



Effects of temperature and surface contamination on D retention in ultrathin Li films on TZM



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ABSTRACT

In this work, we investigate deuterium retention at the Mo–Li interface by studying thin Li films three monolayers thick on a TZM Mo alloy. Li films at temperatures between 315 and 460 K were exposed to a deuterium ion beam and D retention was measured using temperature programmed desorption. In the absence of oxygen, D is retained as LiD, and the relative amount of retained D decreases with increasing substrate temperature. In three-monolayer thick lithium oxide films, the amount of D retained was 2.5 times higher than the amount retained as LiD in the metallic Li film. However, oxygen reduces the thermal stability of D in the film, causing D₂O and D₂ to be released from the surface at temperatures 150–200 K below the LiD decomposition temperature. These results highlight the importance of maintaining a metallic Li layer for high D retention in Li films on TZM at elevated temperatures.

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1. Introduction

Lithium-conditioned plasma-facing components (PFCs) have reduced recycling and improved plasma performance in several magnetic fusion devices [1]. The details of this process are difficult to diagnose in the complex tokamak environment, and quantitative measurements of the influence of temperature and residual gases on deuterium retention in lithium-coated materials are needed. Since tokamaks typically do not operate under ultrahigh vacuum (UHV) conditions, surface reactions with residual gases may occur in the time interval between lithium conditioning and the next discharge. Previous work using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) to measure the oxidation of lithium films on TZM (an alloy composed of 99% Mo, 0.5% Ti and 0.08% Zr) has shown that the top 5 nm of a Li film will be completely oxidized after exposure to 20–40 L (1 L = 1 × 10⁻⁶ Torr-s) of water vapor [2]. Such exposure is common in the intershot interval in tokamaks, and it is therefore important to study how contaminant gases change the surface composition of lithiated PFCs and the effect this has on their hydrogen pumping performance.

Schmitt et al. [3] studied the pumping ability of Li coatings in the Lithium Tokamak eXperiment (LTX) by measuring the vessel

pressure immediately before and after the discharge. They observed a decrease in the pumping ability as the Li layer oxidized after several days in the vacuum chamber. In addition, they found that the pumping ability of hot Li films (at wall temperatures up to 573 K) declined more rapidly than cold Li films (at temperatures below the bulk melting point of 453 K), and they attribute this effect to oxygen segregation to the liquid surface. In retention studies by Sugai et al. [4], the authors found that the capacity for hydrogen uptake in Li during exposure to a DC glow discharge was independent of wall temperature below the Li melting point. Studies by Baldwin et al. [5] on PISCES-B report full uptake of deuterium ions in liquid lithium independent of temperature between 523 and 673 K. They conclude that deuterium is retained as LiD and that uptake continues until the sample is volumetrically converted to LiD, at which point the surface changes to a high recycling material. Subsequent work by Taylor et al. [6] suggests that Li getters oxygen to the surface of graphite substrates and that deuterium is retained in Li–O–D complexes.

We build upon this previous work by studying the deuterium retention at the thin-film limit (i.e., films up to three monolayers thick) in order to investigate the chemistry at the Mo–Li interface. In this paper, we will show results of deuterium retention in three monolayers of Li on TZM for temperatures ranging between 315 and 460 K in an effort to probe both solid and liquid films. The role of oxygen is also assessed by measuring D uptake in oxidized Li films. The samples were exposed to a deuterium ion beam from an electron cyclotron resonance (ECR) plasma, and retention was

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measured by monitoring the evolution of deuterium from the lithiated surface as the sample was heated.

