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Investigation of the damage behavior in CVD SiC irradiated with 70 keV He ions by NEXAFS, Raman and TEM

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ABSTRACT

Chemical vapor deposited (CVD) SiC was irradiated with 70 keV He ions at room temperature. The damage behavior was investigated by near edge X-ray absorption fine structure (NEXAFS) spectroscopy, Raman spectroscopy and transmission electron microscopy (TEM). NEXAFS spectra at the Si K-edge display the obvious decrease in intensity of crystalline peaks and near disappearance of the peak at 1852 eV, suggesting an increase in crystalline disorder resulting from an increased number of Si vacancies caused by irradiation. Raman spectra show the decomposition of crystalline Si-C bonds and the formation of homonuclear (Si–Si and C—C) bonds during irradiation. TEM results show the transition from slight disorder to full amorphization with increasing dose. The dose to amorphization (DTA) is estimated to be about 1 dpa. It is also found that high density of stacking faults in CVD SiC may contribute to the enhancement of amorphization resistance compared to single crystal β-SiC.

1. Introduction

Silicon carbide (SiC) has been considered as a promising material for nuclear applications because of its small neutron capture cross section, good corrosion resistance and high-temperature strength [1,2]. SiC has many polymorphs including α-SiC and β-SiC, among which only face center cubic (FCC) β-SiC shows cubic symmetry [3]. In nuclear reactors, β-SiC is more widely used than α-SiC due to the irradiation induced anisotropic swelling of α-SiC, which can cause intergranular cracking of materials [2,4]. Polycrystalline β-SiC has been used as the coating layer for tri-structural isotropic (TRISO) fuel [5]. Continuous SiC fiber-reinforced SiC-matrix composites (SiC_f/SiC) are developed as candidate materials for core components of nuclear reactors because of the improved toughness compared to ceramic [6–9]. Both the fibers and matrices in SiC_f/SiC are composed of crystalline β-SiC.

Irradiation damage is a critical issue, which will influence the structure stability, thermal properties and mechanical properties of SiC [10–18]. For examples, accumulation of irradiation induced defects causes amorphization [10,11] and swelling[12–14] of SiC. The increased phonon-scattering by these defect clusters degrades the thermal conductivity of SiC significantly [15,16]. Irradiation induced toughening and creep have also been reported [17,18]. In addition, agglomerate He atoms produced through nuclear reactions can form He bubbles and stabilize the vacancy clusters caused by irradiation, resulting in the degradation of mechanical properties and enhanced cavity formation [19–23]. Therefore, to understand these behaviors, it is necessary to carry out a systematic study on the irradiation damage behavior of β-SiC.

Transmission electron microscopy (TEM) techniques are frequently employed to observe the irradiation induced microstructural evolution. Spectroscopic techniques with less destructiveness are also useful to detect irradiation damage. Raman spectroscopy provides information about chemical bonds and has been used widely to study the disorder accumulation caused by irradiation [24–26]. Near edge X-ray absorption fine structure (NEXAFS) spectroscopy offers information about the near-neighbor local structure in materials. Especially, Si K-edge NEXAFS spectra can reveal the crystalline order of SiC [27–29]. Deslandes et al. studied the damage of 3C-SiC caused by H and He ions irradiation with NEXAFS [25]. They reported the disappearance of peaks related to crystalline

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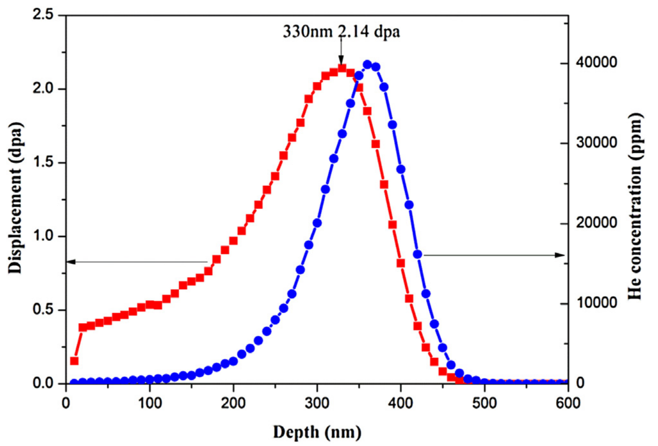

Fig. 1. Depth profiles of damage level (dpa) and He concentration produced by 70 keV He ions in CVD SiC, corresponding to the ion fluence of 5×10^{16} ions/cm^2. Calculations were performed using SRIM-2013, setting the displacement threshold energies to be 21 eV for C and 35 eV for Si.

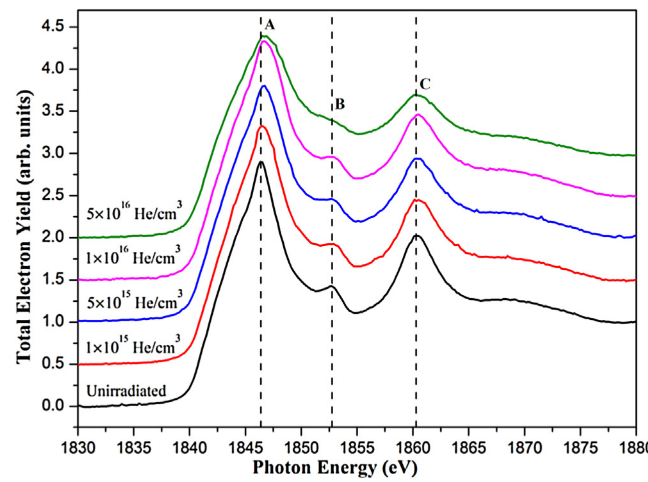

Fig. 2. NEXAFS spectra at the Si K-edge for CVD SiC samples irradiated with 0 (unirradiated), 1×10^{15}, 5×10^{15}, 1×10^{16} and 5×10^{16} ions/cm^2.

