Applications of Atomic Layer Deposition in the Modification of Carbon Nanotubes

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Outline

- **Motivation**
- **What is a Thin Film?**
- **Atomic Layer Deposition (ALD) – a primer**
- **ALD of NiO and *ex situ* reduction**
- **Results of Coated CNTs**
- **ALD deposition of Catalyst Layer for CNT growth**
- **Stray light suppression results**
- **Conclusions Q&A**

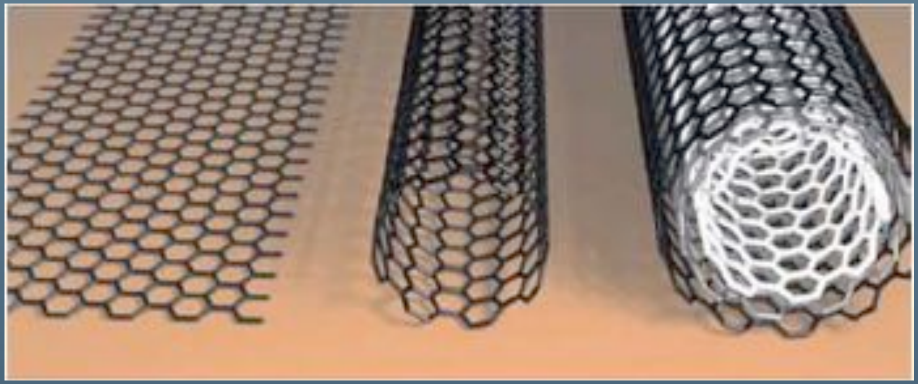
Motivation – Stray Light Control

High contrast scene; Greenland

- **Z306 absorbs 96%; our current piBlack nanotube formulation absorb > 99.5% from the visible to FIR**
- **Improving stray light performance of surface treatments can result in exponential stray light reduction at focal plane**
  - **Enabling new scientific observations with higher – Signal-Noise Ratio - S/N**
  - **Potentially doubling observational efficiencies in high contrast scenes such as those common in Earth science**
  - **Simplifying stray light designs by reducing number of controls required for equivalent performance**

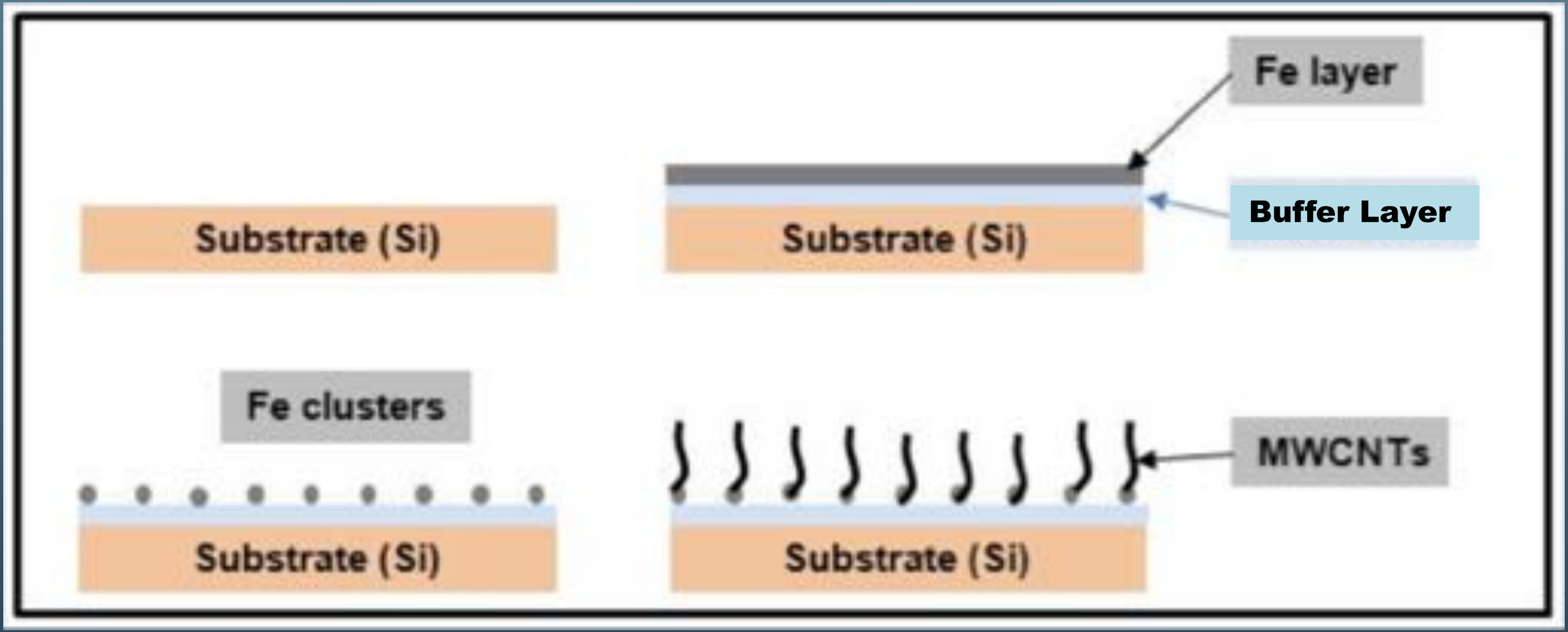
Motivation – Stray Light Control

- Electron mobility in plane of carbon hexagonal matrix is high effectively creating electron gas behavior similar to a metal
- Light interacts with the electrons but confinement in lattice plane results in absorption and thermalization of energy
- This high electron mobility and confinement results in high absorption with little specular reflection



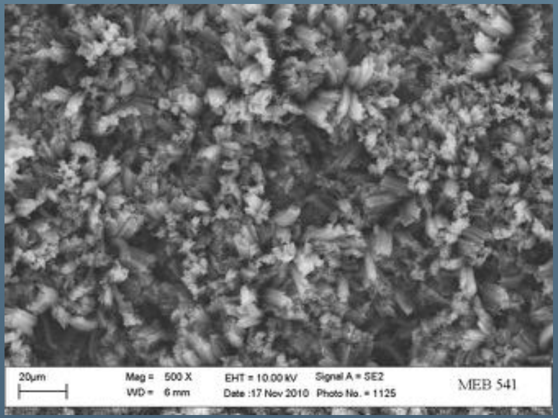
Formation of single and multi-walled carbon nanotubes from graphene. The graphene sheet on the left is rolled to form a single walled nanotube (middle) and multi-walled carbon nanotube (right).

Thermal CVD Growth of CNTs



Stray Light Control – Design Parameters

- **Parameters for optimization of light absorption**
  - **Low density; achieving an effective index of refraction approaching 1 vs graphite (n=4.4) allows reflection at interface to be minimized**
  - **Minimization of amorphous carbon**
  - **Length; long enough to absorb light that gets into nanotube layer**
  - **Orientation; vertically aligned nanotubes are significantly better absorbers than randomly oriented formulations**
  - **Increasing surface roughness of substrate can improve absorption by decreasing interface reflectance as well**
- **These parameters can be tuned during the growth process by adjusting:**
  - **Catalyst thickness, gas flow and composition, substrate preparation**

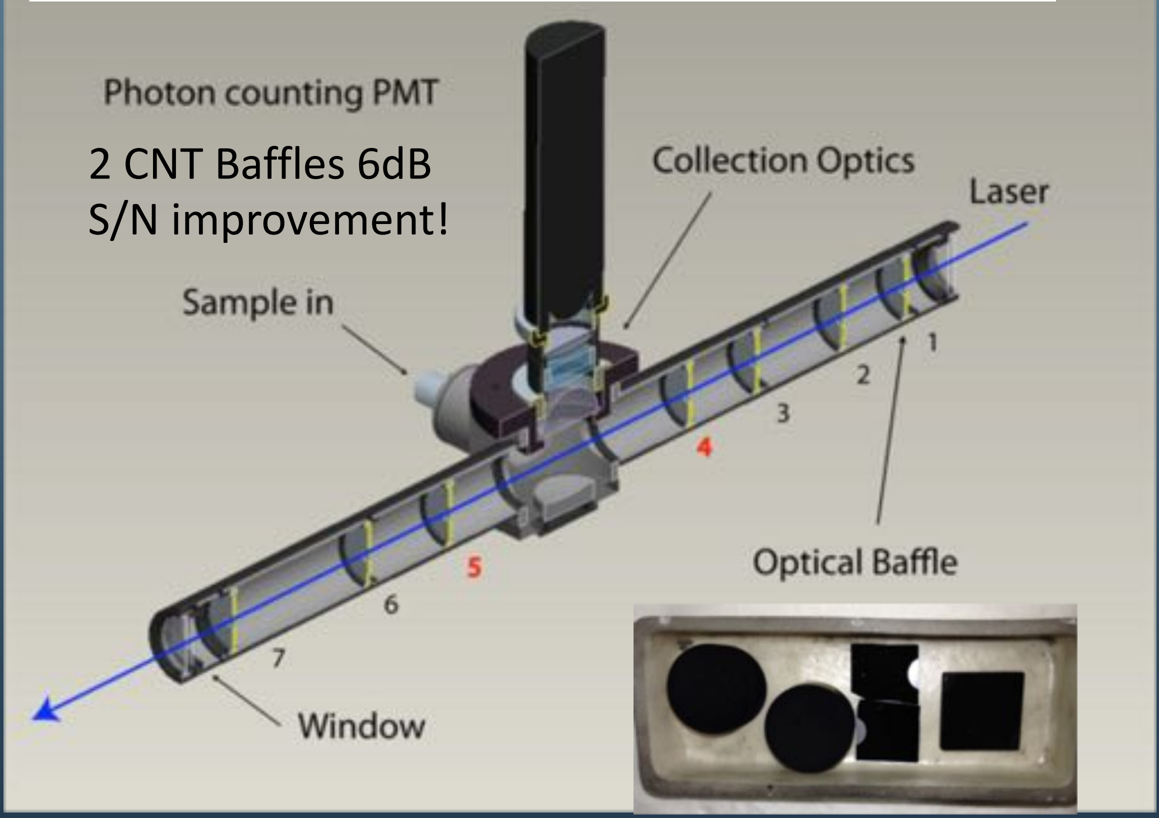


Electron Microscope

Applications and Challenges

Goddard in situ Formaldehyde Laser Induced Fluorescence Experiment (Tom Hanisco-PI)

http://www.atmos-meas-tech.net/8/541/2015/amt-8-541-2015.pdf

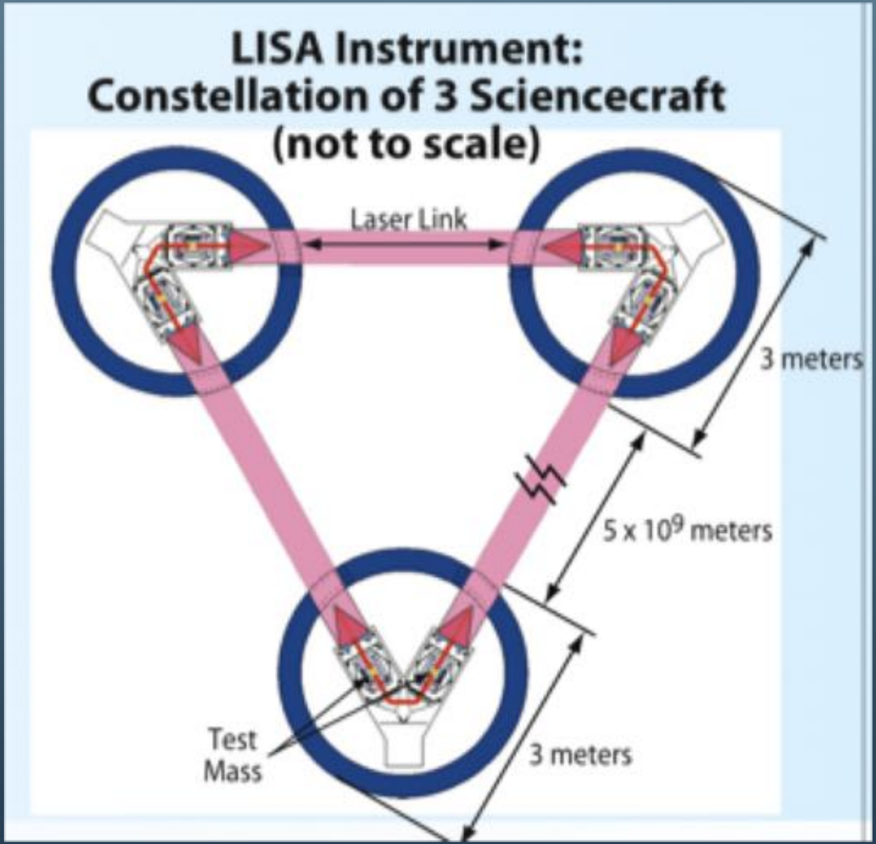


Challenges:
Coating 3D baffles and the inside of cylindrical tubes with catalyst and controlling gas flow during CVD

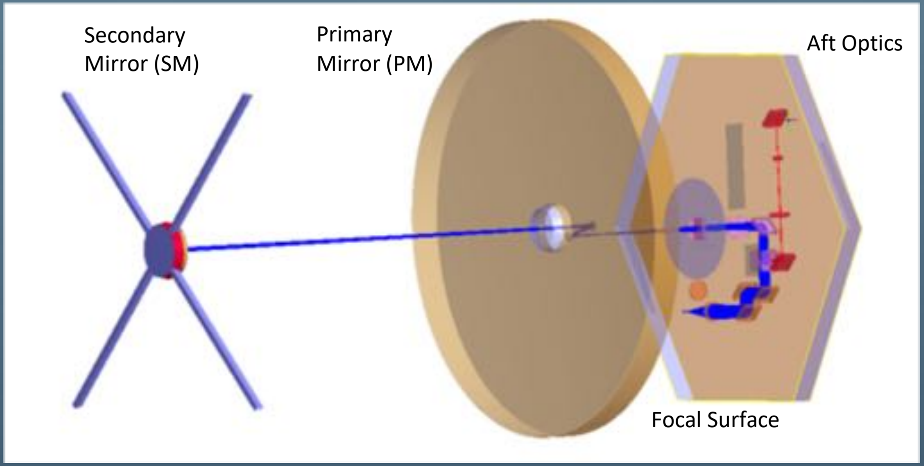
The fluorescence detection cell of the Goddard in situ formaldehyde LIF experiment is shown with a cut-away view. The laser excites the sampled air in the center of the cell.