2. Experimental setup

The experiments were performed in a stainless steel UHV vacuum chamber with a base pressure of 2×10^{-9} Torr pumped by a 170 l/s turbo molecular pump and 440 l/s ion pump. A polycrystalline TZM sample, 8 mm on a side and 0.5 mm thick, was mounted between two Ta posts by spotwelding to 0.015-inch diameter Ta wires. The sample was cleaned using a combination of 1-keV Ar⁺ ion sputtering and chemical cleaning (heating in a background pressure of O₂); however, oxygen contamination remained at the surface as measured by AES (less than 25 at.%), but was mostly likely associated with the grain boundaries. Lithium was deposited onto the TZM substrate by thermal evaporation from a SAES Getters alkali metal dispenser [7]. The surface coverage of Li was calibrated using temperature programmed desorption (TPD) carried out by a 10 K/s linear temperature ramp up to 1200 K. The amount of Li on the surface was determined by measuring the area under the Li desorption curve in TPD and comparing that to the area under the curve for Li desorption from one monolayer of Li. Information on Li desorption from TZM and a discussion of the assignment of the one-monolayer Li TPD curve can be found in Ref. [2]. TPD was conducted by resistively heating the sample and monitoring the desorbed species with a UTI 100C quadrupole mass spectrometer (QMS) with the ionizer in direct line-of-sight of the sample. Temperature control was implemented using a Eurotherm 3508 PID controller, and the temperature was monitored using a type C thermocouple spot-welded to the back of the sample.

Following Li deposition, the chamber was backfilled with D₂ (99.999%, Specialty Gases of America) gas to a partial pressure of 5×10^{-5} Torr via a variable leak valve. Deuterium ions were produced using a tectra GenII ECR plasma source [8] that contains a set of grids for ion extraction and acceleration. The plasma source was operated at a grid bias of 250 V and an extraction voltage of -500 V. The ion current on the sample was measured to be 1 μA with an applied positive bias of 50 V for suppression of secondary electron emission. This is equivalent to a deuterium ion flux of 2×10^{13} cm⁻² s⁻¹. Including the plasma potential, typically 10–20 V [8], the incident ion energy was estimated to be ~265 V. The sample was exposed to the plasma for 100 s, producing a fluence of 2×10^{15} D/cm² (assuming the majority ion species is D₂⁺). The process of Li deposition and ion bombardment occurred at constant substrate temperatures, which ranged between 315 and 460 K. The surface was subsequently oxidized by exposing the sample to O₂ (99.999%, Specialty Gases of America) gas at a partial pressure of 5×10^{-7} Torr for 40 s. Deuterium release was measured by monitoring the partial pressure of D₂ during a temperature ramp of 10 K/s. H₂, HD, H₂O, HDO, D₂O, and Li were also monitored.

3. Results and discussion

3.1. Formation of LiD Films on TZM

A three-monolayer Li film was deposited on TZM and then exposed to the deuterium ion beam. TPD was then performed while monitoring the Li ($m/q = 7$) and D₂ ($m/q = 4$) signals, and the results are shown in Fig. 1. The low temperature Li peak, at 584 K for this Li coverage, represents desorption of Li from a multilayer Li film, as determined by previous TPD studies of Li on TZM [2]. At 663 K for this experiment, Li and D₂ simultaneously desorb from the surface, indicating rate-limited evolution due to LiD decomposition at the surface to liberate both species. Engbaek

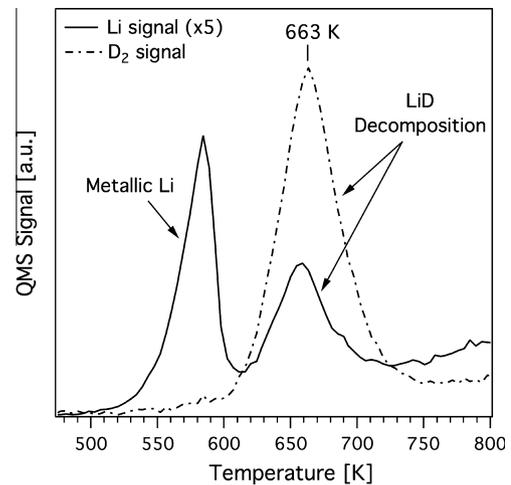


Fig. 1. Li and D₂ TPD traces from a 3 ML Li film on TZM after exposure to 265 V D₂⁺ ions with a fluence of 2×10^{15} D/cm² with the substrate at 315 K. Li (solid line, $m/q = 7$) and D₂ (dashed line, $m/q = 4$) signals were monitored. The peak at 584 K corresponds to desorption of Li from a Li multilayer [2]. Both Li and D₂ desorb at 663 K for these conditions, indicating the thermal decomposition of LiD at the surface [9].

et al. observed the same phenomenon at a similar temperature for LiH on Ni [9]. In their work, the LiH film was formed by depositing atomic hydrogen on a Ni(1 1 1) surface at 100 K, followed by Li deposition. As the temperature was increased during TPD, the atomic hydrogen diffused into the Li film to form LiH. A similar process is likely at work here, as the stopping range of 250 eV deuterium ions in Li is ~15 nm [10]. During the plasma exposure, deuterium ions are implanted in the TZM and then diffuse to the surface promptly or with heating during TPD.

