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Accumulation and recovery of irradiation damage in He^+ implanted α-SiC

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Abstract

In situ RBS/Channeling (RBS/C) has been used to investigate damage accumulation and subsequent annealing behavior in single-crystal wafers of 6H-silicon carbide (α-SiC) irradiated at temperatures from 160 to 300 K with 390 keV He^+ ions to fluences ranging from 7.5×10^{18} to 1.0×10^{20} He^+/m^2. Damage recovery in the irradiated crystals was studied by isochronal annealing at temperatures up to 1170 K. The RBS/C results show that complete amorphization in α-SiC does not occur at 190 K for irradiation fluences up to 1.0×10^{20} He^+/m^2 (0.38 dpa at the damage peak). For a fluence of 4.5×10^{19} He^+/m^2, the relative amount of damage accumulated during irradiation at 190 K is a factor of 5 larger than that accumulated under irradiation at 300 K, which suggests a higher rate of simultaneous point defect recombination at 300 K. In post-irradiation isochronal annealing studies, the integrated damage profile for all irradiated samples decreased exponentially with increasing annealing temperature. At low relative ion fluences and comparable irradiation-induced defect concentrations, the defects produced by He^+ irradiation at 160 K are more difficult to anneal at 300 K than those produced by Si^+ irradiation at 160 K, which suggests that trapping of He atoms at defects may be inhibiting recombination.

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1. Introduction

The 6H polytype of silicon carbide (α-SiC) has a hexagonal crystal structure with a six atomic layer repeat sequence along the c-axis. Silicon carbide is a wide-band gap semiconductor with high thermal conductivity, high-temperature stability, chemical inertness, extreme hardness, small neutron capture cross-section, and good dimensional stability under neutron irradiation. Due to these outstanding properties, SiC has been proposed as a promising candidate material for structural components in fusion energy systems, as an inert host matrix for the burnup of excess weapons plutonium, and for high-temperature, high-power electronic devices. A fundamental understanding of the accumulation and recovery of irradiation damage in SiC is important both to predicting performance in nuclear environments and in using ion-implantation techniques in electronic device fabrication.

Single-crystal wafers of α-SiC with high purity and excellent crystalline quality are commercially available, which has prompted a number of investigations concerned with irradiation effects and annealing behavior. Recent research on SiC has included studies on synthesis and processing [1], irradiation damage formation and annealing [2,3], and the crystalline-to-amorphous phase transition induced by ions [3–6] and electrons [7,8]. The current understanding of damage accumulation and annealing in ion-implanted SiC has recently been reviewed and summarized [9,10]. Much of the work to date suggests that the damage accumulation at room temperature may be greatly influenced by mobile defects at this temperature. In fact, recent studies [3,11] have confirmed the presence of a defect recovery process at

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room temperature. In addition, ion-beam-induced epitaxial recrystallization of amorphous layers in α-SiC has been reported [12,13] at temperatures as low as 750 K.

In a recent investigation [14], the absorption spectra in α-SiC induced by 700 and 1400 keV He^+ irradiation have been compared. A light-absorbing surface layer of slightly damaged crystalline material is formed with a thickness of 1.6 and 3.1 μm for 700 and 1400 keV He^+, respectively. In addition, an interface layer, with a thickness of 0.3 μm, is formed between the surface layer and the substrate, and the index of refraction of this interface layer increases with fluence. Amorphization due to He^+ irradiation has been previously observed in α-SiC [3,5]. Furthermore, a study [3] of damage accumulation in α-SiC irradiated with He^+ at 77 K and at 300 K indicates that significant simultaneous recombination (∼60%) occurs during 30 keV He^+ irradiation at 300 K as compared to 77 K. Other experimental results [3,9,10] suggest that a higher critical damage energy (energy per lattice atom) is needed for lighter ions to produce an amorphous state in α-SiC. Irradiation of SiC with He^+ ions should produce primarily isolated Frenkel pairs on each sublattice. In the case of heavier ions, such as Si^+, molecular dynamics (MD) simulations [15] have shown that a high density of interstitials, vacancies, and anti-site defects are produced in SiC. In addition, the influence of the implanted particle species, particularly a gas species such as He, on damage recovery has not yet received much attention. In the present paper, the results of a study on damage accumulation and thermal recovery behavior in α-SiC irradiated with He^+ ions, as measured by in situ RBS/Channeling (RBS/C), are reported and compared to previous results [11] for defects induced by Si^- ion irradiation.

