RECRYSTALLIZATION KINETICS OF 3C SILICON CARBIDE IMPLANTED
WITH 400 keV CESIUM IONS

by

Daniel Denell Osterberg

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DEFENSE COMMITTEE AND FINAL READING APPROVALS

of the thesis submitted by

Daniel Denell Osterberg

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The following individuals read and discussed the thesis submitted by student Daniel Denell Osterberg, and they evaluated his presentation and response to questions during the final oral examination. They found that the student passed the final oral examination.

Darryl Butt, Ph.D.	Chair, Supervisory Committee
Rick Ubic, Ph.D.	Co-Chair, Supervisory Committee
John Youngsman, Ph.D.	Member, Supervisory Committee
Pushpa Raghani, Ph.D.	Member, Supervisory Committee

The final reading approval of the thesis was granted by Darryl Butt, Ph.D. and Rick Ubic, Ph.D., Co-Chairs of the Supervisory Committee. The thesis was approved for the Graduate College by John R. Pelton, Ph.D., Dean of the Graduate College.

DEDICATION

I would like to dedicate this thesis to my daughter, Tatum Claire Osterberg. She is the unwavering light in my life and has made all of this possible.

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AUTHOR JUSTIFICATION PARAGRAPH

The research summarized in this publication was carried out and authored by Daniel Osterberg to fulfill the requirements of the Material Science and Engineering Master's program at Boise State University. Daniel performed the experiments, recorded and analyzed results, and served as the primary author of the paper. Dr. Darryl Butt provided experimental guidance, analysis of results, financial support, lab space, and editorial support. Dr. John Youngsman aided in the experiments, analysis of results, and provided editorial support on the paper. Dr. Rick Uvic gave project advice, provided discussion of transmission electron microscopy results, and also provided editorial support. Dr. Ivar Reimanis aided this project through project proposals and the critique and review of the paper.

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EXECUTIVE SUMMARY

Silicon carbide has a growing number of industrial applications due to its thermal, electrical, and mechanical properties. There are a wide variety of uses for SiC ranging from abrasives, semiconductors, heating elements, automobile parts, to potential nuclear technology applications. The widespread use of SiC as a semiconductor has been impeded by its low diffusion coefficients, typically requiring very high temperatures and long dwell times. One method for the addition of dopants into SiC is high energy ion implantation. Although this method allows for the doping of SiC, it can also create undesirable microstructural changes in the material. In many cases, the implantation creates a completely amorphous region in the sample surface. A number of studies have been performed on the effects that implantation has on the SiC microstructure, yet there is little data on the kinetics of this annealing or recrystallization process for ion implanted SiC.

To fill this knowledge gap, a thorough analysis of the recrystallization process is needed in order to understand where recrystallization occurs, the overall rates, and activation energies for this process. The objective of this study was to assess the kinetics of recrystallization for polycrystalline SiC implanted with high energy cesium ions. For this research, 400 keV cesium ions were implanted into polycrystalline 3C-SiC coupons to a fluence of 10^{16} ions·cm⁻². The samples were subjected to annealing heat treatments in order to study the recrystallization of the implantation region as a function of temperature

and time. Analysis of the annealed samples was performed using optical profilometry, secondary ion mass spectroscopy (SIMS), and transmission electron microscopy (TEM).

Optical profilometry was used to observe the step height between the implanted and non-implanted regions near the sample edges, as found in Appendix A. This existence of this step height is due to swelling caused by the ion implantation process. Measurements were taken of the as-implanted and post annealed samples treated at 600 – 1100°C for 1 hour increments. This was done in order to observe any densification occurring during the annealing process. Unfortunately, this data could not be used due to the large amount of variance found near the machined sample edges.

SIMS was used to characterize the distribution of cesium versus depth in the as-implanted and annealed samples. This was done to understand what effect the annealing heat treatments had on the dopant profile. Samples treated at 750°C for 8 hours and 725°C for 36 hours indicated 61% and 72% retention of the original implantation with the cesium peak and average shifting towards the sample surface.

Analysis of the implantation region before and after annealing heat treatments was performed using TEM bright field images and selected area diffraction patterns. An in depth understanding of the microstructure is important due to its direct relationship with the mechanical and electrical properties of a material. Analysis of as-implanted samples revealed the creation of 217 ± 2 nm amorphous regions within the sample surfaces. Recrystallization of the implantation region was observed to occur at temperatures $\geq 725^\circ\text{C}$, although densification did not occur until $\geq 800^\circ\text{C}$. The recrystallization of the implantation region occurred primarily from the interface between the amorphous and still crystalline underlying material. This growth was largely non-

uniform in nature, which is attributed in part to the polycrystalline nature of the original samples. The recrystallized microstructure consisted of large grains identified as 3C-SiC along with other fine grained material. Some of the large 3C-SiC grains were shown to share the same orientation as the grains within the undamaged SiC material.

