E-Beam Generated Plasma Etching for Developing High-Reflectance Mirrors for Far-Ultraviolet Astronomical Instrument Applications

By

Manuel A. Quijada

Outline

- ❖ Overview & Objectives
- ❖ FUV Coating Developments at GSFC
  - ✓ Al+MgF_2 (Coating of optics for ICON & GOLD probes)
  - ✓ Al+LiF (SISTINE suborbital program)
- ❖ E-Beam Developments (NRL Collaboration)
  - ✓ Restoring FUV reflectance of aluminum mirrors protected with MgF_2
  - ✓ Oxide removal & passivation of bare Al samples
- ❖ Conclusions
- ❖ Acknowledgments

Overview and Objectives

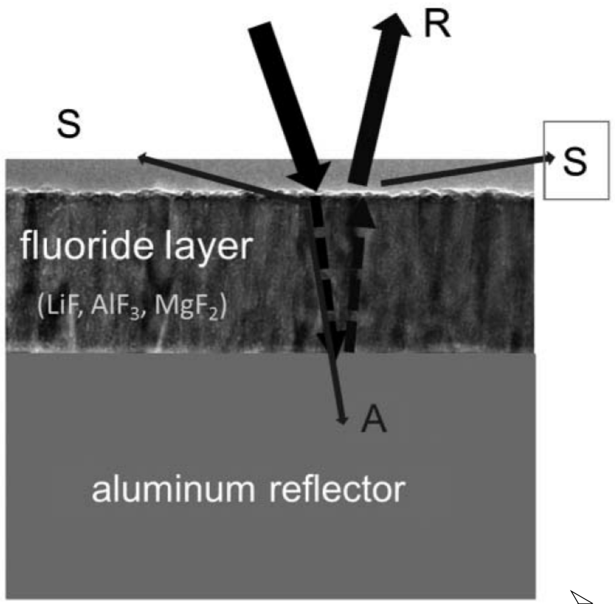
- **Summary of goals**
  - ✓ Deposit high performance FUV to FIR optical broadband coatings by a variety of techniques to produce low-absorption metal-fluoride overcoats to protect and enhanced reflectance of Al mirrors.
- **Driver / Need**
  - ✓ High-performance broadband coatings (90-10,000 nm) have been identified as an "Essential Goal" in the technology needs for a future Large-Aperture Ultraviolet-Optical-Infrared Space Telescope (LUVOIR and HabEx).
  - ✓ Low reflectivity and transmission of coatings in the Lyman Ultraviolet (LUV) range of 90-130 nm is one of the biggest constraints on FUV telescope and spectrograph design.
- **Benefits**
  - ✓ The development of broad-band reflectors based on Al with increased performance in the FUV spectral range will be an enabling technology for an instrumentation platform for astrophysics and optical exoplanet sciences with a shared telescope providing high throughput and signal-to-noise ratio (SNR) over a broad spectral range.

Metal-Fluorides as Protection Layers

Using fluorides as protectors for Al:

(Wilbrandt *et.al. Vol. 53 No. 4 App. Opt. 2014*):

Absorption edges: 116 nm (MgF_2), 110 nm (AlF_3), and 104 nm (LiF)



Optical Constants

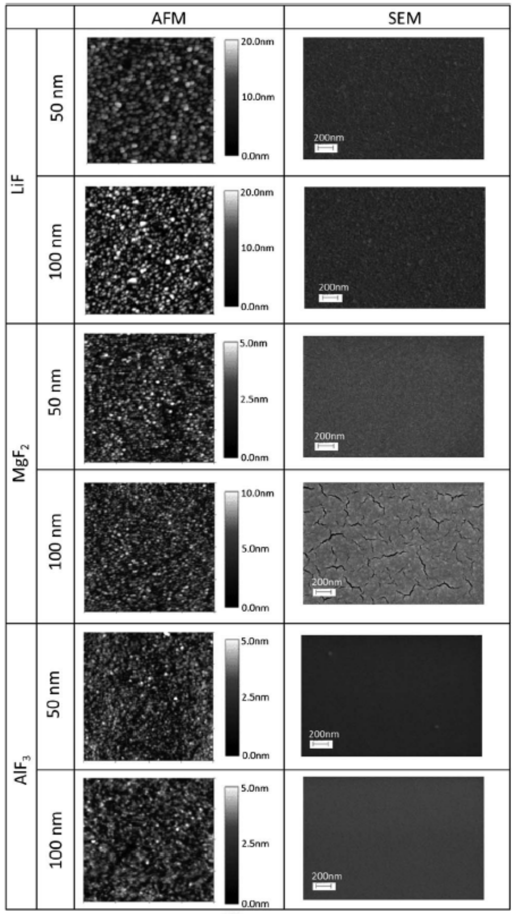
$$R = 1 - A - S$$

Roughness

Overview of Roughness Values for Protected Aluminum Mirrors

Type	Rate in nm/s	σ in Nanometer 1 μm	σ in Nanometer 10 μm
Al+AlF_3 ⇨	0.2	1.34	1.38
	2.0	1.23	1.31
Al+LiF ⇨	0.2	5.81	4.69
	2.0	5.20	4.16
Al+MgF_2 ⇨	0.2	1.39	1.36
	2.0	1.70	1.51

- AlF_3 & MgF_2 exhibit the lowest (comparable) roughness.
- LiF films have significantly higher roughness.
- Surface roughness increases with layer thickness.
- Surface roughness decreases with increased deposition rate.

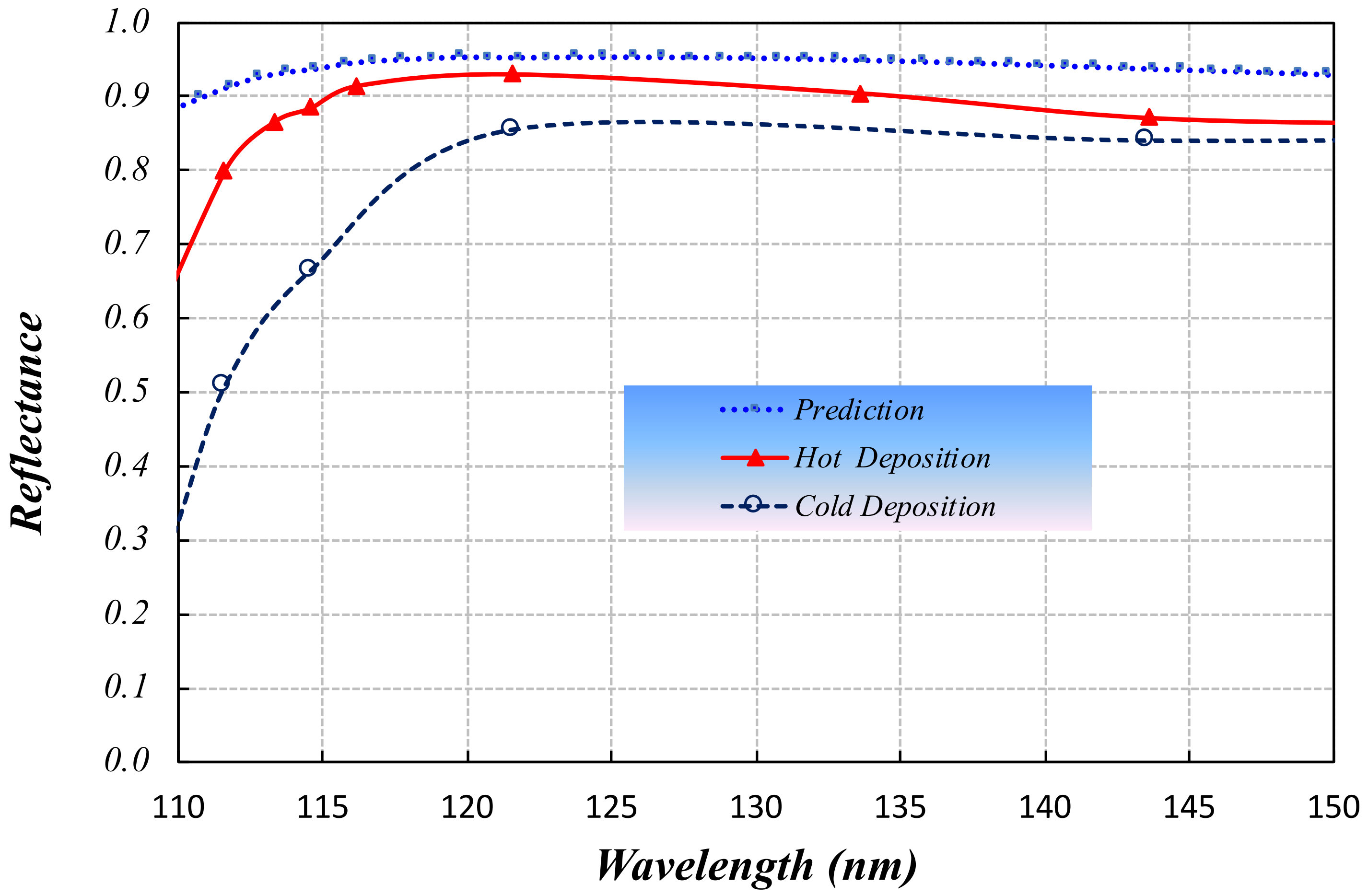


Al+MgF_2 Mirror FUV Performance

- Predicted vs. measured reflectance of bare Al and Al+MgF_2 reflectance (Al: 50.0 nm; MgF_2: 25.0nm)

