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Ion irradiation induced damage and dynamic recovery in single crystal silicon carbide and strontium titanate

Haizhou Xue

University of Tennessee - Knoxville, hxue2@vols.utk.edu

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I am submitting herewith a dissertation written by Haizhou Xue entitled "Ion irradiation induced damage and dynamic recovery in single crystal silicon carbide and strontium titanate." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Materials Science and Engineering.

Yanwen Zhang, Major Professor

We have read this dissertation and recommend its acceptance:

William J. Weber, Kurt E. Sickafus, Maik K. Lang

Accepted for the Council:

Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
Ion irradiation induced damage and dynamic recovery in single crystal silicon carbide and strontium titanate

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Haizhou Xue
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ABSTRACT

The objective of this thesis work is to gain better understanding of ion-solid interaction in the energy regime where electronic and nuclear energy loss are comparable. Such responses of materials to ion irradiations are of fundamental importance for micro-electronics and nuclear applications. The ion irradiation induced modification for the crystal structure, the physical and chemical properties etc. may strongly affect the performance of functional materials that needs to be better understood.

Experimentally, ion irradiation induced damage accumulation and dynamic recovery in SiC [silicon carbide] and SrTiO$_3$ [strontium titanate] were studied in this dissertation project. Five chapters are presented: Firstly, electronic stopping power for heavy ions in light targets was experimentally evaluated for SiC. Secondly, out-surface diffusion of Ag atoms through SiC coating layer was studied by ion implantation and thermal annealing. The result also suggested that a SiO$_2$ [silicon dioxide] thin film might serve as a diffusion barrier. Thirdly, a thermally induced recovery was studied for single crystal SiC. Through well controlled isothermal and isochronal annealing processes, activation energies were estimated and attributed to certain defect migration/recombination mechanisms. The fourth chapter focuses on a competing effect on defect dynamics due to ionization-induced defect recovery in SiC. Recovery of the existing defects resulting from a thermal spike along the ion path was expected, and was experimentally confirmed by using energetic ions. The results suggest a low threshold of electronic stopping power for the ionization-induced recovery. In the last chapter, an example of how the target material responses differently to energy deposition are demonstrated for single crystal SrTiO$_3$. Instead of the recovery that was observed in SiC, a synergy effect of the coupled electronic and nuclear stopping energy deposition leads to formation of amorphous ion tracks.
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CHAPTER I.
INTRODUCTION

1. Stopping power

Ion solid interaction is fundamental to various active research fields and productive industry applications. Benefited from the development of accelerator technologies, ions in a wide energy range from eV to hundreds of GeV can now be produced and injected into targets, including solid, liquid, gas and even the living organism. In general, when an ion reaches the surface of a target, or even before that, the interaction between the ion and target material gets involved that initiate the life change for both the ion and target material. Qualitatively, the ion will loss its energy to slow down, and the target atoms will gain energy to be mobile. Quantitatively, however, the ion-solid interaction is extremely complex. Firstly, a simple way of understanding the complexity of ion-solid interaction is by considering that either the ion or the target is not a single "object". There are numerous nuclei and electrons and their interactions are far beyond the current capability of accurate modeling and calculation. Secondly, during ion irradiation, ions and target material are continually modified. The energies, lattice sites, charge states etc. vary in a time scale of pico-second or less, which greatly adds to the difficulties for studying ion-solid interaction. Moreover, despite of the atomic density of a target material, a tiny amount of incident ions is able to initiate dramatic modifications in physical and chemical properties. For example, in order to modify the band structure and charge density, ppm level of doping by ion irradiation is routinely employed in microelectronic industry. For nuclear material applications, the crystalline-amorphous phase transfer of some ceramics typically occurs at a dose of \(~1\) displacements per atom (dpa), which corresponds to an ion fluence range of \(10^{14} \text{ cm}^{-2}\). To create a significant volume swelling, the
required dose is usually at tens of dpa with the impurity concentration less than 1% at maximum.

In order to improve the knowledge of ion-solid interaction, and to establish theories and models for predicting the ion irradiation induced radiation effects in solid targets, experimental validations are desired. One well accepted approach bases on the fact that in order to make an "interaction" possible, energy transfer during the ion-solid interaction is the essential foundation. By this sense, two different mechanisms of energy transfer are employed to describe the extremely complex, many body interactions, which are the electronic and nuclear stopping powers.

1.1. Nuclear stopping power and displacements of the target atoms

Nuclear stopping power is defined as the energy loss in elastic collisions between the nuclei of target atoms and the projectiles (either ions or recoils). For the charged ions and recoils, the collisions are driven by the Columbic repulsive force. As an approach, the process can be described by a two body elastic collision model which follows the conservation of energy and momentum. The kinetic energy transfer \( T \) in an elastic collision is:

\[
T = \frac{2m_1m_2}{(m_1 + m_2)^2} E_0(1 - \cos \theta^*) \quad \text{(eq. 1-1)}
\]

Where \( m_1 \) is the mass of a projectile, \( m_2 \) is the mass of a target nucleus, \( \theta^* \) is the scattering angle in the center of mass frame of reference. For a head-on collision in which \( \theta^* = 180^\circ \), the energy transfer reaches maximum, and the kinetic factor \( k \) is defined as:
\[ k = \frac{4m_1m_2}{(m_1 + m_2)^2} \]  

(eq. 1-2)

Eq. 1-1 and eq. 1-2 suggest that the energy transfer in an elastic collision depends on the atomic mass of both projectile and target nuclei. A maximum energy transfer occurs when \( m_1 = m_2 \).

After a collision, the target atom will gain kinetic energy and may be displaced away from its original lattice site if the kinetic energy is larger than the displacement threshold energy, \( E_d \). However it does not promise that a defect is created. If the energy transfer is below the threshold, the activated atom will only leave its site temporarily, then return to the equilibrium position after the energy is dispersed by lattice vibration. Only in the case that the transferred energy is above the threshold energy \( E_d \), the displacement becomes permanent and a vacancy is left at the original site. The conception of displacement energy is very important for the theories such as the Kinchin and Pease (K-P) model [1], and for the computer codes such as Stopping and Range of Ions in Matter (SRIM) [2]. In this thesis work, the displacements will be frequently predicted by the SRIM code, and the displacement energies are according to the literature reports. However, it is important to keep in mind that due to the lattice vibration and the anisotropy of crystal structure, \( E_d \) can be orientation-depend, and will vary among atoms at the surface and in the bulk [3]. For a recoil that is displaced from its original lattice site, it will loss energy that eventually rest at an interstitial site or knock-out another target atom to occupy its lattice site, known as a replacement collision. For the ion energies utilized in this thesis work, one energetic ion will cause a series of displacements before it runs out of its kinetic energy, and a collision cascade will be produced.
1.2. Electronic stopping power, ionization and ion track formation

Electronic stopping power is the energy loss due to inelastic collisions between the projectiles and the electrons in a solid target. Compare to the nuclear stopping power for which a two body elastic collision model can serve as a reasonable approach, a quantitative description for electronic stopping power is far more difficult. Firstly the incident ion can interact with multiple electrons in a very short time scale due to a much denser electron concentration than the nuclei. Secondly, in a solid target the electrons of an incident ions or an energetic recoil may be stripped, therefore the charge state of projectiles may be continually modified. Due to the variation of (1) energy of the projectile and (2) electron density of the target material, the variation of charge states and its effects are difficult to be predicted. Thirdly, the ionization induced free electrons will modify the target materials as well as the projectiles. Because of those complexities, it is almost impossible to relay on a universal model to describe the electronic stopping power. In order to better evaluate the electronic stopping power induced effects and provide reasonable predictions, theories for varied combination of ions and targets have been proposed, for example, the Bethe-Bloch formula for the swift ions [4-7] and the LSS-theory (Lindhard, Scharff and Schiott) for the slow-heavy ions [8-9] etc. Based on those theoretical efforts and experimentally measured electronic stopping powers, computer codes such as SRIM can now well predict the electron stopping power for light and medium mass ions. However for the heavy ions, due to the insufficient experimental data, precise prediction is still an issue [10-11], and an example will be discussed in chapter II for Pt ions in SiC.

The electronic stopping power induced ionization will create hot electrons which are able to transfer the heat within a short distance (in an average of mean free path) in solid and interact with other electrons through electron-electron
interaction. The ionized electrons may further transfer energy to the lattice nuclei by electron-phonon coupling. An enhanced lattice vibration equals to an elevated temperature which is localized along the ion path to produce a cylindrical shape hot zone known as the thermal spike. The ionization induced thermal spike will modify the target materials. Firstly it may enhance the recombination of the existed defects such as the Frenkel pairs. Secondly, with an intense energy deposition, temperature within the thermal spike may go above the melting point of a target material. A fast atomic heating and quench (at \( \sim 10^{12} \) s to \( \sim 10^9 \)) process may lead to the formation of amorphous regions, which are the amorphous ion tracks or hilllocks found in metals [12], semiconductors [13] and insulators after high energy ion irradiations [14].

The formation of ion tracks depends on the electronic energy deposition from the ions, and the nature of target materials. For materials with a good thermal conductivity and a high melting point, ion track formation will be suppressed and ionization induced annealing may occur. On the contrary, for some oxides such as \( \text{LiNbO}_3 \), due to their poor thermal conductivities and low melting points, the amorphous ion track can be produced by ions with relatively low electronic stopping powers. It is worth noting that during ion irradiation the target material is continually modified. The physical and chemical properties may vary with the increased defect concentration. As the sequence, ion tracks may be induced with a lower electronic stopping power compares to a pristine single crystal. One example of a synergy effect will be presented in this thesis work in section VI for \( \text{SiTiO}_3 \).
For target materials, the stopping powers are not constants but vary with the energy of ions. As an example, the stopping powers of iodine ion in SiC is plotted as the function of ion energy in Fig. 1-1. At the low energy region, nuclear stopping dominates. As a result, if the irradiation is performed at a large incident angle, medium mass and heavy ions may remove the top layer of target atoms by elastic collisions, known as sputtering. In synthesis of functional materials, sputtering is routinely employed. For example, the ion beam assisted deposition (IBAD) has been employed in the growth of advanced thin films. On the other hand, with a well controlled ion beam flux, the sputtering rate can be modified that ion milling is nowadays a standard technique in sample preparation. In high energy region electronic stopping dominates, where nuclear stopping power is low enough to be negligible. Energetic ions can easily penetrate the coulomb barrier to initiate nuclear reactions. High energy ions produced by large accelerator systems (such as synchrotrons) are of critical importance in the researches of high energy and particle physics.

Within the intermediate energy range, as highlighted in the plot (IM-E) which is from hundreds of keV to tens of MeV. The penetration depth ranges from a few tens of nanometers to a few tens of micrometers. For nuclear material and microelectronics applications, the intermediate energy ions are routinely utilized in ion implantations. Several important ion beam analysis techniques, such as the Rutherford backscattering spectrometry (RBS), elastic recoil detection analysis (ERDA), particle-induced X-ray emission (PIXE) etc. are employing the intermediated energy ions as a probing beam. Regarding to those applications, a comprehensive understanding of the ion-solid interactions for the intermediate energy ions is of fundamental importance. Moreover, as shown in Fig. 1, for the intermediate energy ions in solid materials, the electronic and nuclear stopping
powers can be comparable. The displacements of target atoms and the
ionization-induced effects are coupled together which results in complicated
phenomena. The coupled effects of the intermediate energy ions have not been
well understood yet. The progress in experimental and theoretical studies will
bridge the knowledge gaps of ion-solid interaction and may contribute to the ion
beam modifications.

2. Effects of Ion irradiation induced damage and dynamic
recovery

During ion-solid interaction, nuclear stopping power will cause the displacements
of target atoms, thus may produce point defects, complex defect clusters, and
even small amorphous domains.. A continuous accumulation of point defects will
lead to microstructural damage in the crystal lattice. Structure evolutions, such as
phase transfer, voids and volume swelling, dislocation loops, gas bubble
formation etc may take place as the sequences. On the other hand, driven by the
kinetic energies which are induced by nuclear and electronic energy deposition,
migration and recombination of the existed defects may be enhanced. As a result,
dynamic recovery may occur and compete with the damage production. Due to
the comparable electronic and nuclear stopping powers, for ions within the
intermediate energy range, the coupled damage and dynamic recovery is an
important, practical issue for both fundamental understandings and applications.
More experimental efforts are needed for various combination of ions and target
materials. Also it has been already revealed that there are abundant effects
which may modify the damage accumulation and dynamic recovery processes,
such as the temperature, ions mass/flux effects and the primary bonding type of
target materials.
2.1. Temperature effect

Regarding to the dynamic recovery, for existing point defects to be annealed, a minimum kinetic energy is required to overcome energy barriers for annealing defects in crystals. Firstly, in case a defect is "trapped" in a potential well, a trapping barrier should be overcome that the defect can be mobile. Secondly, point defects, for example an interstitial will need to migrate to encounter a vacancy for recombination. Though the migration of defects may occur through different mechanisms, there are always one or multiple diffusion barriers which consume kinetic energy. Thirdly, a recombination barrier exists before the defect can eventually be annihilated. With an elevated temperature, there is a better chance that the defect gains enough kinetic energy to overcome all the barriers and be annealed. As a result, the damage accumulation will appear less effective as the function of dose, which has been experimentally observed in solids. For example, to single crystal SiC, at low temperature the critical dose for amorphization by ion irradiation employs medium mass ions is $<0.3 \text{ dpa}$ [15-16]. At room temperature, an increased critical dose of 0.35-0.5 dpa is suggested [17-18]. At high temperature, i.e. 420 K under Si ion irradiation, even with a much higher dose the material will not be fully amorphized [19]. The thermally induced annealing has been utilized in crystal growth and post-doping treatments in microelectronics industry. From the research point of view, the temperature effects in damage accumulation during or after an ion irradiation may provide abundant information towards the defect behaviors and the potential barriers exist in the pristine or damaged crystal lattice, which are extremely difficult for directly experimental observations. Also, for applications such as in nuclear reactors, a high temperature is usually combined with high radioactivity, the damage accumulation may vary dramatically from what at room temperature. For example, during a high temperature irradiation, in crystalline SiC, dislocation loops can be produced [20], which is not one of the major defect types induced
by a room temperature ion irradiation. The physical and chemical properties may also be modified differently, which will further influence the performance and reliability of nuclear materials.

2.2. **Ion mass and flux effect**

Energetic ions may experience multiple collisions with the target nuclei to produce collision cascades. According to eq. 1-1, the energy transfer during an elastic collision is a function of ion mass. Also, with the increased ion mass, the collision cross-section is increased, therefore heavy ions usually create larger defect clusters than light ions. As the results, on one hand, larger defect clusters have a better chance to overlap with each other. The defect stimulated amorphization will be enhanced. On the other hand, compares to isolated point defects which are diluted in pristine crystal lattice, a defect cluster or defect complex requires higher energy to be annealed. Therefore, heavy ion may effectively induce higher damage level, which has been observed in materials such as Si [21], InP, GaAs [22] and SiC [23] etc. Besides the ion mass, the flux effect has been suggested to affect the damage accumulation. For example, for proton irradiation on Si, an elevated ion flux induces less damage, and it may be attributed to the diffusion and recombination of point defects between the adjacent ion paths [24]. However for some other materials such as SiC, an increase in ion flux will result in a higher damage level [25]. Another effect from ions is that the impurities induced by ion irradiation, such as the interstitials or substitutions may affect the stability of target materials, which accelerates the damage accumulation, such as the cations in ZrO\textsubscript{2} [26].
2.3. Materials dependence

Besides the temperature and ions mass/flux, the damage accumulation and recovery strongly depends on the nature of target materials. For example, for single crystal SiC, damage accumulation and amorphization at room and low temperature follows a direct impact plus defect stimulated behavior. The disorder level will increase with elevated dose, but the distribution or disorder profile will not experience significant variation. For SiC irradiated with medium mass or heavy ions, fully amorphous is reached at relatively low dose in dpa, i.e. 0.3~0.5 dpa at room temperature. On the other hand, for MgO, a much better radiation tolerance is found that a single crystal is survived from amorphization even with a high dose of tens of dpa. However, with an elevated dose, the damaged layer extends to deeper in depth and goes far beyond the ion range [27]. A much higher mobility of interstitials in MgO compares to SiC is indicated, and the formation and migration of dislocation loops are suggested by the experimental results. Another example is the amorphous ion track formation due to the thermal spike induced melting and fast quench which has been discussed in previous section. Moreover, even for materials with identical components but are different in microstructures, variation in the responses to ion irradiation may take place. For example, grain boundaries may server as sinks for point defects and small defect clusters, which enhances the radiation tolerance for polycrystal and nanocrystal materials [28-29]. It is also found that for a nano-engineered 3C-SiC with a high density of stacking faults, a significant enhancement of radiation resistance is achieved compares to single crystal SiC [30].

