Fast, microfabricated, normal phase TLC plates based on carbon nanotube forest scaffolds

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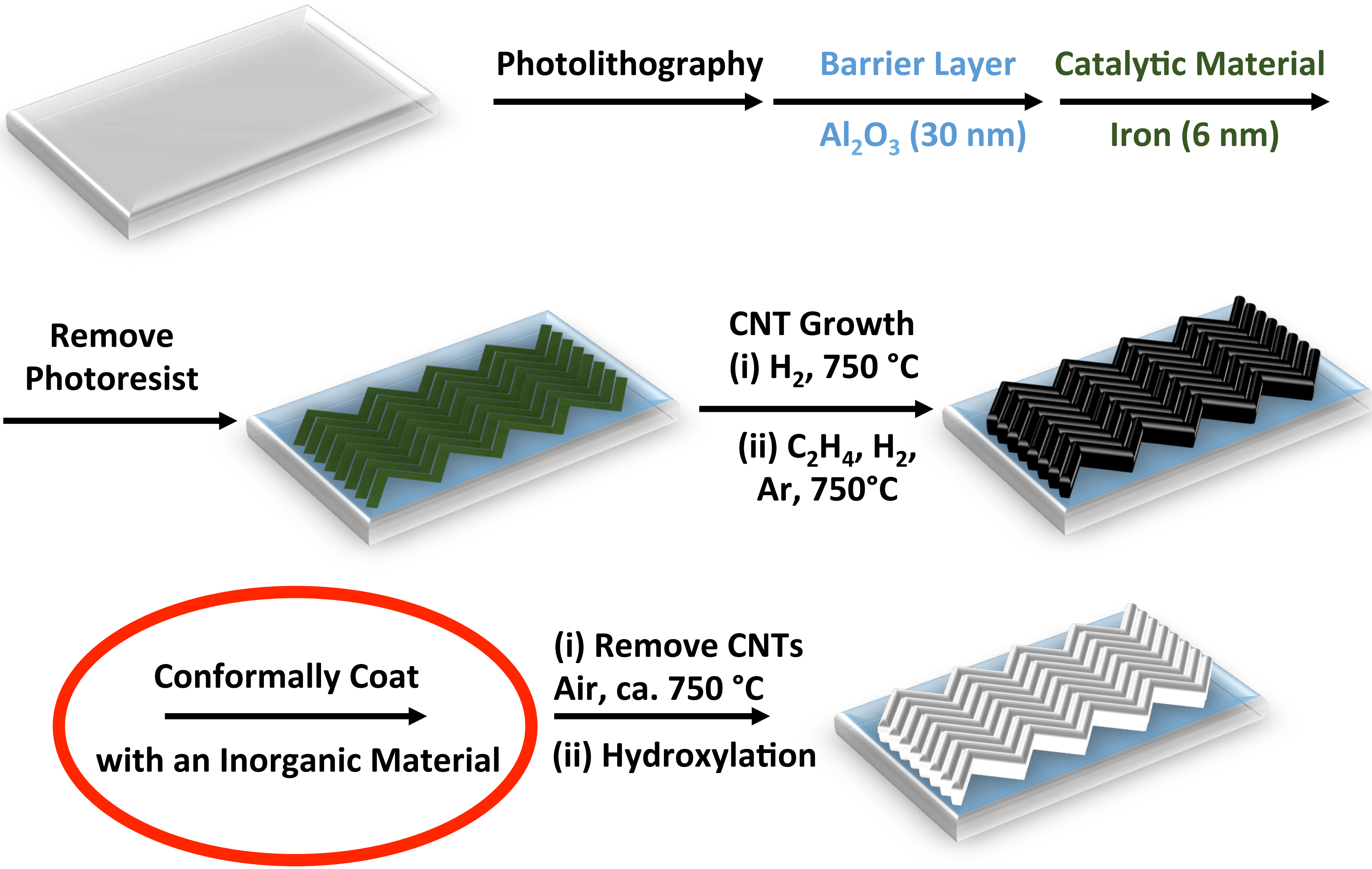
1. Brigham Young University, 2. Diamond Analytics, 3. Justus Liebig University Giessen

Latest Advances in Preparing Microfabricated TLC Plates from Patterned CNT Scaffolds

- Three new advances
  - LPCVD of silicon nitride
    - Fast
    - Very robust plates
    - SiO_2
  - Glass substrates
  - Fluorescent substrates

