

The Response of Ti_3SiC_2 MAX Phase to Ion Energy Dissipation During Energetic Irradiations at Different Temperatures

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Degree

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Dedicated to my mom, Sharon, and my dad, David, for their unending love, support, and encouragement and for by their example, giving me a desire to explore deeper and to learn more. Thank you, it means more than I can completely express.
...and dedicated to my fluffy cat, Mister Worf, too...

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Abstract

The energy dissipation pathways of electronic and nuclear energy loss (S_e and S_n , respectively) during ion irradiations are investigated to evaluate their influence on the damage evolution in Ti_3SiC_2 [titanium silicon carbide] MAX phase. Interest in the unusual properties of $\text{M}_{n+1}\text{AX}_n$ [MAX] phase ceramics for high radiation environments has led to numerous neutron and ion irradiation studies; however, an understanding of the response to energy deposition from high-energy ions is necessary for a comparison between the two irradiation environments. Two novel experiments were developed to compare variation in energy dissipation at constant damage dose: 1) a series of high energy self-ion irradiations at room temperature, 500°C [degrees Celsius] and 880°C , and 2) a sequential irradiation study. Grazing incidence x-ray diffraction and transmission electron microscopy were utilized to characterize structural variation as a function of depth, and integral to this evaluation was the novel adaptation of a method to measure fine changes in lattice strain in hexagonal polycrystals. The results reveal a threshold in S_e , above which the inelastic energy dissipation is a major contributor to the damage evolution in the system, exhibited by increased lattice strain and the formation of a FCC [face centered cubic] phase. High temperature *in situ* irradiation conditions appear to mitigate resulting damage effects, leading to more uniform lattice strain and significant reduction in FCC phase formation. Further, separating the energy loss pathways, the S_n elastic collision cascades are demonstrated to produce Ti and Si anti-site point defects and eventually a structural shift to the FCC phase embedded in the hexagonal structure. While S_e above the threshold adds heat and additional point defects, through a thermal spike and its subsequent shockwaves, there is competition between the dissipation pathways, defined by their ratio. When S_e/S_n is low, the formation of the FCC-type phase is enhanced by the additional defects and energy in the system, but as

S_e/S_n increases, in-cascade annealing by the thermal spike, while insufficient to anneal pre-existing point defects, suppresses the formation of the FCC phase, thus drastically increasing the relative lattice strain in the hexagonal structure and eventually saturating it.

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Chapter 1

Introduction

Nuclear power represents the largest contributor to clean energy worldwide [1], and has been demonstrated over the last 40 years to be a stable baseload source for electrical power [2]. As of 2017 there were 448 reactors in operation worldwide with a net capacity of $392\text{ GW}(e)\cdot\text{hrs}$, supplying over $2.5\text{ PW}(e)\cdot\text{hr}$ of electricity. The U.S. is the largest producer, with 99 nuclear reactors accounting for 20.0% of the electricity supplied [3].

Nuclear energy is considered a clean source of power, with little in the way of gaseous emission wastes associated with climate change, and as such, it is an important resource for the future worldwide energy portfolio [2]. However, the current worldwide fleet of operational reactors is aging; the average age of a reactor is well over 30 years, and the rate of new reactor construction is shrinking [3]. Many of these reactors were designed in the 1960s, the so called Generation II light water reactors (LWRs), including boiling water reactors (BWRs) and pressurized water reactors (PWRs), and began operation in the 1970-90s time frame. Advances in safety and efficiency in the 1990s were incorporated in reactors classified as Generation III reactors, and further advances such as passive heat removal systems were incorporated into current Generation III+ LWRs [4].

While there were advances in safety and economics, the principle of LWR operation hasn't changed as the power density of the core is utilized to generate steam, either through single or multiple loops, which then generates electricity through powering turbines. In the U.S., the license lifetime for reactors is 40 years, with the opportunity to renew for a maximum additional 20 years. Ultimately the lifetime of these reactors is dictated by the continued

safe performance of the materials necessary for their operation: core materials, concrete structures, buried piping, etc [2].

Nuclear reactor cores are attractive from a power density, and self-sustaining reaction perspective, but this results in a very harsh environment for structural materials. The typical ^{235}U fission core has a power density of $\sim 50\text{-}70 \text{ MW}(e) \cdot \text{hrs } m^{-3}$, almost 2 orders of magnitude greater than traditional large scale boiler furnaces [2]. Additionally, higher energy neutrons sustain the fission reaction, yet, along with high-energy gamma radiation, damage and degrade materials by 5 main degradation mechanisms. Neutrons transfer energy through ballistic collisions with other atomic nuclei and can transfer sufficient energy to displace atoms from their lattice sites. This damage is typically quantified by the international standardized dose measurement of the average number of times each atom was displaced, or the displacements per atom (dpa) as developed by Norgett, Robinson, and Torrens (NRT) [2, 5]. It should be noted that while this dose unit of measure is universally used in the field, it does not account for recombination of Frenkel, or interstitial and accompanying vacancy, pairs either through the spontaneous recombination of a pair or saturation of point defects within the recombination radii of vacancies.

There are 5 main degradation mechanisms often observed following neutron irradiation. The increase in Frenkel pairs, subsequent dislocation loops, void and fission gas bubble formation, and interstitial grain segregation all serve to impede dislocation motion, embrittle the material and reduce its toughness. Further, ballistic mixing and irradiation assisted diffusion can result in phase instability, segregation of solutes, and precipitation of or decomposition into secondary and or metastable phases. In extreme cases, this mixing may result in a loss of the crystalline structure or amorphization of the lattice. Dimensional changes also result from irradiation assisted creep and void swelling. This can cause moving parts to jam, can increase stress on pressure vessels and containment systems, and reduce tension in bolt and spring systems. Additionally, diffusion of He from α -particle (He^{2+}) irradiation to form bubbles and segregate to grain boundaries degrades the grain strength, embrittling the material and significantly reducing elongation prior to failure [2].

These very high temperatures ($\sim 325^\circ\text{C}$), intense radiation fluxes and subsequent damage, and corrosive coolant, which is under pressure in the case of PWRs, make for a demanding

environment for materials [2]. What's more, there is research to expand operation lifetimes of current reactors, thus increasing the demand from currently employed materials. With the fleet of current reactors aging, it will be necessary to replace and surpass current technologies with next generation, so called Generation IV, fission and fusion reactor concepts, all of which will demand more from materials [1, 2].

Significantly higher operating temperatures are proposed for concept Generations IV reactors than those currently employed in commercial water cooled reactors [6]. Of hundreds of designs submitted to the U.S. Department of Energy (DOE), the Generation IV International Forum (GIF) has explored 6 concept designs in depth, which use different coolant principles to reach higher operating temperatures than those possible within current water cooled reactors, see Fig. 1.1, courtesy of Zinkle *et al.* [2].

These include the supercritical water-cooled reactor (SWCR), which operates in a similar core dose regime to current Generation II-III+ reactors, but are $\sim 33\%$ more efficient, due to utilizing supercritical water as a coolant to reach higher operating temperatures, $\sim 550^\circ\text{C}$ [1]. The He gas cooled very-high-temperature reactor (VHTR) and gas-cooled fast reactor (GFR) each exceed this operating temperatures with outlet temperatures designed to consistently exceed 850°C , the VHTR in some cases approaching 1000°C . That said, the expected operation dose for these reactors is also comparable to current reactor models [1, 2], and it should be noted that the He gas coolant is inert and not expected to lead to the same embrittlement as in the case of α -particle irradiation described previously.

Two liquid metal-cooled fast reactor concepts, the sodium-cooled fast reactor (SFR) and lead-cooled fast reactor (LFR), are expected to operate at temperatures above 500°C and receive core doses which are often double that seen in current reactors. Finally, the molten salt reactor (MSR), as its name suggests, utilizes a molten pool of fluoride salt in which the fuel is dissolved. It is designed to operate at temperatures up to 800°C and an expected core dose of up to 200 dpa [1, 2]. An additional relatively new reactor concept, the traveling wave reactor (TWR), would be designed to operate for 60 years with a breed-burn once-through cycle which would subject fuel cladding to ~ 600 dpa [2, 7].

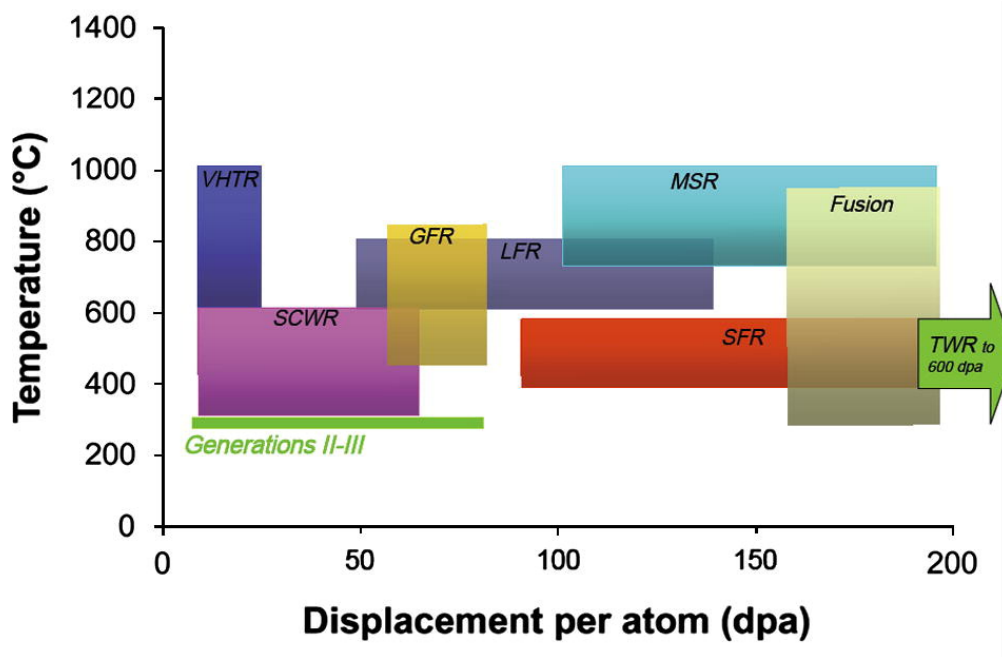


Fig. 1.1 – Expected temperature and lifetime reactor core component doses for Generation IV reactor concepts, as compared to current Generation II-III+ reactors. Includes the very-high-temperature reactor (VHTR), supercritical water-cooled reactor (SCWR), gas-cooled fast reactor (GFR), lead-cooled fast reactor (LFR), sodium-cooled fast reactor (SFR), molten salt reactor (MSR), and traveling wave reactor (TWR) [2].

Based on these more hostile conditions, completely different and new structural materials will be necessary, as currently implemented materials will not survive at these higher temperatures, often more corrosive environments, and greater radiation fluxes and doses for the proposed reactor lifetimes, see Fig. 1.1. Of course, these new materials must possess good mechanical properties, especially at elevated temperatures, and must be able to interface well with the coolant environments, but of paramount importance is still surviving the high radiation flux [2, 6].

There are numerous properties accepted as a good basis for high radiation damage resistance [2, 6]. High point defect recombination sites or sink strength is considered a very important property for resisting radiation damage. These sinks can take the form of precipitates, nano-particle dispersion, grain boundaries, or nanoscale interfaces. However, from a calculated sink strength perspective nanocrystalline grain boundaries and nanocomposite multi-layer interfaces offer calculated sink strengths $\sim 10\times$ that achievable with precipitates or dispersed nano-particles. It should be further noted that proposed

operating temperatures for Generation IV reactor concepts are high enough to anneal many nanocrystalline materials, resulting in grain coarsening and loss of relative sink strength. On the other hand, many nanolamellar composites are thermally stable at extreme temperatures [6].

Low vacancy mobility is another property which can lead to an acceptable saturation of vacancy point defects as immobile vacancies begin spontaneously recombining with interstitials from neighboring formed Frenkel pairs. An important consideration for this is that a large portion of elements have a vacancy mobility temperature threshold that is too low for this to be an engineering consideration in material selection for Generation IV reactors, but several ceramic systems fit these criteria. Another concern, however, is point defect volumetric swelling. Since this engineering design relies on a saturation of vacancies, the resulting swelling of the lattice, especially if anisotropic, may lead to micro-cracking [6].

For high temperature gas-cooled applications, such as the VHTR, ceramics and other passivating high temperature materials are desirable as it is not possible to avoid corrosion and oxidation of metal alloys. However, while nuclear grade graphite is a useful material, its anisotropic swelling, makes it less viable in applications where high damage doses are expected over the lifetime of operation. Further, high thermal conductivity is needed in heat transfer components, so metals, while corroded, are still considered a highly economical option [2].

The $M_{n+1}AX_n$ (MAX) phases are a class of thermodynamically stable ternary carbides and nitrides under consideration for their beneficial properties, which coincide with much of the target material goals. The hexagonal polycrystalline MAX structure is nanolamellar with basal layers of A group elements separating layers of M_2X rhombohedra, where M is an early transition metal and X is either carbon or nitrogen. It is this layered structure that results in a unique combination of properties for ceramic systems, including a high elastic stiffness typical of ceramic systems while retaining a ductility that allows for easy machining. The basal A-layers also lead to a very high thermal conductivity and for many compositions electrical conductivity. They are thermomechanically stable at high temperatures and resist creep and damage due to thermal shock [8]. The Ti-based MAX phases, Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC , were further deemed to have a low neutron absorption cross section that was

comparable to SiC, another candidate material for Generation IV reactor concepts, so low material activation is expected [9]. They are also of interest because layered structures result in a very high theoretical interfacial sink density with a high corresponding strength [6] suggesting a high potential point defect recombination capacity.

Many of the MAX phases have demonstrated a resistance to oxidation and corrosion in many environments because the high surface area of intersecting basal A-layers with exposed surfaces often result in a passivating layer [8]. As such, MAX have been tested in simulated coolant environments proposed for Generation IV reactor concepts. Ti_3SiC_2 and Ti_2AlC were tested in an extended corrosion study in high temperature molten Pb, which revealed Ti_3SiC_2 to be doubly protected by multiple passivating layers while Al solubility in Pb reduced Ti_2AlC performance at extended exposures [10]. Similar studies considered a molten Na environment, where Ti_3SiC_2 , Ti_2AlC_1 , and Cr_2AlC each demonstrated no reaction while Ti_3AlC_2 showed slight change in grain structure believed to be due to Al diffusion via grains into the molten Na [11]. The only environment the Ti-based MAX do not exhibit corrosion resistance in is simulated primary coolant loop water, because the pH of 7.5 makes the passivating SiO_2 and Al_2O_3 layers unstable. That said Cr_2AlC shares many similar properties with Ti-based MAX phases and showed no sign of breaching its Cr_2O_3 layer [12].

These properties and performance make MAX phases an interesting potential material for several of the Generation IV reactor concepts. Possible applications include advanced reactor in-core component such as: corrosion and wear resistant coatings for fuel cladding, fuel cladding and duct/wrapper applications, structural support, structural grid, and pump components [2]. MAX phases have been the subject of numerous neutron and ion-irradiation studies which will be explored in depth in Chapter 2, but summarized here. It has been demonstrated that for the Ti-based MAX phases, radiation damage evolution is typically exhibited as relative strain within the lattice and an increase in TiC concentration, a stoichiometric mismatch impurity [13, 14]. Ti_3SiC_2 , the composition selected for this study, also has a low anisotropic swelling associated with point defect volumetric swelling [6, 14].

It is well established that ion beam irradiation of materials may more rapidly mimic many of the damage events observed following exposure to energetic neutrons, namely elastic collision cascades. Ion beams have the additional capability to fine tune the irradiation

conditions and reach very high damage doses (dpa), via nuclear energy loss, in order to systematically explore damage evolution with little to no radioactivity induced in the material. However, it is important to recognize that energetic ions ($>1\text{ MeV}$), while able to penetrate deep enough into a material to simulate bulk effects, result in a significantly increased proportion of inelastic collisions and ionization per displaced atom associated with electronic energy loss. Further, for medium mass ions, $>90\%$ of energy deposition is due to these electronic effects, which are of sufficient energy that defect migration may be stimulated. Therefore, understanding the influence of electronic energy loss on modification of a material is vital, especially when using ions as a tool to compare with neutron induced radiation damage [4]. The present work seeks to deconvolute the influences of electronic and nuclear energy loss within Ti_3SiC_2 to better understand ion beam modification of the material.

Ti_3SiC_2 was subjected to high-energy Ti ion irradiation to high fluences at room and high temperatures, Chapters 4 and 5, respectively, as well as a sequential irradiation study, utilizing low-energy Au and high-energy Pt and Cl ions, Chapter 6. All ion irradiations were conducted at The University of Tennessee Ion Beam Materials Laboratory (IBML). The high-energy Ti ions were selected to give a wide range in energy deposition over the irradiation depth, specifically a variation in electronic energy loss with depth. The fluences selected allow for both a comparison of damage dose as a function of depth and comparison of said variation in electronic energy loss at comparable doses. The sequential irradiation study was designed to separate the effects of nuclear and electronic energy loss and systematically recombine them to study their interaction.

To quantify fine changes in lattice parameter and estimate phase profile changes, grazing incidence x-ray diffraction (GIXRD) was performed at the Joint Institute for Advanced Materials (JIAM) diffraction facility. To measure fine changes in lattice strain on a lab scale diffractometer, a specialized method to iteratively determine a self-consistent c/a as a function of depth [15] was adapted for the first time to study ion irradiated hexagonal polycrystals. This method has potential for application in other far-from-equilibrium situations for precise measurement of lattice changes in non-cubic systems. Additionally, transmission electron microscopy (TEM), performed in the JIAM microscopy facilities,

provided selected area electron diffraction (SAED) depth profile corroboration and $\mathbf{g}\cdot\mathbf{b}$ defect analysis.

The results reveal that electronic energy loss plays a vital role in the damage evolution of Ti_3SiC_2 and further that there is a low threshold to the onset of its influence. High *in situ* irradiation temperatures are demonstrated to largely mitigate these effects and change the defect morphology. In addition, the separation of nuclear and electronic energy loss reveals a mechanism to describe the structural changes observed in the other studies and that the energy dissipation pathways are in competition, with changes in their ratio resulting in significant variation in the irradiation response. These results have important implications for ion beam interactions with Ti_3SiC_2 . Selection of ions as a tool for comparison with other intense radiation environments, such as those present in nuclear fission reactors, requires consideration of both electronic and nuclear energy deposition for the ion in question. Additionally, tuning the irradiation conditions and thus these effects may allow for control over intentional functionalization of the structure through ion beam modification of the material.

Chapter 2

Literature Survey of MAX Phases and their Response to Neutron and Ion Irradiation

Some of the literature review in this chapter is included in a submission by William Alexander Hanson *et al.* for publication in *Acta Materialia*: W.A. Hanson, M.K. Patel, M.L. Crespillo, F. Zhang, S.J. Zinkle, Y. Zhang, W.J. Weber. Ionizing vs collisional radiation damage in materials: separated, competing, and synergistic effects in Ti_3SiC_2 . *Acta Materialia* Under Review [16]. Any addendum to this submission will be detailed in the Tennessee Research and Creative Exchange (TRACE), where this research dissertation is stored.

2.1 MAX phases

$\text{M}_{n+1}\text{AX}_n$ (MAX) phases are a class of ternary carbides and nitrides, where M is an early transition metal, A is an A group element, and X is either C or N. A current table of possible elements that can form a MAX phase is in see Fig. 2.1 from the list of possible MAX phases as detailed by the Layered Solids Group at Drexel University [17]. These nanolamellar crystalline materials result in a unique combination of thermo-physical properties that make them potentially interesting for applications in demanding environments like those existing in aerospace and advanced fossil and nuclear energy applications [8, 18–22].

IA	IIA											IIIA	IVA	VA	VIA	VII	VIIIA

Fig. 2.1 – A current periodic table of elements that may form a MAX phase.

2.1.1 Structure and applications

When synthesized, a process using high temperature and pressure as detailed extensively elsewhere [20, 23], the $M_{n+1}AX_n$ phases form a polycrystalline, hexagonal structure within the $P6_3/mmc$ space group composed of n layers of M_2X rhombohedra separated by A-element basal monolayers, as seen in Fig. 2.2. This nano-lamellar structure within these materials results in a remarkable combination of properties, not typical for ceramic systems. They have a high elastic stiffness, yet remain ductile enough that they are capable of plastic deformation and being machined using traditional methods, such as turning on a lathe, or computer numerical controlled (CNC) methods, such as milling or electric discharge machining (EDM) [8].

Like many ceramic systems, they possess a high temperature thermomechanical and phase stability, capable of operating at high temperatures ($> 800^\circ C$) in many environments without dissociating into secondary phases. Typically ceramics exhibiting these properties are thermally and electrically insulating; however, due to basal A-layers penetrating the polycrystalline structure, MAX phases are highly thermally conductive. Some compositions even have a high electric and ionic conductivity; Ti_3SiC_2 possesses an electrical conductivity $\sim 1/10$ th that of pure Cu [8, 21, 22, 24].

The combination of these mechanical and thermal properties makes them resistant to thermal shock [8], and the basal monolayers of A-elements often result in a passivating behavior to grant corrosion resistance to many compositions, as was discussed previously in

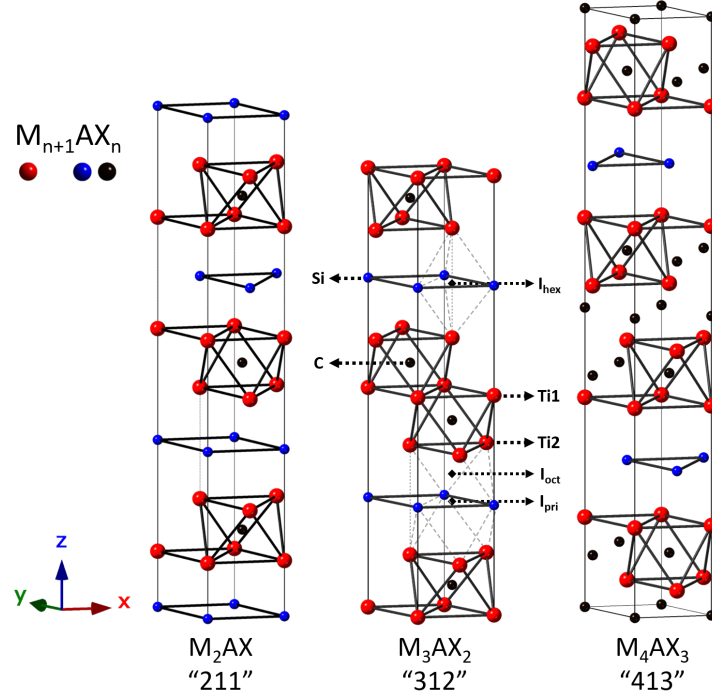


Fig. 2.2 – Examples of the α polymorphs of the “211”, “312”, and “413” $M_{n+1}AX_n$ structures. Enough of each structure has been shown to reveal a complete stacking sequence.

Chapter 1 [10, 11]. Further, analysis of neutron activation within Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC demonstrated that each has a low neutron absorption cross section. Its behavior in this regard is comparable to that of SiC and 3 orders of magnitude lower than Alloy 617, two candidate materials for future generation fission and fusion reactor applications [9].

2.1.2 Structural defects

Defects within the MAX structure can present in multiple forms, including compositional and planar defects. During synthesis of Ti containing MAX phases, the subject of this study, a slight stoichiometric mismatch can result in the formation of TiC_x in the pristine MAX phase [8, 13, 21]. The face centered cubic (FCC) TiC structure shares many similarities with that of MAX phases. In fact, neglecting the A layer in a standard Ti_3SiC_2 cell results in a TiC rock-salt structure with pseudo- $\{111\}$ twin mirror planes present between each Ti_3C_2 rhombohedral unit [8, 21, 25]. TiC is more brittle and less thermally conductive than the MAX phase [20, 21], but it is resistant to swelling [2]. That said, the presence of TiC in

MAX phase bulk can partially offset the beneficial properties of the layered structure for their application in extreme environments [20, 21].

In addition to vacancy point defects, interstitials may form in the structure, but these are typically isolated to sites within and near the basal A-layers, see Fig. 2.2. This will be discussed further in Section 2.2.2 [26–29], but basal confinement is not limited to point defects. Dislocations which form in MAX phases are also confined to the basal planes with a Burgers vector $\mathbf{b} = 1/2[0001]$. As is apparent from the Burgers vector, slip is also confined to a reversible 2d motion along the basal planes, which can result in the formation of basal dislocations [8, 30]. Recently, ripplocations, nano-scale lamellar ripple defects [31], have been observed within the MAX structure resulting in some debate over whether incipient kink bands, coaxial parallel basal dislocation loops, or these bulk ripplocations are responsible for the material’s non-linear elastic deformation properties [8, 32]. In either case, dislocation loops and ripplocations are both observed confined to the 2-d basal layers [33].

2.2 Radiation effects in MAX phases

Several compositions of MAX phases have been the subjects of many irradiation studies, using neutrons and ions; however, the focus of this section will be on current reported response of the Ti-based MAX phase compositions, Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC , which appear largely tolerant of radiation induced damage. In general, radiation damage in these MAX phases has been observed to lead to an increase in TiC concentration and lattice strain, specifically an increase in the c/a ratio of the lattice parameters [13, 14, 29, 30, 34–36], and the following sections will explore the understanding of these responses in more detail.

The material remains crystalline and signatures from MAX appear largely undisordered, even at high doses at a large radiation flux [36, 37]. Further, it has been suggested that the nano-layered structure, specifically the presence of the A-layer, is a primary source for radiation damage resistance for the MAX phase [13, 30, 33, 38], acting as a sink for point defects and a high diffusivity path for recombination [27, 29, 38].

2.2.1 TiC signature changes

The increase of signatures affiliated with TiC within Ti-based MAX phases following both neutron and ion irradiations has been observed and reported many times previously. This apparent change in composition has been observed using multiple techniques. In GIXRD, broad FCC-peaks, believed to be TiC_x , are observed to increase in relative intensity with fluence [13, 39, 40]. Raman spectroscopy shows shift in the spectra from pristine profiles to include some modes typical of $\text{TiC}_{0.67}$ [40]. TEM SAED patterns start to show intensity attributed to TiC structures rather than those of Ti-MAX [41]. Given that increases in the TiC concentration will partially offset the beneficial properties that makes these materials attractive to intense radiation environments, there is interest in understanding the source of these apparent compositional shifts.

However, there is debate in the community over the source of this apparent change in TiC concentration. Some have suggested significant phase change and increases in TiC and other phase content is a decomposition of the MAX phase structure into its MX binary phase [13, 36, 39, 40]. Others propose that rather than decomposing into TiC, intermediate phases of nano-crystalline and amorphous SiC and TiC form, which are likely to reform into Ti_3SiC_2 at elevated temperatures [37]. Still others have proposed that rather than decomposing, another phase transformation occurs which leads to the formation of the β - Ti_3SiC_2 or Ti_3AlC_2 phases [42]. It has also been proposed within the Ti_3AlC_2 MAX composition that rather than decomposing into TiC_x , a structure identical to the FCC-TiC but actually chemically disordered Ti_3AlC_2 may form [41]. Recently a mechanism has been proposed to explain this transformation, whereby the hexagonal Ti_3AlC_2 may form a FCC- Ti_3AlC_2 , through significant Ti-Al anti-site formation [43].

Although there is a lack of agreement on the mechanisms responsible for apparent increases in measured TiC concentration, it appears generally agreed upon and is proposed here that the changes in FCC signatures, whether TiC or otherwise, can still represent a metric for radiation damage within Ti_3SiC_2 and other Ti containing MAX phases. There is, however, challenge in quantifying this change in concentration following irradiation, due to the similarities between the MAX phase and TiC like FCC structures and thus similarities in

both their resulting GIXRD profiles, Raman modes, and SAED patterns. Proposed methods for judging these changes will be discussed in more detail in Chapter 3.

2.2.2 Point defect and dislocation loop behavior

As indicated earlier, in general, point defects within the MAX phases are typically confined to the vicinity of the basal A-layers within the structure. All octahedral sites within the $M_{n+1}X_n$ layer blocks are occupied by the X elements, making it very difficult for interstitials to penetrate them [26–29]. Xiao *et al.* proposed these interstitials reside in-plane on the hexagonal interstitial sites (I_{hex}), see Fig. 2.2, which are the most energetically favorable sites under equilibrium conditions [28]. In contrast, AIMD simulations within the Ti_3SiC_2 composition by Liu *et al.* revealed that interstitials created by threshold displacement events often reside in-plane on the prismatic interstitial sites (I_{pri}), also in Fig. 2.2; though, in many cases, Ti interstitial (Ti_I) also formed split interstitials with neighboring Ti atoms (Ti2 site) above the I_{hex} sites between planes [39]. It has been calculated recently that Ti-Si anti-sites are also a stable defect configuration for Ti_3SiC_2 and that both those and C-Frenkel pairs with interstitials trapped in the basal planes will result in expansion of the c lattice thus increase of the c/a ratio [27–29]. It follows that evidence for this defect confinement will then be observed as a radiation induced strain in the hexagonal structure. This is typically exhibited as an expansion and contraction of the c and a-lattice parameters (c,a-LPs), respectively [13, 14, 29, 30, 34–36].

Both experimental and DFT simulations have demonstrated that the A-layer of the MAX structure readily allows for mobility within the structure, especially at elevated temperatures [38, 44–46], and it has been suggested that this is a primary source of the MAX phase radiation damage resistance [13, 30, 33, 38, 44, 46]. This recovery could occur by proposed migration mechanisms, which suggest vacancy diffusion in this system is largely confined to 2-d motion within the basal layers.

A coupled, interstitialcy mechanism for Si_I migration through the Si layer is significantly faster than the already fast Si_V migration mechanism. This will lead to rapid Si Frenkel pair recombination even at low temperature. Some have suggested this means the aforementioned Ti_{Si} is not likely to form in large concentrations because of Si Frenkel pair recombination

prior to Ti trapping on a Si site, thus confining Ti_I to the Si plane as interstitials [46]. That said, other theoretical work readily demonstrates the formation of the anti-sites as favorable [27–29, 47]. In these cases, it has been proposed that Ti_{Si} may diffuse via the same rapid Si_V mechanism [27].

C_I that form within the Si-layer have a similar bonding structure to that seen in polymorphs of TiC [46], and in the case of forming an anti-site on a Si_V it will have a nearly identical local environment to the Ti_3C_2 layers [36], given the similarity between $M_{n+1}AX_n$ and nanotwinned TiC structures. C_I migration is also faster than C vacancy migration, so it will likely stay in the Si layer to form the aforementioned SiC/TiC like bonding structures as the migration barrier to return to the C-layer is significantly higher than migrating through the Si-layer, recalling that all octahedral sites are occupied in the Ti_3C_2 layers.

Past neutron and ions irradiation studies have demonstrated that damage regimes dominated by elastic collisions can result in dislocations loops and stacking faults that are, again, confined to the basal planes. Specifically dislocation loops have been observed with a Burgers vector of $\mathbf{b} = 1/2[0001]$ [13, 14, 30, 33, 42]. Additionally, it has recently been demonstrated that bulk ripplocations [31, 32], may also form within the basal planes under neutron irradiation. This was demonstrated through extensive tilting through $\mathbf{g} \cdot \mathbf{b}$ invisibility criteria, which resulted in all defects, save the bulk ripplocations, to disappear [33]. However, these bulk ripplocations following neutron irradiation have yet to be identified following ion-irradiation. It should also be noted that both of these planar defects may be present in pristine conditions, so only relative comparison between pristine and different irradiated conditions can give a good reflection of changes.

2.2.3 Elevated *in situ* temperature conditions

Some *in situ* high temperature neutron and ion irradiation studies have been conducted on Ti-MAX phases in the past. It has been demonstrated that typically, Ti_3SiC_2 shows greater radiation damage resistances at higher temperatures [13, 14, 30, 33–35, 42], where only minimal crystalline disorder is observed with minimal swelling and no cracking [14, 35]. Additionally, at very high temperatures ($>700^\circ C$), defect free denuded zones near grain boundaries were observed in Ti_3SiC_2 and Ti_3AlC_2 following neutron irradiations. These

appeared to be isotropic to the grain orientation and the full nature of the denuded zones is not yet known [30, 33].

In general, Ti_3SiC_2 appears to perform better at high temperature in comparison to the other Ti-MAX phases. Under the high temperature neutron irradiation Ti_3AlC_2 showed significant increases in TiC signatures that were not matched by the Ti_3SiC_2 or Ti_2AlC compositions [13]. Further, following high temperature Ni-ion irradiation, Ti_3SiC_2 has a low anisotropic swelling associated with point defect volumetric swelling; meanwhile, both Ti_3AlC_2 and Ti_2AlC do not and often exhibit resultant microcracking at grain boundaries [6, 14]. Under each elevated temperature condition, the strain in the lattice was reduced for Ti_3SiC_2 as compared to both Al containing Ti-MAX phases.

2.3 Comparison of neutron and ion matter interactions

Irradiation with charged particles (ions) is a powerful tool, in use for decades, for understanding the damage evolution of materials exposed to radiation environments. It is well established that elastic collisions with atomic nuclei, known as nuclear energy loss or nuclear stopping power (S_n) during ion irradiations will produce elastic collision cascades and defects similar to those observed following neutron irradiation. There are additional benefits of a greater control over the irradiation environment, reduced irradiation time, and little to no resultant radioactivity following ion irradiation. This is with the recognition that higher energy ions have a significant increase in inelastic collisions with electrons, known as electronic energy loss or electronic stopping power (S_e). These electronic interactions dominate the energy transfer until the energy, and thus velocity, of the ion is reduced sufficiently for the elastic scattering cross section to increase and nuclear stopping power to dominate the interactions [4, 48–52].

It is well established that there is variation in material response between these two energy loss pathways, with metals showing little influence from the electronic excitations. However, early observations showed that ionizing radiation can enhance the diffusion of defects and impurities and even result in annealing of displacive damage in ceramic systems, caused by nuclear energy loss during low-energy, heavy ion irradiation [50, 51, 53, 54]. More

recent studies have demonstrated that the high-energy electrons, so called hot electrons, which result from the electronic energy loss along the ion path, dissipate their energy to neighboring electrons, via electron-electron scattering, and to the local lattice via electron-phonon coupling, leading to significant localized temperature increases, or a thermal spike. Depending on the material system and initial defect concentrations, increasing the ratio of S_e/S_n relating to this thermal spike can enhance the damage and fully amorphize the material along the ion path or fully suppress the damage through in-cascade annealing [55–57]. The importance of this variation in S_e/S_n applies to direct comparison with reactor radiation environments as well, due to intense gamma radiation and electronic energy loss of primary recoils produced by collisions with neutrons. This ratio of S_e/S_n will vary depending on the neutron energy and flux. For example, a ratio of around 4 is typical for liquid metal cooled fast fission reactors while a mixed spectrum LWR, has a S_e/S_n greater than 100 [58].

