Irradiation-Induced Amorphous-to-Crystalline Phase Transformations in Ceramic Materials

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Ceramics are exposed to extreme irradiation environments in numerous applications, including nuclear fuels and claddings, immobilizing and storing nuclear waste, radiation shielding, space exploration and travel, and doping of semiconductors. In such environments, energetic particles impinging on crystalline ceramic materials lead to the creation of damage through various energy transfer mechanisms, culminating in changes to material microstructures, properties, and performance. Although crystalline ceramics have historically been used in practical irradiation-facing applications, amorphous ceramics have recently garnered interest for their unique properties and characteristics, including irradiation tolerance. Amorphous materials are purported to better resist irradiation than crystalline ceramics. The a-to-c transformations can be broadly categorized into three types: (1) athermal, resulting exclusively from either electron or ion irradiation of amorphous material, (2) resulting from the combined effects of heating and either ion or electron irradiation, or (3) epitaxial growth or recrystallization of an amorphous oxide due to ion or electron irradiation.

amorphous-to-crystalline transformations   ceramics   nuclear stopping   electronic stopping

1. Zirconium Dioxide

Roddatis et al. demonstrated that transmission electron microscopy (TEM) beam irradiation of amorphous ZrO_2 films prepared via a self-assembled monolayer method can result in an a-to-c transformation [1]. At a cryogenic temperature of 4.2 K, a 160 kV TEM electron beam at a current density of 0.5 A/cm^2 was able to form crystallites in the as-prepared amorphous film. The size and number of crystallites increased with irradiation exposure time. After 20 min of TEM electron beam irradiation, the crystallites grew to ~10 nm in size, and fast Fourier transform (FFT) analysis of the high-resolution TEM (HR-TEM) images confirmed that the crystallites were structured as tetragonal ZrO_2. To assess whether there was a change in the coordination and film composition as a result of TEM electron irradiation, electron energy loss spectroscopy (EELS) was performed on an as-prepared amorphous sample, a sample irradiated for 5 min with TEM electrons, a tetragonal ZrO_2 powder, and a monoclinic ZrO_2 powder. From the oxygen K-edge spectra, it was found that the amorphous sample lacked a distinct peak at 534 eV, but such a peak was present in both the irradiated sample and the reference standards. Therefore, the EELS results provided evidence for a change in coordination in the amorphous film due to electron irradiation-induced a-to-c transformation. It was also found that the a-to-c transformation occurred faster when amorphous films were irradiated with 200 kV electrons at room temperature compared to with 160 kV electrons at 4.2 K. However, crystallization at room temperature was faster with 200 kV than with 400 kV electron irradiation. While the effects of

temperature and electron energy could not be deconvoluted, the authors explained that this seemingly strange result might be due to inelastic scattering being less probable at higher electron energies and that inelastic electron scattering of electrons on the sample surface plays a role in the electron irradiation-induced structural changes observed [1].

Naguib and Kelly irradiated amorphous ZrO_2 films with Kr ions at energies ranging from 2–35 keV [2]. The amorphous films were prepared by sputtering crystalline ZrO_2 films on Zr foil with Kr or O_2 ions at 6 keV for 75 min, yielding an amorphized layer of ZrO_2. The as-prepared films were confirmed to be amorphous by TEM selected area electron diffraction (SAED). They first investigated the thermally-induced crystallization of amorphous ZrO_2 by TEM in situ pulse heating over 400–540 °C. This was found to result in recrystallization of the amorphous film, and SAED analysis indicated that the resulting crystallites were mainly cubic, with some monoclinic character [2]. As a control, amorphous films were heated in a tube furnace until crystallization was achieved. Samples achieved full crystallization when heated at temperatures between 520–540 °C for 5 min or in air at 400–425 °C for 360 min and showed similar SAED patterns to the pulse-heated sample.

Subsequently, Naguib and Kelly observed athermal irradiation-induced a-to-c transformations as a result of Kr ion bombardment at fluxes ranging from 1–20 $\mu A/cm^2$. As the dose rate (i.e., flux) decreased, the corresponding threshold ion fluence required to induce an a-to-c transformation increased dramatically. The crystallites produced by ion bombardment were found to produce SAED patterns similar to those produced in crystalline films formed by heating alone and yielded crystallite sizes of 80–100 nm and ~700 nm, respectively.