In this thesis work, the target materials studied are single crystal SiC and SrTiO$_3$. The damage accumulation and recovery due to ion irradiation are investigated. Coupled effects of the collision induced displacements, thermal/ionization
induced dynamic recovery as well as the thermal spike generated amorphous ion track are experimentally measured and analyzed.

3. A Brief Introduction to SiC and its radiation effects

Composed by two elements both have leading natural abundance, SiC is considered as an important ceramic and semiconductor material. Though there are over 200 polytypes, the basic unit of SiC is always co-ordination tetrahedron with one of the four Si-C bonds parallel to the c-axis. Figure 1-2 illustrates the structure of three major SiC polytypes, which are 4H, 6H and 3C [31-32]. For 4H and 6H polytypes, the crystal structures are hexagonal with a wider band gap ~3.2 eV and 3.0 eV respectively. For 3C SiC, the crystal structure is cubic, with a narrower band gap of 2.2 eV. For crystalline SiC, the strong IV-IV bonding promises an outstanding hardness, which is 9 in Mohs scale, high elastic modules, which is over 400 Gpa, and good fracture strength [33-34]. Besides its excellent mechanical properties, SiC shows a remarkable thermal stability at elevated temperature. It does not melt but instead the sublime temperature is over 2100 K and the decompose temperature is ~3000 K. The mechanical strength of SiC can also be maintained at high temperature, too. SiC is hard to be etched by the acids, and the oxidization rate is much lower than Si [35]. The combined mechanical strength, thermal and chemical stability makes SiC an ideal material used in a high temperature and environments which require high endurance, such as in automobile industry and astronomy. As one of the wide band gap semiconductors, the break down voltage of SiC is ~10 times higher than Si, the thermal conductivity and the working temperature are much higher [36]. With a good electron mobility, SiC is a promising candidate for the electronic device applications, especially in harsh environments such as high power, high temperature, high frequency etc [37-40]. The primary challenge for SiC as an
electronics material is the growth of high purity, defect free, large size SiC wafer. The difficulties are mainly attributed to an absence of liquid state. By a vacuum sublimation method [41-42], 6H and 4H SiC wafer can now be supplied commercially, however the defect density is still relatively high and the size of wafer is limited.

3C SiC also severs as an important nuclear material. Besides its good thermal conductivity and chemical stability which are crucial for materials working in the fission and fusion reactors, the relatively small neutron displacement cross-section [43], and a low critical temperature for amorphization makes SiC an ideal coating material to provide structural strength and dimensional stability. For example, in gas reactor, SiC is one of the coating layers in the TRISO (tristructural-isotropic) fuel particle [44].

There have been already abundant works focus on the damage accumulation and amorphization mechanisms of SiC, by using ions with varied atomic mass, flux and at different temperatures [45-47]. The ion irradiation induced defect production and amorphization of SiC are relatively better understood. However, at the recovery stage, more comprehensive studies are required, especially the experimental efforts as described in the following:

(1) According to the thermal annealing study, it suggests that for SiC there are multi-stages in the thermally induced recovery, which may indicate different defect types, and their migration and recombination with varied activation energies.

(2) The ionization induced recovery is usually neglected in the previous studies employ the intermediate energy ions. However it has recently been revealed that
the electronic energy deposition may greatly enhance the dynamic recovery, and result in less effective damage accumulation process.

(3) In the fuel particle such as the tristructural-isotropic (TRISO) particle, a SiC coating layer is expected to withhold most of the fission products from releasing. However, the radioactive isotope $^{110m}\text{Ag}$ is determined to diffuse out of the TRISO cell. In this thesis work, the mechanism of Ag diffusion in SiC will be experimentally studied.

4. A Brief Introduction to SrTiO$_3$

Strontium titanate (SrTiO$_3$) is an oxide with perovskite structure at room temperature. SrTiO$_3$, especially its single crystal is of great interests in the microelectronics applications because of its high dielectric constant, good insulating, ferroelectricity, magnetic properties etc. [48-52]. In thin film growth, SrTiO$_3$ has been employed as an outstanding substrate for the synthesis of superconductors and semiconductors [53-55]. SrTiO$_3$ is also considered as a promising material in nuclear applications, especially, for the immobilization of high-level actinide and fission-product nuclear wastes due to its good radiation tolerance and outstanding chemical durability [56-58]. During the long-period storage of nuclear wastes, the alpha-decay will continuous generate high energy alpha particles and heavy recoils which may produce large displacement cascades in the crystal lattice. The accumulation of defects may further cause the degeneration of mechanical properties and chemical stability. Radiation damage from heavy recoils may also produce volume swellings, cracks or other effects that affect the performance of the SrTiO$_3$-based geologic repository. Therefore, in order to improve the reliability of the SrTiO$_3$ and other perovskite
structure materials for nuclear applications, it is necessary to understand their response to ion irradiations.

On the other hand, regarding to the knowledge of stopping powers, and their effects on damage production as well as dynamic recovery in solid, SrTiO$_3$ is a very interesting model material whose damage accumulation and recovery process are shown to be sensitive under ion irradiations. Experimental evidence suggests that the damage accumulation of SrTiO$_3$ is not only affected by the mass of the incident ions [59-61], but also varies with the slightly change of temperature [62-63]. Although a direct-impact / defect stimulated model is proposed to describe the damage accumulation and amorphization process of SrTiO$_3$ under heavy ion irradiation, the mechanism is still unclear, especially for medium and light ions.

In this thesis work, the coupled electronic and nuclear energy depositions and the related effects in SrTiO$_3$ are experimentally studied. Especially, the electronic energy deposition induced amorphous ion track formation is investigated in details. Ion implantations which employ intermediate energy ions and RBS channeling measurements are utilized, which are introduced in the following section.

5. Introduction of experimental methods

5.1. Introduction of the Tandem accelerator

Most of the ion implantations and ion beam analysis for this thesis works are performed in the ion beam materials laboratory (IBML) locates at University of Tennessee, Knoxville [30]. Currently, there are two sources installed on a
Tandem accelerator system. The Alphatross is a gas source for producing He or H ions. By an oscillating electric field, plasma is ignited and positive ions are generated. After a charge exchange with Rb vapor, the positive ions pick up additional electrons and turn to be negative charged. The other source using solid cathodes is the SINCS (Source of Negative Ions by Cesium Sputtering) source which produces a wide range of negative ions from C to Au through sputtering and charge exchange with Cs vapor. The negative ions produced by the sources are extracted into the accelerator tank. For the Tandem accelerator, a high electrostatic potential is built on the terminal shell in the tank, at where also locates a charge exchange chamber filled with low-pressure nitrogen gas. As illustrated in the diagram sketch in Fig. 1-3, the negative ions come out of the source are firstly accelerated by the positive potential on the terminal shell, gains energy $E_{te}$ (the terminal potential). While passing through the charge exchange chamber, the electrons of the energetic negative ions may be stripped by the $N_2$ gas to produce positive ions. The repulsive force from the positive potential on the terminal shell further accelerates the ion to higher energy. Noticing that the positive ions can be single or multiple charges, the finally energy $E_{ion}$ is:

$$E_{ion} = E_{int} + (q + 1) \cdot E_{te} \quad \text{(eq. 2-1)}$$

Where $E_{int}$ is the energy of the negative ions extracted out of the source, $q$ is the charge states of a positive ion after charge exchange with $N_2$. The maximum terminal voltage is $\sim 3.2$ MV for Tandem system in the University of Tennessee, Knoxville. In case of using ion with high charge states, ions with an energy of 20 MeV or higher can be produced with a reasonable particle flux ($\sim 10^{10}$ to $10^{12}$ cm$^{-2}$ s$^{-1}$) to meet the routine needs of ion modification and ion beam analysis such as RBS and ERDA measurements.
5.2. Ion implantation

As discussed in the introduction section, ion implantation technique is very fundamental in material modification, for example, doping for the semiconductors. Also, ion implantation is routinely employed in the researches of radiation effects for nuclear materials. Due to its importance, achieving well-controlled ion implantation becomes one of the requirements for the accelerator facilities. In our Tandem accelerator system, by using the magnetic lens and quadrupole lens, ion beam can be well focused and defocused to create a designated beam spot. The ion/isotope species and charge states are selected by adjustable magnetic fields in order to obtain a monochromic beam at the end-stations. The energy of ions which has been produced in IBML ranges from 700 keV to 27 MeV, and the ion mass is from 1 (H) to 197 (Au) amu.

For a successful ion irradiation to reach desirable dose, a reliable control of the experimental conditions is essential. Firstly, the beam flux needs to be well determined and kept constant during an irradiation. In IBML, UT, the particle flux is calculated based on the ion beam current in a 3×3 mm² beam spot that:

\[ Flux = \frac{I}{\text{area} \cdot q \cdot e} \]

Where \( I \) is the beam current measured by a high sensitive current meter, \( q \) is the charge state of the ions and \( e \) is the charge of single electron (1.602 × 10^{-19} Coulomb). The beam spot size is regulated by two sets of slits locates before the target chamber, as illustrated in Fig. 1-4 (a). The slits offset, and the Faraday cup reading has been well calibrated. The uniformity is ensured by using a couple of raster scanners that are located between the slits and the switching magnet. An ion beam is rastered on both vertical and horizontal directions, the original Gaussian distribution of beam intensity becomes uniform in a designated beam area for ion irradiation, as shown in Fig. 1-4 (b). Moreover, regarding to the
concerns of flux and rastering effects [64], the beam flux (particle flux) are carefully maintained in a serials of experiments. For samples requires exactly an identical condition, such as SrTiO$_3$ whose damage accumulation is very sensitive to ion flux and slight changes in temperature, the beam current before rastering is kept identical as well. Repeatable damage accumulations have been achieved.

For the studies towards revealing the mechanisms in the ion-solid interaction, and for simulating the working conditions of nuclear materials, high and low temperature irradiations are intensively employed. At endstations, a liquid nitrogen cooling system is installed in order to create a low temperature down to ~100 K. High-temperature ion irradiations are assisted by both the filament and electron bombardment heating to reach 1000 K or higher with an ability of temperature control ~1 K. A fast heating and quench can be performed, which will be demonstrated in study of thermally induced recovery for SiC in section IV. Notice that during ion irradiations, the ion beam will deposit energy that lead to an increase of temperature of the sample. An intense ion beam, such as 10 MeV Au$^{3+}$ with a particle flux of $5\times10^{12}$ cm$^{-2}$ s$^{-1}$ may induce an additional increase of temperature to more than 100 K at 400 K, therefore the ion beam induced heating should be considered and temperature compensation by cooling may be needed. For the damage accumulation studies in this thesis works, the ion flux is carefully controlled and the temperature increase is <20 K for ion implantations and RBS measurements to minimize the uncertainty induced by the beam heating.
Rutherford backscattering spectrometry (RBS) measurement bases on the elastic collision between the incident projectile \((M_1)\) and the target nucleus \((M_2)\). In case that \(m_1<<m_2\), the energy of backscattered projectile \((E_i)\) follows:

\[
E_i = E_0 \frac{M_1^2}{(M_1 + M_2)^2} \left( \cos \theta + \left[ \left( \frac{M_2}{M_1} \right)^2 - \sin^2 \theta \right]^{1/2} \right)^2 = kE_0 \quad \text{(eq. 1-3) [65]}
\]

Where \(\theta\) is the scattering angle. If the light incident projectile is backscattered, for certain geometry of detection, such the example shown in Fig. 1-5, a silicon detector is located at an angle \(\beta\) relative to the surface normal direction. By collecting the secondary electrons that are generated in the detector, energy of a backscattered ion can be determined. Employing a multi-channel analyzer, the counts (events) is plotted as the function of energy (channel number). If the solid angle of a silicon detector is small enough compares to the distance from the target, according to eq. 2-2 the energy transfer, or \(k\) factor only depends on \(m_2\) for a fixed detector and the projectile with identical atomic mass \((m_1)\). As the result, if the projectiles are incident at off-crystal channel directions (random geometry), in a RBS spectrum, each edge corresponds to certain elements (or isotopes) with varied atomic mass. The mass resolution of RBS is better for light elements than the heavy elements, because the slope of \(k\) factor decreases with the elevated target atomic mass \(M_2\), as plotted in Fig. 1-6.

RBS also provides reasonable depth resolution. The mechanism is shown in Fig. 1-7 that for a projectile \(A\) that is backscattered at the top surface, the energy follows eq. 2-2 to be \(kE_0\). On the other hand, for another projectile \(C\), while penetrating into the bulk it will continually loss energy due to electronic and nuclear stopping powers. As the result the energy of the backscattered projectile
becomes \( k(E_0 - \Delta E_{\text{in}}(d)) - \Delta E_{\text{out}}(d) \), where \( \Delta E(d) \) is the energy loss as the function of depth \( (d) \). If the stopping powers are well predicted or experimentally determined, then the depth at where the projectile is backscattered can be derived with a depth resolution \( \sim 10 \text{ nm} \).

In a RBS spectrum, the channel number is proportional to the energy of backscattered ions. The counts, on the other hand, are determined by the probability or how often the incident projectiles are backscattered to a given angle. The probability is then described by the Rutherford backscattering cross-section \( d\sigma/d\Omega \), which follows:

\[
\frac{d\sigma}{d\Omega} = \left( \frac{Z_1 Z_2 e^2}{4E} \right)^2 \frac{4}{\sin^4 \theta} \frac{1 - \left( \frac{M_1}{M_2} \sin \theta \right)^2)^{1/2} + \cos \theta}{[1 - \left( \frac{M_1}{M_2} \sin \theta \right)^2]^{1/2}}
\]

(eq. 2-3)

Where \( Z_1 \) and \( Z_2 \) are the atom number of the projectile and target atom, respectively. Unlike the mass resolution which is more favored by the light elements, the backscattering cross-section increases with the atomic number. Figure 1-8 shows a RBS spectrum predicted by the SIMNRA code [66] for a target contains Au, Fe, Si and O with equal atomic fraction (25 at.%) in log scale.

The difference in backscattering yields suggests a clear trend of an enlarged cross-section from light to heavy elements. On the other hand, if the energy of projectile increases, the average closet distance between the projectile and target nucleus will be reduced. The short range nuclear force may get involved that lead to an increase in backscattering probability, known as the non-Rutherford backscattering cross-section. For the light elements with relatively weak signal, non-Rutherford backscattering may significantly enhance the RBS yield to help obtain the elemental distribution and lattice damage information.

According to the elemental sensitivity and depth resolution of RBS, with known the backscattering cross-section, atomic percentage of elements at a certain depth can be derived from the experimentally measured backscattering yields.
Therefore RBS is a powerful tool in determining the composition of target materials, the thickness of multi-layer thin films, and the distribution of impurities etc. Another attractive feature of RBS measurement is that the Rutherford backscattering cross-section only depends on the atomic number and atomic mass. As the result, in determining the composition or distribution using RBS, no reference sample is needed as comparing to other techniques such as secondary ion mass spectrometry (SIMS). The advantages of using RBS in obtaining the elemental profile will be demonstrated in chapter III.

*RBS channeling measurement*

For a regular RBS measurement (random spectrum), a target is treated as solid material with its atoms randomly arranged. However, in a crystal the atoms are arranged in highly ordered periodical microstructure. In chance the ions are incident at certain angles, they will "see" well aligned rows of atoms, with "widely open" channels in between. If an ion travel within those crystal channels and continually experiences small angle scattering as shown in case "B" in Fig. 1-7, backscattering is unlikely to happen. As the result, the RBS yield will be sufficiently lower than the random spectrum. For high quality single crystal, the yield of channeling spectrum is less than 5% of the random yield. Rutherford backscattering spectrometry in channeling geometry (RBS/C) measurement is powerful in detecting defects and impurities in crystals [67-68]. For example, as shown in Fig 1-7, the existence of an interstitial "C" breaks the channeling that leads to an increase of backscattering yield. For the impurities, they can either occupy interstitial or substitutional sites in a crystal lattice. In the former case, it is similar to point defects and the RBS yield will increase in both channeling and random RBS spectra. For the substitutional impurities, the backscattering yield will increases more significantly at off-channel geometry. Therefore, by
employing RBS channeling measurement, the lattice site at where the impurities occupy may be detected.

