SURFACE CHARACTERIZATION OF LI COATINGS AND THEIR INTERACTION WITH PLASMAS FOR FUSION APPLICATIONS VIA ION BEAM ANALYSIS TECHNIQUES

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Abstract

Conditioning of Plasma Facing Components (PFC) is a common practice to improve the plasma performance in both tokamaks and stellarators. The evaporation of thin Li films on the PFC and first wall has given positive results in multiple machines (CDX-U, LTX, TFTR, NSTX, EAST). Reduced recycling and impurity concentration in the plasma are commonly associated with Li. As a consequence, improved energy confinement times and increased stored energy have been observed, in addition to the reduction of Edge Localized Modes (ELMs) frequency. Multiple studies have been dedicated to investigate the surface properties of Li and its interaction with species that are common in fusion environments e.g. H, D, O. As the Plasma Material Interactions (PMI) occur near the surface of the PFC (top 10-100 nm), methods with such probed depths, such as Ion Beam Analysis (IBA) techniques are a remarkable resource to characterize these materials and the effect that plasmas have on them. The Dynamics of ION Implantation and Sputtering Of Surfaces (DIONISOS) is an in-situ analysis facility, designed to expose samples to plasmas and interrogate their surfaces using IBA. The experiment is equipped with a linear plasma source that can produce discharges with fluxes near 10 m\(^{-2}\)s\(^{-1}\) and electron temperatures around to 6 eV. DIONISOS is attached to an ion accelerator, allowing the execution of Elastic Recoils Detection (ERD), Rutherford Backscattering Spectroscopy (RBS) and Nuclear Reactions Analysis (NRA). The facility is also equipped with a Li evaporation system for in-situ deposition of thin films. The combination of modification and analysis tools available in DIONISOS, makes it ideal to study the dynamic and multivariable relationship of Li and plasmas. This work includes in-situ ERD data collected during deposition, erosion and oxidation of thin Li films applied on different substrates. Oxygen concentration near 40% in the Li coatings were measured following 2 hours after their deposition using ERD, in the same way, Li intercalation into a graphite matrix was observed using a 6.5 MeV O\(^+\) beam.

1. INTRODUCTION

The area of Plasma Surface Interactions (PSI) is amongst the most complex and challenging in the context of nuclear fusion devices [1]. The dynamic relationship between plasmas and solids extends over multiple time and length scales, ranging from ps to hr in the former and nm to m in the latter [2]. These interactions occur at the Plasma Facing Components (PFC), such surfaces are modified by the plasma and consequently, the plasma is affected by the PFC response. In the context of Magnetic Confined Fusion (MCF) experiments, it is well known that appropriated conditioning of PFC can lead to improved plasma performance and better operation of the machines [3]. In this way, multiple conditioning techniques have been developed and optimized considering relevant parameters as first wall and PFC materials and regimes of plasma operation. Examples of these conditioning techniques include bake-outs, plasma glow discharges and thin film depositions [4,5]. The deposition of thin films e.g. Si, C or B has been successful applied in several machines e.g. ASDEX, NSTX, ALCATOR C-MOD, EAST) [6-11]. A good example of successful conditioning is the reduction of impurity concentrations in the plasma and consequently \(Z_{\text{eff}}\) and radiated power that have been observed following conditioning with B in ASDEX, NSTX, DIII-D and NSTX. Similarly, data from multiple machines show encouraging results after conditioning with lithium [12,13]. Li has been used in different tokamaks e.g. NSTX, EAST, CDX-U, LTX, yielding considerable improvements in plasma performance mainly due to reduced recycling [12,14–16]. Lithium’s ability to bind hydrogenic species improves wall pumping contributing to flatter temperature profiles and more stable and longer plasma discharges. Edge Localized Modes (ELM) frequency reduction and increased confinement time have also been reported with Li conditioning [14]. Systematic studies in tokamaks, control laboratory studies and computational models have revealed details behind the mechanisms of deuterium retention.
by Li, and, intermediated reactions with oxygen or formation of LiD complexes are recognized as the main paths of D binding [17–19]. However, the extension of the studies of lithium’s interaction with D and O to higher flux densities (~10^20 m^-2) remains an interest issue given the material’s potential for application in reactor scale PFC conditioning. Furthermore, details on Li interaction with different fusion relevant substrates e.g. carbon, tungsten or molybdenum and how plasma exposures affect it remain as relevant issues as well. This work includes characterizations of the response of Li to common residual gases in a vacuum, its interaction with graphite substrates and initial erosion data obtained with Ion Beam Analysis (IBA) Techniques.

