



GSFC • 2015

An Introduction to Atomic Layer Deposition with Thermal Applications

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NASA GSFC Code 545



What is a Thin Film?

Thin film: thickness typically $<1000\text{nm}$.

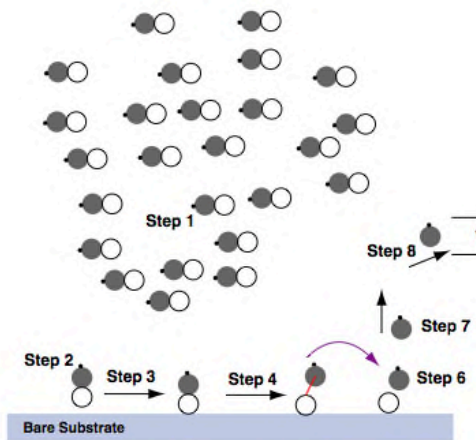
Special properties of thin films: different from bulk materials, it may be –

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

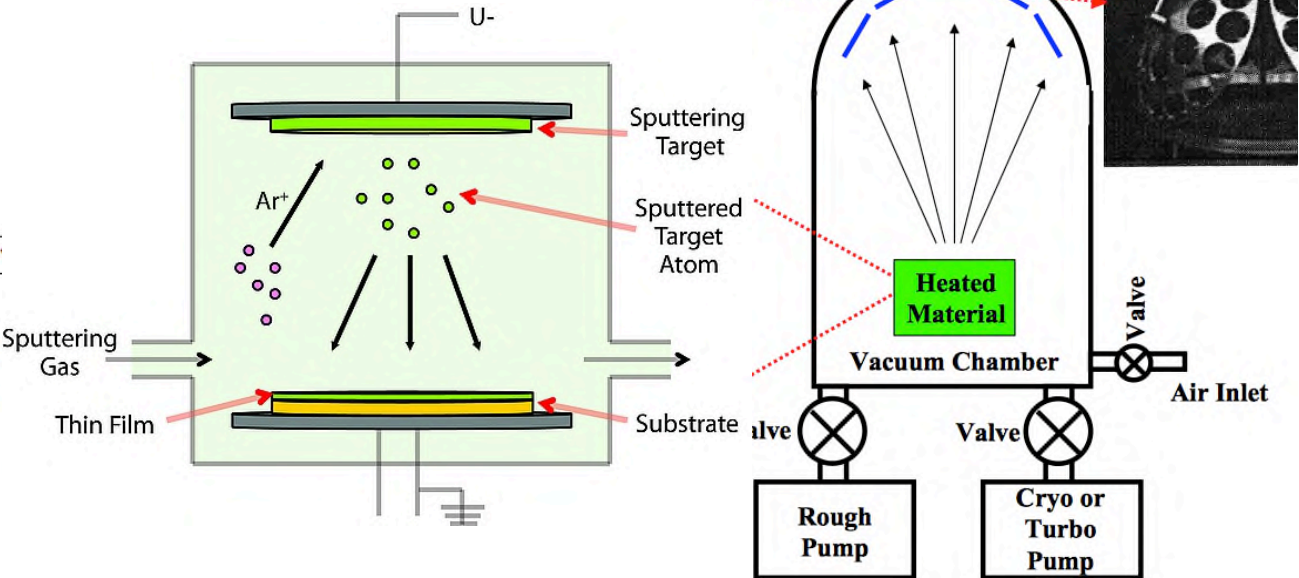


Other Deposition Techniques

CVD Process



1. Precursor gas phase reaction
2. Diffusion
3. Adsorption
4. Surface Process
5. Desorption
6. Diffusion
7. Purge

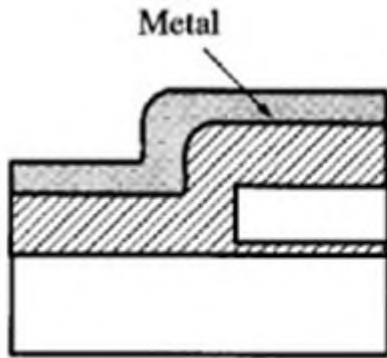




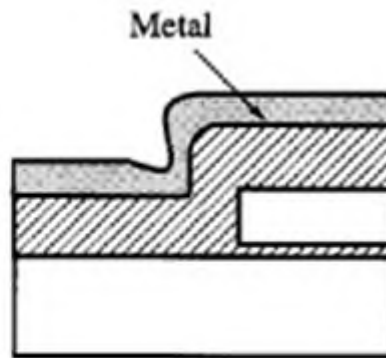
Common Denominator

- 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!

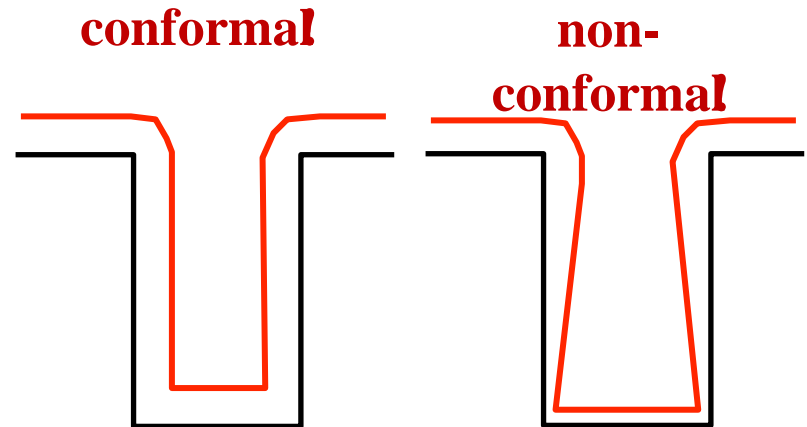
Step Coverage Example!



