# Ultrathin-Layer Chromatography on Nanoengineered Thin Films

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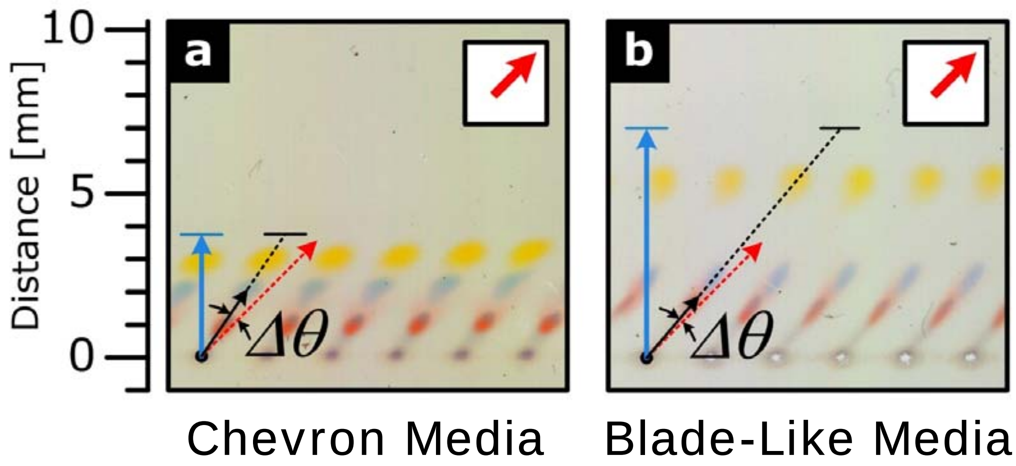
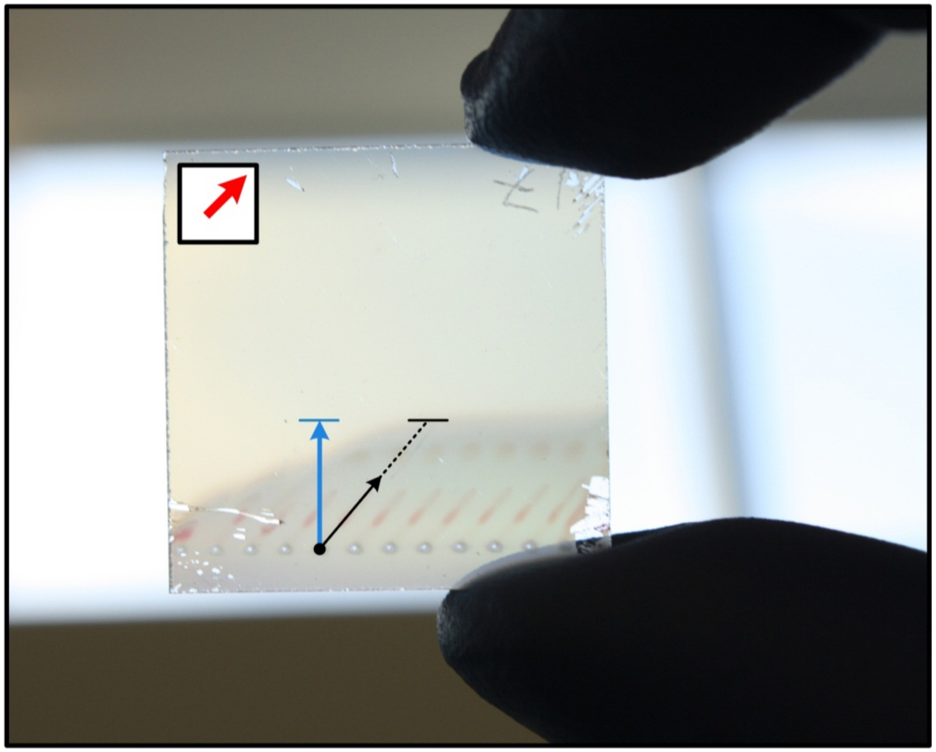
National Research Council Canada
Conseil national de recherches Canada
**National Institute for Nanotechnology**
**Institut national de nanotechnologie**



# Overview



Diagonal dye separation pattern on an anisotropic ultrathin-layer chromatography plate fabricated using glancing angle deposition

Figure from S.R. Jim *et al.*, *Anal. Chem.* (2010).

