SURFACE SCIENCE STUDIES OF SN AND LI FILMS ON REFRACTORY METAL SUBSTRATES FOR FUSION APPLICATIONS

OLUSEYI O. FASORANTI

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Abstract

Liquid metal plasma facing components (LM-PFCs) such as lithium (Li) and tin (Sn) have been proposed as potential solutions to first wall and divertor challenges in tokamak fusion reactors. These liquid metals are of interest due to their regenerative and heat transfer properties which would allow them to withstand high heat and particle fluxes emanating from the plasma. Fundamental investigations of these metals using a surface science approach will yield insights into how they can be optimized for use in the various engineering configurations proposed for a fully functional reactor.

Ultrathin (up to 10 monolayers, ML) pure Li and Sn films in the solid and liquid state were deposited on polycrystalline substrates of molybdenum (Mo), molybdenum alloy (titanium zirconium molybdenum, TZM), tungsten (W), and single-crystal Mo(100). The thermal behavior, film structure, composition, oxidation characteristics and deuterium uptake capabilities of these deposited films were studied under controlled ultrahigh vacuum (UHV) conditions with Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low energy ion scattering spectroscopy (LEIS) and temperature programmed desorption (TPD).

Generally, for Li films deposited on Mo, TZM and W, the monolayer of Li in contact with the substrate is bound much stronger than in bulk Li films, and thermally desorbs at much higher temperatures. Interfacial Li on Mo(poly) has a higher thermal stability than that on TZM(poly), where the limiting values for the desorption activation energies, \( E_d \), are 3.56 and 2.84 eV, respectively, in the low coverage, high temperature desorption tail. LEIS indicates some clustering or interdiffusion of the Li films on the TZM substrate at 500 K. No appreciable irreversible absorption of Li occurs on Mo,
TZM or W under the conditions of these experiments. The Li films grown on the TZM substrate showed non-ideal layering at the monolayer level.

For post-oxidized Li films on TZM, no Li desorption occurred until temperatures above 620 K, and then Li desorbed from the surface via three desorption peaks at temperatures of 860, 990 and 1220 K. The formation of lithium oxide (Li$_2$O) and peroxide (Li$_2$O$_2$), respectively was observed after post-oxidation. The peroxide converts to oxide after heating to 680 K with no Li desorption, and then this film decomposes to liberate Li into the gas phase while leaving oxygen at the TZM surface. Heating the LiO$_x$ films to 1070 K caused oxidation of the substrate to form MoO$_2$ and MoO$_3$, and also a condensed binary lithium molybdenum oxide (Li$_x$MoO$_y$) phase. The LiO$_x$ film at 310 K initially wetted the TZM substrate well and no de-wetting of the LiO$_x$ film occurred prior to evaporation of Li above 680 K. Li deposition on an oxygen-containing TZM surface formed a Li-O-Mo interfacial oxide. This was most clearly seen for the thinnest, sub-monolayer Li films studied. Li desorption from multilayer Li films on oxygen-containing TZM surfaces occurred in a metallic Li multilayer peak and three other oxide-derived peaks at 812, 934 and 1157 K.

Sn films deposited on Mo, TZM and W demonstrated stability up to temperatures of 900 K, and thereafter begin to desorb. Multilayer desorption of these films was observed at temperatures of 1187-1270 K. The Sn monolayer films are stable until very high temperatures of about 1800-1900 K on these substrates. These films formed islands after film deposition at 310 K for all substrates studied, with agglomeration of liquid droplets to form larger clusters occurring after annealing to temperatures greater than 500 K. A complex clustering behavior was seen for the Sn films studied on TZM. The
electronic properties of sub-monolayer Sn on Mo was modified as demonstrated by a -0.4 eV binding energy shift for the Sn 3d core level indicative of strong Sn-Mo electronic interactions. Sn films were found to oxidize rapidly at 800 K to form SnO$_2$ due to facile O and Sn interdiffusion. Deuterium uptake on Sn films at 310-750 K from irradiation using 700 eV D$_2^+$ ions showed lower uptake by liquid Sn compared to solid Sn films. Irradiation of oxidized Sn films by a low flux of 700 eV D$_2^+$ caused reduction of the film to metallic Sn.
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Chapter 1 Introduction

1.1 Research Background and a Commentary on LM-PFCs

The plasma-material interface is a major research area that needs to be properly evaluated to achieve fusion energy. Solid materials such as Mo, W, Be and C have historically been used in the first wall and divertor region but have utilization challenges related to their sustainability in a functional reactor, due to their inability to withstand high heat and particle fluxes that emanate from the plasma boundary. Liquid metals plasma facing components (LM-PFCs) are a strongly considered solution to the high-power and particle flux loads impinging on the first wall and divertor regions of the tokamak. These LM-PFCs can in principle ameliorate lifetime issues caused by surface heat loads. The liquid metals also have excellent regenerative and heat transfer properties due to their relatively large thermal conductivity as well as multiple heat loss channels. For example, heat can be dissipated from these liquid metals due to evaporative heat loss, or heat transfer through convection by a free-surface liquid flow to move the heat around as well as self-regulated vapor shielding effects that can mitigate the heat fluxes that emanate from radiative heating coming from the plasma. These advantages are expected to yield improved plasma confinement times and parameters in experimental tokamaks and in the long term for fusion devices. Also, unlike tungsten (W), these liquid metals do not suffer from material damages in their mechanical properties such as cracking [5], surface morphology changes or blistering [6] or neutron-induced lattice damage. Flowing liquid metal systems will also allow the removal of tritium out of the fusion vessel.
Specifically, Li and Sn are two materials under consideration for use as liquid metals in fusion reactors. Li use in experimental tokamaks has yielded positive effects on plasma performance parameters. This has led to an interest in Li chemistry on high Z metals such as molybdenum (Mo), a titanium zirconium molybdenum alloy (TZM) and tungsten (W). It also has strong chemical reactivity with hydrogen leading to reduced recycling of cold hydrogenic species back into the plasma. This continuous recycling would eventually lead to radiative losses.

Figure 1.1 Temperature dependence of the evaporation rate of various proposed liquid metal materials. Reprinted with permission from Ref. [9] Copyright (2018), AIP Publishing.
Liquid Sn is attractive because it has lower vapor pressures as shown in Fig. 1.1 and thus a lower evaporative flux and higher operating temperature limits in tokamaks. However, questions about the interactions of deuterium with Sn are less studied, especially with regards to how Sn will behave when it interfaces with hydrogenic species at different ion energy and flux distributions.

A key issue in the utilization of liquid metals is interactions with a substrate, especially with regards to wetting. The liquid metals used in fusion devices will be electromagnetically restrained (EMR) in the first wall or restrained by capillary forces as well as surface tension that are dependent on good wetting and contact with a substrate. Moreover, it is important to know the dry out conditions of these liquid metals on different substrates. These key questions will be explored in this thesis.

1.1 Research Goals and Outline

The goals of the work presented herein are to examine the thermal stability, structure, wetting properties, and deuterium uptake of ultrathin Li and Sn films on refractory metal substrates such as Mo, TZM, and W. Refractory metal substrates would likely be used as supports for these films in fusion reactors. Specifically, this thesis will focus on the deposition of ultrathin Li and Sn films at the sub-monolayer, monolayer and multilayer regime and their chemistry with deuterium and oxygen.

The prepared Li and Sn surfaces were examined using Auger electron spectroscopy (AES), low energy ion scattering spectroscopy (LEIS), and X-ray photoelectron spectroscopy (XPS) to evaluate surface composition, structure and thermal stability. Changes in the thermal stability of the films in the presence of O₂ as well as deuterium
release and uptake behavior was evaluated under well-controlled, ultra-high vacuum (UHV) conditions using temperature programmed desorption (TPD).

This work sought to address the following issues:

Binding energies of Sn and Li films on high Z polycrystalline refractory metal substrates to provide an understanding of how these films will behave at conditions of high heat fluxes and the subsequent impact on wetting and dry-out.

- The thermal stability of the films, and surface processes (i.e. diffusion, alloying or clustering) that occur for these films as they are annealed.
- The influence of O-contamination on the interaction of liquid metal films with these substrates, which can come from residual gas in the vacuum chamber or as already adsorbed and absorbed impurities in the substrates.
- The interactions of implanted deuterium ion species with Sn films deposited on W, since deuterium is a fuel utilized in the tokamak.

Chapter 3 will discuss the surface composition, desorption behavior and thermal stability of Li films that were deposited on polycrystalline Mo and a molybdenum alloy, TZM, substrates.

Chapter 4 will examine the thermal stability of LiO\textsubscript{x} films that were deposited on a TZM substrate. TZM was chosen because of its interest as support material in the NSTX experiments at the Princeton Plasma Physics Laboratory (PPPL). Chapter 5 will provide an evaluation of the adsorption, desorption and thermal stability of Sn films on both molybdenum and TZM and their reactivity with oxygen. Chapter 6 will provide a discussion of thin film studies of Sn on a polycrystalline W substrate with a focus on
deuterium ion irradiation of the Sn. Chapter 7 provides a summary of the conclusions from the research conducted for this thesis and offers some suggestions for future work.

The results obtained from this thesis work will guide future uses of liquid metals as plasma-facing components and provide fundamental understanding of the processes important for their use in fusion reactors. This work illustrates the dynamic nature of these films, how they behave in the presence of impurity contamination, and what are the main factors that could be used to improve the use of these films in fusion devices.

The results discussed in Chapter 6 have been presented in academic conferences which have been listed in Ref. [10,11]. Furthermore, the content in Chapter 3, has been accepted for publication in the Journal of Nuclear Materials [12] at the time of printing this thesis.

References


Chapter 2 Experimental Methods

The experiments described in this work were performed in an ultrahigh vacuum (UHV) chamber with instrumentation that consisted of two parts: a 4-axis manipulator arm and an analysis chamber that contained multiple surface diagnostics tools including Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low energy ion scattering spectroscopy (LEIS), and temperature programmed desorption (TPD). The manipulator also accessed a region that allowed for high pressure exposure of gases, and this was separated from the analysis chamber by a gate valve. A schematic of the chamber used is shown in Fig. 2.1.

2.1 UHV Chamber Apparatus

![Figure 2.1 Schematic of the UHV chamber. Reproduced with permission from B.E. Koel, Princeton University.](image)
Analysis of the adsorption, thermal stability, desorption, surface composition, oxygen and deuterium uptake behavior of the ultrathin Li and Sn films on Mo, TZM and W was done in this UHV chamber at a base pressure of $4 \times 10^{-10}$ Torr which rose to $1-2 \times 10^{-9}$ Torr during experiments. The background chamber pressure was achieved using a 300 liter s$^{-1}$ ion pump and titanium sublimation pump, and a 240 liter s$^{-1}$ turbomolecular pump (Pfeiffer Balzer TPU 240) backed by a dual stage rotary vane mechanical pump (Alcatel 2004A). There was also a turbomolecular drag pump (Pfeiffer TMH/TMU 071) backed by a mechanical pump (Alcatel 2004A) that allowed for differential pumping of the manipulator arm.

The analysis chamber was equipped with an electron gun (Kimball Physics, Model EFG-7F-4243, 5 kV) for generation of the electron beam used for Auger electron spectroscopy (AES), a differentially pumped ion gun (PHI Model 04-303, 5 kV) for Ar$^+$ ion sputtering and low energy ion scattering (LEIS), a spherical capacitor analyzer (SCA; PHI Model 10-360) for AES, LEIS, and X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED) optics (PHI model 15-120), a quadrupole mass spectrometer (QMS; UTI 100C), and a dual-anode X-ray source (PHI model 04-548) that can generate either Al K$\alpha$ or Mg K$\alpha$ radiation for XPS. The Mg K$\alpha$ radiation (1253.6 eV) at 300 W was used for all XPS measurements that are presented herein. Oxidation of the films for all experiments was carried out by backfilling the UHV chamber with O$_2$ (Matheson ultrahigh purity 99.99% O$_2$) using a high precision variable leak valve attached to a gas handling line. The line was connected to gas lecture bottles. Exposures reported have not been corrected for ion gauge sensitivity.
AES spectra were taken with an incident beam energy of 3 keV and beam current of 65 nA for all measurements presented. The LEIS measurements were done using a lab scattering angle of 104° with 1 or 2 keV He⁺ ions incident normal to the surface and an SCA pass energy of 939.2 eV. All LEIS scans required took 30 s - 2 min to acquire using a 10 nA beam, and no ion beam sputtering effects were observed when multiple LEIS scans were taken.

All binding energies (BE) for XPS were referenced to the Mo 3d$_{5/2}$ peak at 227.7 eV BE. 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 3d$_{5/2}$ peak at 227.7 eV. Fitting and decomposition of the XPS peaks were done using the CasaXPS program utilizing a mixed Gaussian-Lorentzian peak shape and Shirley background subtraction for the baseline.

2.2 Polycrystalline Sample Mounting and Cleaning

Polycrystalline samples of Mo (ESPI Metals, Ashland, OR; purity 3N8), titanium-zirconium-molybdenum (TZM) alloy (Goodfellow, Huntingdon, England; Mo 99/Ti 0.5/Zr 0.1) and W (ESPI, Ashland, OR; purity 3N8) were used. The Mo and W foil samples (1 cm x 1 cm and a thickness of 0.003” (0.076 mm)) were freshly polished using alumina paste prior to mounting. The TZM sample (1 cm x 1 cm and a thickness of 0.005” (0.125 mm)) was used without polishing. Both samples were rinsed with acetone before mounting into the UHV chamber. The samples were mounted by spotwelding two 0.015 in. (0.38 mm) Ta wires to the back of the samples as heating elements. These were then attached to 0.040 in. (1.01 mm) dia. tantalum rods that were connected to copper
rods using Cu-Be connectors. Resistive heating using a DC power supply enabled heating of the samples to 1900 K. A W 5%Re/W 26% Re thermocouple (Type C) was spotwelded to the samples and used to monitor the temperature with an Eurotherm 3508 controller, which also provided a linear heating rate for TPD. Generally, the samples were cleaned in the UHV chamber first by using 1 keV Ar\(^+\) ion sputtering at room temperature to reduce the O, C and S contamination to a minimum level. Surface carbon was removed by one or more cycles of heating at 1500 K in 5 x 10\(^{-7}\) Torr O\(_2\) for 5-10 min. Oxygen contamination was then reduced by heating the sample to 1900 K in vacuum. Some of the oxygen diffused into the substrate or was trapped in defect sites, and so could not be removed during this cleaning step. Before each Li and Sn adsorption and desorption experiment, the samples were annealed to 1900 K in vacuum to obtain a clean surface. The “clean” Mo AES spectrum indicated 94% Mo and 6% O, with no C after the above cleaning procedure. This oxygen concentration could not be reduced to below 6% despite multiple anneals to 1900 K. We believe that the surface is oxygen-free and this signal arises from oxygen bound in grain boundaries. For the “clean” TZM sample, AES indicates 83% Mo, 4.9% Ti, and 12.9% C.
Figure 2.2 SEM images of samples as received before polishing and mounting into UHV showing the topography of the different metal substrates.
Figure 2.3 AES analysis of the surface composition of Mo, TZM and W after cleaning and before experimental work.

TPD for the cleaned TZM sample showed desorption peaks for $\text{H}_2\text{O}$ and CO at 400 K, as well as $\text{H}_2$ desorption occurring at 400 and 1100 K. There was also C, CO, and $\text{O}_2$ desorption at 1100 K due to CO recombination. The “clean” W sample had a surface composition that was 96% W and 4% O from AES analysis.
2.3 Thin Film Evaporation

The Li films were deposited by physical vapor deposition, i.e., thermal evaporation from a commercially available Li metal dispenser source (SAES Inc.). The physical evaporation source was constructed in-house using the following approach. A Li metal dispenser was attached to stainless-steel rods, that were then connected to electrical feedthroughs using copper-beryllium connectors. The electrical feedthrough was provided with current that when sufficient allowed the Li chromate in the dispenser to thermally decompose and release Li atoms in the gas phase that then condense on the substrate. The amount of Li deposited on the sample surfaces was calibrated by Li TPD measurements. TPD was carried out using the QMS in direct line-of-sight with the sample surface. Since a QMS measures the flux of desorbing particles in TPD experiments, a flux correction to account for the lower sensitivity of the QMS signal to faster moving particles (at higher temperatures) was applied to the QMS signal to properly determine the number of desorbing Li atoms, and these flux-corrected values were used for the integration needed to determine the Li film coverages reported herein. The flux-corrected values were obtained by multiplying the Li QMS signal by $\sqrt{T_{\text{surf}}}$. The particle velocity is proportional to $\sqrt{T}$ and $T=T_{\text{surf}}$ is assumed to describe the translational kinetic energy of the particle.
The Sn films were deposited also by physical evaporation from a custom-made Sn thermal evaporation source. This was constructed by placing one pellet of Sn shot (ESPI Metals, Ashland, OR, purity 6N) into a molybdenum evaporation boat (R.D. Mathis Company, Hi Vacuum Evaporation Sources, Long Beach, CA), which was then covered by a 0.005” Mo foil with a hole in it through which evaporation proceeded. Two 15-mil tantalum wires are spot welded to the molybdenum evaporation boat to allow for ohmic heating. This assembly was then spot-welded to stainless steel rods that were attached to an electrical feedthrough. The amount of Sn deposited on the surface was also calibrated through TPD measurements and all thicknesses and film coverages reported were obtained through TPD. During Sn film evaporation, the chamber pressure rose to about 2 x 10^{-9} Torr. Before experiments, the Li and Sn sources were thoroughly degassed at currents yielding temperatures lower than that needed for evaporation.
2.4 Surface Science Techniques Overview and Set-up

2.4.1 Auger Electron Spectroscopy (AES)

Auger electron spectroscopy is an important technique that is utilized in the analysis of the surface composition of samples such as thin films, powders and other materials. It provides both quantitative and qualitative information and it is also surface sensitive in that it provides information on only the first few layers (sampling depth of 0.4-5 nm) of a sample. [1] A schematic of the Auger electron process at the atomic level is shown in Figure 2.4. The process is a two electron non-radiative transition following the formation of a “hole” (energy level A) in the inner shell or core level of an atom due to ionization by an incoming electron or photon. The ionized atom is in an excited state, and in a relaxation step, an electron from a higher energy level B proceeds to occupy the core hole in energy level A with the released energy from the difference in energy levels ejecting simultaneously a second electron from the atom. [1] This electron is referred to as the Auger electron, and this leaves the atom in a doubly ionized final state. The energy of the Auger electron is defined as:

\[ E = E_A - E_B - E_C \]  \hspace{1cm} (2.1)

with \( E_A \), \( E_B \) and \( E_C \) denoting atomic energy levels that are specific to each element, and as a result the Auger electron has a kinetic energy (KE) that is characteristic of the element from which it is ejected. Scattered and secondary electrons from the primary beam and ionized electrons contribute to the background signal observed in Auger electron spectroscopy and so AES spectra are often shown as derivative signals \( dN(E)/dE \). The peak-to-peak height of these derivative Auger signals is a quantitative measure that
directly relates to the concentration of the element at the surface. This signal, in addition to concentration, will depend on such factors as the ionization and Auger electron transition cross sections and the mean free path $\lambda$ of the ejected electron, which get combined into a sensitivity factor for each element. Quantitative AES has been used primarily in this thesis for thermal stability measurements.

Figure 2.5 (a) Schematic representation of the Auger electron process at the atomic level. Adapted from ref. [1] (b) Depiction of how to measure Auger peak-to-peak height (AppH). [2]

2.4.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a highly surface sensitive technique that can be used to determine the chemical state of surface species that are present in addition to quantitative information about the relative amount of these species. XPS involves bombarding a surface with an X-ray beam of known energy that causes core electrons to be ejected from the sample. [3] These photoelectrons have a kinetic energy
that depends on the photon energy, their binding energy and the work function of the material $\phi$. Analysis of the kinetic energy of the photoelectrons allows for elemental analysis. The KE of the ejected photoelectron is determined by:

$$E_B = E_{\text{photon}} - (E_K + \phi) \quad (2.2)$$

where $E_B$ is the binding energy of the electron and $E_K$ is the electron kinetic energy. The energy of the XPS photoelectrons is within the range of 10-2000 eV.

XPS is defined as a highly surface sensitive technique because the electron escape depth is limited typically to the first 80 Å (8 nm) due to mean free path that allows only photoelectrons near the surface to be detected. [3] Changes in the peak binding energy and width can be used for chemical state identification. For the experiments detailed in this thesis, X-rays were generated using a Mg Kα X-ray source attached to the chamber, and the ejected photoelectrons were analyzed using a hemispherical analyzer similar to the schematic in Figure 2.6.

Figure 2.6 Schematic representation of X-ray photoelectron spectroscopy (XPS) set-up. Adapted from ref. [3].
2.4.3 Low Energy Ion Scattering Spectroscopy (LEIS)

Low energy ion scattering spectroscopy (LEIS) provides very high surface sensitivity (topmost layer detection) compared to the other techniques discussed previously. As shown in Fig. 2.7, LEIS utilizes an incoming ion beam of a specific energy, \( E_0 \) (typically a noble gas such as \( \text{Ar}^+ \) or \( \text{He}^+ \)). The ion is elastically scattered at the surface through a binary collision process leaving with a different energy, \( E_1 \). \( \Delta E \) for the elastically backscattered ions can be used to obtain the mass of the elements in the surface layer through the following equation [4]:

\[
m_2 = m_1 \left( 1 + E_S - 2 \sqrt{E_S \cos \theta_s / (1 - E_S - Q_n)} \right)
\] (2.3)

where \( E_S = \frac{E_1}{E_0} \) and \( Q_n = Q / E_0 \), where \( Q \) accounts for inelasticity in the collision.

Figure 2.7 (Left) Schematic representation of low energy ion scattering (LEIS) at the atomic level. Adapted from ref. [4] (Right) LEIS spectra of TZM after UHV cleaning.
2.4.4 Temperature Programmed Desorption (TPD)

TPD is the primary technique that provides a surface scientist with the ability to determine the kinetics and energetics of desorption products as well as estimate the amounts, i.e. coverages, of the desorbing species. In particular, TPD can be used to determine desorption energies of species, and thus often infer adsorption energies for non-activated adsorption processes. A TPD measurement is typically carried out by exposing the surface of a sample to a gas either by evaporation of a metal or through gas phase exposure with a leak valve. At sufficiently cold sample temperatures and reactivity of the gas, adsorption occurs at the surface. The sample is then brought into line-of-sight with the ionizer of a mass spectrometer as displayed in Fig. 2.8. A linear temperature ramp is applied to the sample. When the sample is at a temperature sufficient to break the physisorption or chemisorption bonds that attach the adsorbate to the substrate, a desorbing flux of species will be obtained that will get ionized in the mass spectrometer leading to subsequent detection. [5] The mass spectrometer can detect the partial pressures of multiple desorption products. The desorption rate can be written as:

\[-\frac{d\theta}{dt} = v_n \cdot e^{\left(-\frac{E_d}{RT}\right)} \cdot \theta^n\]  

(2.4)

where \(v_n\) is the pre-exponential factor, \(\theta\) is the instantaneous adsorbate coverage, \(E_d\) is the desorption activation energy, \(R\) is the ideal gas constant, \(T\) is the temperature and \(n\) is the kinetic order of desorption. This desorption rate as a function of surface temperature can be analyzed through various approaches to provide information about \(n\), \(E_d\), and \(v_n\). The most common approach is the use of Redhead analysis. [5] Using Redhead analysis, one can for example determine if the kinetic order is zeroth, first, or second order based on
the shift of the desorption peak maximum with increasing coverage. TPD was a very important technique in the research herein for calibrating the amount of metal films that were deposited on the substrates studied as well as for quantifying the amount of deuterium that was implanted into the W and Sn-coated W samples prepared in UHV.

![Figure 2.8](image)

Figure 2.8 (Left) Temperature programmed desorption set-up. (Right) A typical TPD spectrum of Sn desorbing from polycrystalline W.

References


Chapter 3

Thermal Stability of Li Films on Polycrystalline Molybdenum Substrates


3.1 Introduction

Research into the use of Li coatings on plasma facing components (PFCs) in tokamaks has shown that Li coatings can improve plasma confinement and performance parameters.[1–3] Liquid Li has also been proposed for use in flowing liquid metal concepts in fusion devices due to its ability to withstand high heat loads, radiation damage, thermal fatigue, decreased hydrogen recycling, and erosion.[4] Lithium was first shown to improve plasma performance in the TFTR reactor[1], but has been used in fusion experiments in T11-M [5], FTU[6], CDX-U[2], LTX[7], EAST[8], and NSTX-U[9]. The Li films used thus far in these various applications have been applied predominately on carbon substrates, but high-Z substrates such as molybdenum, titanium-zirconium-molybdenum alloy (TZM), tungsten (W), and stainless steel (SS) are of increasing interest. Li films on such high-Z PFCs will operate under conditions that will expose them to transient heat fluxes and high-temperatures in the vacuum vessels of these devices, and consequently, it is important to characterize and improve our understanding of the interactions and thermal stability of Li films with these surfaces including at the interface and monolayer level. In addition, Ruzic et al. [10] have proposed a lithium–metal infused trenches (LiMIT) system for heat removal in fusion devices, and so an
improved understanding of Li-substrate interactions would also be helpful to better understand the performance of these systems. Although wetting interactions of Li films on constituent materials of divertors (W, Mo, 316 SS, Ta, and TZM) have been examined [11], we found only one prior study under controlled, ultrahigh vacuum conditions examining the thermal stability of thin Li films on polycrystalline Mo or TZM surfaces[12].

Prior surface science experiments using temperature programmed desorption (TPD) have examined the adsorption and thermal stability of ultrathin (a few adsorbed layer) films of Li on several substrates: Ru(001)[13,14], n-type and p-type Si(100)[15], Ta(poly)[16], Ni(110)[17], , TZM(poly)[12], SS[18] and Mo(110)[19]. All these studies found that Li from multilayer films desorbs with zero-order kinetics, characteristic of Li evaporation, at relatively low temperatures of 540-600 K. Li films exhibit a shift of the desorption temperature to higher values with decreasing Li coverage in the monolayer regime that is characteristic of all adsorbed alkali metals on metal substrates. This is due to an increase in the Li-substrate bond strength that arises from decreasing repulsive lateral interactions between the dipoles of adsorbed alkali metal adatoms that occurs with decreasing Li coverage. The main differences in the desorption behavior of Li from these various substrates arises from different Li-substrate interactions and the concomitant changes in the Li-Li repulsive lateral interactions. Li intermixing with the substrate atoms was also observed on Ni(110) [17] and Si(100) [15] surfaces.

A recent joint experimental and theoretical study of Li adsorption and desorption on a Mo(110) single crystal surface provides the most detailed view available for Li-Mo interactions relevant to Li film thermal stability and our studies. [19] In that work, the Li
desorption energy, $E_d$, increased from 1.91 to 2.79 eV and the onset temperature for Li desorption increased from 489 to 878 K as the Li coverage decreased from one monolayer (a thickness of one atomic layer, 1 ML) to a small coverage of only 0.04 ML. The structure of the Li TPD curve for the monolayer had an onset of desorption at 489 K with a desorption peak at 711 K, and a shoulder at high temperatures that extended from 800 to 1100 K. Theoretical calculations using DFT gave results that matched the measured desorption energies and predicted that Li adatoms at small coverages were bonded at low-coordination defect sites at steps and kinks. Previous Li TPD curves from TZM(poly) showed a high temperature peak at 1040 K at low coverages and two other peaks at 750 and 560 K, indicating $E_d$ values of 2.9, 2.0 and 1.5 eV. [12] All Li was completely desorbed from the Mo(110) and TZM substrates by 1100 K. [12,19] Li monolayer films on a Ni(110) substrate desorb in TPD with peaks at 820, 630, and 540 K, with a low coverage, high temperature peak at 900 K and complete Li desorption by 1000 K.[17] On Ru(001) substrates, the high temperature Li TPD peak occurred at 1050 K at 0.01 ML, with Li fully desorbed at 1200 K.[14,20] Studies on 316 stainless steel showed that the smallest Li dose, producing a submonolayer film, had a Li desorption peak at 942 K (2.52 eV). Li TPD peaks at 732 K (2.05 eV) and 632 K (1.67 eV) at higher Li coverages were attributed to Li desorption from the decomposition of Li compounds.

