Irradiation effects and hydrogen behavior in H_2^+ and He^+ implanted $\gamma\text{-LiAlO}_2$ single crystals

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ABSTRACT

Gamma-phase lithium aluminate ($\gamma\text{-LiAlO}_2$) is a breeder material for tritium, a necessary substance for strategic stockpile and fusion power systems. A fundamental study of structural evolution and tritium diffusion in $\gamma\text{-LiAlO}_2$ under displacive irradiation is needed to fully assess the material performance. This study utilizes ion implantation of protium (surrogate for tritium) and helium in $\gamma\text{-LiAlO}_2$ single crystals at elevated temperatures to emulate the irradiation effects. The results show that at 573 K there are two distinct disorder saturation stages to 1 dpa without full amorphization; overlapping implantation of H_2^+ and He^+ ions suggests possible formation of gas bubbles. For irradiation to $10^{21} \text{ H}^+/\text{m}^2$ (0.36 dpa at peak) at 773 K, amorphization occurs at surface with H diffusion and dramatic Li loss; the microstructure contains bubbles and cubic LiAl_5O_8 precipitates with sizes up to 200 nm or larger. In addition, significant H diffusion and release are observed during thermal annealing.

1. Introduction

Isotope ^6Li -enriched $\gamma\text{-LiAlO}_2$ has been proposed as a promising material for development of neutron dosimeters [1] and has been considered as a candidate for production of tritium in fusion reactor designs [2]. It has also been used as a solid breeder material in support of tritium readiness campaign [3]. Tritium must be produced to secure a steady supply as it is subject to β^- decay with a half-life of 12.3 years. When LiAlO_2 is irradiated under a neutron flux, ^3H and ^4He particles from reaction $^6\text{Li}(n,\alpha)^3\text{H}$ will be emitted at energies of 2.75 and 2.05 MeV, respectively. These energetic particles will initiate damage cascades that lead to generation of point defects in the crystal structure. The accumulation of point defects, formation of

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extended defects and presence of gas species in LiAlO_2 are expected to affect the structural stability, thermomechanical properties, and tritium migration. Previous studies of LiAlO_2 reported in the literature have addressed technical issues of structural defects, volume swelling, micro-cracking, tritium detrapping, diffusion and release using various radiation sources, including x-rays and γ -rays [4,5], electrons [6,7], neutrons [8-12], and ions [13-15]. Modeling of tritium transport [16-18] and molecular dynamics (MD) calculations of threshold displacement energies [19], defect production [20,21] and Li diffusion [22] have also been carried out. However, very few quantitative studies of damage accumulation in LiAlO_2 have been reported to date. Katsui *et al.* used ^2H (surrogate for ^3H) and ^4He ions to irradiate $\gamma\text{-LiAlO}_2$ single crystals at room temperature [23,24] and found a sigmoidal-type dependence of defect concentrations on dose, similar to the generic behavior of many other ceramic materials, such as SiC [25], GaN [26], and SrTiO_3 [27]. The dose-dependent defect accumulation in $\gamma\text{-LiAlO}_2$ at elevated temperatures, such as ~ 573 K that is applied at the Watts Bar Nuclear Unit 1 commercial power plant [28] for tritium production, is currently unknown; tritium diffusion kinetics are subject to change as microstructure evolves. In addition to technological significance, it is of fundamental interest to investigate damage accumulation, microstructural evolution, and tritium transport in $\gamma\text{-LiAlO}_2$ during displacive irradiation at elevated temperatures as well as during post-irradiation thermal annealing. In this study, we use ^1H (surrogate for ^3H) and ^4He ion implantations in single-crystal $\gamma\text{-LiAlO}_2$ to emulate irradiation effects in the temperature range from 300 to 773 K and to study H diffusion and release during thermal annealing.

