Damage evolution of ion irradiated defected-fluorite La$_2$Zr$_2$O$_7$ epitaxial thin films

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Pyrochlore-structure oxides, A$_2$B$_2$O$_7$, may exhibit remarkable radiation tolerance due to the ease with which they can accommodate disorder by transitioning to a defected fluorite structure. The mechanism of defect formation was explored by evaluating the radiation damage behavior of high quality epitaxial La$_2$Zr$_2$O$_7$ thin films with the defected fluorite structure, irradiated with 1 MeV Zr$^+$ at doses up to 10 displacements per atom (dpa). The level of film damage was evaluated as a function of dose by Rutherford backscattering spectrometry in the channeling geometry (RBS/c) and scanning transmission electron microscopy (STEM). At lower doses, the surface of the La$_2$Zr$_2$O$_7$ film amorphized, and the amorphous fraction as a function of dose fit well to a stimulated amorphization model. As the dose increased, the surface amorphization slowed, and amorphization appeared at the interface. Even at a dose of 10 dpa, the core of the film remained crystalline, despite the prediction of amorphization from the model. To inform future ab initio simulations of La$_2$Zr$_2$O$_7$, the bandgap of a thick La$_2$Zr$_2$O$_7$ film was measured to be indirect at 4.96 eV, with a direct transition at 5.60 eV.

1. Introduction

Pyrochlore structure oxides (A$_2$B$_2$O$_7$) are of interest for the wide variety of physical, chemical, and electronic properties exhibited by the more than 500 known A and B-site cation combinations [1]. One particularly interesting property is the resistance of these compounds to structural amorphization when exposed to radiation. This property, along with the ability to incorporate radionuclides such as Pu and Am on the A-site in the pyrochlore structure, has led to much interest in pyrochlore oxides as a stable nuclear waste form [2–4]. Initial work focused on titanate pyrochlores (A$_2$Ti$_2$O$_7$), but zirconate pyrochlores (A$_2$Zr$_2$O$_7$) proved significantly more radiation-tolerant. For example, Ga$_2$Ti$_2$O$_7$ amorphizes at 0.2 displacements per atom (dpa) under 1 MeV Kr$^+$ irradiation at room temperature, while Ga$_2$Zr$_2$O$_7$ can withstand 15 dpa under 1.5 MeV Xe$^+$ irradiation at room temperature without amorphizing [2]. Likewise, Er$_2$Zr$_2$O$_7$ is highly radiation-resistant, while Er$_2$Ti$_2$O$_7$ is not [1].

The remarkable radiation resistance of pyrochlores arises, at least in part, from the unique properties of the pyrochlore crystal structure. The pyrochlore structure (space group Fd$ar{3}$m) is a derivative of the fluorite structure (CaF$_2$, space group Fm$ar{3}$m), with ordered cations on two distinct sites (A and B) and one-eighth of the O sites (the 8a sites in Wycoff notation) vacant [3]. The stoichiometry is formally A$_1$B$_2$O$_6$Y$_{0.12}$, with the A-site occupied by rare earths, actinides, or elements with inert lone-pair electrons of valence 2 + or 3 + and the B-sites occupied by transition or post-transition metals of valence 4 + or 5 + [1,5]; Y = O for pyrochlore oxides but can also be OH or F [2]. The radiation resistance has been shown to be related to the ease with which A- and B-sites can disorder (antisite defects); likewise, disorder can be introduced in the lattice positions of the oxygen vacancies. Thus, superior radiation resistance results from low energetic barriers to transform...
from the ordered pyrochlore to the disordered fluorite structure \[3,6,7\].

The ratio of atomic radii of the A- and B-site cations, r_A/r_B, can be used as a guide to determine whether an A_2B_2O_7 oxide crystallizes in the defected fluorite or pyrochlore structure \[8\]: for r_A/r_B < 1.46, the defect fluorite structure is favored; for 1.46 < r_A/r_B < 1.78, the oxide crystallizes in the pyrochlore structure, and for r_A/r_B > 1.78 less symmetric crystal structures such as the monoclinic perovskite-layered structure (PLS) \[9,10\] or tetragonal (P4_2_1_2) \[11\] structures are energetically preferred. Using this analysis, Gd_2Zr_2O_7 (r_A/r_B = 1.74) is much further from the defected fluorite structure than is Gd_2Sn_2O_7 (r_A/r_B = 1.46); thus, Gd_2Zr_2O_7 can easily transition to the defected fluorite structure upon irradiation, while Gd_2Sn_2O_7 cannot. Likewise, Er_2Zr_2O_7 (r_A/r_B = 1.39) crystallizes in the defected fluorite structure and exhibits high radiation tolerance, while Er_2Sn_2O_7 (r_A/r_B = 1.66) crystallizes in the pyrochlore structure with poor radiation tolerance. A comprehensive study of the lanthanide stannate pyrochlores, Ln_2Sn_2O_7 (Ln = La to Lu and Y) confirmed this trend of increasing radiation tolerance with decreasing r_A/r_B \[12,13\]. A similar analysis of the oxygen positional parameter of the O 48f site, x, compared to that for the ideal pyrochlore structure \(x = 0.3125\) and the ideal (non-defective) fluorite structure \(x = 0.375\), leads to similar conclusions regarding radiation tolerance: those oxides which exhibit x values closer to the ideal fluorite value exhibit higher radiation tolerance than those with x values closer to the ideal pyrochlore structure \[1,7\].