TEM bright field images were taken of the entire FIB sample edge in order to observe the full extent of the recrystallization found in each sample, as found in Appendix B. An image analysis technique was developed and used to convert the TEM images into binary images, which are also shown in Appendix B. This method was used to quantify the recrystallization found within each annealed sample. Results from this study show that the recrystallization rate was faster at higher temperatures and appeared to follow an Arrhenius dependency. The data was fitted to a Johnson-Mehl-Avrami (JMA) equation and yielded activation energy of $482 \pm 54 \text{ kJ}\cdot\text{mol}^{-1}$. The error associated with this activation energy is due to the non-uniform nature of the recrystallization and is likely attributed to the polycrystalline nature of the starting materials.

In summary, this study provides a thorough analysis of the recrystallization of cesium implanted polycrystalline SiC. The implantation was found to create an amorphous surface region of $217 \pm 2 \text{ nm}$. Annealing heat treatments indicate that recrystallization occurs at temperatures as low as 725°C . The final microstructure of the implantation region was found to have retained a majority of the cesium implant and consisted of identifiable 3C-SiC grains along with very fine grained material. The overall activation energy for the recrystallization process was found to be $482 \pm 54 \text{ kJ}\cdot\text{mol}^{-1}$.

ABSTRACT

Polycrystalline 3C silicon carbide was implanted at room temperature with 400 keV cesium ions to a dose of 10^{16} ions·cm⁻². The samples were then annealed at 600 – 1000°C for 0-48 hours in ultra-high purity argon. The implanted zone of each sample was characterized by transmission electron microscopy and secondary ion mass spectroscopy. It is shown that the implantation resulted in a 217 ± 2 nm amorphous region with microstructural damage extending to approximately 250 nm below the surface. Recrystallization of the amorphous region was observed at 725°C, although minimal densification was observed until $\geq 800^\circ\text{C}$. Densification of the annealed samples was observed through the measurement of the implantation region thickness. Through these measurements, the as-implanted sample region was estimated as being 2.6 g·cm⁻³. Transmission electron microscopy revealed that recrystallization generally occurred through nucleation and growth at the interface of the amorphous and polycrystalline material. The recrystallized regions consisted of large identifiable 3C-SiC grains along with fine grained material. Image analysis was used to quantify the fraction of the crystalline phase as a function of time and temperature. The rate of recrystallization was greater at higher temperatures and appeared to follow an Arrhenius dependency. Secondary ion mass spectroscopy analysis demonstrated that most of the cesium was retained within the recrystallized microstructure.

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RECRYSTALLIZATION KINETICS OF 3C SILICON CARBIDE IMPLANTED
WITH 400 keV CESIUM IONS

**Daniel D. Osterberg¹, John Youngsman¹, Rick Ubic^{1,3}, Ivar E. Reimanis²,
and Darryl P. Butt^{1,3}**

¹ Department of Materials Science and Engineering, Boise State University, 1910 University Dr., Boise,
Idaho 83725

² Department of Metallurgical and Materials Science, Colorado School of Mines, 1500 Illinois St.,
Golden, Colorado 80401

³ Center for Advanced Energy Studies, 995 University Boulevard, Idaho Falls, Idaho 83401

Abstract

Polycrystalline 3C silicon carbide was implanted at room temperature with 400 keV cesium ions to a dose of 10^{16} ions·cm⁻². The samples were then annealed at 600 – 1000°C for 0-48 hours in ultra-high purity argon. The implanted zone of each sample was characterized by transmission electron microscopy and secondary ion mass spectroscopy. It is shown that the implantation resulted in a 217 ± 2 nm amorphous region with microstructural damage extending to approximately 250 nm below the surface. Recrystallization of the amorphous region was observed at 725°C although minimal densification was observed until $\geq 800^\circ\text{C}$. Densification of the annealed samples was observed through the measurement of the implantation region thickness. Through these measurements, the as-implanted sample region was estimated as being $2.6 \text{ g}\cdot\text{cm}^{-3}$. Transmission electron microscopy revealed that recrystallization generally occurred through nucleation and growth at the interface of the amorphous and polycrystalline material. The recrystallized regions consisted of large identifiable 3C-SiC grains along with fine grained material. Image analysis was used to quantify the fraction of crystalline phase as a function of time and temperature. The rate of recrystallization was greater at higher temperatures and appeared to follow an Arrhenius dependency. Secondary ion mass spectroscopy analysis demonstrated that most of the cesium was retained within the recrystallized microstructure.

1 Introduction

Silicon carbide (SiC) is an important engineering material due to its excellent high temperature stability and mechanical properties.¹ These properties allow for its use as abrasives, semiconductors, heating elements, automobile parts, as well as potential nuclear technology applications. Although SiC has not seen widespread use in nuclear applications, it has potential for use in fusion reactors and very high temperature nuclear reactors as structural elements, heat

exchangers, fuel cladding, and fuel coatings. SiC resists radiation damage due to its low neutron absorption cross section and its high defect threshold energy.²⁻⁵ The chemical stability of SiC gives it high use temperatures, where it has been shown to maintain its mechanical properties up to temperatures as high as 1200°C.⁶ SiC has also been found to exhibit relatively low diffusion coefficients, typically requiring very high temperatures for the diffusion of most elements.⁷

The low diffusion coefficients along with high use temperatures make SiC a candidate as a diffusion barrier in tristructural-isotropic (TRISO) nuclear fuels.⁸ In the TRISO fuel application, a 50 μm thick polycrystalline 3C-SiC spherical shell within the fuel provides not only a diffusion barrier for fission products but also provides mechanical strength for the multilayered fuel.⁹ Previous research on irradiated TRISO fuels has indicated that certain fission products, such as silver, cesium, and strontium diffuse at higher than anticipated rates through the SiC boundary layer.¹⁰⁻¹² The fast diffusion rates are concerning as one of the main roles of SiC in TRISO fuel is to contain these fission products. Due to the importance of this SiC boundary layer in TRISO fuel, a better understanding of the individual diffusion kinetics for each of these fission products in SiC is required.

