BNL-95199-2011-CP

Polymer Self Assembly for Electronic Devices

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BROOKHAVEN NATIONAL LABORATORY

2006- Brookhaven National Laboratory

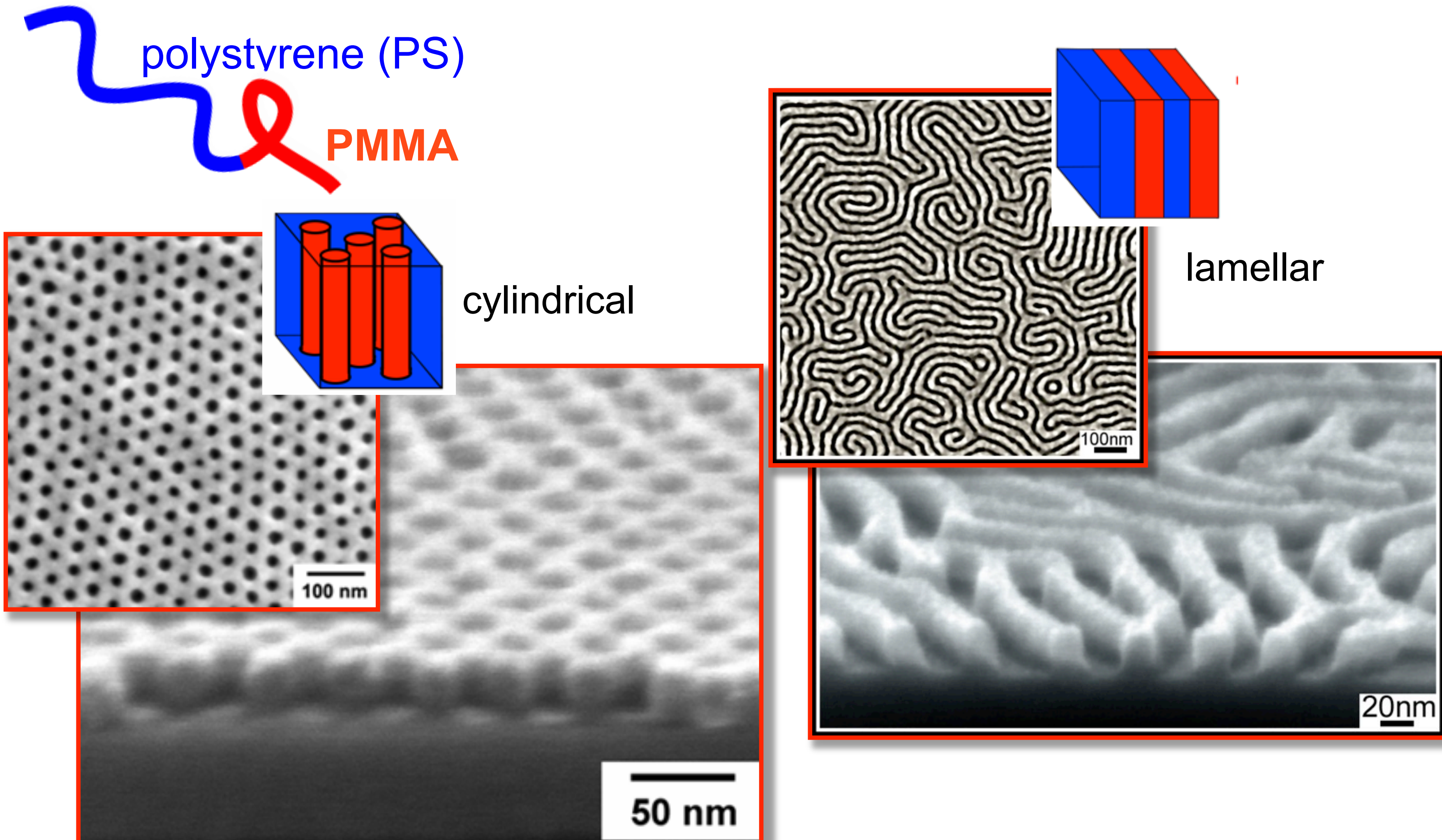
Nanostructured devices for energy conversion

1996-2006: IBM T. J. Watson Research Center

Self assembly for high-performance semiconductor microelectronics

Self-assembled block copolymer films

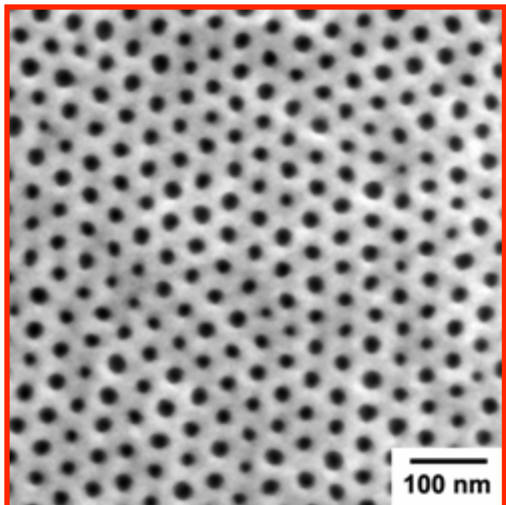
T. P. Russell, M. T. Tuominen (UMass Amherst), C. J. Hawker (IBM) *Adv. Mat.*, **12**, 787 (2000).



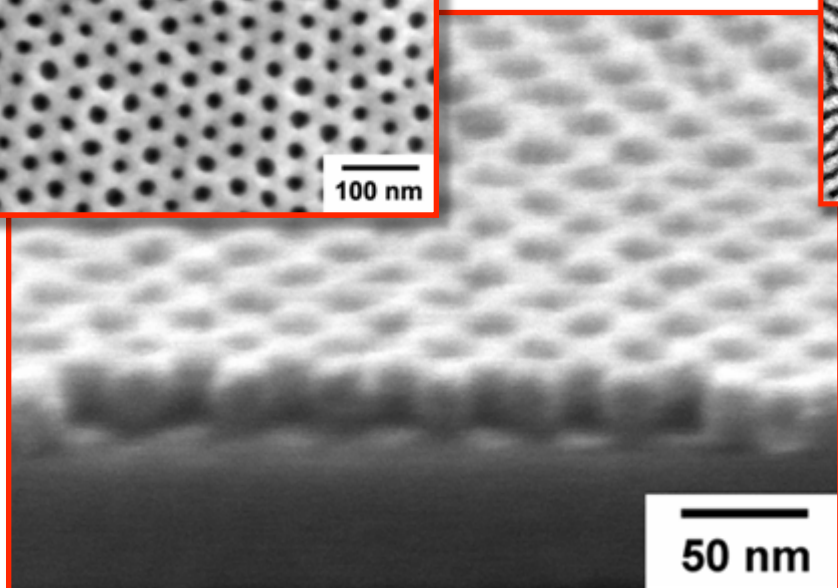
Surface wetting controls pattern orientation

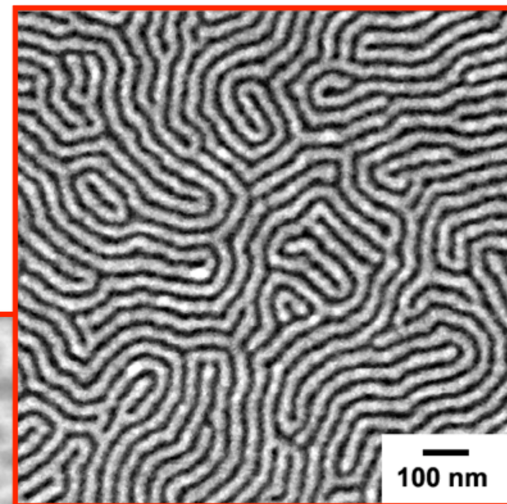
P. Mansky, Y. Liu, E. Huang, T. P. Russell, C. J. Hawker, *Science* **275**, 1458 (1997).

Random copolymer brush controls domain orientation

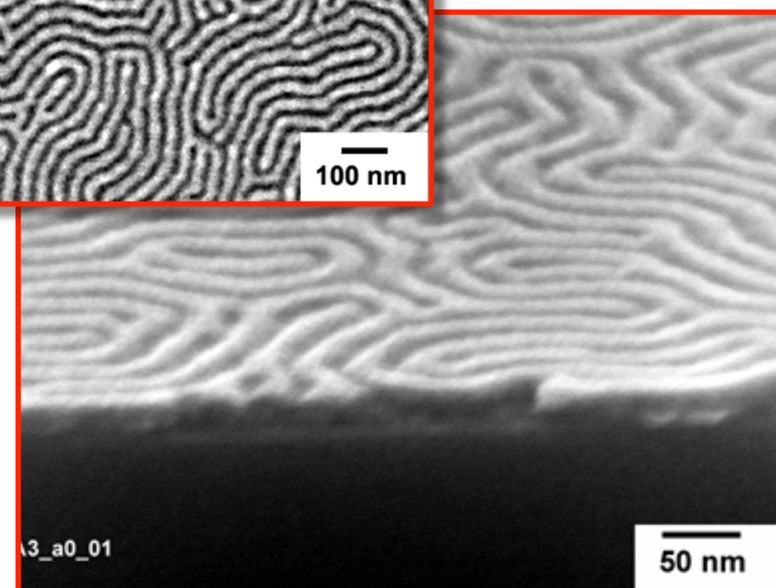


"perpendicular"
cylinders

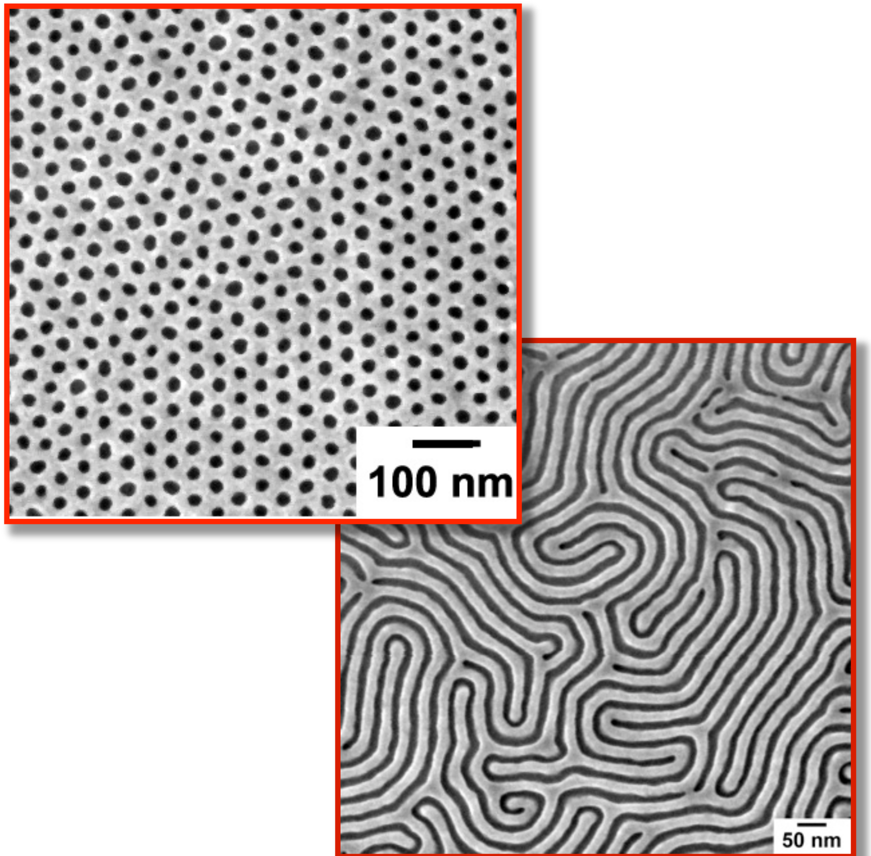




"parallel"
cylinders



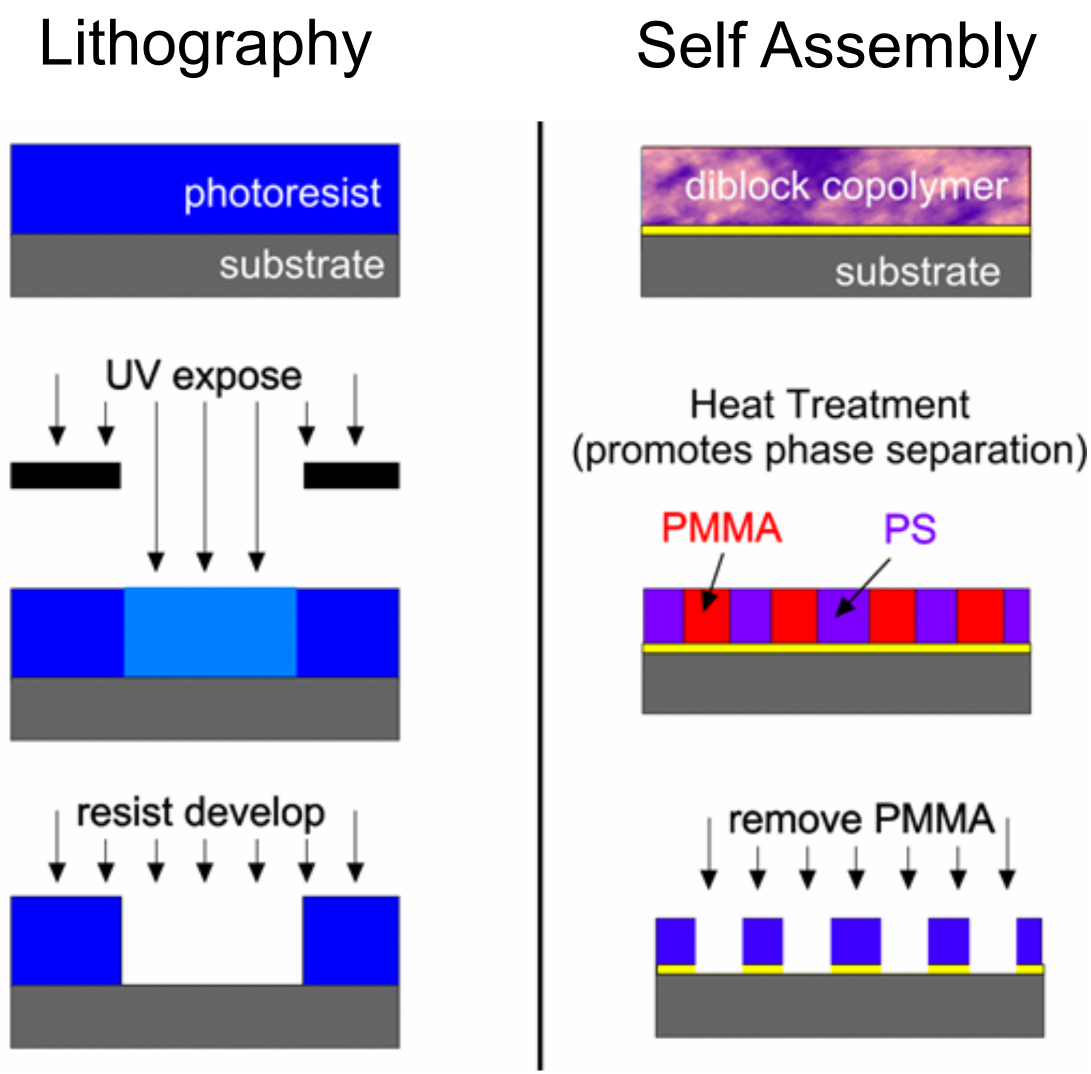
Polymer self assembly for device fabrication