This chapter discusses the strength of Li-substrate interactions for submonolayer Li films, along with the thermal stability of these and thicker Li films, on two polycrystalline substrates, Mo(poly) and TZM(poly), under ultrahigh vacuum conditions using a surface science approach and primarily comparing results from TPD. The results will provide baseline data for the use of polycrystalline Mo and TZM PFCs in NSTX-U
campaigns. [21] The studies reported herein identify similarities and differences between the interactions and thermal stability of Li monolayers and ultrathin films on these substrates and Mo single crystal samples, and also other high-Z PFC materials such as W(poly), 316 SS and Ta(poly). Additionally, we characterize changes that occur in the Li film structure on TZM due to thermal annealing at elevated temperatures using Auger electron spectroscopy (AES) and low energy ion scattering (LEIS).

3.2 Experimental Section

The experiments were performed in an ultrahigh vacuum (UHV) system with a four-axis manipulator and a main chamber equipped with multiple surface analysis capabilities. The base pressure of the chamber was 4 x 10^{-10} Torr, but the pressure rises to 1-2 x10^{-9} Torr during experiments. The chamber was equipped with an electron gun (Kimball Physics, Model EFG-7F-4243, 5 kV) for Auger electron spectroscopy (AES), a differentially pumped ion gun (PHI Model 04-303, 5 kV) for Ar^+ ion sputtering and low energy ion scattering (LEIS), a spherical capacitor analyzer (SCA; PHI Model 10-360) for AES, LEIS, and X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED) optics (PHI model 15-120), a quadrupole mass spectrometer (QMS; UTI 100C) and an X-ray source (PHI model 04-548) that can generate either Al Kα or Mg Kα radiation for XPS. AES spectra were taken with an incident beam energy of 3 kV and beam current of 65 μA. The LEIS measurements were done using a lab scattering angle of 104° with 2 keV He^+ ions incident normal to the surface. All LEIS scans required took 30 s - 2 min to acquire using a 10 nA beam, and no ion beam sputtering effects were observed when multiple LEIS scans were taken.
Polycrystalline samples of Mo (ESPI Metals, Ashland, OR; purity 3N8) and a
titanium-zirconium-molybdenum (TZM) alloy (Goodfellow, Huntingdon, England; Mo
99/Ti 0.5/Zr 0.1) were used. The Mo foil sample (1 cm x 1 cm and a thickness of 0.003”
(0.076 mm)) was freshly polished using alumina paste prior to mounting. The TZM
sample (1 cm x 1 cm and a thickness of 0.005” (0.125 mm)) was used without polishing.
Both samples were rinsed with acetone before mounting into the UHV chamber. The
samples were mounted by spotwelding two 0.015 in. (0.38 mm) Ta wires to the back of
the samples as heating elements. These were then attached to 0.040 in. (1.01 mm) dia.
tantalum rods that were connected to copper rods using Cu-Be connectors. Resistive
heating using a DC power supply enabled heating of the samples to 1900 K. A W
5%Re/W 26% Re thermocouple was spotwelded to the samples and used to monitor the
temperature with an Eurotherm 3508, which also provided a linear heating rate in TPD.
The samples were cleaned in the UHV chamber first by using 1 kV Ar⁺ ion sputtering at
room temperature to reduce the O, C and S contamination to a minimum level. Surface
carbon was removed by one cycle of heating at 1500 K in 5 x 10⁻⁷ Torr O₂ for 5-10 min.
Oxygen contamination was then reduced by heating the sample to 1900 K in vacuum.
Before each Li adsorption and desorption experiment, the samples were annealed to 1900
K in vacuum to obtain a clean surface. The “clean” Mo AES spectrum indicated 94% Mo
and 6% O, with no C after the above cleaning procedure. This oxygen concentration
could not be reduced to below 6% despite multiple anneals to 1900 K. We believe that
the surface is oxygen-free and this signal arises from oxygen bound in grain boundaries.
For the TZM sample, AES indicates 83% Mo, 1.8% Ti, 1.5% O, and 14% C. TPD for the
cleaned TZM sample showed desorption peaks for H₂O and CO at 400 K, as well as H₂
desorption occurring at 400 and 1100 K. There was also C, CO and O\textsubscript{2} desorption at 1100 K due to CO recombination.

The Li films were deposited by physical vapor deposition, i.e., thermal evaporation from a commercially available Li metal dispenser source (SAES Inc.). Before experiments, the Li source was thoroughly degassed at currents yielding temperatures lower than that needed for Li evaporation. The amount of Li deposited on the sample surfaces was calibrated by Li TPD measurements. TPD was carried out using the QMS in direct line-of-sight with the sample surface. Since a QMS measures the flux of desorbing particles in TPD experiments, a flux correction to account for the lower sensitivity of the QMS signal to fast moving particles was applied to the QMS signal to properly determine the number of desorbing Li atoms, and these flux-corrected values were used for the integration needed to determine the Li film coverages reported herein. The flux-corrected values were obtained by multiplying the Li QMS signal by $\sqrt{T_{\text{surf}}}$, where $T_{\text{surf}}$ is assumed to describe the translational kinetic energy of the particle.

3.3 Results and Discussion

3.3.1. Temperature Programmed Desorption Measurements

Lithium films were deposited on polycrystalline Mo and TZM substrates at 300 K. AES after deposition on Mo detected 0.4% O and no C, and on TZM found 0.6% O and 1.6% C. Li (7 amu) TPD curves from Mo are shown in Fig. 3.1 for Li films of $\theta_{\text{Li}} = 0.05$-1.05 ML. The $\theta_{\text{Li}}$ values indicated next to each spectrum were determined based on assignment of the red curve as the saturation monolayer coverage, i.e. $\theta_{\text{Li}} = 1.0$ ML. This assignment was made by analyzing the appearance of the low temperature components of
the Li TPD curves, specifically the leading edge and the appearance of a sharp, zero-order desorption peak signifying desorption from a Li cluster or bulk phase, and determining the TPD trace with the largest area without these features. Importantly, the area under this curve did not increase after deposition of thicker Li films. This assignment is within about 5%, which is sufficient for the experiments reported herein.

We note that other supporting information that is commonly used in surface science experiments was not used here: LEED cannot be used on polycrystalline samples, and quantitative analysis of Li using AES is problematic due to the core-valence-valence nature of the Li transition and its strong sensitivity to electronic structure. The smallest Li coverage of 0.05 ML gave a Li TPD peak at 1279 K (β1) and a smaller peak at 890 K. The high temperature peak could be due to the increased stability of an oxidized Li compound formed by Li reacting with small amounts of oxygen at the surface. Another possible origin for this peak could be tightly bound Li desorbing from grain boundaries. Li in these films was not fully desorbed until 1500 K, which is much higher temperatures than that seen for Mo(110) single crystals [19] and other polycrystalline substrates such as tantalum [12][16] and that seen below for TZM.

With increasing Li coverage on Mo, the peak maximum shifted gradually to lower temperature and occurred at 824 K (β2) for θLi =1.0 ML. The decrease in desorption temperature is caused by repulsive dipole-dipole interactions among Liδ+ adatoms. The appearance of another peak, β3, at 705 K occurred for θLi= 0.88-1.05 ML. This β3 peak could be due to a pre-metallic state of Li in the initial stages of second-layer growth, as was proposed for Li/Ni (110). [17] At θLi >1.0 ML, a lower temperature peak, β4, appeared at 580 K initially. With increasing Li coverage, the β4 peak grew and eventually
developed zero-order kinetics. Based on this behavior, along with previous assignments for Li desorption from other metals [12,13,17,19,22], we assign the $\beta_4$ peak to Li desorption from the beginning of multilayer films characterized by Li-Li interactions. We note that the bulk melting temperature of Li is 453 K, and so Li desorbing from multilayer Li films occurs via evaporation from a liquid state. We conclude that the thermal stability of Li films on polycrystalline Mo substrates is significantly higher than on Mo single crystal substrates, as evidenced by the large loss of Li in a peak at 700 K on Mo(110) [19] compared to the peak above 800 K on polycrystalline Mo and the complete desorption of Li from Mo(110) at 1100 K compared to 1500 K for the Mo(poly) substrate.

The inset in Fig. 3.1 shows a plot of the flux-corrected areas under the Li TPD curves, which is proportional to the amount of desorbed Li, for increasing Li dose times resulting in $\theta_{Li} = 0.05$-1.76 ML. The linear relationship observed indicates that the sticking coefficient of Li on the surface is constant over this coverage range and that no Li is irreversibly absorbed on the Mo substrate, i.e., no Li diffuses deep into the Mo bulk and does not desorb in these experiments.
Figure 3.1 Li TPD traces from Mo for Li coverages from 0.05-1.06 ML. The red curve is used to denote a Li coverage of 1.0 ML. The Li TPD areas given in the inset are flux-corrected values.

Li TPD curves from Li films on a polycrystalline TZM sample are shown in Fig. 3.2. The indicated Li coverages were determined as defined above for Mo. The Li TPD curve indicated in red is from a Li film at close to monolayer coverage, as explained for Mo above, and herein has been assigned as arising from the Li monolayer $\theta_{\text{Li}} = 1.0$ ML. For the lowest Li coverage, $\theta_{\text{Li}} = 0.06$ ML, on TZM, two peaks were observed in Li TPD at 808 and 1030 K (as will be shown more clearly in Fig. 3a), with $\alpha_1$ denoting the 1030 K peak. This curve shows that submonolayer amounts of Li are stable to temperatures of up to near 900 K. With increasing Li coverage, the 1030 K peak shifted gradually to lower temperature to 987 K and saturated near $\theta_{\text{Li}} = 0.2$ ML. Further increases in Li coverage caused Li desorption to shift further to lower temperatures and eventually
formed a peak, $\alpha_2$, at 712 K at monolayer saturation coverage. For $\theta_{Li} > 1.0$ ML, the 712 K peak due to Li-TZM interactions continued to grow indicating that monolayer coverage was not fully completed prior to formation of additional layers. This is indicative of Li surface clustering or the formation of 3D islands of the film. At coverages exceeding one monolayer of Li, the appearance of the Li multilayer peak, $\alpha_3$, was observed initially at 550 K and then at 560 K at $\theta_{Li}=1.38$ ML. The multilayer for coverages with $\theta_{Li} = 5.0$ ML desorb at 600 K. The inset to Fig. 3.2 indicates that on TZM, as on Mo, the Li sticking coefficient was constant over the coverage range of $\theta_{Li} = 0.06$-1.72 ML and that no deposited Li was irreversibly lost into the TZM bulk sample in these experiments.

Figure 3.2 Li TPD traces from TZM for Li coverages from 0.06-1.38 ML. The red curve is used to denote a Li coverage of 1.0 ML. The Li TPD areas given in the inset are flux-corrected values.
A comparison of Li desorption from Mo with that from TZM indicates several notable differences as shown in Fig. 3.3. First, Li has a higher thermal stability overall on polycrystalline Mo compared to TZM. This can be seen in Fig. 3.3a where there is a 250 K difference in the high temperature desorption peak at low Li coverages, i.e., the last traces of Li are not fully desorbed until nearly 1500 K on Mo compared to 1130 K on TZM. Also, Li desorption at these small coverages is dominated by the higher temperature peak on Mo compared to TZM. Such a high temperature Li desorption peak from polycrystalline Mo was unexpected since prior experiments on a Mo(110) single crystal showed that Li was fully desorbed at 1100 K. [19] This could be caused by the interactions of Li with specific low coordination Mo sites on high Miller index planes exposed on the polycrystalline substrate or by Li interactions with oxygen at interfacial sites or grain boundaries, which arises from a small concentration of oxygen in the bulk of the sample. TZM also has oxygen at interfacial sites or grain boundaries, but TZM might not show this high temperature stability due to the presence of Ti in the TZM alloy which binds oxygen more tightly than Mo and may inhibit oxygen interactions with Li at the surface or grain boundaries. Increased thermal stability for Li is also evident in the Li TPD curves on Mo compared to TZM over most of the Li monolayer range, where more Li remained on the surface at a given temperature for Mo than for TZM over the range of 600-1100 K.
Figure 3.3 Comparison of Li TPD traces for (a) 0.06 ML Li/TZM(poly) and 0.05 ML Li/Mo(poly), and (b) 1.38 ML Li/TZM(poly) and 1.05 ML Li/Mo(poly).

These observations for Mo are more clearly visible in Fig. 3.4, which shows the amount of adsorbed Li, as obtained by integrating the flux-corrected Li TPD areas, as a function of temperature for initial coverages of $\theta_{Li}=0.5$, 1 and 1.78 ML on Mo. For initial coverages of $\theta_{Li} \geq 1.0$ ML, a large decrease in Li coverage occurs just below 600 K due to multilayer Li desorption. However, the $\theta_{Li}=0.5$ film remained stable on Mo until 800 K, while this was only stable on TZM to 700 K. The amount of Li that desorbed from Mo above 600 K was independent of the initial Li film coverage.
Figure 3.4 Thermal stability of Li films on Mo(poly) surfaces probed by showing the Li film coverage changes with temperature as determined by flux-corrected Li TPD areas for several initial Li film coverages.

We can determine the activation energy for Li desorption, $E_d$, from the Li desorption peak temperatures ($T_p$) by fitting the desorption curves using the Polanyi-Wigner equation:

$$r_{des} = -\frac{d\theta}{dt} = v_n \cdot exp \left( -\frac{E_d}{RT} \right) \cdot \theta^n$$

(3.1)

where $v_n$ is the preexponential factor, $\theta$ is the instantaneous coverage, and $n$ is the kinetic order of desorption, which in this case is first order with $n=1$. In our analysis of the Li TPD curves we assumed a constant pre-exponential factor of $v_1 = 10^{13} s^{-1}$ and first order desorption kinetics, and calculated Li desorption activation energies as a function of Li coverage by estimating $T_p$ values near the onsets of desorption. These results are shown in Fig. 3.5 for both Mo and TZM substrates. These values for $E_d$ are equal to the
Li adsorption energies, in cases such as those here, where there is no activation energy barrier for adsorption, i.e. Li adsorption is not activated. The value of $E_d$ for Li on Mo at low coverage was 3.52 eV (339.6 kJ/mol) and this decreased rapidly with coverage to 1.94 eV at 0.63 ML, and then finally decreasing to 1.46 eV at monolayer coverage. On TZM, the Li desorption energy is 2.81 eV (271.1 kJ/mol) at 0.06 ML and decreases smoothly to a value of 1.49 eV at monolayer coverage. Li films near one monolayer coverage on Mo and TZM have the same desorption energies, but Li is adsorbed more strongly and desorbs with a higher desorption energy on Mo than on TZM for $\theta_{Li} < 0.77$ ML.

![Graph showing the dependence of Li desorption energy on coverage](image)

Figure 3.5 The dependence of the Li desorption energy on the Li coverage, $\theta_{Li}$, derived from a Redhead analysis of the Li TPD curves from Figs. 1 and 2.

Table 3.1 compares this information on the thermal stability of Li films on Mo and TZM to several other metal substrates. In all case, Li multilayer films begin to desorb near 520 K at an appreciable rate in vacuum during heating in TPD and only a more
stable chemisorbed monolayer remains at the surface after heating to 560 K. This situation arises from relatively weak Li-Li interactions in bulk Li with a corresponding relatively high vapor pressure and a cohesive energy of 1.69 eV.[23] Within the Li monolayer film at the surface, the Li desorption energy, equal to the adsorption energy, probes the Li-substrate interactions. The bonding of Li to the substrate is strongest at low Li coverage and is gradually reduced with increasing coverage, which is caused by electronic effects and dipole-dipole repulsive interactions within the Li adlayer, to values nearly equivalent to that for Li multilayer desorption. Dipole-dipole interactions between Li$^{\delta+}$ adatoms that form due to charge transfer from Li to the substrate account for most of the coverage dependence of $E_d$. An analytical model to account for these dipole-dipole interactions by Albano[24] model was used to simulate fairly well the measured temperature-dependent desorption rates of Li on Mo(110). [19] However, additional coverage-dependent ordering and structural changes within the Li monolayer can cause relatively large changes in the Li desorption rate and give rise to noticeable, large desorption features in the Li TPD curves that typically occur between 700-800 K.

From Table 3.1, the Li films show higher stability on all molybdenum substrates (single crystal, polycrystalline as well as alloy). This indicates that the bonds for Li-Mo > Li-Ru > Li-SS316 > Li-Ta > Li-Ni if there is no impurity contamination leading to compound formation which could contribute to increased stability.
Table 3.1: Maximum Li-substrate binding energies

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$T_p$ (K) ($\theta$, ML)</th>
<th>$E_d$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TZM(poly)</td>
<td>1040 (0.017)</td>
<td>2.85</td>
<td>[12]</td>
</tr>
<tr>
<td>TZM(poly)</td>
<td>1030 (0.06)</td>
<td>2.82</td>
<td>This work</td>
</tr>
<tr>
<td>Mo(poly)</td>
<td>1276 (0.05)</td>
<td>3.52</td>
<td>This work</td>
</tr>
<tr>
<td>Mo(110)</td>
<td>1030 (0.04)</td>
<td>2.82</td>
<td>[19]</td>
</tr>
<tr>
<td>Ni(110)</td>
<td>900</td>
<td>2.46</td>
<td>[17]</td>
</tr>
<tr>
<td>Ru(001)</td>
<td>1000 (&lt;0.01)</td>
<td>2.74</td>
<td>[13,14]</td>
</tr>
<tr>
<td>SS316</td>
<td>942</td>
<td>2.57</td>
<td>[18]</td>
</tr>
<tr>
<td>Ta</td>
<td>913 (0.13)</td>
<td>2.49</td>
<td>[16]</td>
</tr>
</tbody>
</table>

3.3.2 AES Annealing Studies

AES spectra from clean and Li-coated TZM surfaces were obtained and the low energy portion of these are shown in Fig. 3.6. The clean surface is characterized by the Mo 186 eV peak, and other Mo-derived peaks, and a Ti 418 eV peak (not shown), and no detected C, O, or Zr signals. Deposition of Li on the TZM substrate caused the appearance of two Li-derived peaks, at 40 and 50 eV. The 40 eV Li peak is attributed to oxidized Li that results from coadsorption of CO or H$_2$O impurities from background gases, and this peak interconverts to the 50 eV peak after annealing the surface to 450 K and the desorption of impurities. In a prior study of Li adsorption on Ni(110), the presence of a 42 eV Li transition was attributed to arise from an Auger electron exchange process due to interaction of Li with the substrate [17] and similar effects may also occur in our spectra due to Li-Mo interactions. The 50 eV peak is assigned to metallic Li in the film, as done previously. [25] The 50 eV peak intensity increased with increasing Li
deposition, roughly doubling in size from 0.5 to 1 ML, and then increasing from the 1 ML value by a factor of 2.0 and 1.8 for the 2 and 5 ML films. While the Li peak-to-peak height here is not a reliable measure of the Li concentration, due to lineshape changes, these observations are very roughly consistent (as further explained below) with expectations for a Frank-van der Merwe (FM) layer-by-layer growth mode, in which one would expect these signals to be 1.5 and 1.8 times larger than the 1 ML value using an inelastic scattering mean free path, $\lambda_{Li}$ of 4.6 Å at 50 eV in Li.

![Figure 3.6. AES spectra for a clean TZM surface and for deposited films with Li coverages of 0.5, 1, 2 and 5 ML.](image)

Annealing studies of several Li films on TZM were conducted using AES to probe the film thermal stability and interactions of the Li films with the substrate for increasing temperatures, as shown in Fig. 3.7. Li films were deposited onto the TZM substrate at 300 K, annealed for 20 s at the indicated temperatures, and then AES spectra...
were taken after the sample was returned to 300 K. Figs. 3.7(a) and 3.7(b) show the Li 50 eV and Mo 186 eV AES signals (peak-to-peak heights of the Auger transitions in dN/dE mode), respectively, as a function of annealing temperature for Li films of θ_{Li} = 1.0, 2.0, and 4.7 ML. Fig. 3.7(b) shows additional data for θ_{Li} = 0.47. The amount of Li in the deposited films was determined by the Li dose time and confirmed by Li TPD experiments. Due to the nature of AES in general, and in particular for the Li 50 eV AES transition, we do not expect the Li signal plotted in Fig. 3.7(a) to be strictly proportional to the Li coverage, but rather it can be used to probe qualitatively the amount of Li and aspects of the film structure. Two dashed lines are shown on the graphs: one for the melting point of bulk Li, T_m, at 453 K, which represents the upper limit for melting at the Li surface of multilayer Li films, and one for the onset of Li desorption from multilayer films, T_o, at 527 K. We defined T_o as the temperature with 1% of the maximum Li desorption rate in TPD. For the two films exceeding monolayer coverage, changes in the Li signals were seen near the Li melting point and prior to the onset of Li desorption. These could arise from changes in the Li film structure due to desorption of impurities (CO desorption was observed at 370 K), 3D clustering, and melting of Li films thicker than one monolayer near T_m. The large decrease in the Li signals at temperatures above 527 K is due to the loss of Li from the film after the onset of Li desorption. This is consistent with the TPD data, and the coincident Li AES signals above this temperature are consistent with the formation of a Li monolayer film independent of initial film thickness.

The Mo 186 eV AES signals plotted in Fig. 3.7(b) are less sensitive, but more reliable reporters (due to smaller chemical effects on the Mo signal) of changes in the Li
film morphology and coverage with temperature. The Mo AES signal from TZM without any Li as a function of temperature is shown as the top curve for reference. This curve should be temperature independent, if there are no surface composition changes of the other TZM components. The temperature-dependent changes observed in the Mo signal are attributed to the accumulation of contaminants (e.g. CO and H\textsubscript{2}O) during data acquisition and their desorption from the surface at higher temperatures. For the curves for Li films, the changes in the Mo signal with temperature should be complementary to those changes seen for the Li signals, since due to the surface sensitivity of AES, the Mo signal is increasingly attenuated by increasing Li film thickness. For a submonolayer Li coverage, $\theta_{Li} = 0.47$ ML, the Mo signal is attenuated compared to the Li-free surface and is nearly constant until 900 K when the final amounts of Li begin to desorb from the surface and no longer attenuate the Mo signal. For all films that exceed one monolayer or more thickness, $\theta_{Li} \geq 1$ ML, the Mo signal first decreases and then increases near the Li melting point and prior to the onset of Li desorption, consistent with the changes in the Li AES signals and Li film discussed above.

Again, the similar Mo AES signals above $T_o$ at 527 K are consistent with forming Li monolayer films independent of initial film thickness. The Mo signals at 1200 K are below that of the Mo curve without Li due to the presence of atomic oxygen on the surface that does not desorb until higher temperatures. This oxygen was seen in AES spectra after the annealing experiments where completed, which showed a TZM surface composition of 84.2\% Mo, 7.0 \% Ti, 8.8 \% O. Evidently, some additional contamination on the surface is accumulated during the Li film deposition and annealing experiments.
that causes a small attenuation of the clean Mo signal after all Li desorption has occurred by 1200 K.

(a)

(b)

Figure 3.7 Influence of temperature on the (a) Li-50 eV and (b) Mo-186 eV AES signal intensities as measured by peak to peak height for several initial Li film coverages.
Analysis of the AES data can provide insight into the Li film growth mode, i.e., layer-by-layer, layer plus clustering, or clustering, for Li films deposited on TZM at 300 K. The Mo 186 eV Auger electrons have $\lambda_{\text{Mo}}$ of 10.7 Å in Li [26] and one can calculate the attenuation of the Mo 186 eV signal expected due to the deposition of Li films growing in a layer-by-layer mode [27] as:

$$I_{\text{Mo}} = I_{\text{Mo}}^{0} e^{-d \frac{\lambda_{\text{Mo}}}{\cos(\theta)}}$$  \hspace{1cm} (3.2)

where $I_{\text{Mo}}$ is the Mo AES signal intensity, $I_{\text{Mo}}^{0}$ is the Mo AES signal intensity from the clean TZM substrate, $\theta$ is the angle between the surface normal and the electron analyzer axis (90°), and $d$ is the Li film thickness. Based on this calculation, Li film coverages of 1, 2 and 5 ML (determined accurately from TPD) should attenuate the Mo AES signal to values of 75, 56 and 24% that of the original, clean Mo AES signal if the film was growing in a layer-by-layer mode. Our measured values for the Mo AES signals observed of 59, 49 and 43% are very roughly consistent with the model predictions for growth with non-ideal layering, and some clustering in thicker layers, and the strong modification of the Li electronic structure in the monolayer.
3.3.3 LEIS Annealing Studies

LEIS is more surface sensitive than AES and can provide elemental analysis of the topmost atomic layer of a solid. [28] LEIS spectra obtained using 2.0-keV He$^+$ ions are shown in Fig. 3.8 for the initial, clean TZM substrate (bottom curve) and after deposition of a 5-ML Li film on TZM at 300 K. Binary scattering calculations predict peaks from C, O, Ti, Zr, and Mo at 843, 1082, 1643, 1793, and 1810 eV, respectively, and a peak from Li at 390 eV. Prior to Li deposition, no Zr LEIS peaks were seen. As shown in the top curve, the deposition of 5-ML Li eliminates the Mo and Ti signals and strongly alters the shape of the background in the ion scattering spectrum.

![LEIS spectra](image)

Figure 3.8 LEIS curves for (a) the clean TZM(poly) substrate, and (b) 5 ML Li film on TZM. LEIS detected surface atoms of Mo, Ti, O and C for the initial TZM substrate prior to Li deposition.
Figs. 3.9(a)-(c) show data from thermal stability measurements using LEIS for several Li films deposited on TZM at 300 K with initial Li coverages of \( \theta_{Li} = 0.5, 1, 2, \) and 5 ML. The LEIS intensities were calculated using the integrated areas under the scattering peaks. The Mo and Ti LEIS signals were normalized to the signals measured from the clean TZM surface at 300 K and the Li LEIS signal was normalized to that value for the 5 ML Li film at 300 K. As shown in Fig. 3.9(a), the Li LEIS intensities for the 2 and 5 ML Li films after deposition on TZM at 300 K were identical, and the Li LEIS signal changes with heating of these films are nearly the same. The Li signals are unchanged as the temperature is raised until above the onset of desorption from Li multilayer films, \( T_o \), at 527 K. Annealing to 600 K produces a 50% decrease in the signals to about the initial intensity seen for the 0.5 ML Li film. This agrees with the TPD results in Fig. 3.2 that show the 0.56 ML curve has an onset of desorption near 600 K.