Diffusion studies of cesium, a major fission product, are complicated by the fact that Cs has a low melting temperature and is extremely reactive in the presence of moisture or oxygen. Little research has been performed on the diffusion of this fission product due in part to the difficulty in handling Cs safely. One method of simplifying work with cesium is to ion implant it directly into the SiC structure. However, implantation introduces new complications as the ion implantation process can alter the microstructure of the material.

Due to the interest in using SiC as a semiconductor, a large number of ion implant studies have been carried out on the effects that ion implantation has on the SiC structure.¹³⁻⁴⁸ It has been

shown that high energy ion implantation of SiC at room temperature produces an amorphous region at the implantation interface.^{16, 18, 24, 49} The damage caused in SiC has been shown to vary with the implantation rate, angle, dose, temperature, implanted ion, implantation energy, and the structure and phase of the SiC substrate.^{43, 45} It has also been demonstrated that the implantation of high energy ions into SiC microstructure can create volume swelling due to the creation of defects and induced strain in the material.^{25, 31, 37, 43-45, 50, 51} Annealing heat treatments will allow for the re-densification of the implantation region as defects are annealed and recrystallization occurs.

Implantation studies report a wide range of recrystallization temperatures for ion implantation damaged SiC, with values ranging from 700 – 1500°C.^{22, 27, 39, 40, 47, 50} The wide range of reported recrystallization temperatures appears to be related to the variety of characterization equipment used. Typically, analysis of the post-implantation microstructure has been done via X-ray diffraction (XRD),^{20, 31} Rutherford backscattering spectroscopy in channeling mode (RBS-C),^{20, 28, 30, 46, 47, 50} transmission electron microscopy (TEM)^{31, 35, 43, 52} or step height measurements utilizing surface metrology techniques.^{27, 37, 50} In this analysis, TEM was used to evaluate focused ion beam (FIB) cross sections of the implanted surface. Bright-field (BF) imaging and selected area diffraction patterns (SADP) were used to analyze the implanted regions.

2 Experimental

Ion implantation was performed on polycrystalline 3C-SiC coupons (Morgan Advanced Ceramics, Hudson, NH). The SiC coupons (3 mm x 1 mm) were fabricated using a chemical vapor deposition (CVD), which resulted in a grain size of 2-10 μm , as reported by the manufacturer. The samples were of high purity and near theoretical density. Prior to

implantation, the samples were incrementally polished to a 0.25 μm finish using diamond paste. Thirty polished samples were implanted (400 keV implanter, National Electrostatics Corp., Middleton, WI) with 400 keV cesium ions at room temperature to a fluence of 10^{16} ions $\cdot\text{cm}^{-2}$.

TEM samples were prepared using a focused ion beam (Quanta 3D FEG, FEI, Hillsboro, Oregon) in order to retain the very small surface implantation region. A 30 keV gallium ion beam was used to create cross sectional FIB samples that were approximately 12 x 15 μm in size, which were then mounted to 3 mm copper TEM holders, as shown in Figure 1. The sample surface features a platinum layer deposited during the FIB process that protects the surface from the gallium ion beam and is used to mount the sample to the holder. TEM (JEM 2100 HR, JEOL, Tokyo, Japan) bright field (BF) images of the implantation region were taken at 40K or 50K magnification utilizing a 200 keV electron beam. Selected area diffraction patterns (SADP) were used to further evaluate the damage done by the implantation and were also used to identify the phase and orientation of the recrystallized material.

Annealing of the implanted samples was performed in an alumina tube furnace under oxygen-gettered, ultra high purity argon gas. The argon gas was used in order to prevent oxidation of the sample surface during the heat treatment. The oxygen and moisture levels of the argon were measured inline during the heat treatments with typical levels at $\leq .01$ ppm and ≤ 40 ppm, respectively. Heating rates of 300°C per hour were used for these non-isothermal heat treatments with dwell times ranging from 0 to 36 hours. Recrystallization of the implantation regions was evaluated at 725 - 1000°C, as shown in Table 1.

The recrystallization in the implanted samples was largely non-uniform in nature, so a method for evaluating the recrystallization fraction of each sample was developed using image software programs (Photoshop Elements 9, Adobe Systems, San Jose, CA ; ImageJ, NIH,

Bethesda, MD). Bright field TEM images, taken at 40,000 and 50,000 X magnification and SADPs were used to distinguish between the amorphous and recrystallized zones. Contrast of the BF images was enhanced in order to make the recrystallized material more discernable from the amorphous implanted material. The crystalline regions were outlined and a threshold tool was used to create a binary image of the recrystallized regions as illustrated in Figure 2. This technique was applied to the approximately 15 μm implantation edge and was used to calculate the area fraction of the recrystallized material in each sample. In order to account for the variability of the recrystallization, each sample edge was split into 6-7 measurements, each featuring approximately 2 μm of the implant edge. Data from each sampling measurement was used to generate variance bars consisting of one standard deviation, which are used to represent the data scatter.

