Atomic Layer Deposition of Aluminum-Free Silica onto Patterned Carbon Nanotube Forests in the Preparation of Microfabricated Thin-Layer Chromatography Plates

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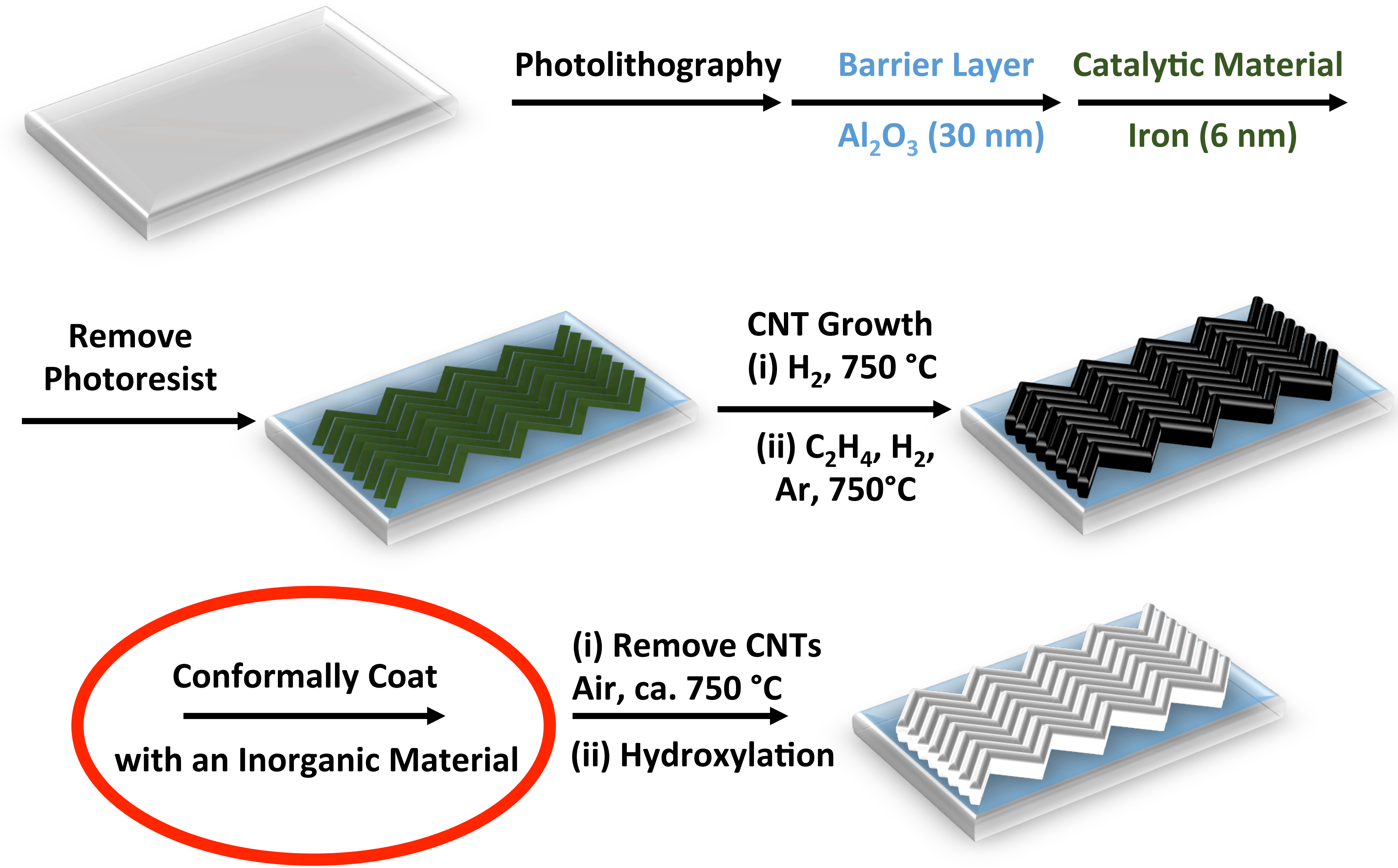
Brigham Young University and Diamond Analytics

The Linford Group, Brigham Young University

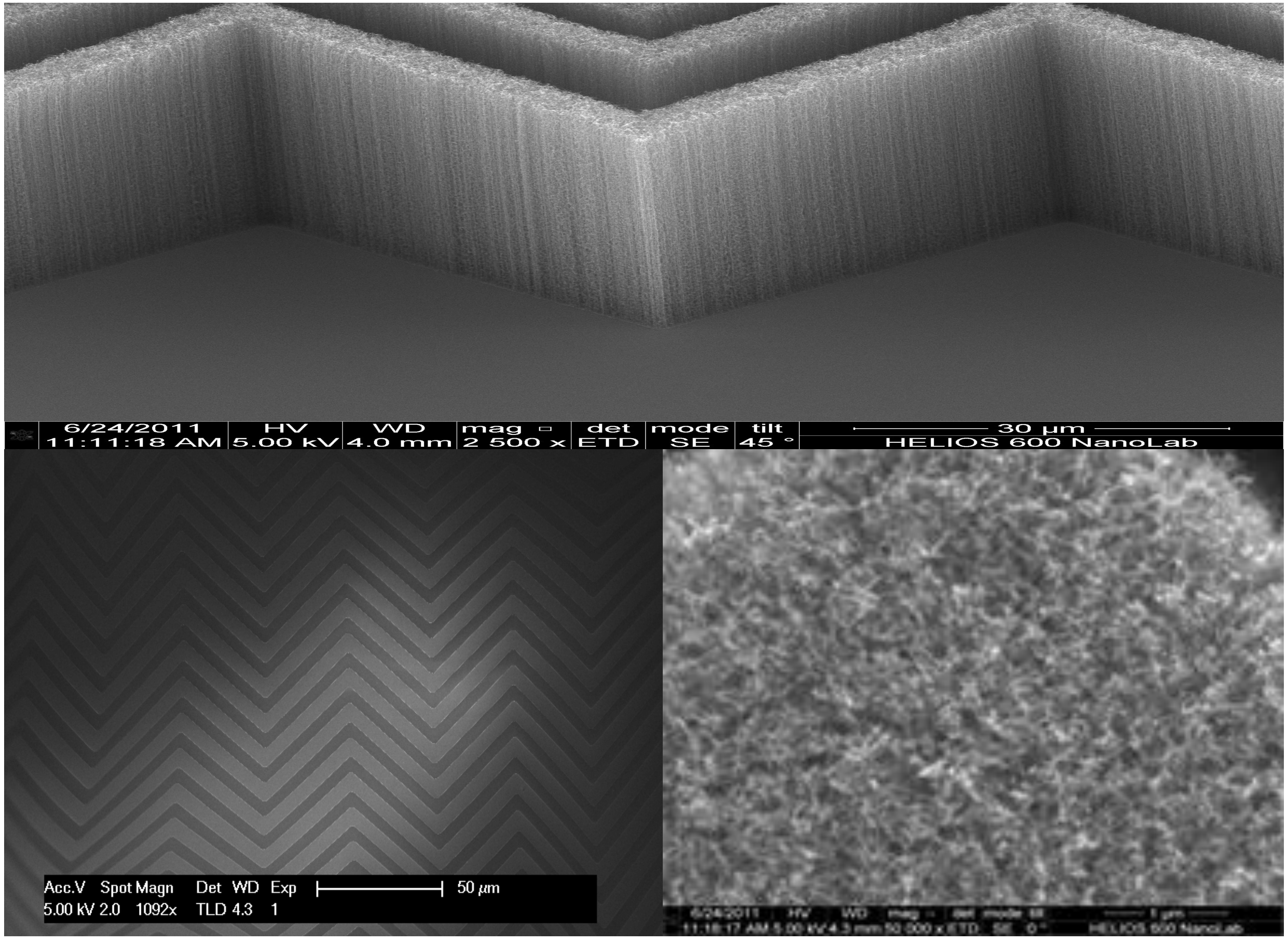
- We specialize in material synthesis and characterization
- Our recent projects
  - Develop new materials for HPLC
  - Develop new materials for digital data storage
  - Develop *microfabricated*, *carbon nanotube* templated TLC plates that are
    - Faster
    - Have higher resolution
    - Have similar selectivity to silica
    - Work with well established analytical protocols