- Higher performance with nanostructuring
- Glancing angle deposition (GLAD)
- GLAD ultrathin-layer chromatography (UTLC) microstructures
- Channel features in anisotropic GLAD UTLC media and their effects on elution
- Final thoughts

# Higher Performance with Nanostructuring

| Stationary Phase Layer Properties | TLC [1,2] (particles, silica gel 60) | HPTLC [1,2] (particles, silica gel 60) | UTLC [1-3] (monolithic, silica gel) | GLAD UTLC [4-7] (columnar $SiO_2$) |
|---|---|---|---|---|
| Typical Thickness (μm) | 100 – 250 | 100 – 200 | 10 | 4.5 – 5 |
| "Characteristic" Size (μm) | 10 – 12 (mean particle size) | 4 – 6 (mean particle size) | 1 – 2 (macropore size) | 0.1 – 0.8 (intercolumn void) |
| Pore Size (Å) | 60 | 60 | 30 – 40 | 20 – 40 |
| Specific Surface Area ($m^2\ g^{-1}$) | 520 | 480 – 540 | ~ 350 | ~ 450 |

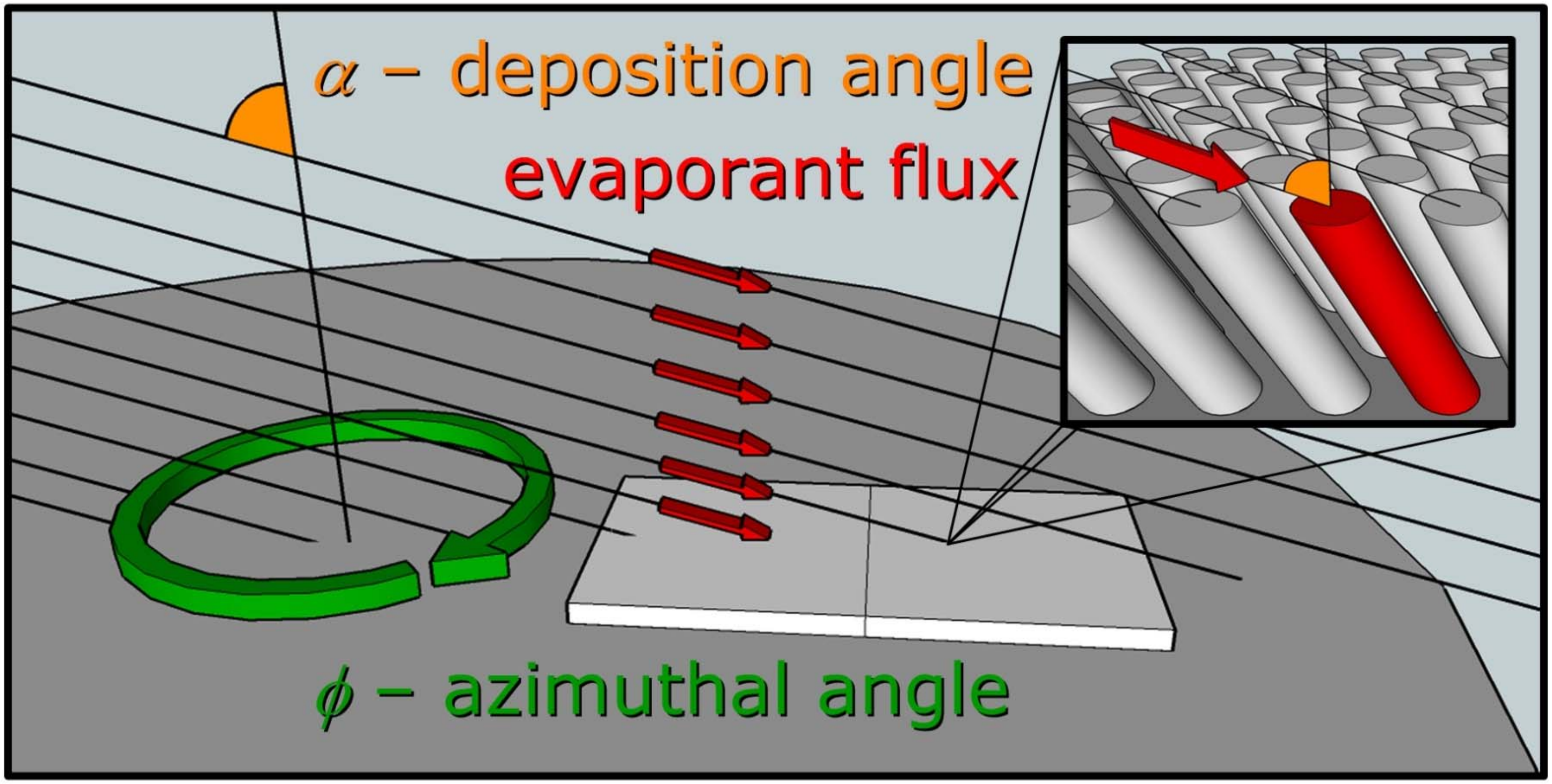
| Representative Elutions | TLC [1-3] | HTLC [1,2] | UTLC [1-3] | GLAD UTLC [4,5] |
|---|---|---|---|---|
| Development Time (s) | > 900 | > 180 | 60 – 360 | < 90 |
| Development Distance (mm) | 70 – 150 | 30 – 70 | 10 – 30 | 10 – 14 |
| Limit of Detection (ng, absorption) | 1 – 5 | 0.1 – 0.5 | 0.5 | < 10 |
| Theoretical Plate Height (μm) | 30 – 75 | 12 – 25 | 80 [3] | 12 – 30 |