2.3.1 Investigating electronic energy loss influences in MAX phases

It has been previously demonstrated that Ti_3SiC_2 irradiated by ions with energy in the regime dominated by electronic stopping power remains crystalline under most irradiation conditions, including thin film, *in situ* irradiations up to 25 dpa [37] and low temperature irradiations. Though a high degree of crystalline disorder may result, the MAX phase structure remains relatively intact and does not fully amorphize [38]. It has been suggested that a low Ti-Si anti-site formation energy for Ti adjacent to the Si layer may contribute to the amorphization resistance by occupying V_{Si} sites [27]. However, it is important to emphasize that a lack of amorphization is not the same as an insensitivity to electronic excitation and ionization effects.

Strain in the c-LP with little to no corresponding volume change was observed following 92 MeV Xe irradiations [59], and a similar response followed 74 MeV Kr irradiations [34]. In both these cases, the structural changes were observed in depth regions where the ion energy loss was dominated by electronic stopping power. However, these results were subsequently compared to low fluence irradiations with 930 MeV Xe ions, and little structural change and

no black spot defects were observed as compared to regions dominated by elastic collisions [34, 59]. Based on this comparison, Ti_3SiC_2 was deemed insensitive to electronic excitations, and the previous observed results were attributed to elastic collisions with atomic nuclei [34]. It should be noted, though, the swift heavy ion irradiations were conducted to a significantly lower fluence, due to experimental constraints to prevent undesired *in situ* sample heating. This means the 930 *MeV* Xe irradiated condition was exposed to an equivalent damage dose that was orders of magnitude lower than the samples it was compared against. It is known that in other material systems that a minimum dose is necessary before electronic excitation results in structural change, and while in materials sensitive to electronic interactions, increasing S_e typically reduces this incubation fluence [60–63], the magnitude of difference between these sample sets would appear to preclude direct comparison. In addition, the same study demonstrated significant variation in the material response following low energy 4 *MeV* Au irradiations, where nuclear stopping power is dominant as compared to the 92 *MeV* Xe and 74 *MeV* Kr irradiations dominated by electronic stopping power [34].

This seems to suggest that the electronic stopping power does, in fact, play a role in the damage evolution, and thus demands further study. Therefore, it is the goal of this research to deconvolute the influences of electronic and nuclear energy loss on the resulting damage evolution observed following ion irradiation of Ti_3SiC_2 .

Chapter 3

Experimental Methods

Some of the experimental methods and theory described in this chapter have been previously published by William Alexander Hanson *et al.* in *Acta Materialia*: W.A. Hanson, M.K. Patel, M.L. Crespillo, Y. Zhang, W.J. Weber. Influence of electronic vs nuclear energy loss in radiation damage of Ti_3SiC_2 . *Acta Materialia* 161 (2018) 302-310. doi:10.1016/j.actamat.2018.09.027 [64], submitted for publication by the same in *Acta Materialia*: W.A. Hanson, M.K. Patel, M.L. Crespillo, F. Zhang, S.J. Zinkle, Y. Zhang, W.J. Weber. Ionizing vs collisional radiation damage in materials: separated, competing, and synergistic effects in Ti_3SiC_2 . *Acta Materialia*. Under Review [16], and submitted for publication by the same in either *Acta Materialia* or the *Journal of Nuclear Materials* under the title: Influence of high temperature ion irradiations on electronic stopping effects and defect morphology in Ti_3SiC_2 . Any addendum to these submissions will be detailed in the Tennessee Research and Creative Exchange (TRACE), where this research dissertation is stored.

3.1 Physical sample preparations

The polycrystalline Ti_3SiC_2 used in this study was synthesized in bulk by the MAX phase Layered Solids research group at Drexel University via hotpressing; complete details for processing have been discussed at length previously and are not pertinent to the discussion here [20, 23].

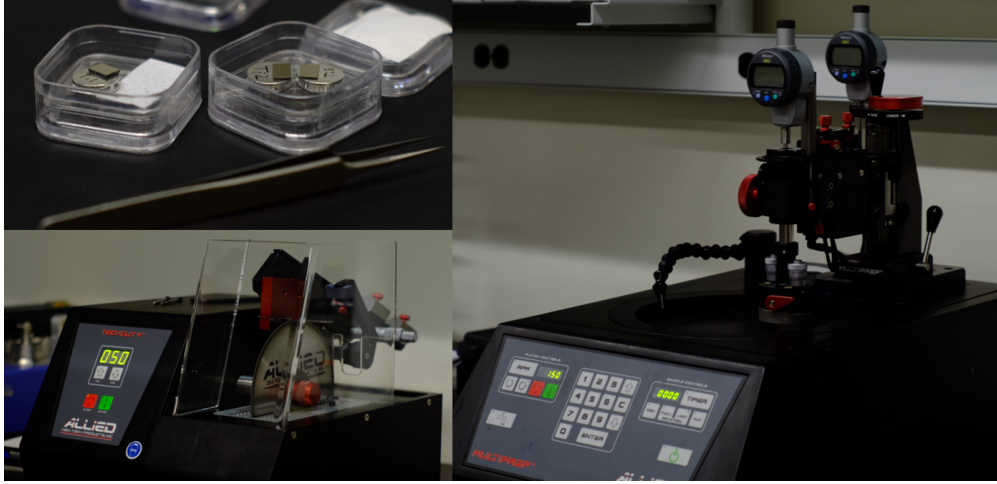


Fig. 3.1 – Sample preparation facilities showing low speed diamond saw, Multi-prep precision polisher, and resultant sample finish in final irradiation dimensions.

Plate sections of samples were cut via low speed diamond saw to roughly $10 \times 10 \times 1.5$ mm and low stress polished with diamond lapping film and finished with $0.05 \mu\text{m}$ colloidal silica and alumina slurry, see Fig. 3.1. To remove any remnants from polishing, samples were ultrasonically washed through a series of deionized water and high purity ethanol, and finally topically cleaned with n-hexane. Final dimensions for irradiations were sectioned again using the low speed diamond saw with sample surfaces mounted tangent to the blade and sample weight counter balanced to minimize contact pressure. The same cleaning procedure was used following sectioning. Polished remnants sectioned from the final irradiation dimensions were retained as pristine conditions, in case needed for future characterization, such as for TEM analysis.

3.2 Ion irradiation conditions

3.2.1 Ion beam materials laboratory

Ion irradiations were conducted at The University of Tennessee Ion Beam Materials Laboratory (IBML) [65]. The IBML is equipped with two ion sources, injection magnet, a 3.0 MV Pelletron tandem accelerator, analyzing magnet, and three active high-energy

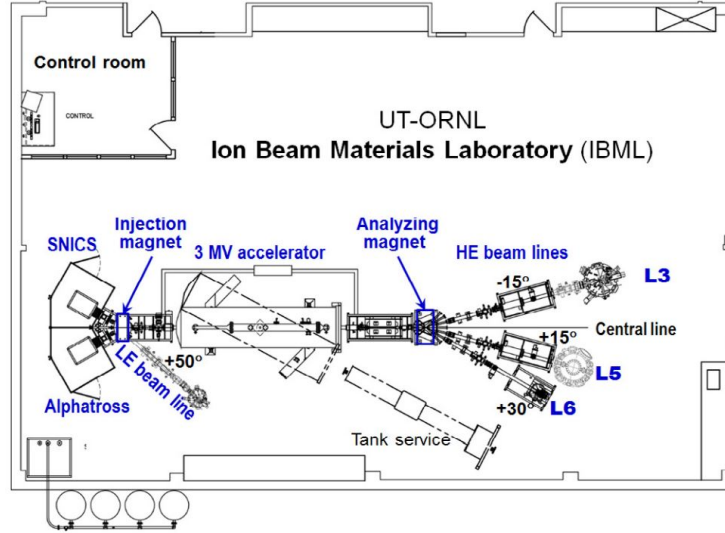


Fig. 3.2 – A diagram of The University of Tennessee Ion Beam Materials Laboratory facility (IBML) [65].

beamlines with a total of 4 endstations, see Fig. 3.2. For this study, the Source of Negative Ions by Cesium Sputtering (SNICS) II source was utilized to produce a negative ion beam.

As many of the negative ions are sourced from compound cathodes, the selected element negative ion beam is bent into the main accelerator central line by the injection magnet. The tandem accelerator pulls the negative ions towards an electrostatic positive source, where a low pressure stripper gas “strips” electrons from the ions. The now positive ions are accelerated a second time from the positive source, their stripped charge state ultimately determining their energy following the second acceleration. The energy of ion is selected using the analyzing magnet to bend the beam into the desired high-energy beamline for the appropriate experimental endstation [65].

All irradiations were conducted in beamline 3 (L3) in the second end station chamber. This chamber was equipped with a Thermionics Northwest Inc. nude W filament heater, which was utilized to produce *in situ* high temperature irradiation conditions. For unelevated, room temperature irradiations, multiple samples were mounted to a large sample extension plate, using carbon tape, along with multiple scintillator sections to check beam footprint and confirm no beam overlap between irradiations, see Fig. 3.3. To ensure beam footprint at the sample surface height, the main scintillator disk is intentionally offset to approximate the sample surface height from the plate. For high temperature irradiations,

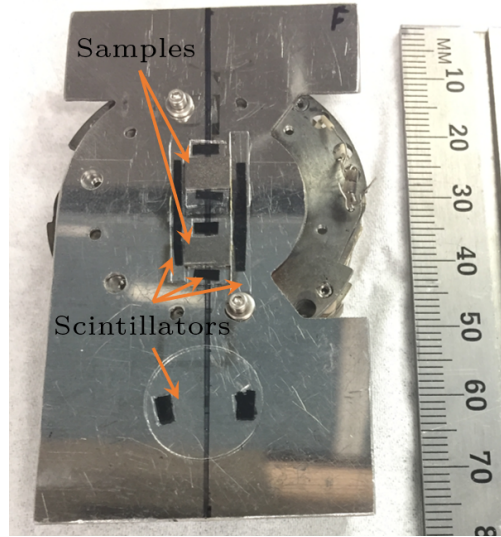


Fig. 3.3 – Two samples mounted to the large sample extension plate using carbon tape. A scintillator disk is included to check beam footprint and is intentionally offset from the plate surface to match the sample surface height. Additional scintillator sections surround the samples to confirm there is no beam overlap

samples were mounted to a Mo sample plate using Ag paint to both adhere the sample to the plate and ensure good thermal contact between the two. This plate is mounted in close proximity to the nude filament, which radiates heat through the highly conductive sample plate to heat the sample. In the case of the 880°C irradiations, Mo clamps were also utilized in securing the sample to the plate as operating conditions are close to the limit of the structural integrity of the Ag paint, see Fig. 3.4. In both high temperature cases, the scintillator disk used to check beam footprint is held with a Mo clamp away from the primary heated region.

Additional Mo clamps secured a type-K thermocouple to the sample surface to monitor temperature during all *in situ* heating experiments. This was done such that the thermocouple was shielded from the ion beam and not in direct contact with the clamps to prevent artifacts due to the beam or “quenching” via direct clamp contact [66], see Fig. 3.4. Temperature during *in situ* heating experiments is controlled via fine adjustments of current through the nude filament. Close monitoring of the sample surface thermocouple, an auxiliary thermocouple located behind the sample plate, and the current through the nude filament provides precise control of sample temperature and redundancy through

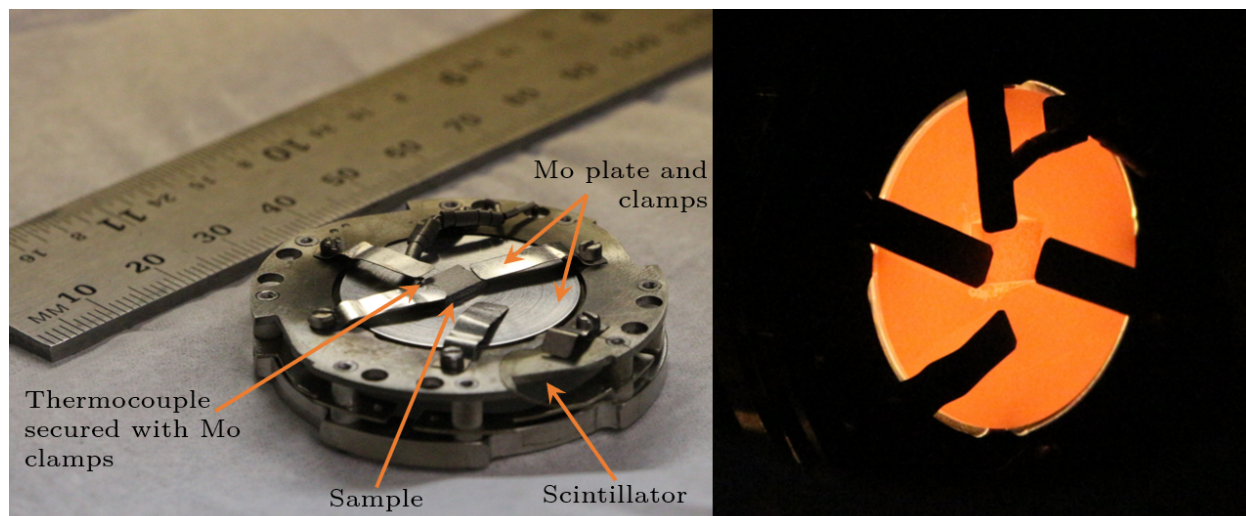


Fig. 3.4 – Sample mounted to high temperature stage using Ag paint and Mo clamps. Note the thermocouple is secured such the measuring filament tip only contacts the sample and not the Mo clamps, but is shadowed from the beam by the clamps.

multiple points of measure. This confidence in recorded temperatures is increased through intermittent temperature measurement of the sample and Mo plate with a pyrometer through the chamber window and is supplemented further through monitoring the exit temperature of N_2 coolant gas from the sample stage.

High temperature constraints within the L3 beamline include nude filament current and stage cooling. The nude W filament begins to degrade rapidly if the current exceeds 9 A; therefore, currents are kept below this threshold to extend the life of the filament. This constrains the maximum temperature by the size and thermal conductivity of the sample. Additionally, the sample stage must be protected from the extreme temperatures and is cooled by N_2 (*g*) evaporated from a N_2 (*l*) dewer. The higher the temperature desired, the higher the gas flow needed from the dewer to cool the sample stage, and thus the shorter irradiation time required to sufficiently protect the stage. Therefore, if high fluence and high temperatures near the limit of the chamber capabilities are desired, higher fluxes may be needed to fit within these cooling time constraints.

3.2.2 SRIM calculations

The ion irradiation experimental parameters were determined using the 2013 edition of The Stopping and Range of Ions in Matter (SRIM 2013) software package. SRIM 2013 has two primary components. One produces the electronic and nuclear stopping power, or energy per unit distance, as well as the estimated ion range tables for any ion matter combination up to $2\text{ GeV}/amu$. The other uses Monte Carlo algorithms to calculate energy deposition, ion ranges, recoil distributions, and vacancy concentrations as a function of depth, through either a Kinchin and Pease approximation of damage cascades or a full damage cascade calculation [67, 68]. It is important to note that these simulations operate on 100 slices of a defined material thickness, so care must be taken to estimate ion ranges and select a cell of appropriate size to maximize the resolution of the simulation. Additionally, each ion simulation is independent of the others [67, 68], so sufficient ions must be selected to statistically trust the calculated behavior as a function of depth.

High fluence Ti ion irradiations

Ab initio molecular dynamics (AIMD) simulations have suggested that Ti is the easiest element to displace from its site, but it is likely to recombine with its own vacancy [47]. These simulations determined weighted average threshold displacement energies of 27.9, 30.6, and 25.7 eV for C, Si and Ti, respectively, which were utilized along with the theoretical density of 4.528 g cm^{-3} to perform 100,000 ion full cascade simulations of 9 MeV Ti as self-ions in Ti_3SiC_2 .

The resulting output files from these simulations allow the calculation of energy deposition, as well as displacements per atom (dpa) and ion concentrations, as a function of depth. Electronic energy loss (S_e) is the ionization due to ions as a function of depth and this summed with the ionization due to recoils is known as the total electronic energy loss. Nuclear energy loss (S_n) is simply the energy imparted to recoils per depth. For full cascade simulations, the number of displacements per depth per ion may be calculated using:

$$\frac{displacements}{nm\ ion} = \left[\left(\sum \frac{vacancies_{element}}{\text{\AA}\ ion} \right) + \left(\frac{No.replacements}{\text{\AA}\ ion} \right) \right] \times \frac{10\ \text{\AA}}{nm} \quad (3.1)$$

Note that like the international measure of damage dose (dpa) for neutron irradiations, this calculated relationship does not represent the total number of Frenkel pairs per ion, but rather the number of displacement events per ion. These may be of low enough energy and range that spontaneous recombination of the interstitial and its vacancy may occur. However, the relationship in Eq. (3.1) between displacements per depth per ion may then be used with a target material density and an ion fluence to calculate the number of displacement events per atom (dpa) within the target material:

$$\text{displacements per atom (dpa)} = \frac{\frac{displacements}{nm\ ion} \times \text{ion fluence} \frac{ions}{nm^2}}{\text{atomic density } nm^{-3}} \quad (3.2)$$

This calculated relationship between damage dose, target, and fluence may be utilized to select an appropriate fluence such that specific damage doses (dpa) are at specific depths in a target material. For Ti_3SiC_2 in this study, the full cascade simulations performed above were used along with Eq. (3.2) to select fluences of $(2.8, 3.5, \text{ and } 4.2) \times 10^{16} \text{ cm}^{-2}$, which results in doses at a depth of $2\ \mu m$ of 20, 25, and 30 dpa, respectively. Fig. 3.5a shows the energy deposition behavior as a function of depth and both the dose and ion concentration profiles vs. depth for a fluence of $4.2 \times 10^{16} \text{ cm}^{-2}$. Meanwhile, energy deposition and damage dose (dpa) for each of the selected fluences over the depths of interest, may be seen in Fig. 3.5b. The 9 MeV Ti ions selected place the ion concentration profile peak well beyond the maximum depth region of interest of $2\ \mu m$, see red highlight in Fig. 3.5a, so there are no chemical or stoichiometric artifacts from excess Ti in the depths probed. However, because it is expected that the ion concentration profile will broaden under high temperature irradiation conditions, due to enhanced interstitial diffusion, the maximum depth probed for any *in situ* irradiation studies must be limited to $1.5\ \mu m$ [4].

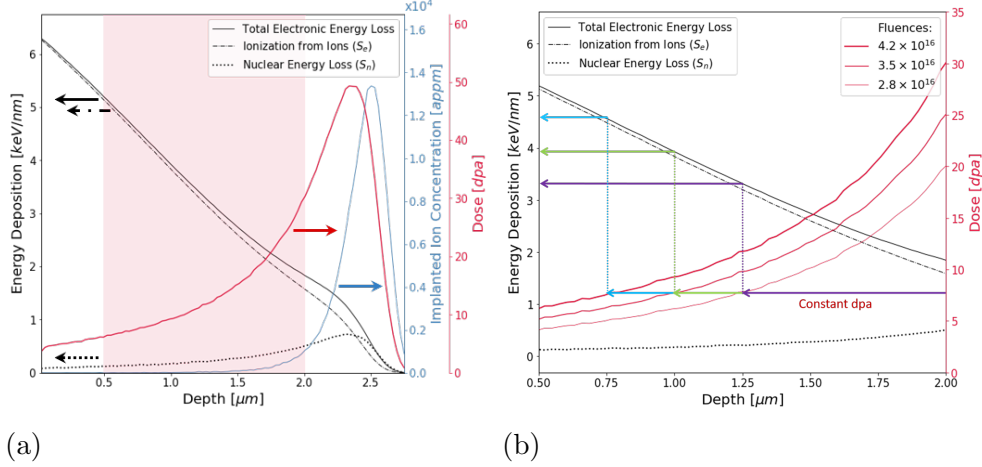


Fig. 3.5 – (a) Energy deposition, damage dose (dpa), and Ti concentration as a function of depth for an ion fluence of $4.2 \times 10^{16} \text{ cm}^{-2}$. (b) Energy deposition and damage dose (dpa) for the three fluences in the present study. The depth region of interest ($0.5 \text{ } \mu\text{m}$ - $2.0 \text{ } \mu\text{m}$) is displayed by a red shaded region in (a) and as the depth range in (b).

Energy deposition experiment

In addition to the 9 MeV Ti ions resulting in variation of local damage dose as a function of depth, the fluences selected provide the opportunity to explore changes in energy deposition at comparable calculated damage doses. As mentioned above, it has been calculated that Ti is the easiest to displace atom [47] as 2/3s of the sites reside along the basal A layer. This means Ti should be the most efficient self-ion for reaching a high damage dose near the end of the ion range where nuclear stopping power is dominant. However, as Ti is a medium mass ion, an energetic ion beam will also result in a high electronic interaction in the regions nearer to the surface. In total, electronic energy loss varies from approximately $5.20 - 1.83 \text{ keV nm}^{-1}$ over the ranges probed of $0.5 \mu\text{m}$ - $2.0 \mu\text{m}$, respectively, as Fig. 3.5 demonstrates.

With the fluences selected it is further possible to probe different depths within each sample, which correspond to the same damage dose (dpa), to compare differing energy dissipation behavior at a comparable dose, see Fig. 3.5b for a specific example. In this case, a dose of 7.6 dpa was selected for comparison; therefore, the depths of 0.75, 1.0, and 1.25 μm were probed in the $(4.2, 3.5, \text{ and } 2.8) \times 10^{16} \text{ cm}^{-2}$ irradiations, respectively, thus comparing electronic energy losses of 4.58, 3.96, and 3.34 keV nm^{-1} , respectively. By simply shifting the

depth probed in each of the fluences, it is possible to compare other such combinations of electronic stopping power at higher and lower constant doses.

Sequential irradiation experiment

While the high-energy Ti ion irradiations and the energy deposition experiment provide variation in electronic energy loss as a function of depth to explore the influence of the stopping power, a subsequent sequential irradiation study will better fully separate dissipation pathways. As indicated earlier in Chapter 2, previous studies in other material systems have used a combination of irradiations to explore independent separate effects of S_e and S_n , typically by introducing initial defects into the material (pre-damaging) through low energy, heavy ion irradiations, where S_n is dominant, and comparing with high-energy ion irradiations, where S_e is dominant. The subsequent recombination of these different energy loss pathways through sequentially performing these irradiations often reveals a synergy or competition between them, whereby the evolving defect concentration affects the energy dissipation of inelastic collisions and vice versus [51, 53, 55, 57, 62, 63, 69].

Full cascade SRIM (v2013) simulations were conducted with the same material and simulation parameters as were implemented to select the high-energy Ti ions [47, 67, 68]. For the nuclear stopping power dominated irradiation, 4 MeV Au was selected, see Fig. 3.6a, because it has sufficient energy to introduce damage to a depth of approximately 0.75 μm in the sample. At the same time, the S_e does not exceed an electronic energy loss of 4 keVnm^{-1} , a threshold to enhanced damage that will be established by the energy deposition experiment in Chapter 4 [64]. A fluence of $5 \times 10^{14} \text{ cm}^{-2}$ was selected, which results in a peak damage dose of 3 dpa at $\sim 0.5 \mu\text{m}$. It will also be established in Chapter 4 that a change in ion concentration of 1000 *appm* is insufficient to result in a measured lattice strain [64]; therefore, the ion concentration peak from this irradiation of $< 250 \text{ appm}$ with inert Au ions should result in no physical or chemical artifacts.

Two ions were selected for the electronic stopping power dominated irradiations: 17 MeV Pt and 14 MeV Cl. Each of these ions has a nearly identical and consistent S_e profile as a function of depth, see Fig. 3.6b and 3.6c, each of which exceeds the aforementioned 4 keVnm^{-1} threshold in electronic energy loss over the depths of interest for this study,

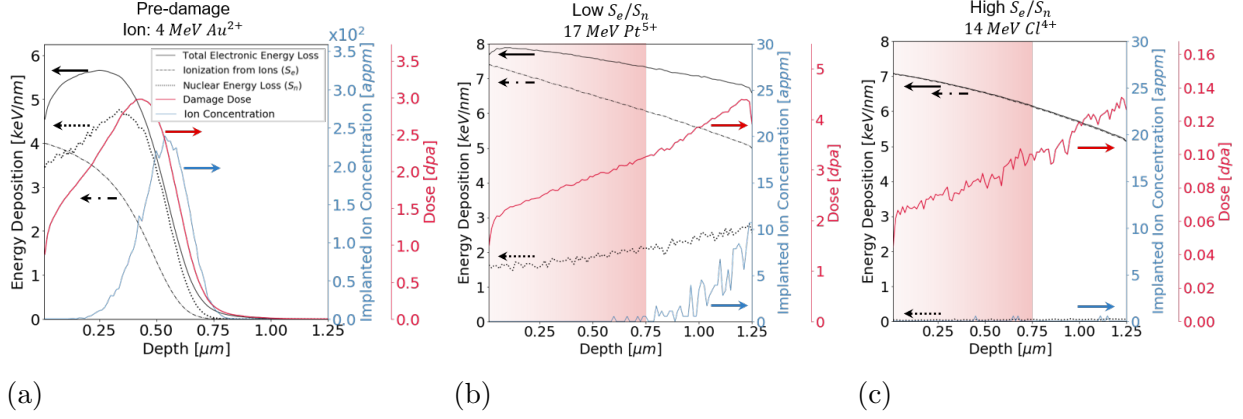


Fig. 3.6 – Energy deposition, damage dose (dpa), and ion concentration as a function of depth for (a) 4 *MeV* Au ions at a fluence of $5 \times 10^{14} \text{ cm}^{-2}$, (b) 17 *MeV* Pt ions at fluence of $1.76 \times 10^{15} \text{ cm}^{-2}$, and (c) 14 *MeV* Cl ions at a fluence of $1.76 \times 10^{15} \text{ cm}^{-2}$. The pre-damaged depth is marked as a red shaded region of interest in (b) and (c).

(0.5 μm -0.75 μm). However, due to the large difference in mass, and associated nuclear scattering cross sections, they each have a vastly different ratio of electronic to nuclear stopping power (S_e/S_n). The same fluence of $1.76 \times 10^{15} \text{ cm}^{-2}$ was selected for both the 17 *MeV* Pt and 14 *MeV* Cl irradiations to result in both similar S_e dose and a damage dose for the Pt ions that matches the Au ion pre-damage dose of 3 dpa, see Fig. 3.6a. Meanwhile, the lower dissipation by nuclear energy loss for Cl results in a significantly lower damage dose, see Fig. 3.6c.

3.2.3 Specific irradiation conditions

To irradiate to a specific fluence with the ions, beam currents are first measured using a faraday cup with an ion beam of known dimension. In this case, a standard $3 \times 3 \text{ mm}$ irradiation area is utilized at the IBML [65]. For example, this allows the calculation of the 9 *MeV* Ti^{3+} ion flux by:

$$\text{ion flux} \frac{\text{ions}}{\text{cm}^2 \text{ s}} = \frac{(\text{beam current } nA) \left(\frac{10^{-9} \text{ A}}{nA} \right) \left(\frac{C/s}{A} \right)}{(0.09 \text{ cm}^2) \left(3 \frac{\text{elementary charge}}{\text{ion}} \right) \left(1.6 \times 10^{-19} \frac{C}{\text{elementary charge}} \right)} \quad (3.3)$$

By regularly measuring the current in this controlled area and measuring irradiation times, it is possible to very accurately determine ion fluence, though a safety margin of 10-15% error in fluence is usually assumed to guarantee accuracy in dose [65].

Three total series of irradiations were conducted over the course of this study. The full details for irradiation conditions are included in Tables 3.1 and 3.2. The ion fluences selected for the 9 MeV Ti^{3+} ion irradiations were $(2.8, 3.5, \text{ and } 4.2) \times 10^{16} \text{ cm}^{-2}$, which correspond to a maximum damage dose of 20, 25, and 30 dpa, respectively, at the maximum depth region of interest ($2.0 \mu m$). For the 4 MeV Au^{2+} ion irradiations a fluence of $5 \times 10^{14} \text{ cm}^{-2}$ was selected, corresponding to a damage dose of 3 dpa at the damage peak. A fluence of $1.76 \times 10^{15} \text{ cm}^{-2}$ was selected for the 17 MeV Pt^{5+} and 14 MeV Cl^{4+} ion irradiations, which correspond to maximum damage dose of 3 dpa and 0.1 dpa, respectively, at the maximum depth region of interest ($0.75 \mu m$).

In all cases the beam was defocussed and slightly wobbled, mildly-rastered, to provide a uniform flux over the sample area: $8 \times 5 \text{ mm}$ for the room temperature irradiations, $4 \times 5 \text{ mm}$ for the elevated temperature irradiations, and $6 \times 4.5 \text{ mm}$ for the sequential irradiations. Samples were oriented with surface normal to the beam. To prevent beam heating and charge accumulation during room temperature, $25^\circ C$, high-energy Ti ion irradiations, beam current and flux were kept below $2 \times 10^{12} \text{ cm}^{-2} s^{-1}$ [66].

The sample stage cooling time constraints, detailed above, demanded a higher beam current than those used during the initial batch of room temperature irradiations; therefore, these fluences were repeated at the higher current, see Table 3.1, with temperature monitored to be approximately $50^\circ C$. This minor $25^\circ C$ beam heating appears consistent with the power density for the increased current, which is $\sim 1 \text{ W}$ for the irradiation dimensions and would therefore result in a low approximate beam heating rate ($< 20^\circ C \text{ s}^{-1}$) that simultaneously saturates for the highly thermally conductive material. For the sequential irradiation study, flux was reduced further and kept below $4.5 \times 10^{11} \text{ cm}^{-2} s^{-1}$ since significantly higher energies per ion were selected.

Table 3.1 –
Summary of the Ti ion irradiation conditions.

Cathode:	TiH ₂		Ions:	9 MeV Ti ³⁺	
Experiment Batch	Irradiation Temperature	Fluences [cm ⁻²]	Measured Current [nA] in (3 × 3 mm)	Equivalent Flux [cm ⁻² s ⁻¹]	
Batch I	25°C	(2.8, 3.5, 4.2) × 10 ¹⁶	~80 (78.5 – 85)	~1.85 (1.82 – 1.97) × 10 ¹²	
Batch II	25°C	2.8 × 10 ¹⁶	~80 (79.8 – 80)	~1.85 × 10 ¹²	
	50°C				
	500°C	(2.8, 3.5, 4.2) × 10 ¹⁶	~140 (116 – 151)	~3.24 (2.69 – 3.50) × 10 ¹²	
	880°C				

Table 3.2 –
Summary of the sequential irradiation study conditions. Equivalent damage dose (dpa) calculated from the damage peak in Fig. 3.6a and maximum depth probed of interest in Fig. 3.6b and 3.6c.

Cathode:	Au	Pt	AgCl		
Ion:	4 MeV Au ²⁺	17 MeV Pt ⁵⁺	14 MeV Cl ⁴⁺		
Energy Regime	Ion	Fluences [cm ⁻²]	Measured Current [nA] in (3 × 3 mm)	Equivalent Flux [cm ⁻² s ⁻¹]	
Low Energy	Au	5 × 10 ¹⁴	8	2.78 × 10 ¹¹	
High Energy	Pt	1.76 × 10 ¹⁵	~25.25 (25 – 25.5)	~3.51 (3.47 – 3.54) × 10 ¹¹	
	Cl		~23.25 (23 – 23.5)	~4.04 (4 – 4.07) × 10 ¹¹	
Sequential	Irradiations				
Experiment Batch	Ion: Low Energy	Ion: High Energy	Total Equivalent Damage Dose	Final Condition	
Batch III	4 MeV Au	–	~3 dpa	Pre-damage	
Batch IV	–	17 MeV Pt	~3 dpa	Low S_e/S_n	
	–	14 MeV Cl	~0.1 dpa	High S_e/S_n	
Batch V	4 MeV Au	17 MeV Pt	~6 dpa	Pre-damage + Low S_e/S_n	
		14 MeV Cl	~3.1 dpa	Pre-damage + High S_e/S_n	

3.3 Grazing incidence x-ray diffraction

All grazing incidence x-ray diffraction (GIXRD) studies were performed using a PANalytical X'Pert³ MRD, see Fig. 3.7, at The University of Tennessee Joint Institute for Advanced Materials (JIAM) diffraction facility. Specific details for the diffractometer, optics, and count times are detailed in Section 3.3.5 and Table 3.3.

3.3.1 X-ray diffraction overview

The basis of diffraction is Bragg's law [70]:

$$n\lambda = 2d \sin \theta \quad (3.4)$$

where $n\lambda$ defines the x-ray wavelength with higher order reflections, d is the d-spacing between the lattice planes, and θ is the angle at which diffraction occurs, the combination of these orientations and spacings colloquially referred to as the Bragg condition. The crystalline structure and atomic positions within that structure define how the material will diffract under the Bragg condition. Specifically the structure factor contribution to intensity is defined by [70]:

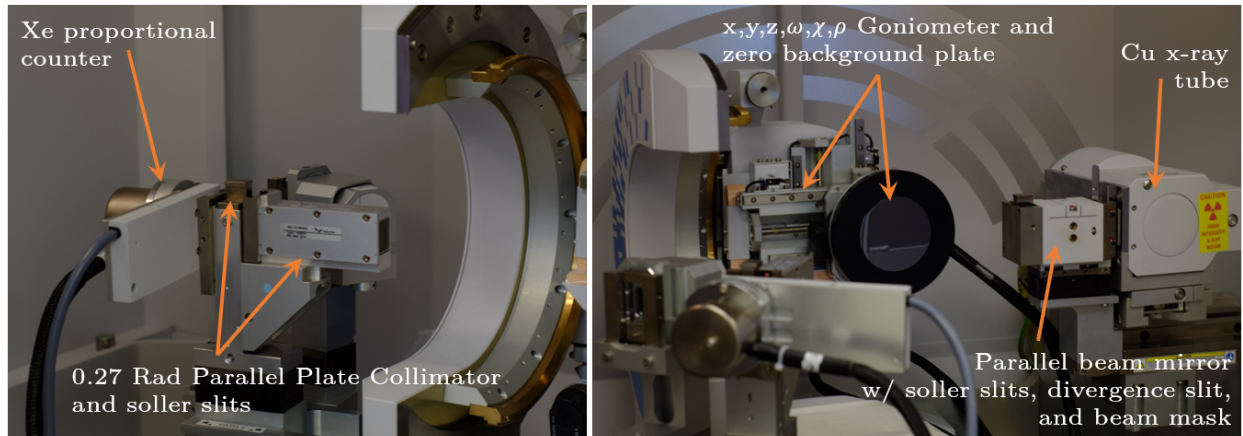


Fig. 3.7 – The diffractometer utilized for this study was a PANalytical X'Pert³ MRD located at the University of Tennessee Joint Institute for Advanced Materials (JIAM) diffraction facility.

$$F_{hkl} = \sum_{j=1}^N f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad (3.5)$$

where f is the atomic scattering factor for an atom located at the fractional coordinates, (x, y, z) , in the unit cell. The structure factor is the primary contributor to diffracted intensity such that $I_{hkl} \propto |F_{hkl}|^2$ and as such determines which planes will result in constructive or destructive diffracted beam interference when meeting the Bragg condition. This determines which diffracted intensities are present in the resulting profile and which are extinctions. Note, the structure factor is independent of crystal system and is purely based on atomic fractional coordinates [70].

