Time dependent chemical interactions of lithium, deuterium, and oxygen on lithium-coated graphite surfaces

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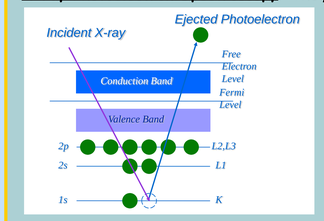
1 Surface Characterization Methods

X-ray Photoelectron Spectroscopy: *The photoelectric process*



- *XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).*
- *The ejected photoelectron has kinetic energy:*

$$KE = h\nu - Binding\ E - Work\ Function$$

- *Energy of ejected photoelectron reveals characteristic information regarding the elemental composition of the substrate.*

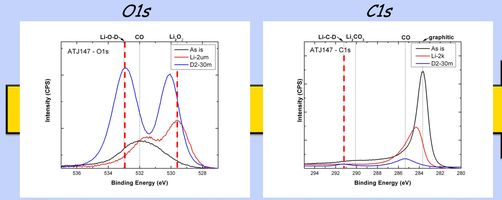
Omicron surface characterization Cluster
(Birck Nanotechnology Center)

Experiment Methods

- XPS performed before and after each process (dwell=0.8ms, step=0.05eV).
- Processes include:
  - Li deposition via lithium evaporator.
  - D^+ bombardment (irradiation) (500 ev/amu).
  - Ar cleaning and annealing (550C) (if needed).

2 Deuterium-Lithium Surface Chemistry

ATJ graphite surface chemistry with 2μm lithium deposition and D^+:



ATJ graphite sample substrate (black) with 2μm lithium conditioning (red), and 30 min deuterium bombardment (blue). Control studies isolate the effect of each process

What happens?

Oxygen:

Li and O interactions are manifest at 529.5 eV in the XPS spectrum.

Li, O, and D interactions, on a graphite substrate, are manifest at 533 eV.

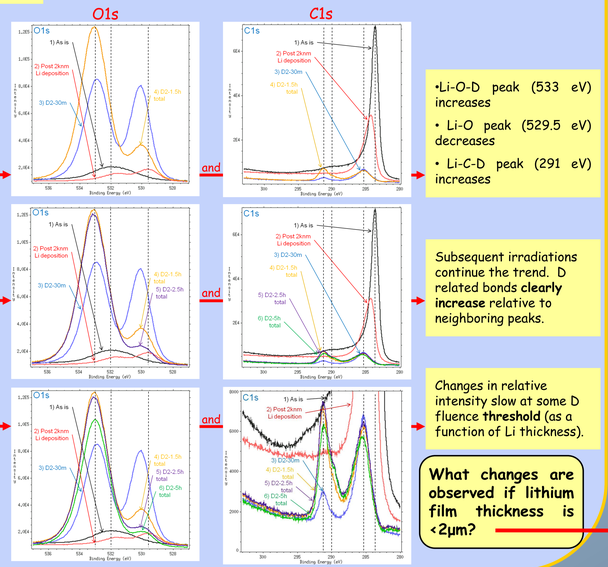
Carbon:

Li, D, and C interactions are manifest at 291 eV.

Time dependent deuterium fluence affects dominating chemical bonds:

Incrementally ***increase deuterium fluence*** to observe changes and response threshold.

XPS Spectra: • Peak shift • New peak = Change in chemical bonds/interactions



- •Li-O-D peak (533 eV) increases
- • Li-O peak (529.5 eV) decreases
- • Li-C-D peak (291 eV) increases

Subsequent irradiations continue the trend. D related bonds **clearly increase** relative to neighboring peaks.

Changes in relative intensity slow at some D fluence **threshold** (as a function of Li thickness).

What changes are observed if lithium film thickness is <2μm?

Abstract

Lithium conditioning of plasma facing components has been used for particle control in fusion devices such as TFTR, CDX-U, FTU, T-11M, TJ-II and NSTX and has yielded improved plasma performance. A PMI probe has been installed on NSTX to provide an in-situ diagnostic for surface chemistry and deuterium retention measurements. Recent controlled laboratory experiments at Purdue University are investigating the chemical functionalities in lithiated graphite and the mechanism by which D is retained. XPS results show that Li reacts readily with residual oxygen in ATJ graphite, and immediately begins to intercalate into the substrate. Additionally, it has been found that Li-O and Li-C react to D proportional to the lithium thickness, suggesting a D saturation threshold. This work investigates the transient nature of the lithium and oxygen functionalities, their response to time varying D flux, and the implications to NSTX.

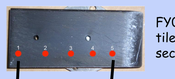
3 Lithium Dose Dependence

Surface chemistry is affected by time dependent parameters:

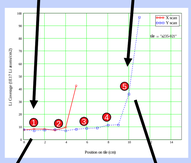
Time dependence

- Lithium fluence (dose)
- Intercalation effects

POST MORTEM ANALYSIS

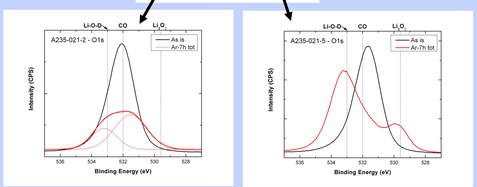


FY08 NSTX post-mortem tile located on the upper secondary passive plate.