There is another useful feature for the RBS/C measurement, as shown in Fig 1-7 "A". Even though the projectiles are incident at channeling directions, it is inevitable that the first several layers of target atoms scatter some projectiles and result in a surface peak in the spectrum. The atoms at the surface are usually with higher energy that easier to be notified. If the re-alignment of the surface atoms occurs, the changes in surface peak can be an important indication shown as an increasing yield from RBS/C measurement [69].

Besides the applications mentioned above, RBS and channeling measurement is routinely used to determine the thickness of films, crystal structure, and even the strain [70]. Comparing to other techniques such as electron-microscope which often requires a time consuming sample preparation, RBS is considered as an convenient, damage-free method for solid targets because normally light ions such as H, He or Li are employed. The light ions penetrate deep into the target, and bring in little displacements in the first one or two micrometers in depth, where is normally the depth of interests. However from our experience, it should be noticed that for RBS measurement, especially when using well focused H and He. For one measurement with reasonable counts, the ion fluence hits the target is in the magnitude of $10^{16}$ cm$^{-2}$. A relatively high concentration of the implanted He or H can be an issue if the sample is then heated to high temperature. Figure. 1-9 shows one SiC sample which experiences RBS measurements to a total fluence of $\sim 5 \times 10^{16}$ cm$^{-2}$ followed by a 700 K annealing in high vacuum. The implanted He migrates to form bubbles, eventually breaks the target surface. On the other hand, for one spot which experiences several RBS measurements, damage level may increase due to the stress or the displacements brought in by
the He ions. Therefore, RBS measurement can be considered as "non-destructive" only with a relatively low ion fluence.
References


Appendix

Fig. 1-1. The stopping powers of iodine ion in SiC, predicted by the SRIM [2] code. The density of SiC is 3.21 g cm\(^{-3}\). "IM-E" refers to intermediate energy range.
Fig. 1-2. The structure of 4H, 6H and 3C SiC.

Fig. 1-3. Diagrammatic sketch of the Tandem accelerator in the University of Tennessee, Knoxville.
Fig. 1-4. The diagrammatic sketch of (a) ion implantation with the 3x3 mm$^2$ size beam spot. (b) Rastered ion beam to create a uniform beam spot.

Fig. 1-5. A schematic diagram of RBS measurement configuration.
Fig. 1-6. k factor for different target atom mass. The incident ion is 2.0 MeV He, with the scattering angle of 155°.
Fig. 1-7. Schematic diagram of the incident projectiles interact with the target atoms in a RBS channeling measurement. The inset is a typical RBS/C spectrum with a surface peak.
Fig. 1-8. The backscattering spectrum predicted by SIMNRA, for a target composed by equal atomic fraction (25 at.%) Au, Fe, Si and C.

Fig. 1-9. He bubbles on the surface of SiC film due to RBS measurement and thermal annealing.
CHAPTER II.
DAMAGE PROFILES AND ION DISTRIBUTION IN PLATINUM-IRRADIATED SILICON CARBIDE
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The irradiations were performed by Dr. W.M. Zhang and Prof Y. Zhang. Data analysis and manuscript preparation was performed by H. Xue. Dr. Z. Zhu performed the secondary ion mass spectrometry measurements. The manuscript was revised by Dr. I. T. Bae, Prof. Zhang and Prof. Weber.

1. Abstract

Single crystalline 6H-SiC samples were irradiated at 150 K with 2 MeV Pt ions. The local volume swelling was determined by electron energy loss spectroscopy (EELS), and a nearly sigmoidal dependence on irradiation dose is observed. The disorder profiles and ion distribution were determined by Rutherford backscattering spectrometry (RBS), transmission electron microscopy, and secondary ion mass spectrometry. Since the volume swelling reaches 12% over the damage region at high ion fluence, the effect of lattice expansion is considered and corrected for in the analysis of RBS spectra to obtain depth profiles. Projectile and damage profiles are estimated by SRIM (Stopping and Range of Ions in Matter). When compared with the measured profiles, the SRIM code predictions of ion distribution and the damage profiles are underestimated due to significant overestimation of the electronic stopping power for the slow heavy Pt ions. By utilizing the reciprocity method, which is based on the invariance of the inelastic energy loss in ion–solid collisions against interchange of projectile and target atom, a much lower electronic stopping power is deduced. A simple approach, based on reducing the density of SiC target in SRIM
simulation, is proposed to compensate the overestimated SRIM electronic stopping power values, which results in improved agreement between predicted and measured damage profiles and ion ranges.

2. Introduction

As a promising material in both nuclear energy and high-power, high-frequency device applications, SiC has attracted much interest because of its wide band gap, high strength, excellent chemical stability, high thermal conductivity and dielectric strength, as well as good resistance to irradiation. In the semiconductor industry, ion implantation inevitably causes damage in the crystal lattice. In nuclear applications, radiation-solid interactions lead to the production and accumulation of point defects, which contribute to microstructure evolution and subsequent changes in physical and chemical properties. Therefore, it is important to understand radiation effects in SiC in order to predict and improve its performance. Efforts to understand radiation effects in SiC have been carried out using molecular dynamics (MD) methods [1-2], as well as experimental approaches employing electron, neutron, or ion irradiations [3-7]. Among various ion species, heavy ions are frequently used in studying radiation effects because they produce high displacements per atom (dpa) in relatively short time.

In this work, irradiation-induced damage profiles and the volume swelling are investigated in 6H-SiC irradiated with 2 MeV Pt ions. Three different ion fluences are chosen to obtain different levels of disorder or amorphization in the lattice. Since it has been reported that SiC may experience significant volume expansion under ion irradiation [8], local volume swelling is determined experimentally as a function of local dose (dpa). For comparison, the damage profiles are calculated by the SRIM (Stopping and Range of Ions in Matter) code [9]. Since the
electronic stopping power predictions of SRIM are based on fits to experimental data, which mainly exist for light elements, the SRIM code provides reasonable predictions for light ions. Experimental studies, however, have shown that SRIM overestimates the electronic stopping power of slow, heavy ions in targets containing light elements [10-12]. Similarly, for medium-mass ions with initial energies near 100 keV·nucleon\(^{-1}\) in Al\(_2\)O\(_3\), MgO, Si\(_3\)N\(_4\) and MgAl\(_2\)O\(_4\) [13], the experimentally measured ion ranges are up to 15% larger than the ranges predicted by SRIM. Recent studies have also shown large overestimation of the electronic stopping power by a factor of 2 for slow heavy ions (up to 50 keV·nucleon\(^{-1}\)) in targets containing light elements, such as Au with energies up to 10 MeV in SiC [10], 1.0 MeV Au in SrTiO\(_3\) [14] and 2.0 MeV Au in GaN [15]. To better estimate the electronic stopping power of heavy ions, a reciprocity method proposed by Sigmund [16] is used to determine electronic stopping powers, which takes advantage of better measured stopping power data for light ions in heavy targets. Based on the reciprocity method, we tested a simple approach by reducing the density of target in SRIM calculations to compensate for the overestimation of electronic stopping powers in order to obtain better predictions of ion ranges and damage profiles. The results from this approach are compared to experimental results in the present work.

3. Experimental Methods

Single crystalline 6H-SiC wafers used in the experiments were grown by Cree Research Inc. (Durham, NC). The Pt ion implantation was performed at 150 K using the 3 MV tandem accelerator facility in the Environmental Molecular Science Laboratory (EMSL) located at Pacific Northwest National Laboratory (PNNL) [17]. To avoid channeling implantation, the 2 MeV Pt\(^{+}\) ion beam was incident at 7 degrees off the surface normal. Samples were irradiated to ion
fluences of 0.21, 0.47 and 22 nm$^2$. To obtain the disorder profiles, Rutherford backscattering spectrometry (RBS) measurements were performed in situ at room temperature, using 2 and 3.5 MeV He$^+$ ions, with a back scattering angle of 150° between the He beam and the Si detector. Both channeling and random RBS spectra were recorded for all the irradiated samples. The Pt ion distribution in the SiC targets was determined by RBS and Time-of-Flight secondary ion mass spectrometer (ToF-SIMS), and the latter was performed on an IONTOF V system (IONTOF GmbH, Münster, Germany). A 2 keV Cs$^+$ ion beam was used as the sputtering beam in the SIMS analysis, and a 25 keV Bi$^+$ beam was employed as the analysis beam. The depth of the sputtering crater is measured by both ZYGO NewView 200 and Dektak 6M profilometers. Transmission electron microscopy (TEM) analysis was performed using a JEOL JEM 2010 electron microscope at EMSL. The samples were prepared by tripod polishing, which was followed with 2.5 to 4 MeV Ar ion thinning. Volume swelling induced by the irradiation was investigated by an electron energy loss spectroscopy (EELS), using the Gatan Image Filter 2000, on the JEOL JEM 2010. The energy resolution for the EELS measurement was 0.1 eV/channel. The local dose in dpa and the ion ranges were predicted by the SRIM2008 code.

4. Results and Discussion

4.1 Disorder profile

Disorder profiles for the Pt ion-implanted SiC was studied by both RBS and TEM characterization. The RBS spectra using 2 MeV He$^+$ and 3.5 MeV He$^+$ are shown in Figs. 2-1(a) and (b), respectively. When the ion fluence increases, the dechanneling yield increases as a result of the accumulated disorder level on the
Si and C sublattices. For the spectra obtained with 2 MeV He\(^+\), only the Si edge is significant and sharp. The C edge can also be clearly observed when using 3.5 MeV He\(^+\) as the analyzing beam, due to the enhanced elastic scattering cross-section for C atoms at higher He\(^+\) ion energies. Through an iterative process, which is described in detail elsewhere [18], the disorder profiles on the Si and C sublattices can be determined. The results are overlaid in Fig. 2-2 with the corresponding cross-sectional TEM images of the irradiated samples. For a low ion fluence (0.21 nm\(^2\)), as shown in Fig. 2-2(a), the maximum disorder level is less than 0.7, and full amorphization is not achieved. The Si disorder profile is in good agreement with the damage region shown by the TEM image. When the ion fluence is increased to 0.47 nm\(^2\), the maximum disorder level reaches 1.0, and a fully amorphized layer is formed from near the surface to the depth at \(~450\) nm, which is confirmed by the corresponding TEM result. With further increase of the ion fluence to 22 nm\(^2\), the disorder curve shows that the fully amorphized layer extends to a depth of \(~650\) nm. However, according to the TEM image, the amorphous SiC layer actually extends much deeper (\(~750\) nm) relative to the disorder profile. In the depth conversion of the RBS spectrum, a theoretical density of 3.21 g/cm\(^3\) is used, and the depth difference may be attributed to the volume swelling that is significant under high dose ion irradiation.

4.2 Pt distribution and volume swelling

The effect of the volume swelling at high ion fluence is also observed in the Pt distribution profile, which was studied by both RBS and SIMS, as shown in Fig. 2-3(a). It can be seen that the peak position of the Pt distribution profile determined by SIMS is at \(~490\) nm, which is 15% deeper than the uncorrected RBS result (\(~425\) nm) where a theoretical density of 3.21 g/cm\(^3\) is used in the depth conversion. It is worth noting that the Cs\(^+\) sputtering beam current is stable
during the ToF-SIMS measurement, therefore, the sputtering rate is considered to be a constant, $c_{\text{sput}}$. The depth at sputtering time $t_1$ is $d = d_{cr} \times t_1/t_{\text{total}}$, which linearly increases with the sputtering time, where $d_{cr}$ is the final depth of the sputtering crater. Consequently, the Pt distribution profile determined by SIMS is based on the actual depth scale with the local density change included. However, for the RBS measurement, a theoretical density of 3.21 g/cm$^3$ is used in the depth conversion without consideration for the volume expansion. It has reported that defect production and accumulation, as well as amorphization leads to volume swelling, which decreases the actual density of the SiC samples [8, 19-20]. As the result, it is possible that there is an underestimation of the depth in Pt distribution profile when the theoretical density is used in the depth conversion.

To determine the local volume swelling in the damage region, EELS measurements were performed. As described in Fig. 2-3(b), a series of spots with diameters less than 25 nm, denoted as 1 to 5, are focused on to the cross-section of the sample that has been irradiated to ion fluence of 22 nm$^{-2}$. The EELS spectra are collected and shown in Fig. 2-3(c).

Besides the zero-loss peak that is attributed to the elastic scattering of the incident electrons, the plasmon energy loss peak, $E_{p(\text{virgin})}$, in the virgin crystal is located at 21.9(6) eV. After irradiation, the plasmon energy loss peak, $E_{p}$, experiences a red shift to 20.7(5) eV in the fully amorphized layer. Since the plasmon energy is proportional to the square root of the number density of valence electrons, described by the relationship $[E_{p(\text{virgin})}/E_{p}]^2 - 1$ [21], the local volume expansion can be determined from the EELS spectra. The results are shown in Fig. 2-3(d). The maximum volume expansion is less than 4% for ion fluence of 0.21 nm$^{-2}$, and reaches 10% when ion fluence increases to 0.47 nm$^{-2}$. As shown in Fig. 2-2(c), further increase of the ion fluence to 22 nm$^{-2}$ does not change the disorder level for the fully amorphous state, but the volume
expansion continues to increase to ~12% over the entire damage region. Such significant volume swelling should be taken into consideration in depth determination from the RBS spectra based on the He$^+$ ion electronic energy loss for both the damage profile and Pt ion distribution. The result derived from the RBS spectra with the correction of volume swelling is included in Fig. 2-3(a), and the peak position shifts to 480 nm, in agreement with the SIMS result, within 5% uncertainty.

4.3 SRIM prediction and local dose (dpa) profile measurements

In order to study the irradiation damage profile, as well as the critical dose for amorphization, SRIM simulations are performed. Displacement energies of 35 eV for Si and 20 eV for C atoms [22] and a density of 3.21 g/cm$^3$ are used. For the high ion fluence (22 nm$^{-2}$) sample, the depth determined from the RBS measurement is corrected according to a volume swelling of 12%, and a reduced density of 2.87 g/cm$^3$ (3.21 g·cm$^{-3}$/112%) is used in the SRIM prediction, which accounts for the reciprocity correction in the electronic stopping power. The predicted Pt distribution and damage (dpa) profiles are shown in Fig. 2-4(a) and (b), respectively. It can be seen in Fig. 2-4(a) that, even when a decrease in the density of SiC is considered, the SRIM-predicted Pt distribution profile is still much shallower (~25%) than the SIMS result. For the low ion fluence (0.21 nm$^{-2}$) sample in Fig. 2-4(b), where the volume swelling is negligible, the SRIM-predicted dpa profile based on the theoretical density also shows a large deviation, as compared with the Si and C disorder profiles determined by the RBS spectra.

Differences between SRIM predictions and experimental results are observed for a series of slow, heavy ions, such as Au, Pb, Cs, Xe etc. [12, 23-24] and also for
other target materials, such as SrTiO$_3$, GaN, and AlN [25-28]. It is believed that SRIM significantly overestimates the electronic stopping power of slow (<25 keV/nucleon) heavy ions. On the other hand, for light ions, the predicted electronic stopping power is within 10% deviation from the experimental data [26, 29-32]. Since it is still a challenge to perform accurate stopping measurement for heavy ions, Sigmund [16, 33] suggests a reciprocity method to estimate electronic stopping cross-sections for heavy ions that are implanted into targets composed by the light elements; these reciprocity stopping cross-sections are constructed using the electronic stopping cross-sections of the light target ions in heavy elemental targets. The reciprocity approach is based on the invariance of the inelastic excitation in ion-atom collisions against interchange of projectile and target. For Pt ion implantation into SiC target, the electronic stopping cross-section, $S_{e_{Pt\,in\,SiC}}$, of the Pt ion can be calculated using the reciprocity approach as follows:

$$S_{e_{Pt\,in\,SiC}}(E) = \frac{1}{2}S_{e_{Si\,in\,Pt}}(E) + \frac{1}{2}S_{e_{C\,in\,Pt}}(E)$$

The unit of $S_e$ is eV/(10$^{15}$ at.cm$^{-2}$), and the unit of $E$ is eV/nucleon in the equation. $S_{e_{Si\,in\,Pt}}$ and $S_{e_{C\,in\,Pt}}$ are calculated by the SRIM code. The total reciprocity stopping cross-section is the sum of the reciprocity-determined electronic and SRIM-predicted nuclear stopping cross-section. After transferring the unit of stopping cross-section to stopping power in eV/A, and the ion energy to MeV, the total stopping power predicted by SRIM (dotted line) and reciprocity (solid line) are shown in Fig. 5(a). For an ion energy of 2 MeV, the difference in total stopping powers predicted by SRIM and by the reciprocity approach is ~34%. The significant overestimation of the stopping power in the SRIM code will result in a shorter ion range and a shallower damage (dpa) profile, as shown in Fig. 2-4. While the improvement based on the reciprocity approach in predicting ion range is well recognized [10, 15], experimental validation is needed. A recent report has shown that the overestimation in the SRIM database already exists for
Si ions in SiC in the low-velocity range [32], demonstrating the importance for accurate electronic stopping power data.