(a)



(b)



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.!



Introduction

Atomics
Layer
Deposition



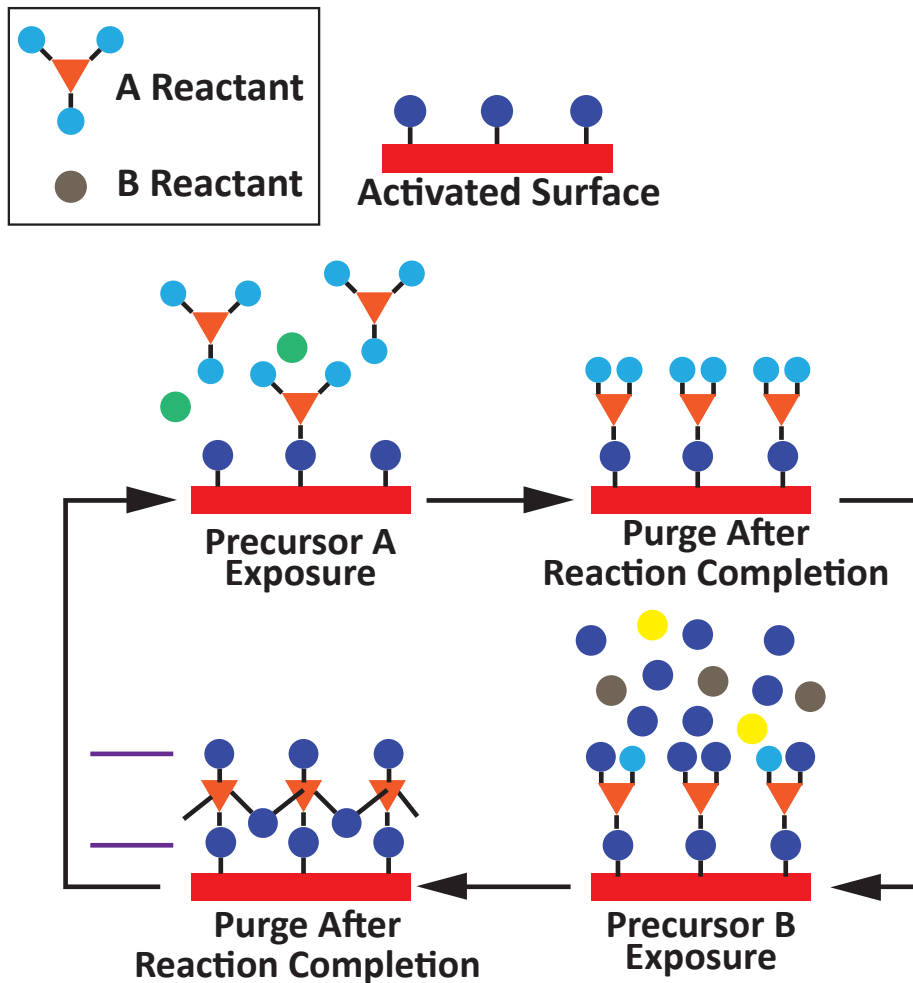
A thin film “nanomanufacturing” tool that allows for the conformal coating materials on a myriad of surfaces with precise atomic thickness control.

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 Procedure



- **A or B exposure = Half Cycle!**
- **A+B = Full Cycle = 1 Monolayer!**
- **Digital Process: ABABABAB!**
- **Not Line of Sight, EVERYTHING GETS COATED!**
- **Substrate Independent**