SiC and the appearance of Si-O peaks, suggesting that disorder and oxidization of SiC had been induced by irradiation.

In view of the general consensus that ion irradiation is an effective way to simulate neutron irradiation with low cost and little radioactivity [30], we have carried out such a study, in which chemical vapor deposited (CVD) SiC samples were irradiated with 70 keV He ions at room temperature to investigate the damage behavior induced by irradiation. The irradiated samples were characterized by NEXAFS, Raman spectroscopy and TEM.

2. Material and methods

The chemical vapor deposited (CVD) SiC samples used in this study are polycrystalline β-SiC produced by Rohm & Hass. The density of CVD SiC is 3.21 g/cm^3. They were cut to blocks with the dimensions of 5mm × 5mm × 2mm. These samples were ultrasonically cleaned in acetone, alcohol, and deionized water to remove the surface dirt and grease and dried by air blowing. Then the samples were irradiated with 70 keV He ions at room temperature using a 100 keV isotope separator located at the Shanghai Institute of Applied Physics, Chinese Academy of Sciences. The irradiation fluences were 1×10^{15}, 5×10^{15}, 1×10^{16} and 5×10^{16} ions/cm^2. The damage level (displacement per atom, dpa) and He concentration profiles were calculated using the Stopping and Range of Ions in Matter (SRIM) 2013 [31], as shown in Fig. 1. The displacement energies of C and Si for calculation are 21 eV and 35 eV, respectively [32]. The irradiation damage depth was about 500 nm. The damage increases firstly with depth, achieving to the peak damage at the depth of 330 nm from the surface, and then decreases with depth rapidly.

The NEXAFS measurements were performed at the spherical grating monochromator (SGM) beamline of the Canada Light Source (CLS), the University of Saskatchewan. The Si K-edge NEXAFS spectra were recorded in steps of 0.2 eV from 1830 to 1880 eV and collected in total electron yield (TEY) mode. All spectra were firstly normalized by the incident photon flux. Then the edge jump (the difference between the pre-edge region and a flat region of the post-edge region) were normalized to unity for the purposes of comparison.

Raman spectra were measured using a Bruker senterra Raman spectrometer coupled with an Olympus microscope that contains an X–Y–Z stage. The 532 nm line of a frequency-doubled Nd-YAG laser was focused on a 1 × l μm^2 spot and collected through a 50× objective. Spectra were collected in the range between 200 and 2000 cm^{-1} with a spectral resolution of about 3–5 cm^{-1}.

Thin specimens for TEM observations were prepared using the focused ion beam (FIB) technique. A layer of tungsten was deposited over the area of interest to prevent damage of the cross-sectional surface of the samples. Initial milling and final polishing were carried out sequentially with 30 keV and 5 keV Ga ions, respectively. The thus prepared TEM samples were examined by a FEI Tecnai G2 F20 S-TWIN TEM with the accelerating voltage of 200 kV.

3. Results

3.1. NEXAFS

It should be noted that the detecting depth of TEY at the Si K-edge is about 10 nm [29], which is far away from peak damage region. The damage levels at the depth of 10 nm are estimated to be 0.0032, 0.016, 0.032 and 0.16 dpa in samples irradiated with different ion fluences. Therefore, NEXAFS results in this study reveal the irradiation damage evolution within 0.16 dpa. The Si K-edge NEXAFS spectra of unirradiated and irradiated SiC samples in TEY are shown in Fig. 2. The spectrum of unirradiated sample presents several well-defined peaks of β-SiC, including the most intense peak A at 1846 eV with a lower energy shoulder peak and two resonance peaks B and C at 1852 eV and 1860 eV. Peak A represents the shape resonance caused by the modulation of the low energetic outgoing photoelectron wave due to multiple scattering on the nearest neighbor atoms [28]. The shoulder peak is attributed to the resonance excitation from Si 1 s to Si 3p–C 2sp hybridized states [28,33]. Peaks B and C correspond to the unoccupied densities of states of p character [34], which are related to the presence of a "medium" and a "short" range order in SiC, respectively [27–29]. For the samples irradiated with 1×10^{15} ions/cm^2, 1×10^{15} ions/cm^2 and 1×10^{16} ions/cm^2 (~0.0032, 0.016 and 0.032 dpa), NEXAFS spectra show no obvious differences as compared to unirradiated sample except that the peaks B were not as sharp as that of unirradiated sample, indicating the weak irradiation damage. However, at the highest dose (5×10^{16} ions/cm^2, ~0.16 dpa), significant change can be observed. The intensities of Peaks A and C decreased obviously. Especially, Peak B became very subtle and broader, indicating the destruction of "medium" term order caused by irradiation. It is noted that the Peaks A and C were still well defined, meaning that the "short" term order were retained.