



Characteristics of lithium thin films under deuterium ion implantation

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Abstract

To clarify characteristics of thin Li films as a plasma facing material, effect of modification of chemical composition of μm -thick deposited Li films introduced during the sample preparation and implantation with 1-keV deuterons on deuterium retention and thermal desorption properties is studied. Accelerator analysis has been employed to measure the thickness, the retention of D, H, O and C in the Li film, while thermal desorption spectroscopy has been utilized to investigate the chemical composition. The Li films exposed to moist atmosphere and subjected to D implantation show almost perfect isotope exchange from LiOH to LiOD. Carbon deposition during ion implantation is found to form a layer mixed with Li. With increasing the deposited amount of C, D_2 desorption behavior approaches that of pure C. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

Low Z materials, such as graphite, Be and Li, are still attractive as a plasma facing material from a view point of minimized radiation loss and possible gettering effect for the oxygen impurities in the case of Li [1–3]. The experiment made in TFTR demonstrated increase in fusion output power and plasma confinement time when the inner graphite limiter was coated with Li [4–7]. However, the effects appear to be still machine-dependent [8], and fundamental research has been continued very actively [9–12]. Recent works have shown similar effects on machine performance. In Ref. [13] is described successful application of a capillary-pore-system-based Li limiter in the T11-M tokamak to enhance heat removal capability and improved plasma parameters. Successful operation of liquid Li limiter in CDX-U spherical torus has also been reported in Ref. [14].

In the present work, in order to examine applicability of Li to a plasma facing material, characteristics of Li thin films implanted with deuterium ions are investigated. Effect of composition change due to exposure to moist atmosphere and ion-beam-induced deposition of polymerized hydrocarbon layer on deuterium retention and thermal desorption (TD) is experimentally examined.

2. Experimental

Li thin film samples were prepared on Mo plates with 0.5-mm thickness by vacuum evaporation in a pressure below 2.0×10^{-5} Pa. The samples were implanted with 1 keV D^+ ions from an ECR ion source with a flux of $3 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ at room temperature in a vacuum below 2.0×10^{-6} Pa under off-beam condition. Taking both secondary electrons and ions into account, the error in the D^+ flux is no more than 50%.

Samples after Li evaporation were transported from the Li evaporation chamber to another chamber by a glovebag filled with Ar unless otherwise specified.

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The Li thin films after the ion implantation were subjected to TD measurements in an electric furnace equipped with a programmable temperature controller and made of a quartz tube maintained at a pressure below 1.0×10^{-6} Pa. The highest temperature attainable was 1000 °C and the temperature was measured with a Pt–Rh thermocouple. All samples in this work were heated at a constant heating rate of 5 °C/min. Particles released from the sample during TD were measured with a quadrupole mass spectrometer.

The samples were also analyzed with Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD) analysis. 3-MeV proton beams and a solid state detector (SSD) located at 160° with respect to the direction of probe beam incidence were used for RBS, while for ERD analysis 5-MeV C^{3+} and an SSD located at 30° were used.

3. Results and discussion

3.1. Implantation into ‘pure’ lithium

Li thin film samples were implanted with deuterium ions with energy of 1 keV, incident flux of 3×10^{14} $cm^{-2} s^{-1}$ and fluence of 5×10^{18} cm^{-2} , and subjected to RBS and ERD analyses. The depth distributions of Li, O and C atoms deduced from the RBS and of H and D from ERD spectra are shown in Fig. 1. Thickness of Li sample was 4.3 μm . The areal densities of D and impurities, O, H and C are 4.3×10^{17} , 5.1×10^{17} , 1.0×10^{17} and 3.8×10^{17} cm^{-2} , respectively, from the surface to the depth of 1500 nm for D.

