



High-throughput screening of adhesion and release in nanoimprint lithography

*Christopher M. Stafford, Hyun Wook Ro, Ronald L. Jones,
Michael J. Fasolka, Christopher L. Soles*

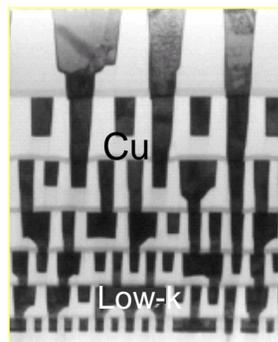
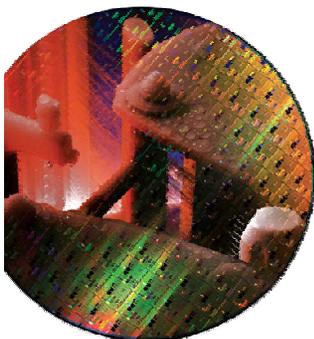
*Polymers Division
Materials Science & Engineering Laboratory
National Institute of Standards and Technology*



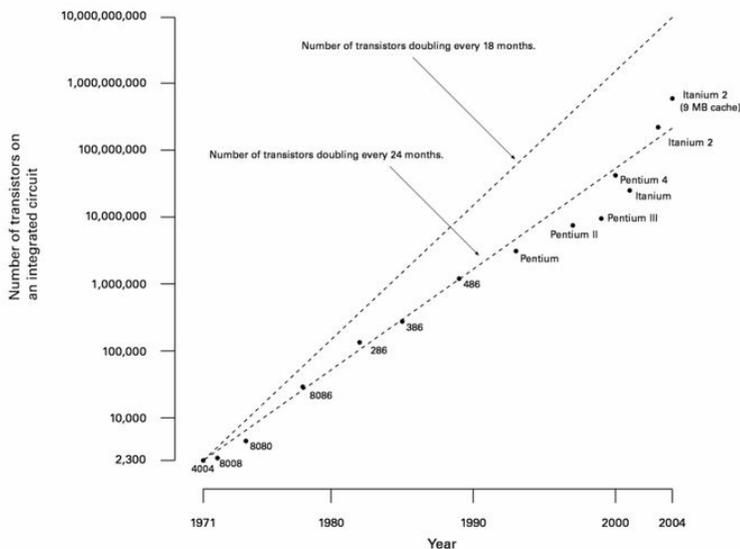


Introduction

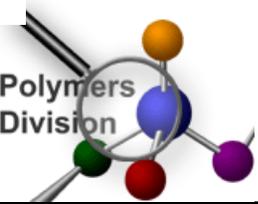
- Advanced microprocessors are comprised of multilevel interconnects of Cu and low-k material with the minimum feature size approaching 50 nm.



Moore's Law



- As features continue to get smaller, current technologies will not be able to keep up with Moore's Law...
- Nanoimprint lithography (NIL) is a low-cost, high-resolution next-generation lithographic technique.



Nanoimprint Lithography

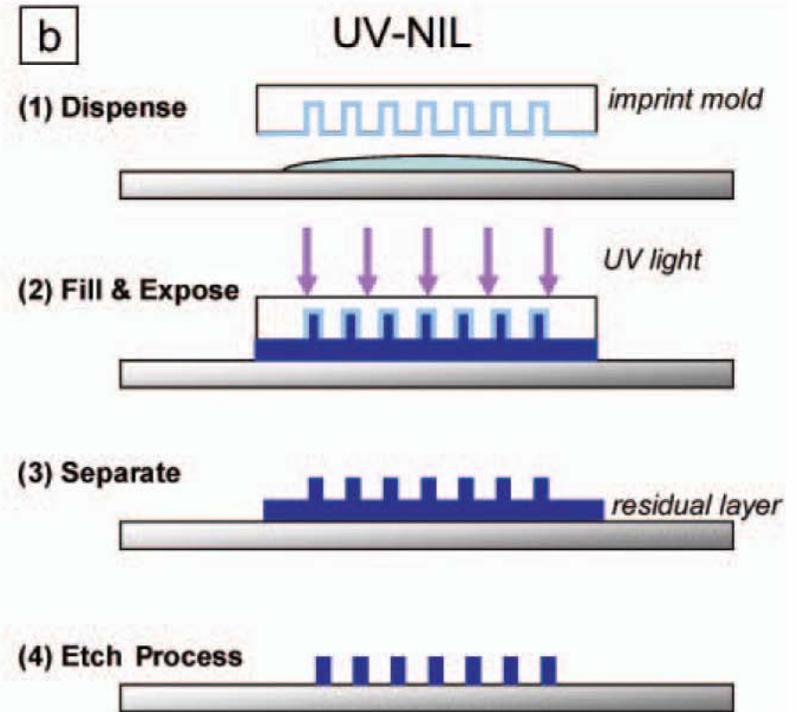
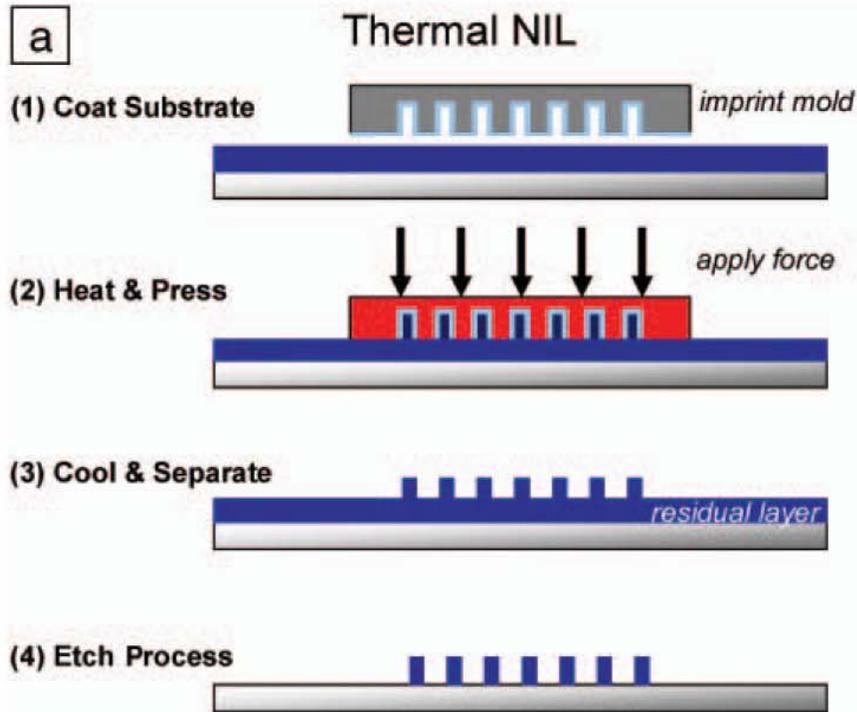
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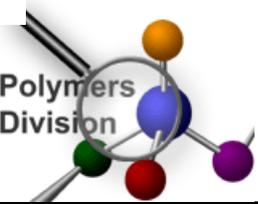
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S.Y. Chou *et al.*, *Appl. Phys. Lett.* **67**, 3114 (1995)

C.G. Willson *et al.*, *Proc. SPIE* **3676**, 379 (1999).

