Thermal stability of oxidized ultrathin Li films on TZM for plasma facing components

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1. Introduction

Utilization of solid and liquid lithium (Li) films has been proposed for the first wall and divertor regions in fusion devices. Conditioning of plasma facing components (PFCs) with solid Li coatings improved plasma performance and confinement time in experiments in TFTR [1], T-11M [2], FTU [3], CDX-U [4], LTX [5], EAST [6], DIII-D [7] and NSTX-U [8]. Although the reasons for this are currently not well understood, these improvements have been attributed to lowered H recycling [9,10], edge density changes [11], and suppressed edge localized modes (ELMs) [12]. Li is also attractive as a liquid metal PFC due to its low melting point and high chemical reactivity that allows it to efficiently getter hydrogen. However, this high chemical reactivity causes Li to react with background or residual gases (e.g. H₂O and CO) present in the vacuum chamber of these devices. Oxygen can also come from diffusion of impurities from the bulk and grain boundaries of substrates supporting the Li films. In either case, oxidation of Li films alters the surface composition and can form new compounds with very different chemical and physical behavior than metallic Li, as shown via offline characterization by surface science experiments [13–15] and the Materials Analysis Particle Probe (MAPP) [16]. In the case of hydrogen retention, metallic and oxidized Li films have shown comparable hydrogen retention capabilities, but the mechanisms by which hydrogen is chemically retained is different between the two systems [16–18]. In metallic Li, hydrogen is retained as LiH/LiDi [17,19] while in Li₂O, hydrogen is retained in part as LiOH/LiOD [17,20]. Further understanding retention of hydrogen, erosion, redeposition, and thermal stability of oxidized Li films is important for advancing Li PFC applications.

Studies of oxidation of bulk Li and Li films have also been motivated by applications in electrochemistry and catalysis. Previous laboratory experiments have focused on measuring the oxidation rate and identifying the intermediates and reaction products formed [21–26]. Hoenigman and Kiel found that exposure of poly-
crystalline Li films to 100 L O₂ produced an O 1 s peak at 530.6 eV binding energy (BE) in X-ray photoelectron spectroscopy (XPS) assigned to Li₂O formation [21]. Oxidation of the Li film proceeded more slowly with water and produced two O 1 s XPS peaks; one at 530.6 eV BE assigned to Li₂O accounted for 85% of the oxygen at the surface, and one at 533.5 eV BE assigned to lithium hydroxide (LiOH) accounted for the rest and arose from H₂O dissociation on the film. A later study using O₂ and H₂O as oxidants established that a monolayer of Li₂O was formed on the surface regardless of oxidant with low amounts of hydroxide at the surface from H₂O oxidation [27]. This oxide monolayer did not passivate the surface, and oxidation using O₂ continued up to a thickness of 1600 Å. Depositing Li films on a pre-oxidized Ni(110) substrate, denoted by the authors as a Ni(110)-O surface, was found to reduce the oxidized Ni substrate [28].

Herein, results are presented from surface science studies of the oxidation of Li films deposited on a titanium-zirconium-molybdenum (TZM) alloy, a high-Z (high atomic number) substrate of interest, and the thermal stability of the oxides formed in ultrahigh vacuum (UHV) vessels, TZM is of interest in part due to its improved mechanical strength at elevated temperatures compared to pure Mo [29], high resistance to creep [30], and proven corrosion resistance against liquid metals, which has led to its use as a substrate for Li in the limiter region for current fusion devices such as EAST [31] and FTU [32]. Our investigations utilized a multi-technique approach for surface characterization including XPS, temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and low-energy ion scattering (LEIS). These experiments extend the prior research by Skinner et al. [12] and provide information on the effects of post-annealing on the nature of oxidized lithium films and interactions that occur between the film and substrate that are relevant for PFCs subject to high temperatures.

2. Experimental Methods

Experiments were performed in an UHV system with a 4-axis, long-transfer manipulator and attached load lock chamber connected to the main surface analysis chamber. The main chamber base pressure was 4 × 10⁻¹⁰ Torr and rose to 1–2 × 10⁻⁷ Torr during experiments. Equipment included: 3-kV Kimball Physics (EFG-7F/4243) electron gun for AES; PHI (04–303) differentially pumped ion gun for LEIS and Ar⁺ ion sputtering; PHI (10–360) spherical capacitor analyzer (SCA) for AES, LEIS, and XPS; PHI (04–548) X-ray source for either Al Kα or Mg Kα radiation for XPS; and a U10 100C quadrupole mass spectrometer (QMS) for residual gas analysis and TPD.

The TZM alloy sample (Goodfellow, Huntingdon, England) had a stated bulk composition of Mo:Ti:Zr of 99:0.5:0.1 at.% (no other impurities or their amounts were specified). The TZM sample had dimensions of 1 cm x 1 cm and a thickness of 0.005 in. (0.125 mm) and was mounted by spotwelding two 0.015 in. (0.38 mm) Ta wires to the back of the sample that were attached to larger Ta rods connected to Cu rods using Cu-Be connectors. A DC power supply was used to resistively heat the sample to 1900 K for cleaning and for TPD. A W-5%Re/W-26% Re thermocouple was spotwelded to the TZM sample to monitor the temperature. The sample was cleaned by cycling the use of 1-kV Ar⁺ ion sputtering of the sample at 310 K to reduce O, C, and S contamination to minimum levels, heating at 1500 K in 5 × 10⁻⁷ Torr O₂ for 5–10 min. to remove carbon, and annealing the sample to 1900 K in vacuum to reduce surface oxygen. Before each experiment, the sample was reconditioned by heating to 1900 K for 5 s. AES of the cleaned TZM substrate indicated a surface composition of 83.1 at.% Mo, 1.8 at.% Ti, 15 at.% O and 13.7 at.% C, with no Zr detected, and was measured prior to each experiment.

Li films were deposited on the TZM substrate by physical evaporation from a commercially available alkali metal dispenser (AMD; SAES Inc.). Before experiments, the Li source was thoroughly outgassed at a temperature below that needed for evaporation. The amount of Li deposited on the surface was calibrated by using TPD measurements. Oxidation was carried out by backfilling the UHV chamber with O₂ (Ultra-high purity 99.99% O₂; Matheson) by using a variable leak valve attached to a stainless steel gas handling line connected to the O₂ lecture bottle. Exposures of 20 L O₂ were carried out using 1 × 10⁻⁷ Torr O₂ for 200 s.