2. Experimental procedures

In this study, both low-energy (390 keV) He^+ ion implantation and high-energy (2.0 MeV) He^+ RBS/C analysis have been performed using a 3.4 MV tandem accelerator within the Environmental Molecular Sciences Laboratory (EMSL) at the Pacific Northwest National Laboratory (PNNL) [16]. The samples used in this study were n-type α-SiC (6H-polytype) <0 0 0 1>-oriented single crystal wafers (Cree Research, Inc.). Samples were irradiated at 190 K to ion fluences of 7.5×10^{18}, 1.5×10^{19}, 4.5×10^{19}, and 1.0×10^{20} He^+/m^2 and at 300 K (room temperature) to 4.5×10^{19} He^+/m^2. In addition, a pair of samples were irradiated at 160 K with 390 keV He^+ to 6.1×10^{19} He^+/m^2 and with 550 keV Si^+ to 7.5×10^{17} Si^+/m^2, which produced comparable defect concentrations in the samples for comparative annealing studies. Shallow (near-surface) irradiation-induced damage, which could be readily analyzed by 2.0 MeV He^+ ion channeling, was produced by tilting each sample by either an angle of 60° (for 390 keV He^+ irradiation) or 30° (for 550 keV Si^+ irradiation) relative to the incident beam. The damage profile produced under these conditions for the 390 keV He^+ implantations, based on SRIM-97 and a threshold displacement energy of 25 eV, is illustrated in Fig. 1 for a fluence of 1.5×10^{19} He^+/m^2. During the ion implantation, a relatively low ion flux was used ($<10^{16}$ ions/m^2/

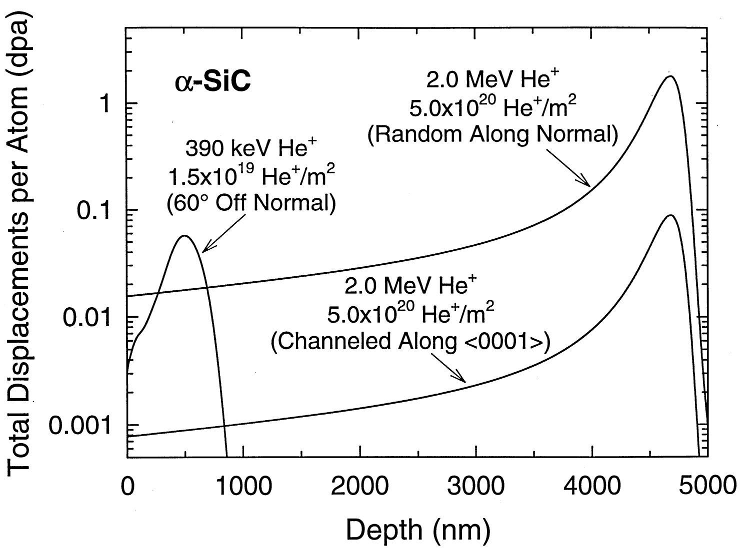

Fig. 1. Damage profiles, based on SRIM-97 and a displacement energy of 25 eV, for irradiation with 390 keV He^+ ions at 60° off the surface normal to a fluence of 1.5×10^{19} He^+/m^2 and for the 2.0 MeV He^+ analysis (RBS/C) beam along the <0 0 0 1> surface normal, under both random and channeling conditions, to a typical fluence of 5.0×10^{20} He^+/m^2.

s), and no temperature increase was observed on the target, nor was any expected because of the high thermal conductivity of SiC. The size of the irradiated spot was 1.2×1.2 mm^2, and the cross section profiles of the incident beams were uniform within this size.