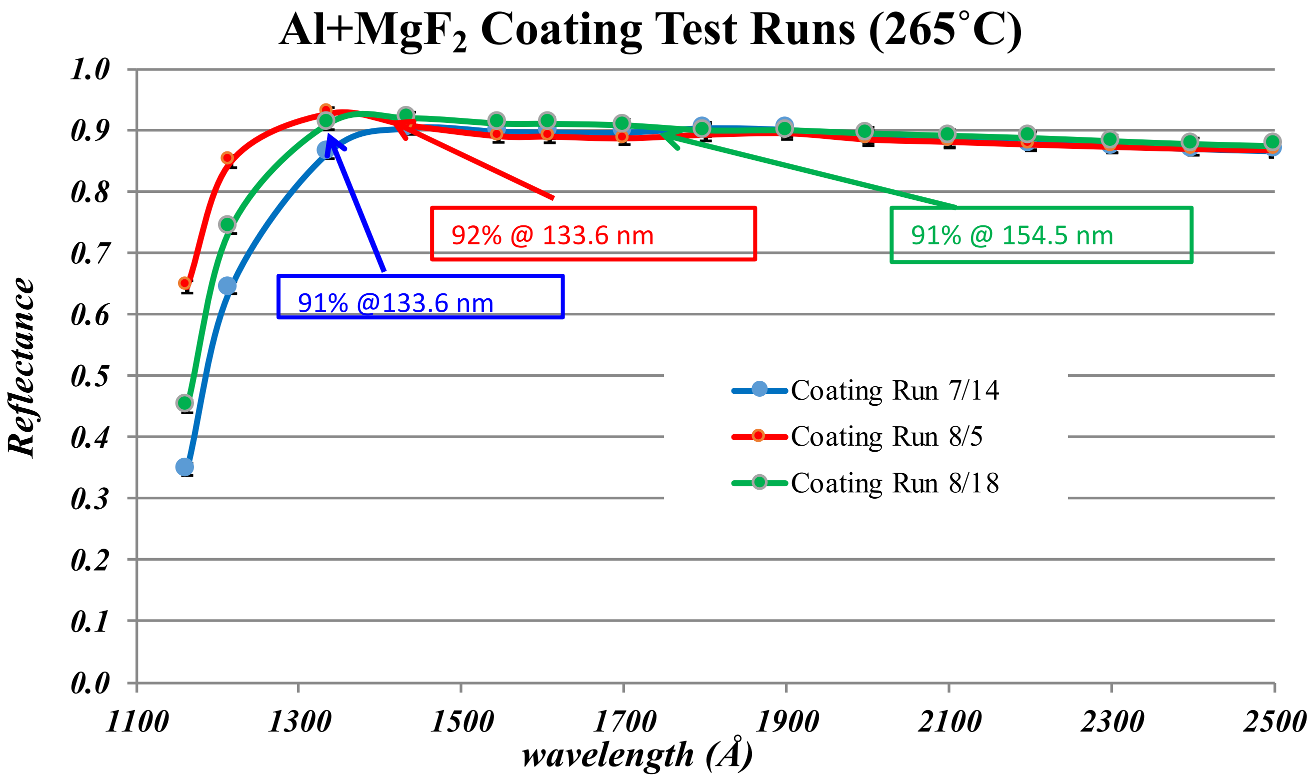
- Enhanced performance is obtained by heating (~220°C) substrate during MgF_2 deposition

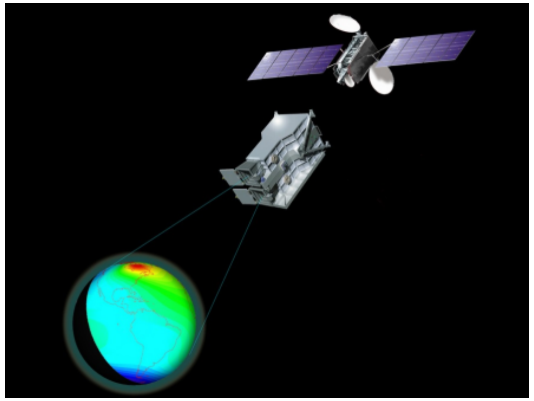
- Reflectance > 90% at λ > 121.6 nm (vs. 84% for "cold deposition")



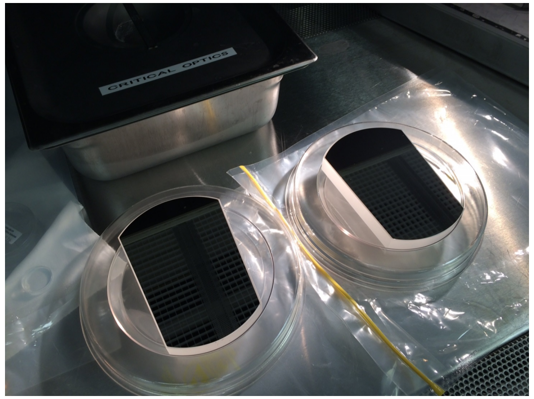
ICON/GOLD Coating Tasks

- ICON (Ionospheric Connection explorer): Study Earth's low-orbit ionosphere sun interactions
- GOLD (Global-scale Observations of the Limb and Disk) : Imager to map Earth's thermosphere & ionosphere





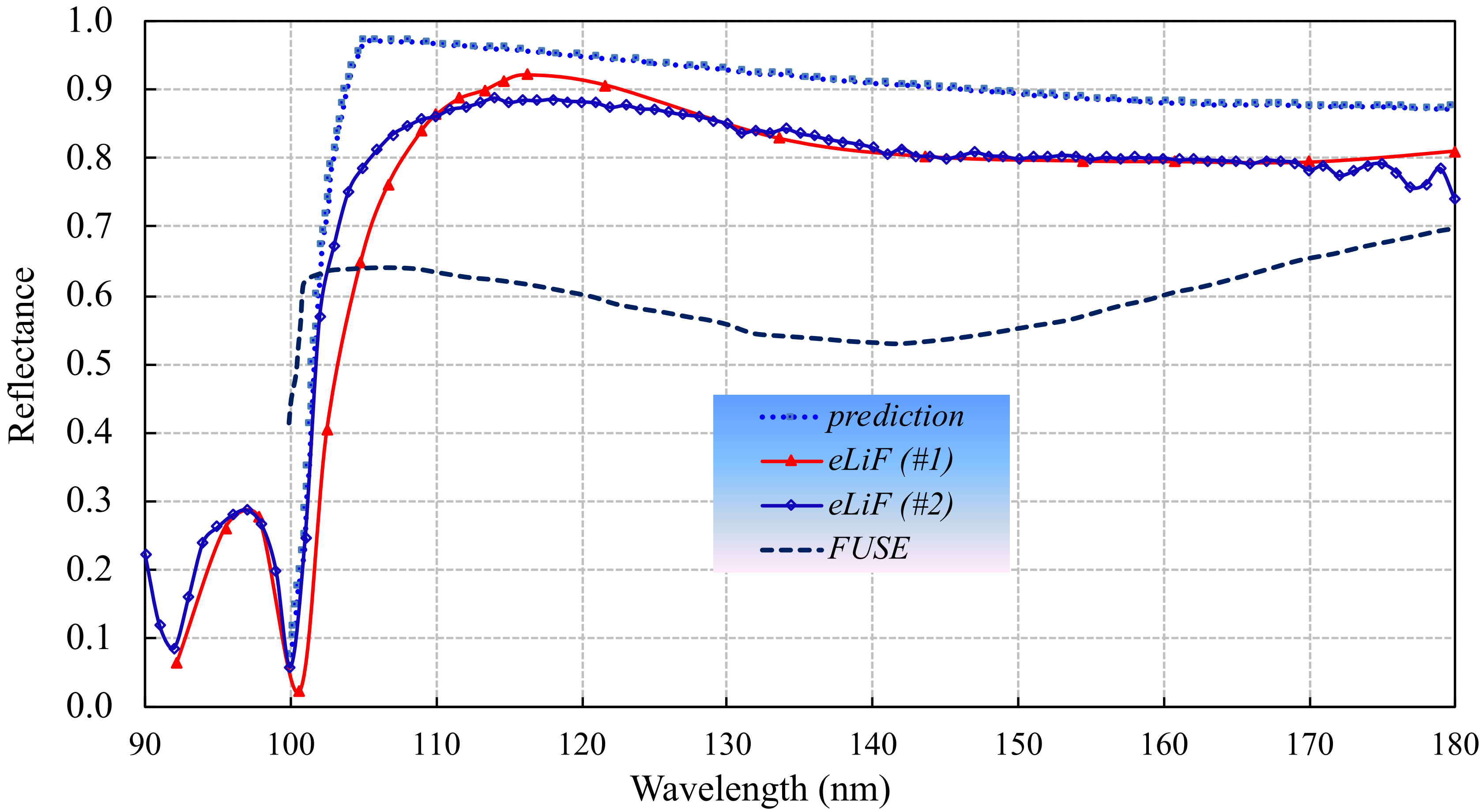
ICON satellite scheduled to launch on 11/7/18



ICON Optics

- A total of 12 optics ranging in size from 26 mm to 264 mm
- Coatings are optimized to produce reflectance over 90% in the 134-156 nm range

Optimization Al+LiF (eLiF) Hot Coatings



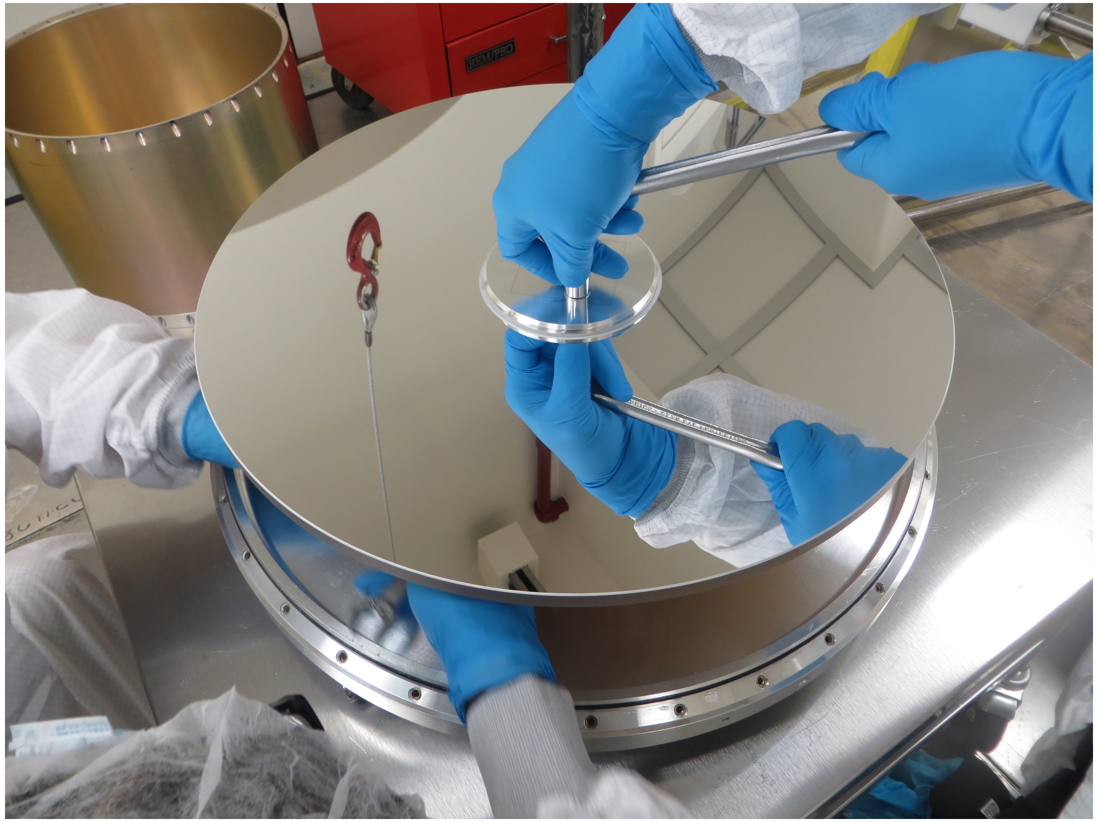
Coating runs to optimize FUV reflectance of AL+LiF (eLIF) in preparation for coating the 0.5-meter SISTINE primary.