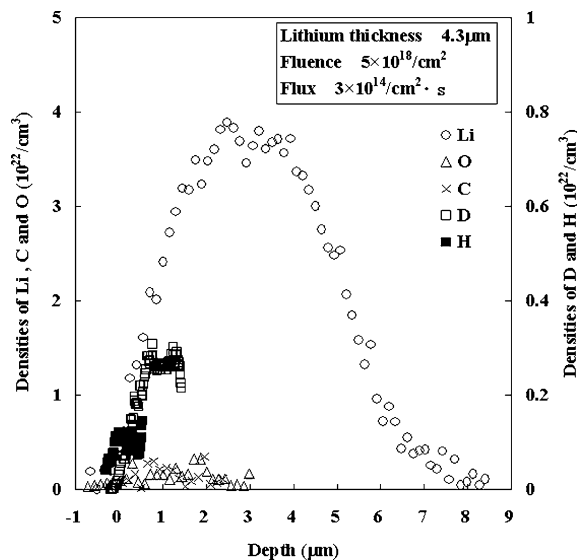


Fig. 1. Depth distributions of Li, D, H, O and C in the pure Li sample implanted with 1-keV deuterons.

We notice rather low retention probability of the sample for D, i.e., rather high reflection/reemission coefficient of D for the sample. The density ratio of H to O, $n_H/n_O = 0.2$, suggests that the Li film has absorbed a little amount of H_2O to form LiOH. C atoms appear to be introduced by the ion-beam-induced polymerization process described later in Section 3.3.

The samples were then subjected to TD measurements; they were heated up to 900 °C from room temperature in a vacuum below 1.0×10^{-6} Pa. The TD spectrum of D_2 is shown in Fig. 2, where the temporal variation of the partial pressure of D_2 gas is expressed as a temperature dependence. The D_2 desorption curve has a single peak at 560 °C with a relatively narrow FWHM. No appreciable amount of emission of D_2O nor HDO was observed.

Commercially available standard samples of LiH and LiOH show the TD spectra shown in Fig. 3(a) for H_2 and (b) for H_2O . The H_2 release from the LiH sample having a melting point of 680 °C shows two peaks at 350 and 650 °C. The latter is a result of the reaction, $LiH + Q_1 (= 0.939 \text{ eV}) \rightarrow Li + (1/2)H_2$. On the other hand, the LiOH sample releases very little amount of H_2 , while H_2O is released at 440 °C just below the melting point of 450 °C as a result of the endothermic reaction, $LiOH + Q_2 (= 0.452 \text{ eV}) \rightarrow (1/2)Li_2O + (1/2)H_2O$.

Similarity of Fig. 2 to Fig. 3(a) suggests that the Li film irradiated with D ions incorporates D atoms in the form of LiD. We notice, however, the peak temperature is slightly shifted to a lower temperature. A possible reason for this shift is an isotope effect, or coexistence of a small amount of LiOH which could lower the binding energy of D in the Li/LiOD lattice.

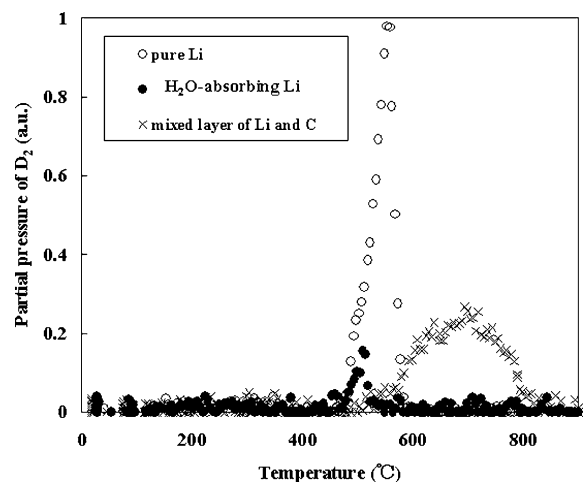


Fig. 2. TD spectra of D_2 for 1-keV deuteron implanted samples; the pure Li (open circles), the H_2O -absorbing Li (closed circles) and the mixed layer of Li and C (crosses).