2. Structure and properties of $\gamma\text{-LiAlO}_2$

Lithium aluminate was first synthesized in 1906 [29]. At least five LiAlO_2 allotropes have been identified to date, with the most studied structures being trigonal (α phase), orthorhombic (β phase) and tetragonal (γ phase) [30]. Nuclear engineers are particularly interested in $\gamma\text{-LiAlO}_2$ because it is a high-temperature phase and has demonstrated acceptable performance under neutron radiation to a high burnup for tritium production [3]. Fig. 1 shows the $\gamma\text{-LiAlO}_2$ crystal structure in units of tetrahedra, created from commercial software CrystalMaker [31]. The crystal has tetragonal symmetry (space group $P4_12_12$) with lattice constants $a = 0.51687$ nm and $c = 0.62679$ nm at room temperature [32]. The specific gravity corresponds to 2615 kg/m^3 [32] (atomic density $9.555 \times 10^{28} \text{ at./m}^3$) and the melting point ≈ 2023 K [17]. Symmetry operations are a fourfold rotation about the $[001]$ axis and twofold rotations about the $[100]$, $[010]$ and $[110]$ axes. The Li and Al atoms are located at the centers of oxygen tetrahedra. Each LiO_4 tetrahedron shares a common edge with an AlO_4 tetrahedron. The $\text{LiO}_4\text{-AlO}_4$ pairs are connected via common tetrahedron vertices and form a three-dimensional lattice, as shown in Fig. 1. Chemical bonds between aluminum and oxygen are

Fig. 1. Perspective view of tetragonal $\gamma\text{-LiAlO}_2$ crystal structure with LiO_4 and AlO_4 represented in yellow and green tetrahedra, respectively.

significantly covalent, while those between lithium and oxygen are predominantly ionic [33]. In general, γ -LiAlO₂ has exhibited dimensional stability, chemical inertness, and acceptable tritium release behavior under neutron irradiation. The material can withstand the rigors of long-term irradiation at high temperatures and under large temperature gradients [34,35]. γ -LiAlO₂ also has an outstanding thermal conductivity under suitable operating conditions [36].

3. Experimental details

Single-crystal (001)-oriented γ -LiAlO₂ substrates (10 mm $\times$ 10 mm $\times$ 0.5 mm) with one-side polish were obtained from MTI Corporation (Richmond, CA). Ion implantation and subsequent Rutherford backscattering spectrometry (RBS) under $\langle 001 \rangle$ -axial channeling conditions (RBS/C) were performed using the 140 kV ion implanter and 1.7 MV Ionex Tandetron, respectively, at Texas A&M University. 80 keV H₂⁺ molecular ions (equivalent to 40 keV H⁺ ions) were implanted 60° off the surface normal to fluences ranging from 2×10^{20} to 3×10^{21} H⁺/m² at 573 K. The elevated temperature for implantation was chosen because the value is typical for neutron irradiation to produce tritium [28]. The large tilting angle was used to produce a shallow damage layer for convenience of RBS/C analysis of atomic displacements. A magnetically rastering system was applied during ion implantation to achieve large-area uniform implantation (5 mm $\times$ 5 mm or 5 mm $\times$ 10 mm). The implantation was manually interrupted once about every 15 min to check the beam current, which was found to be fairly stable in most cases during the course of implantation. The beam current is averaged over the time period and the ion flux is typically on the order of 2×10^{17} ions/m²/s. Additional samples were implanted under the same geometry to 10^{21} H⁺/m² at various temperatures ranging from 300 to 773 K. Overlapping implantation of 80 keV H₂⁺ and 90 keV He⁺ ions as well as the reverse sequential implantation in γ -LiAlO₂ were also performed to an equal ion fluence of 10^{21} ions/m² for each of the ion species at 573 K. The detailed implantation conditions are given in Table 1.

The depth profiles of the atomic displacements and implanted H and He have been simulated using SRIM-2013 [37], where the surface sputtering/monolayer collision step mode was chosen to eliminate

artifacts into the sample damage by the energetic light ions in the near surface region. In the simulation, the threshold displacement energies of $E_d(\text{Li}) = 22$ eV, $E_d(\text{Al}) = 84$ eV and $E_d(\text{O}) = 37$ eV were adopted from a molecular dynamics (MD) simulation [19]. The simulation results show that for 40 keV H^+ ion implantation at 60° off normal, the maximum atomic displacement rate in LiAlO_2 is 0.031 displacements/nm/ion at the peak depth of ~ 150 nm [full width at half maximum (FWHM) ≈ 170 nm], leading to a conversion factor of 3.2×10^{-4} dpa/(ion/nm²), where dpa stands for displacements per atom. The dose thus calculated could be as large as a factor of 2 compared to that from quick Kinchin-Pease mode [38], but it will not affect the major data interpretation in this study. The simulated H peak maximum is located at ~ 210 nm with FWHM ≈ 170 nm. The highest ion fluence (3×10^{21} H^+/m^2) applied in this study corresponds to a dose of ~ 1 dpa and ~ 18 at.% H at their respective peak maxima. Similarly, the conversion factor for 90 keV He^+ ion implantation at 60° off is 2.5×10^{-3} dpa/(ion/nm²) at ~ 220 nm (FWHM ≈ 270 nm) and the He profile is peaked at ~ 310 nm with FWHM ≈ 260 nm.