Applications and Challenges

Laser Interferometer Space Array (LISA) Gravity Wave Sensor (Telescope PI – Jeffrey Livas)



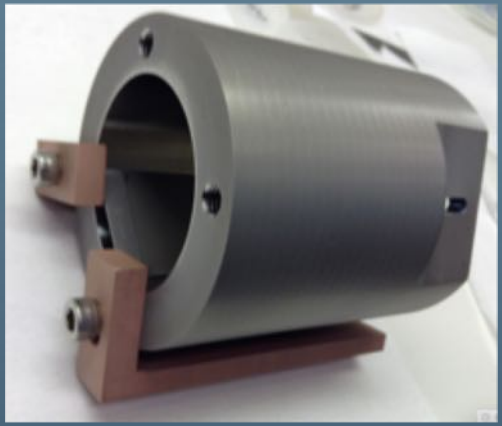
Constellation of 3 Sciencecraft with linked Telescopes



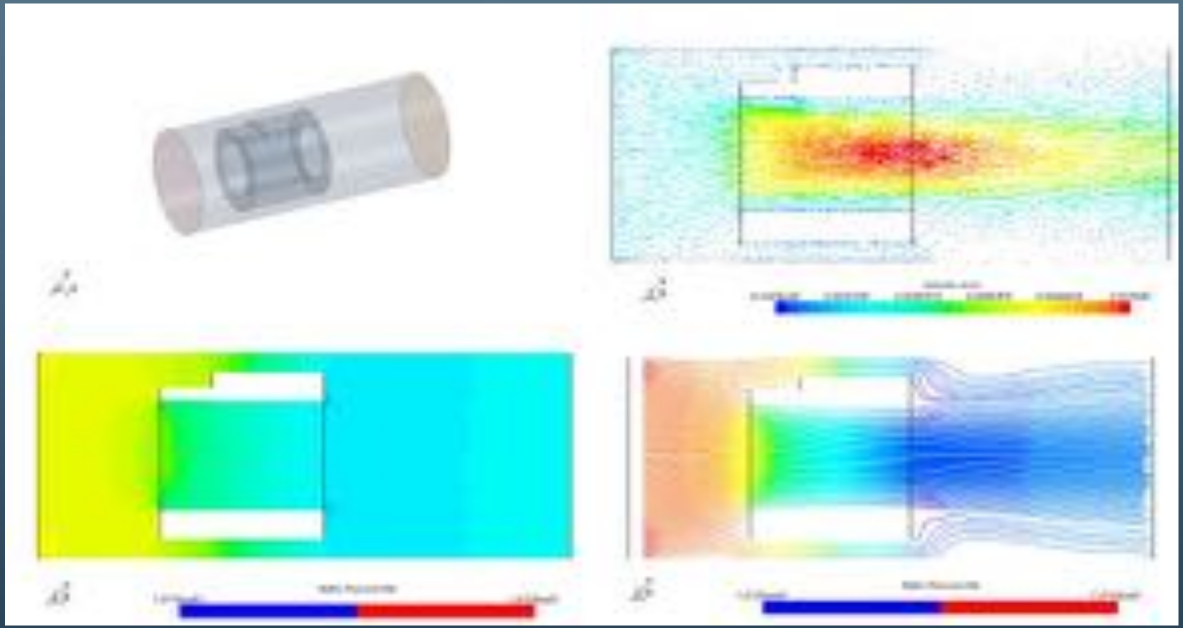
- **LISA Stray Light Challenge**
  - **Telescope used in duplex**
  - **Tx beam is 10^9x intensity of Rx Beam**
  - **Tx beam reflected/scattered off of center of telescope secondary mirror (SM) must be suppressed by 10^9**

Applications and Challenges

Solar Coronagraph – PI Doug Rabin



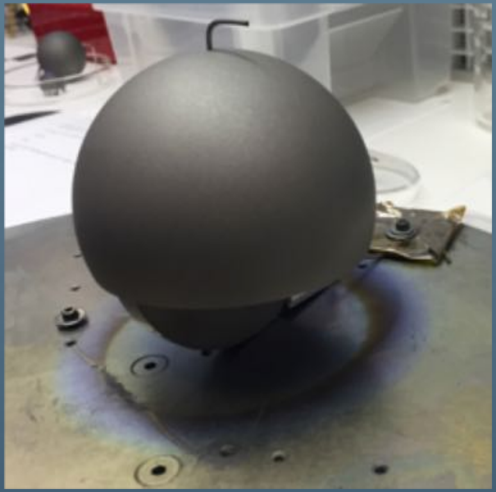
Challenge:
3D Catalyst Deposition, CVD flow control
Solution: Catalyst sputtering, tapered boat

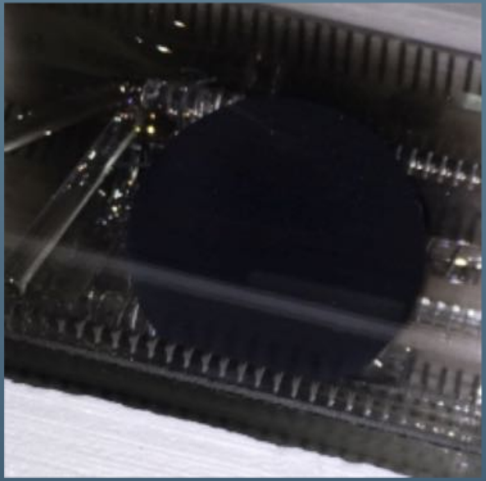


https://www.nasa.gov/content/goddard/nasa-ultra-black-nano-coating-to-be-applied-to-3-d-new-solar-coronagraph/#.Vj_a0Uar8ZM

Applications and Challenges

Spherical Occulter Coronagraph CubeSat (SpOC Cube) – PI Phil Chamberlin





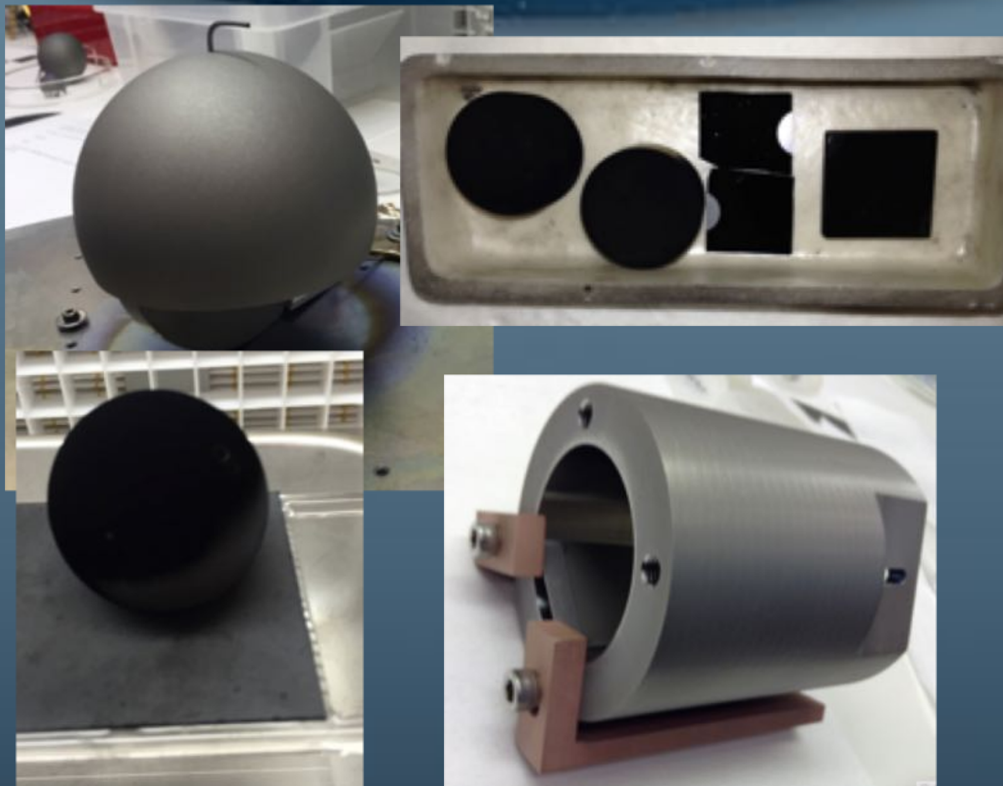
Challenges to fabricating spheres include:

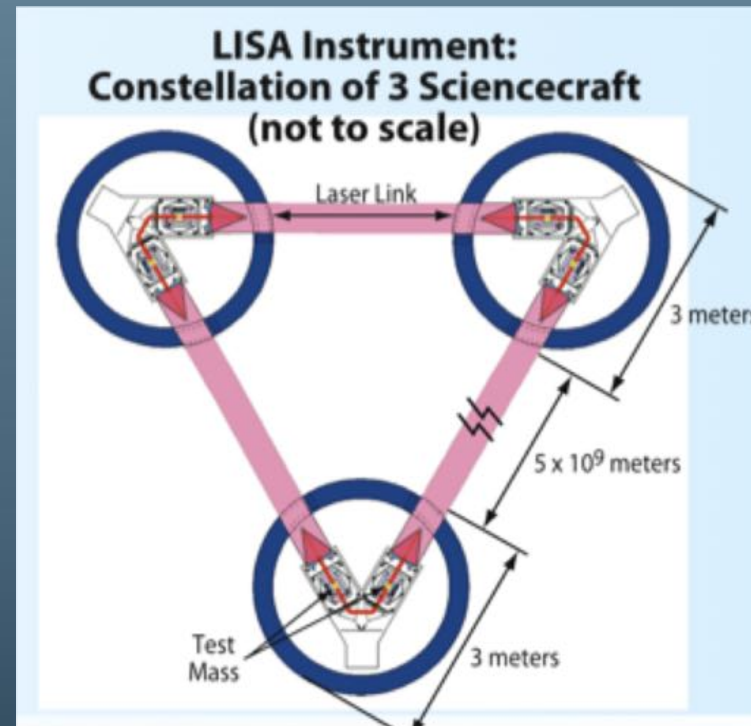
1. **Uniformly depositing catalyst on a sphere during physical vapor deposition**
2. **Controlling the gas flows during the chemical vapor deposition phase to prevent shadowing and uneven growth**

Three titanium spheres from ½” to 3” in diameter were fabricated to provide pathfinder elements for testing the theory

https://gsfctechnology.gsfc.nasa.gov/Coronagraph.html

Challenge





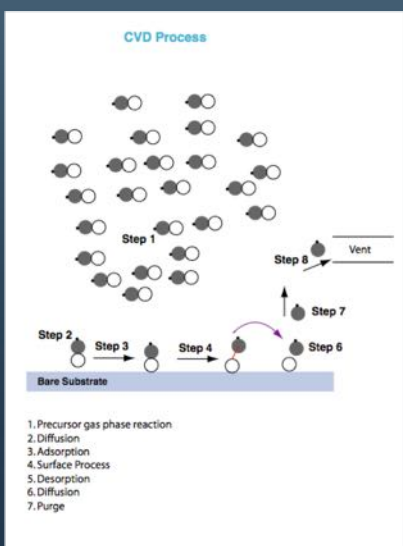
The deposition of the catalyst is in terms of: uniformity, thickness control, material regardless of geometry is paramount. Flat surfaces are easy!

