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4 Anisotropic expansion and amorphization of Ga₂O₃ irradiated with 946 MeV Au ions
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Abstract

The structural response of β -Ga₂O₃ to irradiation-induced electronic excitation was investigated. A polycrystalline pellet of this material was irradiated with 946 MeV Au ions and the resulting structural modifications were characterized using *in situ* x-ray diffraction analysis at various ion fluences, up to $1 \times 10^{13} \text{ cm}^{-2}$. Amorphization was induced, with the accumulation of the amorphous phase following a single-impact mechanism in which each ion produces an amorphous ion track along its path. Concurrent with this phase transformation, an increase in the unit cell volume of the material was observed and quantified using Rietveld refinement. This unit cell expansion increased as a function of ion fluence before saturating at 1.8%. This effect is attributed to the generation of defects in an ion track shell region surrounding the amorphous track cores. The unit cell parameter increase was highly anisotropic, with no observed expansion in the [010] direction. This may be due to the structure of β -Ga₂O₃, which exhibits empty channels of connected interstitial sites oriented in this direction.

Introduction

Gallium sesquioxide, Ga₂O₃, is a multifunctional wide-bandgap material that exhibits optical transparency [1,2], electrical conductivity [3], and luminescence [4,5]. Due to this unique combination of properties, it has diverse applications. This material has found use as a high-temperature oxygen gas sensor [6], a blue luminescent phosphor [4,5], an anti-reflective coating for GaAs semiconductors [7], a deep-ultraviolet transparent conducting oxide [2,8], and a wide-bandgap semiconductor for ultrahigh-voltage switching applications in power electronics devices [9–11]. Ga₂O₃ is also a component of nuclear reactor fuels made from Pu recovered from dismantled nuclear weapons, due to the use of Ga as a Pu alloying element [12,13]. The

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4 properties of Ga_2O_3 , and hence its performance in these applications, are strongly influenced by
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6 the presence of defects. For example, oxygen vacancies act as shallow donors with low
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8 activation energies [3]. Thus, its electrical conductivity [3,6,8,14], optical absorption [14], and
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10 cathodoluminescence [5] all increase with oxygen vacancy concentration. In contrast, Ga
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12 vacancies act as trapping centers for charge carriers, decreasing electrical conductivity [15].
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16 One method for the controlled introduction of defects to a material is exposure to a beam
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18 of energetic ions. Irradiation with ions of low velocity (*i.e.* low specific energy) directly causes
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20 atomic displacement in the target material through elastic nuclear collisions between the
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22 accelerated ions and the atoms comprising the material. In contrast, ions of high mass and
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24 velocity (*i.e.* specific energies of ~ 1 MeV or greater) deposit the majority of their energy to the
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26 electronic subsystem of the target material through inelastic interactions. This electronic energy
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28 loss yields dense ionization along the roughly linear paths of these swift heavy ions, producing a
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30 cascade of excited electrons in the conduction band. As the electron cascade cools, electron-hole
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32 recombination occurs. Ionization and recombination can produce atomic displacements through
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34 various processes, including the decay of self-trapped excitons to Frenkel pairs, destabilization of
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36 the atomic structure following the excitation of electrons from bonding to anti-bonding states,
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38 and the production of nanometric thermal spikes due to phonon emission during non-radiative
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40 recombination [16–18]. Through these mechanisms, ion beam processing allows for direct
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42 modification of the structures and properties of materials. The response of materials to irradiation
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44 in this high specific energy regime is also of interest for the development of nuclear fuels, which
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46 are irradiated by energetic nuclear fission fragments [19], and electronic devices for spacecraft,
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48 which are irradiated by cosmic rays [20].
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Few data are available regarding the response of Ga_2O_3 to particle irradiation. A single study [15] reports the generation of Ga Frenkel pairs and a decrease in electrical conductivity following irradiation with neutrons, which deposit energy to a material via nuclear collisions, yet no corresponding studies of this material's response to irradiation in the electronic energy loss regime have been reported. In the present study, the effects of swift heavy ion irradiation on the atomic structure of $\beta\text{-Ga}_2\text{O}_3$ have been characterized. The β -phase was studied because this is the most stable of the five polymorphs of Ga_2O_3 between ambient and melting temperatures [21,22]. $\beta\text{-Ga}_2\text{O}_3$ exhibits a monoclinic structure ($C2/m$ space group) shown in Fig. 1. Ga cations occupy two distinct $4i$ sites in distorted tetrahedral and octahedral coordination with O anions. Octahedra are edge-sharing with adjacent octahedra, while tetrahedra are corner-sharing with adjacent octahedra and tetrahedra.

