Vacancy effects on the formation of He and Kr cavities in 3C-SiC irradiated and annealed at elevated temperatures

Hang Zang ^{a,*}, Weilin Jiang ^{b,*}, Wenbo Liu ^a, Arun Devaraj ^b, Danny J. Edwards ^b, Charles H. Henager Jr. ^b, Richard J. Kurtz ^b, Tao Li ^a, Chaohui He ^a, Di Yun ^a and Zhiguang Wang ^c

Abstract

Polycrystalline 3C-SiC was sequentially irradiated at 400 and 750°C with 120 keV He²⁺ and 4 MeV Kr¹⁵⁺ ions to 10¹⁷ and 4×10¹⁶ cm⁻², respectively. The Kr¹⁵⁺ ions penetrated the entire depth region of the He²⁺ ion implantation. Three areas of He²⁺, Kr¹⁵⁺ and He²⁺ + Kr¹⁵⁺ ion implanted SiC were created through masked overlapping irradiation. The sample was subsequently annealed at 1600°C in vacuum and characterized using cross-sectional transmission electron microscopy and energy-dispersive x-ray spectroscopy. Compared to the He²⁺ ion only implanted SiC, He cavities show a smaller size and higher density in the co-implanted SiC. At 25 dpa, presence of He in the co-implanted 3C-SiC significantly promotes cavity growth; much smaller voids are formed in the Kr¹⁵⁺ ion only irradiated SiC at the same dose. In addition, local Kr migration and trapping at cavities occurs, but long-range Kr diffusion in SiC is not observed up to 1600°C.

Keywords: He and Kr cavities; vacancy effect; high-temperature annealing; ion irradiation; 3C-SiC

1. Introduction

Due to its excellent high-temperature stability, low neutron capture cross-sections, and good irradiation resistance, silicon carbide (SiC) has been considered as one of the most promising candidate materials for advanced nuclear applications, such as fuel cladding in fission reactors and structural components in fusion reactors [1,2]. Volume swelling in SiC irradiated at temperatures between the critical amorphization temperature (228°C for Au ion irradiation [3]) and 1000°C originates from production and accumulation of point defects and interstitial clusters (dislocation loops). It saturates after a dose of a few displacements per atom (dpa). Voids in SiC are formed when irradiation temperature is above 1000°C, where single vacancies become mobile [4,5]. Voids induced volume swelling has been found to increase with irradiation dose monotonically without saturation [6]. Void formation and microstructural evolution in SiC under high-temperature irradiation has been a topic of considerable scientific interest and technological significance. It is known that presence of He as a nuclear reaction product has an enormous effect on void formation and swelling during neutron irradiation [7]. As a

structural material in fusion reactors, SiC will receive a high flux of 14 MeV neutrons that induce transmutation in SiC, leading to generation of helium whose concentration is 1-2 orders of magnitude higher than in the fission environment [8]. Calculations by Sawan *et al.* [9] predict that ~2.2 at.% He are generated in SiC irradiated with the high-energy neutrons at an accumulative dose of 123 displacements per atom (dpa). The impact of helium at such a high concentration on cavity formation and swelling in SiC during irradiation is currently unknown.

Interaction between He atoms and irradiation-induced point defects leads to material swelling and physical property degradation. According to recent calculations by Li *et al.* [10], a small cavity of ~0.55 nm in size in 6H-SiC can accommodate up to 14 He atoms. An *in-situ* transmission electron microscopy (TEM) study [11,12] of He ion pre-implanted SiC has showed a He cavity size distribution with the most probable sizes at 1.75 nm and 3.75 nm at He concentrations of 0.8 at.% in nano-engineered SiC after Kr²⁺ ion irradiation to 10 dpa at 700°C [11]. Compared to thermally annealed SiC, the growth rate of He cavities during ion irradiation is reduced [12] due to He atoms displaced out of the cavities by collision cascades, showing that there is a strong effect of irradiation conditions on the growth behavior of He cavities. To date, only a few studies have focused on the defect-clusters and swelling caused by high-dose He ion implantation in SiC at high temperatures. Barbot *et al.* [13] have showed that swelling remains unchanged in 400°C implanted 4H-SiC after annealing at 500-1400°C, but increases significantly in 750°C implanted 4H-SiC after annealing at 1000-1700°C. However, the dependence of swelling on He concentration in SiC has not yet been reported. This study focuses on vacancy concentration effects on cavity formation and growth in 3C-SiC under irradiation of He, Kr, and He + Kr ions and subsequent annealing at high temperatures. The effects are studied as a function of the He cavity size and concentration. The mobility of Kr in 3C-SiC at high temperatures will also be discussed.