- Large area patterning (~cm^2)
- Small feature sizes (<20nm)
- High feature density (>$10^{10}/cm^2$)
- Periodic structures (<40nm pitch)
- Reasonable size uniformity (σ~10%); little uniformity in ordering
- Dimensions (somewhat) tunable
- Materials are semiconductor process compatible
- Process tooling already in existing manufacturing infrastructure

Polymer self assembly similar to lithography

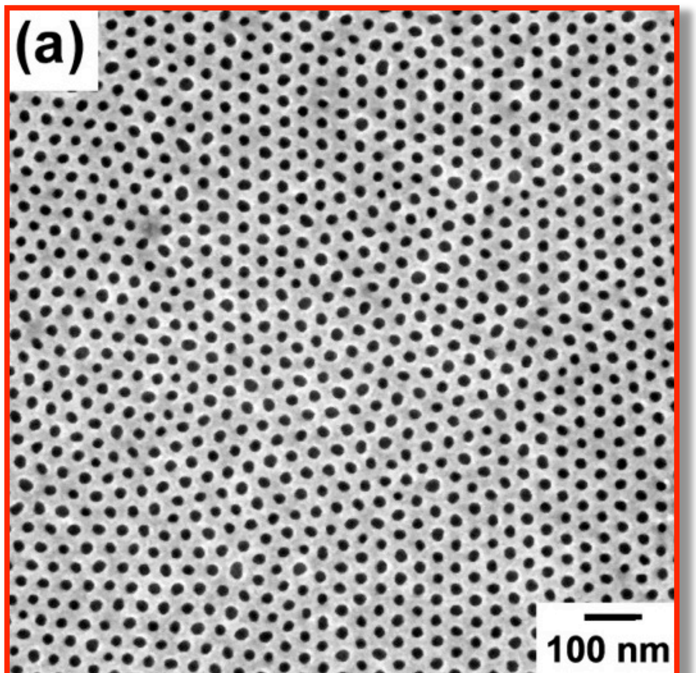
1. apply material
2. form latent image
3. create image contrast

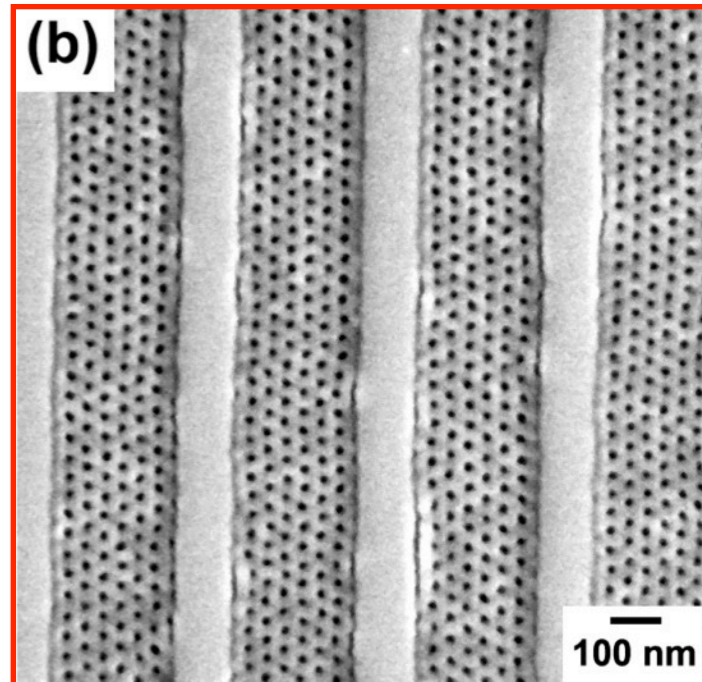


Non-self-aligned vs. self-aligned patterning

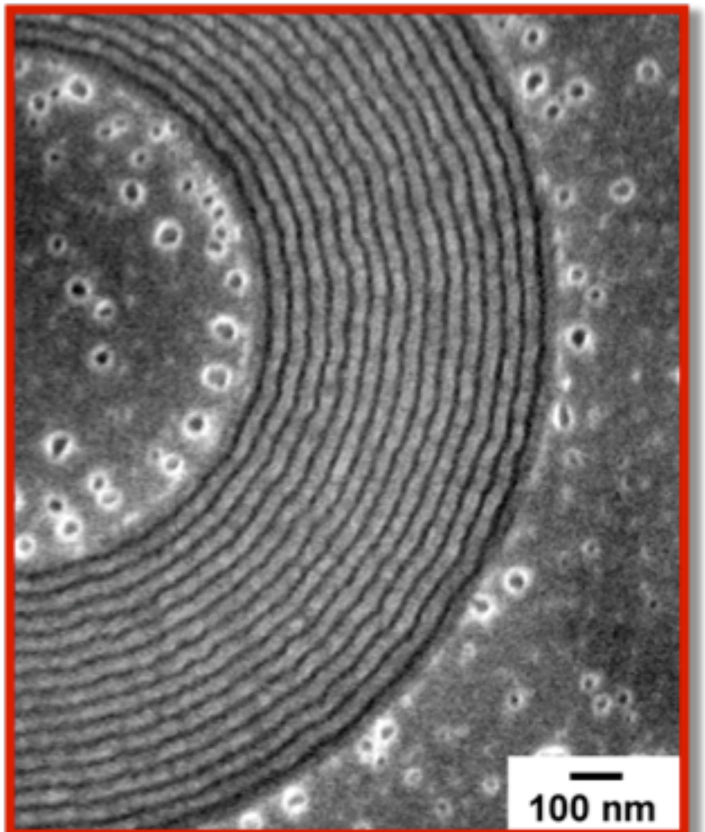
NO registration = useful for nanostructuring materials
- domain size uniformity

YES registration = lithography
- reduced defectivity
- known domain positions





Block copolymer lithography



Amazing recent advances:

Massachusetts Institute of Technology
Caroline Ross, Karl Berggren

Hitachi Global Storage Technologies
Ricardo Ruiz,
with Paul Nealey (Univ. Wisconsin)

IBM Almaden Research Center
Joy Cheng

Some lithography requirements questions

How scalable is block copolymer self assembly?

What are ultimate limits on size, pitch?

How smooth are the self-assembled pattern features?

targets (ITRS): CD: 3σ= 2.3nm; LWR: 3σ= 1.2nm

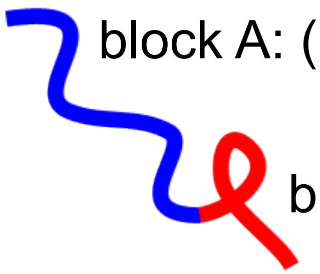
Can we create/integrate robust fabrication processes?

pattern formation

pattern develop

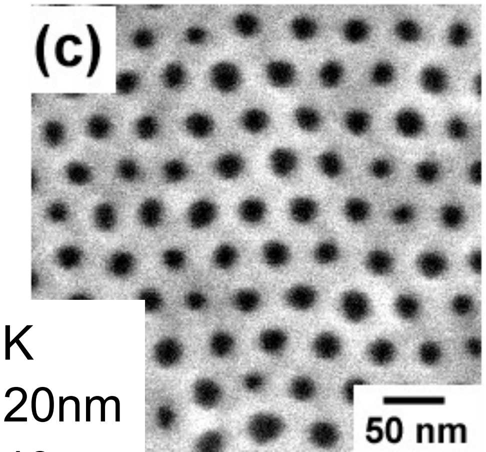
plasma etch resistance

Pattern scalability

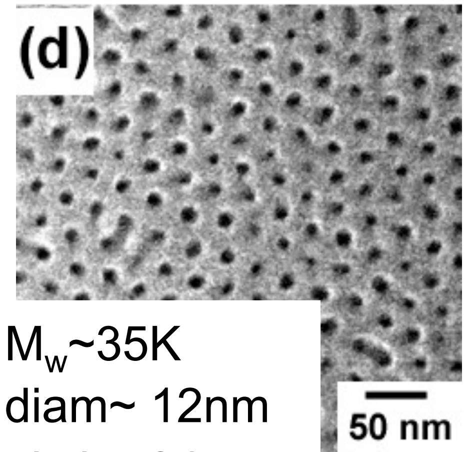


block A: (PS)

block B: (PMMA)



M_w~60K
diam~ 20nm
pitch~ 40nm



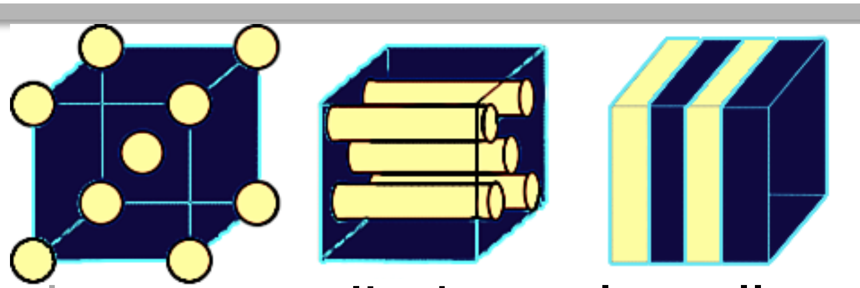
M_w~35K
diam~ 12nm
pitch~ 24nm

- need **χN> 10** for good pattern formation
- intrinsic pattern dimension set by **L_0 (in nm) ~ $N^{2/3} * \chi^{1/6}$**
- so, minimum feature size: $L_{0min}\text{(in nm)} \sim \dfrac{4.6}{\sqrt{\chi}}$

~27nm in PS:PMMA

χ ↑ for smaller features

Pattern feature roughness



spheres cylinders lamellae

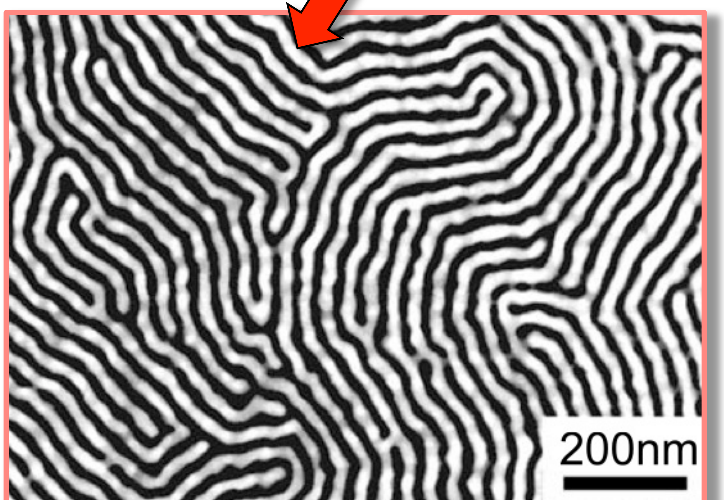
block interface width set by:

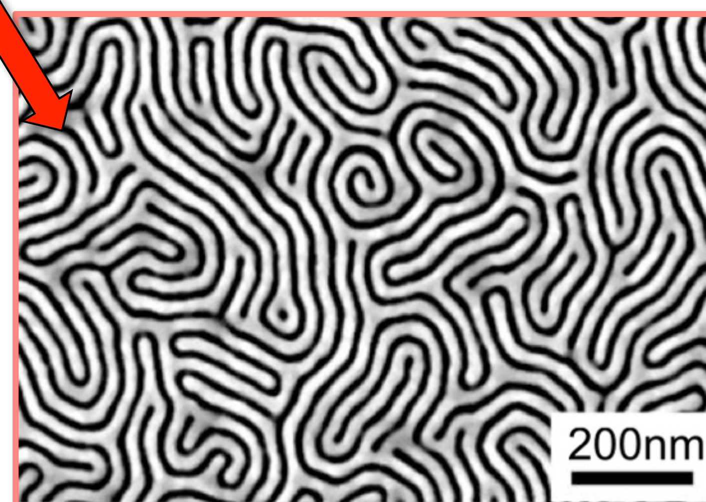
$$\Delta(\text{in nm}) \sim \frac{2}{\sqrt{6\chi}}$$

~4nm in PS:PMMA

Need χ↑ for sharper interfaces

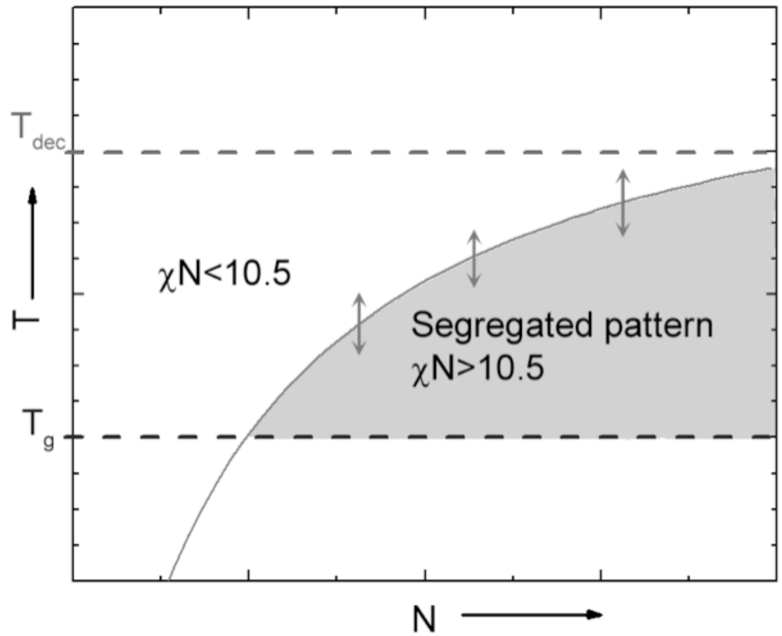
But, need interdiffusion (χ ↓) to heal defects