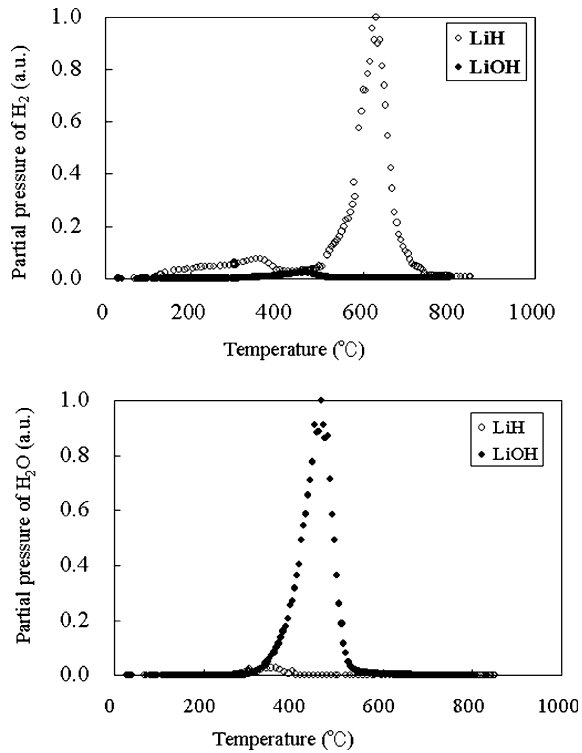


Fig. 3. TD spectra of H₂ (a) and H₂O (b) for standard samples of LiH (open circles) and LiOH (closed circles).

3.2. H₂O absorption of lithium thin film

Effect of H₂O absorption on the D retention and TD characteristics of Li films has been examined by controlled exposure of the film to atmosphere before ion implantation. The samples were implanted with essentially the same conditions as those in the preceding section. Fig. 4 shows the density distributions in a 4.2- μm -thick Li film. The areal densities of 1.3×10^{17} , 1.8×10^{17} and $2.5 \times 10^{18} \text{ cm}^{-2}$ are deduced from the spectra of D, H and O, respectively. Ratio of the areal density of O to that of Li is 0.1, indicating transformation of about 10% of Li to LiOH.

Shown in Fig. 2 is the TD spectrum of D₂ for this sample, which has a single peak with reduced amplitude at a somewhat lower temperature of 510 °C than for the pure Li. The origin of the D₂ should be the reaction $\text{LiD} + \text{Q}'_1 \rightarrow \text{Li} + (1/2)\text{D}_2$. The sample also shows a desorption spectrum of HDO with a single peak at 300 °C, which may originate either in the reaction $\text{LiOH} + \text{LiOD} + 2\text{Q}'_2 \rightarrow \text{Li}_2\text{O} + \text{HDO}$ or in the reaction $\text{LiOH} + \text{LiD} + \text{Q}_3 \rightarrow 2\text{Li} + \text{HDO}$.

The integrated amounts of D₂, HDO and D₂O released from several samples are plotted in Fig. 5 as a function of degree of transformation to LiOH expressed as atomic density ratio of O to Li in the depth range of O

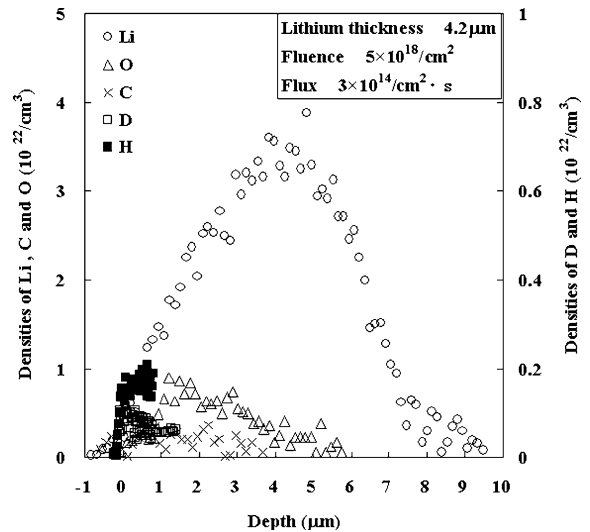


Fig. 4. Depth distributions of Li, D, H, O and C in the H₂O-absorbing Li sample implanted with 1-keV deuterons.