LEIS measurements were done at a lab scattering angle of 104° with 1–2 keV He⁺ ions incident normal to the surface with a sample current of 10 nA and an SCA pass energy of 939 eV. All BEs for XPS were referenced to the Mo 3d₅/₂ peak at 227.7 eV BE [33]. A pass energy of 50 eV for the SCA was used for XPS, and this gave a full width half-maximum (FWHM) of 1.4 eV for the Mo 3d₅/₂ peak at 227.7 eV BE. XPS spectra herein were acquired using Mg Kα X-rays at 1253.6 eV. Fitting and decomposition of XPS peaks were done using the CasaXPS program and utilizing a mixed Gaussian-Lorentzian peak shape and a Shirley background subtraction for the baseline.

3. Results and Discussion

3.1. Post-oxidized Li films on TZM

The thermal stability of post-oxidized ultrathin (1–5 ML, monolayer) Li films on a TZM substrate was studied by using TPD, XPS, and LEIS. For these measurements, either 3.5 ML (0.7 nm) or 5 ML (1.0 nm) Li films were deposited, with the amount of Li calibrated by TPD. Further details on the method of Li film calibration can be found in our previous report [34]. Oxidation of the Li film was subsequently performed by exposing the film at 310 K to 20 L O₂, and these post-oxidized Li films are herein referred to as LiOₓ films.

3.1.1. TPD of LiOₓ films

A Li (7 amu) TPD trace from a LiOₓ film formed by oxidation of an initial 5 ML Li film is shown in Fig. 1a. No appreciable Li multilayer TPD peak was observed, which from prior experiments on clean Li films occurs near 800 K [34], and this indicates that the Li film was completely oxidized by the procedure utilized. The
LiO film was stable until 620 K, after which decomposition lead to three distinct Li desorption features, with peaks at 860, 990, and 1220 K. The last trace of Li from this LiO film was not fully desorbed from the TZM surface until 1400 K.

Fig. 1 shows three additional Li TPD curves: (b) from a post-oxidized 3.5 ML (0.7 nm) Li film, and from a similar oxidized film after pre-annealing for 20 s to (c) 880 K and (d)1070 K, temperatures just before desorption of the higher two Li TPD peaks. The peak at 860 K is more prominent in curve (b) compared to that in curve (a) and this could be associated with the lower coverage of the oxidized film and the larger influence by the TZM substrate. Additional TPD experiments (not shown) show that the peaks at 990 and 1220 K grow with increasing Li precovrage, while the 860 K peak saturates for thicker LiO films. It was discovered during oxidation of lower Li coverages that the feature at 990 K could be further resolved and is composed of two desorption peaks at 935 and 989 K. Both the 990 and 1220 K peaks shifted to lower temperatures as the Li coverage increased while using constant oxygen exposures. When the Li coverage was kept constant at 5 ML and the O₂ exposure was increased, the 990 K peak was found to dominate for small O₂ exposures, i.e. a Li-rich environment in which the Li film was partially oxidized and the Li multilayer peak was still present, and the 1220 K peak grew rapidly for large O₂ exposures, i.e. O-rich environments. To help assess if the peaks observed arise from distinct phases, we annealed the films to two different temperatures. An 880 K anneal removed the 860 K feature and retained the other two desorption states, while an 1070 K anneal removed all but the peak located at 1160–1220 K. Since these pre-annealing experiments did not significantly modify the maximum desorption temperatures for the different peaks observed, we conclude that Li desorbs from decomposition of the LiO film through at least three distinct phases at well-defined temperatures. No coincident desorption in the signals for Li and O or O₂ was observed in TPD over the temperature range of 300–1100 K. This indicates that the lithium oxide phases in these films do not have sufficient vapor pressure to be observed desorbing in TPD, but rather decompose during TPD to desorb Li and retain oxygen at the TZM surface up to a temperature of 1100 K. Such decomposition and subsequent desorption of an alkali metal after oxide formation has been observed for NaO films formed on Si(111) [35], although this is not always the case, e.g. coincident signals for K and O were observed in TPD after both were co-deposited on Pt(111) [36]. In our studies, a substantial amount of oxygen is lost from the surface at 1220 K, as was observed by XPS (see Section 3.1.2). Finally, TPD was used to determine the Li coverage change with temperature, and it was found for the oxidized 5 ML Li film that 0.5 ML Li (10% of the film) desorbed after heating to 880 K, and 3.5 ML Li (70% of the film) desorbed after heating to 1070 K. This analysis assumes that the peaks observed are due to Li desorption rather than Li signals from an ionization cracking fragment (and thus requiring a different Li QMS sensitivity than that for Li atoms) of some Li-containing desorbing species, e.g. LiO and other compounds discussed in detail later.

There are several potential explanations for the origins of the three Li desorption peaks in Fig. 1. One is that the peaks arise from decomposition of different lithium oxide compounds that co-exist either after oxidation at 310 K or are formed during heating of the films during TPD. This explanation is quite plausible since lithium is known to form multiple compounds with oxygen, i.e. Li₂O, Li₂O₂, α,β-Li₂O, Li₂O₂, and Li₂O₂ as reported for the Li-O phase diagram [37]. Decomposition of these compounds may occur and desorb Li at different temperatures in reaction rate-limited desorption peaks. In this case, subsequent desorption of Li during heating in TPD reduces the LiO stoichiometry of the film, and this could also lead to formation of new compounds that have different decomposition temperatures. One other factor is the unknown role of the TZM substrate in altering (either stabilizing or destabilizing) lithium compounds in the oxidized film due to intimate involvement of interfacial Li and O atoms/ions at the TZM substrate surface, which is primarily composed of Mo as we determined by ISS and AES.