Experimental methods

$\beta\text{-Ga}_2\text{O}_3$ powder was uniaxially compacted into a pellet of 12 mm diameter and 3 mm height using a pressure of 30 MPa. The pellet was sintered in air at 1450 °C for 30 hours to achieve suitable density and crystallinity, while also removing any water present. X-ray diffraction (XRD) was performed after sintering to ensure that the sample retained the $\beta\text{-Ga}_2\text{O}_3$ structure and had grain sizes above 1 μm , to avoid potential effects of nanocrystallinity on the radiation response. The pellet was fixed with epoxy resin to copper sample holders prior to irradiation and analysis.

Irradiation and *in situ* XRD were carried out at the M2 beamline of the GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany. The sample was irradiated with a beam of 946 MeV Au ions at room temperature, under vacuum. The beam spot size was 2.25 cm^2 , such

that the entire beam-facing surface of the pellet was irradiated. The ion flux was maintained below $1.8 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ to prevent bulk heating of the sample. Before exposure to the ion beam, and at ion fluences of $1 \times 10^{11} \text{ cm}^{-2}$, $5 \times 10^{11} \text{ cm}^{-2}$, $8 \times 10^{11} \text{ cm}^{-2}$, $1 \times 10^{12} \text{ cm}^{-2}$, $3 \times 10^{12} \text{ cm}^{-2}$, $5 \times 10^{12} \text{ cm}^{-2}$, $8 \times 10^{12} \text{ cm}^{-2}$, and $1 \times 10^{13} \text{ cm}^{-2}$ the sample was characterized by XRD.

This beamline is equipped with an *in situ* x-ray diffractometer, allowing for collection of XRD data without removal of the sample from the irradiation vacuum chamber. The diffractometer is a 4-circle device with a Cu-K $_{\alpha}$ source operated in point focus geometry and a position-sensitive detector. XRD patterns were recorded over the range $2\theta = 25\text{-}62^{\circ}$ with a collection time of 60 s. With an ion range of 27 μm in Ga $_2$ O $_3$, according to calculations using the SRIM code [23], the irradiation- modified region was thicker than the penetration depth of the x-rays, ensuring that only the modified region was probed. Because the x-ray beam spot diameter was larger than that of the pellet, additional signal was obtained from the copper sample holder onto which the pellet was mounted. After each XRD measurement, exposure of the sample to the ion beam was resumed and irradiation proceeded until the next ion fluence step was achieved and the measurement process was repeated.

The XRD data were analyzed by Rietveld refinement [24] using the software Fullprof [25]. Unit cell parameters were refined as a function of ion fluence, based on shifts in the angular positions of the peaks. Diffraction peaks from the copper sample holder, which is highly resistant to radiation-induced structural modification, were used as a standard in quantitative phase analysis to measure the β -Ga $_2$ O $_3$ phase fraction as a function of ion fluence, based on changes to its refined scale factor.

Results

XRD patterns collected prior to irradiation were consistent with a well-crystallized β - Ga_2O_3 phase. Three modifications to the XRD patterns were observed with increasing ion fluence: attenuation of the initial diffraction maxima, growth of a low-intensity, diffuse band in the range $2\theta \approx 25$ - 40° , and angular shifts of the initial diffraction maxima to lower values of 2θ . These modifications are evident in the data shown in Fig. 2, which displays representative diffraction patterns at various ion fluences up to $1 \times 10^{13} \text{ cm}^{-2}$.