3.3.2 The grazing geometry

Due to the attenuation of x-rays in materials, it is possible to control the penetration depth by selecting an incident grazing angle, ω , so that diffracting x-rays only have sufficient energy to escape the material for detection above a certain depth. The attenuation of x-rays in materials is defined by the following relation [71]:

$$I = I_0 e^{\mu t} \quad (3.6)$$

where μ is the material linear attenuation coefficient, t is the thickness traveled, and I_0 and I are the incident x-ray intensity and the intensity at thickness t , respectively [71]. By considering the x-ray refractive index of the material and the attenuation behavior, it is possible to determine the penetration depth of a parallel x-ray beam within a material as a function of its incident grazing angle. This is defined by the following relationships in [72]:

$$D(\omega) = \frac{\lambda\sqrt{2}}{4\pi \left[\sqrt{(\omega^2 - \omega_c^2)^2 + 4\delta_i^2} + \omega_c^2 - \omega^2 \right]^{1/2}}, \text{ where :} \quad (3.7)$$

$$\begin{aligned}
\omega_c &= \sqrt{2\delta} & \delta_i &= \lambda \left(\frac{\mu}{4\pi} \right) \\
\delta &= N_a \left(\frac{e^2}{2\pi m c^2} \right) \left(\frac{Z\rho}{A} \right) \lambda^2 = 2.701 \times 10^{-6} \left(\frac{Z\rho}{A} \right) \lambda^2
\end{aligned} \tag{3.8}$$

where ω and ω_c are the incident and critical grazing angles, δ and δ_i are the real and imaginary refractive index components, λ is the x-ray wavelength in $\text{\AA}$, μ is the linear absorption coefficient, Z is the average atomic number, A is the average atomic mass in amu , ρ is the mass density in g/cm^3 , N_a is Avagadro's number, e and m are the charge and mass of an electron, and c is the velocity of light [72].

The X-ray Interactions with Matter data tables, developed by The Center for X-ray Optics [73], tabulate the x-ray attenuation behavior in most elements and provide a tool for calculating the x-ray penetration depth in most compounds as a function of grazing angle, see Fig. A3.1 in Appendix A.3. TiC is a slightly better x-ray attenuator than Ti_3SiC_2 , and x-ray penetration behavior as a function of grazing angle is proportionate between the two materials. A linear relationship exists between phase concentration and the corresponding x-ray attenuation; therefore, given the expected variation in FCC-type profile contribution demonstrated in the literature, whether TiC or FCC-MAX, a rough concentration estimation allows for more precise selection of x-ray penetration depth, see Fig. A3.1. That said, it is generally conventional to use consistent grazing angles to make comparisons between samples, so the error in the selected penetration depths should be considered. To that end, an upper bound of 20% error is assumed in the TiC concentration estimations, which, due to the similarity between Ti_3SiC_2 and TiC x-ray attenuation, results in an average maximum calculated depth error of $0.04 \mu m$ for the selected grazing angles. This means the depths probed between samples may be considered consistent and the variation in penetration depth intervals selected for this study ($0.25 \mu m$) is significant.

Another factor to consider when selecting grazing angles is beam footprint. As the grazing angle is reduced, the beam footprint increases in area, especially at the low angled needed for the shallowest depth probed. It is vital that undesired regions are either positioned such that they remain unexposed to the x-ray beam or masked to prevent diffraction. In the

case of the high temperature irradiations discussed in Section 3.2.3, the clamps utilized to both fix the sample and protect the thermocouple monitoring sample surface temperature also prevent the irradiation of small corners of the sample, as shown in Fig. 3.4. The strain variation is expected to be fine; therefore, to prevent needing to deconvolute irradiated peak signal from pristine peak signal present due to these regions on already small sample surfaces, a combination of these strategies was employed. Precise measurement of the beam footprint was undertaken utilizing an alignment fluorescent disk to minimize the pristine region's exposure on the sample surface. In addition, Au was sputter coated over pristine regions to attenuate the x-ray beam, such that any x-rays intersecting the regions would not be able to penetrate the Au layer, diffract, and still have sufficient energy to escape and be detected. Au was selected for this masking task because it is a good x-ray attenuator and its polycrystalline x-ray profiles do not majorly overlap or interfere with the position of the Ti_3SiC_2 peaks.

3.3.3 Pristine analysis

Given the precision in strain analysis employed in this study, the pristine or pre-irradiated condition of each sample was carefully characterized prior to irradiations to ensure uniformity in starting lattice parameters between samples. GIXRD profiles were gathered for each pristine sample, probing depths of $0.5\ \mu\text{m}$ - $2.0\ \mu\text{m}$ in each. The profiles were then corrected as detailed below for the grazing geometry and peak fit using Origin-pro [74]. The fit peaks were indexed and ANOVA statistical analysis was performed, using the same software, comparing the indexed peak positions among samples. The ANOVA revealed a maximum statistical variance of 8.53×10^{-4} *degrees* 2θ within the peak positions which is statistically insignificant [74]. Therefore the samples may be treated as statistically equivalent in the pristine condition and samples held in the pristine condition may be used for future analysis as an accurate representation of the former pristine condition of irradiated samples.

3.3.4 Strain analysis and the iterative c/a method

Accurate changes in lattice parameters (LPs) between pristine and ion-irradiated conditions cannot be directly determined from peak position shift within hexagonal systems alone because the ratio between the c-LP and a-LP (c/a) must first be known [15]. It should be noted that there are many ways to arrive at this ratio. It may be determined by performing Rietveld refinements [75]; however, most software developed for this method do not fully account for x-ray absorption due to the grazing angle [76]. Additionally, it has been demonstrated that damage within the structure further complicates performing detailed analysis using this method [36]. Given that GIXRD is vital to this study and structural damage in some form is expected following ion irradiation, Rietveld analysis is not utilized in this study. It is also possible to select a c/a ratio from literature sources. That said, given previous ion irradiation results in this system, which demonstrate lattice distortion [13, 14, 30, 34, 36], it is unrealistic to assume the c/a ratio remains undistorted, thus making literature c/a ratios not viable for this application. Furthermore, c/a can be directly calculated by selecting peaks that isolate contributions to the c and a-LPs, such as the (008) or (110), respectively. The issue with this method is that it severely limits the number of peaks that can contribute to the calculation. Finally, the method utilized in this study is to use all the peaks measured to iteratively determine a c/a value that is self-consistent. To the best of the author's knowledge this is the first time this method has been applied to determine structural changes in lattice parameter within ion-irradiated hexagonal materials. As such, the method and its adaptation will be described in great detail in the following sections.

Integral to the iterative c/a method is measurement of d-spacing and peak positions from multiple ψ , to determine temporary stress tensors describing the system. Traditionally, this is accomplished by varying the incidence angle ω , and thus ψ , while measuring resultant peak position and d-spacing, as seen in the Fig. 3.8a, in what is known as the $\sin^2 \psi$ method for polycrystalline samples. By measuring at multiple ψ of a fixed (hkl), and rotating the sample about ϕ , it is possible to develop a picture of the stress tensor in the lab basis. However, this method does not allow for control over the depth probed within the sample, so other methods

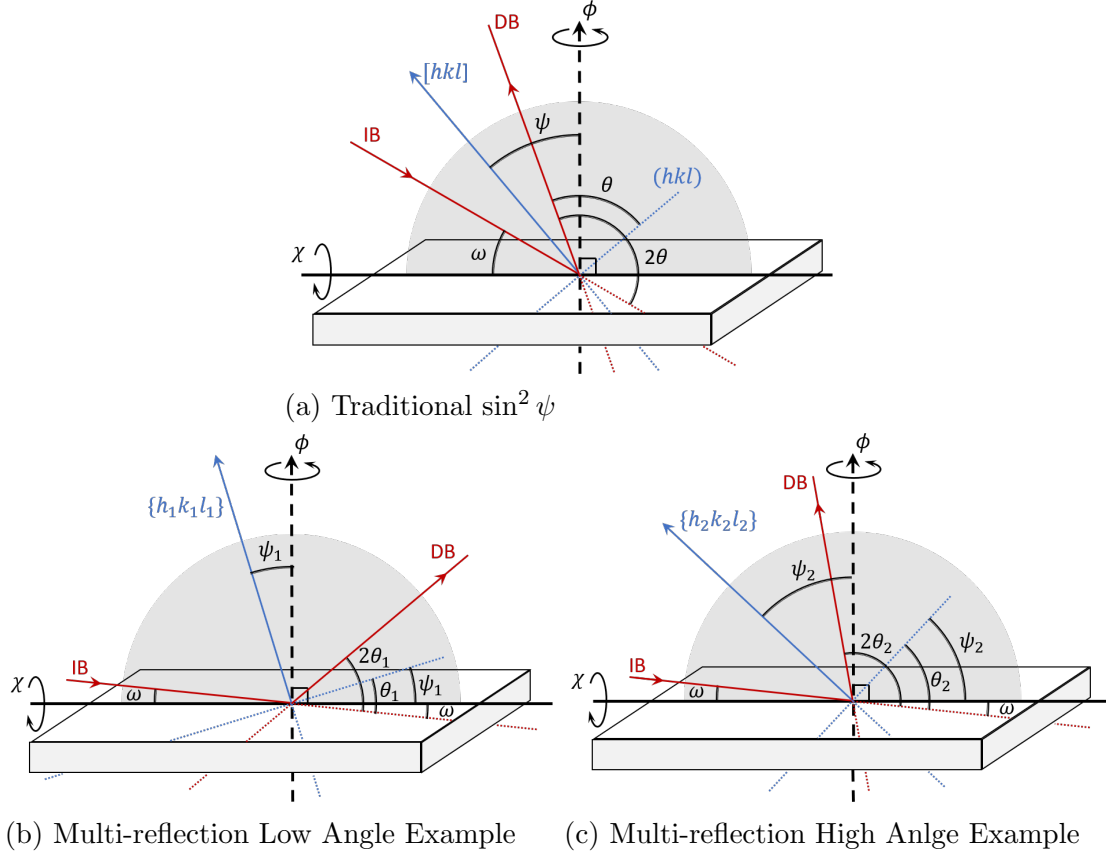


Fig. 3.8 – Comparison between the diffraction geometries for traditional $\sin^2 \psi$ and the multireflection method.

have been developed to achieving this control. The multi-reflection method accomplishes this by fixing the incidence angle, ω , and measuring the peak position of multiple reflections. In this way, multiple ψ are effectively measured at each measured reflection given the relationship, $\psi_{(hkl)} = \theta_{(hkl)} - \omega$, as demonstrated in Fig. 3.8b and 3.8c [15, 71], all while fixing the depth probed through the grazing geometry.

It should be noted that while using this method, χ is fixed at 0 such that angles measured in ω , ψ , and θ all take place in a plane normal to the sample surface. Further, ϕ may also be varied in this method, as it is in the $\sin^2 \psi$ method, to develop a complete picture of the stress tensor relative to the lab basis. However, this is not necessary for developing the temporary tensors utilized to determine a self-consistent c/a as texture has been demonstrated to not affect the c or a -LPs determined by this method. Therefore, in this case, ϕ is arbitrary and may be treated as zero, so long as all grazing ω are gathered consistently from the

same rotational orientation for each sample [15, 77, 78]. To implement the iterative c/a method described below, python 3.6 [79] scripts were written utilizing jupyter notebooks [80], and some of the jupyter cells used for the implementation are included with comments in Appendix B.

Correcting raw grazing profiles

The GIXRD profiles were corrected for Lorentz-polarization and absorption (LPA) effects on intensity, as these can influence the peak position. The Lorentz-polarization contribution to intensity is defined as a function of diffracted angle by [15, 71]:

$$LP(2\theta) = \frac{1 + \cos^2 2\theta}{\sin^2 \theta} \quad (3.9)$$

The absorption contribution to, or detracton from, relative intensity is dependent on both the fixed incident grazing angle, ω , and the diffracted angle as [15]:

$$Ab(2\theta) = \frac{1 + \tan(\theta - \omega) \cot \theta}{2} \quad (3.10)$$

It should be noted that refraction can also have a possible influence on peak position, but the incident angles selected for this study are large enough to make these effects negligible [15]. To correct the intensity of the profile, first the background is stripped and then intensity is corrected for LPA at each measured 2θ value in [15]:

$$I_{cor}(2\theta) = \frac{I_{exp}(2\theta) - I_{bkg}(2\theta)}{LP(2\theta)Ab(2\theta)} \quad (3.11)$$

where I_{exp} and I_{cor} are the experimentally measured and corrected intensities, I_{bkg} is the background intensity, and LP and Ab are the LPA contributions to intensity.

The c/a iterative method

The corrected profiles by the above method are indexed, and the peaks were fit using Origin-Pro [74], see Fig. A3.2 in Appendix A.3 for an example. These fit peaks may then be used within the iterative method. The first step in the iterative method is to assume a c/a value

from the literature and use the indexed peak locations in the relationship to determine the a-LP for each peak:

$$\begin{aligned} \langle a(\phi, \psi) \rangle_{(hkl)} &= \langle d(\phi, \psi) \rangle_{(hkl)} \cdot \\ &\cdot \left\{ \left[\frac{4}{3} \cdot (h^2 + hk + k^2) \right] + \frac{l^2}{(c/a)^2} \right\}^{\frac{1}{2}} \end{aligned} \quad (3.12)$$

$$\psi_{(hkl)} = \theta_{(hkl)} - \omega \quad (3.13)$$

where a is the calculated a-LP, d is the experimentally measured d-spacing for each peak, and ψ is determined by peak location and incident grazing angle, ω , as defined previously by the multi-reflection geometry in Fig. 3.8b and 3.8c. Once the a-LPs are calculated for each peak using Eq. (3.12), they are used to find the values for the stress tensor (σ_{ij}) and initial a-LP (a_0) via least squares fit of the relationship in Eq. (3.14) [15]:

$$\langle a(\phi, \psi) \rangle_{(hkl)} = [F_{ij}(hkl, \phi, \psi) \cdot \sigma_{ij}] a_0 + a_0 \quad (3.14)$$

where $F_{ij}(hkl, \phi, \psi)$ are the X-ray Elastic Constants (XECs) determined previously based on sample orientation as detailed in the next section using the method defined by Victor Hauk and Baczmanski *et al.* [71, 81] with known elastic properties for Ti_3SiC_2 [22]. Once σ_{ij} and a_0 are known, Eq. (3.14) is used again in reverse to determine theoretical values for the a-LP for each peak, once again based off the already determined XECs. These calculated a-LP values are used with the experimentally determined d-spacings in Eq. (3.15) as defined by the relations in Eq. (3.16) [15].

$$y = px, \text{ where :} \quad (3.15)$$

$$\begin{aligned}
p &= \frac{1}{(c/a)^2} & x &= l^2 \\
y &= \left[\frac{\langle a(\phi, \psi) \rangle_{(hkl), calc}}{\langle d(\phi, \psi) \rangle_{(hkl), exp}} \right]^2 - \left[\frac{4}{3} \cdot (h^2 + hk + k^2) \right]
\end{aligned} \tag{3.16}$$

A linear fit is performed on Eq. (3.15) to find the slope and thus a calculated c/a ratio as defined in Eq. (3.16). This new c/a is then inserted in Eq. (3.12) in place of the assumed c/a from the first cycle, and the processes is repeated iteratively until c/a has converged on a single value. This c/a may then be used to determine the c and a -LPs for the pattern using the multiple reflections present and Eq. (3.12) one last time, the mean and standard deviation of which may be reported for the profile. This technique not only determines a more accurate c/a value than what may be estimated given the expected lattice distortions, it utilizes all fit peaks to determine c/a , thus returning a value that is self-consistent across the diffraction profile [15]. Further, this method has been tested to be stable, and the quality of the initially assumed c/a value from the literature only determines the number of iterations needed for the c/a to converge on a self-consistent value; even an intentional 80% error in the initial assumed c/a does not influence the converged c/a value.

X-ray elastic constants (XECs)

The general relationship between the stress tensor solved for in Eq. (3.14) and the x-ray elastic constants (XECs) is described in [71, 81]:

$$\begin{aligned}
F_{ij}(hkl, \phi, \psi) \cdot \sigma_{ij} &= \frac{1}{2}s_2 [\sigma_{11} \cos^2 \phi \sin^2 \psi + \sigma_{22} \sin^2 \phi \sin^2 \psi + \sigma_{33} \cos^2 \psi] \\
&+ \frac{1}{2}s_2 [\sigma_{12} \sin 2\phi \sin^2 \psi + \sigma_{13} \cos \phi \sin 2\psi + \sigma_{23} \sin \phi \sin 2\psi] \\
&+ s_1 [\sigma_{11} + \sigma_{22} + \sigma_{33}]
\end{aligned} \tag{3.17}$$

where (hkl) are the miller indices, ψ and ϕ are defined for each (hkl) by the multi-reflection geometry in Fig. 3.8b and 3.8c, σ_{ij} is the stress tensor solved for in Eq. (3.14). The XECs, s_1 and s_2 may be described through different models. The Voigt model assumes a homogenous

strain of different crystallites and as such, s_1 and s_2 are independent of (hkl) and crystal symmetry and may be described by [71]:

$$\begin{aligned} s_1 &= \frac{-3}{2} \cdot \frac{x + 4y - 2z}{(x - y + 3z)(x + 2y)} \\ \frac{1}{2}s_2 &= \frac{15}{2x - 2y + 6z} \end{aligned} \tag{3.18}$$

$$x = c_{11} + c_{22} + c_{33}$$

$$\text{where : } y = c_{12} + c_{13} + c_{23}$$

$$z = c_{44} + c_{55} + c_{66}$$

where c_{ij} are the elastic stiffness tensor values for the material. In contrast, the Reuss model assumes a homogenous stress across the sample and as such the XECs s_1 and s_2 will be dependent on (hkl) . In a hexagonal system these are described by [71]:

$$\begin{aligned} s_1 &= \frac{1}{2} \gamma_i \gamma_j (\delta_{mn} - \gamma_m \gamma_n) S_{ijmn} \\ \frac{1}{2}s_2 &= \frac{1}{2} \gamma_i \gamma_j (3\gamma_m \gamma_n - \delta_{mn}) S_{ijmn} \\ \gamma_1 &= (1 - H^2)^{1/2} \cos \rho \\ \text{where : } \gamma_2 &= (1 - H^2)^{1/2} \sin \rho \\ \gamma_3 &= H , \\ \text{and : } H^2 &= \frac{l^2}{(4/3)(c/a)^2 (h^2 + hk + k^2) + l^2} \\ \rho &= \operatorname{arccot} \left(\sqrt{3} \frac{h}{2k + h} \right) \end{aligned} \tag{3.19}$$

where S_{ijmn} is the elastic compliance tensor for the material.

The Reuss model technically provides a superior determination of the XECs as it allows the XECs to vary depending on the (hkl) under investigation, which is important to account

for when high elastic anisotropy is present in a material. However, it has been demonstrated that the end resulting self-consistent c/a and stresses calculated using the Voigt and Reuss models are virtually identical. Further, the Voigt model was shown to more accurately determine c/a than the Reuss model in cases of low elastic anisotropy [15]. Given the minor elastic anisotropy in Ti_3SiC_2 [8] and the simplicity in implementation, the Voigt model was selected for XEC determination in this material.

3.3.5 Specific diffraction experiment conditions

Grazing incidence x-ray diffraction (GIXRD) profiles were gathered at the Joint Institute for Advanced Materials (JIAM) diffraction facility using a PANalytical X'Pert³ MRD in grazing geometry equipped with a Cu x-ray tube, Si parabolic parallel beam mirror, a 0.27° parallel plate collimator, and a Xe gas proportional counter. For a full list of optics utilized in alignment and the experiments, see Table 3.3. The scans were performed at increasing incidence angles, ω , in all samples to probe depths from $0.5\ \mu\text{m}$ - $2.0\ \mu\text{m}$ in $0.25\ \mu\text{m}$ intervals, providing a depth profile of the pristine and irradiated conditions. As stated earlier, ω was calculated using the x-ray penetration depth relation demonstrated in Fig. A3.1.

Full profile scans, $7\text{-}82^\circ\ 2\theta$, were gathered for each condition at a count time of $3\ \text{s}/\text{step}$, but this was increased in the case of the pristine analysis for batches beyond the first to $3.5\ \text{s}/\text{step}$ to compensate for the smaller sample size needed for high temperature and sequential irradiations. It was later determined that the extra time was not necessary to improve the counting statistics for these full profile scans, so later full profile scans for these were gathered at $3\ \text{s}/\text{step}$. To improve the counting statistics in critical regions of peak fitting, longer count times were used to scan over reduced ranges for shallower depths probed. A full list of the scan parameters is included in Table 3.3. This was not always necessary for deeper regions probed where scattering signal was reduced enough that improving the counting statistics had a negligible effect on quality of peak profiles.

In all cases, scans were gathered in batch files so a consistent alignment was utilized for a given sample such that fine adjustments to ω were equally consistent. In the cases where a reduced range was gathered, these scans were performed in the batches immediately

Table 3.3 –

Summary of the optics and parameters used in the GIXRD experiments on the PANalytical X'Pert³ MRD.

Optics:	Alignment	Experiment			
Incident Beam Path	2 mm mask, parallel beam mirror, 0.04 rad Soller slits, 1/32° divergence slits, Cu/Ni manual beam attenuator	2 mm mask, parallel beam mirror, 0.04 rad Soller slits, 1/8° divergence slits,			
Diffracted Beam Path	0.27 parallel plate collimator, receiving slit, large 0.04 rad Soller slits, Xe gas proportional detector	0.27 parallel plate collimator, large 0.04 rad Soller slits, Xe gas proportional detector			
Experiment	Sample Condition	Scan Type	Range	Step Size	Time/step
Batch I Room Temperature Experiment	Pristine	Full Profile	7-82° 2θ	0.02°	3 s
		Full Profile	7-82° 2θ	0.02°	3 s
	Ion Irradiated	Reduced Range	33-45° 2θ	0.02°	6 s
			57-64° 2θ		7 s
			70-80° 2θ		8 s
Batch II High Temperature Experiment	Pristine	Full Profile	7-82° 2θ	0.02°	3.5 s
		Full Profile	7-82° 2θ	0.02°	3 s
	Ion Irradiated	Reduced Range	33-45° 2θ	0.02°	6 s
			57-64° 2θ		7 s
			70-80° 2θ		8 s
Batch III-V Sequential Irradiations Experiment	Pristine	Full Profile	7-82° 2θ	0.02°	3.5 s
		Full Profile	7-82° 2θ	0.02°	3 s
	Ion Irradiated	Reduced Range	32-47° 2θ	0.02°	9 s
			57-65° 2θ		
			70-81° 2θ		

following their full profile counterparts such that both the alignment and ω are identical between full profile and reduced range scans. All scans were performed on a Si off-axis oriented single crystal wafer, which serves as a zero-background plate to reduce the signal from goniometer sample plate; however, totally eliminating the background scattering profile is unavoidable and accounted for in the profile corrections discussed previously.

3.4 Raman spectroscopy

Raman spectroscopy was used as a tool to corroborate some observations based on grazing diffraction profiles made in Chapter 6 and was performed at the Raman lab in the Materials Science and Technology (MST) Division of Oak Ridge National Laboratory (ORNL). The experiment parameters utilized were determined based on previous methods reported in the literature [40], on colleague recommendations, following the diffraction experiment results, and on facility capabilities. A Horiba LabRaman HR evolution with 785 *nm* laser was used to gather scans over the wavenumber range of 70-1800 cm^{-1} with a 600 *gr mm*⁻¹ grating, 5 × 20 *s* count times, and a 100× objective.

3.5 Transmission electron microscopy

Transmission electron microscopy (TEM) was performed using a double tilt stage in a ZEISS Libra 200 HT FE MC at an accelerating voltage of 200 *kV*, at the JIAM electron microscopy facility, see Fig. 3.9, to obtain micrographs and gather selected area electron diffraction patterns to analyze structural changes at deeper regions without surface contributions. The electron microscope was equipped with a field emission gun and monochromator, resulting in a near parallel beam without the use of a condenser aperture.

3.5.1 Focused ion beam lamella preparation

TEM lamella were prepared from pristine and irradiated conditions using a ZEISS Auriga Crossbeam scanning electron microscope (SEM) equipped with a field emission gun and a Ga focused ion beam (FIB), also at the JIAM electron microscopy facility. Pt was deposited

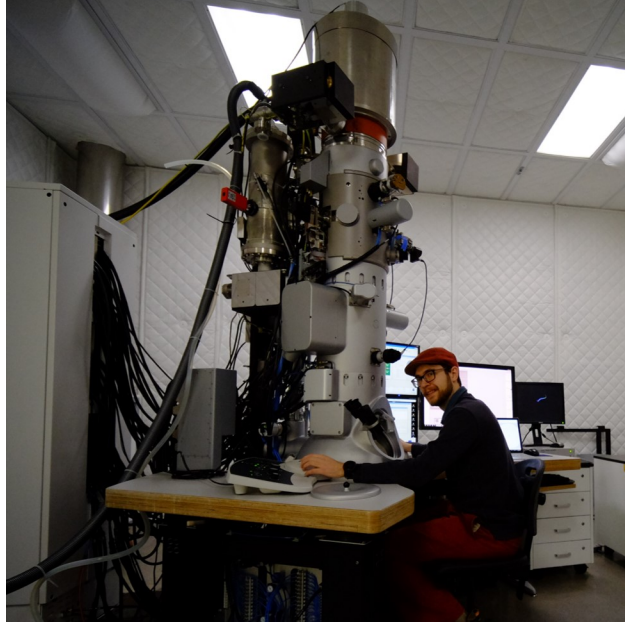


Fig. 3.9 – The transmission electron microscope (TEM) utilized for this study was a ZEISS Libra 200 HT FE MC located at the University of Tennessee Joint Institute for Advanced Materials (JIAM) electron microscopy facility.

on the surface to minimize artifacts from the milling procedure and protect the irradiation surface such that estimation of depth from the surface observed in TEM would be possible. Lamella were trenched, normal to the irradiation surface, taking care to only use larger probes (30 kV and $>2\text{ nA}$) away from the lamella cross section, and initially polished to a thickness of $\sim 1\text{-}2\text{ }\mu\text{m}$ before being welded to a W needle with Pt and material redeposition using a 30 kV , 100 pA probe. The lamella were then cut free of the trench, lifted out of the material surface, and transferred to a Cu lift out grid, where they were welded there using the same probe currents and deposition gas, before being cut free of the W needle. Trenching normal to the surface and lifting the lamella out results in a view orientation in the final, thinned lamella that is in cross section with the irradiation surface, thus allowing for characterization of irradiation depth by viewing normal to the ion path. Lamella were intentionally oversized to allow final thinning and polishing at least $1\text{ }\mu\text{m}$ away from regions where welding with larger probes occurred, to avoid artifacts of the weld, see Fig. 3.10 and A3.3, and final thinning and polishing were conducted with a maximum probe of 30 kV , 50 pA , reducing the milling current while thinning to minimize polishing surface amorphization. Fortunately, as previously mentioned, MAX phases are highly resistant to amorphization [37]. Crystalline

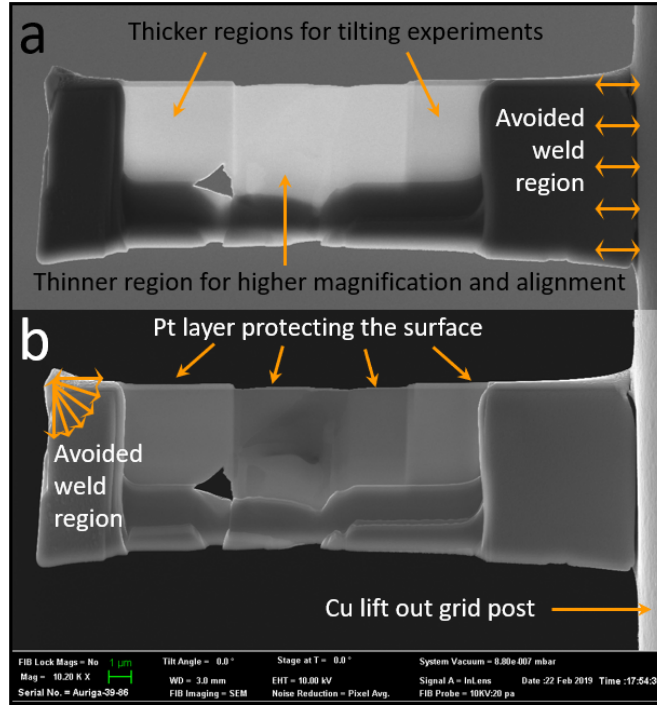


Fig. 3.10 – SEM micrographs of TEM lamella prepared using FIB lift out and polishing to produce a very thin region for high magnification imaging and alignment surrounded by regions left thicker for diffraction experiments, such as **g·b** and convergent beam electron diffraction (CBED). The lamella is imaged with secondary electron (a) and InLens (b) detectors.

orientation and tilting experiments were vital to this study; therefore, large regions thick enough for convergent beam electron diffraction and other tilting experiments, such as **g·b**, were included at final polishing probe quality in addition to regions thinned for higher magnification and alignment, see Fig. 3.10 and A3.3.

3.5.2 Electron diffraction overview

Electron diffraction works on the same principles as Eq. (3.4), except n is incorporated into d such that $1/2$, $1/3$, etc of real spacings between lattice planes are considered rather than second, third, etc order reflections. In this case, the electron diffraction pattern is defined by a zero-loss, undiffracted intensity and surrounding intensities which satisfy the Bragg condition in Eq. (3.4) at a distance defined by a vector $\mathbf{g}$, which is inversely proportional to the d-spacing by: $|\mathbf{g}| = |1/d|$ [82].

Selected area electron diffraction

Selected area electron diffraction (SAED) is a powerful tool for complimenting the depth profiles gathered using GIXRD. GIXRD, by its nature of using x-ray attenuation to control depths probed, will always contain some signal from shallower depths than the target depth probed, even if the relative intensity of this signal is reduced by scattering. SAED, by contrast, makes use of an aperture in the image plane to only allow portions of the beam that passed through a “selected area” (SA) of the sample to reach the detector, thus filtering the regions of the sample from which electron diffraction patterns are gathered. Since the samples are in cross section to the ion path, an SAED depth profile is possible through control over placement of the SA aperture. An added advantage for the Libra 200 is that since a condenser aperture is not required to produce near parallel illumination of the sample, the condenser apertures are utilized as SA apertures in this TEM. The apertures are still in the image plane of the microscope, but by using the condenser apertures instead of a more conventional SA aperture, the image of the sample is filtered by which portions of the sample are illuminated by the electron beam. This means that regions from which diffraction signal is not desired are not illuminated in the first place; therefore, they are unable to diffract, giving additional confidence in the regions the SAED patterns are collected from.

Brightfield (BF) / Darkfield (DF) contrast

Contrast in any TEM micrograph is determined by changes in the local diffracting condition of the lattice, whether disturbed by a defect, strain, lattice mismatch, etc. This means the contrast is highly orientation dependent, and is defined by the diffraction patterns. Integral to this study is the use of brightfield (BF) and darkfield (DF) contrast, which are simply images produced using either the zero-loss or diffracted beam, respectively. To most effectively produce this contrast, the sample lamella is tilted as close as possible to the Bragg condition for a diffracted plane defined by a vector $\mathbf{g}$, maximizing its relative intensity to make it closer to that of the zero-loss beam and creating a so called two-beam condition. A small objective aperture is then inserted in the diffraction plane to only allow either the zero-loss or diffracted intensity to pass through, and the beam illumination tilt is utilized to

conveniently alternate between the two intensities without the need to mechanically move the aperture. What results in the image plane is the ability to rapidly switch between contrast limited to the zero-loss beam, brightfield contrast, and the inverse of this contrast, produced from only the diffracted beam, darkfield. Alternating between paired images in brightfield and darkfield contrast, BF/DF pairs, can allow changes in contrast to be easier to observe. There are many forms of two-beam condition that can produce useful BF/DF pairs, including kinematical and weak beam; however, a two-beam dynamical condition is typically used in this study as the signal for the diffracted beam used in the DF image is maximized, thus increasing the range of contrast observed when alternating between the resulting BF/DF pairs [82, 83].

3.5.3 $\mathbf{g} \cdot \mathbf{b}$ method

Defects, such as dislocations, will have contrast that changes when tilted down specific viewing directions, so it is possible to use tilting experiments and the so called invisibility criterion to determine their character. Since contrast is highly orientation dependent, observation of dislocations is easiest when tilting to a two-beam condition near a zone axis that allows for its observation and examining the resultant BF/DF paired contrast images. The resulting contrast for the defect is then dependent on the dot product of the $\mathbf{g}$ vector defining the two-beam condition and the Burgers vector, $\mathbf{b}$, which defines the defect. When $\mathbf{g} \cdot \mathbf{b} > 0$, the defect will have contrast; however, when tilted to a $\mathbf{g}$ vector where $\mathbf{g} \cdot \mathbf{b} = 0$, there is a significant loss in contrast for the defect, making it invisible, or near-invisible, hence the name invisibility criterion. It is, therefore, possible to use tilting to test the effect on the contrast of a visible dislocation to determine its Burgers vector [82, 83].