The Li LEIS signals are nearly constant for temperatures of 600-900 K despite the desorption of Li from the substrate seen in TPD. This could be due to either a coverage-dependent ion neutralization probability for Li scattering or the presence of contamination that oxidized these submonolayer Li films and therefore made them more stable until desorption at temperatures greater than 900 K. After 900 K, these films show a gradual decrease to zero at 1200 K. The signal for the 1-ML Li film decreases upon heating until 500 K and then follows roughly the curves for the thicker Li films. The lower than expected intensity for the as-deposited 1-ML Li film could arise from either some 3D clustering or contamination, or both. The 0.5-ML Li film has a Li LEIS signal intensity initially that is close to one-half that of the thick Li films as would be expected, and with heating follows roughly the curves obtained for heating the thicker Li films.
The Mo LEIS signals shown in Fig. 9(b) provide complementary information to that in Fig. 9a, since the surface atoms are primarily Li or Mo and so increases in the Mo signal should occur as the Li signal decreases due to uncovering of the Mo substrate by clustering or desorbing Li atoms. The increase in the Mo LEIS signal near $T_m$ and below $T_o$ for the multilayer films indicates 3D clustering in the Li film. After desorption of any Li exceeding the monolayer, the Mo LEIS signal gradually increases with temperature, with a much sharper rise above 900 K, and finally at 1200 K attains the Mo LEIS signal corresponding to the initial TZM surface.

As shown in Fig. 9(c), for the $\theta_{\text{Li}} = 1, 2$ and 5 ML Li films, no Ti LEIS signal is detected until the substrate is heated above 500 K. After Li films exceeding one monolayer are desorbed by heating to 600 K, a Ti LEIS signal is observed, but with large variations in size depending on the initial amount of deposited Li. This probably arises from the different amounts, for different deposited Li films, of oxygen on the surface from impurities such as CO and H$_2$O, which could preferentially adsorb on the Ti and increase the surface concentration of Ti during annealing.
Figure 3.9 Thermal stability of Li films on TZM probed by LEIS for several initial Li film coverages. Changes in the LEIS signals for (a) Li, (b) Mo, and (c) Ti are shown as the substrate annealing temperature was increased.

A comparison of the TPD data Fig. 3.2 with the LEIS data shown in Fig. 3.9(a) is shown in Fig. 3.10 and enables us to make conclusions about the nature of the Li film as the temperature is increased above 300 K. To evaluate the amount of Li left on the surface as measured by TPD after annealing, we used the onset of desorption and the flux-corrected TPD areas. Onset temperatures of 522, 583, 711, 772 and 925 K corresponded to coverages of $\theta_{Li} = 0.06, 0.13, 0.26, 0.56$ and 0.77 in TPD respectively. Prior to and at 600 K, there is good agreement between the TPD data and the Li LEIS annealing plot. However, at 700 K and above LEIS indicates much more Li than does TPD, which is due to contamination that accumulates during the sequential LEIS
measurements and stabilizes surface Li. Nonetheless, we can conclude that with heating there is no significant diffusion of Li out of the deposited film into the grain boundaries or TZM subsurface regions since the LEIS signal intensities indicate Li surface layer concentrations at or exceeding those determined by Li TPD at all temperatures from 500 – 1200 K.

Figure 3.10 A comparison of the temperature dependence of the Li LEIS signals and Li TPD areas for a 5 ML Li film on TZM.

3.4. Conclusions

The thermal stability of thin Li films on two polycrystalline substrates, pure molybdenum and a molybdenum alloy (titanium zirconium molybdenum, TZM), has been studied under UHV conditions using a multi-technique surface science approach. Li TPD results show that Li in films thicker than one monolayer thermally desorb in a peak at 560-600 K. Li monolayer films on both substrates show stronger Li-Mo bonding than
Li-Li bonding in the thicker Li films, however Li in the monolayer, in contact with the substrate metal, begins to desorb at only slightly higher temperatures. On Mo, the Li monolayer is characterized by a broad thermal desorption feature from 600 - 850 K and a high temperature tail with Li remaining on the surface until 1500 K. The Li monolayer on TZM shows a prominent and well-defined desorption peak near 700 K and a shoulder near 1000 K, with Li remaining on the surface until 1100 K. These results show an unusually high thermal stability of Li films on a Mo(poly) substrate compared to TZM(poly), single-crystal Mo(110) surfaces, and other metal substrates. This could be caused by the interactions of Li with specific low coordination Mo sites on high Miller index planes exposed on the polycrystalline substrate or by Li interactions with oxygen at interfacial sites or grain boundaries. No irreversible intermixing of Li with either the Mo or TZM substrates was observed, as evidenced from studies of TPD and surface spectroscopy. Evidence in LEIS was found for 3D-clustering in Li films at or exceeding one monolayer on TZM when heated at temperatures of 300-400 K. Li AES and Mo AES attenuation measurements were roughly consistent with Li film growth with non-ideal layering, and some clustering in thicker layers, at room temperature, and LEIS also shows no exposed Mo or Ti atoms for Li films thicker than 2 ML on the TZM substrate. These results provide benchmark thermal stability data that will assist in understanding Li film behavior on high-Z substrates at temperatures that may be found in fusion devices. In particular, such data on the Li monolayer stability on these substrates is important for “dry-out” conditions and rewetting phenomena.
References


Chapter 4

Thermal Stability of Oxidized Ultrathin Li films on TZM for Plasma Facing Components

4.1 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 was shown to improve plasma performance and confinement time in experiments in TFTR [1], T11-M [2], FTU [3], CDX-U [4], LTX [5], EAST [6], and NSTX-U [7]. Although the reasons for this are currently not well understood, these improvements have been attributed to lowered H recycling [8,9] and suppressed edge localized modes (ELMs) [10]. 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 poses a potentially problematic issue because Li is likely to react with background or residual gases (e.g. H$_2$O 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 even potentially form new compounds with very different chemical and physical behavior than metallic Li. Understanding erosion, redeposition, hydrogen retention, and thermal stability of oxidized Li films is important for advancing Li PFC applications.

In NSTX the base vacuum pressure was about 1 x 10$^{-8}$ Torr, and this rose to about 3 x 10$^{-6}$ Torr for 100-600 s or possibly longer during intershot intervals. Prior lab-based
studies showed that Li surfaces are readily oxidized by 20-40 L (Langmuir; 1x10^6 Torr s) of water vapor (or CO about four times slower).[11] Li oxidation was also observed using in-vacuo measurements of Li-coated samples of PFCs in LTX using the Materials Analysis Particle Probe (MAPP). [12]

Studies of oxidation of bulk Li and Li films has also been motivated by applications in electrochemistry and catalysis and laboratory experiments have measured the oxidation rate and identified the intermediates and reaction products formed. [13–18] Hoenigman and Kiel [13] found that exposure of polycrystalline Li films to 100 L O\(_2\) produced an O 1s peak at 530.6 eV binding energy (BE) in X-ray photoelectron spectroscopy (XPS) assigned to Li\(_2\)O formation. Oxidation of the Li film proceeded more slowly with water and produced two O 1s peaks in XPS: one at 530.6 eV BE assigned to Li\(_2\)O accounted for 85% of the oxygen at the surface, and one at 533.5 eV BE assigned to lithium hydroxide (LiOH) accounting for the rest and arising from H\(_2\)O dissociation on the film. A later study using O\(_2\) and H\(_2\)O as oxidants established that a monolayer of Li\(_2\)O was formed on the surface regardless of oxidant with low amounts of hydroxide at the surface from H\(_2\)O oxidation. [19] This oxide monolayer did not passivate the surface, and oxidation using O\(_2\) continued up to 1600 Å. Another study looked at the effect of depositing Li films on an O-Ni(110) surface which was oxidized by preadsorbed oxygen. Here, the Li was found to reduce the oxidized Ni substrate. [20] Studies on Li film oxidation can also be compared to previous investigations of the formation and thermal stability of other metal oxide films such as SiO\(_2\)[21,22], TiO\(_2\) [23–27]. FeO\(_x\) [28], Al\(_2\)O\(_3\) [29] and MgO [30].
This chapter presents results from surface science studies of the oxidation of Li films coated on a “high-Z” substrate (containing elements with a high atomic number (Z)) of a titanium-zirconium-molybdenum (TZM) alloy and the thermal stability of the oxides formed in ultrahigh vacuum (UHV) vessels. These investigations used a multitechnique approach of temperature programmed desorption (TPD), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and low-energy ion scattering (LEIS) for surface characterization. These experiments extend the prior research by Skinner et al. [11] 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 plasma facing components subject to high temperatures found in fusion devices such as NSTX and LTX.

4.2 Experimental Section

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 base pressure of the surface analysis chamber prior to experiments was $4 \times 10^{-10}$ Torr and rose to $1-2 \times 10^{-9}$ Torr during experiments. The chamber was equipped with a 3 kV Kimball Physics (EFG-7F-4243) electron gun for AES, a PHI (04-303) differentially pumped ion gun for LEIS and Ar\(^+\) ion sputtering, a PHI (10-360) spherical capacitive analyzer (SCA) for AES, LEIS, and XPS, a PHI (04-548) X-ray source that can generate either Al K\(\alpha\) or Mg K\(\alpha\) radiation for XPS, and a UTI 100C quadrupole mass spectrometer (QMS) for residual gas analysis and TPD.
The titanium-zirconium-molybdenum (TZM) alloy sample (Goodfellow, Huntingdon, England) had a bulk composition of Mo:Ti:Zr of 99:0.5:0.1 at.%. 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 sample back and attached to larger Ta rods connected to Cu rods using Cu-Be connectors. Current was passed through this assembly using a DC power supply for resistive heating of the sample to temperatures of 1900 K. 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 at 310 K to reduce O, C and S contamination to minimum levels, heating at 1500 K in 5 x 10\(^{-7}\) Torr O\(_2\) 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 heated to 1900 K for 5 s to retain cleanliness. AES of the cleaned TZM substrate before each experiment indicated a surface composition of 83.1% Mo, 1.8% Ti, 1.5% O and 13.7% C, with no Zr detected.

Li films were deposited on the TZM substrate by physical evaporation from a commercially available dispenser (SAES Inc.) Li getter source. 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 via TPD measurements. Oxidation was carried out by backfilling the UHV chamber with O\(_2\) (Matheson ultra-high purity 99.99% O\(_2\)) by using a variable leak valve attached to a gas handling line connected to a lecture bottle. Exposures reported have not been corrected for ion gauge sensitivity.
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 939.2 eV. All binding energies (BE) for XPS were referenced to the Mo 3d\(_{5/2}\) peak at 227.7 eV BE. \[31\] 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 3d\(_{5/2}\) peak at 227.7 eV. XPS spectra herein were acquired using Mg K\(\alpha\) X-rays at 1253.6 eV. Fitting and decomposition of the XPS peaks were done using the CasaXPS program utilizing a mixed Gaussian-Lorentzian peak shape and Shirley background subtraction for the baseline.

4.3 Results and Discussion

4.3.1 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 (1 nm) or 5 ML (1.5 nm) Li films were deposited, with the amount of Li calibrated by TPD. Oxidation of the Li film was subsequently performed by exposing the film at 310 K to 20 L O\(_2\) (1 x 10\(^{-7}\) Torr O\(_2\) for 200 s), and these post-oxidized Li films are herein referred to as LiO\(_x\) films.

4.3.2 TPD of LiO\(_x\) Films

A Li (7 amu) TPD trace from a LiO\(_x\) film formed by oxidation of an initial 5 ML Li film is shown in Fig. 4.1a. No appreciable Li multilayer TPD peak was observed, which from prior experiments on clean Li films occurs near 600 K \[32\], and this indicates
that the Li film was completely oxidized by the procedure utilized. The LiO\textsubscript{x} film was stable until 620 K, after which decomposition leads to three distinct Li desorption features, with peaks at 860, 990, and 1220 K. The last trace of Li from this LiO\textsubscript{x} film was not fully desorbed from the TZM surface until 1400 K.

Fig. 4.1 shows three additional Li TPD curves: (b) from a post-oxidized 3.5 ML (1 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 total coverage of the oxidized film on which there would be more influence by the TZM substrate.

![Li TPD Curve](image)

Figure 4.1 Li TPD (amu=7) after (a) 20 L O\textsubscript{2}/5 ML Li/TZM at 330 K; (b) 20 L O\textsubscript{2}/3.45 ML Li/TZM; (c) 880 K annealing of oxidized 3.45 ML Li film; (d) 1070 K anneal of oxidized 3.45 ML Li film. 20 L of O\textsubscript{2} = 1 \times 10^{-7} \text{Torr for 200 s.}
Additional TPD experiments (not shown) show that the peaks at 990 and 1220 K grow with increasing Li precoverage, while the 860 K peak saturates for thicker LiO\textsubscript{x} films. To help assess if the peaks observed arise from distinct phases, annealing to two different temperatures was carried out. The 880 K anneal removed the 860 K shoulder leaving the other two desorption states, while the 1070 K anneal left only the peak located at 1160-1220 K. It was observed that the preannealing of the films did not significantly modify the maximum desorption temperatures for the different peaks observed, indicating that Li desorbs from decomposition of the LiO\textsubscript{x} film through at least three distinct phases at well-defined temperatures. No coincident desorption of Li with either O or O\textsubscript{2} was observed in TPD, indicating that lithium oxide(s) in these films decomposes at temperatures below those needed for developing appreciable vapor pressure and desorption. The decomposition mechanism leads to retaining of all the oxygen at the TZM surface after Li desorption as was observed later in XPS measurements. TPD was used to obtain an analysis of 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 with a different Li QMS sensitivity than Li atoms) of some Li-containing desorbing species, e.g., LiO.

There are several potential explanations for the origins of these three Li desorption peaks. One is that the peaks arise from decomposition of different lithium oxide compounds that coexist either after oxidation at 310 K or are formed during heating of the films during TPD. This is quite plausible since lithium is known to form multiple
compounds with oxygen, i.e. Li₂O, Li₃O₂, α,β-LiO, Li₂O₂, and LiO₂, as reported for the Li-O phase diagram. [33] Decomposition of these compounds will occur at different temperatures and desorb Li at different temperatures in reaction rate-limited peaks. In this case, the subsequent desorption of Li during heating reduces the Li:O stoichiometry of the film during TPD. This could also lead during TPD to formation of new compounds that have different decomposition temperatures. One other factor is the potentially important 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 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 (LiₓMoOᵧ) compound. A prior report observed that Li₂O reacted with molybdenum and TZM to form Li₄MoO, which decomposes upon heating to liberate Li₂MoO₄ in the vapor phase. [34] The evaporation of lithium molybdate (Li₂MoO₄) and its presence in the vapor phase had been observed previously. [35,36] To assess the role of lithium molybdate desorption and decomposition 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. 4.2. 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, Li₃O₂, LiO, Li₂O₂ and LiO₂), pure molybdenum oxide phases (Mo, MoO, MoO₂, and MoO₃), and the binary oxide phase, Li₂MoO₄ (LiMo, Li₂Mo, Li₃O, LiMoO, LiMoO₂, LiMoO₃, Li₂MoO, Li₂MoO₂, Li₃MoO and
Li₂MoO₂). The known fragmentation pattern for Li₂MoO₄ is Li⁺, Li₂MoO₄⁺, MoO₂⁺, MoO₃⁺, Li₂O⁺ and LiO⁺ with a ratio of 100:10:2.5:2.3:1.0:0.5. [35] 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, we assign the Li peak at 1159-1220 K to arise at least in part from a cracking fragment due to desorption of Li₂MoO₄, which is desorbed in a peak at 1196 K, with an onset at 1092 K, as indicated in Fig. 4.2 (along with other signals not shown) from Mo, Li₂Mo, MoO, MoO₂, MoO₃, LiMoO₃, Li₂MoO, Li₂MoO₂, Li₃MoO and Li₃MoO₂. Another peak at 1182 K was observed for signals corresponding to LiMoO and LiMoO₂. Li₂O a fragment that had been prior observed for lithium molybdate ionization, did not yield a signal. On Mo(100), only a signal for LiO (21 amu) was observed in TPD for any of the LiₓOᵧ masses monitored as listed above. The LiO is likely both a desorption product from a pure lithium oxide phase and mass fragment coming from the desorption of a binary oxide phase such as the lithium molybdate that was observed. This is assumed to be the case because the LiO TPD line-shape mirrors that for the high-temperature Li TPD with a peak maxima at 1196 K until the other mass fragments that came from the binary oxide phase for Mo(100). We note that this peak appears on Mo(100) at 1196 K which is similar in temperature to that on TZM at 1159-1220 K, which supports concluding that the same oxide phases were formed on these two substrates.
Figure 4.2 TPD signals of multiple masses after oxidation of 5 ML of Li on Mo(100). Masses followed in amu where, Li=7, LiO=23, Mo=96, MoO=112, MoO$_2$=128 (not shown), MoO$_3$=144, LiMoO=119 (not shown), LiMoO$_2$=135, LiMoO$_3$=141 (not shown), Li$_2$MoO=126 (not shown), Li$_2$MoO$_2$=142, Li$_2$Mo=109, Li$_3$MoO=131 (not shown), Li$_3$MoO$_2$=147 (not shown).
4.3.3 XPS of Annealed LiOₓ Films

XPS was utilized to characterize the chemical nature of the oxidized 5 ML Li film and TZM substrate at 310 K and the changes that occurred after heating. XPS spectra for the Mo 3d, Li 1s and O 1s regions are shown in Fig. 4.3a. The Li 1s peak is partially obscured by the overlapping Mo 4s peak of the substrate. In the bottom curves of Fig. 4.3a, the Li 1s peak for the oxidized Li film appeared at 55.6 eV binding energy (BE) and the O 1s spectra show peaks at 529.5 and 532.1 eV BE. The Li 1s peak BE agrees with a prior report of 55.8 eV for oxidized Li. [13] We can assign the two O 1s peaks to lithium monoxide (Li₂O) and lithium peroxide (Li₂O₂), respectively. [37,38] In studies of the interaction of Li with solid oxygen, Qiu et al. assigned O 1s peaks from Li₂O at 530-530.5 eV, Li₂O₂ at 532.5-533 eV, and the superoxide (LiO₂) at 534.5 eV. [37] Prior work has also assigned a peak at 533.5 eV to OH species [13], but we don’t favor this assignment in our work because this peak is still present at temperatures higher than those where water or hydrogen desorption was observed by TPD. Under standard state conditions, Li₂O₂ formation (ΔG = -136.5 kcal/mol) and Li₂O formation (ΔG = -134 kcal/mol) are similarly thermodynamically favorable. [37] The O 1s spectra in Fig. 4.3a do not show a clearly identifiable peak at 534.5 eV from a superoxide component after Li oxidation, and so we did not include fitting this possible component. The Mo 3d spectra contain the spin-orbit split 3d₅/₂ and 3d₃/₂ components and at 310 K are fit well using only metallic molybdenum peaks indicating that Mo was not oxidized. This indicates that the interfacial oxygen from the LiOₓ film bonds at the surface more like a chemisorbed layer rather than incorporating the Mo to form an ionic or “oxidic” Mo environment under

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these conditions. Attenuation of the Mo 3d$_{5/2}$ peak from clean TZM by 27.4% upon formation of the 5 ML LiO$_x$ film was observed.

Upon heating the LiO$_x$ film, the Li 1s peak decreases in size significantly by 1070 K and disappears by 1400 K, consistent with Li desorption observed in TPD. However, the O 1s peak intensity is constant at temperatures up to 1070 K, confirming that the LiO$_x$ film on TZM primarily decomposes upon heating as opposed to evaporating. 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 temperatures of 1090-1400 K due to desorption of species such as LiO, MoO$_3$, or Li$_2$MoO$_4$ species.

As seen in Fig. 4.3a, no changes occur in the Mo 3d line shape or peak intensity for heating to 680 or 880 K. However, upon annealing to 1070 K, changes occur and the Mo 3d spectra can be decomposed into three components, giving three Mo 3d$_{5/2}$ peaks: metallic Mo(0) at 228 eV BE, Mo(IV) at 229.5 eV, and Mo(VI) at 233.2 eV, the latter two due to oxidized Mo compounds. A zoomed-in view of the Mo 3d XPS spectrum at 1070 K is shown in Fig. 4.3b. with both oxides composed of 15% of the data envelope. At this temperature, a chemical reaction occurs between the LiO$_x$ film and the Mo in the substrate, presumably through place exchange and/or incorporation of oxygen into the top Mo layer to form oxidized Mo compounds [39], including formation of Li$_4$MoO$_5$ [34,40] The Mo(IV) and Mo(VI) peaks disappear after heating further to 1400 K, consistent with our TPD data indicating desorption of species such as MoO$_3$ or Li$_2$MoO$_4$ at 1070 K-1400 K. The Mo 3d signal recovered to 95.8% of its original value after heating to 1400 K due to desorption of Li and oxygen, but even heating to 1800 K did not remove all from the
A prior study involving oxidation of Mo(110) at 1000 K found desorption signals for MoO$_3^+$ and MoO$_2^+$ at 1400-1600 K in TPD. [22] From the results of this study, MoO$_3$ monomers and dimers were believed to desorb from thick films at 1400 K and from a monolayer at 1600 K. This does not agree with our experimental TPD results in which MoO$_3$ species desorb at 1200 K leaving more metallic Mo at the surface. Therefore, the MoO$_3$ formed is coming from the lithium molybdate phase which decomposes earlier than molybdenum oxides. Annealing to 1800 K leaves a TZM substrate with primarily metallic Mo 3d peaks with an O 1s peak at 530.1 eV BE due to diffusion of oxygen.

The Li 1s intensity (peak area) increased by 20% from its original value upon heating from 310 to 680 K, (which coincides with conversion of the Li$_2$O$_2$→Li$_2$O + O$_2$). The Li 1s intensity is then 80% of its original value when the film is annealed to 880 K, and then 43.2% of its original value at 1070 K relative to the initial Li signal intensity at 310 K and is eliminated at 1400 K. The increase in the Li 1s peak may arise from a less rough film or a structural change, and the decrease at or above 880 K 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 Li:O stoichiometries since very large changes in these intensities were observed previously [11] during oxidation of solid Li. These changes may occur due to changes in Li density, mean free path for inelastic scattering, and in intensities of satellite features (shake up and shake off processes) that affect the main line intensity.

As the LiO$_x$ films are annealed from 310-880 K, the O$_2^-$ component peak area under the O 1s data envelope becomes larger with a concurrent decrease in the O$_2^{2-}$ peak.
area from the conversion of peroxide, $O_2^{2-}$ species to oxide, $O^{2-}$ species due to the low stability of the peroxide. Peroxide conversion to oxide has been observed in other systems such as MgO films on Mo(100). [30] The O 1s peaks after heating to 1070 K or higher were not decomposed into components since they are likely to be multiple oxygen species and we have no clear structure in the peak to guide us. There is likely either an interfacial $Li_2O$ film on an oxidized molybdenum surface, or $Li_4MoO_5$ species. After annealing to 1400 K, the disappearance of the $Mo(IV)$ and $Mo(VI)$ peaks in the Mo 3d spectra shows that no oxygen is chemically bound to molybdenum. The oxygen species retained at these temperatures is bound to the grain boundaries, diffused into the subsurface region of the substrate or arising from $TiO_2$ or $ZrO_2$. The O 1 signal decreases in intensity further upon annealing to 1800 K as mentioned earlier either due to diffusion of O atoms into the bulk outside the depth resolution of XPS or due to desorption of oxygen.
The Li/O ratio as the LiO$_x$ film is annealed at the indicated temperatures is shown in Fig. 4.4. The ratio was calculated using the peak area intensity of Li and O, normalized to atomic sensitivity factors. 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 O1s spectra that indicate a 3:1 ratio of Li$_2$O to Li$_2$O$_2$. The Li/O ratio initially rises as the film is annealed to 680 K due to interconversion of the peroxide to the oxide. It is known from TPD that the no Li begins to desorb at this
temperature. 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. At this temperature, both lithium and molybdenum oxides coexist together.

![Graph showing the effect of temperature on the Li/O XPS ratio of the LiOₓ film after 20 s anneals.](image)

Figure 4.4 The effect of temperature on the Li/O XPS ratio of the LiOₓ film after 20 s anneals.

It is noteworthy that XPS of the LiOₓ films thermally annealed at 1070 K shows that the Mo atoms on the TZM substrate are oxidized by reaction with Li₂O. A similar interaction was observed for SiO₂ films supported on Mo(100).[21] When these films were annealed to 1400-1700 K, SiO₂ was reduced to volatile SiO. The molybdenum oxides are more volatile than Mo and begin to evaporate at 1400 K. There were no measurable changes in the Mo 3d XPS spectra for LiOₓ anneals at T <1070 K suggesting no interaction with the substrate at lower temperatures.
4.3.4 LEIS of LiO\textsubscript{x} Films

Low energy ion scattering (LEIS) spectra of the clean TZM substrate and Li and LiO\textsubscript{x} films are shown in Fig. 4.5a. The bottom curve shows the Mo, Ti, and O peaks characteristic of the TZM surface. Zr may be present but is not resolvable from Mo in these spectra. Depositing 5 ML of Li on the surface eliminates the Mo and Ti peaks, but causes a characteristic change in the background signal, and cause the appearance of a Li signal at 390 eV. The deposited Li film was pure and no oxygen LEIS signal was observed. The absence of any substrate signals (Mo or Ti) indicates that Li wets the surface and there was no large 3D clustering that lead to uncovered TZM surface regions. Subsequent oxidation of the Li film at 310 K by a 20 L O\textsubscript{2} exposure produced the curve labeled as “LiO\textsubscript{x}”, in which the Li signal significantly attenuated and an O peak appeared at 1090 eV. The LiO\textsubscript{x} film also completely wets the TZM surface, and no de-wetting of the LiO\textsubscript{x} film occurred prior to evaporation of Li and heating to 1000 K. The small Li signal after oxidation is expected from the solid crystal structure of Li\textsubscript{2}O which is an antifluorite structure with a low-index surface composed of oxygen atoms with Li atoms buried in the second layer.[41] The Li LEIS peak never reappears after subsequent heating as indicated. The O LEIS intensity increases with annealing temperature, and this is shown quantitatively in Fig. 4.5b. The O LEIS intensity slowly increased from 300-700 K, prior to Li desorption, due to an increased concentration of O in the surface layer that could arise from diffusion of additional oxygen to the surface layer or changes in the structure of the surface compounds. There is a rapid increase in the O LEIS after heating above 900 K due to Li desorption from the surface. This desorption process likely reveals oxygen at the TZM interface and an increase in the O concentration. A Ti LEIS peak
appears at 900 K just after the first desorption state at 860 K that was observed by TPD. The first desorption at 860 K (See Fig. 4.1) either uncovers some of the TZM substrate or causes a structural change such as clustering of the oxide film which could lead to exposure of Ti atoms on the surface. Ti as opposed to Mo is first observed from Li desorption presumably due to oxygen-induced segregation and formation of TiO$_2$. The Mo substrate signal was not observed until 1000 K after the LiO$_x$ films decompose and Li desorbs (see Fig. 4.1). Further oxygen-induced segregation of Ti to the surface was observed after completion of the annealing measurements. The calculated Ti/Mo ratio for TZM is 0.23 which increases to 1.02 for the case of the LiO$_x$/TZM surface heated to 1700 K.

