Dependence of LTX plasma performance on surface conditions as determined by *in situ* analysis of plasma facing components

M. Lucia[a]*, R. Kaita[a], R. Majeski[a], J.P. Allain[b], F. Bedoya[b], T. Abrams[a], R.E. Bell[a], D.P. Boyle[a], M.A. Jaworski[a], J.C. Schmitt[a]

[a]*Princeton Plasma Physics Laboratory (PPPL), Princeton, NJ 08543, USA*
[b]*University of Illinois at Urbana-Champaign (UIUC), Urbana, IL 61801, USA*

Abstract

The Materials Analysis and Particle Probe (MAPP) diagnostic has been implemented on the Lithium Tokamak Experiment (LTX) at PPPL, providing the first *in situ* surface characterization of tokamak plasma facing components (PFCs). MAPP samples were exposed to argon glow discharge cleaning (GDC), lithium evaporations, and hydrogen tokamak discharges inside LTX. Samples were analyzed with x-ray photoelectron spectroscopy (XPS), and alterations to surface conditions were correlated against observed LTX plasma performance changes. Argon GDC caused the accumulation of nm-scale metal oxide layers on the PFC surface, which appeared to bury surface carbon and oxygen contamination and thus improve plasma performance. Lithium evaporation led to the rapid formation of a lithium oxide (Li_2O) surface; plasma performance was strongly improved for sufficiently thick evaporative coatings. Results indicate that a 5 h argon GDC or a 50 nm evaporative lithium coating will both significantly improve LTX plasma performance.

1. Introduction

Understanding the interplay between surface conditions and plasma performance is a key aspect in the continuing advancement of magnetic confinement fusion research. Indeed, various metrics of tokamak plasma performance are affected by such plasma facing component (PFC) surface conditions as elemental composition, chemical state, and physical morphology [1]. Plasma performance in modern fusion devices is typically well-analyzed with a variety of plasma diagnostic systems, but surface condition analysis is often limited to a qualitative narrative of wall-conditioning techniques—baking, glow discharge cleaning (GDC), boronization, *etc*. In this light, surface analysis techniques can provide a quantitative and analytic foundation for describing surface condition.

Past experiments have attempted either to reconstruct the surface history of an *ex situ* campaign-integrated PFC sample following air exposure [2] or else to reproduce tokamak conditions in offline experiments [3]. This work details the first *in situ* surface analysis of a tokamak PFC. This analysis has been accomplished via the Materials Analysis and Particle Probe (MAPP) diagnostic [4], a collaborative effort between PPPL and UIUC. MAPP is designed for sample surface analysis on timescales as brief as one plasma discharge.

For this study, MAPP's x-ray photoelectron spectroscopy (XPS) analysis capability was used to study samples exposed to argon GDC, lithium evaporations, and hydrogen plasma discharges in the Lithium Tokamak Experiment (LTX) at PPPL. Experiments sought to correlate the nanoscale changes in PFC surface composition observed with MAPP XPS to the macroscopic changes in LTX plasma performance observed with LTX's suite of more traditional plasma diagnostics. Such a correlation would ideally inform the optimization of LTX wall conditioning techniques going forward.

2. Materials and methods

LTX is a spherical torus magnetic confinement device (R_0 = 40 cm, a = 26 cm) [5][Fig. 1(a)]. Plasma discharges are limited by four conducting toroidal quadrants, creating a shell conformal to the plasma. The shell quadrants (hereafter, "shells") are composed of 0.16 cm 304L stainless explosively bonded to 0.95 cm OFHC copper, providing a combination of good lithium compatibility and high thermal conductivity. Up to μm-scale lithium coatings can be applied evaporatively to the shells, providing a lithium PFC over 75% of the plasma's edge. Two toroidal breaks, two poloidal breaks, and eight mid-shell penetrations allow for diagnostic access. The shells are independently heatable to 325 °C, allowing for operation with a liquid lithium PFC. LTX base pressure is typically 5×10^{-8} Torr, mostly H_2 and N_2, but it transiently exceeds 10^{-4} Torr due to hydrogen fueling with each plasma discharge. Lithium evaporation in this work is accomplished by a two-step process. Liquid lithium is first dropped onto a pre-heated (300 °C) lower shell via a hole in the bottom of a resistively heated crucible, forming a macroscopic pool of lithium on the shell bottom. An electron beam is then used to heat the pool above 450°C.