The D₂ release peak shown in Fig. 1 was not observed when only one monolayer of Li was deposited on the surface. Previous work has shown that the Li monolayer begins to desorb from TZM above 700 K, and the desorption temperature continues to increase with decreasing Li coverage [2]. This indicates strong Li–Mo bonding that is stable in the presence of deuterium; however, LiD can form when multilayer Li is present and Li–Li bonding dominates. Note that the D₂ peak near 700 K in Fig. 1 is not due to the decomposition of LiOD, as previous work has shown that LiOH decomposes between 450 and 650 K to liberate Li₂O and H₂O [11]. No H₂O ($m/q = 18$), HDO ($m/q = 19$), or D₂O ($m/q = 20$) was evolved during these TPD experiments.

3.2. Temperature dependence of D retention in ultrathin Li films

The process of depositing three monolayers of Li followed by D₂⁺ ion exposure was conducted while the substrate was maintained at various constant temperatures. The relative amount of deuterium retained as LiD was determined by performing TPD and measuring the area of the D₂ desorption peak shown previously in Fig. 1. This experiment was repeated for eight different substrate temperatures ranging from 315 to 460 K. The results are plotted in Fig. 2 and show that the relative retention drops exponentially with temperature. Approximately 40% less deuterium is retained for the film at 350 K than at 315 K. However, at temperatures above 400 K, little change in the deuterium retention was observed. The amount of oxygen at the TZM surface prior to Li deposition was measured with AES and did not vary with temperature. Additionally, the substrate temperature was changed between experiments in a nonsequential manner in order to eliminate any experimental bias.

An explanation for the temperature dependence of D retention is that the Li film may not be uniform and clustering may occur at low temperatures, causing the formation of Li islands several

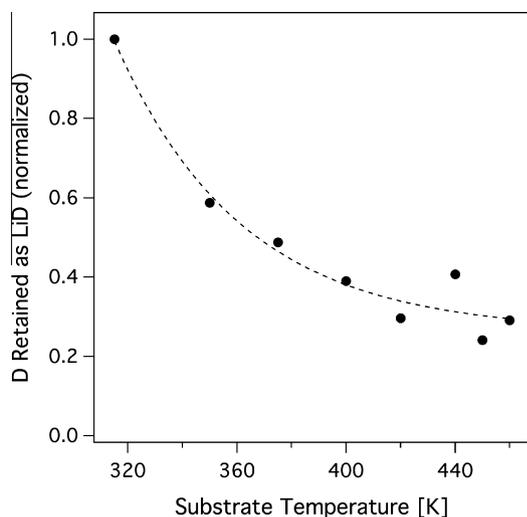


Fig. 2. The amount of deuterium retained as LiD in a 3 ML Li film was measured at different substrate temperatures using TPD. The decrease in relative D retention with increasing substrate temperature is described well by an exponential fit.

atomic layers thick. LiD may form in these islands where Li–Li bonding dominates, but not in areas where the film is thinner. Surface melting may also play a role, as the surface melting temperature can be several hundred degrees lower than the bulk [12]. The oxygen contamination at the TZM surface could inhibit the formation of LiD, and the effect of oxidation on D retention is addressed in the following section. To better understand the origin of this temperature dependence, further work will be conducted on single-crystal Mo substrates, where oxygen contamination can be eliminated and with thicker films where island formation is less likely to influence the results. Future work will also use spectroscopic techniques, that are sensitive to the first 1–3 layers, such as low energy ion scattering and high resolution electron energy loss spectroscopy, to determine if oxygen segregates to the surface and inhibits LiD formation at higher temperatures.