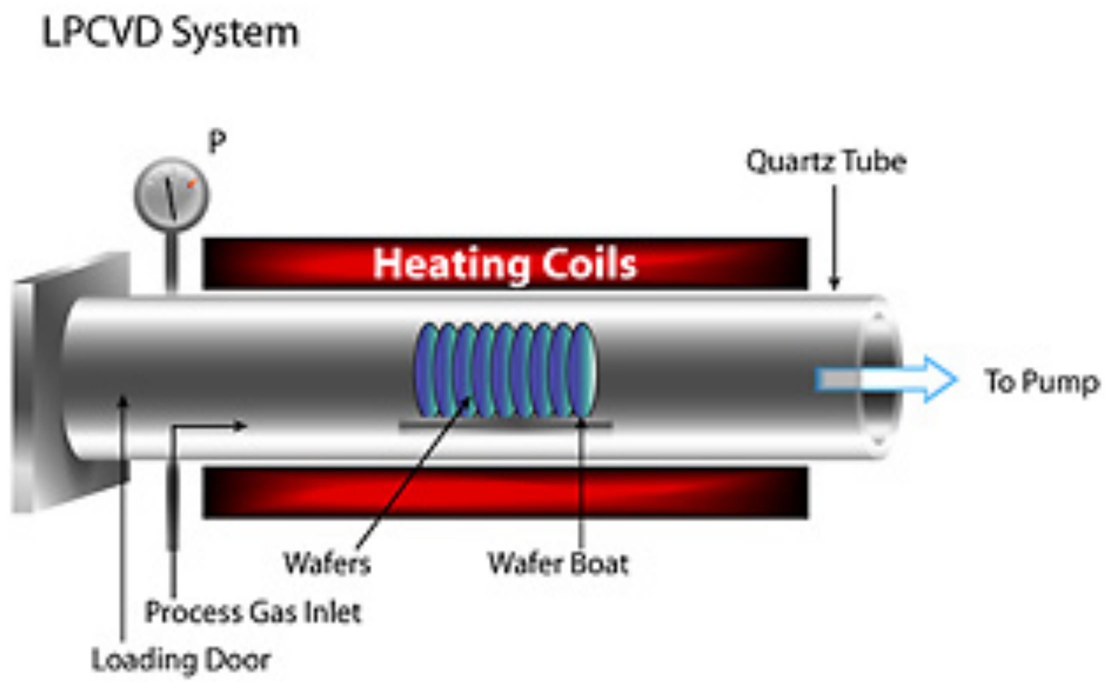
From CNTs to TLC Plates



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 pl
distortion on patterned carbon and Al_2O_3-primed carbon nanotube forests. *J. Chromat. A.* **2012**, *1257*, 195-203.

Low Pressure Chemical Vapor Deposition

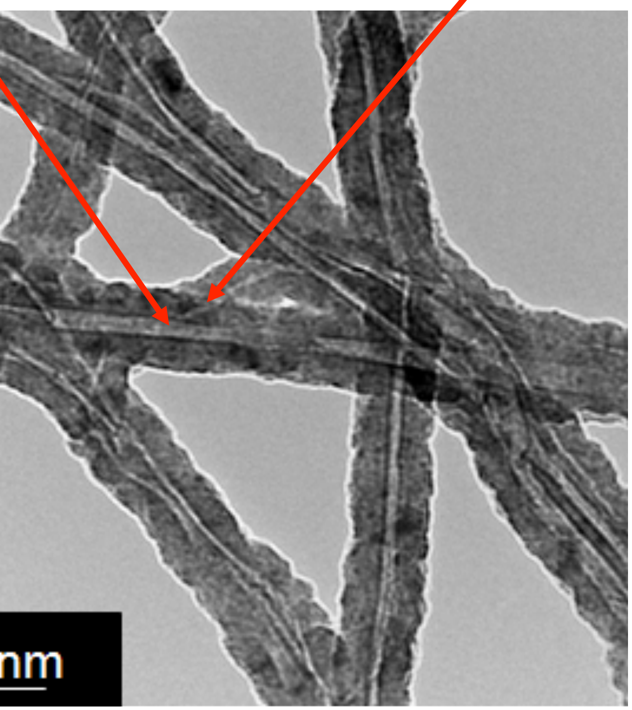
Reagent gasses continuously flow, and volatile biproducts are continuously remov



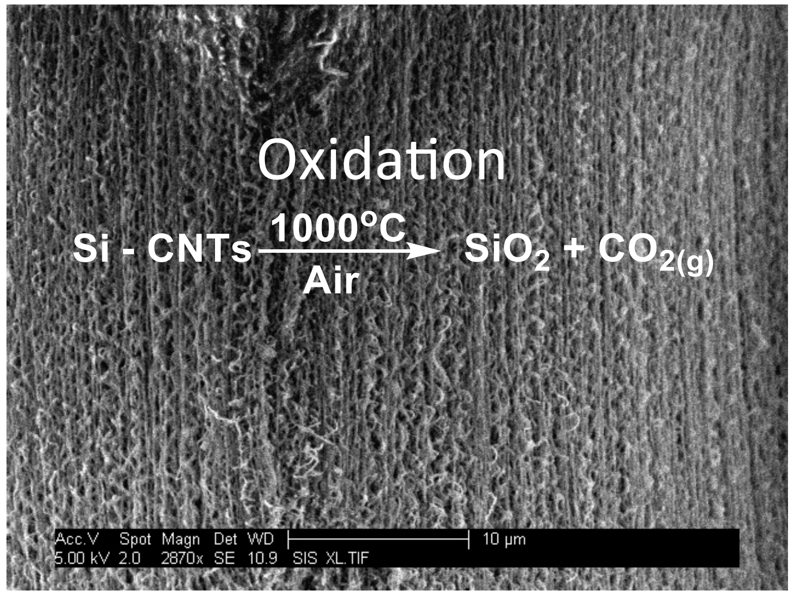
Images from 1. http://www.dowcorning.com/content/etronics/etronicschem/etronics_newcvd_tutorial3.asp?DCWS=Electronics&DCWSS=Chemical+Vapor+Deposition
2. http://sindhu.ece.iisc.ernet.in/nanofab/twikii/bin/view/Main/LPCVD