The MAPP head carries four small (d = 0.94 cm) interchangeable sample disks, and it is mounted on a bellows drive so that it can be inserted into the LTX plasma chamber [Fig. 1(b)] and then retracted into a private analysis chamber [Fig. 1(c)], which can be sealed and pumped independently. MAPP base pressure is typically 5×10^{-8} Torr, mostly H_2O and CO_2, rising as high as 1×10^{-7} Torr when biasing the x-ray source filament. This present work used MAPP's x-ray photoelectron spectroscopy (XPS) capability to measure elemental composition and chemical state information of the sample surfaces. For XPS, MAPP houses a PSP Vacuum TX400 x-ray source and a Comstock AC-900 electrostatic energy analyzer. Energy calibration was performed using single-point reference either to Au-4f from a gold sample or to C-1s or F-1s from some adventitious surface component, as available. Atomic

fractions for elemental composition were calculated as a ratio of peak areas above a Shirley background, accounting for empirical elemental sensitivity factors [6].

3. Argon glow discharge cleaning

3.1. Experimental

Gold and 316 stainless MAPP samples were exposed to two argon glows inside LTX. Glows were struck with an electrode inserted through the outboard toroidal break and biased 600 VAC against grounded shells. Neutral argon pressure was 3 mTorr, and the glow appeared visibly uniform throughout the volume between shells. For both exposures, the MAPP head was located flush with the shells through the outboard toroidal break [Fig. 1(c)].

The first glow (hereafter, "pre-lithium glow") occurred prior to any lithium evaporation after machine venting and cleaning. The glow lasted 13 h spaced over several days, but MAPP was only exposed for a continuous 1.5 h, with XPS scans completed immediately before and after exposure. LTX plasma discharges were conducted before and after the glow to gauge its effect on plasma performance.

The second glow (hereafter, "post-lithium glow") occurred following three months of occasional lithium evaporation on three of the shells, altogether totaling ~1 g. Glow duration was 5.2 h, but in this case MAPP was exposed for the entire time. XPS scans were completed immediately before and after the glow exposure, and intermediate survey scans were taken 0.3 h and 1.5 h into the glow.

3.2 Results

Following the pre-lithium glow, both the gold and 316 stainless samples acquired a 12 ± 2 at. % Fe and 6 ± 1 at. % Cr signature, where neither was previously present on either sample surface. At the same time, the Au-4f signal disappeared from the gold sample. Both

surfaces gained a significant amount of oxygen, and the Fe-2p peak structure of each suggested both reduced and oxidized iron, respectively at 707 eV and 710 eV.

Compared to pre-glow discharges, post-glow discharges lasted more than twice as long and had almost triple the plasma current [Fig. 2]. Spectroscopic C II and O II filterscopes both recorded less total emission from plasma discharges after the glow, but no direct comparison of impurity concentration is possible because temperature data was not available for these discharges.

Following the post-lithium glow, all MAPP samples had acquired a coating of lithium and oxygen thick enough that no other elements were visible. The intermediate survey scans reveal that the coating built up progressively during the entire 5.2 h period. A second peak appears in both the C-1s and O-1s regions, attributable to Li-C and Li-O bonding, while the C-C bonding peak in the C-1s region almost completely disappears [Fig. 3].