In a similar study, Leteurtre and Soullard created amorphous ZrO_2 films prepared by sputtering crystalline ZrO_2 with O_2 ions [3]. The resulting amorphous films were then irradiated with 1 MeV Kr ions. While these irradiation conditions did not consistently result in a homogeneous a-to-c transformation, TEM analysis of the irradiated amorphous films exhibited distinct diffraction spot patterns in regions having higher electron transmission, indicating at least partial a-to-c transformation. The authors attributed this to the effects of collision cascades creating zones with differentiated order.

2. Titanium Dioxide

Kern et al. conducted experiments in which electrolytically deposited amorphous TiO_2 films on polished AISI 316 steel substrate were irradiated with a scanning electron microscope (SEM) electron beam at 20 kV under beam currents of 24 μA, 250 nA, 30 nA, and 10 nA [4]. The samples were mounted to a heating stage that was either held at room temperature or 250 °C, and the irradiation time was varied between 1 and 600 s. Results showed evidence of a decrease in film thickness by ~20 nm when irradiated at 10 nA and by ~40 nm when irradiated at 30 nA or higher beam current. The change in film thickness was the result of electron-stimulated O desorption in the amorphous TiO_2 film and reduction of TiO_2 to TiO [4]. Some of the irradiation conditions resulted in a phase transformation from an amorphous state to anatase TiO_2 as identified via Raman spectroscopy. Specifically, the amorphous-to-anatase transformation occurred locally after irradiation with 24 μA for 600 s at room temperature. Increasing temperature accelerated the rate of transformation; when the sample stage was preheated to 250 °C,

the transformation occurred after only 60 s at the same beam current. Both experimental temperatures were below the 440 °C thermally-induced crystallization temperature of electrolytically deposited amorphous TiO_2 films [4][5]. Local heating from the electron beam may have contributed to, but could not completely explain, the lower phase transformation temperatures under irradiation.

Smith and coworkers investigated the effects of proton irradiation on amorphous TiO_2 nanotubes and found that 200 keV proton irradiation at a fluence of 2.18×10^{17} ions/cm^2 at both room temperature (RT) and a higher temperature (HT) of 250 °C resulted in varying degrees of a-to-c phase transformations [6]. TEM and SAED analysis showed that irradiation at RT resulted in a partial phase transformation of the amorphous material to anatase and rutile TiO_2, while irradiation at 250 °C resulted in the formation of only the disordered rutile phase. Rings corresponding to anatase (101) and rutile (101) and (111) were indexed in the RT irradiated sample, while only rings corresponding to the rutile phase were visible in the SAED for the HT sample. The presence of a disordered rutile phase was also confirmed by Raman spectroscopy and EELS. Based on the phase diagram of TiO_2, the crystallization to the anatase phase generally requires thermal annealing temperatures > 400 °C, and the rutile phase requires temperatures > 600 °C [6][7]. In a sense, this corroborates Kern's [4] finding that increasing irradiation temperature accelerated the a-to-c transformation. Additionally, thermal annealing of TiO_2 nanotubes at >600 °C is generally not a viable method for synthesizing rutile TiO_2 nanotubes because it results in the collapse of the nanotube structure [6]. However, SEM analysis showed that the proton irradiation did not significantly change the morphology of the nanotubes. Therefore, it was highlighted that a new avenue to create crystalline nanostructures through ion irradiation on amorphous starting materials.

3. Aluminum Oxide

Liu et al. investigated the effects of electron irradiation of amorphous Al_2O_3 that led to an a-to-c transformation [8][9]. The as-prepared samples were 300 nm thick layers of amorphous Al_2O_3 on dislocation-free ⟨100⟩

B-doped Si wafers. Electron irradiation was conducted using a TEM electron beam operating at 100 keV at a dose rate of 100 mA/cm^2. When the exposure time was varied over 1–16 min at a dose rate of 100 mA/cm^2, near-spherical trigonal Al_2O_3 crystallites formed in the bulk layer of Al_2O_3, and dendrites formed at the Al_2O_3/Si boundary. As irradiation time increased, the size and number of crystallites in the amorphous layer increased, while the dendrites remained unchanged. The size of crystallites began to approach a steady state after about 5 min, and the crystallite density plateaued after an irradiation time of 10 min. A critical electron beam dose rate was required for the a-to-c transformation to occur. Specifically, when the particles were irradiated at 10 mA/cm^2, no a-to-c transformation occurred [8]. The authors initially thought that thermal activation from the electron beam due to local heating was the main cause of the a-to-c transformation [8]. However, in a follow-up publication, the estimated temperature contribution was found to not be significant enough to be a factor in the mechanism for the observed a-to-c transformation [9]. The authors subsequently proposed that electron irradiation-induced defects were a more likely cause for the a-to-c transformation [9].