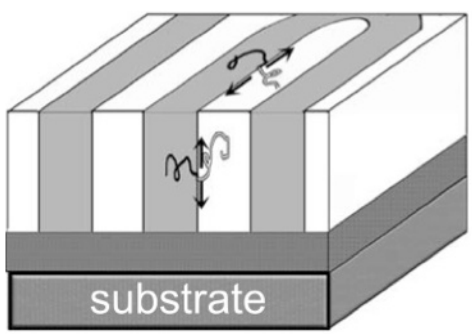




(?: Lamellae are always smoother than cylinders)

Pattern feature roughness





block interface width set by:

$$\Delta(\text{in nm}) \sim \frac{2}{\sqrt{6\chi}}$$

~4nm in PS:PMMA

use T-dependence of χ to control Δ and heal defects

$$\chi \sim A + B/T$$

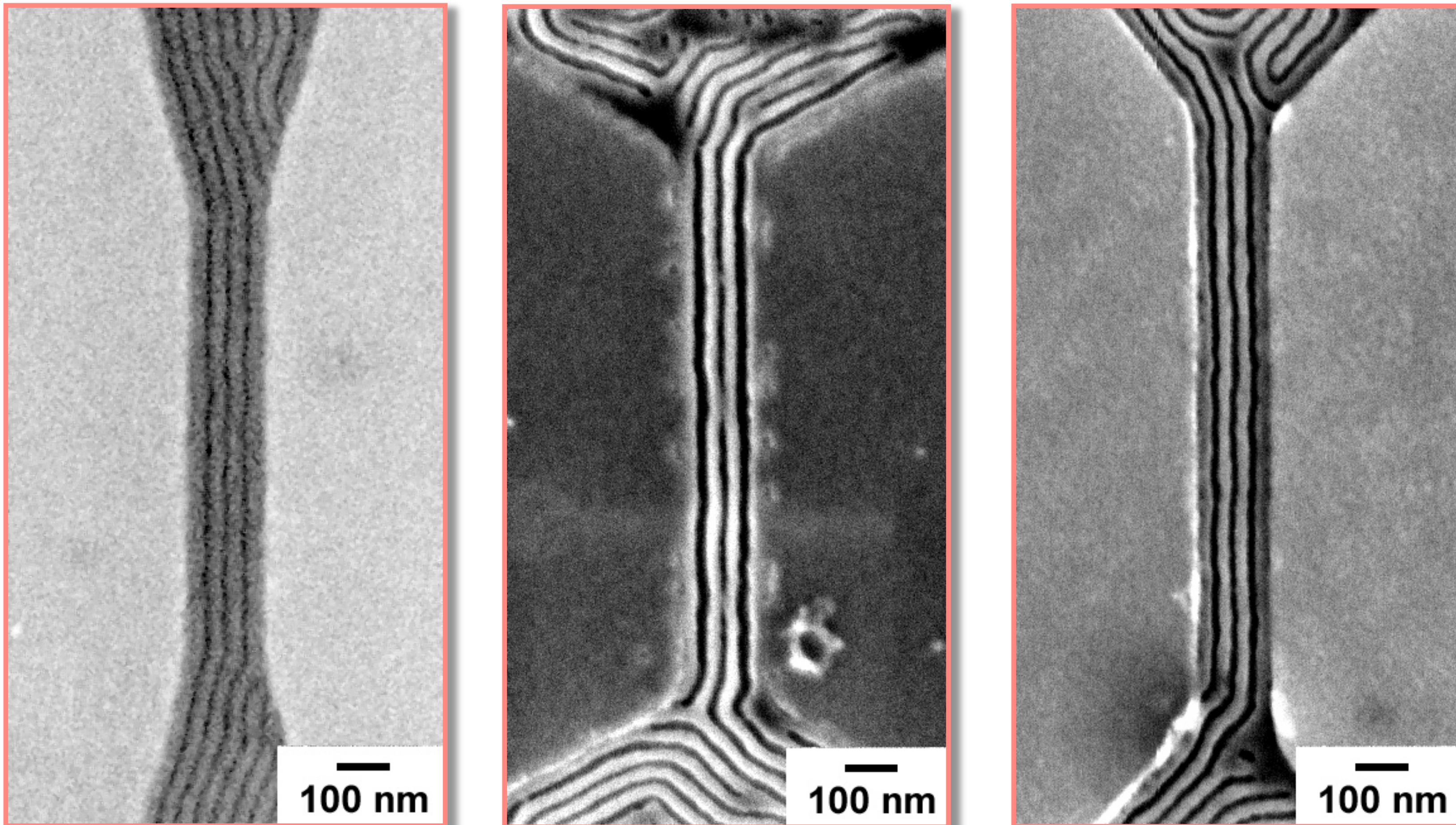
e.g.,

GOOD: PS-b-P2VP: strong T-dependence of χ

NOT-SO-GOOD: PS-b-PMMA: little T-dependence

See, for example, Hammond, Kramer, *et al.*, *Macromolecules* **38**, 6575 (2005).

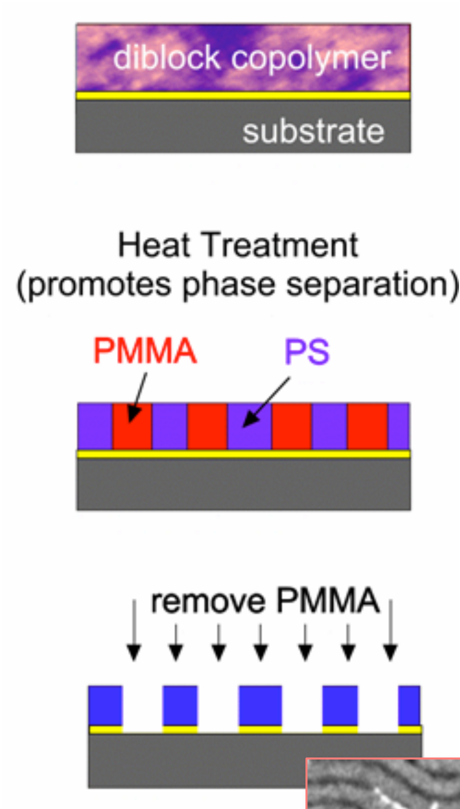
Pattern develop

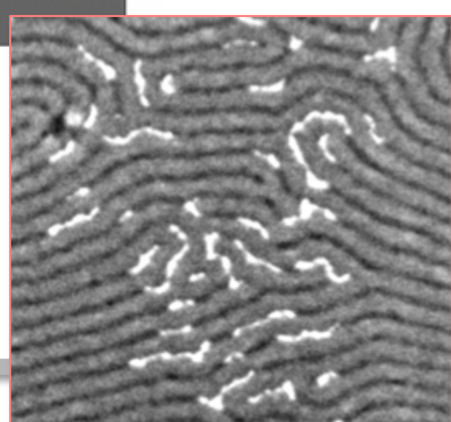


as formed (no develop)
PS and PMMA present

UV exp.+ liquid develop
PMMA removed; some collapse

O_2 plasma develop
PMMA removed; lose PS





Good

Lithography by self assembly

Better?

Self assemble the active structure itself

- Localize inorganic precursors within block copolymer micelles (in solution)
- Load inorganic precursor after self-assembled pattern formation (from solution)
- Control surfactant/polymer block interactions to localize surfactant-capped nanocrystals

U.S. DEPARTMENT OF ENERGY

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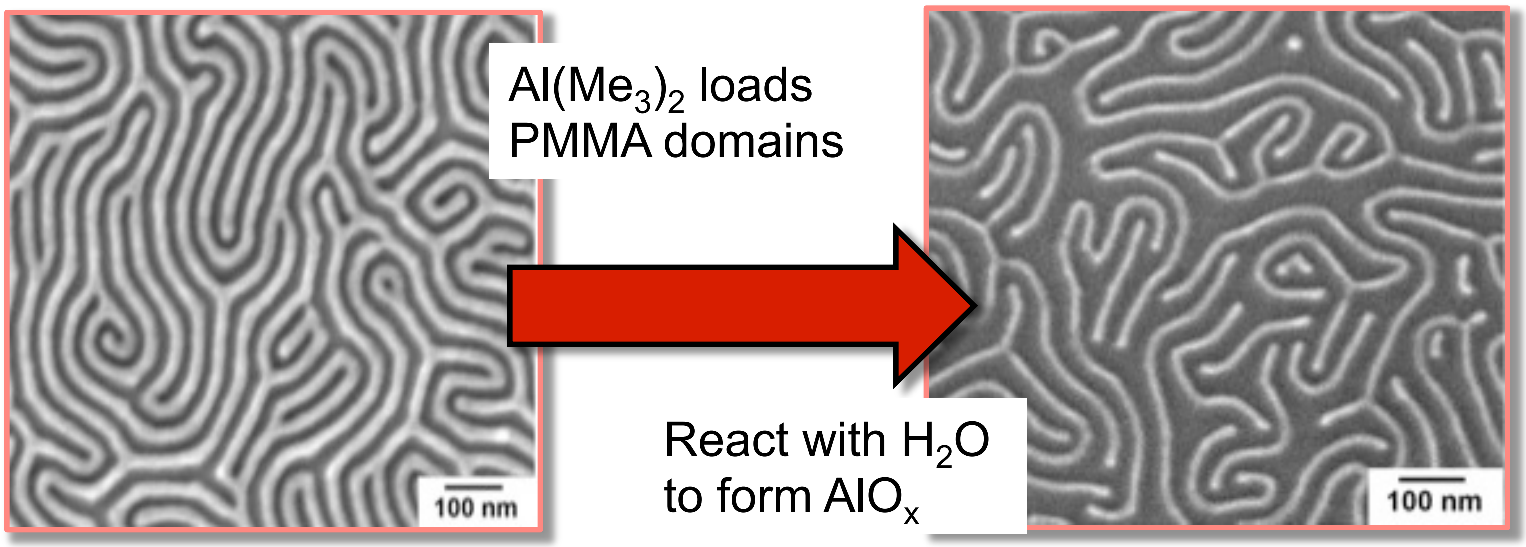
“Pattern Develop”

Q. Peng et al., Adv. Mat. 22, 5129 (2010).

Idea: Selectively load domains with inorganic precursor from **vapor phase**



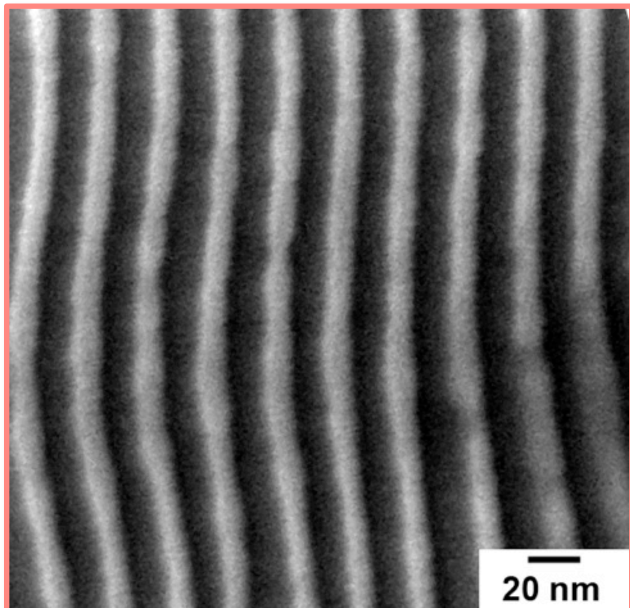
Lamellar PS-b-PMMA

AlOx pattern (polymer removed)

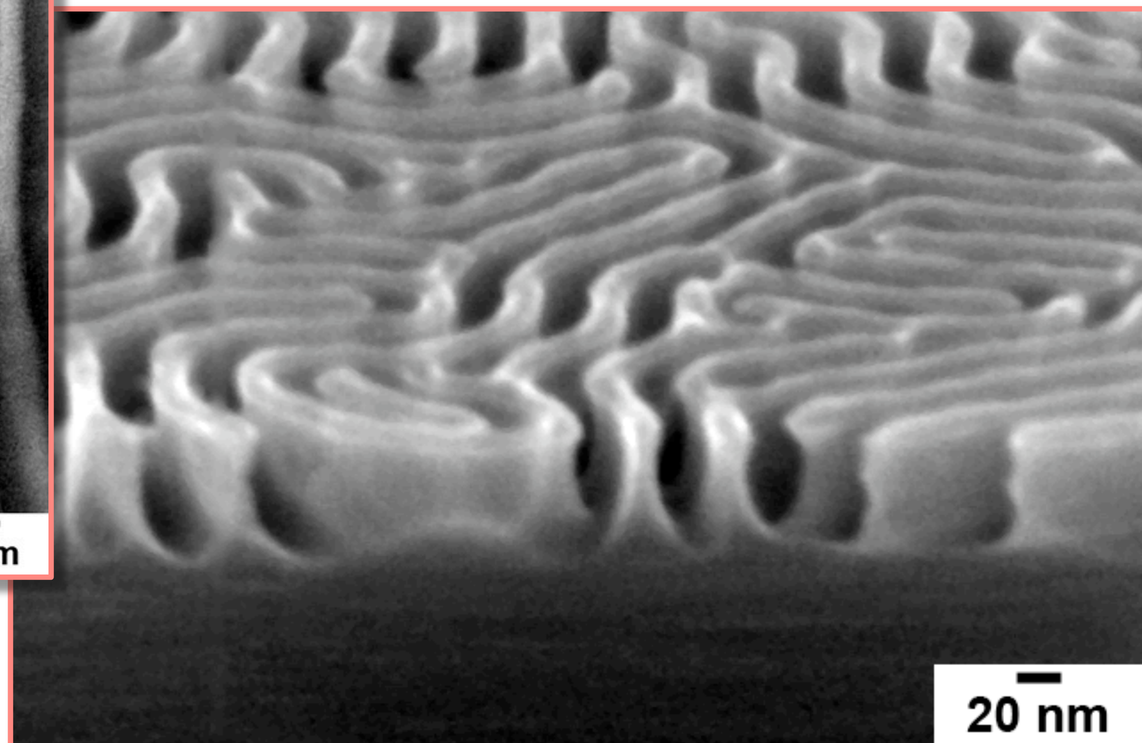
Plasma etch resistance

Converting PMMA domains to AlOx:

- prevents resist collapse during "develop"
- increases plasma etch resistance

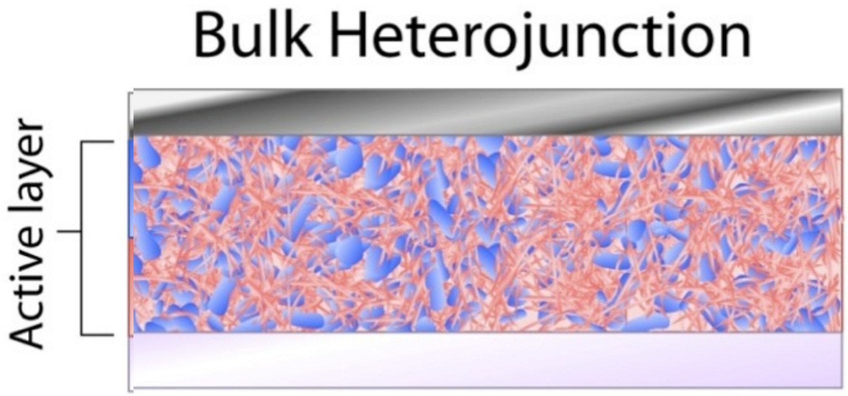


AlOx pattern (polymer removed)

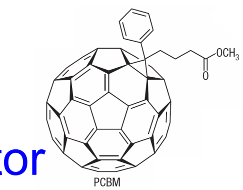


Etched silicon grating

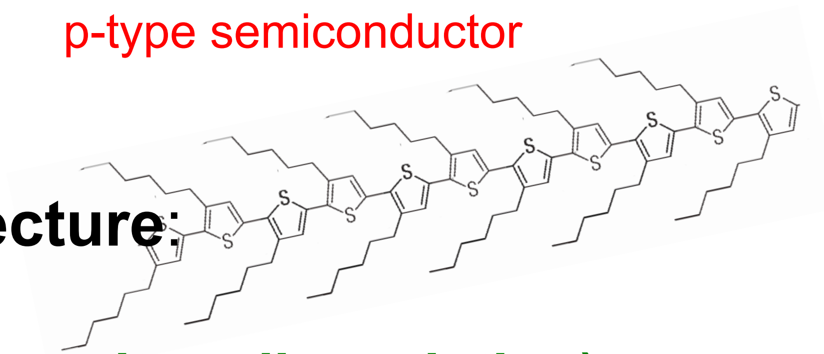
Organic semiconductor solar cell design



C60 derivative
n-type semiconductor



polythiophene (P3HT)
p-type semiconductor



Consequences of device architecture:

Good:

- **High interface density (good for exciton dissociation)**

Bad:

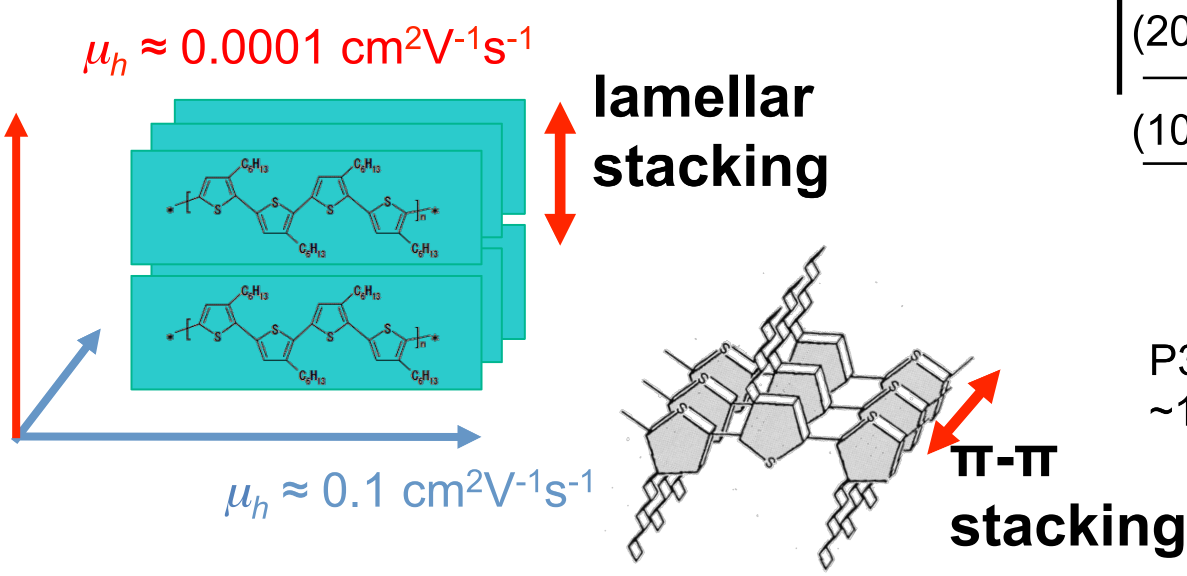
- **High interface density (increased recombination)**
  esp. problematic with poor electronic mobilities

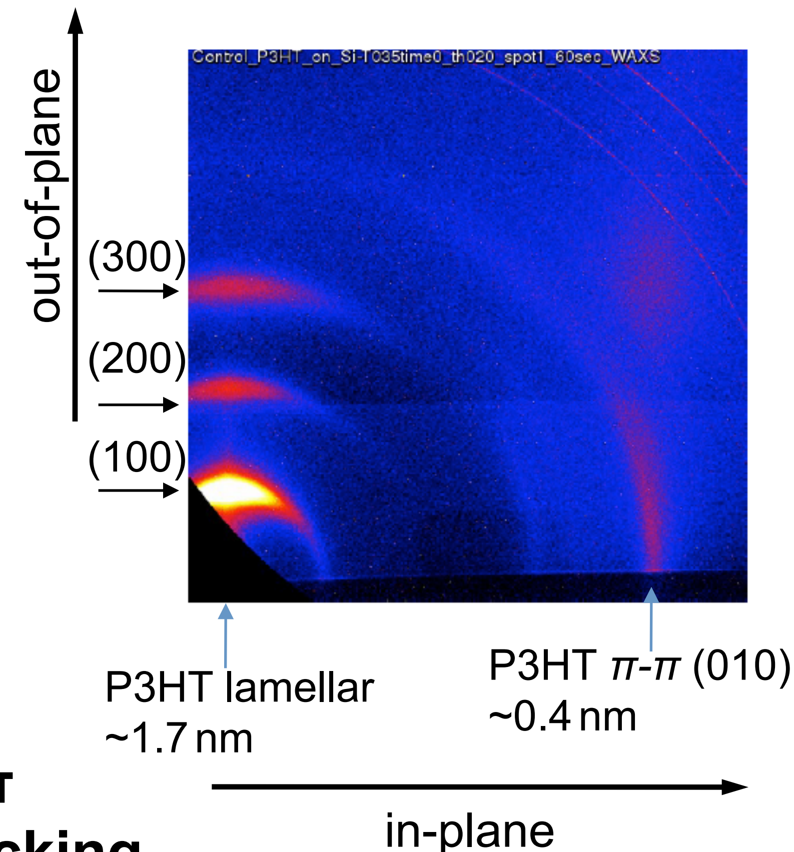
P3HT structure and electronic properties

Regioregular polythiophene (P3HT) is a semi-crystalline polymer

P3HT has “good” mobility perpendicular to lamellar stacking

P3HT has poor mobility along lamellar stacking direction

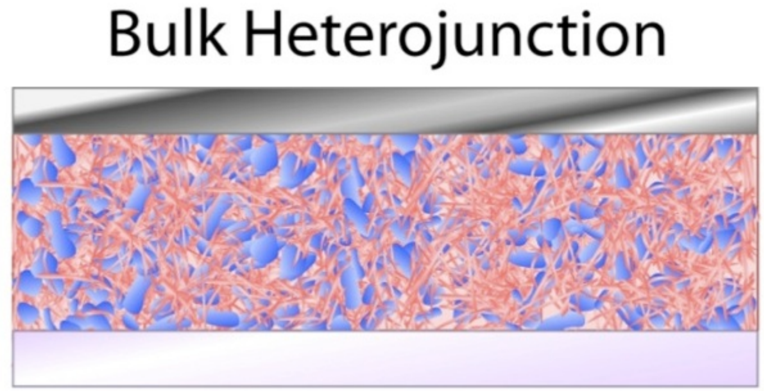




Organic semiconductor bulk heterojunction

Self-organization occurs on two length scales

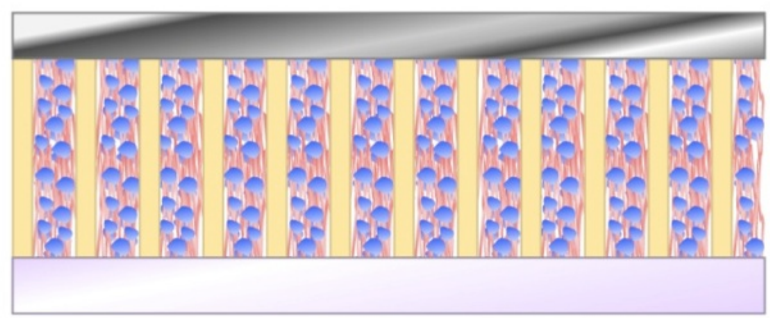
- *spinodal decomposition to form domains*
- *blend components crystallize*



Good device performance requires trapping in non-equilibrium state

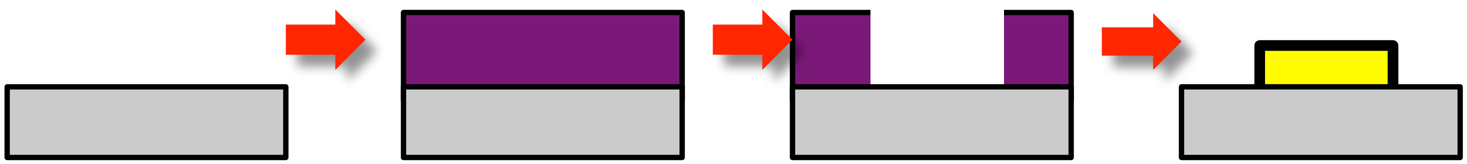
Idea: Confine blend material to nanometer-scale volumes

- *Control/stabilize phase separation (i.e., keep domains small)*
- *Change structural order?*
- *Change material properties?*



How to pattern an organic material?

Typical lithography: Use organic materials (resists) to pattern inorganics

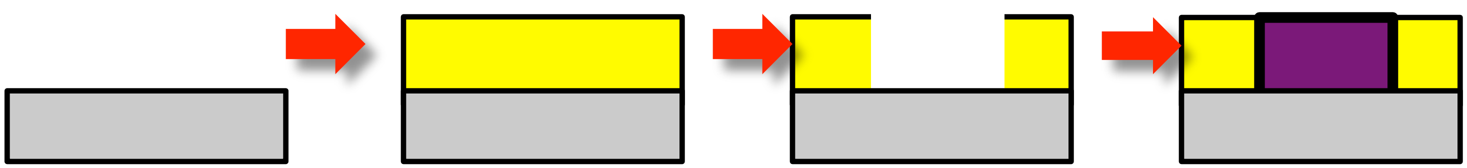


apply organic (resist)

pattern organic

transfer pattern to inorganic (e.g. metallization)