The thicknesses of the implantation regions were measured from the TEM BF images. These measurements were taken from the sample edge to the depth where observable recrystallization had occurred near the still crystalline SiC. The reduction observed in this implantation region thickness was used to estimate the densification that occurred at various annealing temperatures. The baseline for all density estimates was the SiC sample annealed at 1000°C for 48 hours. This sample exhibited a large amount of densification and for experimental purposes was assumed to be close to the theoretical density of 3.21 $\text{g}\cdot\text{cm}^{-3}$. Based off of assumed density and visible width of the implant region of the 1000°C sample, the density of the as-implanted region could be estimated.

SIMS (IMS 6F, Cameca, Cedex, France) was used to characterize the cesium concentration versus depth of the as-implanted and several of the annealed samples. This analysis was performed utilizing a primary beam of 5 kV oxygen ions.

3 Results and Discussion

3.1 Initial Characterization

TEM BF images and SADPs of the as-implanted SiC samples demonstrated that the implantation created an amorphous layer 217 ± 2 nm in thickness, as shown in Figure 3. Below this region, SADPs were used to identify the still crystalline substrate as 3C-SiC, demonstrated in Figure 4. The depth of this amorphous region was comparable to values reported by Audren and Friedland where 300 and 360 keV implantations of cesium led to the formation of 150 and 190 nm amorphous regions in 6H-SiC, respectively.^{15, 53}

SIMS was used to determine the cesium content and depth of the cesium implantation in the as-implanted samples as found in Figure 5. The implanted cesium was found to have a maximum depth of approximately 250 nm based on the lower detectable limit of approximately $10^{17} - 10^{18}$ atoms·cm⁻³ for cesium. The peak concentration of cesium within the implanted surface was 1.4×10^{21} atoms·cm⁻³ found at a depth of 112 nm. Integration of this data in the as-implanted samples, from 0-300 nm, yielded a total implant dose of 1.0×10^{16} atoms·cm⁻², which agrees with the ion fluence found during the implantation process, thus validating the calibration of the SIMS and implantation process.

3.2 Heat Treatments and Recrystallization

TEM characterization indicated that no observable recrystallization occurred within the implantation zones after annealing at 600 or 700°C for 1 hour. Recrystallization did occur at 725°C, although at a relatively slow rate, with full recrystallization occurring at approximately 36 hours. The upper temperature explored for the kinetics of recrystallization in this study was 900°C due to the fact that the rate of recrystallization was very high above this temperature.

SADPs taken from the SiC sample treated at 900°C for 1 hour indicate a large degree of recrystallization, as shown in Figure 6.

Recrystallization in the implanted samples was found to occur primarily at the interface of the amorphous implantation region and the underlying polycrystalline 3C-SiC. This recrystallization appeared to nucleate just below the amorphous region depth of 217 ± 2 nm found in the as-implanted samples. In the sample treated at 725°C for 4 hours, recrystallization appeared to have nucleated at a depth of 263 ± 3 nm. This value is within the cesium implantation depth of approximately 250 nm confirmed by SIMS. Initial nucleation and growth in all of the annealed samples occurred just below the interface between the amorphous and still crystalline material.

The recrystallized microstructure consisted of large grains along with very fine grains grown from the undamaged SiC substrate. Past research on single crystal 6H-SiC microstructures has indicated that uniform epitaxial growth occurs from the still crystalline substrate, along with the nucleation and growth of 3C-SiC grains.^{16, 22, 49, 52} In comparison, the recrystallization observed in this study was largely non-uniform in nature. This is attributed to the polycrystalline nature of the samples used in this work. Bright field images of the annealed implantation region suggest that some of the large grains may share the same orientation as the 3C-SiC substrate, as illustrated in Figure 7. SADPs were used to show that large grains within the recrystallized implantation region share the same orientation as grains within the substrate, as found in Figure 8. The SADPs were indexed and found to be that of 3C-SiC, which indicates that the recrystallized grain is also 3C-SiC, as demonstrated in Figure 9. In some cases it was found that this preferred growth only occurred on a small portion of the much larger oriented grains in the substrate. Identification of the crystalline structure of the fine grains within the implant region

was difficult due to their very small size. Literature has shown the formation of 3C-SiC grains in implanted 6H-SiC at temperatures comparable to the ones used in this work, which suggests that the fine grains could be 3C-SiC.^{22, 40, 47, 52}

3.3 Densification

During heat treatments, the thickness of the amorphous region decreases as defects are annealed, the material recrystallizes, and the area redensifies. Previous work performed by Nipoti and McHargue utilized surface step height measurements, taken between implanted and non-implanted regions, to observe the densification that occurs during annealing.^{37, 50}

Densification studies indicate that the density of implanted SiC can decrease 10-25% due to point defects and strain induced by the implantation process.^{43, 45, 50, 51} Measurement of the implantation region widths were taken of all of the heat treated samples in order to study the densification of the implant region at each annealing temperature and time, shown in Figure 10.

