Surface blistering of ion irradiated SiC studied by grazing incidence electron microscopy

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Abstract

We present the structural analysis of surface blisters on SiC crystals heavily irradiated by He^+ and H^+ ions using grazing incidence electron microscopy and electron energy-loss spectroscopy. The shapes of the blisters were similar to those observed in silicon as the target, but the critical fluence and skin structure of the H-blisters were considerably different from those in silicon, while the He-blisters had features very similar to the case of silicon. The differences between silicon and SiC can be tentatively explained by the differences of binding energies of Si–Si, Si–C, Si–H and C–H. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

A blistering phenomenon has been often observed on material surfaces exposed to high-temperature plasma and/or gas ion irradiation for long-term use in nuclear environments. The phenomenon has been generally considered to occur by accumulation of implanted gas atoms or molecules along the layer corresponding to their projected range, followed by the gas pressure pushing up the surface layer. A few examples of the cross-sectional observations confirmed that a high density of gas bubbles actually coalesced into a spacious opening in the matrix [3,4].

The present research group has recently applied grazing incidence electron microscopy (GIEM) to the blisters on silicon surfaces. Since this method allows us a detailed non-destructive structural analysis and requires no tedious sample preparation procedures specific to TEM, it is effectively applicable to any materials, brittle or ductile [5]. The GIEM observation revealed that morphologies and skin structures of blisters by H^+, D^+ or He^+ bombardment on silicon surfaces are very different [1,2]. Moreover blisters by H^+ or D^+ irradiation are formed at a much smaller fluence than that of He^+

irradiation. Those differences could be attributed to the chemical reactivity between the implant and the target material as well as the energy deposition (mainly the nuclear stopping) brought by the implant species. It is therefore a natural extension of the study to examine the blistering on other target materials with different physical/chemical properties.

Silicon carbide (SiC) is considered as one of the candidate materials for the first wall of fusion reactors due to its high-temperature properties, small neutron capture cross-section and high chemical stability, and its fundamental properties under energy particle irradiation have been both intensively and extensively investigated. In addition, SiC is a covalent binary system with the same tetrahedral local coordination as silicon, though its chemical and physical properties are very different from those of silicon. Thus, to examine the surface blistering on SiC can provide additional and essential information to tackle its formation mechanism at further length, which is the motivation of the present study.

2. Experimental

The experimental setup of GIEM has been described in detail previously [1,5]. The sample was a $\langle 0001 \rangle$-oriented 6H–SiC wafer, one side of that was electro-chemically polished. The wafer was cut into a rectangular

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parallelepiped block of 2 mm × 1 mm × 1 mm. Each block was mounted on a single-hole grid with the shiny side edge-on to the center of the grid. The shiny polished side of the sample was irradiated with H^+ and He^+ ions at room temperature. The ion energies were selected to be 16 and 19 keV, respectively for H^+ and He^+ irradiation to give nearly the same projected range ($\simeq$230 nm) as the previous studies on Si [1]. GIEM observation and electron energy-loss spectroscopy (EELS) measurements were carried out using the Jeol JEM-200CX equipped with the Gatan Digi-PEELS model 766.

3. Results

3.1. GIEM observations

A GIEM image of the SiC surface irradiated with He ions at the fluence of 2.0×10^{22} m^{-2} is shown in Fig. 1(a) and (b), an enlarged one among the blisters with its diffraction pattern inset. The structure of the He-blister skin is an amorphous mesh including a high density of He-bubbles, as shown in the figures. These apparent features are very similar to the He-blisters on silicon surface.

On the other hand, no blister was observed at the fluence below 2.0×10^{22} m^{-2} for H^+ irradiation. A perspective and an enlarged H-blister at the fluence of 4.0×10^{22} m^{-2} are shown in Fig. 1(c) and (d), together with the diffraction pattern. The structure of the blister skin is also amorphous but its shape is flatter than that

of the He-blister. The thickness of the blister skins seems rather uniform unlike those of He-blisters.

3.2. EELS measurements

Representative EELS spectra in the plasmon energy-loss region obtained from the central part of the H- and He-blister are shown in Fig. 2. The peak at 21.5 eV corresponds to the bulk plasmon of SiC. The K-shell