La_2Zr_2O_7 has been investigated as a model zirconate pyrochlore material that exhibits relatively poor radiation resistance. La_2Zr_2O_7 is relatively far from the fluorite structure, with r_A/r_B = 1.61 and O 48f = x = 0.332 \[14\]. An irradiation study of a polycrystalline monolith of La_2Zr_2O_7 with 1.5 MeV Xe+ found that the material amorphized at a dose of 5.5 dpa at room temperature. A fit of the amorphization temperature as a function of temperature found a critical amorphization temperature of ~310 K; above this temperature, recrystallization processes dominate and the material cannot be amorphized \[1\]. Because this study utilized transmission electron microscopy (TEM) to identify the onset of amorphization, the degree of damage that occurred at a given temperature as a function of dose could not be measured. Without this data, it is difficult to determine the damage mechanism. Theoretical molecular dynamics (MD) simulations of ion-induced defect cascades in La_2Zr_2O_7 confirmed that a low yield of cation antisites, interstitials, and vacancies was the primary material response \[15\]. This was interpreted as the beginnings of a transition towards the disordered fluorite state, and follow-up simulations revealed that the key defect process is the generation of cation Frenkel pairs (interstitial + vacancy) \[16\]. More recent ab initio MD calculations found that the threshold displacement energies for both cations and anions are higher, and cation and anion Frenkel pair formation energies are lower, in La_2Zr_2O_7 than in Nd_2Zr_2O_7 and Sm_2Zr_2O_7 \[14\]. These predictions correlate with the enhanced ion-beam-induced radiation resistance observed for A_2Zr_2O_7 (A = Nd, Sm, Gd) pyrochlores relative to La_2Zr_2O_7 \[1\]. Likewise, MD simulations predicted that substitution of Ti for a fraction of the Zr in La_2Zr_2O_7 would be detrimental to the radiation tolerance, since the A-site to B-site exchange energy increases with the addition of Ti \[17\].

To better understand the mechanisms of ion-induced radiation damage in pyrochlores such as La_2Zr_2O_7, it is preferable to study single crystal specimens. In contrast to polycrystalline powders, which are typically limited to a determination of the amorphization dose, the level of radiation damage in single crystal specimens can be more easily quantified (without contributions from grain boundary effects) with techniques such as TEM \[18\] or Rutherford backscattering spectrometry (RBS) in the channeling geometry (RBS/c) \[19,20\]. Synthesis of bulk single crystals can be difficult and time-consuming, but deposition of epitaxial thin films can be done relatively quickly and easily, and dopants can be introduced in a controlled manner. Epitaxial thin films are suitable for ion-induced radiation damage studies \[21\], and are particularly amenable to RBS/c. In contrast to textured La_2Zr_2O_7 thin films deposited by solution methods \[22,23\], there have been few reports of epitaxial La_2Zr_2O_7 films synthesized by vacuum deposition methods \[24,25\]. Here we present the results of 1 MeV Zr+ ion irradiation of La_2Zr_2O_7: epitaxial thin films which have crystallized in the defected fluorite structure. With RBS/c data collected from these films as a function of dose, we obtain detailed information on the mechanism of damage accumulation in defected-fluorite La_2Zr_2O_7, as well as an accurate measure of the dose required for full amorphization. The conclusions drawn from the RBS/c analysis are supported by scanning transmission electron microscopy (STEM) cross-sectional images collected at key dose levels. These results are compared to previous reports \[1\] detailing radiation damage accumulation in pyrochlore La_2Zr_2O_7.

2. Experimental

Thin films of La_2Zr_2O_7 were deposited by pulsed laser deposition at a substrate temperature of 850–900 °C in a background pressure of 25 mTorr O_2. A KrF laser operating at 1 Hz was used to ablate the ceramic targets with a fluence of ~2 J/cm^2. La_2Zr_2O_7 films were deposited from a ceramic La_2Zr_2O_7 target. Final film thicknesses were nominally 500 Å on 1 × 1 cm^2 single crystal SrTiO_3 (STO), LaAlO_3 (LAO), and 8% Y:ZrO_2 (yttria-stabilized zirconia, YSZ) substrates. Except where noted below, substrates were adhered with colloidal silver paint to a 1” diameter Si(001) wafer to prevent the diffusion of metals (such as Mo) from the sample holder to the substrate; an additional benefit of this sample mounting arrangement is the improved thermal contact to the thin Si wafer, which allowed efficient heating of the substrate to the temperatures employed in this work. X-ray diffraction (XRD) patterns were collected on a Philips X’Pert Materials Research Diffractometer (MRD) using Cu Kα radiation monochromated with a hybrid mirror/4 crystal monochromator. High-resolution 0–20 scans, Φ scans, and reciprocal space maps (RSMs) were collected with fixed-slit detector optics. Ellipsometry data was collected as a function of incident photon energy with a variable-angle spectroscopic ellipsometer (V-VASE, J.A. Woollam) at angles of 50°, 60°, and 70°. Data were fit using the WVASE software program.