[1] S.K. Poole and C.F. Poole, *J. Chromatogr. A.* (2011); [2] ChromBook 2008|09, Merck KGaA, Darmstadt, Germany (2008); [3] H.E. Hauck and M. Schulz, *J. Chromatogr. Sci.* (2002); [4] S.R. Jim *et al.*, *Anal. Chem.* (2010); [5] A.J. Oko *et al.*, *J. Chromatogr. A.* (2011); [6] K.M. Krause *et al.*, *Langmuir* (2010); [7] K.M. Krause *et al.*, *Microporous Mesoporous Mater.* (2011).

# Glancing Angle Deposition (GLAD) and UTLC Microstructures

*Shadowing and Sculpting*
*Architectures, Advantages, and Applications*
*GLAD Microstructures and Elution*
*Channel Features in Anisotropic Media*
*Migration in Anisotropic Microstructures*

# Shadowing and Sculpting

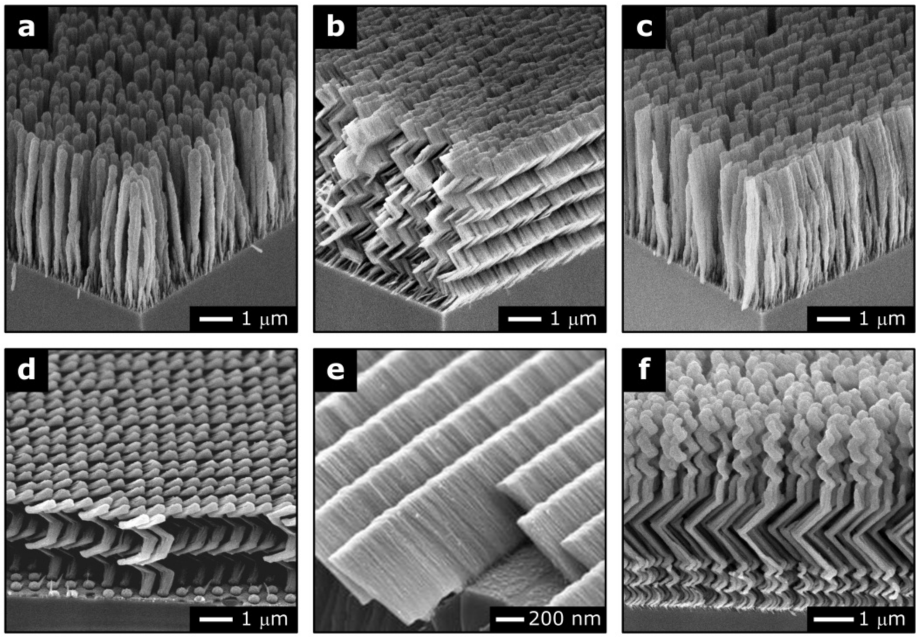



Glancing angle deposition couples self-shadowing with substrate motion control to sculpt columnar thin films of useful morphologies.