The evolution in the intensities of both the initial β -phase peaks and the broad radiation-induced band are evidence of a transformation from the β -phase to an amorphous phase, which proceeds with increasing ion fluence. The attenuation of the peaks corresponding to the β -phase indicates a decrease in the crystalline fraction, while the broad irradiation-induced band is characteristic of the diffuse scattering arising from solids with aperiodic structures [26]. Thus, the energy deposited by 946 MeV Au ions is sufficient to drive this material from its initial, equilibrium phase into a non-equilibrium, amorphous phase. By analyzing the accumulation of this phase as a function of ion fluence, information about the irradiation-induced phase transformation mechanisms can be obtained [27]. Fig. 3 shows the crystalline fraction of this material, f_c , as a function of ion fluence, determined by refinement of the XRD data. Because no evidence of phases other than the β - and amorphous phases is observed at any ion fluence, f_c is equal to $1 - f_a$, where f_a is the amorphous fraction. From Poisson statistics, a model of the accumulation of the amorphous phase and depletion of the crystalline phase as a function of ion fluence can be developed. The best fit to the data in Fig. 3 is achieved using a model that assumes that each impinging ion generates a cylindrical amorphous ion track along its path, via a single-impact mechanism [27]. From this single-impact model, an equation for f_c (equal to $1 - f_a$) can be derived, which is fit to the data in Fig. 3 and has the form:

$$f_c(\Phi) = e^{-\sigma\Phi} \quad (1)$$

where σ is the cross-sectional area of the cylindrical, amorphous region of an ion track and Φ is the ion fluence. Deviation of the accumulation of the amorphous phase from single-impact behavior, as would be the case if multiple impacts of an accelerated ion with a volume of material were necessary to induce the crystalline-to-amorphous transformation, would yield sigmoidal behavior of $f_c(\Phi)$ at low ion fluences, which is not observed in the experimental data. Thus, the initial linear decrease in the crystalline fraction, followed by saturation at higher ion fluences, is evidence of a single-impact mechanism and the formation of an amorphous ion track following each swift heavy ion impact. Fitting of the data in Fig. 3 to Eq. 1 yields an ion track cross-sectional area of $54 \pm 5 \text{ nm}^2$, corresponding to a track diameter of approximately 8 nm, assuming cylindrical geometry.

Interestingly, at the highest ion fluences achieved there remains in the XRD data (Fig. 2) signal of very low intensity corresponding to the crystalline phase. As show in Fig. 3, this indicates that complete amorphization is not achieved by an ion fluence of $1 \times 10^{13} \text{ cm}^{-2}$, despite the predictions of the single-impact model. This model is an idealized representation of damage accumulation in irradiated materials, and does not account for simultaneous recovery processes associated with thermal-spike induced annealing [27]. If these recovery processes induce limited recrystallization of amorphous material concurrent with amorphization of the ion track cores, a dynamic equilibrium will be achieved at high ion fluences, wherein a small fraction of the material will remain crystalline. The minor residual crystallinity observed here at high ion fluences is consistent with such steady state behavior.

The final modification observed in the diffraction patterns, shifts of the diffraction maxima to lower diffraction angles with increasing ion fluence, is evidence of expansion of the