LPCVD of *Silicon* onto CNTs

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

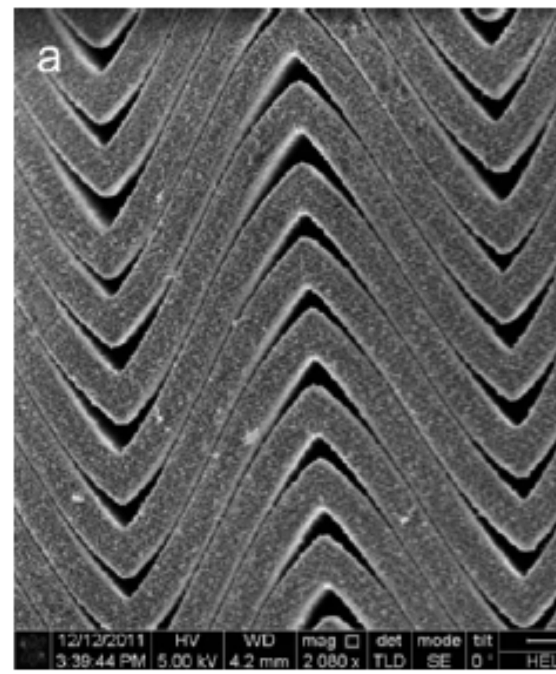


TEM image of silicon coated CNTS



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 re
in feature distorti

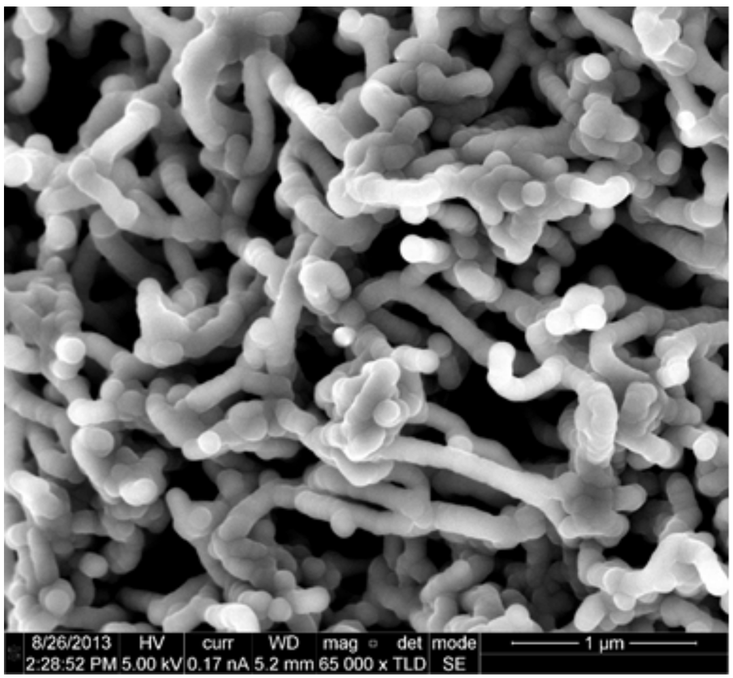


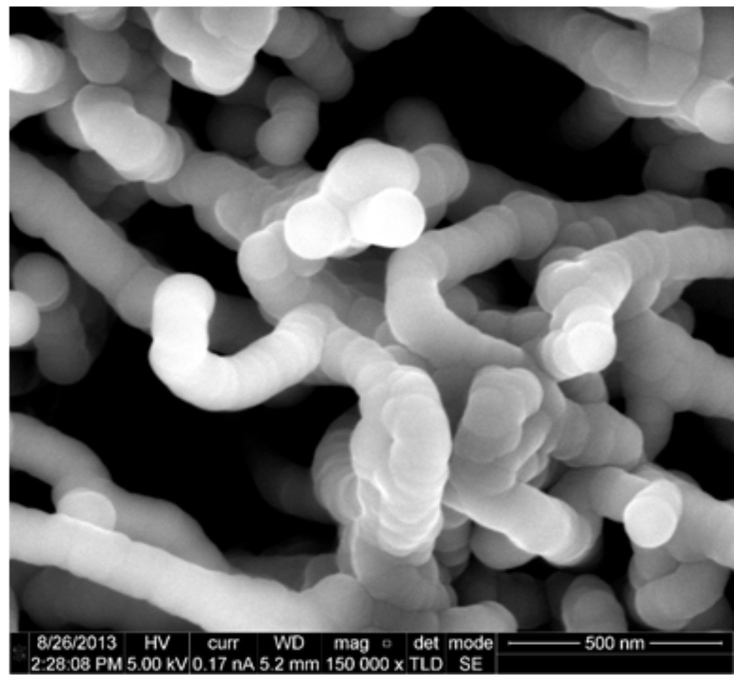
SEM of features after oxidatio

LPCVD of *Silicon Nitride* onto CNTs

$$SiH_2Cl_{2\,(g)} + NH_{3\,(g)} \xrightarrow{780^{\circ}C} Si_3N_{4\,(s)} + HCl_{\,(g)}$$