Figure from S.R. Jim *et al.*, *Anal. Chem.* (2010).

# Architectures, Advantages, and Applications

Representative scanning electron micrographs of GLAD morphologies



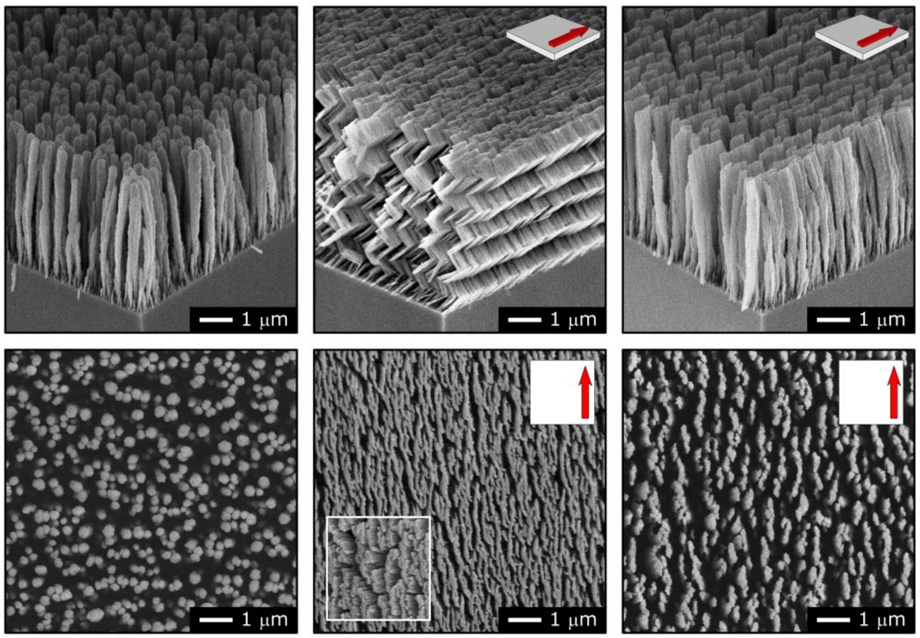

(a) Vertical post, (b) chevron, (c) blade-like, (d) helical, (e) nanoribbon, and (f) hybrid structures.

- *Key Capabilities*
  - Excellent control over porosity and architecture
  - Variety of materials
  - Patented single-step technology compatible with microfabrication
- *Applications*
  - Rapid relative humidity sensors
  - Optical and photovoltaic devices
  - Planar chromatography

Images reproduced from (a-c) S.R. Jim *et al.*, *Anal. Chem.* (2010); (d) P.C.P Hrudey *et al.*, *Proc. SPIE* (2005); (e) J.J. Steele *et al.*, *J. Mater. Sci.: Mater. Electron.* (2007); (f) A.C. van Popta *et al.*, *Proc. SPIE* (2004).