Finally, we propose an additional explanation that one or more of the peaks could be due to desorption or decomposition of a lithium molybdenum oxide (Li₆MoO₄) compound. Prior reports observed that Li₂O reacted with Mo and TZM to form Li₃MoO₄, which decomposed upon heating to liberate Li₂MoO₄ in the vapor phase [38,39]. This reaction occurred measurably within the temperature range of 1073–1223 K in vacuum. In addition, evaporation of lithium molybdate (Li₂MoO₄) from the solid binary oxide and its presence in the vapor phase has been observed previously [40,41]. Reaction of alkali oxides with their metal substrates to form surface binary oxides has been observed several times, e.g. a ternary compound of cesium tungsten bronze was formed for O/Cs/W at 900 K [42], and for Li, K, and Na deposited on Ni(110)-O, binary oxides of LiNiO₂, KNiO₂, and Na₂NiO₂ were formed [28]. To assess the role of binary oxide decomposition and desorption in our Li TPD results, we performed additional studies involving oxidation of 5 ML Li films on a Mo(100) single crystal surface, as shown in Fig. 2. Multiple signals during TPD were monitored simultaneously corresponding to the parent ions and possible ionization cracking fragment ions that might arise from desorption of Li, pure lithium oxide phases (O, Li₂O, Li₂O₂, LiO, Li₂O₂, and Li₂O), pure molybdenum oxide phases (Mo, MoO, Mo₂, and Mo₃O), and the binary oxide phase Li₂MoO₄ (LiMo, Li₂Mo, LiO, LiMoO, Li₂Mo₂, Li₂MoO₂, Li₂Mo₂O, Li₂Mo₂O₂, LiO, and Li₂Mo₂O₃). The known fragmenta-

![Fig. 2. TPD signals of multiple masses after oxidation of 5 ML of Li on Mo(100). Signals followed in amu were: 7 (Li), 23 (LiO), 96 (Mo), 112 (MoO), 144 (MoO₂), 119 (LiMoO), 135 (LiMo₂O), 141(LiMo₃O), 126 (Li₂MoO), 142 (Li₂MoO₂), 109 (Li₂Mo), 131 (Li₂MoO₂), and 147 (Li₃MoO₂).](image-url)
tion pattern for Li$_2$MoO$_4$ is Li$^+$, Li$_2$MoO$_4$$^+$, MoO$_2$$^+$, MoO$_3$$^+$, Li$_2$O$^+$, and LiO$^+$ in a ratio of 100:10:2.5:2.3:2.0:0.5 [40]. We were not able to monitor signals above 150 amu due to a limitation in our QMS. Based on our results, and those highlighted by the curves shown in Fig. 2, the Li peak observed on TZM at 1159–1220 K has a small contribution from a cracking fragment due to desorption of Li$_2$MoO$_4$, which can be deduced to occur near 1196 K, with an onset at 1092 K, as indicated in Fig. 2. Other signals with peaks in TPD near 1196 K (some not shown) assigned to Mo, Li$_2$Mo, MoO, Mo$_2$, LiMoO$_4$, Li$_2$MoO$_4$, Li$_2$MoO, and Li$_2$MoO$_3$ cracking fractions were observed. Another peak at 1182 K was observed for signals corresponding to LiMoO and LiMoO$_2$. On Mo(100), only a signal at 21 amu (LiO) was observed in TPD when monitoring any of the Li$_x$O$_y$ masses as listed above. This LiO TPD peak, which occurs at 1176 K, was coincident in temperature and shape with the high temperature Li TPD peak from the oxidized film on Mo(100) (bottom curve, Fig. 2). This Li TPD curve shows a similar shape and desorption peak temperature as that from TZM (Fig. 1a), which leads to the conclusion that the same oxide phases were formed on these two substrates. In Fig. 2, relative intensities of the Li$^+/LiO^+$ signals is 300, which is higher than the value of 200 found by Yamagami et al. [40]. This suggests that another oxide phase (likely Li$_2$O) different from other oxide phases due to the desorbing Li$^+$ fragment [39]. This is reasonable since solid Li$_2$MoO$_4$ is known to decompose to gaseous Li$_2$MoO$_4$ and solid Li$_2$O. We propose that Li$_2$O forms from decomposition of the binary oxide phase and is not evolved into the gas phase, but further decomposes to desorb Li and LiO. We did not observe Li$_2$O desorption in TPD at the temperatures studied, although this was expected from a prior report [43].

Comparison of the areas of the TPD signals for Li$^+$/MoO$_2$$^+$:MoO$_3$$^+$:LiO$^+$ were determined to be 100:0.7:0.4:0.3, which shows lower molybdenum oxide fragment intensities compared to that found by Yamagami et al [40]. Furthermore, prior studies of the oxidation of single crystals of Mo(100) [44] and Mo(110) [45] resulted in Mo, MoO, Mo$_2$, and Mo$_3$ fragment peaks that had matching line shapes and desorption peaks at ≥1400 K, which is at a higher temperature than the 1206 K molybdenum oxide derived fragments observed in our results. Both of these observations indicate that these TPD signals in our studies arise due to decomposition and desorption of the binary oxide rather than simply formation of a pure molybdenum oxide phase. In other studies that formed bulk lithium molybdenum oxides, a Li$_2$Mo$_3$O$_4$ signal was observed at 1500 K [38], which is higher than in our results and is likely due to the difference in pressures studied. Another contribution to the difference in temperatures could be due to destabilization of the ultrathin binary oxide film by the TZM substrate.