2. Experimental procedures

Materials used in this study include polycrystalline 3C-SiC with micrometer sized grains (prepared using chemical vapor deposition by Rohm and Haas Company) and monocrystalline 6H-SiC (obtained from Tiankeblue Semiconductor Company). All the implantation experiments were performed at the 320 kV Multidisciplinary Research Platform for Highly Charged Ions at the Institute of Modern Physics, Chinese Academy of Sciences. A 120 keV He²⁺ ion beam was rastered over a masked sample to insure uniform He implantation to $1 \times 10^{17} \text{ cm}^{-2}$ at 400°C. An elevated-temperature for irradiation was used to avoid full amorphization of the material. Subsequent thermal annealing at 750°C for 3 h in vacuum ($< 2 \times 10^{-3} \text{ Pa}$) was conducted to recover some of the implantation-induced defects. These samples were further implanted with a mask using 4 MeV Kr¹⁵⁺ to $4 \times 10^{16} \text{ cm}^{-2}$ at 750°C. Three regions in the 3C-SiC sample were created for this study, including He-implanted (Sample A), Kr-implanted (Sample B) and He + Kr co-implanted regions (Sample C). Figure 1 shows a schematic diagram, illustrating the sequential overlapping ion irradiations and the resulting Samples A, B and C. A tube furnace was used for

Table 1 Sequential overlapping He²⁺ and Kr¹⁵⁺ ion implantation and thermal annealing conditions for 3C- and 6H-SiC.

Material	1st Implantation	Fluence	Imp.	1st Ann.	2ed Implantation	Fluence	Imp.	2ed Ann.
	Ion; Energy	(cm ⁻²)	Temp.	Temp.; Time	Ion; Energy	(cm ⁻²)	Temp.	Temp.; Time
	(keV)		(°C)	(°C; h)	(MeV)		(°C)	(°C; h)
3C-SiC (A)	He ²⁺ ; 120	1×10 ¹⁷	400	750; 3	-	-	-	1600; 3
3C-SiC (B)	-	-	-	750; 3	Kr ¹⁵⁺ ; 4	4×10 ¹⁶	750	1600; 3
3C-SiC (C)	He ²⁺ ; 120	1×10 ¹⁷	400	750; 3	Kr ¹⁵⁺ ; 4	4×10 ¹⁶	750	1600; 3
6H-SiC	He ²⁺ ; 120	1×10 ¹⁷	400	750; 3	Kr ¹⁵⁺ ; 4	4×10 ¹⁶	750	1600; 3

subsequent thermal annealing at 1600°C for 3 h in vacuum ($<3 \times 10^{-1}$ Pa). The furnace was initially evacuated to 4.3×10^{-3} Pa. As the temperature increased to 1600°C, the pressure increased to 0.1 Pa. When the 3 h annealing process was completed and the furnace temperature decreased to room temperature, the pressure returned to 3.6×10^{-3} Pa. A 6H-SiC wafer was also implanted and annealed under the same conditions as Sample C and was used as a reference for compositional analysis. The ion implantation and thermal annealing parameters in this study are summarized in Table 1.

The depth profiles of the displaced atoms and implanted ions were calculated using SRIM-2013 code [14] under a full-damage cascade mode. The threshold displacement energies for Si and C sublattices in SiC were chosen to be $E_d(\text{Si}) = 35$ eV and $E_d(\text{C}) = 21$ eV [15], and the specific gravity of the SiC

Fig. 1. Sequential irradiation of a 3C-SiC at 400 and 750°C with 120 keV He²⁺ and 4 MeV Kr¹⁵⁺ ions to 10^{17} and 4×10^{16} cm⁻², respectively. Three regions in the 3C-SiC sample were created through masked overlapping irradiation, including He-implanted (Sample A), Kr-implanted (Sample B) and He + Kr co-implanted regions (Sample C).

Fig. 2. SRIM results of the displacements per atom, He and Kr atomic concentrations in SiC implanted with (a) 120 keV He ions (Sample A), 4 MeV Kr ions (Sample B), and He + Kr ions (Sample C).

sample was taken as the theoretical value of 3.21 g/cm^3 . The dpa and ion concentration distributions in Samples A, B and C are shown in Figs. 2(a), (b) and (c), respectively. From the simulation results, the peak concentration of 7 at. % He is located at the depth of $\sim 510 \text{ nm}$ in Samples A and C (Figs. 2(a) and (c)), and that of 1 at. % Kr at $\sim 1500 \text{ nm}$ in Samples B and C (Figs. 2 (b) and (c)). The doses at the He peak correspond to 4 and 25 dpa, respectively. One of the main aims of this work is to study the vacancy concentration effects on the size and density of the He cavities in Samples A and C during thermal annealing at 1600°C .

Sample C was initially analyzed using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with the sputtering and analyzing beams of 2 keV Cs^+ and 50 keV Bi_3^{++} , respectively. Elastic backscattering analysis or non-Rutherford backscattering spectrometry (non-RBS) for reference sample 6H-SiC, instead of Sample C due to a too small implantation area for the analysis, was performed at a scattering angle of 160° using 2.56 MeV H^+ ions. Cross-sectional TEM specimens for Samples A, B and C were prepared using focused ion beam (FIB, FEI Quanta). Conventional TEM, high angle annular dark field (HAADF) scanning TEM (STEM) and energy dispersive spectroscopy (EDS) were performed using both an FEI Tecnai G2 TEM and a JOEL ARM 200cF Cs-corrected TEM/STEM, both operating at an accelerating voltage of 200 kV . The ARM TEM was equipped with an enhanced EDS system, providing high detection sensitivity based on a silicon drift detector collecting x-rays from samples at a nominal collection angle of 0.98 Sr .