In this study, it was found that although recrystallization of the implantation region begins at temperatures as low as 725°C, there was no observed change in the implantation region thickness. The recrystallization and lack of densification found in the 725°C treated samples suggest that it is a highly defect filled microstructure. At temperatures $\geq 800^\circ\text{C}$, there is an observed reduction in the implantation region thickness. This apparent densification of the implanted region matches well with previous step height studies performed by Hofgen.²⁷

Annealing at 1000°C for 48 hours creates significant densification, where the thickness of the implant region is reduced by 50 nm when compared to the sample treated at 725°C for 4 hours. By assuming that the 1000°C treated sample is at the theoretical density of $3.21 \text{ g}\cdot\text{cm}^{-3}$ for SiC, the density of the as-implanted region can be estimated as being approximately $2.6 \text{ g}\cdot\text{cm}^{-3}$. This represents a 23% decrease in density due to the ion implantation process.

3.4 Recrystallization Kinetics

The recrystallization fraction of each annealed SiC sample was analyzed using the method described in the experimental section. In this process, it was apparent that the nucleation and growth observed in the implantation region was anisotropic and dependent upon the orientation of the grains in the polycrystalline substrate, as observed in Figure 11. The local differences in the recrystallization growth rates indicate different rates of nucleation and growth for different 3C-SiC orientations. The measurement methodology used in this analysis gives an average recrystallization rate and activation energy for all grain orientations found in the polycrystalline 3C-SiC microstructure.

The recrystallization fraction for each annealing treatment was plotted versus time in order to observe the kinetics of the recrystallization process found in Figure 12. It is observed from the recrystallization data that the rate of recrystallization increased with temperature and to a reasonable approximation followed a characteristic Avrami fit.⁵⁴ Analysis was done using a simple recrystallization and growth equation, the Johnson-Mehl-Avrami equation (JMA).⁵⁴⁻⁵⁶

$$x(t) = 1 - \exp((-k * t)^n)$$

Where $x(t)$ is the fraction recrystallized with respect to time t , k is a temperature dependent rate constant, and n is the dimensionality of growth coefficient, which describes the kind of nucleation and growth that is occurring. This equation can then be re-written as:

$$\ln[-\ln(1 - x(t))] = \ln(k) + n * \ln(t)$$

If the data follows JMA behavior, then the plot of $\ln(t)$ vs. $\ln[-\ln(1 - x(t))]$ will yield a straight line with a slope of n and an intercept of $\ln(k)$, as seen in Figure 13. It was observed from this that data there was an overall linear fit with slope values ranging from 0.4 to 1.1.

Dimensionality of growth values ($n \leq 1$) indicates 1-D growth during the recrystallization process.

The y-axis intercepts found in Figure 13 yielded the natural log of the temperature dependent rate constants, $\ln(k)$. Using the JMA equation, a plot of $\ln(k)$ vs. T^{-1} will yield a slope of $\frac{E_a}{R}$, as found in Figure 14. Plotting these values gives us a fairly linear plot with an approximate activation energy of $482 \pm 54 \text{ kJ}\cdot\text{mol}^{-1}$. An activation energy of $667 \pm 20 \text{ kJ}\cdot\text{mol}^{-1}$ for the recrystallization of an amorphous SiC derived from a polymer precursor was found by Kurtenbach et al. in a DTA/TGA study.⁵⁷

3.5 Cesium Retention

SIMS analyses of several of the annealed samples were carried out in order to quantify the amount of remaining cesium within the recrystallized or partially recrystallized microstructures. Results for samples treated at 750°C for 8 hours and 725°C for 36 hours indicate that there was retention of cesium within the microstructure, illustrated in Figure 15. The cesium peak for these two samples was located at 110 and 108 nm, respectively. This represents a slight shift of the peak toward the surface when compared to the 115 nm peak found in the as-implanted samples. Integration of the SIMS data yields $6.1 \times 10^{15} \text{ atoms}\cdot\text{cm}^{-2}$ for the sample treated at 750°C for 8 hours and $7.2 \times 10^{15} \text{ atoms}\cdot\text{cm}^{-2}$ for the sample treated at 725°C for 36 hours, which represents 61% and 72% retention rates of the original cesium implantation, respectively. The SIMS data also indicated that there was no discernable diffusion of cesium into the original undamaged 3C-SiC microstructure. The cesium loss and shift agrees with previous cesium implantation work performed by Audren and Friedland, where there was also no detectable diffusion of cesium into the bulk SiC microstructure.^{15, 53} The selective shift of cesium

towards the sample surface indicates there may be slightly different diffusion rates for the undamaged 3C-SiC and the recrystallized material.