Image from: M.D. Steward and C.G. Willson, *MRS Bulletin* **30**, 947 (2005).



Adhesion to Patterned Surfaces

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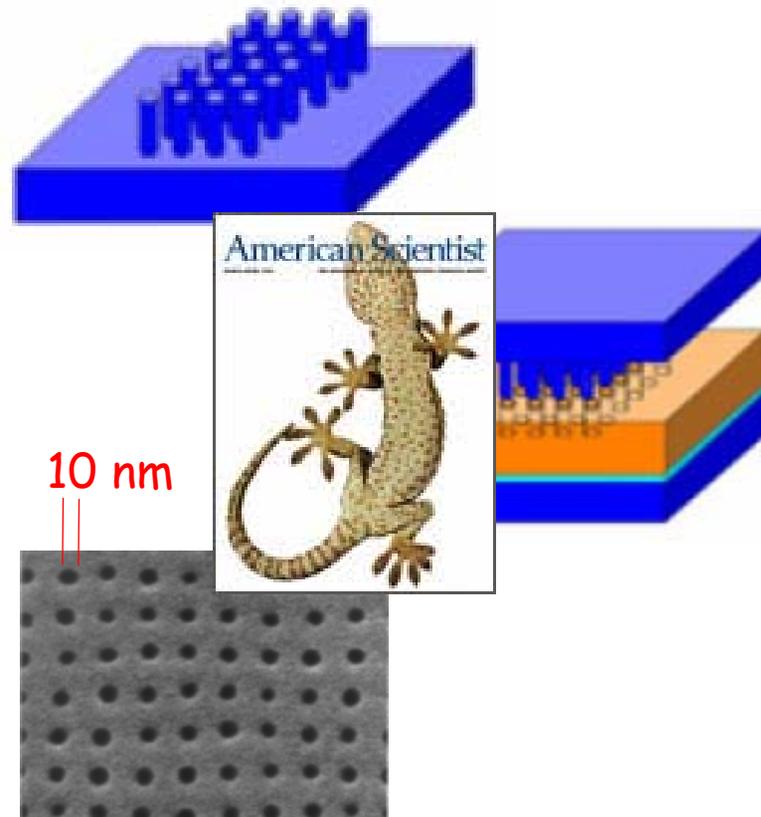
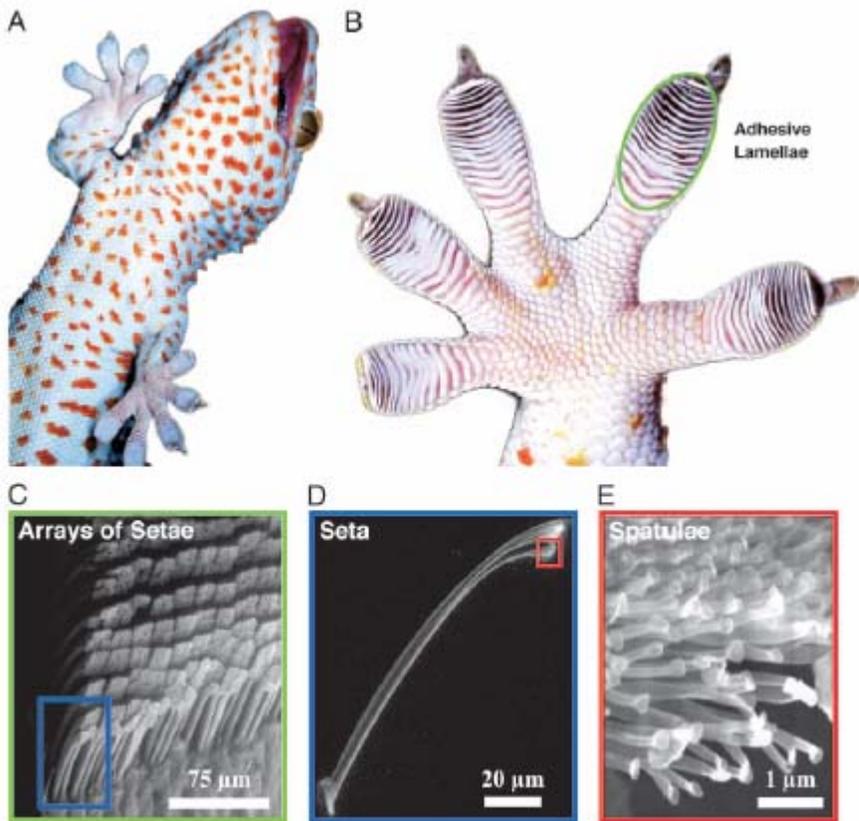
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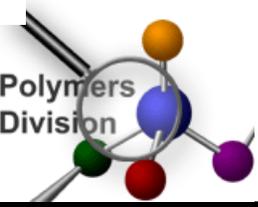
Lessons from mother nature

Implications for Nanoimprint



- Nanoscale spatulae provide enormous surface area
- van der Waals interaction huge

- Surface forces / van der Waals interactions will be important!