3.3. D retention in oxidized Li films

Three monolayers of Li were deposited on TZM at 400 K and were then fully oxidized by backfilling the chamber with O₂ gas to a partial pressure of 5×10^{-7} Torr for 40 s. This lithium oxide film was then exposed to the D₂⁺ ion beam. Fig. 3 shows D₂ TPD from this surface (curve a), and for comparison we also plot D₂ TPD from TZM with no Li after the same D₂⁺ exposure (curve b) and an oxidized Li film that was not exposed to the D₂⁺ ion beam (curve c). No D₂ gas is evolved in curve (c) of Fig. 3, as expected. In the absence of Li, a D₂ desorption peak at 520 K was observed, as shown in curve (b). This peak results from the diffusion and desorption of D that has been implanted in TZM via the ion beam. Four to five times more D₂ is retained when D₂⁺ ions were incident on Li oxide than in TZM without any Li, as was observed by comparing the D₂ release peak areas in curves (a) and (b). However, the desorption peak at 570 K in curve (a) is not the result of LiD decomposition.

An additional experiment was performed in which the Li film was first exposed to the D₂⁺ ion beam before being oxidized. Fig. 4 shows the D₂ TPD trace prior to oxidation (dashed curve) indicating formation of LiD, as evidenced by the release of D₂ gas near 700 K. After oxidation, however, LiD no longer exists at the surface and D₂ gas is released at 550 K as shown in the solid curve. The results of Figs. 3 and 4 show that the presence of oxygen inhibits LiD formation at the surface and reduces the thermal stability of

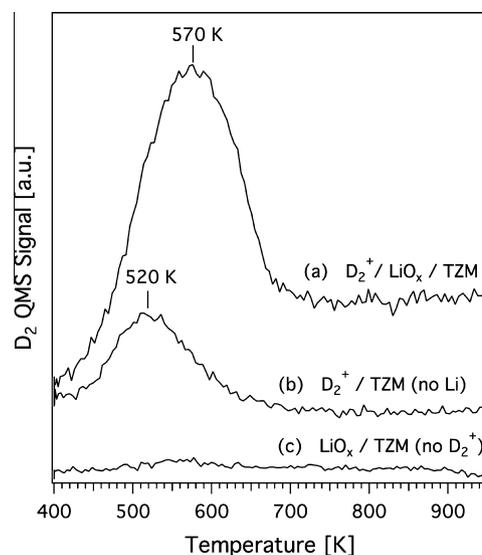


Fig. 3. D₂ TPD from: (a) a 3 ML lithium oxide film on TZM after exposure to 265 V D₂⁺ ions at a fluence of 2×10^{15} D/cm², (b) TZM surface with no Li after exposure to 265 V D₂⁺ ions at a fluence of 2×10^{15} D/cm², and (c) a 3 ML film of lithium oxide on TZM without exposure to D₂⁺ ions.

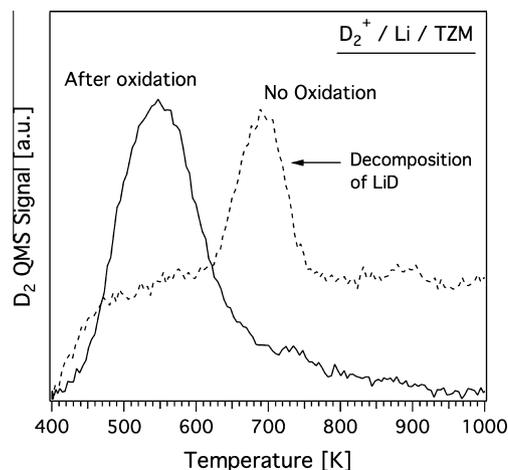


Fig. 4. D₂ TPD from a 3 ML Li film exposed to 265 V D₂⁺ ions at a fluence of 2×10^{15} D/cm² at 400 K before (dashed curve) and after (solid curve) oxidation. The presence of oxygen increases the amount of D retained at the surface but destabilizes the LiD film.

deuterium in the film. D₂⁺ exposure on the lithium oxide film also resulted in the evolution of D₂O at 500 K (not shown). Note that the amount of D retained in the three-monolayer thick lithium oxide film was 2.5 times higher than the amount of D retained as LiD in the metallic Li film, as determined by comparing the areas under the D₂ TPD curves in Fig. 4. However, the D retained in the lithium oxide film begins to desorb around 400 K, and most of the D in the film is released from the surface at temperatures below that of LiD decomposition. These results show that at temperatures below about 400 K, oxidation improves D retention in Li films on TZM, but highlights the importance of maintaining a metallic Li layer to retain D in the film at temperatures above 400 K.