The implanted samples were analyzed at room temperature in vacuum (8×10^{-6} Torr) using 2 MeV He^+ RBS/C at a scattering angle of 160° along the $\langle 001 \rangle$ crystallographic axis of $\gamma\text{-LiAlO}_2$. The RBS/C beam spot was $1 \text{ mm} \times 1 \text{ mm}$ with a beam current of ~ 10 nA. A random spectrum was collected at the fixed tilting angle of 7° with the sample kept rotating around an axis perpendicular to the tilt over the range from -3° to 3° . The integrated charge for each spectrum was 10 μC , equivalent to an ion fluence of 6×10^{19} He^+/m^2 . Time-of-flight secondary ion mass spectrometry (ToF-SIMS) at the Environmental Molecular Sciences Laboratory (EMSL) located at the Pacific Northwest National Laboratory (PNNL) was employed to study H diffusion behavior with 1.0 keV O_2^+ ions as a sputtering beam and 25 keV Bi^+ ions as an analyzing beam. While Cs^+ ions are usually selected for sputtering to achieve a higher H detection sensitivity [39], O_2^+ ions are used in this study primarily because both H and Li need to be analyzed simultaneously. The sputtered crater area was $300 \mu\text{m} \times 300 \mu\text{m}$ and the analysis was performed at the center of the crater with an area of $50 \mu\text{m} \times 50 \mu\text{m}$ or $100 \mu\text{m} \times 100 \mu\text{m}$. A thin layer of Au was deposited onto the backside of each sample to minimize charging effects. An electron gun was also used during SIMS measurements to compensate the charge. The depth scale for the SIMS data was calibrated by measuring the crater depth with a Veeco Dektak 150 stylus profilometer. It should be noted that all the SIMS measurements were performed outside the RBS/C spots except for one sample that was implanted at 300 K and measured both inside and outside the RBS/C spot to evaluate 2 MeV He^+ irradiation effects on H diffusion. An additional sample implanted to 10^{21} H^+/m^2 at 300 K without RBS/C measurements was used to study thermal annealing behavior of H. Isochronal anneals for 4 h at 573, 673 and 773 K in air (Table 1) were applied with a ramp-up time of 2 h and ramp-down rate of 2 K/min or less. Before and after each annealing step, SIMS was performed in close proximity to minimize possible non-uniformity effects of ion fluence. In addition to H depth profiling, Li concentration was simultaneously measured up to the depth of 650 nm beyond the implantation damage band.

A cross-sectional thin specimen for $\gamma\text{-LiAlO}_2$ implanted to 10^{21} H^+/m^2 at 773 K was prepared using a FEI Helios 600 Nanolab system of focused ion beam (FIB) and scanning electron microscope (SEM) at EMSL. Ga^+ ions at 30 and 5 keV were used for cutting/thinning and polishing the specimen, respectively. The specimen was examined using a FEI aberration-corrected Titan 80–300 scanning transmission electron microscope (STEM) at EMSL with a spatial resolution of better than 0.1 nm at an operating voltage of 300 kV. Both bright-field transmission electron microscope (TEM) and high-angle annular dark field (HAADF) STEM were used to examine the damage band and microstructures.

4. Results and discussion

4.1. Defects and microstructures

4.1.1. Damage accumulation

A sequence of RBS/C spectra for γ -LiAlO₂ implanted with H₂⁺ ions to various ion fluences at 573 K are shown in Fig. 2(a). Also included in the figure are a RBS/C spectrum and a random spectrum from an unimplanted area. The depth scale for element Al, shown on the top axis, is estimated based on the SRIM database [37] with the assumption of surface energy approximation [40]. The minimum yield, $\chi_{\min}$, from the channeling spectrum for pristine γ -LiAlO₂ is determined to be only ~3.3%, indicating that the as-received sample had high crystalline quality in the near-surface region of interest. The inset in Fig. 2(b) illustrates γ -LiAlO₂ crystal structure viewed along the <001> axis, exhibiting wide open space for ion channeling. Apparent damage peaks on both the Al and O sublattices are observed in the RBS/C spectra around channel numbers 450 and 270, respectively. As O spectra are completely overlapped with the higher-yield Al spectra, only Al lattice disorder is discussed in this study. From Fig. 2(a), the damage peak is barely visible at 2×10^{20} H⁺/m², but grows significantly at 4×10^{20} H⁺/m². It remains at a similar intensity up to 10^{21} H⁺/m² although the damage level near the surface rises, starting from 8×10^{20} H⁺/m². Further increase in the ion fluence to 2×10^{21} H⁺/m² leads to an abrupt increase in the peak intensity, and then stay at the level to the highest applied ion fluence of 3×10^{21} H⁺/m². No complete amorphization occurs under the irradiation conditions.

