

## DEUTERIUM TREATMENT EFFECTS ON LITHIUM AND TIN-LITHIUM SPUTTERING IN SOLID AND LIQUID PHASE

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The absolute sputtering yields of  $D^+$ ,  $He^+$  and  $Li^+$  on solid, liquid lithium and liquid tin-lithium have been successfully measured and modeled at low energies in the Ion-surface InterAction Experiment (IIAX). IIAX is used in this work to determine the dependence of Li erosion on the use of hydrogen isotopes to treat liquid metal surfaces of both liquid lithium and liquid tin-lithium. Earlier data from IIAX demonstrates that for  $He^+$  bombardment of solid phase lithium, the physical sputtering yield is reduced by deuterium treatment of the surface. In this work data for  $D^+$  bombardment of solid phase lithium is presented also shows similar sputtering reductions. In the case of tin-lithium both in the solid and liquid phase, deuterium treatment does not affect the absolute sputtering yield of lithium. The secondary sputtered ion fraction of lithium atoms has also been measured in IIAX and the effect of deuterium coverage is discussed. In IIAX, a Colutron ion source is used to create and accelerate  $He^+$  or  $D^+$  onto a 100 mm<sup>2</sup> metal target, with an influx of the order of  $10^{14}$  ions/cm<sup>2</sup>/sec. The metal targets are heated past their melting point to the desired temperature, where the surface oxide layer is plasma cleaned by a hollow cathode source with an influx in the order of  $10^{17}$  ions/cm<sup>2</sup>/sec and immediately irradiated with  $D^+$  or  $He^+$  ion beams. The evaporated flux at the desired temperature is measured before and after beam irradiation. Modeling of the absolute sputtering yield is accomplished by VFTRIM3D, a variant of the TRIM-SP code.

### 1. Introduction

The use of lithium as a first wall or divertor plasma-facing component (PFC) has been the focus of recent studies on advanced limiter/divertor systems [1]. Lithium in both solid and liquid phase has been examined and its erosion measured in the Ion-surface Interaction Experiment [2, 3]. Lithium alloys have also been considered. For example much work was done in the 1980's on the use of solid Cu/Li alloys [4-6]. Recently the lithium sputtering yield from liquid-phase tin-lithium has been measured [7]. These studies and measurements have demonstrated that lithium and its alloys may be good alternate PFC's for future advanced fusion devices. Modeling and measurements of solid and liquid lithium and its alloys result in less-than-unity physical sputtering yields

[2, 3] for temperatures less than 400 °C, which prevent runaway events. Not only is lithium advantageous due to its low  $Z$  and relatively good thermophysical properties, but also due to its ability to absorb impinging species. The ability of lithium to strongly absorb impinging D-T ions may lead to a high temperature/ low density or “low recycling” regime [8].

If lithium is used in its liquid state, it allows continuous recovery of damaged surfaces exposed to the large heat fluxes in the reactor wall and divertor regions. Results of lithium physical sputtering in the solid state [2] show lower yields than previously predicted [9]. This was due to preferential sputtering of implanted deuterium atoms. The present study attempts to determine the effect of implanted hydrogen isotopes in both solid and liquid-phase lithium and its alloys on the physical sputtering yield of lithium at low energies and glancing incidence.

## 2. Experiment

The Ion-surface InterAction Experiment (IIAX) is designed to measure the absolute, angular resolved and self-sputtering yields of many particle/target combinations (see Figure 1) [2]. A Colutron ion source is used to create and accelerate gaseous or metal ions onto a 0.018-cm<sup>2</sup> liquid metal target with an influx in the order of 10<sup>14</sup> ions/cm<sup>2</sup>/sec. Gaseous ions are obtained by means of electron-impact ionization while the lithium metal ions are obtained by thermionic emission from a LiCl powder. The bombarding ions are mass-selected through an  $E \times B$  filter and decelerated near the target by a five-element cylindrical electrostatic lens system. Complete details of the system can be found in earlier papers [2, 3, 7]. The target can be rotated in order to provide variation in the angle of incidence. 45-degree incidence was used based on the average angle of incidence a gyrating particle makes where the magnetic field lines cross the divertor plates at oblique incident angles.