3.1.2. XPS of annealed LiO$_x$ films

XPS was utilized to characterize the chemical nature of the oxidized 5 ML Li film and TZM substrate at 310 K and changes that occurred after heating. XPS spectra for the Mo 3d, Li 1s, and O 1s regions are shown in Fig. 3a. The Li 1s peak is partially overlapped by the Mo 4s peak of the substrate. In the bottom curve of Fig. 3a for the oxidized Li film at 310 K, the Li 1s peak is at 55.6 eV BE, which agrees with a prior report of 55.8 eV for oxidized Li prepared from vapor deposited films on tantalum foil [21]. The corresponding O 1s spectra show peaks at 529.5 and 532.1 eV BE, which we tentatively assign to lithium monoxide (LiO) and lithium peroxide/hydroxide (Li$_2$O$_2$/LiOH), respectively [46,47]. Clear assignment of the peak at 532.1 eV to a single species is challenging due to results showing that LiOH and Li$_2$O$_2$ have overlapping XPS peaks near that BE [48]. In studies of the interaction of Li with condensed oxygen, Qiu et al. assigned O 1s peaks from Li$_2$O at 353–530.5 eV, Li$_2$O$_2$ at 532.5–533 eV, and the superoxide (LiO$_2$) at 534.5 eV [46], while a peak at 533.5 eV has been assigned to OH species [21]. Residual gas analysis shows a small H$_2$O pressure in the chamber that could react with Li to form small amounts of LiOH. Under standard state conditions, formation of Li$_2$O$_2$ (ΔG = −136.5 kcal/mol) and Li$_2$O (ΔG = −134 kcal/mol) are both thermodynamically favorable [46]. The O 1s spectra in Fig. 3a do not show a significant peak at 534.5 eV, which rules out the presence of Li$_2$O. No additional XPS experiments were done to obtain information.
on the nature of the oxide layer at the surface and subsurface interfaces, though Li$_2$O is known to form over Li$_2$O$_2$ when these two oxides are present [49]. The Mo 3d spectra contain the spin-orbit split 3d$_{5/2}$ and 3d$_{3/2}$ components and can be fit well using only single peaks from metallic Mo(0). This indicates that Mo was not extensively oxidized, but these spectra do not probe sensitively the interfacial Mo atoms. This indicates that most of the oxygen forms an LiO$_x$ film rather than incorporating into the Mo to form Mo oxides.

Heating the sample causes the Li 1s peak to decrease in size significantly by 1070 K and to disappear by 1400 K, consistent with Li desorption observed in TPD. However, the O 1s peak intensity (peak area) is constant at temperatures up to 1070 K, confirming that the LiO$_x$ film on TZM primarily decomposes upon heating as opposed to evaporating or desorbing oxygen. Heating to 1400 K causes the O 1s intensity to drop to 46% of the original value, indicating that oxygen leaves the TZM surface at 1090–1400 K. TPD results indicate that this is due to LiO desorption and the decomposi-
tion of Li$_2$MoO$_3$ into volatile species that desorb and yield oxygen-containing mass species such as LiO$^+$, MoO$_{2+}$, Li$_2$MoO$_{2-}$, etc. as already discussed.

As seen in Fig. 3a, no significant changes occur in the Mo 3d spectrum for heating to 680 or 880 K. However, upon annealing to 1070 K, the Mo 3d spectrum changes and, as shown in Fig. 3b more clearly, can be decomposed into three components, with Mo 3d$_{5/2}$ peaks at 227.7, 229.5, and 232.9 eV BE, assigned to Mo(0), Mo(VI), and Mo(VI). The detection of Mo(VI) could arise from Li$_2$MoO$_3$ (as discussed above) or Mo$_2$O$_3$, and the larger Mo(VI) peaks could be due to other binary oxides or MoO$_2$. The oxidized Mo components comprise 15.8% of the Mo 3d intensity. At this temperature, a chemical reaction occurs between the LiO$_x$ film and the Mo substrate to oxidize the Mo interfacial layers to form either Mo oxides [50] or binary oxides of lithium and molybdenum, such as Li$_2$MoO$_5$ [38,51], that would give rise to a Mo(VI) signal. Several other binary oxide phases could be formed. The solid state quasi-binary phase diagram of lithium oxide-molybdenum (VI) oxides shows four intermediate phases of Li$_2$MoO$_3$, Li$_2$MoO$_4$, Li$_2$MoO$_{2+}$, and Li$_2$MoO$_{2-}$ [52], while the Li-O-Mo(VI) phase diagram is composed of Li$_2$MoO$_3$, Li$_2$MoO$_{2+}$, and Li$_2$MoO$_{2-}$ [53]. The Mo(VI) and Mo(VI) peaks decrease substantially after heating further to 1400 K, consistent with our TPD data indicating desorption of species such as MoO$_3$ or Li$_2$MoO$_3$ at 1070–1400 K. It seems clear that binary lithium molybdenum oxide compounds, and not only molybdenum oxide phases, exist in these films and this is supported by the XPS data. The TPD results in 3.1.1 show desorption of species containing both Li and Mo, and MoO$^+$, Mo$_2$O$^+$, and Mo$_3$O$_{2+}$ signals near 1200 K. Prior studies of the oxidation of a Mo(100) single crystal observed in TPD desorption of Mo$_2$O$_3$ and MoO$_2$ at 1400–1600 K, where MoO$_2$ monomers and dimers were desorbed from thick oxide films at 1400 K and from a monolayer at 1600 K [45]. Our XPS studies indicate that the lithium molybdate phase(s) are more volatile and also decompose at lower temperatures than these molybdenum oxides.

The Mo 3d signal intensity increases significantly (to 95.8% of the clean surface value) after heating to 1400 K due to desorption of most of the oxidized film, but even heating to 1800 K did not remove all oxygen. Annealing to 1800 K leaves a Li-free TZM substrate, with metallic Mo 3d peaks and a reduced O 1s peak at 530.1 eV BE. This O 1s intensity is the same as that measured from a freshly cleaned TZM substrate, which is present due to some oxygen in the subsurface region or located in the grain boundaries.

Finally, the Li 1s intensity increased by 20% from its original value upon heating from 310 to 680 K, and the conversion of Li$_2$O$_2$/LiOH to Li$_2$O in the O 1s spectra occurs over the same range. No desorption of molecular oxygen (O$_2^+$ signal) was observed in TPD. The mechanism by which the peroxide/hydroxide is reduced to Li$_2$O is unknown in this case. After heating to 880 K, the Li 1s intensity decreases to 80% of its original value, then to 43% of its original value after heating to 1070 K, and is eliminated after heating to 1400 K. The increase in the Li 1s peak must arise from a structural change in the film, but the decrease between 680 to 880 K and higher temperatures is due to desorption of Li from the TZM substrate. No change in the Li 1s peak position occurred during heating. We note that the Li 1s peak intensities are difficult to use to assign LiO stoichiometries since a large increase in the Li 1s intensity was observed previously [13] during oxidation of solid Li. This increase could arise from changes in Li density, mean free path for inelastic scattering, or intensities of satellite features (shake up and shake off processes) that affect the main line intensity.