3. Results and discussion

3.1. Overall microstructure

ToF-SIMS results (data not shown) for Sample C suggest that there is an oxide layer on the sample surface with a thickness of $\sim 300 \text{ nm}$, which contains mainly Si and O with a nearly constant atomic ratio over the entire thickness. The oxygen concentration decreases abruptly to zero at the depth of the surface layer. A non-RBS result for a 6H-SiC wafer subjected to the same implantation and annealing conditions as for Sample C is shown in Fig. 3, together with the simulation result from SIMNRA [16]. The Kr and O peaks are well resolved from the SiC spectrum. The data suggests that the surface layer is silicon oxide, consistent with the SIMS result.

Figure 4 shows low-resolution TEM images for a general view of the microstructures in the

Fig. 3. Non-RBS spectrum, along with the SIMNRS result, for 6H-SiC implanted with He^{2+} and Kr^{15+} ions and annealed at 1600°C .

near-surface region of Samples A, B and C, where the surface layer is clearly exhibited. From Fig. 4(a), the He peak is located at ~770 nm from the surface of the top layer after thermal annealing, in contrast to the SRIM prediction for a depth of ~510 nm in SiC. The difference (~260 nm) is close to the thickness (~300 nm) of the surface layer. The data comparison suggests that the surface layer might be a deposited film, rather than an oxidized SiC layer during furnace annealing at 1600°C unless the He ion stopping powers in SiC are generally overestimated by ~50% in the SRIM database, which is not likely. In the annealing experiment, a similar deposition layer was also observed on the crucible surface of the furnace after annealing. Possible reasons for the surface deposition include the use of the new furnace without pre-conditioning. Partial exfoliation of the film from the SiC surface was observed after the thermal annealing. However, presence of this layer does not affect the major results and conclusions in this study, as will be discussed below.

Both the He and Kr cavities in the implanted and annealed samples are clearly visible. Also shown in the figures are the SRIM results for the He and Kr depth profiles with a depth scale indicated. The small difference in the profiles between the experiment and simulation is likely due to the uncertainty of the electronic stopping powers in the SRIM database [17]. The He cavity band is located in the depth range of 300-550 nm in (Fig. 4(a)), while the Kr cavity band is between 1200-1800 nm (Fig. 4(b)). These two cavity bands are well separated without profile overlap, as shown in Fig. 4(c). The TEM results in Fig. 4 also show a surface layer of ~300 nm in thickness, which is consistent with the SIMS and non-RBS results. Apparently, presence of this surface layer does not affect the behavior of the buried He or Kr cavity bands as both the He and Kr distributions are well separated from

Fig. 4. Low-resolution bright-field TEM images of (a) He ion implanted (Sample A), (b) Kr ion implanted (Sample B) and (c) He + Kr ion implanted (Sample C) 3C-SiC.

the SiC surface.

3.2. He ion implanted 3C-SiC

A bright-field low-resolution TEM image for Sample A is shown in Fig. 5(a). The width of the He cavity band is determined to be ~ 200 nm, which is consistent with the SRIM simulation (Fig. 2(a)). The high-resolution TEM image near the He peak shown in Fig. 5(b) reveals an image overlap of He cavities due to specimen thickness. The cavities are generally spherical, but some large cavities also show facets. The size distribution of the He cavities estimated from Fig. 5(b) is shown in Fig. 5(c). Very small cavities (<3 nm in size) are hardly resolvable due to image overlap and are excluded in the estimation. The size range is found to be fairly large, with cavity size up to

~ 34 nm. Based on the counted cavities, the average size is ~ 15 nm with a density of $\sim 9.4 \times 10^{16} \text{ cm}^{-3}$. This result is significantly different from Barbot's report [18], where the cavity sizes of up to 50 nm in 4H-SiC were observed as a result of 50 keV He^+ ion implantation to $1.0 \times 10^{17} \text{ cm}^{-2}$ at 750°C and annealed at 1500°C for 0.5 h. The difference could be attributed to a higher He-vacancy cluster concentration in the sample implanted at 750°C . Previous reports [11,19] have indicated that when SiC is irradiated with He ions to a high dose at 750°C , interstitial loops are formed with a supersaturated vacancy concentration. Since He de-trapping from He-vacancy clusters in SiC occurs at 1127°C [20] and vacancies become mobile in SiC at 1000 to 1100°C [21], the cavity size is determined by the combined effects of He and vacancy migrations and interactions during thermal annealing process. Further discussion is provided in section 3.4. It should be noted that unlike nanocrystalline SiC, where a majority of point defects produced during ion irradiation at elevated temperatures [22] could reach grain boundaries and be annihilated, the effects in polycrystalline SiC with micrometer sized grains in this study are not dominant and its disordering behavior is not very different from its monocrystalline counterpart.

3.3. Kr ion implanted 3C-SiC

Figure 6(a) shows a HAADF STEM image of Kr cavities near the profile peak of the implanted Kr (~ 1500 nm deep) in Sample B. The corresponding EDS map of Kr in the same area is shown in Fig. 6(b). Clearly, the microscopic features in the two images exactly overlap, indicating that all the cavities are filled with Kr gas. After a high-dose Kr ion implantation at 750°C , a supersaturated concentration of vacancies was produced in the SiC. Upon annealing at 1600°C , vacancies become mobile leading to

Fig. 5. (a) Bright-field TEM image of helium cavities in Sample A around the depth of 450 nm, (b) a high-resolution image near the depth of the He peak, and (c) size distribution of helium cavities estimated from (b), excluding those smaller than 3 nm.