From CNTs to TLC Plates



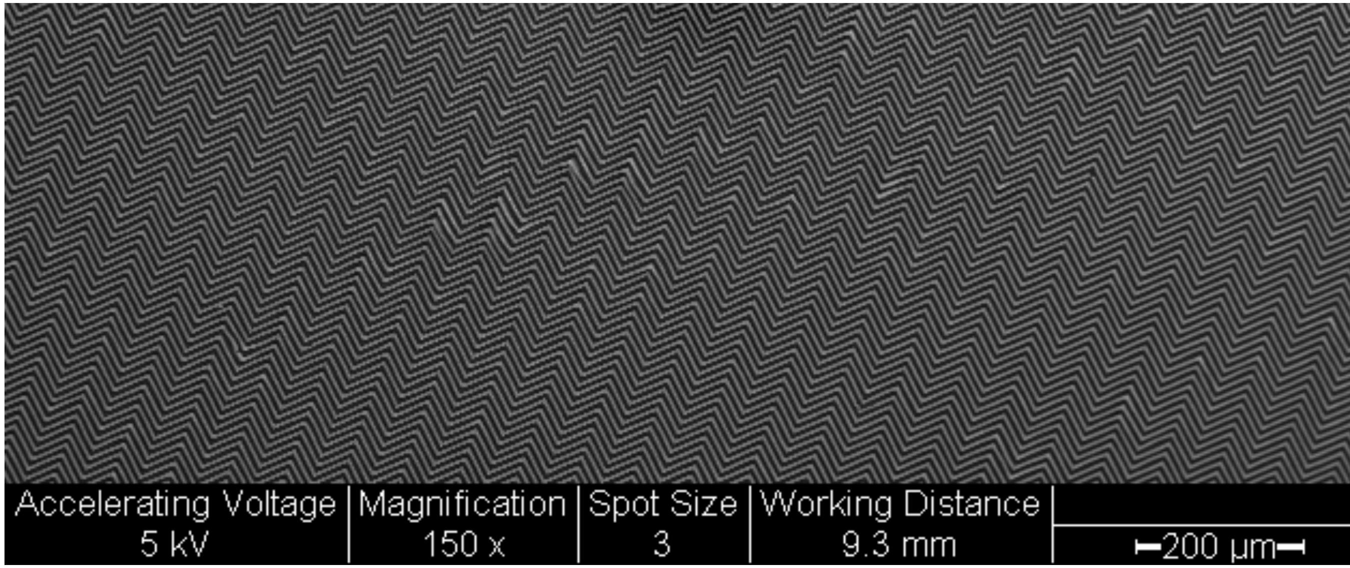
sen, D. S.; Kanyal, S. K.; Gupta, V.; Vail, M. A.; Dadson, E. A.; Engelhard, M.; Vanfleet, R.; Davis, R. C.; Linford, M. R. Stable, microfabricated thin layer chromatography plates
ume distortion on patterned carbon and Al_2O_3-primed carbon nanotube forests. *J. Chromat. A.* **2012**, *1257*, 195-203.

Material Characterization



Kanyal, S. S.; Jensen, D.S.; Miles, A, J.; Dadson, A. E.; Vail, M. A.; Olsen, R.; Scorza, F.; Nichols, J.; Vanfleet, R.; Davis, C; Linford, M. R. Effects of catalyst thickness on the fabrication and performance of carbon nanotube-templated thin layer chromatography plates. *J. Vac. Sci. Technol. B.* **2013**, *31*, 031203

Why Coat and Remove the CNTs?