Our approach: Use inorganic materials to pattern organics



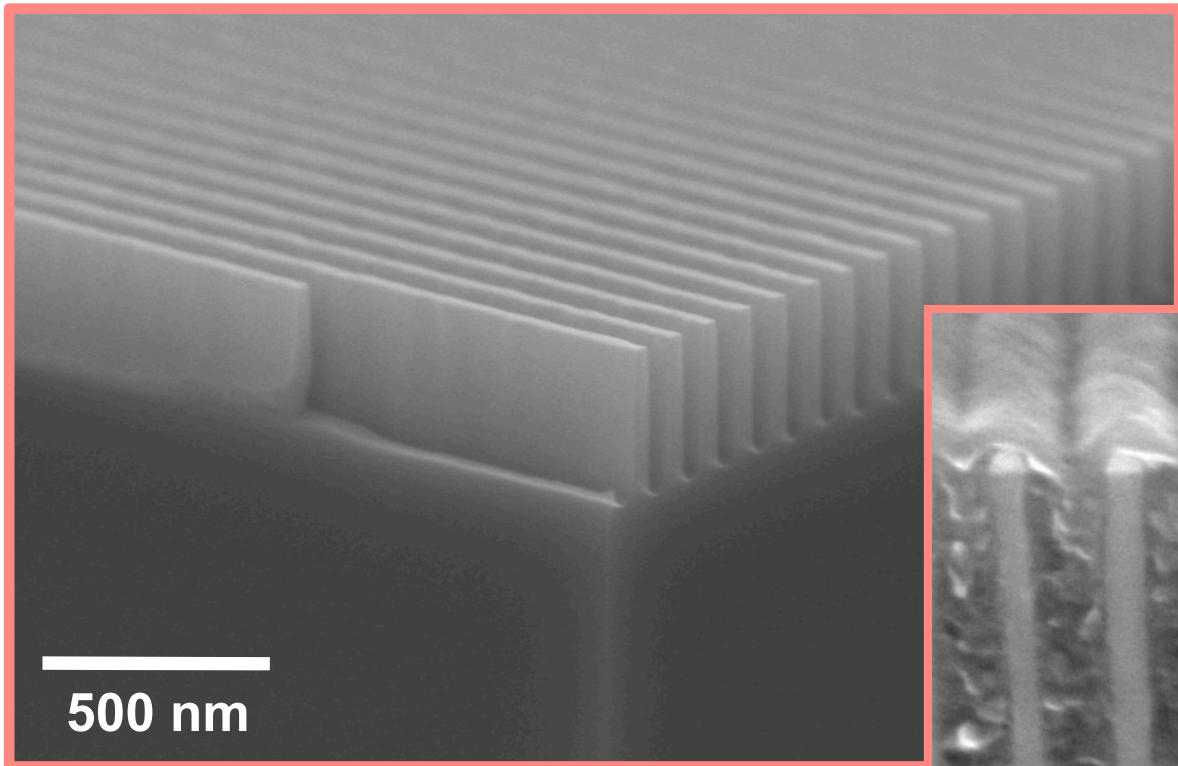
apply inorganic

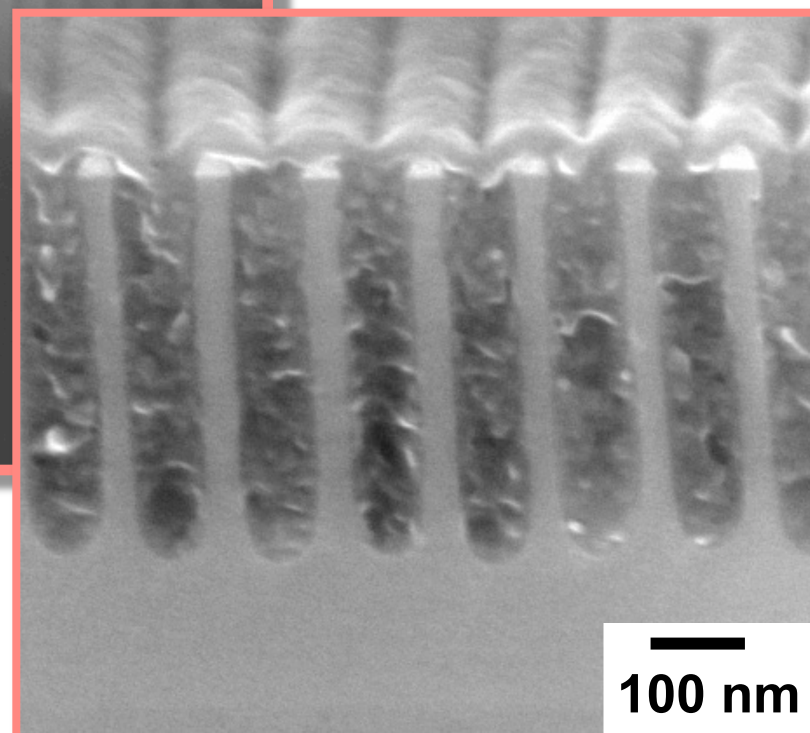
pattern *inorganic*

transfer pattern to organic

Controlling P3HT crystal orientation

Dan Johnston, CFN



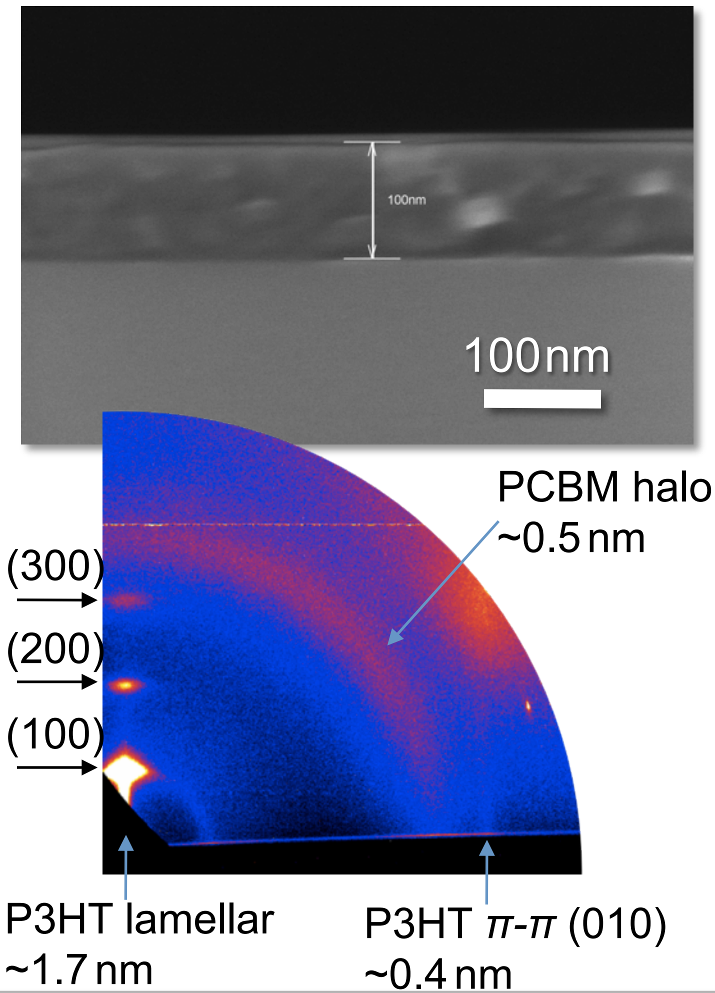


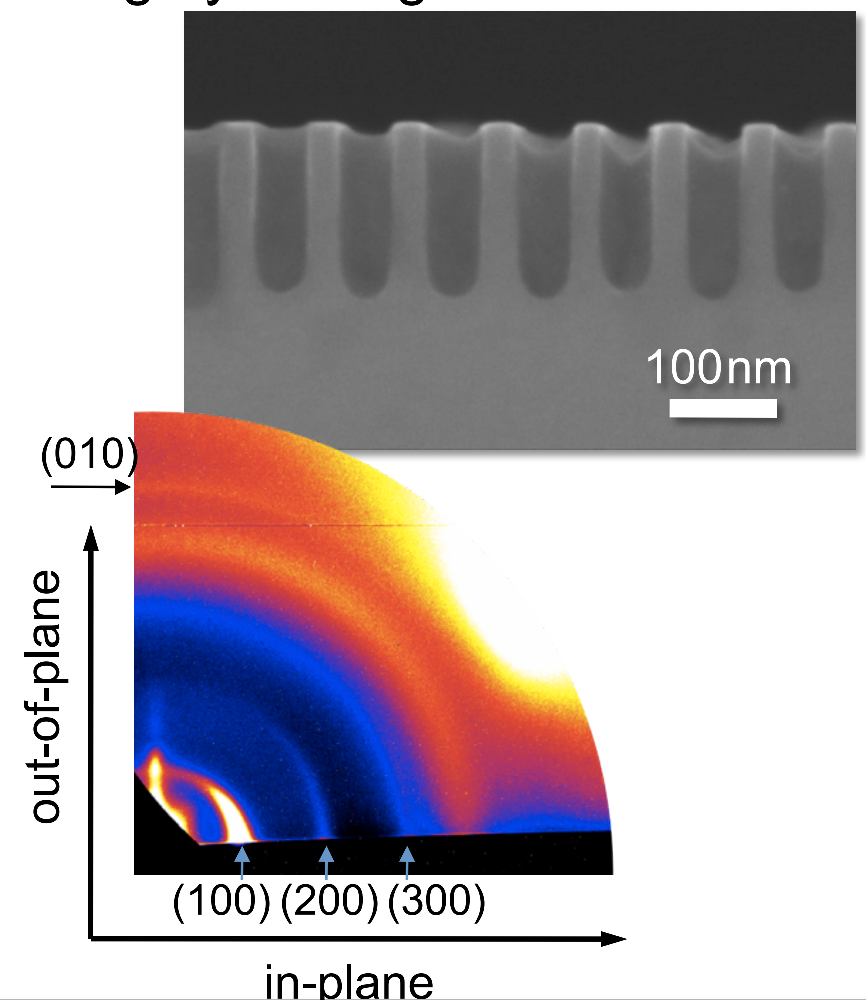
- 40nm linewidth
- variable pitch
- ~0.5 um line depth
- 2x2 mm^2 area

Controlling P3HT crystal orientation

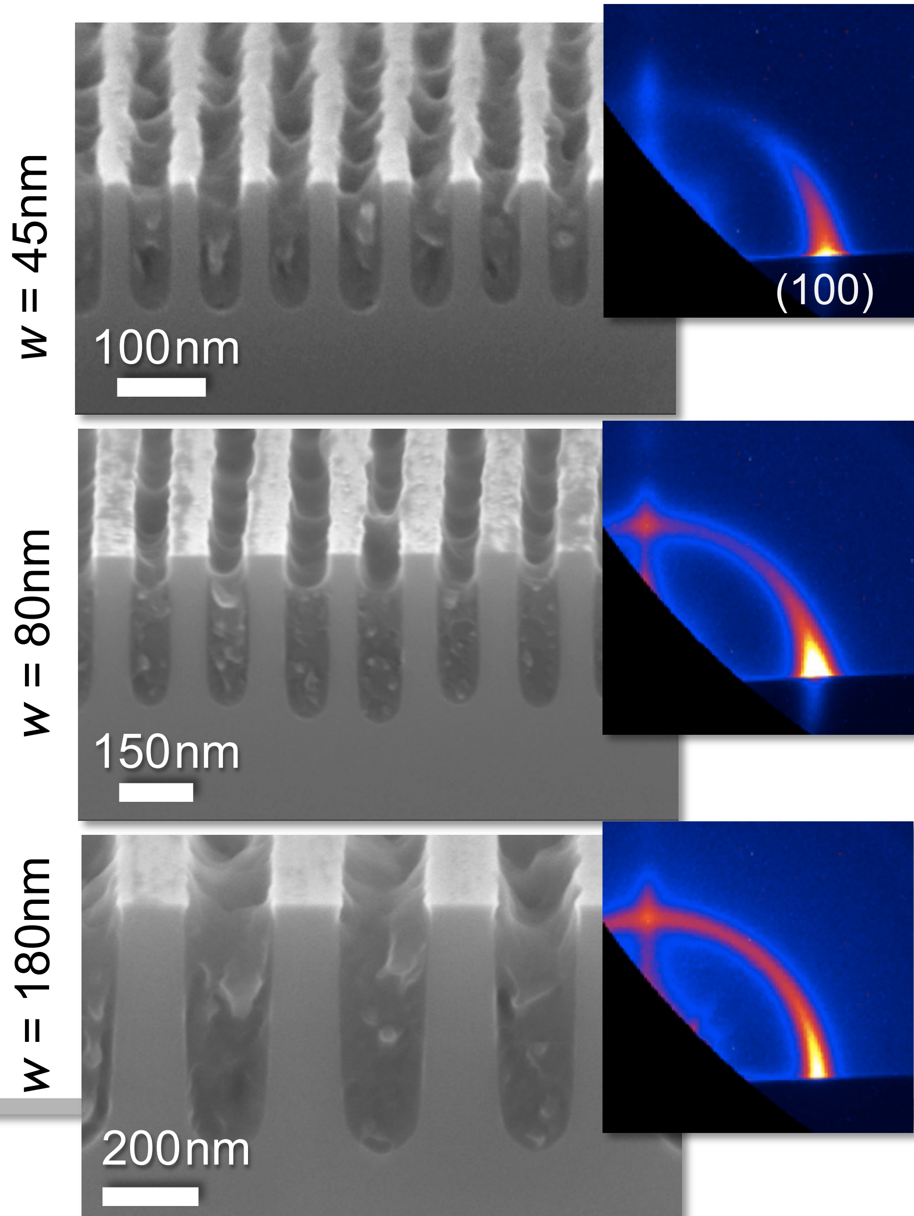
Dan Johnston, CFN

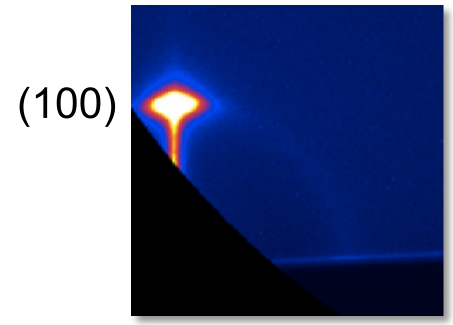
Grating re-orients P3HT crystal stacking by 90 degrees