Zhou and Sood used two ion irradiation conditions to first form an amorphous layer in an α-axis oriented single crystal sapphire (α-Al_2O_3), then subsequently induce epitaxial crystallization in that amorphous layer [10]. Amorphous layers on single crystal α-Al_2O_3 samples were generated by irradiating with 100 keV In ions to a fluence between 0.7 and 2.7×10^{16} ions/cm^2. The amorphized layers were then irradiated with 1.5 MeV Si ions to a fluence of 3×10^{16} ions/cm^2 at 400 °C. Rutherford backscattering and channeling (RBSC) measurements showed that a thin amorphous layer was successfully created on the surface of the α-Al_2O_3 after the initial In ion irradiation. RBSC spectra after the 400 °C Si irradiation, then showed signs of recrystallization to a γ-Al_2O_3 phase, consistent with that formed through 700 °C thermal annealing. These results demonstrated that epitaxial recrystallization of amorphous Al_2O_3 is possible at lower temperatures when used in conjunction with Si ion irradiation.

In a more recent study of amorphous films on single crystal (0001) α-Al_2O_3, Ning et al. found that epitaxial growth of γ-Al_2O_3 in the amorphous layer could be induced via irradiation with either 360 keV Ar^{2+} ions or 180 keV O^+ ions [11] at various temperatures. RBSC spectra of the amorphous films before and after irradiation indicated that epitaxial recrystallization of γ-Al_2O_3 had taken place, and this was confirmed by cross-sectional TEM and SAED. When comparing SAED patterns of the unirradiated and O ion irradiated films, a diffraction pattern appeared that was consistent with orientation-related epitaxial growth of γ-Al_2O_3 from the original single crystal layer [11]. The ion beam-induced epitaxial growth between 400 and 600 °C produced films with higher epitaxial quality than those produced by annealing alone at 800 °C. This improvement in quality was attributed to the elimination of {111} twin boundaries in the γ-Al_2O_3 layer due to ion channeling effects during the irradiation.

Finally, Sina et al. showed that epitaxial crystallization of γ-Al_2O_3 on α-Al_2O_3 could be accomplished via two-step ion irradiation at room temperature [12]. In their study, α-Al_2O_3 samples were irradiated with Zr^+ ions at 175 keV to fluences ranging from 7.5×10^{15} to 1.5×10^{16} ions/cm^2 and then subsequently irradiated with O^+ ions at 55 keV to fluences that corresponded with 25% of the maximum displacement damage dose produced by the initial Zr^+ ion irradiation. The lower Zr^+ ion fluence (7.5×10^{15} ions/cm^2) specimens had buried polycrystalline (but not amorphous) regions at depths that corresponded to the maximum Zr^+ ion range calculated by SRIM; subsequent irradiation with O^+ ions changed little. Meanwhile, in samples that were irradiated to higher Zr^+ ion fluences of 1.5×10^{16} ions/cm^2, a sub-surface amorphous layer appeared at depths of 20–65 nm, which corresponded to the peak damage calculated by SRIM simulations [12].

4. Silicon Oxide

Upon ion irradiation, a-to-c transformations have been observed in the Si regions of SiO after SiO transformed into both Si and SiO_2 [13][14]. Rodichev et al. [13] irradiated SiO at room temperature with 575 MeV Ni and 863 MeV Pb ions to fluences of 10^{11} ions/cm^2 and 10^{13} ions/cm^2, respectively. They observed the transition of SiO to Si and SiO_2 through infrared (IR) spectroscopy, in which the Si-O bond for SiO at 1000 cm^{-1} shifted to 1035–1055 cm^{-1}, which was consistent with the Si-O bond for SiO_2. TEM images of the irradiated samples confirmed these results with two distinct regions observed: one with light-contrasting amorphous zones and the other being localized dark-contrasting zones attributed to high-Z number contrast. Si nanocrystals were believed to be present due to the lattice fringes in the dark-contrast regions within the HR-TEM images. These darker regions were located in a track

within the material in a crystal-like arrangement. The number of dark regions increases with ion fluence. The authors concluded that two types of transformations occurred. The first involved short-range diffusion where SiO converted to Si and SiO_2, wherein the Si aggregates were small and mixed with SiO_2 and were thus unresolvable in TEM. The second type of transformation that occurred was diffusion over several atomic distances close to the ion track, which accounted for the oxygen concentration near the core of the ion track and rearrangement of Si atoms into nanocrystals.