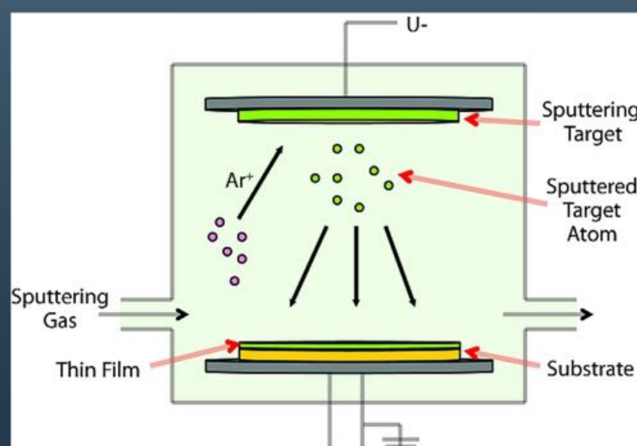
What is a Thin Film?

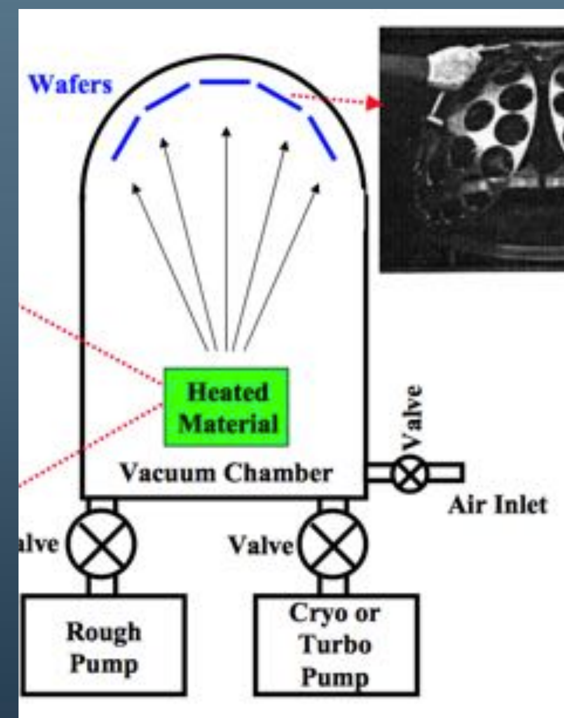
Thin film: thickness typically <1000nm.

Special properties of thin films: different from bulk materials, it may be –

- Not fully dense
- Under stress
- Different defect structures from bulk
- Quasi - two dimensional (very thin films)
- Strongly influenced by surface and interface effects



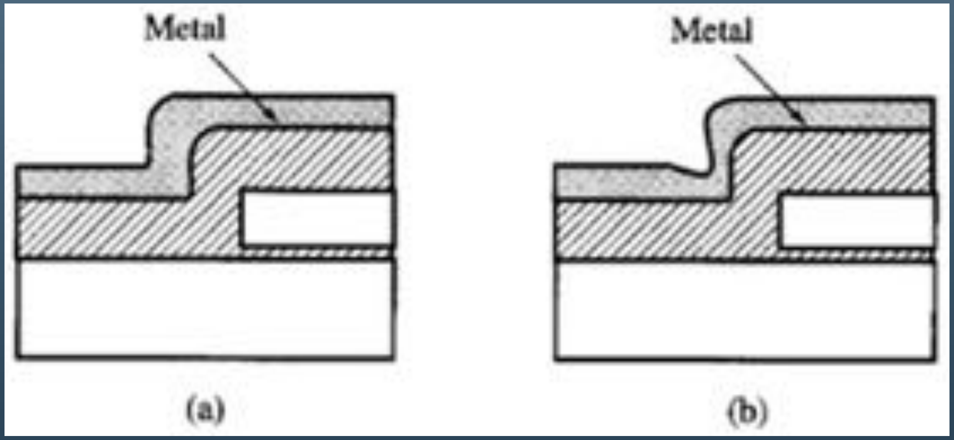


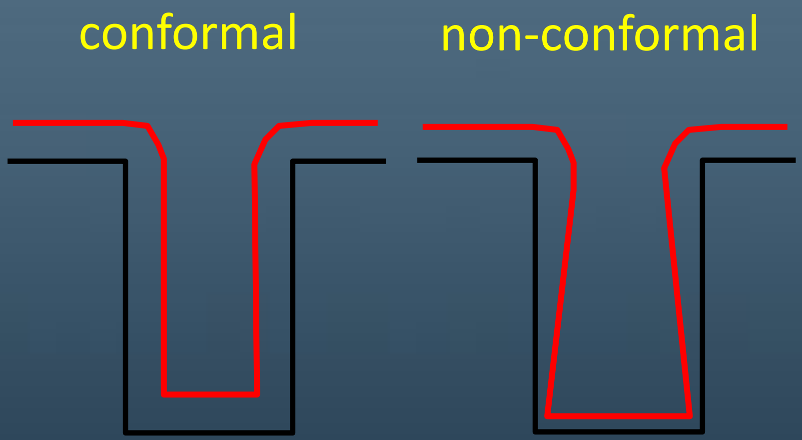


Common Denominator

- Deposition only occurs on substrates that "see" the target.
- Plasma process can damage the substrate
- Poor thickness control
- Poor Step Control
- High Pressure High Temperature Environment

Step Coverage Example





Step coverage of metal over non-planar topography.
(a) Conformal step coverage, with constant thickness on horizontal and vertical surfaces.
(b) Poor step coverage, here thinner for vertical surfaces.

Atomic Layer Deposition

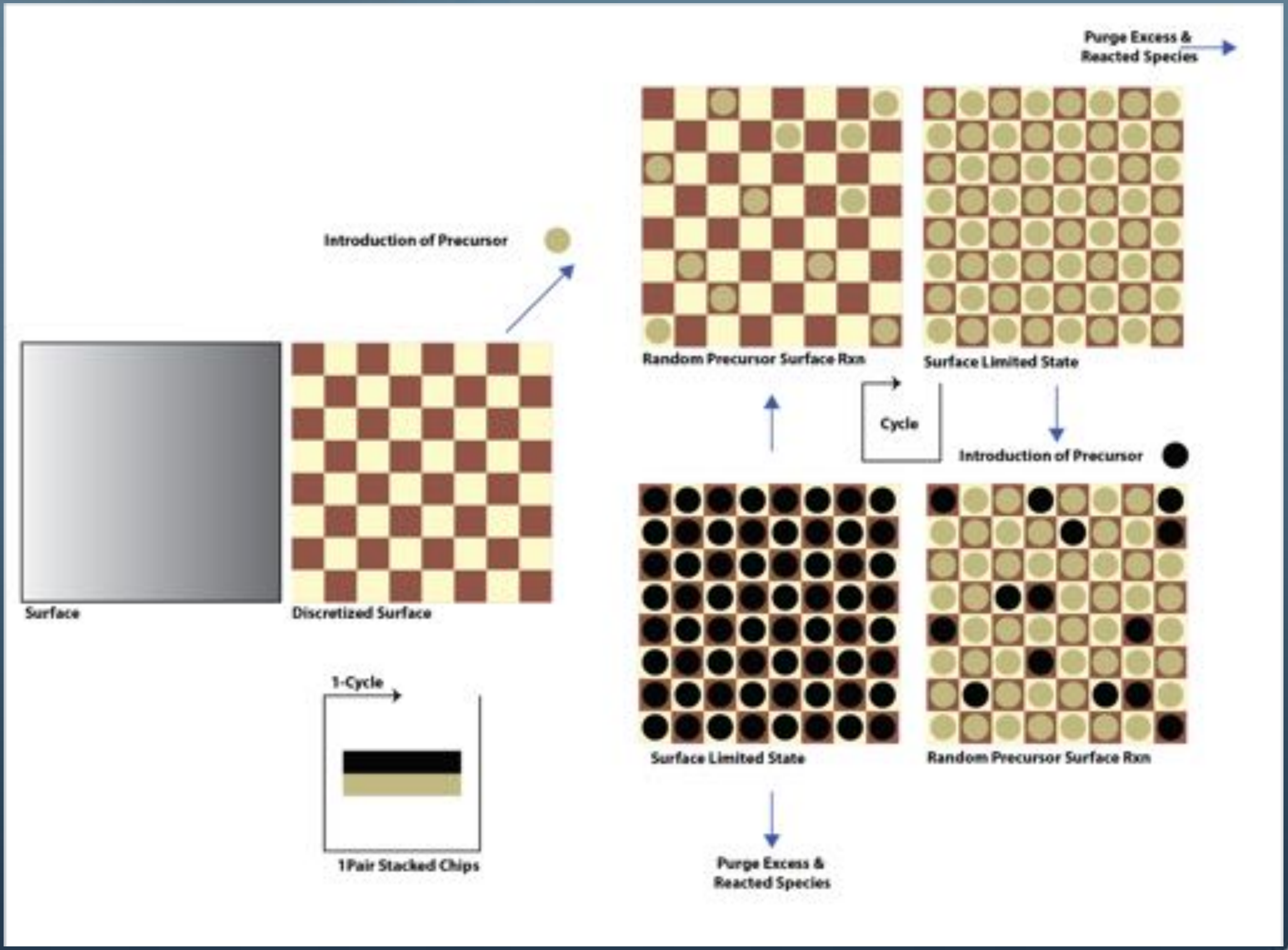
Atomic
Layer
Deposition

} **A thin film"nanomanufacturing" tool that allows for the conformal coating of materials on a myriad of surfaces with precise atomic thickness control.**

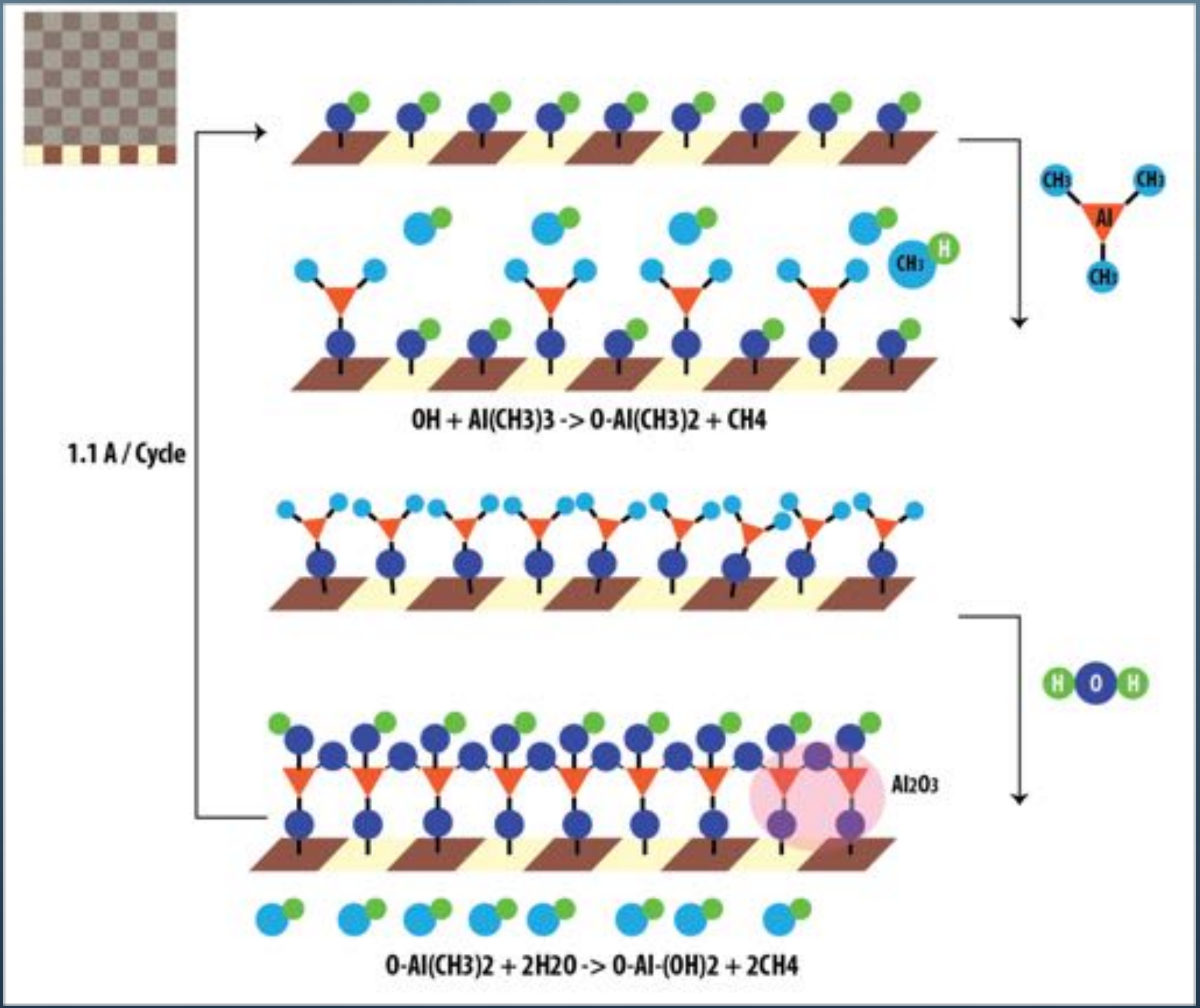
Based on:

- **Paired gas surface reaction chemistries**
- **Benign non-destructive temperature and pressure environment**
  - **Room temperature -> 250 °C (even lower around 45 °C)**
  - **Vacuum**

ALD Analogy (Checkers)



ALD Analogy Chemistry

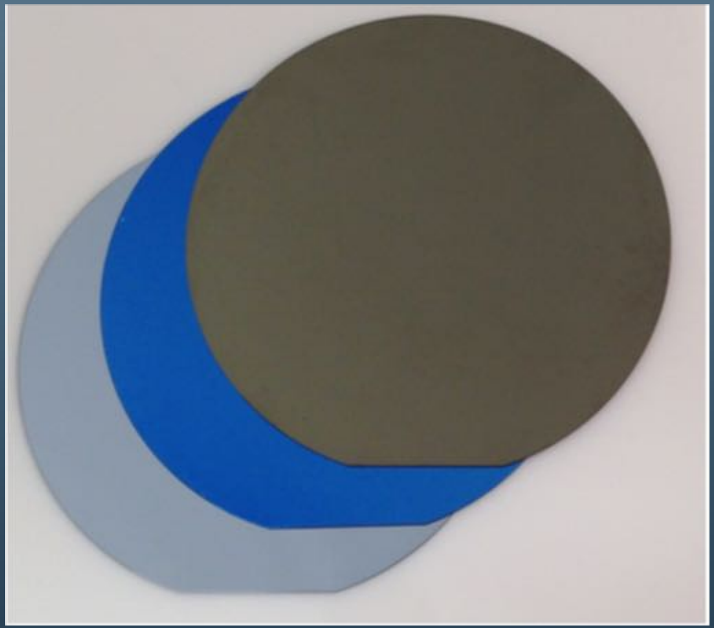


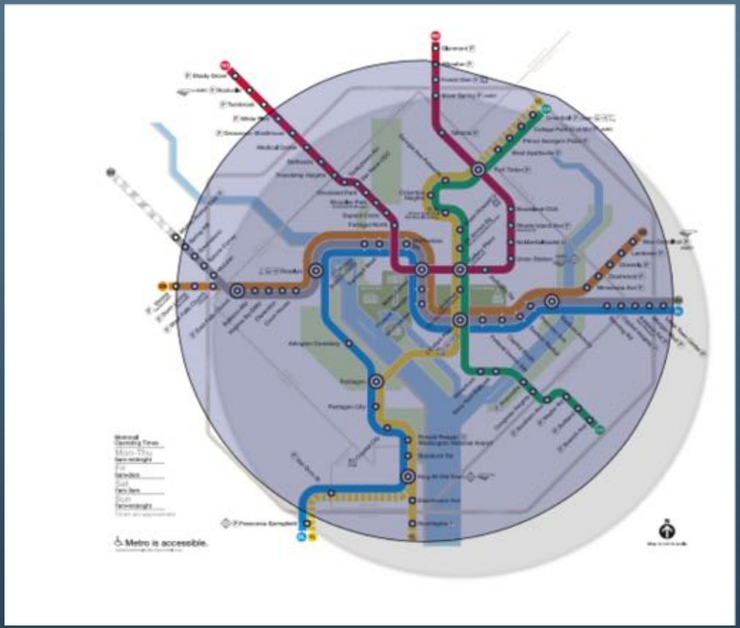
ALD

Precursor A + Precursor B → Solid film + Gas by-products

Cyclic operation: A → purge → B → purge → A → purge → ···

Atomic-level thickness control ...

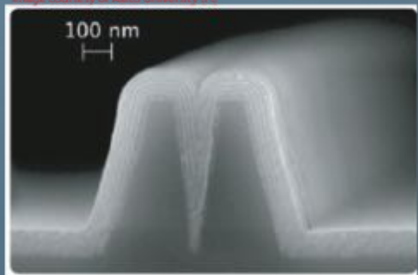


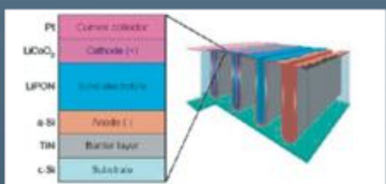


... equivalent to a 60 µm layer over a city-sized wafer

ALD Advantageous Property

Artificial trench filled with an ALD nanolaminate
Image courtesy of Aalto University (FI)





Schematic of a 3D battery integrated in a Si- substrate. The cross-section shows the various functional layers in the battery stack as well as the candidate materials.
Knoops, H.C.M. et al., ECS Trans., 25 (2009) pp. 333-344

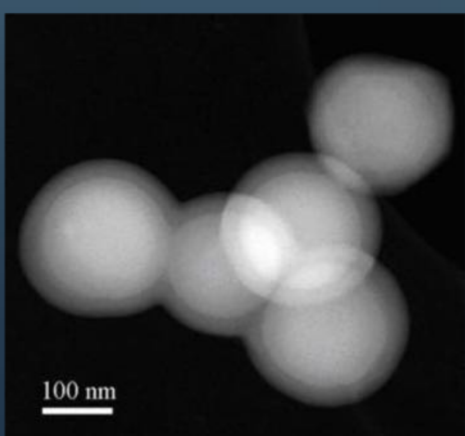
Epitaxial Growth

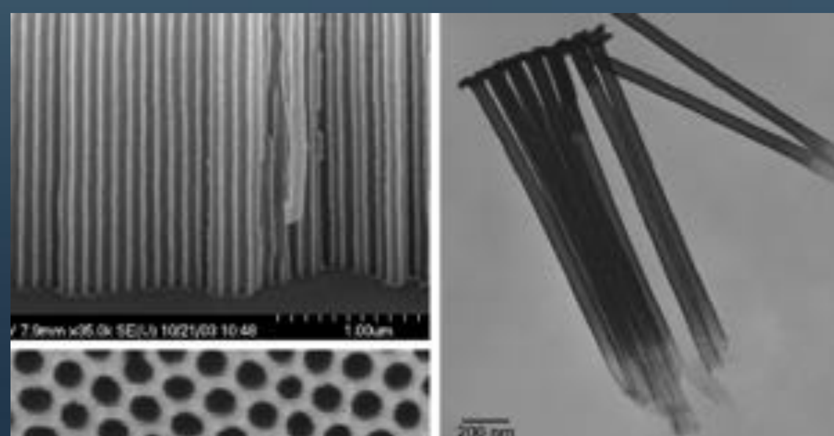
Multilayer consisting of:
Al2O3 - 25 nm
TiN - 20 nm
Al2O3 - 25 nm
Dr. Fred Roozeboom, NXP Semiconductors Research and Dr. Erwin Kessels, University of Technology, Eindhoventd

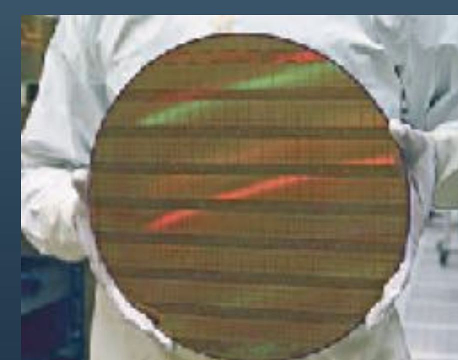
Batch Process

Coating Silver with Aluminum Oxide
http://www.glassonweb.com/

Substrate Independence







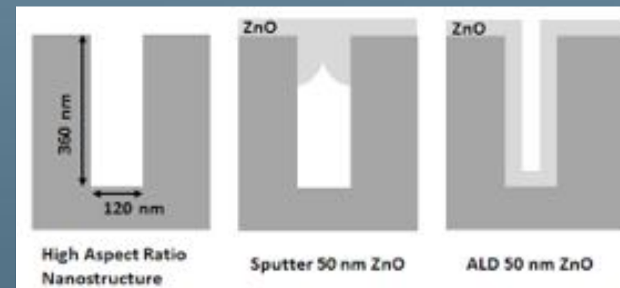
ALD Material Systems

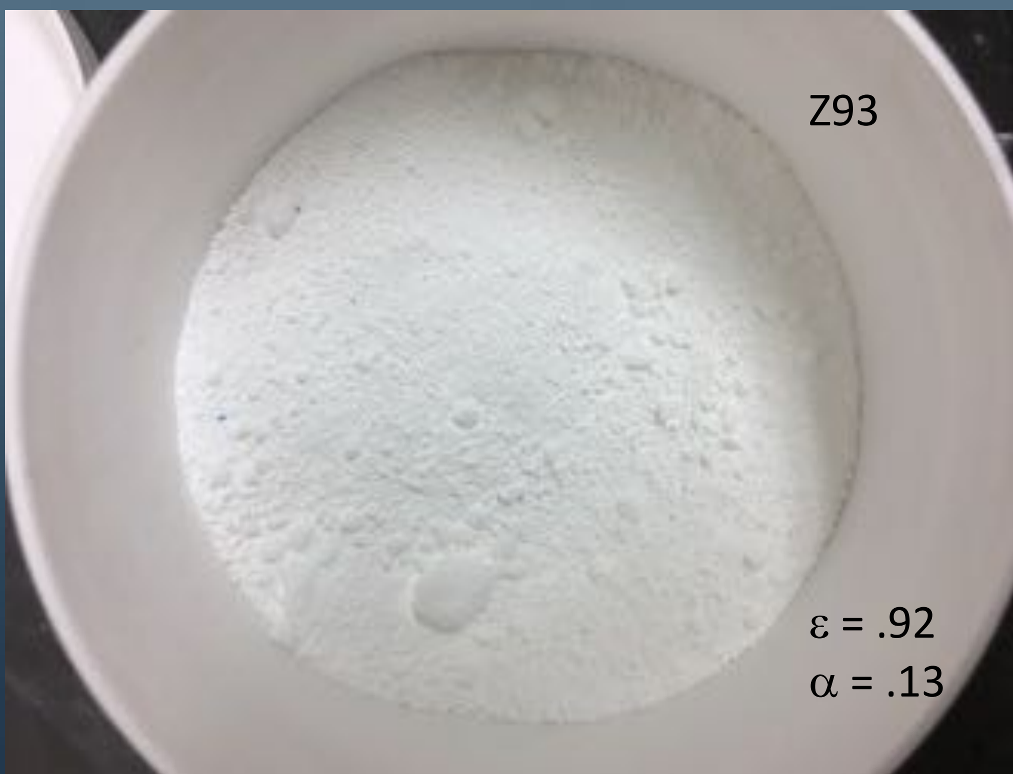
• Gordon, Roy (2008). Atomic Layer Deposition (ALD): An Enable for Nanoscience and Nanotechnology. PowerPoint lecture presented at Harvard University, Cambridge, MA.