Nanoimprint Lithography

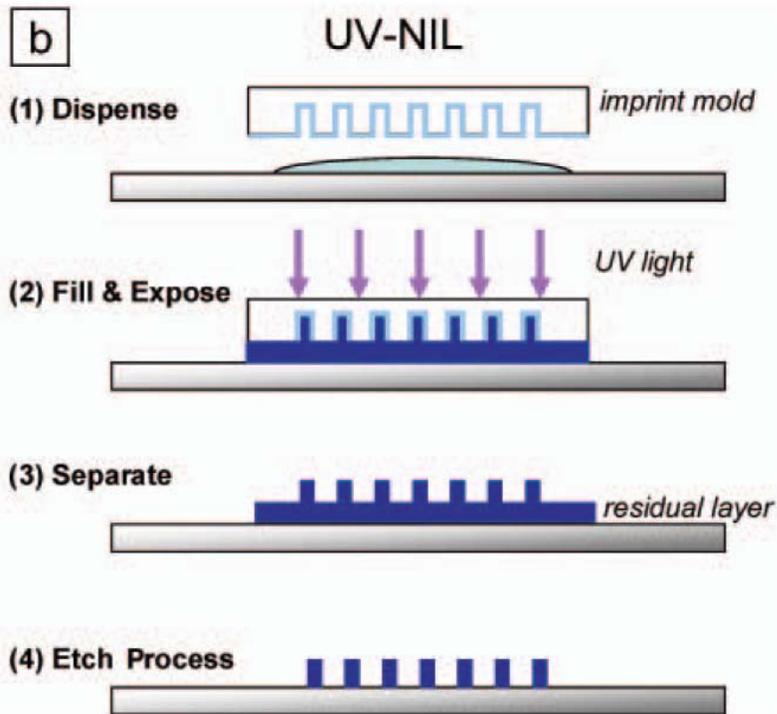
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ADVANTAGES

- Cheap and Easy Process
- No Feature Size Limitations
- High Throughput

DISADVANTAGES

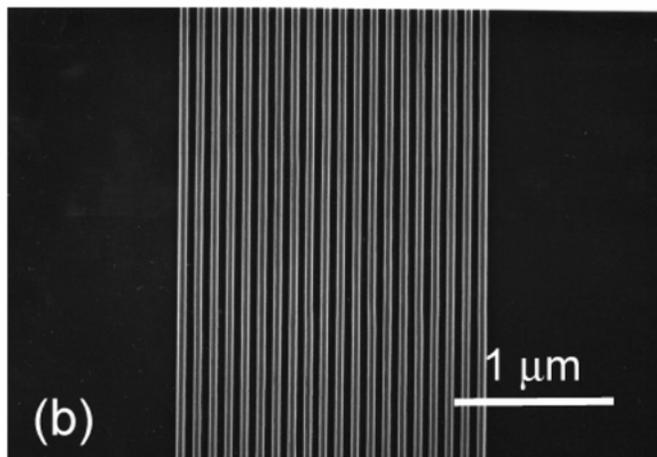
- Mold Adhesion to the resist
- Unknown or Varying Residual Layer Thicknesses

APPLICATIONS

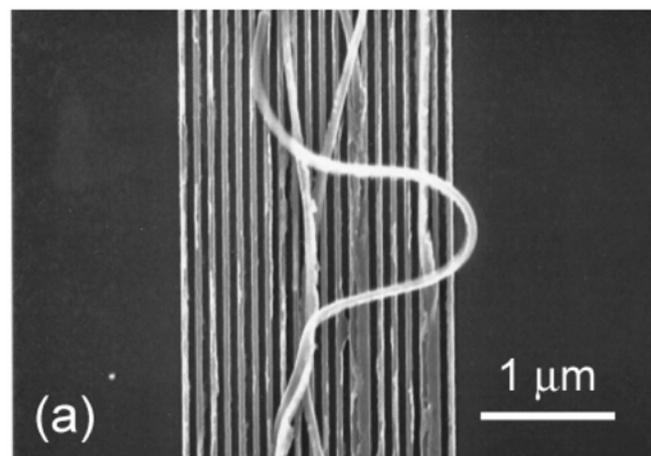
- Semiconductor chips
- Nanofluidic devices



mold

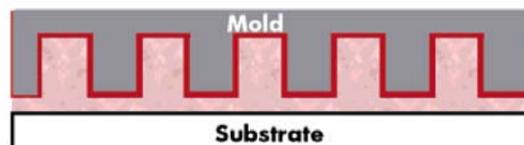


mold after imprinting



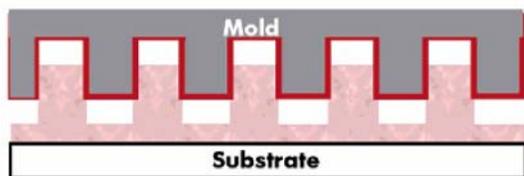


Adhesion in UV-NIL

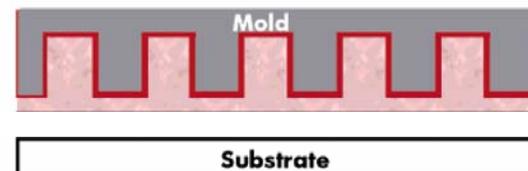


$$G_i = A_{r-s}\gamma_{r-s} + A_{r-m}\gamma_{r-m}$$

Case I



Case II



$$G_f = A_{r-s}\gamma_{r-s} + A_{r-m}(\gamma_r + \gamma_m)$$

$$G_f = A_{r-m}\gamma_{r-m} + A_{r-s}(\gamma_r + \gamma_s)$$

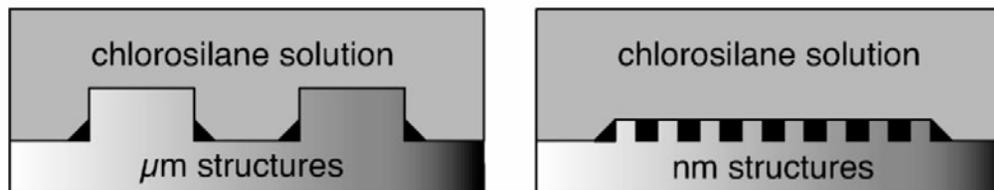
$$\Delta G_{detach} < \Delta G_{adhere}$$

$$A_{r-m}(\gamma_r + \gamma_m - \gamma_{r-m}) < A_{r-s}(\gamma_r + \gamma_s - \gamma_{r-s})$$



Treatment of Mold

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■ insufficient wetting

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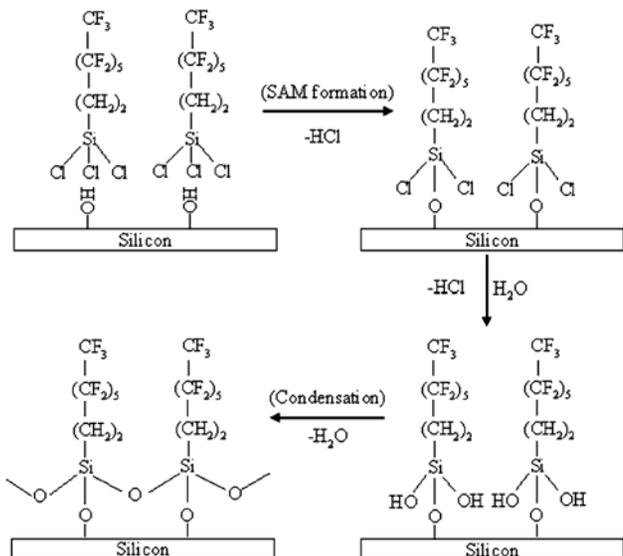


Table 1. Water Contact Angle and Ellipsometric Thickness of the Vapor-Phase SAMs Formed Under Different Conditions

sample preparation	sessile contact angle (deg) (water)	ellipsometric thickness (nm)
1 cycle w/o water vapor	100	0.66
1 cycle	108	0.64
2 cycles	112	0.94
3 cycles	113	0.95

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M. Beck *et al.*, *Microelectronic Engineering* **61- 62**, 441 (2002).