$$Si_3N_{4\,(s)} \xrightarrow[\text{Air, 48 h}]{1000^{\circ}C} SiO_{2\,(s)}$$





LPCVD silicon nitride *before* oxidation

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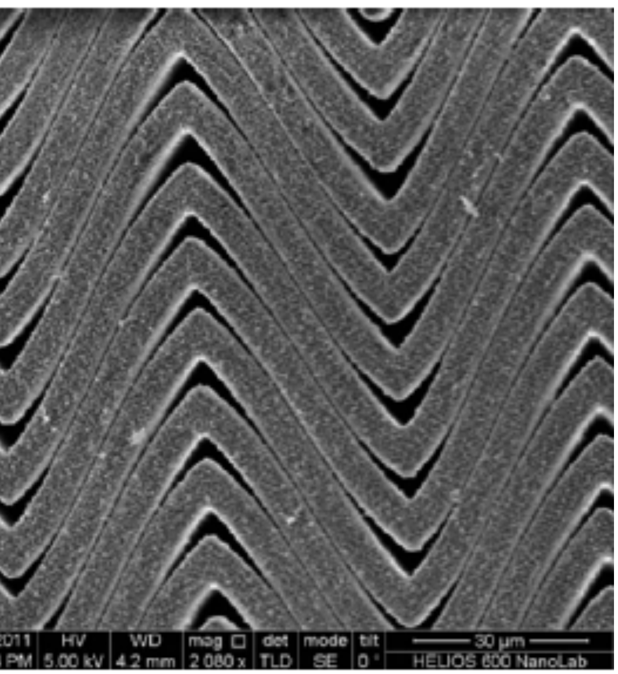
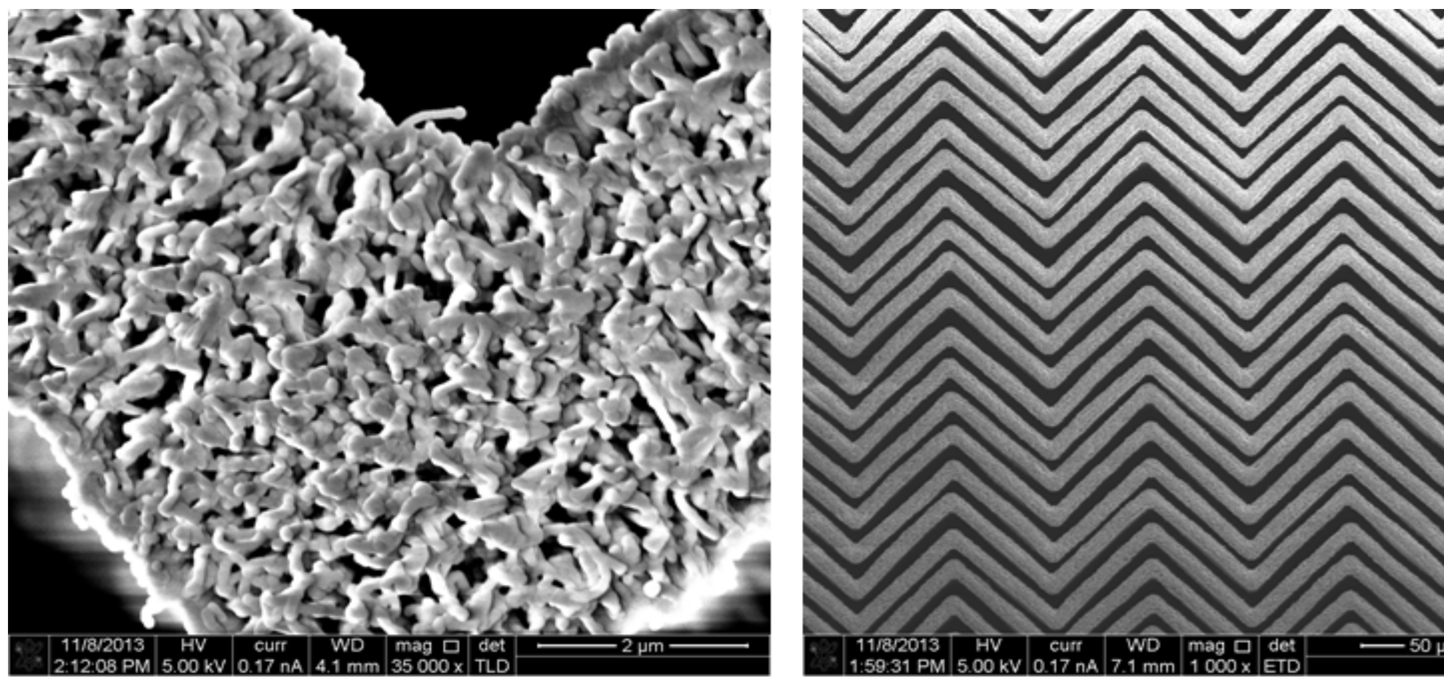