3.3 Discussion

Glow discharge cleaning has a long history as a wall-conditioning method in magnetic confinement fusion devices, and the plasma performance improvement following the pre-lithium glow demonstrates its effectiveness in LTX. H.F. Dylla reports that an argon glow ion fluence of 1×10^{23} m^{-3} completely removed surface carbon contamination from stainless [7]. In this work, the MAPP sample surface carbon was halved in the 1.5 h pre-lithium glow, and it was almost completely removed in the 5.2 h post-lithium glow. Exact LTX glow parameters are unknown, but assuming a typical glow discharge with $T_e = 5$ eV and $n_i = 1 \times 10^{16}$ m^{-3}, argon ion fluence would be 4×10^{23} m^{-2} for the pre-lithium glow (only 5×10^{22} m^{-2} for MAPP exposure portion) and 2×10^{23} m^{-2} for the post-lithium glow. These values are in good agreement with Dylla.

However, physical sputtering of carbon as the wall conditioning mechanism is not consistent with the observed accumulation of iron, chromium, and oxygen on both gold and 316 stainless MAPP samples. In addition, W. Eckstein calculates a threshold energy of 70 eV for argon on carbon, but only 20 eV for argon on iron and chromium [8]; the 70 eV ion energy is not possible in a glow discharge, but the 20 eV ion energy should be available from an argon glow's $5T_e$ sheath potential. Absent chemical sputtering effects that aren't possible with inert argon, only the metal components of the LTX shell should be sputtered. The resulting wall conditioning mechanism would be the re-deposition of a thin Fe_2O_3/Cr_2O_3 layer everywhere on the surface of the LTX shells; carbon impurities would thus be sequestered, and oxygen impurities would be bound in the metal oxide. This would account for the better plasma performance because fewer impurities would enter the plasma, as reflected in the reduced plasma C II and O II filterscope signals.

In fact, the stoichiometry of the MAPP results is consistent with a thin Fe_2O_3 and Cr_2O_3 layer accounting for 40% of the XPS signal distributed uniformly over the now-buried original carbon-dominated surface, which still accounts for the remaining 60% of the XPS signal. Given the first-order attenuation law for photoelectron signal [9], the thickness d of such an ideal uniform layer can be calculated:

$$I(z) = I_0 exp\left[\frac{-z}{\lambda_X \cos \theta}\right] \qquad (1)$$

$$d = \lambda_m \cos \theta \log\left[1 + \left(\frac{\lambda_c}{\lambda_m}\right)\left(\frac{S_m}{S_c}\right)\right] \qquad (2)$$

where S is the signal from the carbon/metal oxide, λ is the photoelectron inelastic mean free path of the carbon/metal oxide, and θ is the angle of the energy analyzer from the surface normal. For the relevant parameters here, $d = 0.3$ nm ≈ 1 ML. With the assumption that glow-induced sputtering and re-deposition occurs uniformly over LTX, a sputter yield can be

estimated as the ratio of Fe/Cr atoms on the MAPP samples to total Ar fluence: $Y_{Ar \to Fe,Cr} = 1 \times 10^{-4}$, which is at least consistent with sputter yields just above the threshold energy.

A similar calculation is possible for the post-lithium glow, where MAPP results suggest that lithium is sputtered from the LTX shells and re-deposited around the vessel. With the different parameters, $d = 2.0$ nm ≈ 7 ML and $Y_{Ar \to Li} = 4 \times 10^{-4}$. Future work should diagnose plasma discharges immediately before and after a post-lithium glow in order to determine the effect of these lithium re-deposition levels on LTX plasma performance.

4. Lithium evaporation and passivation

4.1. Experimental

LTX shell (copper-backed 304L stainless) and TZM molybdenum alloy MAPP samples were exposed to three electron beam evaporations from the lower shell lithium pool. In each case, the MAPP head was located flush with the shells through the outboard toroidal break, so the evaporation from the pool was line-of-sight to the samples. XPS scans were completed immediately before and after each evaporation. Estimates of lithium evaporation rate were possible via measurements from a back-shell thermocouple directly beneath the lithium pool. Given the lithium vapor pressure curve $P_{Li}(T_{Li})$, total evaporated mass was given by Langmuir evaporation:

$$\Gamma_{vap}(T_{Li}) = \frac{P_{Li}(T_{Li})}{\sqrt{2\pi m_{Li} T_{Li}}} \tag{3}$$

yielding 3 ± 1 mg, 100 ± 40 mg, and 80 ± 30 mg for the three evaporations. Based on the geometry of lithium pool and MAPP head, these masses were converted to MAPP sample coating thicknesses: 1.6 ± 0.4 nm, 60 ± 20 nm, and 50 ± 20 nm, respectively.