SRIM is a widely used code for prediction of stopping power, ion range and local damage profiles in ion implantation and irradiation damage research. For current application using heavy ions, one approach of reducing the density of SiC target in the SRIM code to adjust the total stopping power has been tested. For Pt ion implantation into SiC, if the target density is reduced by 25% (75% of the original density), the total stopping power (dash line) predicted by SRIM agrees well with the reciprocity results in the ion energy range from 1 to 4 MeV, as shown in Fig. 2-5(a). A detailed calculation with full damage cascades is performed using the reduced SiC target density (75% of theoretical density). Both the Pt distribution and dpa profiles based on the reduced density are determined and compared with experimental results in Fig. 5. As the density of the target decreases, the predicted Pt distribution profile shifts to greater depths and becomes broader. When the density is reduced to 75%, as discussed above, the total stopping power determined by the SRIM code agrees well with the reciprocity approach, and the SRIM-predicted profile based on the reduced target density is within 5% of that determined by SIMS and RBS measurements, as illustrated in Fig. 2-5(b). The dpa profiles follow the same trend. While the density is reduced to 75%, the predicted dpa profile is consistent with the disorder profiles under low ion fluence (Fig. 2-5(c)). The conversion factor from ion fluence (ion nm$^{-2}$) to local dose (dpa) is 0.417. When the ion fluence increases to 0.47 nm$^{-2}$, a relatively thick (~450 nm) fully amorphized layer is formed, and the irradiation dose is 0.195 dpa at the damage peak. To further test this simple approach for correcting SRIM calculations, based on reduced density to compensate for the overestimation of SRIM electronic stopping powers, MD simulations of 700 eV and 1 MeV Au ion implantation into SiC were performed using the electronic stopping powers calculated by the reciprocity method, as well as the reduced-density SRIM
predictions. The predicted Au ion distribution profiles from both methods agree well with each other, and also in agreement with the experimental SIMS results. This work is described in detail elsewhere [33]. The above discussion indicates that the SRIM predictions based on a reduced density is a simple and effective way to compensate the overestimation of the electronic stopping power in the SRIM code and give a better ion range prediction. One should note, however, that the reduced density used in the SRIM program has no physical basis.

By using the dpa profile predicted with the reduced target density, the relationship between the local irradiation dose (dpa) and volume swelling can be determined, which is shown in Fig.2-6. For low and medium ion dose, the volume swelling shows a sigmoidal dependence on dose. This indicates that the volume expansion caused by irradiation is closely related to the damage in the lattice, especially, to the production and accumulation of the point defects, which result from the displacement of the lattice atoms. For medium and high ion fluence irradiations, the SiC layer has been fully amorphized. However, the volume swelling keeps increasing with further irradiation, as shown in Fig. 6, and finally reaches 12% at high dose. According to our previous study, increases in volume swelling after amorphization may be attributed to an increase of defect states and short-range chemical disorder in the amorphous layer [34]. Compared to results in the literature where an average volume swelling over the damaged region is used in correcting depth profiles [8, 35-36], there is an advantage in using local EELS measurements. Since the local volume swelling can be determined from EELS, more accurate corrections in depth scale can be made by integrating the local volume expansions over depth. This will allow for more accurate interpretation of RBS data, and the comparison and interpretation of results obtained using different techniques, such as RBS, SIMS and TEM.
5. Conclusion

Ion implantation with Pt ions was performed in 6H-SiC to study the disorder profiles and Pt ion distributions. Significant volume swelling occurs under high ion fluence irradiation, which is responsible for the deviation between the Pt ion profiles determined by RBS and SIMS. The volume swelling exhibits a sigmoidal dependence on irradiation dose. It is found that SRIM significantly overestimates the electronic stopping power, which leads to relatively shallow dpa profiles and ion ranges compared to the experimental results. A reciprocity approach is applied to estimate the stopping power, and an approach of reducing the target density in SRIM simulation to compensate for the overestimated electronic stopping power is tested. The SRIM predicted Pt distribution, as well as dpa profiles, agree well with the experimental results when the density is reduced by 25%.

6. Acknowledgements

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References

Appendix

Fig. 2-1. RBS spectra obtained using (a) 2 MeV He$^+$ ions; (b) 3.5 MeV He$^+$ ions.
Fig. 2-2. The Si disorder profiles overlaid on the cross-sectional TEM images of the irradiated samples at ion fluences of (a) 0.21 nm$^{-2}$ (low), (b) 0.47 nm$^{-2}$ (medium), and (c) 22 nm$^{-2}$ (high).
Fig. 2-3. (a) The Pt ion distribution determined from the SIMS and RBS spectra with/without the volume swelling correction. (b) A cross-sectional TEM image of SiC indicating the spots showing where the EELS spectra were taken. (c) The EELS spectra from the sample with ion fluence of 22 nm$^2$. (d) The volume expansion as a function of depth.
Fig. 2-4. Comparisons of (a) the SRIM-predicted Pt distribution with the SIMS result of the high-fluence sample (22 nm$^{-2}$), and (b) the SRIM-predicted dpa profile with the disorder profiles of both Si and C sublattices measured from RBS for the low-fluence sample (0.21 nm$^{-2}$). The SRIM predictions are shallower than the experimental profiles.
Fig. 2-5. (a) The total stopping power predicted by SRIM (dash) and derived by the reciprocity method (solid). (b) Pt distribution profile of the high-fluence sample (22 nm²) and (c) disorder profile of the low-fluence sample (0.21 nm²). Also included in (b) and (c) are the SRIM predictions based on reduced target density.
Fig. 2-6. The dependence of volume swelling on dose.
CHAPTER III.
AG OUT-SURFACE DIFFUSION IN CRYSTALLINE SILICON CARBIDE WITH AN EFFECTIVE SILICON DIOXIDE DIFFUSION BARRIER

The ion irradiation was performed by Y. Zhang and V. Shutthanandan. Data analysis and manuscript preparation was performed by H. Xue. H. Y. Xiao performed the Density Functional Theory simulation, while Z. Zhu did the secondary ion mass spectrometry measurement. Prof. L.L. Snead and Lynn A. Boatner provide suggestions to this work and got involved in the revision. Prof. W. J. Weber and Y. Zhang are the advisor who leaded this project.

1. Abstract

For applications of tristructural isotropic (TRISO) fuel particles in high temperature reactors, release of radioactive Ag isotope \( ^{110m}\text{Ag} \) through the SiC coating layer is a safety concern. To understand the diffusion mechanism, Ag ion implantations near the surface and in the bulk were performed by utilizing different ion energies and energy-degrader foils. High temperature annealing was carried out on the as-irradiated samples to study the possible out-surface diffusion. Before and after annealing, Rutherford backscattering spectrometry (RBS) and secondary ion mass spectrometry (SIMS) measurements were employed to obtain the elemental profiles of the implanted samples. The results suggest little migration of buried Ag in the bulk, and an out-diffusion of the implanted Ag in the near-surface region of single crystal SiC. It is also found that a SiO\(_2\) layer, which was formed during annealing, may serve as an effective barrier to reduce or prevent Ag out diffusion through the SiC coating layer.
2. Introduction

Silicon carbide (SiC) is a promising structure material under harsh environments due to its superior physical and chemical properties, including high mechanical strength, excellent chemical stability, outstanding dielectric properties, low thermal expansion, as well as its small neutron absorption cross-section [1-8]. In high-temperature nuclear reactors, SiC is employed as one of the four coating layers in the tristructural isotropic (TRISO) coated particles to provide structural strength and dimensional stability in high temperature, high radiation environments. It is also expected that the SiC layer serves as the first containment barrier to withhold the radioactive fission products, especially atoms such as Cs, Xe, and Ag, from releasing out of the fuel particles. However, it has been reported that at the operation temperature of high temperature gas-cooled reactor (HTGR), Ag atoms, include one of its isotopes ($^{110m}\text{Ag}$), release from intact TRISO particles [9-10]. The half-life of $^{110m}\text{Ag}$ is 253 days and releases a highly energetic $\gamma$ upon decay. Deposition of the released $^{110m}\text{Ag}$ may lead to serious safety issues as well as other practical operational issues within the nuclear plant.

To reduce or prevent the release of Ag from the SiC coating layer in TRISO, it is of crucial importance to develop a fundamental understanding of the diffusion mechanism. A simple Fickian diffusion model, in which the diffusion rate increases with temperature has been investigated [10-12]. However, the predicted diffusion coefficients are not in good agreement with each other, a significant difference of several magnitudes still exists. On the other hand, evidence has been proposed that the grain structure is a key issue in Ag diffusion. Petti et al. compared Ag release from TRISO particles with different SiC grain size, samples containing small equiaxed grains showing a lower diffusion rate than the ones containing larger columnar grains [13]. Khalil et al.’s ab initio
calculation suggests that the Ag diffusion coefficient is \(3.7 \times 10^{-18} \text{ m}^2/\text{s}\) in the \(\Sigma 3\) grain boundary, compared to \(3.9 \times 10^{-29} \text{ m}^2/\text{s}\) in the bulk [14]. In addition, a low energy (360 keV) Ag ion implantation experiment performed by Friedland supports a Fickian grain boundary diffusion mechanism [15]. However, it is worth noting that, in Friedland’s experimental work, the Ag distribution profile is only \(~100 \text{ nm}\) in depth. Employing the ATLAS accelerator facility, Maclean et al. performed high-energy implantation to produce Ag profiles buried deeper than 10 \(\mu\text{m}\) inside the polycrystalline SiC bulk. After 210 and 480 hours annealing, no Ag migration was observed [16]. It raises the possibility that besides the grain boundary, the out-surface diffusion also plays an important role in the release of Ag at high temperature. Friedland et al. [12] and Jiang et al. [17] have experimentally observed Ag diffusion toward the surface in both crystalline and amorphous SiC at high temperature, respectively. Recently ab initio calculations also suggest that Ag prefers to absorb at the surface, and the mobility of Ag is relatively high on the surface [18].

In the present work, Ag profiles near the surface as well as buried inside the SiC bulk are produced by varying Ag ion energy in combination with energy-degrader foils. Annealing is applied to initiate the migration of Ag atoms and simulate the operation condition of HTGR. Before and after annealing, RBS spectra were collected for each sample. Taking advantage of the elastic collisions between the incident ions and target atoms, which provide mass selectivity, RBS is a widely utilized non-destructive technique for determining target composition. Moreover, because of the electronic stopping power, the energy of the detected He ions decreases with increasing depth at which the ion is backscattered, which provides reasonable depth resolution. Through the combination of mass and depth resolution, RBS measurements provide Ag distribution profiles, and any redistribution of the Ag is easily determined from changes in the RBS elemental spectra.
3. Experimental

Single crystal 4H-SiC wafers grown by Cree, Inc. were used in this study. The Ag implantation was performed employing the 3.0 MV electrostatic tandem accelerator facility within Environmental Molecular Sciences Laboratory (EMSL) at the Pacific Northwest National Laboratory (PNNL) [19]. The Ag ion implantation was carried out at a tilt angle of 10° off the surface normal to avoid channeling effects. In order to compare the near-surface out-diffusion with the diffusion in the bulk, Ag profiles at different depths were produced by implantation utilizing varied ion energies produced by passing the incident ion beam through Al foils with different thickness. (a) The buried Ag profile was produced by 2.0 MeV Ag implantation to an ion fluence of $1.6 \times 10^{16}$ cm$^{-2}$ in a bare SiC wafer (sample 1). (b) In order to produce a shallower Ag distribution near the surface (sample 2), a nominal 1.5 µm Al foil was attached in front of the SiC wafer as the energy degrader foil. Implantation with 4.0 MeV Ag$^+$ to an ion fluence of $2.4 \times 10^{16}$ cm$^{-2}$ was carried out with the Al foil. Both implantations were performed at 650 K, which is higher than the critical temperature for amorphization of 4H-SiC (450 K) [20]. After ion implantations, the Al foil was removed; samples were annealed at 1273 K for 48 hours in an Ar atmosphere. Before annealing, the disorder profiles were determined by RBS channeling measurements along the <0001> direction using a 2.0 MeV He$^+$ beam and a backscattering angle of 150°. The Ag distribution profiles before annealing were determined from the RBS spectrum at random geometry. After annealing, both RBS and Time-of-Flight secondary ion mass spectrometer (ToF-SIMS) measurements were performed to obtain the distribution of Ag and other elements.
4. Results

Virgin and random RBS spectra of the pre-implanted SiC sample are shown in Fig. 1(a). The virgin spectrum refers to the RBS measurement along the \(<0001>\) direction for the pristine single crystal SiC before irradiation, and represents the nominally defect-free level or a level associated with the low concentration of intrinsic defects. The random spectrum, obtained by off-axis rocking of the sample, is equivalent to the backscattering spectrum for fully amorphous SiC. The ratio of the scattering yield between the virgin and random spectrum is less than 3%, which suggests the high crystalline quality of the starting crystals. Prior to the measurements of the as-implanted SiC, an energy calibration was performed using Mo, Au and intrinsic SiC samples to determine the linear relation between the channel number and the energy of the backscattered He ion. The RBS results for sample 1 (bare SiC) and sample 2 (Al foil attached SiC) before annealing are shown in Fig. 1(b) and 1(c) in solid lines. Employing the energy calibration result, each peak (or edge) is attributed to certain elements, which are Si, C and Ag respectively. The peaks corresponding to the implanted Ag are shown in details in the insets. It can be seen in sample 2 that the Ag peak shifts to higher channel numbers, indicating that the Ag distribution is relatively close to the surface. On the other hand, the Ag peak of sample 1 is located at a lower channel number and partly overlaps with the silicon edge, which indicates that a buried Ag profile is produced.

After annealing at 1273 K in an Ar atmosphere, the RBS measurements were performed on both samples under identical experimental conditions. The annealing results are shown in Fig. 1(b) for sample 1 and (c) for sample 2 as dashed lines, along with the RBS spectrum before annealing (solid lines). A new peak appears at channel number \(~340\), which is attributed to the oxygen at the surface. According to Fig. 1(c), carbon is found depleted at the surface layer after
annealing, because the carbon edge shifts to lower channel number in the RBS spectrum. The silicon edge does not shift, and the reduced RBS yield suggests that the atomic concentration of Si decreases. Regarding the appearance of the O peak after annealing, the growth of a SiO$_2$ thin layer on the surface is indicated. With regard to the Ag distribution, as shown in the inset image of Fig. 1b, after annealing there is no evidence of the migration of Ag, which is buried in the bulk (sample 1). On the contrary, a decrease in the RBS yield is observed for the Ag profile in sample 2 (Fig. 1c), which may be attributed to a decrease in the Ag concentration due to Ag release from the SiC surface. The Ag edge shifts to a lower channel number, similar to the carbon, and the implanted Ag is found depleted in the near-surface region.

From the RBS spectra, the SiO$_2$/SiC structure, as well as Ag concentration profiles can be determined by utilizing the SIMNRA code [21], and the results are shown in Fig. 2(a) and 2(b), for samples 1 and 2, respectively. The Ag concentration profiles confirm that during annealing there is no observable migration of the buried Ag, both in sample 1, and for sample 2 beyond 350 nm in depth. On the other hand, as illustrated in Fig. 2(b), in the surface region of sample 2, the concentration of Ag decreases after annealing. The reduction of Ag may be attributed to Ag out-diffusion, in which Ag first migrates towards the surface and then desorbs from the sample.

As discussed in the introduction, RBS is a commonly used, non-destructive technique to provide depth distribution profiles for elements. However, the depth resolution and elemental sensitivity of RBS is relatively poor for light elements such as O and C. While the Ag ion fluence reaches $10^{16}$ cm$^{-2}$, the scattering yield is still low because of the limited backscattering cross-section for medium mass atoms. In SIMNRA, the concentration of Ag is determined by simulating the target layer by layer with varied thickness and Ag concentration to fit the RBS
spectrum. The accuracy of the simulation is, therefore, limited by the resolution and detection efficiency of RBS. In order to better evaluate the Ag diffusion, SIMS measurements were carried out after annealing to provide elemental profiles with better depth resolution and higher sensitivity. Unlike RBS and the SIMNRA simulation, SIMS cannot determine the atomic concentration in units of atom/cm$^3$ or at. % without a reference. In order to obtain the Ag concentration profiles, two assumptions are proposed: First, there is little release of Ag in sample 1, which is supported by the RBS results. If the total amount of the implanted Ag is assumed to be a constant ($1.6 \times 10^{16}$ cm$^{-2}$), the conversion of SIMS yield (counts) to Ag concentration can be determined. The second assumption is that the sensitivity of SIMS for Ag remains constant between the measurements for sample 1 and sample 2. As a result, even though the implanted Ag may deposit in the Al foil or be released from sample 2, the Ag concentration can be estimated by comparing the SIMS yield of sample 2 to sample 1. Based on these assumptions, the Ag concentration profiles are determined and overlaid with the RBS results, as presented in Fig. 2.