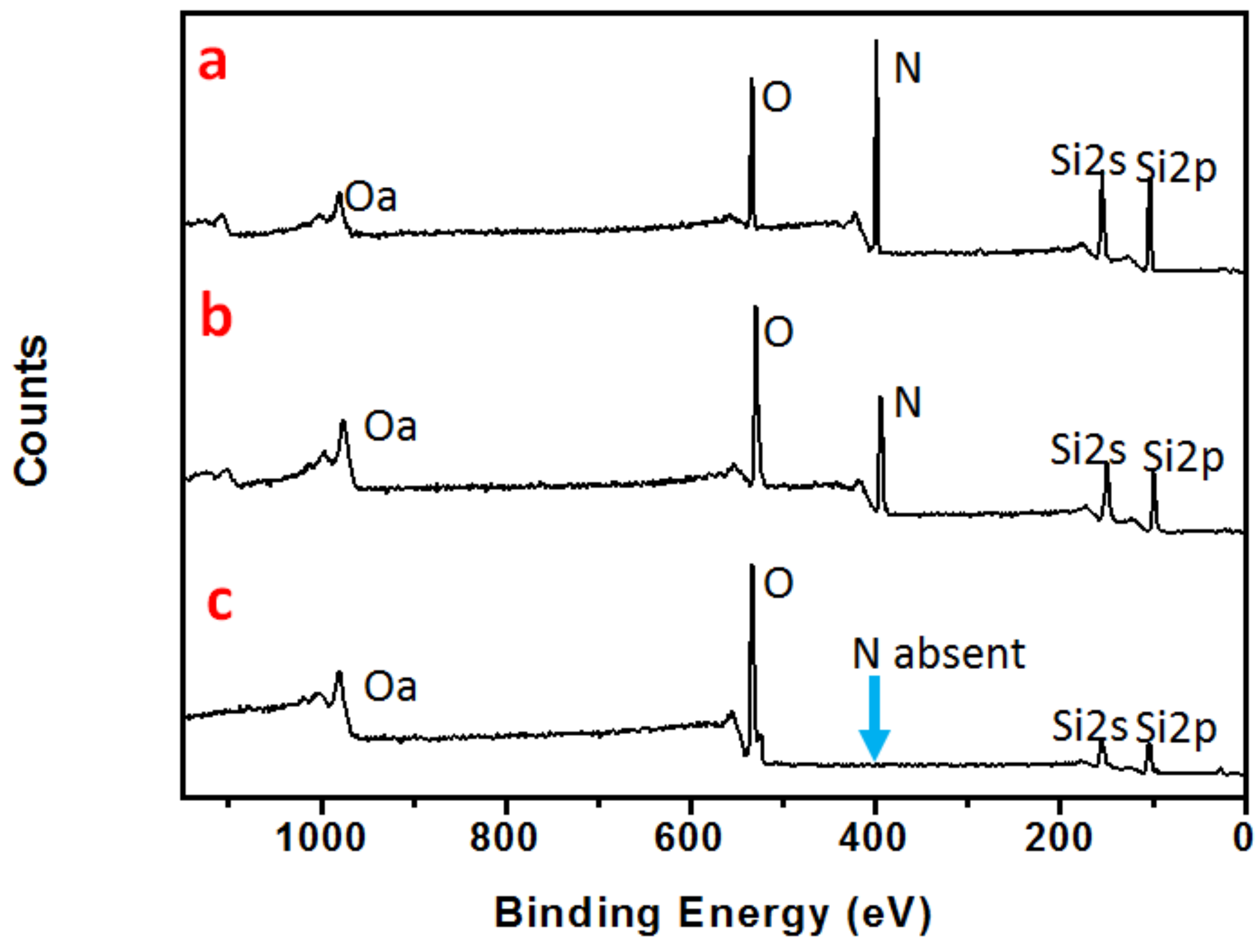
LPCVD silicon after oxidation



LPCVD silicon nitride *after* oxidation

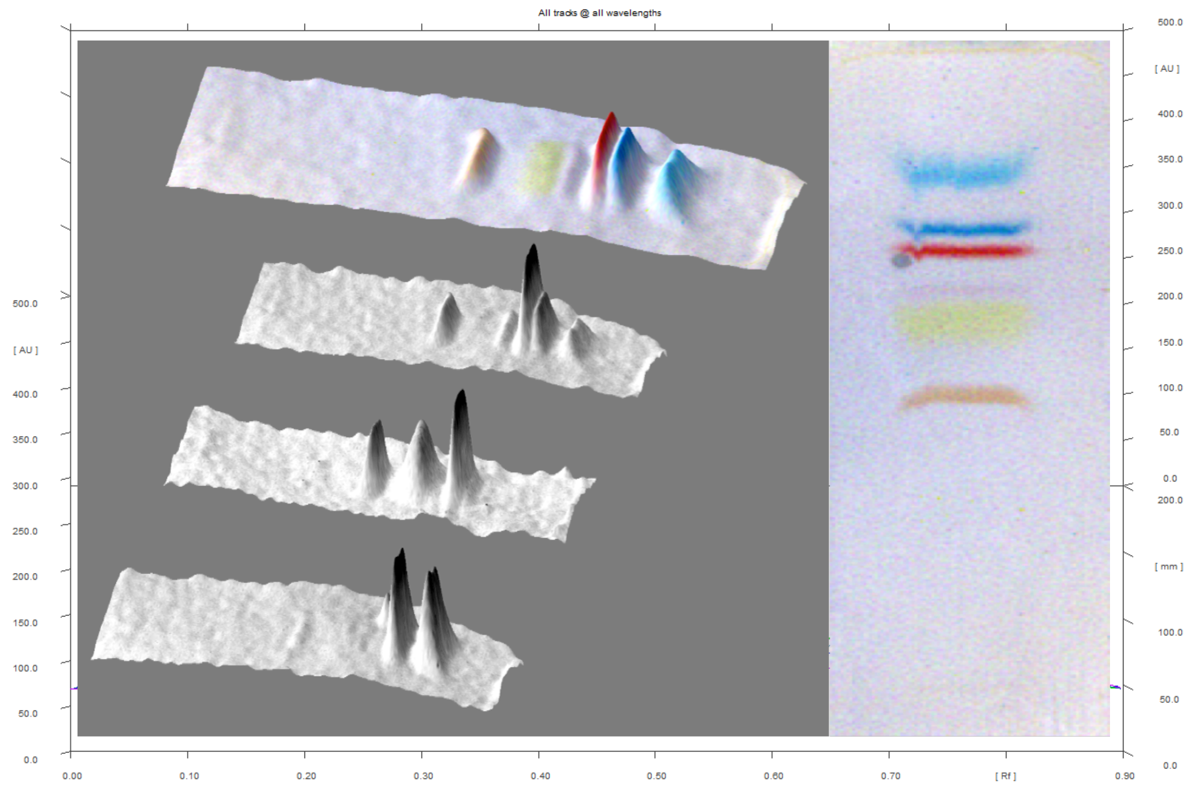
Nitrogen Can Be Completely Removed from the Near Surface Region of the Si_3N_4 plates