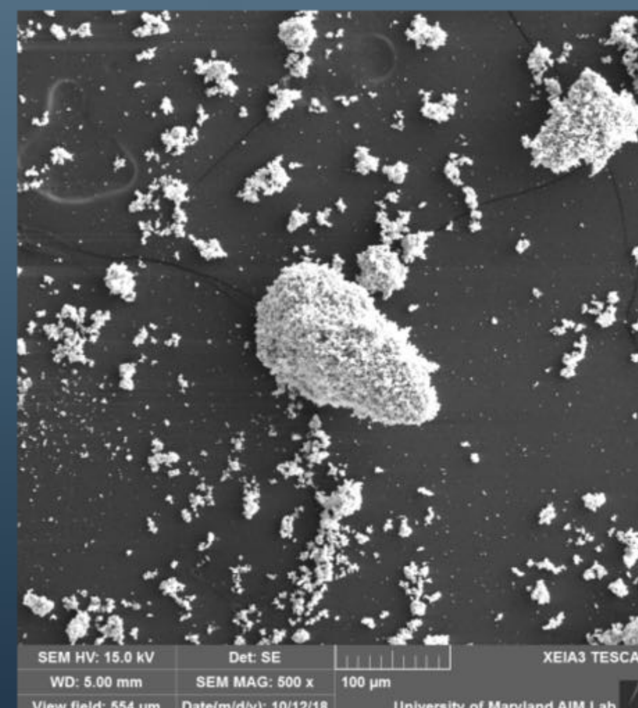
• Elam, Jeffrey (2007). ALD Thin Film Materials. Argonne National Laboratory

High Aspect Ratio (Radiator Pigments)

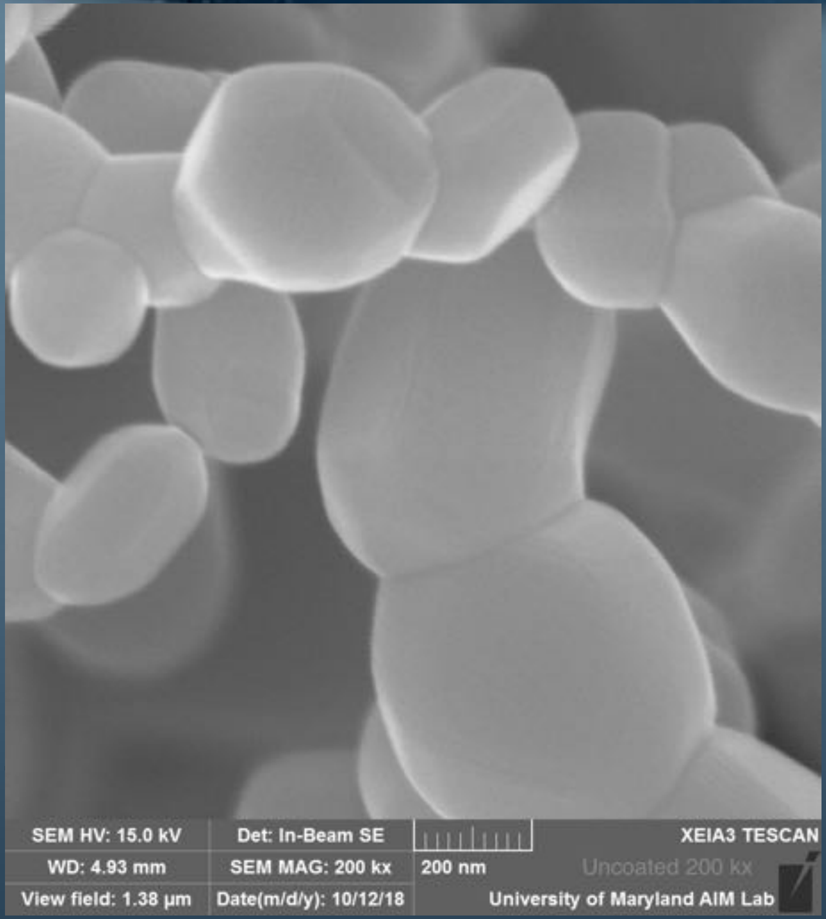
AZ TECHNOLOGY



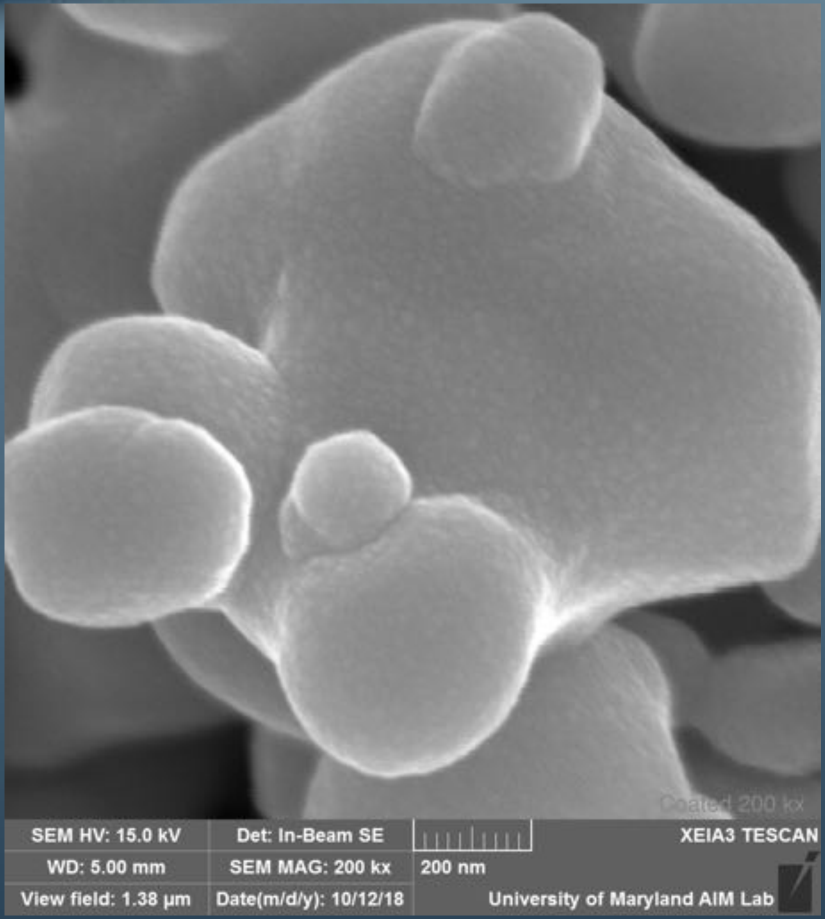




Results

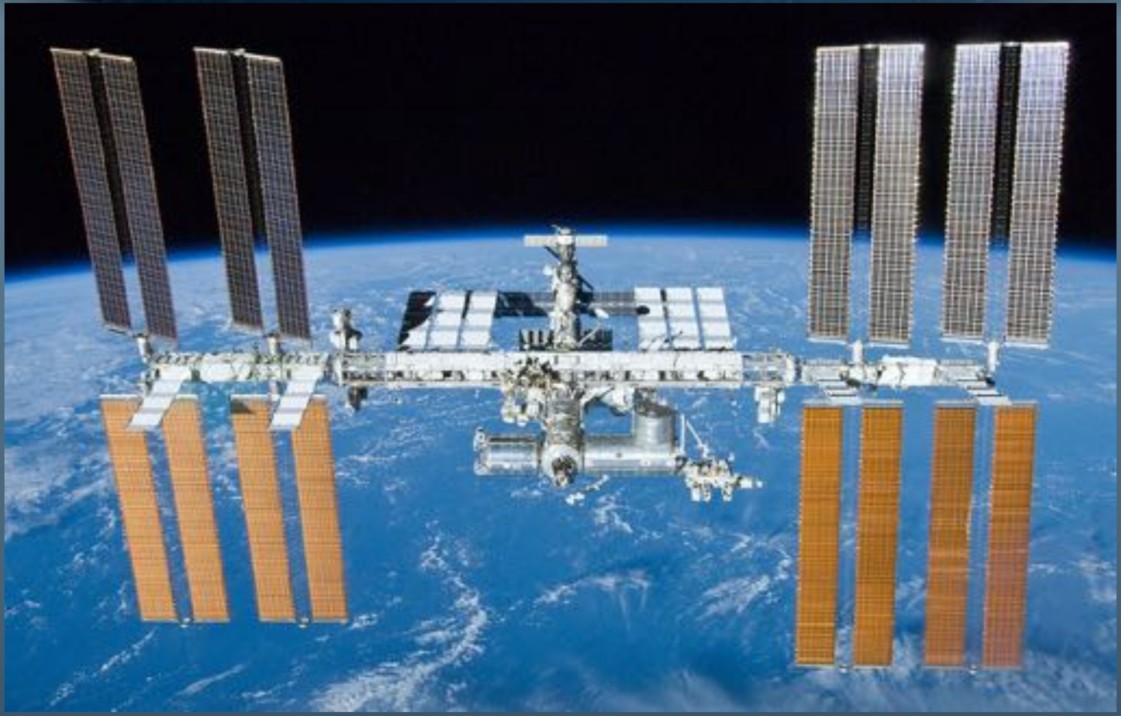


Uncoated Pigment



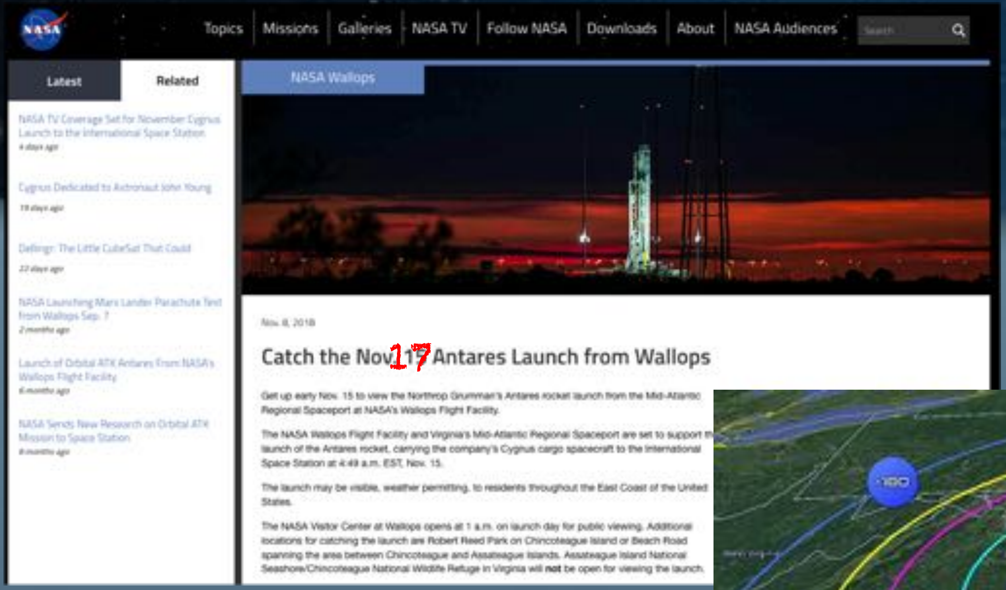
Coated Pigment

ISS Opportunity - MISSE-FF



The Materials ISS Experiment Flight Facility (MISSE-FF) with MISSE Sample Carriers (MSCs) in the fully open position exposing samples/experiments to the harsh environment of space in low-Earth Orbit (LEO). Image courtesy of Alpha Space.

An earlier MISSE mission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NASA Wallops

Nov. 8, 2018

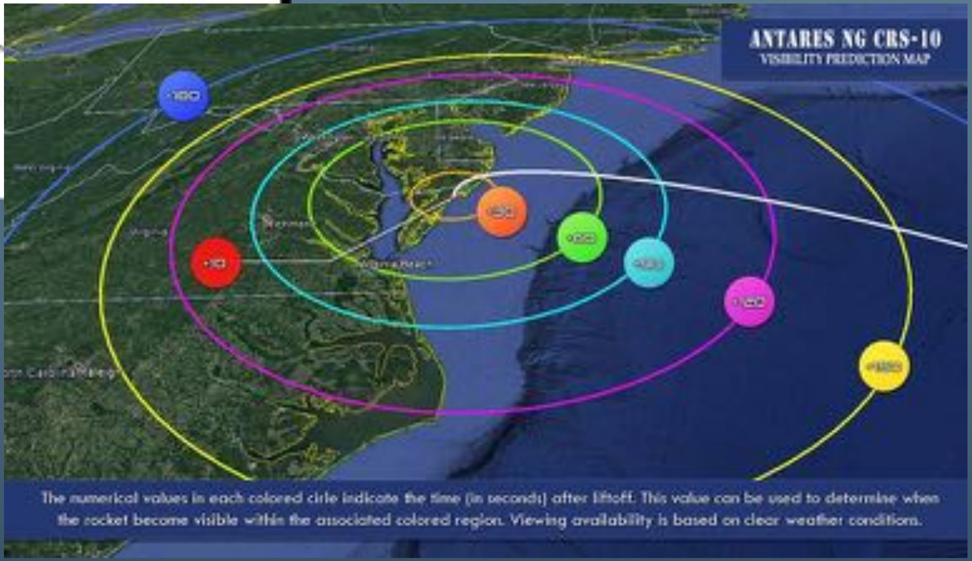
Catch the Nov ~~15~~ 17 Antares Launch from Wallops

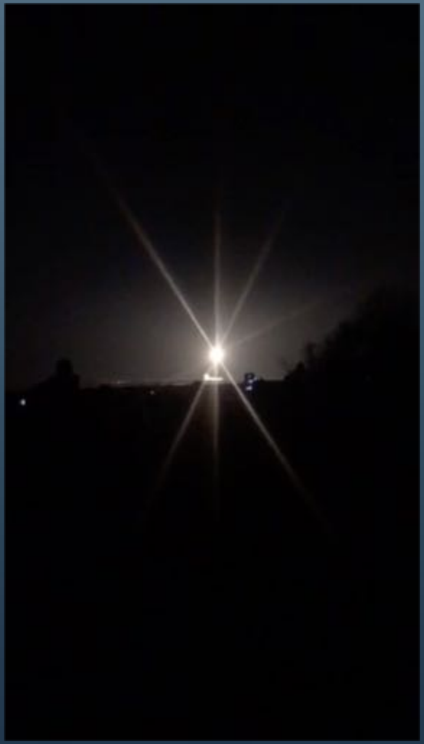
Get up early Nov. 15 to view the Northrop Grumman's Antares rocket launch from the Mid-Atlantic Regional Spaceport at NASA's Wallops Flight Facility.