2. METHODS

Since the bulk of the PSI occur near the top surface of the PFC (nm to µm deep), experimental techniques that focus on surface analysis are commonly used e.g. X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) or Temperature Programed Desorption (TPD). In this way, Ion Beam Analysis (IBA) becomes a relevant tool for PSI/PFC research. IBA techniques vary in depth range from nm to µm with the additional advantages of being sensitive to hydrogenic species and non-destructive. IBA techniques include some frequently used for post-mortem analysis of materials e.g. Nuclear Reactions Analysis (ERD), Rutherford Backscattering Spectroscopy (RBS) and Proton-Induced X-ray Emission (PIXE).

The Dynamics of ION Implantation and Sputtering Of Surfaces (DIONISOS) is an in-situ PMI research facility designed for irradiation and survey of PFC materials, combining controlled plasma exposures with IBA techniques (Fig. 1a). The device is equipped with a helicon plasma source with a Nagoya type II antenna, powered by a 1.5 kW RF (13.6 MHz) supply. The plasma is magnetically confined by a set of four Helmholtz coils with a maximum in axis magnetic field of 0.1 T. The ion flux is usually in the order of 10^22 m^-2 s^-1, with electron temperatures just below 6 eV in the case of He plasmas. For deuterium, the ion flux decreases approximately one order of magnitude while conserving the same values of temperature [20].

DIONISOS is attached to a Cockcroft-Walton tandem ion accelerator with a maximum potential of 1.7 MV. The accelerator is equipped with two ion sources; one versatile sputtering ion source, capable of producing a wide spectrum of beams of any material that can be deposited on the cathode tip. The second is a plasma source, capable of producing H, He or He^3 beams. The accelerator is equipped with a suite of focusing electrostatic lenses, quadrupoles, steering plates and bending magnets that allow proper positioning and focusing of the beams downstream on the DIONISOS target holder [20,21].

![Image](a)

FIG 1. (a) The DIONISOS chamber with the main diagnostics and modification sources labeled. (b) Al film sample coated with Li during one of the experiments presented in this work.

2.3 Samples preparation

Lithium was deposited on the samples using a custom designed evaporator with a focusing cone that allows a well-defined deposition on the surface of the samples. The resulting Li spot is an ellipse with ~7.0 mm major and ~4.0 mm minor radius (Fig. 1b). The thickness of the Li spot can be controlled with the deposition time [22].
For the oxidation measurements Li was deposited on a polished Al plate. This substrate was used to allow better measurement of the oxygen (since Al is a light metal) while preventing issues with intercalation of the Li as it would be the case with a graphite substrate. The thickness of this coating was around 1500 nm. Following the deposition, the analysis beam was kept on the sample and additional spectra was collected during two additional hours. A similar sample preparation was used for the plasma erosion measurements.

In the case of the intercalation measurements, ATJ graphite samples were cut 1x1 cm squares (2.65 mm thick) and mechanically polished to mirror finish. A Li layer of 10 µm was deposited on the surface of the sample and spectra was collected during deposition and during one additional hour after the end of the deposition.

### 2.2 Ion Beam Analysis (IBA)

In this work, Elastic Recoil Detection (ERD) was performed using two different beams, selected to provide the best resolution for the specific aspect of the sample studied during the particular experiment. In this way, measurements of oxidation of the Li coatings were performed using a 5 MeV He\(^{+4}\), whereas the measurements of intercalation and those acquired during plasma exposures and intercalation were executed with a 6.5 MeV O\(^{+4}\) beam. The helium beam was created with a plasma source and focused to a 1.0 mm diameter spot using a quadrupole triplet. The oxygen beam was created with a sputtering source with and a lithium oxide cathode, the spot size was again around 1.0 mm. The current at the target location was 5.0 nA for helium and 15 nA for oxygen. The recoiled and scattered particles were measured with a solid-state Si detector biased to 40V, the total acquisition time varied from 120 s for the measurements performed with the He beam to 60 s for those acquired with the O beam. Atomic contents and concentrations were calculated from ERD data using SimNRA [23] simulations.

### 2.3 Plasma irradiations

The plasma irradiations were performed using He gas. The He flux varied between 1.5x10\(^{22}\) and 3.5x10\(^{23}\) He\(^{+}\).m\(^{-2}\).s\(^{-1}\) for all the irradiations, corresponding to changes in power supplied to the antenna (800 to 1000 W). The sample was exposed to a total fluence of 1.2x10\(^{24}\) He\(^{+}\).m\(^{-2}\). The current to the magnetic field coils was 120 A corresponding to 40% of the maximum magnetic field. All the ERD scans were taken in between irradiations, and each scan took 100 s.