SISTINE Primary Mirror

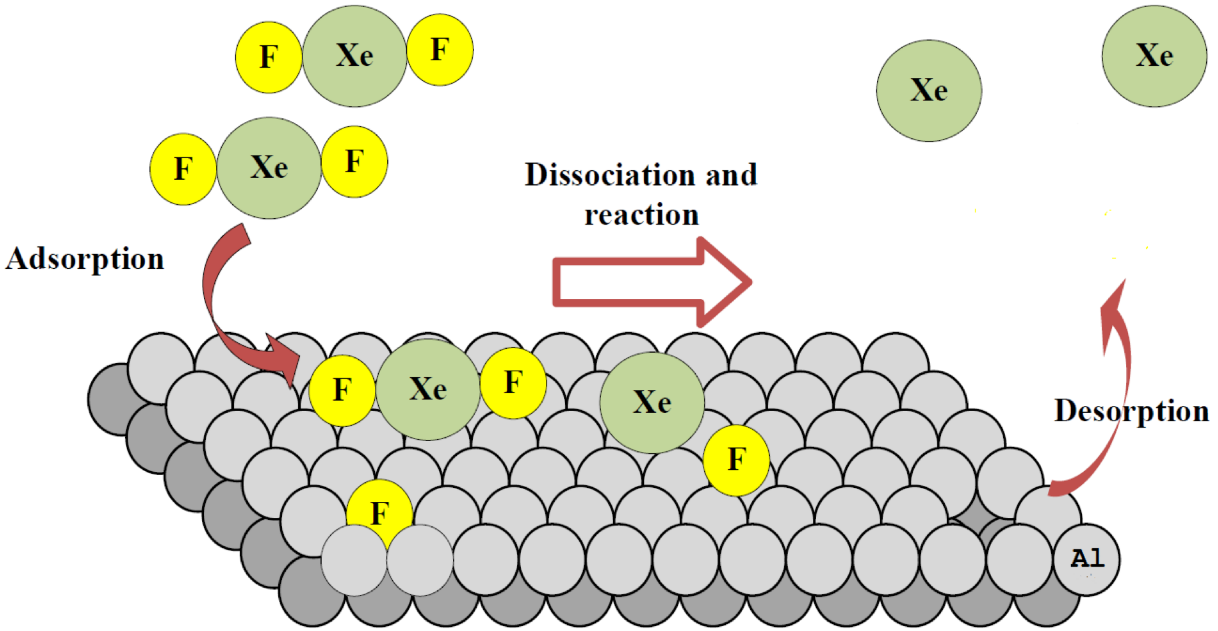
SISTINE: Suborbital Imaging Spectrograph for Transition region Irradiance from Nearby Exoplanet host stars

PI: Kevin France (University of Colorado)

Javier Del Hoyo



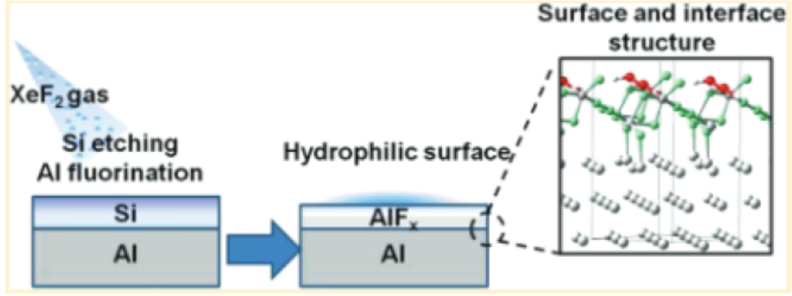
Hybrid PVD Passivation/Fluorination Al Mirrors



Reactive fluorine compound with low bond energy used (e.g. XeF_2 with 133.9 kJ/Mole)

Heating of the XeF_2 may also be used if compound is not sufficiently reactive for increased selectivity.

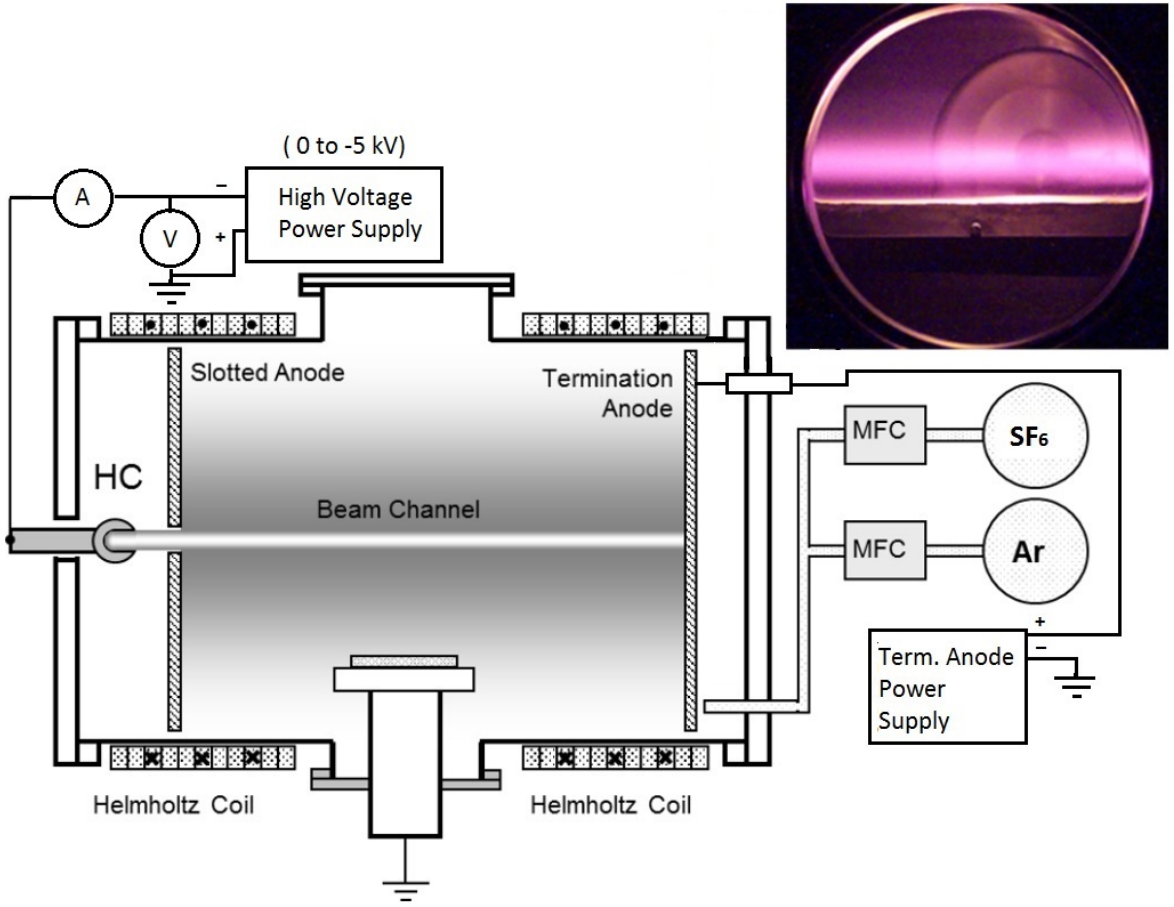
XeF_2 is a dry-vacuum based method of reaction and requires no plasma or other activation minimizing damage to substrate.



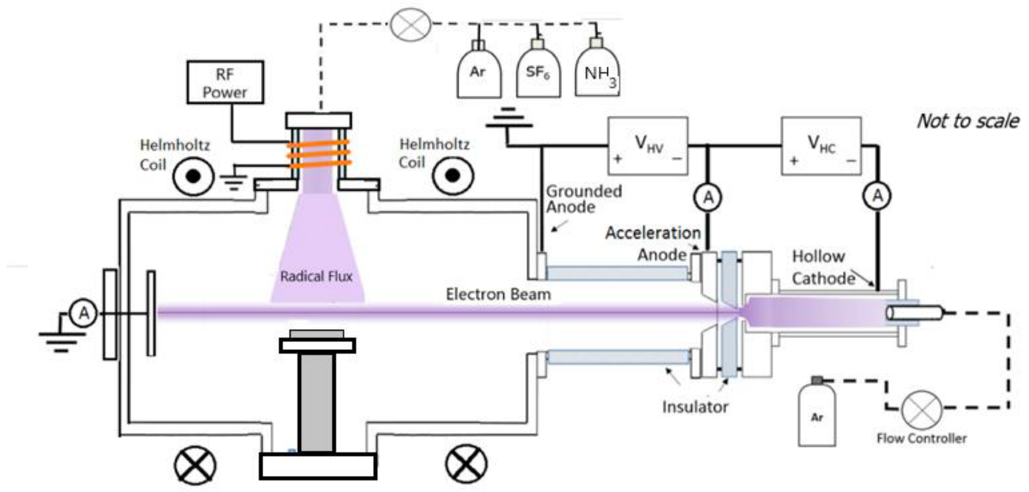
Roodenko *et.al.* J. Phys. Chem. C Vol. **115**, 21351, 2011

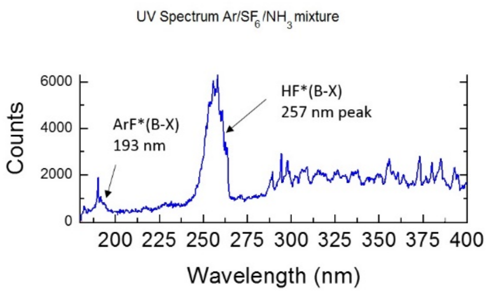
LAPPS Reactor at NRL

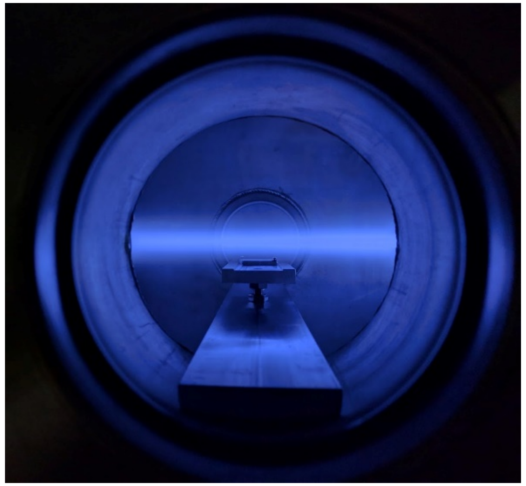
- The US Naval Research Laboratory's Large Area Plasma Processing System (LAPPS), which employs an electron beam generated plasma for etching and fluorination of Al samples.
- The schematic diagram illustrates the processing reactor, whereas the image on the upper right corner is a view of the plasma through a 6-inch port.