The NASA Wallops Flight Facility and Virginia's Mid-Atlantic Regional Spaceport are set to support th[e] launch of the Antares rocket, carrying the company's Cygnus cargo spacecraft to the International Space Station at 4:49 a.m. EST, Nov. 15.

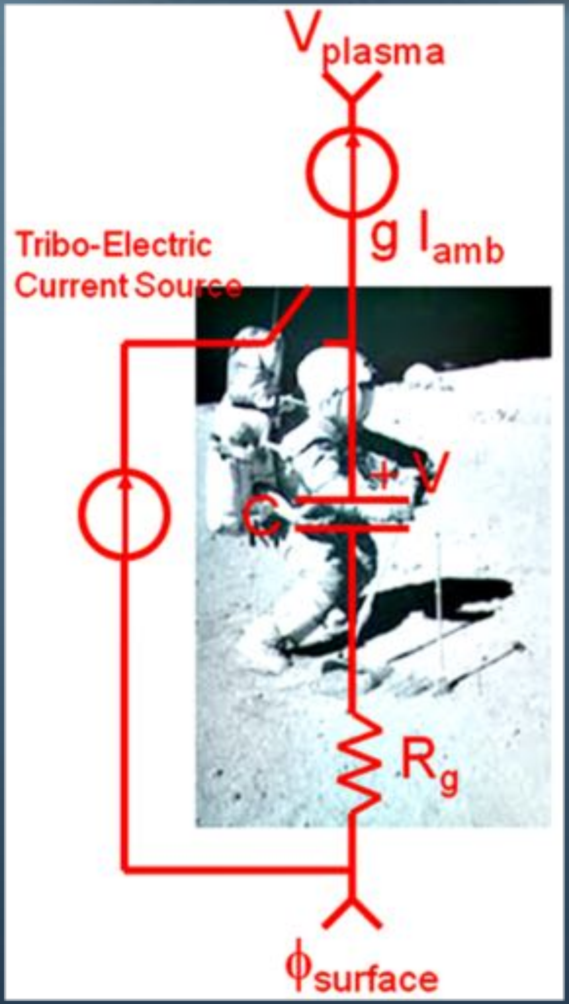
The launch may be visible, weather permitting, to residents throughout the East Coast of the United States.

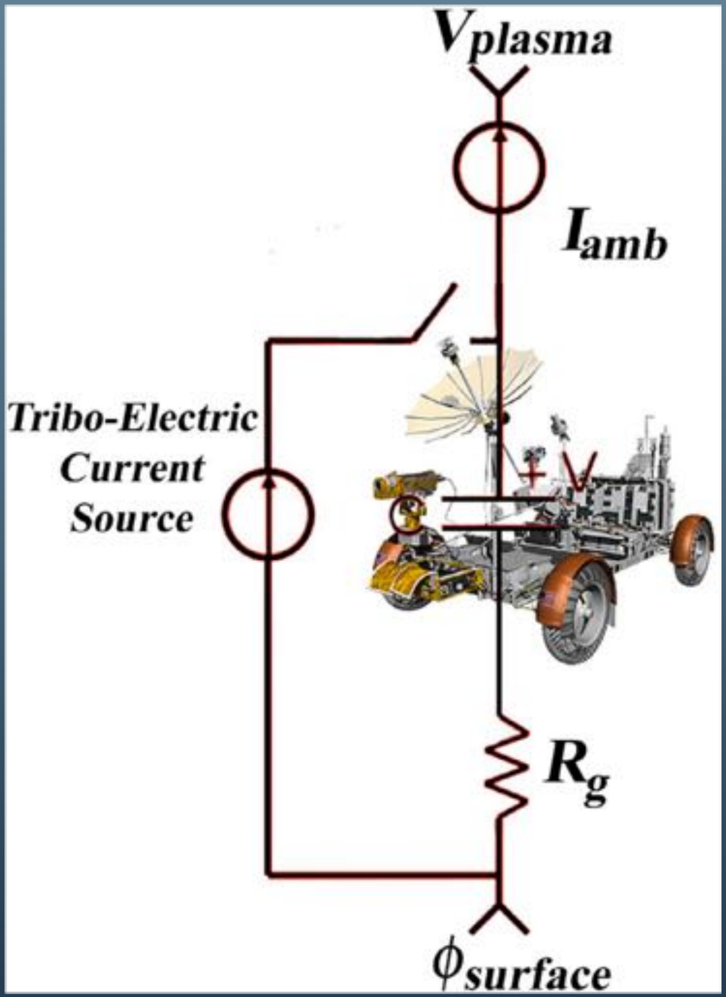
The NASA Visitor Center at Wallops opens at 1 a.m. on launch day for public viewing. Additional locations for catching the launch are Robert Reed Park on Chincoteague Island or Beach Road spanning the area between Chincoteague and Assateague Islands. Assateague Island National Seashore/Chincoteague National Wildlife Refuge in Virginia will **not** be open for viewing the launch.





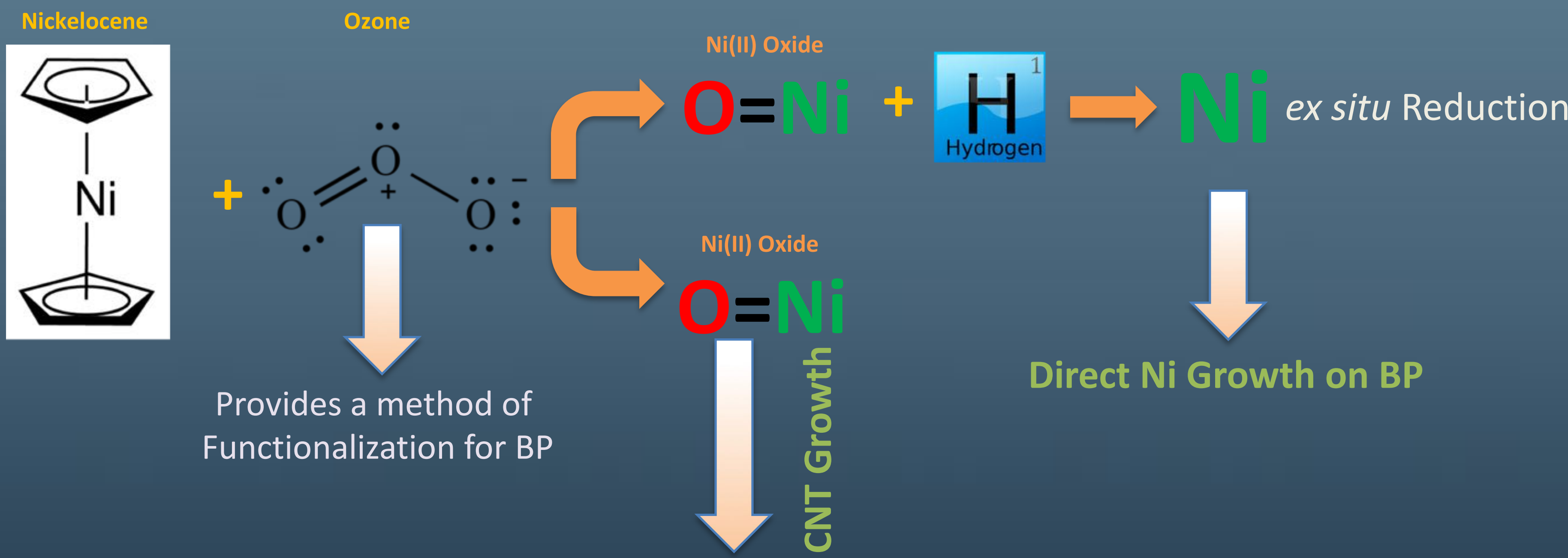
Potential Applications





Element of choice (Ni)

Reaction Pathway



- During Growth Process Ni(II) Oxide reduces to Ni
- Ni (II) Oxide is Oxygen rich and reduction results in 40% decrease in thickness
- Resulting in Ni Cluster

Experimental Procedures

Reactor Parameters:

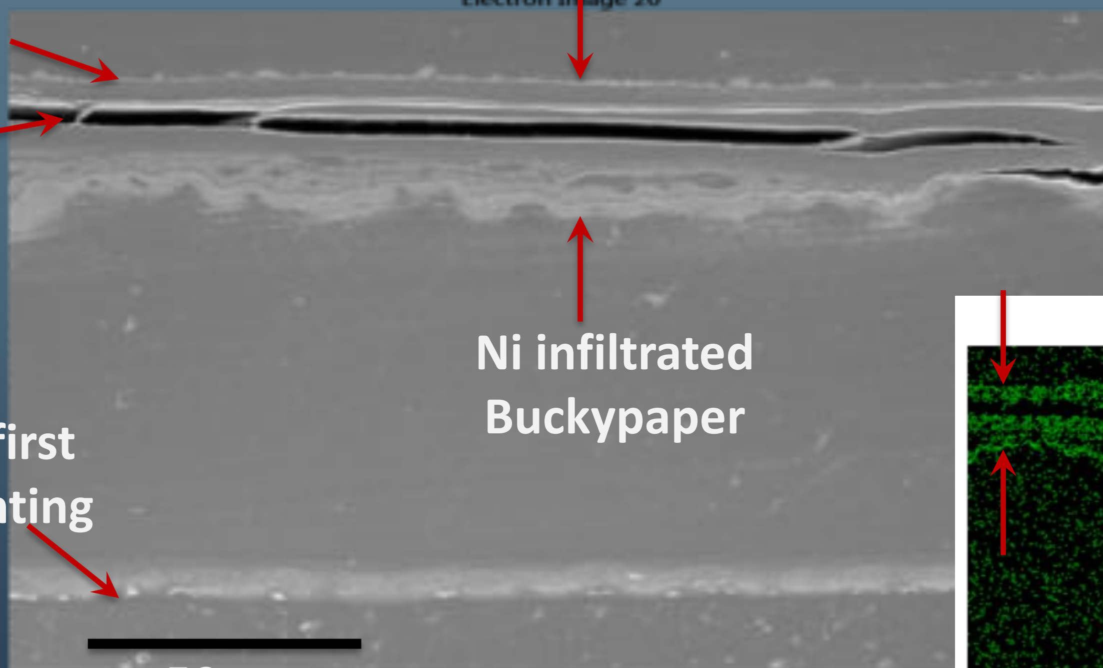
Reactor Temperature: 245 C
Ni Precursor Temperature: 90 C
Argon Flow Rate: 20 SCCM
Ozone Weight Percent: 8%
Ozone Flow Rate: 20 SCCM

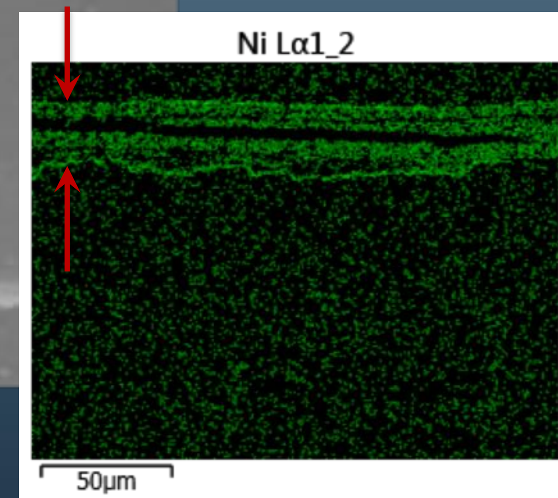
Ni Pulse Time: .6 Sec (2*.3 sec)
Ni Residence Time: 15 Sec
Ozone Pulse Time: .2 Sec
Ozone Residence Time: 15 Sec