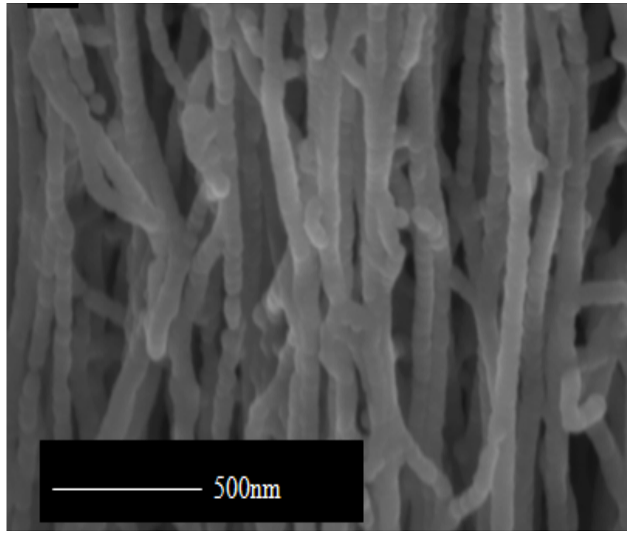


Pros

- High surface area
- Micropatternable

Cons

- Black
- Nonpolar
  - Not highly wettable
- CNT forests have very poor mechanical stability



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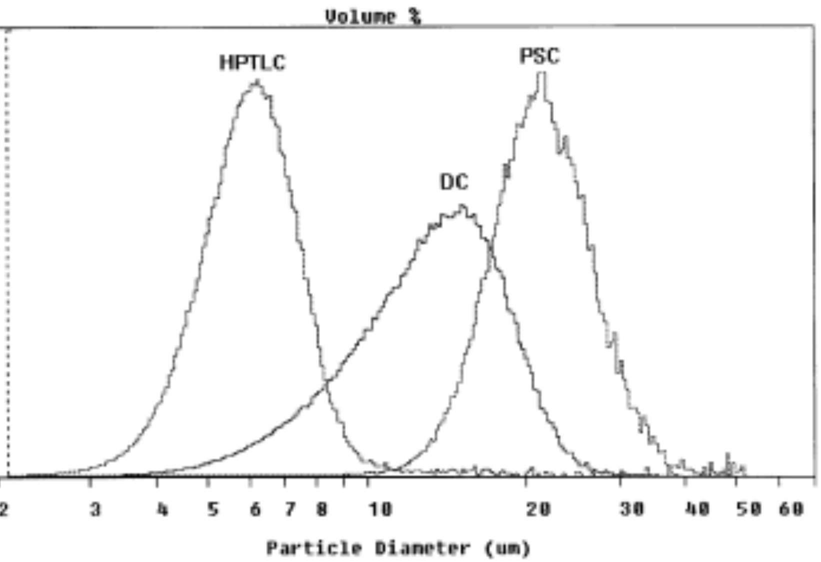
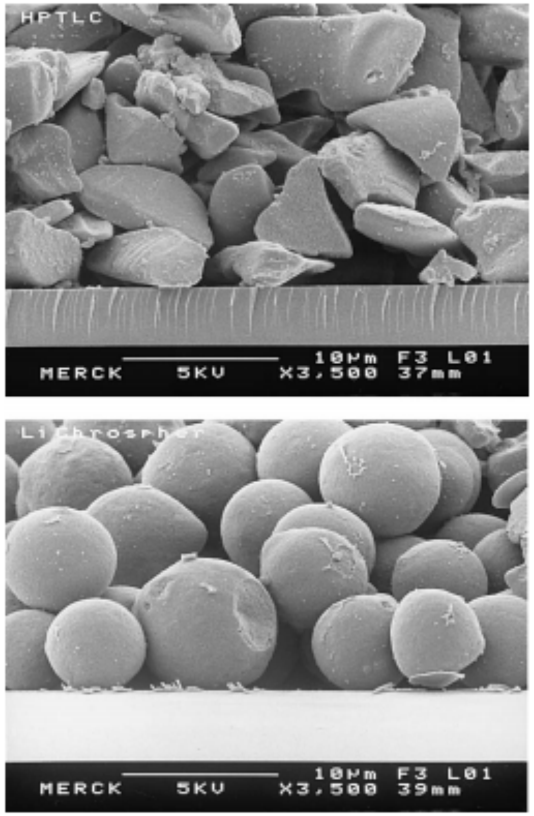
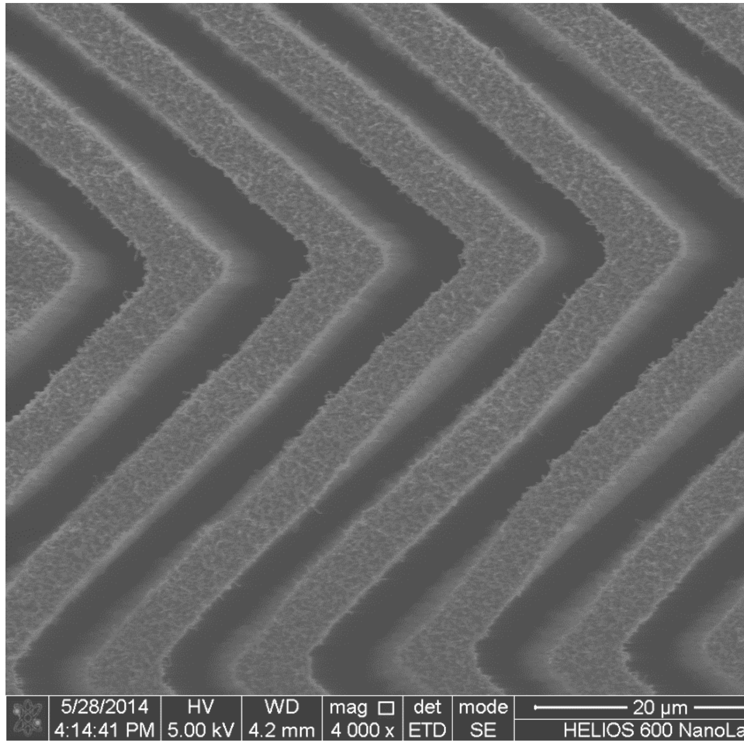
Theoretical Advantages



rticle size distributions for HPTLC, TLC, and
eparative Scale TLC Plates[1].



SEM of Merck Si 60 particles (top) and Merck LiChroSpher F_{254} Si 60 particles (bottom)[1].