Periodic Table of ALD Films

H 1	<div><div>O:Oxide N:Nitride M:Metal P:Phosphide/Asenide S:Sulphide/Selenide/Telluride</div><div>C:Carbide F:Fluoride D:Dopant</div></div>																He 2						
<div>Li 3</div>	<div>Be 4</div>																	<div><div>N B 5</div><div>D</div></div>	<div><div>C 6</div></div>	<div><div>N 7</div></div>	<div><div>O 8</div></div>	<div><div>F 9</div></div>	<div>Ne 10</div>
<div>Na 11</div>	<div><div>Mg 12</div><div>F</div></div>																	<div><div><div>N M Al 13</div><div>P</div><div>D</div></div></div>	<div><div><div>N M Si 14</div><div>C</div></div></div>	<div><div>P 15</div></div>	<div><div>S 16</div></div>	<div><div>Cl 17</div></div>	<div>Ar 18</div>
<div>K 19</div>	<div><div>Ca 20</div><div>S F</div></div>	<div><div>Sc 21</div></div>	<div><div><div>N M Ti 22</div><div>S</div></div></div>	<div><div>V 23</div></div>	<div><div>Cr 24</div></div>	<div><div><div>N M Mn 25</div><div>S D</div></div></div>	<div><div><div>N M Fe 26</div><div>M</div></div></div>	<div><div><div>N M Co 27</div></div></div>	<div><div><div>N M Ni 28</div><div>M</div></div></div>	<div><div><div>N M Cu 29</div><div>S D</div></div></div>	<div><div><div>N M Zn 30</div><div>S F D</div></div></div>	<div><div><div>N M Ga 31</div><div>P D</div></div></div>	<div><div><div>N M Ge 32</div><div>M</div></div></div>	<div><div>As 33</div></div>	<div><div>Se 34</div></div>	<div><div>Br 35</div></div>	<div>Kr 36</div>						
<div>Rb 37</div>	<div><div>Sr 38</div><div>S F</div></div>	<div><div>Y 39</div></div>	<div><div><div>N M Zr 40</div></div></div>	<div><div><div>N Nb 41</div></div></div>	<div><div><div>N M Mo 42</div></div></div>	<div><div><div>N M Tc 43</div></div></div>	<div><div><div>N M Ru 44</div><div>M</div></div></div>	<div><div><div>N M Rh 45</div><div>M</div></div></div>	<div><div><div>N M Pd 46</div><div>M</div></div></div>	<div><div><div>N M Ag 47</div><div>M</div></div></div>	<div><div><div>N M Cd 48</div><div>S</div></div></div>	<div><div><div>N M In 49</div><div>S P</div></div></div>	<div><div><div>N M Sn 50</div><div>S D</div></div></div>	<div><div><div>N M Sb 51</div><div>D</div></div></div>	<div><div>Te 52</div></div>	<div><div>I 53</div></div>	<div>Xe 54</div>						
<div>Cs 55</div>	<div><div>Ba 56</div><div>S</div></div>	<div><div><div>N La 57</div><div>S F</div></div></div>	<div><div><div>N M Hf 72</div><div>S F C</div></div></div>	<div><div><div>N M Ta 73</div></div></div>	<div><div><div>N M W 74</div></div></div>	<div><div><div>N Re 75</div></div></div>	<div><div><div>N Os 76</div></div></div>	<div><div><div>N M Ir 77</div><div>M</div></div></div>	<div><div><div>N M Pt 78</div><div>M</div></div></div>	<div><div>Au 79</div></div>	<div><div>Hg 80</div><div>S</div></div>	<div><div>Tl 81</div></div>	<div><div><div>N M Pb 82</div><div>S D</div></div></div>	<div><div><div>N Bi 83</div></div></div>	<div><div>Po 84</div></div>	<div><div>At 85</div></div>	<div>Rn 86</div>						
<div>Fr 87</div>	<div>Ra 88</div>	<div>Ac 89</div>	<div>Rf 104</div>	<div>Db 105</div>	<div>Sg 106</div>	<div>Bh 107</div>	<div>Hs 108</div>	<div>Mt 109</div>															
									<div><div><div>N Ce 58</div><div>D</div></div></div>	<div><div><div>N Pr 59</div></div></div>	<div><div>Nd 60</div></div>	<div><div>Pm 61</div></div>	<div><div><div>N Sm 62</div></div></div>	<div><div><div>N Eu 63</div><div>D</div></div></div>	<div><div><div>N Gd 64</div></div></div>	<div><div><div>N Tb 65</div><div>D</div></div></div>	<div><div><div>N Dy 66</div></div></div>	<div><div><div>N Ho 67</div></div></div>	<div><div><div>N Er 68</div><div>D</div></div></div>	<div><div><div>N Tm 69</div><div>D</div></div></div>	<div><div><div>N Yb 70</div></div></div>	<div><div><div>N Lu 71</div></div></div>	
									<div>Th 90</div>	<div>Pa 92</div>	<div>U 93</div>	<div>Np 94</div>	<div>Pu 95</div>	<div>Am 96</div>	<div>Cm 97</div>	<div>Bk 98</div>	<div>Cf 100</div>	<div>Es 101</div>	<div>Fm 102</div>	<div>Md 104</div>	<div>No 4</div>	<div>Lr 4</div>	

Acknowledgements!

- 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!



Advantageous Property

Precise Thickness Control

Thickness = \mathcal{F} (# monolayers)

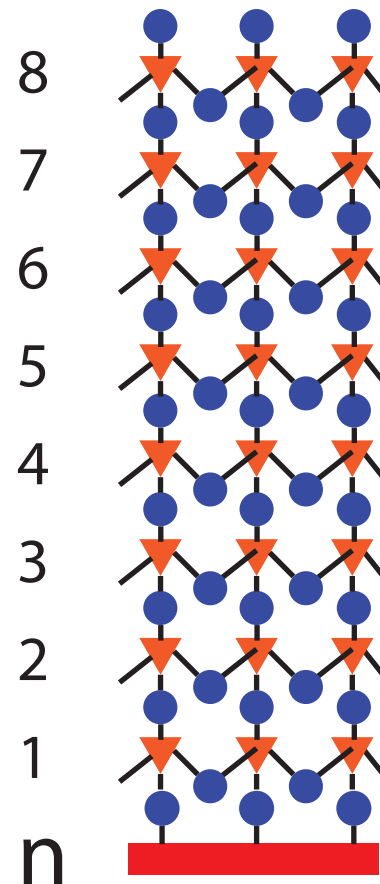
Example:

If 1 monolayer = 1 Å

monolayers = 7

Thickness = 7 Å

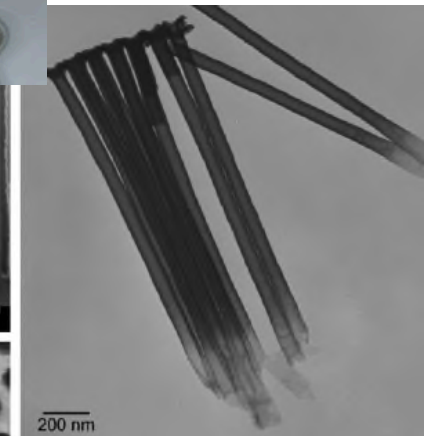
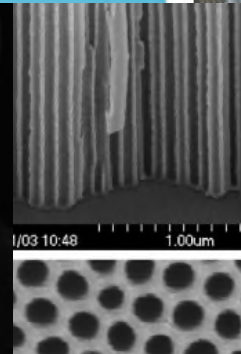
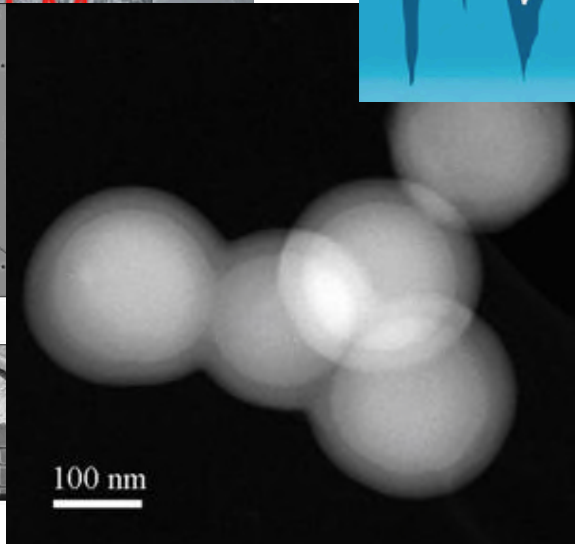
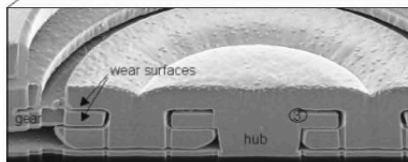
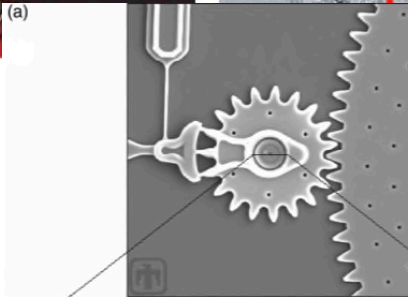
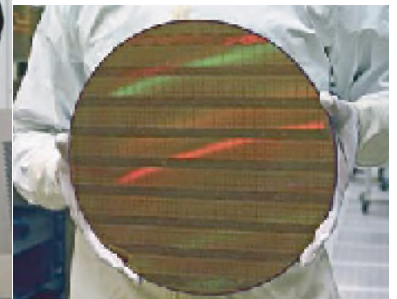
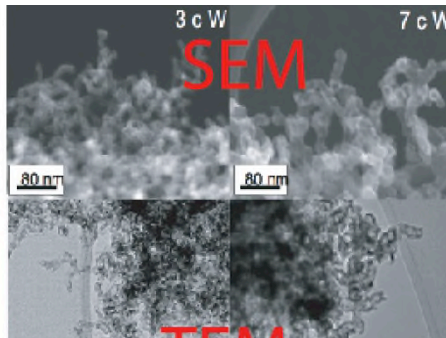
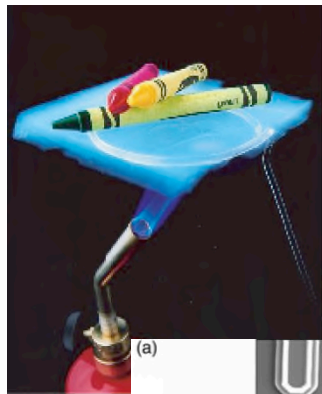
Reproducibility





Advantageous Property

Substrate Independence

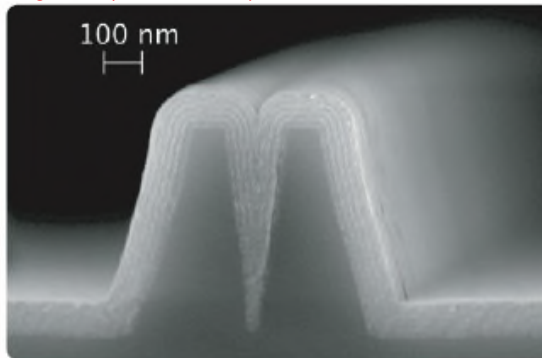




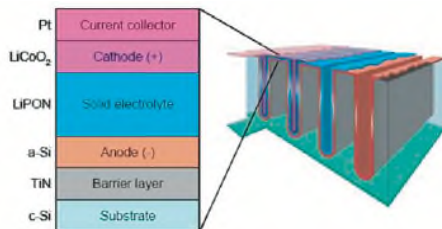
Advantageous Property

Epitaxial Growth

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



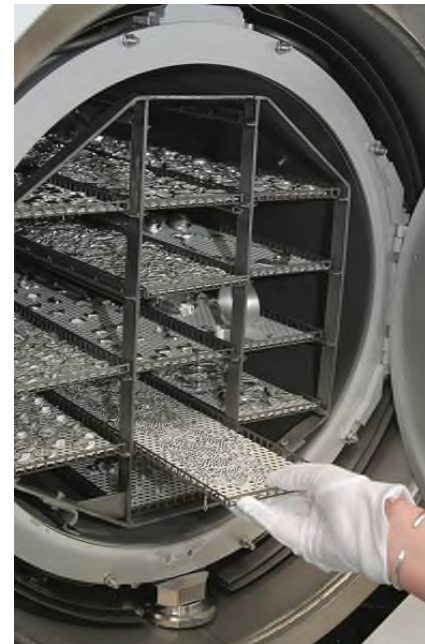
Multilayer consisting of:
Al₂O₃ - 25 nm
TiN - 20 nm
Al₂O₃ - 25 nm
Dr. Fred Roozeboom, NXP Semiconductors Research and
Dr. Erwin Kessels, University of Technology, Eindhoven