Following implantation, the damaged regions in the crystals were analyzed in situ by 2.0 MeV He^+ RBS/C from the irradiation temperature (160 or 190 K) up to 1170 K in a <0 0 0 1>-axial channeling geometry. Backscattering particles were detected with a Si barrier detector at an angle of 150°. The 0.6×0.6 mm^2 analyzing beam was centered in the implantation beam spots. During each isochronal annealing step, the samples were maintained at the given temperature, to within ±5 K, for 20 min. This thermal condition was achieved by adjusting the e-beam heater parameters (e.g., filament current and bias voltage) while a constant flow of liquid nitrogen was maintained. Conventional chromel–alumel thermocouples were used for the measurement of temperatures on the sample front surface. In order to minimize additional defect recombination in the damaged region, RBS/C measurements were performed at a temperature well below the anneal temperature to insure the annealing process was quenched. For annealing temperatures between 160 and 300 K, the RBS/C measurements were carried out near 160 K; for annealing above 300 K, the RBS/C was carried out at room temperature. The accurate measurement of the target current and, thus, determination of the ion fluence were made possible for both ion implantation and ion-beam analysis by applying a positive voltage of 300 V to the target. The relative incremental damage induced by the 2.0 MeV He^+ analysis beam is also included in Fig. 1 for a typical analysis fluence of 5.0×10^{20} He^+/m^2 under both random and channeling conditions along the <0 0 0 1> surface normal. The effect of the damage induced by the RBS/C analysis is relatively minor, as discussed below.

3. Results and discussion

3.1. *Influence of 2.0 MeV He^+ analysis beam*

It is important to consider to what extent the high-energy (2.0 MeV) helium analyzing beam contributes to the damage being measured. Due to the small beam size in this study, the analyzing-beam fluence was relatively high, typically from 2.0×10^{20} to 5.0×010^{20} He^+/m^2 for each RBS/C spectrum, particularly when compared to the 390 keV He^+ implantation fluences (7.5×10^{18}–1.0×10^{20} He^+/m^2). Damage profiles in α-SiC have been simulated using SRIM-97 for implantations with 390 keV He^+ to 1.5×10^{19} He^+/m^2 (60° off surface normal) and for 2.0 MeV He^+ at 5.0×10^{20} He^+/m^2 (along the surface normal). The results are shown in Fig. 1. SRIM-97 assumes a random structure in the simulations; however, in the case of channeling along a crystallographic direction, the elastic scattering interactions are considerably reduced. The minimum backscattering yield measured along <0 0 0 1> in the virgin α-SiC single crystals in this study is 2.3% relative to the random yield. This reflects the reduction in elastic scattering and is a reasonable estimate of reduction in damage production due to channeling in virgin samples when the incident beam is along <0 0 0 1>. Using a more conservative value of 5% for the relative damage production under <0 0 0 1> channeling conditions, the damage produced by 2.0 MeV He^+ irradiation in virgin α-SiC during RBS/C analysis along the <0 0 0 1> direction is also shown in Fig. 1 for a typical analysis fluence of 5.0×10^{20} He^+/m^2. The amount of damage actually produced by the 2.0 MeV He^+ will vary between the two limiting curves shown in Fig. 1, depending on the induced-damage in the subsurface region analyzed. Clearly, the damage introduced by RBS/C analysis is only a few percent of that introduced by the 390 keV He^+ implantation under all conditions. At the lowest implantation fluence for 390 keV He^+ in this study (7.5×10^{18} He^+/m^2), where the damage (dechanneling yield) is only a few percent above the virgin condition, the RBS/C analysis contributes only about 5% to the total damage in the peak damage region (500 nm depth). At the highest fluence for the 390 keV He^+ (1.0×10^{20} He^+/m^2), where the damage (Fig. 2) is about 50% of the random level, the RBS/C beam fluence was reduced to 2.0×10^{20} He^+/m^2, and its contribution to the total observed damage is only about 2% in the damage peak region. Consequently, despite the high RBS/C ion fluences used in this study, the overall contribution of the RBS/C measurements to the defect concentration is small (<5%). This has been confirmed by 2.0 MeV He^+ irradiations at significantly higher fluences (up to 3.6×10^{21} He^+/m^2), which indicate a 2% increase in the minimum yield for random irradiations about <0 0 0 1> and less than 1% increase in the minimum yield for channeled irradiation along the <0 0 0 1> direction.