(a) as deposited Si_3N_4 film
(b) oxidized at 600 °C, 48 h
(c) oxidized at 1000 °C, 48 h



Separation on an LPCVD Silicon Nitride TLC Plate

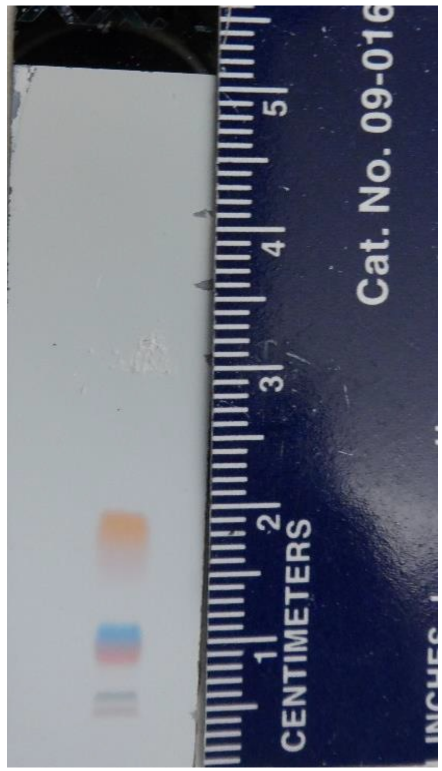
- s: Food dye mixture
- tance: 45 mm
- time: ca. 5 min
- ness: Plates can be washed
  sed dozens of times
- ocessing: Color enhanced for
  ation
- nt: 2 – 3 times as fast as a
  rcial plate



Densitometer scan at different wavelengths

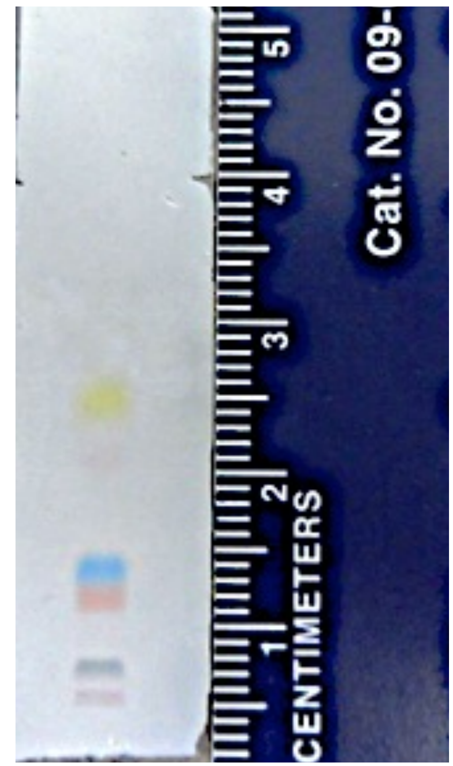
Separations from our Lab at BYU on LPCVD Silicon Nitride TLC Plates

- ication: Plates (i) and (ii) made different masks
- ytes: CAMAG test dye mixture
- distance: 25 mm (i and ii), 35 (iii)
- on time: (i) 1 min 10 s, (ii) 1 min , (iii) 3 min 15 s
- t size: 3 mm
- bile phase: *t*-butyl benzene
- nidity: 21% (typical)
- perature: 22 C (typical)
- ment: 2 – 3 times as fast as mercial plates



(i)

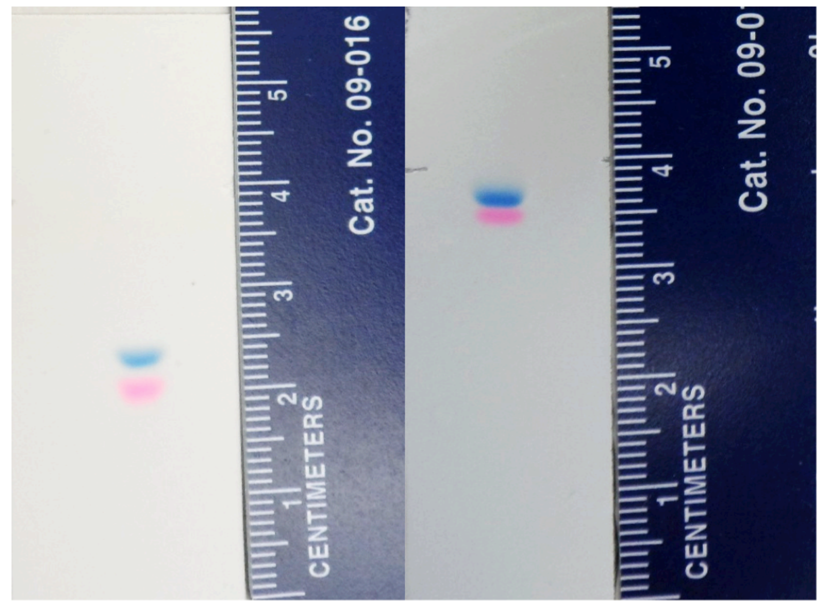
(ii)



(iii)

Separation of two dyes: BB7 and Rhodamine

- Separation of BB7 and rhodamine dye on
  - (a) Merck TLC plate
  - (b) M-TLC-plates.
  - Development solvent: EtOAc:MeOH:H_2O (75:15:10)
  - Run times: 1 min 15 s and 3 min 43 s for M-TLC and Merck TLC plates, respectively



(a) (b)