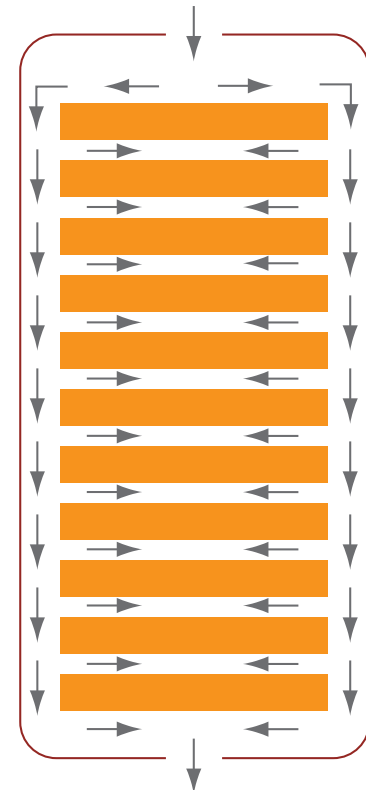
Schematic of a 3D battery integrated in a Si-substrate.
The cross-section shows the various functional layers
in the battery stack as well as the candidate materials.
Knoops, H.C.M. et al., ECS Trans., 25 (2009) pp. 333-344



Batch Process



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

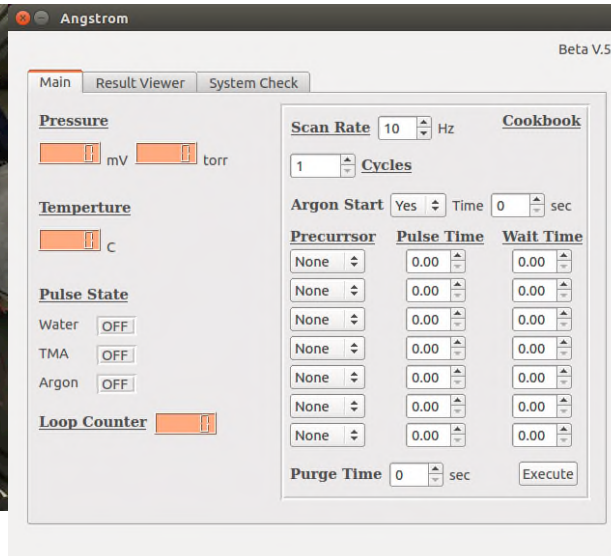
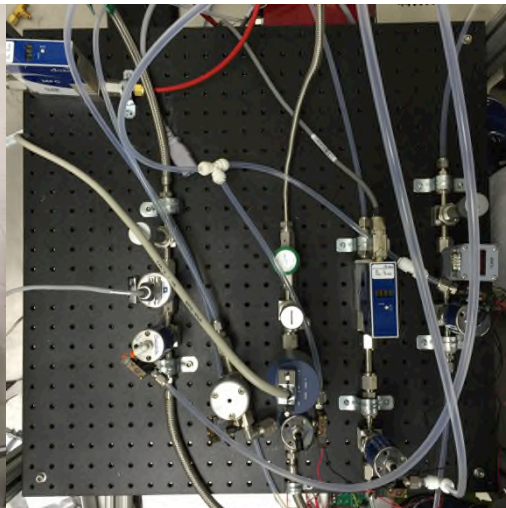
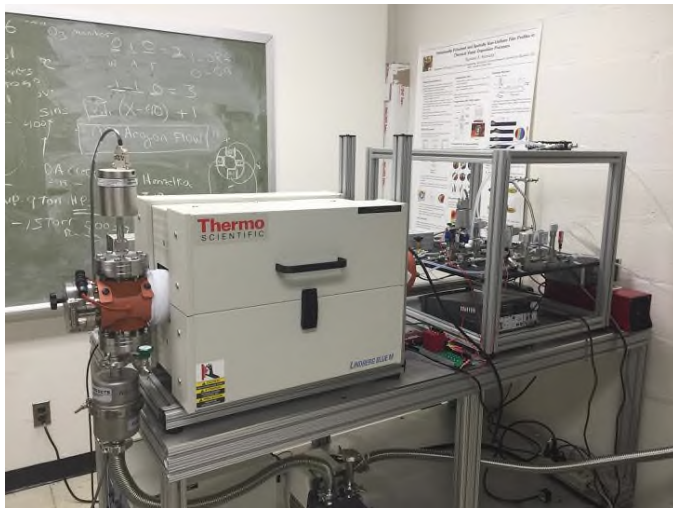
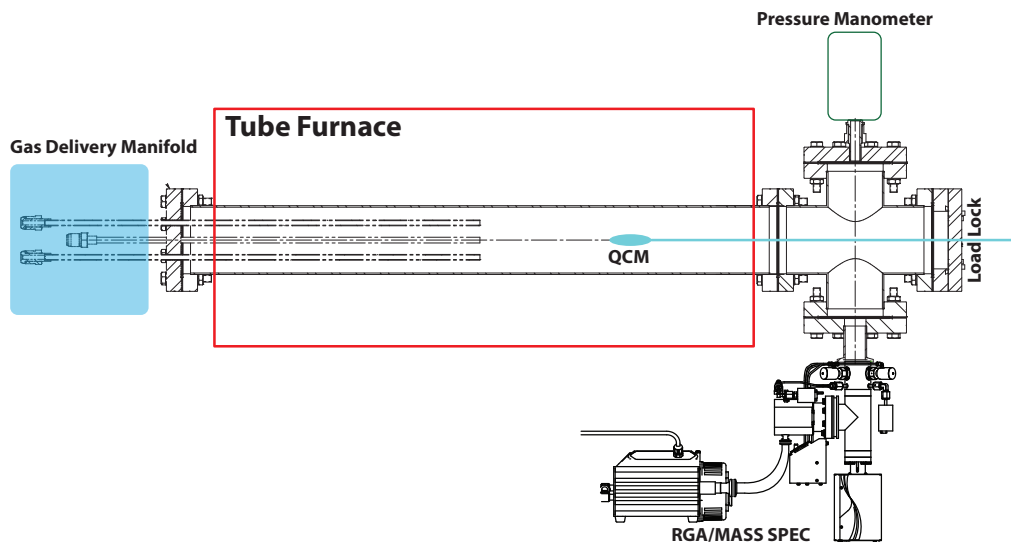