Although the 2.0 MeV He^+ RBS/C analysis is not absolutely non-destructive, particularly relative to extremely low-level damage, it induces only a low-level, linear background contribution to the total damage. Since the dechanneling profiles induced for most implantation fluences in the current study exhibit a well-defined damage peak, any linear background contributions (<5%) introduced by the RBS/C measurements are effectively subtracted using standard RBS/C data analysis methods [17]. In the current study, the integrated damage profiles are used to characterize both the relative damage produced by 390 keV He^+ implantation and that remaining after annealing at different temperatures; consequently, the influence of the 2.0 MeV He^+ RBS/C

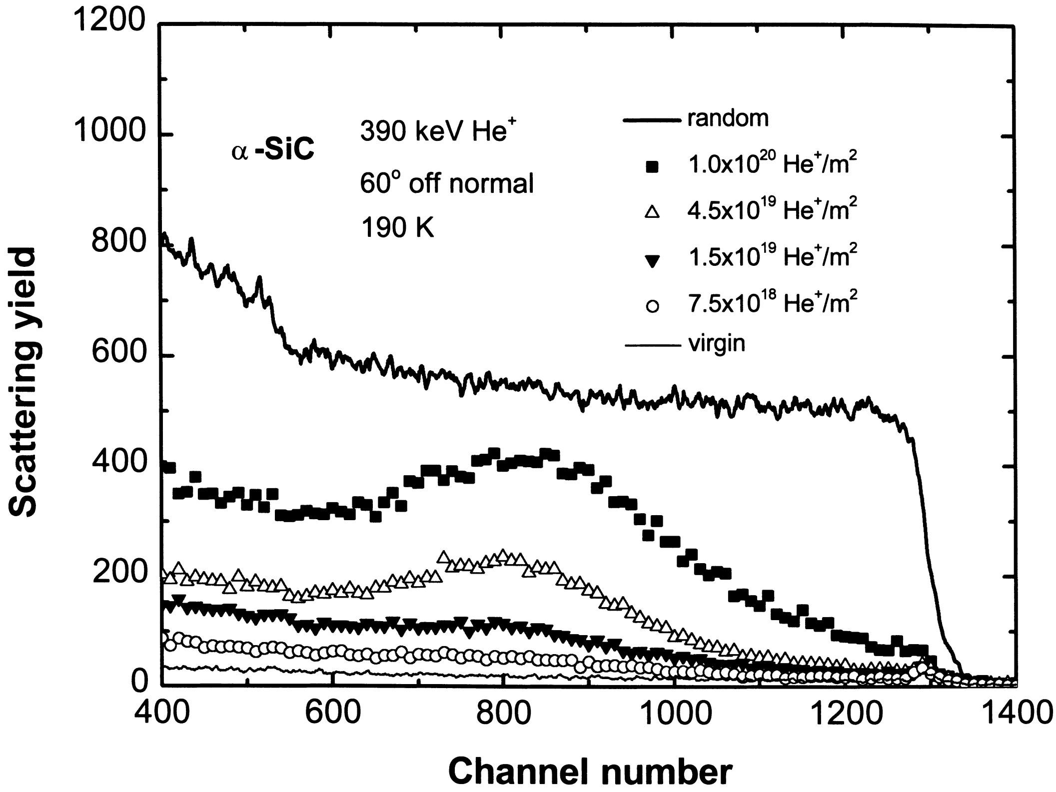

Fig. 2. 2.0 MeV He RBS/C spectra taken in situ for a <0 0 0 1> α-SiC single crystals implanted (60° off the surface normal) at 190 K with 390 keV He^+ ions. Also included are a random spectrum and a channeling spectrum from a virgin area.

beam on the analysis of the results is considered insignificant (less than 5%). In addition, it is expected that the incremental damage induced by each RBS/C analysis will readily anneal during subsequent isochronal annealing at higher temperatures; consequently, cumulative effects are not anticipated.

3.2. Damage production

A series of 2.0 MeV He RBS/C spectra for samples implanted (60° off surface normal) at 190 K with 390 keV He^+ to various fluences (7.5×10^{18}, 1.5×10^{19}, 4.5×10^{19} and 1.0×10^{20} He^+/m^2) are shown in Fig. 2; also included are a random-equivalent spectrum and a virgin (non-irradiated) spectrum. The channeling spectrum for the undamaged (virgin) crystal gives a minimum yield of about 2.3% under the experimental conditions. At a fluence of 7.5×10^{18} He^+/m^2, an increase in the backscattering yield is observed, but a peak in the damage spectrum is not yet apparent. For ion fluences greater than 10^{19} He^+/m^2, a peak in the damage profile (backscattering yield) is readily observable in each spectrum. The damage peaks have been estimated to correspond to a depth of about 500 nm under the experimental geometry employed. At the highest fluence (Fig. 2), which corresponds to a displacement dose of 0.38 dpa at the damage peak, the accumulated damage is well below the random-equivalent level (estimated to be about 50% disordered). This result indicates that a completely amorphous layer is not produced in α-SiC at this depth and temperature (190 K) after implantation with 390 keV He^+ to a fluence of 1.0×10^{20} ions/m^2. However, some amorphous domains may be present at this damage level as observed previously at similar damage levels by cross-sectional transmission electron microscopy in Ar^+ irradiated α-SiC [10]. These data (Fig. 2) are in good agreement with the results reported previously by Grimaldi et al. [3]. Under the irradiation conditions of this study, SRIM-97 results predict that a fluence of about 2.0×10^{20} He^+/m^2 is required to reach the critical damage energy for complete amorphization of SiC under He^+ irradiation [3], if defect recombination effects are not important at this temperature (190 K).