LAPPS Plasma Operation







- The injection of a 2 keV beam into the background gas will directly ionize and dissociate the gas.
- Beam energy well above ionization threshold
- Higher beam energy = more efficient ionization

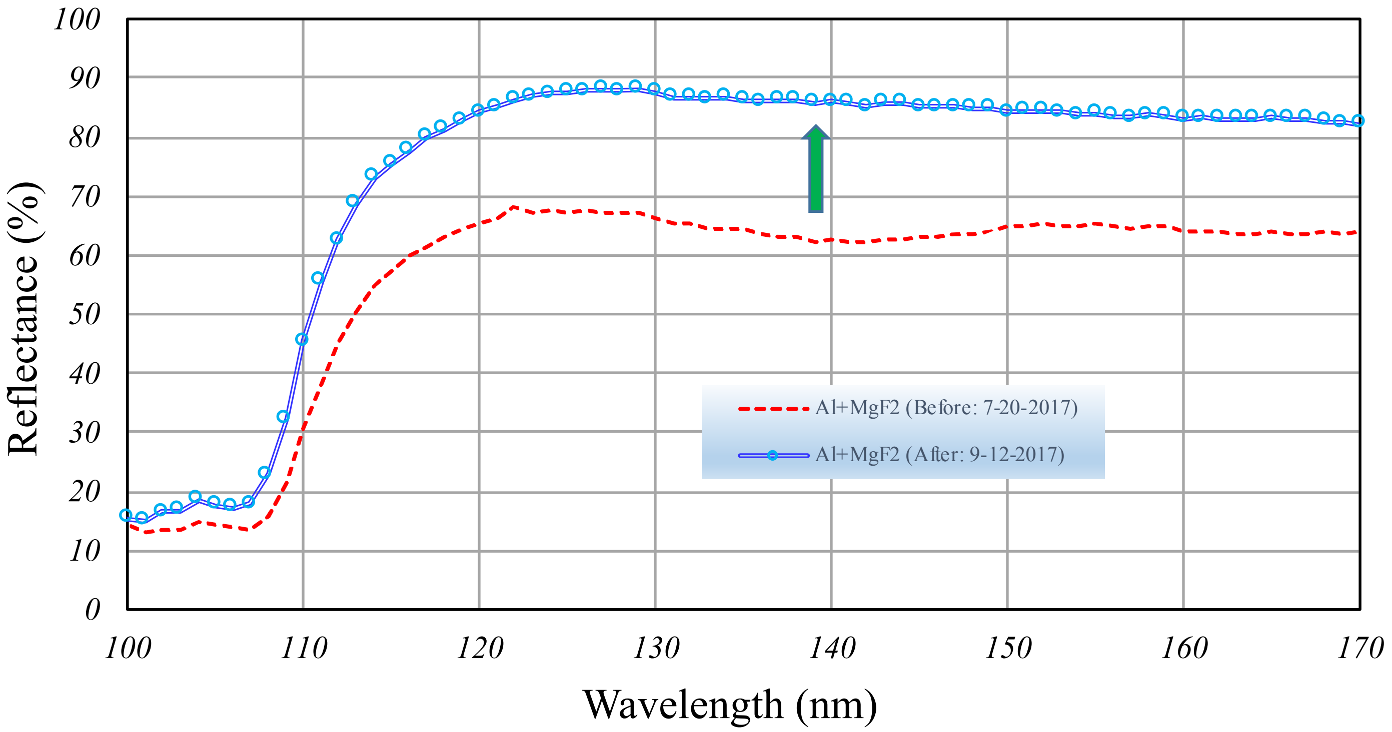
Operating Parameters

- Gas manifold: Ar, SF_6, NH_3
- Flow rates: Ar (150 sccm); Molecular gases (0.5 sccm, SF_6 and 2.5 sccm NH_3)
- Pressure: 75 mTorr

- Process Time 240 s
- Beam Energy 2.5 keV, Cathode Current 20 mA

LAPPS E-Beam Treatment of Al+MgF_2

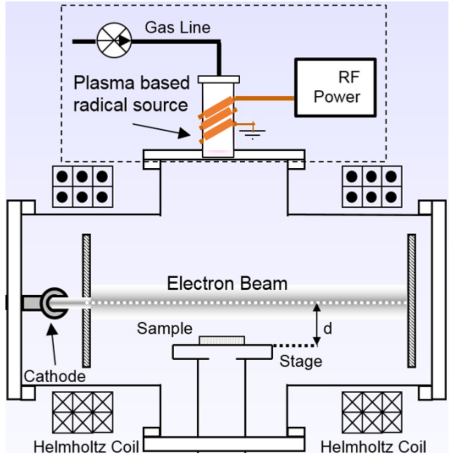
Al+MgF_2 Coatings before and after plasma etch/passivation @ NRL



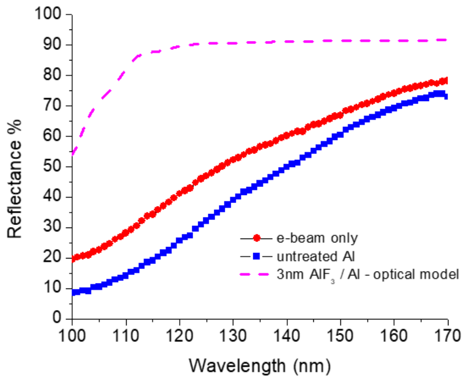
- Recent reflectance measurements of Al+MgF_2 coating made in 2011.
- Sample was treated at the NRL LAPPS reactor and re-measure reflectance again.
- Results indicate a gain in FUV reflectivity of around 20% over most of spectral range.
- Samples has remained stable after a second round of measurement (after plasma treatment at NRL).