G.-Y. Jung *et al.*, *Langmuir* **21**, 1158 (2005).



Adhesion

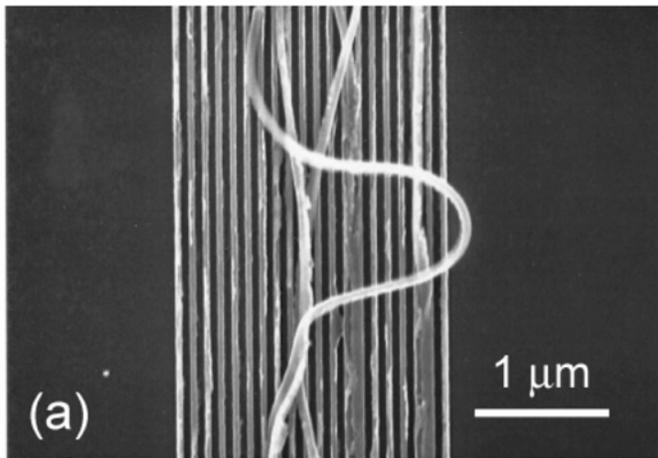
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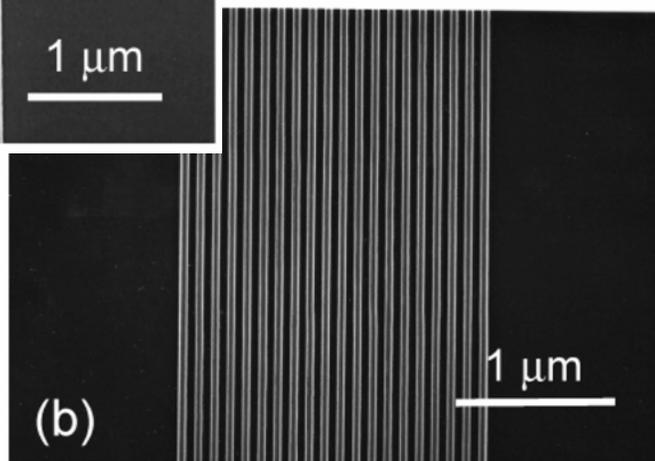
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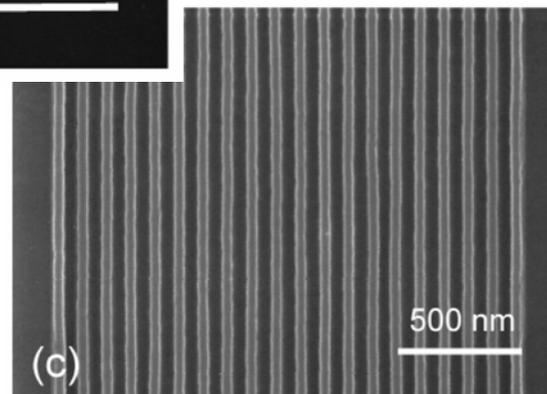
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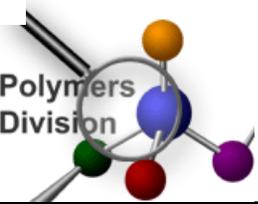
Mold w/ high adhesion (untreated or solution phase)



Mold w/ low adhesion (vapor phase)



Imprinted lines (fidelity)



Adhesion

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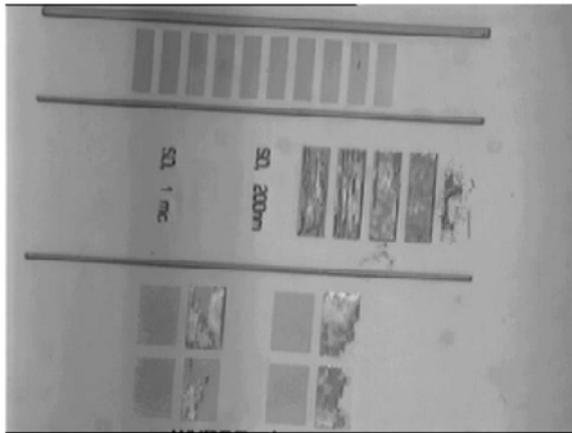
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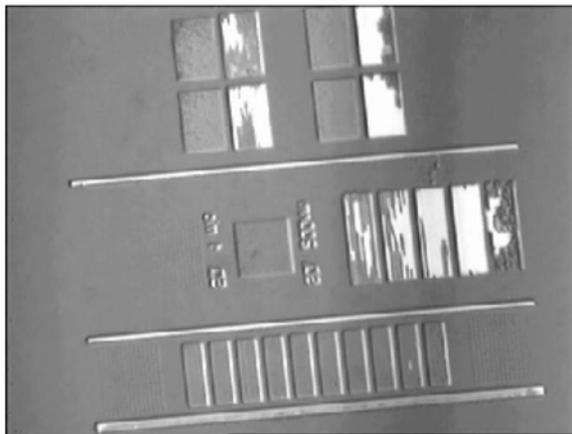
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Liquid phase

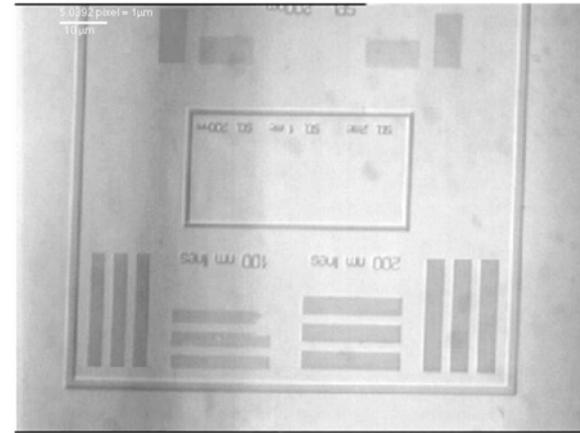


(a)