Ion irradiations were performed with 1 MeV Zr+ ions at fluences ranging from 3.98 × 10^{13} to 7.96 × 10^{14} ions/cm^2 produced by a 1.7 MV tandem accelerator at the Texas A&M University Ion Beam Lab. Zr+ ions were incident on the sample at room temperature and an angle of 7° off normal. A corner of the sample, approximately 4 mm × 4 mm, was defined by masking the sample with a thick Al foil prior to irradiation. Displacements per atom (dpa) were calculated using the SRIM software, assuming a displacement energy of 50 eV \[1\] (in reasonable agreement with later theoretical predictions \[14,15\]), which resulted in a predicted average damage rate of 0.8 vacancies/ion² Å in the La_2Zr_2O_7 film. Films were analyzed before and after irradiation by RBS in the random and channeling (RBS/c) directions. RBS data were generated with 2 MeV He⁺ incident on a ~1.5 × 1.5 mm area of the film, and collected at a detector angle of 160°. Aligned spectra were obtained by adjusting the goniometer to the surface normal of the specimen. Random spectra were acquired by tilting one axis to a fixed value of 7° and rocking another axis of the goniometer by ±3° during acquisition. Various levels of charging were observed for different analysis locations and ion doses, affecting the backscattering yield and (to a lesser extent) the energy scale. To correct for this, individual channeling data were normalized such that the La peak of the...
respective random backscattering spectra matched across all measurements.

Samples were prepared for STEM using an FEI Helios NanoLab Dual-Beam Focused Ion Beam (FIB) microscope and a standard lift out procedure. High-angle annular dark field (STEM-HAADF) images were collected using a Cs-corrected JEOL ARM 200-CF microscope operated at 200 keV, with a 1 Å probe size, a convergence angle of 27.5 mrad, and a collection angle of 83 mrad. Geometric phase analysis (GPA) was performed using the FRWR Tools plugin [26] with the YSZ substrate selected as a reference region.

3. Results

3.1. Crystalline structure and epitaxy

The pyrochlore crystal structure of La$_2$Zr$_2$O$_7$ is closely related to the cubic fluorite structure of YSZ, although the lattice parameter difference ($a_{La2Zr2O7} = 10.786 Å$ [24] and $a_{YSZ} = 5.125 Å$) leads to a lattice misfit of $\delta = (a_{La2Zr2O7} / a_{YSZ}) - 100\% = 5.3\%$. Despite this misfit, high quality epitaxial La$_2$Zr$_2$O$_7$(111) thin films can be obtained on YSZ(111) substrates, as shown in Fig. 1(a).

Only (111) reflections are observed in the 0–20 scan. Surprisingly, only reflections with even index l are observed; the (111) (10.68°, 20) and (333) (43.49°, 28) reflections of the pyrochlore structure [27] are not present. This indicates that the cations in the La$_2$Zr$_2$O$_7$ film have not ordered in the pyrochlore crystal structure, as expected, but instead the film has crystallized in the defected-fluorite structure. Despite this, the finite thickness fringes flattening the La$_2$Zr$_2$O$_7$(222) peak indicate that the film exhibits well-ordered crystallinity with sharp and smooth interfaces. The RSM in Fig. 1(b) shows the YSZ(133) and La$_2$Zr$_2$O$_7$(266) reflections. The single spot observed for the La$_2$Zr$_2$O$_7$(266) reflection confirms the epitaxial relationship with the YSZ substrate. From the $q_{xy}$ position of the film reflection relative to that of the substrate, the film appears to be relaxed, as expected from the large $\delta$ and film thickness.