Fig. 6. (a) HAADF STEM image of Sample B and (b) EDS map of Kr in the area of (a).

formation of vacancy clusters and voids. The observed Kr gas-filled cavities suggest that local Kr migration and trapping at the cavities in SiC occur at the high temperature. The results may validate a first principles calculation [23] that shows that Kr can be trapped at vacancies. From Fig. 6, there is a distribution of Kr cavity size with a peak value of ~ 20 nm near the Kr profile peak at the depth of ~ 1500 nm, where the atomic concentration of Kr is ~ 1 at. % and the local dose is ~ 50 dpa (Fig. 2(b)). The high production rate of vacancy clusters by Kr ions could suppress the cavity growth due to creation of a high concentration of nucleation sites, as have been previously observed for Xe ion implanted SiC [24].

Bright-field TEM images of Sample B at the depth of ~ 600 nm are shown in Figs. 7(a)-(c) under different imaging conditions. The observed features show a bright contrast in under-focus mode (Fig. 7(a))

Fig. 7. Bright-field TEM images of cavities in Sample B at the depth of ~ 600 nm: (a) under-focused, (b) over-focused, (c) high resolution, (d) SAED pattern; (e) and (f) are the EDS spectra at the depths of 300 and 1500 nm from the surface, respectively.

Table 2 Size and density of voids in 3C-SiC irradiated and annealed under various conditions.

Particle species	Energy (MeV)	Irradiation temp.(°C)	Dose (dpa)	Annealing temp.(°C)	Void size (nm)	Void density (cm ⁻³)	Ref.
Neutron	>0.1	1460	9.6	-	5.7	6.6×10 ¹⁶	Kondo, <i>et al.</i> [25]
Si ²⁺	5.1	1400	10	-	~4.0	2.0×10 ¹⁶	Katoh, <i>et al.</i> [5]
Si ²⁺	5.1	1400	30	-	~4.0	1.3×10 ¹⁸	Katoh, <i>et al.</i> [5]
Si ²⁺	5.1	1350	20	-	~4.1	4.6×10 ¹⁶	Lin, <i>et al.</i> [4]
Mg ⁺	0.2	400	53	1300 (12h)	~4	-	Jiang, <i>et al.</i> [26]
Kr ¹⁵⁺	4	750	25	1600 (3h)	~3	~4.0×10 ¹⁷	This work

and a darker contrast in over-focused mode (Fig. 7(b)), indicating that those features are cavities. Analytical results from the high-resolution TEM image (Fig. 7(c)) suggest that the spherical cavities in this depth region exhibit a small average size (~3 nm) and a high density (~4×10¹⁷ cm⁻³) with a local dose of 25 dpa. The selected area electron diffraction (SAED) pattern shown in Fig. 7(d) indicates that the probed region is crystalline 3C-SiC with a [110]-zone axis. The EDS results of the cavities at the depths of 300 and 1500 nm are shown in Figs. 7(e) and (f), respectively. While Kr peak at 1500 nm is evident in the EDS spectrum, it is absent at 300 nm. The Kr absence is also expected at 600 nm from Figs. 4(b) and (c), suggesting that the small cavities shown in Figs. 7(a)-(c) are voids. They were formed as a result of high-temperature vacancy clustering in the near-surface region penetrated by the energetic Kr ions. Both small Pt and O peaks are also observed in the EDS spectra due to the FIB process and likely surface oxidation of the TEM specimen, respectively.

It has been reported that void formation occurs during neutron irradiation to doses >1-2 dpa at elevated temperatures (> 1000°C) [25]. Voids have also been observed during heavy-ion irradiation to >10 dpa at irradiation temperatures above 1000°C [4,5]. Our previous study [26] shows that 1300°C annealing of a Mg-ion irradiated 3C-SiC at 400°C to a dose of ~53 dpa leads to possible formation of tetrahedral voids of ~4 nm in size. In the present study, small voids are observed in Sample B (Figs. 7(a)-(c)) near the surface region, where the Kr concentration is negligible. However, the voids are spherical, not tetrahedral in shape as observed by others [25,26]. According to Price's report [27], void shape can change from tetrahedral to quasi-spherical as the migration and aggregation of voids is accelerated with increasing annealing temperature. This has been found in 3C-SiC after neutron irradiation at 1500°C followed by annealing at 1800-2000°C. Table 2 summarizes the size and concentration of neutron and heavy-ion irradiation induced voids at various temperatures and doses in SiC.

