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

Matthew R. Linford¹, Andrew E. Dadson, Gertrud Morlock, Supriya S. Kanyal, Cody Cushman, Tim Häbe

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

Photolithography → Barrier Layer → Catalytic Material
Al$_2$O$_3$ (30 nm) → Iron (6 nm)

Remove Photoresist

CNT Growth
(i) H$_2$, 750 °C
(ii) C$_2$H$_4$, H$_2$, Ar, 750°C

Conformally Coat with an Inorganic Material

(i) Remove CNTs Air, ca. 750 °C
(ii) Hydroxylation

Low Pressure Chemical Vapor Deposition

Reagent gasses continuously flow, and volatile biproducts are continuously removed.

2. http://sindhu.ece.iisc.ernet.in/nanofab/twiki/bin/view/Main/LPCVD
LPCVD of *Silicon* onto CNTs

\[
\text{Si}_4(\text{g}) \xrightarrow{\text{530°C}, 10 \text{mtorr}} \text{Si}_2(\text{s}) + 2\text{H}_2(\text{g})
\]

Volume expansion results in feature distortion.

LPCVD of Silicon Nitride onto CNTs

\[
\text{SiH}_2\text{Cl}_2(\text{g}) + \text{NH}_3(\text{g}) \xrightarrow{780°C} \text{Si}_3\text{N}_4(\text{s}) + \text{HCl}(\text{g})
\]

\[
\text{Si}_3\text{N}_4(\text{s}) \xrightarrow{1000°C \text{ Air, 48 h}} \text{SiO}_2(\text{s})
\]

LPCVD silicon nitride *before* oxidation
LPCVD of *Silicon Nitride* onto CNTs

\[ \text{SiH}_2\text{Cl}_2 (g) + \text{NH}_3 (g) \xrightarrow{780^\circ C} \text{Si}_3\text{N}_4 (s) + \text{HCl} (g) \]

\[ \text{Si}_3\text{N}_4 (s) \xrightarrow{1000^\circ C \text{ Air, 48 h}} \text{SiO}_2 (s) \]

LPCVD silicon after oxidation

LPCVD silicon nitride *after* oxidation
Nitrogen Can Be Completely Removed from the Near Surface Region of the $\text{Si}_3\text{N}_4$ plates

(a) as deposited $\text{Si}_3\text{N}_4$ film
(b) oxidized at 600 °C, 48 h
(c) oxidized at 1000 °C, 48 h
Separation on an LPCVD Silicon Nitride TLC Plate

- Analytes: Food dye mixture
- Distance: 45 mm
- Time: ca. 5 min
- Robustness: Plates can be washed and reused dozens of times
- Data processing: Color enhanced for visualization
- Comment: 2 – 3 times as fast as a commercial plate

Densitometer scan at different wavelengths
Separations from our Lab at BYU on LPCVD Silicon Nitride TLC Plates

Fabrication: Plates (i) and (ii) made with different masks
Analytes: 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
size: 3 mm
Mobile phase: t-butyl benzene
Humidity: 21% (typical)
Temperature: 22 C (typical)
Comment: 2 – 3 times as fast as commercial 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:H₂O (75:15:10)
- Run times: 1 min 15 s and 3 min 43 s for M-TLC and Merck TLC plates, respectively
Two Quick Teasers

Transparent (glass) substrates
Fluorescent plates
New Observations:

- Need to find high temperature substrate
- Somewhat challenging problem
- Most glasses soften and/or deform at elevated temperatures
- Adapt process to somewhat lower temperatures
- Transmission mode detection is important for 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

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

Patterned CNT forests grown on a high temperature glass
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
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