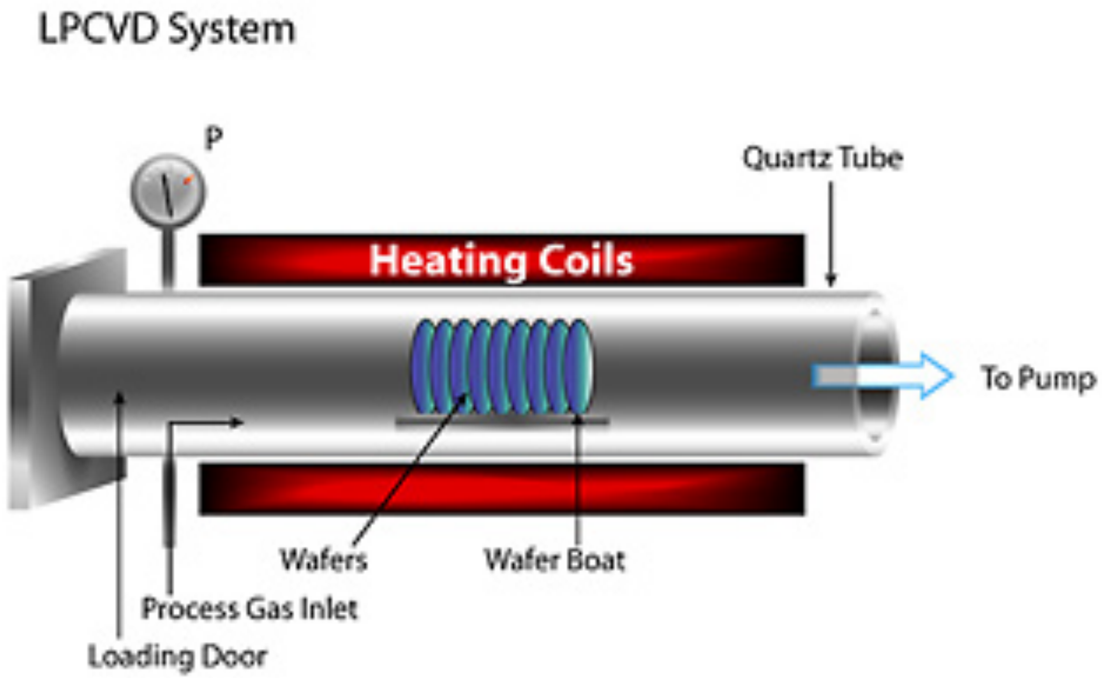


SEM of a micropatterned Si nanowire pla
We can control hedge and channel widtl
within a few tenths of a micron!

1. Hahn-Deinstrop, E. *Applied Thin-Layer Chromatography: Best Practices and Avoidance of Mistakes.* 2nd ed. Wiley-VCH Verlag GmbH & Co; KGaA, Weinheim, 2007.

Method 1. Low Pressure Chemical Vapor Deposition

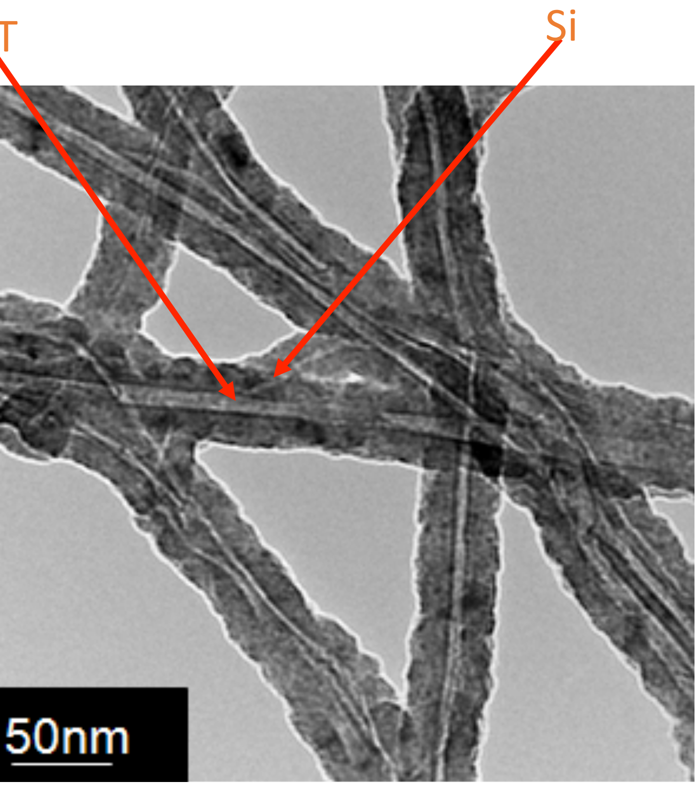
Reagent gasses continuously flow, and volatile biproducts are continuously removec



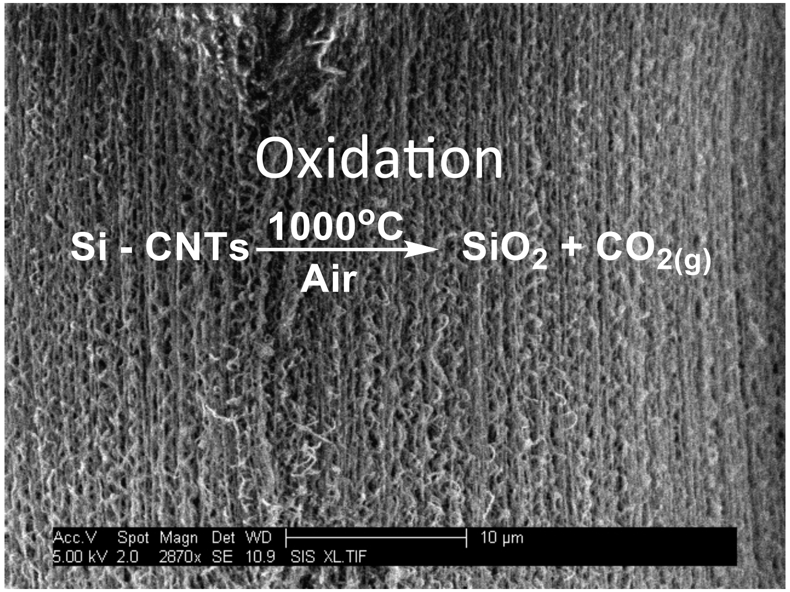
Images from 1. http://www.dowcorning.com/content/etronics/etronicschem/etronics_newcvd_tutorial3.asp?DCWS=Electronics&DCWSS=Chemical+Vapor+Deposition
2. http://sindhu.ece.iisc.ernet.in/nanofab/twikii/bin/view/Main/LPCVD