The data in Fig. 7 also suggest that there is no long-range Kr diffusion in SiC at temperatures up to 1600°C. The diffusion behavior of fission products, such as Ag, Cs, Kr, and Xe [28-32] in SiC and related materials at high temperatures has been an active subject of research over the past decades due to the fact that SiC has been used as a cladding material for nuclear fuels (such as UO₂) in the TRISO particle design [33]. Many metallic fission products, including Ag, are found to start diffusing in SiC at ~1200°C. A recent report [34] suggests the possibility that void mediated Ag transport due to the change in

microstructure of the 3C-SiC at elevated temperatures plays a role. This interpretation is consistent with void formation due to mobile vacancies in neutron- or ion-irradiated SiC at the high temperatures [5,26,35] for Ag diffusion. In contrast, diffusion of Kr and Xe in SiC does not occur at 1500 and 1400°C, respectively, as reported by Friedland *et al.* [36,37] This study provides evidence that there is no significant long-range Kr diffusion in 3C-SiC at temperatures up to 1600°C. Apparently, effective trapping of Kr at cavities of varied sizes is responsible for the immobility of the gas species, as shown in Fig. 6. The results from this study suggest that SiC can effectively confine fission gas Kr at very high temperatures and may find potential applications as a nuclear waste form.

3.4. He + Kr co-implanted 3C-SiC

Figure 8(a) shows a low-resolution view of He cavities around the He profile in Sample C. A higher-resolution image for the He cavities at the peak (~510 nm) is shown in Fig. 8(b), and the size distribution of the He cavities estimated from Fig. 8(b) is shown in Fig. 8(c). The maximum diameter of the He cavities is determined to be ~27 nm, but most of the cavities are much smaller. For the convenience of comparing cavity sizes in samples A and C, a statistical analysis has been made for

Fig. 8. (a) Bright-field TEM image of helium cavities in Sample C around the depth of 450 nm, (b) a high-resolution image near the depth of the He peak, and (c) size distribution of helium cavities estimated from (b), excluding those smaller than 3 nm.

Table 3 Size and density of the cavities in SiC implanted with He and Kr ions and annealed at high temperatures.

Sample	He Imp. Temp. (°C)	He Peak Con. (at.%)	Kr Imp. Temp. (°C)	Local Dose [§] (dpa)	Ann. Temp.(°C); Time (h)	Ave. Cavity Size (nm)	Ave. Cavity Density (cm ⁻³)	Ref.
3C-SiC (A)	400	7	-	4	1600; 3	15 ^{&}	~9.4×10 ¹⁶ ^{&}	This work
3C-SiC (B)	-	-	750	25	1600; 3	3	~4.0×10 ¹⁷	This work
3C-SiC (C)	400	7	750	25	1600; 3	9 ^{&}	~1.4×10 ¹⁷ ^{&}	This work
4H-SiC	400	4	-	2	1400	7±2 nm	-	Barbot, <i>et al.</i> [13]
4H-SiC	750	8	-	4	1500; 0.5	mainly 50 nm	-	Barbot, <i>et al.</i> [13,18]
4H-SiC	750	8	-	4	1700; 0.5	mainly 200 nm	-	Texier, <i>et al.</i> [41]

[§] At the depth of 450 nm for 3C-SiC (A) and (C) and at 600 nm for (B).

[&] Only for cavities larger than 3 nm.

cavities larger than 3 nm in Sample C as performed for Sample A. The results indicate that the cavities in Sample C have an average size of 9 nm with a density of $\sim 1.4 \times 10^{17} \text{ cm}^{-3}$. The size and density of the cavities in SiC produced under various implantation and annealing conditions from this study and literature are summarized in Table 3. Compared to Sample A at 4 dpa, the average cavity size is slightly smaller and density is larger in Sample C at 25 dpa with the same He depth profile. This result suggests that a higher dose or vacancy concentration leads to formation of smaller He cavities with a higher concentration. The small He clusters are probably formed during the first He^{2+} ion implantation due to a high concentration (7 at. %) of He [38]. The vacancies produced in the second Kr^{15+} ion implantation plays a key role in the growth of the cavities during annealing at 1600°C. Compared to Sample A, the smaller size and higher density of the cavities in Sample C may be understood because a higher vacancy concentration increases the probability for He-vacancy interaction, resulting in more nucleation sites for He cavity formation in the cavity growth stage. Formation of more He cavities consumes more He atoms, leading to an overall smaller He cavity size. In addition, comparison of the data in Figs. 8(b) for Sample C and 7(c) for Sample B suggests that there is a very significant effect of the presence of He atoms on cavity growth. The presence of He atoms results in a much larger cavity size at the same dose (25 dpa) and under the same annealing conditions. The results again suggest He trapping and aggregation at vacancies in SiC is the primary mechanism for growth of He cavities during the annealing process in this study.