Deposition under similar conditions on LAO(001) results in epitaxial (001)-oriented La$_2$Zr$_2$O$_7$ films, as presented in Fig. 1(c). A very large lattice mismatch of $\delta = -0.2\%$ is possible if the La$_2$Zr$_2$O$_7$(001) film rotates by 45° about the surface normal. In addition to the strong La$_2$Zr$_2$O$_7$(001) diffraction peaks, an additional peak is observed in the 0–20 pattern (marked with an asterisk in Fig. 1(c)), which is assigned as Mo(110) arising from contact with the Mo sample holder during deposition. Fig. 1(d) presents a φ scan of the La$_2$Zr$_2$O$_7$(440) and LAO(110) in-plane peaks. The four-fold symmetry of the La$_2$Zr$_2$O$_7$(440) reflections reveals a single in-plane orientation for this film, and the relationship with the four-fold LAO(110) peaks confirms the expected epitaxial orientation between film and substrate: the La$_2$Zr$_2$O$_7$ film rotates by 45° relative to the LAO substrate. In the (001) orientation, the out-of-plane diffraction patterns of pyrochlore and fluorite structures are identical. A search for the (333) in-plane diffraction peak (not shown) did not reveal any diffraction intensity, indicating that this film has crystallized in the defected fluorite structure. Deposition of La$_2$Zr$_2$O$_7$ on STO(001) might be expected to result in a similar epitaxial relationship as La$_2$Zr$_2$O$_7$/LAO(001), despite the somewhat larger lattice mismatch ($\delta = -2.3\%$); however, as indicated in Fig. 1(e), (111)-oriented La$_2$Zr$_2$O$_7$ films result instead; as with the La$_2$Zr$_2$O$_7$ film deposited on YSZ(111) and discussed above, the (333) reflection is not observed, confirming that this film also possesses the defected fluorite structure. The (111) orientation of the pyrochlore structure is a low-energy surface, although a recent modeling study found the (110) surface to be the lowest-energy surface [28]. As illustrated by the very weak and unevenly spaced peaks in the phi scan of the La$_2$Zr$_2$O$_7$(440) reflection in Fig. 1(f), no preferential in-plane orientation exists. Thus, La$_2$Zr$_2$O$_7$/STO(001) can be considered, at best, textured in the out-of-plane direction, but the film is not epitaxial.

The film structure results obtained by XRD are corroborated by RBS/c measurements of the La$_2$Zr$_2$O$_7$ films deposited on STO(001), YSZ(111), and LAO(001), as shown in the RBS random and channeling spectra in Fig. 2(a), and scans of the La peak region of interest as the film is rocked through the channeling direction in Fig. 2(b). In all cases, the single crystal oxide substrate exhibits strong channeling (channel number < ~380 in Fig. 2(a)), with LAO(001) returning the lowest yield. Due to the difficulty in separating the La signal due to the film from that of the substrate for La$_2$Zr$_2$O$_7$/LAO(001), the minimum yield ($I_{\text{min}} = I_{\text{channeling/random}}$, where $I$ is the yield in counts) was calculated for the Zr peak (after subtraction of the LA background) and found to be 14%. The angular scan for this film in Fig. 2(b), which was obtained for the La peak, indicates a similar channeling yield but is likely influenced by La channeling in the LAO substrate. In Fig. 2(a), a somewhat higher yield of 21% is obtained for the La peak from the La$_2$Zr$_2$O$_7$/YSZ(111) heterostructure (for reference, the minimum yield obtained for a bare YSZ substrate is 12%). In this case, the La peak in the channeling direction exhibits clear surface and interface peaks in addition to the yield from the bulk of the film. The surface peak arises from backscattering from the top surface of the film, where no shadowing can occur. The interface peak indicates the presence of disorder at the film/substrate interface. The fairly low $I_{\text{min}}$ values for these two films are consistent with the well-ordered epitaxial structure observed by XRD (Fig. 1). In contrast, the La$_2$Zr$_2$O$_7$ film on STO(001) exhibits essentially no channeling ($I_{\text{min}} = 96\%$), as confirmed by the identical La and Zr backscattering peak intensities in the random and channeling directions in Fig. 2(a), and the lack of features exhibited by the angular scan in Fig. 2(b). This is actually somewhat surprising considering the XRD results in Fig. 1(d) and (e), which indicated an out-of-plane texture in the (111) direction. Although the film grains are oriented randomly in-plane, RBS/c in the out-of-plane direction normal to the film surface should still reveal some degree of channeling. The lack of channeling indicates the presence of film defects that were not detected by XRD, suggesting that more local probes are needed.

3.2. Irradiation with 1 MeV Zr$^+$

Inspection of Fig. 2(a) reveals that La$_2$Zr$_2$O$_7$/STO(001) is the ideal choice for the irradiation study because both the La and Zr peaks are well-separated from the substrate Sr peak. Unfortunately, the La$_2$Zr$_2$O$_7$ film deposited on STO(001) is not epitaxial and thus shows no channeling, making it impossible to monitor the increase of disorder in the film with increasing dose. Instead, La$_2$Zr$_2$O$_7$/YSZ(111) was chosen as an alternative for the irradiation measurements. Although only the La peak from the film can be analyzed due to interference of the Zr peaks from the film and substrate, the La peak is well-resolved, with clear surface, bulk, and interface regions. Each region can be monitored independently to ascertain whether disorder or amorphization occurs preferentially in a particular region.

The effect of 1 MeV Zr$^+$ irradiation on the La backscattering peak collected in the channeling geometry is illustrated in Fig. 3(a) as a function of ion dose (dpa). As the La$_2$Zr$_2$O$_7$ film is irradiated, the channeling yield for the La peak decreases, indicating that disorder is increasing. For low ion doses (0.5–2 dpa), the characteristic “U” shape of the channeling peak remains, indicating that the disorder in the bulk of the film is less than at the interface (I), and the surface backscattering peak (S) can be resolved. The approximate positions of these three regions are shown as shaded areas in Fig. 3(a). As the dose increases to ~4 dpa, this characteristic shape
disappears and the distinction between interface, bulk, and surface regions can no longer be made.