4 Conclusion

The damage and recrystallization kinetics of cesium ion implanted 3C-SiC were characterized by TEM and SIMS. The cesium ions were implanted at 400 keV to a dose of 10^{16} ions·cm⁻². The ion implantation process creates an amorphous region of 217 ± 2 nm with observed damage extending to ≈ 250 nm. Recrystallization of the amorphous region was facilitated by annealing samples from 600 – 1000°C, 0 – 36 hours in ultra high purity argon. An image analysis technique was developed in order to quantify the kinetics of the recrystallization. In this analysis, the following results were observed:

- For times of 4 hours or less, recrystallization was observed at temperatures $\geq 725^\circ\text{C}$. Densification of the implantation region was not observed until temperatures $\geq 800^\circ\text{C}$. The recrystallization without densification indicated the formation of a highly defected microstructure. The density of the implant region in the as-implanted was estimated to be approximately $2.6 \text{ g}\cdot\text{cm}^{-3}$, which represents a 23% drop in density due to the ion implantation.
- The majority of the nucleation and growth in the annealed samples occurred at the interface between the amorphous and polycrystalline material. This nucleation and growth was anisotropic in nature due to the polycrystalline nature of the 3C-SiC starting material. Some of the recrystallized grains were found to have the same orientation as the grains on which they were nucleated and were identified as being 3C-SiC.

- It is shown that the fraction of recrystallized phase can be fitted to a Johnson-Mehl-Avrami (JMA) equation, which is typically used to describe isothermal nucleation and growth kinetics. The model yielded an apparent activation energy of 482 ± 54 kJ·mol⁻¹.
- SIMS analysis of heat treated samples indicated a loss of cesium along with an overall shift of the cesium peak and average concentration towards the implantation surface. Samples treated at 750°C for 8 hours and 725°C for 36 hours were shown to retain 61% and 72% of the original cesium implantation, respectively. There was also no discernable diffusion of cesium into the undamaged 3C-SiC bulk microstructure.

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Tables

Table 1. Experimental annealing heat treatment temperatures and times for the cesium implanted SiC samples.

Heat Treatment (°C)	Time (min)
As Implanted	0
600	60
700	60
725	240, 480, 720, 1200, 1680, 2160
750	60, 120, 240, 480, 600
775	30, 60, 240, 240, 360, 480
800	30, 45, 60, 90
900	0, 60
1000	2880

Figures

Figure 1. SEM images of a FIB sample created from an implanted SiC sample annealed at 800°C for 1 hour. The sample is mounted to a copper TEM holder and allows for the analysis of approximately 15 μm of the ion implanted surface.

Figure 2. TEM bright field image demonstrates the variability found in the recrystallization of the implanted SiC sample annealed at 725°C for 20 hours. In order to quantify the recrystallization found in the samples, binary images were generated of the amorphous (A) and crystalline areas (C).

Figure 3. TEM bright field images and selected area diffraction patterns of as-implanted SiC indicate the creation of a 217 ± 2 nm amorphous region.

Figure 4. Selected area diffraction from the as-implanted SiC sample (Figure 3) indicates the original material as being 3C-SiC.

Figure 5. SIMS data for the cesium content vs. depth for the as-implanted SiC sample indicates a maximum depth of approximately 250 nm. TEM bright field images of the as-implanted SiC sample indicated the amorphous region extended down to 217 ± 2 nm. Recrystallization was found to occur at depth of 263 ± 3 nm for samples annealed at 725°C for 4 hours.

Figure 6. TEM bright field images of the SiC sample annealed at 900°C for 1 hour indicate recrystallization of the implantation region.

Figure 7. TEM bright field images indicate that some of the large grains in the implant region appear to share the same orientation as the undamaged 3C-SiC material.

Figure 8. Selected area diffraction patterns taken of a SiC sample annealed at 725°C for 36 hours indicated that a large grain in the implant region shared the same orientation as the grain in the undamaged 3C-SiC.

Figure 9. The selected area diffraction pattern taken from the sample annealed at 725°C for 36 hours (Figure 8) was indexed and identified as being 3C-SiC.

Figure 10. Using TEM bright field images, the implantation region thickness was measured after each annealing heat treatment. Reduction in this thickness was found at temperatures $\geq 800^{\circ}\text{C}$ and is due to the redensification of the implantation region.

Figure 11. Binary images were created from the recrystallization found in the TEM bright field images. These images represent the entire edge of the FIB sample made from the SiC sample annealed at 725°C for 4 hours. Using these binary images, the recrystallization area percent was calculated for each annealing treatment.

Figure 12. The recrystallization percent for each annealing heat treatment was obtained through analysis of the TEM bright field images. The variance bars indicate the variability of the recrystallization in each sample surface.

Figure 13. This is a fit of the recrystallization data to the Arrhenius model. The data was found to have an overall linear fit. The intercept values were found using the linear fit and the experimental variability in this measurement was found through the use of 95% confidence intervals.

Figure 14. The plot of each temperature dependent rate constant ($\ln(k)$) vs. $1/T$ yielded an activation energy of $482 \pm 54 \text{ kJ}\cdot\text{mol}^{-1}$.

Figure 15. SIMS data for an as-received sample, sample annealed at 750°C for 8 hours, and a sample annealed at 725°C for 36 hours were analyzed for cesium content. The annealed samples indicate a slight shift of the cesium peak towards the surface along with an overall loss of cesium. There was also no apparent diffusion of cesium into the undamaged bulk 3C-SiC microstructure.