As a final comment, it is useful to compare these results and conclusions to those by Taylor et al. [6] in similar studies with lithiated graphite substrates. Even though the intercalated Li in the carbon matrix they studied is different chemically from our ultra-thin Li films on TZM, our results and conclusions are consistent.

They concluded that in the presence of oxygen, for concentrations that were between 25% and 40%, O–D bonding was the primary mechanism for D retention in lithiated graphite [6]. We draw a similar conclusion from our lithium oxide film data, which showed the importance of O–D bonding in D retention in these films, consistent with the well-known chemistry resulting from the stronger O–D bond compared to the Li–D bond. In addition, our results also showed that in the absence of oxygen, D could be retained to higher temperatures in metallic Li films due to LiD formation.

4. Conclusions

In this work, we investigated deuterium retention at the Mo–Li interface by studying Li films up to three monolayers thick on TZM substrates. LiD was formed on TZM by exposing a multilayer Li film to a D_2^+ ion beam. The formation of LiD was evidenced by the simultaneous release of D_2 and Li near 700 K during temperature programmed desorption. The Li deposition and D_2^+ exposure process was repeated several times while holding the substrate temperature constant at different values ranging between 315 and 460 K. The Li films were observed to retain less D, which is associated with the formation of LiD, as the substrate temperature was increased. This effect may result from oxygen segregation to the surface or differences in the three-dimensional structure of the Li film at different temperatures. Further work will be conducted on thicker films and on substrates with less oxygen contamination.

The effect of oxidation on D retention and the thermal stability of D at the surface was studied by exposing the Li film to O_2 gas before and after D_2^+ exposure. D_2^+ exposure on the lithium oxide film resulted in the evolution of D_2O at 500 K and D_2 at 570 K. Oxidation

of the Li film after D_2^+ exposure resulted in D_2 release at 550 K. However, D_2^+ exposure on the metallic Li film resulted in no D_2O evolution and D_2 gas was evolved near 700 K, where LiD decomposition occurs. The amount of D retained in the three-monolayer thick lithium oxide film was 2.5 times higher than the amount of D retained as LiD in the metallic Li film. However, because of the reduced thermal stability, most of the D retained in the lithium oxide film was released from the surface before the temperature for LiD decomposition was reached. The results highlight the importance of maintaining a metallic Li layer and shows that oxygen can be detrimental to D retention in Li films on TZM at elevated temperatures.

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References

- [1] M. Ono et al., *Nucl. Fusion* 52 (2012) 037001.
- [2] C.H. Skinner et al., *J. Nucl. Mater.* 438 (2013) S647.
- [3] J.C. Schmitt et al., *J. Nucl. Mater.* 438 (2013) S1096.
- [4] H. Sugai, M. Ohori, H. Toyoda, *Vacuum* 47 (1996) 981.
- [5] M.J. Baldwin et al., *Nucl. Fusion* 42 (2002) 1318.
- [6] C.N. Taylor et al., *J. Appl. Phys.* 114 (2013) 223301.
- [7] SAES Getters USA, Inc. 1122 East Cheyenne Mountain Blvd., Colorado Springs, CO 80906, USA. <<http://www.saesgetters.com>>.
- [8] R. Anton et al., *Rev. Sci. Instrum.* 71 (2000) 1177.
- [9] J. Engbaek et al., *Surf. Sci.* 600 (2006) 1486.
- [10] J.F. Ziegler, J.M. Manoyan, *Instrum. Methods B35* (1989) 215.
- [11] L.N. Dinh et al., *J. Nucl. Mater.* 295 (2001) 193.
- [12] J.W.M. Frenken, J.F. van der Veen, *Phys. Rev. Lett.* 54 (1985) 134.