Hydrogen Reduction:
5 Hours
450 C
5% Hydrogen in Argon
Flow Rate 550 sccm

Results - SEM & EDS of Ni coated buckypaper

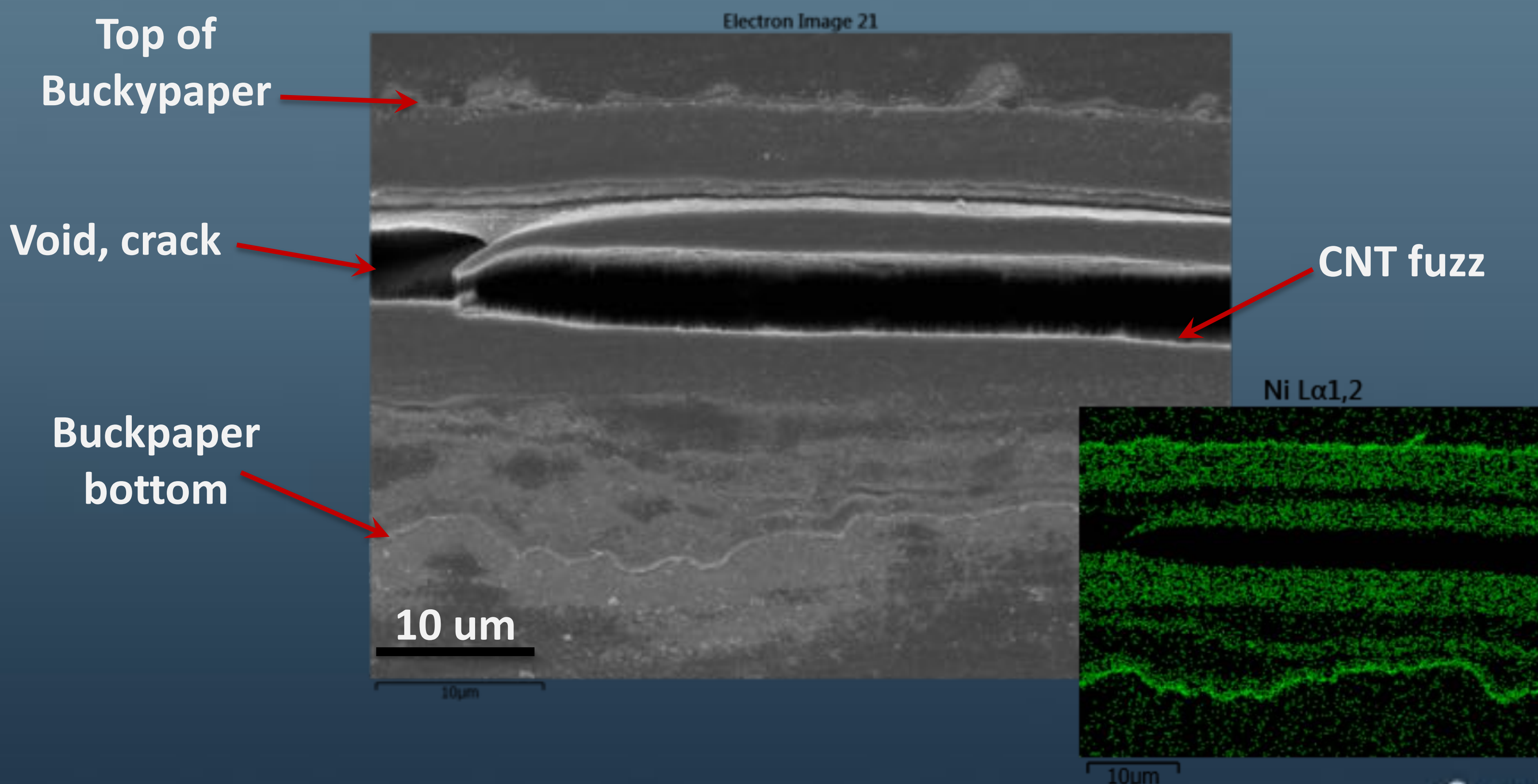
Cross-sectional, edge view of the coat paper, 500 cycles of NiO – then reduced; mounted in metallographic epoxy: a crack frequently found in infiltrated region.





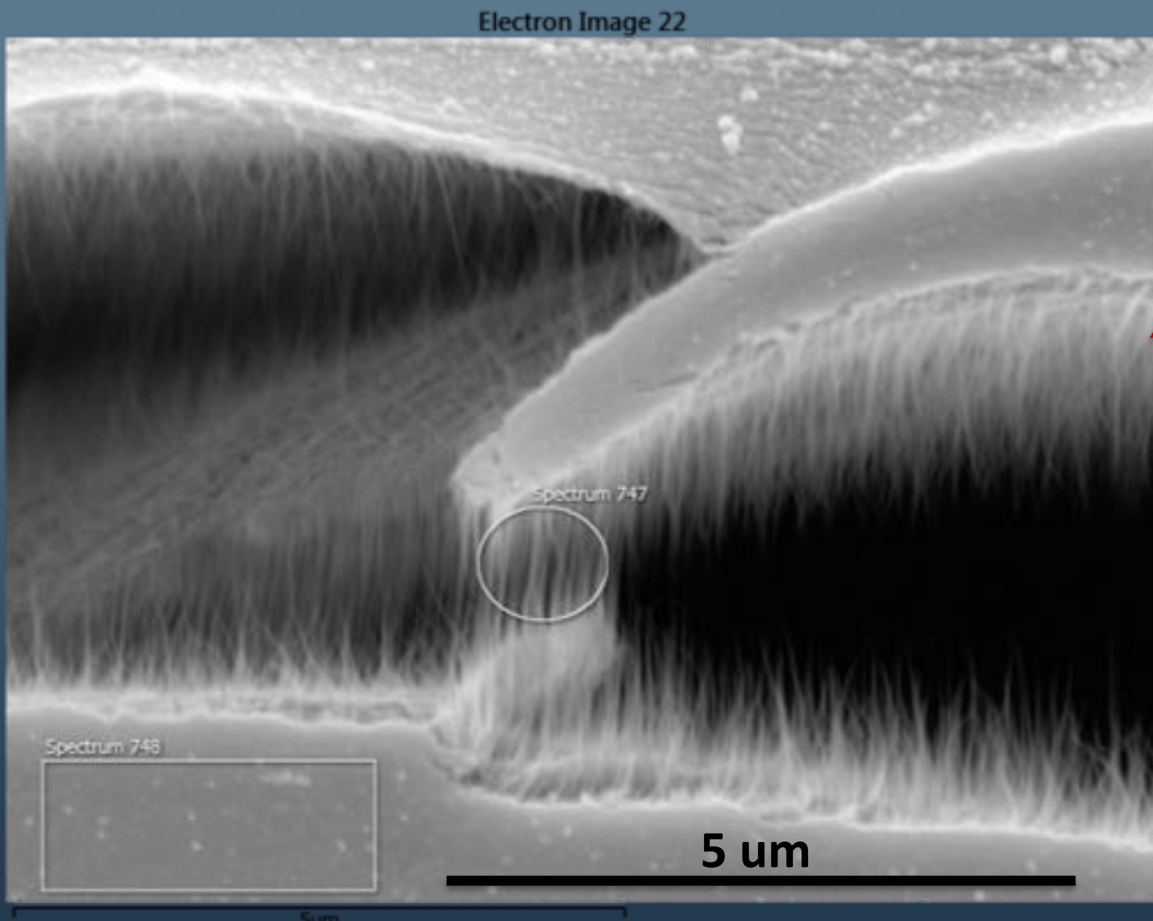
Results - 500 cycles NiO-reduced

Closer view of the cracked area in the Buckypaper; Ni appears to be throughout the Buckpaper thickness.



500 cycles NiO-reduced

Closer view of the CNT in cracked area; showing less Ni than we would like, and more O than we would like.