5. Discussion

The SIMS-determined Ag profiles are in good agreement with the RBS results. It is confirmed that the implanted Ag diffuses towards the surface and is released out of sample 2. Inside the SiC bulk, no migration is detected for both samples. As MacLean et al. suggested, surface diffusion through a nano-crack may play a crucial role in the release of Ag from a SiC coating layer [16]. The surface diffusion mechanism has also been studied recently by ab initio calculations [18]. The calculations were carried out using Density Functional Theory (DFT) within the framework of general gradient approximation, as implemented within the Vienna Ab Initio Simulation Package (VASP) [22]. All calculations were spin-
polarized, and the exchange-correlation terms were described using the Perdew and Wang (PW91) functional [23-24]. The interaction between ions and electrons was described using the projector augmented wave method [25]. A supercell consisting of six Si layers, six C layers and a vacuum region of 16 Å was used. The dangling bonds of the bottom atoms were saturated by hydrogen atoms. Convergence with respect to a plane-wave cutoff energy of 450 eV and a Monkhorst-Pack k-point sampling of 3×3×1 were verified. The fourth surface layer was taken as the bulk-like state and Ag diffusion from the fourth surface layer to the surface state was studied. The diffusion pathway along the direction perpendicular to the surface was fixed and complete structural optimizations were then performed. The energy profiles relative to the surface state for Ag diffusion from the fourth to first slab layer are shown in Fig. 3 (original presented in ref. 18), in which the configuration at the A point represents Ag adsorption on the surface, and B, C, D and E points correspond to Ag adsorbed in the first, second, third and fourth surface layer, respectively. It turns out that Ag diffusion from the fourth layer to surface state is an exothermic process and easily takes place, i.e., Ag migration from the surface state into bulk SiC needs to overcome a huge energy barrier. The energy barrier for Ag desorbing from the surface is determined to be 0.85 eV. It is worth noting that for real materials that experience ion irradiation, defects are produced and accumulated, and the damaged crystals are at a relatively unstable state due to both damage and local ionization. Vacancies and local charge re-distribution may modify the migration barriers and provide easy paths for Ag out-diffusion to occur. Such complexity is beyond the capacity of the DFT calculation. However, the DFT result provides important indications that firstly, if redistribution of Ag occurs, the net diffusion of Ag is suggested to be from the bulk to the surface. Secondly, in a high temperature environment, the energy barrier may be overcome so that Ag desorption takes place. The loss of Ag from the SiC surface may keep the concentration gradient.
As a result, diffusion may continue and eventually create a concentration difference that can be experimentally observed.

Besides the decrease of Ag concentration at the surface region, by taking advantage of its high depth resolution, SIMS provides detailed elemental profiles for Si, C and O. From inspection of the results from sample 2, a sharp interface located at ~55 nm can be clearly observed in the Ag distribution profile, at which the Ag concentration rapidly drops to ~0. An accumulation of Ag at the deeper side of the interface indicates that the Ag diffusion towards the surface is obstructed. According to the SIMS yields, O and C profiles are plotted in Fig. 4 and overlaid with the Ag yield. In Fig. 4(a), the depletion of carbon at the surface region confirms the formation and growth of the SiO$_2$ layer during annealing. For the O concentration, three spots with different irradiation histories were measured by SIMS, including: (a) virgin SiC for which neither ion implantation nor RBS measurements have been performed, (b) sample 1 for which the implanted Ag atoms were buried inside the SiC bulk, and (c) sample 2 with Ag profile at the surface region. For all three spots, SiO$_2$ layers are formed, but with varying thickness. At spot (a), the thickness of the SiO$_2$ layer is less than 10 nm, which agrees with the study of Vickridge et al. where the oxidization rate of single crystal SiC is relatively low [26]. For sample 1 and sample 2, the incident ions, as well as the recoils, lead to displacements of the target atoms, which result in damage to the crystalline structure. At the surface, the SRIM-predicted displacement doses are 9.2 dpa (displacements per atom) and 41 dpa for sample 1, and sample 2, respectively. The displacement energies are 35 eV for Si, and 20 eV for C in the SRIM simulations [27]. While the SiC was not fully amorphized at 650 K according to the RBS channeling measurement, continuing displacement due to further irradiation will induce more damage to the crystal lattice [20, 28], which may be responsible for the increased thickness of the SiO$_2$ layer because the defects may enhance the diffusion of O. For sample 2,
the Ag and O profiles are plotted in Fig. 4(b). The interface between the SiO$_2$ layer and SiC substrate is located at 55-60 nm, and as discussed above, the Ag concentration rapidly drops to ~0 at 55 nm. These results indicate that the SiO$_2$ film may work as an effective diffusion barrier to obstruct the Ag out-diffusion. The statement is in agreement with an insignificant diffusion coefficient for Ag in SiO$_2$ reported by Nason et al. [29].

The idea of using SiO$_2$ as the barrier to withhold Ag from releasing out of the SiC coating layer is interesting because the thermal oxidation of SiC is relatively economical and easy to achieve. The growth mechanism has been intensively investigated [30-31]. In an effort of further exploring the potential of SiO$_2$ in reducing Ag release, near-surface implantation should be performed by employing a similar method, as for sample 2, where various ion fluences can be used in implantation to obtain Ag profiles from shallow to deep. Annealing at higher temperatures with longer time may be carried out to further confirm if the Ag diffusion can be stopped by the SiO$_2$ layer under extreme condition over a long time. The formed SiO$_2$ and the SiC lattice can be studied by high resolution TEM to determine the nano-scale structures as well as the concentration or distribution of the defects and cracks, and their relation to the Ag diffusion as well as the oxidization.

6. Conclusion

The release of a radioactive Ag isotope from the SiC coating layer in TRISO fuel particle can result in serious safety concerns in the operation of high temperature fission reactors. To investigate the diffusion mechanism, Ag ion implantations were performed to obtain Ag distribution profiles both buried inside the bulk and at the surface region of single crystal 4H-SiC. After implantation, high
temperature annealing was carried out. The RBS results before and after annealing suggest that a SiO₂ layer forms on the surface of SiC. While no migration is observed from the buried Ag, out-diffusion of the Ag in the surface region is evident. The Ag release out of the SiC wafer may be attributed to the relatively low adsorption energy at the surface. The out-diffusion of Ag at the surface is confirmed by the SIMS measurements. According to the SIMS results, there is no Ag concentration in the SiO₂ layer, and Ag diffusion is obstructed by the thin SiO₂ layer, which may serve as an effective barrier to prevent Ag from diffusing out of the SiC coating layer.

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References

Fig. 3-1. RBS spectra of (a) the pristine single crystal 4H-SiC wafer used in this study, and (b) sample 1 and (c) sample 2 before (solid line) and after (dash line) annealing. Edges corresponding to Ag, Si, C and O are indicated.
Fig. 3-2. Ag distribution profiles (in atomic percentage) determined from the RBS (squares for before and triangles for after annealing) and SIMS (solid line, after annealing) measurement results of (a) sample 1 and (b) sample 2.
Fig. 3-3. Adsorption energy of Ag at the surface (A), 1st to 4th layer (B-E) and at the free state (F). High energy barrier exists for Ag to diffuse into the bulk SiC, and an energy barrier of 0.85 eV is needed to overcome for the Ag at the surface to desorb from the SiC sample. The original plot was presented in ref.18.
Fig. 3-4. SIMS determined (a) O yield of the virgin spot, sample 1 and sample 2, and C yield of sample 2. (b) O and Ag yields of sample 2, the abrupt decrease of O and increase of Ag yields are detected at an interface located at 55-60 nm.
CHAPTER IV.
THERMALLY INDUCE DYNAMIC RECOVERY OF RADIATION DAMAGE IN SINGLE CRYSTAL 3C-SIC
Manuscript under preparation, this work was an invited talk for the 23th Conference on Application of Accelerators in Research and Industry, 2014.

Authors: H. Xue, M. Crespillo, Y. Zhang and W. J. Weber

The experiments were performed by H. Xue and M. Crespillo in the ion beam materials laboratory at University of Tennessee, Knoxville. The data analysis was performed by H. Xue. Prof. Y. Zhang and W. J. Weber were the advisors and leader of the project.

1. Abstract

Thermally induced dynamic recovery of radiation defects in single crystal 3C-SiC is studied. Initial damage was produced by low-energy Si irradiations, both isochronal and isothermal annealing were sequentially performed at varied temperatures from 150 K to 1000 K. By employing a short temperature interval in the isothermal annealing, detailed damage evolution as a function of temperature was obtained. At least two recovery stages were suggested between 200 K and 300 K, and above 350 K. For the isothermal annealing, it is found that the recovery rate is significant within the first one minute, and for the isolated point defects, a lower activation energy is indicated. According to the results from both isochronal and isothermal annealing, activation energies were estimated, and may be attributed to the recombination of close Frenkel pairs and migration of Si interstitials.
2. Introduction

SiC is considered as an important material for nuclear applications. In a radioactive environment, high energy neutrons and recoils will continually produce defects in the crystal lattice. The accumulation of defects may further lead to amorphization, production of dislocation loops, volume swelling etc. The performance as well as the reliability of SiC-based materials may thus be affected. On the other hand, for applications such as in the fission reactors, temperature usually rises to several hundreds K or above 1000 K. The target atoms will gain relatively high kinetic energies to be more mobile. The migration as well as recombination of radiation-induced defects may occur and compete with the damage production. To meet the urgent needs of accurate predictions and evaluations of radiation damage, ion irradiation is routinely utilized as a highly efficient, low residual radioactivity surrogate to simulate energetic neutrons and recoils. Therefore, a better understanding of the damage accumulation and thermally induced recovery under ion irradiations and thermally-induced recovery is of fundamental importance to ensure safe applications in nuclear industrial. The damage accumulation of SiC at room or low temperature, on one hand, is relatively better understood and described by a direct impact/defect-stimulated mechanism [1]. On the other hand, at elevated temperature, it is found that the damage accumulation process becomes much less effective [2-3]. For single crystal SiC the critical temperature for amorphization is ~450 K [4], above which SiC will not be fully amorphized. Those evidences indicate that the thermally-induced recovery of defects that are created by ion irradiations occurs, and is enhanced with increasing temperature.

Due to the time scale, dimension and the perturbation from the characterizations, a direct observation of defect recovery is extremely difficult, especially for the bulk materials. Moreover, the migrations and recombination of varied defect
types are coupled together, which add to the complexity of the thermally-induced recovery. Fortunately, the effects due to dynamic recovery can be relatively accurately determined utilizing in-direct characterizations, such as the measurements of damage levels before and after an annealing process. Moreover, the process for defect migration and recombination will consume certain energy to overcome the corresponding energy barriers to enable the reactions. Activation energies may be estimated according to a dynamic recovery model. By combining systematic experimental efforts with the theoretical and simulation works, activation energies may be further associated to the migration and recombination of varied defect types to reveal the corresponding recovery mechanisms. Dynamic recovery in SiC has been investigated by employing thermal annealing together using different characterization methods including deep level transient spectroscopy [5-6], photoluminescence [7], positron annihilation spectroscopy [8-9] etc. According to the literature reports, multi-stages of recovery are identified from room temperature to above 2000 K, with each stage corresponds to specific activation energy. In this project, dynamic recovery of radiation damage in single crystal 3C-SiC is studied by utilizing the Rutherford backscattering spectrometry in channeling geometry (RBS/C) measurements. RBS is considered as a non or low-damage method for determining the composition of solid materials, the elemental profile, and film thickness etc. Moreover, for a single crystal material, RBS/C measurement is powerful in detecting the point defects induced by ion irradiations [10], crystalline to amorphization phase transfer [11], strain [12] etc. In the study on recovery of irradiation induced defects, RBS/C shows its unique advantage because the measurement can be performed in-situ before and after an ion irradiation as well as after each annealing cycles. Furthermore, RBS/C measurement is able to provide detailed information towards the variation of disorder level with a reasonable depth resolution. Especially, RBS/C shows a high sensitivity on
interstitial type defects that the evolutions of defect concentration can be well tracked.

3. Experimental Methods

SiC wafers used in this serial of works are commercially available in NOVA Electronic Materials. The sample is 3.8 μm thickness, single crystal 3C-SiC (001) film deposited on a silicon substrate. Room temperature Si implantations were performed at the UT-ORNL Ion Beam Materials Laboratory (IBML) locates at the University of Tennessee, Knoxville [13]. Firstly, a sample was cooled down to low temperature ~140 K and a 900 keV Si⁺ irradiation was employed to produce an initial damaged region. High and low initial disorder fractions of ~0.53 and ~0.27 were produced by Si ion fluences of 2.7x10¹⁴ and 1.6x10¹⁴ cm⁻², respectively. After the low energy Si irradiations, RBS/C measurement using 3.5 MeV He⁺ was performed at ~140 K to determine the initial disorder fraction. Low flux of Si and He ions was ~1x10¹² cm⁻² s⁻¹ and each beam spot was relatively small to ensure that the elevation of temperature due to beam heating is <15 K. After an initial damage was created, both isochronal and isothermal annealing were performed to initiate the dynamic recovery. In an isochronal annealing, the pre-damaged SiC sample was heated to a designate temperature and kept for an identical time of 30 minutes. Multiple isochronal annealing cycles were carried out from 170 K to 1000 K, with relatively small temperature intervals of 30 to 50 K to obtain detailed damage evolution information. In the isothermal annealing, the initial damaged samples were heated to an identical temperature, but were kept for varied time length from 10s to 1 hour. Isothermal annealing was performed at temperatures of 213, 243, 273, 308, 403 and 703 K, respectively. After each annealing, the sample was quenched to at least 100 K below the annealing temperature, or to 150 K. RBS/C measurement was then carried out. All the ion
irradiations, annealing and RBS/C measurements were performed in-situ in a high vacuum chamber.

4. Results

The RBS spectra of isothermal annealing were plotted in Fig. 4-1 for samples with high and low initial damage. For seeing clearly, only parts of the spectra are plotted. A continuous decrease of the counts (RBS yield) suggests that the recovery is enhanced by the elevated annealing temperature, both for high and low initial damages. For 3.5 MeV He+, its ion range is ~10 μm, therefore the implanted He is buried inside the Si substrate which should not affect the lattice structure of SiC. However at low temperature, the background RBS yield is found increases \( i.e. \) at channels from 500-750 which indicates that some damage was induced by the He ions, especially due to the measurements at low temperature. Based on an iterative method, the disorder fractions of Si sub-lattice can be determined from the RBS/C spectra. For the damage peak, the disorder faction is shown in Fig. 4-2. A clear trend of thermally induced recovery is suggested, and the results from high and low initial damages agree well with each other.

According to the isothermal annealing results, below 200 K, little recovery is observed. The first recovery stage (region "I") is between 200 K and room temperature (RT). However, slightly above RT, the increased heating power does not further result in an observable recovery within 30 minutes. A second recovery stage is above 350 K, and there is another "step" at where the recovery rate appears decrease between 550 K and 600 K. With a further increase of temperature, the disorder fractions of the samples with high and low initial damage are getting closer, but the crystal structures have not been fully restored at 1000 K. The residual disorder at high temperature indicates that for some
defect types such as di-vacancies, defect clusters or amorphous domains etc., more kinetic energy may be required to overcome the recovery barriers, which agrees with the annealing studies at higher temperature [6, 8].

The isochronal annealing provides a detail trend of how the recovery rate varies with elevated temperature. It is worth noting that for the relatively "flat" regions in the curves, thermally-induced recovery is not absolutely "frozen" but in a much slower rate. One demonstration is performed on a 3C-SiC sample which was irradiated by 900 keV Si ions at low temperature, and annealed at RT for 30 minutes. The disorder fraction after annealing was determined to be ~0.72 at the damage peak. After a storage in high vacuum at room temperature for 1 month, the disorder fraction decreases to 0.52. The much slower but continuous recovery also indicates that a rate function may be employed to describe the thermally-induced recovery. According to the isochronal annealing results, the temperatures for isothermal annealing were determined and the experiments were carefully controlled. Because for the isothermal annealing, one sample with an initial damage will be repeating annealed and measured, but can only work for one temperature. In order to compare the results at different temperatures, it is critical to produce an identical initial damage under low temperature Si irradiations. By employing a stable Si ion beam with identical particle flux, we were able to create similar initial disorder fractions which are within 10% of variation, as demonstrated in Fig. 4-3. Furthermore, a fast heating and quench is essential to enable a short time annealing. In this work, by using a filament plus electron bombardment assistant heating, and a high flux liquid nitrogen cooling system, sharp heating and cooling was achieved for short annealing time such as 10 s.