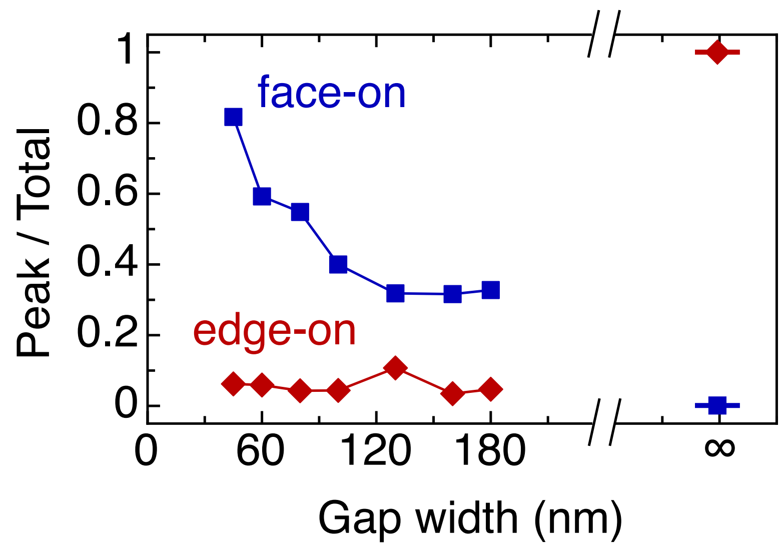


Controlling P3HT crystal orientation



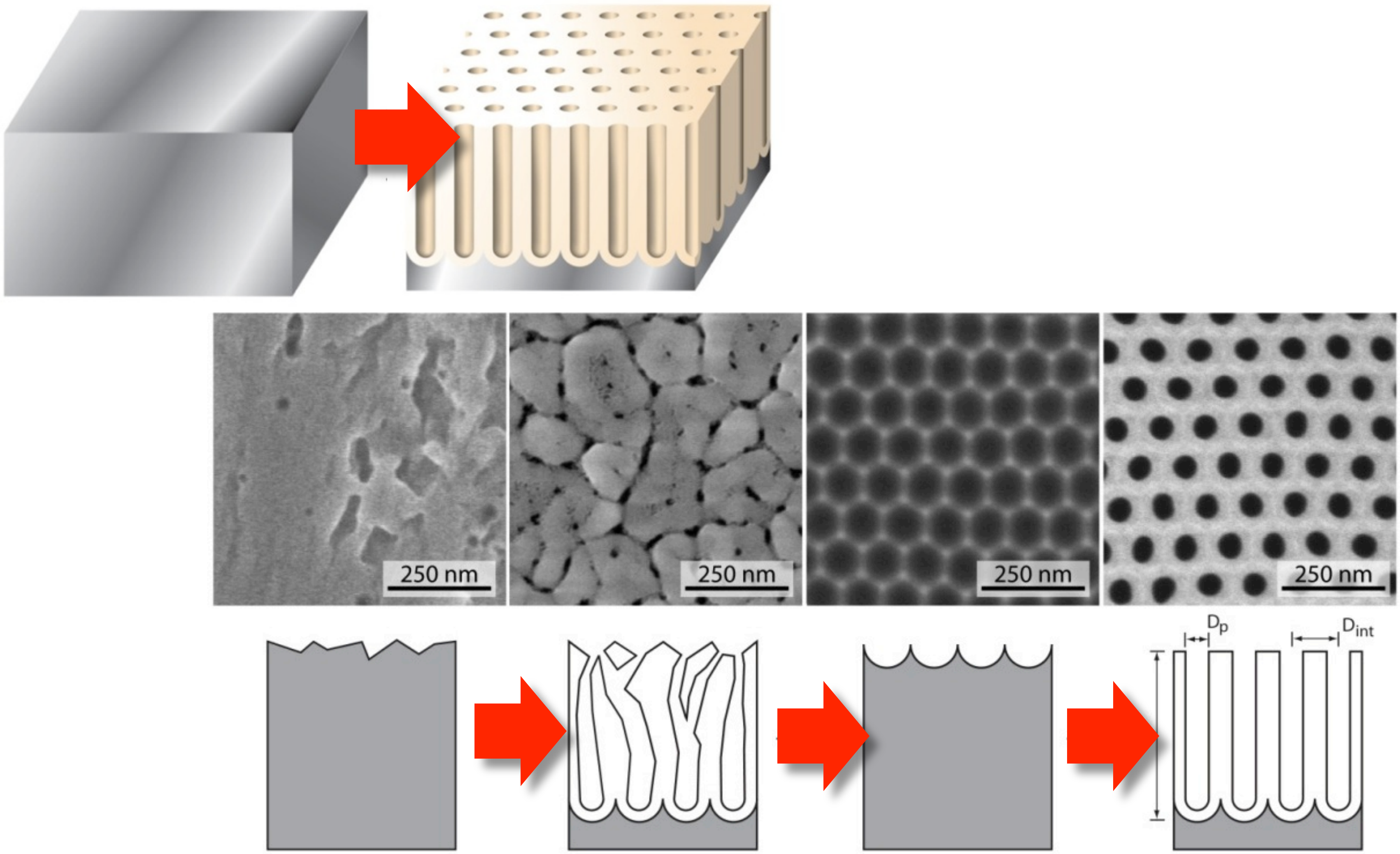


flat substrate

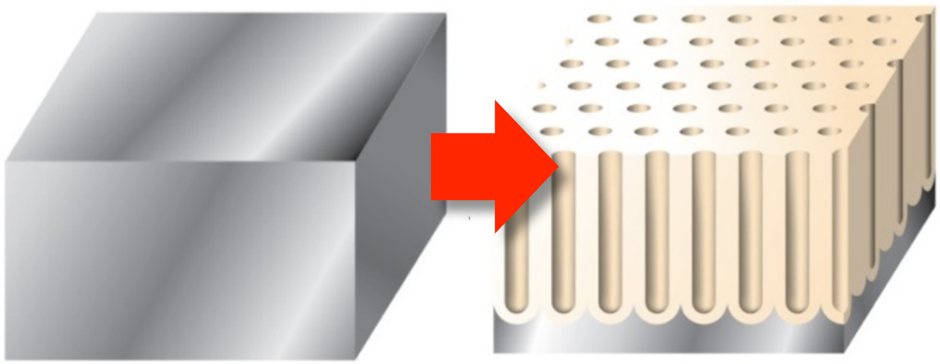


Self assembly of porous aluminum oxide

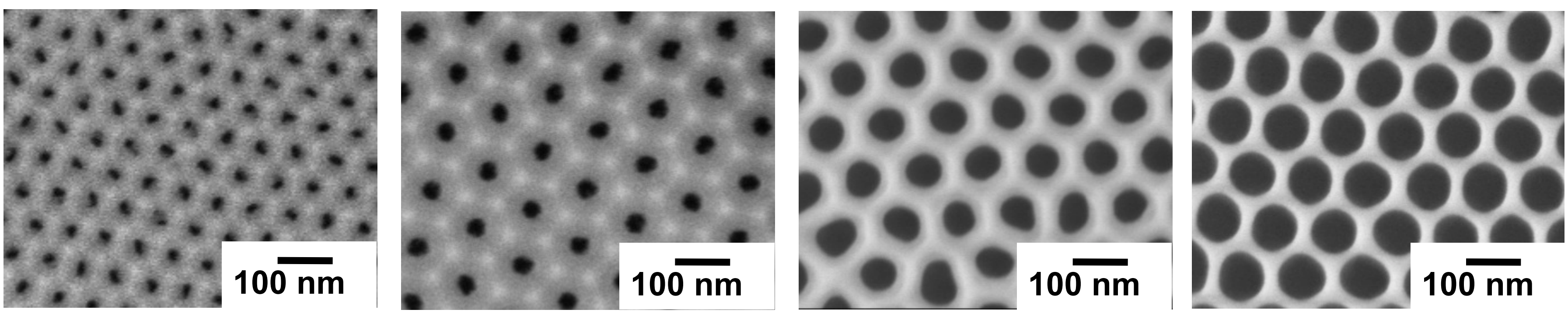
H. Masuda and K. Fukuda, Science **268** 1466 (1995).



Self assembly of porous aluminum oxide



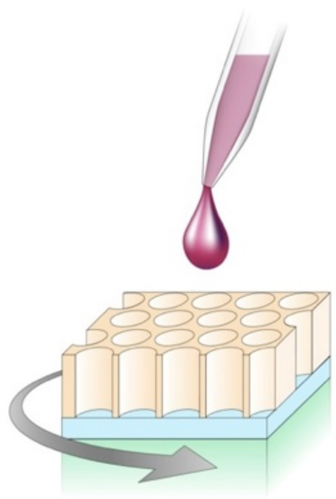
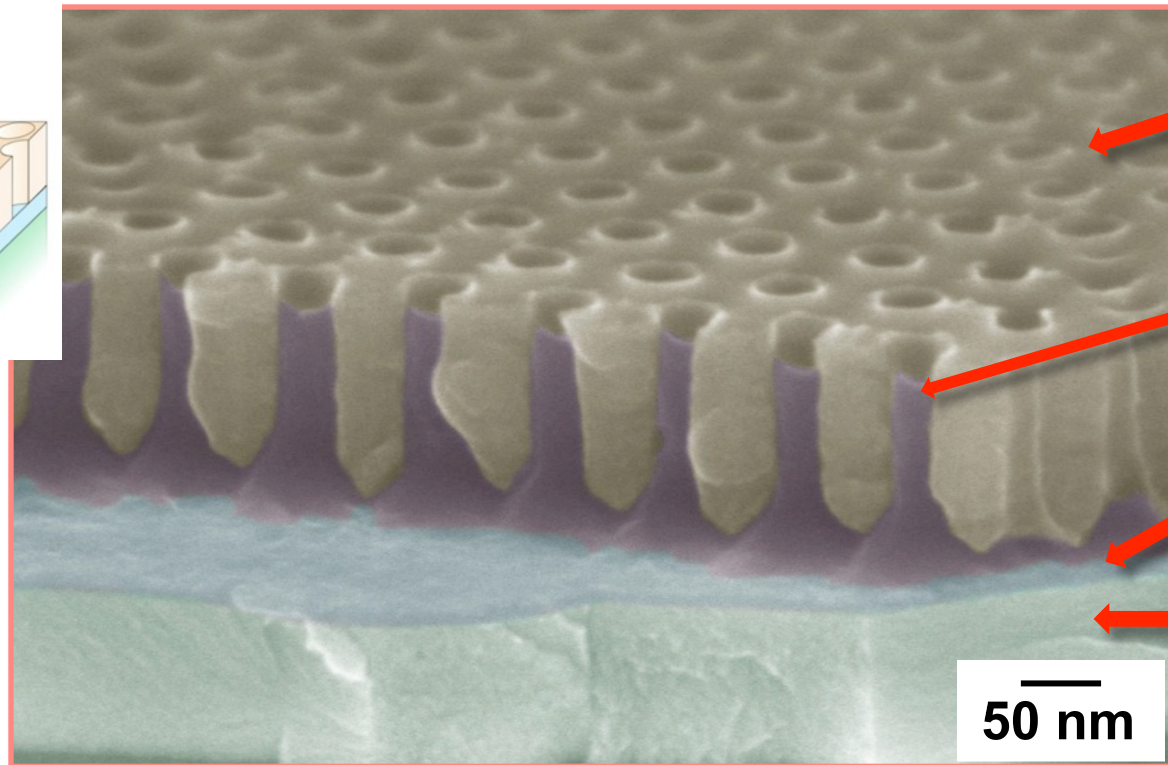
- Tunable nanometer-scale dimensions (size, separation, porosity)
- Extreme aspect ratios possible
- Large-area patterning
- Reasonable size uniformity
- Chemically and thermally robust
- Optically transparent
- Electrically insulating



20 nm 35 nm 65 nm 85 nm

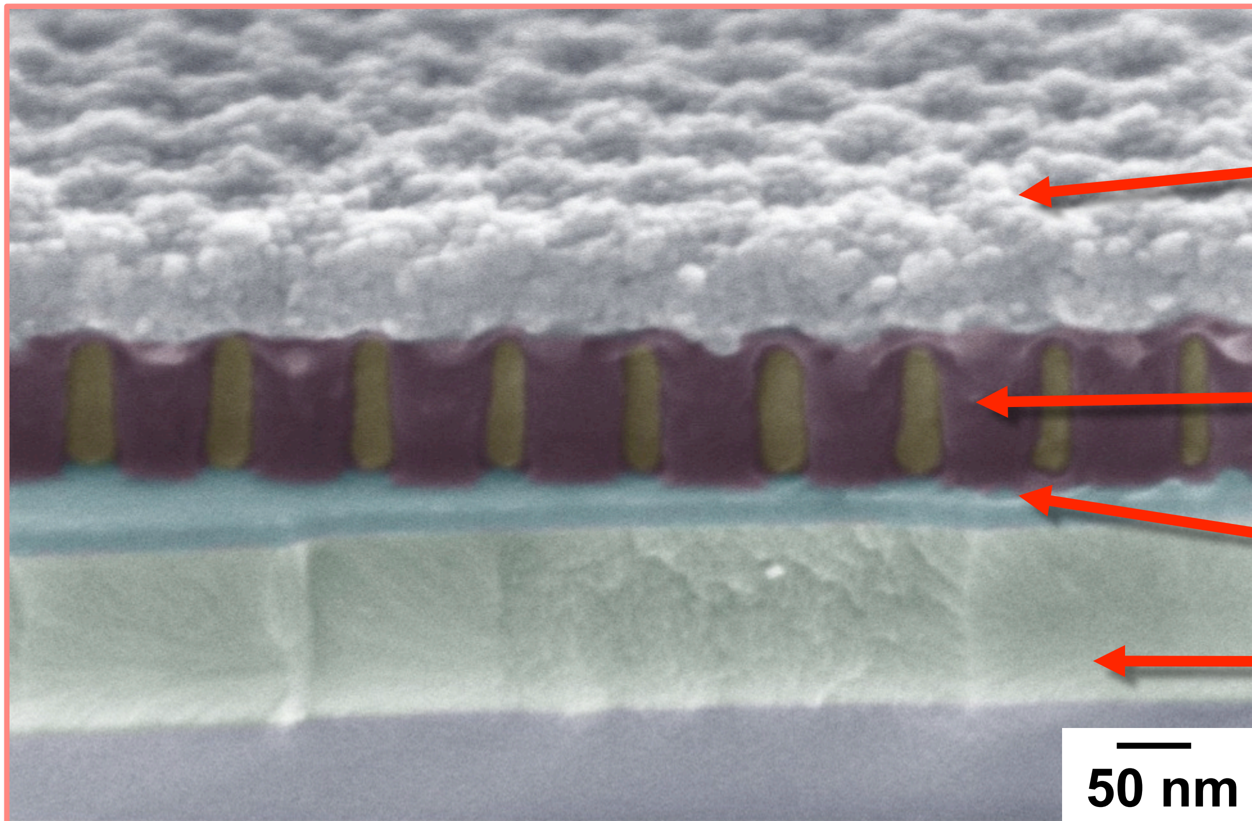
Patterning organic semiconductors

Jon Allen, CFN

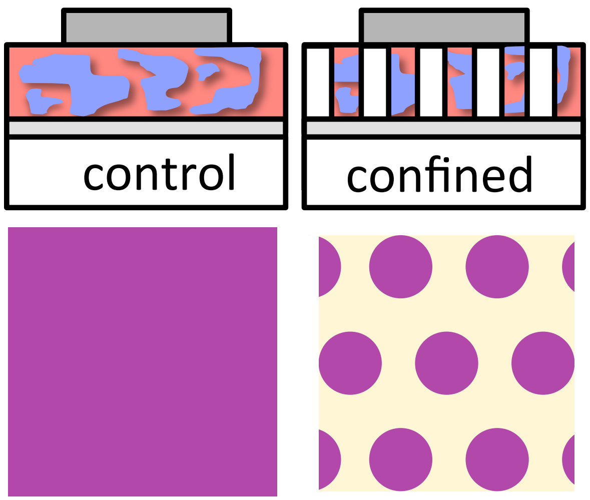
Patterned organic semiconductor solar cell