The relative disorder on the Al sublattice in γ -LiAlO₂ is obtained from the RBS/C spectra [Fig. 2(a)] using an iterative procedure [41,42] that is based on dechanneling from the actual defect concentration present. The procedure extracts the probability of close encounters between the energetic particles and the displaced atoms, which is directly proportional to the defect concentration. Fig. 2(b) shows disorder accumulation as a function of dose in dpa at the damage peak located at ~230 nm, which is somewhat larger than the SRIM prediction (150 nm) and is likely due to the overestimation of the electronic

Fig. 2. (a) 2 MeV He⁺ RBS/C spectra along the <001> axis in γ -LiAlO₂ single crystal irradiated 60° off normal with 80 keV H₂⁺ ions to a range of ion fluences at 573 K. Also included are random and channeling spectra from an unimplanted area, and (b) damage accumulation on the Al sublattice at the damage peak as a function of dose in dpa. Inset in (b): <001> axial view of γ -LiAlO₂ crystal structure.

stopping powers for slow ions in the SRIM database. The dashed line is a spline fit to the data points. It appears that the relative Al disorder saturates at 0.29 between 0.1 and 0.3 dpa, followed by disorder saturation at 0.54 between 0.6 and 1.0 dpa, indicating that simultaneous recovery of defects in γ -LiAlO₂ is considerable during ion irradiation at 573 K. Similar disordering behavior was also observed in single-crystal GaN irradiated with Au²⁺ ions at room temperature [26], where a high-concentration planar defects were generated and they acted as efficient sinks to mobile point defects [43].

4.1.2. Effects of implantation temperature

Fig. 3 shows RBS/C spectra for γ -LiAlO₂ implanted to 10^{21} H⁺/m² at various temperatures. For irradiation at 300 K, a well resolved damage peak appears without full amorphization. The result is similar to a previous report on γ -LiAlO₂ irradiated with 10 keV D₂⁺ ions to 10^{21} D⁺/m² at room temperature [24]. As temperature increases to 573 K, more simultaneous recovery of defects occurs and less residual defect concentrations are retained. At 673 K, even less damage is accumulated at the depth of the peak maximum, as expected. However, a high dechanneling yield emerges at the surface, where the electronic energy deposition process is dominant. This behavior may be associated with the material decomposition or dissociation induced by ion irradiation at the elevated temperature. When the temperature increases to 773 K, Al channeling spectrum reaches the level of the random spectrum from the surface to the depth of 200 nm, indicating that the surface material is no longer a single crystal aligned with the incident He⁺ beam. As will be discussed in section 4.1.4., the material in this layer was fully amorphized. The anomalously strong surface peak shown in Fig. 3 for 673 K might also be associated with the surface amorphization.

4.1.3. Effects of prior H₂⁺ implantation

Due to the fact that both energetic ³H and ⁴He particles are generated from neutron reaction with ⁶Li in γ -LiAlO₂, it is important to study the synergic effects of the interactions among the gas species and implantation defects. The RBS/C results from the two different sequences of ion implantations to 10^{21} H⁺/m² and 10^{21} He⁺/m² at 573 K are shown in Fig 4. Also included in the figure is

Fig. 3. 2 MeV He⁺ RBS/C spectra along the <001> axis in γ -LiAlO₂ single crystal irradiated 60° off normal with 80 keV H₂⁺ ions to 10^{21} H⁺/m² at various temperatures. Also included are random and channeling spectra from an unimplanted area.