Li and Mo are also both oxidized at 1100 K, as shown by XPS. When all Li has been desorbed, the O LEIS signal is highest at 1500 K due to the large concentration of oxygen at the TZM surface. The decrease in the O LEIS signal at 1700 K is due to desorption of oxide species or diffusion of O atoms into the bulk.
Figure 4.5 (a) LEIS study of the thermal stability of the LiOₓ films formed from 20 L O₂/5 ML Li/TZM. (b) Oxygen LEIS signal as a function of temperature for the annealed LiOₓ films.
The overall chemistry occurring on the post-oxidized surface is:

Li monoxide formation (310 K, 20 L O₂): \(4\text{Li (s)} + \text{O}_2 (g) \rightarrow 2\text{Li}_2\text{O (s)}\) \hspace{1cm} (4.1)

Lithium peroxide can be formed through these two channels:

Li peroxide formation: \(4\text{Li (s)} + 2\text{O}_2 (g) \rightarrow 2\text{Li}_2\text{O}_2 (s)\) \hspace{1cm} (4.2)

Li peroxide formation: \(2\text{Li}_2\text{O (s)} + \text{O}_2 (g) \rightarrow 2\text{Li}_2\text{O}_2 (s)\) \hspace{1cm} (4.3)

Li peroxide decomposition (310 K < T ≤ 680 K):

\(2\text{Li}_2\text{O}_2 (s) \rightarrow 2\text{Li}_2\text{O} (s) + 2\text{O}_2 (g)\) \hspace{1cm} (4.4)

Li₂O decomposition and Li desorption (T= 620 (onset) - 990 K (T_p)):

\(\text{Li}_2\text{O (s)} \rightarrow \text{Li} (g) + \text{O (on Mo and Ti)}\) \hspace{1cm} (4.5)

The molybdenum oxides formed at 1070 K can occur through either these reaction channels:

\(\text{Li}_2\text{O (s)} + \text{Mo (s)} \rightarrow \text{MoO}_3 (s) + \text{MoO}_2(s) + 2\text{Li (s)}\) \hspace{1cm} (4.6)

\(\text{Li}_2\text{O (s)} \rightarrow 2\text{Li(s)} + 1/2\text{O}_2 (s) \text{ (ad on Mo)}\) \hspace{1cm} (4.7)

\(\text{Mo(s)} + 4 \text{ Li (g)} + 1/2\text{O}_2 (g) \rightarrow \text{Li}_4\text{MoO}_5 (s)\) \hspace{1cm} (4.8)

\(\text{Li}_4\text{MoO}_5 (s) \rightarrow \text{Li}_2\text{MoO}_4(g) + \text{Li}_2\text{O(g)}\) \hspace{1cm} (4.9)

The peak observed at 1200 K could be due to decomposition of lithium molybdate or Li-oxide desorbing from a molybdenum oxide surface. The reaction of lithium-oxide with a TZM substrate has been observed to form \(\text{Li}_4\text{MoO}_5\) in the solid phase \[42\]

We can also not rule out the formation of Lithium Titanate:

\(2\text{Ti(s)} + 4\text{Li} (s)+ 3\text{O}_2 (g) \rightarrow 2\text{Li}_2\text{TiO}_3 (s)\) \hspace{1cm} (4.10)
4.3.5 Li Adsorption on O/TZM

In these experiments, a 20 L O2 exposure was given on TZM at 310 K prior to deposition of Li films. Based on XPS, this forms a chemisorbed oxygen layer and does not lead to extensive oxidation of the TZM. Molecular oxygen is known to dissociate on molybdenum to form adatoms. [43] The surface composition of the TZM is 83% Mo, and so the surface can be roughly approximated to be primarily composed of Mo atoms.

Fig. 4.6a shows LEIS spectra of the surface before and after chemisorption of O atoms. The ion scattering spectra for the clean TZM prior to oxygen exposure has mainly peaks from Mo, Ti, O and C. Exposure of the TZM to 2 L of oxygen leads to a disappearance of the C peak, a growth in intensity of the O peak by a factor of 4, and an attenuation of the Mo and Ti peak. The Ti/Mo LEIS peak ratio also increases from 0.14 to 0.25 which suggests more Ti atoms are on the surface after exposure. Subsequent O2 exposure from 2 to 20 L does not lead to any significant growth in the O peak as seen in Fig. 4.6b. There are also no reportable changes in the Mo and Ti peak intensities after 5 to 20 L oxygen exposure. The existence of Mo and Ti peaks in the LEIS spectra after saturation exposure of O2 indicates that not every Mo and Ti surface atom is bonded with O-atoms. XPS measurements of the TZM after 20 L O2 exposure confirm that the Mo atoms are not oxidized and their interaction is with chemisorbed O atoms due to the presence of only Mo 3d metallic line shapes. We assumed that Ti was oxidized although we did not follow the Ti 2p core level. At 20 L room temperature exposure, the TZM surface would be covered with 1.1-1.5 ML of O atoms using previous reports on the saturation coverage on single crystal and polycrystalline Mo. [44,45] The Auger spectra indicates 81.4% Mo, 6.1% Ti and 12.5% O on the surface. This latter value represents an
upper limit on the oxygen concentration since this assumes a homogeneous bulk concentration. The TZM surface created by this exposure is referred to as O/TZM.

Figure 4.6 (a) LEIS measurements of the surface oxidation of a TZM substrate (b) LEIS peak area intensity changes as a function of oxygen exposure.
4.3.6 TPD and XPS Results

Pure Li films of varying thicknesses were deposited on the O/TZM surface. Li TPD curves for these films are shown in Fig. 4.7. The Li coverages indicated in the figure were obtained based on the Li dose time, which had been previously calibrated for the Li evaporator using TPD from a metallic Li film. However, calibrating based on the Li evaporator dose time did not match the TPD areas obtained from Li on O/TZM. This was discovered when the Li TPD signal for each film deposited on O/TZM was integrated and compared it to a 1 ML coverage of Li on clean TZM and is due to the differing sensitivities of the QMS for Li coming from multilayer Li films relative to that from the decomposition and evaporation of Li-oxides. We have therefore provided both the coverage obtained from a prior calibration of the evaporator and that coming from comparing the integrated Li TPD areas from O/TZM referenced to a 1 ML TPD area in parentheses henceforth.

The lowest Li coverage, $\theta_{Li}=0.25 \ (0.08)$, leads to the formation of a peak at 1196 K. At this coverage, the Li is in an O-rich environment with Ti and Mo atoms present. The desorbed Li is due to desorption of interfacial Li-oxide species or binary oxide phases (Li$_x$MoO$_y$ if we place it in context of the post-oxidation experiments. With increasing amounts of Li deposited, a new Li TPD peak appeared at 1157 K. After deposition of $\theta_{Li}=1.0(0.66)$ an additional peak appeared at 923 K, and after deposition of $\theta_{Li}=2.0(1.01)$ another peak at 793 K appeared and the 925 K peak decreased in size. Deposition of $\theta_{Li}=3.0(1.92)$ lead to the formation of the Li multilayer and all three high temperature Li peaks at 812, 934 and 1157 K. A Li multilayer is formed for large depositions of Li since there is insufficient oxygen available to oxidize all the deposited
Li. However, the TPD results does not reveal information on what compounds are initially present after oxidation at 310 K.

Figure 4.7 A series of Li-TPD curves from O/TZM at different coverages. The coverages in the figure show the amount of Li deposited based by calibration with the evaporator. The calibration by TPD using a 1 ML TPD are placed in parentheses. The coverages, $\theta_{Li}$ (ML) studied are: 0.25(0.08), 0.5 (0.23), 1 (0.66), 2 (1.01), 3 (1.92), 4 (2.27) and 5 (3.04).

Fig. 4.8 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 Li and LiO$_x$ films, we obtain useful information on the modification of the thermal stability of Li films due to the presence of surface oxygen contamination on 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 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 is observed for the 4 ML Li film. Using the desorption peak temperature of the first peak above that of the Li multilayer, indicates 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 changes to 233 K for 1 ML Li. For the thicker films, surface oxygen contamination of the TZM substrate does not affect the thermal stability of the bulk of the Li film and Li primarily desorbs in the unaltered Li multilayer peak. However, the Li monolayer that ultimately remains upon heating desorbs 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.
Figure 4.8 A comparison of TPD curves of Li on TZM and O/TZM. The amount of Li and the corresponding area as referenced to 1 ML of Li on clean TZM which is indicated in bracket. Estimated coverage is to be 1.1-1.5 ML of O atoms on TZM.

XPS studies were done to examine chemical modifications that occur when Li is deposited on an-oxygen covered TZM surface and these results are shown in Figure 4.9. The Mo 3d spectra shown in the left panel are unchanged after 20 L O\textsubscript{2} exposure and showed only metallic components indicating that Mo was not oxidized. As shown in the right panel by the O 1s spectra, the initial TZM sample retained some oxygen, assigned to O chemisorbed on Mo or Ti, or to be due to the formation of TiO\textsubscript{x} either on the surface or
in grain boundaries. The O 1s peak shifts 0.2 eV to lower binding energy after 20 L O2 exposure from the high coverage of chemisorbed oxygen at the surface. These observations are consistent with previous studies showing that very high (2000 L) O2 exposures on Mo at very high temperatures of 900-1200 K were required to form oxides such as MoO, MoO2 and MoO3. [43]

Results of the XPS characterization of the surface 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 Figure 4.9. Li deposition caused no new peaks or peak shifts in the Mo 3d spectra. The Mo 3d5/2 peak area drops to 93.7% of its original value from the clean TZM after 20 L oxygen exposure to form the chemisorbed O atoms on the TZM. Further addition of a 0.5 ML Li film reduces it to 89.3% of its signal intensity and 5 ML Li to 61%. The Li 1s peak appears at a position indicative of oxidized Li state. From the O 1s spectra, there is a +0.4 eV positive shift in the binding energy when 0.5 ML of Li is deposited on the O/TZM. The deposited 0.5 ML Li on the O/TZM is in an oxygen rich environment. This shift arises from formation of a submonolayer of interfacial lithium oxide containing either or both Li-O-Mo or Li-O-Ti bonding at the surface. For the 5 ML Li film, the O 1s peak has nearly the same binding energy indicating the presence of the interfacial oxide. The calculated Li/O ratio for the 5 ML film is 2.51 indicating an Li-rich environment while that for the 0.5 ML film is 0.94 which is O-rich.
Figure 4.9 XPS of 0.5 and 5 ML Li films on O/TZM at 310 K showing the Mo 3d, Li 1s and O 1s core-level signals.

In separate experiments, 0.5, 1, and 5 ML Li films deposited on O/TZM at 310 K were annealed to various temperatures and probed by XPS as shown in Fig. 4.10. In Fig. 4.10a, for 310 K adsorption of 0.5 ML Li on O/TZM there a binding energy shift of +0.28 eV shift which is similar to the +0.36 eV shift observed in prior experiments. Annealing to 650 K and 850 leads to a reduction in the binding energy by – (0.2-0.3 eV) due to changes in the interfacial oxide structure. From TPD measurements in Figure 4.7, we see that the 0.5 ML Li on O/TZM does not desorb at this temperature. After a 1400 K anneal, Li is fully desorbed. The oxygen observed in the O 1s signal is due to oxygen
that has diffused into the subsurface region or grain boundaries or chemically bound to Ti or Zr atoms.

The O 1s spectra for the 5 ML Li on O/TZM case is shown in Fig. 4.10c. Annealing the sample to 500 K causes a 0.2 eV shift in the O 1s peak. Annealing to 680 and 900 K causes substantial desorption of Li from the film and shifts of -0.7-0.9. This creates an interfacial oxide but the composition is not clear since the O 1s peak for Li$_2$O has a similar BE. For a 1050 K anneal the O 1s line shifts by 0.5 eV which likely due to the formation of molybdenum oxides on the surface.
Figure 4.10 Changes in the O 1s signal for (a) 0.5 ML, (b) 1 ML Li and (c) 5 ML on O/TZM during annealing of the films.
**Li on Oxygen covered TZM**

Interfacial oxide (310 K): \[ \text{Li (s)} + \text{O (ad)} + \text{Ti (s)} + \text{Mo (s)} \rightarrow \text{Li}_2\text{O (s)} + \text{Ti (s)} + \text{Mo (s)} \] (4.11)

Li₂O decomposition and desorption (\(T_p=812\) and 934 K): \[ \text{Li}_2\text{O (s)} \rightarrow \text{Li (g)} + \text{O (ad)} \] (4.12)

Li₅MoO₇ decomposition/desorption (\(T_p =1157\) K): \[ \text{Li}_5\text{MoO}_7 (s) \rightarrow \text{Li}_2\text{MoO}_4(g) + \text{Li}_2\text{O(g)} \] (4.13)

4.4 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 (H₂O 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 4.3.2 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. 4.11. In the absence of oxygen, as shown in the bottom 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. As shown in the middle TPD curve, Li films subjected to extensive post-oxidation to form a Li₂O/Li₂O₂ mixed oxide film are more thermally stable and Li does not begin to desorb until 620 K with peak maximums at 860, 990 and 1220 K. Oxidation increases the onset of Li desorption by 100 K and significant Li desorption/material erosion is inhibited by 250 K. Moreover, a large fraction of the Li coating remains on the surface until oxide decomposition leads to a peak at 1220 K. The top TPD curve in Fig. 10 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 was
insufficient to oxidize the entire 3 ML Li film that was deposited (~ 0.5 ML Li desorbs in the metallic Li peak). The peaks at 812, 938 for the 3 ML Li/O/TZM are believed to be the same as the 860 and 990 K peaks that are present in the 20 L O\textsubscript{2}/5 ML Li/ TZM system. The 1155 K peak is formed at low coverages of Li and saturates with increasing thicknesses for Li/O/TZM confirming that it is an interfacial Li-oxide state. This peak overlaps with the another state, the 1220 K peak seen in post-oxidation that continues to grow with increasing Li thickness and oxygen exposure. Multiple masses where monitored by TPD but no coincident desorption of LiO was observed for Li desorbing on an oxygen-covered TZM surface.

Figure 4.11 Li QMS signals from 6.47 ML Li/TZM (bottom curve), 20 L O\textsubscript{2}/5 ML Li/TZM (middle curve) and 3 ML Li/O/TZM (top curve).
The 3 ML Li film is about 10 Å (1 nm) and the coatings used in NSTX-U are much thicker (a few microns) than this. At sufficiently high temperatures, oxygen from the bulk or grain boundaries of the molybdenum CPS system could diffuse continuously to the Li films to form lithium-oxides. This would lead to a situation where there is a liquid Li overlayer with solid Li$_2$O layer formed at the interface due to reaction with interfacial oxygen. More extensive oxidation by post-oxidation leads to higher thermal stability but increase in stability however is accompanied by a much higher melting point of the LiO$_x$ compounds (Li$_2$O mp = 1711 K; LiO mp=stays solid) than pure Li (mp = 453 K) and this has important implications for flowing liquid Li systems.

The formation of these Li-oxides can also lead to defective wetting which can affect the success of the capillary pore system (CPS) as well as change the flow properties of the liquid.

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 LiO$_x$ films as a function of temperature. Although these results are for ultra-thin 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, the implications for fusion devices are presented: (1) For a Li film oxidized by residual gases at 310 K, energetic D$_2^+$ ions will interact with a film that is composed of a mixed lithium oxide/peroxide system. Due to the presence of an additional O atom, the peroxide is expected to make more water when it interacts with the ions. This will also depend on the energy and stopping range of the ions in the film. (2) At temperatures of 680 K and higher, any peroxides formed will be converted to Li$_2$O. Li$_2$O
will be the main lithium-oxide compound interfacing with incoming deuterium particles. (3) For unusually high temperatures >1000 K, it is expected that the oxygen will be incorporated into the TZM to form molybdenum oxides and potentially titanium oxides. Depending on the stopping range of the ions in the films, deuterium implantation could also involve interactions with both molybdenum oxides and lithium oxides.

4.5 Conclusion

The thermal behavior of LiO\textsubscript{x} films prepared by either post-oxidation of deposited Li films or by the deposition of Li films on an oxygen-precovered surface was studied by using TPD, XPS and LEIS on a titanium-zirconium-molybdenum (TZM) alloy substrate under UHV conditions. These 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 5 ML LiO\textsubscript{x} 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 initially the decomposition and desorption of lithium oxide Li\textsubscript{2}O (860 and 990 K) and the subsequent decomposition of solid lithium molybdate Li\textsubscript{4}MoO\textsubscript{5} and evaporation of Li\textsubscript{2}MoO\textsubscript{4} (1220 K). The onset for Li desorption from the LiO\textsubscript{x} films is 100 K higher than that from metallic Li films, demonstrating the higher stability of the oxides. XPS showed the formation of a mixed oxide phase of lithium monoxide Li\textsubscript{2}O and lithium peroxide Li\textsubscript{2}O\textsubscript{2} upon oxidation of the Li film at 310 K. Li\textsubscript{2}O\textsubscript{2} is thermally unstable and decomposed to Li\textsubscript{2}O when annealed to 680 K. XPS also showed that at 1070 K, Mo in the TZM substrate was oxidized to form Mo(IV) and Mo(VI) species, with at least some
presence of the lithium molybdate Li₄MoO₅. 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. LEIS experiments of the oxidized Li
films confirm the wetting of TZM by LiOₓ films at room temperature.

The deposition of sub-monolayers of Li on an oxygen-precovered TZM substrate
at 310 K lead 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.

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Chapter 5

Surface Science Studies of Sn and SnO Films Supported on Molybdenum Substrates

5.1 Introduction

Liquid metals are under consideration as plasma facing components. Lithium (Li) [1–6], tin (Sn) [7,8], lithium-tin eutectics (Li-Sn) alloy (30 at.% Li) [8–10] and gallium (Ga) [11–13] are the candidate materials chosen as liquid metals primarily based on the unique beneficial properties that each of these metals possess. The use of Li leads to lower recycling of cold D atoms back into the plasma which has been attributed to its success in improving plasma confinement parameters. As a result, it is the most widely used and studied liquid metal. However, the high evaporation rate of Li at higher temperatures will place limitations on the operating wall temperature of a functional tokamak. Ga, on the other hand, has a low melting point ($T_m=303$ K) and a wide range in which it is in the liquid state due to its high boiling point. Sn and Ga have beneficial neutron activation and transmutation properties. However, Ga has shown to be incompatible with several metal substrates due to corrosion effect especially in the presence of impurities leading to an interest in Sn which is compatible with Mo and W. [14]

Sn, in addition to its relatively low chemical reactivity and low melting point (505 K), also has a lower vapor pressure than Li expanding the operating temperature limit of the tokamak. Sn is also not expected to getter deuterium due to the volatility of SnD$_4$ which circumvents issues associated with tritium inventory balance in a fusion reactor. Sn is
therefore expected to operate under a high recycling regime. Moreover, its power exhaust capabilities have been predicted to be up to 20-25 MW/m². [15]

Although studies on Sn are beginning to gain traction, their use in a functional tokamak is still in the nascent stages and laboratory studies results on key salient properties are still absent in literature. Some investigations have looked at the deuterium retention behavior of Sn in ISSTOK fusion devices [8], its erosion/re-deposition behavior through the linear device Pilot-PSI [16], corrosion compatibility with Mo and W [14] and its secondary electron emission properties. [17] For functional reactor studies, a liquid Sn limiter has also been examined at FTU. [18] Experiments using a tin filled-CPS system at Magnum-PSI and TEXTOR have been carried out and indicated temperature enhanced sputtering and formation of a vapor cloud which was observed when Sn samples were exposed to the divertor-type plasmas of Magnum PSI at FOM. One major issue observed is that de-wetting of the liquid metal in the CPS system affected material performance and that oxide reduction by H₂ or heat treatment was pre-requisite for good wetting at moderate temperatures in Sn-Mo and Sn-W combinations. [19]

Sn if used either as a solid surface coating or in any of the engineering configurations suggested for flowing liquid metals will experience high heat fluxes due to radiative heating emanating from the plasma edge. Its utilization, therefore, in the first wall or divertor region of a magnetic fusion device will require an understanding of its thermal behavior. Also, since Sn is a high Z metal, the evaporation of Sn atoms into the plasma core could lead to cooling of the discharge, and radiative collapse consequently leading to a reduction in discharge performance. The effects of impurity on Sn is still an open question. While Sn is relative inert compared to Li, Sn could potentially form volatile
compounds with oxygen and carbon which can evaporate into the plasma. The presence of impurities can also lead to defective wetting and modify fluid flow on the substrate.

Consequently, fundamental studies on the thermal stability of Sn especially on refractory metal substrates (i.e. Mo, TZM and W) of interest are still required to accomplish a tin-filled CPS system. These investigations will provide insight into material compatibility, wetting, impact on plasma degradation and other potential benefits and limitations of Sn films in a CPS.

Sn has been studied in the surface science community using multiple techniques to examine the adsorption, growth, alloying and desorption of Sn atoms from various substrates such as Mo (100)[20], Mo(110)[21–23], Al(100)[24], Al(111)[25], Cu(111)[26], Ni(111)[27], Si(001)[28], Cu(100)[29], and Rh(111) [30] and Pd(110) [31]. The oxidation of Sn particles, thin films, and bulk samples on multiple substrates to form SnO and SnO₂ have also been subject to multiple investigations over the past 30 years [32–38]. These were for applications in catalysis, gas sensors and semiconductor devices. However, there are no studies of the thermal stability of Sn films on polycrystalline Mo and TZM or the effect oxidation on refractory-metal supported films.

This chapter will present results that will augment understanding of the wetting, alloying, heat-flux resistance and overall nuclear safety aspects of solid and liquid Sn films deposited on molybdenum substrates. The techniques used were AES, LEIS, TPD and XPS. The paper is structured in the following manner. The first section will examine and compare the thermal stability of deposited Sn films on polycrystalline molybdenum and TZM substrates. These results will provide answers with regards to the interactions
of Sn atoms with these substrates. The second section will focus on the post-oxidation of liquid Sn films using XPS at temperatures of interest in fusion devices. The oxygen is expected to come from water, carbon monoxide and carbon dioxide residual gases in the tokamak chambers. The third part of the paper looks at how Sn films will behave on an oxygen-covered TZM substrate to simulate situations where the refractory metal substrate possesses close to or over a monolayer coverage of oxygen as contamination in fusion devices. This pre-existing oxygen can come through diffusion from the bulk or O atoms trapped in the grain boundaries. These investigations will aid in understanding how solid and liquid Sn coatings will interact with molybdenum substrates of interest when interfaced with high heat fluxes.

5.2 Experimental Section

The work described herein were performed in an ultrahigh vacuum (UHV) system with the base pressure of the chamber kept at $4 \times 10^{-10}$ Torr. The structure of the chamber has been as well as aspects related evaporation procedure has been discussed earlier in other chapters. Polycrystalline samples of Mo (ESPI Metals, Ashland, OR; purity 3N8) and a titanium-zirconium-molybdenum (TZM) alloy (Goodfellow, Huntingdon, England; Mo 99/Ti 0.5/Zr 0.1) were used. Extensive details of sample preparation and cleaning both prior to UHV mounting and in UHV have been discussed in prior work.[39]

Briefly, the LEIS measurements were done using a scattering angle of $104^\circ$ with 1 keV He$^+$ ions incident normal to the surface. Each LEIS spectra was a scan that took 1 min to acquire using a 10 nA beam. No ion beam sputtering effects were observed when multiple LEIS scans were taken for submonolayer Sn films.
The Sn films were deposited by physical vapor deposition from a thermal evaporation source made in-house to allow for clean film deposition. This source was constructed by placing a Sn shot (ESPI Metals, Ashland, OR, purity 6N) into a molybdenum evaporation boat (R.D. Mathis Company, Hi Vacuum Evaporation Sources, Long Beach, CA). Two 15 mil tantalum wires are spot welded to the molybdenum evaporation boat to allow for ohmic heating. These were then spot-welded to stainless steel rods attached to a rotary electrical feedthrough. Before experiments, the Sn source was thoroughly outgassed at currents yielding temperatures lower than evaporation. TPD was used to calibrate the amount of deposited Sn. TPD was carried out using the QMS in direct line of sight with the sample surface with a linear temperature ramp of 6 K/s. Since a QMS measures the flux of desorbing particles in TPD experiments, a flux correction to account for the dependence of the QMS signal on the particle kinetic energy (desorption temperature) was applied to the QMS signal to properly determine the number of desorbing Sn atoms, and these flux-corrected values were used for the Sn film coverages reported herein. This correction was done by multiplying the received QMS signal by $\sqrt{T_{surf}}$.

For XPS analysis, all binding energies were referenced to the Mo 3d 5/2 XPS peak at 227.7 eV. The pass energy of the spectrometer was set at 50 eV for this work. At this pass energy, the Mo(3d 5/2) peak exhibited a full width half-maximum (FWHM) of 1.4 eV which we have taken as the instrument resolution. The peak position and FWHM for the tin oxide was determined by taking the Sn 3d core-level after complete oxidation of 7 ML of Sn film at 800 K for which metallic Sn contribution to the signal was negligible. The areas of the spin orbit splitting for the Sn 3d spectra for both the metal and the oxide (5/2:3/2) were maintained at 1.5. The Sn 3d peak binding energy positions and FWHMs
for the oxide and the metal were fixed for all the decomposed curves. The XPS spectra in this paper were obtained using Mg Kα X-rays at (1253.6 eV). Decomposition of the XPS peaks were done using CasaXPS, with curve fitting by using a Shirley background subtraction and mixed Gaussian-Lorentzian peak shape. The O₂ (Matheson ultra-high purity 99.99% O₂) used for film oxidation was leaked into the chamber using a Varian leak valve connected to a gas handling system attached to the chamber.

5.3 Results and Discussion

5.3.1 Thermal Stability of Ultrathin Sn Films on Mo and TZM

Sn films at different coverages were deposited on polycrystalline Mo and TZM substrates at 310 K. AES before Sn deposition on Mo detected 95.3% Mo, 4.7% O, and no C and on TZM 88.3% Mo, 2.9% Ti, 1.7% O and 7.1% C. After 6 ML Sn deposition, AES on Mo showed 66.1% Mo, 28.1% Sn, 5.9% O and no C while for 7.23 ML Sn on TZM found 74.7% Mo, 21.6% Sn, 3.9 % O and no Ti or C. Oxygen surface concentration increased after deposition due to small amounts of outgassing from the Sn evaporator source during evaporation and deposition of the film.

Sn (amu=118.8) TPD curves from Mo are shown in Fig. 5.1 for Sn film coverages of θ_{Sn} = 0.28-5.5 ML. The θ_{Sn} values indicated next to each spectrum were determined based on assignment of the 1.0 ML curve shown in Fig. 5.1 as the saturation monolayer coverage. This curve was chosen as the monolayer curve due to the saturation of the growth of the monolayer curve and the absence of a prominent or populated multilayer peak. As seen in Fig. 5.1, deposition of the smallest sub-monolayer Sn coverage at 0.28
ML gave rise to a TPD peak, \( \beta_1 \), at 1481 K (4.15 eV). This high-temperature peak is indicative of Sn-Mo binding interactions.

As the Sn coverage is increased, the \( \beta_1 \) peak temperature decreases slowly to lower temperatures, and has a final position at 1415 K (3.90 eV). The smallest coverage studied on polycrystalline Mo was 28% of a monolayer, but it is expected based on this trend that lower coverages will yield stronger interactions, leading to higher temperatures and higher desorption energies. Another low-temperature peak, \( \beta_2 \), appears at 1171 K (3.2 eV), which was assigned to Sn-Sn multilayer interactions that arises from evaporation/sublimation of metallic Sn films. This peak has been observed in earlier Sn desorption studies on Mo(110).[21] Fig. 5.1 also depicts thicker multilayers of Sn films from \( \theta_{\text{Sn}} = 1.9-5.5 \) ML. It can be the seen from this plot, that the Sn multilayer peak continues to grow as the Sn surface concentration increases with the peak demonstrating zero-order desorption kinetics at high coverages. The \( \beta_2 \) multilayer peak shows a shoulder at low temperatures for the 2.3 and 2.6 ML Sn coverage which disappears for higher coverages. The presence of this low temperature shoulder can be attributed either to the influence of the substrate on the Sn second layer leading to perturbed atoms or small amounts of alloying of the Sn with the Mo substrate. The inset in Fig. 5.1 displays the Sn QMS signal emanating from zero desorption of a thick 23 ML (6.5 nm) Sn film. The multilayer peak is shown most clearly for this film at 1270 K (3.5 eV) which matches prior reports in literature of the heat of evaporation of Sn which is 3.1 eV/atom.