LPCVD of Silicon onto CNTs

$$SiH_{4(g)} \xrightarrow[10\ \text{mtorr}]{530°C} Si_{(s)} + 2H_{2(g)}$$

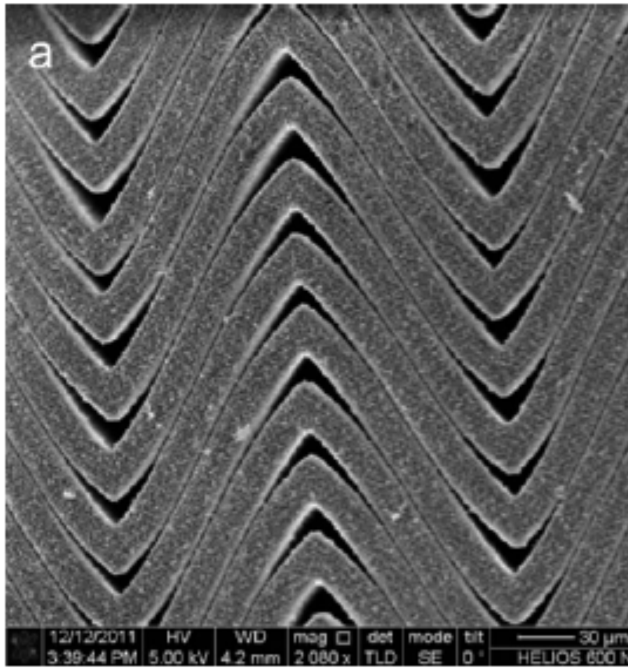


TEM image of silicon coated CNTS



Song, J.; Jensen, D. S.; Hutchison, D. N.; Turner, B.; Wood, T.; Dadson, A.; Vail, M. A; Linford, M. R.; Vanfleet, R. R.; Davis, R. C.; Carbon-nanotube-templated Microfabrication of porous silicon-carbon materials with application to chemical separations. *Adv. Funct. Mater.* **2011**, *21*, 1132-1139

Volume expansion resu
in feature distortion

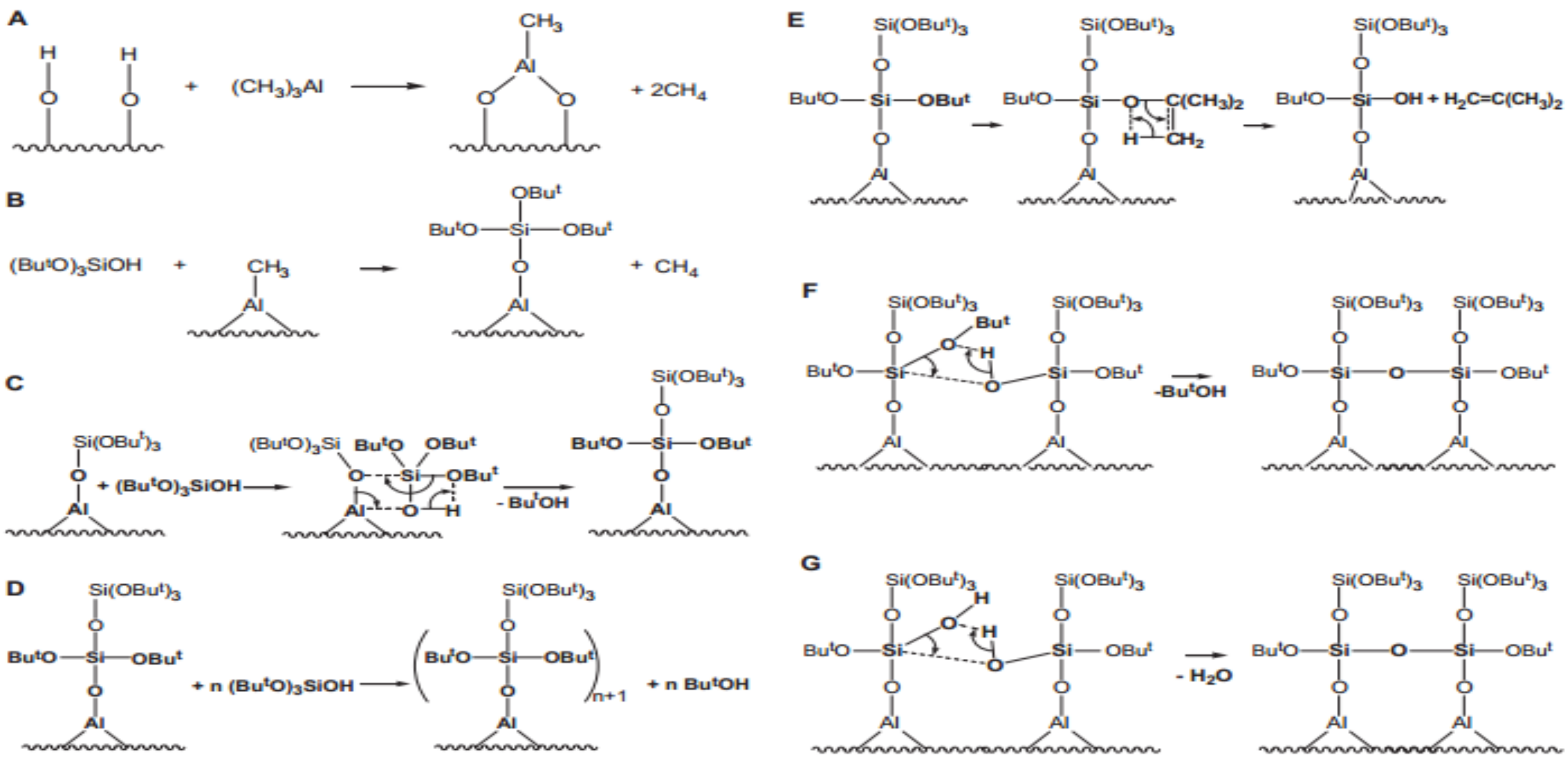


SEM of features after oxidation

Method 2. Psuedo Atomic Layer Deposition (Ψ-ALD)

ast ALD of SiO_2 (ca. 13 nm/cycle)

- $Al(CH_3)_3$ catalyzed growth of SiO_2 from tris(*t*-butoxysilanol)
- No volume expansion during CNT removal



Scheme 1.