To quantify the level of disorder in the film, the fraction of amorphous material within the film was calculated from the intensity of the La backscattering peak at a given ion dose ($I_{\text{irradiated}}$) as $(I_{\text{irradiated}} - I_{\text{channeling}})/(I_{\text{random}} - I_{\text{channeling}})$. The value of $I_{\text{irradiated}}$ was taken as the average of the counts in the interface peak region, the film bulk region, or the surface peak region, as indicated by the shaded areas in Fig. 3(a), or the area under the entire La backscattering peak. The values of $I_{\text{random}}$ and $I_{\text{channeling}}$ were taken from the unirradiated film. The amorphous fraction of LaZr2O7 as a function of ion dose is plotted in Fig. 3(b). A monotonic increase in amorphization is observed to a dose of 6 dpa, after which amorphization appears to plateau; at 10 dpa, the LaZr2O7 film exhibits a very similar fraction of amorphous material as at a dose of 6 dpa. Subtle differences in damage rate can be seen for the interface, bulk, and surface regions. The disorder in the surface peak region increases quickly at low doses, then increases more slowly at higher doses. In contrast, the interface peak increases more slowly initially, then at higher doses the damage rate increases. The film bulk region appears to exhibit a plateau at 2 dpa, but more data points as a function of dose are required to confirm this trend.

To correlate the RBS results to structural changes in the film, cross-sectional STEM-HAADF images were collected from three areas, corresponding to nominally pristine LZO and ion doses of 2
dpa and 10 dpa. As shown in Fig. 4(a), the nominally pristine LZO crystal structure is cubic, as expected. The superstructure indicative of the pyrochlore crystal structure [1] is not observed in fast Fourier transform (FFT) of the image, consistent with the assessment by XRD that this film possesses the defected fluorite structure. This cross-section was collected from an area between the pristine region utilized for He\textsuperscript{+} RBS channeling alignment and the 2 dpa Zr\textsuperscript{+} region, and thus a low level of damage may have occurred from either He\textsuperscript{+} or Zr\textsuperscript{+} irradiation (or both). Evidence of this damage is also observed as a surface amorphous region in some of the STEM images (not shown), and the observation of ion tracks on the film surface (see inset to Fig. 4(a)); the STEM cross-section was collected from an area between ion tracks). Fig. 4(b–c) show details of the LZO/YSZ interface, indicating the presence of misfit dislocations to accommodate the lattice mismatch between the film and substrate. GPA analysis was used to calculate the in-plane strain component (\(\varepsilon_{xx}\)) relative to the substrate and highlight the location of the misfit dislocations. The dislocations are spaced 7–8 nm apart and act to relax the film strain, yielding a 3–4% in-plane expansion relative to the substrate, in good agreement with our XRD measurements. Fig. 5(a–b) show that, after a dose of 2 dpa, the top portion of the film has transformed to a damaged layer consisting of substantial amorphization. The thickness of this damaged layer in the region imaged in Fig. 5(b) is approximately 8 nm. Some radiation-induced amorphization (~4 nm) is also observed at the LZO/YSZ interface in certain regions, although in other regions the LZO exhibits crystallinity in contact with the YSZ substrate. The central portion of the film remains crystalline; as with the nominally pristine film shown in Fig. 4, the superstructure indicative of the pyrochlore crystal structure is not apparent in the lattice image or the associated FFT. The thickness of this crystalline region, in the areas which exhibit amorphization at the YSZ interface, is also observed as a surface amorphous region in some of the STEM images (not shown), and the observation of ion tracks on the film surface (see inset to Fig. 4(a); the STEM cross-section was collected from an area between ion tracks). Fig. 4(b–c) show details of the LZO/YSZ interface, indicating the presence of misfit dislocations to accommodate the lattice mismatch between the film and substrate. GPA analysis was used to calculate the in-plane strain component (\(\varepsilon_{xx}\)) relative to the substrate and highlight the location of the misfit dislocations. The dislocations are spaced 7–8 nm apart and act to relax the film strain, yielding a 3–4% in-plane expansion relative to the substrate, in good agreement with our XRD measurements.
approximately 26 nm. The original film thickness was 56 nm, which indicates that FIB sample preparation of the STEM cross-section has removed some of the amorphous film at the surface. If the assumption is made that, other than a 26 nm thick central region of crystalline material, the rest of the 56 nm thick film has amorphized, an amorphous fraction of 0.53 can be estimated. The RBS channeling results shown in Fig. 3(b) indicated an amorphous fraction of 0.46 at a dose of 2 dpa, which matches well with the ratio of damaged to crystalline regions in the STEM images.