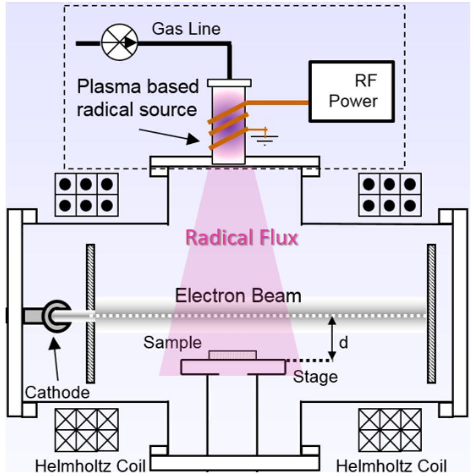
Bare Al Sample Treatment @ LAPPS

- Effect of E-beam + Radical Source

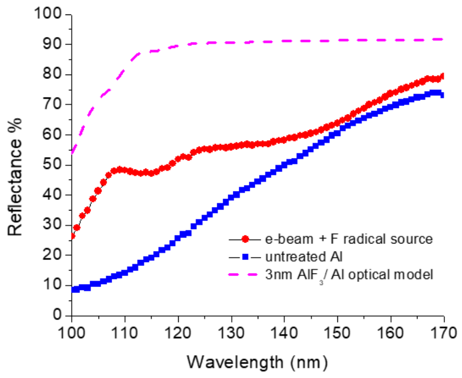


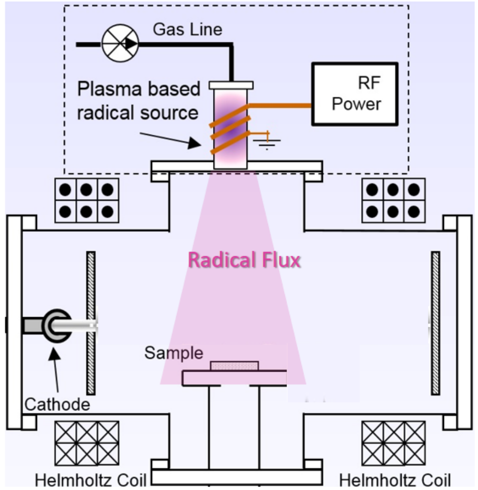
Electron Beam Only



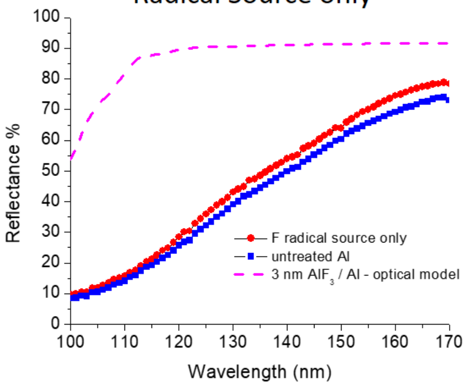


Electron Beam+Radical Source





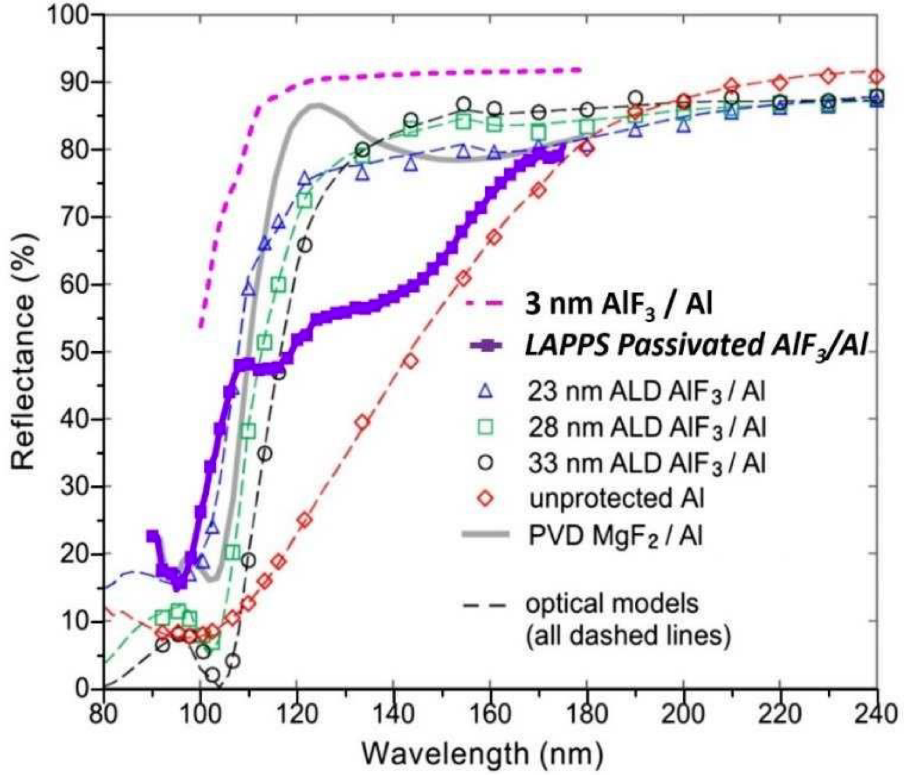
Radical Source only

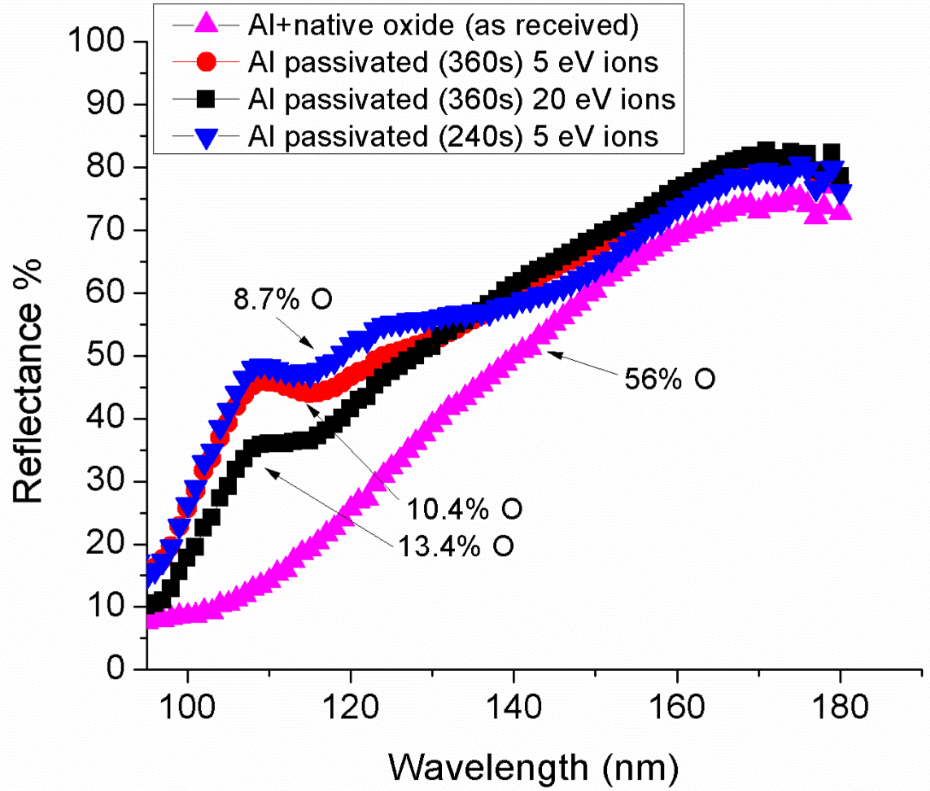


XPS Data

• As Received	36% Al / 64% O / 0% F
• E-beam only	25% Al / 25% O / 50% F
• Radical source	38% Al / 36% O / 26% F
• E-beam+Radicals	**23% Al / 9% O / 68% F**

FUV Reflectance versus Oxygen content

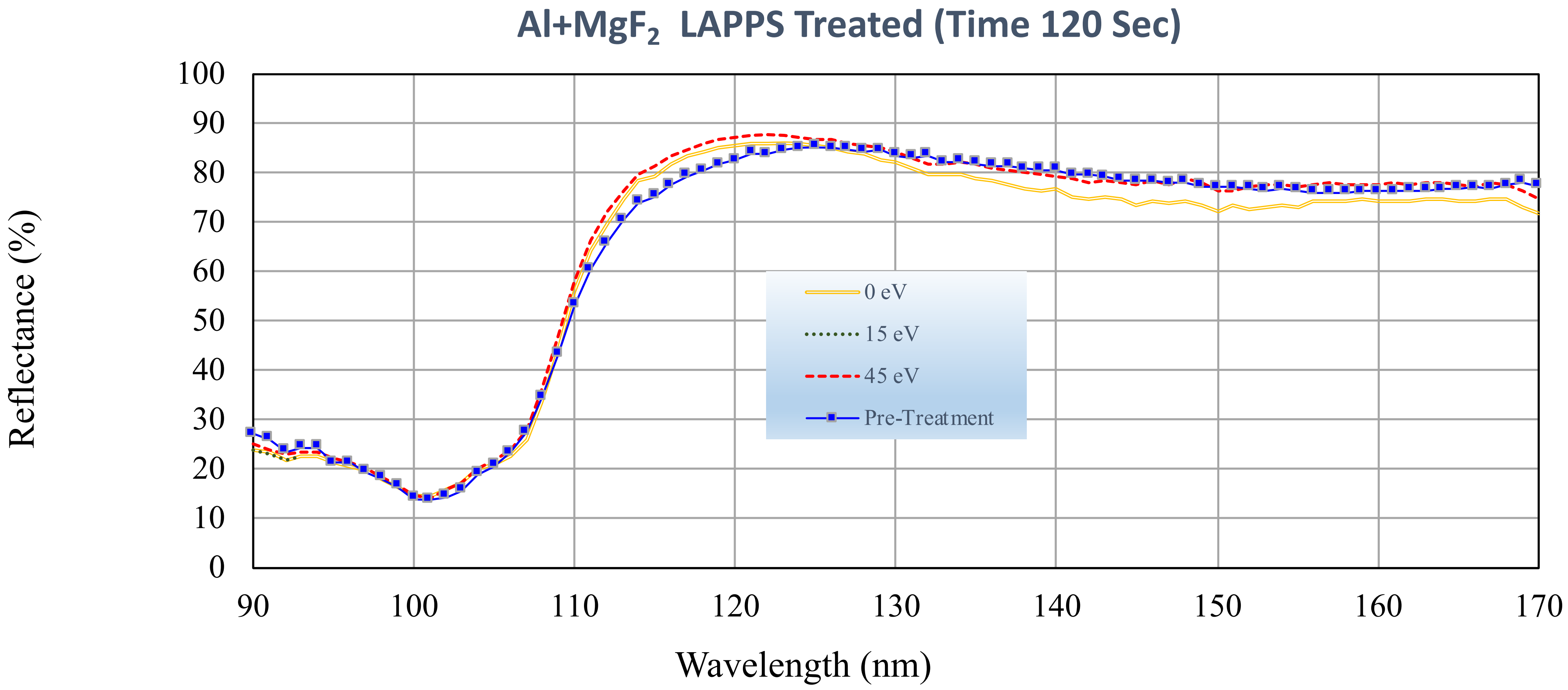




FUV Reflectance for Ebeam + Radical Source Treatments with varying treatment time and varying ion energy

- Correlating XPS results with process conditions seems hint at two possible trends
- First – increased ion energy led to slightly higher oxygen content
- Second – longer exposure time led to slightly higher oxygen content
- Overall – higher oxygen content was correlated with decreased FUV reflectivity

Al+MgF_2 LAPPS Treatment



XPS Results

Element	Untreated (%)	Treated (%)
Mg	26.29	26.98
C	11.33	6.87
O	4.31	9.05
F	58.07	57.10

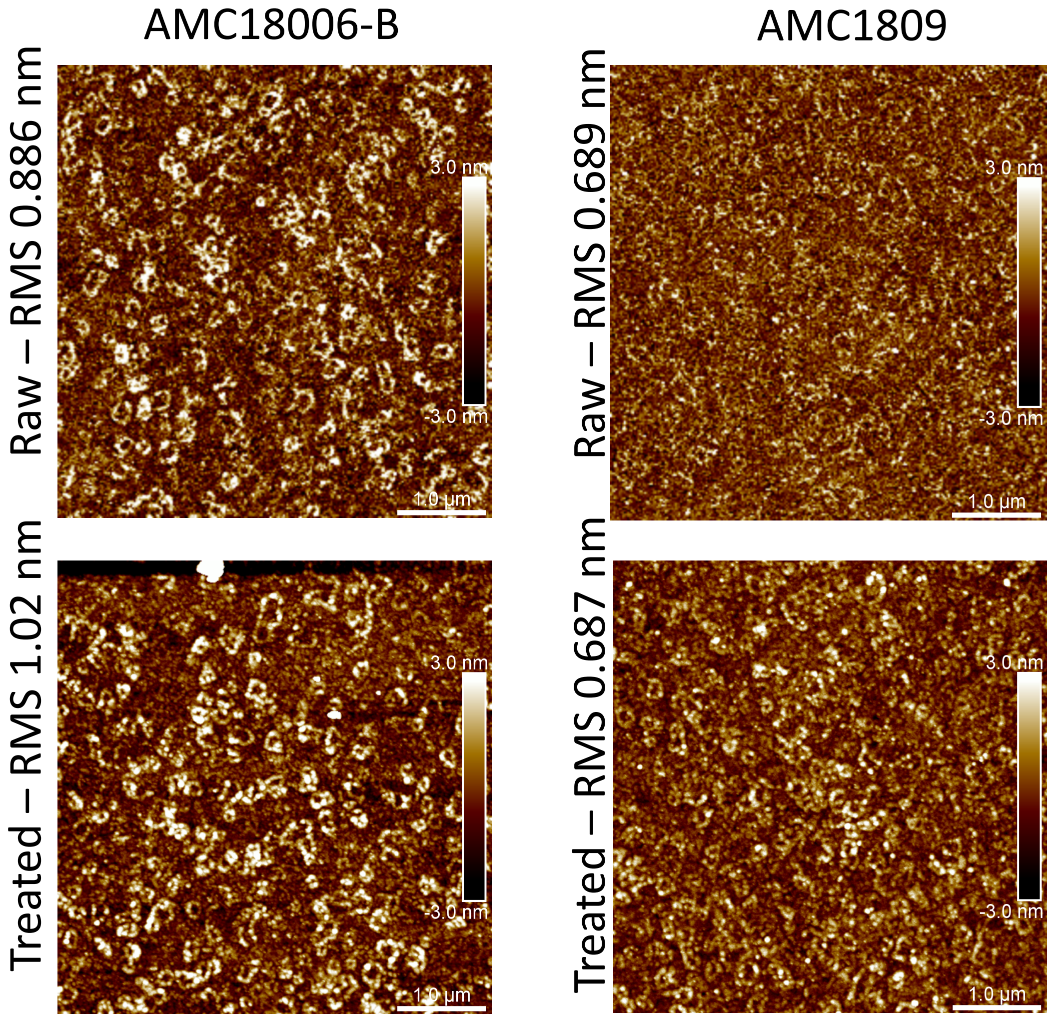
Element	Untreated (%)	Treated (%)
Mg	24.54	24.76
C	11.93	6.63
O	4.31	8.83
F	59.21	59.78

-samples homogenous (bulk not significantly different from surface) before & after treatment

-both samples show evidence of magnesium carbonate in the films, significantly reduced post-treatment -both samples show evidence of oxy-fluoride species

-plasma treatment appears to <u>reduce magnesium carbonate to magnesium oxy-fluoride</u>

AFM Results



- For both samples the as received and post treatment RMS roughness is very low indicating smooth films.
  - AMC18006-B: 0.886 nm RMS roughness increased to 1.02 nm RMS roughness. This increase is minimal.
  - AMC1809: 0.69 nm RMS roughness was unchanged post plasma treatment
- The lack of changes in surface morphology indicate that the enhanced reflectivity observed in the FUV is likely due to the reduction of magnesium carbonate.
- **This appears to indicate that the plasma is performing a cleaning function in that it is removing carbon contamination from the surface while leaving the remainder of the film unchanged.**

Conclusions

- Two success stories for coating optics for ICON/GOLD satellite missions and optics of SISTINE low orbit payload instrument.
- We studied the feasibility of using the LAPPS reactor (developed at NRL) that employs a low energy- e-beam to etch away the native oxide layer from Al samples as well as improving reflectance of Al+MgF_2 coatings.
- Initial trial runs of oxidized Al coatings with NLR LAPPS reactor showed improved FUV reflectance with treatment with the LAPPS e-beam in combination with a radical (fluorine) source.
- Chemical analysis confirmed presence of F bonds on the surfaces of Al samples (with reduced concentration of O) that correlated with improved FUV reflectance.
- Treatment of Al+MgF_2 samples show positive changes (increase in FUV reflectivity), while AFM analysis indicates that LAPPS treatment does not increase surface roughness of these samples.