After each isothermal annealing cycle, RBS/C measurement was performed. As the examples, the results for high initial disorder fraction (~0.53) at 308 K and
403 K are plotted in Fig. 4-4. Recovery is suggested for both temperatures. At 403 K, the decrease in disorder fraction as a function of annealing time is more significant than at 308 K which suggests a more effective thermally induced recovery. Notice that 403 K is within the second recovery stage above RT, therefore the isothermal annealing result shows a good consistence with the isochronal annealing. In order to quantitatively evaluate the role of temperature and annealing time, recovery is estimated by the decrease of disorder fraction refers to the initial damage, and the evolution of disorder fraction at varied temperatures are shown in Fig. 4-5 for (a) low initial damage and (b) high initial damage.

5. Discussion

According to the isothermal annealing results, firstly, the majority of recovery occurs within the first one minute. After 30 minutes, the recovery rate becomes much insignificant, which confirms that the time interval chosen for the isochronal annealing is reasonable. Another feature of the isothermal annealing results is that the relative recovery rate is higher for the low initial damage than the high initial damage. For example, for an initial disorder fraction ~0.53 at 243 K, the recovery is ~5% after 300 s relative to the initial damage. However for a lower initial disorder ~0.27, the disorder fraction already decreases ~15% in the first 30 s. Also for a high temperature of 703 K, for a low initial damage the recovery has almost been completed in the first 10 s. On the other hand, for a high initial damage, noticeable recovery can be observed within ~130 s. The lower recovery rate for high initial damage may be attributed to defect concentration and configuration: For the individual point defects which are diluted in the crystal lattice, the activation energy for recovery is lower than the complex defects or the defect clusters, which is suggested by the RBS/C studies performed by W. Jiang
et al [14]. For the two recovery stages indicated by the isochronal annealing, the activation energies can be estimated by employing a rate equation [15]:

\[
df/dt = F(f, q_1, q_2 \cdots q_n) \exp(-E/kT) \quad \text{(eq. 4-1)}
\]

Where \( f \) is the disorder fraction; \( t \) is the annealing time; \( q_1 \sim q_n \) are variables other than time and temperature \( (T) \), depends on the previous history of the samples. For the samples with identical history and initial damage, the activation energies can be calculated from eq. 4-1 according to the isothermal annealing results that:

\[
\ln(t_i) = \ln C + E/kT_i \quad \text{(eq. 4-2)}
\]

Where \( t_i \) is the annealing time for reaching certain disorder fraction at temperature \( T_i \). Or by employing both isochronal and isothermal annealing results, the activation energies can be calculated as:

\[
\ln(\Delta \tau_i) = \ln(\Delta \tau_j) + E/kT_a - E/kT_j \quad \text{(eq. 4-3)}
\]

Where \( \Delta \tau_i \) is the time interval in an isothermal annealing (with a temperature \( T_a \)) reaches the same amount of recovery as an isochronal annealing, which is at a temperature of \( T_j \) and annealing time \( \Delta t_j \). In the estimations of activation energies, \( \Delta \tau_i \) are chosen to be 0.03, 0.04 and 0.05 in disorder fraction. The results for the first recovery stage (200 K to RT) are shown in Fig. 4-6.

From both methods of employing (1) results of the isothermal annealing and (2) combined results of the isothermal and isochronal annealing processes, the estimations suggest an activation energy of 0.36-0.45 eV for the samples with high initial damage. For the samples with low initial damage, the activation
energy is estimated to be 0.17-0.25 eV. As discuss above, the variation may be attributed to the effect of defect concentration. The experimentally determined activation energies are in good agreement with a previous study for 6H-SiC at low temperature [16]. On the other hand, according to the molecular dynamics (MD) simulation [17], for the close-pairs of vacancies and interstitials with a distance <0.7 \( a_0 \) (lattice constant), they are not stable at room temperature and the activation energy for recombination is 0.24-0.38 eV, which are confirmed by our results.

For the second recovery stage above RT, by employing both the isothermal and isochronal annealing results, the activation energies are estimated to be 0.93 ± 0.26 eV for the high initial damage, and 1.24 ± 0.41 eV for the low initial damage. At elevated temperature, the energy barriers for recovery may become relatively insignificant, as compared to the kinetic energies of the defects, also the recovery rate is much faster compared to the experimental time scale, as seen in Fig. 4-6. For varied initial defect concentrations, the isothermal annealing and the fitting according to the rate equation may not be able to determine the slight differences. On the other hand, the disorder fraction is calculated for the Si sub-lattice. For Si interstitials, \textit{ab initio} calculations suggest a migration energy of ~0.8 eV [18-19], therefore if the migration barrier is higher than the recombination barrier [20], at high temperature region the recovery may be mainly attributed to the migration and recombination of Si interstitials.

6. Conclusion

Thermally induced recombination was investigated by annealing the pre-damaged single crystal 3C-SiC. Recovery of the radiation damage is determined
by employing the RBS/C measurements. In order to determine the activation energies, both isochronal and isothermal annealing were performed in well controlled experimental conditions. From 150 K to 1000 K, at least two recovery stages are suggested, with relatively stable temperature regions at low temperature and near RT. The activation energies are estimated to be 0.17-0.45 eV for the first stage between 200 K and RT, and ~1.0 eV for the second stage above 350 K, which are in good agreement with the literature reports for 6H-SiC and with the simulation works. It is also indicated that the defect concentration may modify the activation energy of recovery, especially at low temperature. We further attribute the activation energies to different mechanisms of recovery. At the low temperature region, the recombination of close-pair vacancies and interstitials may dominate. Above 350 K, the migration of Si interstitials may occur and recovery may take place. As for future works, the disorder fraction for the C lattice will be determined in order to study the carbon vacancies and interstitials related mechanisms.
References

Appendix

Fig. 4-1. RBS/C spectra of the isochronal annealing for sample (a) with a relatively high initial damage (~0.53) and (b) with a low initial damage (~0.27).
Fig. 4-2. The evolution of disorder fraction according to the isochronal annealing, in which at least two recovery stages, as notes in "I" and "II" are noticeable.
Fig. 4-3. Initial damage produced by 900 keV Si irradiations, for the isothermal annealing studies.
Fig. 4-4. Isothermal annealing results for temperatures of (a) 308 K and (b) 403 K.
Fig. 4-5. Evolution of the disorder fraction as the function of annealing time in isothermal annealing processes, for (a) low initial damage and (b) high initial damage.
Fig. 4-6. Estimation of the activation energies for the first recovery stage (below RT), (a) & (b): high initial damage, using isothermal results & combined isothermal and isochronal results, respectively; (c) & (d) low initial damage, using isothermal results & combined isothermal and isochronal results, respectively.
CHAPTER V.
IONIZATION INDUCED DYNAMIC RECOVERY FOR
INTERMEDIATE ENERGY SI ION IRRADIATED 3C-SILICON
CARBIDE
Manuscript under preparation.

Authors: H. Xue, P. Liu, Y. Zhang and W. J. Weber

This serial of experimental works and data analysis were designed and performed by H. Xue. P. Liu was a co-researcher in the experiments. Prof. W. J. Weber and Y. Zhang were the advisors and leaders of the project.

1. Abstract

The irradiation-induced recovery is studied by employing Si ion on single crystal 3C-SiC. The ion energies are chosen within the intermediate energy range, and the electronic stopping power is less than 4 keV nm$^{-1}$. Experimentally, the disorder fractions are determined by the RBS/C measurements, and analyzed as a function of dose. At different depths, with increasing electronic energy loss and ionization-to-displacement ratio, the damage accumulation slows down while the critical dose for amorphization increases. It is proposed that the ionization-induced recovery is responsible for the less effective damage accumulation process, and for the researches and applications which routinely employ the ions in the intermediate energy range, ionization induced recovery may need to be taken into consideration to better predict the radiation induced damage and recovery.
2. Introduction

As a promising wide-bandgap semiconductor, silicon carbide (SiC) has great potential for the high-temperature, high-power, high-frequency device applications. SiC is also an important nuclear material due to its relatively small neutron absorption cross-section and high performance at elevated temperature [1-2]. For microelectronics and nuclear applications, radiation damage is inevitable either from doping or energetic particles that are produced in nuclear reactions. The energetic ions or neutrons will cause the displacements of target atoms and production of point defects. As a sequence, continuous damage accumulation may lead to amorphization and volume swelling which eventually lead to the degradation of materials or even safety concerns. Therefore, in order to improve the performances and the reliability of SiC based materials and devices, it is of great importance to understand the mechanisms of irradiation-induced damage accumulation, especially, the coupled defect production and dynamic recovery processes.

In the past several decades, the radiation effects of SiC have been intensively studied by using ions with varied atomic mass, implantations at elevated temperature and single crystal SiC targets of different polytypes etc. [3-6]. From those efforts, the atomic-level defects production is relatively better understood based on an elastic collision model. A direct impact/defect simulated mechanism is proposed to describe the ion irradiation induced amorphization of SiC [7]. However dynamic recovery is rather complex. Firstly the driving force involves simultaneously thermal, ionization, and other factors. Secondly, ionization from electronic energy deposition is believed to stimulate the diffusion and recombination of the defects, thus enhances the dynamic recovery. However, for the ions within the intermediate energy range (0.5-50 MeV), especially for the ions with electronic stopping power less than 5 keV nm\(^{-1}\), it was less of solid
experimental evidences for the ionization induced recovery for SiC [8], compares to the oxides i.e. SiO$_2$ [9], Ca$_2$La$_8$(SiO$_4$)$_6$O$_2$ [10] and SrTiO$_3$ [11] etc. Recently, with an increased interest towards ionization related effects of SiC, a few experimental works that focus on the coupled effects of the irradiation-induced displacement and dynamic recovery have been reported: Utilizing a dual beam system, simultaneously ion irradiation on single crystal 6H-SiC using 900 keV I and 36 MeV W ions was performed by L. Thome et al. A suppression of damage accumulation due to the ionization induced recovery was observed. Y. Zhang et al. reported that after a 21 MeV Si irradiation on single crystal 4H-SiC which is pre-damaged by a 900 keV Si implantation, annealing occurred which was attributed to the ionization induced recovery [12]. By studying the irradiation-induced amorphization using electron and ions from Ne to Au, W.J. Weber and L.M. Wang et al. revealed that the critical dose for amorphization increased and the critical temperature decreased with an elevated ratio between the ionization and displacement [13]. Inspired by those studies, one of the simplest ion irradiation, which is Si implantation on single crystal 3C-SiC was studied in this work. The idea bases on the fact that for 5 MeV and 1.5 MeV Si ions, ionization and the ratio of ionization-to-displacement ($r_{i,d}$) at the near surface region are considerable higher than at the damage peak. In previous damage accumulation studies, usually the disorder fraction was analyzed as a function of dose only for the damage peak. As a result, most of the information related to the ionization was ignored due to the energy deposition profile. In the presented work, with the displacement and ionization well predicted by the SRIM code [14], experimentally the damage accumulation at different depths are obtained by the Rutherford Backscattering Spectrometry in Channeling geometry (RBS/C) measurements to evaluate the role of ionization.
3. Experimental methods

SiC samples used in this study are from NOVA Electronic Materials. The sample is 3.8 μm thickness, single crystal 3C-SiC (001) film deposited on a silicon substrate. Room temperature Si implantations were performed at UT-ORNL Ion Beam Materials Laboratory (IBML) located at the University of Tennessee, Knoxville [15] by employing a 3 MV Tandem accelerator. Two samples were irradiated with (1) 5.0 MeV Si$^{2+}$ incidents at 60° off the surface normal direction in order to produce a shallow damage profile; (2) 1.5 MeV Si$^+$ irradiated at 7° off the surface normal to avoid the channeling effect. The ion flux are 1.4×10$^{12}$ cm$^{-2}$ s$^{-1}$ and 3.8×10$^{12}$ cm$^{-2}$ s$^{-1}$ for 5 MeV and 1.5 MeV irradiations, respectively. For each sample, on a series of spots the ion fluence were chosen from 9.0×10$^{13}$ to 1.2×10$^{16}$ cm$^{-2}$ to create elevated damage levels until full amorphization was reached. In order to obtain an entire damage profile for each ion fluence, before and after an irradiation, 3.5 MeV He$^+$ RBS/C measurements were performed in-situ at room temperature. The stopping power profiles and the displacement profiles (in dpa) were predicted by the detailed calculation with full damage cascade in SRIM 2008 code. The threshold displacement energy is 35 eV for Si and 20 eV for C sub-lattice [16] in SRIM simulation.

4. Results and discussion

Fig. 5-1 shows the SRIM predicted displacement and ionization (from electronic energy deposition of ions and recoils) profiles, together with the electronic and nuclear stopping powers for (a) 5 MeV Si$^{2+}$ irradiated at 60° off the surface normal direction; (b) 1.5 MeV Si$^+$ at 7°. Noticing that for the irradiation performed at 60° relative to the sample’s surface perpendicular direction, the ionization is divide by 2 in order to compensate the geometry effect (along the surface normal
or along the irradiation direction) when compared with the electronic stopping power. For both ion energies, the displacement peak locates at ~1000 nm, and at near surface region the displacements are considerable less. In contrary, the ionization has its maximum at the surface, which is 7.0 keV nm\(^{-1}\) for 5.0 MeV and 2.2 keV nm\(^{-1}\) for 1.5 MeV Si ion. As a result, the \(r_{i-d}\) ratio will decrease substantially while the ion penetrating into the bulk. Another feature of the SRIM prediction is that the electronic energy loss of the ion contributes most to the ionization, especially at the near surface region. Meanwhile the displacement profile has its trend well fits the nuclear stopping power. It indicates that both the ionization and displacement are dominated by the energy loss from the incident ions.

For the purpose of characterizing the irradiation induced damage in single crystal materials, RBS/C measurement is routinely utilized. Besides its low/none damage production in the targets, one of the most attractive advantages of RBS/C measurement is that the entire damage profile can be well determined from the spectrum by using a reasonable combination of ion and energy. In this work, 3.5 MeV He\(^+\) was employed in order to better separate the signal from the Si and C sub-lattice. The spectra were collected on a pristine region, and on the spots irradiated with different ion fluences. The RBS/C spectra are plotted in Fig 5-2. (a) and (b), for the 5.0 MeV and 1.5 MeV Si irradiations, respectively. The ion fluences are in the unit of ion per cm\(^2\). According to the spectra, firstly, it shows good self-consistency that the counts, or backscattering yield, continually increases with the elevated ion fluence. Secondly, for the 5 MeV Si irradiation at 60°, ion fluence was chosen to be 8.0×10\(^{13}\) to 1.9×10\(^{15}\) cm\(^{-2}\). At the damage peak the backscattering yield gradually increases from close to the virgin counts to full amorphization. For the 1.5 MeV Si irradiation, relatively higher ion fluences were employed from 4.0×10\(^{14}\) to 1.2×10\(^{16}\) cm\(^{-2}\) in order to produce high defect concentration not only around the damage peak. According to Fig. 5-2 (b), it is
confirms that eventually fully amorphized layer extends to the near surface region at where the ionization and $\rho_{i-d}$ are much higher than at the damage peak. By combining the results from both irradiations, detailed damage accumulations at different depths can be derived, which offers a good case for studying ionization induced effects under ion irradiations.