Building off a Commercial Reactor

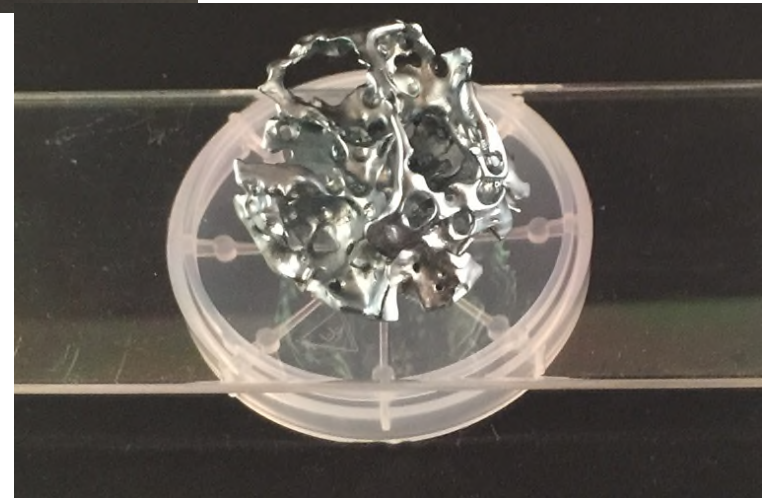
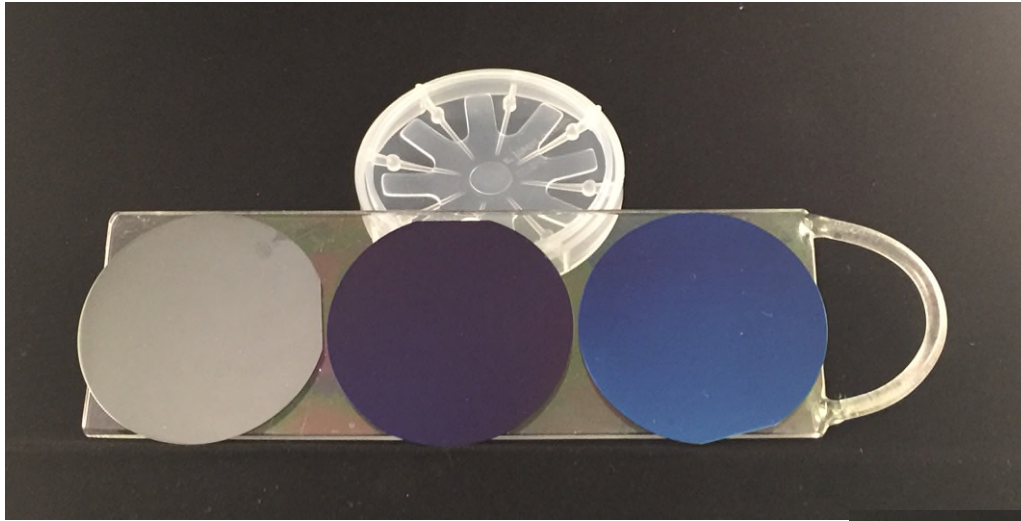
Commercial Options