Fig. 4. 2 MeV He⁺ RBS/C spectra along the <001> axis in γ -LiAlO₂ single crystal irradiated with H₂⁺ and He⁺, He⁺ and H₂⁺, and sole H₂⁺ ions to 10^{21} ions/m² each at 573 K. Also included are random and channeling spectra from an unimplanted area.

the result from sole H_2^+ ion implantation to $10^{21} \text{ H}^+/\text{m}^2$ at 573 K for comparison. Apparently, the dechanneling yield is significantly higher when H_2^+ ions are per-implanted. An accurate interpretation for the data is not available at this time. However, it may be worthwhile to note that a similar study has been reported for SiC [44], where He bubble formation and growth via He^+ ion implantation are greatly enhanced by pre-injection of H atoms. While further studies are still needed, formation of gas-pressurized bubbles in the $\gamma\text{-LiAlO}_2$ is possible, which could lead to an enhancement in the dechanneling yield because presence of bubbles can distort the local crystal structure.

4.1.4. Microstructures and precipitates

TEM study has been performed for $\gamma\text{-LiAlO}_2$ implanted to $10^{21} \text{ H}^+/\text{m}^2$ at 773 K. Fig. 5(a) shows a conventional low-resolution bright-field TEM image for an overall view of the sample surface region. The Pt and C layers were deposited prior to FIB preparation of the cross-sectional TEM specimen for protection of the sample surface from sputtering and irradiation damage. A damage band is clearly exhibited in bright contrast with a thickness of $\sim 500 \text{ nm}$. FIB created a thinner, wedge-shaped surface layer with a brighter contrast [Fig. 5(a)]. The material is fully amorphized from the surface to a depth of $\sim 200 \text{ nm}$, showing a uniform contrast that does not change with rotation of the specimen. This thickness is consistent with the RBS/C data for 773 K in Fig. 3. The agreement suggests that volume swelling in the amorphized layer is not noticeable. As will be discussed below in section 4.2.1., this layer has a dramatic Li loss that could effectively mitigate the amorphization-induced volume swelling, leading to an insignificant net dimensional change.

From Fig. 5(a), solid-state faceted precipitates are formed with sizes up to 200 nm or larger at depths between 200 and 500 nm. The rectangular shape of the precipitates at the jagged interface suggests that the precipitates have a preferred growth direction along the [001] axis of $\gamma\text{-LiAlO}_2$. Nucleation of the precipitates could be a result of ion-beam irradiation induced predominant production of Li interstitials, decomposition or dissociation of $\gamma\text{-LiAlO}_2$ single crystal at 773 K, followed by significant Li diffusion out of the region (see section 4.2.1.), and finally phase transformation driven by local lattice stress. The bright feature near the surface in the bright-field TEM image of Fig. 5(a), which appears as a dark contrast in the HAADF STEM image in Fig. 5(b), is a gas-pressurized bubble, where the surface shows an extruding curvature. The bubbles observed mainly near the surface are formed in an ellipsoid shape with the long axis parallel to the surface, and have a size of up to 100 nm or larger with spacing of 600 –

Fig. 5. (a) Bright-field TEM micrograph of $\gamma\text{-LiAlO}_2$ implanted to $10^{21} \text{ H}^+/\text{m}^2$ at 773 K, (b) HAADF STEM micrograph of the sample with inserted diffraction patterns from matrix and precipitates, and (c) gas-pressurized bubbles formed at the surface.

Fig. 6. HAADF STEM micrographs at (a) low resolution, (b) higher resolution, (c) interface, and atomic-level resolution for (d) γ -LiAlO₂ and (e) cubic LiAl₅O₈ precipitate in γ -LiAlO₂ implanted to 10^{21} H⁺/m² at 773 K. Insets in (d) and (e) are crystal structures and FFT patterns from images (d) and (e), respectively.

700 nm, as shown in Fig. 5(c). The HAADF STEM image in Fig. 5(b) shows the atomic number (Z) contrast. The image intensity is approximately proportional to $Z^{1.7}$ due to screened elastic scattering of electrons [45] and to the occupancy in the atomic column [46]. Clearly, the average Z of the precipitates is larger than that of γ -LiAlO₂ as the precipitates show a brighter contrast. The selected area electron diffraction (SAED) pattern in the inset of Fig. 5(b) shows expected intensity maxima for single-crystal γ -LiAlO₂ [100], while that for the precipitates is complex and needs a more careful analysis (see below).