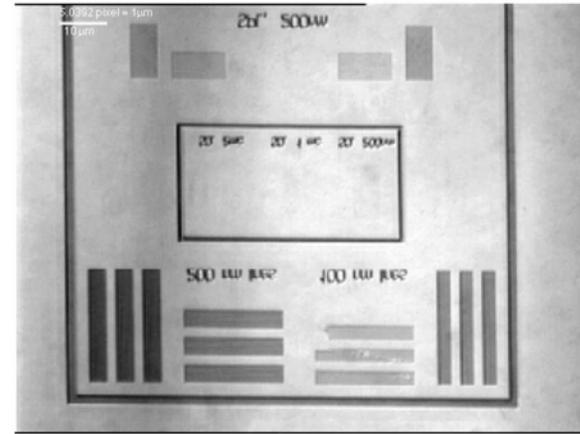


(b)

Vapor phase



(a)



(b)



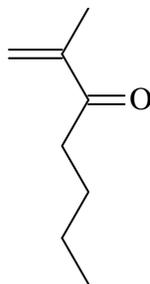
Application of C&HT

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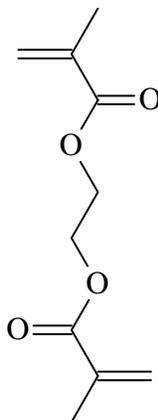
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- Optimization of adhesion / release can be time-consuming, and quality control in nanoimprint is ill-defined and typically off-line
- High-throughput screening offers rapid assessment of new candidate materials and can define appropriate operating windows and tolerances:
 - new suppliers
 - new formulations
 - change in processing conditions

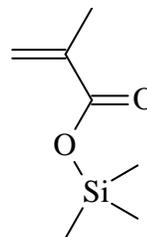
Model system



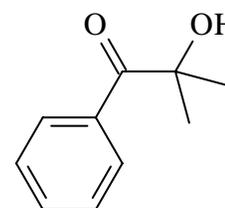
butyl methacrylate



ethylene glycol dimethacrylate

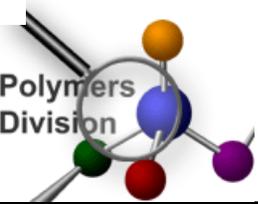


trimethylsilyl methacrylate



Darocur 1173

Recipe from: M .D. Dickey *et al.*, *AICHE Journal* **51**, 2547 (2005).

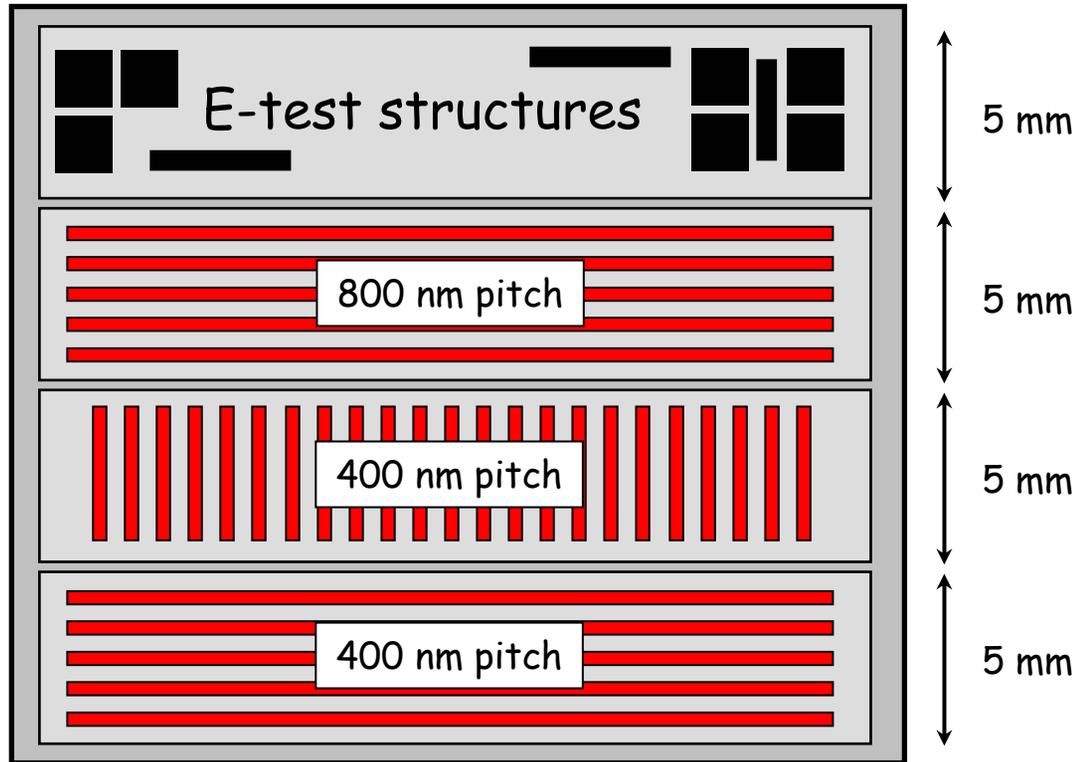


Imprint Mold

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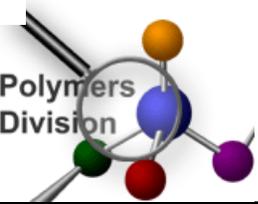
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Height - 400 nm