In order to obtain information concerning the effects of simultaneous defect recombination during ion irradiation at different temperatures, a comparative experiment was performed under identical irradiation conditions and fluences (60° off surface normal, 390 keV He^+ ions,

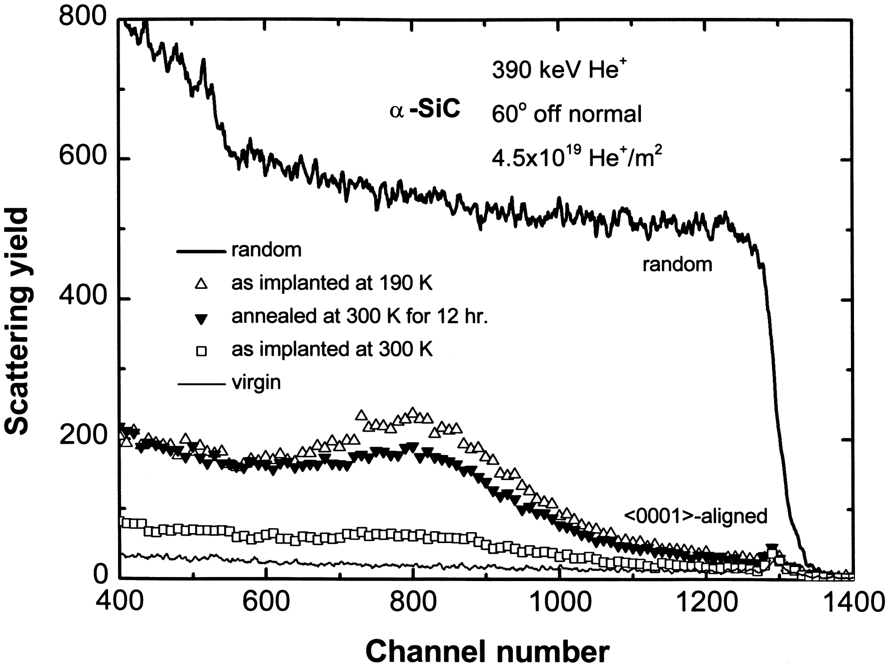

Fig. 3. 2.0 MeV He RBS/C spectra for a <0 0 0 1> α-SiC single crystals implanted (60° off surface normal) at 190 K and 300 K with a fluence of 4.5×10^{19} He^+/m^2 ($E_{He} = 390$ keV). Also included are the spectrum for the sample implanted at 190 K and annealed at 300 K for 12 h, a random spectrum, and a channeling spectrum from a virgin area.