Two Quick Teasers

Transparent (glass) substrates

Fluorescent plates

Transparent Substrate

w Observations:
eed to find high
mperature
bstrate
- Somewhat
  challenging
  problem

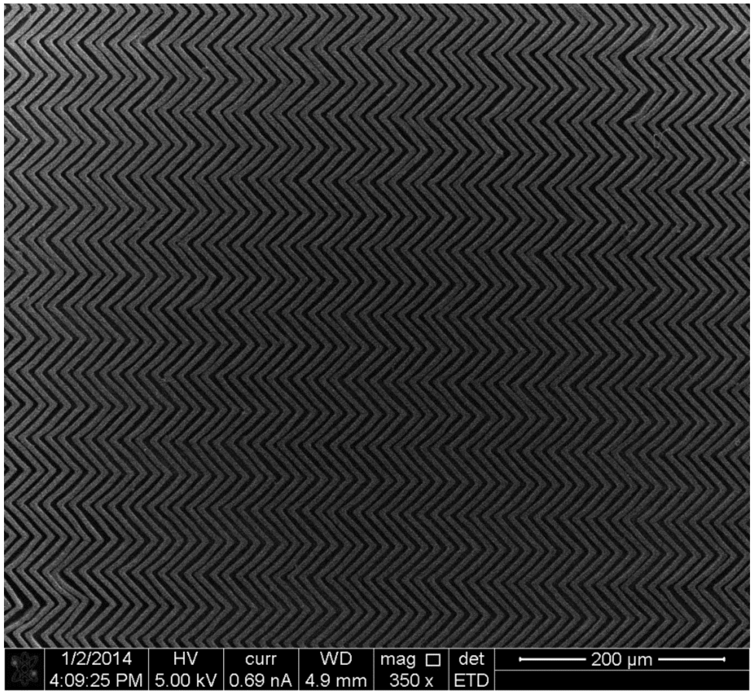
ost glasses soften
nd/or deform at
evated
mperatures
dapt process to
omewhat lower
mperatures
ansmission mode
etection is important
r TLC scanners

720 °C for 48 h
One substrate unaffected, another bends slightly, another to a significant degree

620 °C for 48 h
Flat as a board

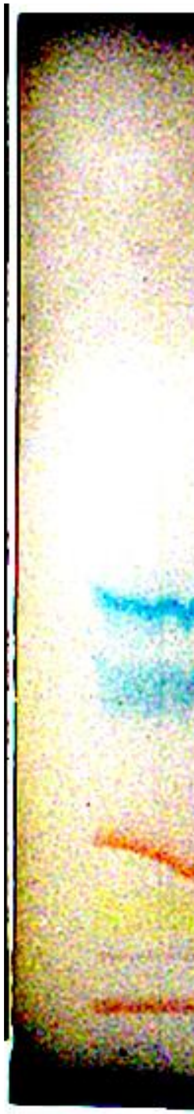
Transparent Substrate

- The lithography changes a little on a different substrate
- Still optimizing



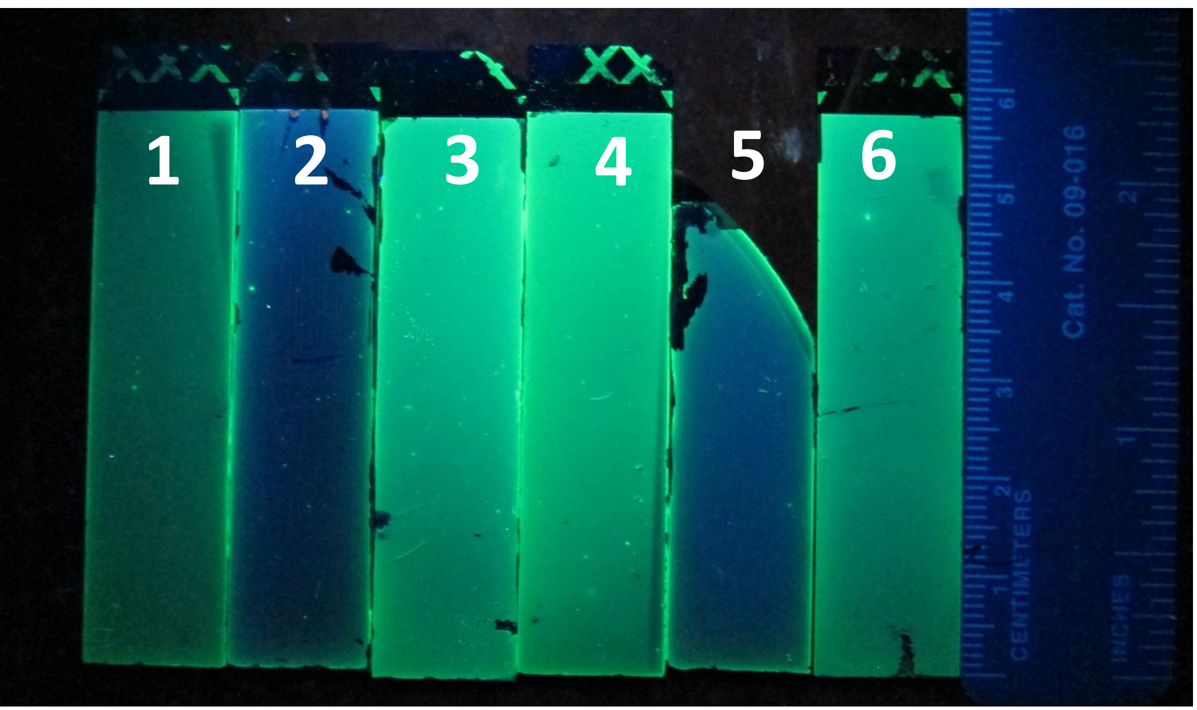
Patterned CNT forests grown on a high temperature glass

- Separation of a food dye mixture on a glass TLC plate.
- Color enhanced for easy visualization of spots.