Extensive tilting experiments can be required to locate the invisibility criterion and thus **b**. Fortunately, defects, including dislocations and interstitial dislocation loops, are well characterized in this MAX phase in both pristine and irradiated material, and they are known to typically reside in the basal plane with a $\mathbf{b} = 1/2[0001]$ [8, 14, 30]. Therefore, viewing down one of the prismatic zone axes parallel to the basal plane, such as the $[11\bar{2}0]$ will give contrast to the defects. Subsequent tilting to a two-beam condition near this zone axis with a $\mathbf{g}$ vector that results in a $\mathbf{g} \cdot \mathbf{b} = 0$ will make them disappear and confirm their

Burgers vector. For example, if near the aforementioned $[11\bar{2}0]$ zone axis, tilting to a two-beam condition with a $\mathbf{g}$ of either $[1\bar{1}00]$ or $[\bar{1}100]$ will result in near zero contrast for defects with a Burgers vector of $\mathbf{b} = 1/2[0001]$.

In addition, this method may be used to distinguish between basal dislocations and bulk ripplocations. It has been demonstrated that no invisibility criterion will result in a loss of contrast for bulk ripplocation defects [32]; therefore, if no $\mathbf{g}\cdot\mathbf{b}$ condition makes a defect invisible, it may be a ripplocation. These have been observed in this manner recently following high temperature neutron irradiation by D. Tallman *et al.* [33].

Chapter 4

Room Temperature High Fluence Irradiations

The results discussed in this chapter were previously published by William Alexander Hanson *et al.* in *Acta Materialia*: W.A. Hanson, M.K. Patel, M.L. Crespillo, Y. Zhang, W.J. Weber. Influence of electronic vs nuclear energy loss in radiation damage of Ti_3SiC_2 . *Acta Materialia* 161 (2018) 302-310. doi:10.1016/j.actamat.2018.09.027 [64]. The experimental conditions for the ion irradiations and subsequent characterization experiments performed for this room temperature analysis are detailed fully in Chapter 3 and Tables 3.1 and 3.3 and will not be repeated here.

4.1 GIXRD results

4.1.1 Profile disorder and peak shift

Full GIXRD profiles of deepest, shallowest and an intermediate depths of interest are shown in Fig. 4.1 with reduced ranges expanded for the shallowest depth probed. For ease of viewing, all profiles have had their backgrounds stripped and have been normalized with relative intensity staggered vertically. It is expected from the damage profile calculated and shown in Fig. 3.5a that the majority of damage as seen by peak broadening and shifting as well as phase intensity changes will increase with depth as the damage dose does; however,

that is not the case observed here. In shallower depths, broad disordered FCC-type peaks, typically associated with TiC, dominate the relative intensity. Ti_3SiC_2 peaks are visible at all depths and show little to no signs of broadening, though it is difficult to judge in shallower depths where the relative intensity of the FCC-type peaks is dominant. Shifting of the (008) and (110) peaks, see expanded views at ~ 40.8 and 60.3° 2θ , respectively, is clearly visible in the $0.5\ \mu\text{m}$ profiles but not in deeper regions, where calculated damage dose (dpa) is higher. This indicates the presence of strain in the lattice at these shallower depths and will be explored further below.

Peak shifting is more clear when examining GIXRD profiles about the (110) peak of Ti_3SiC_2 for three different fluences and the pristine condition, shown in Fig. 4.2, with relative intensity normalized and staggered; in addition, the relative intensity is also plotted as a heat map in the background. Each profile was collected from a different depth such that an equivalent damage dose of 7.6 dpa is probed for each fluence while electronic energy loss is varied, as demonstrated in Fig. 3.5b. Since the pristine profiles for each depth appear equivalent in peak position, the deepest corresponding depth is also indicated. Initial observations clearly show an apparent increase in TiC at all depths with broad disordered FCC-type peaks dominating the relative intensity of the profiles when probing shallower depths. The Ti_3SiC_2 phase is easily observed, contributing intensity at all depths, and appears to show little to no signs of broadening in the peaks, though like in Fig. 4.1, it is difficult to judge given the relative intensity of the FCC-type peaks at the shallowest depths probed. Peak shifting is also only evident in the shallower depths probed. This is especially clear when comparing depths probing comparable damage doses as shown in Fig. 4.2. For example, the three irradiated profiles shown in Fig. 4.2 probe different depths at the consistent damage dose of 7.6 dpa, and the (110) peak clearly shifts to higher *degrees* 2θ with decreasing depth probed. This indicates a contraction of the a-LP relative to pristine values at depths where electronic stopping power dominates.

Past studies have also observed major broadening in GIXRD peak profiles apparently isolated to peaks attributed to TiC while broadening of MAX peaks by comparison is observed to be less significant [36, 39]. A possible source for these isolated intensity changes can be seen by examining the structure factors of disordered Ti_3SiC_2 supercells, including

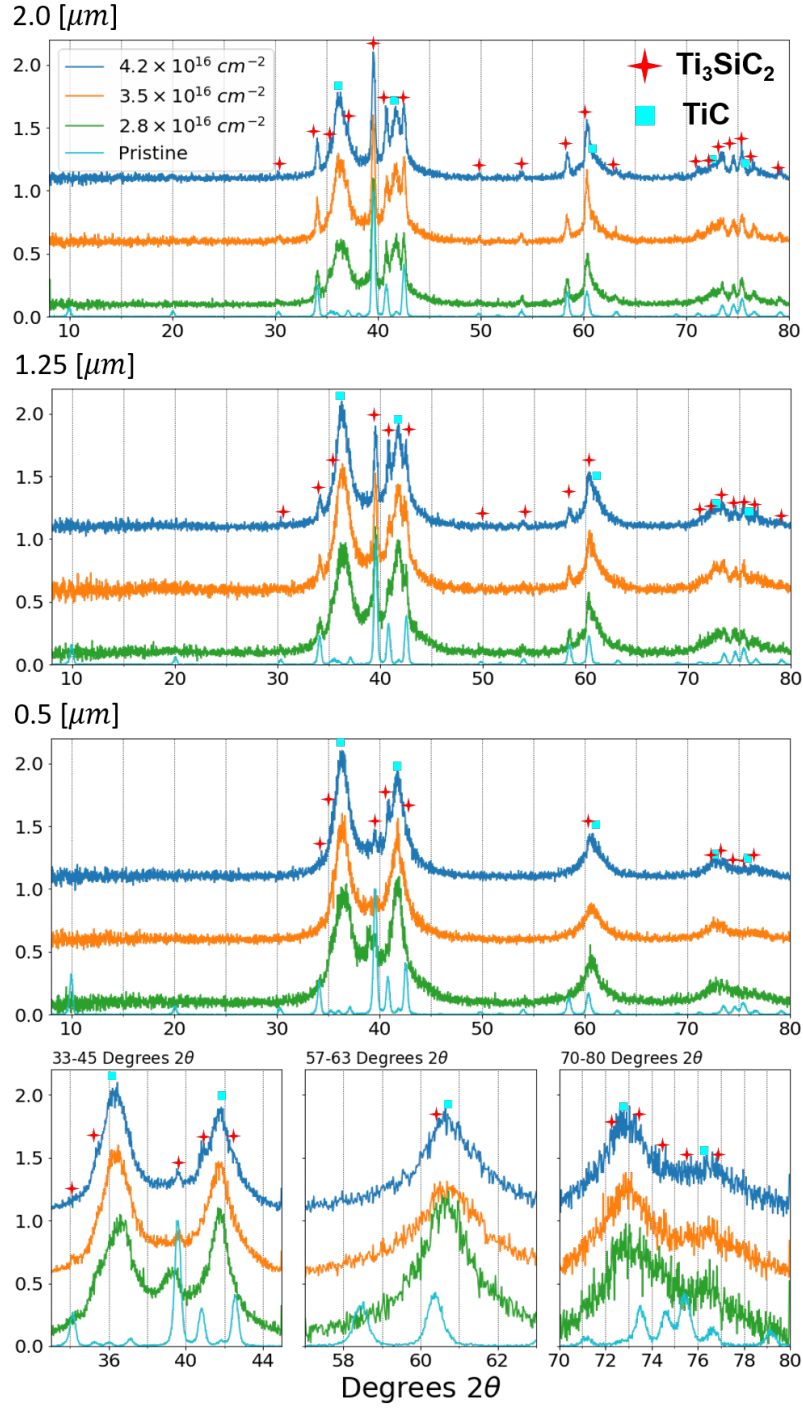


Fig. 4.1 – Full diffraction profiles for 2.0, 1.25, and 0.5 μm depths probed for the pristine and irradiated conditions with expanded views of the shallowest depth probed.

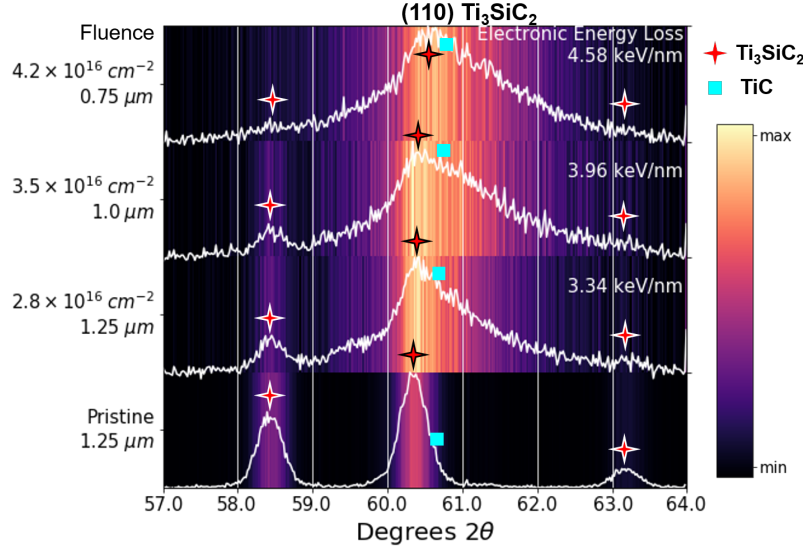


Fig. 4.2 – (110) peak profiles obtained from Ti_3SiC_2 irradiated at three different fluences. Each profile was collected from a different depth that corresponds to the same damage dose (7.6 dpa).

defects, as proposed by Liu *et al.* [47]. Minor peak intensity is observed in the profiles of partially disordered supercells near where TiC is expected in the profile. Given the largely unbroadened nature of the MAX profiles observed, this could suggest that a partially disordered MAX structure may contribute to the broad observed intensity at these peak sites rather than a full decomposition of the MAX phase into the TiC_x binary phase. It has been previously proposed that the Ti_3AlC_2 composition, which shares its structure with Ti_3SiC_2 , may form a chemically disordered structure that exhibits peak profiles similar to TiC_x [41]. The potentially convoluted contribution to the broad intensity near the TiC peak positions makes it difficult to quantify exactly any changes in concentration, but qualitatively it is clear that the relative intensity increases with decreasing depth and increasing electronic energy loss, as illustrated in Fig. 4.2. This parallels what is observed in the SAED patterns and discussed below in Fig. 4.6a and 4.6b, where intensity attributed to a nano-twinned FCC structure, such as twinned TiC_x , is observed. Given this evidence alone, a precise mechanism cannot be postulated; however, the separate effects study in Chapter 6 provides a more thorough discussion of these structural contributions to the GIXRD profiles, and proposes a mechanism for their formation.

4.1.2 Lattice parameter analysis

Utilizing the iterative self-consistent c/a method detailed in Section 3.3.4, lattice parameters for each condition have been determined as a function of depth, as shown in Fig. 4.3a and 4.3b. The pristine profile shows consistent c and a -LPs without statistical change, and the irradiated samples have c and a -LP values comparable to pristine values at deeper regions, 1.25-2.0 μm , where the damage dose is higher. As indicated by the (110) peak shifting in Fig. 4.2, all observed lattice strain is isolated to the shallower regions, where the damage dose is lower and electronic stopping power is dominant. At a fluence of $2.8 \times 10^{16} \text{ cm}^{-2}$, contraction of the c -LP and expansion of the a -LP are evident while for a fluence of $4.2 \times 10^{16} \text{ cm}^{-2}$, the opposite behavior, with c -LP expansion and a -LP contraction, is apparent. This latter result is similar to previous behavior under predominantly ballistic damage conditions [13, 14, 30, 36]. At the intermediate fluence of $3.5 \times 10^{16} \text{ cm}^{-2}$, only minor contraction of the a -LP and expansion of the c -LP are observed.

By applying the similar groupings of damage dose at different depths, it is possible to compare lattice strain in the system as a function of the energy deposition, as shown in Fig. 4.3c and 4.3d. At this point, a trend is clearly visible that in each grouped case, increases in electronic energy loss correlate to relative expansion in the c -LP and contraction in the a -LP. Further, these trends only begin when electronic energy loss exceeds a threshold of 4 $keVnm^{-1}$. Reexamining the peak shifting at 7.6 dpa in Fig. 4.2, the shifting of the (110) peak is clear at depths where electronic energy loss exceeds 4 $keVnm^{-1}$, and FCC relative intensity dominance in the profile increases with increasing electronic energy loss. This threshold will be discussed in more detail in Section 4.3.

The observed lattice strain results may be explained by interstitials trapped within the A-layers. Xiao *et al.* proposed these interstitials reside in-plane on the hexagonal interstitial sites (I_{hex}), which are the most energetically favorable sites under equilibrium conditions. In contrast, AIMD simulations by Liu *et al.* revealed that interstitials created by threshold displacement events often reside in-plane on the prismatic interstitial sites (I_{pri}); though, in many cases, Ti interstitial (Ti_I) also formed split interstitials with neighboring Ti atoms (Ti_2 site) above the I_{hex} sites between planes. In either case, these proposed defect diffusion

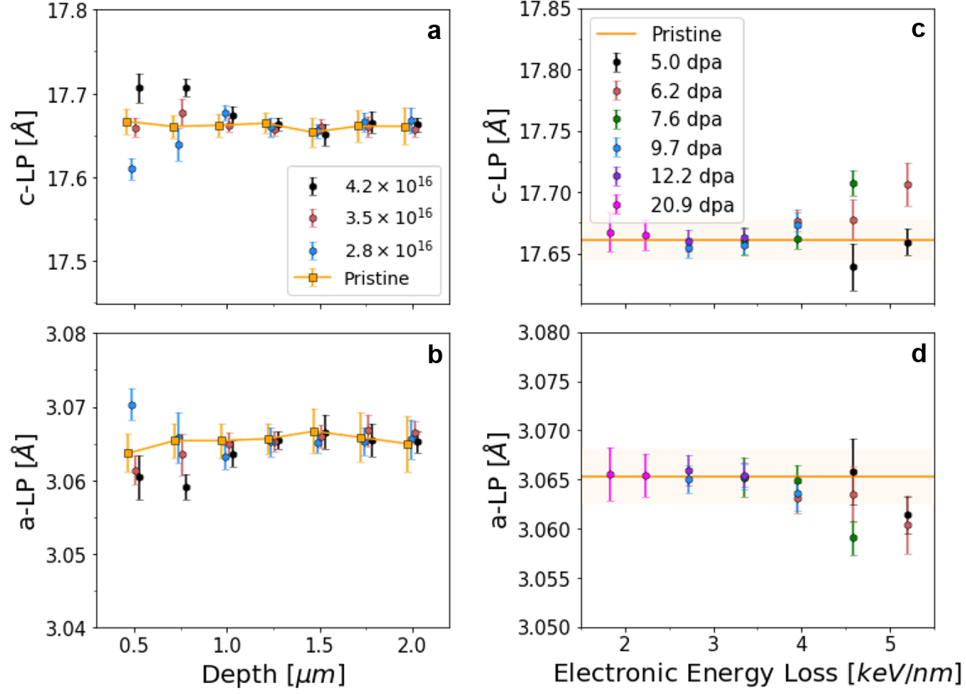


Fig. 4.3 – Lattice parameters (LPs) of the pristine and room temperature ion irradiated conditions (a-b) as a function of depth and (c-d) as a function of electronic energy loss.

mechanisms and sites could account for the changes in lattice parameter observed in the shallowest regions in Fig. 4.3a and 4.3b.

It has been calculated recently that Ti-Si anti-sites should also result in expansion and contraction of the c and a-LP, respectively, while C Frenkel pairs should lead to expansion of the a-LP and less expansion of the c-LP [27–29]. Given the similarity of their in-plane site occupancy, it is expected that Ti_I would have a similar influence on the c and a-LPs; though, in the case of the split Ti_I s, c-LP expansion and a-LP contraction is expected. The results in Fig. 4.3a and 4.3b, could be explained by initially trapped C_I and Ti_I within the basal layers, which with increased ion fluence either saturate or migrate to sites adjacent to the basal layer, thus resulting in the apparent relaxation to pristine LP values at the intermediate fluence. It should be acknowledged that it is possible that the seeming reverse in strain observed could be relaxation with increasing fluence from strain induced via polishing. However, given the consistent LPs recorded in the pristine sample at each depth in comparison to ion-irradiated samples when they were still pristine, this seem unlikely.

4.2 TEM results

The TEM lamella were oriented on the $[2\bar{2}01]$ zone axis and SAED patterns were gathered with the selected area aperture exposing approximately $0.25\ \mu\text{m}$ diameter section of the sample, as illustrated in Fig. 4.4 to 4.6. The $[2\bar{2}01]$ zone axis is advantageous because the MAX structure has near extinctions; meanwhile a nano-twinned FCC structure, such as TiC, has significant intensity contribution in the same orientation. Looking at the depth profiles from the irradiated surface of both the most and least exposed samples, 4.2×10^{16} and $2.8 \times 10^{16}\ \text{cm}^{-2}$ in Fig. 4.4 and 4.5, respectively, it is clear that the material is highly crystalline with only slight ring intensity, likely an artifact from FIB lamella preparation in this region. The $4.2 \times 10^{16}\ \text{cm}^{-2}$ irradiated sample shows intensity believed to be due to nano-twinned TiC strongly at shallowest depths and significantly weaker at greater depths. The $2.8 \times 10^{16}\ \text{cm}^{-2}$ irradiated sample shows the same intensity in the shallower depths, but signal again returns to near extinction levels typical of the Ti_3SiC_2 phase at depths further from the irradiated surface in the 1.25 to $2.0\ \mu\text{m}$ range. This appears to corroborate what was observed previously in the GIXRD results where Ti_3SiC_2 profiles were strong in relative intensity at greater depths probed, while broad FCC-type profiles were still visible, recalling that grazing incidence techniques include a signal from regions shallower than the desired depth; though, this signal is weaker.

These SAED depth profiles, which are isolated from irradiation surface conditions, further suggest that structural changes occurred in the near surface regions where electronic stopping power dominates, rather than where predicted damage dose is greater. By comparing the SAED patterns at two depths of the comparable dose of $7.6\ \text{dpa}$, as indicated by the example in Fig. 3.5b and Fig. 4.2, it is possible to once again see the influence of the S_e threshold to structural change. The nano-twinned FCC intensity is only visible in Fig. 4.6a, where electronic energy loss slightly exceeds $4\ \text{keVnm}^{-1}$. On the other hand, near extinctions are present in Fig. 4.6b, where electronic energy loss is slightly less than $4\ \text{keVnm}^{-1}$; though, each region corresponds to an equivalent damage dose of $7.6\ \text{dpa}$.

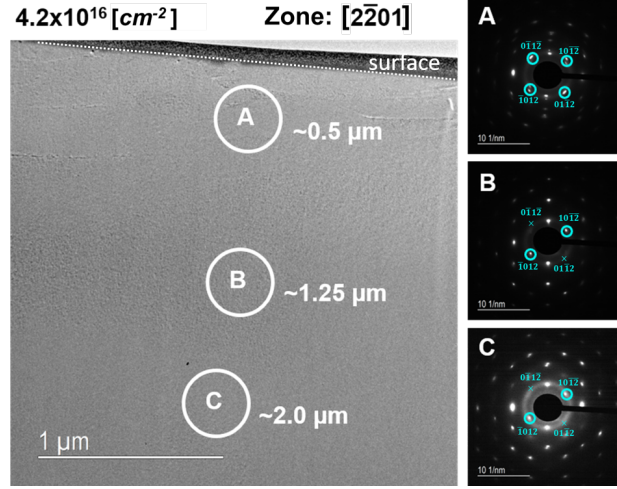


Fig. 4.4 – TEM micrograph of the room temperature $4.2 \times 10^{16} \text{ cm}^{-2}$ fluence with SAED depth profiles with aperture positioned at 0.5, 1.25, and 2.0 μm (A-C, respectively) from the irradiated surface. Blue rings encircle intensity believed to be due to a nano-twinned FCC structure, such as TiC, while near extinction values typical of the Ti_3SiC_2 are not encircled.

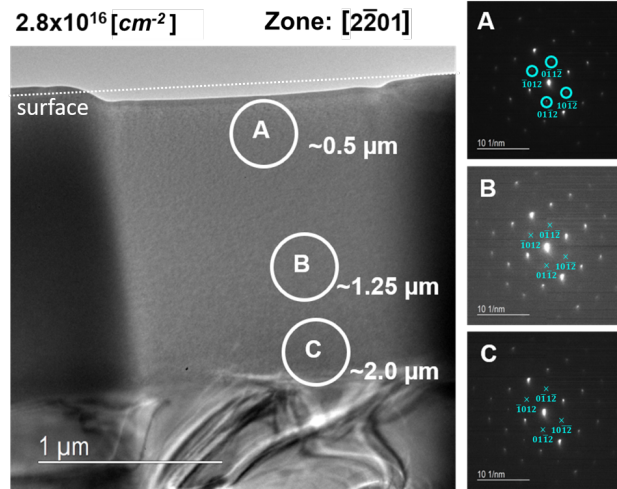
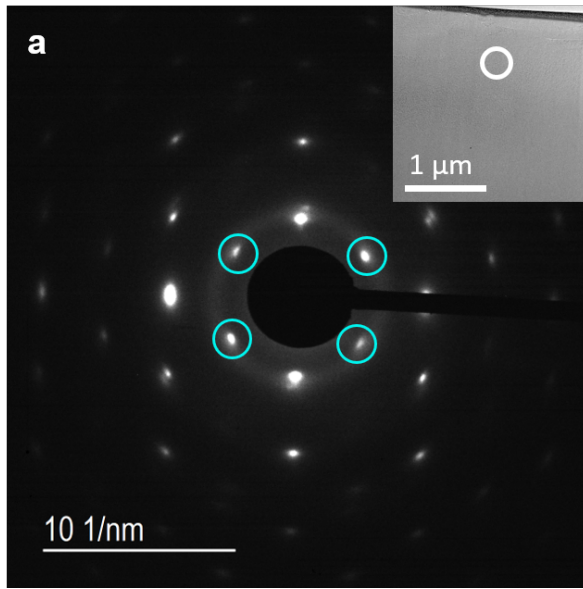


Fig. 4.5 – TEM micrograph of the room temperature $2.8 \times 10^{16} \text{ cm}^{-2}$ fluence with SAED depth profiles with aperture positioned at 0.5, 1.25, and 2.0 μm (A-C, respectively) from the irradiated surface. Blue rings encircle intensity believed to be due to a nano-twinned FCC structure, such as TiC, while near extinction values typical of the Ti_3SiC_2 are not encircled.

Depth: $\sim 0.75 \mu\text{m}$
Electronic Energy Loss: 4.58 [keV/nm]



Depth: $\sim 1.25 \mu\text{m}$
Electronic Energy Loss: 3.34 [keV/nm]

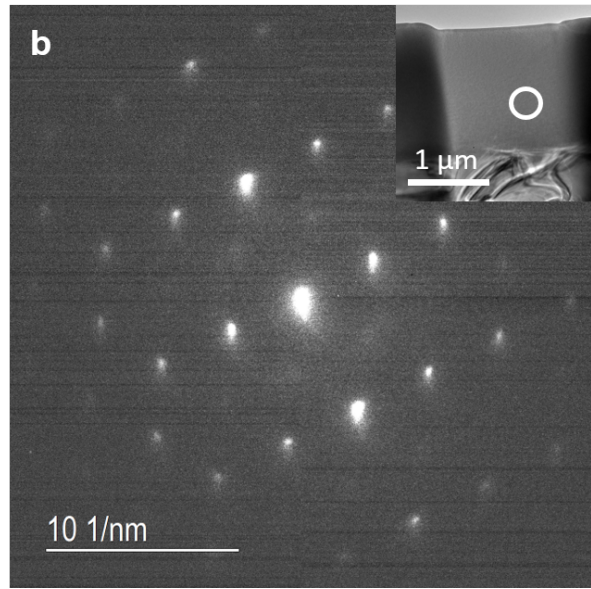


Fig. 4.6 – SAED patterns with corresponding TEM micrographs (insets) illustrating the selected area aperture location for the (a) 4.2×10^{16} and (b) $2.8 \times 10^{16} \text{ cm}^{-2}$ fluences. In each sample the orientation is about the $[2\bar{2}01]$ zone axis and the aperture is placed to probe an irradiation depth consistent with a damage dose of 7.6 dpa. Blue rings encircle intensity believed to be due to a nano-twinned FCC structure, such as TiC, in (a) while near extinction values typical of the Ti_3SiC_2 are observed in (b).

4.3 Threshold in electronic energy loss

A clear correlation has been observed between the near surface LP strain behavior and the electronic stopping power, as shown in Fig. 4.3c and 4.3d. At comparable doses, increasing electronic energy loss results in increased c-LP expansion and a-LP contraction above an apparent 4 keVnm^{-1} threshold in electronic stopping power. The same can be said for apparent TiC concentration increases in the near surface regions above the same threshold, Fig. 4.6a and 4.6b. In the past, little defect production or lattice strain has been attributed to electronic energy loss at levels below 28 keVnm^{-1} [34], but to the author’s knowledge the influence of S_e hasn’t been explicitly explored at fluences such as those employed in this study. Further, without the self-consistent c/a method utilized here, the strain effects may not have been readily visible within the lab-scale testing environment.

While this observed strain, where electronic stopping power dominates, might be attributed to an artifact of surface irradiation effects, this may be discounted for multiple reasons. Surface effects are typically exhibited as defect-free denuded zones adjacent to free surfaces and grain boundaries that are often limited to the first 100-200 nm of depth [4]. For this study, the shallowest depth probed is well beyond this typical depth of influence. Additionally, following high temperature neutron irradiation studies, defect-free denuded zones were only observed when irradiation temperatures exceeded 735°C [30, 33], which suggests higher temperatures are needed for irradiation assisted annealing of defects near free surfaces and grain boundaries. Therefore, there shouldn’t be much in the way of surface effects within Ti_3SiC_2 during RT irradiations.

It is likely these electronic effects are not due solely to electronic energy loss of single ions within the MAX structure. The ionization energy from a single 9 MeV Ti ion transferred to the lattice via electron-phonon coupling is likely insufficient to account for the observed defect production and eventual strain. It has been demonstrated that there is often a synergy between electronic energy loss and evolving defect concentrations, whereby evolving defects can significantly affect the dissipation of electronic energy loss, such that the thermal spike is more radially confined and greatly increased in temperature [55–57, 62, 63, 84, 85]. For example, if a similar behavior is assumed between Ti_3SiC_2 and

SiC, an electronic stopping power of 4 keV nm^{-1} results in thermal spike of $\sim 1000 \text{ K}$, and 6 keV nm^{-1} a spike $> 1600 \text{ K}$ [56]. In a recent study, Xue *et al.* found SiC to have an electronic energy loss threshold of 1.0 keV nm^{-1} for in-cascade annealing, a self-healing phenomenon [55]. Conversely, it has been shown in zircon that even when electronic energy loss is below 1.0 keV nm^{-1} there is an additive effect between the electronic and nuclear stopping powers that increases damage production [62]. In another case, the electronic energy loss, exceeding a threshold of 7 keV nm^{-1} , was shown to interact synergistically with pre-existing defects in strontium titanate to form damage tracks with diameter linked to the increasing S_e and defect concentration [63]. Another example can be seen in pure, unstabilized, monoclinic zirconia, which readily transforms into a tetragonal phase at low fluences when electronic energy loss exceeds a 12 keV nm^{-1} threshold [86].

The present study's results may parallel the behaviors in the latter oxide examples, strontium titanate [63] and zirconia [86], as exceeding an electronic energy loss threshold of 4.0 keV nm^{-1} results in increases in the c/a ratio and diffraction intensity resembling nano-twinned TiC, or other FCC structure, in the SAED patterns. This seems to suggest that above this low threshold, electronic energy loss contributes to enhanced defect production, and thus lattice strain, while also contributing to some form of phase transition. It is important to emphasize the apparent independence of this threshold from damage dose. Below the 4 keV nm^{-1} threshold, damage doses as high as 30 dpa in the $4.2 \times 10^{16} \text{ cm}^{-2}$ sample show no signs of strain relative to pristine values and have no signature from a nano-twinned FCC visible in the SAED patterns. Meanwhile, the opposite occurs at lower damage dose in regions where electronic energy loss exceeds the 4 keV nm^{-1} threshold.

These results confirm that these structural changes are more influenced by variation in electronic stopping power rather than increases in damage dose. It is further important to note that this is a true threshold in the energy dissipation to structural change. While nuclear stopping power is significantly higher at depths below the 4 keV nm^{-1} threshold, as can be seen in Fig. 3.5a, it is clearly demonstrated that the majority of energy dissipation is still due to electronic energy loss effects. Yet, being below the threshold in electronic stopping power, the structural changes are not observed. There are also implications for future comparison between neutron and ion irradiation results. Electronic energy loss must

be taken into consideration when selecting ions for studying irradiation damage events within this material. The next chapter, Chapter 5, will explore the influence of temperature and analysis of defects, while Chapter 6 will better separate the ion energy loss pathways.

Chapter 5

High Temperature High Fluence Irradiations

Some results in this chapter have been submitted by William Alexander Hanson *et al.* for publication in either Acta Materialia, Scripta Materialia, or the Journal of Nuclear Materials under the title: Influence of high temperature ion irradiations on electronic stopping effects and defect morphology in Ti_3SiC_2 . Any addendum to this submission will be detailed in the Tennessee Research and Creative Exchange (TRACE), where this research dissertation is stored. As in the previous chapter, the experimental conditions for the *in situ* high temperature ion irradiations and subsequent characterization experiments performed for this comparison to room temperature are detailed fully in Chapter 3 and Tables 3.1 and 3.3 and will not be repeated here.

5.1 GIXRD results

5.1.1 Profile disorder and peak shift

Full GIXRD profiles for the $2.8 \times 10^{16} \text{ cm}^{-2}$ fluence at each irradiation temperature for the deepest, shallowest, and an intermediate depth are shown in Fig. 5.1, and the same are plotted for the 3.5 and $4.2 \times 10^{16} \text{ cm}^{-2}$ fluences in Fig. A5.1 and A5.2 in Appendix A.5. For ease of viewing, the backgrounds were stripped and intensity was normalized and staggered.

As in the previous room temperature study, also shown in Fig. 5.1, at the shallowest depth probed for unelevated temperature irradiation conditions, the relative intensity is mainly dominated by broad FCC-type peaks. These broad FCC-type peaks are markedly absent in both the 500°C and 880°C irradiation conditions, suggesting that bulk annealing may prevent the structural change. It also appears that the slight increase in temperature to 50°C , due to beam heating, resulted in a reduction in the broad FCC profile relative intensity, compared to the true room temperature condition (25°C). For this repeated flux irradiation, the broad dominance of FCC-type peaks in the near surface area is also partially reduced as compared to the previous study. The pristine condition for this study appears to be more pure than that used in the initial study, so this may have played a role in the amount of FCC-type signal following ion irradiation. As before, the Ti_3SiC_2 MAX peaks appear to be largely unbroadened, but in the shallower depths shifting of peaks isolated to a single lattice direction such as (008) and (110) becomes evident at temperature less than 880°C . At the greater depths probed, as in the room temperature study, the MAX peaks intensity is more readily visible. In the case of the 880°C condition, the profiles are almost unchanged from those of the pristine condition; though, some relative intensity, which may be left over TiC from the pristine state, is visible.

5.1.2 Lattice parameter analysis

Once again utilizing the iterative c/a method, Section 3.3.4, lattice parameters for each condition were found with depth, plotted in Fig. 5.2. Clearly, in the unelevated conditions, shown in Fig. 5.2a and 5.2b, strain is again isolated to the near surface regions, where dose is lower and electronic stopping power is dominant. The reduction in flux to reproduce the original room temperature irradiation conditions at the $2.8 \times 10^{16} \text{ cm}^{-2}$ fluence resulted in a comparable magnitude in strain, both in the c and a -LPs, to those of the original study, see Fig. 4.3a and 4.3b. Once again it is clear that strain appears to recover toward pristine values at the intermediate dose of $3.5 \times 10^{16} \text{ cm}^{-2}$. Interestingly, the slight increase in temperature from 25°C to 50°C resulted in a slight increase in relative strain magnitude at the shallowest depths; though, the precise reason for this will not be apparent until Chapter 6. In the case of both high temperature conditions, see Fig. 5.2c to 5.2f, the relative strain of the c and

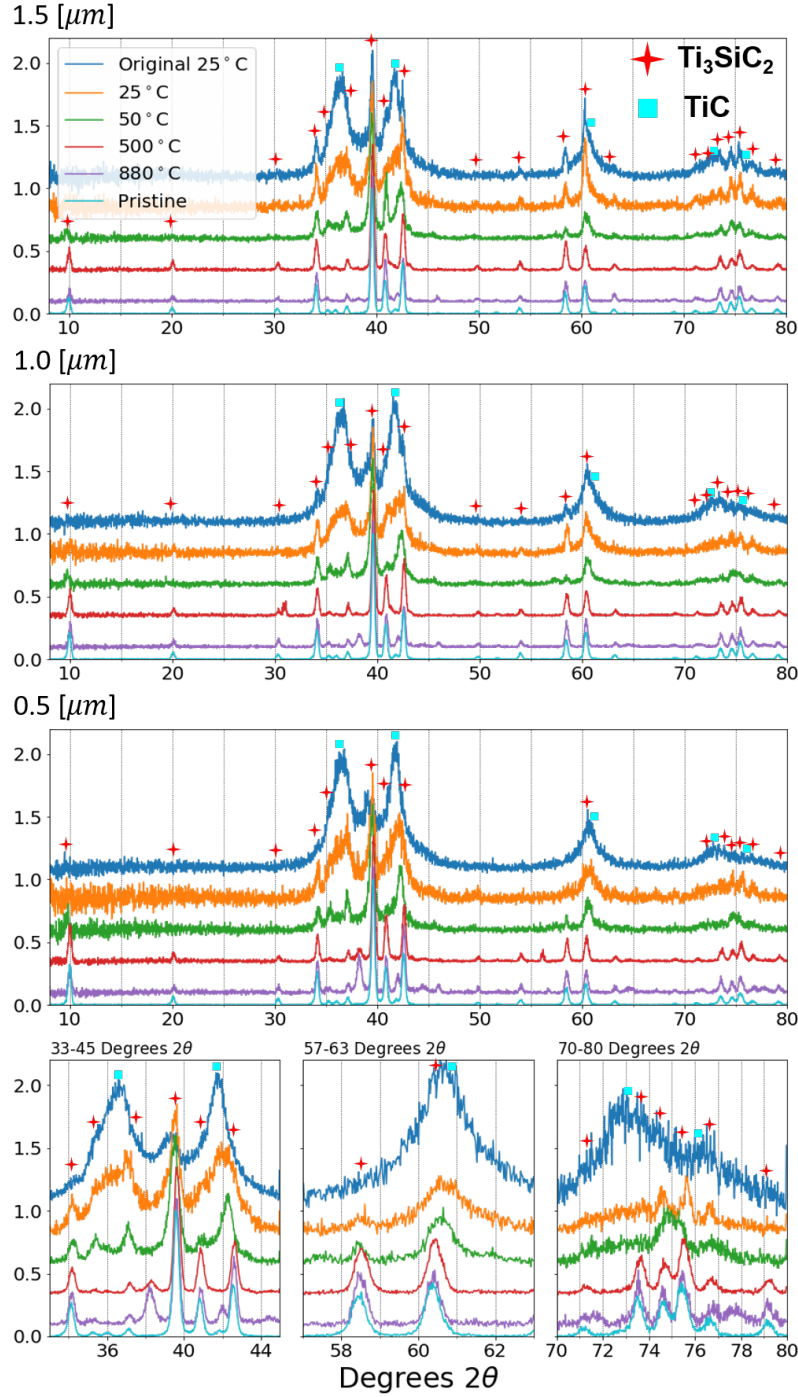


Fig. 5.1 – Full diffraction profiles for 1.5, 1.0, and 0.5 μm depths probed for the pristine condition and $2.8 \times 10^{16} \text{ cm}^{-2}$ fluence at each of the *in situ* irradiation temperature conditions with expanded views of the shallowest depth probed. Included is the $2.8 \times 10^{16} \text{ cm}^{-2}$ fluence from Fig. 4.1, and extended counting statistics for reduced ranges are detailed in Table 3.3.