From the RBS/C spectra, the disorder fractions of Si sub-lattice were determined by an iterative procedure [17] and plotted as a function of depth in Fig. 5-3 (a) and (b) for 5 MeV and 1.5 MeV Si irradiations, respectively. The disorder fraction is 0 for the pristine SiC, and reaches 1 for the fully amorphized layer. Shown from the disorder profiles, the damage level increases with increasing ion fluence, however the distribution of the defects does not shift, which suggests that the net diffusion of radiation-induced defects is negligible. In Fig. 5-3 (c), the disorder fraction at the damage peak is plotted as a function of displacement (in dpa). For the 5.0 MeV and 1.5 MeV irradiations, the results are consistent. The critical dose for full amorphization is determined to be ~0.5 dpa, which is in agreement with a previous study which employs 550 keV Si\(^+\) implantation on 4H-SiC [12]. It is also worth noting that, for 1.5 MeV Si irradiation with an ion fluence of $1.2 \times 10^{16}$ cm\(^{-2}\), the maximum atomic concentration of the implanted Si is ~0.6 at.% at 1050 nm in depth. To be consistent with the results shown in Fig. 3 (c), it is believed that such a slightly change in chemical stoichiometry does not lead to an observable effect within the resolution of the RBS/C measurement. Secondly, at the damage peak, as illustrated in Fig.1, for 5 MeV Si\(^{2+}\) which was incident at 60° off the surface perpendicular direction, the electronic stopping power is 0.59 keV nm\(^{-1}\), and for 1.5 MeV Si\(^+\) at 7°, it is 0.53 keV nm\(^{-1}\). Therefore in case any irradiation-induced recovery occurs, there should not be a significant difference at the damage peak, and the coupled displacement with recovery should result in similar damage levels for different energies, as demonstrated in Fig 5-3 (c).
As mentioned in the discussion of the SRIM predicted energy deposition profiles, at near surface region or at the intermediate depth between the sample surface and the damage peak, ionization is relatively more intense compared to the damage peak. The $S_\text{e} : S_\text{n}$ ratio increases toward the surface. In Table 1, the ionization, $S_\text{n}$, $S_\text{e}$ and their ratio at depths of 300 nm, 500 nm, 1000 nm for 5 MeV, and at 250 nm, 500 nm, 990 nm for 1.5 MeV Si irradiation were summarized. Also from the disorder profiles, the disorder fraction was plotted as a function of displacement in Fig. 5-4 at different depths. The results suggest a less effective damage accumulation at 500 nm compares to at the damage peak. Furthermore, at the near surface region, the damage accumulation becomes even slower as a function of dose. The critical dose for amorphization is determined to be $\sim$1.2 dpa at 250 nm for the 1.5 MeV Si irradiation. Noting that the SRIM predicted displacements are Frenkel pairs and replacements that are created by the ions as well as the energetic recoils in the collision events. On the other hand, for the ions in the intermediate energy range, the defects production and amorphization of SiC is well established based on the ballistic collision displacements [18-19]. Therefore in the damage accumulation studies of SiC using a single ion or isotope species, if the displacement is identical, the variation in damage accumulation should be attributed to a varied recovery rate. One example is the thermally induced recovery, which is studied by ion irradiations at elevated temperature, i.e. 1.1 MeV Al$_2$$^{2+}$ implantation at temperature from 150 K to 450 K for single crystal 4H-SiC [25]. An increase of the critical dose for amorphization is attributed to the thermally enhanced migration and recombination of point defects. Nevertheless, in the presented study, temperature may not be the primary driving force since the surface and damage peak ($\sim$1000 nm) are very close spatially. Moreover the irradiation–induced beam heating is negligible because of a relatively low flux was employed. Therefore the enhanced dynamic recovery may be ionization dominated as reported by using ion irradiations with higher energies, i.e. 21 MeV Si and 36 MeV W.
On the other hand, according to the critical dose study at elevated temperature, it suggests that the thermally induced recovery becomes prominent only when the temperature is close to the critical temperature for amorphization. Around room temperature, for irradiation using ions with medium atomic mass, i.e. Ar or Al, the damage accumulation of SiC does not shift much from the low temperature result [20-21]. Also in this study, by considering that the critical dose for amorphization at the damage peak (0.5 dpa) is sufficiently lower than at 500 nm (~0.8 dpa) or 250 nm (~1.2 dpa), if assuming the thermally induced recovery is much insignificant compares to the ionization effects, the critical dose $D$ has a general expression at room temperature ($T_{RT}$) that [10]:

$$D = D_0 / \left[1 - (\sigma_r / \sigma_d) \exp(-E_{irr} / kT_{RT})\right] \quad (\text{eq.5-1})$$

Where $\sigma_r$ is the irradiation-induced recovery cross-section, $\sigma_d$ is the damage cross-section. $D_0$ is the amorphization dose at 0 K without the flux effect. $E_{irr}$ is the activation energy for the irradiation-induced recovery. According to Eq. (1), at room temperature, the critical dose $D$ is inversely proportional to the ratio between $\sigma_r$ and $\sigma_d$. Further more if assume that $\sigma_r$ is proportional to the ionization, and $\sigma_d$ is proportional to the displacement, $D$ should be inversely proportional to the ratio between ionization and displacement ($r_{i-d}$). For the 1.5 MeV Si irradiation, the critical dose $D$ can be estimated from the disorder profiles at 250, 350, 500, 800 and 990 nm when a full amorphization was reached. In Fig. 5-5, $1/D$ is plotted as a function of $r_{i-d}$ as shown in rhombus icons. An inversely proportional trend is suggested. Moreover, according to the studies by W. J. Weber et. al.[10, 13], $E_{irr}$ is suggested to be ~0.12 eV. With assuming $D_0$~0.4 dpa, $\sigma_r: \sigma_d$ can be estimated and plotted as a function of $r_{i-d}$, too, which is shown in Fig. 5-5 in circle icons. The $\sigma_r: \sigma_d$ ratio shows a proportional trend to $r_{i-d}$, further confirms the role of ionization induced recovery. For 1.5 MeV Si ion, its electronic stopping power is only ~1.7 keV nm\(^{-1}\), therefore, the ionization induced recovery may needs to be carefully evaluated in applications which employ the intermediate energy ions,
and further efforts will be needed regarding to the ionization induced dynamic recovery.

5. Conclusion

Ion irradiations on single crystal 3C-SiC were performed using 5 MeV and 1.5 MeV Si ions, which are within the intermediate energy range. The disorder fractions were determined *in-situ* by the RBS/C measurements. By utilizing a series of ion fluences, detailed damage accumulation were obtained not only at the damage peak but also in the near surface region at where the ionization is dominating. The result suggests that the damage accumulation process becomes slower and the critical dose for amorphization increases with an increased ionization-to-displacement ratio. We believe it is an evidence for the ionization induced dynamic recovery, which may be available with a surprisingly low threshold of electronic stopping power down to \(~1.7\) eV nm\(^{-1}\) or less. Noticing that a large proportion of the ion implantations as well as the ion beam analysis are performed using the ions in the intermediate energy range, the ionization induced recovery is important for with both scientific interests and practical applications that will need to be further understood.
References

Appendix

Fig. 5-1. SRIM predicted displacement (shown in dash line), electronic stopping power (dot line), nuclear stopping power (dash-dot line) and ionization (solid line) profiles for (a) 5 MeV Si$^{2+}$ irradiation at 60° off surface normal direction and (b) 1.5 MeV Si$^+$ with an incident angle of 7°.
Fig. 5-2. RBS/C spectra measured by employing 3.5 MeV He\(^+\), for (a) 5 MeV Si\(^{2+}\) irradiation at 60° off surface normal direction and (b) 1.5 MeV Si\(^+\) irradiation at 7°. The unit of ion fluence is ion per cm\(^{-2}\).
Fig. 5-3. Disorder fractions calculated by an iterative procedure for (a) 5 MeV Si$_{2}^{+}$ irradiation at 60° off surface normal direction and (b) 1.5 MeV Si$^{+}$ irradiation at 7°. For 5 MeV irradiation, some results are not plotted in order for clarity. (c) Disorder fraction as the function of displacement at the damage peak for 5 MeV and 1.5 MeV Si irradiations.
Fig 5-4. Damage accumulation as a function of displacement, at the near surface region (250 nm or 300 nm), intermediate depth (500 nm) and damage peak for (a) 5 MeV Si$^{2+}$ irradiation at 60° off surface normal direction and (b) 1.5 MeV Si$^+$ irradiation at 7°.
Fig. 5-5. Left Y axis: the estimated ratio between the irradiation induced recovery cross-section and damage cross-section, plotted as a function of $r_{i-d}$. Right Y axis: the inverse of the critical dose for amorphization, which shows an inversely proportional dependence to $r_{i-d}$. Linear fitting is plotted in dash line.
Table 1. Summary of the ionization energy deposition, electronic stopping and nuclear stopping power of the ions, as well as the ratio between the electronic and nuclear stopping power at the near surface region, intermediate depth and the damage peak.

<table>
<thead>
<tr>
<th>Depth (nm)</th>
<th>1.5 MeV Si irradiation, 7° off</th>
<th>5.0 MeV Si irradiation, 60° off</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (nm)</td>
<td>250 nm</td>
<td>300 nm</td>
</tr>
<tr>
<td>Ionization/S_{e-ion} (keV nm^{-1})</td>
<td>1.75/1.68</td>
<td>6.34/3.13</td>
</tr>
<tr>
<td>S_{n-ion} (keV nm^{-1})</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>S_{e-ion} : S_{n-ion}</td>
<td>15.3</td>
<td>34.8</td>
</tr>
</tbody>
</table>

* For 5 MeV Si irradiation, the sample was tilted 60° off the surface normal direction, therefore the ionization is ~2 times of the electronic stopping power due to the geometry.
CHAPTER VI.
MODIFICATION OF THE SYNERGY INDUCED ION TRACKS IN SRTIO3 BY THE DEFECT CONCENTRATION AND ELECTRONIC STOPPING POWER
Manuscript under preparation.

Authors: H. Xue, P. Liu, K. Jin, W. J. Weber and Y. Zhang

This serial of experimental works and data analysis were designed and performed by H. Xue. P. Liu was a co-researcher in the experiments, and K. Jin was involved in the discussions and analysis. Prof. W. J. Weber and Y. Zhang were the advisors and leaders of the project.

1. Abstract

Synergy effect of the coupled electronic and nuclear stopping powers in single crystal SrTiO$_3$ has been investigated. It is experimentally confirmed that the nuclear stopping power induced defects will significantly reduce the threshold of electronic stopping power for the formation of amorphous ion tracks. As the result, a fast ionization-induced damage accumulation and amorphization is observed in regions with initial damage created by low-energy ion irradiations. By employing a direct impact model, the amorphous cross-sections can be estimated. The correlation of defect concentration and the electronic stopping power with the amorphous cross-section are further established. Those evidences suggest a possibility of selectively producing nanometer scale, amorphous ion tracks into a crystalline structure, with the ability of modifying the spatial topographies by utilizing simple ion irradiations in the intermediate energy range.
2. Introduction

Nowadays, ion irradiation has become an important and routinely utilized tool to modify band structure and charge density of the semiconductors. On the other hand, it is well known that for the nuclear materials, ion irradiation has been proved as a high efficiency, low cost surrogate tool to simulate defects production, volume swelling and phase transfer etc. induced by the energetic neutrons and recoils. Regarding to those applications, it is important to predict materials response to ion irradiations, and to evaluate the potential hazards for working in radioactive environments. Therefore, a comprehensive understanding of ion-solid interaction becomes an urgent need. Because of the complexity of ion-solid interaction, a well accepted approaching is to separate the energy deposition from ions into (a) nuclear stopping power ($S_n$), which is the elastic energy loss to atomic nuclei; and (b) electronic stopping power ($S_e$), which is the inelastic energy loss to target electrons. The knowledge towards $S_n$ is relatively better established by an elastic collision model. It is believed that $S_n$ is responsible for the displacements of target atoms, the production of point defects and defect clusters. The electronic stopping power, however, is relatively much less understood. Especially, at the intermediate energy region from several hundreds of keV to tens of MeV, $S_e$ and its coupling effects with $S_n$ may lead to complex phenomena, which modify the target materials in different ways. For example, for materials such as SiO$_2$ [1] CeO$_2$ and ZrO$_2$ [2], the $S_e$ produced defects are linearly additive to the damage accumulation in ion irradiations. On the other hand, migration and recombination of point defects may be enhanced by $S_e$ resulting from the ionization-induced thermal spike,. As the result, annealing of the defects and recovery of the damaged crystalline structure may occur for materials such as SiC [3-4]. Recently, a synergy effect has been found for single crystal SrTiO$_3$. Experimental evidences and simulation results suggest that the
existence of Frenkel pairs and other defects, which are induced by $S_n$, may significantly reduce the threshold of $S_e$ to form amorphous ion tracks [5]. It appears that the damage level is being boosted very efficiently during the ion irradiations, and crystalline-amorphous transformation takes place at an unexpected low dose in dpa (displacements per atom).

In the presented work, the synergy effect of SrTiO$_3$ is further investigated. The motivation, on one hand, is to improve the understanding of the coupled effects of electronic and nuclear stopping powers. A practical concern is that for the nuclear applications, i.e. SrTiO$_3$ as one of the materials for the immobilization of nuclear wasters [6-7], synergy may have significant impact on damage accumulation. As the sequences, the reliability of materials may decay and lead to the potential safety issues. On the other hand, taking advantage of the synergy effect, amorphous ion tracks with diameters of several nanometers can be selectively planted into a crystalline lattice. A certain level of control for the amorphous cross-section may be achieved. Moreover, SrTiO$_3$ is one of the important micro-electronics materials [8-10]. Especially, at its interface with other dielectric oxides and selenides such as LaAlO$_3$ [11-13] and FeSe [14], or at the interface between its crystalline and amorphous phases [15], the unique electronic and ferromagnetic properties attract intensive research interests. By taking advantage of the synergy effect, ion implantation shows its potential to serve as a fast, economical tool for creating continues, nanometer scale interface, which may be inspiring in the devices applications.

Experimentally, in this series of works, ion irradiations with different ion species and energies were performed on high quality, single crystal SrTiO$_3$. In order to understand the synergy effects between the electronic and nuclear stopping powers, samples with different irradiation histories were produced. After the irradiations, Rutherford backscattering spectrometry in channeling geometry
(RBS/C) measurements were employed to determine the damage levels with a good depth resolution. The evolution of damage level becomes an important indication of how the electronic and/or nuclear stopping power modifies microstructure of the target material.

3. Experimental methods

Single crystal SrTiO$_3$ samples used in this work are $<100>$ wafers from MTI Corp. The ion implantations and RBS/C measurements were performed at the Ion Beam Materials Laboratory (IBML) located at the University of Tennessee, Knoxville by employing a 3 MV Tandem accelerator system [16]. In order to produce initial damaged regions with a low to medium defect concentration, firstly low-energy ion irradiations employed 700 keV O or 900 keV Au were performed on a pristine SrTiO$_3$. The initial damage shows a peak distribution, with a maximum disorder fraction ranges from 0.10 to 0.72. Then relatively high energy irradiations using 21 MeV Ni, 20 and 12 MeV Ti, 21 MeV Cl and 12 MeV O ions were applied to pristine SrTiO$_3$ as well as to the regions with initial damage. Except the 700 keV O irradiation which was $60^\circ$ off the surface normal direction, other irradiations were performed at a geometry in which the incident ion beam was several degrees off the surface normal to avoid the channeling effect. The ion fluences for the high energy irradiations were from $10^{11}$ to $10^{14}$ cm$^{-2}$ in order to obtain separated to overlapped ion paths. Before and after each ion irradiation, RBS/C measurement using 3.5 MeV He$^+$ ions was performed in-situ to determine the disorder profile. All the ion irradiations and RBS/C measurements were carried out at room temperature in a high vacuum.
4. Results and discussion

For low energy ions, their $S_e$ are relatively low and far from the theoretical threshold value (~12 keV/nm) for the formation of amorphous ion tracks predicted by a two temperature model [17]. The damage production and amorphization are mainly attributed to $S_n$ induced displacements, and the kinetics is described by a direct-impact/defect-stimulated model [18]. On the other hand, the high energy ions were chosen with varied $S_e$ from 3.0 to 9.8 keV/nm that are predicted by the SRIM2008 code [19]. The dominating $S_e$ produces intensive ionization which creates a high temperature zone along the ion path, know as the thermal spike. Meanwhile, due to a negligible $S_n$, few defects are expected to be induced by the elastic collisions in the first 500 nm in depth. Therefore logically, if $S_e$ is not expected in producing point defects and amorphous domains, little damage will be brought in, which is confirmed by the RBS/C results shown as the inset of Fig. 1(a): For both 20 MeV and 12 MeV Ti irradiations on pristine SrTiO$_3$, there are only slightly increases in the backscattering yield (counts) even with a relatively high ion fluence ($8.3\times10^{13}$ cm$^{-2}$).