A plasma cup is used to provide plasma cleaning of the target leading to the removal of any oxides or other impurities from the surface. This method also allows for the saturation of deuterium within the top surface of lithium and its alloys in the solid and liquid phase, simulating plasma-facing wall conditions within a fusion reactor. Saturation levels give a one-to-one ratio for implanted deuterium ions in solid and liquid lithium. The dose levels reached with plasma cup are of the order of 10<sup>16</sup> to 10<sup>18</sup> ions. A dual quartz crystal oscillator unit is rotated in front of the target to collect the sputtered flux, measuring the absolute sputtering yield. The QCO unit is mounted on a manipulator and thus its spatial and angular position with respect to the target is known. More details can be found in earlier papers as mentioned above.

## 3. Data Analysis

Analysis of the absolute sputtering yield of lithium is done by correlating the frequency variation in the crystal signal with the time period of ion beam dose. The calculation of the absolute sputtering yield is then possible after accounting for sputtering of QCM deposited material by highly incident energetic reflected particles, the sticking

coefficient of sputtered atoms onto the QCM crystal and the ion fraction of sputtered atoms. A mass balance is then used to set up the analytical expression for the absolute sputtering yield. The mass deposited on the crystal, which corresponds to the mass loss from the lithium sample,  $M_d$  due to both evaporation and physical sputtering is shown to be:

$$M_d = D f_i S^{QCM} Y \Omega m_{Li_2O} \quad (1)$$

$D$  is the total ion dose,  $S^{QCM}$  is the sticking coefficient defined as  $1 - R_j^{QCM}$  which corresponds to the reflection coefficient for sputtered species  $j$  off the QCM crystal surface and are calculated by VFTRIM-3D,  $Y$  is the absolute sputtering yield,  $\Omega$  is the fraction of the normalized distribution of sputtered particles collected by the QCM crystal,  $f_i$  is a factor accounting for the ion fraction of sputtered species ranging from 1.5 to 1.8 and  $m_{Li_2O}$ , the mass of lithium oxide deposited on the QCM deposition crystal. The mass deposited on the QCM crystal as measured by the Leybold Inficon XTC/2 monitor is defined as:

$$M_{QCM} = \frac{\Delta f}{f} M_{crystal} \quad (2)$$

$\Delta f$  is the frequency change measured from the raw frequency difference between the deposition and reference crystal data.  $M_{crystal}$  is the mass of the crystal given by the manufacturer, and  $f$  is the initial frequency of the QCM crystal. The  $M_{QCM}$  term incorporates the mass loss due to sputtering from reflected deuterium or helium neutrals from the lithium surface. The reflection coefficient of deuterium or helium atoms,  $R_j$  ( $j$  for the species type), the sputtering coefficient of energetic neutrals impinging on the QCM crystal surface,  $Y_j^{QCM}$ , and the corresponding solid angle subtending these reflected neutrals,  $\Omega_j$ , are factored into the mass variation of the QCM in this manner:

$$M_{QCM} = \frac{\Delta f}{f} M_{crystal} \left( 1 + R_j Y_j^{QCM} \Omega_j \right) \quad (3)$$

However, the factor  $R_j Y_j^{QCM} \Omega_j$  gives only about a 5-10% change in the lithium yield, well within the 25-30% error bars of the data. A mass balance between the mass loss from the lithium sample and the mass gained on the QCM deposition crystal results in the expression for the absolute sputtering yield of lithium:

$$Y = \frac{1}{D f_i S^{QCM} \Omega m_{Li_2O}} \frac{\Delta f}{f} M_{crystal} \left( 1 + R_j Y_j^{QCM} \Omega_j \right) \quad (4)$$

#### 4. Modeling and Simulation

Simulation is done with the VFTRIM-3D model, which simulates surface roughness [10] under the basic TRIM framework [11]. VFTRIM-3D has been used for a variety of systems with success [12]. In VFTRIM-3D the surface binding energy (SBE) applies the heat of sublimation of the material as a key parameter at these low energies. The

version of VFTRIM-3D uses an equipartition between the local Oen-Robinson inelastic energy loss model and a non-local Lindhard-Sharff inelastic energy loss model.