CONCLUDING CHAPTER

This analysis consisted of an in depth TEM study of the recrystallization kinetics of polycrystalline 3C-SiC implanted with high energy cesium ions. It was found that the 400 keV implantation of cesium ions into polycrystalline 3C-SiC, to a fluence of 10^{16} ions·cm⁻², creates an amorphous region of 217 ± 2 nm. Secondary ion mass spectroscopy analysis of the implantation region indicates that the cesium was implanted to a maximum depth of approximately 250 nm. Subsequent annealing of the implanted samples indicates that recrystallization occurred in samples treated at temperatures $\geq 725^{\circ}\text{C}$. Measurements taken of the implantation region thickness in the annealed samples indicates that a reduction occurs at treatments temperatures $\geq 800^{\circ}\text{C}$. These thickness measurements were used to calculate the as-implanted density as being approximately $2.6 \text{ g}\cdot\text{cm}^{-3}$.

The nucleation and growth was found to occur just below the interface between the amorphous and still crystalline sample regions. The recrystallization rate was found to be non-uniform along the implantation edge, which is attributed to the polycrystalline nature of the started sample materials. The recrystallized microstructure consisted of very fine grains along with larger grains, which appeared to share the same orientation as the undamaged 3C-SiC. Using selected area diffraction patterns, some of these large grains were identified as being that of 3C-SiC.

SIMS analysis of heat treated samples indicated a loss of cesium along with an overall shift of the cesium peak and average concentration towards the implantation surface.

Samples treated at 750°C for 8 hours and 725°C for 36 hours were shown to retain 61% and 72% of the original cesium implantation, respectively. There was also no discernable diffusion of cesium into the undamaged 3C-SiC bulk microstructure.

Bright field TEM images were used to evaluate the recrystallization that occurred in the annealed samples. An image analysis technique was developed in order to measure the recrystallized percent of each sample. This was done by converting the bright field images into binary images. Through use of this technique, it was found that the recrystallization rate increased with temperature and followed an Avrami type fit. The Johnson-Mehl-Avrami (JMA) equation was used to fit the kinetics of the data and an activation energy of 482 ± 54 kJ·mol⁻¹ was found.

This work adds to the existing literature on the kinetics of recrystallization for implanted SiC. Further work on this project would include additional annealing times and temperatures along with further analysis of the recrystallized microstructure. Convergent beam TEM techniques could be employed to gain a better understanding of the phase of the recrystallized material. Further analysis should be done on the relationship between grain orientation and recrystallization rate of the amorphous material. It may also be of interest to implant at elevated temperatures in order to limit the damage done to the microstructure.

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APPENDIX A

Implantation Surface Analysis – Optical Profilometry Data

Figure A1. Bright field images of the as-implanted SiC sample surface show the contrast between the implanted surface and the non-implanted edge. This non-implanted region is an artifact of the holder used during the implantation process.

Sample #1			Sample #2		
	Average	StDev		Average	StDev
Untreated #1 A	25.6	9.5	Untreated #2 A	32.7	7.6
Untreated #1 B	24.1	4.6	Untreated #2 B	33.1	8.4
Untreated #1 C	33.1	7.9	Untreated #2 C	na	na
Untreated #1 D	26.2	7.3	Untreated #2 D	25.1	5.5
Untreated #1 Average	27.2	8.0	Untreated #2 Average	30.3	8.0
Treated #1 (600°C) A	20.8	7.4	Treated #2 (700°C) A	14.4	9.3
Treated #1 (600°C) B	24.4	5.1	Treated #2 (700°C) B	33.6	5.7
Treated #1 (600°C) C	23.6	4.9	Treated #2 (700°C) C	39.0	6.4
Treated #1 (600°C) D	16.1	4.2	Treated #2 (700°C) D	5.8	6.3
Treated #1 Average	21.2	6.2	Treated #2 Average	23.2	15.3

Sample #3			Sample #4		
	Average	StDev		Average	StDev
Untreated #3 A	29.8	10.9	Untreated #4 A	93.9	19.2
Untreated #3 B	38.6	18.3	Untreated #4 B	181.3	53.1
Untreated #3 C	51.1	44.0	Untreated #4 C	15.4	11.2
Untreated #3 D	64.4	40.4	Untreated #4 D	127.1	40.5
Untreated #3 Average	46.0	32.1	Untreated #4 Average	104.4	69.7
Treated #3 (800°C) A	22.9	9.9	Treated #4 (900°C) A	124.9	51.1
Treated #3 (800°C) B	38.1	13.1	Treated #4 (900°C) B	83.1	23.9
Treated #3 (800°C) C	88.9	24.2	Treated #4 (900°C) C	86.8	10.4
Treated #3 (800°C) D	31.0	13.7	Treated #4 (900°C) D	68.1	28.7
Treated #3 Average	45.2	30.4	Treated #4 Average	90.7	37.4

Figure A2. Listed are the measurements taken of the step height differences between the as-implanted regions and the edge non-implanted SiC sample surface for samples annealed at 600 – 900°C for 1 hour. Four measurements were taken of each sample surface before and after annealing heat treatments. The data showed a large amount of variance which is attributed the slight rounding of the sample edges that may occur during machining.