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4 β -Ga₂O₃ unit cell. As shown in Fig. 4, these angular shifts do not occur in a uniform manner, and
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6 instead depend strongly on the Miller indices, (*hkl*), corresponding to each diffraction maximum.
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8 This is indicative of anisotropic expansion of the unit cell, wherein the unit cell parameters *a*, *b*,
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10 and *c*, increase at different rates during irradiation. From refinement of the diffraction patterns,
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12 these unit cell parameters were measured as a function of ion fluence, with the results shown in
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14 Fig. 5. Because this unit cell expansion is a result of ion-matter interactions, it will not occur
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16 homogeneously throughout the sample, instead being confined to an ion influence region, similar
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18 to the irradiation-induced amorphization process. However, because the magnitude of this
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20 expansion is relatively small, compared to the angular resolution associated with these XRD
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22 measurements, diffraction maxima from the modified and unmodified material volumes cannot
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24 be accurately distinguished. Instead, this heterogeneous modification gives rise to apparent
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26 angular shifts of the diffraction maxima, as the relative intensities of the initial peaks decrease
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28 and those of peaks from the modified crystalline material, having slightly larger lattice
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30 parameters, increase. Thus, the measured unit cell parameters are effectively a weighted average
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32 of the unit cell parameters of the two regions (the undamaged, initial unit cell parameter region
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34 and the damaged, high unit cell parameter region), with the contribution of each to the measured
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36 value weighted by relative volume of each region. Because the amorphous volume does give rise
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38 to sharp diffraction maxima, it does not contribute to the measurement of unit cell parameters.
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48 Over all ion fluences for which XRD data were collected the unit cell expansion is highly
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50 anisotropic, with *a* exhibiting a greater increase than *c*, and *b* showing minimal change. As with
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52 the amorphous fraction data, the unit cell parameters for which expansion occurred exhibit an
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54 initial linear increase followed by saturation at higher ion fluences. Saturation occurs at
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56 expansions of approximately 1.4% for *a* and 0.4% for *c*, resulting in a unit cell volume expansion
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of 1.8%. This behavior is consistent with a single-impact mechanism for this modification of the atomic structure, wherein each ion induces unit cell expansion of the material within an influence region having a specific cross-sectional area [27]. From the single impact model, an equation for the evolution of each lattice parameter as a function of ion fluence can be derived, given by:

$$\left[\frac{\Delta d}{d_0} \right] (\Phi) = \left[\frac{\Delta d}{d_0} \right]_{sat} (1 - e^{-\sigma \Phi}) \quad (2)$$

Where $[\Delta d/d_0]$ is the fractional change in the d -spacing associated with the lattice parameter, $[\Delta d/d_0]_{sat}$ is the fractional change in d -spacing at which the measured expansion saturates once it has been induced throughout the entire sample volume, σ is the effective cross-sectional area of the unit cell expansion influence region, and Φ is the ion fluence. For the unit cell parameters that increase in response of swift heavy ion irradiation, a and c , saturation of this modification occurs at a much lower ion fluence than does that of the crystalline-to-amorphous transformation (Fig. 3). This indicates a more rapid accumulation of volume in which unit cell expansion has been induced, as compared with the accumulation of the amorphous phase, corresponding to a larger cross-sectional area for the ion track region within which expansion is induced. Fits of the data in Fig. 5 to Eq. 2 yield cross-sectional areas of $\sigma = 194 \pm 15 \text{ nm}^2$ for the expansion of a and $\sigma = 346 \pm 72 \text{ nm}^2$ for the expansion of c .

Discussion

The formation of cylindrical amorphous ion tracks, so called “latent tracks,” is a common feature of the swift heavy ion irradiation response of many oxide materials [28]. Amorphization within these tracks signifies a very high density of atomic displacements resulting from modified interatomic interactions and the rapid transfer of energy from the excited electron cascade to the atomic subsystem (the electronic and atomic subsystems typically equilibrate within a few