existence. Naturally, the density of LiD decreases with increasing LiOH density. It should be noted that D₂O is observed for the samples with high density of LiOH. Appearance of D₂O molecules implies that isotope exchange has occurred to form LiOD in the LiOH phase under implantation of D⁺ ions, since the D₂O molecules can be synthesized only through the reaction of two LiOD; $2\text{LiOD} + 2\text{Q}'_2 \rightarrow \text{Li}_2\text{O} + \text{D}_2\text{O}$.

The isotope exchange has been more typically observed in the case of the D⁺ implantation of the sample with a 0.8- μm -thick Li layer with pre-exposure to at-

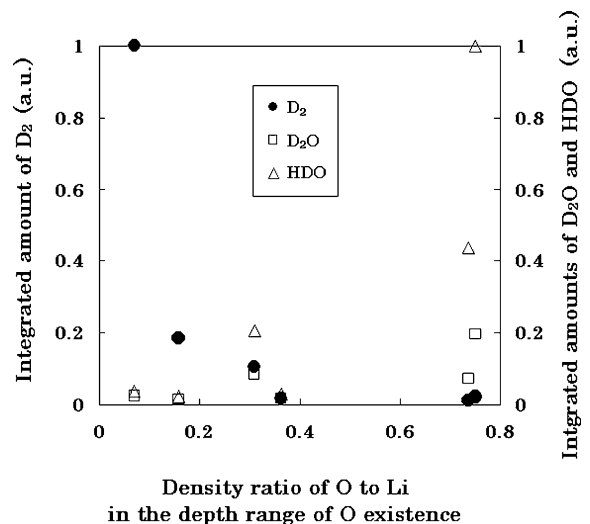


Fig. 5. Dependence of integrated amounts of D₂, D₂O and HDO in the TD spectra on atomic density ratio of O to Li in the depth range of O existence.

mosphere. The areal densities of D, H and O were 3.6×10^{17} , 2.5×10^{17} and $2.1 \times 10^{18} \text{ cm}^{-2}$, respectively, and the atomic density ratio of O to Li was 0.6. In the TD measurements for this sample, no emission of D_2 was observed, while single peaks of D_2O and HDO were observed at 360 and 350 °C, respectively. This means that the LiD phase is remaining with hardly appreciable density in this sample. The atomic density of H on the implanted area decreased in comparison with that on a non-implanted area in this sample by almost the same amount as that of the retained deuterium. It should be noted, however, that the temperatures of maximum release of D_2O and DHO in the TD measurement are somewhat lowered in comparison with that of H_2O release in the standard sample shown in Fig. 3(b).

3.3. Lithium thin film with carbon deposition

When a sample is bombarded by an ion beam, a deposited layer of hydrocarbon is observed to grow on the target sample as a result of radiation-induced polymerization of residual hydrocarbon impurities coming from the vacuum system and residing on the surface [15]. In the present work on the Li film as a plasma facing material, this phenomenon is utilized for introduction of C atoms onto the sample. This could be an eccentric simulation of co-deposition of wall material atoms and fuel particles, which would affect the retention properties of a plasma facing material and is one of the important problems to be investigated.