* Courtesy of Intel



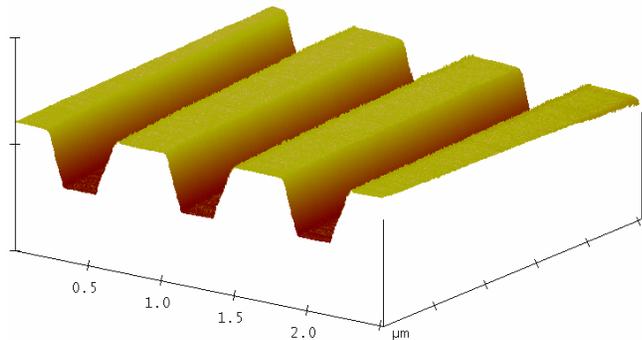
Imprint Mold

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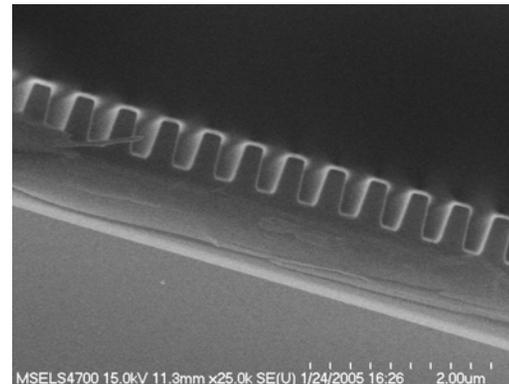
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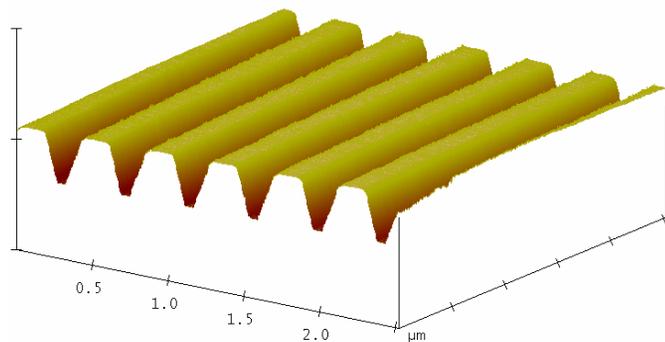
800 nm pitch



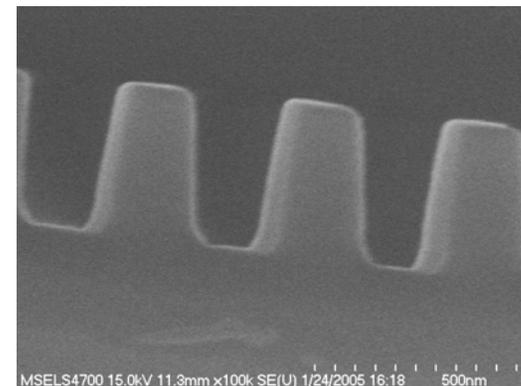
pitch (AFM) - 800 nm
height (AFM) - 403 nm



400 nm pitch



pitch (AFM) - 415 nm
height (AFM) - 354 nm



← AFM likely not reaching bottom of pattern

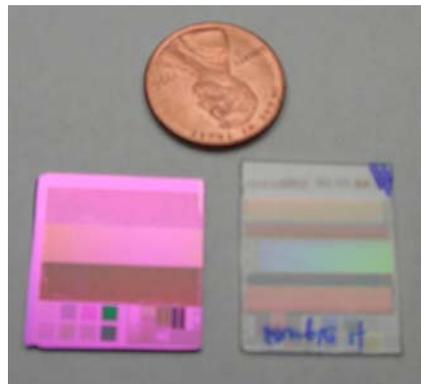
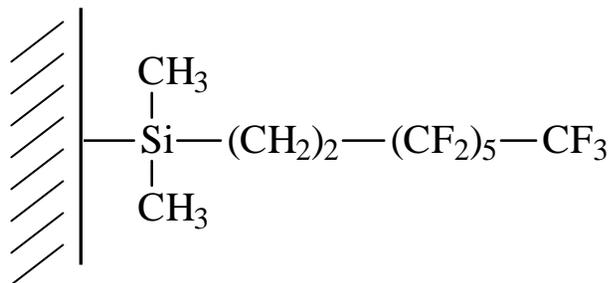