Considering the changes in the O 1s spectra as the LiO$_x$ films are heated, Li$_2$O and Li$_2$O$_2$/LiOH were the only phases identified in the LiO$_x$ film since an O 1s peak corresponding to Li$_2$O was not observed. We note that conversion of Li$_2$O$_2$ to Li$_2$O species has been observed in bulk studies of Li$_2$O$_2$ [49] and similarly in other metal oxide systems such as MgO films on Mo(100) [54], and this could account for the changes in relative intensities in the spectra. However, the temperatures for these changes could be strongly affected by interactions with the substrate. The O 1s binding energy of Li$_2$O increases during annealing due to a decrease in crystallinity and/or changes in structural ordering of the film [55–57]. The O 1s peaks after heating to 1070 K or higher were not decomposed into components since they are likely to arise from multiple oxygen species and we have no clear structure within the peak to guide us. As stated above, there is a lithium molybdenum oxide species, which could be Li$_2$MoO$_3$ as well as other complex interfacial Li$_2$MoO$_x$$_2$ species. The O 1s decrease from heating from 1400–1800 K is not from desorption of O$_2$ since this was not observed in TPD. After annealing to 1400 K or above, smaller Mo(VI) and Mo(VI) peaks in the Mo 3d spectra shows that little oxygen is associated with molybdenum oxides, but rather the oxygen retained is bound to the grain boundaries, diffused into the subsurface region of the substrate, or is associated with TiO$_2$ or ZrO$_2$. Ti and Zr XPS peaks were not followed during the annealing experiments in order to limit XPS data collection times. As stated in Section 2, AES spectra determined that the clean surface contained only 1.8 at.% Ti and no detectable Zr. At temperatures above 900 K, LEIS (discussed in Section 3.1.3) detected Ti but no appreciable level of Zr in the top surface layer. As such, we attribute the O 1s signal from 1400–1800 K largely to O chemisorbed on Mo and associated with TiO$_2$, with little contribution from ZrO$_2$. We note that Ti and Zr bond with oxygen and carbon in the bulk and at grain boundaries, and these oxides and carbides play an important role in the bulk mechanical behavior of TZM [29,30,58].

The Li/O ratio as the LiO film is annealed to the temperatures shown in Fig. 3 was calculated using the peak area intensity of Li and O, normalized to atomic sensitivity factors [22]. The results show the film goes from a Li-rich stoichiometry to an O-rich stoichiometry due to desorption of the Li. The ratio at 310 K is 1.36 which is consistent with the O 1s spectra that indicate a 3:1 ratio of Li$_2$O to Li$_2$O$_2$/LiOH. The Li/O ratio initially rises as the film is annealed to 680 K due to interconversion of the peroxide/hydroxide to the oxide. After annealing to 880 K, the Li/O ratio drops to ~1. At this temperature, a fraction of the Li has desorbed leaving adsorbed oxygen. In the 1070 K case the Li/O ratio is 0.61 which is an environment that is O-rich indicative of a complex binary oxide in which Li and Mo exist in an oxidized state.

3.1.3. LEIS of LiO$_x$ films

Low energy ion scattering (LEIS) spectra of the clean TZM substrate and Li and LiO$_x$ films on TZM are shown in Fig. 4. The bottom curve shows Mo (1810 eV), Ti (1643 eV), and O (1090 eV) LEIS
peaks characteristic of the TZM surface. Zr may be present but the Zr peak, calculated to be at 1793 eV, is not resolvable from the Mo peak in these spectra. Depositing 5 ML of Li on the surface eliminates the Mo and Ti peaks, causes a characteristic change in the background signal, and causes the appearance of a Li signal at 390 eV. The deposited Li film was pure with only a very small O LEIS signal observed. The absence of any Mo or Ti substrate signals shows that Li wet the TZM surface and left no uncovered TZM regions. Subsequent oxidation of this Li film at 310 K by a 20 L O₂ exposure produced the curve labeled as “LiOₓ”, in which the Li signal was eliminated, and an O peak appeared. The LiOₓ film also completely wet the TZM surface, and furthermore no de-wetting of the LiOₓ film occurred prior to heating to 1000 K and evaporation of Li. Only a small Li signal after oxidation is expected from the crystal structure of solid Li₂O, which is an antifluorite structure with a low Miller-index surface composed of O atoms with Li atoms buried in the second layer [59]. Another explanation for changes in the Li signal could be matrix effects leading to changes in the neutralization probability (i.e. changes in the neutralization during scattering from a given atom as a function of its chemical environment) as observed during oxidation of Ce atoms [60]. The O LEIS intensity increases with annealing temperature, slowly increasing by a factor of 1.4 from 300–900 K, prior to significant Li desorption, and then rapidly increasing by a factor of 2.3 upon heating from 900 to 1500 K, with a small decrease after heating further to 1700 K. As before, these intensity changes could arise from morphological or composition changes in film structure accompanied by Li desorption (see Fig. 1). At 900–1000 K, a Ti LEIS peak appears from the TZM substrate, presumably due to oxygen-induced segregation of Ti and formation of TiO₂. There was no similar growth in the Zr LEIS peak in the range of 900–1000 K or at higher temperatures. The Mo substrate signal was observed at 1000 K after more of the LiOₓ film decomposed and Li desorbed. Further oxygen-induced segregation of Ti to the surface occurred after heating to 1700 K. The Ti/Mo ratio in LEIS was 0.23 for clean TZM, and this increased to 1.02 after the LiOₓ/TZM surface was heated to 1700 K. The decrease in the O LEIS signal at 1700 K is likely due to diffusion of O atoms into the bulk since no O₂ desorption was observed from TPD [61]. The presence of an O LEIS peak at 1800 K (not shown) indicates that O is still present at the surface after annealing to high temperatures and has not all diffused into the bulk. Oxygen atoms are likely trapped at the surface in grain boundaries or as TiO₂.