### 3. RESULTS

#### 3.1 Deposition and passivation of Li coatings on Al

Figure 2 shows the simulated data obtained with the SimNRA software by modeling a thick Al substrate coated with a thin layer of Li. The lithium layer has defined contents of oxygen and hydrogen. In the model the incident analysis beam was set to be 5 MeV He\(^{+3}\).

The model shown in Fig. 1 was used to analyze the data collected during the Li deposition and its later passivation, this includes the calculation of the amounts of each constituent in the sample (Fig. 3b). The spectrum shows peaks belonging to O at (channel number 276), Li (channel number 210), H (channel number 355) and Al (channel number 40). As a consequence, the spectrum of a clean Al surface would show a combination of H and O high energy edges. As Li is deposited on the substrate, a decrease in the counts of the O edge would be expected in addition to a progressive grow of the Li edge, the resultant spectrum would be similar to that shown in Fig. 2, depending on the Li, O and H concentration in the deposited layer.

Fig. 3a shows the ERD data collected during the Li deposition on an Al sample (1.5 µm thick). In addition, the figure includes the data obtained after the deposition ended, hence measuring the passivation of the Li layer. The data shown in Fig. 3a were normalized to the average value of the counts between
channels 40 and 50, this, to compensate potential variations in the He$^+$ beam current. The labels in the figure corresponds to the time after starting the deposition, which ended after 121 min (dotted line). The solid thick continuous line (0) belongs to the Al substrate previous to any Li evaporation. The lines labeled 67, 83 and 99 (thin continuous) show a progressive decrease in the counts of the high energy edge of the traces, while the section of the spectra relating to the Li peak remains relatively high. This is interpreted as a decrease in the content of oxygen of the surface layer i.e. freshly deposited Li layer, at the same time that the Li content of this layer increases. It can be noticed that traces 99 and 110 show a slight increase in the counts at high energy end, implying a small increase in the oxygen content of the layer, this can be explained by a possible decrease in the Li vapor flux from the evaporator, which in turn would decrease the deposition rate, allowing more time for the residual gases in the DIONISOS chamber to react with the freshly deposited Li.

Following the end of the deposition (121 min), the evolution of the Li layer was monitored during ~2 hours i.e. traces 148, 175 and 241. During this time the oxygen content in the sample increased, as it can be seen by the increasing counts of the high energy edge. These results can be seen more clearly in Fig. 3b where the contents of Li, H and O measured with ERD are plotted as a function of time. As shown in the figure, in the early stages of the deposition, the Li layer remains fairly pure i.e. the oxygen content is around 10% with a small increase towards the end of the deposition where the oxygen content reaches approximately 12%. Following the end of the deposition, the oxygen concentration of the Li layer raises following an almost logistic trend, with a rapid increase in the early stages of the passivation almost doubling in the first 60 min, and reaching an asymptotic behavior after 120 min (240 min in Fig 3b) where the concentration of O is just under 40%. Further measurements done ~21 hr. after the deposition shown similar concentrations of O, further confirming the logistic trend followed by the oxidation process. Skinner et al. reported similar observations using XPS and thick Li samples [24].

**3.1 He$^+$ plasma erosion of Li layer**

Fig. 4a shows the ERD spectra collected in between irradiations of a thin (1.25 µm) Li layer deposited on an Al substrate. The spectra are shown at different fluence steps as the irradiation progressed with the trace labeled 0.00 being the pre-irradiation freshly deposited Li layer. Features similar to those mentioned in the discussion of Fig. 3a can be noticed in Fig. 4a, in this case, the initial sample state is that of a surface with low oxygen concentration.
with a noticeable Li edge (channel 210). As the helium plasma fluence increases, the content of oxygen in the Li layer increases resulting in a decrease in the Li edge. The progressive transition from a mostly metallic Li layer, to a lithium oxide surface and finally to a profile that closely resembles that of an Al surface (as shown in Fig. 3a) can be seen in the figure.

![Graph showing ERD data and thickness of the Li layer as a function of He+ fluence](image)

**FIG 4.** (a) ERD data collected during erosion of and Li layer deposited Al using He+ plasmas in DIONISOS, the label shows the accumulated fluence after each irradiation. (b) Thickness of the Li layer as a function of He+ fluence, the figure includes estimated values of erosion that use the fluence and defined sputtering yields to obtain the resulting thickness. The data labeled Y cte. were obtained the same value of sputtering yield through the whole range of fluences, whereas the data labeled Y var. were resulted from calculations that assumed a change in the yield following the increase in power to the plasma around 5.8x10^{23} He+/m^2.