[21] The bulk melting temperature of Sn is at 505 K therefore the Sn multilayer desorption is through evaporation from liquid state droplets or films.
At $\theta_{\text{Sn}} \geq 0.98$ ML, a lower temperature peak at 1058 K is also present which is due to a Sn mass fragment coming from a tin-oxide. This is confirmed by TPD where coincident desorption of SnO (amu=134) with the Sn QMS signal (amu=118.8) at 1058 K was observed. The peak temperature for desorption of the tin oxides shifted to lower temperatures of 1007 K as the film thickness increased. This is presumably because for low coverages, the oxides formed are interfacial and in contact with the Mo substrate. The Mo substrate stabilizes the interfacial tin oxides, leading to higher desorption temperatures. The tin oxides could be formed either by reaction of gas phase Sn with residual gas oxidants during the film deposition and desorption process or by Sn films reacting with O contamination already present in the surface or bulk of the Mo.
Figure 5.1 Sn TPD traces from polycrystalline Mo for coverages of $\theta_{\text{Sn}}$=0.28-5.5 ML. The inset shows a thick coverage of Sn (23 ML) on Mo.

Sn films on Mo are stable till temperatures of 1700 K which agree with AES studies that are discussed later. The rising tail observed at or above 1800 K is from Sn
outgassing coming from the heating elements of the sample and not from desorption of Sn from the substrate.

Sn TPD curves from TZM are presented in Fig. 5.2 for $\theta_{\text{Sn}} = 0.16$-$4.2$ ML. The monolayer assignments are also done using a similar procedure as that for Mo, where the curve just after onset of multilayer desorption is denoted as the 1.0 ML curve and used for subsequent calibrations. Desorption for the lowest coverage of Sn studied at 0.16 ML led to the appearance of a peak, $\alpha_1$, at 1600 K (4.50 eV). This peak, also shifted to lower temperatures as the coverage increased with a final peak position at 1560 K (4.37 eV). Sn atoms remain on the TZM substrate till temperatures of 1750 K, with the rising tail as discussed earlier on Mo being an artifact due to outgassing of Sn adsorbed on the heating elements.

When the coverage reached $\theta_{\text{Sn}} = 1.0$ ML, a peak, $\alpha_2$, appeared at 1165 K which we have assigned to multilayer desorption of the films in agreement with results from Mo and also previous literature reports. [21] This peak also grows with increasing coverage with zero-order desorption kinetics. The inset in Fig. 5.2 shows Sn desorption from a 19 ML (5.3 nm) Sn film on TZM with the multilayer peak at 1187 K (3.3 eV). The difference in the peak temperature of the multilayer insets in Fig. 5.1 and Fig. 5.2 is due to the differences in Sn coverages as well as minor temperature measurement differences that could occur due to sample mounting.

A tin oxide desorption peak was absent from both the Sn and SnO QMS signal for all coverages studied on TZM. The absence of tin oxides after deposition and desorption can be explained by the initial lower O surface concentration on the “clean” TZM
compared to Mo before Sn deposition, as well as the role of Ti and Zr in binding the oxygen strongly, thereby preventing interaction with Sn. Titanium especially reacts with oxygen to form TiO$_2$ which could reduce any tin oxide formed on the surface through the reaction of SnO (s) + Ti (s) → TiO$_2$ (s).

Figure 5.2 Sn TPD traces from TZM for coverages of $\theta_{\text{Sn}}$=0.16-4.2 ML. The inset shows a thick coverage of Sn (19 ML) on TZM.
It is pertinent to discuss the TPD of the Sn films on the molybdenum substrates in comparison to each other, as well as to prior studies of Sn on single crystal substrates. The Sn films demonstrate similar desorption character on Mo and TZM alloy substrate with some minor differences. For the Sn on Mo, the Sn films does not begin to desorb until 900 K, after which they desorb due to the presence of SnO, which has a higher vapor pressure than Sn. Sn on TZM, in comparison, does not begin to desorb from the substrate until temperatures of 960 K, due to the absence of tin-oxide formation. The smallest amount of Sn remains on the polycrystalline Mo and TZM till temperatures of 1700 and 1750 K, respectively. Prior results of Sn adsorption and desorption on Mo (110) report that the last amount of Sn does not completely desorb until 1700 K. [21] This indicates similar stability at high temperatures for the Sn on polycrystalline Mo, TZM and single crystal Mo(110) despite the presence of grain boundary sites in the first two substrates which were expected to have an effect on Sn desorption. One would expect tighter binding of Sn atoms to the grain boundaries of the Mo and TZM substrate compared to Mo(110). Previously reported Sn TPD results from Mo(110) showed three peaks, the multilayer peak at $\theta_{\text{Sn}} > 1$ ML, and two peaks at 1300 and 1500 K for $\theta_{\text{Sn}} < 1$ ML. The exact origin of the 1300 K and 1500 K peak were not discussed by the researchers. For the single crystal studies, the double peak character of the monolayer desorption state observed as opposed to a single peak is due to a phase-transition that occurs for Mo(110). The peak at 1300 attributed to Sn desorption from the reconstructed Mo(110) surface was not observed on either polycrystalline Mo or TZM.

The activation energy for Sn desorption, $E_d$, was determined from the Sn desorption peak temperatures ($T_p$) by fitting the desorption curves using the Polanyi-
Wigner equation. The desorption energies measured from this analysis indicated that the binding interaction energies varied from 3.93-4.15 eV for coverages of 0.28-1.0 ML of Sn on Mo. For the case of TZM, the variation was from 4.37-4.50 eV for $\theta_{\text{Sn}} = 0.16$-1.35 ML. This is an average range of 0.15 eV (40 K) showing that changes in binding interactions going from 16% of a monolayer to a complete monolayer for TZM, and 28% of a monolayer to a complete monolayer for Mo are minor compared to Li desorption from these substrates. In our prior work on Li films studied on Mo and TZM, the desorption energy varied from 1.5-2.0 eV for Mo, and 1.5-2.5 eV for TZM for similar coverage ranges. This indicates that the Sn-Sn lateral interactions are less repulsive than Li, and that the Sn likely forms close-packed 2D islands as opposed to ordered superstructures like that observed on alkali metal adsorption systems which tend to have strong repulsive dipole-dipole interactions. The high temperature monolayer desorption peak for similar coverages of Sn on polycrystalline Mo matched with literature values for single crystal Mo(110). [21] Sn on TZM ($\theta_{\text{Sn}}=0.16$, $T_p=1600$ K) showed slightly higher stability for a roughly similar Sn coverage on single crystal Mo (110) ($\theta_{\text{Sn}}=0.14$, $T_p=1550$ K).

The changes in the Sn film coverage with temperature for Sn desorbing from Mo and TZM is shown in Fig. 5.3. These curves provide an estimate of the amount of Sn remaining on the surface during the desorption process within limit since TPD measures desorption rates. In Fig. 3a, the 5.5 ML Sn curve intersects with that for the monolayer (1.0 ML) and sub-monolayer (0.5 ML) films at temperatures just over 1300 K. The lack of complete convergence at high temperatures is due to the impact of the Sn outgassing component on the results. At 1250 K, there is 1.0 ML of Sn left on the surface, and at
1300 K, there is 0.5 ML left on the surface. For the 8.2 ML Sn on TZM, at 1200 K, the amount of Sn left on the surface is 1.1 ML and at 1450 K is 0.4 ML. All the Sn curves for TZM reach a nexus at 1450 K after which they begin to gradually decrease in amount till complete removal of Sn adatoms at 1800 K. The spurious differences in Sn amounts after 1450 K is again because of the outgassing artifact.
Figure 5.3 Thermal stability of Sn films on (a) Mo and (b) TZM surfaces probed by showing the Sn film coverage changes with temperature as determined by flux-corrected Sn TPD areas for several initial Sn film coverages.
This result is further confirmed from annealing experiments on Sn films deposited on the Mo and TZM and probed with AES. These experiments aid in understanding at what temperatures important surface processes such as diffusion, surface redistribution/clustering and alloying occur for adsorbates on metallic systems. In these experiments, Sn films of various thicknesses were evaporated onto the Mo and TZM, and then annealed at 20 s at the indicated temperature setpoints on the x-axis and then cooled to 300 K. The Sn MNN 430 and Mo MNN 186 eV Auger spectra were then taken. Based on a prior AES study, it was observed that the TZM surface was primarily composed of Mo. The Mo 186 energy transition was therefore monitored for the substrate. Furthermore, this energy transition had a larger signal compared to Ti and therefore a more sensitive reporter of surface processes. The intensities reported were obtained from the Auger peak-to-peak heights (Ap-pH). The Sn/Mo ratio from these measurements is shown in Fig. 5.4(a) and Fig. 5.4(b). The Sn/Mo ratio was used as a standardization approach to eliminate any effects that could arise due to experimental errors such as sample positioning or differences in beam currents between experiments.

The AES spectra obtained after initial adsorption of the film at 310 K was used to evaluate if the growth mode of Sn on Mo and TZM conformed to one of these: (1) layer-by-layer, (2) island growth and (3) layer plus island.

A Frank van der Merwe (FM) layer-by-layer growth kinetics of the film can be described by the equation below:

\[
I_{Mo} = I_{Mo}^0 e^{-d \lambda \cos(\theta)} \quad (5.2)
\]

\[
I_{Sn} = I_{Sn}^0 (1 - e^{-d \lambda \cos(\theta)}) \quad (5.3)
\]
where $I_{Mo}$ is the Mo AES signal intensity, $I'_{Mo}$ is the Mo AES signal intensity from the clean TZM substrate, $I_{Sn}$ is the Sn AES signal intensity, $I'_{Sn}$ is the Sn AES signal from a bulk Sn sample and $\theta$ is the angle between the surface normal and the electron analyzer axis ($90^\circ$), and $d$ is the Sn film thickness. For Sn on Mo in Fig. 5.4a, four different coverages were studied to span submonolayer to multilayer scenarios. These $\theta_{Sn}=0.6$, 1.4, 4 and 6 ML gave Mo signals that were 64.7, 50.3, 48.5 and 40.1 % of the original Mo signal coming from the substrate with no deposited Sn ($I'_{Mo}$). The expected attenuation for a layer-by-layer growth using Eqn. 5.2 with $\lambda_{Mo}=7.51 \, \text{Å}$ and $d= 2.8 \, \text{Å}$ is 59.3, 22.5 and 10.7% for films $\theta_{Sn}\geq 1.4$ ML. Using Eqn. 5.3, if the Sn films grow by a layer-by-layer growth the calculated theoretical values indicate that the Sn AES signal of the 4 and 6 ML film should be larger than that of the 1.4 ML Sn by a factor of 2.19 and 2.74, respectively. This is higher than the obtained experimental values of 1.3 and 1.68. Both these results indicate non-ideal layering for the Sn films for coverages of 1.4 ML with significant 3D clustering and island formation at thicker coverages of 4 and 6 ML. This growth behavior is similar to prior studies which showed that for Sn on Mo(110) the Sn atoms grow layer by layer until the first 2 layers and then begin to grow by 3D clusters. [21]
Figure 5.4 Influence of temperature on the Sn/Mo AES ratio for Sn films on (a) Mo and (b) TZM as measured by peak to peak height for several Sn film coverages. Films deposited at 310 K and annealed for 20 s.
6 and 4 ML Sn films on Mo demonstrate a consistent, complex thermal behavior prior to multilayer desorption. The Sn/Mo AES ratio for these films decreases substantially when they are annealed to 500 K, and continues to do so till 600 K. This could be due to either structural rearrangements such as further clustering of the Sn atoms or interdiffusion into the substrate. However, the Sn/Mo ratio for the 0.6 ML Sn coverage is stable during annealing which weakens the argument for Sn loss by interdiffusion into the substrate. Furthermore, the temperatures at which the Sn/Mo AES signals are decreasing are at or just over the bulk melting point of Sn indicating the formation of liquid droplets that grow due to enhanced lateral diffusion and coalesce to form larger droplets through well-established processes such as ostwald ripening, cluster migration or sintering. The signal rises again when annealed to 800 K back to 100% of its original value for 4 ML film, and to 86% of its original value for 6 ML Sn film. This was then followed by a decrease after annealing the film to 900 K. This could be due to deagglomeration of the liquid clusters formed, modifications in the layer structure and surface redistribution changes such as diffusion of Sn in and out of the surface. The Sn/Mo AES ratio increases again at T > 900 K and reaches a maximum at 1100 K. This rise is attributed to the desorption of tin oxides. Annealing to 1200 K, led to a drop in the signal due to multilayer desorption.

Prior to multilayer desorption for the 1.4 ML film, there is no reportable drop in the Sn/Mo AES ratio at 600 K for the 1.4 ML Sn film, which suggests that the surface process occurring at this temperature is characteristic of thick 3D multilayer films. After 600 K, the curve behavior for the 1.4 ML film mirrors that of the 6 and 4 ML Sn/Mo AES ratio curves. At 1300 K, the Sn/Mo ratio of the 6, 4 and 1.4 ML films converge.
indicating a similar surface concentration of approximately 0.6 ML. Small amounts of Sn remain present on the surface till temperatures of 1700 K demonstrating high temperature stability but no Sn is left after annealing to 1800 K.

The sub-monolayer Sn films at 0.6 ML are stable till temperatures of 1000 K, and begin to desorb after that agreeing with TPD measurements for the 0.69 ML films in Fig. 1. The initial reduction in the Sn/Mo signal for the 0.6 ML film at a 1000 K is due to formation and desorption of small amounts of interfacial tin oxide from the surface. Oxygen can accumulate on the surface during experiments either from the electron gun or residual gases which could then interact with the Sn films. The Sn/Mo ratio of all the films decreases linearly after this temperature due to desorption from the substrate until all the Sn is desorbed by 1800 K.

Similar experiments were done for various coverages of Sn films on the TZM with results presented in Fig. 5.4(b). For this substrate, the three different coverages of $\theta_{\text{Sn}}=0.41, 1.1$ and 7.2 ML gave Mo AES signals at 300 K that were 57, 58.7 and 44.56 % of the original Mo AES signal coming from TZM with no deposited Sn ($I_{\text{Mo}}^0$). The calculated theoretical values for Mo signal attenuation by the 1.06 and 7.2 ML Sn films were 67.5 and 6.8%, respectively. For layer-by-layer growth using Eqn. 5.3 it is expected that the Sn AES signal for the 7.2 ML film should be larger than that of the 1.1 ML Sn by a factor of 4, but experimental values indicated that it was 1.04 times as much. These results are also consistent with non-ideal layering for the first 1 ML, and significant clustering/island formation afterwards for 7.2 ML films.
During annealing of the Sn/TZM, the Sn/Mo signal for a 7.2 ML coverage increases slightly at 450 K, due to a decrease in the Mo AES signal (not shown). The Sn AES signal remains constant at this temperature. This is caused by surface redistribution of the Sn that does not change the average Sn AES signal or could also arise adsorption of the impurities that reduce the Mo signal. The Sn/Mo AES ratio for the 7.2 ML film decreases substantially when it is annealed to 600 K as was also observed on Mo at a temperature just after the bulk melting temperature of Sn and could also be attributed to formation and agglomeration of liquid Sn droplets on the TZM surface. The Sn/Mo ratio increases at T > 600 K, and continues to rise till 1050 K due to deagglomeration of the clusters/surface rearrangement. The observed decrease in the Sn/Mo ratio after temperatures of 1050 K is due to multilayer desorption of the films consistent with TPD. The Sn/Mo AES ratio signal for the 0.41 and 1.1 ML Sn films are both relatively stable till 750 K, and then begin to decrease after until multilayer desorption. The decrease in the Sn/Mo AES ratio continues after complete multilayer desorption at T>1050 K for 1.1 ML film, and till the onset of submonolayer which occurred at T>1050 K for the 0.41 ML film. However, the Sn AES signal (not shown) for both the sub-monolayer and monolayer film remains constant till temperatures of 1050 K while the Mo AES signal begins to rise rapidly at temperatures between 750-1050 K for both the sub-monolayer and monolayer films. The rise of the Mo AES signal for the 2D films could also be due to structural changes such as alloying, diffusion or 2D close packed island formation that don’t significantly change the Sn AES signal intensity. The thermal behavior of the films of 0.41 and 1.1 ML whereby the Sn/Mo AES ratio decreases for temperatures of 750-1050 K contradicts that observed for that at 7.2 ML for which the Sn/Mo signal rises at
this temperature. The clustering of the multilayer films can be inferred from TPD measurements. The Sn monolayer feature at $\alpha_1$ for the TZM substrate does not saturate until coverages of 2.17 ML. After annealing at 1100 K, 7.23 ML and 1.1 ML films lose substantial amounts of Sn leaving $\sim$0.41 ML on the surface as indicated by the Sn/Mo AES ratio. After 1200 K, Sn concentration decreases linearly until it is completely desorbed from the substrate at 1800 K. The increase in the Sn/Mo ratio for Sn films on Mo that occurred above 900 K, and was assigned to tin oxide desorption was not observed in annealing measurements for TZM further confirming the absence of the oxide.

Additional annealing measurements were performed using XPS to study the thermal stability of the Sn films for coverages $\theta_{Sn}=10$, 4 and 1.2 ML on Mo. In addition to providing chemical state information, XPS has a different probing depth than AES due to the larger mean free path (m.f.p) of the analysis electrons. Annealing measurements followed a similar procedure to that for AES, and the metallic Sn 3d$_{5/2}$ (484.8 eV) and Mo 3d$_{5/2}$ (228 eV) core levels were followed in addition to an oxidized Sn 3d$_{5/2}$ component (486.7 eV). The XPS intensities reported are obtained from the areas under the XPS curves.

Fig. 5.5(a) shows the Mo 3d$_{5/2}$ XPS intensity for the films as a function of temperature. For 10 ML and 4 ML Sn, the Mo 3d$_{5/2}$ XPS signal rises as the film is annealed to $T>300$ K, and continues to rise until 600 K. In contrast, the Sn 3d$_{5/2}$ XPS intensity drops as the 10 and 4 ML Sn films are annealed to 600 K. The changes in both the substrate and adsorbate core-level intensities are consistent with the results observed for the AES. For the 10 and 4 ML film, the Mo 3d$_{5/2}$ and Sn 3d$_{5/2}$ signal do not change
after subsequent annealing measurements indicating that the Sn clusters have reached
their equilibrium size. The complex thermal behavior observed for the Sn/Mo AES
curves for the thick 6 ML and 4 ML Sn films on Mo was not observed for the XPS
studies. The Sn 3d$_{5/2}$ signal also rises when the film is annealed to temperatures at or
greater than 1000 K due to loss of the SnO which previously attenuated the Sn AES
signal. There was no change in the Mo 3d signal during the desorption of the SnO
indicating that the substrate was not uncovered during this process. The loss of Sn is
more pronounced at 1200 K for the 4 ML film compared to the 10 ML Sn, which loses a
lot of Sn after annealing at 1300 K. At 1300 K, the amount of Sn on the surface for the 4
and 10 ML Sn films converge and then decrease linearly due to monolayer desorption
until complete removal at 1800 K. For 1.2 ML films, the Mo 3d$_{5/2}$ and Sn 3d$_{5/2}$
demonstrates stability, with small rises that could be attributed to noise, until a decrease
at 1100 K from onset of loss of Sn. The Mo 3d$_{5/2}$ increases at 1300 K for all three films,
and becomes less sensitive to Sn desorption afterwards.

The 4 ML Mo 3d$_{5/2}$ signal was lower than that of the other 2 films after multilayer
desorption which could be due to impurities adsorbing during experiments preventing the
Mo 3d$_{5/2}$ from reaching its original value.

The oxidized component of Sn 3d$_{5/2}$ showed that a small fraction of the Sn film
that was deposited on the Mo substrate was already oxidized in agreement with Sn TPD
results which confirmed the desorption of SnO. The tin oxide (SnO) Sn 3d XPS peak
(486.7 eV) was deconvoluted from the metallic Sn peak (484.88 eV), and followed as a
function of temperature for three films as shown in Fig. 5.5 (c). The amount of tin oxide
that was initially formed decreased with the thickness of the deposited Sn film. As the Sn
film was annealed to higher temperatures, the amount of tin oxide increased with a saturation value reached at temperatures of 500-800 K. The formation of tin oxide is thermally enhanced highlighting the presence of an activation barrier for oxygen penetration and diffusion into the film and the reaction of tin to form the oxide. Mo 3d\textsubscript{5/2} core-level BE and FWHM remained constant during this process confirming no interaction of oxygen with the substrate. Tin oxide desorption also led the SnO XPS signal to decrease after a 900 K anneal and it is eliminated at 1200 K.
Figure 5.5 XPS studies of the influence of temperature on the signal intensities of:

(a) Mo 3d$_{5/2}$ (b) metallic Sn 3d$_{5/2}$ and (c) the oxidized component of Sn 3d$_{5/2}$. The signal intensities were measured by the peak area for several Sn film coverages. (d) Binding energy change for a 10 ML bulk multilayer film compared to a 0.5 ML sub-monolayer film on Mo.
An initial 0.1 eV decrease (not shown) in the metallic Sn 3d\textsubscript{5/2} XPS binding energy when the 10 ML Sn film was annealed to temperatures at or greater than 900 K was observed. There was a further shift in the Sn 3d\textsubscript{5/2} core level after further anneals. The Sn 3d core levels fully shifted to lower binding energies after anneals of 1300 K due to the influence of the molybdenum substrate on the Sn electronic properties. This is clearly shown in Fig. 5(d) where the Sn 3d core level signal from 0.5 ML of Sn is shifted by 0.4 eV due to charge transfer. This occurs due to the electropositive nature of Mo, which influences the electron density of state of Sn. This binding energy shift demonstrates the strong electronic Sn-Mo interactions that are present.

5.3.2 Low Pressure Oxidation of Liquid Sn Films Deposited on Mo

The oxidation of 7 ML (2.1 nm) of Sn films at or above the bulk melting temperature (T\textsubscript{m}=505 K) was studied using XPS. Previous investigations of gaseous oxidation of tin and its alloys have been limited to Sn in the solid state or at exactly the bulk melting temperature.[33,40–44] For the studies presented herein, the oxidation behavior of the liquid films examined fell within a temperature range of 500-800 K. To ensure consistency, a constant amount of Sn was deposited and then exposed to oxygen at exposures that ranged from 0-500 L. After each exposure the Sn 3d and O 1s core level features were taken with results shown in Fig. 5.6. Deconvolution of the Sn 3d core level for the initially deposited Sn films at different temperatures shows the presence of two peaks at binding energies of 484.6 eV and 486.2 eV which were assigned to metallic Sn and a Sn (II) oxide (SnO), respectively. This assignment agrees with prior reports of the
binding energy position of Sn 3d in metallic Sn compared to oxidized Sn. [45] Although it should be noted that the binding energy shifts for the oxide relative to the metal can vary depending on if the sample is a polycrystalline foil, powder, single crystal or thin film in addition to energy referencing errors. The oxidized Sn 3d component was distinguished from Sn(IV) due to concurrent valence band measurements matching literature.[36,46] Distinguishing these two oxide phases through XPS measurements is not trivial. [47] Only one single oxide phase was observed even after exposure at 500 L O₂.

From the Sn 3d core level deconvolution, the metallic component of the initially deposited films was determined to be 79% (500 K), 77.1 % (600 K), 74.3% (700 K), 68% (800 K) of the total Sn 3d data envelope with the rest being composed of oxidized Sn. This showed roughly constant amount of metallic Sn upon deposition, and prior to oxidation. In Fig. 5.6(a), the Sn film at 500 K which is close to the bulk melting temperature (Tₘ=505 K) and is therefore at a solid-liquid interface shows an increase in the SnO component after exposure to 100 L O₂ and a corresponding decrease in the metallic Sn 3d component. As the O₂ exposure increases, the oxidized Sn 3d at 486.2 eV representative of the SnO increases while that for the metallic Sn 3d at 484.6 attenuates for all films (complete spectra not shown). Complete oxidation for the film kept at 500 K, was not achieved for the highest exposures (500 L) studied. Similar XPS spectra is shown in Fig. 5.6 for the endpoint exposures of liquid Sn films at 600, 700 and 800 K. Spectra comparison shows that the higher the liquid film temperature, the more SnO was formed after exposure to 500 L of O₂. Furthermore, for the complete data discussed later it was
observed that the oxidized Sn 3d peak increased much more rapidly as the bulk liquid Sn temperature was raised.

Figure 5.6 XPS spectra showing the (a) Sn 3d$_{5/2}$ and (b) O 1s core levels during the oxidation of 7 ML Sn films at or above liquid temperatures of T(K) = 500, 600, 700 and 800 K.
The origin of this temperature enhanced oxidation is at the very least three-fold and can be better understood by considering the three steps required for the formation of the oxide film:

**Step 1:** Sn (s) + O₂ (g) → Sn + 2O (ad)  (Dissociation)

**Step 2:** O (ad) diffusion and transport into film bulk

**Step 3:** Sn + 2O (ad) → SnO (s) (Oxidation and bond formation)

The second step corresponding to the diffusion of dissociated O in the bulk, is rate limiting and necessary for oxidation of the Sn leading to their dependence on temperature.

The structure of the Sn film which is also affected by the annealing can influence the oxidation rate, with layers and large 3D crystallites leading to different rates of oxygen uptake. The annealing measurements in Fig. 5.4(a) show differences in the Sn/Mo AES ratio for Sn films on Mo at 500, 600, 700 and 800 K. These differences as discussed earlier could be due to structural rearrangements and redistribution of Sn that could influence oxygen uptake.

O 1s signal for these films are shown in Fig. 5.6(b) with binding energy of 530.0 eV and the same FWHM for all the exposures and Sn temperatures studied. This value falls within the range of prior reports of the O 1s peaks binding energies for extended SnO, SnO films and high-purity polycrystalline powers of about 529. 7-531.4 eV. [36] The O 1s signal increased with increasing liquid Sn film temperature. It is challenging to distinguish the chemical nature of the oxygen that is observed for the O 1s signal since this could rise to a variety of oxygen containing species in addition to bonded oxygen.
(Sn-O) such as hydroxyl groups, oxygen at the Sn/TZM interface or oxygen absorbed in the bulk of the Sn film.

This is illustrated in Fig. 5.7(a) which shows changes in the O 1s intensity, as derived from the peak area, as a function of the oxygen exposure for different film temperatures. The initial sticking coefficients for the O atoms on the Sn film, obtained from the slopes of the curves, is roughly constant for all temperatures. The initial O uptake for these films is rapid between exposures of 0-50 L and by 100 L O₂ exposure, the O 1s intensity has obtained 50-60% of their limiting values. The rate of rise in the O 1s signal is slower at exposures between 300-500 L especially for films at temperatures of 500-600 K. This is presumably due to less Sn sites at the near surface region becoming less available for bond formation with oxygen. Consequently, formation of tin-oxide is diffusion limited in this exposure leading to saturation. As more SnO is formed in the near surface/surface region, this will serve as a diffusion barrier for the oxygen slowing down penetration into bulk of the Sn sample leading to case of metallic Sn atoms protected beneath a capping, passivated oxide layer.