Computational runs for deuterium-treated solid lithium were modeled using a surface, which consisted of 50 a/o Li and 50 a/o D, consistent with deuterium concentration measurements [13, 14]. The model used a surface binding energy of 1.68 eV based on the heat of sublimation for solid lithium. The value of 1.68 eV for the surface binding energy of solid-phase lithium has been measured in plasma-surface interactions experiments in PISCES-B [15]. The bond energy ( $BE$ ) – the energy to break a bond in the bulk – was taken as  $BE = 0.1 SBE$ .

Modeling for liquid-phase lithium is done with the VFTRIM-3D model using a fractal dimension of 2.00. To determine the surface composition we note again experimental data from H. Sugai [13], that shows the hydrogen solubility in lithium is one to one. As the temperature is increased and lithium reaches the liquid state, deuterium atoms will begin diffusing to the bulk and form Li-D bonds in subsequent layers below the surface [3, 16]. Therefore, computational runs are modeled with the first layer composed of 100% Li and subsequent layers below with a homogeneous mixture of Li and D with a one-to-one ratio. For solid Li, the surface comprises of a one to one mixture of D and Li as stated earlier. This model is confirmed by comparing the D-saturated solid and liquid lithium modeling results to the experimental sputtering results [3]. Using a 100% Li layer for both, or using a 50%-50% layer for both do not reproduce the data. Further detail is provided in earlier references [2, 3, 7].

Tin-lithium simulations are conducted by VFTRIM-3D as well for both solid and liquid phase. To determine the surface composition to be modeled for liquid tin-lithium, we note the experimental results of B. Bastasz [17]. Li atoms migrate to the surface upon melting. Therefore, computational runs modeling liquid tin-lithium are modeled with the first layer composed of 100% Li. Subsequent layers are modeled using the 80%Sn and 20% Li composition. Further details are provided in experimental and modeling work done for the Sn-Li system [7].

## 5. Sputtering theory and semi-empirical models

In order to complement simulation work, a widely known semi-empirical model for physical sputtering is used to gain a better physical understanding of lithium sputtering. The theoretical development by P. Sigmund of physical sputtering based on a transport model has been successfully used, coupled to experimental data and appropriate scaling factors resulting in an empirical relation known as the “Bohdansky Formula” [18, 19], for normal incidence.

$$Y(E_o, \alpha = 0^\circ) = Q_s^{KrC}(\epsilon) \left[ 1 - \left( \frac{E_{th}}{E_o} \right)^{2/3} \right] \left( 1 - \frac{E_{th}}{E_o} \right)^2 \quad (5)$$

This empirical relation can be expressed as a function of the angle of incidence. A revised formula, which used the treatment by Yamamura et al. [20] results in the following relation, so equation (5) becomes:

$$Y(E_o, \alpha) = Y(E_o, \alpha = 0^\circ) \frac{1}{(\cos \alpha)^f} \exp \left[ f \left( 1 - \frac{1}{\cos \alpha} \right) \cos \alpha_{opt} \right] \quad (6)$$

Details on the semi-empirical parameters can be found in respective references [18, 19]. In addition to the revised Bohdanský formula, an expression is used to model the deuterium saturation of the solid lithium target as a multi-component surface. In this case the expression derived by P. Sigmund [21] and N. Andersen [22] based on the linear cascade theory gives the partial sputtering yield,

$$Y_{Li} = Y(E_o, \alpha) \frac{c_{Li}}{c_D} \left( \frac{M_D}{M_{Li}} \right)^{2m} \left( \frac{U_D}{U_{Li}} \right)^{1-2m} \quad (7)$$

Where  $c_D$  is the concentration of deuterium atoms in a lithium matrix and  $c_{Li} = 1 - c_D$ . The  $U_i$ 's correspond to surface barrier for each component. The  $Y(E_o, \alpha)$  is the absolute sputtering yield, as given in equation (6), if no other component than lithium was present on the surface. The expression in equation (7) will be referred to as the Bohdanský-Sigmund-Yamamura (BSY) model. The expression can account for the surface treatment of lithium with deuterium atoms assuming a 50% Li – 50% D surface coverage and that one has a homogeneous composition profile. A homogeneous composition means at least over the depth of origin of the sputtered species. Preferential sputtering, as seen in our results, is expected for the lightest component and for the least bound species. The BSY model was not utilized for the Sn-Li system in this work.