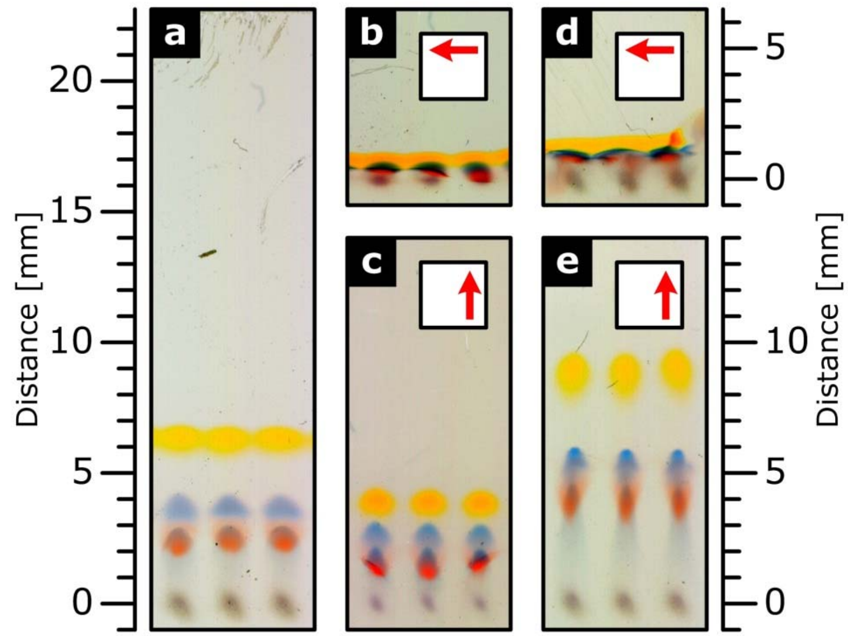
# GLAD Microstructures and Elution

Micrographs of macroporous GLAD thin film separation media




Vertical Post (Isotropic) | Chevron (Anisotropic) | Blade-Like (Anisotropic)

Scanned images of developed GLAD UTLC plates



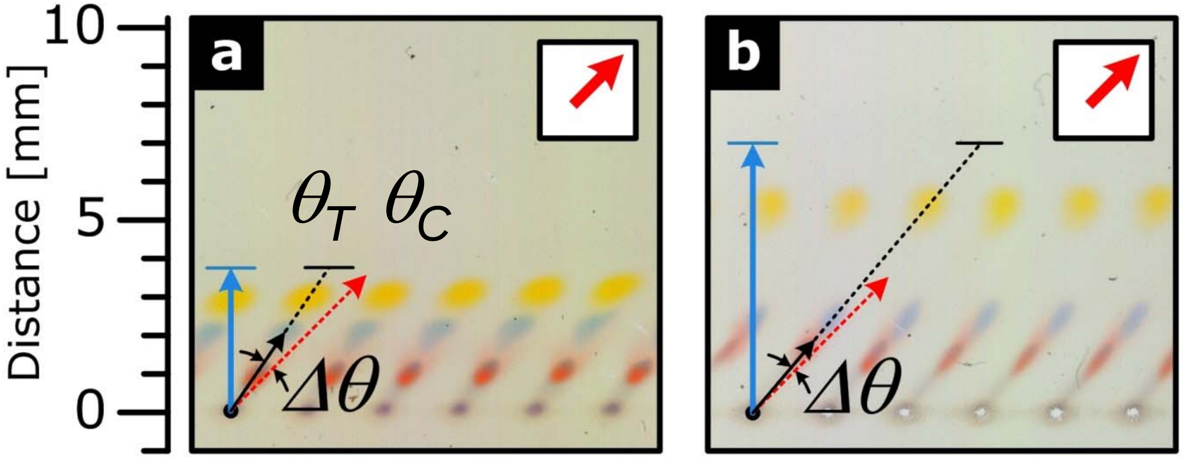

Vertical Post (Isotropic) | Chevron (Anisotropic) | Blade-Like (Anisotropic)

Figures modified from S.R. Jim *et al.*, *Anal. Chem.* (2010).

