is only slightly in excess of that of a vacancy ($\Delta v/\Omega = -0.50$) [21]. From Raman spectroscopy and XRD, an amorphization of the crystal was clearly observed only in silicon as broad peaks at 17–27 (2θ deg., CuKα) by XRD and by Raman peaks at 480 cm^{-1}, which was assigned to an amorphous phase [22,23]. In silicon, an amorphous phase is formed as a result of neutron irradiation over a fluence of 10^{25} n/m^2 [23] besides vacancy clusters or interstitial clusters [24]. This result was supported by the molecular dynamic simulation result of Rubia et al. [25] 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 is much greater than that of diamond, therefore the homogeneous formation of small sp^2 clusters may induce the lattice expansion [12].

A further basic difference during irradiation is the vacancy mobility. The mobility of interstitials is high in all three materials, in spite of the high mobility of vacancies only in silicon. Large differences in radiation response between silicon and diamond or silicon carbide correspond basically to the differences in melting point and Debye temperature despite of similar geometric structures.

5. Conclusion

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

(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 slightly greater than that of silicon carbide. Lattice swelling decrease starts around the irradiation temperature up to 1200 °C, but full recovery is not completed due to the presence of sp^2 clusters up to 1300 °C.

(2) Silicon carbide shows similar response to neutron irradiation like diamond, but does not transform into other crystalline or non-crystalline forms unlike diamond. Therefore, most point-like defects, mainly interstitials and vacancies, were distributed throughout the original crystal and then they should annihilate after high temperature annealing at 1400 °C by recombination.

(3) Silicon was partly amorphized. 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 vacancies at irradiation temperature, different from that of diamond and silicon carbide, should be a cause of irradiation response.

Acknowledgements

We would like to thank Professor M. Kakihana of Tokyo Institute of Technology for assistance in Raman spectroscopy and useful discussions. This work was partly supported by the collaborative research program of the Materials and Structures Laboratory, Tokyo Institute of Technology. The irradiation experiment was kindly supported by the staff of the O-arai branch, Institute of Materials, Tohoku University.

References

[1] L.H. Rovner, G.R. Hopkins, Nucl. Technol. 29 (1976) 274.
[2] G.P. Pells, J. Nucl. Mater. 122&123 (1984) 1338.
[3] F.W. Clinard Jr., G.F. Hurley, R.W. Klaffky, Res Mech. 8 (1983) 207.
[4] G.R. Hopkins, R.J. Price, Nucl. Eng. Des./Fus. 2 (1985) 111.
[5] S.J. Zinkle, E.R. Hodgson, J. Nucl. Mater. 191–194 (1992) 58.
[6] A. Kasugai, K. Sakamoto, K. Takahashi, M. Tsuneoka, T. Kariya, T. Imai, O. Braz, M. Thumm, J.R. Brandon, R.S. Sussman, A. Beale, D.C. Ballington, Rev. Sci. Instrum. 69 (1998) 2160.
[7] K. Sakamoto, A. Kasugai, M. Tsuneoka, K. Takahashi, T. Kariya, Y. Mitsunaka, Rev. Sci. Instrum. 70 (1999) 208.
[8] W. Primak, L.H. Fuchs, P.P. Day, Phys. Rev. 103 (1956) 1184.
[9] V.A. Nikolaenko, V.I. Karpukhin, At. Energy 82 (1997) 81.
[10] V.A. Nikolaenko, V.I. Karpukhin, At. Energy 79 (1995) 603.
[11] N.F. Pravdyuk, V.A. Nikoraenko, V.I. Karpuchin, V.N. Kuznetsov, in: D.J. Litter (Ed.), Property of Reactor Materials and Effects of Radiation Damages, Butterworth, 1962, p. 57.
[12] V.A. Nikolaenko, V.G. Gordeev, Radiat. Eff. Def. Sol. 139 (1996) 183.
[13] S.A. Khasawinah, G. Popovici, J. Farmer, T. Sung, M.A. Prelas, J. Chamberlain, H. White, J. Mater. Res. 10 (1995) 2523.
[14] M. Yoshikawa, Y. Mori, H. Obata, M. Maegawa, G. Katagiri, H. Ishida, A. Ishitani, Appl. Phys. Lett. 67 (1995) 694.
[15] M. Yoshikawa, N. Nagai, M. Matsuki, F. Fukuda, G. Katagiri, H. Ishida, A. Ishitani, N. Nagai, Phys. Rev. B 46 (1992) 7169.
[16] D.T. Morelli, T.A. Perry, J.W. Farmer, Phys. Rev. B 47 (1993) 131.
[17] C. Kittel, Introduction to Solid State Physics, 7th Ed., John Wiley, New York, 1996.
[18] E.L. Kern, D.W. Hamitt, H.W. Deem, H.D. Sheels, Mater. Res. Bull. 4 (1969) S25.
[19] F.W. Clinard Jr., L.W. Hobbs, in: R.A. Johnson, A.N. Orlov (Eds.), Physics of Radiation Effects in Crystals, Elsevier Science, 1986, p. 387.
[20] A.R. Chelyadinskii, Sov. Phys. Solid State 18 (1976) 506.
[21] W. Mayer, H. Peisl, J. Nucl. Mater. 108&109 (1982) 627.
[22] M. Coeck, C. Laermans, R. Provoost, R.E. Silverans, Mater. Sci. Forum 258–263 (1997) 623.
[23] B. Schröder, H. Wild, E. Minninger, J. Nucl. Mater. 108&109 (1982) 685.
[24] R. Oshima, T. Kawano, R. Fujimoto, J. Nucl. Mater. 212–215 (1994) 293.
[25] T. Diaz de la Rubia, M.-J. Caturla, M. Tobin, Mater. Res. Soc. Proc. 373 (1995) 555.