When amorphous SiO was irradiated with 80 keV He ions at a fluence of 7×10^{20} ions/cm^2, small circular precipitates were observed by Walters et al. [14]. The precipitates exhibited an electron diffraction pattern matching closely with crystallized Si. During irradiation, the sample reached 850 °C. To ensure that the crystallization was an effect of irradiation and not thermal annealing, the researchers thermally annealed the samples at 900 °C. Following 60 min exposure to 900 °C, there were no changes, suggesting that the crystallites formed as a result of irradiation. Walters and coworkers also found that the crystallization as a function of dose was non-linear and instead followed an S-shaped curve described by the Avrami equation. Below a flux of 2×10^{18} ions/m^2·s, the authors state that, similar to other non-metallic materials, amorphous SiO requires extended diffusion to form the observed precipitates.

SiO_2 has been investigated with neutral atom, ion, and electron irradiation [15][16], and a-to-c transformations were found with neutral atom and electron irradiation. When Mizutani et al. irradiated SiO_2 with 400 eV Ne neutral atoms or Ne ions to a fluence of 2×10^{17} atoms/cm^2 or ions/cm^2, RBS showed that O was preferentially sputtered by the Ne ion, creating an O-deficient, Si-rich layer on the surface of the ion irradiated sample [15]. By contrast, neutral Ne atom irradiation did not create a chemical deficiency or enrichment at the surface. Auger electron spectroscopy (AES) showed that the neutral Ne atom irradiated sample changed to a different phase, although its chemical composition was maintained, whereas the Ne ion irradiated sample showed AES peaks associated with Si and SiO_x, indicating chemical separation.

When neutral Ne atom irradiation was conducted at a lower energy of 350 eV and to a lower fluence of 1×10^{17} atoms/cm^2, TEM analysis exhibited darker regions, suggesting crystalline phases were formed, though electron diffraction patterns could not be obtained due to the small size of the crystallites. Using Ne ions at the same energy of 350 eV to the same fluence of 1×10^{17} ions/cm^2, however, no layers or regions having different contrast were found, even with the Si-rich surface layer. Furthermore, following neutral Ne and Kr atom irradiation (both at 350 eV, 1×10^{17} atoms/cm^2), reflection high-energy electron diffraction (RHEED) analysis showed diffraction rings associated with α-cristobalite and α-quartz, respectively. These results suggested that both Ne and Kr neutral atom irradiations caused a-to-c transformations, whereas the ion irradiations did not. The authors suggested that a greater extent of crystal growth may have occurred due to successive neutral irradiations. They also noted that since the two crystalline phases (α-cristobalite and α-quartz) were not found in the same sample, but rather one phase induced by Kr and one induced by Ne, the neutral beam irradiation conditions determine the pressure and temperature processes governing which crystalline phase will form. They also found that the preferential sputtering of O with the ionic counterparts (e.g., Kr^+ and Ne^+) prevented crystallinity changes due to the higher density of Si in

the samples. They suggested that with neutral beam irradiation, local hotspots were formed by the bombardment of neutral atoms on the surface atoms.

Other work by Du et al. using 200 kV electron irradiation of amorphous SiO_2 to a dose of 10^{18} C/m^2 showed that rather than SiO_2 crystallizing, Si crystallized in two steps [16]. Initially, in the amorphous SiO_2 sample, amorphous Si formed and then eventually crystallized with continued electron irradiation. The authors stated that the bonds were broken by creating an O vacancy from the knock-on displacement as a result of energy transferred from the electron irradiation. Because of the O vacancies, the Si atoms then aggregated towards one another. They then argued that the beam heating decreased the nucleation barrier, while knock-on displacement increased the potential energy above the ground state, thus leading to the crystallization of Si.