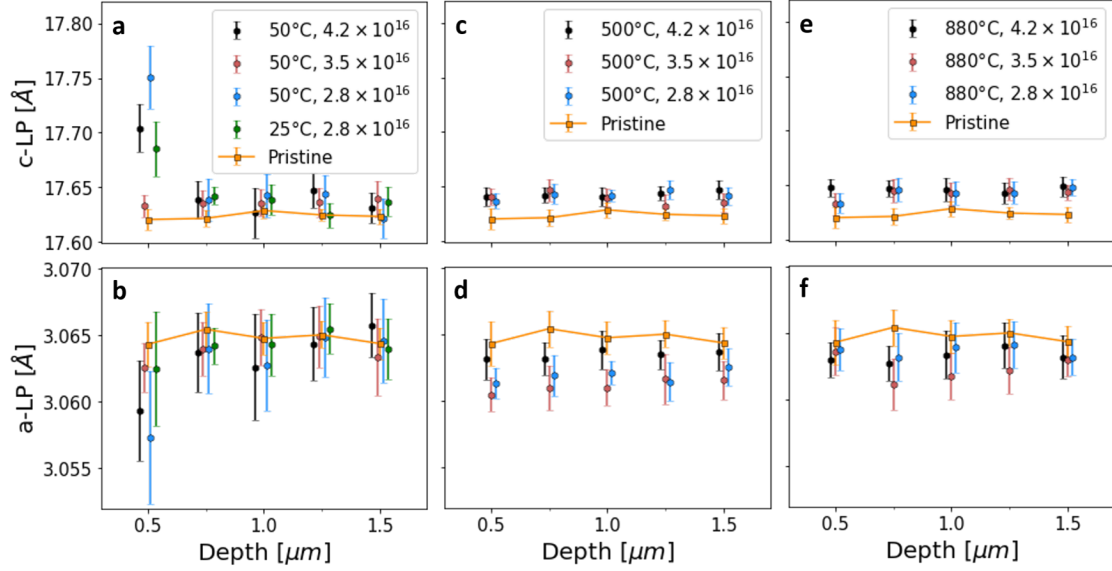


Fig. 5.2 – Lattice parameters (LPs) of the pristine and ion irradiated conditions as a function of depth following (a-b) room temperature, (c-d) 500°C , and (e-f) 880°C *in situ* ion irradiations.

a-LPs appears more uniform with depth for each fluence. However, the a-LP appears to recover at the shallowest depth for the 880°C condition in Fig. 5.2f.

These main effects behaviors between temperature and fluence may be more easily observed by comparing the determined self-consistent c/a for each depth, see Fig. 5.3a and 5.3b. In Fig. 5.3a, for unelevated conditions, distortion of the c/a in the near surface regions appears to partially recover at an intermediary dose. Further, this $3.5 \times 10^{16} \text{ cm}^{-2}$ fluence's c/a distortion appears more uniform with depth as compared to the lower and high fluences. Conversely, the c/a distortion following high temperature irradiations appears largely unchanged by fluence for each depth. In Fig. 5.3b, c/a vs irradiation temperature demonstrates that at the shallowest region, where electronic stopping power is dominant, increasing the irradiation temperature for the 2.8 and $4.2 \times 10^{16} \text{ cm}^{-2}$ conditions results in reducing the c/a distortion. However, for the intermediate $3.5 \times 10^{16} \text{ cm}^{-2}$ condition, the 500°C temperature leads to greater c/a distortion. At greater depths, the c/a distortion is closer to pristine values, but appears to increase slightly with irradiation temperature.

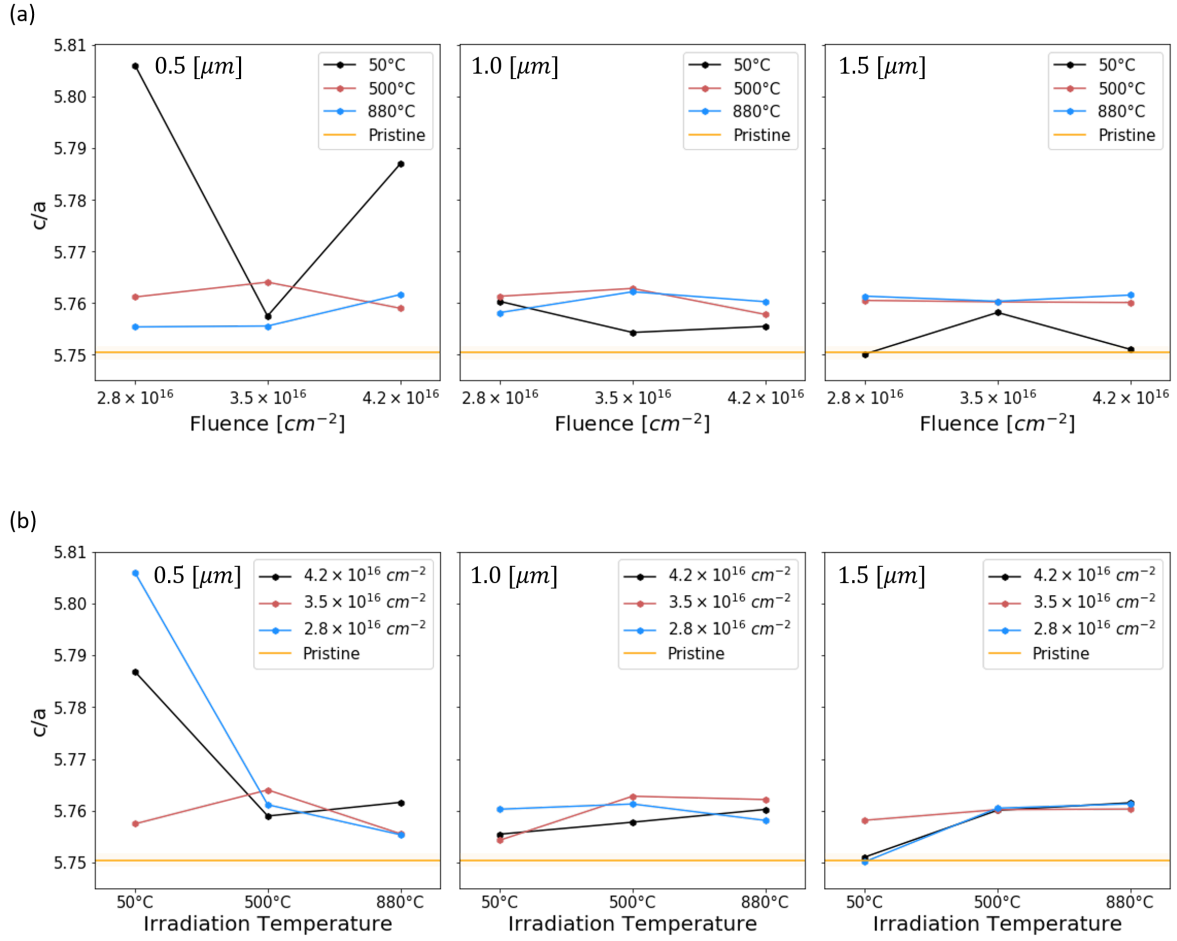


Fig. 5.3 – The iterative method determined self-consistent c/a (a) vs fluence and (b) vs *in situ* ion irradiation temperature.

5.2 Influence on electronic stopping power threshold

Using the same methodology to group comparable doses, as in the original energy deposition experiment in Fig. 3.5b, 4.3c and 4.3d, it is possible to once again compare the relative lattice strains observed with electronic energy loss, see Fig. 5.4. The minimum 4 keV nm^{-1} threshold in S_e still appears, and the magnitude of the strains observed at the highest electronic energy loss are greater than those observed in the original room temperature study, Fig. 4.3c and 4.3d; though, these are reduced closer to the threshold by comparison. This change in relative strain appears correlated to the reduced FCC phase dominance observed in the near surface regions for the 50°C conditions as compared to the reproduced 25°C condition; though, as indicated in the previous section, the precise mechanism behind this correlation will be clearer in Chapter 6. As for the high temperature *in situ* irradiation conditions, given the GIXRD profiles and resulting lattice parameter results, it appears that the effects of electronic energy loss above the threshold are largely mitigated by the bulk annealing during irradiation, so no trends are apparent through comparing relative lattice strain and S_e for these cases.

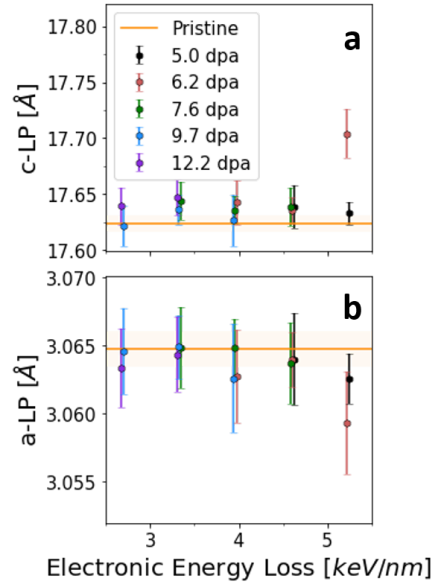


Fig. 5.4 – Lattice parameters (LPs) calculated as a function of electronic energy loss in (a) and (b) for the unelevated irradiation condition.

5.3 TEM: defect behavior

Given the changes in relative lattice strain response observed as a result of lattice parameter changes, analysis of the change in defect behavior is needed. As was previously described in Chapter 2, planar defects are well defined in this material system to be confined to the basal planes. As such, planar defects, whether perfect dislocation planes, dislocation loops, or stacking faults, are best viewed by imaging near a prismatic zone axis such as the $[11\bar{2}0]$ or the $[01\bar{1}0]$. Given the reduced tilt angles to satisfy possible visibility and invisibility criterion in the former, it is the preferred zone axis, but both may be used successfully for these tilting experiments. These dislocations, as indicated by the literature review earlier, are known to have a Burgers vector of $\mathbf{b} = 1/2[0001]$ [8, 14, 30]; therefore, invisibility criterion, as defined in Section 3.5.3, will be met when tilting to a $\mathbf{g}$ of $[1\bar{1}00]$ or $[2\bar{1}\bar{1}0]$, respective to the zones above.

Before exploring the influence of ion irradiation and elevated *in situ* irradiation temperatures, it is important to observe the defects typical within the pristine material. Fig. 5.5 shows brightfield (BF) and darkfield (DF) micrographs in two-beam conditions near the $[11\bar{2}0]$ zone axis and demonstrates that while the pristine condition does contain dislocations, they are typically <100 nm in diameter and relatively isolated. Further, the Burgers vector of the dislocations is confirmed to be $\mathbf{b} = 1/2[0001]$ by the loss of contrast when tilting from a $\mathbf{g}$ of $[\bar{1}101]$ ($\mathbf{g} \cdot \mathbf{b} = 1$) in Fig. 5.5b to a $\mathbf{g}$ of $[\bar{1}100]$ ($\mathbf{g} \cdot \mathbf{b} = 0$) in Fig. 5.5c.

A first look at the influence of *in situ* irradiation temperature can be made in Fig. 5.6 by imaging down the $[11\bar{2}0]$ zone axis, comparing the various irradiation temperatures at the same fluence ($2.8 \times 10^{16} \text{ cm}^{-2}$). It is possible to make initial observations of black spot defects and the presence of dislocation loops in each case, though the contrast in Fig. 5.6a, makes them very difficult to see. It is also observed that significantly higher concentrations of the dislocation loops follow the high temperature *in situ* irradiation conditions, Fig. 5.6b and 5.6c, and these appear to be more uniform with depth as compared to the unelevated irradiation condition. However, because of the low contrast, quantity of black spot defects, and the lack of strain contrast, it is very difficult to image the defects themselves, so two-beam conditions and BF/DF contrast will be used for the remaining analysis.

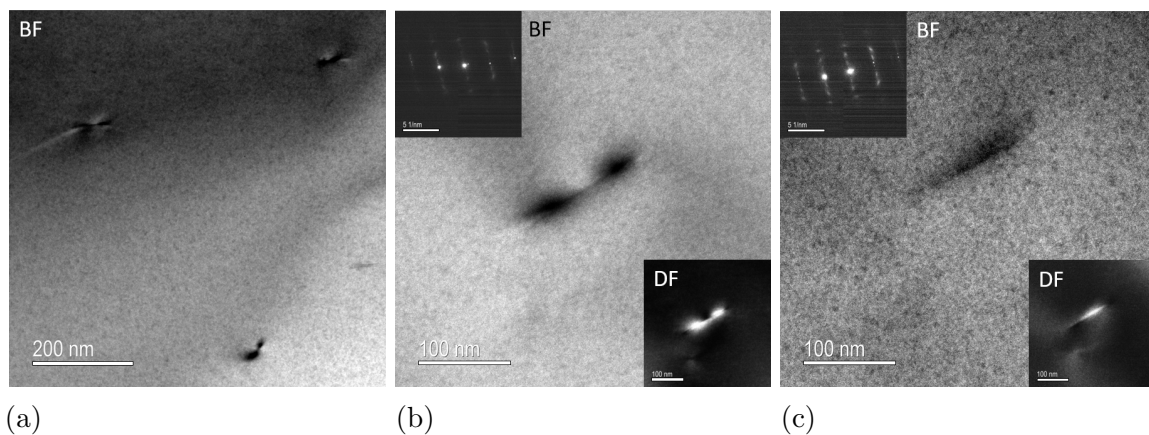


Fig. 5.5 – (a) and (b) Brightfield (BF) TEM micrographs of typical interstitial dislocation, possibly a partial loop, present in the pristine condition using a two-beam condition near the $[11\bar{2}0]$ zone axis with a $\mathbf{g}$ of $[\bar{1}101]$ as shown in the SAED pattern upper left inset in (b). When $\mathbf{g}$ is tilted to $[\bar{1}100]$ in (c), there is a loss in contrast for the defect, suggesting invisibility criterion is met. Paired, darkfield micrographs of the corresponding defects are shown in the lower right insets of (b) and (c).

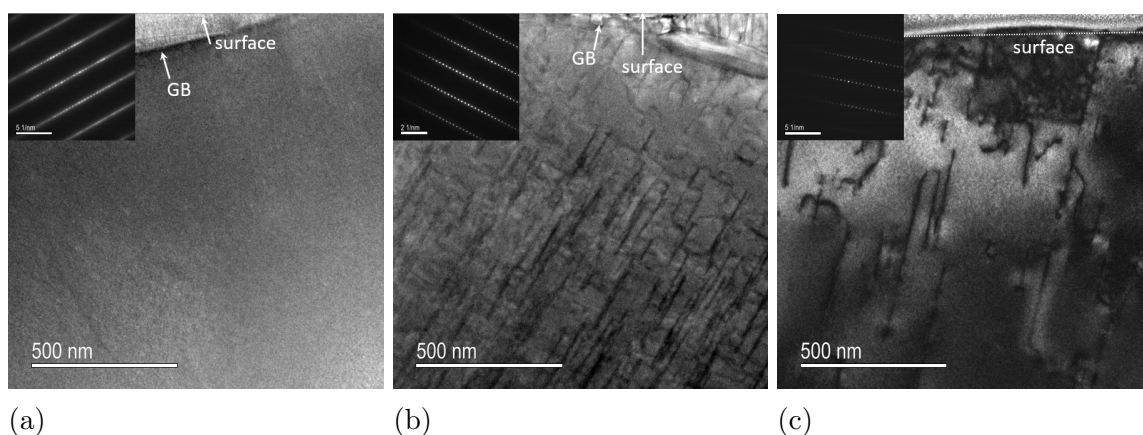


Fig. 5.6 – TEM micrographs near the irradiation surface for the $2.8 \times 10^{16} \text{ cm}^{-2}$ fluence at (a) 50°C , (b) 500°C , and (c) 880°C *in situ* irradiation temperatures. Each was imaged down the $[11\bar{2}0]$ zone axis, shown in inset SAED pattern, revealing black spot defects and dislocation loops in each.

To best explore the character of the defects present, the 880°C irradiation temperature for the $2.8 \times 10^{16} \text{ cm}^{-2}$ fluence was selected as shown in Fig. 5.7, which explores the invisibility criterion about the $[11\bar{2}0]$ zone axis. An overview BF micrograph and magnified view BF/DF paired micrographs for two $\mathbf{g}$ vectors are demonstrated: 1) a $\mathbf{g}$ of $[1\bar{1}01]$ in Fig. 5.7a and 2) a $\mathbf{g}$ of $[1\bar{1}00]$ in Fig. 5.7b. The loss of contrast for dislocation loops when tilting from the $\mathbf{g}$ vector in Fig. 5.7a to that in Fig. 5.7b, confirms that the $\mathbf{g} \cdot \mathbf{b} = 0$ invisibility criterion is met and the dislocation loops share the $\mathbf{b} = 1/2[0001]$ from the pristine condition. Further, it should be noted that there is a lack of Fresnel fringe contrast shift with focus and tilting of the loops, suggesting they are interstitial dislocation loops (IDLs). This matches with the IDLs observed in the literature following irradiation [14, 30] and makes sense given the low vacancy mobility and a literature demonstrated resistance to form bubbles without high fluences of He ions [87, 88].

The IDL diameter is observed to change with distance from the irradiation surface. Within a $\sim 350 \text{ nm}$ region from the surface, IDLs appear relatively small at $< 75 \text{ nm}$ with a few larger exceptions. A pileup of $\sim 50 \text{ nm}$ dislocation loops is observed at a stacking fault in the blue and green regions in Fig. 5.7a and 5.7b, respectively; though, there is little contrast for the stacking fault itself at this orientation. Beyond this region, in the bulk of the grain, IDLs are significantly larger, $\sim 240 \text{ nm}$, see the orange and yellow regions in Fig. 5.7a and 5.7b, respectively. This variation in size will be explored in depth in comparison to other *in situ* temperature conditions below.

There may be a few instances of contrast retention under the $\mathbf{g}$ of $[1\bar{1}00]$; though, these mainly appear as the partially dissociated Frank loops, intermediate to stacking fault tetrahedra, and examples of which are observed in the upper right corner of the blue and green magnified regions. In the past, extensive bulk ripplations, which share the appearance of IDLs but lack any invisibility criteria, have been observed following high temperature neutron irradiation [33]. While there may be some retention of contrast for some dislocations, example in the yellow region in Fig. 5.7b, this contrast is significantly less than that observed previously for bulk ripplations, suggesting it is more likely due to the stacking fault, which is pinning the IDL. While it is possible that small diameter ripplations may be present,

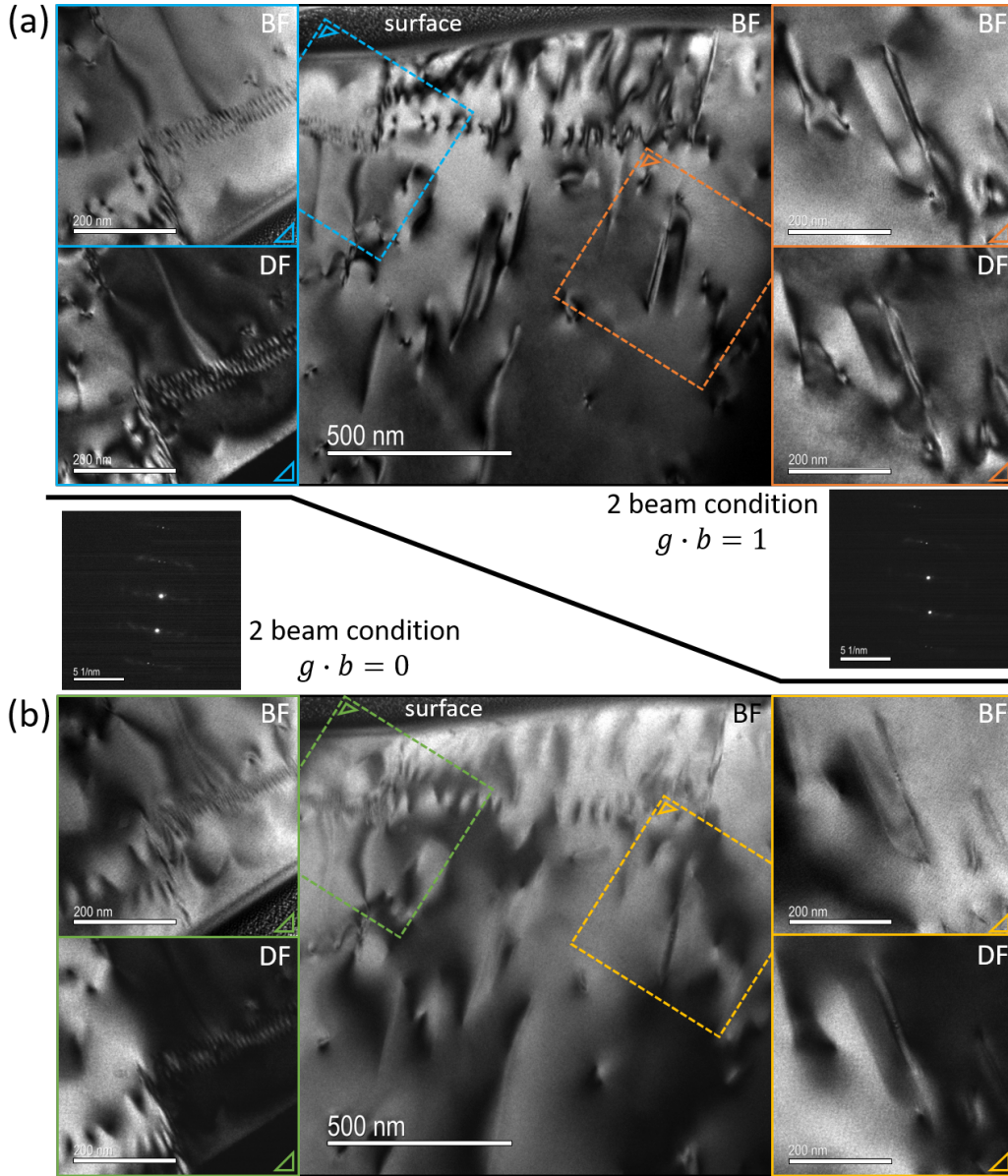


Fig. 5.7 – Brightfield and darkfield TEM micrographs of the 880°C *in situ* irradiation condition at a fluence of $2.8 \times 10^{16} \text{ cm}^{-2}$, imaged near the $[11\bar{2}0]$ zone axis. A two-beam condition was used with a $\mathbf{g}$ of $[1\bar{1}01]$ in (a) and $[1\bar{1}00]$ in (b), shown in their corresponding SAED patterns. Dislocation loops are clearly observed in (a), but contrast is lost when the $\mathbf{g}$ vector is changed in (b) indicating the $\mathbf{g} \cdot \mathbf{b} = 0$ invisibility criterion is met. Higher magnification brightfield, darkfield pairs are included and correspond to their adjacent colored, dashed boxes, with fiducial marks to indicate orientation change due to magnification rotation. The blue and green regions in (a) and (b), respectively, show a dislocation pileup at a stacking fault of $\sim 50 \text{ nm}$ dislocation loops near the irradiation surface. The orange and yellow regions in (a) and (b), respectively, show larger ($\sim 290 \text{ nm}$) dislocation loops further from the irradiation surface.

the lack of clear contrast and observed quantities demonstrated in the literature previously suggests they would be the exception rather than the rule in this case.

Examining Fig. 5.8, an analysis of the unelevated *in situ* irradiation conditions for the $2.8 \times 10^{16} \text{ cm}^{-2}$ fluence is conducted, comparing the 50°C slightly beam heated, due to a higher irradiation flux, condition to that of the true room temperature condition. A similar defect morphology is observed in each condition, with a large concentration of black spot defects across the samples and strain due to IDLs observed. Like in the 880°C sample above, a $\sim 350 \text{ nm}$ region from the irradiation surface is observed in the 25°C sample in Fig. 5.8c and 5.8d, where dislocation loops are generally $< 100 \text{ nm}$ ($\sim 90\text{-}135 \text{ nm}$) with a few exceptionally large ($\sim 100\text{-}250 \text{ nm}$) loops. A similar $\sim 350 \text{ nm}$ region is observed in the 50°C sample; though this region borders a grain boundary (GB) instead. This suggests that this region behavior is not associated with the irradiation depth, but with a boundary related to high interstitial diffusivity regions, or defect sinks, such as the irradiation surface or GBs in this case.

Beyond this region surrounding the sinks, IDL diameter variation in each sample remains with many significantly $< 100 \text{ nm}$ and many observed as partially dissociated Frank loops, with occasional full stacking fault tetrahedra. While the behavior near the sinks does not appear correlated with a distance from the irradiation surface, beyond that boundary region the IDLs appear to reduce in diameter then abruptly ceases at $\sim 1 \mu\text{m}$ from the irradiation surface in each sample. $1 \mu\text{m}$ from the irradiation surface corresponds to where electronic energy loss for the 9 MeV Ti ion drops below the 4 keV nm^{-1} threshold in S_e . This suggests that for unelevated irradiation temperatures, an electronic energy loss exceeding the 4 keV nm^{-1} threshold assists in the consolidation of defects into relatively small IDLs and eventually partially dissociated Frank loops.

It should be acknowledged that even using BF/DF pairs, it is very difficult to estimate the loop diameter in these samples due to the overall reduced contrast. That said, it may be judged that the two unelevated conditions' response is very similar, and since the contrast in the 50°C sample is clearer, due to the reduced tilt angle necessary to reach the $[11\bar{2}0]$ zone axis, it may be substituted for the 25°C sample for demonstrating the unelevated 9 MeV

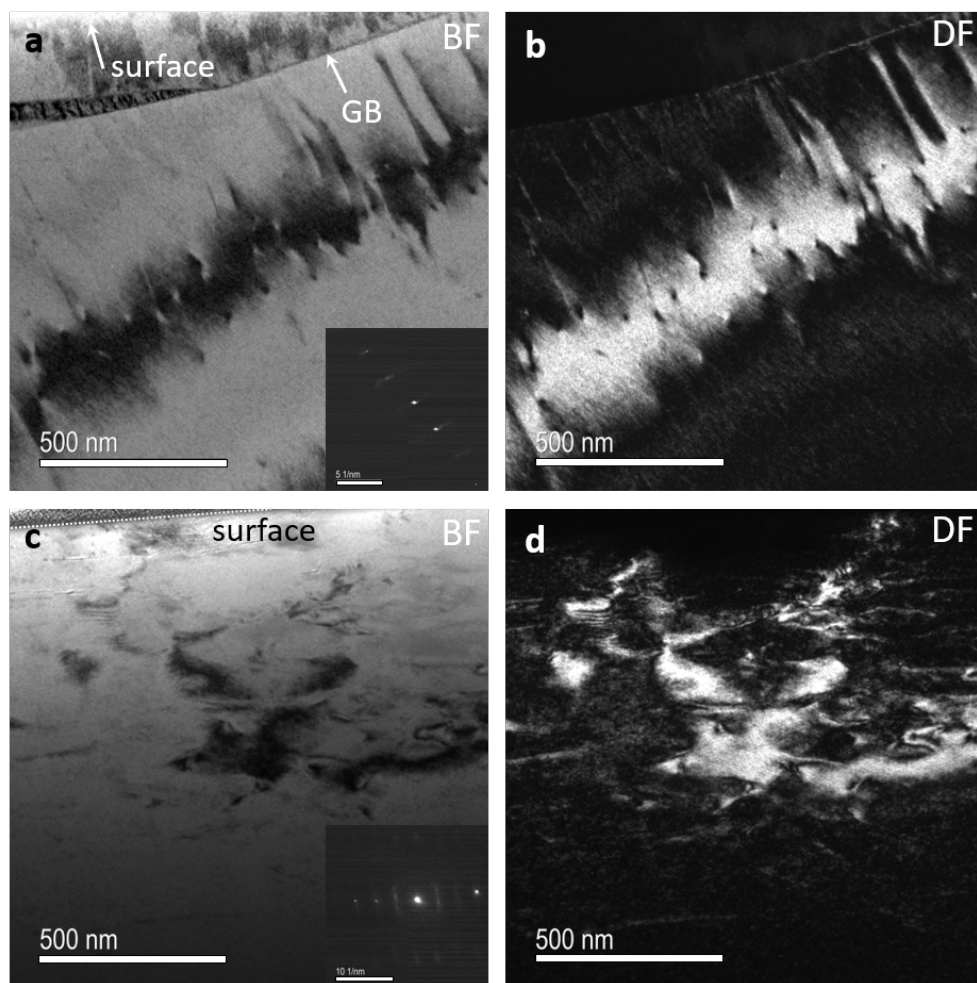


Fig. 5.8 – Brightfield, darkfield paired TEM micrographs of $2.8 \times 10^{16} \text{ cm}^{-2}$ fluence with effective *in situ* irradiation temperatures of 50°C (a and b) and 25°C (c and d), each imaged in a 2 beam condition near the $[11\bar{2}0]$ zone axis with a $\mathbf{g}$ vector of $[1\bar{1}00]$ and $[3\bar{3}00]$, respectively shown in the SAED insets in (a and c).

Ti condition. This will reduce focus depth-of-field issues for future analysis utilizing SAED depth profiles in Chapter 6.

Moving forward to consider the influence of high *in situ* temperatures on the defect behavior, Fig. 5.9 and 5.10 are paired figures showing BF/DF pairs of the 500°C and 880°C temperatures for the 2.8, 3.5, and 4.2×10¹⁶ cm⁻² fluences. Like in the pristine and unelevated conditions, the IDLs observed following both high temperature conditions meet the invisibility criteria to indicate a $\mathbf{b} = 1/2[0001]$, see the split BF/DF contrast micrographs in Fig. 5.9b, 5.9d, 5.10b and 5.10d. Starting with the 500°C condition for comparison, the bulk of the grains show large, uniform concentrations of IDLs with variation in diameter, ~230 nm with some >350 nm, for the 2.8×10¹⁶ cm⁻² fluence in Fig. 5.9a. This apparent uniformity of IDLs with depth could explain the reduced and more uniform relative lattice strain observed with depth in Fig. 5.2c and 5.2d, since it is known clustering of point defects into IDLs will serve to relax both the structure and relative strain [13, 30]. At the higher fluence, 4.2×10¹⁶ cm⁻² in Fig. 5.9c, this average diameter appears slightly reduced at ~150 nm, but it is likely that these IDLs are renucleated within loops whose diameters have exceeded the lamella thickness. This increase in IDL concentration is consistent with the more relaxed strain compared to lower fluences in Fig. 5.2c and 5.2d.