As discussed in section 3.2, the temperature of He ion implantation plays an important role in determining the cavity size in SiC during post-implantation annealing at high temperature. This is shown in Table 3, where a larger cavity size is resulted from He ion implantation at 750°C compared to 400°C. This behavior may be attributed to a lower vacancy concentration due to more simultaneous recovery during irradiation at the higher temperature, which is consistent with the results above. In addition, a higher concentration of He-vacancy clusters is expected to form in the higher-temperature irradiated SiC prior to annealing. The presence of the clusters could also help grow larger size of cavities during thermal annealing above 1000°C. Sawabe *et al.* [39] studied swelling of heavily neutron-irradiated SiC at various intermediate temperatures (480-735°C) after annealing up to 1500°C, and their results showed that there was macroscopic swelling of the samples irradiated above 735°C due to void formation along grain boundaries. However, no voids were observed after the annealing of a sample irradiated at 480°C. The different results were attributed to interstitial dislocation loops developed during irradiation at the higher temperatures, leaving behind excess vacancies that form voids during post-irradiation annealing at 1500°C. During neutron irradiation at the lower temperature (480°C), annihilation of independent point defects is less probable and a subsequent thermal annealing up to 1500°C leads to a nearly complete combination of the more balanced concentrations of interstitials and vacancies in the SiC structure. Barbot *et al.* [13] have also found a strong increase of surface swelling in 4H-SiC irradiated with He ions at 750°C after annealing at temperatures above 1100°C, but no significant swelling when irradiated at 400°C after the same annealing. In this study, high concentrations of implanted He and vacancies are introduced sequentially in Sample C, potentially leading to formation of He-vacancy clusters during the

second stage of Kr^{15+} ion irradiation, which served as growth centers of He cavities during subsequent annealing at 1600°C . Similar effects of sequential irradiation-induced hardening in alloys due to formation of He-vacancy complexes have also been reported [40]. From Table 3, it is also seen that at the same implantation temperature (400°C) for Sample A and 4H-SiC in Ref. [13], higher He concentration and annealing temperature lead to formation of larger He cavities in SiC. Due to the presence of the surface oxide layer, the swelling magnitude due to He cavities could not be determined accurately. Further studies will be performed to determine the relationship between He cavity size and swelling in SiC.

4. Conclusions

He and Kr cavities with a wide range of size distributions are observed in He^{2+} , Kr^{15+} and $\text{He}^{2+} + \text{Kr}^{15+}$ ion-implanted 3C-SiC around their depth profiles following thermal annealing at 1600°C . Under the implantation conditions, He cavities of up to 34 nm in size are formed in He^{2+} ion-implanted 3C-SiC and the size decreases to 27 nm for the $\text{He}^{2+} + \text{Kr}^{15+}$ ion co-implanted SiC. Under the same He concentration profile, a higher vacancy concentration results in a higher density of cavities with smaller sizes. This study also provides evidence that at the same dpa, presence of high-concentration He atoms in SiC leads to much larger He cavities during high-temperature annealing. The results suggest that processes involving He-vacancy interactions, He trapping and He aggregation at vacancy sites are responsible for nucleation and growth of He cavities in SiC at 1600°C , where both vacancies and He atoms are mobile. In addition, Kr cavities of up to 20 nm in size are formed in this study. Local Kr migration and trapping at all cavity sizes are observed, but long-range diffusion does not occur up to 1600°C . This property could be useful to confine Kr (a fission gas) in SiC as a wasteform at high temperatures.

Acknowledgment

We are grateful to Todd Allen (INL) for providing the CVD SiC samples in this study, Guiqiu Zheng (MIT) for sample polishing, Jinyu Li and Huiping Liu (IMPCAS) for ion implantation, Jiandong Zhang and Zihua Zhu (PNNL) for SIMS measurement, and to Xuemei Wang and Lin Shao (Texas A&M University) for RBS analysis. Zang was financially supported by China Scholarship Council during his visit to PNNL. This study was supported by the National Natural Science Foundation of China (no. 11405124) and the U.S. DOE Office of Fusion Energy Sciences under Contract DE-AC05-76RL01830.

References

- [1] G. Newsome, L.L. Snead, T. Hinoki, Y. Katoh, D. Peters, Evaluation of neutron irradiated silicon carbide and silicon carbide composites, *J. Nucl. Mater.* 371 (2007) 76–89. doi:10.1016/j.jnucmat.2007.05.007.
- [2] L.L. Snead, T. Nozawa, M. Ferraris, Y. Katoh, R. Shinavski, M. Sawan, Silicon carbide composites as fusion power reactor structural materials, *J. Nucl. Mater.* 417 (2011) 330–339.

