Crystal Nucleation Behavior Caused by Annealing of SiC Irradiated with Ne at Liquid Nitrogen Temperature or at 573 K

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1. Introduction

Silicon carbide (SiC) is a promising material, in view of its potential ability to wide applications, in areas such as semiconductors,1 optical2 and optoelectronic devices,3 fusion reactors,4 and high-temperature gas-cooled reactors.5 In the nuclear application fields, irradiation behaviors of SiC must be an important subject to study. Ion implantation and subsequent removal of the radiation damages are also important for technological steps in the device-processing field. Thus, up to date, many researchers have conducted irradiation studies on SiC6–10.

In our previous study, we made annealing treatments to SiC specimens amorphized with Ne irradiation at room temperature and showed that specimens irradiated with higher fluence provide greater number of crystal nucleation sites than those irradiated with lower fluences.10 Fluence dependence of the crystal nucleation behavior attracts attention in view of application studies, such as solid phase epitaxy11 of ion beam induced amorphous SiC, as well as basic studies. We have reported10 that a cause of the fluence dependence may be a structural change of amorphous SiC and/or an increase in a density of implanted gas atoms. However, it was difficult to clarify which one played more important role by varying only the ion fluence as a variant. Accordingly, we have investigated the influence of the fluence of different implanted gas atoms.12 In the study, we selected Ne and He as irradiation ion species to vary the rate of implanted inert gas atoms to the elastic displacement damage (gas atom/peak dpa); the peak ion implantation of He was estimated to be about 5 times as large as that of Ne for the same peak dpa. We have found that the greater number of crystal nucleation sites can be generated with smaller dpa in the case of He ion irradiation than in the Ne irradiation. It seemed from these results that the density of the implanted inert gas atoms would promote the crystal nucleation.

Inui et al.13 made annealing treatments to SiC specimens amorphized by electron irradiation and reported the occurrence of epitaxial growth of the crystals subjected to annealing at 1173K for 30 minutes for specimens irradiated to critical amorphization fluence. On the other hand, for a specimen irradiated to a fluence well above the critical level, both of the crystal nucleation and epitaxial growth occurred. These results suggested that further increase of the disordered structures of amorphized SiC led to an increase in the number of crystal nucleation sites.

In our previous study,14 we carried out irradiations to SiC specimens with Ne ions at temperatures from 573 to 673 K, and found that the irradiation with Ne at temperatures well over 573K was so high to examine the dependence of the crystal nucleation behavior on the amorphous structure that amorphization did not occur in the depth region where a number of Ne atoms existed.14

In the present study, we have tried to see the effect of the amorphous structure on crystal nucleation behavior, by selecting liquid nitrogen temperature and 573K for the irradiation temperature in order to get different amorphous structures for the same amount of implanted gas atoms.

2. Experimental

The specimen used in this study was CVD-β-SiC, purchased from Furuiuchi-Kagaku Ltd. It was subjected to dimpling and Ar ion etching for TEM observation. Major impurity concentration in mass ppm contained in the specimen are: 130Cr, 62Mn, 43V, 13Ti, 200V, 400.

The irradiation and annealing were carried out in a TEM (JEM-2000FX of JEOL Ltd.), with a thermal field emission gun, linked with an ion accelerator.

The ion species was J(30 keV) Neþ. The
incident angle of the ion beam was about 30 degree to the observation direction. Ion flux was $3.1 \times 10^{17} \text{Ne}^+/\text{m}^2/\text{s}$. Used ion fluences were 1.9 and $2.3 \times 10^{20} \text{Ne}^+/\text{m}^2$. Irradiation temperatures were 573 K and liquid nitrogen temperature (hereafter referred to as LT).

The dpa and implanted Ne ions were distributed to the depth of about 80 nm and the peak depths were estimated to be about 23 and 37 nm from the irradiated surface of the specimen for the dpa and Ne ion distribution, respectively. The peak dpa and peak Ne concentration were estimated to be $8.35 \text{dpa}$ and $2.45 \text{at}\%$ for the fluence of $1 \times 10^{20} \text{Ne}^+/\text{m}^2$, respectively, from TRIM-98 calculation. 15)

After the irradiations, specimen temperatures were returned to room temperature (RT), and then they were annealed in the TEM at 1273 K for 30 minutes and then returned to RT spending over 2 h.

3. Results and Discussion

Figure 1 shows a schematic illustration of an annealed specimen in a case when the crystal nucleation occurs in it. Changes in bright field images with annealing in specimens irradiated with fluence of $1.9 \times 10^{20} \text{Ne}^+/\text{m}^2$ at 573 K and about 98 K are shown in Figs. 2 and 3, respectively. Those with annealing in specimens irradiated with fluence of $2.3 \times 10^{20} \text{Ne}^+/\text{m}^2$ at 573 K and about 98 K are shown in Figs. 4 and 5, respectively.