Looking to the 880°C *in situ* condition in Fig. 5.10, once again there are large IDLs with high variation in diameter, ~240 nm with some >380 nm, observed near the center of the grains with occasional small loops <100 nm in diameter. As compared to the 500°C condition, the loops in this grain bulk are slightly larger in each case, but appear to be in lower concentrations compared to the relatively lower high temperature condition. Looking at both high temperature conditions, the ~350 nm boundary around sinks with reduced IDL diameter, typically <75 nm with occasional larger loops ~100-200 nm, is present in each sample. In the case of the 880°C samples, the region bounding the irradiation surface has a higher concentration of relatively small IDL pileups than the 500°C samples, which could explain the relaxation in relative lattice strain toward pristine values observed in Fig. 5.2e and 5.2f. It is interesting to note that in the case of the unelevated *in situ* irradiation temperatures, the ~350 nm region bounding the sinks, while consistent in IDL diameter behavior as compared to the high temperature irradiations, represents the largest diameter

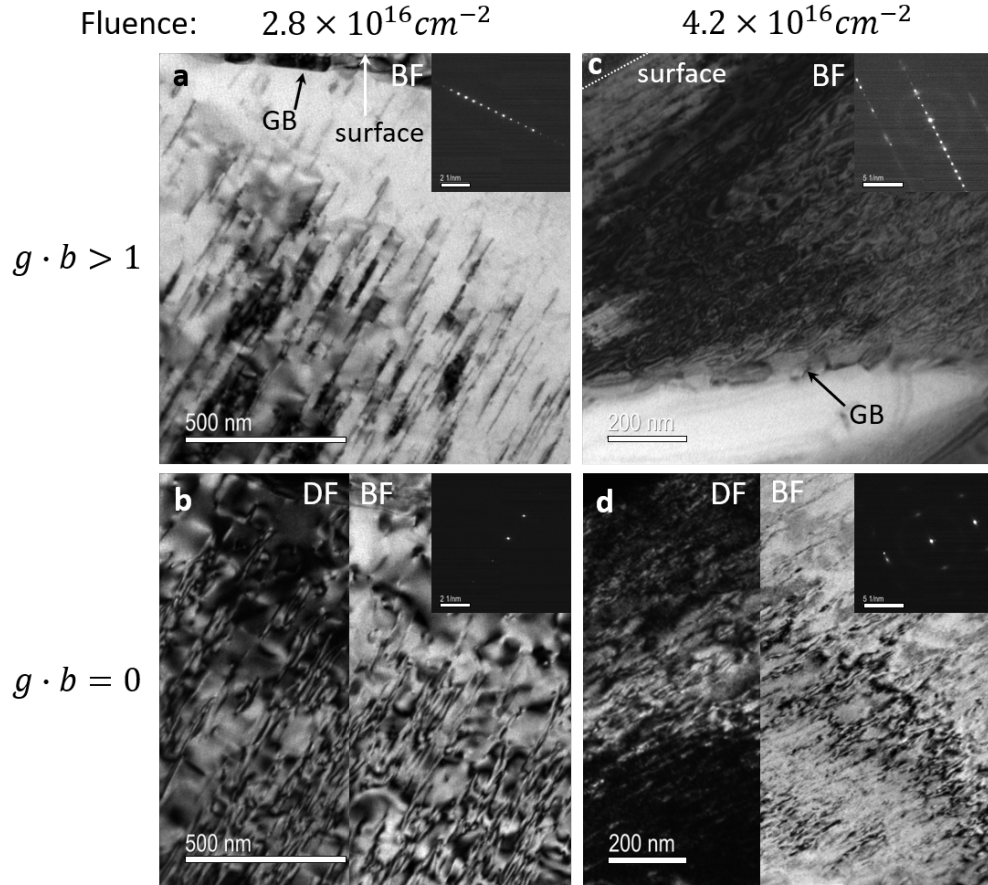


Fig. 5.9 – Brightfield and darkfield TEM micrographs of the 500°C *in situ* irradiation temperature for fluences $2.8 \times 10^{16} \text{ cm}^{-2}$ (a and b) and $4.2 \times 10^{16} \text{ cm}^{-2}$ with SAED insets indicating orientation. (a and c) are brightfield micrographs imaged near the $[11\bar{2}0]$ and $[01\bar{1}0]$ zone axes, respectively, and dislocation loops are clearly visible while in (b and d) their contrast is lost when tilting to $\mathbf{g}$ vectors of $[1\bar{1}00]$ and $[2\bar{1}\bar{1}0]$, respectively. Note the contrast is split over the region between brightfield and darkfield contrast using this two-beam condition.

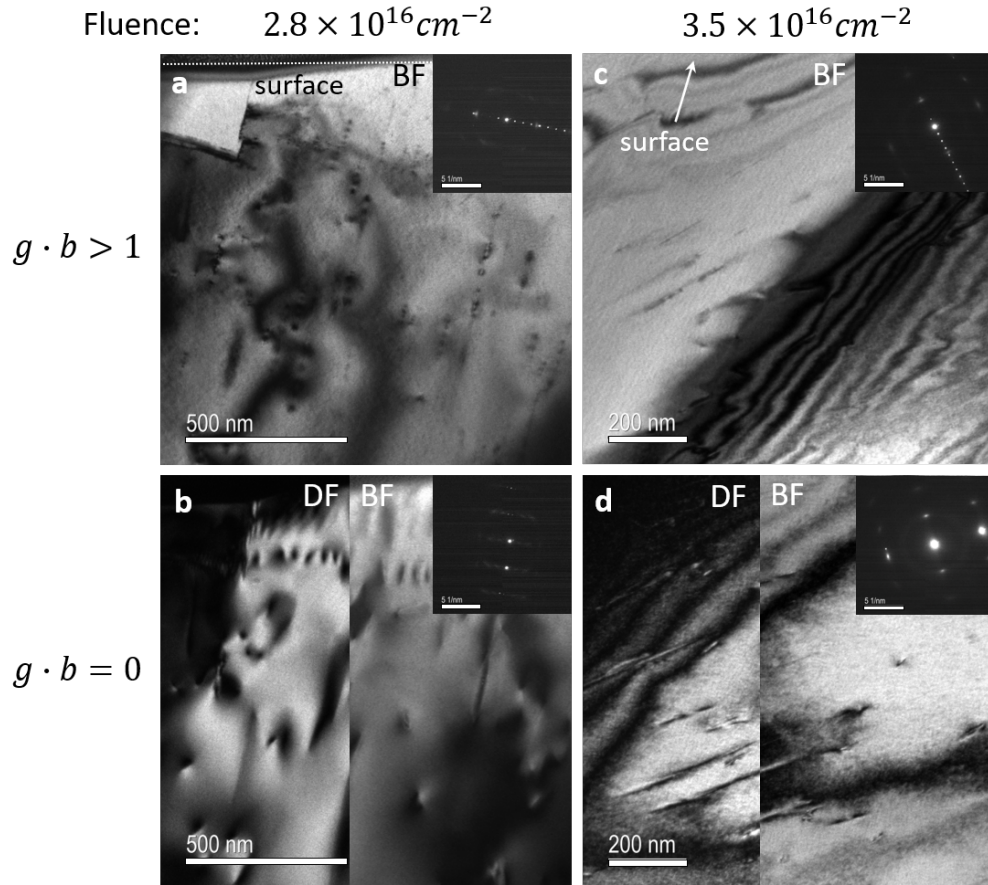


Fig. 5.10 – Brightfield and darkfield TEM micrographs of the 880°C *in situ* irradiation temperature for fluences $2.8 \times 10^{16} \text{ cm}^{-2}$ (a and b) and $3.5 \times 10^{16} \text{ cm}^{-2}$ with SAED insets indicating orientation. (a and c) are brightfield micrographs imaged near the $[11\bar{2}0]$ and $[01\bar{1}0]$ zone axes, respectively, and dislocation loops are clearly visible while in (b and d) their contrast is lost when tilting to $\mathbf{g}$ vectors of $[1\bar{1}00]$ and $[2\bar{1}\bar{1}0]$, respectively. Note the contrast is split over the region between brightfield and darkfield contrast using this two-beam condition.

IDLs for those low temperatures. This, combined with the observed cutoff in defect contrast of both IDL and partially dissociated Frank loops at the $4 \text{ keV nm}^{-1} S_e$ threshold in Fig. 5.8, suggests that at least for unelevated conditions, the IDL diameter will increase with electronic energy loss above the threshold, ultimately limited by the region bounding sinks.

In summary, elevated *in situ* temperatures during irradiation appears to largely mitigate many of the structural changes observed previously in Chapter 4. Broad FCC profile intensity is noticeably lacking in all GIXRD depths probed for 500°C and 880°C irradiations, and even a 25°C increase to a 50°C *in situ* temperature reduced FCC profile intensity for the low to unelevated temperature irradiations. High temperature conditions also resulted in a more uniform c/a distortion with depth, likely due to the formation of many large diameter IDLs in the bulk of grains. A $\sim 350 \text{ nm}$ boundary, where IDL diameter was reduced to typically $< 100 \text{ nm}$ in diameter, was observed near sinks, such as GBs and the irradiation surface, at each irradiation temperature. In the 880°C case, this allowed for a greater pileup of $\sim 50 \text{ nm}$ IDLs, which results in additional relaxation in near surface c and a-LP relative strain. For the unelevated conditions (25 and 50°C), the previously observed 4 keV nm^{-1} threshold in electronic energy loss still plays a vital role in the damage evolution of the material, with c/a distortion increasing with S_e above the threshold and remaining near pristine values below it. Further, it appears that IDL formation is limited to irradiation depths with S_e exceeding this threshold in electronic stopping power, and these loops increase in diameter with S_e to the limit established by the $\sim 350 \text{ nm}$ region bounding sinks. This influence of *in situ* temperature and the electronic energy loss threshold will be revisited, while more directly exploring the two ion energy dissipation pathways, in the following chapter, Chapter 6.

Chapter 6

Sequential Irradiations: Separated, Competing, and Synergistic Effects

Some results in this chapter have been submitted by William Alexander Hanson *et al.* for publication in *Acta Materialia*: W.A. Hanson, M.K. Patel, M.L. Crespillo, F. Zhang, S.J. Zinkle, Y. Zhang, W.J. Weber. Ionizing vs collisional radiation damage in materials: separated, competing, and synergistic effects in Ti_3SiC_2 . *Acta Materialia*. Under Review [16] and submitted by the same for publication in either *Acta Materialia* or the *Journal of Nuclear Materials* under the title: Influence of high temperature ion irradiations on electronic stopping effects and defect morphology in Ti_3SiC_2 . Any addendum to these submissions will be detailed in the Tennessee Research and Creative Exchange (TRACE), where this research dissertation is stored. As in the previous chapters, the experimental conditions for the ion irradiations and subsequent characterization experiments performed are detailed fully in Chapter 3 and Tables 3.1 to 3.3 and will not be repeated here.

6.1 GIXRD results

6.1.1 Profile disorder and peak shifting

The reduced range grazing incidence x-ray diffraction (GIXRD) profiles for the pristine condition and each of the five damage states, including combinations of 4 *MeV* Au to a

fluence of $5 \times 10^{14} \text{ cm}^{-2}$ and 17 MeV Pt and 14 MeV Cl to a fluence of $1.76 \times 10^{15} \text{ cm}^{-2}$, are plotted in Fig. 6.1. The profiles had their backgrounds stripped, were normalized, and their relative intensity plotted in the background as a heat map to display shifting of peaks between profiles more clearly. They are also vertically staggered in order of increasing S_e/S_n with Au ion pre-damaged material plotted higher than samples only exposed to high S_e ions. Also included is a profile from a depth of $0.5 \mu\text{m}$ probed in the 25°C 9 MeV Ti sample irradiated to a fluence of $2.8 \times 10^{16} \text{ cm}^{-2}$ from the study in Chapter 5, as this corresponds to an S_e of $\sim 5.1 \text{ keV nm}^{-1}$ and a damage dose of ~ 4 dpa, similar to the electronic stopping power and dose achieved by the Pt and Cl and the Au and Pt irradiations, respectively.

It may be observed immediately that broad FCC-type peaks, previously attributed to TiC [64] and marked with blue boxes, are present in each sample pre-damaged with 4 MeV Au ions, and are highly dominant in samples irradiated with 17 MeV Pt ions. As detailed by full cascade SRIM (v2013) [67, 68] simulations, plotted in Fig. 3.6a and 3.6b, there is a significant nuclear energy loss contribution to each of these ion energy depositions. These diffraction results are corroborated by similar behavior of broad FCC-type peaks dominating the relative intensity of grazing profiles of several MAX compositions, including Ti_3SiC_2 , exposed to even lower energy Au ions at very high fluences, $\sim 4 \times 10^{16} \text{ cm}^{-2}$ [43]. On the other hand, Ti_3SiC_2 irradiated with 14 MeV Cl ions, which have a low S_n , shows little to no intensity from these broad peaks; though, there is a comparable S_e with depth behavior to the high-energy Pt ions, see Fig. 3.6c. This variation in S_e/S_n with similar S_e may be observed as peak shifting in Fig. 6.1, where peaks closely aligned with the c and a axis shift to lower and higher *degrees* 2θ , respectively. This is especially evident when observing peaks such as the (104), (008), and (105) in Fig. 6.1a, the (109) in Fig. 6.1b, and the (1012) and (118) in Fig. 6.1c, each of which shifts to a lower *degrees* 2θ , indicating a relative expansion of the c-LP. Meanwhile, the principle peak parallel with the a-axis, the (110), can be seen to shift to higher *degrees* 2θ in Fig. 6.1b, which corresponds to a slight contraction of the a-LP. The shifting of c-LP dominated peaks may also be readily observed in the full profiles plotted in Fig. A6.1 in Appendix A.6. It is interesting to note that this shifting appears isolated from dose, given that the greatest peak shifts are observed following the Cl ion irradiations, which induced the lowest damage dose, but had the highest S_e/S_n per ion.

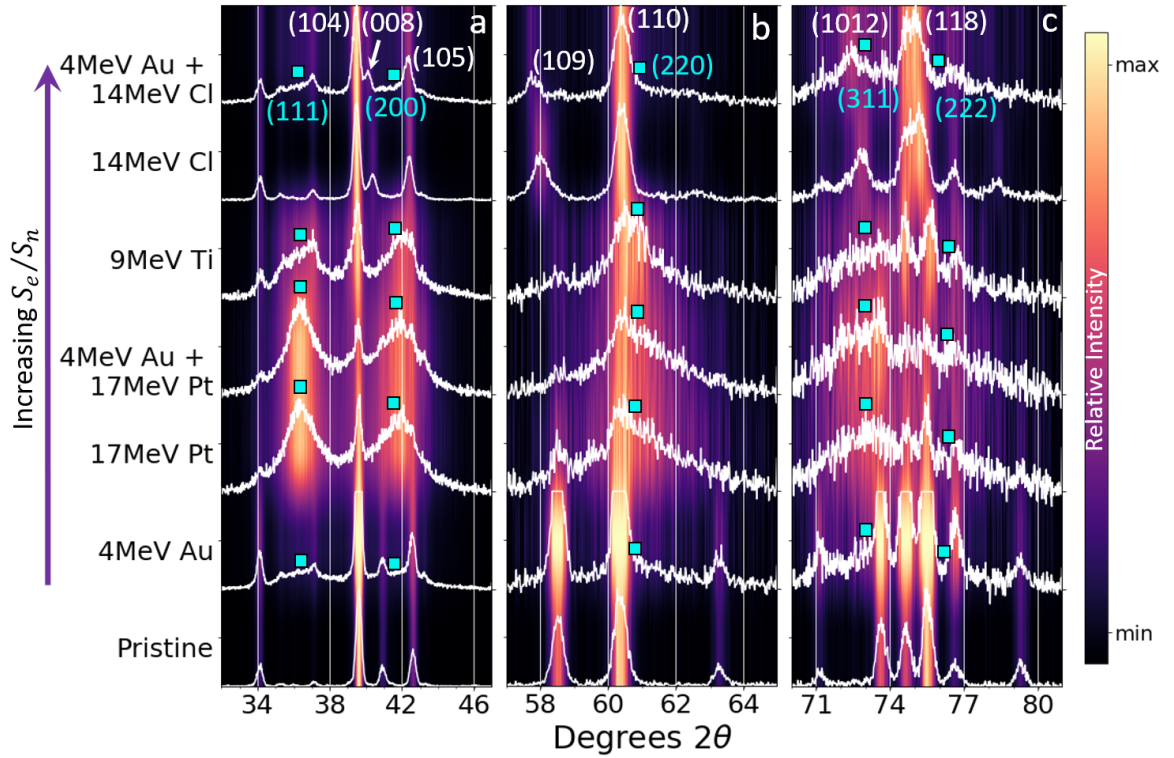


Fig. 6.1 – GIXRD profiles of the subranges (a) $32\text{--}47^\circ\ 2\theta$, (b) $57\text{--}65^\circ\ 2\theta$, and (c) $70\text{--}81^\circ\ 2\theta$ at a depth of $0.75\ \mu\text{m}$ comparing pristine and irradiated conditions with increasing S_e/S_n , including the 25°C lowest fluence ($2.8 \times 10^{16}\ \text{cm}^{-2}$) $9\ \text{MeV}$ Ti irradiation from Chapter 5 at a depth of $0.5\ \mu\text{m}$, which represents a similar S_e and damage dose [64]. Broad FCC-type peaks are marked with square annotations.

6.1.2 Mechanism proposed for FCC-type peaks

The broad FCC-type peaks observed in these diffraction profiles have been previously observed following high fluence 4 *MeV* Au, 2 *MeV* I, 700 *keV* C, and 9 *MeV* Ti ion irradiations. They were attributed to TiC based on their position in reciprocal space and the presence of a small amount of initial impurity in the pristine material [34, 36, 39, 40, 64]. However, in light of the recent results in Ti_3AlC_2 , which shares its structure with the subject of this study, a FCC-MAX phase transition should be considered as a mechanism behind the FCC-type profiles observed in Fig. 6.1 [41, 43]. Ti-Si anti-site defects are likely following ballistic mixing via elastic collision cascades, as both Ti and Si are relatively easy to displace [47] and the proposed defect is known to have a favorably low formation energy [27–29]. It is further proposed that irradiation assisted diffusion, along with ballistic mixing, may result in a site shift for the previous Si A-layer to the $\beta\text{-Ti}_3\text{SiC}_2$ position, see Fig. 6.2a and 6.2b, thus continuing the stacking sequence already present in the former Ti_3C_2 layers while also creating interstitial sites for C_{int} identical to the typical C site position. This may result in a MAX structure, which retains the Ti_3SiC_2 stoichiometry, but effectively lacks the A-layer and encompasses an embedded twinned FCC structure, shown in Fig. 6.2c and with FCC type cell drawn in Fig. 6.2d to demonstrate the $\{111\}$ twins [25].

From a diffraction standpoint this proposed mechanism seems plausible. It is important to recognize the similarity of diffraction planes of this defined hexagonal structure to the twinned FCC structure embedded inside it. The hexagonal $\{103\}$, $\{105\}$, $\{110\}$, $\{1012\}$, and $\{203\}$ peaks are emphasized in the structure factor by the Ti-Si anti-sites and also intersect the FCC-MAX $\{111\}$, $\{200\}$, $\{220\}$, $\{311\}$, and $\{222\}$, respectively, as seen in Fig. 6.2e to 6.2i. Further, slight distorting of the hexagonal lattice results in a complete overlap with these FCC positions, as observed experimentally.

Of note is the presence of these broad FCC-MAX profiles only following irradiation with 17 *MeV* Pt ions, 9 *MeV* Ti ions, and 4 *MeV* Au ions. These broad peaks are markedly absent when pristine material is irradiated with 14 *MeV* Cl ions; though, their intensity may increase slightly when pre-damaged material is irradiated under the same conditions. This seems to suggest that only ions with a larger nuclear stopping power component will

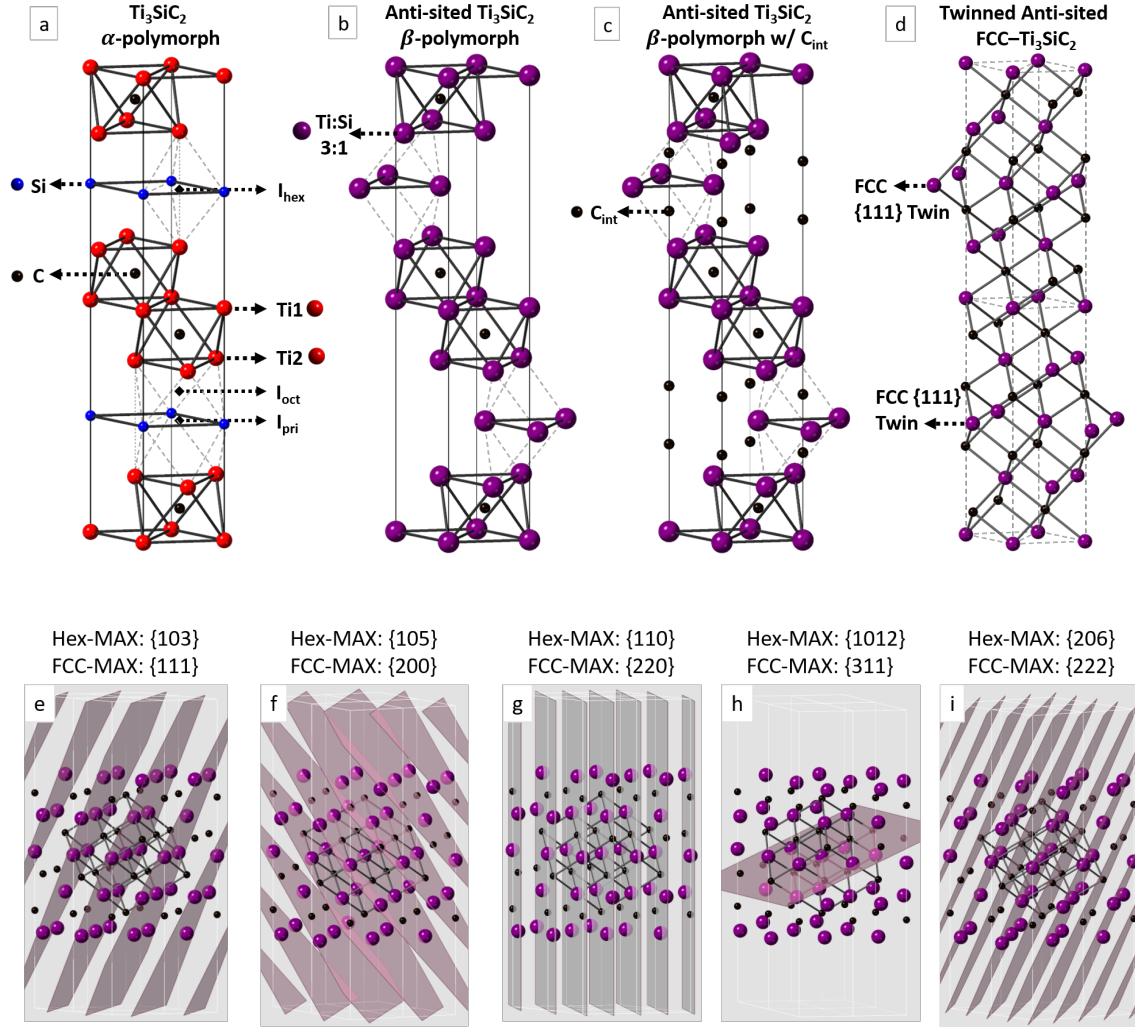


Fig. 6.2 – (a) α -polymorph of Ti_3SiC_2 with unoccupied interstitial sites labeled. (b-c) β -polymorph of Ti_3SiC_2 with Ti-Si anti-sites and C_{int} on octahedral sites in the latter. (d) Identical structure to (c) but with the unit cells redrawn to show 111-twinned FCC- Ti_3SiC_2 . (e-i) illustrates the shared planes between the hexagonal unit cell and the embedded FCC unit cell.

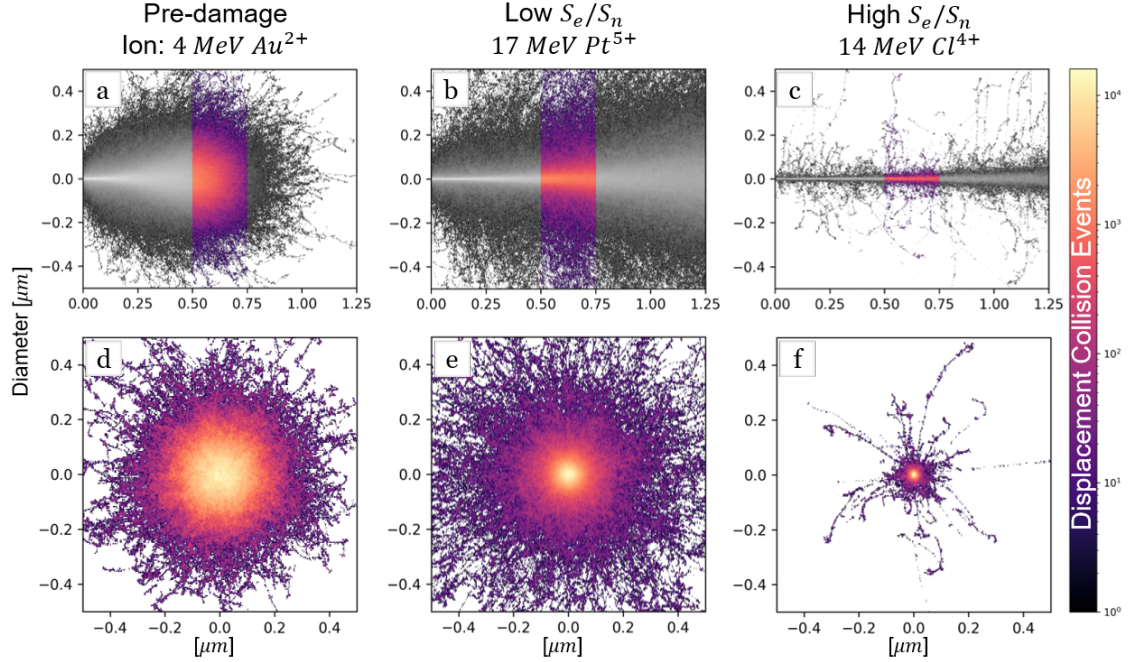


Fig. 6.3 – Collision events for 5000 ions each from the SRIM (v2013) [67, 68] simulations plotted in Fig. 3.5a and Fig. 3.6. (a-c) Collision cascade events vs depth for 4 MeV Au, 17 MeV Pt, and 14 MeV Cl, respectively. (d-f) Radial collision cascade events over the depth range of 0.5 μm -0.75 μm as indicated by the colored bands in (a-c), respectively.

lead to this FCC-MAX formation, resulting in the necessary Ti-Si anti-site formation. This observation is consistent with profiles gathered in the literature that exhibit these broad FCC-type profiles also contain a larger S_n component [34, 36, 39, 40, 64]. Evidence for the significant increase in ballistic efficiency of the larger S_n can be easily seen by examining the collision cascades, plotted using pysrim [89] for 5000 of the simulation ions calculated in Section 3.2.2 as a function of depth in Fig. 6.3a to 6.3c and radially over the highlighted depths of 0.5 μm -0.75 μm in Fig. 6.3d to 6.3f.

6.2 Raman Spectroscopy: supporting GIXRD results

The pristine and irradiated Raman spectra are plotted in Fig. 6.4. There are Raman active modes present in the pristine Ti_3SiC_2 spectra at 159, 190, 222, 275, 370, 620, and 676 cm^{-1} . Following Au pre-damaging irradiations and high-energy Pt irradiations, the modes centered

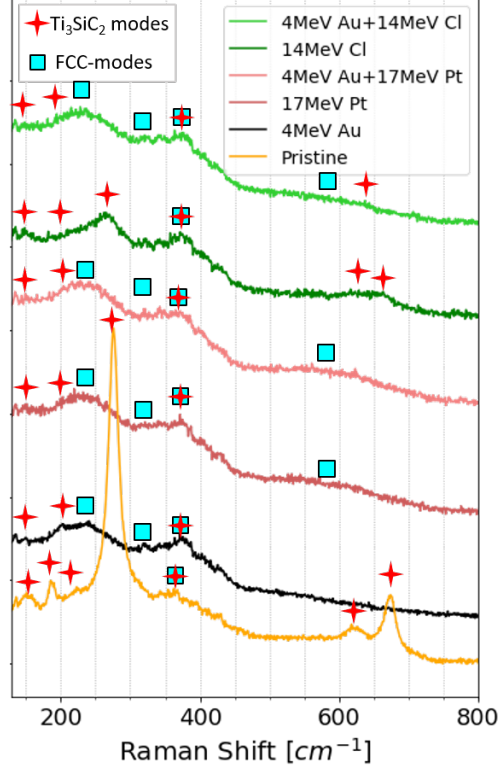


Fig. 6.4 – Raman shift over the range of 70-800 cm^{-1} comparing pristine and ion irradiated conditions with increasing S_e/S_n .

at 190, 275, and 676 cm^{-1} lose their intensities, and the mode at 370 cm^{-1} , which is attributed in common between Ti_3SiC_2 and $TiC_{0.67}$ is sharpened slightly. Additional modes attributed to $TiC_{0.67}$ appear about 250 and 340 cm^{-1} , and a broad mode appears about 596 cm^{-1} . The already broad modes centered at 222 and 370 cm^{-1} remained following each irradiation state; however, the mode at 159 cm^{-1} is broadened following Au pre-damaging and high-energy Cl irradiations and may be lost following high-energy Pt irradiations. Unlike the heavy ion irradiations, the very intense modes at 275, 620, and 676 cm^{-1} remain following high-energy Cl irradiations, though they lose intensity, broaden, and shift to slightly lower frequencies. Note that in this case, the 9 MeV Ti ion irradiation is not included in this comparison because its energy dissipation varies significantly with depth, while the energy dissipation with depth is mainly flat for the ions in this sequential irradiation study.

Examination of the Raman spectra in Fig. 6.4 appears to corroborate the above proposal of both the FCC-MAX phase formation and its link to a larger S_n component. All $TiC_{0.67}$

defect modes are present in the Ti_3SiC_2 spectra; though, they are shifted and the order of the C-sites makes them far more intense and sharp [90]. Since, the FCC-MAX shares its Ti:C ratio and structure with $\text{TiC}_{0.67}$, most notably its effective lack of the basal A-layers, it is proposed that the following established $\text{TiC}_{0.67}$ modes should apply to the FCC-MAX structure as well. Spectra from samples exposed to a greater nuclear stopping power, whether from pre-damaging with low energy Au or exposure to high-energy Pt, show decrease in intensity from MAX related modes and increase in their $\text{TiC}_{0.67}$ counterparts.

The nuclear stopping power dominated profiles lose most intensity from the Ti_3SiC_2 A_{1g} modes, c-axis movement of C-Ti-C, at 275, 312 (likely hidden beneath the noise) and 676 cm^{-1} while gaining broad intensity from their $\text{TiC}_{0.67}$ counterparts at 340, 372 and 661 cm^{-1} (also likely buried in the background). The E_{1g} mode, a-axis movement of C-Ti-C in symmetry about the basal A-layers, is also lost in these cases and replaced by broad intensity near its counterpart at 596 cm^{-1} [8]. The formation of C Frenkel pairs and interstitials as described in the above FCC-MAX phase structure could explain this as the C occupancy in the Ti-octahedra approaches that seen in $\text{TiC}_{0.67}$, thus resulting in the more broad, shifted modes [90]. Further, the E_{2g} mode, a-axis movement of C-Ti-Si, mode at 222 cm^{-1} broadens and is joined by its $\text{TiC}_{0.67}$ shifted counter part at about 250 cm^{-1} [8]. Once again, the spectra for the condition with Cl ion irradiation, where S_n is significantly lower, does not include these additional $\text{TiC}_{0.67}$ modes, save a slightly sharper mode at 370 cm^{-1} , which again is shared between Ti_3SiC_2 and $\text{TiC}_{0.67}$. This condition further retains the A_{1g} and E_{1g} modes albeit broadened by local defects and slightly shifted from 275, 620, and 676 cm^{-1} . It should be noted that while the $\text{TiC}_{0.67}$ modes are present, the MAX phase does not appear to be eliminated. The E_{2g} modes, unique to Ti_3SiC_2 and located at 159 and 222 cm^{-1} , each require the basal A-layer and retain much of their intensity following each irradiation condition, only broadening slightly [90, 91]. These results further suggest that nuclear stopping power is principally responsible for the formation of the FCC-type phase embedded in the MAX structure.

6.3 Lattice Parameter Analysis

The iterative method detailed previously was used to determine a self-consistent c/a over each depth range probed in irradiated and pristine samples, and subsequent c and a -LPs were calculated. The lattice parameters for the irradiated conditions are plotted as a function of S_e/S_n in Fig. 6.5 with the pristine c and a -LPs shown as a horizontal line for reference. As in Fig. 6.1, the c and a -LPs from the previous Ti irradiation condition are plotted in Fig. 6.5 as well. Comparing the relative strain of each condition to S_e/S_n confirms the initial peak shifting observations in Fig. 6.1 and reveals a trend. As S_e/S_n increases, the c/a distortion appears to increase and eventually saturate; the c and a -LP expansion and contraction, respectively, saturate by an S_e/S_n of ~ 150 in Fig. 6.5. Further, pre-damaged samples show a relative strain from pristine values that is greater than the sum of the strains for both the low energy Au ion irradiations and high-energy Pt or Cl ion irradiations; though, the trend of increasing c/a distortion remains correlated with an increase in S_e/S_n .

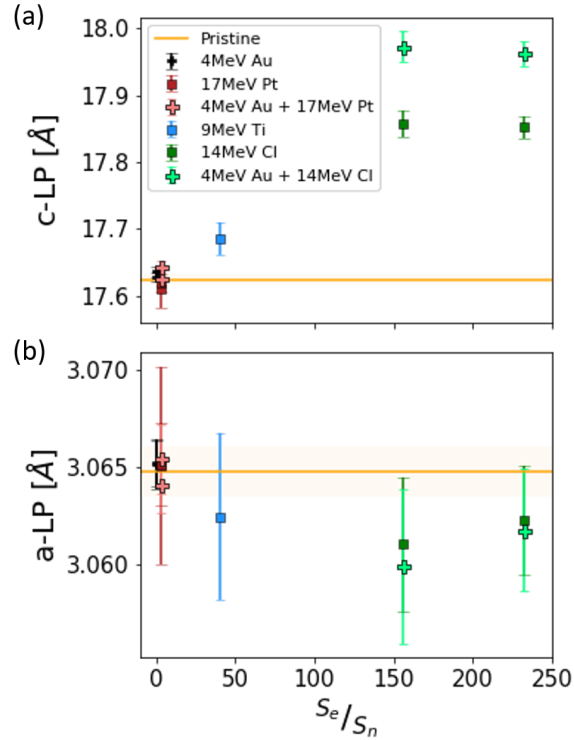


Fig. 6.5 – (a) and (b) c and a lattice parameters (c and a -LP, respectively) plotted as a function of the ratio of electronic to nuclear stopping power (S_e/S_n).

In each case, the high-energy Cl irradiations resulted in a significant expansion of the c-LP and contraction of the a-LP while high-energy Pt resulted in much less relative strain, and low energy Au showed little change from pristine values. Recall that the 14 *MeV* Cl and 17 *MeV* Pt S_e versus depth behavior is comparable, and each was irradiated to the same $1.76 \times 10^{15} \text{ cm}^{-2}$ fluence to ensure a similar overall S_e deposition, which exceeds the previously observed 4 keV nm^{-1} threshold to lattice strain following Ti ion irradiations [64]. In this case, however, Cl has a significantly greater S_e/S_n than Pt and the resulting relative strain increase is equally large and appears to saturate over an S_e/S_n ratio of 150, suggesting that when the 4 keV nm^{-1} threshold in electronic energy loss is surpassed, the ratio between inelastic and elastic energy dissipation becomes more important. This is corroborated by the inclusion of the 25°C repeated 9 *MeV* Ti ion irradiation condition, which has a similar S_e ($\sim 5.1 \text{ keV nm}^{-1}$) to the high-energy Pt and Cl irradiations and damage dose (~ 4 dpa) to the Au and Pt irradiations. Its resulting relative strain in c and a-LPs each fall directly on the trend established by the conditions in this study. Inelastic energy dissipation can lead to the formation of point defects, which add to the strain observed. The ionization energy from the high-energy Cl and Pt ions, once transferred to the lattice via electron-phonon coupling, will result in a large thermal spike, expected to easily exceed 1500 K in the pristine Ti_3SiC_2 , based on inelastic thermal spike calculations in SiC [56]. This large, rapid temperature differential has been demonstrated to result in a shock wave in the lattice, which can easily displace local atoms to the surrounding lattice [92], likely resulting in Frenkel pairs and even Ti-Si anti-site formation. Since the typical sharpness in the pristine principle modes of the Raman spectra is due to the highly ordered C atoms, their slight broadening and shifting in the spectra of the 14 *MeV* Cl irradiated samples is evidence for their displacement to interstitial lattice sites. That said, based on the previous observations, it is likely the inelastic collisions are not solely responsible for the strain observed in Fig. 6.5, but rather serves to exacerbate the defect production caused by elastic scattering events, which will be discussed below in Section 6.5.