5. Silicon Carbide

Silicon carbide is another ceramic material that has also demonstrated a-to-c transformations upon irradiation with Xe and Si ions. Amorphous SiC samples were prepared by Zhang et al. and then irradiated with 5 MeV Xe to a fluence of 1.15×10^{16} ions/cm^2 at 700 K [17]. The amorphous film of SiC formed randomly oriented crystalline grains homogeneously distributed throughout the material. While amorphous regions remain, the crystalline grains are of the 3C-SiC polymorph with a cubic structure consistent with the known zinc-blende structure of the 3C-SiC polymorph [18]. SAED patterns demonstrating the cubic crystalline structure formed are shown as an inset. The crystalline grains contained stacking faults, identified by the shoulder peak at ~33.7° in the grazing incidence X-ray diffraction (GIXRD) spectrum and confirmed by TEM and Raman spectroscopy. The authors confirmed that the a-to-c transformation was irradiation-induced by conducting thermal annealing at 700 K and finding this was too low a thermal annealing temperature to induce crystalline grain nucleation and growth without irradiation.

The amorphous SiC to crystalline 3C-SiC transformation was also seen under 300 keV Si irradiation to a fluence of 1×10^{17} ions/cm^{-2} at 500 °C and 1050 °C by Heera et al. [19]. In their study, a series of samples were investigated at 500 °C, where one was thermally annealed, and the other was Si ion irradiated. The thermally annealed sample showed no changes from its original amorphous structure, whereas the ion irradiated sample demonstrated both epitaxial and polycrystalline crystallization. Although the ion irradiation-induced crystallization was not homogenous, neither epitaxial nor polycrystalline crystallization could be achieved at 500 °C through thermal annealing alone. The authors suggested that the polycrystalline layer consisted of two main zones, one of 6H-SiC and the other of 3C-SiC, resulting from ion beam-induced random nucleation and subsequent ion beam-enhanced grain growth. A series of samples were also studied at 1050 °C, and it was shown that the sample became fully crystalline following thermal annealing alone. The crystalline thermally annealed sample consisted of columns of hexagonal SiC, aligning with the underlying 6H substrate, though slightly inclined with respect to the substrate. The crystallinity under ion irradiation at 1050 °C was substantially improved, showing almost perfect epitaxial 6H-SiC with a near-surface columnar structured layer and aligned 3C-SiC grains. The overall number of 3C-SiC grains in the ion irradiated sample was smaller than the thermally annealed sample at elevated temperatures.

The effects of 690 keV Xe ion irradiation at dose levels of 10^{15}, 5×10^{15}, and 10^{16} ions/cm^2 on amorphous MoSi$_2$/SiC nanolayered composites were investigated by Lu et al. [20]. Initial electron diffraction showed that the alternating layers of MoSi$_2$/SiC were amorphous. Following Xe$^+$ irradiation, the layers lost their structural integrity, MoSi$_2$ turned into a metastable hexagonal C40 phase, and the SiC began to spheroidize. This behavior occurred at all doses, although the changes were more pronounced with increasing dose. HRTEM showed that the C40 MoSi$_2$ grains were nanocrystalline, while the SiC spheroidization indicated microstructural coarsening. These results from the irradiated sample indicated that the energy of the Xe ions enhanced diffusion similar to thermal annealing at 500 °C, although the irradiating particle energy is not sufficient to fully crystallize the SiC layer.

6. Silicates

Silicates are classified as any derivative of A$_x$B$_y$SiO$_z$ excluding SiO and SiO$_2$ and have exhibited a-to-c transformations under both electron and ion irradiation. Electron irradiation has been shown to induce compositional changes and crystallization in some silicates [21][22], while others exhibited epitaxial recrystallization [23]. Meldrum et al. studied the recrystallization of zircon (ZrSiO$_4$) using two-stage irradiations [24]. First, amorphous ZrSiO$_4$ was created by irradiating a natural crystalline zircon with 1.5 MeV Kr to a dose of 9×10^{14} ions/cm^2 to ensure complete amorphization. Then, 200 keV electron irradiation at a beam current of 90 A/cm^2 induced crystallization zones among the amorphous regions. Upon recrystallization, the diffraction patterns showed that the crystallites adopted cubic or tetragonal ZrO$_2$ structures. When lowering the beam energy below 200 keV, zircon was unable to crystallize within a reasonable experimental time. The authors determined the maximum temperature increase due to beam heating to be only 19 °C, suggesting that thermal effects have little contribution to the observed crystallization [25].