The maximum uptake as measured by the O 1s intensity at exposures of 500 L O₂, which is proportional to the amount of oxygen retained in the Sn film increases as the bulk temperature of the Sn film is raised from 500 to 800 K.
Figure 5.7 XPS study of the oxidation of 7 ML of liquid Sn Films on Mo at temperatures of 500, 600, 700 and 800 K: (a) O 1s intensity and (b) SnO/(Sn+SnO) conversion ratio as a function of exposure. The intensities were determined by the area under the curve.
The 600 K film shows a slight enhancement in saturation O uptake (1.16 times that of the 500 K film). However, the O uptake increases substantially when the film temperature is raised to 700 K and 800 K with the O 1s signal intensity being 1.83 and 2.25 times that of the 500 K Sn film at 500 L. For the Sn films kept at 700 and 800 K, the oxygen uptake is the same till exposures greater than 200 L, where uptake is higher for the 800 K Sn film. The higher temperature provides sufficient energy to surmount the activation barrier required for the dissociation and penetration steps of the reaction as mentioned earlier.

To further understand the influence of the temperature on SnO formation, the ratio of the areas of Sn\textsuperscript{2+} component of the Sn 3d core level to that of the metallic Sn is presented in Fig. 5.7(b). This parameter represents the conversion rate of the metal to the oxide. The curves for the 500 and 600 K Sn films show roughly the same metal to oxide conversion rate. The minor divergence at oxygen exposures > 300 L can be attributed to experimental errors from high exposure measurements. Although the conversion rate was the same for these two temperatures, the O 1s uptake (See Fig 5.7(a)) was different. At first guess, one might attribute this to the mean free path of the O 1s photoelectrons compared to that of the Sn 3d photoelectrons. However, the K.E. of the O 1s photoelectrons at 723 eV (\(\lambda_{O1s}=18.19\) Å) is close to that of Sn 3d at 769 eV (\(\lambda_{Sn3d}=18.97\) Å). The additional oxygen observed for the 600 K Sn film can be attributed to chemisorbed oxygen on the surface, dissolved oxygen in the bulk that is not chemically bonded to Sn or interfacial oxygen. XPS depth resolution is 3\(\lambda\) so about 12 ML for the Sn film if the lattice constant for a tin-oxide unit cell is taken to be 4.7 Å. These measurements therefore follow the complete oxidation behavior of the 7 ML Sn films.
The conversion rate to oxide for the films at temperatures of 700 and 800 K is noticeably larger than that for those at 500 and 600 K specifically at exposures of O₂ ranging from 0-200 L. Partial oxidation could only be achieved for liquid Sn films at temperatures of 500, 600 and 700 K at 500 L O₂ exposure. For films at 800 K, the ratio approached 1.0 after oxidation at 200 L due to complete conversion to tin oxide (SnO). Despite all metallic Sn been converted to SnO after 200 L O₂ exposure for 800 K Sn films in Fig. 7(b), the O1s peak area continues to rise at exposures >200 L as displayed in Fig. 7(a). This indicates that oxygen continues to be incorporated into the SnO film not through bond formation but bulk dissolution into the amorphous SnO film formed or occupation of interfacial SnO/Mo sites. The fraction of Sn that is oxidized after 500 L exposure was determined from XPS to be 0.5 (500 K), 0.5 (600 K), 0.8 (700 K) and 1.0 (800 K).

The absence of an inflection point in the O 1s signal during exposure provide additional support that only one type of oxide was formed during the oxidation. The complete oxidation of the Sn film at high temperatures indicates that alloying or subsurface diffusion of the Sn does not occur at high temperatures since if that were the case then some of the Sn atoms would be inaccessible to oxygen and this would also be reflected in the oxygen uptake of the film.

The substrate is inert during the reaction since the Mo 3d intensity, binding energy or FWHM did not change during oxidation (not shown). All chemically bonded oxygen can be completely attributed to the formation of tin oxide films due to the presence of only metallic BE features in the Mo 3d5/2 (228.0 eV) and 3d3/2 (232 eV) core levels for all the O₂ exposures studied. The presence of chemisorbed oxygen at the Sn-
Mo interface cannot be ruled out especially at high temperatures where increased O mobility would allow for inward diffusion and transport as for the 800 K Sn film case. It can also be inferred from this result that no significant structural rearrangements such as the formation of large thin oxide clusters occurred as the metallic Sn films were being oxidized to form SnO since such a change is expected to cause attenuation of the Mo 3d emission.

TPD measurements were used to evaluate the effect of oxygen exposure on the thermal stability of the oxidized films. 7 ML of both solid (310 K) and liquid (800 K) Sn films were exposed to 500 L of O₂ and a TPD trace taken as displayed in Fig. 5.8 for Sn (amu=118.8), SnO (amu=134) and O (amu=16). SnO₂ (amu=150) was also followed but did not show a peak. Fig. 5.8(a) shows the Sn and SnO QMS signal coming from desorption of a solid 310 K Sn film exposed to 500 L of O₂. Both signals show the presence of two desorption peaks at temperatures lower than that of the Sn multilayer, and these have been denoted for discussion purposes as γ₁, 1044 K and γ₂, 966-981 K. These peaks are due to the evaporation of SnO which has a higher vapor pressure than metallic Sn. The SnO QMS signal also showed a small but relatively broad peak at 1200 K of unknown chemical origin. The Sn film at 310 K is partially oxidized after 500 L exposure as evidenced by the presence of a multilayer peak at 1200 K. A broad O peak was also present in the TPD spectrum with a peak that coincided with the γ₁ peak therefore coming from fragmentation of the SnO.

TPD traces of liquid Sn films at 800 K is presented in Fig. 5.8(b). The oxygen exposure and θSn were kept the same as the 310 K film to allow for direct comparison. For the liquid Sn film, TPD indicated that the film was completely oxidized which is
supported by the absence of a multilayer peak in the Sn QMS signal. The only peaks observed for the Sn and SnO QMS signal come from cracking components of $\gamma_1$ and $\gamma_2$ that were previously observed for the 310 K Sn oxidation. A fully oxidized Sn film will therefore desorb at temperatures 150-210 K lower than metallic Sn multilayer. All the tin oxide is completely desorbed by 1200 K, with a thermal stability that is 500 K lower than that of the metallic Sn which completely desorbs at 1700 K. One consideration is the stability of Sn at the monolayer level to oxidation. Sn binding to Mo at the monolayer level could stabilize the interfacial Sn preventing oxidation. However, this was not observed from the TPD traces for the oxidized films, since all the metallic Sn including that at the monolayer level is converted to tin oxide.

Figure 5.8 TPD traces from 7 ML Sn exposed to 500 L O$_2$ at (a) 310 K (solid Sn) (b) 800 K (liquid Sn). The masses followed were Sn (amu=118), SnO (amu=134) and O (amu=16). The liquid Sn is completely oxidized at this temperature as indicated by the
absence of the Sn multilayer in the Sn QMS signal while the solid Sn is partially oxidized.

The two different peaks $\gamma_1$ and $\gamma_2$ can be attributed to changes in the vapor pressure of SnO nanoparticles during nucleation and growth of oxide particles. This is commonly referred to as the Kelvin effect, where a change in vapor pressure due to a curved liquid is higher than that in contact with a flat surface. Herein it is proposed that the low temperature peak arises from curvature regions within the tin oxide nanoparticles that lead to a higher vapor pressure. Since the tin oxide evaporated and was not reduced and decomposed to metallic Sn, disproportionation to form SnO$_2$ via transitional intermediate oxides such as Sn$_2$O$_3$ or Sn$_3$O$_4$ [48–50] was not observed.

In comparison to other sources of the oxidation of Sn, results show that the Sn films studied here are oxidized faster than what is found in literature for room temperature oxidation [45] Comparatively, in an earlier study, 3.4 ML of Sn on Pd at room temperatures exposed to 500 L O$_2$, yielded Sn 3d signals where the SnO component was 5% of the Sn 3d data envelope. From this study, the maximum amount of Sn film oxidized is 45% of the Sn 3d data envelope after $10^{11}$ L exposure. While direct comparisons in exposures are not always accurate due to differences in pumping and gas dosing, they provide a rough estimate. Our results point to the rapid and complete oxidation of 7 ML Sn films at 800 K compared to only 45% in AF Lee et al.’s study which utilized pressures larger by a factor of $10^9$. This highlights the important role of temperature in driving oxidation rates of liquid Sn.
5.3.3 Sn Films on O/TZM

A TPD spectra monitoring QMS signals for Sn (amu= 118.8) and SnO (amu =134) for a 3 ML Sn film desorbing from O/TZM (red and blue curve) and TZM (black curve) is shown in Fig. 5.9. The O/TZM surface was formed from exposure of the TZM to 20 L of O₂. SnO₂ (amu=150) desorption was not observed from TPD spectra of Sn desorption from TZM and O/TZM. During desorption from TZM(black curve), only the characteristic Sn multilayer peak is observed, and a broad monolayer desorption feature that extends till 1800 K. No desorption of SnO in both the Sn and SnO QMS signals was observed for metallic Sn initially deposited and desorbed from TZM. For 3 ML Sn film desorbing from O/TZM, the Sn QMS signal (red curve) shows the presence of a peak at 996 K, assigned to the evaporation of SnO, in addition to the multilayer and monolayer features. The assignment was confirmed by coincident desorption of SnO (blue curve) as well as the similarity in peak desorption temperature with the TPD observations for post-oxidation of liquid Sn films in Fig. 5.8. These confirm that multilayer Sn on an oxygen covered surface led to the desorption of SnO.

The earlier evaporation of the SnO, and presence of a monolayer feature in Fig. 5.9 suggests that the formed SnO particulates diffuse to the surface prior to desorption, leaving a metallic Sn metal overlayer beneath the oxide film. This is further confirmed in LEIS measurements of the thermal stability of the tin oxides formed on TZM.

The amount of SnO formed by deposition and desorption of Sn on O/TZM surface was obtained by finding the difference in metallic Sn coverage for Sn desorbing
from a TZM surface and that from O/TZM. This was calculated as 0.9 ML of Sn metal atoms being converted to SnO.

The absence of any additional peaks in the Sn TPD trace provides some evidence that only one tin oxide phase was formed from these desorption experiments. In prior TPD experiments for the complete oxidation of Sn films, two desorption peaks were observed. Only the peak at 996 K which is close in shape and \( T_p \) to the \( \gamma_1 \) peak in Fig. 5.8 was observed for Sn on O/TZM while the second lower temperature peak at 966-981 K was absent. The substrate used for this experiment was TZM and so Ti could have an impact. Nevertheless, it would seem that the oxygen concentration plays a role in the formation of the dual oxide peaks observed in the TPD for the post-oxidation of the liquid metal Sn films in Fig. 5.8.

Sn films of variant coverages were deposited on an oxygen covered TZM surface, and Sn QMS signal was monitored during the subsequent desorption of these films as shown in Fig. 5.10 (a). The goal was to monitor the evolution and growth of the SnO in an oxygen-limited environment. The coverages indicated in the plots are obtained from prior calibrations using metallic Sn films desorbing from an oxygen-free “clean” TZM. The peak maxima for the SnO desorption continues to shift to higher temperatures as the amount of Sn deposited increases demonstrating desorption is zero order. The inset in Fig. 5.10(a) shows lower film coverages of, \( \theta_{\text{Sn}} = 1.3, 1.7 \) and 2.2 ML. 1.3 ML is composed primarily of desorption from SnO and monolayer desorption, while a substantial amount of the multilayer peak of the 1.7 ML film is completely converted to SnO with the rest of the Sn atoms desorbing as monolayers from TZM.
Figure 5.9 TPD of 3 ML of Sn from TZM and O/TZM. The masses monitored were Sn (amu=118.8) and SnO (amu=134). The black curve shows the Sn QMS signal for desorption of Sn from a clean TZM substrate with no pre-adsorbed oxygen. The red curve is the Sn QMS signal from a Sn film desorbing from TZM pre-adsorbed with oxygen. The blue dashed line shows the corresponding SnO QMS signal from the Sn film desorbing from O/TZM.

At increasing Sn coverages, $\theta_{\text{Sn}} = 2.2, 2.9, 4.9, 5.6$ ML three main peaks were observed, depending on the dose, for SnO evaporation (996 K), multilayer (1159 K) and a peak at 1315 K. Due to limitations in interfacial oxygen concentration, the films at thicker coverages are not completely converted to tin oxide as demonstrated by the growing multilayer peak. The SnO peak continues to grow also with increasing Sn
coverage and reaches it limiting value at coverages of 4.9-5.6 ML. It was initially expected that as the coverage increased, the Sn atoms would fully consume all O atoms first to form SnO, and then later grow as multilayer films, but that was not observed. This could suggest inhomogeneous distribution of O atoms or the formation of Sn islands with some of the Sn layers not initially accessible to oxygen atoms.
Figure 5.10 TPD traces of $\theta_{\text{Sn}}=1.3, 1.7, 2.2, 2.9, 4.9$ and $5.6$ ML desorbing from a TZM substrate with a surface saturated with chemisorbed O atoms. (a) Sn (amu =118.8) QMS signal with inset showing lower coverages. (b) SnO (amu=134) QMS signal.
The SnO QMS signal for these films was also monitored and shown in Fig. 5.10(b). For the lowest amount (1.28 ML) of Sn on O/TZM a broad peak structure is formed which grows to form a well-defined sharp peak at 950 K for 1.73 ML Sn. This shifts to higher temperatures after 2.18 ML but the peak temperature does not increase significantly with increasing Sn coverage on O/TZM. The desorption onset for the SnO at all the coverages studied is just above 800 K with complete evaporation of the SnO by 1200 K. From plotting the TPD areas of the SnO peaks as a function of coverage, it was observed that the amount of SnO formed increases linearly with the amount of Sn that is deposited on O/TZM. The 1315 K peak that was observed on the Sn QMS signal was absent in the SnO QMS signal indicating that does not a fragment from SnO.

These results indicate that for a liquid Sn film concept in a tokamak, O contamination on a TZM surface could reduce the thermal stability of the Sn film by 100 K due to the formation SnO. This SnO is an additional high Z component that can evaporate into the plasma and affect performance. QMS signals were observed for O (amu=16) at peak maxima of 969 K and O₂ (amu=32) at 929 K during desorption of 5 ML of Sn from O/TZM.

To evaluate the chemical nature of Sn on O/TZM at temperature ranges of 300-1800 K, XPS measurements were performed for a 5 ML Sn film deposit. XPS spectra is shown for these in Fig 5.11(a). Sn 3d spectra for 5 ML Sn film on O/TZM indicates that upon deposition of Sn on the O/TZM, there is formation of SnO on the surface. The metallic Sn 3d₅/₂ position was at 484.7 eV and that of the oxidized Sn component at 486.5-486.7 eV. It was assumed like the post-oxidation experiments, that the oxide formed is SnO. The SnO component is 12% of the Sn 3d XPS data envelope at 300 K.
This increases when annealed to 500 K (13.5%) and just before evaporation of SnO to 18.8% of the Sn 3d envelope. The deposited Sn is still primarily composed of metallic Sn at 800 K. Increased amounts of SnO with temperature confirms that SnO formation is thermally activated. Increased mobility of the O atoms into the film can explain the increased SnO formation with temperature as well as redistribution of already formed SnO which would lead to an increase in the overall detected XPS intensity. When the films are annealed to 1230 K, the SnO and leaves metallic Sn on the substrate as seen from Sn 3d core levels also consistent with what was observed from TPD measurements in Fig. 5.10. The Sn 3d core level at 1230 K had a binding energy of 484.2 eV representative of Sn/Mo interactions. After 1800 K, Sn loss is complete.

The Mo 3d core level binding energies and FWHM showed only metallic components during the annealing measurements from 300-1800 K. Mo is therefore not oxidized before and after deposition as well as during annealing of Sn on O/TZM. Additionally, the Mo 3d intensities were constant when annealed from 300-800 K, though changed after multilayer desorption at 1230 K. The Ti 2p core level for the TZM was not followed although Ti has a high affinity for reacting with oxygen to form TiO$_2$ and could have been oxidized before and during annealing.

The O 1s core level has a binding energy at 530.1 eV over the 300-1800 K range. The intensity of the O 1s core level is stable from temperatures of 300-500 K, and then increases by 18% when annealed to 800 K. Structural changes that affect the overall O 1s intensity is responsible for this increased intensity. After annealing to 1230 K, the O 1s intensity drops to 60% of its original value at 800 K due to evaporation of the SnO. There
is still oxygen on the surface presumably chemically bonded to Ti at the interface or adsorbed on the surface as oxygen species.
Figure 5.11 (a) Influence of temperature on the XPS spectra for 5 ML of Sn films on an oxygen covered TZM surface. The oxidized component of the Sn 3d$_{5/2}$ core-level intensity increased with increasing annealing temperature. (b) LEIS scans of the surface for clean TZM, O/TZM surface (20 L of O$_2$ on TZM) and (c)/TZM after Sn film deposition and annealing to 1800 K. The peaks identified and their kinetic energy (eV) locations were Mo (857), Ti (763), C (423) and O (518).

A LEIS spectrum was taken of the 5 ML Sn/O/TZM system after the 1800 K anneal with results displayed in Fig. 5.11. The TZM surface is initially composed of Ti, Mo, C and O. Exposure of the TZM substrate to 20 L of O$_2$ (red curve) changed the surface composition and led to growth of the O peak signal, suppression of the Ti and Mo peaks, and disappearance of the C peak but the surface is not fully covered with O.
However, after 1800 K anneals (blue curve), the Ti/Mo ratio increased due to segregation of Ti to the surface of the substrate. Although no Ti 2p spectra was taken, it can be inferred that this segregation is due to the formation of a TiO$_2$/Mo surface.

These results combined with prior confirm rapid uptake at high temperatures in Fig 5.7 due to inward diffusion of O atoms to the Sn bulk, and the progressive formation of SnO from thicker Sn films in contact with O atoms adsorbed on the interface, confirms outward diffusion into the film.

5.3.4 LEIS Study of Room Temperature Oxidation of Sn Films on TZM

LEIS spectra displayed in Fig. 5.12 were taken for a 5 ML Sn film exposed to 500 L of O$_2$ and annealed to multiple temperatures. The film is partially oxidized based on XPS measurements which showed that it was comprised of 25% SnO and 75% metallic Sn. The initial TZM surface was composed of Mo (857 eV), Ti (763 eV), C (423 eV) and O (518 eV) as seen in the red curve in Fig. 5.11. After deposition of 5 ML of Sn on TZM, a peak appeared at 884 eV due to kinematic scattering of 1 keV He$^+$ ions from Sn atoms on the surface with concurrent disappearance of the Mo, Ti, and C peaks. An O peak was still identified in the spectra presumably coming from either diffusion of O from the grain boundaries on the substrate or during deposition of the film. The Sn LEIS peak overlapped with that for Mo (854 eV) but prior LEIS experiments using Ar$^+$ ions to resolve the peaks (not shown) indicated that 5 ML of Sn completely covers and wets the surface of TZM at room temperature.

After oxidation with 500 L of O$_2$, there was a 10% attenuation of the Sn signal, but the O LEIS intensity (as measured by area) doubled by a factor of 2. The presence of Sn
atoms on the surface could either be structural where Sn and O atoms are both present on
the surface of SnO or occur because of the partial oxidation of these films. There are
multiple configurations for the partially oxidized film, for example, the top layer could
have a homogeneous capping SnO layer with metallic Sn buried underneath or in another
case the top surface layer could be composed of segregated SnO and metallic Sn.

No Mo or Ti signal was observed after partial oxidation of the Sn film indicating that
O₂ exposure did not lead to any structural rearrangements that led to uncovering of the
substrate. The Sn/SnO mixed film formed was annealed to temperatures of 500-1800 K as
seen in Fig. 5.12. Generally, the surface composition was composed of Sn and O atoms
until temperature anneals at 1300 K. As the substrate was uncovered during subsequent
anneals of the film, a Ti peak appeared at 1300 K, that continued to grow till complete
desorption of the oxide film. An Mo shoulder also appeared at 1100 K which fully
formed into a peak due to desorption of the metallic Sn. No Sn remained on the surface
after 1800 K anneals consistent with all previous spectroscopy and TPD measurements.
Figure 5.12 (a) LEIS of partially oxidized 5 ML of Sn films on a TZM substrate at 310 K and the thermal stability of the SnO film formed. (b) Effect of temperature on the O LEIS signal for the annealed SnO films.
The O LEIS intensity (from peak area) is shown in Fig. 5.12(b). The O LEIS signal increased as the Sn/SnO mixed film was annealed to temperatures of 300-900 K. This increase is attributed to the diffusion of unbonded O atoms to the surface, structural and morphological changes in the film structure that could have increased O concentration or signal sensitivity or consistent with a scheme in which the SnO diffuses to the surface before desorption. After heating to 1100 K, the O LEIS signal decreased due to SnO desorption but was not eliminated confirming that all the Sn is not bonded to available oxygen. At 1100 K, from Fig. 5.12(a), the surface is composed only of Sn and so this cannot be O atoms bonded to the Mo or Ti interface. This oxygen is assigned to come from either chemisorbed O atoms or hydroxyl groups adsorbed on Sn.

As the Sn multilayer evaporates to leave a monolayer, and the subsequent monolayer desorption to uncover the TZM, the oxygen signal increases rapidly due to interfacial O atoms bonded to the Ti or Mo atoms. At temperature ranges of 1300-1700 K, there are both interfacial Mo, Ti, Sn and O on the surface. Although speculative, the partial oxidation observed for the 310 K Sn film, could be due to the O atoms preferentially bonding to Ti or Mo at the interface explaining the large rise in the O LEIS signal intensity as the substrate is uncovered. Noteworthy, that the O LEIS intensity could be influenced by other factors such as ion neutralization probability and shadow coning amongst other things, and so is not a reliable monitor of surface concentration.

A carbon signal (not seen due to the scale) appears after the annealing of the mixed Sn/SnO film coming from inter-diffusion from the TZM substrate or from dissociative adsorption of CO during the oxidation. No reportable changes were observed for the Sn LEIS signal intensity for anneals of 500-1100 K. Although some intensity fluctuations...
where observed, they fell within ±6% of each other and was attributed to experimental error.

5.4 Implications for the Use of Sn as a Plasma Facing Component (PFC)

The metallic Sn films studied on these molybdenum substrates have very high stability both at the multilayer and monolayer level compared to Li films. Multilayer metallic Sn on both Mo and TZM starts to evaporate at 1000 K, while Li films start to desorb at 520 K as displayed in Fig. 5.13 (a-b). This 480 K increase in onset of desorption makes Sn a more sustainable material in regions within the tokamak that are under high heat fluxes. The earlier onset of desorption of Sn observed in Fig. 5.13(a) on Mo is due to the presence of tin-oxide (SnO). The peak maxima ($T_p$) for multilayer desorption, which is the temperature at which the desorption rate is fastest, is 550-585 K higher for Sn ($T_p=1270$ K) compared to Li ($T_p=600$ K) due to lithium’s higher vapor pressure. Sn has a melting point of 505 K, and the operating temperature range of liquid Sn before the onset of multilayer desorption is 495 K, while for liquid Li with a melting point of 453 K is only 70 K. These results highlight the advantages of using liquid Sn for high temperature applications.

On the question of dry-out conditions of these two liquid metals on molybdenum substrates, the Sn monolayer films were observed to persist on both molybdenum substrates at higher temperatures than the Li films. Furthermore, the Li monolayer is not completely removed from polycrystalline Mo till temperatures of 1500 K but the Sn atoms remain on the surface till temperatures of 1800 K. This is even more prominent for the case of Li films on TZM, for which dry-out from the substrate occurs at 1100 K and
there is 700 K improvement when Sn is used. We can therefore conclude for all cases that
the Sn-Mo ($\theta_{\text{Sn}}=0.28 \text{ ML}, E_D=4.15 \text{ eV}$) bonds are therefore stronger than the Li-Mo
($\theta_{\text{Li}}=0.25, 2.3 \text{ eV}$) and the heat of sublimation of Sn, 3.5 eV is higher than that for Li
sublimation at 1.6 eV.

AES of Sn on molybdenum at room temperature and during annealing showed
that clustering of Sn occurred on both Mo and TZM to varying degrees for ultrathin 6-7
ML films. However, there is not sufficient data to determine if de-wetting of the substrate
occurred during annealing. Structural rearrangements of the Sn on the surface can
potentially influence its surface chemistry and interaction with deuterium ion particles.

The thermal enhancement observed for the oxidation of the Sn films is
noteworthy in situations where the residual gas composition in UHV chambers can
significantly affect surface composition of the liquid metal. Oxidants such as CO and
H$_2$O can be present in the fusion reactor and combined with high temperature liquid Sn
walls can lead to the formation of tin-oxide. This can lead to defective wetting of the film
on the substrate, changes in the thermal conductivity and heat transfer properties, vapor
shielding effects and fluid flow rates.

It can also be inferred from the results that the hotter the wall temperature, the
amount of SnO formed. In events in which the temperatures of the wall exceed 600 K, the
Sn film will be expected to rapidly oxidize to form SnO. Such high temperatures can
arise due to transient events such as edge localized models (ELMS) which can cause high
heat fluxes that allow the wall temperatures reach 800 K. Results presented here indicate
that for thin Sn films, oxygen uptake will become an even more salient issue for $T \geq 700-$
800 K. This of course depends on O migration parameters (diffusivity, solubility and permeation) into the Sn film and thickness of the liquid metal layer.
Figure 5.13 TPD traces of the Li QMS signal (amu=7) from multilayer Li films (black curves) compared to Sn QMS signal (amu=118.8) from multilayer Sn films (red curves) deposited on (a) Mo ($\theta_{Li}=1.05$, $\theta_{Sn}=1.9$) and (b) TZM ($\theta_{Li}=1.38$, $\theta_{Sn}=2.2$). (c) Comparison of post-oxidized Li films to that of Sn films that were deposited on molybdenum substrates of interest.

The thermal stability of oxidized Li films deposited on TZM was discussed extensively in Chapter 4. The oxidation of the Li and Sn films on molybdenum substrates show some interesting differences. The SnO formed from oxidation of the metallic Sn evaporates at temperatures of 996-1044 K while the LiO$_x$ decomposes leaving oxygen on the substrate at peak maxima temperatures of 860 and 990 K. This poses a concern since Sn is already a high Z material, and the combined evaporation of Sn and O into the plasma will increase impurity contamination. The formation of oxides increased
the stability of the Li films compared to metallic Li. Stability being defined by the desorption onset temperature. On the other hand, oxide formation in Sn reduced the formed film stability relative to metallic Sn. Regardless the onset of desorption of oxidized Sn films (850 K), is still higher than that for the oxidized Li films (620 K).

The oxidized Li films were found to interact with the TZM substrate as observed by the desorption of several Li$_x$MoO$_y$ mass fragments that are believed to come from a lithium molybdate complex. The molybdenum substrate is however inert during Sn film oxidation.

The interactions of Li and Sn with oxygen-covered TZM substrates also showed some interesting differences. At high coverages, Li films on oxygen-covered TZM formed phases that desorbed at peak temperatures that matched that of post-oxidized Li films on TZM. The Sn films on such prepared surfaces were only able to make the high temperature peak at 996-1044 K, and not the lower temperature shoulder demonstrating the important role of oxygen concentration in formation of this peak. Regardless of these differences, both Li and Sn films demonstrate affinity to form oxides with oxygen covered TZM surfaces.