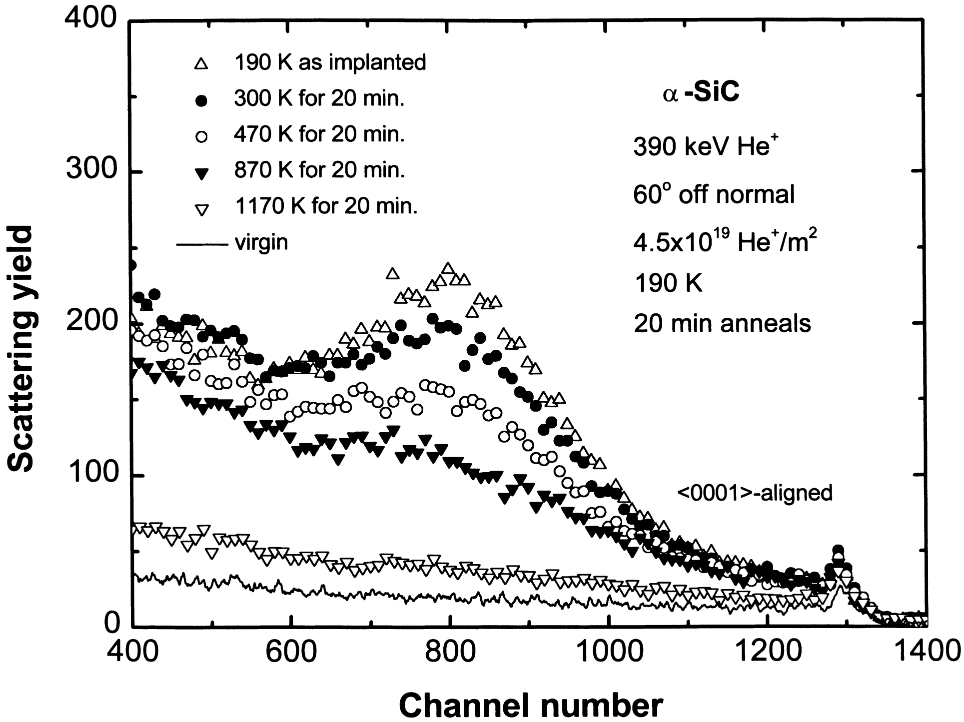

Fig. 4. 2.0 MeV He RBS/C spectra for a <0 0 0 1> α-SiC single crystal implanted at 190 K to a fluence of 4.5×10^{19} He^+/m^2 ($E_{He} = 390$ keV) and subsequently isochronally annealed at different temperatures for 20 min. Also included is a virgin spectrum.

4.5×10^{19} He^+/m^2) at 190 and 300 K. The as-implanted damage profiles for these samples, which are shown in Fig. 3, indicate significant differences in the damage accumulated at these two temperatures. The total defect concentration generated at 190 K is about a factor of 5 larger than that produced at 300 K. These data imply that significant simultaneous defect recombination (~80%) is occurring during implantation at 300 K, which is in reasonable agreement with the results of Grimaldi et al. [3], who reported about 60% recombination in α-SiC irradiated with 30 keV He^+ at 300 K to higher fluences. Post-irradiation annealing at 300 K of the sample implanted at 190 K does decrease the observable defect concentration in the damaged region (see solid triangles in Fig. 3); however, the damage peak is still much higher than that produced by irradiation at 300 K.

3.3. Defect annealing

Recovery of the accumulated damage in the α-SiC crystals depends on annealing temperature and time. The thermal recovery of the damage in the sample irradiated at 190 K to a fluence of 4.5×10^{19} He^+/m^2 is illustrated in the RBS/C spectra, shown in Fig. 4, for a series of isochronal (20 min) anneals at temperatures up to 1170 K. In general, the degree of disorder in the damaged region diminishes monotonically with increasing annealing temperature. The damage recovery at 300 K after a 20 min anneal (full circles), is clearly visible in the spectra shown in Fig. 4. The accumulated damage in this sample is almost completely recovered after annealing at 1170 K.

The relative integrated defect densities in all the samples irradiated at 190 K (Fig. 2) have been estimated by extracting the net areas of the damage peaks in the <0 0 0 1>-axial channeling spectra, as described by Holland et al. [18]. To minimize statistical errors, experimental spectra were smoothed using averages of five adjacent points before extraction. The relative integrated defect concentrations as a function of annealing temperature are shown in Fig. 5, where the defect concentrations have been normalized to the maximum value obtained for the highest fluence (1.0×10^{20} He^+/m^2) in this study. The damage recovery data obtained for the different ion fluences exhibit an exponential decay of the relative defect concentration with increasing annealing temperature. Similar dependence was also observed for α-SiC crystals irradiated with 550 keV Si^+ [11].