The first evaporation (hereafter, "2-nm evaporation") was a 6 min beam run at 0.80 kW beam power on a 260 °C pre-heated lower shell. No argon glows, lithium evaporations, or plasma discharges had occurred in LTX for 46 d prior to this evaporation. Afterward,

LTX was operated for 10 plasma discharges to determine the evaporation's effect on plasma performance.

The second evaporation (hereafter, "60-nm evaporation") was a 5 min beam run at 1.30 kW power followed (after a 20 min duty cycle break) by a 6 min beam run at 1.45 kW power on a 310 °C pre-heated lower shell and the beam operated first for 5 min at 1.30kW power, then for 6 min at 1.45kW power, with a 20 min duty cycle break in between. Following this evaporation, LTX was operated for 13 plasma discharges.

The third evaporation (hereafter, "50-nm evaporation") was a 6 min beam run at 1.45 kW beam power on a 320 °C pre-heated lower shell. This evaporation marked the beginning of a 3 d passivation experiment. LTX was operated for 2 plasma discharges (to estimate reproducibility) at each of 2 h, 20 h, 41 h, and 70 h after the evaporation. XPS scans were performed immediately before and after each pair of plasma discharges to decouple ambient passivation from plasma passivation.

4.2. Results

Following the 2-nm evaporation, a lithium signature appeared on both LTX shell and TZM MAPP samples; however, it was not strong enough to completely attenuate the signals from the substrate metals. The carbon/oxygen ratio dropped significantly after the evaporation, and the lithium/oxygen ratio settled around two. Post-evaporation plasma performance was comparable to that with bare stainless shells: Discharges lasted 9-10 ms, with plasma current peaking at 8-10 kA and average density peaking at 1.7-2.1 $\times$ 10^{18} m^{-3}. Triple Langmuir probes had been installed on the centerstack and lower shell, and these measured edge electron temperatures of 15-20 eV and 6-8 eV, respectively.

The 60-nm and 50-nm evaporations coated the LTX shell sample with enough lithium that the substrate metal signals were completely attenuated. The carbon signature was also

greatly suppressed, particularly in the 50-nm evaporation, while the lithium/oxygen ratio settled around two within a few hours of evaporation and remained unchanged during the three-day passivation test.   Plasma performance improved strongly following the 60-nm evaporation [Fig. 4], with 38-40ms discharges that peaked at 52-54kA plasma current and 2.3-2.7 × 10^{18} m^{-3} average density.   The centerstack and lower shell triple probes measured a slightly hotter edge plasma, at 20-25eV and 10-15 eV, respectively.   In comparison with historical filterscope data from passivated lithium walls, the post-evaporation C II and O II emission was reduced by an order of magnitude, but the Li I and Li II emission was increased by an order of magnitude.

Plasma performance was not strongly changed in the 70 h period following the 50-nm evaporation [Fig. 4].   Discharge plasma current reached the same maximum, but decayed slightly more quickly, resulting in a 3-4ms shorter discharge.   Average plasma density ramped up more quickly, but it never reached a higher maximum due to the shorter length of discharges.

4.3. Discussion

The 60-nm and 50-nm evaporations saturate the XPS probe depth, but MAPP results from the 2-nm evaporation can be used to benchmark against the validity of the thermocouple evaporation model.   In this evaporation, the average substrate metal (Fe, Cr, Mo) was attenuated 89 ± 1 %.   A slight reworking of (2) allows calculation of the required lithium layer for the observed attenuation: $d = 2.3 \pm 0.1$ nm.   Given neglected potential errors in the geometrical conversion factor and in the assumption of a uniform coating, the agreement with the model is quite good.