Deuteron implantation into the 4.8- μm -thick Li sample was performed under a condition favorable for the ion-beam-induced hydrocarbon deposition; a worse vacuum of $2.0 \times 10^{-5} \text{ Pa}$ and a lower flux of $2 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$. The RBS measurement of the sample shows that a mixed layer of Li and C having a density ratio of 0.4 is formed with areal densities of D, H, O and C being 7.7×10^{17} , 1.0×10^{17} , 1.5×10^{18} and $2.4 \times 10^{18} \text{ cm}^{-2}$, respectively. The TD spectrum of D_2 has a single peak at 510 °C, which indicates that substantial amount of Li is yet retained in the form of LiD.

In a more extreme case of a 0.1- μm -thick Li sample implanted with a deuteron flux of $5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, we cannot identify the Li atoms in the RBS spectrum, while the areal densities of D, H and C are 8.5×10^{17} , 4.2×10^{16} and $1.9 \times 10^{18} \text{ cm}^{-2}$, respectively. The TD spectrum of D_2 shows a single broad peak extending from 500 to 820 °C and centered at 700 °C as shown in Fig. 2. As the carbon deposition proceeds, the D_2 desorption peak shifts to the higher temperature with a broadened FWHM, and approaches to that of graphite implanted with deuterons [16]. The above results might imply that in a fusion device with Li coating and C as a

plasma facing material, re-deposition of C atoms could change the D retention properties of the Li layer to increase the TD temperature.

Study on the mechanism responsible for the peak shift in terms of molecular orbital theory is in preparation. Graphite shows a unique property known as ‘intercalation’; alkaline metal atoms are incorporated between the layered structure of graphite [17]. It is of interest to study how this mechanism is related to the present results.

4. Conclusion

Deuterium retention properties of Li films have been studied with use of 1-keV deuteron beams taking account of chemical deformation possibly encountered in fusion devices; absorption of H_2O from surrounding atmosphere and re-deposition of sputtered C atoms used as wall components. The results obtained are as follows. Incident D ions are incorporated in Li as LiD, while LiOH formed by exposure to moist atmosphere retains D in the form of LiOD, as a result of isotope exchange, which releases D atoms in the form of D_2O and/or HDO at an elevated temperature lower than that for D_2 release from LiD. Carbon atoms introduced during ion beam implantation forms a mixed layer of Li and C, which has both of Li and graphite properties as far as D retention is concerned.

References

- [1] H. Sugai, M. Ohori, H. Toyoda, *Vacuum* 47 (1996) 981.
- [2] H. Sugai et al., *J. Nucl. Mater.* 220–222 (1995) 254.
- [3] T. Hino et al., *J. Nucl. Mater.* 258–263 (1998) 612.
- [4] J.A. Snipes et al., *J. Nucl. Mater.* 196–198 (1992) 686.
- [5] D.K. Mansfield et al., *Phys. Plasmas* 3 (1996) 1892.
- [6] C.H. Skinner et al., *J. Nucl. Mater.* 241–243 (1997) 214.
- [7] D.N. Ruzic et al., *J. Nucl. Mater.* 266–269 (1999) 1303.
- [8] J.T. Hogan, C.E. Bush, C.H. Skinner, *Nucl. Fusion* 37 (1997) 705.
- [9] J.N. Books et al., *J. Nucl. Mater.* 290–293 (2001) 185.
- [10] J.P. Allain, D.N. Ruzic, *Nucl. Fusion* 42 (2002) 202.
- [11] R.P. Doerner et al., *J. Nucl. Mater.* 290–293 (2001) 166.
- [12] A. Hassanein, *J. Nucl. Mater.* 302 (2002) 41.
- [13] V.A. Evtikhin et al., *Fusion Eng. Des.* 49&50 (2000) 195.
- [14] G.Y. Antar et al., *Fusion Eng. Des.* 60 (2002) 157.
- [15] Moeller et al., *Nucl. Instrum. and Meth.* 182&183 (1981) 297.
- [16] H. Atsumi, S. Tokura, M. Miyake, *J. Nucl. Mater.* 155–157 (1988) 241.
- [17] S. Kato et al., *J. Nucl. Mater.* 266–269 (1999) 406.