Thin regions near the hole, made for TEM observation, of the specimens were completely amorphized by the irradiations for all four irradiation conditions as seen in the electron diffraction images shown in Figs. 2(a), 3(a), 4(a) and 5(a). Many defect contrasts were observed in the crystalline-remaining regions in the cases of 573 K irradiations [see the regions where the crystalline contrasts appeared in Figs. 2(a) and 4(a)]. Dense bubbles were also observed in the whole of the ion implanted region except the very thin region near the hole of the specimens for all four irradiation conditions [see
Figs. 2(a), 3(a), 4(a) and 5(a). In the thin region, since most of the gas ions passed through there easily, i.e., the implanted gas ions were negligible small in number, the density and size of the bubbles were also negligible small. Generally, the size of the bubbles observed was very small, a few nm in diameter when the fluence was $1.9 \times 10^{20} \text{Ne}^+/\text{m}^2$, whereas it was around 5–8 nm in diameter at the largest when the fluence was $2.3 \times 10^{20} \text{Ne}^+/\text{m}^2$ for both irradiation temperature cases, i.e., 573 K and LT.

Crystal nucleation was observed after the annealing in the specimens irradiated to the fluence of $2.3 \times 10^{20} \text{Ne}^+/\text{m}^2$ for both irradiation temperature cases [see the electron diffraction images in Figs. 4(b) and 5(b)]. No effect of the irradiation temperature on the crystal nucleation occurred within the present experimental range. On the other hand, the volume fraction of the amorphous region in the annealed specimens appeared to be larger in the case of LT irradiation as seen in the electron diffraction images [see Figs. 4(b) and 5(b)].

Halo rings remained in the electron diffraction image as seen in Fig. 5(b). There is, however, a possibility that the difference might be due to a small error in Ne ion flux. A probable cause for the fact that no effect of the irradiation temperature on the crystal nucleation occurred is one or two of the following ones:

a) The concentration of the implanted inert gas atoms played more important roll than the amorphous structure in the crystal nucleation behavior under the condition that a large volume fraction of the inert gas bubbles was formed in amorphous SiC. (The number of the implanted gas atoms would be independent of the irradiation temperature and the temperatures were too low for the implanted gas atoms to diffuse long distances in the as-irradiated specimens; as a result, they produced a great number of bubbles there.)

b) The amorphous structure was independent of the irradiation temperature in this experimental range.

c) Crystal nucleation behavior was independent of amorphous structure in this experimental range. It was found that the volume fraction of the amorphous structure was different for the different irradiation temperatures, which implies that the amorphous structures formed at 573 K and 98 K might have differed in its stability. On the other hand, the amount of implanted gas atoms
would be independent of irradiation temperature. It seems, therefore, that a main cause why the crystal nucleation behavior showed no dependence of the irradiation temperature was that the implanted gas atom played more important role than that of the amorphous structure.

It is interesting to note that few numbers of the bubbles were changed when the amount of the fluence was more than a certain value, which meant that the volume fraction of the bubbles had much more effect than the number of the bubbles.

Debye-Sherrer rings from the nucleated crystals well fitted to the net pattern [see Fig. 4(c)] of the matrix region [see Fig. 1]. There appeared, however, no ring corresponding to (200) of $\beta$-SiC, as seen in Fig. 4(c). The $\beta$-SiC corresponds to “3H”-SiC and (200)$_{\beta}$ corresponds to (1012)$_{3H}$. On the other hand, the rings corresponding to (0003)$_{3H}$, (111)$_{3H}$, (1120)$_{3H}$, (220)$_{3H}$, and (1123)$_{3H}$, (311)$_{3H}$ were clearly observed. In addition, streaks were observed in the diffraction patterns from a small region including the small amount of the nucleated crystals [see the streak shown with the white arrow in Fig. 4(d)]. Therefore, it seems certain that the nucleated and grown crystals were SiC with disordered stacking sequence.

Concerning the bubbles, the following phenomena have been found in the regions to which epitaxial growth had not yet reached [see Fig. 1] even in the LT irradiation case. [see Figs 5(c) and (d)]:

1) Bubble coalescence occurs only in nucleated and grown crystals.
2) No changes in the size and shape of bubbles were observed in the region outside the nucleated crystals.

It should be noted that it is difficult to confirm whether the bubble coalescence occurs even in the amorphous SiC or only in the crystalline SiC in the matrix region [see Fig. 1]. It has been suggested that the Ne bubble coalescence occurs only when the atoms rearrange for recrystallization at 1273 K. While no effect of the irradiation temperature on the crystal nucleation behavior occurred within the present experimental range, it appeared certain that the concentration of the implanted gas atoms played more important roll than the amorphous structure in the crystal nucleation behavior. It is therefore essential to take the effect of implanted gas atoms, in the case that the implanted gas atoms are inert gas,
as well as those of amorphous structure and stoichiometry into consideration on the crystal nucleation behavior in the case of amorphization caused by the ion irradiation. To study an amorphous structure formed by means of quenching of liquid specimen, that can be a suitable method for the study of the effect of amorphous structure, may be an alternative way.

4. Conclusions

(1) No effect of irradiation temperature on crystal nucleation behavior was observed within the present experimental range. It appeared certain, however, that the concentration of implanted inert gas atoms played more important roll than the amorphous structure on the crystal nucleation behavior under the condition that the inert gas bubbles were formed in amorphous SiC.

(2) Bubble coalescence was observed in the crystallized area after annealing in the specimens irradiated to the fluence of \(2.3 \times 10^{20}\text{Ne}^+/\text{m}^2\) at both of 573 K and liquid nitrogen temperature. No change in the bubble state was observed in the region outside the bubble-coalesced region after annealing even in the case of LT irradiation.

(3) Crystal nucleation sites were increased as the fluence of irradiation was increased.

(4) It appeared that the nucleated and grown crystals were SiC consisting of disordered stacking sequence.

REFERENCES