Despite a wide variation in lithium coating thickness among the three evaporations, the surface lithium-oxygen ratio always tended to about two, suggesting the formation of

9

Li$_2$O. While LiOH is favored in bulk reaction between lithium and water, various studies have reported a preference for Li$_2$O in high vacuum [3][10]. J.R. Hoenigman and R.G. Keil have observed Li$_2$O forming exclusively up to 10^2 L H$_2$O exposure and preferentially up to 10^3 L H$_2$O exposure [11]; for the current cold-shell $P_{H_2O} = 2 \times 10^{-9}$ Torr in LTX, these doses respectively correspond to 14 h and to 6 d. Interestingly, this latter time period coincides somewhat with the observed rate of post-lithium decay for LTX plasma performance. This suggests that Li$_2$O is still capable of pumping hydrogen ions, while LiOH is not. A similar but longer passivation experiment should be performed, lasting at least two weeks.

5. Conclusions

Surface analysis results from argon GDC imply that a 2 nm surface layer of metal (Fe, Cr, or Li) oxide effectively sequesters surface carbon impurity. For plasma performance considerations, this indicates optimum argon glow duration of 10 h on bare stainless shells and 5 h on lithium-coated shells. Plasma performance demonstrates substantial improvement with 50 nm evaporative lithium coatings, but not with 2 nm coatings. Accordingly, lithium evaporation should be performed with the lower shell pre-heated to near maximum temperature and with the electron beam run at near maximum power. The discrepancy here between an effective 2 nm glow-induced shell coating and an ineffective 2 nm evaporation-induced shell coating requires further study. Uniformity of lithium coating coverage may be the key difference; the argon GDC appeared to re-deposit the lithium very uniformly, while the beam evaporation coats only two shell quadrants.

References

[1] H.W. Kugel *et al.*, Phys. Plasmas **15**, 056118 (2008)

[2] C.N. Taylor *et al.*, J. Appl. Phys. **109**, 053306 (2011)

[3] R. Sullenberger, MS thesis, Princeton University, 2012.

 [4] C.N. Taylor *et al.*, Rev. Sci. Instrum. **83**, 10D703 (2012)

[5] R. Majeski *et al*., Phys. Plasmas **20**, 056103 (2013)

[6] D. Briggs and M.P. Seah, eds. *Practical Surface Analysis, Vol. 1*. John Wiley & Sons, 2e.: New York, 1992.

[7] H.F. Dylla, J. Vac. Sci. **6** (3), 1276-1287 (1988)

[8] R. Behrisch and w. Eckstein, eds. *Sputtering by Particle Bombardment*. Springer: Berlin, 2007.

[9] L.A. Giannuzzi and F.A. Stevie. *Introduction to focused ion beams instrumentation, theory, techniques, and practice*. Springer, 1e.: New York, 2005.

[10] H. Sugai *et al.*, J. Nucl. Mater. **220-222** (1995) 254-258

[11] J.R. Hoenigman and R.G. Keil, App. Surf. Sci. **18** (1984) 207-222

Figure captions

Fig. 1 – (a) A cutaway projection of LTX; (b) MAPP head in exposure position; (c) MAPP head in analysis position.

Fig. 2 – Various measures of LTX plasma performance immediately before (red) and immediately after (blue) the pre-lithium argon GDC.

Fig. 3 – Changes observed in C-1s and O-1s peaks of 316 stainless MAPP sample, with traces from immediately before (red), immediately after (blue), 12 hours after (black), and 8 days after (magenta) the post-lithium argon GDC.

Fig. 4 – Various measures of LTX plasma performance immediately before (red), immediately after (blue), and 3 days after (black) the 50-nm lithium evaporation.

Figures