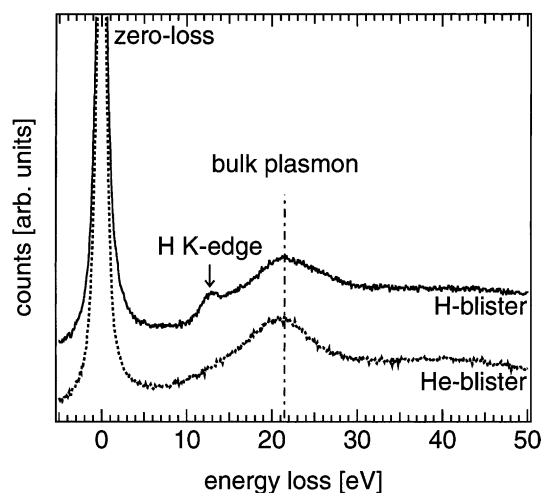

Fig. 2. EELS spectra acquired from the center part of the He- and H-blister. These spectra were normalized with the height of zero-loss peak and then offset vertically.
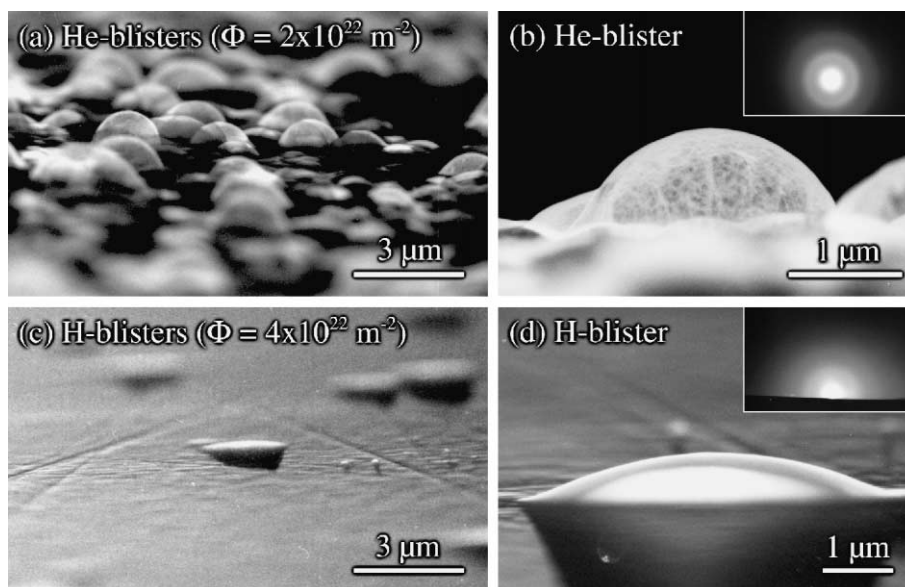

Fig. 1. GIEM images obtained for He^+-irradiated (a) and H^+-irradiated (c) SiC; (b) and (d) are enlargements of a blister with its diffraction pattern inset in each sample.
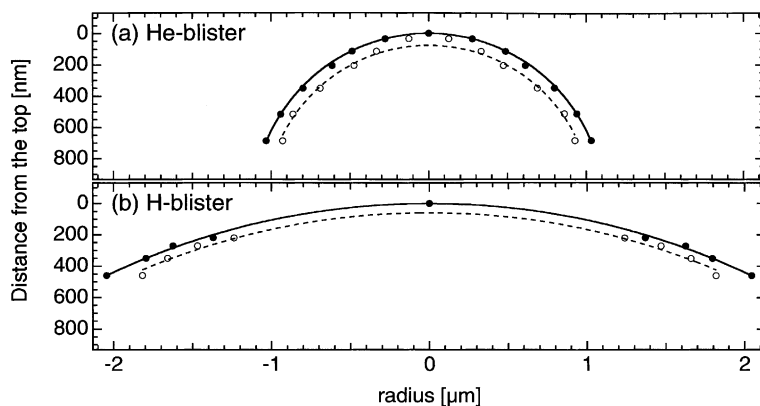
Fig. 3. Derived cross-sectional structures of (a) He-blister and (b) H-blister. The solid circle represents the outer boundary of the blister skin and the open circle the inner boundary. The curves were computed using concentric circle functions.

absorption edge of hydrogen is clearly seen at 13.6 eV, which is an unambiguous evidence of a high density of H_2 molecules incorporated inside the H-blister. The He K-shell absorption edge, however, is not apparently visible unlike the case of silicon [1], probably because the large bulk plasmon peak superposes on the He K-edge.

The specimen thickness t, through which the incident electron travels, is given by

$$t/\lambda = \ln(I_t/I_0), \qquad (1)$$

where I_0 is the zero-loss (elastic scattering) intensity, I_t is the total electron intensity reaching the spectrometer and λ is the electron mean free path for energy-loss (165 nm for SiC using the jellium model) [6]. One can thus estimate the path length of electrons through the sample, which enables us to delineate the cross-sectional view of the blister. The obtained cross-sectional structures for H- and He-blisters are shown in Fig. 3(a) and (b), and the radii of curvature and the thickness of H- and He-blister skins are tabulated in Table 1, with comparison of the results of silicon and SiC. Note that the thickness

of the blister skins is much less than the projected range ($\simeq 230$ nm) calculated with a Monte-Carlo simulation code, TRIM-98 [7]. This is partly based on the large plastic deformation for the dome-like protrusions to develop and partly based on a considerable amount of outward atomic flow or evaporation, which is discussed in Section 4.