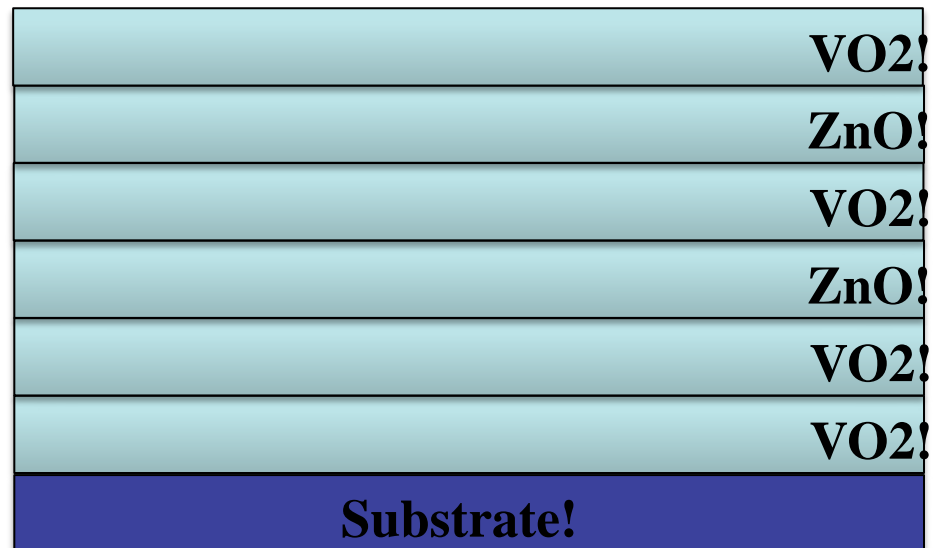
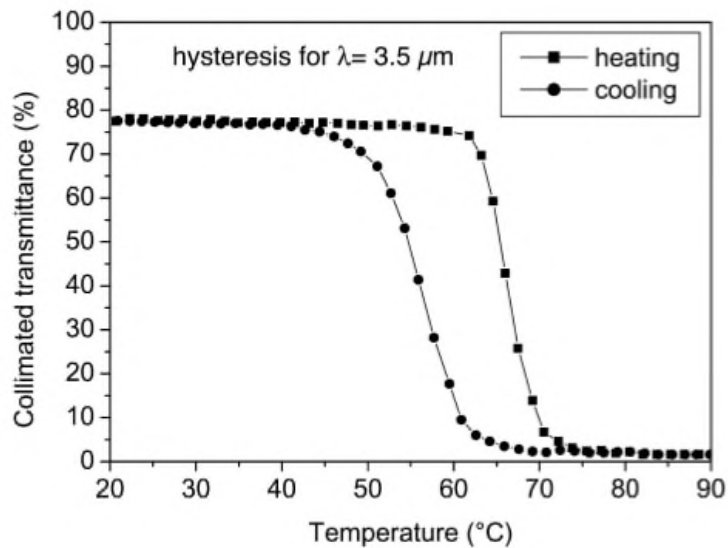
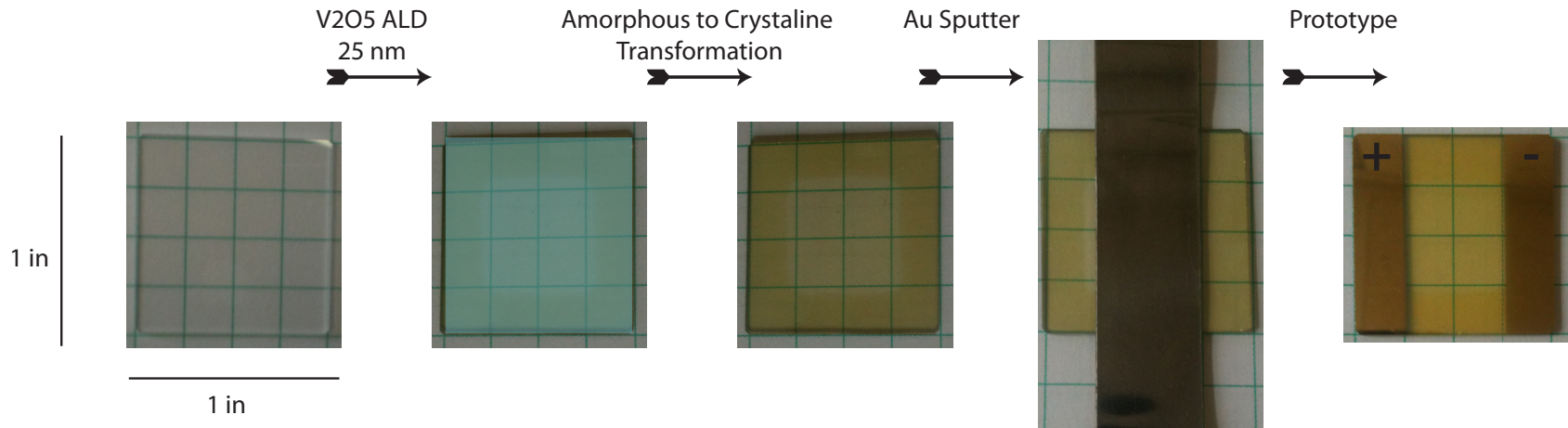


Thermal Applications and Results





Passive Thermal Films





ZnO

$E = hc/\lambda$, where: !

f = frequency in Hertz (Hz = $1/\text{sec}$) !

λ = wavelength in meters (m) !

c = the speed of light (299792458 m/s)!

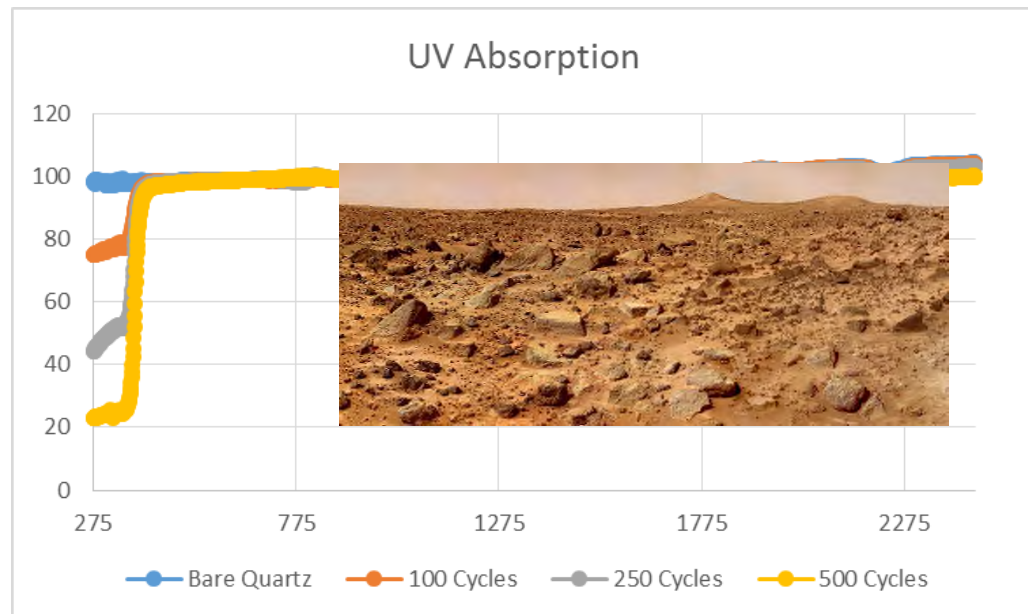
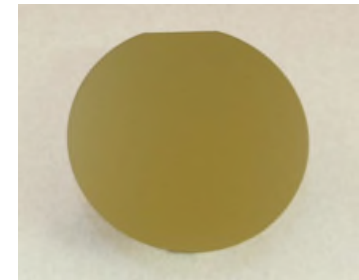
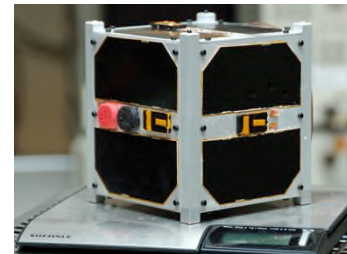
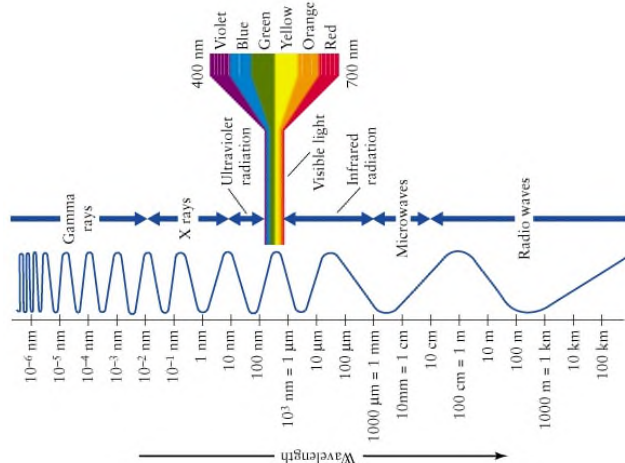
E = energy in electron Volts (eV) !