6.4 TEM: structural change corroboration

A series of SAED depth profiles, oriented on the $[11\bar{2}0]$ zone axis are shown in Fig. 6.6 to 6.8 and 6.10 and may be used to further corroborate both the GIXRD and Raman spectroscopy results, supported by the results from Chapter 5. Examining the profile of the nuclear stopping power dominated Au irradiations in Fig. 6.6b to 6.6d, the FCC-type twinned structure for the shared orientation, Fig. 6.6g and 6.7g, is very clear, as simulated in Fig. 6.6f. Additionally, the α - Ti_3SiC_2 structure, simulated in Fig. 6.7f, is visible in Fig. 6.6b to 6.6d gaining in relative intensity until it is the only phase present in Fig. 6.6e, which is beyond the 4 *MeV* Au ion range. It should be noted at this point, that during the thinning preparation of the TEM lamella, the Au irradiation depth showed some signs of preferential thinning, even in regions intentionally left thick for tilting alignments, despite milling parameters being matched to those utilized in other samples. That said, the results displayed here are not believed to be artifacts of the preparation process as these are typically exhibited as amorphous halos, observed previously in the SAED patterns in Fig. 4.4 and 4.5. These SAED patterns by contrast, while highly disordered as indicated by the diffuse spots for the $\{111\}$ twinned FCC-type structure, exhibit no such halos, and further, the α - Ti_3SiC_2 structure, visible at each depth from the irradiation surface, is highly ordered and crystalline with fine spots.

Comparing the results for low energy Au irradiation in Fig. 6.6 to those of an unelevated temperature high-energy Ti irradiation in Fig. 6.7, it is possible to see the influences of electronic stopping power on the FCC-MAX formation. The FCC twins are not nearly as dominant in Fig. 6.7b to 6.7d, though their diffuse intensity is still present at the appropriate positions in reciprocal space: FCC-type $\{111\}$ and $\{002\}$ in the vicinity of the MAX $\{103\}$ and $\{105\}$, respectively. This is even observed across the grain boundary observed in Fig. 6.7a and 6.7b in a grain slightly misoriented from the defined $[11\bar{2}0]$ zone. Further, the periodicity present in the relative intensity of the MAX profile is more characteristic of the β - Ti_3SiC_2 polymorph at these depths, but appears to return to the α - Ti_3SiC_2 structure by Fig. 6.7e, which is close to where S_e drops below the 4 *keV nm⁻¹* threshold. This would seem to corroborate that when electronic energy loss exceeds the threshold, it exacerbates the

predominantly elastic process of producing β -Ti₃SiC₂ with anti-site defects and then eventual FCC-MAX, as nuclear stopping power for this ion at this irradiation depth is significantly lower than the Au ion in Fig. 6.6.

As in the GIXRD results, the SAED depth profiles for high-energy Cl irradiations in Fig. 6.8 represent a contrast to those in Fig. 6.6 and 6.7 as it shows no relative intensity from either FCC-type twins or the β polymorph at any irradiation depth probed. α -Ti₃SiC₂ appears to be the dominant structure present at each depth, Fig. 6.8b to 6.8d; though, there is significant diffuse streaking parallel to the [0001] direction, which indicates a high density of defects and is expected given the large apparently saturated lattice strain observed in Fig. 6.5. However, an interesting parallel may be drawn between the Cl irradiation results and the high temperature Ti irradiations, in the defect behavior observed. Fig. 6.9 shows a series of BF and BF/DF split contrast micrographs of a magnified region, each imaged near the [11 $\bar{2}$ 0] zone axis, and examining Fig. 6.9b and 6.9c, it is clear that the IDLs still obey the same $\mathbf{g} \cdot \mathbf{b} = 0$ invisibility criterion, indicating a Burgers vector of $\mathbf{b} = 1/2[0001]$. Like the previous samples imaged in the high temperature study in Chapter 5, a ~ 350 nm region at the irradiation surface shows a high concentration of small diameter IDLs (~ 75 nm) with occasional loops >100 nm in diameter and some partially dissociated Frank loops. Beyond this range, larger loops are observed with variation in diameter, ~ 135 nm with a few <100 nm and a few >250 nm, as seen in the 880°C irradiations. However, the strain contrast observed at these irradiation depths is more similar to that observed in the unelevated temperature irradiations in Fig. 5.8. Based on their similar GIXRD profiles, it is unsurprising that the SAED depth profiles for the 500°C irradiation with 9 MeV Ti to a fluence of $2.8 \times 10^{16} \text{ cm}^{-2}$, Fig. 6.10b to 6.10d, is very similar to that of the high-energy Cl irradiation; no contribution from either the FCC-MAX or β -Ti₃SiC₂ is observed at any of the depths probed. However, unlike the unelevated temperature irradiations, the *in situ* annealing reduces the number of point defects as well, eliminating the diffuse streaking in the SAED patterns, also consistent with the more uniform and relaxed latticed strain observed in Fig. 5.2c and 5.2d.

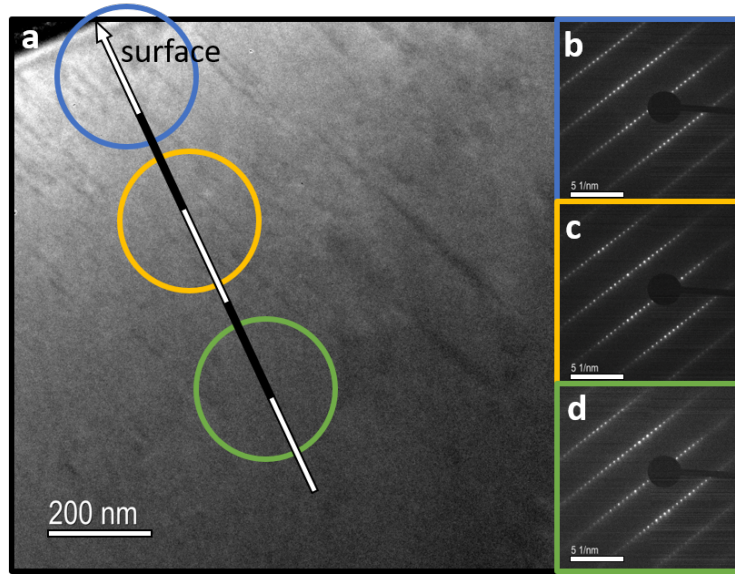


Fig. 6.8 – Depth profile in 14 *MeV* Cl irradiated sample with (a) overview (b-d) SAED patterns.

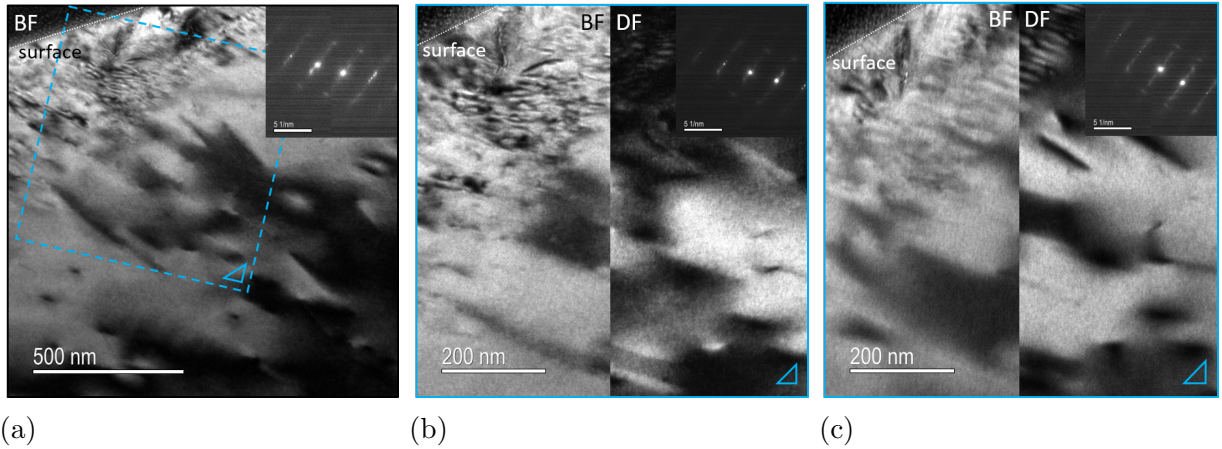


Fig. 6.9 – (a) Brightfield TEM micrograph of the 14 *MeV* Cl ion irradiated condition in two-beam conditions near the $[11\bar{2}0]$ zone axis with a $\mathbf{g}$ of $[\bar{1}10\bar{1}]$, SAED inset indicates orientation. (b and c) Brightfield, darkfield pairs at an increased magnification of the colored, dashed region in (a) with fiducial marks and SAED insets to indicate orientation. Note the contrast is split in (b and c) between brightfield and darkfield contrast using the two-beam conditions with $\mathbf{g}$ of $[1\bar{1}01]$ and $[1\bar{1}00]$, respectively, the latter resulting in a loss of contrast for dislocation loops observed in each micrograph.

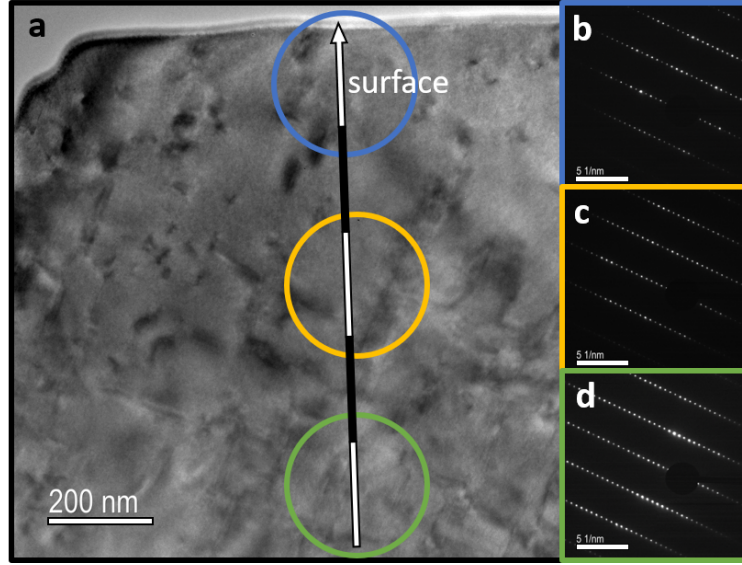


Fig. 6.10 – Depth profile in 500°C 9 MeV Ti irradiated sample with (a) overview (b-d) SAED patterns.

6.5 Implications of these proposed effects

Though the nuclear scattering cross section is small for both high-energy ion irradiations, Fig. 6.3b, 6.3c, 6.3e and 6.3f clearly demonstrates that collision cascades will stochastically occur for each ion. It was demonstrated earlier that elastic collisions from a higher nuclear energy loss contribution are necessary to form the FCC-MAX phase, but there is a clear distinction in the FCC profile intensity between 4 MeV Au and 17 MeV Pt; though, the damage dose (~ 3 dpa) is similar. It has been demonstrated recently in the literature that low energy Au ions require a fluence roughly 2 orders of magnitude greater than that employed here ($\sim 1 \times 10^{16} \text{ cm}^{-2}$) to produce FCC-MAX profiles with relative intensity similar to those observed following the high-energy Pt irradiation [43]. Recall that formation of the FCC-MAX involves a site shift to form the β -Ti₃SiC₂ polymorph, so the added energy deposition from the 17 MeV Pt ion thermal spike could effectively reduce this barrier to forming the FCC-MAX. This is consistent with the depth profile analysis from the previous study, which demonstrated that with other contributions being equal, increasing electronic energy loss above the 4 keV nm^{-1} threshold leads to an increase in FCC-type relative intensity [64].

This sort of S_e threshold for enhanced phase transformation to a higher symmetry phase has been observed in other material systems in the past, most notably in zirconia. Pure, unstabilized zirconia has a monoclinic structure that, following high fluence irradiations at low temperatures with 340 *keV* Xe ions, partially transforms to a higher symmetry tetragonal phase [93]. However, when irradiating at room temperature with ions where S_e exceeds a 12 *keV nm⁻¹* threshold, the percent phase transformed increases significantly, in fact, linearly with S_e , and the fluence to reach the saturated transformation is reduced by over two orders of magnitude [86]. Therefore, the enhanced transformation from α -Ti₃SiC₂ to FCC-MAX with added {111} twin symmetry by S_e exceeding a 4 *keV nm⁻¹* threshold is not unprecedented.

It also appears the relationship between the thermal spike radii and the radial distribution of collision events is vital to this phase formation as the 14 *MeV* Cl irradiations do not show a clear, if any, increase in a FCC-MAX profile or evidence of FCC twins in the SAED patterns; though, there is an equivalent S_e deposition to the 17 *MeV* Pt irradiations. This suggests that while an S_e greater than the 4 *keV nm⁻¹* threshold will exacerbate the formation of FCC-MAX by nuclear stopping power, increasing the S_e/S_n will eventually suppress the effect. This is corroborated in the reduced FCC-MAX to MAX phase profile intensity at a similar S_e and damage dose following 9 *MeV* Ti ion irradiation, see Fig. 6.1, as the S_e/S_n of this condition lies between that of the high-energy irradiations of this study. This is not to say that Ti-Si anti-site and C Frenkel pair production due to the stochastic elastic collisions and inelastic thermal spike shock waves are not occurring, but rather the formation of FCC-MAX is suppressed by annealing as the thermal spike exceeds the radii of collision events. Additional evidence for this in-cascade annealing may be seen when recalling the comparison in Fig. 5.1 between the room temperature $2.8 \times 10^{16} \text{ cm}^{-2}$ 9 *MeV* Ti irradiation to its higher flux counterpart from the high temperature irradiation study in Chapter 5. The increased flux, reflected by the minor increase in *in situ* irradiation temperature from 25°C to 50°C, results in additional annealing by the thermal spike, and thus a greater suppression of the FCC-MAX formation. All that said, this in-cascade annealing does not appear to be sufficient to “heal” pre-existing FCC-MAX nor anneal resulting point defects, such as anti-sites, which lead to the large relative lattice strain. The broad peaks in both the diffraction and Raman profiles for pre-damaged material irradiated with the high-energy Cl ions attest to this as

do the diffuse streaking in the SAED patterns of pristine material irradiated with the same. However, it does appear to be sufficient to result in larger diameter IDL behavior similar to that following 880°C *in situ* annealing conditions, rather than reduced IDL diameter with irradiation depth which eventually ceases when S_e is reduced below the 4 keV nm^{-1} threshold, as observed following the unelevated Ti ion irradiations in Fig. 5.8. This is unsurprising given that the 14 MeV Cl ion S_e profile is greater in magnitude and relatively flat with depth, as compared to the 9 MeV Ti ion irradiations, resulting in a more uniform in-cascade anneal for the depths probed in this study.

The above effects may be observed indirectly through the significant increase in relative strain of the c and a-LPs with increasing S_e/S_n when the FCC phase does not increase. It has been previously observed that the inclusion of FCC TiC reduced irradiation swelling and other anisotropic lattice distortion in microstructures [2]; therefore, it is expected that the formation of a FCC phase, whether TiC_x or a FCC-MAX embedded in the hexagonal MAX structure, would perform similarly. In fact, the strain is reduced in magnitude to near pristine values following the low energy Au and high-energy Pt irradiations, where increased FCC formation was observed, and the minor strain that does result, lacks the high anisotropy typical of the hexagonal structure. Conversely, if FCC-MAX phase formation is suppressed, while point defects and Ti-Si anti-sites are allowed to form, the relative strain of the c/a would therefore increase, as is seen comparing between Fig. 6.1 and 6.5. Again further evidence may be seen when comparing the $2.8 \times 10^{16}\text{ cm}^{-2}$ fluence for the 9 MeV Ti irradiations to its higher flux counterpart from the high temperature study, see the $0.5\text{ }\mu\text{m}$ depth in Fig. 5.2a and 5.2b. Just as the higher flux condition shows a greater FCC-MAX suppression, it also shows the greater relative lattice strain for the same fluence. What is more, in the case of high-energy Cl irradiation, where the formation of additional FCC phase appears fully suppressed, the relative strain appears to saturate and values are comparable to those calculated for a high Ti-Si anti-site concentration in an otherwise pristine Ti_3SiC_2 lattice [29]. Diffraction results from a previous study appear to corroborate this as following irradiation with high S_e and S_e/S_n ratios exceeding 270, a nearly identical maximum c-LP strain is measured without observing the broad FCC-type peak profiles. It should be noted that following swift heavy ion (SHI) irradiation, changes in diffraction profiles have not

been observed [34]. Following the proposed suppression of the FCC-MAX formation by the thermal spike, this makes sense, as S_e/S_n will be significantly higher for the ion; however, there is also a lack of lattice strain. It is possible, with such a low nuclear stopping cross section, the production of defects is insufficient to result in a measurable strain, suggesting a minimum S_n or relative dose to damage by this mechanism. Alternatively, in the SHI regime, the thermal spike may achieve a significantly higher temperature, leading to localized melting and relaxation of any resulting lattice strain, suggesting a maximum S_e , above which strain is not observed. However, the energy regimes of this study are not attuned to answer this question, and further postulation would be speculative. For now, what may be suggested is a second threshold of a ratio of $S_e/S_n > 100$ to suppress FCC-MAX phase formation and maximize relative c/a strain when ion energy is $< 1 \text{ MeV}/amu$.

It may also be observed that while additional FCC-MAX phase formation is suppressed by the high S_e/S_n , the contribution of pre-existing defects serves to significantly increase the saturated relative strain magnitude. This increase is well beyond that of an additive contribution and represents a synergy between the inelastic energy dissipation and evolving defect concentration, whereby the thermal spike is more radially confined and thus increases the temperature differential and subsequent shock-wave [55, 57, 62, 63, 69, 84, 85]. This radial confinement may be sufficient to prevent complete annealing of the pre-damaged FCC-MAX phase by high-energy Cl ions but not to suppress increased formation of the phase.

In summary, the effects of electronic and nuclear energy dissipation during ion irradiation of Ti_3SiC_2 have been found to be competing and synergistic for different ratios of electronic to nuclear energy loss. Nuclear energy loss results in elastic collision cascades, leading to the formation of a FCC-MAX phase with Ti-Si anti-site defects. This FCC phase serves to partially relax the structure and resist the overall anisotropic c/a distortion. Intense electronic energy loss above an S_e threshold of 4 keVnm^{-1} serves to exacerbate this effect, through the thermal spike adding energy to the lattice and increasing point defects through shock waves. However, increasing the ratio of S_e/S_n serves to add sufficient energy over the radial distribution of collision events that formation of the FCC-MAX phase is suppressed, thus maximizing relative strain for energy regimes $< 1 \text{ MeV}/amu$. There is a threshold for this ratio of $S_e/S_n > 100$, where the FCC-MAX phase formation is fully suppressed and

lattice strain is saturated. Further, there is a synergy between pre-existing defects and electronic energy loss, whereby the effects of the thermal spike are more radially confined, thus significantly increasing the resultant strain. These results further illustrate that the interaction of both electronic and nuclear energy dissipation pathways is vital to the study of irradiation effects of materials such as Ti_3SiC_2 .

Chapter 7

Conclusions

Some of the discussion of results and recommendations in this chapter are included in a submission by William Alexander Hanson *et al.* for publication in Acta Materialia: W.A. Hanson, M.K. Patel, M.L. Crespillo, F. Zhang, S.J. Zinkle, Y. Zhang, W.J. Weber. Ionizing vs collisional radiation damage in materials: separated, competing, and synergistic effects in Ti_3SiC_2 . *Acta Materialia*. Under Review [16].

7.1 General Summary

The goal of this dissertation was to better understand the roles of energy dissipation, electronic and nuclear energy loss, on the ion-matter interactions in the Ti_3SiC_2 MAX phase. This was accomplished through a series of novel ion irradiation experiments: 1) a series of the high-energy self-ion irradiations at room (Chapter 4) and elevated *in situ* temperatures (Chapter 5), and 2) a series of sequential irradiations to separate the energy loss effects (Chapter 6). Integral to this research was the novel adaptation of a specialized method for iteratively determining a self-consistent ratio of the c and a lattice parameters (c and a-LP, respectively), as a function of depth probed, to the study of ion irradiated hexagonal polycrystals. This allowed for analysis of fine changes in relative lattice strain as a function of the energy deposited by the ions.

The 9 MeV Ti irradiations were designed such that damage evolution resulting from variation in the self-ion's electronic energy loss could be studied at a constant damage dose.

This comparison revealed that not only does electronic stopping power play a vital role in the structural changes, but there is also a low threshold in electronic energy loss to its onset at 4 keV nm^{-1} . Above this threshold, there is enhanced formation of a FCC phase, observed in both GIXRD and SAED depth profiles, and increasing electronic energy loss results in increased c/a distortion from pristine values. High temperature irradiations appear to mitigate these effects, suppressing the formation of the FCC phase and resulting in a more uniform and reduced strain with depth. Additionally, the high temperature irradiations reveal a boundary region of $\sim 350 \text{ nm}$ surrounds defect sinks, such as grain boundaries and the irradiation surface, within which irradiation induced interstitial dislocation loops are reduced in diameter, typically $< 100 \text{ nm}$.

The sequential irradiation of Ti_3SiC_2 with 4 MeV Au followed by 14 MeV Cl and 17 MeV Pt ions, respectively, were designed to separate the ion energy loss pathways to explore their independent effects before systematically recombining them to study their interaction. The separation of the effects revealed that elastic collision cascades, nuclear energy loss (S_n), is responsible for the formation of Ti and Si anti-site defects that eventually result in a FCC-MAX phase embedded in the β polymorph of the Ti_3SiC_2 structure. Above the previously established threshold of 4 keV nm^{-1} , inelastic collisions with the electrons, electronic energy loss (S_e), leads to increased c/a distortion and significantly enhances the formation of the FCC-MAX phase, through additional energy in the system via the thermal spike and additional point defects produced by shockwaves therein. However, the combination of S_e and S_n , through the sequential irradiations, reveals that the energy loss pathways are in competition, defined by their ratio (S_e/S_n). When S_e is greater than the threshold and S_e/S_n is small the formation of the FCC-MAX is initially enhanced, but as S_e/S_n increases, the FCC-MAX formation is suppressed by in-cascade annealing via the thermal spike. This annealing by the thermal spike, unlike *in situ* annealing during irradiation, is insufficient to relax the structure and “heal” point defects, regardless of whether they are pre-existing or produced by the elastic collision cascades. However, it does allow for the retention of the α -MAX structure, thus resulting in increased c/a distortion, which eventually saturates.

As a foundation for the motivations of this study was analysis of some past results in the literature, it is important to reevaluate them here. Relative lattice strain has been

calculated for c and a-LPs reported in the literature following room temperature 92 *MeV* Xe and 74 *MeV* Kr irradiation to doses comparable to those reached by the 14 *MeV* Cl irradiations of this study [34, 60] and are shown in Fig. 7.1. These results continue the trend initially observed in Chapter 6, confirming that c-LP strain saturates by an S_e/S_n of 150 while the a-LP strain appears to saturate above an S_e/S_n of 250. Additionally, like those following high-energy Cl irradiations in this study, the GIXRD profiles used to calculate the reported LPs show no broad FCC-type peaks [34]. Therefore, the initial observation in Chapter 2 that these literature results suggested an influence of electronic energy loss on the damage evolution in Ti_3SiC_2 is correct, and what's more they corroborate the results of this study. It is also important to reevaluate past results in the literature from low energy, heavy ions below the threshold, to demonstrate further consistency with those of this study. Hence, Fig. 7.1 includes relative lattice strains calculated from c and a-LPs reported in the literature following 7 *MeV* Xe irradiations [42]. However, it should be noted that error was not reported in the literature with these lattice measurements, so error has been conservatively estimated at 0.1% of the measured lattice strain and included as error bars. The literature data was gathered from irradiation depths where the dose is similar to the 4 *MeV* Au irradiations of this study, and the material response appears largely similar. Like the 4 *MeV* Au irradiations, the GIXRD profiles and SAED patterns from the $[11\bar{2}0]$ zone axis reported for the S_n dominated irradiation show evidence of $\{111\}$ type FCC-twins and the β - Ti_3SiC_2 structure like those of similar energy regimes in Chapter 6. Further, the relative lattice strain is also reduced in magnitude and shows a minor increase in both c and a-LPs, which is another demonstration of the reduction, following FCC-MAX formation, in the typical anisotropic c/a distortion in α - Ti_3SiC_2 that results from radiation damage.

7.2 Implications of the results

The implications of these results for the selection of ion species and energy regimes for irradiation studies in MAX phases cannot be overstated. Typically, higher energy (10-50 *MeV*) medium mass self-ions and light ions are recommended to extend the safe analysis depth range and avoid artifacts due to surface effects and ion concentration profiles [4].

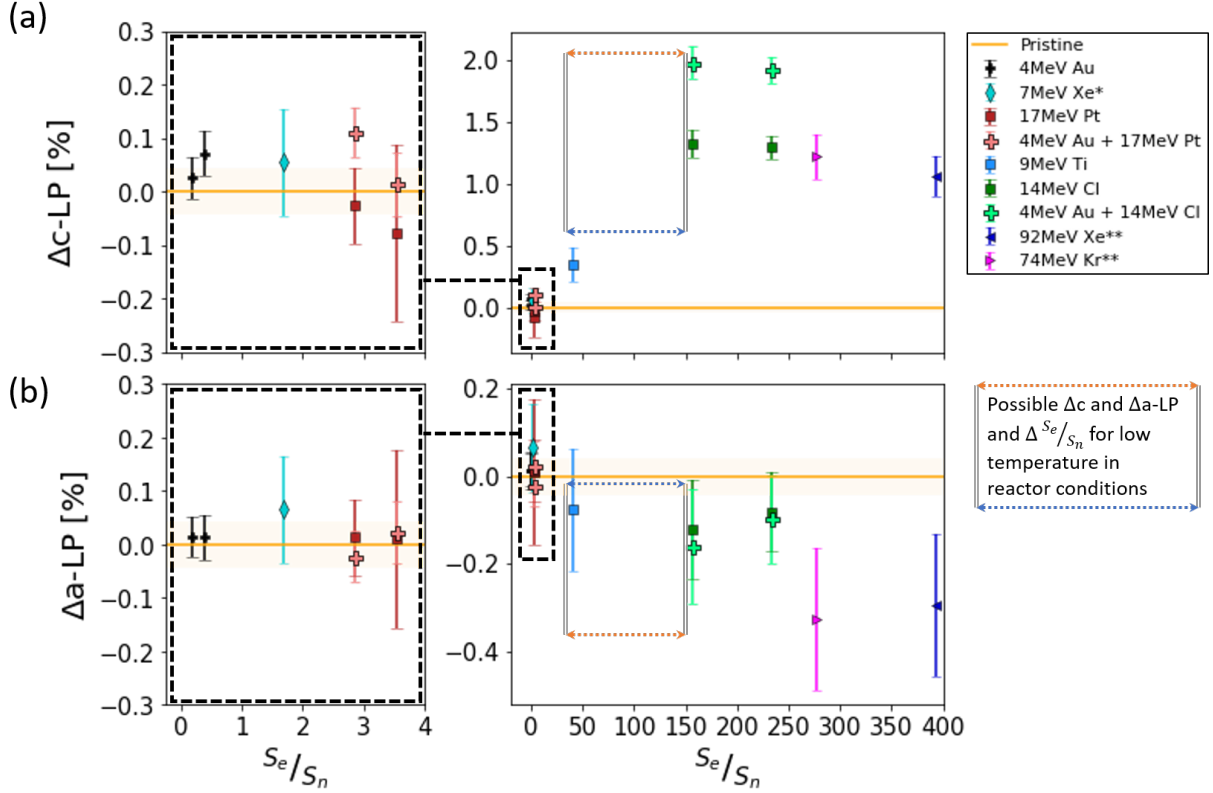


Fig. 7.1 – (a) and (b) relative Δc and Δa lattice parameter (Δc and Δa -LP, respectively) strain as a function of the ratio of electronic to nuclear stopping power (S_e/S_n) with an expanded view of the low range of S_e/S_n . Included are Δc and Δa -LP values from this work (Fig. 6.5) as well as 7 MeV Xe* ion irradiations to 3 dpa [42], 92 MeV Xe** ion irradiations to 0.14 dpa, and 74 MeV Kr** ion irradiations to 0.09 dpa [34, 60] from the literature. Additionally, a region of possible Δc and Δa -LPs plotted against $\Delta S_e/S_n$ based on low temperature in-reactor studies [13, 33] is proposed.

However, for this composition, two additional constraints are now recognized as vital to the selection of ions. Exceeding a low threshold in S_e dramatically increases the effect of FCC-MAX formation, resulting from the elastic collision cascades. At the same time, radial confinement of the ballistic processes, when S_e/S_n is large, suppresses this phase formation and enhances measured lattice strain. Additionally, as energy loss pathways will change with depth for ion irradiation, an appropriate depth probe must be selected for subsequent characterization, such that the S_e/S_n is consistent.

It is possible to draw some correlations between the ion irradiation results of this study and other intense radiation environments. In the case of direct comparison with different reactor environments, the 14 MeV Cl ions have a comparable S_e/S_n to a mixed spectrum LWR such as the High Flux Isotope Reactor (HFIR). On the other hand, the 17 MeV Pt ions may be compared with a fast fission reactor environment such as the Materials Open Test Assembly (MOTA) located at the former Fast Fission Test Facility (FFTF) [58]. Direct comparison of the results of this study and these reactor environments is limited as operational temperatures significantly exceed the room temperature *in situ* conditions from this study. That said, the lower *in situ* elevated temperature ion irradiation conditions observed in this study in Chapter 5 and the literature [14], as well as previous neutron irradiations in-reactor [30, 33], have been observed to only partially mitigate the effects of lattice strain. This would suggest that the direct influence of the energy loss pathways observed here are expected to remain consistent in reactor, albeit annealed out if operating temperatures are sufficiently high. In fact, examining some lower temperature in-reactor neutron irradiation results [13, 33], and estimating probable S_e/S_n operation ranges based off dose rates and power density, it is possible to propose a region of possible Δc and Δa -LP in Fig. 7.1a and 7.1b, respectively. While the region is conservative in size, there is a reasonable probability for results in the regions to continue the trend established by this study. It is further interesting to note that the outer bounds of the regions suggest that sequential irradiation studies may more closely emulate the ballistic collision cascades and continuous ionizing radiation of in-reactor conditions as compared to single high-energy ion cascade events.

Other considerations may be made regarding the formation of the FCC-MAX structure. It may be desirable to intentionally use ions with a large nuclear stopping power to functionalize Ti_3SiC_2 by forming the FCC-MAX structure, which has not been reported as synthesized through other means. The formation of this structure has already been demonstrated to allow the lattice to remain largely relaxed, near pristine values, and other FCC structures of similar composition, such as TiC_x , are known to be resistant to the anisotropic swelling that is typical in hexagonal systems [2]. This new structure has the added advantage of a high density of $\{111\}$ twin interfaces, which are likely to impart a large defect sink strength, and thus irradiation resistance, to the structure that is greater than other FCC ceramic materials of similar composition [6]. Additionally, the high density of $\{111\}$ twins, on the former basal layers of the MAX structure, may preserve some of the ductile character of the MAX structure. Formation of the FCC-MAX structure in Ti_3AlC_2 , which shares its structure with Ti_3SiC_2 , has already been demonstrated using low energy, high fluence Au irradiations [43]. Therefore, given the similarity of their structures and properties, it is anticipated that a similar enhancement of the FCC-MAX formation will occur in this composition following irradiation with high-energy, heavy ions, so long as $S_e > 4 \text{ keV nm}^{-1}$ and S_e/S_n is kept near parity (<10). Tuning of the functionalized range of material would then be possible through selecting ions and energies to retain this energy loss ratio and magnitude for the ion range desired. This type of ion beam modification may not be limited to the M_3AX_2 structures, as following low energy, heavy ion irradiation to high fluences, the Ti_2AlC , Ti_4AlN_3 , and Ti_2AlN MAX compositions each show similar FCC-type peaks to those observed in Ti_3AlC_2 and Ti_3SiC_2 GIXRD profiles [43]. Given the previously observed similarity to high-energy Pt S_e/S_n , it may even be possible to allow this material to functionalize naturally under a fast fission reactor environment [58]. In-reactor at higher operating temperatures, the structure may reach an equilibrium of forming functionalized FCC-MAX while annealing to α -MAX and may then be more resistant to anisotropic swelling.

With these considerations, care should be taken when selecting ions as a tool for direct comparison to bulk elastic collision environments, such as those under neutron irradiation in-reactor, and high-energy self-ions may not always be the appropriate tool for making such

comparisons in Ti_3SiC_2 . That said, the competition between these ion energy dissipation pathways represent a fascinating phenomenon, one that may prove to be useful in engineering design, and therefore warrants further study.

7.3 Potential paths forward

At the close of this dissertation, it seems appropriate to propose future avenues of study.

Of particular interest is the stability and properties of the FCC-MAX structure formed via ion beam modification with a large nuclear stopping power. This represents a newly defined structure that, to the knowledge of this author, is not formed via other means of material processing. Therefore, its influence on the beneficial properties that make MAX phase ceramics attractive for intense radiation environments is of paramount importance.

A sequential irradiation experiment in the reverse of that performed here is proposed where a high-energy, medium mass ion irradiation, such as Cl, is followed by a low-energy, heavy ion irradiation, such as Au. This would explore the capability of a nuclear stopping power dominated energy regime to form the FCC-MAX structure, when the c and a-LPs are already highly distorted, and at the same time would explore the capacity of the FCC-MAX formation to relax said saturated c/a distortion. Along similar lines, a dual beam irradiation study is suggested, using the same pairs of ions. The goal of this experiment would be to explore the interaction between the in-cascade annealing of the high-energy ions and the high concentration of elastic collision cascades of the heavy ions.