Low γ Mold

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flat silicon

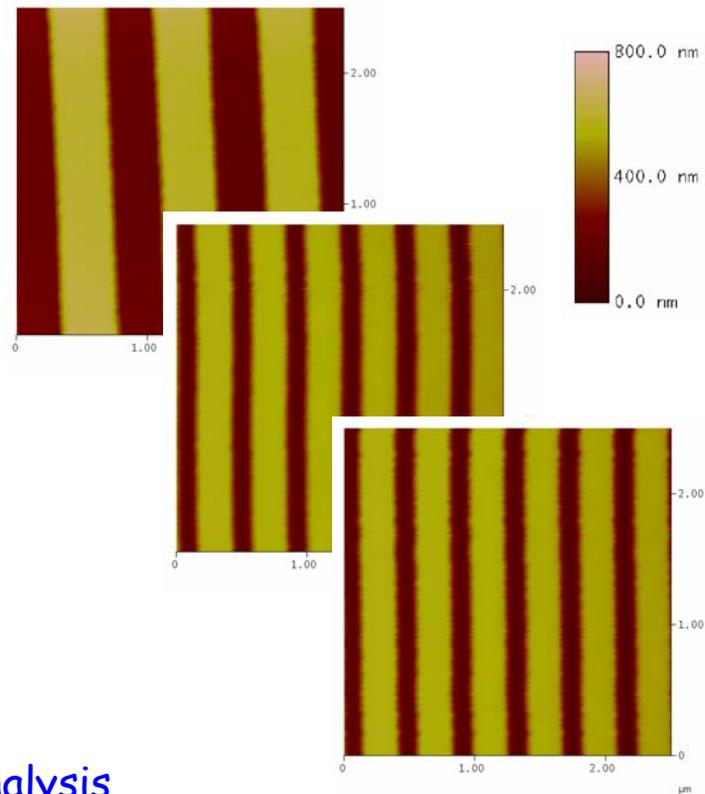
$$\theta_A/\theta_R = 111/95$$

mold

$$\theta_A/\theta_R = 150/129 \text{ (800 nm pitch)}$$

$$\theta_A/\theta_R = 151/141 \text{ (400 nm pitch)}$$

AFM of imprinted material



AFM analysis

	1	mold	2	3	mold
pitch	801	800	418	418	415
height	393	403	388	389	354



Intermediate γ Molds

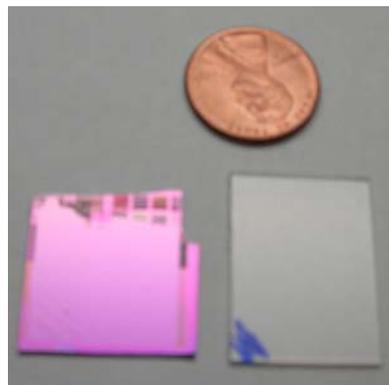
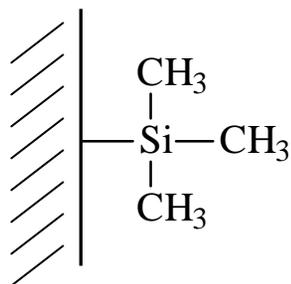
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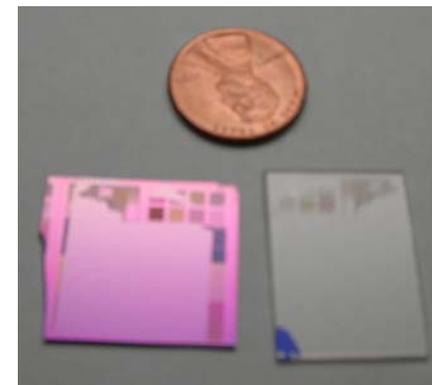
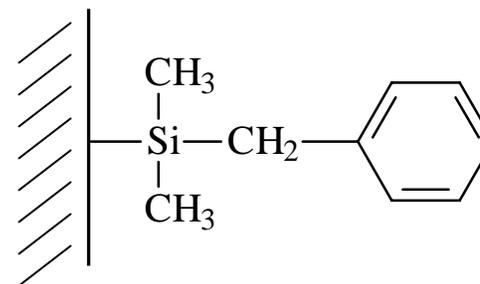
flat silicon

$$\theta_A/\theta_R = 93/79$$

mold

$$\theta_A/\theta_R = 150/\text{pins (800 nm pitch)}$$

$$\theta_A/\theta_R = 149/\text{pins (400 nm pitch)}$$



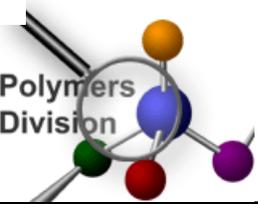
flat silicon

$$\theta_A/\theta_R = 79/57$$

mold

$$\theta_A/\theta_R = 148/\text{pins (800 nm pitch)}$$

$$\theta_A/\theta_R = 148/\text{pins (400 nm pitch)}$$



Surface Energy Gradients

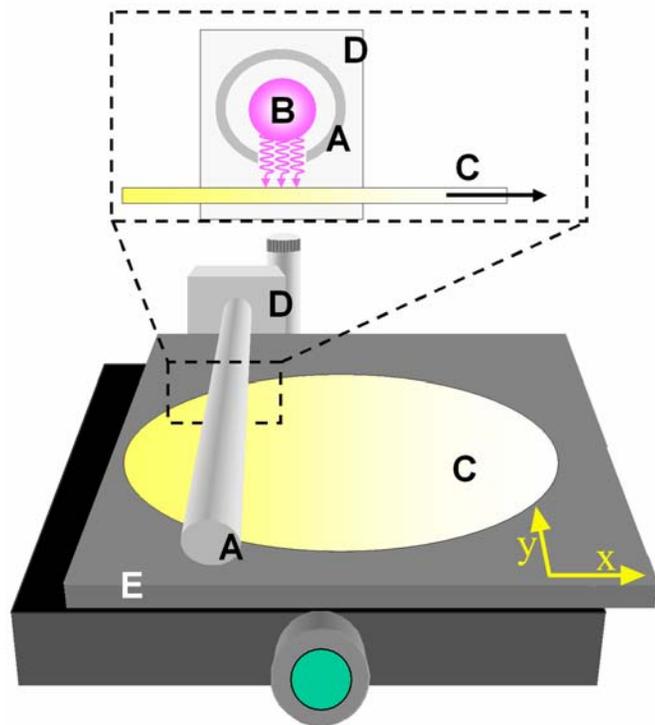
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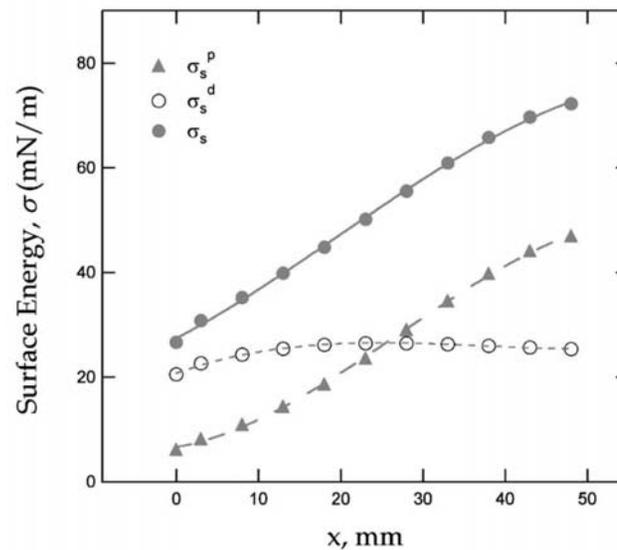
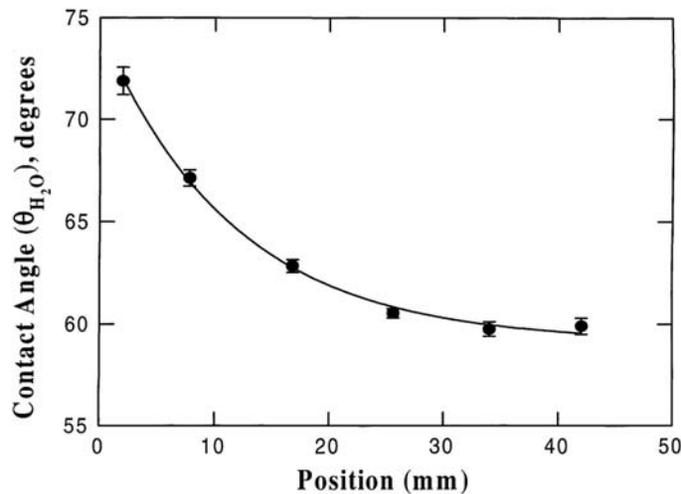
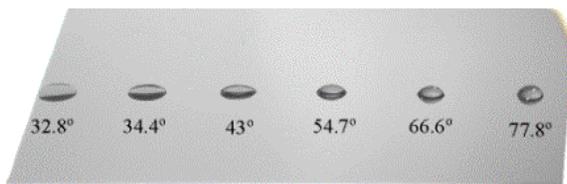
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Automated contact \angle measurements