The question of if Sn forms an intermetallic surface alloy was not answered from the data presented. Previous reports have suggested a Sn-Mo surface alloy on single crystal Mo(110) at 800 K, though the evidence presented is sparse. [21,22] Although the Sn-Mo bulk phase diagram shows that Sn forms MoSn$_2$ and Mo$_3$Sn compounds with Mo [51] However, lattice mismatch for Sn atoms on Mo is expected because the Sn has an atom radius of 1.45 Å and is smaller than that of Mo at 1.9 Å. The surface energy of Sn is
also lower than that of Mo, making it less thermodynamically possible for surface alloy formation to occur as opposed to a Sn overlayer.

5.5 Conclusions

The interaction of Sn films with polycrystalline molybdenum substrates (pure Mo and a TZM alloy) in the absence and presence of oxygen has been studied by the combined use of XPS, TPD and LEIS to provide new information on surface phenomena relevant to applications of Sn coatings on PFCs in fusion experiments and reactors. The results indicate that pure Sn films are stable in vacuum until temperatures of 900-1000 K, after which evaporation of Sn multilayers occurs in a peak near 1187-1270 K for TPD measurements on both substrates. Monolayer Sn films are not completely removed from both substrates until temperatures of 1800 K. Repulsive Sn-Sn lateral interactions cause desorption energies to range from 3.9-4.15 eV for coverages of $\theta_{\text{Sn}}$=0.3-1.0 ML on Mo and 4.4-4.5 eV for $\theta_{\text{Sn}}$ = 0.16-1.4 ML on TZM. The electronic character of these submonolayer Sn films was influenced by the Mo substrate, as confirmed by a 0.4 eV BE decrease for the Sn 3d core level in XPS. The clustering of liquid Sn droplets on both substrates was also observed from AES measurements.

Low pressure oxidation using $O_2$ of a 7-ML liquid Sn film were studied at four temperatures of 500, 600, 700 and 800 K up to exposures of 500 L $O_2$. An increased oxidation rate of metallic Sn to tin oxide $\text{SnO}_2$ was observed as the substrate temperature was increased. This may be attributed to increased sticking and dissociation of gas phase $O_2$, increased interdiffusion rates of O and Sn, and/or surmounting some other activation energy barrier in tin-oxide formation. $\text{SnO}$ evaporation occurs in TPD at 966 and 1044 K,
which is attributed to the Kelvin effect during nucleation and growth of the oxide. Tin oxide decomposition and/or desorption of SnO occurs at 230 K lower temperature than metallic Sn evaporation, and thus the thermal stability of oxidized Sn is therefore less than that of metallic Sn.

In experiments where 5 ML Sn films were deposited on an oxygen-precovered TZM surface, tin oxide was formed at room temperature and then increased in concentration during annealing of the films. SnO evaporated in only a single peak at 996 K in TPD. A Sn multilayer TPD peak was also present due to limitations in the amount of oxygen available to oxidize all of the Sn film, with otherwise similar thermal stability and behavior for the formation of tin oxide through either post-oxidation and Sn deposition on oxygen-precovered surfaces. These results provide additional fundamental understanding of the interactions and thermal stabilities of Sn films and coatings for utilization as plasma-facing components in fusion experiments and reactors.

References


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Chapter 6

Low Flux Deuterium Ion Interactions with Solid and Liquid Sn Films Supported on a W Substrate

6.1 Introduction

Liquid metals (LM) are being studied as a potential solution to the high heat fluxes that occur in fusion devices. The regenerative properties of the liquid surface and vapor-shielding effects are some of the advantages that would come from their utilization as a PFC. Metals such as lithium (Li)[1], gallium (Ga)[2] or tin (Sn)[3] have been suggested as well as a lithium-tin (Li-Sn) alloy (30 at. % Li) which is expected to display the advantageous properties of both its constituent elements [4]. Li has received the most attention as a liquid metal PFC and has been used in various engineering configurations and functional magnetic fusion devices due to being low Z and having a low melting point (453 K) [1,5,6]. However, lithium’s evaporation rate poses a problem as temperature increases thereby limiting its utilization in certain regimes.

The other two elements, Ga and Sn have not received the same level of attention as Li though there have been a growing number of both laboratory and fusion device studies to obtain measurements on how these materials will behave when in contact with the plasma. Sn, especially, has a lower vapor pressure and lower chemical reactivity than the other material options of Li and Ga. [7,8] The vapor pressure of Sn is at least five orders of magnitude higher than that of Li. It therefore has operating temperature limit than the other candidate metals. Sn also has a higher surface tension by a factor of 1.7 than Li at 300°C (573 K) and is therefore more stable.
If Sn is interfaced with the plasma in a functional reactor it will experience large particle fluxes coming from the deuterium fuel. Deuterium ion chemistry with Sn films either in the solid or liquid state would be necessary to understand how these films will respond when in contact with the plasma. There have been some recent studies to examine the material properties of interest in Sn especially in comparison with Sn-Li. In a functional reactor its erosion/re-deposition behavior through the linear device Pilot-PSI [9] and secondary electron emission studies. [10] A liquid Sn limiter has also been examined at FTU. [11] Work by Allain et al have looked at the absolute sputtering yield of solid and liquid phases of tin using incident 300-1000 eV H$, D^+$, and He$^+$ particles. The results showed sputtering yields of about 0.038-0.107 Sn atoms for each D$^+$ ion on a solid Sn sample. There was no significant difference in the sputtering yield of solid Sn and liquid Sn at temperatures just above the melting point [12] Deuterium retention on Sn films using ISSTOK plasmas yield less than 0.1% retention ratios which are low but comparable to that W. [13] The studies were done using nuclear reaction analysis (NRA), and the origin or mechanism of deuterium uptake was not discussed in detail.

Laboratory experiments have looked at the thermal decomposition of tin hydride on glass and tin surfaces. [14] Hydrogenic interactions with Sn has also garnered interest in the field of next generation EUV lithography. Sn is used a fuel in the plasma, and leaves deposits on the lithography window. The Sn is etched with atomic or plasma generated hydrogen. Ugur et al. initially examined the generation and decomposition of volatile tin hydrides monitored by in situ quartz crystal microbalances. Results showed that upon atomic hydrogen exposure of a Sn coated crystal surface, only one SnH$_4$ molecule was generated per 90 000 incident H radicals. [15] In this study, the tin hydride on Sn surfaces
is volatile and evaporates. The tin hydride is chemically unstable, and when in contact with a metal surface such as Au decomposes.

Sn etching with hydrogen radicals and inductively coupled plasma reactive ion etching to clean EUV optics is a well characterized technique. [16–19] Prior surface science work has also looked at the adsorption and reaction of gaseous H(D) atoms with D(H) adatoms on Pt(111) and Sn/Pt(111) surface alloys. [17] In addition, Voss et al. also looked at adsorption of thermal D atoms on Sn/Pt(111) surface alloys. [18] Studies have also quantified the decomposition of SnH₄ molecules on metal and metal oxide surfaces such as TiO₂ and ZrO₂.[20–22]

This section will discuss the interactions of low flux, low energy deuterium ions with ultrathin Sn and mixed Sn/SnO films deposited on a W substrate. This is aimed at evaluating the effect of Sn-coatings on deuterium release behavior and deuterium uptake from W. These studies will combine an evaluation of both solid and liquid Sn films. The film thickness was of 7 ML (2.1 nm) for both the Sn film and mixed Sn-SnO film. The range of the ion fluxes and energies used for the study was, \( \Gamma = 0.03-3.3 \times 10^{12}/cm^2s^{-1} \) and 100-700 eV. W was chosen as a substrate in this study due to its pervasive use as a plasma-facing material in multiple studies and the plethora of data on the interactions of deuterium with W. Deuterium release and uptake measurements were measured using Temperature programmed desorption (TPD). X-ray photoelectron spectroscopy (XPS) was used to examine any sputtering effects and structural, concentration or chemical state changes that occur during deuterium irradiation.
6.2 Experimental Section

The experiments are performed in an ultrahigh vacuum (UHV) system, with a 4-axis long arm transfer manipulator system and an antechamber. The base pressure of the chamber prior to experiments is less $2 \times 10^{-10}$ Torr. The chamber is equipped with multiple surface analysis instrumentation.

The polycrystalline tungsten (W) foil (ESPI, Ashland, OR) was cut and freshly polished into dimensions of 1cm x 1cm with a thickness of 3 mil (0.003”). The W was then chemically cleaned with acetone before mounting onto the UHV chamber. The sample was mounted by spot-welding two 15 mil (0.38 mm) Ta wires to the back of the sample to enable resistive heating. This was then attached to two 45 mil tantalum rods to create the heating assembly. This assembly is then attached to the copper rods coming from the manipulator using copper-beryllium connectors. A W-5% Re/W-26% Re thermocouple (Type C) was used to monitor the temperature of the sample. This method of sample mounting allowed the crystal to be resistively heated to temperatures of 1900 K. The polycrystalline W was cleaned using a mixture of 1 kV Ar⁺ sputtering at room temperature to reduce O, C and S contamination to minimum level. Bulk carbon was removed by oxygen-anneals at 1500 K for 5-10 minutes. The oxides where then eliminated by annealing the sample to 1900 K. Before each experiment, the foil was annealed to 1900 K for 5-10s to retain cleanliness.

The Sn films were deposited by physical evaporation from a laboratory made Sn thermal evaporation source. This was constructed by placing a Sn shot (ESPI Metals, Ashland, OR, purity 6N) into a molybdenum evaporation boat (R.D. Mathis Company,
Hi Vacuum Evaporation Sources, Long Beach, CA). Two 15 mil tantalum wires are spot welded to a tungsten evaporation boat to allow for ohmic heating. These where then spot-welded to stainless steel rods attached to a rotary electrical feedthrough. The Sn evaporation source was thoroughly outgassed at temperatures lower than required for evaporation before experiments were performed. The amount of Sn deposited on the surface was calibrated through TPD. During Sn film evaporation, the chamber of the pressure increased to about 2 x 10^{-9} Torr. All thicknesses and film coverages reported are from the TPD measurements.

The prepared Sn films were irradiated with deuterium ion beams at energy ranges of 100-700 eV from a differentially pumped ion source (PHI Model 04-303, 5 kV). A 1 cm x 1 cm raster was applied on the sample to ensure complete exposure of the surface to the ions. The beam currents measured on the samples were 5 nA (100 eV), 16 nA (350 eV), 74 nA (500 eV) and 534 nA (700 eV). This corresponded to fluxes of 0.03-3.33 x 10^{12} ions/cm^2s^{-1}.

The tin oxides studied were prepared by depositing the metallic Sn films on the W, and back-filling the chamber with oxygen by leaking from a lecture bottle (Matheson ultra-high purity 99.99% O_2) through a variable leak valve into the chamber. The films were exposed to a 1000 L of O_2 and held at temperatures of 750 K. The presence of the metallic Sn 3d_{5/2} core level line after oxidation indicated the films were partially oxidized.

All binding energies for the XPS were referenced to the W 4f_{7/2} XPS peak of 31 eV. The pass energy of the spectrometer was set at 44.75 eV for this work. At this pass energy, the W(4f_{7/2}) peak exhibited a full width half-maximum (FWHM) of 1.4 eV which
we have taken as the instrument resolution. Deconvolution of the XPS peaks were done using CasaXPS, with curve fitting by using a Shirley background subtraction and mixed Gaussian-Lorentzian peak shape.

6.3 Results and Discussion

6.3.1 Interaction of Sn films with W

Sn TPD curves from polycrystalline W are shown in Fig. 6.1 for $\theta_{Sn} = 0.07-5.9$ ML. The monolayer was assigned to the curve just after onset of multilayer desorption and is the denoted 1.0 ML curve shown more prominently in in Fig. 6.1(b). This curve was used for subsequent calibrations that are presented in this chapter. Desorption for the lowest coverage of Sn studied at 0.07 ML led to the appearance of a peak, $\chi_1$, at 1525 K (4.2 eV). This peak shifted to lower temperatures due to repulsive interactions as the coverage increased with a final shoulder position at 1384 K (3.8 eV) for a $\theta_{Sn} = 1.0$ ML. This represented a range of 141 K (0.4 eV) going form 7% of a monolayer to a complete monolayer as shown in Fig.6.1 (c). Sn atoms remained on the W surface till temperatures of 1700 K.

At $\theta_{Sn} = 1.0$ ML, a peak, $\chi_2$, appeared at 1115 K which has been assigned to multilayer desorption of the films in agreement with prior results from Mo, TZM and also previous literature reports. [23] This peak also grows with increasing coverage with zero-order desorption kinetics. A SnO peak was observed originating from Sn reacting with gas phase oxygen during deposition or desorption.
Figure 6.1 Sn TPD from W at coverages of 0.07-5.9 ML.
Li TPD curves from polycrystalline W are shown in Fig. 6.2 for $\theta_{\text{Li}} = 0.07$-1.9 ML for comparison with that of Sn films from W. The lowest amount of Li atoms at 0.07 ML tightly bound to W, desorb at peak maxima temperatures of 1192 K (3.28 eV). At Li coverage of 0.2-0.31 ML, the Li monolayer structure is split into a three-peak structure with temperatures at 793 (2.2 eV), 876 (2.38 eV) and 931 K (2.54 eV). The 793 and 876 K peaks continue to grow until a monolayer is reached and the 931 K peak saturates into a shoulder at $\theta_{\text{Li}} = 0.84$. The Li monolayer peak structure is altered at coverages $\theta_{\text{Li}} \geq 1.3$ ML due to Li-induced surface reconstruction of the W surface.

Figure 6.2 Li TPD from W at coverages of 0.07-1.9 ML.
The monolayer at multilayer coverages desorb through two features at 751 and 931 K with a broad high temperature tail that extends to 1500 K. The Li therefore remains on the W surface till temperatures of 1500 K, while Sn atoms remain on the surface till 1700 K. The Li monolayer desorption spectra from W demonstrates more complexity than that observed on Mo or TZM or for Sn on all the surfaces that were studied.

Spectroscopy was used to monitor the surface processes that occur as the Sn films were being annealed to temperatures before and after multilayer desorption. The indicators $T_m$, refers to the Sn bulk melting temperature at 505 K, and $T_o$ is the multilayer desorption onset. The 7 ML Sn AES signal and the Sn/W ratio starts to decrease in Fig. 6.3 when the films are annealed to temperatures at or greater than 450 K, this continues till temperatures of 900 K. This is due to agglomeration of the 3D liquid Sn films into large sized droplets/clusters. As the droplets grow larger the Sn auger signal decreases. This is further confirmed by the increase of the W AES signal with temperature. At $T(K)=1000$, the Sn AES signal increases with a concurrent drop in W AES signal due to desorption of the tin oxide layers which was observed in TPD. One explanation put forward in literature for this drop, is that more Sn becomes incorporated in the 2D layer.[23] This might play a role in our experiments. 1200 K anneals leaves less than 0.65 ML Sn on the surface for both 7.9 and 1.0 ML films. The 0.65 and 1.0 ML Sn, W and Sn/W AES signals remain unchanged till temperatures greater than 1000 K, indicating that no inward diffusion of Sn into the W bulk exceeding the depth detection limit of AES occurs for the sub-monolayer and monolayer films within the explored temperature range of 450-1000 K. Furthermore, this further confirms that the clustering observed for
multilayer Sn films is absent at the monolayer and submonolayer coverages. The linear decrease in the Sn AES for all three coverages at $T(K) \geq 1200$ K occurs from monolayer desorption. However, the formation of a surface Sn-W alloy could not be confirmed by using Auger spectroscopy.

(a)
Figure 6.3 Influence of temperature on the Sn, W and Sn/W AES ratio for Sn films on W. Films deposited at 310 K and annealed for 20 s.
The dependence of both the Sn and W LEIS signal on temperature is presented in Fig. 6.4. For this experiment, 1 kV of Ar\(^+\) was used to resolve the Sn and W peaks. 7.9 ML Sn films completely cover the W substrate till temperatures of 1000 K despite the W AES signal increasing with annealing as seen in Fig. 6.3. The Sn therefore completely wets the surface at least to the monolayer level with large islands on top for thick films. The Sn LEIS signals for 7.9 and 1.0 ML show a reproducible complex phenomenon at temperatures of 1000 K where the Sn LEIS signal continues to rise till temperatures of 1500 K despite desorption of the monolayer. This could be due to aspects related to the technique used. The ion scattering signal depends not only on surface concentration but also on the statistical cross-section of interaction between the ion and surface atoms. The ion neutralization probability, and hence observed LEIS signal has an angular dependence which could change depending on the structure at the sub-monolayer level. One other explanation, is that inter-diffusion into the bulk for multilayer films, and the Sn diffuses out at temperatures greater than 1100 K, and continues to do so till temperatures of 1500 K. A subsurface W-Sn alloy only a few layers thick could also be formed which decomposes. This is further confirmed by the observed decrease in the 0.65 and 1.0 ML Sn LEIS signals at 400-500 K which would be more sensitive to changes in one atom thick layers.

Thermal stability measurements for 10 and 5 ML Sn films using XPS are shown in Fig. 6.5 and are consistent with clustering of multilayers observed for 7.9 ML Sn films by AES. The W 4d signal continues to rise till 1200 K, after multilayer desorption, when it becomes less sensitive to changes in the surface. The Sn 3d core level curve mirrors that of Sn AES line shape. The oxygen signal was monitored to evaluate the impact of
impurities on the thermal stability measurements. The O 1s signal rises due to formation and outward diffusion of SnO, and is eliminated after desorption of the tin oxide. The O 1s increases from 1350-1900 K as the W substrate becomes uncovered from desorption of the monolayers leaving interfacial O atoms.

The alteration of the electronic character of sub-monolayer Sn films on W as inferred by the Sn 3d core level structure is shown in Fig. 6.6. The Sn 3d binding energy shifts by -0.4 eV due to charge transfer and the electropositive nature of W. This shift is the same as that observed for Sn on Mo. No changes were observed for the W 4f core level BE.
Figure 6.4 Influence of temperature on the Sn and W LEIS signals for Sn films on W. Films were deposited at 310 K and annealed for 20 s.
Figure 6.5 Influence of temperature on the Sn, W and Sn/W XPS ratio for multilayer Sn films on W. Films were deposited at 310 K and annealed for 20 s.

Figure 6.6 Sn 3d XPS binding energy shifts for multilayer Sn films compared to that for sub-monolayer Sn films. The W 4f signal remained unmodified by the presence of Sn.
6.3.2 Oxidation Behavior of Ultrathin Sn Films on W

7 ML of metallic Sn was deposited on polycrystalline W and oxidation studies were performed using O₂ within the exposure range of 5-500 L at temperatures relevant to fusion reactor walls. The main motivator was because in some situations, the Sn coatings in the tokamak chamber will be in contact with oxidants (CO and H₂O) that can modify their chemical state. These experiments, were done to study to what extent liquid phase oxidation will have an impact on the surface composition of ultrathin Sn films supported on a W substrate. The Sn 3d and O 1s core-levels were monitored for the different exposures. Valence band measurements indicated that only the stannous oxide phase (SnO) was present throughout the 5-500 L exposures. The ratio of the oxidized Sn component to the total area under the Sn 3d XPS data envelope, SnO/(Sn+SnO) 3d, was used as a parameter for evaluating the extent of film oxidation.

Exposure of the liquid Sn films supported on W induced significant oxidation as shown in the SnO/(Sn+SnO) 3d ratio plot in Fig. 6.7. The rate of oxidation of ultrathin Sn films at temperatures in the liquid state (505, 625 and 750 K) was higher than that for solid state (310 K). This is due to increased rates of inward diffusion into the Sn bulk. The rate of oxidation and oxygen uptake (as measured by the O 1s signal) of the 625 and 750 K films were found to be the same. This indicates that temperature plays less of a role in metal to oxide conversion at temperature ranges of 625-750 K. At exposures of 500 L, the oxide component was 30% (310 K), 41% (505 K), 45% (625 K) and 54% (750 K) of the Sn 3d data envelope indicating partial oxidation of the films.

The SnO/(Sn+SnO) 3d ratio and O 1s signal rose linearly as a function of exposure for all temperature cases. Using the 310 K solid films as a baseline, the O 1s
signal intensity after 500 L O$_2$ exposure for 505 K films were 1.4 times higher, and 625 and 750 K films 2 times higher than that of the solid indicating that oxygen uptake was also affected by temperature. The W 4f signal (not shown) intensity, BE and FWHM remained unchanged during oxidation, and so it can be concluded that the W was inert throughout the oxidation process.

Sn films oxidized on molybdenum (Fig. 5.7) were completely oxidized when held at temperatures of 800 K (the SnO/(Sn+SnO) 3d ratio approached 1). The Sn films on tungsten were partially oxidized at 750 K (SnO/(Sn+SnO) 3d ratio approached 0.54), the highest temperature studied. The partial oxidation of the Sn on W could be explained by the inter-diffusion of Sn into the W or alloying to form a W-Sn which would retard the oxidation rate as proposed earlier based on LEIS thermal stability measurements. An uptake plot for the oxidation of solid and liquid multilayers Li films at $\theta_{Li}$=5 and 15 ML, and the sub-monolayer regime is shown in Fig. 6.7 for comparison. Li is more chemically reactive than Sn to oxygen, and so uptake is rapid with saturation oxygen uptake reached after 10-20 L O$_2$ exposure. Generally, the thicker the Li films, the larger the saturation oxygen uptake. However, the liquid Li films at 456 K retained less oxygen at saturation exposures than the solid Li films for all multilayer thicknesses. This is due to one of the Li oxide phases being unstable at high temperatures. Consequently, this blocks a channel for oxygen consumption.

LEIS scans of the oxidized Sn surface were obtained after 500 L exposure and are presented in Fig. 6.8 (a). The oxidized Sn surfaces are composed of both a Sn peak at 884 eV and O peak at 517 eV for all oxidation temperatures. The O LEIS intensity area as shown in Fig. 6.8 (b) was obtained, and it was discovered that more oxygen was on the
surface with increasing oxidation surface temperature. The oxidized Sn at temperatures of 505, 625 and 750 K was cooled down to 310 K, and the O LEIS areas taken after cooling are indicated as colored data points. The amount of surface oxygen was the same at 505 and 625 K after cooling to 310 K, but for the 750 K, there was more surface oxygen.

TPD measurements in Fig. 6.8 (c) of the oxidized films show negligible differences in the SnO desorbed and the presence of prominent Sn multilayer peak further confirming the partial oxidation of the films.
Figure 6.7 Conversion to oxide ratio and the O 1s XPS binding energy shifts for multilayer Sn films exposed to molecular oxygen. The oxidation of Li films at various thicknesses also solid and liquid temperatures is provided for comparison purposes.
Figure 6.8 LEIS spectra and TPD signal after oxidation experiments for the Sn films at bulk temperatures.
6.3.3 Deuterium Ion Interactions with Metallic Sn Films on W

Sn films were deposited on the polycrystalline W substrate and irradiated with a monoenergetic deuterium ion beam. The ion energies used for this study varied between 100-700 eV. The fluxes incident on the W sample varied depending on the ion energies and were within the range of \(0.03-3.3 \times 10^{12} \text{ D}_2^+ \text{ cm}^{-2} \text{s}^{-1}\). The fluxes were calculated by measuring the beam current from the sample after a 50 V bias was applied to increase the collection efficiency. The experimental set up and the expected ion-interactions is displayed in Fig. 6.9. Ion-irradiation on the W sample was used as control, since the stopping range of 700 eV \(\text{D}_2^+\) exceeds the thickness of the ultrathin Sn coatings used in this study as calculated by TRIM calculations.

![Figure 6.9 Schematic of \(\text{D}_2^+\) irradiation experiment and the expected interactions with the surface.](image)

Several experiments were first undertaken as an initial step to understand the interactions of the W-Sn system with deuterium ions. TPD signals were taken from a W and 7 ML Sn coated sample with no deuterium ion irradiation and this is depicted in Fig. 6.10 for the temperature range of 300-1000 K. Both W and 7 ML Sn/W showed no D$_2$ desorption peaks. A small HD peak was observed for the 7 ML Sn/W which is due to recombination of H and D atoms already adsorbed on the surface. This is expected since a residual gas analysis of the chamber vacuum shows the presence of D$_2$ gas.

Figure 6.10 QMS signal from clean W and from a 7 ML Sn film coating.
The W and 7 ML Sn/W, were also exposed to 500 L of D$_2$ gas through a leak valve, and a subsequent TPD was taken with results shown in Fig. 6.11. D$_2$ and HD desorption were observed at peak maxima of 404 and 419 K, respectively for W. These peaks are from recombination of surface adsorbed hydrogenic atom species since there is very negligible incorporation of hydrogen in the subsurface of tungsten. [24–27] For W, H$_2$ desorption was also seen at higher temperatures due to isotopic effects and water formation (H$_2$O, D$_2$O and HDO) at peak temperatures between 369-379 K is observed forming presumably from the recombination of H or D atoms with surface hydroxyl groups. The HD and D$_2$ desorption peaks observed for the 7 ML Sn film exposed to gas phase deuterium, closely match the line shape and peak maxima for that from W. Consequently, they originate from small amounts of adsorbed D atoms dissociated on exposed W surface and not from chemisorption on the Sn clusters. Another potential origin is due to absorption of D atoms into the bulk of Sn to finally reside on the Sn/W interface. These species are weakly bonded, and diffuse out and recombine at ~400 K. While water formation was observed via HDO desorption, for 7 ML Sn/W, the presence of Sn eliminated the D$_2$O peak.

To elucidate the mechanism by which the deuterium ions are retained in the Sn-coated W sample, two modes of exposure were performed. In the first case, the W sample was first pre-irradiated with deuterium ions, and after that Sn was deposited. For the second, referred to as post-irradiation, Sn was first deposited, and then deuterium exposure occurred after. The results shown in Fig. 6.12 indicate that the pre-irradiated case retained more deuterium (1.76 times) than the post-irradiated case as indicated by the TPD areas. The peak maxima for post-irradiation (405 K, 1.08 eV) is close to that for pre-irradiation (414 K, 1.1 eV) and the similarity in line shape indicates that the implanted deuterium in
the subsurface region desorb through the same states regardless of the exposure method. Therefore, the order of the ion irradiation did not have an effect on the D₂ release behavior from a 7 ML Sn-coated W.

Figure 6.11 QMS signal from W and 7 ML Sn film coating after 500 L D₂ exposure.
Figure 6.12 D$_2$ TPD from 7 ML Sn film coating after 700 eV D$_2^+$ exposure. Two modes of exposure. Post-irradiation of Sn film coating (black curve) and pre-irradiation before Sn deposition (red curve).

D$_2$ desorption from an uncoated W substrate at 310 K after 700 eV D$_2^+$ ion exposure is displayed in Fig. 6.13 with two broad desorption peaks at 445 (1.2 eV) and 652 K (eV). Our results agreed with prior work on polycrystalline W. [28] The 445 K peak has been assigned prior in literature to be due to desorption from adsorption sites or natural defects such as grain boundaries, while the peak at 652 K was assigned previously to radiation induced defects such as vacancies. [28] A high temperature 720 K peak observed in prior reports due to vacancy clusters was not observed in our experiments due to our low energies and fluxes which would not cause such significant radiation damage. Addition of sub-monolayer Sn ($\theta_{\text{Sn}}=0.25$ and 0.5 ML) to W, reduced the size of the 445 and 652 K peak. A new D$_2$ peak appeared at 419 K for 0.5 ML of Sn, which grew and dominated the D$_2$ QMS
signal for 7 ML Sn on W irradiated with deuterium ions. The presence of Sn therefore attenuates D\textsubscript{2} desorption from radiation induced defects although does not eliminate it. The effect of Sn sub-monolayers and multilayers on W are twofold, the first is the destabilization of D\textsubscript{2} desorption and release, leading to lower peak desorption temperatures and the second is that less deuterium is retained in the Sn-W system than polycrystalline W.