Acknowledgments

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NASA Goddard Space Flight Center, Greenbelt, MD 20771

David Boris, & Scott Walton:

Plasma Physics Division, Naval Research Laboratory, Washington, DC 20375

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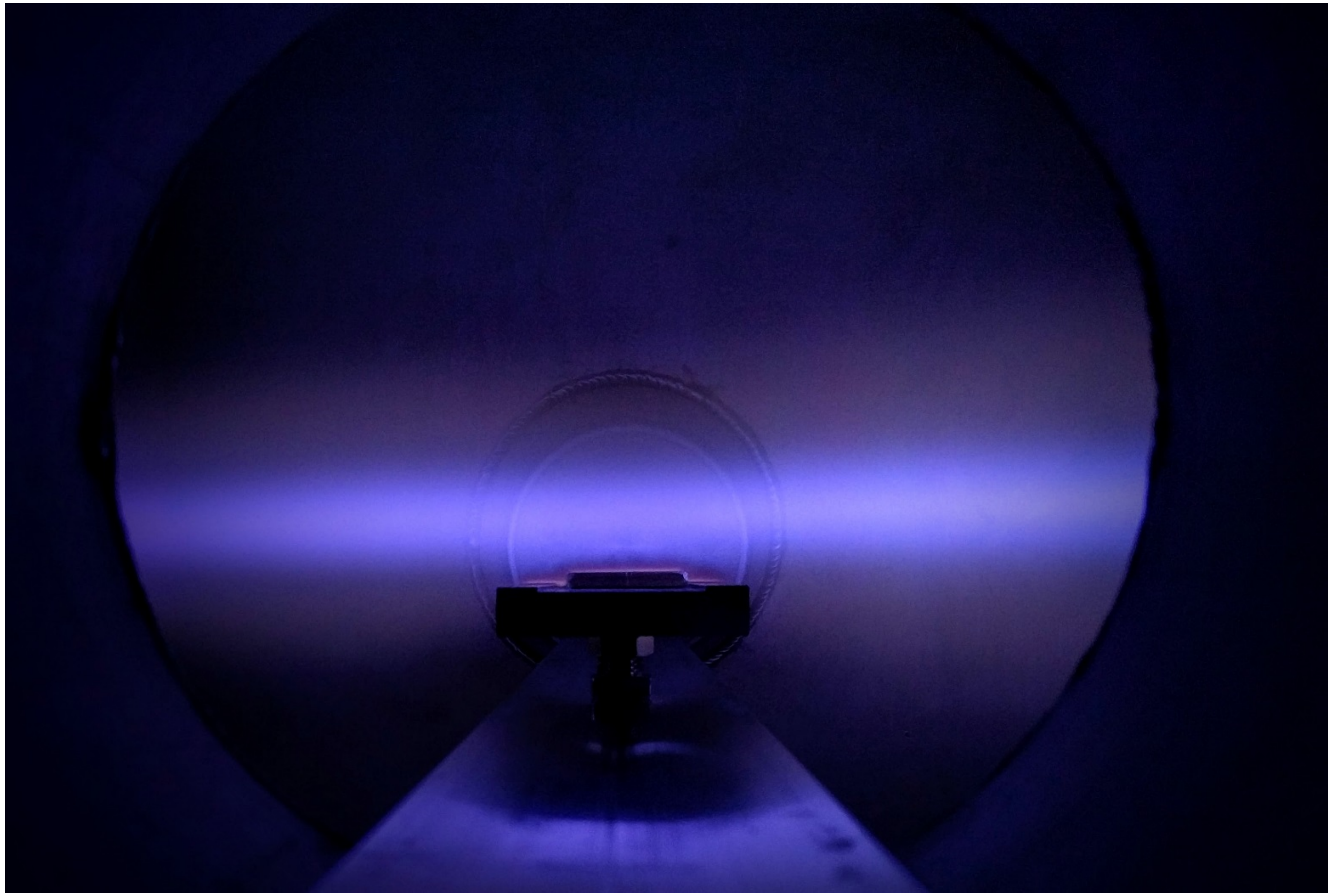
- *GSFC FY18 Internal Research & Development (IRAD) Program*
- *DRB & SWG supported via NRL based program*

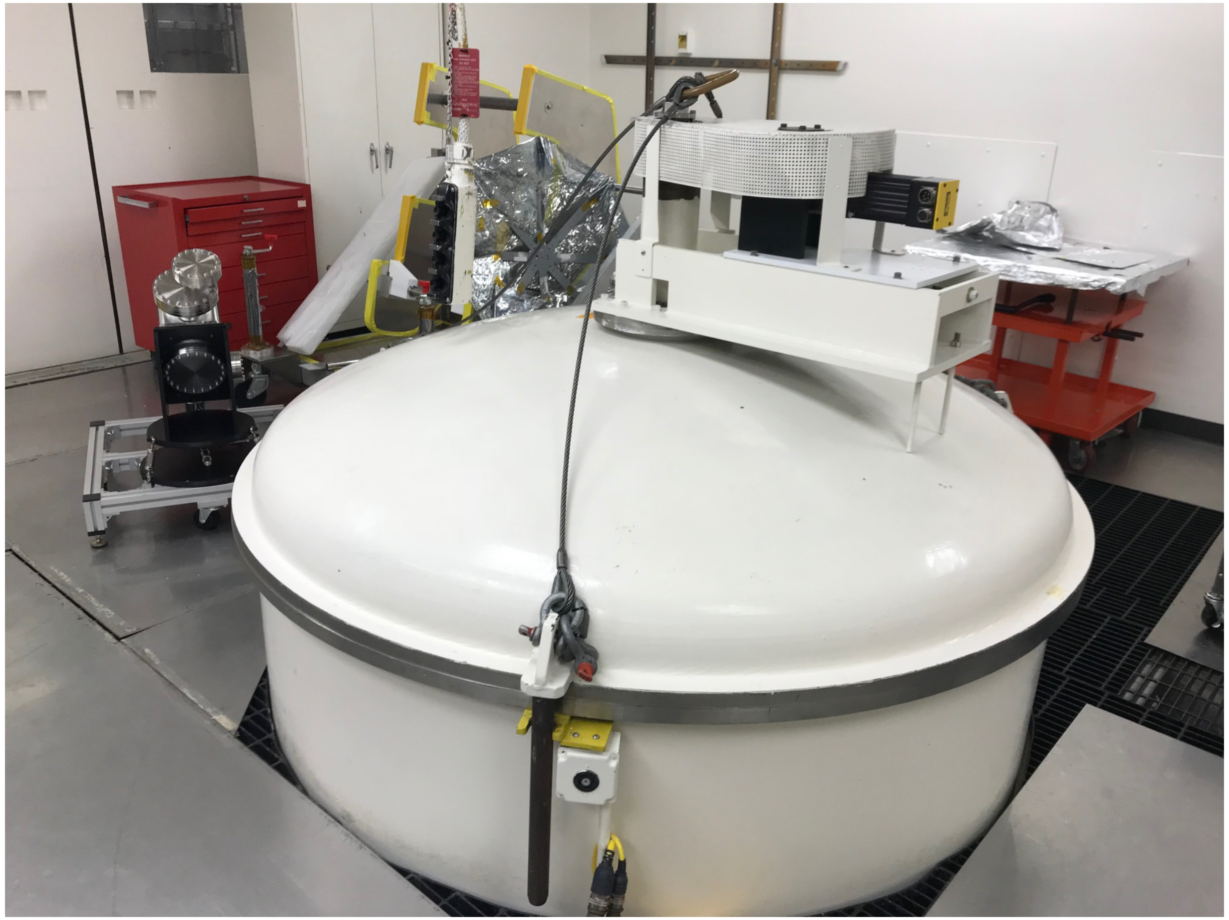
Backup Slides

How are e-beam generated?

- The injection of a 2 keV beam into the background gas will directly ionize and dissociate the gas.
- Beam energy well above ionization threshold
- Higher beam energy = more efficient ionization

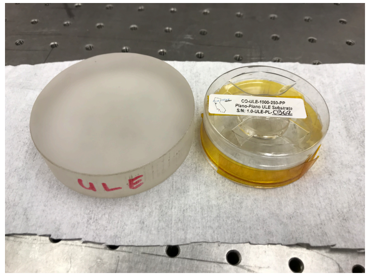


Ion-Assisted PVD Deposition



Deposition of a ion-assisted physical vapor deposition (IAPVD) of FUV-optimized Al+metal fluoride overcoats (LiF, MgF2, and Al+AlF_3) in the large 2-meter coating chamber.

- ✓ Pumping system, deposition controller and PVD power supplies upgraded over the last year.
- ✓ Procurement of various types of glass substrates (ULE and Zerodur) to evaluate effect of heating on surface figure & wave-front error to demonstrate process on substrates traceable to LUVOIR.