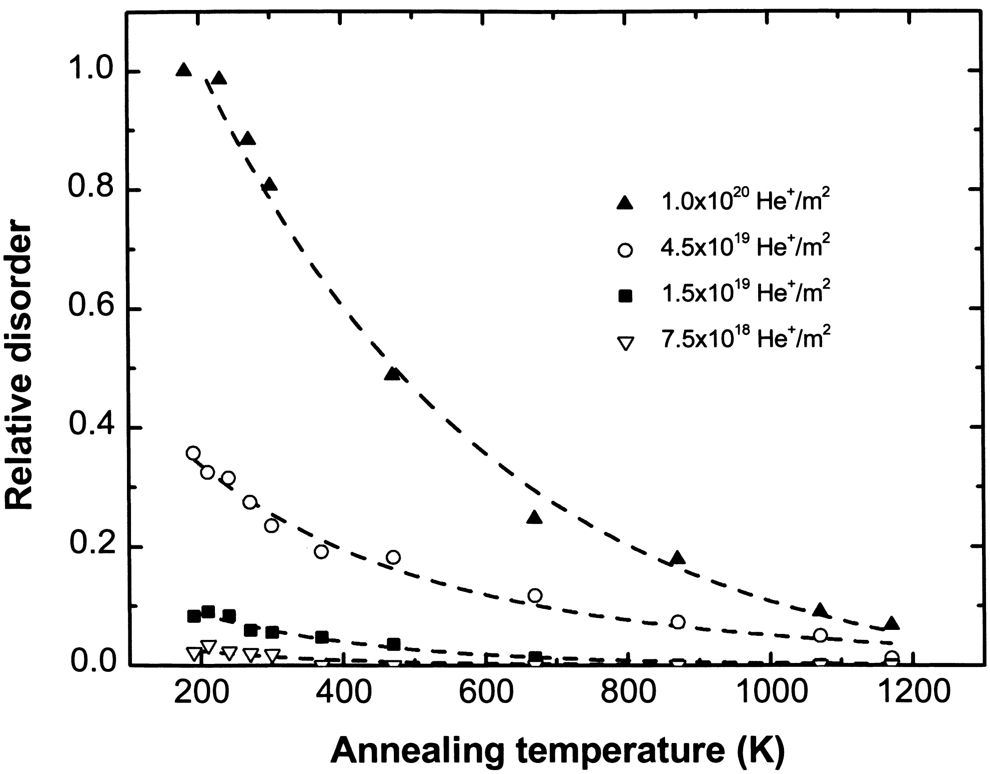

Fig. 5. Relative defect concentration as a function of annealing temperature for different implantation fluences ($E_{He} = 390$ keV, 60° off the α-SiC surface normal) at 190 K. Symbols indicate the experimental data and the dashed lines are exponential decay fits to the data.

The data in Figs. 3–5 show that defect annealing is not very significant at 300 K, even after 12 h, for α-SiC implanted with He^+ at 190 K. Because the type of damage induced by different ion species and the different ion species themselves may affect defect recovery processes, a comparative irradiation experiment at 160 K with He^+ and Si^+ ions has been conducted in order to observe relative defect annealing at 300 K. Samples were irradiated to either 6.1×10^{19} He^+/m^2 (0.23 dpa at the damage peak) or 7.5×10^{17} Si^+/m^2 (0.04 total dpa at the damage peak), which produced a comparable and relatively low defect concentration in each case. Based on previous studies [10], amorphous domains should not be present at these low damage levels. The results indicate that a significantly higher number of displaced atoms are required under He^+ irradiation to produce a defect concentration comparable to that under the Si^+ irradiation. This suggests that simultaneous recovery rates are higher at this temperature for He^+ irradiation than for Si^+ irradiation, and recombination of He^+-induced defects is active even at 160 K. The annealing behavior for α-SiC implanted at 160 K with 6.1×10^{19} He^+/m^2 is shown in Fig. 6. The irradiation damage undergoes some partial recovery at 300 K after 12 h, and further annealing at 670 K (Fig. 5) does not lead to complete recovery. Also included in Fig. 6 is the annealing behavior of the sample irradiated at 160 K with 550 keV Si^+ ions. After annealing at 300 K for 10 h, the RBS/C spectrum for the Si^+-irradiated sample is indistinguishable from the virgin spectrum, which indicates that within experimental error the damage recovery is complete. Convincing explanations for this experimental observation are not yet available, but this behavior might be partially attributed to the helium atoms, which could be effectively trapped interstitially in the crystal structure or at irradiation-induced defects. The presence of trapped helium may inhibit defect migration and recombination in SiC, which could impact the behavior of SiC in fusion reactor environments. The theory of interstitial defects trapping at impurities in metals is well developed [19] and suggests the formation of immobile defect complexes and alteration of the defect annihilation kinetics. Such behavior has been previously reported in UO_2 irradiated with alpha particles [20], where defect recovery studies have shown evidence for stable helium-vacancy complexes. Additional studies are necessary to understand the annealing behavior of defects induced by different ion