- doi:10.1016/j.jnucmat.2011.03.005.
- [3] W. Jiang, Y. Zhang, W.J. Weber, Temperature dependence of disorder accumulation and amorphization in Au-ion-irradiated 6H-SiC [48], *Phys. Rev. B - Condens. Matter Mater. Phys.* 70 (2004) 1–8. doi:10.1103/PhysRevB.70.165208.
 - [4] Y.-R. Lin, C.-S. Ku, C.Y. Ho, W.T. Chuang, S. Kondo, J.J. Kai, Irradiation-induced microstructural evolution and swelling of 3C-SiC, *J. Nucl. Mater.* 459 (2015) 276–283. doi:10.1016/j.jnucmat.2015.01.040.
 - [5] Y. Katoh, N. Hashimoto, S. Kondo, L.L. Snead, A. Kohyama, Microstructural development in cubic silicon carbide during irradiation at elevated temperatures, *J. Nucl. Mater.* 351 (2006) 228–240. doi:10.1016/j.jnucmat.2006.02.007.
 - [6] L.L. Snead, Y. Katoh, S. Connery, Swelling of SiC at intermediate and high irradiation temperatures, *J. Nucl. Mater.* 367–370 A (2007) 677–684. doi:10.1016/j.jnucmat.2007.03.097.
 - [7] S.J. Zinkle, W.G. Wolfer, G.L. Kulcinski, L.E. Seitzman, II. Effect of oxygen and helium on void formation in metals, *Philos. Mag. A* 55 (1987) 127–140. doi:10.1080/01418618708209804.
 - [8] D. Guo, C. He, H. Zang, P. Zhang, L. Ma, T. Li, X. Cao, Re-evaluation of neutron displacement cross sections for silicon carbide by a Monte Carlo approach, *J. Nucl. Sci. Technol.* 53 (2016) 161–172. doi:10.1080/00223131.2015.1028502.
 - [9] M.E. Sawan, Y. Katoh, L.L. Snead, Transmutation of silicon carbide in fusion nuclear environment, *J. Nucl. Mater.* 442 (2013) S370–S375. doi:10.1016/j.jnucmat.2012.11.018.
 - [10] R. Li, W. Li, C. Zhang, P. Zhang, H. Fan, D. Liu, L. Vitos, J. Zhao, He–vacancy interaction and multiple He trapping in small void of silicon carbide, *J. Nucl. Mater.* 457 (2015) 36–41. doi:10.1016/j.jnucmat.2014.10.062.
 - [11] C.H. Chen, Y. Zhang, E. Fu, Y. Wang, M.L. Crespillo, C. Liu, S. Shannon, W.J. Weber, Irradiation-induced microstructural change in helium-implanted single crystal and nano-engineered SiC, *J. Nucl. Mater.* 453 (2014) 280–286. doi:10.1016/j.jnucmat.2014.07.020.
 - [12] C.J. Pawley, M.F. Beaufort, E. Oliviero, J. a Hinks, J.F. Barbot, S.E. Donnelly, An in-situ TEM investigation of He bubble evolution in SiC, *J. Phys. Conf. Ser.* 371 (2012) 12052. doi:10.1088/1742-6596/371/1/012052.
 - [13] J.F. Barbot, M.F. Beaufort, M. Texier, C. Tromas, Swelling and stacking fault formation in helium implanted SiC, *J. Nucl. Mater.* 413 (2011) 162–165. doi:10.1016/j.jnucmat.2011.04.022.
 - [14] J.F. Ziegler, J.P. Biersack, U. Littmark, *The Stopping and Range of Ions in Solids*, Pergamon, New York, 1985; available at <http://www.srim.org>.
 - [15] R. Devanathan, W.J. Weber, Displacement energy surface in 3C and 6H SiC, *J. Nucl. Mater.* 278 (2000) 258–265. doi:10.1016/S0022-3115(99)00266-4.
 - [16] M. Mayer, *SIMNRA User's Guide*, Garching, Germany, 1997; available at <http://simnra.software.informer.com>.
 - [17] Y. Zhang, I.T. Bae, K. Sun, C. Wang, M. Ishimaru, Z. Zhu, W. Jiang, W.J. Weber, Damage profile and ion distribution of slow heavy ions in compounds, *J. Appl. Phys.* 105 (2009). doi:10.1063/1.3118582.
 - [18] J.F. Barbot, S. Leclerc, M.-L. David, E. Oliviero, R. Montsouka, F. Pailloux, D. Eyidi, M.-F. Denanot, M.-F. Beaufort, A. Declémy, V. Audurier, C. Tromas, Helium implantation into 4H-SiC, *Phys. Status Solidi.* 206 (2009) 1916–1923. doi:10.1002/pssa.200881468.
 - [19] S. Kondo, T. Hinoki, A. Kohyama, Synergistic Effects of Heavy Ion and Helium Irradiation on