It can be posited that the effects observed can from two mechanisms. The first is that Sn is serves as a protective barrier for W, reducing the impact of radiation damage or directly affecting the population of vacancy sites due to different hydrogen migration parameters (diffusion, solubility and permeability) in Sn than W. This less likely as observed from the results in Fig. 6.12. The second is that D\textsubscript{2} release from vacancies is blocked by the presence of Sn.

Figure 6.13 D\textsubscript{2} TPD from sub-monolayer Sn films after 700 eV D\textsubscript{2}\textsuperscript{+} irradiation at fluence of 4 x 10\textsuperscript{15} D\textsubscript{2}\textsuperscript{+} per cm\textsuperscript{2}.
The magnitude of radiation induced-defects are dependent on ion energies and fluences, and this was explored with results shown in Fig. 6.14. W and 7 ML Sn-coated W samples were exposed to D$_2^+$ at progressively lower energies of 100, 350 and 500 eV with correspondingly lower fluences. For these three ion energies, more deuterium was retained on W with the difference narrowing at 500 eV exposure. The D$_2$ release character was the same regardless of the ion energy used for both W and 7 ML Sn-coated samples. For all cases, the Sn reduced the desorption temperatures for implanted D atoms.

Figure 6.14 D$_2$ TPD from 7 ML of Sn irradiated with different D$_2^+$ at various ion energies. The ion energies studied were 100, 350, and 500 eV in addition to 700 eV.
This is further illustrated by measurements of the fluence dependence of D₂ desorption from deuterium ion irradiated W and 7 ML Sn-W shown in Fig 6.15 and Fig. 6.16. At low fluences for W, the 605 K peak appears prominently and then saturates at fluences of 1 x 10¹⁵ D₂⁺/cm². The lower temperature 450 K peak continues to grow with increasing fluences. The peak shifts to lower temperatures finally settling at 416 K indicative of second order desorption. All the implanted deuterium has desorbed from the bulk of the W with a high temperature tail by 700-800 K. For the 7 ML Sn-coated W sample, at the lowest fluence studied at 5 x 10¹³ D₂⁺/cm² a peak appears at 393 K due to recombination of D atoms from a Sn surface. All the implanted D is released by 500 K for the Sn/W system at fluences of 0.5-2 x 10¹⁴ D₂⁺/cm² and the 618 K peak that was present on W is absent. At fluences ≥1 x 10¹⁵, the high temperature at 635-674 K develops like that observed for W, leading to increased stability of D atoms on the Sn-coated W with D continuing to desorb till 800 K. At higher fluences, Sn becomes less effective in suppressing the high temperature shoulder observed in the D₂ desorption spectra though D₂ continues to desorb at peak maxima of 8-20 K lower than uncoated W. At fluences ≥1.2 x 10¹⁶ D₂⁺/cm², a D₂ desorption peak was observed at 496 K for 7 ML Sn/W which was not observed for W. This peak was further observed when we irradiated the 7 ML Sn/W sample with 2.4 x 10¹⁶ D₂⁺/cm² and results from the presence of Sn.
Figure 6.15 D$_2$ TPD from a W (black curves) and 7 ML-Sn coated W substrate (red curves) irradiated with 700 eV D$_2^+$ ions at various ion fluences.
Figure 6.16 D\textsubscript{2} TPD from a W and 7 ML-Sn coated W substrate irradiated with 700 eV D\textsuperscript{2+} ions at different fluences elucidating the differences in the desorption behaviors.

HD, HDO and D\textsubscript{2}O signals were observed during deuterium ion irradiation as shown in Fig. 6.17. The W and 7 ML Sn/W samples will have adsorbed H, -OH, -OD species. Diffusion limited desorption of water and HD is therefore expected. No SnD\textsubscript{4} evaporation/desorption was observed throughout all desorption experiments that were performed on irradiated Sn/W. The HD TPD from W at low fluences (0.5-2 x 10\textsuperscript{14} D\textsubscript{2}/cm\textsuperscript{2}) has a peak at 500 K, with the appearance of another peak at 414 K at higher fluences. Both the 414 K peak and 500 K shoulder continue to be populated at high fluences. The 600 K D\textsubscript{2} peak from radiation defects was not present in the HD signal. The desorption spectra for HD from 7 ML Sn/W is remarkably different from that from W with the first peak appearing at 419 K which continues to grow. There is no literature evidence of adsorption of H or D atoms on Sn surfaces, so this peak is assigned to recombination of subsurface D atoms with interfacial H atoms located at the boundary of Sn/W. However, one cannot rule
out the presence of adsorbed or absorbed H atoms in the Sn bulk. The 496 K peak observed at fluences \( \geq 1.2 \times 10^{16} \text{D}_2^+ / \text{cm}^2 \) is absent from the HD spectra. D$_2$O desorption is observed at \( T_p \) of 400 and 520-600 K, and HDO desorption at \( T_p = 383-387 \) K, for both W and 7 ML Sn/W indicating that this is coming from -OD and -OH groups on W. This is further confirmed by the similarity of the line-shapes of their TPDs.

Less deuterium as D$_2$ was retained in the 7 ML Sn/W than uncoated W except at a fluence of \( 1.2 \times 10^{16} \text{D}_2^+ / \text{cm}^2 \) as shown in Fig. 6. 19. This was also true for deuterium retained as HD or HDO for all fluences. More D$_2$O was formed on 7 ML Sn/W than W for fluence range of \( 0.2-4 \times 10^{15} \text{D}_2^+ / \text{cm}^2 \). Due to the differing mass spectrometer sensitivities for D$_2$, HD, D$_2$O and HDO, the peak areas cannot be summed up. However, it can be concluded that more deuterium was retained overall for the W samples as D$_2$ and HD compared to 7 ML Sn/W at 310 K.
Figure 6.17 Complete TPD of all the signals that come from irradiation of the W and 7 ML Sn/W samples at fluences of: (a) $4 \times 10^{15} \text{ D}_2^+$/cm$^2$ (b) $1.2 \times 10^{16} \text{ D}_2^+$/cm$^2$. 
Figure 6.18 TPD for HD, D₂O and HDO signals from a clean W and 7 ML-Sn coated W substrate irradiated with 700 eV D₂⁺ ions at various fluences.
Figure 6.19 Uptake plot for D₂, HD, D₂O and HDO signals from a clean W and 7 ML-Sn coated W substrate irradiated with 700 eV D₂⁺ ions at various fluences.

7 ML Sn/W held at the Sn bulk melting temperature (505 K) was irradiated with 700 eV D₂⁺ at various fluences with the D₂ desorption spectra from this shown in Fig. 6.20. At this temperature, the Sn forms agglomerated droplets as observed from AES. A single broad desorption peak at 656 K for high fluences is observed for this system. This peak is a result of the thermal stability of the D₂ as opposed to a new chemical state. This peak grows rapidly with fluence and appears to saturate at 1.2 x 10¹⁶ D₂⁺/cm². Noteworthy is that more deuterium as D₂ is retained in the 505 K 7 ML Sn/W than for the W sample.
Figure 6.20 D$_2$ uptake plot from liquid 7 ML-Sn coated W substrate irradiated with 700 eV D$_2^+$ ions at various fluences.

The influence of temperature on the D$_2$ desorption behavior is further illustrated in Fig. 6.21. While for 310 K D$_2^+$ ion irradiation, D$_2$ from Sn/W is released at peak maxima lower than of W, for T(K) ≥ 450, the reverse occurs. The D$_2$ is released from W at temperatures 30-50 K lower than that of 7 ML Sn/coated W. However, the D$_2$ TPD line shape for all temperatures studied are similar for W and Sn/W except broader with a higher temperature tail for the latter case suggesting that W plays a role in desorption kinetics. Interestingly, while no D$_2$ desorption was observed from ion-irradiated W at 650 K, a feature at 788 K was observed for D$_2$ desorption from 7 ML Sn/W. This result was reproducible at several ion gun energies and substrate conditions (results not shown) and this state has been attributed to desorption from a W-Sn surface alloy state. From Fig. 6.22, it is observed that liquid Sn on W at T(K) ≥ 450 increased D$_2$ uptake by a factor of ~2. The amount of deuterium retained as D$_2$ decreased with temperature for both W and 7 ML Sn/W.
Figure 6.21 D$_2$ uptake plot from a clean W and 7 ML-Sn coated W substrates irradiated with 700 eV D$_2^+$ at a fluence of $4 \times 10^{15}$ D$_2^+$/cm$^2$ at temperatures of 310, 450, 505, 550, 650 and 750 K.
Figure 6.22 Temperature dependence of the $D_2$ uptake plot on a polycrystalline W and 7 ML-Sn coated W substrate irradiated with 700 eV $D_2^+$ ions at a fluence of $4 \times 10^{15}$ $D_2^+/cm^2$.

The QMS signals for HD, HDO and $D_2O$ desorbing from both samples at the different temperatures studied. Less HD is retained on 7 ML Sn/W than W with all gone at 550 K. More $D_2O$ is formed on Sn/W than for the W at all the temperatures studied. All $D_2O$ for W is gone at temperatures of 505 K, while for 7 ML Sn/ $D_2O$ desorption persists till temperatures of 650 K.
Figure 6.23 QMS signal from the W and 7 ML Sn film at the different temperatures studied after irradiation with 700 eV D$_2^+$ ions at a fluence of $4 \times 10^{15}$ D$_2^+/\text{cm}^2$. (a) D$_2$ signals and (b) HD, D$_2$O and HDO signals.
XPS was taken before and after deuterium ion irradiation of the 7 ML Sn/W at various temperatures to evaluate any modifications in the chemical state (through differences in BE and FWHM) or changes in concentration of Sn, and the results are shown in Fig. 6.24. For multilayer Sn films on W irradiated with deuterium ions, no chemical state changes were observed and the Sn 3d\(_{5/2}\) BE was centered at 484.8 for all temperatures studied before and after deuterium ion irradiation. The constant Sn 3d intensity before and after irradiation of the Sn films at 310 K, indicates that the 700 eV D\(_2^+\) ions do not significantly sputter the Sn film within the detection limit of XPS. At temperatures T(K) ≥ 450, the Sn 3d signal decreased due to clustering of the Sn films prior to irradiation. For 7 ML Sn/W irradiated with deuterium ion at temperatures of 505-750 K, it was observed that the Sn 3d signal increased after irradiation due to ion-induced structural changes and rearrangement of the Sn multilayers on W. No reportable changes in the W 4f signal was observed after ion irradiation.

Although multiple prior reports in literature have shown that Sn is etched by interactions with atomic hydrogen [15] and hydrogen/deuterium plasma, this was not observed in our experiments. Volatile SnD\(_4\) is formed by the exothermic reaction:

\[
\text{Sn + 4D} \rightarrow \text{SnD}_4 \quad (\Delta G = -625.5 \text{ kJ/mol})
\]

The measured reaction probability of Sn for H atoms by Ugur et al. was calculated to be 90000 H atoms to generate one SnH\(_4\) molecule. [15] This matched reaction probability estimates that were obtained by forming tin deuteride using a hydrogen plasma source by Braginsky et al. [21] For the highest deuterium fluence provided to the Sn coated W surface at 1.2 x 10\(^{16}\) D\(_2^+\)/cm\(^2\) it is expected that 1.3 x 10\(^{11}\) SnD\(_4\) is generated (an upper limit estimate since ions are used) which is below the 1% monolayer detection (1 x 10\(^{13}\))
limit of TPD and much lower than that for XPS. A fluence of D atoms or energetic ions of $9 \times 10^{16}$ D$_2^+$/cm$^2$ is required to etch a monolayer of Sn from the surface as tin deuteride. This low reaction probability is due to a high recombination of H/D atoms to evolve gas phase hydrogen. H$_2$ formation with ($\Delta G = -203.3$ kJ/mol H) is more favorable than SnD$_4$ formation ($\Delta G = -156.4$ kJ/mol H). Tin hydride is also very chemically unstable and is thermally decomposed on contact with metallic surfaces to release gas phase hydrogen. The presence of W could catalyze the decomposition of any SnD$_4$ formed at the interface during outward diffusion of the D atoms from the W bulk leading to evolution of deuterium gas.
Figure 6.24 XPS of the Sn 3d core levels of the 7 ML Sn films before (blue curve) and after (red curve) 700 eV D$_2^+$ ion irradiation. The temperatures studied were 310, 450, 505, 550, 650 and 750 K. The black curve is the Sn 3d XPS signal after deposition of the film.
6.3.4 Low Flux 700 eV Deuterium Ion (D$_2^+$) Interactions with Mixed Sn/SnO$_2$ Films

The interaction of 700 eV D$_2^+$ ions with mixed Sn/SnO$_2$ films was studied. The SnO$_2$ films were prepared by depositing 7 ML of Sn onto a W substrate, and exposing the Sn film to 1000 L of O$_2$ at temperatures of 750 K, and then cooled down to 310 K. The films were partially oxidized as indicated by the presence of metallic Sn 3d peak after exposure. Partial oxidation of the Sn films is explained by diffusion or alloying of the Sn with the W substrate within the XPS analysis depth limit. The initial fraction of the Sn 3d doublet that was composed of SnO$_2$ after oxidation and before ion irradiation was determined to be for the film kept at 330 K to be 65%, 525 K to be 74%, and 750 K 67%. These films will be referred to as a mixed Sn/SnO$_2$ film henceforth.

Sn 3d$_{5/2}$ of the mixed Sn/SnO$_2$ as a function of deuterium ion fluence is shown in Fig. 6.25 for films held at temperatures of 310, 525 and 750 K. Generally, as the partially oxidized Sn/SnO$_2$ film is bombarded with D$_2^+$ ions, the Sn 3d$_{5/2}$ intensity coming from SnO$_2$ decreases, with a concurrent increase in metallic Sn 3d component. This indicates that the oxidized Sn is being reduced to metallic Sn due to impact of the deuterium ions either by physical or chemical sputtering process or possibly both. For the highest fluence studied at $2.35 \times 10^{16} \text{D}_2^+/\text{cm}^2$, the SnO$_2$ is not completely reduced to Sn when Sn/SnO$_2$ is kept at 310 K. At this temperature, 20% of the Sn 3d envelope is composed of the oxide component. However, at the same fluence, complete reduction of the SnO$_2$ to metallic Sn is observed for deuterium irradiated mixed Sn/SnO$_2$ held at temperatures of 525 and 750 K.
Thermal enhancement of the reduction process by deuterium ions is further illustrated in Fig. 6.26. The SnO$_2$ 3d intensity decreases exponentially for all temperatures studied till it was completely removed for the 525 and 750 K case. For all fluence points, there was less SnO$_2$ for high temperature cases. This is also true for the O 1s signal which decayed exponentially with increasing deuterium fluence. Despite the complete reduction of the SnO$_2$ to metallic Sn, for 525 K, a O 1s signal was observed at high fluences, due to O not chemically bonded to Sn and either adsorbed on the metallic Sn surface as O atoms or hydroxyl or from O containing species located at the Sn/W interface. The corresponding metallic Sn and conversion ratio of Sn/(SnO$_2$+Sn) grew with deuterium ion irradiation. The observed thermal enhancement of the process indicates that the SnO$_2$ is reduced to metallic Sn by a chemical sputtering mechanism (SnO (s) + D$_2^+$ → Sn (s) + D$_2$O).

Desorption spectra from the mixed Sn/SnO$_2$ films at 310 and 750 K after irradiation with deuterium ions at 2.35 x 10$^{16}$, is shown in Fig. 6.27. The sharp D$_2$ desorption feature at 496 K that was observed for metallic Sn irradiated with deuterium at fluences of 1.2 x 10$^{16}$ D$_2^+/cm^2$ in Fig. 6.16, is also observed as a HD and D$_2$ desorption feature at 484 K for the reduced Sn/SnO$_2$ film at 310 K. This points to a dynamic process where the metallic Sn formed from the reduction of the SnO$_2$ interacts with the incoming deuterium ions. D$_2$O desorbs through a broad peak at 608 K. No D$_2$, HD, D$_2$O, HDO desorption features was observed in the TPD for the 750 K case.
Figure 6.25 XPS spectra showing reduction of the oxide during 700 eV D$_2^+$ irradiation of the 7 ML Sn/SnO$_2$ film at fluxes of 3.3 x 10$^{12}$ D$_2^+$ cm$^{-2}$s$^{-1}$. (a) 310 K (b) 525 K (c) 750 K.
Figure 6.26 Changes in the XPS intensity (as measured by the peak area) for the 7 ML Sn/SnO₂ film during 700 eV D²⁺ irradiation at fluxes of 3.3 x 10¹² D²⁺ cm⁻² s⁻¹. (a) metallic Sn 3d, (b) O 1s, (c) oxidized Sn 3d and (d) reduction ratio.
Figure 6.27 QMS signal after 700 eV D$_2^+$ irradiation of 7 ML mixed Sn/SnO$_2$ film on W substrate at (a) 310 K and (b) 750 K.
6.5 Conclusions

Thermal stability, oxidation rate and deuterium uptake measurements were performed on Sn films deposited on a polycrystalline W substrate using AES, XPS, LEIS and TPD. Sn from deposited films did not begin to desorb from the substrate until temperatures of 900 K, above which SnO desorbs followed by Sn multilayer and subsequent Sn monolayer desorption. Sn monolayers remain on W up to temperatures of 1700-1800 K. TPD of Li films on W showed Li-induced reconstruction of the substrate after deposition of 1 ML of Li. Sn multilayers and monolayers on W desorb at higher temperatures than for Li films on W. Clustering of liquid Sn films on W at temperatures of 450-900 K was observed by both AES and XPS. A -0.4 eV BE shift in the Sn 3d core level peak showed that W modified the electronic structure of sub-monolayer Sn films. Deuterium uptake measurements at 310 K show that a Sn coating on W causes less deuterium to be retained for fluences of 0.05-4 x 10^{15} D_2^+/cm^2. In similar experiments at substrate temperatures of 450-550 K, deuterium uptake was larger for Sn-coated W samples by a factor of two than uncoated W samples. While no deuterium was observed to be retained on W at 650 K, Sn-coated samples retained deuterium at this temperature. No deuterium uptake was observed on either the W and Sn-coated W substrates at 750 K. For mixed SnO_2/Sn films, deuterium irradiation led to reduction of the oxide component to metallic Sn, with rapid reduction at 750 K. Films initially composed of 67% tin oxide were completely reduced to metallic Sn at this temperature, with a chemical sputtering mechanism playing an important role in the reduction process.
References


Chapter 7

Conclusions and Future Work

The thermal stability of metallic and oxidized Li and Sn films has been studied on two polycrystalline molybdenum substrates. For metallic Li films, the Li TPD results show that Li in films thicker than one monolayer thermally desorb in a peak at 560-600 K. Li monolayer films on both substrates show stronger Li-Mo bonding than Li-Li bonding in the thicker Li films, however Li in the monolayer, in contact with the substrate metal, begins to desorb at only slightly higher temperatures. On Mo, the Li monolayer is characterized by a broad thermal desorption feature from 600 - 850 K and a high temperature tail with Li remaining on the surface until 1500 K. The Li monolayer on TZM shows a prominent desorption peak near 700 K and a shoulder near 1000 K, with Li remaining on the surface until 1100 K. These results show an unusually high thermal stability of Li films on a Mo(poly) substrate compared to TZM(poly), single-crystal Mo(110) surfaces, and other metal substrates. This could be caused by the interactions of Li with specific low coordination Mo sites on high Miller index planes exposed on the polycrystalline substrate or by Li interactions with oxygen at interfacial sites or grain boundaries. No irreversible intermixing of Li with either the Mo or TZM substrates was observed, as evidenced from studies of TPD and surface spectroscopy. Evidence in LEIS was found for 3D-clustering in Li films at or exceeding one monolayer on TZM when heated at temperatures of 300-400 K. Li AES and Mo AES attenuation measurements were roughly consistent for Li film growth with non-ideal layering, and some clustering
in thicker layers, at room temperature, and LEIS also shows no exposed Mo or Ti atoms for Li films thicker than two monolayers on the TZM substrate.

TPD measurements of oxidized Li films demonstrated that the 5 ML LiO$_x$ films prepared by post-oxidation of Li are stable until temperatures of 620 K, after which they desorb in three main peaks. The desorbing Li atoms observed on the QMS arise due to decomposition of pure lithium oxide phases (LiO$_x$) and decomposition of Li$_4$MoO$_5$ and evaporation of lithium molybdate (Li$_2$MoO$_4$). The desorption onset for the LiO$_x$ films is 100 K higher than the desorption onset for metallic Li films demonstrating the higher stability of the oxides. The 860 K shoulder and 990 K peak observed on the Li TPD is tentatively attributed to decomposition and desorption of Li-oxide films and the 1220 K peak to decomposition and desorption of Li$_x$MoO$_y$. XPS shows the formation of a mixed oxide phase of Li$_2$O/Li$_2$O$_2$ upon oxidation of the film at 310 K. Lithium peroxide is thermally unstable and reduced to lithium monoxide when annealed to 680 K. At 1070 K, O atoms react with the Mo atoms of the TZM substrate to form MoO$_2$ and MoO$_3$ species as indicated by XPS. These are proposed to arise due to the presence of a lithium molybdate species as observed from prior experiments. Molybdenum oxides can only be formed at conditions of very high temperature (> 1000 K) and high oxygen exposures (>80 L) indicating that Li promotes molybdenum oxidation through the formation of Li$_2$O. The Li$_2$O then reacts with molybdenum to form lithium molybdate species. Additionally, LEIS experiments of the oxidized Li films confirm the wetting of TZM by LiO$_x$ films at room temperature.

The deposition of sub-monolayers of Li on an oxygen-covered TZM substrate at 310 K lead to the formation of interfacial lithium-oxide species. A new chemical state
was observed when the interfacial Li oxide was annealed to higher temperatures. The interfacial Li oxide decomposes and desorbs by a single broad peak temperature of 1126 K. The presence of a multilayer peak in the Li QMS signals showed that Li films 3-5 ML thick deposited on the O/TZM were not fully oxidized by chemisorbed O. Nevertheless, these films made LiO$_x$ that desorbed through oxide phases that closely matched that of the post-oxidized films.

Sn films were observed to be thermally stable until a temperature range of 900-1000 K, after which zero-order desorption of the Sn multilayer occurs at temperatures of 1187-1270 K for both molybdenum substrates. The Sn monolayer begins to desorb at 1050 K, just after multilayer desorption. Monolayer Sn films are not completely removed from both substrates until temperatures of 1800 K. Sn-Sn lateral interactions are largely repulsive, with desorption energies ranging for 3.93-4.15 eV for coverages of $\theta_{\text{Sn}}$=0.28-1.00 ML on Mo and 4.37-4.50 eV for $\theta_{\text{Sn}}$ = 0.16-1.35 ML on TZM. Mo also influenced the electronic character of interfacial submonolayer Sn films which was confirmed by a 0.4 eV decrease in the BE of the Sn 3d core level in XPS. The clustering of liquid Sn droplets on both substrates was observed from AES measurements.

Low pressure oxidation of 7 ML liquid Sn films were studied at four temperatures of 500, 600, 700 and 800 K up to exposures of 500 L O$_2$. An increased conversion rate of the metallic Sn to tin oxide was observed as the temperature was increased. This thermal enhancement may be attributed to increased sticking and dissociation of gas phase oxygen, increased O diffusion rates into the subsurface of the Sn metal, or overcoming the activation barrier for tin-oxide formation. The tin oxide formed evaporates as SnO in peaks at temperatures of 966 and 1044 K. The presence of two desorption states during
evaporation of the tin oxide is tentatively attributed to the Kelvin effect. As observed by TPD, the SnO desorption peaks are at lower temperature than the temperature for metallic Sn sublimation, and so the thermal stability of post-oxidized Sn is less than that of metallic Sn.

For 5 ML Sn films deposited on an oxygen-covered TZM surface at room temperature, tin oxide was formed. The tin oxide concentration increased during thermal annealing of the films. The tin oxide evaporated with only one single Sn peak at 996 K. A Sn multilayer peak was also present due to limitations in the amount of oxygen available to react with the Sn atoms.

TPD of Li films on W show Li-induced reconstruction of the substrate after deposition of 1 ML of Li. The Sn films demonstrate higher thermal stability than Li films at the multilayer and monolayer level on W. Agglomeration of multilayer liquid Sn films on W was observed by both AES and XPS measurements. Deuterium uptake measurements show that at 310 K, a Sn coating on W destabilizes D₂ release from the substrate. Furthermore, less deuterium is retained either as D₂ or HD on Sn-coated W for fluences of 0.05-4 x 10¹⁵ D₂⁺/cm². Destabilization of deuterium release also occurred for submonolayer coverages of Sn atoms. The reverse was observed for 7 ML Sn films on W kept at temperatures of 450-650 K. Deuterium uptake was larger for Sn-coated W samples by a factor of two than uncoated W samples at temperatures of 450-550 K. Additionally, while no deuterium uptake and release was observed on W at 650 K, Sn-coated samples retained deuterium. At substrate temperatures of 750 K irradiated with deuterium ions, no deuterium release was observed for both W and Sn-coated W samples. For mixed SnO-Sn films, deuterium ion irradiation led to reduction of the oxide.
components to metallic Sn. Reduction is thermally enhanced pointing to the dominance of a chemical sputtering mechanism.

These results increase our fundamental understanding of the interactions and temperature conditions required for the utilization of Sn films as a plasma-facing component. Just a monolayer of Sn coating on W can affect deuterium release at high temperatures that may be encountered in fusion devices.

Suggestions for future work that could be explored include examining the interactions of Sn films with deuterium atoms and ions at high fluxes. This is due to the low cross section of reactions of deuterium atoms with the Sn films as calculated by prior researchers for SnD$_4$ formation. This cross section is also dependent on the incident energies and temperatures. High flux measurements can be used to evaluate the etch rate for Sn films due to deuterium adsorption or implantation which is important for evaluating Sn material loss and the subsequent impact on plasma radiative heat losses arising from evaporation of SnD$_4$. Moreover, while SnD$_4$ is known to evaporate at room temperature, high flux irradiation ($>10^{16}$ atoms cm$^{-2}$s$^{-1}$) of cold Sn can allow observation of the tin-deuteride by HREELS and its subsequent desorption temperature in vacuum by TPD. The interaction of Sn films with other PFC substrates such as SS316 should also be explored as an extension of this work. Only oxygen was studied in this work, and other gases such as CO, H$_2$O and CO$_2$ remain unexplored both in this thesis and in literature.

Additionally, for the oxidized Li films studied, it was discovered that Li molybdate was formed at 1070 K. The thickness of the Li molybdate formed increased with the initial Li coverage present prior to oxidation and thermal annealing. The
interaction of the Li molybdate with deuterium ions has not yet been explored and would be of interest to the fusion community. Future studies could evaluate the thermal stability of Sn-Li films by mixing these elements on substrates of interest and studying their deuterium retention behavior. Additionally, studies on Ga due to its low melting point, may also be of interest and are amenable to study by physical vapor deposition on refractory substrates in UHV.