Fig. 6 shows a series of HAADF STEM images at different resolutions for γ -LiAlO₂ implanted to 10^{21} H⁺/m² at 773 K (the same sample as in Fig. 5). Also included in the figure are the insets for simulated Al lattices and fast Fourier transformation (FFT) patterns. The STEM image in Fig. 6(c) shows a thick amorphous boundary between the precipitate and matrix. The lattice contrasts from both γ -LiAlO₂ and precipitate are apparent, indicating that their zone axes are parallel. Figs. 6(d) and 6(e) show atomic-level resolution HAADF STEM images for γ -LiAlO₂ and a precipitate, respectively, with sample-drift corrections made. Calculations of d -spacing from the reciprocal lattice of γ -LiAlO₂ were performed based on the lower left SAED pattern in Fig. 5(b). Not surprisingly, the best match of the diffraction patterns between the experiment and simulation suggests that the crystal is tetragonal γ -LiAlO₂ with zone axis [100]. The calculated lattice constants $a \approx 0.53$ nm and $c \approx 0.64$ are accurate within 2% to the database [32]. The STEM image in Fig. 6(d) also matches with the computed Al lattice pattern in γ -LiAlO₂ [100], providing a confirmation for the identified zone axis. Similar calculations were also performed for the

FFT patterns in Figs. 6(d) and 6(e). While the result for γ -LiAlO₂ is consistent with that from its SAED pattern shown in Fig. 5(b), the calculation also suggests that the precipitate is cubic-structure LiAl₅O₈ with zone axis [211]. The lattice constant was determined to be $a \approx 0.78$ nm, accurate within 2% to the database $a = 0.79$ nm [47]. As expected, the computed Al lattice pattern in the inset of Fig. 6(e) also confirms the precipitate orientation. The result agrees with a previous TEM study [6] of γ -LiAlO₂ under 200 keV electron irradiation, although the orientation relationship between the cubic LiAl₅O₈ and tetragonal γ -LiAlO₂ was not established in that study.

In a separate electron irradiation study of γ -LiAlO₂ [7], a similar diffraction pattern to that in the upper right inset of Fig. 5(b) was reported; it was concluded that the precipitate was LiAl₅O₈ with zone axis [111]. This conclusion appears to be in contradiction to our result. In fact, a detailed analysis of our SAED pattern indicates that it is a superimposition of two sets of patterns from precipitates LiAl₅O₈, as indexed in Fig. 7. One set of the diffraction spots is grouped in rectangles for [211] oriented LiAl₅O₈, and the other in hexagons for [111] oriented LiAl₅O₈. The complex pattern is a result of simultaneous diffractions from many nano-sized precipitates with both orientations because the electron beam spot for SAED was relatively large, as indicated in Fig. 5(b).

As discussed, precipitates with a rectangular shape have zone axis [211]; precipitates with zone axis [111] are likely to correspond to a triangular shape that is also observed in Fig. 6(a) and labeled in Fig. 6(b). Obviously, both zone axes [211] and [111] of the precipitates LiAl₅O₈ are parallel to the axis [100] of matrix γ -LiAlO₂. According to Fig. 7, plane (01 $\bar{1}$) in the two differently oriented precipitates is also parallel, and so is plane (0 $\bar{1}$ 1) in the precipitates. Similar to the procedure described in [48], further examinations along multiple zone axes of the precipitates are needed to establish their complete orientation relationships with the matrix.

Previous report [7] also showed SAED evidence for LiAl₅O₈ to be further transformed to hexagonal α -Al₂O₃ under electron irradiation. However, the SAED data from this study does not show a distinct pattern for the corundum phase. One of the major differences between the two studies is the source of irradiation. At this time, it cannot be ruled out that Al₂O₃ is present in an amorphous or highly disordered state under the ion-beam irradiation conditions in this study. The amorphized surface layer with highly depleted Li (see section 4.2.1.) is possible to contain aluminum oxide. Not surprisingly, we also observed susceptibility of γ -LiAlO₂ crystal to 300 keV electron beam, as evidenced by the black vertical lines from electron beam scans [Fig. 6(b)]. In contrast, similar scans across the precipitates do not produce such lines, suggesting that LiAl₅O₈ is more resistant to irradiation-induced decomposition than γ -LiAlO₂.

Fig. 7. SAED pattern of cubic LiAl₅O₈ precipitates in γ -LiAlO₂ implanted to 10^{21} H⁺/m² at 773 K. [211] and [111] zone axes in the LiAl₅O₈ precipitates are parallel to γ -LiAlO₂ [100].