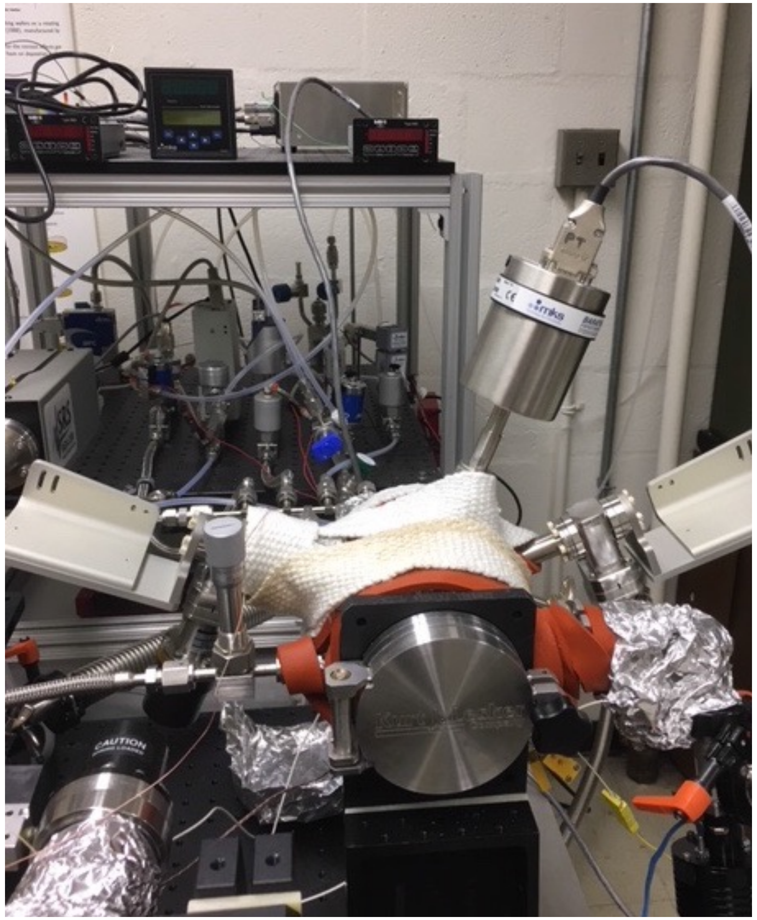
Ion-Assisted Coating Deposition

Procurement & installation of electron-gun for ion-assisted deposition to create more densely packed metal-fluoride coatings.

View of Ion gun in operation inside 2-meter Chamber.

- Hollow Cathode (for operation without a filament).
- Deposition systems with critical dimensions greater than 1meter
- Favorable film properties in packing density, stress, environmental stability and stoichiometry
- Process Gases: Ar, Xe, Kr, O2, N2, Organic Precursors.
- Process: Pre-Cleaning, Surface Modification, Ion Beam Assisted Deposition, Direct Deposition

ALD Reactor System for AlF_3 Deposition



Atomic Layer Deposition (ALD) reactor at the University of MD.

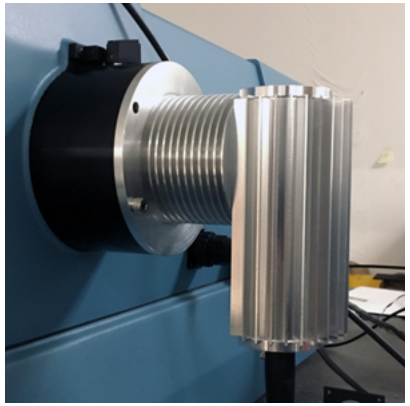
General-purpose ALD reactor features:

- The ALD process utilizes solid state halide precursors (TiF_4 and Trimethyl Aluminum (TMA) for the deposition of AlF_3 films.
- Solid state precursors precursor manifold plumbed for Ar, TMA, water, DEZn' room for 3 additional precursors.
- Optical access ports for real-time ellipsometry.
- Exhaust gate valve for "exposure" –mode operation.
- Accepts up to 2 inch substrates.
- Residual Gas Analyzer.

Lyman-Alpha Optical Monitor

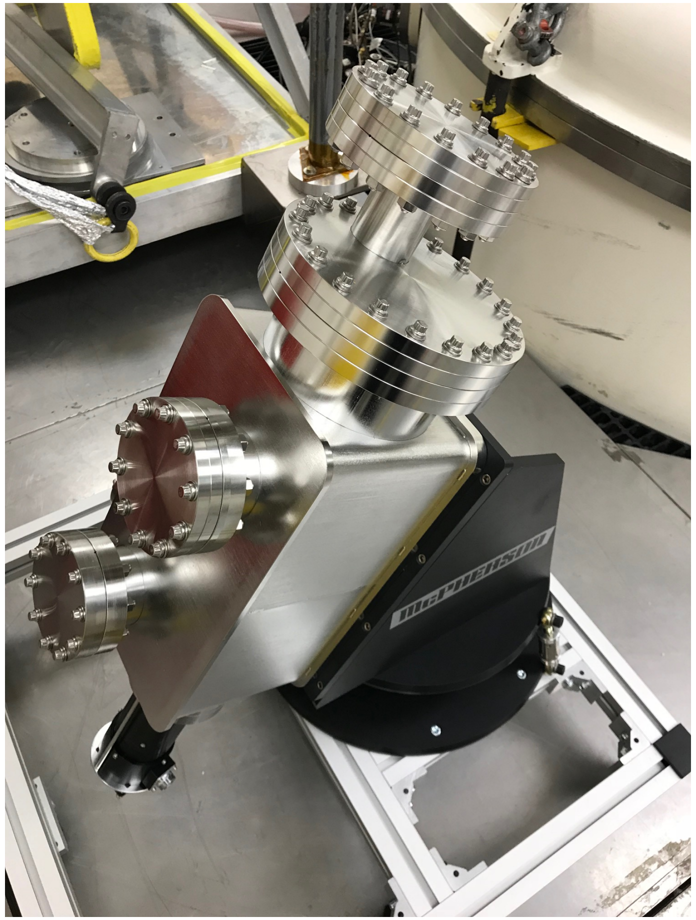
Collimator with 10 mm c.a.

- Procurement & installation of an in-situ optical monitor (λ = 121.6 nm); source, detector, port window, etc.
- System will produce a collimated beam that will manage to deliver the collected light to a 10mm spot over a meter away. It uses a ISO NW40KF flanges for mounting and beam path.



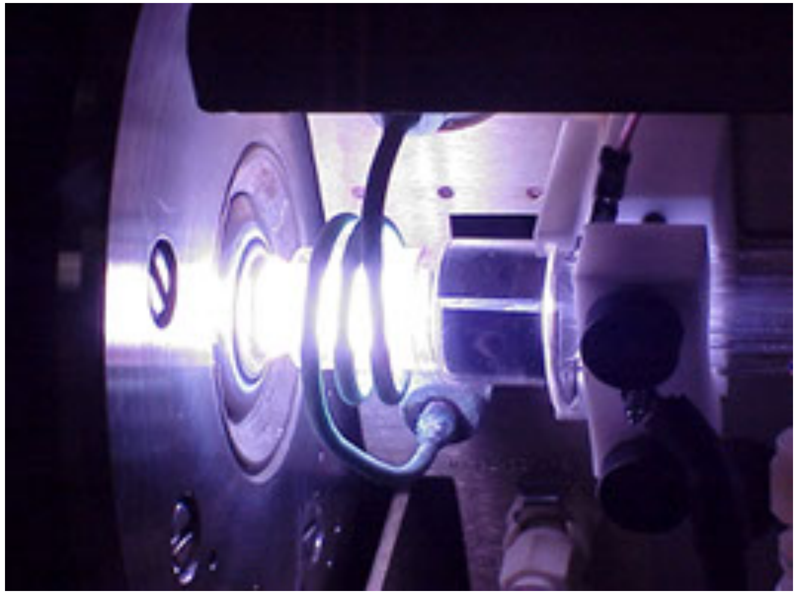
D_2 source with strong Lyman-Alpha output (MgF_2 window).

PMT Detector



Complete Assembly as delivered

Where does the oxygen come from?



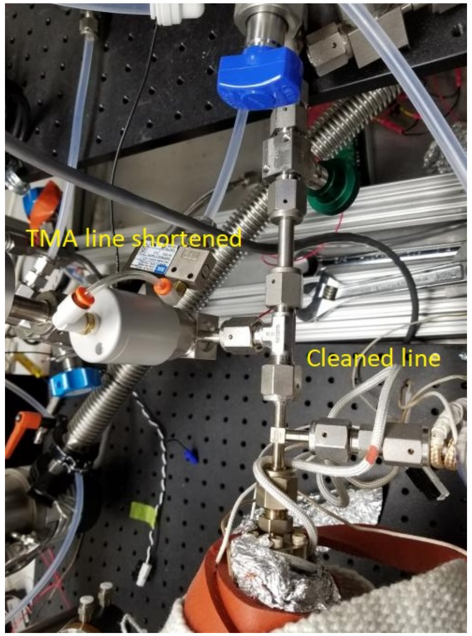
Two possibilities

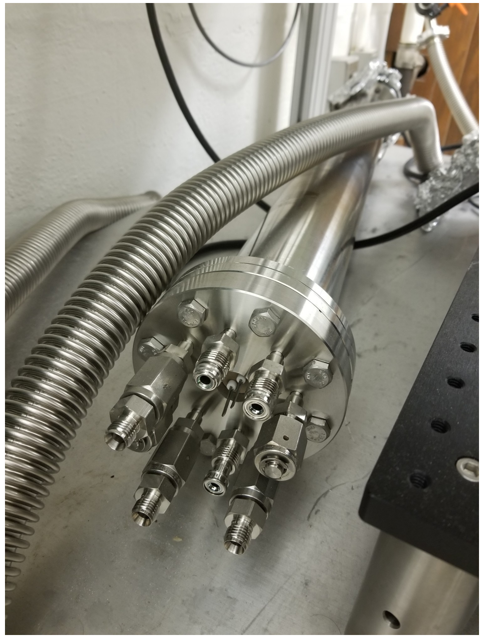
- Residual oxygen in the surface layer that we can't remove

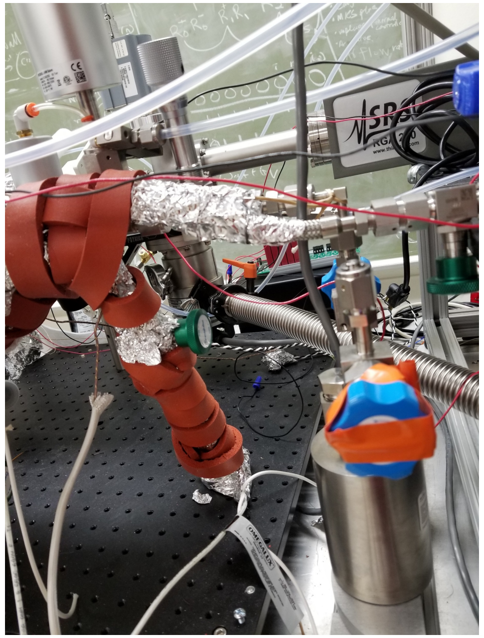
- The quartz wall of the inductively coupled plasma source is etching and depositing oxygen in the film.
    - $SiO_2 + 4F \rightarrow SiF_4 + O_2$

- Eliminating SiO_2 will eliminate one source of O contamination.