Further irradiation to 10 dpa does not continue to uniformly thicken the surface damage layer, as illustrated in Fig. 5(c); in this case, the damage layer possesses a thickness of approximately 14 nm compared to a total film thickness 46 nm, with an uneven and somewhat poorly defined interface between the amorphized surface layer and the central crystalline region. At this higher ion dose, the majority of additional damage has occurred at the LZO/YSZ interface. In Fig. 5(c), the average thickness of the amorphous region at the interface is approximately 9 nm.

Pitting of the substrate is observed at regular intervals, as shown in Fig. 5(d), likely originating from the misfit dislocations shown in Fig. 4(b–c). However, it is difficult to ascertain whether the misfit dislocations promoted damage in these regions, or conversely if they acted as...
sinks for radiation-induced damage [21] while the areas between dislocations experienced higher damage levels. In some places, the amorphous regions at the interface and surface infringe on the central crystalline region, and touch or nearly touch. In these regions, evidence of faceting of the crystalline material is evident; this faceting is likely along a direction equivalent to the corner-sharing TiO$_6$ octahedra in the pyrochlore (112) direction [29]. An estimate of the ratio of amorphous to crystalline regions in the STEM image in Fig. 5(c) is 0.40, which is well below that found by RBS/c (0.87). This discrepancy may be explained by fact that the crystalline region in the center of the film is partly damaged. Thus, a fraction of the backscattering observed in RBS/c occurs in this region, whose amorphous level cannot be quantified from the STEM images. The estimate of amorphous fraction also does not account for the amorphous regions which have infringed on the central, crystalline region. Nonetheless, the STEM images confirm that the LZO film has not fully amorphized at a dose of 10 dpa.

3.3. Electronic structure of La$_2$Zr$_2$O$_7$

The electronic structure of La$_2$Zr$_2$O$_7$ is not well established, which hinders efforts to model the radiation damage properties of the material [14]. To this end, the optical properties as measured by spectroscopic ellipsometry of a 3000 Å thick La$_2$Zr$_2$O$_7$ thin film deposited on YSZ(111) are presented in Fig. 6. The XRD patterns of this film were similar to those presented in Fig. 6(a and b), indicating that the film possesses the defected fluorite structure and the epitaxial strain has been relaxed. In the visible light region (~1.8–3.5 eV), the index of refraction of La$_2$Zr$_2$O$_7$ ranges from 2.09 to 2.20, which matches well with the index of refraction determined by Kinata et al. [30] on a bulk sample of polycrystalline pyrochlore La$_2$Zr$_2$O$_7$ in a similar wavelength range. The bandgap values of defected-fluorite La$_2$Zr$_2$O$_7$ are determined from the Tauc plots in Fig. 6(b–c). A direct bandgap of 5.60 eV and indirect bandgap of 4.96 eV are determined by extrapolating the linear region of each plot to zero. From this analysis, defected-fluorite La$_2$Zr$_2$O$_7$ is found to be an indirect-gap semiconductor. As summarized in Table 1, these bandgap values are considerably larger than those measured experimentally on polycrystalline powder material with the pyrochlore structure (3.5–3.9 eV) [31,32]. Density functional theory (DFT) calculations which model the pyrochlore structure typically predict bandgap values in the range of 4.0–4.2 eV [31,33,34], although a recent ab initio molecular dynamics calculation predicted a bandgap of 3.33 eV [14]. In most cases, the bandgap prediction was assumed to be an underestimate of the true value, due to the well-known deficiency of both the local density approximation (LDA) and Perdew-Burke-Emzerhof (PBE) functionals in correctly accounting for electron correlation effects [14,34]. Interestingly, analysis of the pyrochlore La$_2$Zr$_2$O$_7$ band structure predicted by DFT indicates that the lowest-energy band transition should be direct [31,33,34], while the experimental results in Fig. 6 indicate that defected-fluorite La$_2$Zr$_2$O$_7$ possesses an indirect bandgap. Analysis of the optical properties of La$_2$Zr$_2$O$_7$ at photon energies >6 eV may provide a more accurate measure of the indirect bandgap value, but are not possible with the current ellipsometry setup.

4. Discussion

Several physical models have been proposed for the evolution of amorphization as a function of ion dose [18,35]. Among these, Gibbons [19] discussed a defect accumulation model (also referred to as a cascade overlap model), which assumes that the defects and disorder created by each irradiation-induced collision cascade accumulate in the sample until the defect concentration exceeds the critical concentration necessary for amorphization; this tends to occur when individual collision cascades overlap. The cascade overlap model predicts a sigmoidal dependence of amorphous fraction on ion dose, as is typically observed for light ion irradiation (i.e., He$^+$. For example, synthetic coesite (a high pressure polymorph of SiO$_2$) was found to amorphize through a cascade overlap model when irradiated with 1.5 MeV Kr$^+$. As an alternative, Gibbons [19] also proposed a direct amorphization model, which predicts that the highly disordered region generated by each collision cascade is quenched more rapidly than recrystallization can occur. Analogous to the rapid thermal quenching employed to create glasses, this rapid quenching of the collision cascade results in an amorphous core surrounded by crystalline material. As the ion dose increases, these small amorphous volumes accumulate until the entire material is amorphized. In this model, the amorphous fraction follows an exponential dependence on ion dose, as is observed for heavy ion irradiation. For example, zircon (ZrSiO$_4$) mineral samples irradiated by naturally-occurring U were found to follow the direct amorphization model [37].