# Channel Features in Anisotropic Media

- *Development track deviation angle ($\Delta\theta$) as a measure of the "extent of anisotropy":*

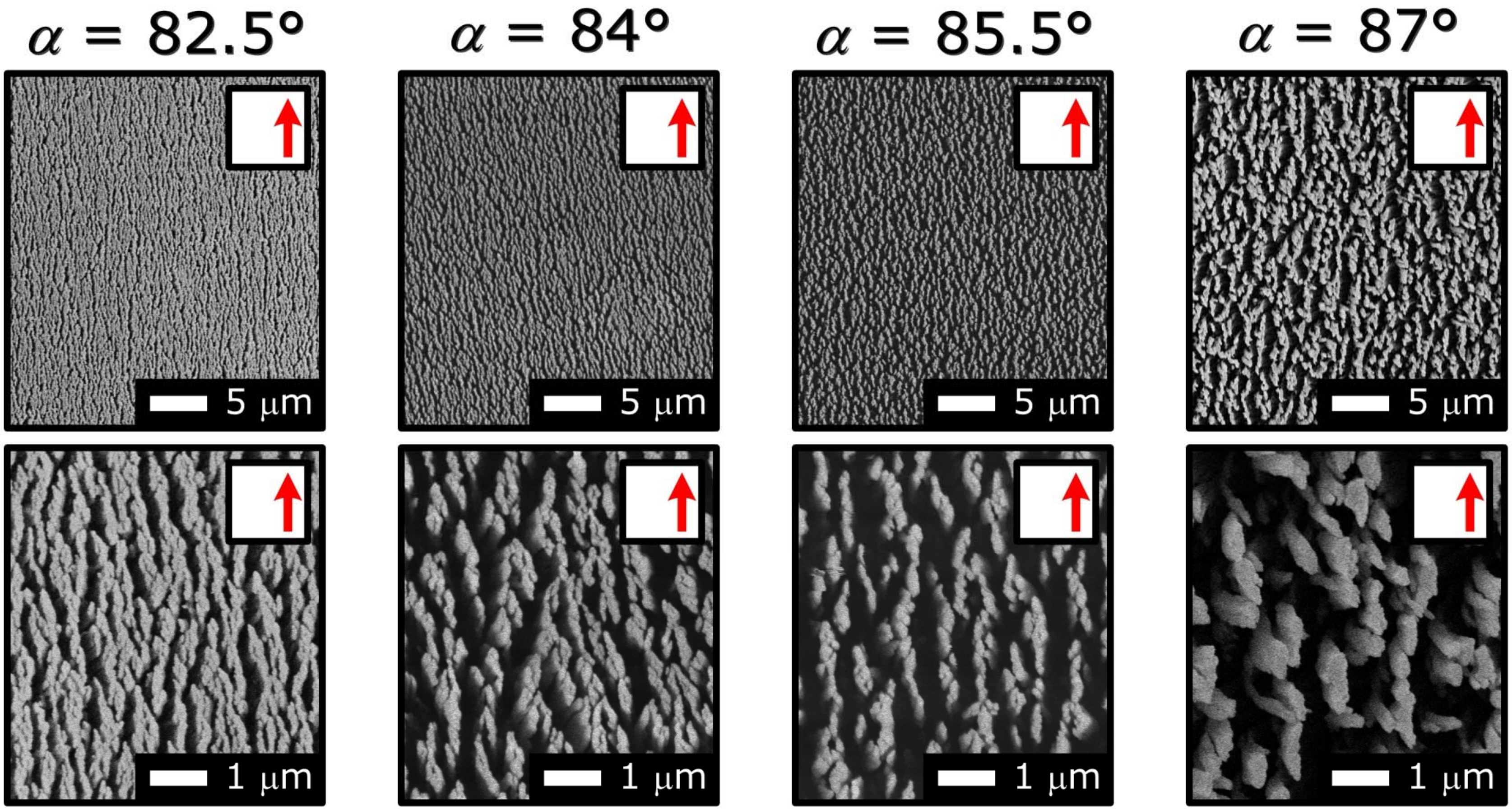
$$\Delta\theta = \theta_C - \theta_T \quad (1)$$




| Chevron Media | Blade-Like Media |
|---|---|
| $\theta_C$ = 45° | $\theta_C$ = 45° |
| → $\Delta\theta$ = 10° ± 2° | → $\Delta\theta$ = 5° ± 2° |

Figure modified from S.R. Jim *et al.*, *Anal. Chem.* (2010).