Sample #5			Sample #6		
	Average	StDev		Average	StDev
Untreated #5 A	25.4	8.6	Untreated #6 A	50.8	11.1
Untreated #5 B	69.0	48.1	Untreated #6 B	54.7	39.0
Untreated #5 C	127.9	25.8	Untreated #6 C	30.1	4.8
Untreated #5 D	42.8	11.0	Untreated #6 D	35.9	18.3
Untreated #5 Average	66.3	47.7	Untreated #6 Average	42.9	12.8
Treated #5 (1000°C) A	21.9	3.8	Treated #6 (1100°C) A	50.0	11.0
Treated #5 (1000°C) B	21.0	14.3	Treated #6 (1100°C) B	54.7	39.0
Treated #5 (1000°C) C	38.0	10.3	Treated #6 (1100°C) C	30.1	4.8
Treated #5 (1000°C) D	17.4	7.2	Treated #6 (1100°C) D	35.9	18.3
Treated #5 Average	24.6	23.8	Treated #6 Average	42.7	23.8

Figure A3. Listed are the measurements taken of the step height differences between the as-implanted regions and the edge non-implanted SiC sample surface for samples annealed at 1000 – 1100°C for 1 hour.

	As Implanted Step Height (nm)		Heat Treated Step Height (nm)	
	Average	StDev	Average	StDev
600°C	27.2	8.0	21.2	6.2
700°C	30.3	8.0	23.2	15.3
800°C	46.0	32.1	45.2	30.4
900°C	104.4	69.7	90.7	37.4
1000°C	66.3	47.7	24.6	23.8
1100°C	42.9	12.8	42.7	23.8

Figure A16. Step height measurements taken using an optical profiler indicate a large amount of variance for the samples annealed at 600 - 1100°C for 1 hour. There was no discernable relationship between treatment temperature and the reduction of the step height due to the large variability found in the measurements.

APPENDIX B

TEM Bright Field and Binary Images of SiC Recrystallization

Figure B17. TEM BF images of a cesium implanted SiC sample after a heat treatment of 725°C for 4 hours.

Figure B18. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 725°C for 4 hours.

Figure B19. TEM BF images of a cesium implanted SiC sample after a heat treatment of 725°C for 8 hours.

Figure B20. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 725°C for 8 hours.

Figure B21. TEM BF images of a cesium implanted SiC sample after a heat treatment of 725°C for 12 hours.

Figure B22. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 725°C for 12 hours.

Figure B23. TEM BF images of a cesium implanted SiC sample after a heat treatment of 725°C for 20 hours.

Figure B24. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 725°C for 20 hours.

Figure B25. TEM BF images of a cesium implanted SiC sample after a heat treatment of 725°C for 28 hours.

Figure B26. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 725°C for 28 hours.

Figure B27. TEM BF images of a cesium implanted SiC sample after a heat treatment of 725°C for 36 hours.

Figure B28. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 725°C for 36 hours.

Figure B29. TEM BF images of a cesium implanted SiC sample after a heat treatment of 750°C for 1 hour.

Figure B30. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 750°C for 1 hour.

Figure B31. TEM BF images of a cesium implanted SiC sample after a heat treatment of 750°C for 2 hours.

Figure B32. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 750°C for 2 hours.

Figure B33. TEM BF images of a cesium implanted SiC sample after a heat treatment of 750°C for 4 hours.

Figure B34. Binary image generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 750°C for 4 hours.

Figure B35. TEM BF images of a cesium implanted SiC sample after a heat treatment of 750°C for 8 hours.

Figure B36. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 750°C for 8 hours.

Figure B37. TEM BF images of a cesium implanted SiC sample after a heat treatment of 750°C for 10 hours.

Figure B38. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 750°C for 10 hours.

Figure B39. TEM BF images of a cesium implanted SiC sample after a heat treatment of 775°C for 0.5 hours.

Figure B40. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 775°C for 0.5 hours.

Figure B41. TEM BF images of a cesium implanted SiC sample after a heat treatment of 775°C for 1 hour.

Figure B42. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 775°C for 1 hour.

Figure B43. TEM BF images of a cesium implanted SiC sample after a heat treatment of 775°C for 4 hours.

Figure B44. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 775°C for 4 hours.

Figure B45. TEM BF images of a cesium implanted SiC sample after a heat treatment of 775°C for 6 hours.

Figure B46. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 775°C for 6 hours.

Figure B47. TEM BF images of a cesium implanted SiC sample after a heat treatment of 775°C for 8 hours.

Figure B48. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 775°C for 8 hours.

Figure B49. TEM BF images of a cesium implanted SiC sample after a heat treatment of 800°C for 0.5 hours.

Figure B50. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 800°C for 0.5 hours.

Figure B51. TEM BF images of a cesium implanted SiC sample after a heat treatment of 800°C for 1 hour.

Figure B52. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 800°C for 1 hour.

Figure B53. TEM BF images of a cesium implanted SiC sample after a heat treatment of 800°C for 1.5 hours.

Figure B54. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 800°C for 1.5 hours.

Figure B55. TEM BF images of a cesium implanted SiC sample after a heat treatment of 900°C for 0 hours.

Figure B56. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 900°C for 0 hours.

Figure B57. TEM BF images of a cesium implanted SiC sample after a heat treatment of 900°C for 1 hour.

Figure B58. Binary images generated from the TEM bright field images of the recrystallization found in the cesium implanted SiC sample treated at 900°C for 1 hour.