Jon Allen, CFN

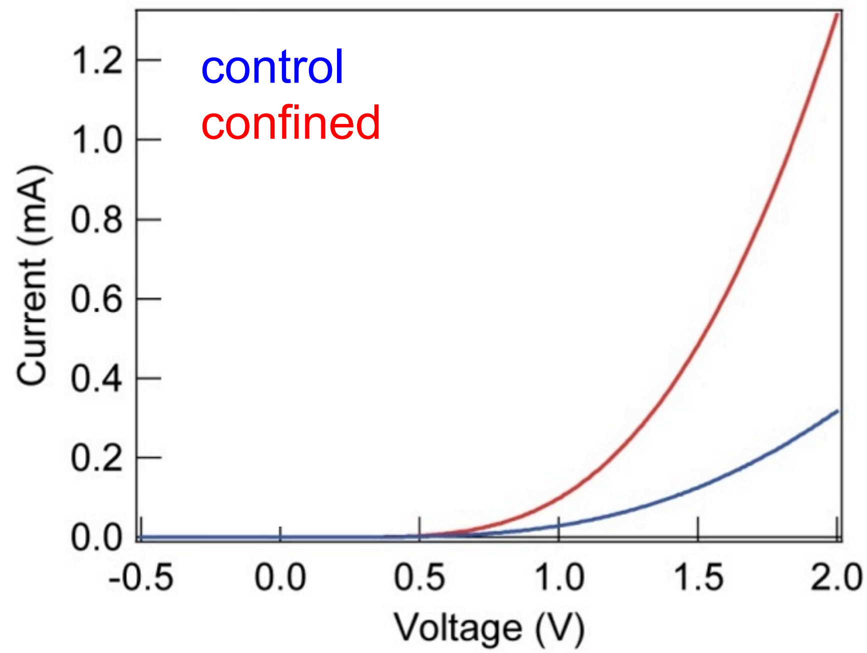


Nanostructured organic semiconductor performance

Confined devices carry **~5x MORE current** in forward bias despite containing **~3x LESS material**

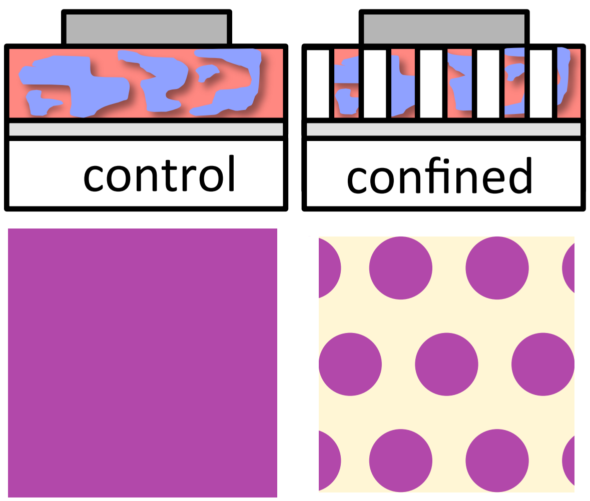


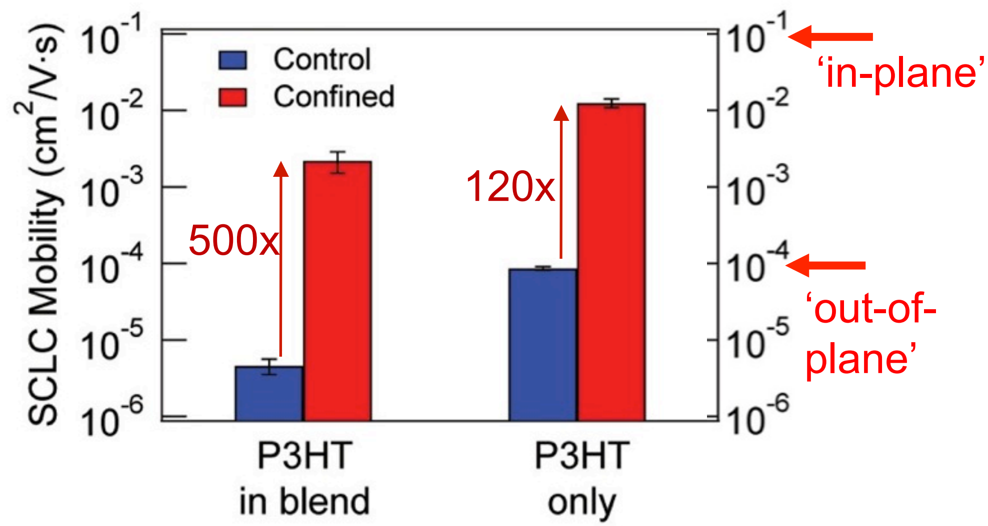
Confined area is 37% of device area



Nanostructured organic semiconductor performance

P3HT hole mobility **enhanced ~500X** by confinement

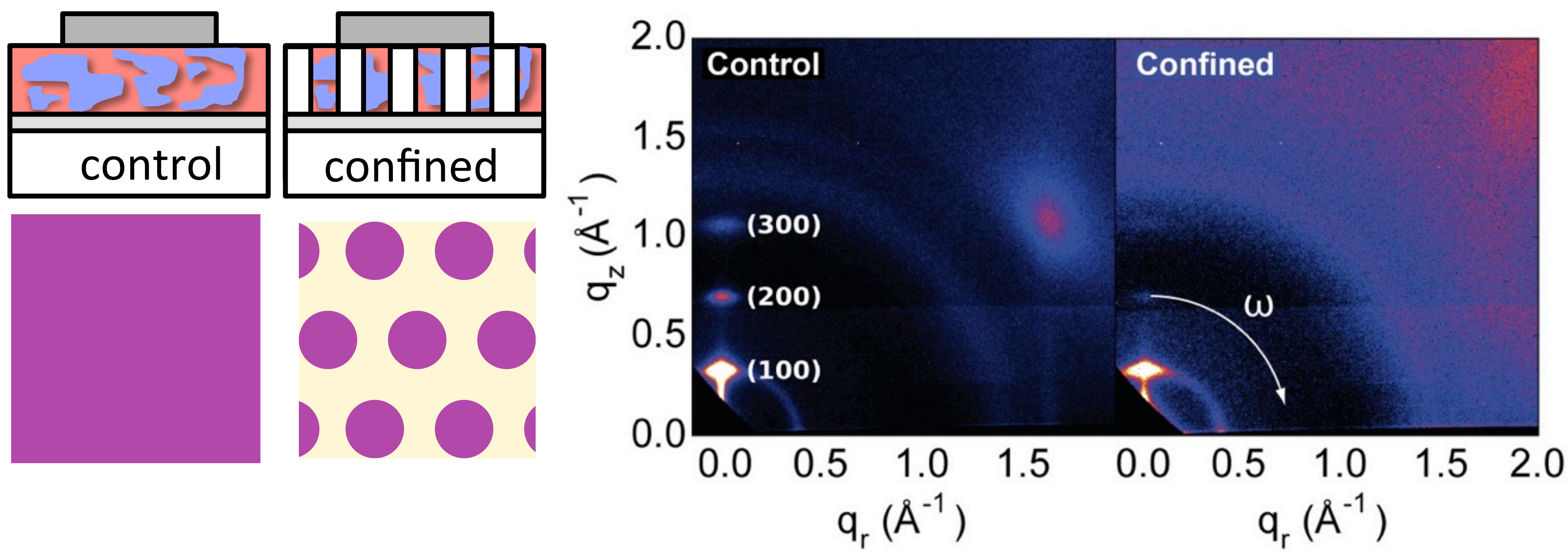




P3HT enhancement first reported by
K. M. Coakley, M. D. McGehee et al., *Adv. Funct. Mat*. **15**, 1927 (2005).

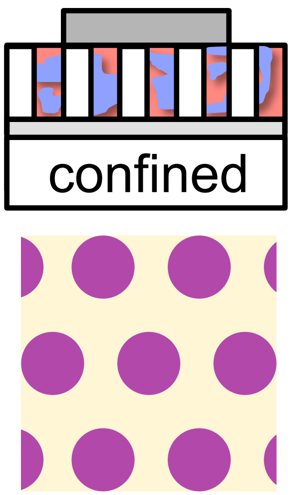
Confined organic semiconductor structure

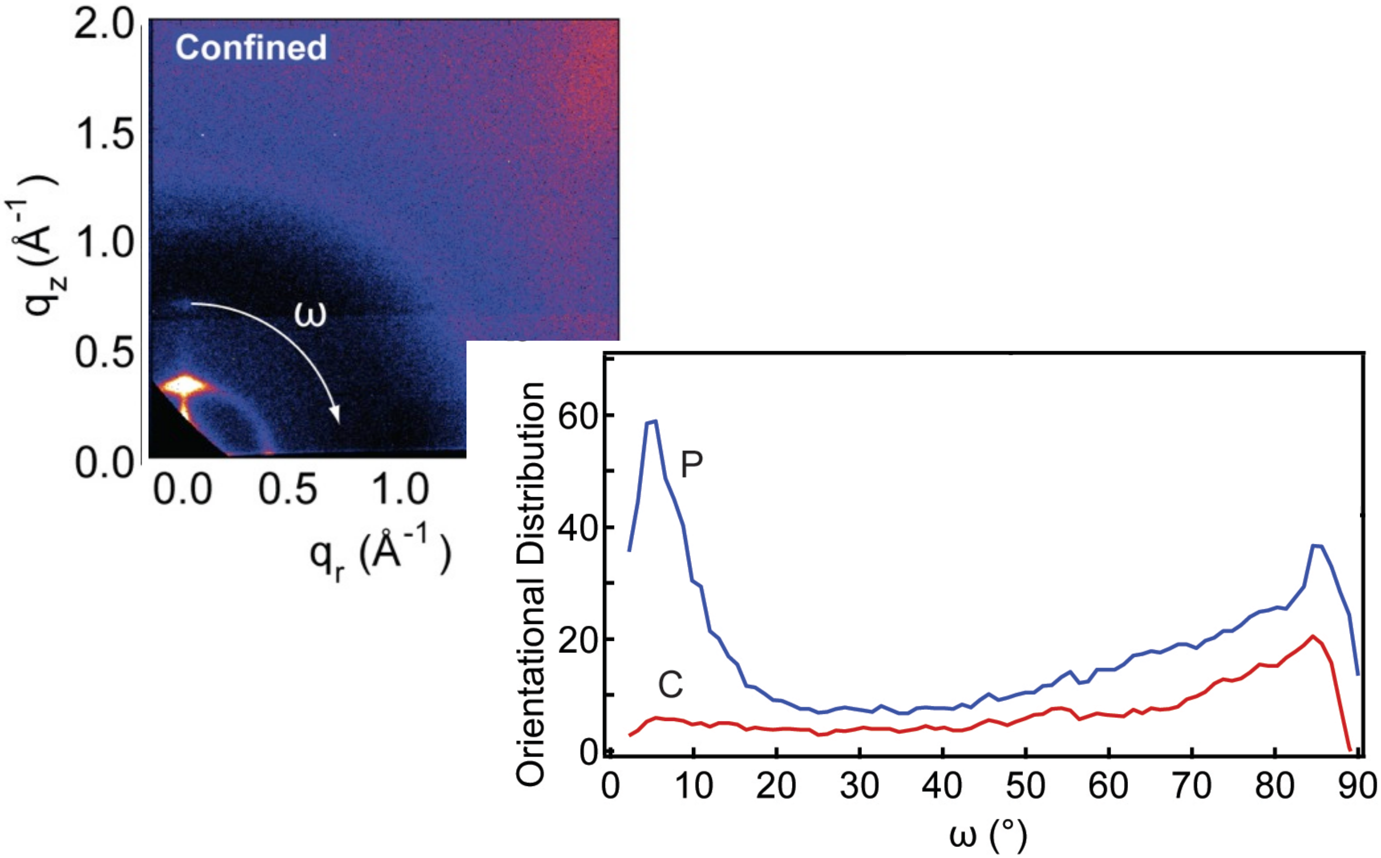
- No evidence for 90 degree P3HT reorientation
- Rather, confinement disrupts polymer ordering
  - Reduced scattering intensity (less crystallinity)
  - Reduced P3HT crystallite size (20nm to 16nm)



Confined organic semiconductor structure

P3HT mobility enhancement instead due to suppressed perpendicular lamellar stacking



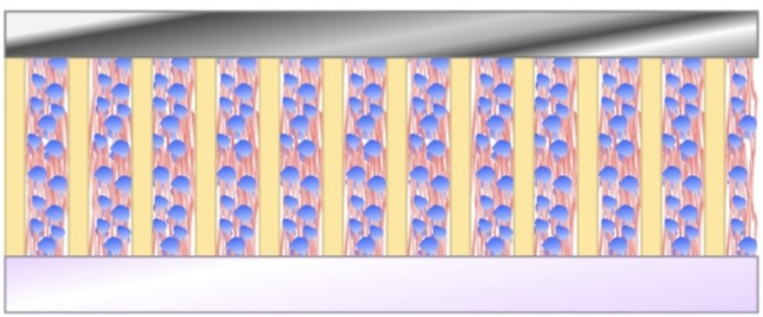


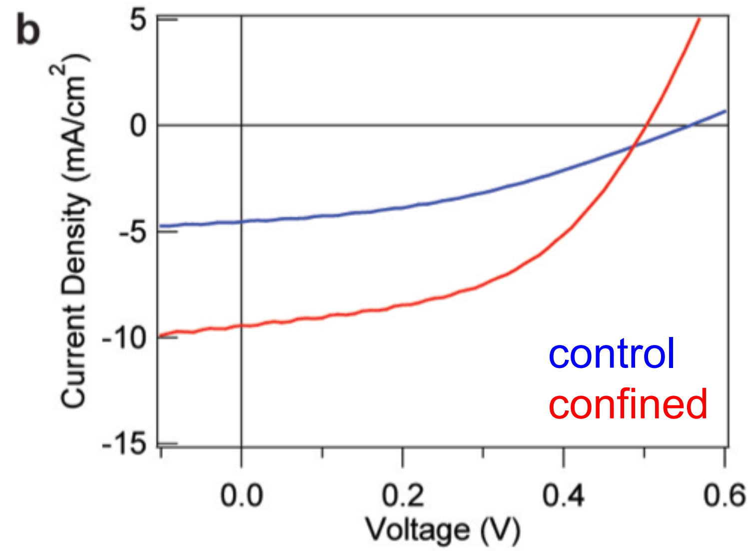
Nanostructured organic semiconductor performance

Confined P3HT:PCBM produces **~2x** the photocurrent density of an equivalent volume of unconfined material

(P3HT mobility increases by $>10^2$)

Why not more photocurrent improvement?