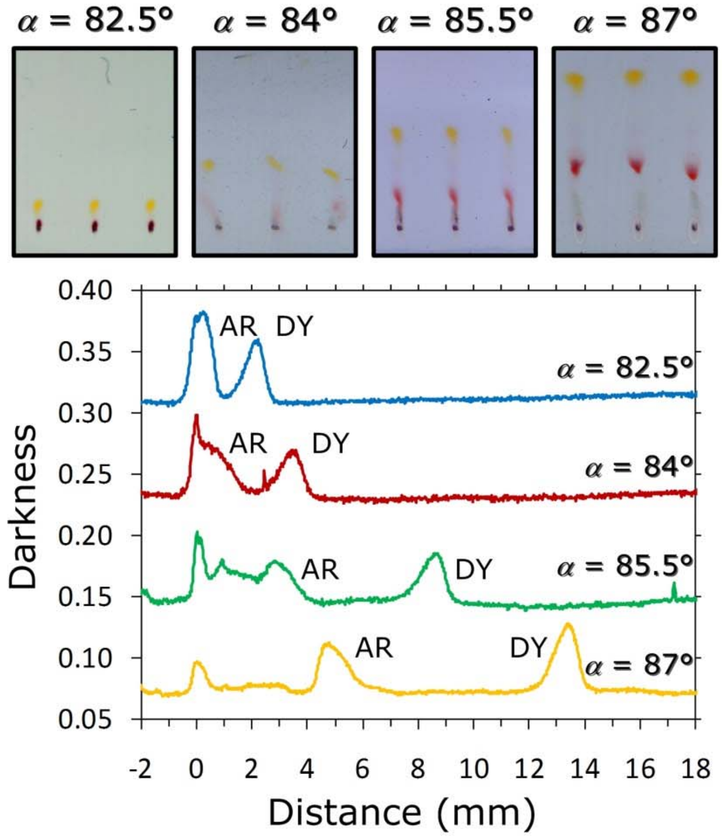
# Migration in Anisotropic Microstructures