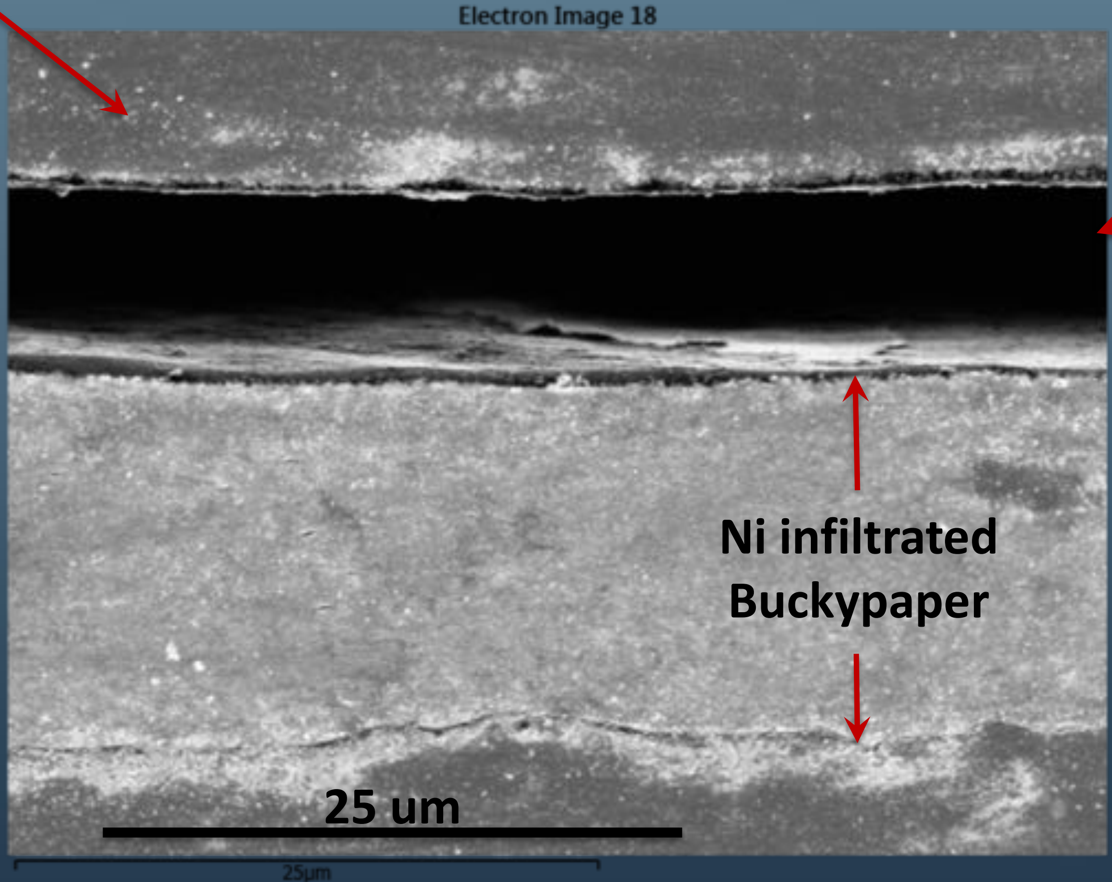
CNT

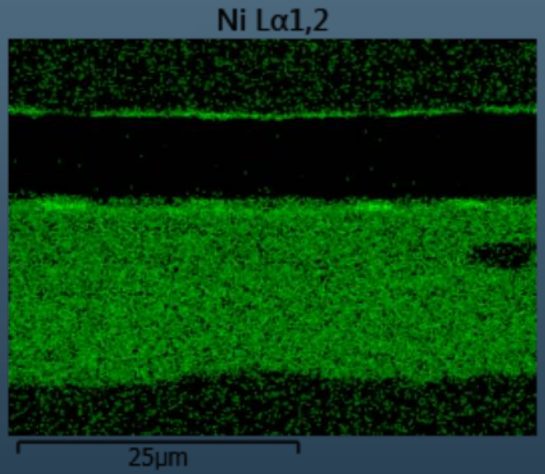
Spectrum 747	At%
C	94.1
O	3.9
Ni	2.0

Spectrum 748	At%
C	92.2
O	5.7
Ni	2.1
N	0.0

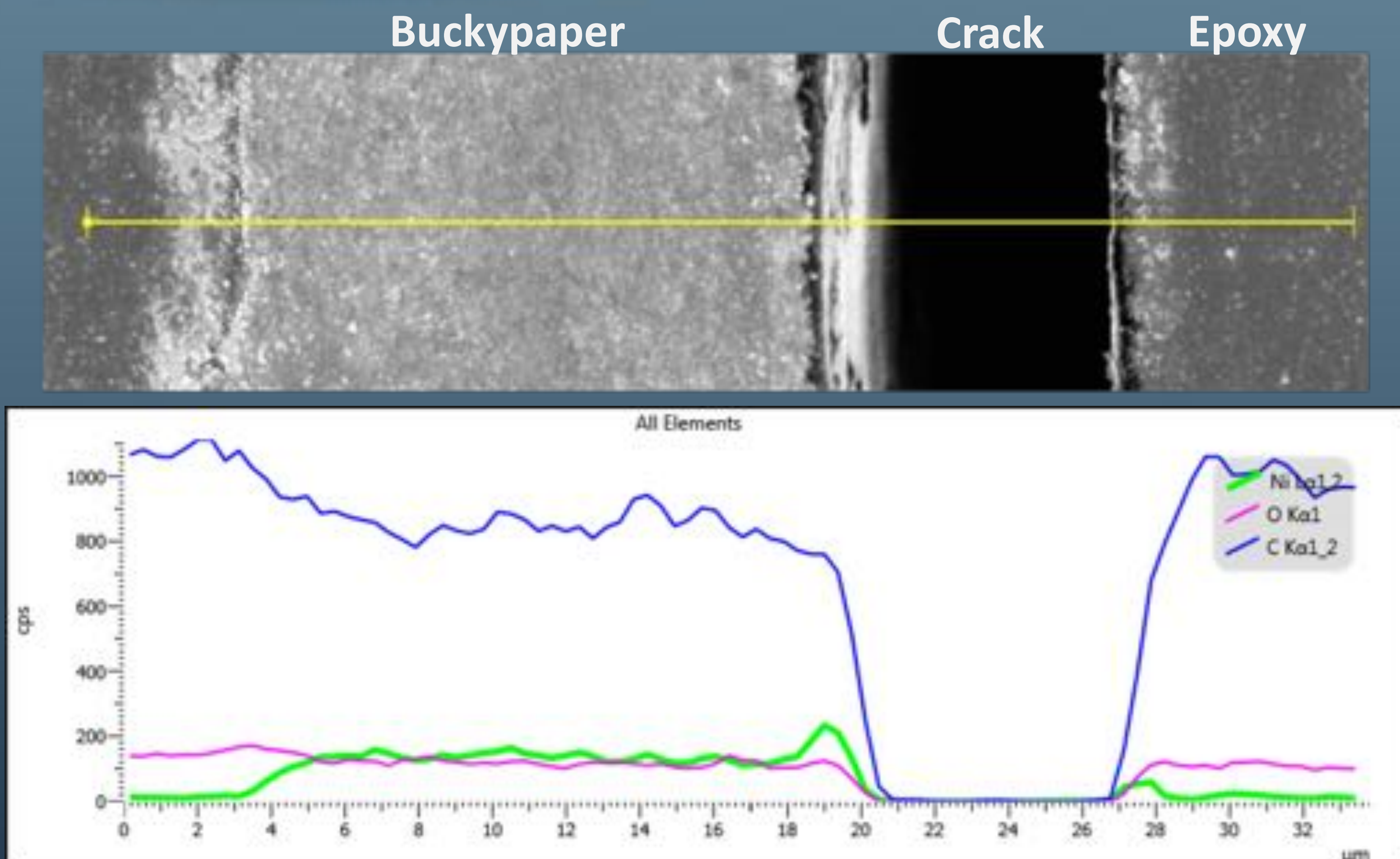
1000 cycles NiO-reduced

Buckypaper subjected to more deposition cycles showing good Ni penetration into the paper.





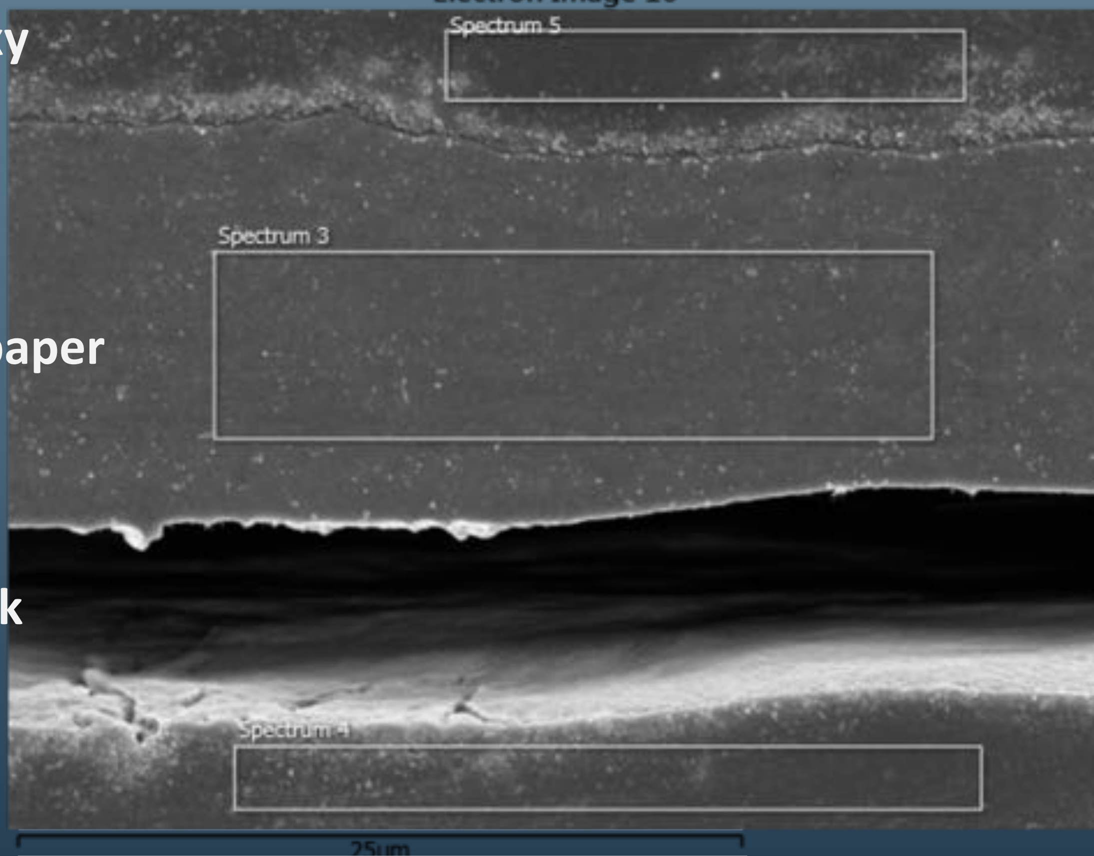
Composition line scan across 1000 cycles NiO-reduced



500 cycles NiO-NOT reduced

Unreduced sample has twice the O content in the paper.

Electron Image 16



Epoxy

Buckypaper

Crack

25 um

Spectrum 5

	At%
C	90.4
O	9.6
Ni	0.0

Spectrum 3

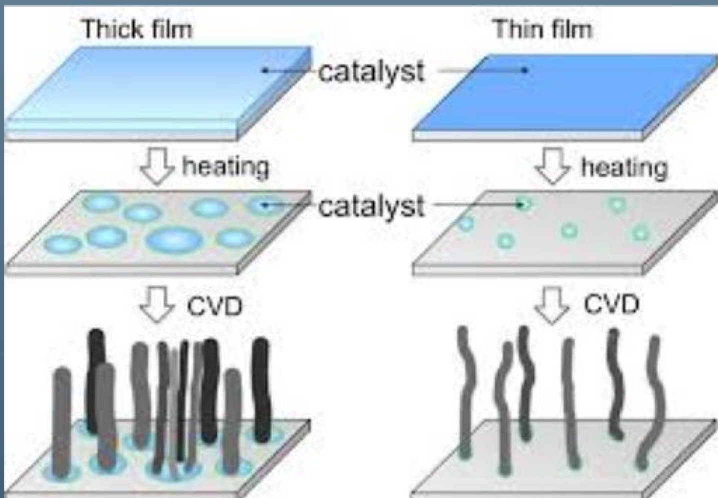
	At%
C	87.1
O	10.2
Ni	2.7

Spectrum 4

	At%
C	89.1
O	10.9
Ni	0.0

Growth of CNT & ALD

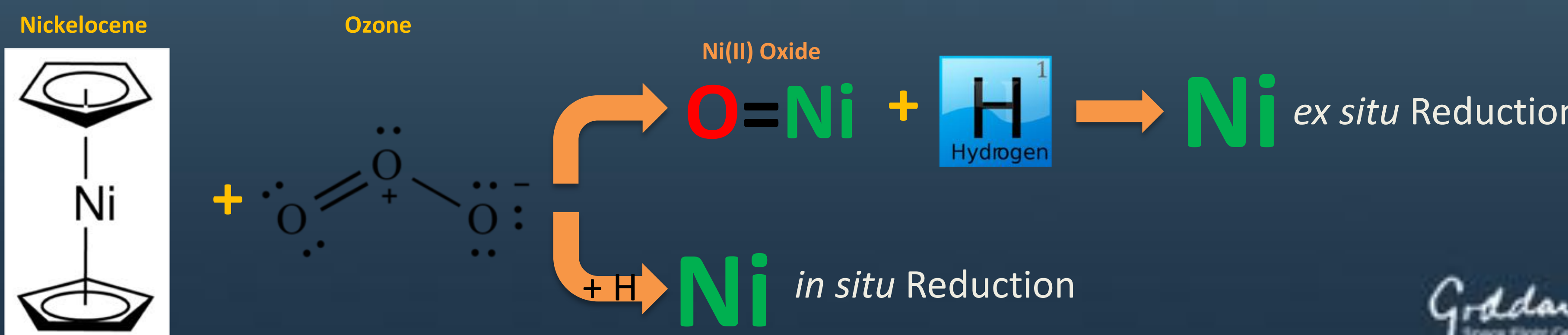
Typical Growth of CNTs



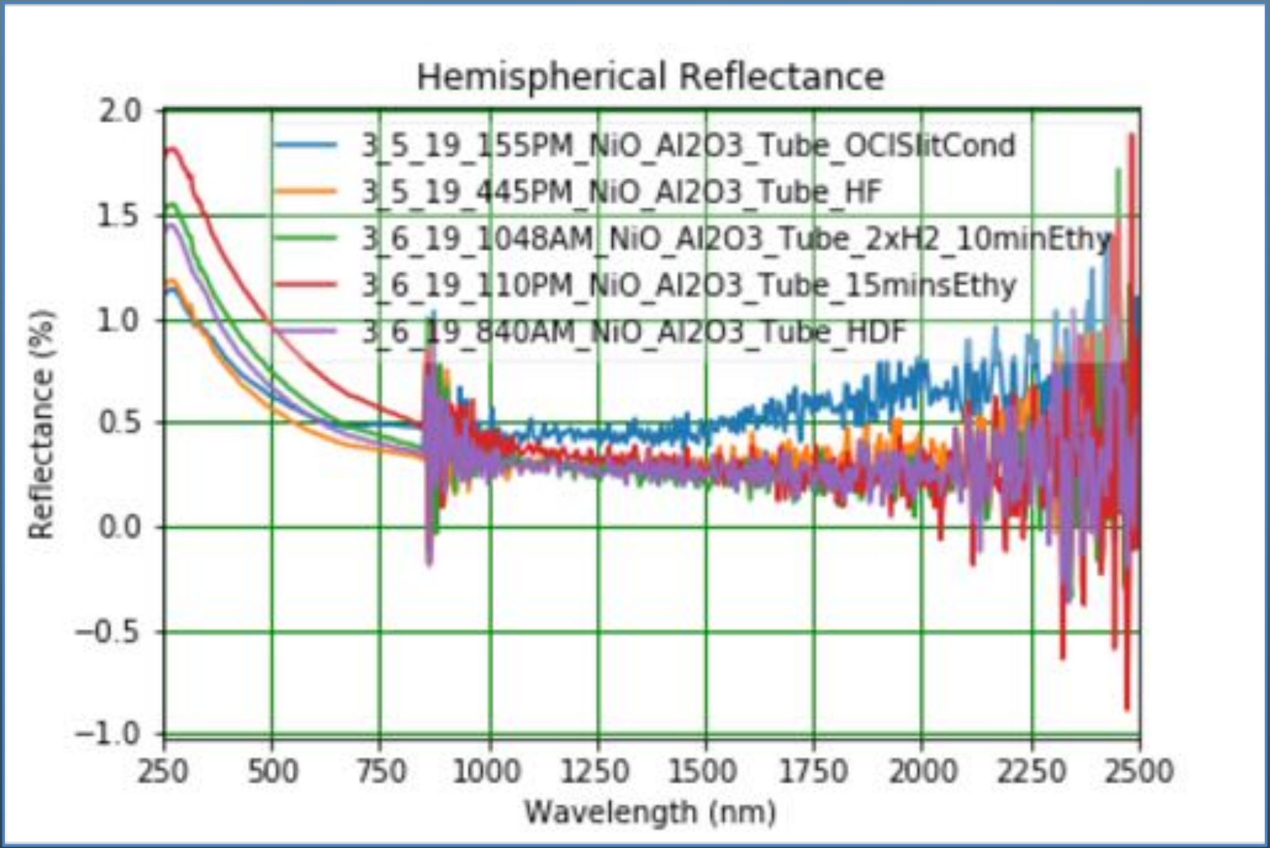
Substrate + Catalyst + Gas = CNNT
Si,Ti, flat, 3d + Iron,Ni + Ethylene

ALD of Catalyst (Ni)

Precursors and Reaction Pathway



Initial Results



Acknowledgments

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