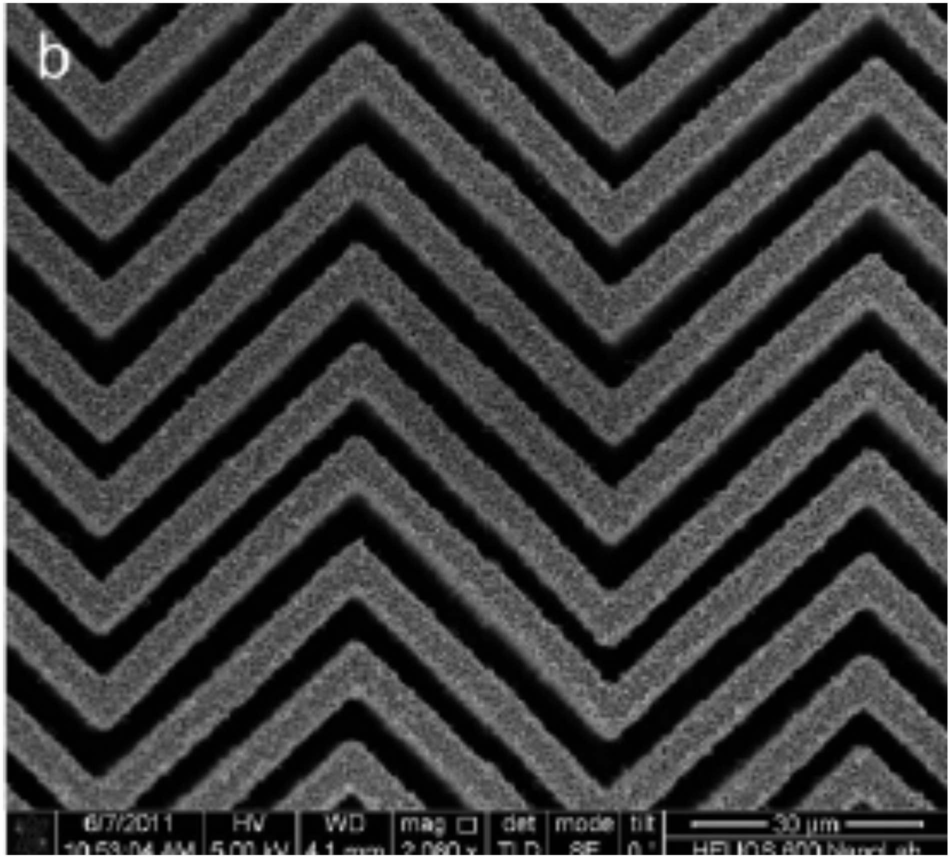
Hausmann, D.; Becker, J.; Wang, S.; Gordon, R.G. Science 2002, 298 (5592), 402 - 406

Ψ-ALD

Advantage
- No volume expansion of features upon CNT removal

Disadvantage
- Left Al(III) in the plates
- Caused serious peak tailing

Solution
- Create an amino (APTES) phase
- Good separations possible



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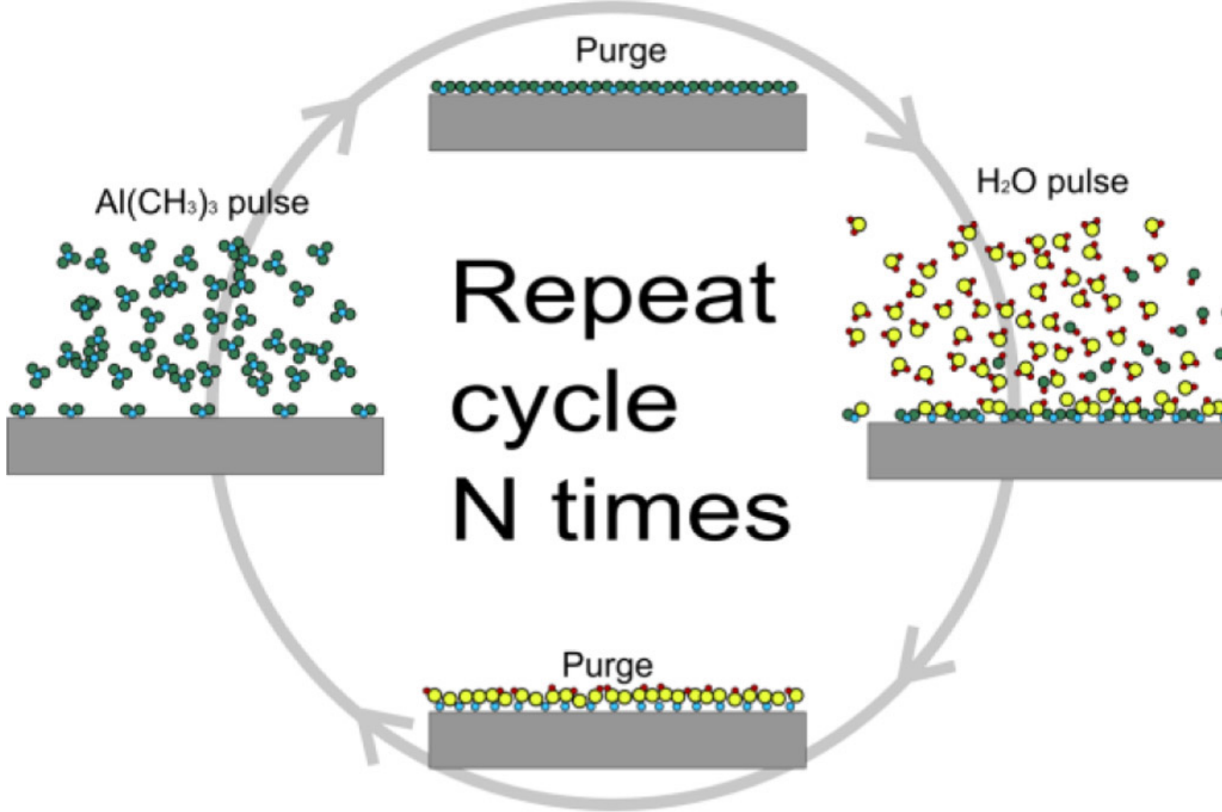
Method 3. (True) Atomic Layer Deposition (ALD)

Goals:

- Reduce impurities, e.g., Al(III)
- Produce normal phase plates

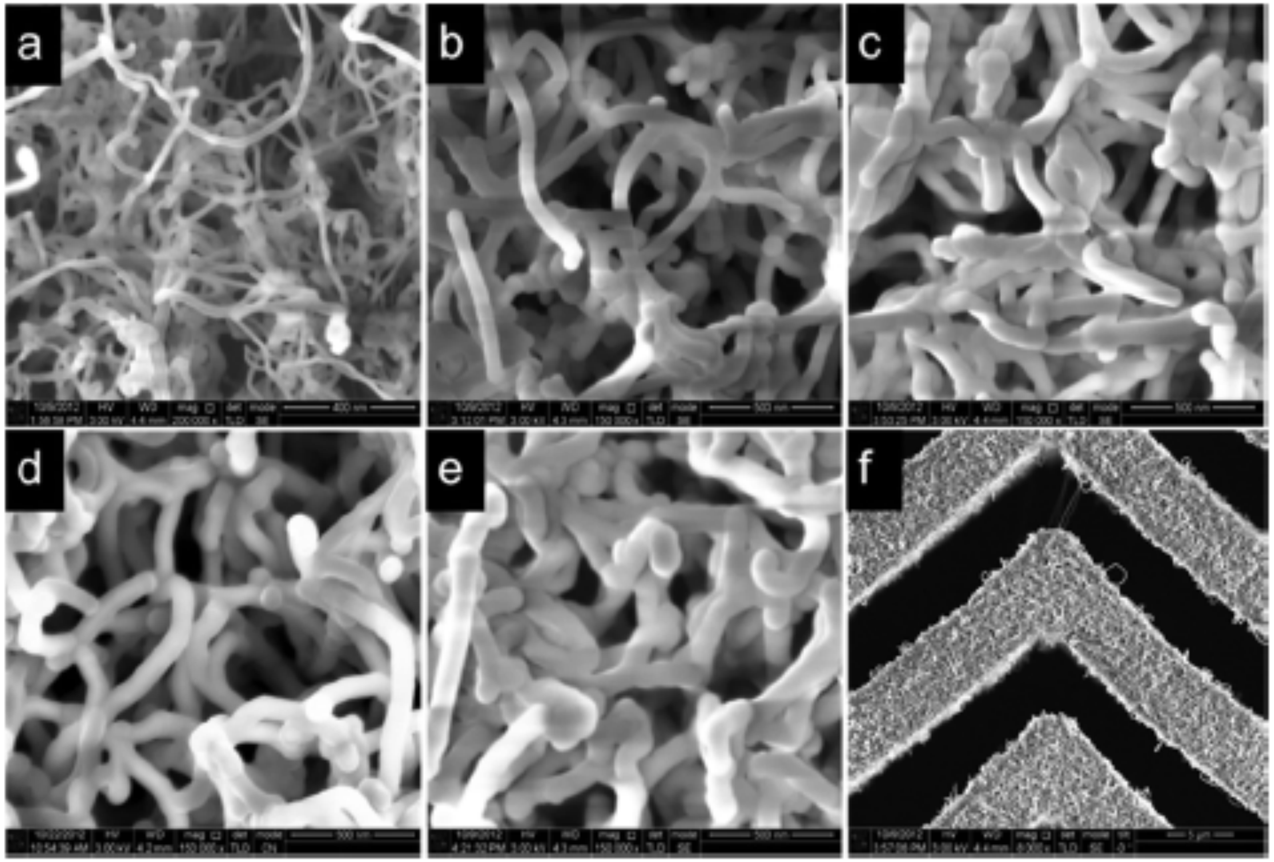
Process:

- Reagents
  - A: AP LTO 330 (proprietary SiO_2 precursor, Air products inc).
  - B: Ozone



en from: http://spie.org/x86946.xml

True ALD Results



Carbon nanotubes coated by true ALD in the presence of silicon witness wafers which showed thicknesses of (a)20 nm, (b) 30 nm, (c) 40 nm, (d) 50 nm and (e) 60 nm. (f) A top view of TLC plate microstructure.