ALD Reactor Re-configuration







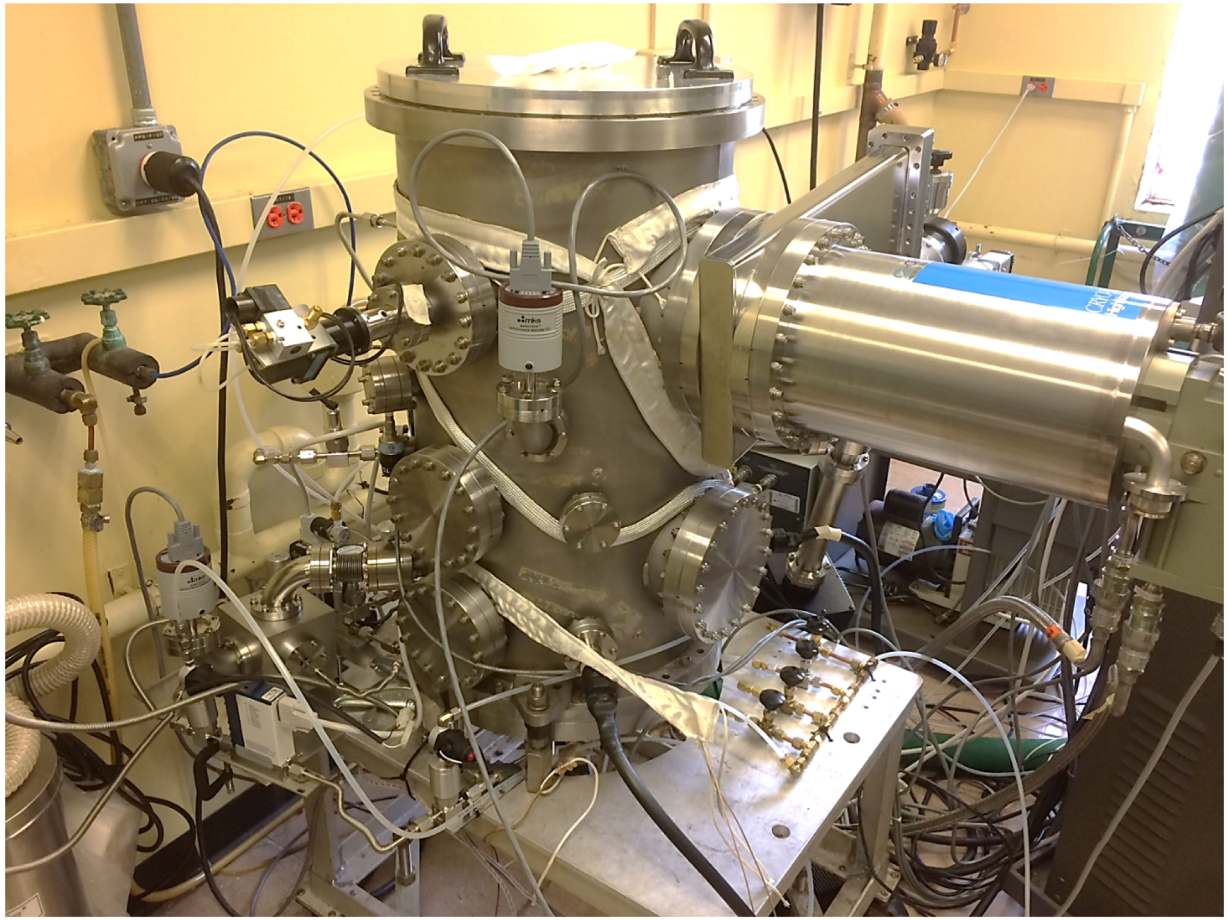
- ✓ The UMD graduate student (Mr. Alan has worked on the reconfiguration shown in these pictures to prevent pre-mixing into reactor.
- ✓ Scanning Electron Microscope (SEM) images of sample grown in the previous ALD reactor configuration and determined TiF4 particles growth.
- ✓ The SEM report seems to indicate that titanium generally segregated from the aluminum (see table below).

Single Input Precursor System Features:

- ➢ Prevent pre-mixing into reactor.
- ➢ Heating the Argon gas during ALD growth.

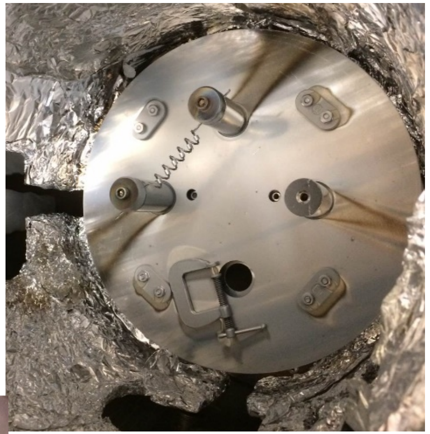
Spectrum Label	Aluminum	F, Ti	Carbon Tape F, Ti
C	13.67	16.77	54.00
O	61.18	29.58	22.18
F	4.02	37.28	16.28
Al	20.95	2.69	1.89
Ti	0.18	13.68	5.66
Total	100.00	100.00	100.00

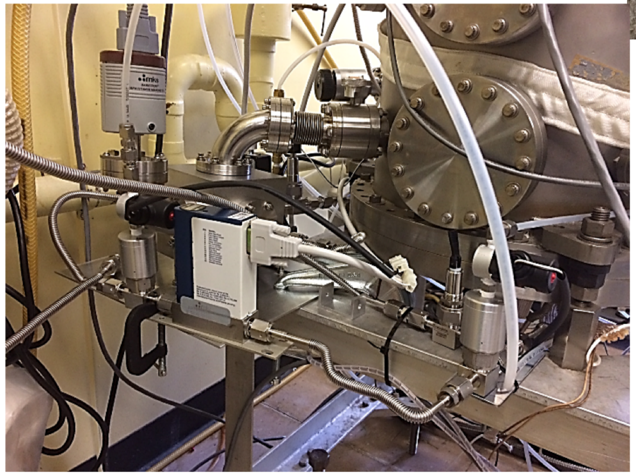
Fluorination in Research Coating Chamber



UHV Research Chamber capable of thin film physical vapor deposition (PVD) and passivation.

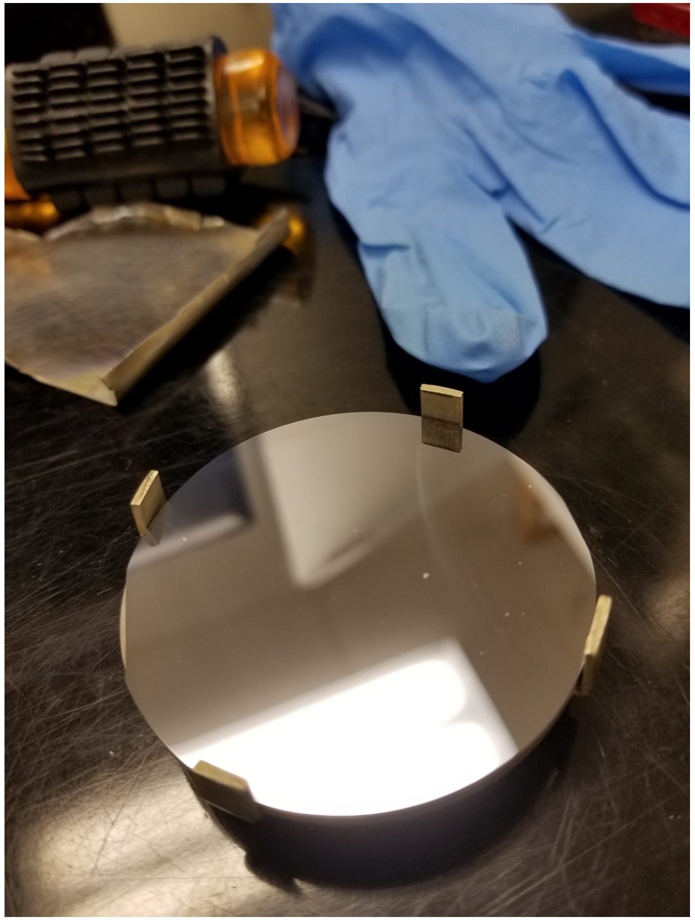
Inside of chamber PVD components.



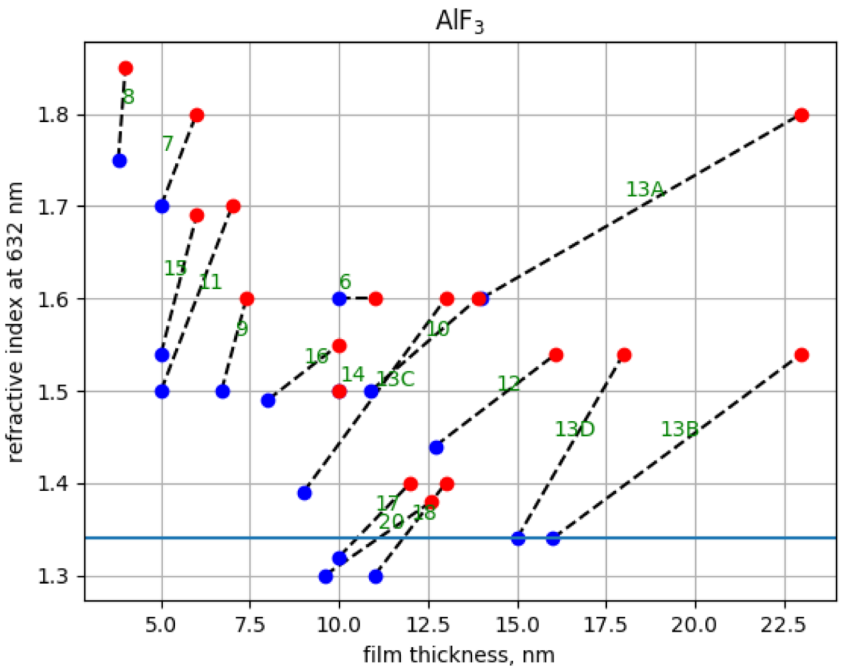


XeF_2 Gas feed components capable of continuous flow or pulsed flow.

Latest run of AlF_3 currently looking promising



Index Variation with Thickness



Successful growth of nominal AlF_3 films with good uniformity (Runs 17, 18, and 20)

Trend in obtaining a nominal refractive index value:

1) increasing total number of ALD cycles
2) decreasing reactor temperature
3) decreasing purge argon gas flow

Moving forward:

- Continue refining AlF_3 ALD recipe.
- Ellipsometry characterization for film
- Future growth on Al surfaces (to cap Al+AlF_3 or Al+LiF)

Vent Pipe Installation

Vent pipe installation completed this past summer.

Abatement system

Plan forward: All hardware updates have been completed to perform fluorination experiments with XeF_2 gas within the next 1-2 months.