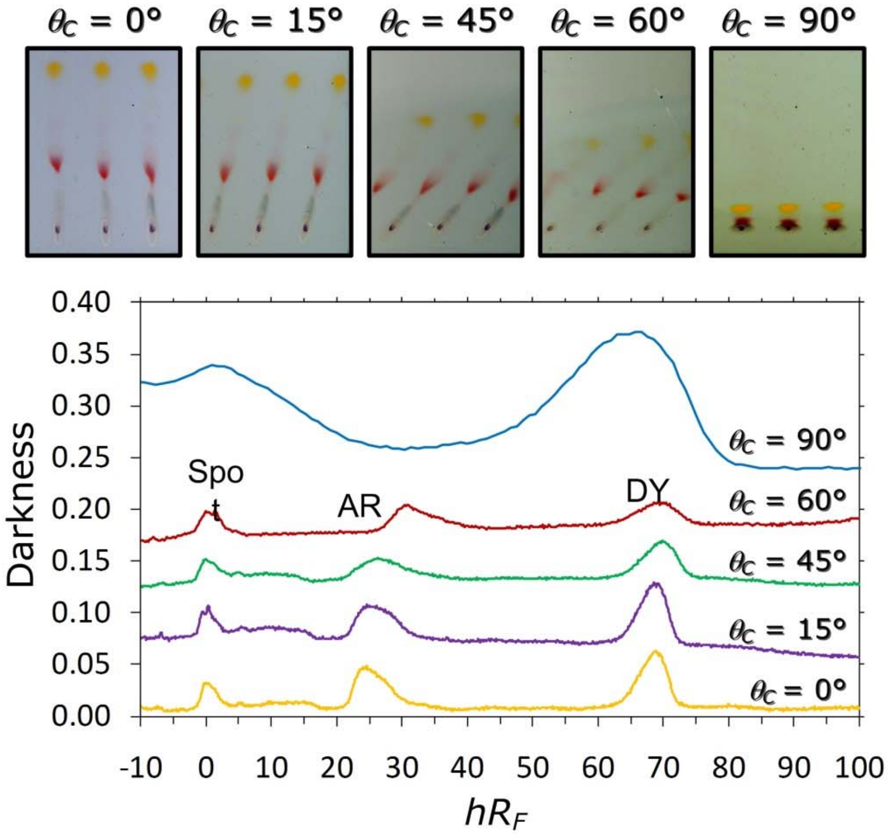

Low and high magnification top view SEM micrographs of ~ 5 μm thick $SiO_2$ blade-like films fabricated with varied deposition angle ($\alpha$)

Figure modified from A.J. Oko *et al.*, *Anal. Chem.* (2011).

# Migration in Anisotropic Microstructures




Along-channel ($\theta_C$ = 0°) chromatograms for GLAD UTLC plates of varied porosity (varied deposition angle, $\alpha$)




Chromatograms for $\alpha$ = 87° blade-like plate with channels oriented at varied angles ($\theta_C$)

Figures modified from A.J. Oko *et al.*, *Anal. Chem.* (2011).

# Final Thoughts

*Conclusions*
*Acknowledgements*
*Further readings on the GLAD technique and on GLAD UTLC*

# Conclusions

- Planar chromatography performance improves with stationary phase microstructure engineering.
- GLAD provides excellent control over the porosity and architecture of columnar UTLC microstructures.
- Anisotropic GLAD UTLC media exhibit channel features that strongly influence analyte migration velocities, separation track orientations, and spot broadening.
- Ongoing research aims to combine the benefits of anisotropic media with post-processing and better-suited chromatography instrumentation to produce a high-performance GLAD UTLC system.

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## Further reading on GLAD UTLC


1. A.J. Oko, S.R. Jim, M.T. Taschuk, M.J. Brett, "Analyte migration in anisotropic nanostructured ultrathin-layer chromatography media", *Journal of Chromatography A* 1218(19), 2661-2667 (2011).
2. S.R. Jim, M.T. Taschuk, G.E. Morlock, L.W. Bezuidenhout, W. Schwack, M.J. Brett, "Engineered Anisotropic Microstructures for Ultrathin-Layer Chromatography", *Analytical Chemistry* 82(12), 5349–5356 (2010).
3. G.E. Morlock, C. Oellig, L.W. Bezuidenhout, M.J. Brett, W. Schwack, “Miniaturized planar chromatography using office peripherals”, *Analytical Chemistry* 82(7), 2940-2946 (2010).
4. L.W. Bezuidenhout, M.J. Brett, “Ultrathin layer chromatography on nanostructured thin films”, *Journal of Chromatography A* 1183(1-2), 179-185 (2008).


## Further reading on the GLAD technique and applications


1. M.T. Taschuk, M.M. Hawkeye, M.J. Brett, “Glancing Angle Deposition,” *Handbook of Deposition Technologies for Films and Coatings: Science, Applications and Technology*, P. Martin (ed.), Oxford, United Kingdom: William Andrew (Elsevier), 621-678 (2010).
2. M.J. Brett, M.M. Hawkeye, “New materials at a glance,” *Science* 319(5867), 1192-1193 (2008).
3. M.M. Hawkeye, M.J. Brett, “Glancing angle deposition: Fabrication, properties, and applications of micro- and nanostructured thin films,” *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 25(5), 1317-1335 (2007).



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