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4 picoseconds of the ion impact [18]), followed by rapid quenching of the thermal spike via the
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6 diffusion of heat to the surrounding matrix (typically over tens of picoseconds [18]). This
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8 quenching serves to “freeze” the melt-like structure of the excited ion track volume, such that it
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10 is recovered to ambient conditions as a metastable phase.
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14 As with amorphization, unit cell expansion is characteristic of the response of many
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16 oxides to irradiation with swift heavy ions, having been observed in, for example, ZrO_2 [29,30],
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18 CeO_2 [31–33], ThO_2 [33,34], and UO_2 [35,36]. Possible sources of this expansion are stresses
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20 applied to the crystalline material, resulting from density changes in the amorphous tracks, and
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22 the accumulation of defects that distort the structure in their local environment and reduce atomic
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24 packing efficiency. Stresses exerted by the amorphous volume must be tensile to cause unit cell
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26 expansion, which would require the formation of over-dense amorphous tracks. Volume
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28 contraction of the in-track material concomitant with an increase in density would exert tensile
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30 stress on adjacent crystalline material. While limited data concerning the densities of ion track
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32 interiors has been reported, both molecular dynamics simulations and small angle x-ray
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34 scattering experiments by Kluth *et al.* [37] show that tracks in amorphous SiO_2 are under-dense.
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36 Similarly, direct scanning transmission electron microscopy observation of ion tracks in CeO_2 by
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38 Takaki *et al.* [38] showed a decrease in the density of the track core region. These results are
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40 consistent with the rapid quenching of a high temperature track core to ambient conditions, such
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42 that the inefficient atomic packing of the melt-like region is preserved. Furthermore, unit cell
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44 expansion has been observed in numerous oxides that do not adopt an amorphous phase in
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46 response to irradiation with swift heavy ions, such as fluorite-structured ZrO_2 , CeO_2 , ThO_2 , and
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48 UO_2 [29–36]. Expansion in these materials is instead typically ascribed to the accumulation of
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There also exist several discrepancies between the accumulation of unit cell expansion observed here and the effects of possible stresses arising from density changes to the amorphous material. The observed unit cell expansion saturates at ion fluences far below those at which amorphization is complete (Figs. 3 and 5). Stresses resulting from in-track density changes would increase continuously as amorphization proceeded, as would the unit cell expansion if such stresses were its cause. Additionally, the anisotropy of the observed unit cell expansion is inconsistent with the known elastic properties of β -Ga₂O₃. High pressure experiments [39,40] show that, under hydrostatic stress conditions, this material is softest in the [100] and hardest in the [001]. Thus, the formation of over-dense amorphous tracks in a polycrystalline pellet of random crystallite orientation would be expected to produce unit cell expansion that is greatest in *a* and least in *c*. In contrast, the data presented in Fig. 5 shows that expansion of *c* is significantly greater than that of *b*, which shows no expansion, within experimental error. Based on this evidence, the observed unit cell expansion in β -Ga₂O₃ irradiated with swift heavy ions is attributed to the accumulation of defects in a crystalline ion track shell region. The formation of a defect-rich shell around an amorphous track core is consistent with previous observations of such shells in, for example, Gd₂Ti_{2-x}Zr_xO₇ materials irradiated with swift heavy ions [41–44]. If the defect concentration in a shell region concentric with an amorphous track core is low enough that the crystalline structure is maintained, microstrain will result as interstitial atoms push away adjacent atoms, while atoms adjacent to vacant sites relax towards those vacancies. The expansive effect of the interstitial defects typically dominates the relaxation near vacancies, such that the net effect is expansion of the structure.

To assess possible sources of the anisotropy of the observed unit cell expansion, the incorporation of interstitial defects in the β -Ga₂O₃ structure must be considered. These

defects typically occupy interstitial sites between polyhedra, which allows for minimization of the microstrain required to incorporate the defect and of the associated lattice energy increase. As shown in Fig. 1, the interstitial sites in the Ga_2O_3 structure are unique in that they form distinct channels along the [010]. Therefore, defects occupying these interstitial sites will exert forces on adjacent atoms in the [100] and [001], while having minimal effect in the [010] due to the lack of adjacent atoms in this direction on which to exert Coulombic repulsive forces. This is consistent with the observed lack of measurable increase in b , the unit cell parameter in the [010], as a function of ion fluence.

The large cross-sectional areas derived for the unit cell expansion influence region (Eq. 1, Fig. 5), relative to those of amorphization, are consistent with expansion resulting from defect formation in the crystalline periphery of the ion tracks. While amorphization is induced within ~4 nm of each swift heavy ion path, in a region within which very high energy densities are deposited during ion-solid interaction, the most energetic electrons excited by swift heavy ion irradiation typically travel a few hundred nanometers in the radial track direction before relaxation [18]. Thus, as a swift heavy ion traverses the solid, energy is deposited to the material over a much larger radial area than that within which the resulting energy densities are sufficient for amorphization. However, the deposited energy density typically decreases as a function of radial distance from the ion path, giving rise to a radial decrease in defect concentration [34]. At distances from the ion path for which the induced defect concentration is low enough that crystallinity is maintained (*i.e.*, amorphization does not occur), unit cell expansion of the crystalline phase occurs. Thus, the defects that cause unit cell expansion of the crystalline portion of each ion track are produced within a track shell having a comparatively large area, yielding the more rapid saturation of unit cell expansion, compared to amorphization, that was observed.