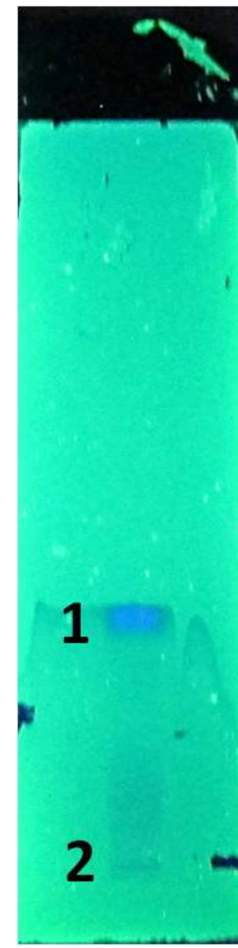


Making a Fluorescent Plate

Deposited ZnO(s) into the silicon nitride plates
ALD of dimethylzinc (DMZ) and water
Depending on deposition conditions, plates show green fluorescence
Fluorescence good with 254 nm excitation
Analytes on the plates quench the fluorescence
The chromatography doesn't change – same selectivity

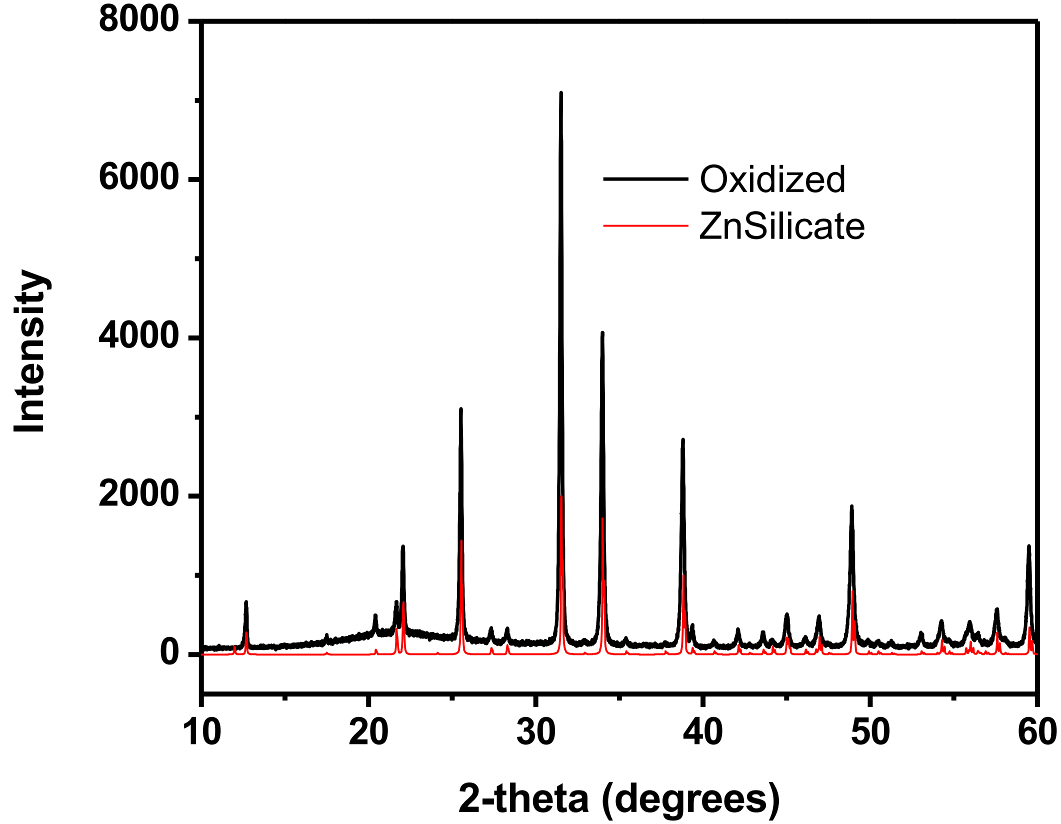


Analytes: caffeine (1) and phenacetin (2)
Mobile phase: chloroform:methanol:acetic acid (80:15:5 v/v/v)



Making a Fluorescent Plate

Intriguing result:



Conclusions

LPCVD of silicon nitride leads to good silica TLC plates

- No deformation of features
- No nitrogen left by XPS after oxidation
- Good separations of food dyes, CAMAG dye mixture, and other dyes
- Plates are very robust – can be washed and reused multiple times
- Separations comparable in resolution to those on HPTLC plates, but 2 – 3 times faster

Glass substrates being developed

- Photolithography is possible
- Preliminary separations performed

Fluorescent plates

- Progress towards the production of a fluorescent plate
- Preliminary separations

Acknowledgements

The Linford Group, BYU Chemistry Dept.

r. Mathew R. Linford

upriya S. Kanyal

nubhav Diwan

hupinder Singh

Wang Hao

ung Chuan-Hsi

US Synthetic

ndrew Dadson

Michael Vail

avid S. Jensen

ndrew Miles

BYU Physics Dept.

Dr. Robert C. Davis

Dr. Richard Vanfleet

BYU Integrated Microfabrication Facility

University of Utah Nanofab Facility

This project was funded by US Synthetic (Diamond Analytics)