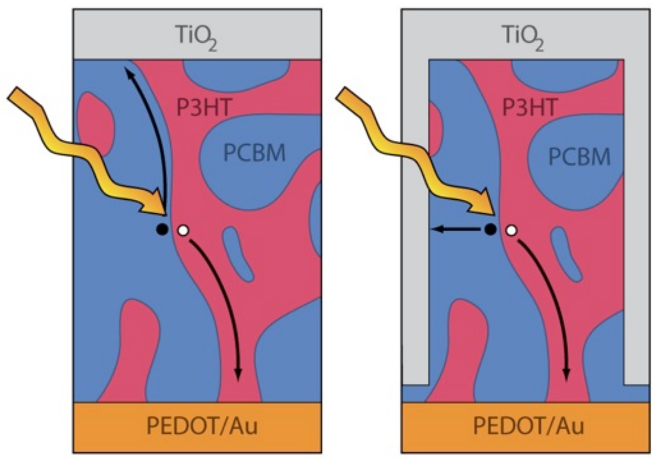




Performance limited by the worse of the **two** semiconductor mobilities

Improving electron collection in confined solar cells

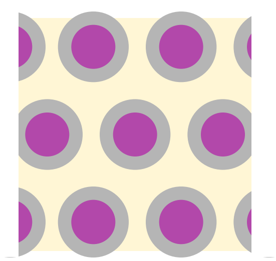
Introduce radial contact to shorten electron collection pathway

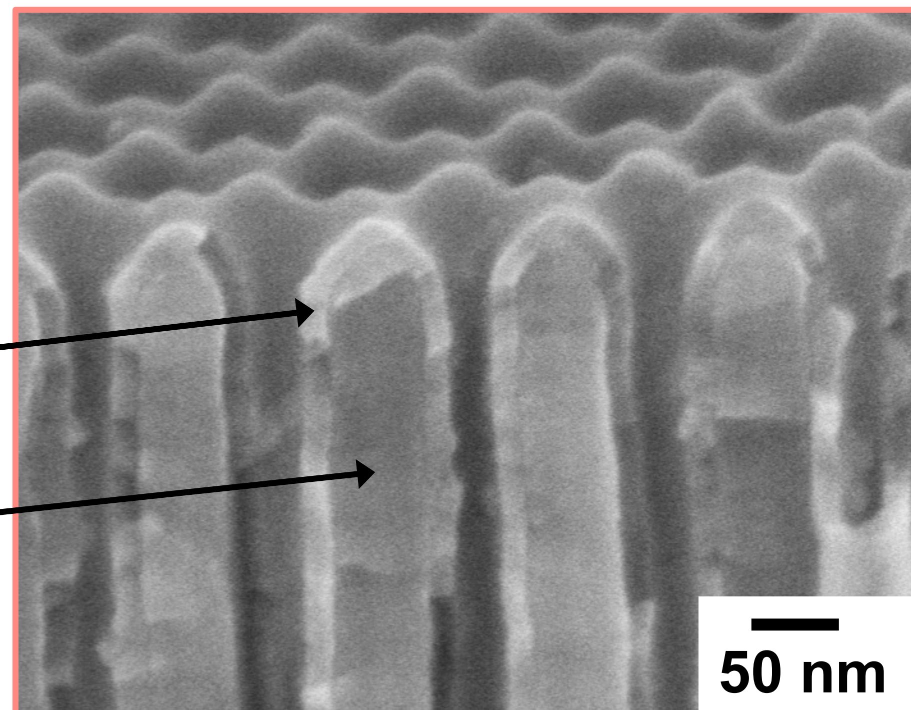


planar radial

TiO_2 (electron acceptor)

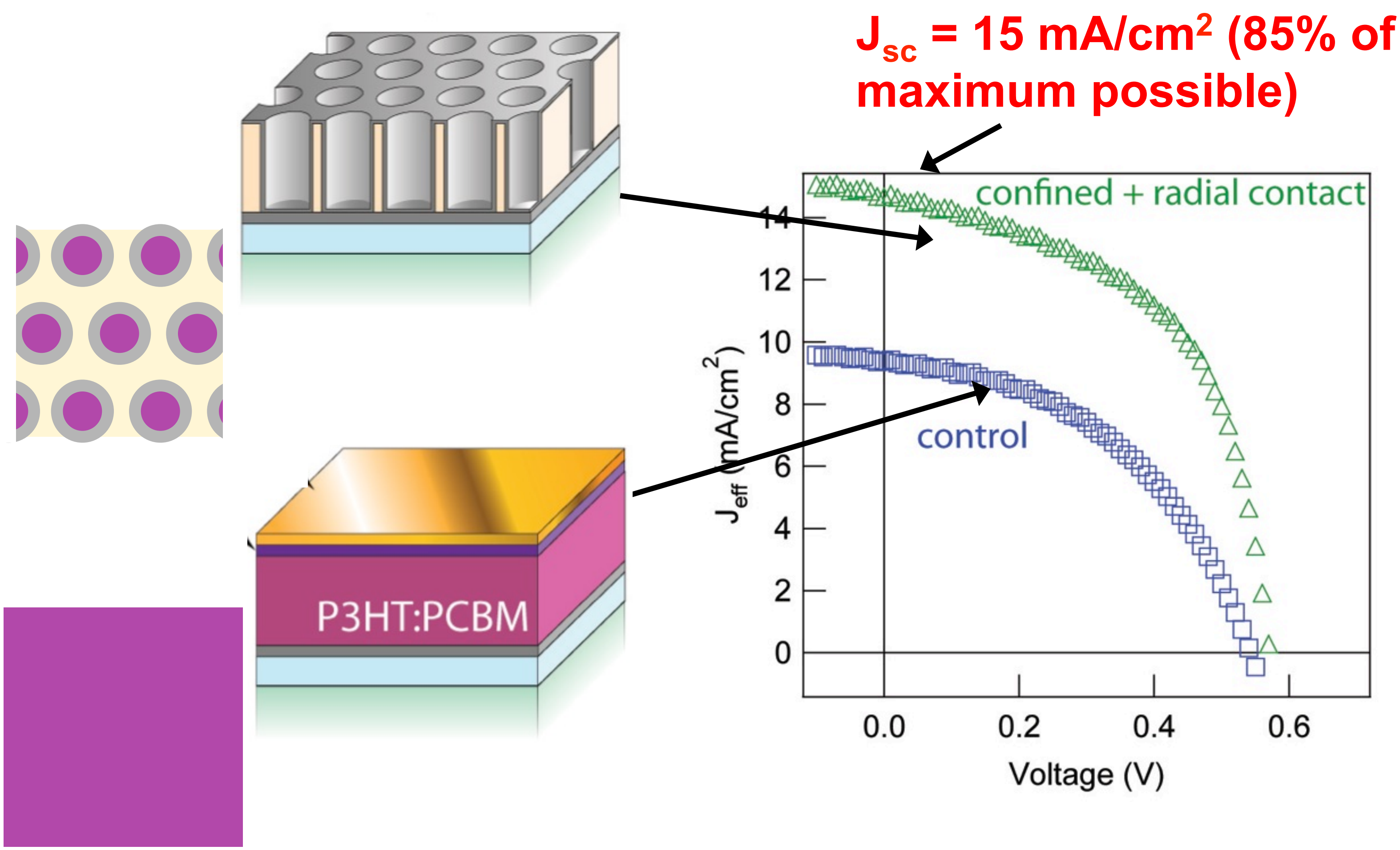
AlOx (template)





Improving electron collection in confined solar cells

Confined material performs ~50% better than control



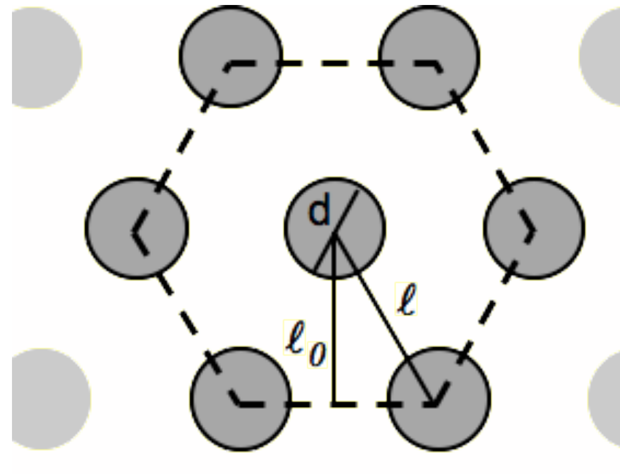
Leveraging confined polymer advantages

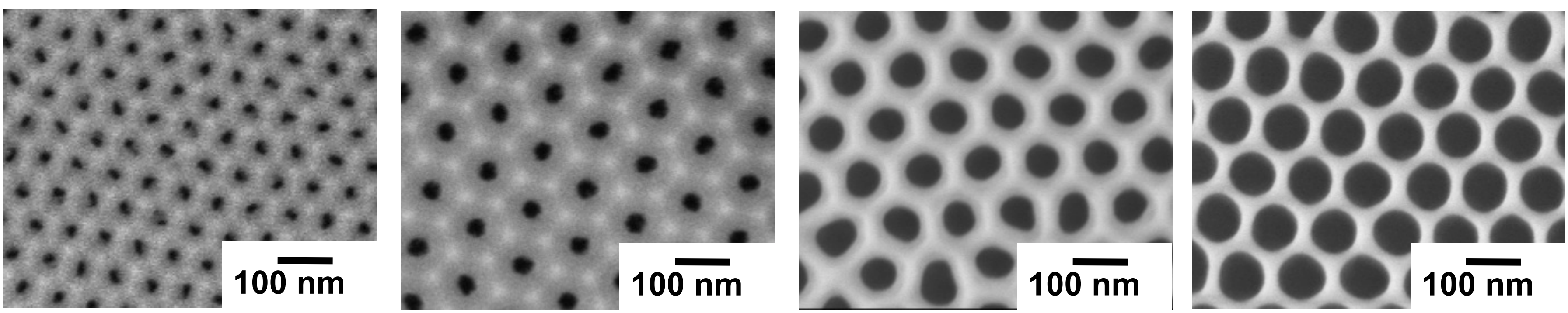
How to best take advantage of performance improvements?

Maximize template porosity (ϕ)
(i.e., minimize wasted space)

$$\phi = \frac{\pi}{2\sqrt{3}}\left(\frac{d}{\ell}\right)^2 \approx 0.9\left(\frac{d}{\ell}\right)^2$$

90% porosity possible



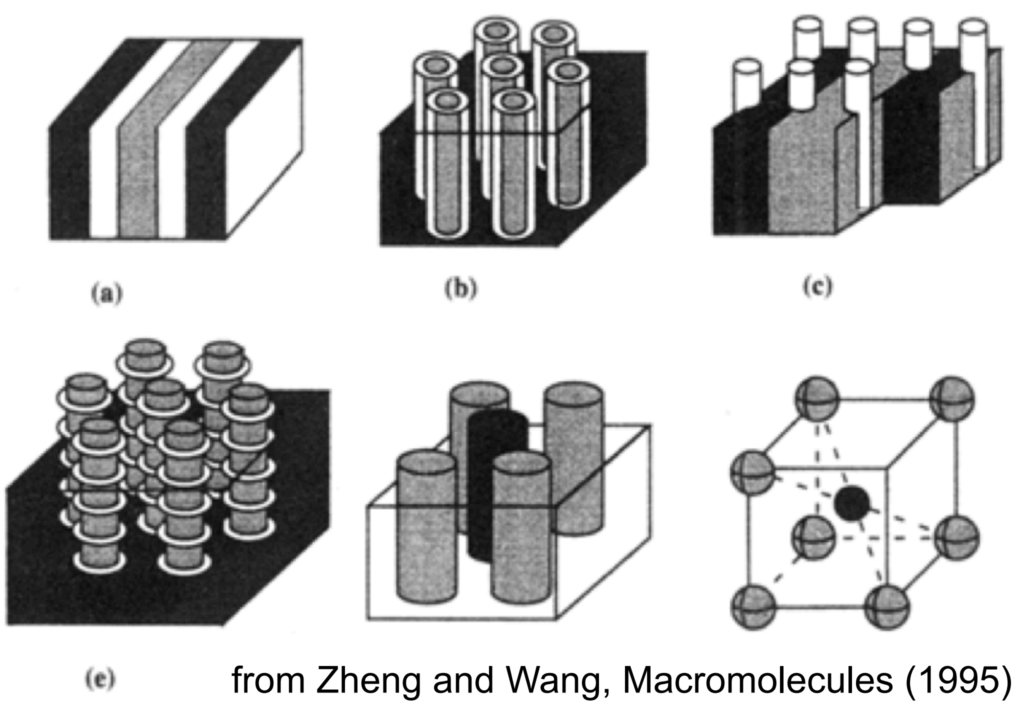


20 nm | 35 nm | 65 nm | 85 nm

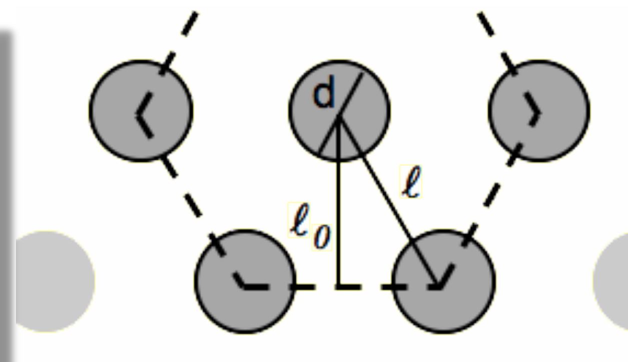
Leveraging confined polymer advantages

How to best take advantage of performance improvements?

Can we make the entire coaxial structure with polymers?



from Zheng and Wang, Macromolecules (1995).



Message

Self assembly:
- Is a tool for device fabrication (similar to lithography)
- Provides access to sub-lithographic length scales

Self assembly for semiconductor devices
- Significant challenges to application to technology
- Significant advances from groups around the world

Self assembly as a tool for understanding photoconversion and improving performance
- Controlling organic semiconductor structure
- Changing organic semiconductor electronic properties

Acknowledgements

IBM group members:

Ricardo Ruiz (now at Hitachi)
Ying Zhang (now at TSMC)
Kathryn Guarini

CFN group members:

Jon Allen
Dan Johnston

X-rays:

Kevin Yager
Htay Hlaing (SUNY Stonybrook)
Xinhui Liu
Ben Ocko

Work supported by Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy

U.S. DEPARTMENT OF ENERGY
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