## 6. Results and Discussion

Deuterium treatment of lithium surfaces has demonstrated a clear effect on the sputtering yield of lithium. This was evident in other measurements of solid phase lithium, where a 60% reduction in the sputtering yield of lithium occurred after treatment with a deuterium plasma. The implanted deuterium atoms are sputtered preferentially, thus leading to an effective reduction of lithium sputtering. This effect is also noted in similar deuterium surface treatment studies of liquid lithium [3]. In this particular case implanted deuterium atoms readily diffuse to the lithium bulk as the temperature increases. In addition there are radiation-induced segregation processes that drive deuterium atoms to the surface. Therefore, a net amount of deuterium atoms will exist on the surface and subsurface layers of the hot lithium sample.

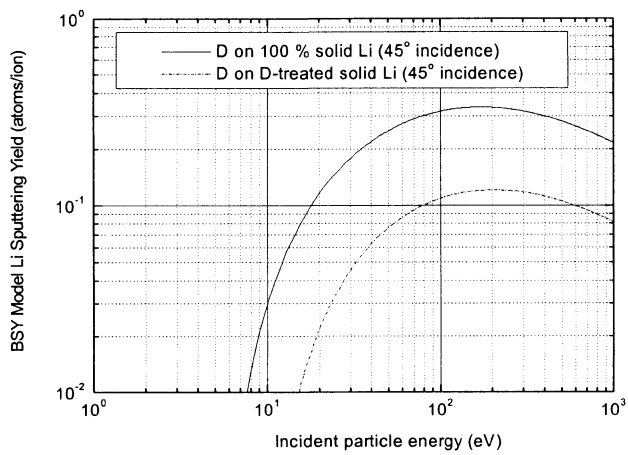


Figure 1. BSY Model lithium sputtering yield by D bombardment at 45-degree incidence for D-treated and non D-treated solid lithium surface.

The effect of deuterium treatment of the lithium surface on lithium sputtering from deuterium and helium bombardment is shown in Figures 1-2 as calculated from the BSY model. In Figure 1 the lithium sputtering yield as calculated using the BSY Model is shown for deuterium bombardment at 45-degree incidence. These results are consistent with experimental data in IIAX, as well as simulation data from VFTRIM3D [2]. One notes that in the case of deuterium bombardment the lithium sputtering yield threshold increases as the surface is treated with deuterium. This occurs due to additional deuterium atoms on the surface preferentially sputtered compared to lithium atoms, thus reducing the lithium sputtering yield.

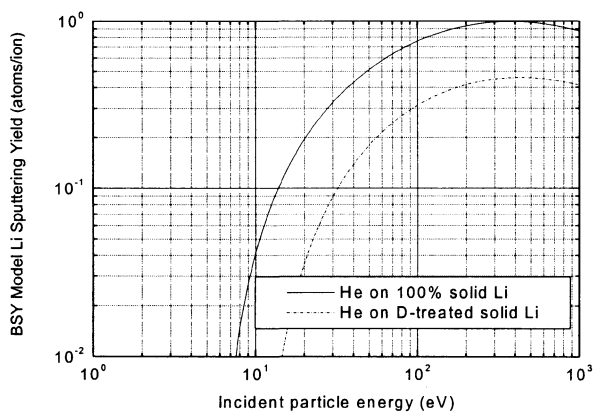


Figure 2. BSY Model lithium sputtering yield by He bombardment at 45-degree incidence for D-treated and non D-treated solid lithium surface.