Based on our results so far, the following model is proposed for reactions in the post-oxidized Li film on a TZM substrate. Metallic Li deposited on TZM is oxidized at 310 K by 20 L of O₂ to form Li₂O by the reaction: 4Li (s) + O₂ (g) → 2Li₂O (s). Lithium peroxide can be formed via two reactions: 4Li (s) + 2O₂ (g) → 2Li₂O₂ (s), or 2LiO (s) + O₂ (g) → 2Li₂O₂ (s). LiOH can be formed by reaction of H₂O from the background gas with Li (2Li + H₂O → LiOH + LiH), Li₂O (Li₂O + H₂O → 2LiOH), or LiO₂ (2Li₂O₂ + 2H₂O → 4LiOH + O₂). As the surface temperature increases, in the range of 310 to 1700 K, all of these Li oxides, produced primarily of Li₂O, decompose at several distinct temperatures that we can observe by the accompanying Li desorption (see Fig. 1) and leave interfacial oxygen at the surface that reacts to form TiO₂ and lithium molybdenum oxides, including Li₄MoO₄, near 1700 K. Li₂MoO₄ decomposes into lithium molybdate (Li₂MoO₄) which desorbs near 1200 K and lithium oxide (Li₂O) [39] which further decomposes and desorbs Li and LiO.

3.2. Li adsorption on oxygen-precovered TZM (O/TZM)

In these experiments, TZM at 310 K was exposed to 20 L of O₂ prior to deposition of Li films, and the pre-oxidized TZM substrate is herein referred to as O/TZM. XPS results (provided below) show that this forms a chemisorbed oxygen layer and does not lead to extensive oxidation of the TZM. This is consistent with prior reports demonstrating that molecular oxygen dissociates on both Ti and Mo to form an overlayer of O adatoms after a 20 L O₂ exposure at ambient temperatures [44,62]. The Ti/Mo peak ratio in LEIS (not shown) of the TZM surface increased from 0.14 (for the “clean surface”) to 0.25 after oxygen exposure, which is associated with more Ti present at the TZM surface after oxidation. The coverage of O atoms in the chemisorbed oxygen layer at the TZM surface is likely near 1.1–1.5 the density of the Mo atoms in the surface layer of TZM, based on previous reports of the saturation coverage of chemisorbed oxygen on single crystal molybdenum surfaces [61,63].

3.2.1. TPD results

Pure Li films of varying thickness were deposited on the O/TZM surface. Li TPD curves for these films are shown in Fig. 5. The Li coverages reported in Fig. 5 were calculated based on the Li dose time, which is linear with Li coverage and was calibrated previously for the Li evaporator using Li TPD from a metallic Li film. Li coverages derived from Li dose time should be the same as those from the areas under the Li TPD curves, however we observed different values. This situation arises when the Li mass spectrometer signal is produced from desorption of Li compounds in addition to Li vapor. The ionization and cracking of these complex Li species produce a Li ion signal, but with different and unknown sensitivities. Therefore, the Li TPD curve area is no longer necessarily pro-

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**Fig. 4.** (a) LEIS spectra for monitoring the thermal stability of the LiOₓ films formed from a 20 L O₂ exposure on a 5 ML Li film on TZM.
portional to the Li coverage on the surface. Thus, we have provided hereon both the Li coverage ($\theta_{\text{Li}}$ in ML) obtained from the Li dose time and also values from the measured integrated Li TPD areas from O/TZM referenced to the 1 ML Li TPD area in parentheses.

The lowest Li coverage, $\theta_{\text{Li}}=0.25$ (0.08), led to the formation of a peak at 1196 K. The temperature of this peak is the same as the highest temperature peak observed in the Li desorption spectra of post oxidized lithium films, making it likely that this peak arises from the Li signal from desorption of a binary oxide phase (Li$_2$MoO$_4$). At this low coverage, the interfacial Li is in an O-rich environment that facilitates interactions with Ti and Mo atoms, apparently forming complex binary oxide phases during heating. With increasing amounts of Li deposited, a new Li TPD peak appeared at 1157 K, which is presumably also due to a Li signal from a second binary oxide decomposition product, one which has a higher vapor pressure. The interfacial oxide formed on the surface from 0.25–0.5 ML Li deposition is extremely stable and does not form any of the Li-decomposition products observed at lower temperatures ranges of 800–1000 K. After deposition of $\theta_{\text{Li}}=1.0$ (0.66), an additional peak appeared at 923 K. After deposition of $\theta_{\text{Li}}=2.0$ (1.01), another peak at 793 K appeared, and the 923 K peak decreased in size. Deposition of $\theta_{\text{Li}}=3.0$ (1.92) led to the formation of the metallic Li multilayer and three high temperature Li peaks at 812, 934, and 1157 K. The peak at 1157 K saturates with increasing thicknesses of Li films on O/TZM. A metallic Li multilayer is formed after large deposits of Li since there is insufficient oxygen available to oxidize all the deposited Li. Although the result shows that different lithium oxide phases form depending on the initial coverage of Li deposited on O/TZM and these have different vapor pressures and thermal stabilities, the temperatures that these compounds are formed is not revealed by the TPD measurements, and so one needs additional temperature-dependent spectroscopic information.

Fig. 6 directly compares Li TPD curves from clean TZM with those from O/TZM for the same Li film coverages. Using the Li desorption onset and peak temperatures from the pure Li and oxidized Li films, we obtain useful information on the modification of the thermal stability of Li films due to the presence of surface oxygen contamination of TZM substrates. The differences in desorption onsets become smaller as the Li films become thicker since eventually there is not enough oxygen to influence all of the Li in the film. For the 0.5 ML Li case, the desorption onset increases from 560 K on TZM to 920 K for O/TZM. The 1 ML Li film has a desorption onset of 490 K that is shifted to 722 K on O/TZM. The 2 ML Li film on TZM starts to desorb at 477 K while this is shifted to 572 K on O/TZM, and no change in the peaks was observed for the 4 ML Li film. Using the desorption peak temperature of the first peak above that of the Li multilayer, we observe that the Li film thermal stability is increased by 422 K when oxygen is on the surface for a 0.5 ML Li film, and this changed to 233 K for 1 ML Li. For the thicker films, surface oxygen contamination of the TZM substrate did not affect the thermal stability of the bulk of the Li film, and Li primarily desorbed in the unaltered metallic Li multilayer peak. However, the Li monolayer that ultimately remained upon heating this film desorbed at 141 K higher temperature from O/TZM for the initial 2 ML Li case, and little change is observed for the 4 ML case on O/TZM.