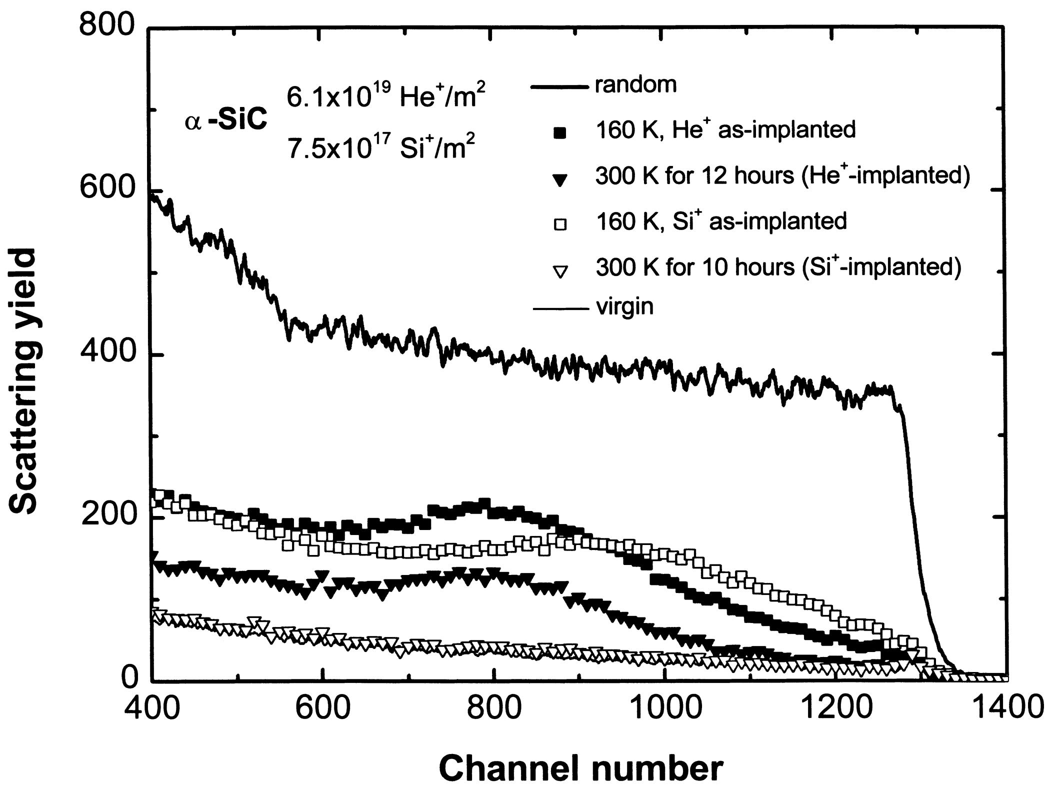

Fig. 6. 2.0 MeV He RBS/C spectra for a <0 0 0 1> α-SiC single crystal implanted (60° off surface normal) at 160 K to a fluence of 6.1×10^{19} He^+/m^2 ($E_{He} = 390$ keV) and subsequently annealed at 300 K for 12 h. Similar spectra are shown for a <0 0 0 1> α-SiC single crystal implanted at 160 K to a fluence 7.5×10^{17} Si^+/m^2 ($E_{Si} = 550$ keV) and subsequently annealed at 300 K for 10 h (from Ref. [11]). Also included are random and virgin spectra.

species and the possible effects of helium trapping in SiC, including the measurements of implanted ion profiles and locations in the crystal structure.

4. Conclusions

The total defect concentration induced in α-SiC at 190 K by irradiation with 390 keV He^+ ions is 5 times larger than that induced at 300 K, indicating that in the latter case significant simultaneous recombination of irradiation-induced defects takes place during the implantation process. Isochronal annealing studies of the irradiated SiC indicate an exponential decrease of residual damage with increasing temperature. In samples irradiated at 160 K with either He^+ or Si^+ ions to produce a comparable low defect concentration, annealing studies at 300 K indicates that only partial recovery of the He^+ implantation damage is possible, while the Si^+ implantation damage undergoes complete recovery. Trapping of helium atoms at defect sites is proposed as one of the possible mechanisms that may lead to the observed reduction in defect recombination at 300 K. Such behavior could impact the performance of SiC in fusion reactor environments.

Acknowledgements

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