h = Plank's constant ($6.626068 \times 10^{-34} \text{ m}^2\text{kg/s}$)!

$E_{\text{ZnO}} = 3.3 \text{ eV}$!

$\lambda_{\text{ZnO}} \sim 375 \text{ nm}$!

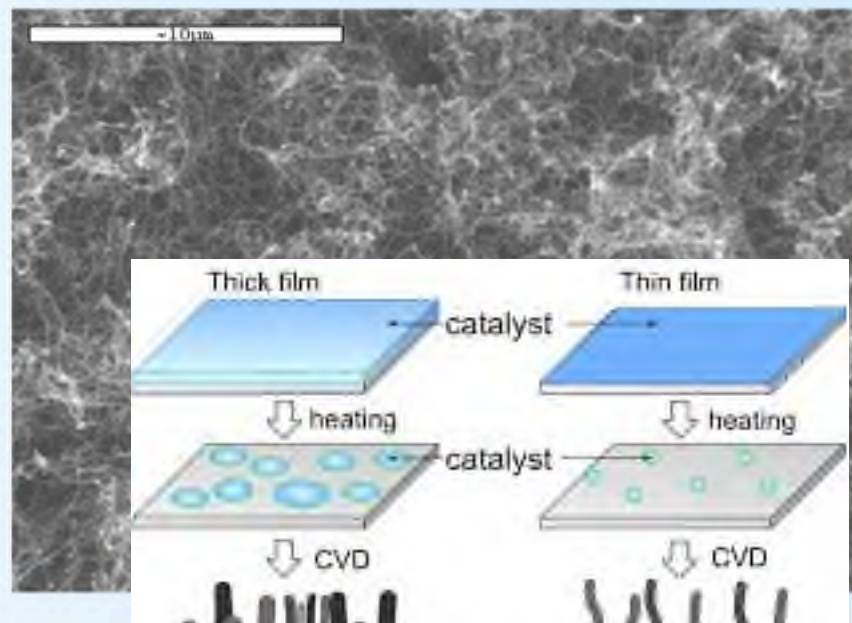
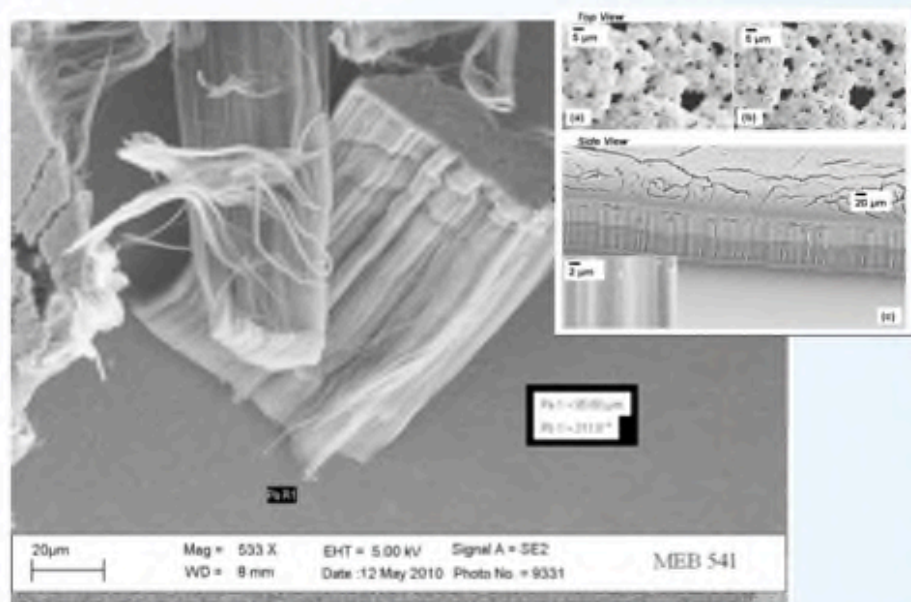
! ! ! ! !





Blacker Than Black Carbon Nanotubes

Fe ALD on Complex Geometries for Carbon Nanotube Growth



Substrate + Catalyst + Gas = CNNT!

Si, Ti, flat, 3d + Iron + Ethylene!

!

Blacker than NASA Z306 Paint 10X Darker!



Atomic Oxygen Protection



100 nm on Kapton!

1000 Cycles!

155 °C!

Al_2O_3 !

**GPM Funded an experiment!
at Glenn to determine AO effects!
on materials.!**

!

**99% mass retention after a simulated!
5 year flux!**



Questions?