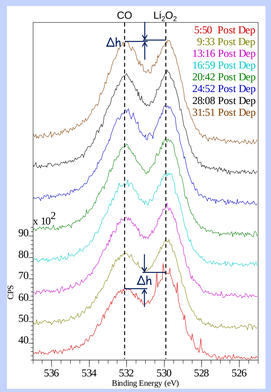
Ion beam analysis for Li coverage.[1] Analysis shows a single tile having Li rich and low Li regions.
W.L. Wampler

Ion beam analysis shows that both regions have comparable D coverage. [2]



Low Li region on tile ***did not*** produce the functionalities characteristic of deuterium retention.

Li rich region on the same tile ***produces*** the functionalities characteristic of deuterium retention.



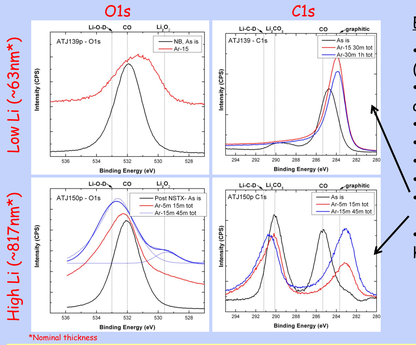
Above, as time after deposition increases (5 min, 50 sec, etc.) the relative height (Δh) of the Li-O bonds to the Li-O-D bonds ***decreases***. Intercalation of lithium is a time dependent function and has been studied extensively.[3]

How do sections 2 & 3 connect to PMI in NSTX?

- Section 2: Controlled experiments show correlation between D retention and Li-C and Li-O bonding.
- Section 3: The amount of Li on surface dictates retention viability.
- Section 4: PMI probe elucidates on D-Li interactions.

4 PMI Probe Results

Samples were exposed to NSTX plasmas via PMI probe during several experiments. Samples provided shot by shot comparison of surface chemistry and D retention measurements.

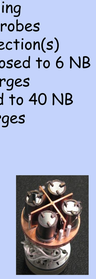


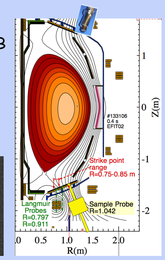
*Nominal thickness

Experimental specifications:

- 4 samples on a 2" dia. Probe (2x ATJ graphite, Si, and Si/Pd)
- Secure, disruption- proof mechanical attachment
- 16 thermocouple wires connections
- Thermal cooling
- 2 Langmuir probes
- Heater connection(s)
- Samples exposed to 6 NB heated discharges
- ATJ exposed to 40 NB heated discharges

Lane Roquemore

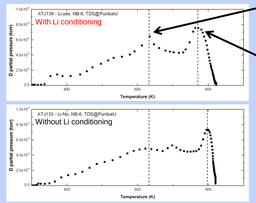




Samples exposed to NSTX plasmas with ***sufficient lithium*** coverage (100-500 nm for a polished surface) had peaks congruent to the Li-O-D and Li-C-D functionalities observed in control studies.

Thermal desorption spectroscopy TDS:

- Samples exposed to NSTX plasma
- PMI probe retracted into analysis chamber
- Samples heated to ~800 C
- TDS peaks correspond to effect release of D.
- Multiple peaks indicate multiple bonds



With Li conditioning, 600 K peak consists of weaker bonds

800 K peak indicates stronger covalent bonds of D to Li, O, and/or C.

Results are consistent with gas balance measurements by C.H. Skinner (JO4.00008).

5 Conclusions

- ❑ Lithium thickness is a fundamental parameter in deuterium retention. A ***nominal minimum threshold*** thickness exists between 100 and 500 nm.
- ❑ Lithium is always bound to ***oxygen and carbon***, when present.
- ❑ *Working hypothesis:* ***D atoms are weakly bound*** (based on TDS and XPS analysis) in regions near lithium atoms bound to either oxygen or the carbon matrix (fundamentally different to non Li conditioned graphite).

Discussion

- ❑ Li, O, and D interactions, on a graphite substrate, are manifest at 533 eV. Peak dominates with larger D fluence , indicating that a given lithium thickness has a finite deuterium capacity.
- ❑ Li, D, and C interactions are manifest at 291 eV. Relative peak energy increases with increased D fluence. Changes cease to occur at a presently unknown D fluence threshold.
- ❑ Li and O interactions, on a graphite substrate, are manifest at 529.5 eV in the XPS spectrum. Peak diminishes with larger D fluence, indicating that D^+ binds with and consumes the Li-O bonds manifest at 529.5 eV.
- ❑ Future work will: 1) utilize Raman Spectroscopy to measure the D hybridization state, 2) study surface morphology effects.

Acknowledgements

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[1] W.L. Wampler, "Ion Beam Analysis of Lithium on Tiles from NSTX" SNL, 2007.
[2] W.L. Wampler, "Ion Beam Analysis of Deuterium on Tiles from NSTX" SNL, 2007.
[3] N. Itou, H. Toyoda, K. Morita and H. Sugai, J. Nucl. Mater. 290 (2001), p. 281.