3.2.2. XPS results

XPS studies were done to examine chemical modifications that occur when Li is deposited on an-oxygen covered TZM surface at 310 K, and these results are shown in Fig. 7. The Mo 3d spectra shown in the left panel are not significantly changed after 20 L O$_2$ exposure and showed only metallic components indicating that Mo was not extensively oxidized. As shown in the O 1s spectra, the cleaned TZM sample retained some oxygen, assigned either to O chemisorbed on Mo or Ti or oxidized Ti on the surface or in grain boundaries. The O 1s peak increases in area and shifts 0.2 eV to lower BE from the higher coverage of chemisorbed oxygen at the surface after 20 L O$_2$ exposure. These observations are consistent with previous studies showing that very high (2000 L) O$_2$ exposures on Mo at very high temperatures of 900–1200 K were required to form oxides such as MoO$_x$, MoO$_2$, and MoO$_3$ [44].

XPS spectra following deposition of 0.5 and 5 ML Li on O/TZM at 310 K is shown in the top two sets of curves in Fig. 7. Li deposition caused no new peaks or peak shifts in the Mo 3d spectra. The Li 1s peak for both the 0.5 and 5 ML films has a BE indicative of an oxidized Li state. The O 1s peak exhibits a $+0.4$ eV positive shift in the BE when 0.5 ML of Li is deposited on the O/TZM. This shift arises from formation of a submonolayer of interfacial lithium oxide containing either or both Li-O-Mo or Li-O-Ti bonding. For the 5 ML Li film, the O 1s peak has the same binding energy as that of the 0.5 ML Li film, indicating also the presence of an interfacial oxide. The calculated Li/O ratio for the 5 ML film is 2.5, indicating a Li-rich environment, while that for the 0.5 ML film is 0.94, which is O-rich.

In separate experiments, 0.5, 1 (not shown), and 5 ML Li films deposited on O/TZM at 310 K were annealed to various temperatures and probed by XPS as displayed in Fig. 8. In Fig. 8a, following deposition of 0.5 ML Li on O/TZM at 310 K, annealing to 650 K and 850 K leads to a reduction in the O 1s peak binding energy by 0.2–0.4 eV possibly due to changes in either the interfacial oxide structure and bonding or surface morphology. TPD measurements in Fig. 6 show that no Li desorbs at these temperatures and so this shift cannot be attributed to Li loss. After a 1400 K anneal, Li is fully desorbed, and oxygen is left on the oxidized substrate. Fig. 8b shows that annealing the 5 ML Li on O/TZM sample to 500 K caused the O 1s peak to shift 0.2 eV higher BE. Annealing to 680 and 900 K causes substantial desorption of Li from the film and shifts of the O 1s peak to 0.7–0.9 eV lower BE. This annealing creates an interfacial oxide characterized by an O 1s peak similar to that for Li$_2$O. Further annealing to 1050 K causes the O 1s peak to shift by $+0.4$ eV, which is likely due to the formation of lithium molybdenum oxides on the surface. This is supported by the iden-
Fig. 6. Comparisons of Li TPD curves from Li films deposited on TZM and O/TZM surfaces. The labeled amounts of deposited Li in the figures are referenced to the deposition of 1 ML of Li on clean TZM. Information on the O/TZM surface is given in the text.

Fig. 7. Mo 3d, Li 1s, and O 1s XPS spectra from TZM and O/TZM surfaces, along with spectra after deposition of 0.5 and 5 ML Li films on an O/TZM surface at 310 K. The XPS spectrum for the 50–75 eV BE region for the 20 L O₂/TZM sample (not shown) was unchanged from that of clean TZM.
greater than 900 K, indicating that the binary oxides are formed within a temperature range of 900–1050 K. The results for Li films deposited on oxygen pre-covered TZM suggest the formation of an interfacial lithium oxide containing either or both Li–O–Mo or Li–O–Ti bonding at 310 K. Subsequent annealing causes decomposition and desorption of Li in TPD (T_p=812 and 934 K) followed by LiMoO_5 decomposition and desorption in TPD (T_p =1157 K) assigned in part to: LiMoO_5 (s)→ Li_2MoO_4(g) + Li_2O (s), where the Li_2O formed immediately decomposes to Li and LiO.

3.3. Implications for lithium-coated plasma facing components

The solid or liquid Li coatings that are used in fusion devices can be oxidized by reactions with residual gases (H_2O and CO) in the vacuum vessels or dissolved oxygen in the grain boundaries of the metal substrates. The post-oxidation experiments reported here in Section 3.1 are most closely related to the former case and experiments with Li films deposited on the oxygen-precovered TZM surfaces are relevant to the second case. The effects of oxygen on the thermal stability of Li films by post-oxidation and deposition on an O/TZM substrate are compared in Fig. 9. In the absence of much oxygen, as shown in the bottom Li TPD curve, multilayer metallic Li films on TZM are stable until 520 K where the Li in the multilayer begins to desorb in the multilayer peak at 606 K. The Li monolayer on TZM is much more tightly bound, and Li desorption is not complete until 1200 K where any oxygen impurities cause small lower temperature peaks. As shown in the middle curve, Li films subjected to extensive post-oxidation to form a Li_2O/Li_2O_2/LiOH mixed oxide film are more thermally stable than without oxygen, and Li does not begin to desorb until

Fig. 8. O 1s XPS spectra from TZM and O/TZM surfaces, along with spectra after deposition of (a) 0.5 ML and (b) 5 ML Li on an O/TZM surface and annealing of the Li films.