In the cascade overlap model (specifically, the cascade double overlap model [19]), the rate of amorphization as a function of ion dose, $D$, is given by [37]:

$$f_a = 1 - \left[ 1 + B_D D + \frac{1}{2} B_D^2 D^2 \right] e^{-B_D D}$$

(1)

where $f_a$ is the fraction of amorphous material, $B_D$ is the total area of disordered or damaged material (projected onto the material surface) [19], and the ion dose, $D$, is given as total ions/cm$^2$. In Fig. 3(b), the best fit of the defect accumulation model (Equation (1)) to the

![Fig. 6. Optical coefficients extracted from fits to spectroscopic ellipsometry data collected on 3000 Å La$_2$Zr$_2$O$_7$/YSZ(111). Insets: Tauc plots of (shv)$^2$ and (shv)$^{1/2}$ vs. photon energy and linear extrapolations to determine the direct and indirect bandgap values, respectively.](image)
experimental amorphization data for La$_2$Zr$_2$O$_7$ is plotted. A value of $B_d = 1.73 \times 10^{-14}$ cm$^2$ was found to best fit the amorphous fraction calculated from La backscattering data averaged over the entire region. Clearly, the sigmoidal shape of the model curve is not reproduced in the experimental data, and the discrepancy between model and experiment increases at higher ion doses. In contrast, the direct amorphization model fits the data well at ion doses up to 6 dpa. The direct amorphization model is given by [19,37]:

$$f_a = 1 - e^{-B_d S_d}$$

(2)

where $B_d$ is analogous to $B_d$ in Equation (1) (i.e., the total area of amorphous material, projected onto the film surface). A value of $B_d = 4.54 \times 10^{-15}$ cm$^2$ was found to fit the amorphous fraction calculated from the entire La backscattering region satisfactorily for ion doses $\leq$ 6 dpa. This value of $B_d$ corresponds to a radius of 380 Å for each amorphous cluster generated by an implanted ion, if a cylindrical geometry of the collision cascade is assumed [19].

A disorder accumulation model has also been developed [20,38], in which the amorphous fraction ($f_a$) is given by a direct impact/direct-stimulated model which includes both direct-impact amorphization and growth of the amorphous region at the crystalline/amorphous interface stimulated by defects, cascades, or implanted ions [39]:

$$f_a = 1 - \frac{(\sigma_s + \sigma_t)}{(\sigma_s + \sigma_0) \exp[(\sigma_s + \sigma_t)d]}$$

(3)

where $\sigma_s$ and $\sigma_t$ are the cross-sections for direct and stimulated amorphization, respectively ($\sigma_s$ is analogous to $B$ in Eqns. (1) and (2) above). Because ion channeling analysis is sensitive to both amorphization and the presence of interstitials and small interstitial clusters in crystalline regions, the total relative disorder, $S$, is given by:

$$S = f_a + S_d$$

(4)

where $S_d$ is the relative disorder from interstitials in the crystalline regions of the material. The dependence of $S_d$ on ion dose is given by a simple point defect accumulation model, multiplied by the probability, (1-$f_0$), of a defect being generated in the crystalline region:

$$S_d = S_{d0}[1 - \exp(-BD)](1-f_0)$$

(5)

where $S_{d0}$ is the saturation value for the defect-induced disorder observed along a specified ion channeling direction and $B$ is proportional to the effective recombination volume for the interstitial defects giving rise to $S_d$. The best fit of Eqn. (4) to the amorphization data as a function of dpa is presented in Fig. 3(b), and the fit parameters are given in Table 2. The model is able to fit the data well, including the slight plateau between 1 and 2 dpa. The resulting $\sigma_s$ and $\sigma_t$ values from the fit are one to two orders of magnitude smaller than those obtained at 300 K for the Sm sublattice of Sm$_2$Ti$_2$O$_7$ ($\sigma_{fi} = 1.0$ dpa$^{-1}$, $\sigma_{fi} = 66$ dpa$^{-1}$) [20]. This is intuitively reasonable, given the ease with which the bulk single crystal of Sm$_2$Ti$_2$O$_7$ was amorphized (full amorphization at 0.1–0.15 dpa) compared to the La$_2$Zr$_2$O$_7$ epitaxial film in Fig. 3(b), which has not reached full amorphization at 10 dpa. However, the mechanism of amorphization appears to be somewhat similar for both materials: in both cases, $\sigma_f$ is significantly larger than $\sigma_0$. In addition, the value of $B = 10$ dpa$^{-1}$ is somewhat larger than that obtained for La$_2$Zr$_2$O$_7$.