4.2. H and Li diffusion and release

4.2.1. Effects of implantation temperature

The implanted H in γ -LiAlO₂ at different temperatures was analyzed using ToF-SIMS at room temperature outside the RBS/C spots near the edge areas of the implantation. The absolute H concentration is subject to an error bar due to non-uniformity and uncertainty of charge integration. In addition, corrections for charging effects during SIMS varied with samples. The H profiles are normalized to the peak areas for a comparison of the peak shape. The normalization [49] follows

$$I_H^{norm}(i) = 100 I_H(i) / [w \sum I_H(j)], \quad (1)$$

where $I_H(i)$ is the H intensity at channel number i and w is the channel width (or depth step). This procedure does not alter the FWHM of the peak, but allows for the SIMS data measured under different conditions (dwelling time of sputtering beam, beam current, charging compensation, etc.) to be plotted in one figure for a direct comparison. H diffusion can be reflected by the change in the peak shape.

The peak-area-normalized depth profiles of the implanted H in the as-implanted samples at various temperatures are shown in Fig. 8(a). The shift of the H peak is small from 300 to 573 K although some peak broadening occurs. An apparent peak shift to a smaller depth, accompanied by peak narrowing at 673 K, is observed. Repeated measurements show that the data are reproducible. Further increase in the implantation temperature to 773 K leads to formation of a fine structure with double peaks, which might originate from the two distinct depth regions of fully amorphized material (0 – 200 nm) and highly concentrated precipitates (200 – 500 nm) observed in Fig. 5(a). In general, the change in the H profile shape suggests H diffusion (and likely release from the sample as well) during ion implantation at the elevated temperatures. The result is consistent with the bubble formation at the surface (Fig. 5) at 773 K.

Fig. 8(b) shows the normalized Li yields as a function of depth in the sample at different implantation temperatures. The Li profile is normalized to Al yield that is assumed to remain largely unchanged over the depth at all the applied temperatures up to 773 K. This assumption is supported by the data for 773 K in Fig. 3, where the RBS yields of Al in the near-surface region of the implanted and unimplanted

Fig. 8. ToF-SIMS depth profiles of (a) H and (b) Li in γ -LiAlO₂ single crystal irradiated 60° off normal with 80 keV H₂⁺ ions to 10²¹ H⁺/m² at various temperatures.

samples are statistically the same. Further calibration of the normalized yield was conducted based on the Li/Al yield ratio from the unimplanted γ -LiAlO₂ at the depths between 550 and 600 nm, where the material was not affected by the implantation. This procedure largely eliminates the factors affecting the SIMS yields from the experimental conditions and allows for a direct comparison of the relative Li concentrations at different implantation temperatures. The data in Fig. 8(b) suggests that Li concentration in γ -LiAlO₂ remains unchanged over the depth during implantation at 300 K to 10^{21} H⁺/m². For implantation at 573 K, diffusion and release of ~15 at.% Li relative to the initial concentration take place in the near-surface region (within ~200 nm). More Li loss is observed at higher irradiation temperatures. The Li depth profile shows a pit-shaped curve that is reproducible but not yet fully understood at this time. Within the depth of 300 nm, ~90 at.% Li atoms were released to vacuum ($\sim 10^{-5}$ Torr) from γ -LiAlO₂ during implantation to 10^{21} H⁺/m² at 773 K. In contrast, thermal annealing in the absence of ion implantation does not essentially lead to Li loss at 773 K, as shown in Fig. 8(b).

4.2.2. Effects of energetic He⁺ ion irradiation

Fig. 9 shows the area-normalized H profiles from expression (1) in γ -LiAlO₂ implanted to 10^{21} H⁺/m² at 300 K before and after 2 MeV channelled He⁺ ion irradiation to 6×10^{19} He⁺/m² at 300 K. The energy of 2 MeV He⁺ ions in the near-surface region (<500 nm) is dissipated predominantly through the processes of electronic excitation and ionization of the target atoms. Based on the SRIM database [37], the ratio of the deposited electronic to nuclear energy into LiAlO₂ from 2 MeV non-channelled He⁺ ions is on the orders of 10^3 . It is known that electronic energy deposition by ion irradiation can enhance atomic diffusion in solid materials [50]. From Fig. 9, the irradiation does not lead to a significant H redistribution in the γ -LiAlO₂. Possible factors contributing to the observed behavior may include a low rate of electronic energy deposition (~ 0.3 keV/nm for random incidence), small ion fluence (6×10^{19} He⁺/m²), and low irradiation temperature (300 K).