4. Discussion

4.1. Morphology of blisters and their skins

In the case of silicon as the target material, the structure of blister skins exhibited to be highly defective monocrystalline, an admixture of amorphous and randomly oriented nano-crystals, and fully amorphous for H^+, D^+ and He^+ irradiation, respectively. Their structural differences are to be reported in further detail in separate papers, but these features roughly reflect the magnitude of the nuclear stopping power of implant species [1,2]. The same principle holds for the blister

Table 1
Experimental conditions and structural parameters for He- and H-blister

Target	Ion species	Accelerating voltage (kV)	Fluence (m^{-2})	Radius of curvature (nm)	Effective skin thickness (nm)	Structure of blister skin
SiC	He^+	19	2.0×10^{22}	1100	78	Amorphous with high density of bubbles
	H^+	16	4.0×10^{22}	4800	59	Amorphous having uniform thickness
Si	He^+	16	2.0×10^{22}	1200	100	Amorphous with high density of bubbles
	H^+	13	1.0×10^{22}	3400	85	Single crystal original, orientation remains

structure on SiC, which is much more easily amorphized than silicon by irradiation.

However, in contrast to the fact that the radius of curvature was larger for H(D)-blisters than for He-blisters on silicon, corresponding to the much less gas pressure or total fluence, the radius of curvature of H-blisters was still much larger than that of the He-blisters on SiC in spite of the much more implanted atoms. This means that the implanted hydrogen atoms did not effectively work for the blistering and that the internal gas pressure was smaller in SiC. This point is discussed again in Section 4.2.

4.2. Critical fluence for blistering

In the case of blistering on silicon, He-blistering required the ion fluence about twice as much as that for H(D)-blistering to obtain a similar blister density although the effective internal gas pressure in He-bubbles should be nearly twice as much as that in H(D)-bubbles for the same number of atoms involved. It follows that hydrogen can considerably enhance the blistering in silicon. A clue to solve this problem was given by the projected thickness images by energy-filtering electron microscopy [8]: the H(D)-blister skin has a rather uniform thickness while the He-blister skin is porous due to a high density of bubbles. The implanted hydrogen atoms effectively terminate broken Si–Si bonds along the projected range, which induces micro-cracks followed by coalescence into large cracks to facilitate the blistering. This is very similar to the mechanism of 'smart cut' for producing the SOI structure [9] and we call this effect as the 'chemical effect' of implanted species.

In the present case of SiC, the H-blister seems to have rather uniform thickness, which suggests that the same mechanism works in the H-blistering as in Si. However, the H-blister density is still much less than that of He-blisters, as shown in Fig. 1(a) and (c) although the total fluence of (c) is much more than (a).

These different features in the blistering on Si and SiC likely originate from differences in the binding energies of Si–Si (3.39 eV/atom), Si–C (4.68 eV), Si–H (3.10 eV) and C–H (3.51 eV) [10]. The hydrogen atoms first break the chemical bonding of Si–Si and Si–C, respectively, in case of silicon and SiC as the target, but more energies should be necessary to break the Si–C bonds than Si–Si ones. Moreover, since the Si–C bonds are more stable than the other possible combinations of chemical bonds by more than 1 eV, successive irradiation may give rise to restore the once formed Si–H and/or C–H bonds to Si–C ones and released hydrogen atoms can diffuse away out of the sample surface. After the matrix is fully disordered, hydrogen can start to terminate effectively the broken bonds so as not to increase the total energy significantly, and the blistering proceeds in the way similar to the silicon–hydrogen system.

Note that the skin thickness of the H-blister in SiC is thinner than that in silicon although the projected range is similar, as shown in Table 1. According to the context of the present discussion above, this can be explained by considering that the hydrogen atoms released from the Si–H and C–H states diffuse to the surface and probably escape away as the forms of H_2, CH_4 and/or SiH_4, the latter two of which can reduce the effective thickness of the H-blister skins.

5. Conclusions

Surface blistering on a SiC crystal irradiated by H^+ and He^+ was studied with GIEM and associated EELS. The structures of the H- and He-blister skins were both amorphous unlike the case of H- and D-blisters in silicon, which reflects much easier irradiation induced amorphization of SiC. Furthermore, H-blistering required a much higher H-fluence, about twice as much as that required for He-blistering, in contrast to the fact that hydrogen acts much more effectively on blistering than helium in silicon.

The observed features of the H-blistering in SiC can be tentatively explained by the stability of chemical bonding between silicon, carbon and hydrogen. In the case of SiC, Si–C bonds are most stable rather than making S–H and/or C–H bonds, which hinders the crack formation and propagation, generally enhanced by the hydrogen termination of broken bonds. This assumption is, however, still based on speculations and need to be confirmed experimentally in future.

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