Given the high temperature Ti ion irradiation results, the stability of the FCC-MAX structure formation under high-energy heavy ion irradiation should be evaluated under *in situ* high temperature conditions to see if the enhanced formation of the FCC phase is offset by bulk annealing. Along similar lines, an in-reactor study in a fast fission environment where S_e/S_n is low is proposed to evaluate the formation of the FCC-MAX structure at a bulk scale. A long term SHI irradiation study to a low dose ~ 0.1 dpa would provide insight into the very high S_e and S_e/S_n regimes at damage doses comparable to those achieved following high S_e/S_n irradiations in this study.

The question of compositional effects on the threshold in electronic energy loss itself may be useful to explore as well. That Ti_3AlC_2 appears to show more order and intensity for the resulting FCC and β -polymorph type signatures seems to indicate that it more readily undergoes the phase transition to FCC-MAX than Ti_3SiC_2 [42, 43]. This may suggest a lower threshold in electronic stopping power to enhancing the phase formation and perhaps a higher required S_e/S_n for its suppression. In either case, a systematic exploration of the electronic effects in the sister composition to the subject of this study appears warranted. Additionally, these studies could be expanded beyond evaluating Ti-based MAX phases. Other compositions, such as Nb_4AlC_3 , have shown similar, broad FCC-type peaks following extensive irradiation with low-energy ions [43] and should be explored to see if a similar threshold in electronic energy loss is present outside the Ti-based MAX phases. Of a similar interest is the response of Cr_2AlC to similar conditions, given its superior corrosion performance in simulated primary coolant loop water, which make it potentially interesting for both LWR and SCWR applications, where Ti-based MAX phases cannot form passivating barriers [12].

Of course, there is always room for theoretical work to explore mechanisms and support experimentation. Density functional theory has already provided useful insight into the point defect structures and behaviors and their influence on the MAX structure, but the types of interactions observed here in Ti_3SiC_2 and in other compositions in the literature, namely the formation of the FCC-MAX structure, will require the larger scale defect interactions possible only in molecular dynamic (MD) simulations. It has been noted previously [47, 94], and is echoed here, that the lack of empirical interatomic potentials for Ti_3SiC_2 and other compositions with the $\text{M}_{n+1}\text{AX}_n$ structure remains a barrier to MD investigations. However, it is also recognized that it is not a trivial problem to generate these necessary potentials, given the odd, complex mixture of covalent, ionic, and metallic bonding character that allows for this unique structure. Hopefully, as research continues in this material system, appropriate potentials will be developed to explore and support the mechanisms and phase transformations discussed in this work.

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Appendices

A Additional Figures

A.3 Supplemental Figures: Chapter 3

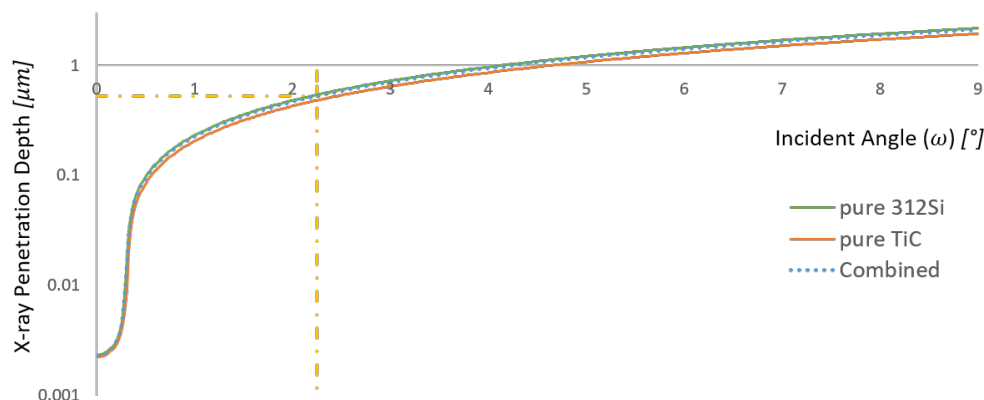


Fig. A3.1 – X-ray penetration depth vs. grazing angle for Ti_3SiC_2 and TiC as calculated using the X-ray Interactions with Matter data tables developed by The Center for X-ray Optics [73].

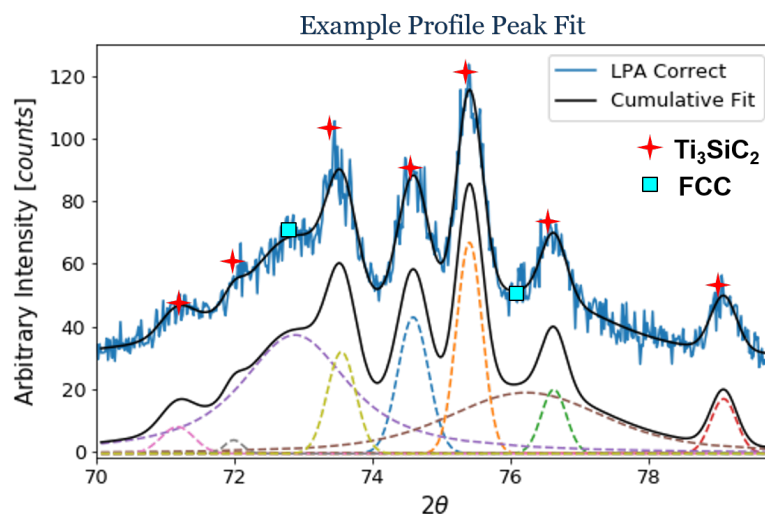


Fig. A3.2 – Example of experimental GIXRD profile with background stripped and intensity corrected for Lorentz polarization and x-ray absorption (LPA) contributions with the individual peaks fitted and along with their cumulative profile. Profiles were vertically staggered for ease of viewing.

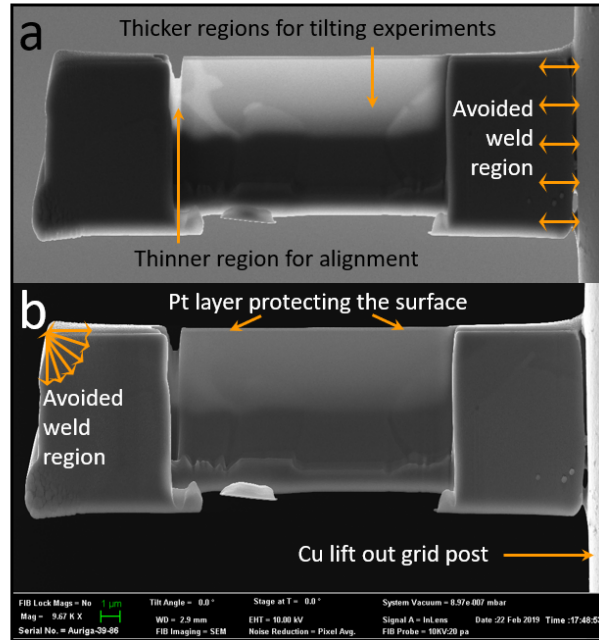


Fig. A3.3 – SEM micrographs of TEM lamella prepared using FIB lift out and polishing to produce a region just thick enough for diffraction experiments, such as $\mathbf{g \cdot b}$ and convergent beam electron diffraction (CBED). A very thin region is included to the side for high magnification alignments. The lamella is imaged with secondary electron (a) and InLens (b) detectors.

A.5 Supplemental Figures: Chapter 5

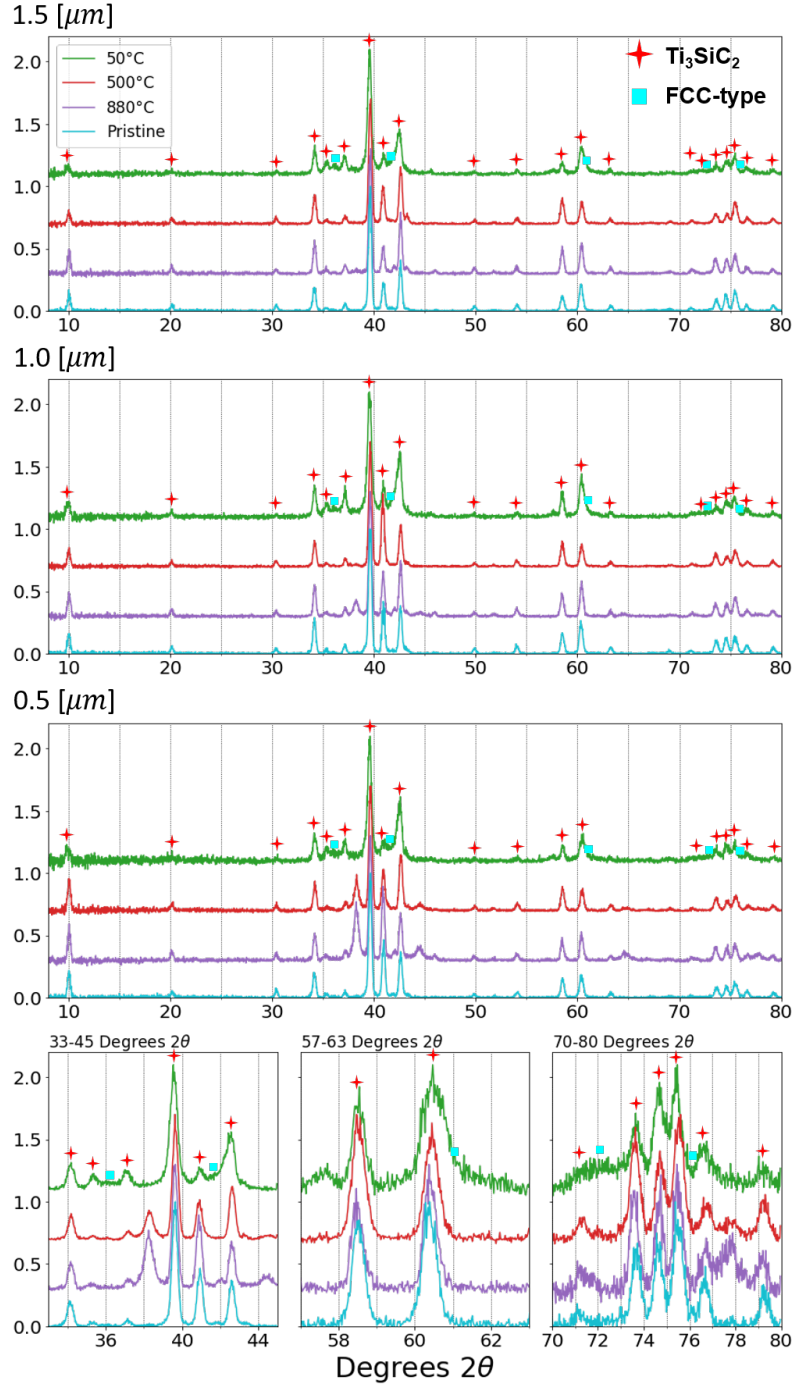


Fig. A5.1 – Full diffraction profiles for 1.5, 1.0, and 0.5 μm depths probed for the pristine condition and $3.5 \times 10^{16} \text{ cm}^{-2}$ fluence at each of the *in situ* irradiation temperature conditions with expanded views of the shallowest depth probed. Extended counting statistics for reduced ranges are detailed in Table 3.3.

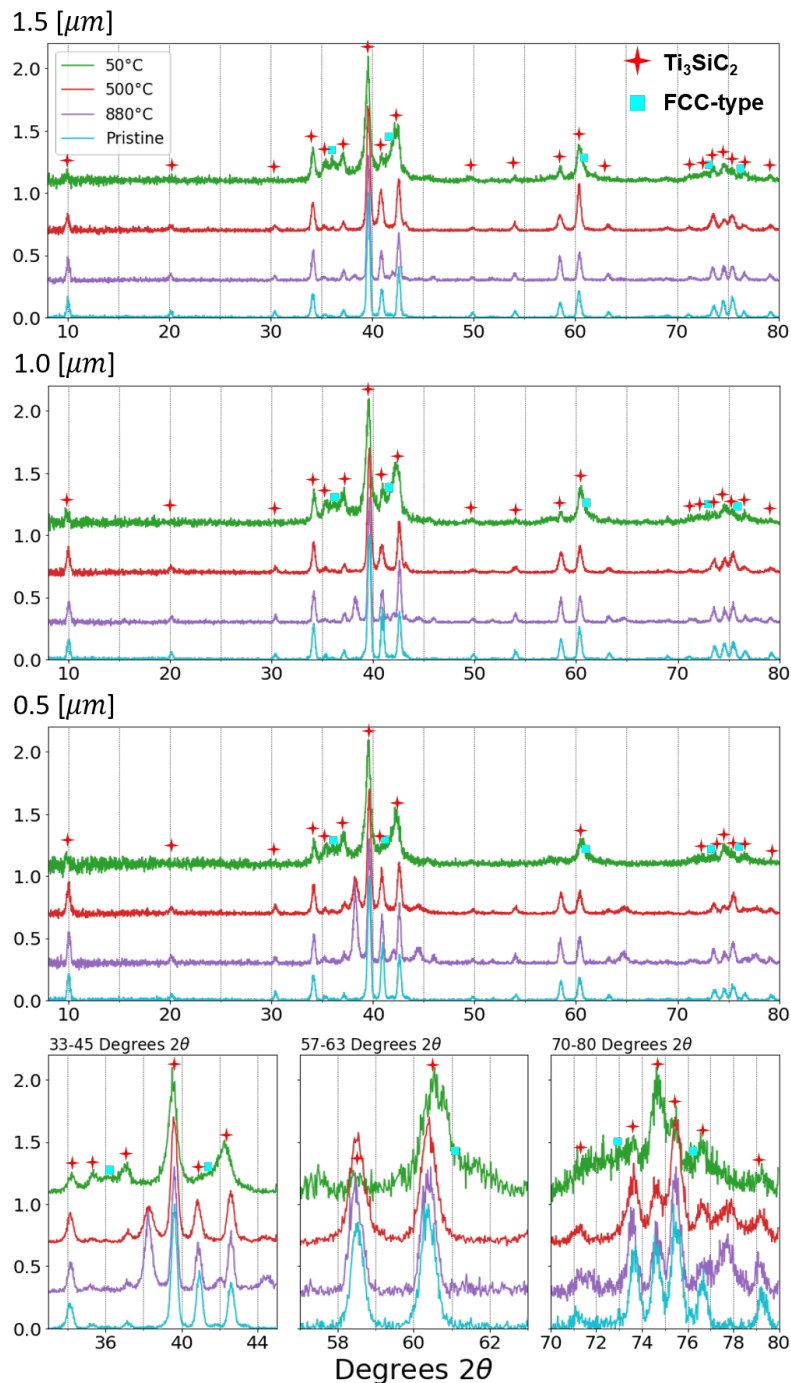


Fig. A5.2 – Full diffraction profiles for 1.5, 1.0, and 0.5 μm depths probed for the pristine condition and $4.2 \times 10^{16} \text{ cm}^{-2}$ fluence at each of the *in situ* irradiation temperature conditions with expanded views of the shallowest depth probed. Extended counting statistics for reduced ranges are detailed in Table 3.3.

A.6 Supplemental Figures: Chapter 6

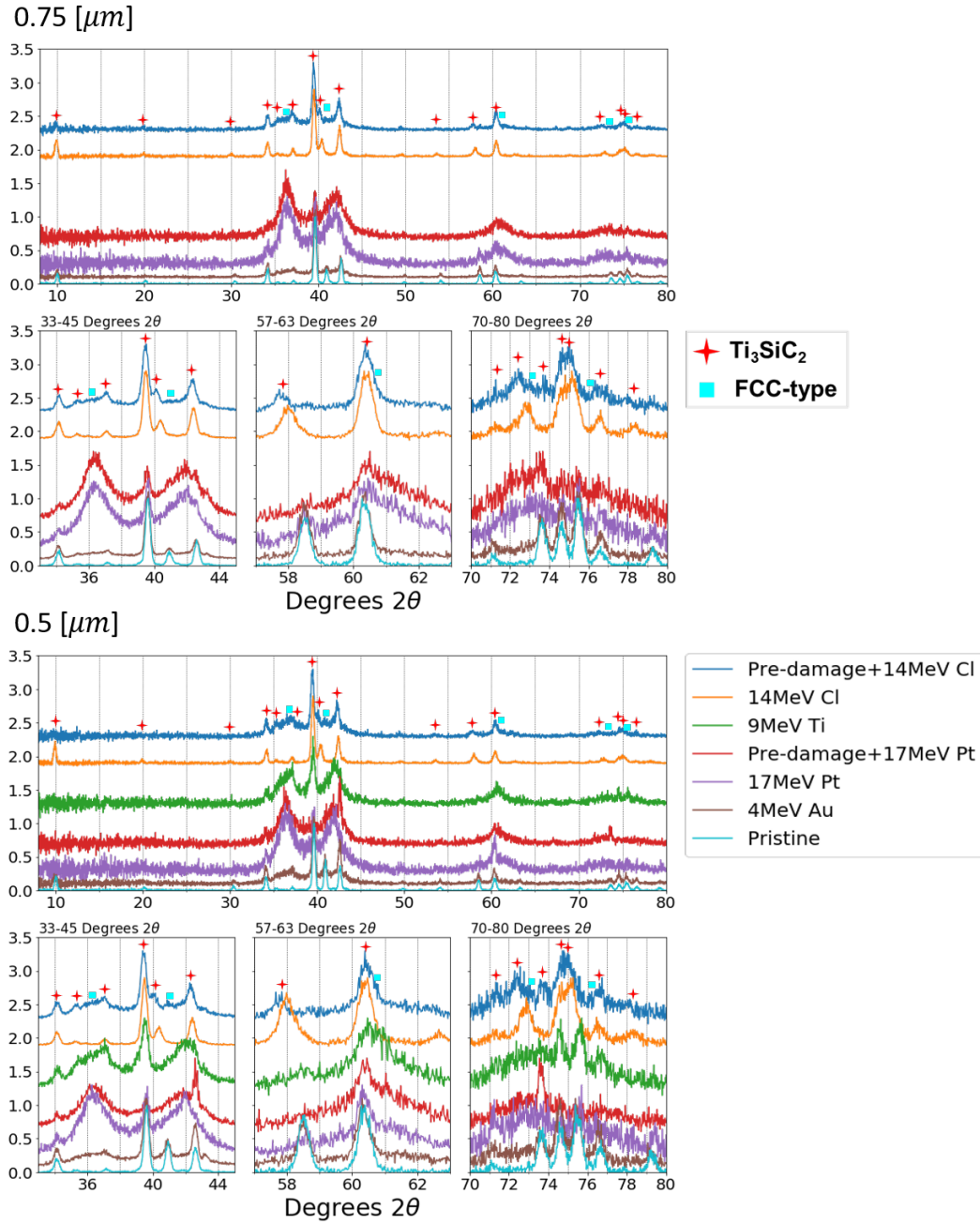


Fig. A6.1 – Full GIXRD profiles of the Au ion pre-damaged and subsequent high energy ion irradiations. Grazing angles were selected to probe 0.5 μm -0.75 μm in the material for each profile and extended counting statistics for reduced ranges are detailed in Table 3.3. Included is a repetition of the $2.8 \times 10^{16} \text{ cm}^{-2}$ fluence 9 MeV Ti ion irradiation from the previous study, probed to a depth of 0.5 μm , roughly matching the S_e and damage dose for this study.

B Python Scripts

Python 3.6 [79] was utilized to process, store, and analyze much of the data gathered in this study. Of particular usefulness were jupyter notebooks [80] for use as executable cells for the rapid adaptation and implementation of the iterative c/a method. Included here are some of scripts and cells written to implement the equations and methods detailed in Section 3.3.4. Note that this appendix is only intended to give a sense of the implementation of the iterative method and is not an exhaustive inclusion of every code line used in the characterization and analysis, as the current version of the script is not material generalized. References for the adaptation of this method to the study of ion irradiated hexagonal polycrystalline materials should be directed to the first publication of this study, where it was first implemented: William Alexander Hanson *et al.* in Acta Materialia [64].

B.1 Initial Packages

These are the initial packages that preamble all jupyter notebooks written for this research project. Dictionaries are used to store many data values as the keys may also be used as a kind of data value in addition to the value they point to within their dictionary, and these dictionaries are saved in “.json” file types. As such, the classes for “NPEncoder” and “NPDecoder” are defined here to encode numpy arrays to be correctly stored in the dictionaries when saved as a JSON file and then correctly reinitialize the numpy arrays when reloading the JSON files into the script.

```
%matplotlib inline
import numpy as np
import matplotlib.pyplot as plt
import json
import pandas as pd
import scipy
import statistics as st
from scipy import stats
from scipy.optimize import minimize
class NPEncoder(json.JSONEncoder):
    def default(self, obj):
        if isinstance(obj, np.ndarray):
            return obj.tolist()
        return json.JSONEncoder.default(self, obj)
class NPDecoder(json.JSONDecoder):
    def __init__(self, **kwargs):
```

```

        json.JSONDecoder.__init__(self, **kwargs)
        self.parse_array = self.JSONArray
        self.scan_once = json.scanner.py_make_scanner(self)
    def JSONArray(self, s_and_end, scan_once, **kwargs):
        values, end = json.decoder.JSONArray(s_and_end, scan_once, **
                                              kwargs)

        return np.array(values), end
import os

```

B.2 Definitions

This section contains many of the definitions required to run the iterative method; however, again this is not an exhaustive code listing. Shorthand definitions are not included here for brevity, as they simply make the script easier to read. For example:

```

def sindg(x):
    return np.sin(np.deg2rad(x))

```

simply allows the calling of the $\sin(x)$ function without having to convert x from experimentally measured [*degrees*] typical in diffraction measurements to the [*radians*] the numpy operation requires. There are many such other definitions, but they are not included here as their functions are similarly self explanatory. However, of particular import is the indexed (hkl), which are stored as the string keys for their peak position values in the sample dictionary data sets, so the following definition converts this string key into the individual h , k , and l numerical values.

```

def hkl(hkl_s):
    if '-' in hkl_s:
        prevneg = False
        h_occ = False
        k_occ = False
        l_occ = False
    for i in range(len(hkl_s)):
        if hkl_s[i]=='-':
            prevneg = True
        elif i==0:
            h = hkl_s[i]
            h_occ=True
        elif prevneg:
            if h_occ and k_occ and l_occ:
                l = l+hkl_s[i]
            elif h_occ and k_occ:
                l = hkl_s[i-1]+hkl_s[i]
            l_occ = True

```

```

        elif h_occ:
            k = hkl_s[i-1]+hkl_s[i]
            k_occ = True
            prevneg = False
        elif i == 1:
            h = hkl_s[i-1]+hkl_s[i]
            h_occ = True
            prevneg = False
    else:
        if h_occ and k_occ and l_occ:
            l = l+hkl_s[i]
        elif h_occ and k_occ:
            l = hkl_s[i]
            l_occ = True
        elif h_occ:
            k = hkl_s[i]
            k_occ = True
    return int(h),int(k),int(l)
else:
    if len(hkl_s)==3:
        return int(hkl_s[0]),int(hkl_s[1]),int(hkl_s[2])
    elif len(hkl_s)==4:
        return int(hkl_s[0]),int(hkl_s[1]),int(hkl_s[2]+hkl_s[3])

```

The following definitions are used in defining the x-ray elastic constants (XECs) based off peak index (*hkl*) and position.

```

def LSS_macrostress_a0(parameters):
    sig11,sig22,sig33,sig12,sig13,sig23,a0 = parameters
    if XECmodel == 'voigt':
        eq = 0
        for hkl_s, peakLP in m312si_aLP.items():
            prev_eq = eq
            psi = dtt2psi(m312si_peakpos[hkl_s],omega)
            eq = prev_eq+(((s2['s2'])*(sig11*cosdg(phi)**2*sindg(psi)**2+
                                sig22*sindg(phi)**2*sindg(
                                psi)**2+sig33*cosdg(psi)
                                **2)+s2['s2']*(sig12*
                                sindg(2*phi)*sindg(psi)**
                                2+sig13*cosdg(phi)*sindg(
                                2*psi)+sig23*sindg(phi)*
                                sindg(2*psi))+s1['s1']*(
                                sig11+sig22+sig33))*a0+a0
                                ) - peakLP)**2

        return eq
    else:
        print('No XECmodel defined')
        return 'error'

def macro_a0_2_aLP(sig,a0,peakpos,s1,s2):
    psi = dtt2psi(peakpos,omega)

```

```

return ((s2*(sig['11']*cosdg(phi)**2*sindg(psi)**2+sig['22']*sindg(phi)
)**2*sindg(psi)**2+sig['33']*
cosdg(psi)**2)+s2*(sig['12']*
sindg(2*phi)*sindg(psi)**2+sig['
13']*cosdg(phi)*sindg(2*psi)+sig[
'23']*sindg(phi)*sindg(2*psi))+s1
*(sig['11']+sig['22']+sig['33']))
*a0+a0)

def s_voigt(C_ten):
    x = C_ten['11']+C_ten['22']+C_ten['33']
    y = C_ten['12']+C_ten['13']+C_ten['23']
    z = C_ten['44']+C_ten['55']+C_ten['66']
    s1 = {'s1':-3/2*(x+4*y-2*z)/((x-y+3*z)*(x+2*y))}
    s2 = {'s2':15/(2*x-2*y+6*z)}
    return s1,s2

```

These definitions are for the relationships in Eqs. (3.15) and (3.16).

```

def c_a_from_linR(m_aLP,mPP):
    x_hkl = {}; y_hkl = {}
    for hkl_n, peak in mPP.items():
        h,k,l=hkl(hkl_n)
        x_hkl.update({hkl_n:calc_x_hkl(l)})
        y_hkl.update({hkl_n:calc_y_hkl(m_aLP[hkl_n],dtt2dspace(mPP[hkl_n])
, h,k,l)})

    x = np.array(list(x_hkl.values()))
    y = np.array(list(y_hkl.values()))
    plt.plot(x,y,'o')
    slope = linR_slope(x,y)
    return slope**(-1/2)

def calc_y_hkl(a_hkl,d_hkl,h,k,l):
    return (a_hkl/d_hkl)**2-4/3*(h**2+h*k+k**2)

def calc_x_hkl(l):
    return l**2

def linR_slope(x,y):
    slope, y_int, r_val, p_val, std_err = stats.linregress(x,y)
    return slope

def c_a2_c(a,c_a):
    return a*c_a

```

B.3 Iterative c/a method

These cells are material parameters that must be input to use the iterative method below. The example here is for a data set from one of the 9 MeV Ti ion irradiations gathered at a depth of 0.5 μm .

```
# dataset parameters
sample = '9MeV_Ti'
depth = '0o5um'
omega = omegaDict[sample+'_'+depth.replace('o','.')]
print(omega)
phi = 0
overwritingdictionary = False
newdictionary = False

# material and model parameters
xtalsys = 'hex' # hexagonal = hex, cubic = cubic
XECmodel = 'voigt' # voigt or reuss
# Stiffness tensor
C_ten = {
    '11':365,
    '12':125,
    '13':120,
    '33':375,
    '44':122
}
C_ten = fillC_Ten(C_ten,xtalsys) # fills in full tensor
S_ten = StoC(C_ten) # converts stiffness to compliance
```

This cell shows how the data set desired is imported from and exported to a saved JSON file. The data dictionary keys and values are the indices in (*hkl*) notation and their measured peak positions in *degrees 2 θ* , respectively.

```
m312si_peakpos = json.load(open(sample+'_'+depth+'_312Si_peakpos.json','r')
                             ,cls=NPDecoder)
json.dump(m312si_peakpos, open(sample+'_'+depth+'_312Si_peakpos.json','w')
          ,cls=NPEncoder)
```

The following script cell is the iterative method itself. The loop here will iterate until the c/a has converged such that there is a $< 10^{-6}\%$ change between iterations, but it will also terminate after 20 cycles to prevent diverging infinite loops. That said it typically converges within 11 iterations.

```
# Generate Blank dictionaries
m312si_aLP = {}; m312si_cLP = {}

# c/a assumed starting point
assumed_c_a = 5.76
```

```

c_a = assumed_c_a
keepgoing = True
counter = 0
while keepgoing:
    # Calculate XECs from hkl_s
    if XECmodel == 'voigt':
        s1,s2 = s_voigt(C_ten)

    counter = counter+1
    print(counter)

    # Populate/update LP dictionary from dspacing values using
    # current c_a value
    for hkl_s, peak in m312si_peakpos.items():
        m312si_aLP.update({hkl_s:hex_dtt2aLP(peak,hkl_s,c_a)})

    config = {
        "x0": [0,0,0,0,0,0,3.076],      # Parameters / initial guess
        "method": 'Powell',
    }

    vari = minimize(LSS_macrostress_a0,**config)
    a0 = vari.x[6]
    sig = {'11':vari.x[0], '22':vari.x[1], '33':vari.x[2], '12':vari.x[3], '13':
           ':vari.x[4], '23':vari.x[5]}

    aLP_calc = {}
    for hkl_s,peak in m312si_peakpos.items():
        if XECmodel == 'voigt':
            aLP_calc.update({hkl_s:macro_a0_2_aLP(sig,a0,peak,s1['s1'],s2[
                's2'])})
    c_a_calc = c_a_from_linR(aLP_calc,m312si_peakpos)

    print(c_a_calc,a0)
    if abs(c_a - c_a_calc) < .00000001:
        keepgoing = False
    elif counter > 20:
        keepgoing = False

    c_a = c_a_calc

    for hkl_s, peak in aLP_calc.items():
        print(hkl_s, '___original___',m312si_aLP[hkl_s], '___calc___',peak)
print(sample+'_'+depth)

```

Once the above script is finished iterating, the final c and a-LPs are calculated from the experimentally determined peak positions and the converged c/a value:

```

for hkl_s, peak in m312si_peakpos.items():
    m312si_aLP.update({hkl_s:hex_dtt2aLP(peak,hkl_s,c_a)})
    m312si_cLP.update({hkl_s:c_a2_c(m312si_aLP[hkl_s],c_a)})

```


C Project Publishing

C.1 Peer-reviewed Journal Publications

- [64] W.A. Hanson, M.K. Patel, M.L. Crespillo, Y. Zhang, W.J. Weber. Influence of electronic vs nuclear energy loss in radiation damage of Ti_3SiC_2 . *Acta Materialia*. 161 (2018) 302-310. doi:10.1016/j.actamat.2018.09.027.
- [16] W.A. Hanson, M.K. Patel, M.L. Crespillo, F. Zhang, S.J. Zinkle, Y. Zhang, W.J. Weber. Ionizing vs collisional radiation damage in materials: separated competing, and synergistic effects in Ti_3SiC_2 . *Acta Materialia*. Under Review (Submitted Jan 24, 2019)

C.2 Conference Presentations

(MS&T2017) Materials Science and Technology Annual Conference

- Pittsburgh, PA | Oct 2017
- “Structural Characterization of Nanolayered Response in Select MAX Phase Ceramics to High Fluence Self-ion Irradiation.” W.A. Hanson, Y. Zhang, W.J. Weber.
- Oral Presentation

(TMS2018) The Minerals, Metals & Materials Society Annual Conference

- Phoenix, AZ | Mar 2018
- “Irradiaion Temperature Influence on Nanolayered Response in Select MAX Phase Ceamics to High Fluence Self-ion Irradiation.” W.A. Hanson, Y. Zhang, W.J. Weber.
- Oral Presentation

(IBMM2018) 21st International Conference on Ion Beam Modification of Materials

- San Antonio, TX | Jun 2018
- “Effects of Temperature and Electronic Energy Loss on the Irradiation Response of Ti₃SiC₂ to Self-Ions.” W.A. Hanson, Y. Zhang, W.J. Weber.
- Oral Presentation

(NuMat2018) The 5th Nuclear Materials Conference

- Seattle, WA | Oct 2018
- “Influence of Electronic Stopping Threshold on Damage Evolution in Ti₃SiC₂ Irradiated with 9 MeV Ti ions.” W.A. Hanson, Y. Zhang, W.J. Weber.
- Poster Presentation | 2nd Best Poster Award

Vita

William Alexander Hanson grew up in Laurel, MD, son to David P. Hanson and Sharon L. Hanson. In 2014, he graduated from Drexel University in Philadelphia, PA with his B.S. degree in Materials Science and Engineering and a minor in Nuclear Engineering, magna cum laude. He also graduated with Distinction from Drexel's Pennoni Honors College, which required broadening his education through significant additional coursework outside his major field of study and a capstone project worthy of honors. Alex was inducted into the PA Zeta chapter of Tau Beta Pi, the engineering honors society. He served two terms as the chapter president and saw 300% increase in membership induction rates and involvement and attended the 2013 annual convention as the chapter delegate. In 2014, he was inducted into the PA Alpha chapter of Alpha Sigma Mu, the materials science and engineering honors society.

During the course of his B.S. degree, Alex worked for Carpenter Technology Corp. in the Alloy Research and Development and Product Processing Technology departments over two, six-month Co-ops in 2011 and 2013. He was also heavily involved in undergraduate research throughout his education, working as a research assistant in the Layered Solids group on development of novel MAX phase ceramics, starting in 2009. Early in 2013, he joined the Dynamic Characterization group to begin research, which culminated in his capstone project, evaluation of fission product surrogate diffusion in model TRISO systems, utilizing *in situ* transmission electron microscopy annealing experiments. Following his graduation from Drexel, Alex began the pursuit of his Ph.D. in Materials Science and Engineering at the University of Tennessee, Knoxville, as a Chancellors Fellow working under the mentorship of Prof. William J. Weber in the Irradiation Effects in Materials Group. He focused his research efforts on understanding nuclear vs. electronic energy loss effects during ion irradiation

of MAX phase ceramics, evaluating the influence of the different energy loss pathways on the damage evolution in the layered solid. He has presented his research at several major conferences, in both oral and poster formats, received several awards, and published multiple peer-reviewed journal articles over his course of study at the University of Tennessee.

Alex served as a mentor from 2015 to 2017 for the ASM Materials Education Foundation Materials Camp, hosted by the Oak Ridge chapter of American Society for Materials, International (ASM). Outside of this academic service, he has been an active member of the Hospitaller Order of St. John of Jerusalem, Knights Hospitaller since 2010 and received the accolade of Knighthood in 2017. He is also involved at Legacy Church, Knoxville as a sound engineer and in service with the Emerald Youth Foundation. Following the completion of his Ph.D. at the University of Tennessee, Knoxville in February, 2019, Alex began work as a postdoctoral research associate working in post irradiation examination at Idaho National Laboratory, located in Idaho Falls, ID.