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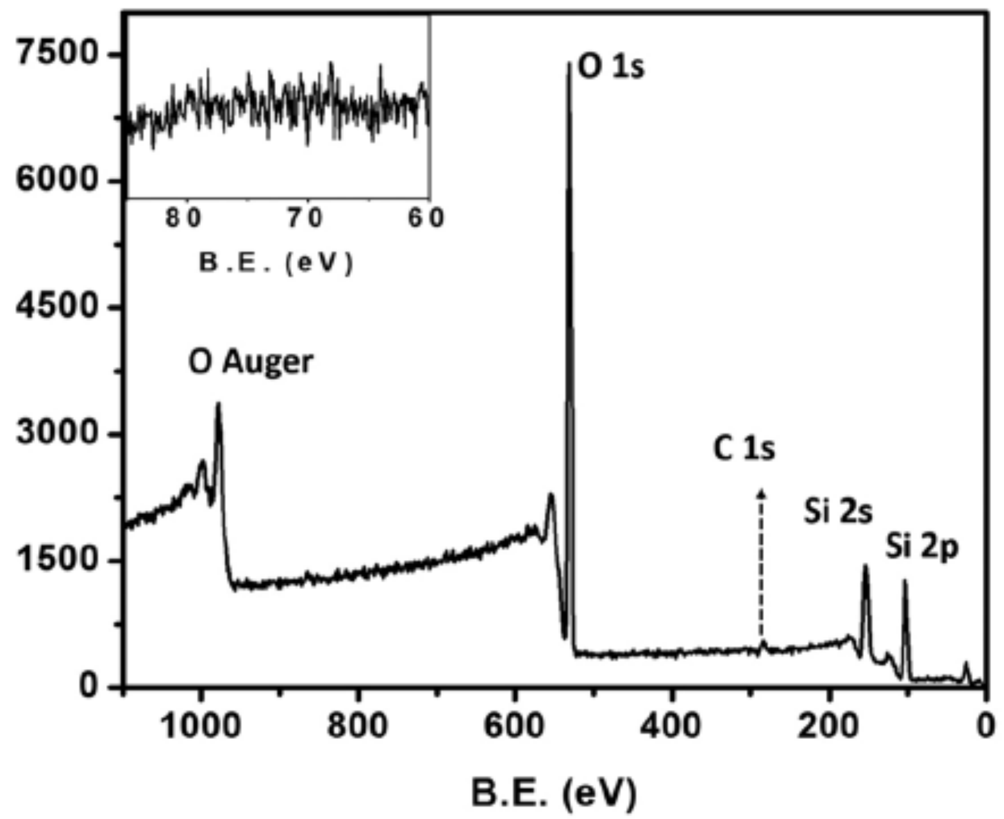
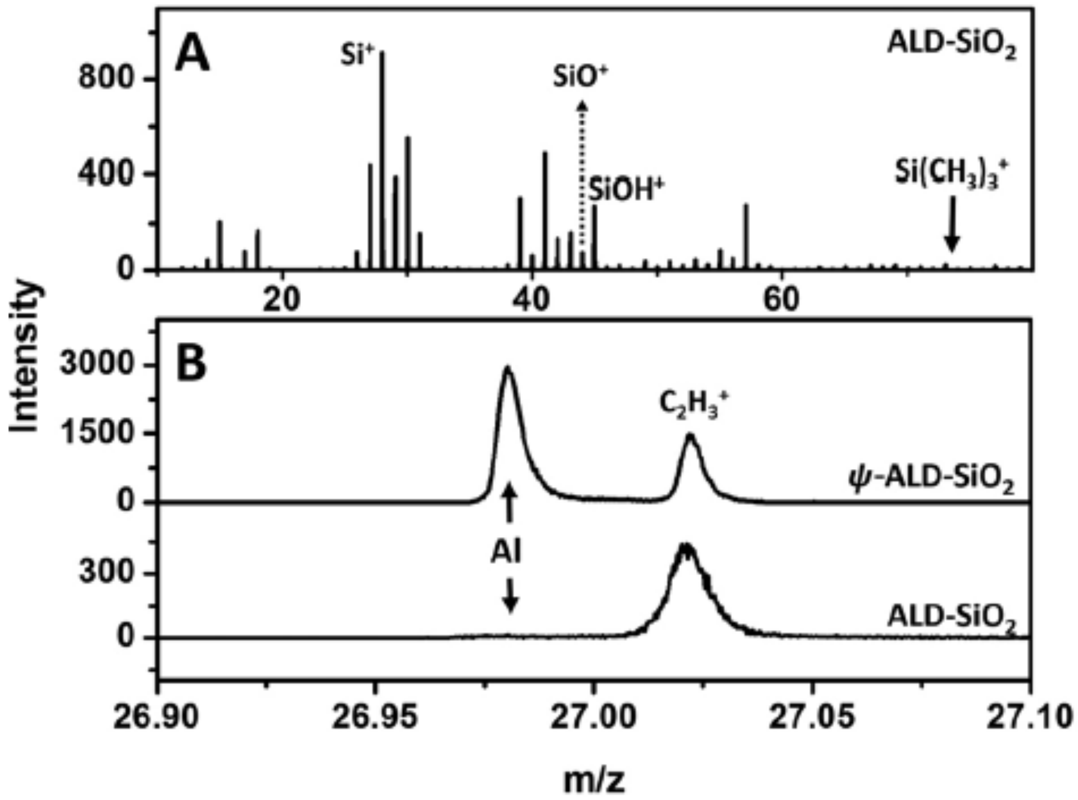
True ALD: No Al(III)



XPS of a true ALD TLC plate. No aluminum signal at 73 eV (narrow scan shown in inset).



(a) ToF-SIMS mass spectrum of a True ALD plate.

(b) Zoomed in view of m/z 27 region. The top trace shows aluminum in a Ψ-ALD plate, but no aluminum in a True ALD plate.

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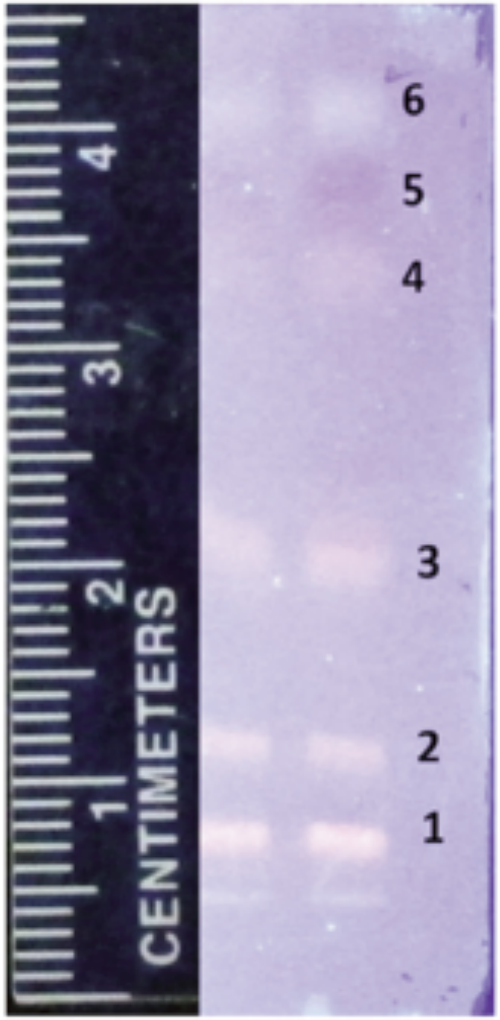
True ALD TLC Plates

vantages
- No tailing
- Fast development (2 – 4x faster than Merck HPTLC)
- Good efficiencies

sadvantages
- Plates not robust
- ALD is slow

Mobile phase: *t*-butylbenzene
Development time: 2 minutes

(1) 39,876 plates/m
(2) 127,868 plates/m
(3) 133,157 plates/m
(4) 126,230 plates/m
(5) 127,475 plates/m
(6) 139,336 plates/m



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Conclusions

- Investigated a series of inorganic materials to coat CNTs in microfabricated HPTLC plates
  - Si by LPCVD
  - SiO_2 by Ψ-ALD
  - SiO_2 by (true) ALD
- (True) ALD of SiO_2 gave the best results
  - A true SiO_2 plate, no Al impurity
  - But not very robust
- Even better results will be shown in the next talk by Dr. Linford!

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Dr. Richard Vanfleet

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