The single-impact model [27] from which track cross-sectional areas were derived only distinguishes between modified and unmodified regions, and does not account for gradual variation in the defect concentration (and therefore in the unit cell expansion) within a single ion track. Therefore, in this analysis, the crystalline ion track shells are idealized as discrete regions within which a specific value of expansion, $[\Delta d/d_0]_{\text{sat}}$, is induced. These assumptions in the analysis are necessitated by the aforementioned XRD resolution constraints, which prevent more precise analysis of the spatial variation of unit cell expansion within ion tracks. Thus, the cross-sectional areas reported here for the unit cell expansion influence region should be considered qualitative. This is not the case for the track areas reported for amorphization, as this modification of the atomic structure of Ga_2O_3 does not exist on a continuum, but rather constitutes the formation of distinct amorphous regions of specific dimensions in an otherwise crystalline matrix.

Conclusions

XRD patterns collected from $\beta\text{-Ga}_2\text{O}_3$ irradiated with 946 MeV Au ions exhibited three changes with increasing ion fluence: loss of intensity of the initial diffraction maxima, growth of a broad signal at low 2θ arising from diffuse scattering by an amorphous phase, and shifts in the angular positions of the initial peaks due to unit cell expansion. The accumulation of the amorphous fraction followed single-impact behavior, indicating that each incident ion produced an amorphous ion track. The unit cell expansion was not consistent with stresses caused by density changes in the amorphous material, and was instead attributed to the accumulation of defects in a shell region around the amorphous cores of the ion tracks. Significant anisotropy was observed in this expansion, with the unit cell parameter b showing no increase as a function of

ion fluence, within experimental error. This may be related to the structure of the β -phase, which exhibits empty channels oriented along the [010], allowing for the incorporation of defects into interstitial sites with minimal structural expansion in this direction.

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Fig. 1. The crystal structure of β -Ga₂O₃ projected in various crystallographic directions. Small green circles represent Ga atoms and large red circles represent oxygen atoms. The distorted octahedral and tetrahedral coordination of Ga is indicated by the transparent polyhedra.

Fig. 2. Representative XRD patterns corresponding to several of the ion fluences at which data was collected. With increasing ion fluence, Φ , the initial β -Ga₂O₃ decrease in intensity, while a broad, diffuse scattering band grows in the range $2\theta \approx 25$ -40°. Peaks marked with an asterisk, which show no change with ion fluence, correspond to the metallic Cu sample holder.

Fig. 3. The evolution of the crystalline fraction, f_c , with ion fluence, as measured by refinement of the XRD data. Error bars represent the uncertainty associated with the refinement. The data are fit with Eq. 1, as shown by the dashed line, yielding an amorphous track cross-sectional area of $\sigma = 54 \pm 5 \text{ nm}^2$.

Fig. 4. XRD patterns of β -Ga₂O₃ before irradiation and following irradiation to an ion fluence of $\Phi = 5 \times 10^{11} \text{ cm}^{-2}$. A selected 2θ is shown to emphasize the angular shifts of the diffraction peaks to higher 2θ following irradiation. The peak shifts are non-uniform, showing dependence on the peak Miller indices, (hkl) , as labelled.

Fig. 5. The change in the three unit cell parameters a , b , and c , as a function of ion fluence. The data are fit with Eq. 1, as shown by the dashed lines. The expansion of the unit cell is highly

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4 anisotropic, with a increasing to a greater extent than c , and c increasing to a greater extent than
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7 b , at each ion fluence. Saturation of the expansion occurs at 1.4% for a and 0.4% for c . No
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9 systematic expansion of b is observed. The error bars represent the uncertainty associated with
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FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5