Figure 2 shows bombardment by He ions at 45-degree incidence for both a D-treated and non D-treated lithium surface. In this case helium atoms effectively sputter lithium with an energy transfer factor of 93% compared to 88% for collisions with implanted deuterium atoms. We note a similar behavior of an increase of lithium sputtering yield threshold mainly due to the existence of deuterium atoms at interstitial sites.

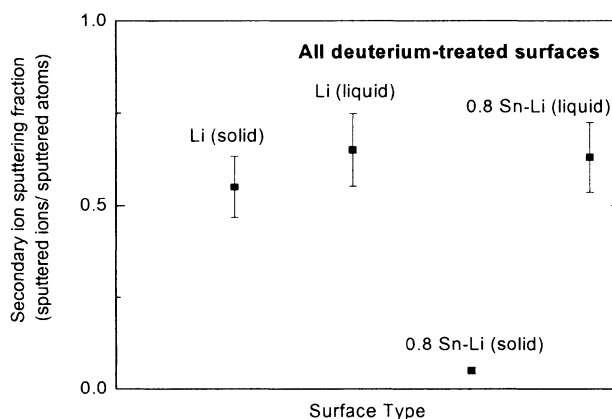


Figure 3. Secondary ion fraction of sputtered lithium atoms as a function of surface phase type for deuterium-treated surfaces.

Figure 3 shows the influence of surface phase for both lithium and tin-lithium on the secondary ion fraction of sputtered lithium atoms for deuterium-treated surfaces. These results show that for tin-lithium in solid phase less than 5% of sputtered lithium atoms are in an ionic state. The case for deuterium-treated surfaces of pure lithium in both solid and liquid phase shows fractions ranging from 55-65%. For liquid tin-lithium the secondary ion fraction is similar for pure lithium implying the segregation of lithium to the surface [7].

Further investigations will consider the effect of deuterium surface treatment on lithium sputtering yield at a variety of surface temperatures. An increase in surface temperature of lithium surfaces has shown a strong lithium sputtering dependence on temperature [23]. Furthermore, treatment of liquid lithium and liquid lithium alloy surfaces with deuterium vary in their effect on lithium sputtering as the temperature of the liquid metal is increased. This is due to a variety of mechanisms discussed in another work [23].

Figures 4 and 5 show IAX experimental data for  $D^+$  and  $He^+$  bombardment of D-treated and non D-treated solid lithium. The D-treated lithium-sputtering yield is measured to be significantly lower than bombardment with no deuterium treatment. The chemical state of the lithium surface is relevant since the incident oxygen flux to the surface is similar to the incident ion flux. As explained before, preferential sputtering is expected for the lightest component and for the least bound species. The deuterium is sputtered preferentially and the surface, in time, is enriched in lithium.

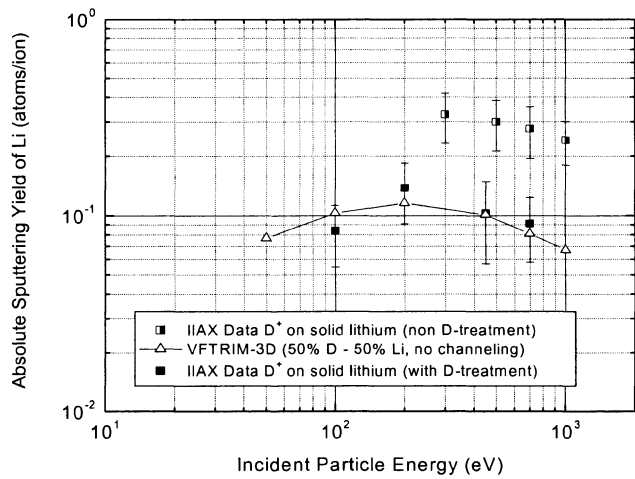


Figure 4. Energy dependence of 45-degree incidence D<sup>+</sup> bombardment on non D-treated and D-treated solid lithium measurements and VFTRIM-3D simulation.

However, at our doses and doses found in typical plasma-facing conditions in tokamaks, the one to one ratio of lithium matrix atoms and saturating-deuteride species is kept over the depth of origin of sputtered species as a constant flux of deuterium atoms impinges on the lithium sample and a source of implanted deuterium atoms segregate to the surface over the time of dose. Another factor is the competition between preferential sputtering on the one hand, and mixing or segregation on the other.