Fig. 9. Li TPD curves from 6.47 ML Li/TZM (bottom curve), 20 L O_2/5 ML Li/TZM (middle curve), and 3 ML Li/O/TZM (top curve).
over 700 K with peaks at temperatures of 860, 990, and 1220 K. The 860 K peak could come from particular interfacial compound structures/clusters and the 990 K peak could come from desorption and decomposition of lithium-deficient oxide phases, Li$_2$O$_{1-x}$, that are formed after Li desorption. Post-oxidation increases the onset of Li desorption by 200 K, and significant Li desorption and material loss does not occur until 250 K higher temperatures. Moreover, a large fraction of the Li coating remains on the surface until binary oxide decomposition leads to Li loss in a peak at 1220 K. The top TPD curve in Fig. 9 is for a Li film deposited on an oxygen-precovered O/TZM surface. In this case, there are four desorption peaks that are at 572, 812, 938, and 1155 K. The amount of oxygen available for oxidation of the Li film is very limited in this case (1.1–1.5 ML O) and is insufficient to oxidize the entire 3 ML Li film that was deposited, and so ~0.5 ML Li desorbs in a peak at 572 K. TPD peaks at 812 and 938 K for the 3 ML Li/O/TZM curve are believed to have the same origin as the 860 and 990 K peaks that are present in the 20 L O$_2$/5 ML Li/ TZM system. The 1155 K peak is formed at a lower coverage of Li and saturates with increasing Li thicknesses for Li$_x$/O/TZM indicating that it is an interfacial binary Li$_2$MoO$_4$ state whose formation is strongly dependent on the oxygen concentration at the interface. This peak overlaps with another state causing the 1220 K peak that was observed in post-oxidation experiments, which continues to grow with increasing Li thickness and oxygen exposure. This peak arises from formation of lithium molybdenum binary oxide(s) of the same high temperatures for increasing Li and oxygen amounts and decompose in TPD to desorb gas phase oxide species that produce signals at more than a half-dozen amu values as shown in Fig. 2.

A 3 ML Li film is about 6 Å (0.6 nm) and the coatings used in NSTX-U and LTX are much thicker (hundreds of nanometers to micron scales) than this. At sufficiently high temperatures, oxygen from the bulk or grain boundaries of molybdenum in a CPS system could diffuse to the surface and react with the Li films to form lithium oxides. This would lead to a situation where there is a liquid Li overlay with solid Li$_2$O layer or Li$_4$MoO$_9$ formed at the substrate interface due to reaction with interfacial oxygen. More extensive oxidation by post-oxidation via residual gasses leads to higher thermal stability of Li, but the increase in stability is accompanied by a much higher melting point of the Li$_x$O$_y$ compounds (e.g. Li$_2$O mp = 1711 K) than pure Li (mp = 453 K), which has important implications for flowing liquid Li systems.

One primary motivation for studying the thermal stability of these lithium oxide films is to provide a fundamental understanding of how deuterium retention will change due to chemical state and structural changes that occurs on Li$_x$O$_y$ films as a function of temperature. Although these results are for ultrathin Li films, if it is assumed that the thick Li coatings used in the divertor region of fusion devices have oxides with similar thermal stabilities, there are several implications for fusion devices. For a Li film oxidized by residual gasses at 310 K, energetic D$^+$ ions will interact with a film that may have a surface composed of a mixture of lithium oxide, peroxide, hydride compounds. While hydrogen retention in metallic Li and Li$_2$O is believed to be comparable, the hydrogen retention behavior of LiOH and Li$_2$O is not yet understood. Also, if high temperatures of >1000 K occur due to high heat flux, ELMs, or disruptions, one could expect that binary oxides, e.g. lithium molybdenum oxides, could be formed that could liberate Mo into the gas phase and radiatively cool the plasma.

4. Conclusion

Experiments were performed to improve our fundamental understanding of how lithium-oxide films will behave at elevated temperatures that may arise from high heat loads on PFCs during fusion experiments. The thermal behavior of ultrathin (~5 ML) Li$_2$O films formed by either post-oxidation of deposited Li films or by the deposition of Li films on an oxygen-precovered titanium-zirconium-molybdenum (TZM) alloy surface was studied by using TPD, XPS, and LEIS under UHV conditions. The 5 ML Li$_2$O films prepared by post-oxidation of Li were stable until temperatures of 620 K, after which they desorbed in three main peaks in TPD. Desorption of Li from the surface is attributed to the decomposition and desorption of lithium oxide, Li$_2$O (860 and 990 K) and then the decomposition of solid lithium molybdates in the Mo(V) and Mo(VI) state with subsequent evaporation of binary oxides, including Li$_2$MoO$_4$, and fragments of Li$_2$O (1220 K). One of these solid lithium molybdates could be Li$_4$MoO$_9$. The onset for Li desorption from a Li$_2$O film is 100 K higher than that from a metallic Li film, demonstrating the higher stability of the oxides. XPS showed the formation of a mixed oxide phase of lithium monoxide Li$_2$O and lithium peroxide/hydride Li$_2$O/LiOH upon oxidation of the Li film at 310 K. Li$_2$O/LiOH are thermally unstable and began to decompose to Li$_2$O when annealed to 680 K. XPS also showed that at 1070 K, Mo in the TZM substrate was oxidized to form Mo(V) and Mo(VI) species. Molybdenum oxides typically can only be formed at conditions of high temperature (> 1000 K) and high oxygen exposures (> 80 L) indicating that Li promotes molybdenum oxidation through a solid-state reaction. LEIS experiments of the oxidized Li films confirm the wetting of TZM by Li$_2$O films at room temperature. In addition, the deposition of sub-monolayers of Li on an oxygen-precovered TZM substrate was also investigated that may be relevant to dryout conditions of PFCs. Deposition of Li films at 0.5 ML on O/TZM at 310 K led to the formation of an interfacial lithium oxide species that decomposes and desorbs Li in a single broad peak at 1126 K in TPD that closely matched that of the post-oxidized films. Overall these results highlight the increased thermal stability of oxidized lithium over that of lithium metal and the importance of accounting for Mo impurity transport into the plasma via formation of volatile lithium molybdate compounds at high temperatures.

Declaration of Competing Interest

None.

CRediT authorship contribution statement

O. Fasoranti: Conceptualization, Methodology, Investigation, Validation, Formal analysis, Writing - original draft, Writing - review & editing. E.T. Ostrowski: Formal analysis, Writing - review & editing. B.E. Koel: Conceptualization, Writing - review & editing, Supervision, Funding acquisition.

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