Fig. 4b shows the change in the thickness of the deposited layer as a function of fluence measured with ERD. The progressive erosion of the layer produced by the plasma can be seen in the figure. Two estimations of erosion are also provided in the plot. First, labeled Y cte., is a sequence of data points obtained with the assumption of a constant sputtering yield for all the irradiations, these data reproduce fairly well the measured values with increasing error as the fluence increases, such difference can be due to the fact that the sample changed in composition i.e. oxygen content during the irradiation thus changing the sputtering yield. Furthermore, the discrepancy between predicted and calculated data becomes larger after 5.8x10^{23} He+/m^2 where the power supplied to the antenna increased from 800 to 1000 W, this change could have produced a change in the energy of the incident He+ ions, increasing the sputtering yield and producing faster sputtering than that predicted by the calculations. In an effort to illustrate this point, Fig. 4b also includes a set of data obtained with a variable sputtering yield (Y var.) in this case, the yield changes from 0.055 to 0.150 in the transition of power going into the plasma. In this second case, the values of thickness more closely reproduce those obtained experimentally.

### 3.3 Li deposition and intercalation in graphite substrates

Fig. 5a displays a SimNRA simulation of a Li layer deposited on graphite and analyzed using a 6.5 MeV oxygen beam. The simulation allows to see the growth of the Li layer such that increments in the maximum counts of the Li peak (high energy edge at 800) would be related to the content of Li in the layer while increments in the width of the peak would be related to the increase of the thickness of Li layer. This model can be used to analyze the data shown in Fig. 5b. This figure shows the ERD data collected during the deposition of Li on a polished graphite sample. As the plot shows, when more Li is deposited on the sample with increasing time, the Li peak not only grows in intensity i.e. counts, but its low energy side extends towards lower channel numbers hence implying an
increment in thickness. However, a more careful analysis of the traces, and a comparison with the peak shown in Fig. 5a provides insights on the Li/C interface.

The peak in Fig. 5a is symmetric, which indicates that the Li layer in the model has a uniform concentration. In contrast, the peak depicted in Fig. 5b, shows a clear asymmetry, since the low energy edge decreases with a less steeped slope than the high energy side. This implies that the Li measured by the oxygen beam shows a gradient in concentration through the depth of the sample, hence implying intercalation of the Li into the carbon matrix. As the time increases, both the intensity and width of the Li peak increase, these increments respond to two main reasons; the Li vapor flux incident on the surface of the graphite sample is arriving to the surface at a high enough rate that the concentration of oxygen on the surface remains low, and, the thickness of the layer is progressively increasing. This means that both the intercalated Li layer is reaching more depth into the graphite, consequently increasing the Li concentration in the near surface regions and, the thickness of the Li that is actually on top of the graphite substrate is growing as well.

The phenomena of Li intercalation in graphite is very relevant in the context of PFC since the graphite can act as storage that, allows replenishment of Li following any potential sputtering from the plasma. In addition, Li has been reported to reduce the chemical and physical sputtering of carbon and, furthermore it has been shown that the Li-C-O surpasses the D retention capabilities of C or Li independently [25].

4. CONCLUSIONS

We have used IBA and in particular ERD analysis to measure the deposition, oxidation, erosion and intercalation behavior of Li. According to the ERD data, the Li coatings deposited in the conditions observed in DIONISOS i.e. pressure around 1.3x10^{-5} Pa (1.0x10^{-7} Torr), with partial pressures around 1.3x10^{-6} Pa (1.0x10^{-8} Torr) oxidize following a logistic type behavior with 40% oxygen content as asymptote. The coatings developed such concentration in the first two hours of reacting with the residual gases in the chamber, however only a small change was observed beyond that period and measurements taken more than 20 h after the end of the deposition revealed similar oxygen contents in the layers. Sputtering of Li, using He’ plasmas was measured using ERD. The experimental data was compared with simple quantifications of erosion and reasonable agreement was observed when assuming a variation of the sputtering yield of the Li layers as a response of an increase in the power used for the discharge. Finally, the intercalation behavior of Li into a graphite matrix was observed using ERD. Using an oxygen beam it was possible to observe the diffusion of Li deep into the graphite substrate and the accumulation of a layer on the surface of the sample.
Lithium’s great potential as PFC makes it an interesting subject for research and development as an alternative solution to PMI issues. Given its complex chemical behavior and the highly dynamic interaction mechanisms with solids, atmospheric gases and hydrogenic species, further studies towards a complete understanding of its properties can still be laid out. With the data shown in this work we have demonstrated the great potential and impressive utility of IBA to characterize lithium systems e.g. Li-C and Li-Al. The methods presented in this work i.e. beam species and energies, will be used and extended into quantitatively studies of fuel retention and general plasma response of Li coatings on different materials e.g. W and TZM substrates. Such studies can contribute to our complete understanding of this low-Z material, which in turn would allow the definition of better operational points and optimal application of Li in reactor scale machines.

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REFERENCES