4.2.3. Thermal annealing

Isochronal annealing (4 h) at 573, 673 and 773 K in air was performed for γ -LiAlO₂ implanted to 10^{21} H⁺/m² at 300 K. The as-implanted sample was measured near the center of the implantation area by ToF-SIMS prior to annealing. After each annealing step, the measurement was repeated in a nearby region.

Fig. 9. ToF-SIMS depth profiles of H in γ -LiAlO₂ single crystal irradiated to 10^{21} H⁺/m² at 300 K before and after 2.0 MeV channelled He⁺ ion irradiation to 6×10^{19} He⁺/m² at 300 K.

Fig. 10. ToF-SIMS depth profiles of H in γ -LiAlO₂ single crystal irradiated to 10^{21} H⁺/m² at 300 K and isochronally annealed at 573, 673 and 773 K for 4 h each in air.

The four analytical SIMS spots were within an area of $2\text{ mm} \times 2\text{ mm}$ and presumably had the same ion fluence. The SIMS results are shown in Fig. 10 with the H yields normalized to the respective Al yields and calibrated using the Li/Al yield ratio from the as-implanted sample around the depth of 500 nm. This procedure, similar to that for Fig. 8(b), allows for a quantitative comparison of the relative H retention in the annealed samples. From Fig. 10, a significant out-diffusion of H is observed at the annealing temperature of 573 K. The intensity of the H profile becomes noticeably lower at 673 K. After annealing at 773 K, a sharp, reproducible H peak emerges around the depth of 250 nm, which is not yet well understood and needs further studies for clarification. Based on the total H contents (peak area) at 300 K, there are 24 at.%, 52 at.% and 76 at.% H atoms released from the sample after 4-h isochronal annealing at 573, 673 and 773 K, respectively. It should be noted that SIMS measures H atoms in the structure. H_2 gas bubbles in solids cannot be detected effectively by SIMS [51] because when bubbles rupture due to material sputtering, gas is released to vacuum immediately.

5. Conclusions

The results from this study indicate that the relative disorder on the Al sublattice in $\gamma\text{-LiAlO}_2$ single crystal irradiated with H_2^+ ions at 573 K saturates at 0.29 between 0.1 and 0.3 dpa and at 0.54 between 0.6 and 1.0 dpa. A higher dechanneling yield from $\gamma\text{-LiAlO}_2$ sequentially implanted to $10^{21}\text{ H}^+/\text{m}^2$ and $10^{21}\text{ He}^+/\text{m}^2$ at 573 K is observed, suggesting possible formation of gas-pressurized bubbles in the crystal structure. H diffusion and Li loss occur during implantation at elevated temperatures (573 – 773 K). Although there is no noticeable irradiation-enhanced diffusion of H in 300 K implanted $\gamma\text{-LiAlO}_2$ under 2 MeV channeled He^+ ion irradiation to $6 \times 10^{19}\text{ He}^+/\text{m}^2$ at 300 K, 4-h isochronal annealing of the sample shows significant H release of 24 at.%, 52 at.% and 76 at.% H at 573, 673 and 773 K, respectively. $\gamma\text{-LiAlO}_2$ is completely amorphized from surface to the depth of $\sim 200\text{ nm}$ with $\sim 90\text{ at.}\%$ Li release after implantation to $10^{21}\text{ H}^+/\text{m}^2$ at 773 K; in addition to the formation of gas bubbles at the surface within the amorphized layer, cubic-structure LiAl_5O_8 precipitates of sizes up to 200 nm or larger are observed at the rear jagged interface. The solid-state precipitates are surrounded by an amorphous layer in the $\gamma\text{-LiAlO}_2$ matrix and are present with two orientations [211] and [111] that are parallel to $\gamma\text{-LiAlO}_2$ [100].

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Table 1Experimental conditions for ion implantation and thermal annealing of γ -LiAlO₂.

Implantation Sequence	Ion	Energy (keV)	Fluence (10^{20} ions/m ²)	Temperature (K)	Tilt (°)
I	H ₂ ⁺	80	2,4,6,8,10,20,30	573	60
II	H ₂ ⁺	80	10	300,573,673,773	60
IIIa	H ₂ ⁺	80	10	573	60
IIIb	He ⁺	90	10	573	60
IVa	He ⁺	90	10	573	60
IVb	H ₂ ⁺	80	10	573	60

4-h isochronal annealing at 573, 673 and 773 K in air for γ -LiAlO₂ implanted with H₂⁺ ions to 10^{21} H⁺/m² at 300 K