While Meldrum's work did not observe a compositional change associated with the amorphization or subsequent a-to-c transformation, Carrez et al. saw a compositional change followed by crystallization during 300 keV electron irradiation of MgSiO$_3$ at room temperature [22]. Initial SAED showed diffuse rings indicative of amorphous samples, but as the fluence increased above 5×10^{16} electrons/cm^2, small structures began forming on the surface of the sample too small for SAED identification. Above a fluence of 3×10^{17} electrons/cm^2, the material crystallized to MgO as indicated by new diffraction rings. With increasing electron fluence, the rings became progressively sharper, indicating growth of the initial nuclei and newly formed crystallites. The newly formed structure was associated with periclase MgO, though as the fluence increased to 5×10^{18} electrons/cm^2, the periclase rings disappeared, and new rings attributed to forsterite MgO appeared. As the crystallites formed, so did the number of MgO-rich and MgO-poor domains. The authors suggested that SiO$_2$ and MgO were not miscible under the experimental conditions, and the oxide separation is unsurprising as the phase diagram displayed a liquid immiscibility at high temperatures within the composition range of interest. They suggested that the sample went through two stages during irradiation. In the first stage, the sample was unstable and decomposed into MgO and SiO$_2$; in the second stage, nanosized MgO crystallites formed. The nucleation and growth processes were activated by radiation-enhanced diffusion as a result of ionization processes as well as a thermodynamic driving force for crystallization. The paper did not report on the phase evolution of the SiO$_2$ under irradiation.

Other silicates which displayed crystallization as a result of Kr and Xe ion irradiation were $ZrSiO_4$, $ThSiO_4$, and $HfSiO_4$, as reported by Meldrum et al. [21]. $ThSiO_4$ and $HfSiO_4$ were irradiated with 800 keV Kr ions, and $ZrSiO_4$ was irradiated with 800 keV Xe ions. When $ZrSiO_4$ was irradiated at temperatures above 900 K, the single crystal samples initially became amorphous and then, with increasing dose, decomposed into its component oxides: tetragonal ZrO_2 and amorphous SiO_2. This decomposition was similar to their previous results attained by electron irradiation [24], possibly demonstrating the immiscible properties of ZrO_2 and SiO_2. $HfSiO_4$ similarly decomposed when heated to above 950 K into tetragonal HfO_2 and amorphous SiO_2. With $ThSiO_4$, a similar irradiation-induced decomposition occurred at 1000 K into monoclinic $ThSiO_4$ containing a network of distorted huttonite and randomly oriented ThO_2. However, this decomposition process in $ThSiO_4$ occurred with slower kinetics than the decompositions in $ZrSiO_4$ and $HfSiO_4$, and regions demonstrated more intense electron diffraction rings rather than rapid and complete crystallization. To determine whether the decomposition occurred due to thermal annealing alone, the ion beam amorphized samples were heated to 1100 K and held for 30 min without irradiation; neither crystallization nor decomposition occurred, so the authors concluded that the decomposition was associated with ion irradiation.

7. Other Ceramic Materials

Jiang et al. demonstrated that an a-to-c transformation could be induced in amorphous ZrC by irradiating with 30 keV He^+ ions at an ion flux of 1.79×10^{13} ions/cm^2-s to various fluences at 593 K [26]. The sample was prepared by depositing amorphous ZrC on a layer of crystalline ZrC using magnetron sputtering. At a fluence of 1.08×10^{16} ions/cm^2, nanocrystals were visible in TEM cross-sections. At fluences ranging from 3.23 to 6.45×10^{16} ions/cm^2, SAED analysis showed evidence of increased crystallization in the amorphous ZrC layer; i.e., diffuse rings corresponding to crystalline ZrC domains appeared at a fluence of 1.08×10^{16} ions/cm^2 and the SAED patterns became more defined as the fluence increased. Additionally, irradiated samples were annealed at a temperature of 723 K to determine if heating at elevated temperatures would affect the morphology or crystallinity of irradiation-induced nanocrystals, but no significant changes were observed. The mechanism for the a-to-c transformation was primarily explained as a diffusion-assisted mechanism via the thermal spike model. Essentially, He^+ irradiation transfers much of its energy to electrons in the target material and causes a sharp increase in temperature along the ion path, causing adjacent atoms to diffuse more rapidly. A related correlation between atomic distributions of Zr and C and the irradiation-induced crystallization was observed using EDS analysis of the sample cross-sections. This analysis found that the observed a-to-c transformation tended to occur at depths where the relative concentration of C was lower, and this concentration gradient occurred near the interface between the amorphous and crystalline layers of ZrC. Therefore, He^+ irradiation seemed to preferentially form ZrC crystals near the amorphous-to-crystalline interphase where the C concentration was lower, and irradiation enhanced diffusion of Zr and C atoms would cause crystallites to gradually develop closer to the sample surface as the C to Zr ratio was decreased as a result of ion irradiation [26].