- Microstructural and Dimensional Change in β -SiC, *Mater. Trans.* 46 (2005) 1388–1392.
doi:10.2320/matertrans.46.1388.
- [20] E. Oliviero, M.F. Beaufort, J.F. Barbot, A. Van Veen, A. V. Fedorov, Helium implantation defects in SiC: A thermal helium desorption spectrometry investigation, *J. Appl. Phys.* 93 (2003) 231–238.
doi:10.1063/1.1527974.
- [21] M. Bockstedte, A. Mattausch, O. Pankratov, Ab initio study of the migration of intrinsic defects in 3C-SiC, *Phys. Rev. B.* 68 (2003) 205201. doi:10.1103/PhysRevB.68.205201.
- [22] W. Jiang, L. Jiao, H. Wang, Transition from irradiation-induced amorphization to crystallization in nanocrystalline silicon carbide, *J. Am. Ceram. Soc.* 94 (2011) 4127–4130.
doi:10.1111/j.1551-2916.2011.04887.x.
- [23] A. Charaf Eddin, L. Pizzagalli, First principles calculation of noble gas atoms properties in 3C-SiC, *J. Nucl. Mater.* 429 (2012) 329–334. doi:10.1016/j.jnucmat.2012.06.022.
- [24] C.H. Zhang, Y.M. Sun, Y. Song, T. Shibayama, Y.F. Jin, L.H. Zhou, Defect production in silicon carbide irradiated with Ne and Xe ions with energy of 2.3 MeV/amu, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms.* 256 (2007) 243–247. doi:10.1016/j.nimb.2006.12.010.
- [25] S. Kondo, Y. Katoh, L.L. Snead, Cavity swelling and dislocation evolution in SiC at very high temperatures, *J. Nucl. Mater.* 386–388 (2009) 222–226. doi:10.1016/j.jnucmat.2008.12.095.
- [26] W. Jiang, H.J. Jung, L. Kovarik, Z. Wang, T.J. Roosendaal, Z. Zhu, D.J. Edwards, S. Hu, C.H. Henager, R.J. Kurtz, Y. Wang, Magnesium behavior and structural defects in Mg⁺ ion implanted silicon carbide, *J. Nucl. Mater.* 458 (2015) 146–155. doi:10.1016/j.jnucmat.2014.12.071.
- [27] R.J. Price, Neutron irradiation-induced voids in β -silicon carbide, *J. Nucl. Mater.* 48 (1973) 47–57.
doi:10.1016/0022-3115(73)90077-9.
- [28] W. Jiang, W.J. Weber, V. Shutthanandan, L. Li, S. Thevuthasan, Thermal and dynamic responses of Ag implants in silicon carbide, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms.* 219–220 (2004) 642–646. doi:10.1016/j.nimb.2004.01.134.
- [29] D. Shrader, S.M. Khalil, T. Gerczak, T.R. Allen, A.J. Heim, I. Szlufarska, D. Morgan, Ag diffusion in cubic silicon carbide, *J. Nucl. Mater.* 408 (2011) 257–271. doi:10.1016/j.jnucmat.2010.10.088.
- [30] W. Jiang, C.H. Henager, T. Varga, H.J. Jung, N.R. Overman, C. Zhang, J. Gou, Diffusion of Ag, Au and Cs implants in MAX phase Ti₃SiC₂, *J. Nucl. Mater.* 462 (2015) 310–320. doi:10.1016/j.jnucmat.2015.04.002.
- [31] E. Friedland, N.G. van der Berg, T.T. Hlatshwayo, R.J. Kuhudzai, J.B. Malherbe, E. Wendler, W. Wesch, Diffusion behavior of cesium in silicon carbide at T>1000°C, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms.* 286 (2012) 102–107. doi:10.1016/j.nimb.2011.11.048.
- [32] J.B. Malherbe, Diffusion of fission products and radiation damage in SiC, *J. Phys. D. Appl. Phys.* 46 (2013) 27. doi:10.1088/0022-3727/46/47/473001.
- [33] B.G. Kim, Y. Choi, J.W. Lee, Y.W. Lee, D.S. Sohn, G.M. Kim, Multi-layer coating of silicon carbide and pyrolytic carbon on UO₂ pellets by a combustion reaction, *J. Nucl. Mater.* 281 (2000) 163–170.
doi:10.1016/S0022-3115(00)00365-2.
- [34] R.A. Coward, C.R. Winkler, W.A. Hanson, M.L. Jablonski, M.L. Taheri, Transmission electron microscopy investigation of Ag diffusion mechanisms in β -SiC, *J. Nucl. Mater.* 457 (2015) 298–303.
doi:10.1016/j.jnucmat.2014.11.116.
- [35] S. Kondo, Y. Katoh, L.L. Snead, Unidirectional formation of tetrahedral voids in irradiated silicon carbide,

- Appl. Phys. Lett. 93 (2008). doi:10.1063/1.3005650.
- [36] E. Friedland, K. Gärtner, T.T. Hlatshwayo, N.G. van der Berg, T.T. Thabethe, Influence of radiation damage on xenon diffusion in silicon carbide, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 332 (2014) 415–420. doi:10.1016/j.nimb.2014.02.109.
- [37] E. Friedland, T.T. Hlatshwayo, N.G. van der Berg, M.C. Mabena, Influence of radiation damage on krypton diffusion in silicon carbide, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 354 (2015) 42–46. doi:10.1016/j.nimb.2014.11.011.
- [38] C. Zhang, S.E. Donnelly, V.M. Vishnyakov, J.H. Evans, Dose dependence of formation of nanoscale cavities in helium-implanted 4H-SiC, J. Appl. Phys. 94 (2003) 6017–6022. doi:10.1063/1.1611630.
- [39] T. Sawabe, M. Akiyoshi, K. Ichikawa, K. Yoshida, T. Yano, Microstructure of heavily neutron-irradiated SiC after annealing up to 1500 °C, J. Nucl. Mater. 386–388 (2009) 333–337. doi:10.1016/j.jnucmat.2008.12.322.
- [40] C. Heintze, F. Bergner, M. Hernández-Mayoral, R. Kögler, G. Müller, A. Ulbricht, Irradiation hardening of Fe–9Cr-based alloys and ODS Eurofer: Effect of helium implantation and iron-ion irradiation at 300 °C including sequence effects, J. Nucl. Mater. 470 (2016) 258–267. doi:10.1016/j.jnucmat.2015.12.041.
- [41] M. Texier, B. Pichaud, M.-F. Beaufort, J.-F. Barbot, Structural disordering and extended defects produced by He-implantation in silicon carbide, J. Phys. D. Appl. Phys. 46 (2013) 485105. doi:10.1088/0022-3727/46/48/485105.