Previous MD simulations of the ion irradiation properties of pyrochlore La$_2$Zr$_2$O$_7$ by Chartier et al. [15,16] predicted a low yield of cation antisites, interstitials, and vacancies as a result of irradiation. This low yield of defects occurs as La$_2$Zr$_2$O$_7$ transitions towards the disordered fluorite state. Ion implantation of a polycrystalline La$_2$Zr$_2$O$_7$ sample by 1.5 MeV Xe$^+$ by Lian et al. [1] partially corroborated these results. At low ion doses, La$_2$Zr$_2$O$_7$ tended to form a disordered fluorite structure observed by in situ TEM, as predicted by the MD simulations, but as the dose increased, the material amorphized; total amorphization (as judged by the loss of diffraction features in selected area electron diffraction patterns) occurred at a dose of 5.5 dpa.

The amorphization data presented in Fig. 3(b) indicates that, at low ion irradiation dose, the defected-fluorite La$_2$Zr$_2$O$_7$ film amorphizes more readily than either the direct amorphization or cascade overlap models would predict. Inclusion of stimulated amorphization ($\sigma_t$) in the disorder accumulation model (Eqn. (3)) is required to adequately fit the data in the low-dose regime. The best-fit parameters shown in Table 2 indicate that stimulated amorphization is more influential than direct amorphization ($\sigma_f$).

The STEM image presented in Fig. 5(b) clearly shows an amorphous layer which has formed in the surface region of the film; in this region, we can conclude that growth of the amorphous region at the crystalline/amorphous interface after the radiation damage has occurred, stimulated by defects, cascades, or implanted ions, is a primary amorphization mechanism in La$_2$Zr$_2$O$_7$. As the irradiated dose increases, similar amorphization appears at the La$_2$Zr$_2$O$_7$/YSZ(111) interface. Interestingly, though, the amorphous regions do not easily encroach on the center portion of the La$_2$Zr$_2$O$_7$ sample. Instead, they tend to form a disordered fluorite structure in the STEM image in Fig. 5(d). As the damage level increases, the film becomes more resistant to amorphization, in agreement with the previous MD simulations [15,16]. Surprisingly, though, while Lian et al. [1] observed full amorphization of pyrochlore La$_2$Zr$_2$O$_7$ at a dose of 5.5 dpa, in this work the epitaxial film of defected fluorite La$_2$Zr$_2$O$_7$ exhibited an amorphous fraction of only 78% at a dose of 6 dpa; this damage level did not increase as the dose was increased to 10 dpa. Clearly, the surface and interface of the epitaxial thin film play a large role in the amorphization mechanism at lower doses, in contrast to the spatially uniform amorphization observed in large-grained polycrystalline pyrochlore-structure La$_2$Zr$_2$O$_7$ [1]. The resistance of thin film La$_2$Zr$_2$O$_7$ to amorphization at higher doses, however, may be related to the difference in structure between La$_2$Zr$_2$O$_7$ which originally possessed the pyrochlore structure but has disordered into a defected fluorite-type structure as a result of irradiation, and La$_2$Zr$_2$O$_7$ which is fully disordered as-synthesized.

Two plateaus in the damage accumulation data presented in Fig. 3(b) are evident: a weak plateau in the range of 1–2 dpa, and a clear plateau between 6 and 10 dpa. These plateaus cannot be explained by the presence of recombination centers. Instead, they typically correspond to the formation of extended planar defects such as stacking faults and dislocation loops, facilitated by the high mobility of interstitials during irradiation near the critical amorphization temperature [35,36]. Lian et al. [1] predicted that the critical amorphization temperature for La$_2$Zr$_2$O$_7$ above which amorphization does not occur, is ~310 K. Thus, the room temperature irradiation in the current study is close to the critical

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<td>$\sigma_s$</td>
<td>0.08 dpa$^{-1}$</td>
</tr>
<tr>
<td>$\sigma_t$</td>
<td>0.55 dpa$^{-1}$</td>
</tr>
<tr>
<td>$S_{d0}$</td>
<td>0.33</td>
</tr>
<tr>
<td>$B$</td>
<td>2.64 dpa$^{-1}$</td>
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temperature, and the formation of planar defects is a possible source of the observed damage plateaus. These planar defects may play a role in the observed change in amorphization behavior observed by STEM: at doses up to 2 dpa, most of the amorphization occurs in the top half of the film, but at higher doses, this surface amorphous region remains relatively static, and further amorphization is observed at the film/substrate interface.

5. Conclusions

The structural and optoelectronic properties of epitaxial, defected fluorite structure La$_2$Zr$_2$O$_7$ thin films were explored. Epitaxy was realized on YSZ(111) and LAO(001) substrates, but not a function of ion dose considerably higher than the critical amorphization dose observed at a dose of approximately 8 dpa. A dose of 10 dpa is also observed by STEM: at doses up to 2 dpa, most of the amorphization to reformation of planar defects. The results presented here can be used to refine the models developed to predict the radiation response of pyrochlore oxides, and provide insight into the underlying physical mechanisms of radiation-induced defect formation.

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