On the other hand, for the initial damaged regions, after high energy ion irradiations the damage levels increase significantly, and fully amorphous has been achieved at a low dose in dpa. As an example, the RBS/C spectra are shown in Fig. 6-1(a) for 20 MeV Ti irradiated SrTiO$_3$ with an initial disorder fraction ~0.14 in maximum. To clarity purpose, only parts of the curves correspond to ion fluences from $1.7\times10^{12}$ to $8.3\times10^{13}$ cm$^{-2}$ are plotted. According to the RBS/C spectra, the backscattering yield increases significantly for both Sr and Ti sub-lattices. Employing an iterative process which is described in details in our previous report [20], the disorder fraction of Sr sub-lattice can be determined. The results are plotted in Fig. 6-1(b) as the function of depth, for which “0” corresponds to the pristine single crystal, and “1” indicates a fully
amorphous phase. It is found that an increase of disorder fraction only takes place within the initial damaged region, which ends at ~250 nm in depth. In the pristine SrTiO$_3$ bulk beyond the damage profile that is created by 900 keV Au irradiation, little disorder is further induced. Fully amorphous has been reached with a Ti ion fluence of $1.7 \times 10^{13}$ cm$^{-2}$ at the damage peak. According to the SRIM prediction, the displacements induced by $S_n$ (<0.0005 dpa) of the Ti ions is negligible. Therefore, this extremely effective damage accumulation and amorphization should be attributed to the intensive energy deposition by $S_e$. The production of amorphous ion tracks is suggested, as we experimentally observed in a 21 MeV Ni irradiated SrTiO$_3$ [5].

According to the two temperature model [21], for an amorphous ion track to form in a crystalline lattice, melting followed by a fast quench is essential. During the high energy ion irradiations, the lattice vibration along the ion path is enhanced by $S_e$ via electron-electron scattering and electron-phonon interactions. Temperature therefore rises and may go above the melting point of the target material. In the heating up stage, energy deposition by the ions and thermal conductivity of the target materials play crucial roles in determining the localized temperature. For the target material, defects, especially the vacancies will scatter the phonons to reduce their mean free path. As a result, thermal conductivity may decrease with an increased defect concentration, especially for the insulators [22]. Due to the decay of thermal conductivity, heat can not be efficiently dispersed, which produces a higher temperature within the thermal spike in the pre-damaged region compared to a pristine SrTiO$_3$. Therefore, the electronic stopping power which is required for the ion tracks formation may be reduced. A MD simulation has been performed and the result suggests that for single crystal SrTiO$_3$ with a low concentration of Frenkel pair (1%), irradiation using 21 MeV Ni is sufficient to produce amorphous ion tracks [23]. The
simulation result agrees well with our experimental observation that at the surface with a low initial disorder fraction (<0.05), a fast amorphization still occurs.

By taking advantage of a peak distribution of the initial damage profile and the depth resolution of RBS/C measurements, we were able to further study the relation between the defect concentration and the ion tracks. As discussed above, for the high energy ions, S\textsubscript{n} induced displacements can be negligible. Without an effective production of defect clusters, the defect-stimulated growth of the amorphous domains is suppressed in the first 1 μm in depth. The direct production and overlapping of continues amorphous ion tracks are therefore considered as the dominating mechanisms in the damage accumulation. A direct impact model [24-25] is employed in order to estimate the amorphous cross-section ($\sigma_a$) as the function of Ti ion fluence ($\Phi$):

$$f_a = 1 - (1 - f_0) \exp(-\sigma_a \cdot \Phi)$$

(eq. 6-1)

Where $f_0$ is the initial disorder faction induced by 900 keV Au irradiation, $f_a$ is the disorder fraction after a 20 MeV Ti irradiation. One example is plotted in Fig. 6-2(a) for an initial disorder fraction of ~0.14. Noticing that if the damage level is close to fully amorphous, the relaxation of strain due to crystalline-amorphous phase transformation may get involved, also the ion track may overlap at high ion fluences, therefore the ion fluences which result in high disorder fractions (>0.4) are not employed in the fitting. By applying the direct impact model to different depths of the disorder profile, the amorphous cross-section shows a monotonically increase with the initial disorder faction, as plotted in Fig. 6-2(b). The RBS/C determined disorder fraction is proportional to the concentration of point defect, which may be the major defect type induced by S\textsubscript{n} during the low energy ion irradiations. Therefore, the results suggest that the S\textsubscript{n} induced defects may be responsible in modifying the amorphous cross-section of ion tracks.

According to the trend of the amorphous cross-section as shown in Fig. 6-2(b), a schematic drawing of the ion tracks produced by 20 MeV Ti is illustrated in Fig. 6-
3(a). It is expected that spindle-shape ion tracks are formed within the initial damaged region. Moreover, with assuming the cross-section is circular, the track diameter is of several nanometers which may be modified by the initial damage. This observation is interesting because unlike the hundreds of MeV or GeV energy ions whose production usually requires a large accelerator facility, intermediate energy ions from relatively smaller systems such as the Tandem accelerators can be employed to produce discontinues tracks. A designated energy and a stable beam flux can be designed. Therefore, initial damage can be induced with well modified distribution profiles, amorphous ion tracks may thus be further induced into crystalline materials with a certain level of control for their locations, lengths and diameters. The spatial topographies include but are not limited to the spindle-like shape. For example, by simply using the ions and energies employed in this work, 700 keV O together with 900 keV Au irradiations followed by a 20 MeV Ti irradiation may produce "dumbbell" ion tracks. An imaginary representation is illustrated in Fig. 6-3(b).

Besides the defect concentration and the sequentially decrease in thermal conductivity, according to the two temperature model, another critical factor which determines the ion track formation is the S_e of the ions. Notice that for the low energy ion irradiations, the damage accumulation shows a regular, S_n dominated behavior. No indication for the formation of ion tracks is available. A new threshold of S_e is expected below 20 MeV Ti, at which melting along the ion path occurs. S_e at different values may be used to modify the amorphous cross-section in combination with the pre-existing defects at variable concentration. As mentioned in the introduction section, electronic stopping power is one of the fundamental concepts in the ion-solid interaction. The efforts towards understanding synergy effects between S_n and S_e does not only improve the two temperature model, but may also provide important references for theoretical and modeling efforts towards a better understanding of ion-solid interaction. In the
presented work, in order to create varied $S_e$ and minimize $S_n$, ions such as 21 MeV Ni ($S_e$=9.8 keV/nm), 20 and 12 MeV Ti ($S_e$=7.1 keV/nm), 21 MeV Cl ($S_e$=7.3 keV/nm) and 12 MeV O ($S_e$=3.0 keV/nm) are employed. For all those combinations of ion species and energies, within the initial damaged regions, the formation of ion tracks are suggested by the RBS/C results. However, with similar initial disorder fractions between 0.10~0.15, the damage accumulations are observed to have different efficiency as a function of ion fluence. For example, the required ion fluence for 21 MeV Ni to reach fully amorphous is $\sim 8.0 \times 10^{12}$ cm$^{-2}$, but the critical dose increases to $2.0 \times 10^{13}$ cm$^{-3}$ for 21 MeV Cl ions.

Another evidence for the critical role of $S_e$ in determining the amorphous cross-section is shown in Fig. 6-4(a). For an identical initial damage and an ion fluence of $1.7 \times 10^{13}$ cm$^{-2}$, the disorder fractions created by the 12 MeV and 20 MeV Ti irradiations are different. For the 20 MeV result, fully amorphous was reached. However, a much lower disorder fraction was induced after under 12 MeV irradiation. Since for both 20 MeV and 12 MeV Ti, $S_n$ can be negligible as demonstrated in the inset of Fig. 1(a) for the pristine SrTiO$_3$, the difference in damage accumulations should be attributed to the difference in $S_e$.

Moreover, we compare the disorder profiles which are created by (1) 20 MeV Ti irradiation with an ion fluence of $1.7 \times 10^{13}$ cm$^{-2}$ and (2) 12 MeV Ti with an ion fluence of $8.3 \times 10^{13}$ cm$^{-2}$. it always appears that the 12 MeV ions lead to higher disorder fractions before the damage peak ($\sim 100$ nm). However at the region deeper than the damage peak, the disorder fractions are getting close or the 20 MeV curve appears higher. As shown in Fig. 6-4(b), from 50 to 150 nm in depth, the $S_e$ of 20 MeV Ti ion decreases from 8.6 to 8.5 keV/nm. Meanwhile for 12 MeV Ti ion, its $S_e$ changes with a larger slope from 7.1 to 6.9 keV/nm, which may be responsible for the evolution of the relative disorder fraction. Another
possibility is that for an initial disorder fraction $\sim 0.10$, an electronic stopping power of $\sim 7$ keV/nm is approaching to the threshold for the ion track formation. Therefore even a slight decrease in $S_e$ may lead to an observable variation.

By utilizing the direct impart model, the amorphous cross-sections induced by ions with varied $S_e$ are estimated. For an initial disorder fraction between 0.10 and 0.15, the results are plotted in Fig. 6-5. A trend that the amorphous cross-section is enlarged with the increased $S_e$ is evident. According to the current result, a linear fitting predicts an electronic stopping power of 6.8 keV/nm to be the threshold. This estimation is in good agreement with the experimental observation for the 12 MeV Ti irradiation. Below the threshold, it is believed that the temperature along the ion path is insufficient to reach the melting point of SrTiO$_3$, and ion track formation is therefore prohibited or much suppressed. An experimental verification is performed, in which a 12 MeV O ($S_e=3.0$ keV/nm) irradiation was applied on a pre-damaged SrTiO$_3$ sample with an initial disorder fraction $\sim 0.72$ at the peak. According to the disorder profile as shown in Fig. 6-6, with an elevated O ion fluence, the disorder fraction is monotonically decreasing, which is similar to the ionization induced recovery found in SiC [4]. The result confirms that the ionization from the ions can modify the target materials by either promoting the dynamic recovery, or by inducing the amorphous domains such as ion tracks. Also, the modification may be controllable by carefully choosing electronic stopping power with an appropriate initial defect concentration.
5. Conclusion

Synergy effect of the coupled electronic and nuclear stopping powers in single crystal SrTiO$_3$ is studied. With a low to medium initial defect concentration, a much lower threshold of S$_e$ for the formation of amorphous ion tracks is suggested based on the results from the RBS/C measurements. The amorphous cross-sections of the ion tracks are estimated by utilizing a direct impact model. A proportional relation between the amorphous cross-section and the initial disorder fraction is indicated. Moreover, by employing varied combinations of ion mass and energies, the role of S$_e$ in determining the formation of ion tracks is evident. The amorphous cross-section is found to be increased with higher S$_e$, and for a certain initial disorder fraction, our prediction for the threshold value of S$_e$ is in good agreement with the experimental observations. Furthermore, the lengths and the amorphous cross-sections of the ion tracks may be modified to induce amorphous structures with designated topographies and to create continues nanometer scale crystalline-amorphous interface for application requirements. In the future works, the mechanism of the ion track formation will be further investigated. We are looking forward to revealing the roles of different defect types, i.e. point defects, defect clusters etc. in the synergy effect. More detailed relations between the amorphous cross-section and the defect concentrations & S$_e$ are expected to be established quantitatively.
References

Appendix

Fig. 6-1. (a) The RBS spectra of 20 MeV Ti irradiated single crystal SrTiO$_3$ with the initial damage created by a 900 keV Au irradiation. The inset are the RBS spectra for 12 and 20 MeV Ti irradiations on pristine SrTiO$_3$, with an ion fluence of $8.3 \times 10^{13}$ cm$^{-2}$. (b) The disorder fraction profiles determined from the RBS/C spectra.
Fig. 6-2. (a) One example of the fitting according to the direct impact model, in order to determine the amorphous cross-section for the 20 MeV Ti irradiated SrTiO$_3$ with an initial disorder fraction $\sim$0.14. (b) The amorphous cross-section as a function of initial disorder fraction, for different depths before and after the damage peak which is located at $\sim$100 nm.
Fig. 6-3. (a) Schematic drawing of the spindle-like amorphous ion tracks which are produced by 20 MeV Ti irradiation in the pre-damaged SrTiO$_3$. (b) Imaginary representation for the initial disorder profile produced by a 900 keV Au irradiation (white curve), 60 degree off the surface normal direction together with a 700 keV O irradiation (red curve), 7 degree off the surface normal direction. Then a 20 MeV Ti irradiation is applied to create the dumbbell-shape ion tracks.
Fig. 6-4. (a) The disorder profiles determined from the RBS/C spectra, for 12 MeV Ti irradiations with ion fluences of $1.7 \times 10^{13}$ cm$^{-2}$ (squares) and $8.3 \times 10^{13}$ cm$^{-2}$ (circles), compared with the result of 20 MeV Ti irradiation to an ion fluence of $1.7 \times 10^{13}$ cm$^{-2}$ (triangles). (b) The electronic stopping powers of 20 MeV and 12 MeV Ti ions in the pre-damaged region.
Fig. 6-5. The amorphous cross-sections of the ion tracks as the function of $S_e$, for 21 MeV Ni, 20 and 12 MeV Ti and 21 MeV Cl ion irradiations on SrTiO$_3$ with an initial disorder fraction between 0.10 and 0.15. A linear fitting is applied.
Fig. 6-6. The disorder profile of 12 MeV O ion irradiated SrTiO$_3$ sample with an initial disorder fraction of \(~0.72\).
CHAPTER VII.
CONCLUSION

Ion irradiation induced damage and dynamic recovery in crystalline SiC and SrTiO$_3$ are studied experimentally, both crystals are important microelectronics and nuclear materials. Practical issues relates to the applications of SiC based materials, including stopping powers prediction and release of radioactive fission products, were studied. Based on Pt ion implantation and SIMS measurements, we were able to obtain the distribution profile of Pt and compared it with the SRIM code prediction. An overestimation of electronic stopping power in SRIM is suggested for heavy ions in light targets. Regarding the Ag release from a SiC coating layer in fuel particles, an out-surface diffusion mechanism is suggested based on the experimental evidences. We further proposed a potential solution that a thermally grown SiO$_2$ thin film may sever as a diffusion barrier.

While ion-induced radiation damage in SiC are relatively more predictable and repeatable, which has been demonstrated in the damage accumulation studies using ion with varied energies and flux, surprises, excitedments and even confusions are still exist. New knowledge is obtained as shown in the very recent works on ionization-induced dynamic recovery in single crystal SiC. In this thesis work, a thermally induced recovery of the radiation damage in 3C-SiC was firstly investigated in details. By employing both the isothermal and isochronal annealing methods, activation energies were determined and attributed to the migration and recombination of varied defect types. The thermally induced recovery is a good start point for a systematic study of the ionization induced recovery, where we show that ionization-induced thermal spike may play a crucial role in the recovery of radiation damages. In this thesis work, simple damage accumulations were employed. We were focusing not only on the evolution of disorder level at the damage peak, but also at the regions with varied
ionization-to-displacement ratios. The results are inspiring that even a relatively low electronic stopping power of $<2$ keV/nm may modify the damage accumulation due to the ionization-induced recovery, which may needs to be carefully considered in the applications such as ion implantation and ion beam analysis.

Besides the ion species and energies, another critical factor in ion-solid interaction is the nature of a target material itself. Unlike SiC for which ionization only enhances the recovery, a synergy effect which boosts the damage production and amorphization is suggested for SrTiO$_3$. Defects were initially produced by the nuclear stopping power induced displacements, intense electronic stopping power was then deposited using relatively high energy ions. The RBS/C measurements suggest that amorphous ion tracks were produced at an electronic stopping power below the threshold of track formation in a pristine crystal, and crystalline to amorphous phase transformation occurs much more effectively than the contributions by the separated electronic and nuclear stopping powers. The roles of the defect concentration and electronic stopping power in the synergy effect were evident, and potential applications in nano-scale materials modification were discussed briefly.
VITA

Haizhou Xue was born in Anhui province in China. He is the only son in his family with parents are both doctors in hospital. In 2002, He graduated from the NO.1 High School of Hefei, and attended to the Sun Yat-sen University which is located at Guangzhou. While enjoy the famous Guangdong foods and his college life, he started to build his background in mathematic and physics. Haizhou received his bachelor degree in the Department of Physics in 2006, then he joined Prof. Xiaoping Wang’s group in Hefei National Laboratory of Physical Sciences at the Micro-scale in the University of Science and Technology of China. In pursuing his master degree of condensed matter physics, Haizhou focused on the optical properties of advance semiconductors. He did a serial of studies on ZnO nanowires by using the cathodoluminescence characterization. Since 2010, Haizhou started his Ph.D. studies in the Department of Materials Science and Engineering in the University of Tennessee, Knoxville. Supervised by Prof. Yanwen Zhang and Prof. William J. Weber, Haizhou’s projects mainly focus on the ion irradiation induced damage and dynamic recovery in silicon carbide and strontium titanate. During his Ph.D studies, Haizhou published more than 10 first author or co-author papers. He is also one of the main operators for the Tandem accelerator system in the ion beam materials laboratory in the University of Tennessee, Knoxville.