Allen and coworkers studied the effects of Kr ion irradiation on the crystallization of $CoSi_2$ thin films [27]. The samples were partially crystallized from TEM electron beam irradiation operated at 300 kV prior to ion irradiation.

Further crystallization was observed after 1.5 MeV Kr^+ irradiation to a fluence of 8.5×10^{14} ions/cm^2 at 300 K. The authors suggested that the prior electron irradiation led to a profuse number of crystallites with sizes that fell within the critical to supercritical size range that enabled the crystallites to continue to grow via subsequent ion irradiation-assisted recrystallization. The authors then irradiated another as-deposited film with 1.5 MeV Kr at a lower fluence of 3.4×10^{14} ions/cm^2 at 300 K, then thermally crystallized the sample at 450 K. The irradiated portion of the sample showed higher crystallization rates, about double those of the non-irradiated portion of the sample. Additionally, when the ion dose was lower, specifically 3.4×10^{13} ions/cm^2 at 300 K, the number density of crystallites was 30% lower, but the crystallite growth rates in the irradiated and non-irradiated portions of the sample were the same. This suggested that low-dose ion irradiation prior to thermal crystallization sufficiently induced critical or supercritical-sized crystallite nuclei that assisted in thermal crystallization.

Som et al. used two-step ion implantation and irradiation to induce recrystallization of an implanted Si_3N_4 layer in Si [28]. Initial implantation of 100 keV N ions into a Si wafer at 300 °C to a fluence of 8×10^{17} ions/cm^2 created an amorphous Si_3N_4 layer while the Si above and below this layer remained crystalline. Subsequent irradiation with 100 MeV Ag ions was conducted to a fluence of 10^{14} ions/cm^2. The implanted layer remained amorphous when the Ag ion irradiation was carried out at 150 °C, but the implanted layer crystallized when the Ag ion irradiation was carried out at 200 °C or higher. Using HRTEM, the *d*-spacing of the implanted then irradiation-crystallized layer matched with that of the hexagonal α-Si_2N_4 phase. This implanted layer *d*-spacing did not match that of the crystalline Si layers above and below it, so the authors suggested that the Ag ion irradiation caused the crystallization. The crystallization was explained by irradiation defect creation in the Si substrate. That is, as the Ag ions penetrated through the multi-layered structure and deposited in the substrate, they created vacancies and interstitials in the crystalline Si. These point defects were available at the amorphous/crystalline (a/c) interfaces between the layers and migrated through thermal diffusion. The vacancies in the amorphous layer enabled thermal vibrations of Si and N atoms to occur more freely and unconstrained, thus inducing redistribution that resulted in the crystallization of one monolayer at the a/c interface. These monolayers then progressed inward from both a/c interfaces bounding the amorphous layer.

Finally, Meldrum et al. used two-step irradiation to induce recrystallization of phosphates, namely $ScPO_4$ and $LaPO_4$ specimens [24]. The amorphous $ScPO_4$ and $LaPO_4$ were made by first irradiating single crystals with 1.5 MeV Kr to fluences of 4×10^{14} ions/cm^2 and 2×10^{15} ions/cm^2, respectively, to ensure complete amorphization. The amorphized specimens were subsequently irradiated with a 200 keV electron beam at a beam current of 1.45 A/cm^2 at ambient temperature. The $LaPO_4$ showed facile crystallization in mere seconds under the electron beam, whereas it took about 10 times as long for $ScPO_4$ to fully recrystallize under the same electron beam conditions. When the electron beam current was increased, the crystallite size decreased for both phosphates, though crystallites in $ScPO_4$ were consistently about 50% larger than those in $LaPO_4$. When both materials were subjected to thermal annealing over a temperature range of 200–300 °C, solid phase epitaxy was achieved over a period of 1–3 h. To investigate the temperature increase as a result of electron beam heating, the Fisher model was utilized

and showed that the temperature increased within the range of 4–40°C [25]. By contrast, temperatures in excess of 400 °C are needed to thermally anneal the amorphized samples for recrystallization.

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