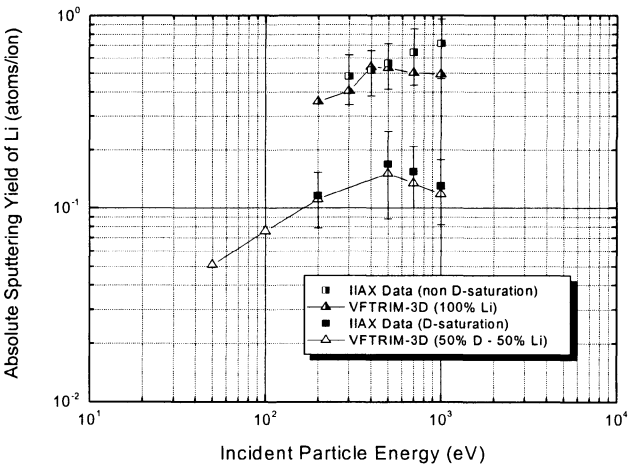


Figure 5. Energy dependence of 45-degree incidence He<sup>+</sup> bombardment on non D-treated and D-treated solid lithium measurements and VFTRIM-3D simulation.



These latter effects are less pronounced here since we have a surface that is “soaked” with deuterium atoms and not an alloy composed of deuterium and lithium constituents. Therefore preferential sputtering mechanisms are justified as a viable interpretation. Binding of deuterium and lithium atoms is less likely than deuterium atoms penetrating and sitting at interstitial sites in BCC solid lithium.

The next case to consider is the effect of deuterium treatment of tin-lithium in the solid phase. Figure 6 shows this effect to be negligible thus eluding to the fact that tin-lithium in solid phase may not uptake much hydrogen. However, in liquid phase this is more difficult to measure for this particular alloy. In Figure 6 only the lithium sputtering from liquid-phase tin-lithium is shown, future work will measure deuterium uptake on lithium alloys at high temperatures.

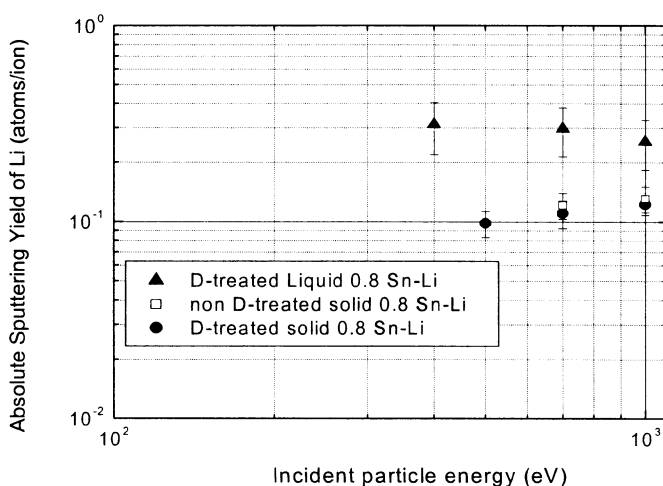


Figure 6. Lithium sputtering from D-treated and non D-treated tin-lithium in liquid and solid phase from helium bombardment at low energies and oblique incidence.

## 7. Conclusion

To summarize the effect of deuterium uptake on lithium sputtering from both solid-phase and liquid-phase lithium and lithium alloys has been measured and studied. Implantation of deuterium ions into solid and liquid-phase lithium demonstrates a strong reduction in lithium sputtering. This is primarily due to preferential sputtering of deuterium atoms due to their weak binding and low mass. Deuterium uptake in solid-phase tin-lithium is not observed. The secondary sputtered ion fraction of lithium is measured to be about 55-65% for solid-phase and liquid-phase lithium, as well as for liquid-phase tin-lithium. For solid-phase tin-lithium this high secondary sputtered ion fraction is not observed implying the segregation of lithium to the surface of tin-lithium at high temperatures as observed in other experiments.

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