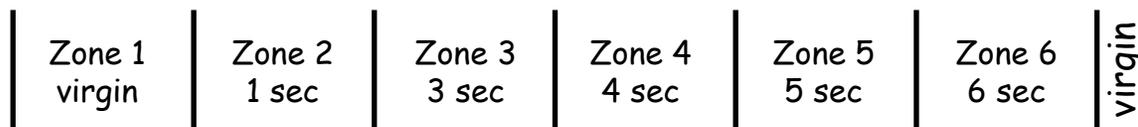
Surface Energy Gradient #1

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step size - 0.1 mm

Zone	1	2	3	4	5	6
θ_A/θ_R	146/127	146/125	143/119	140/116	137/109	-

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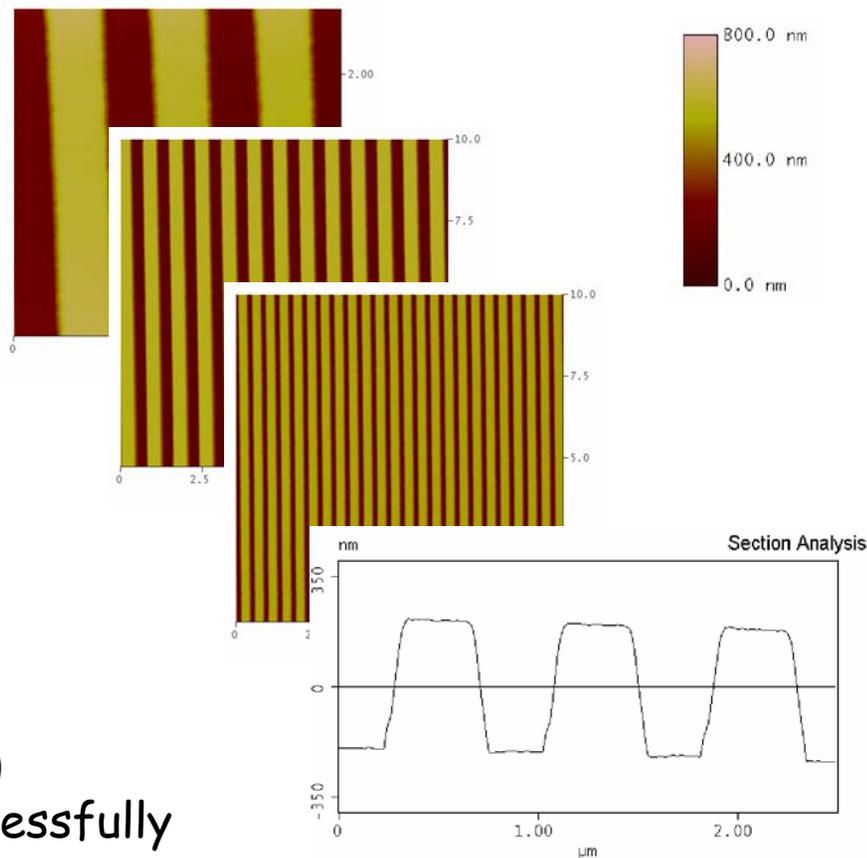
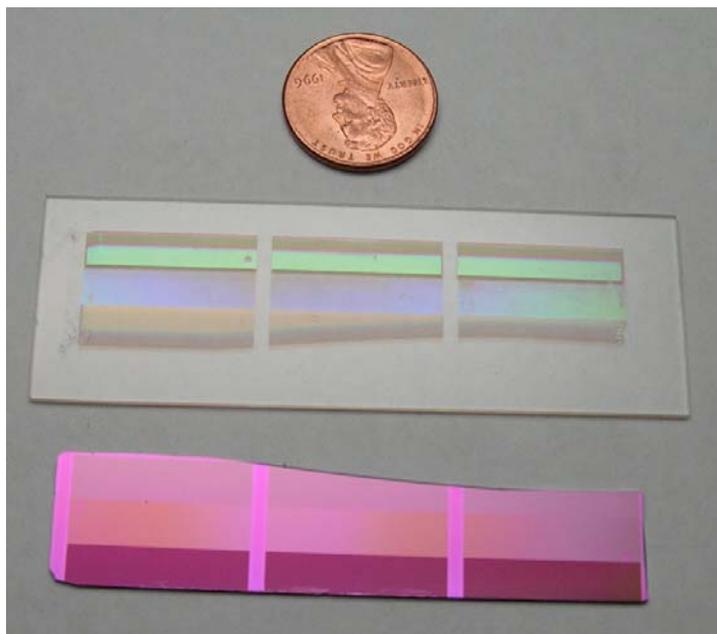


Surface Energy Gradient #1

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- Gradient is shallow (high-resolution)
- All zones transferred patterns successfully

	mold	1	2	3	4	5	6
pitch	800	801	796	796	801	791	796
height	403	393	402	421	378	392	406



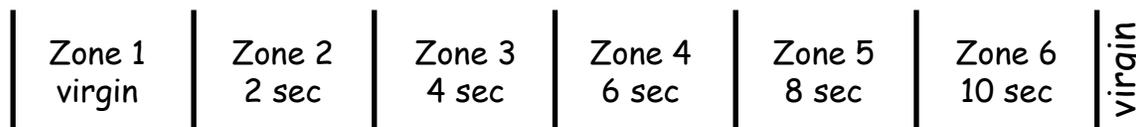
Surface Energy Gradient #2

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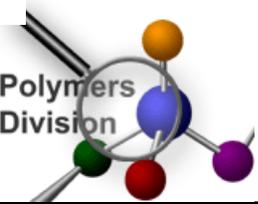
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step size - 0.1 mm

Zone	1	2	3	4	5	6
θ_A/θ_R	145/127	145/101	102/pins	81/pins	53/pins	wets

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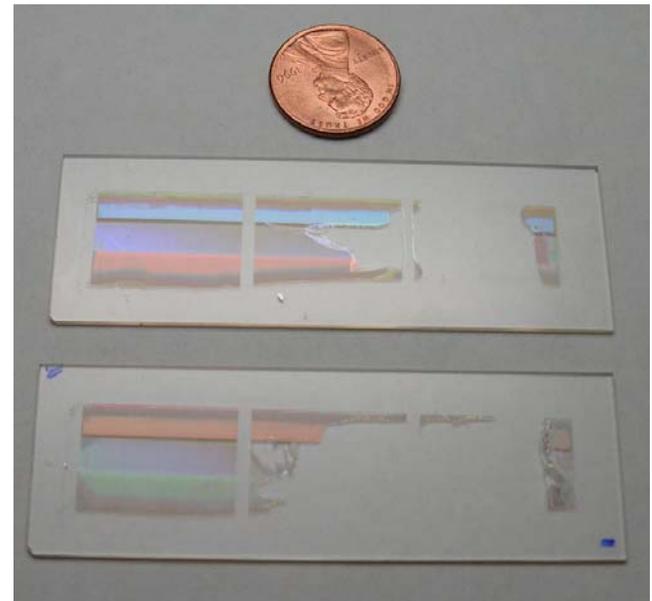
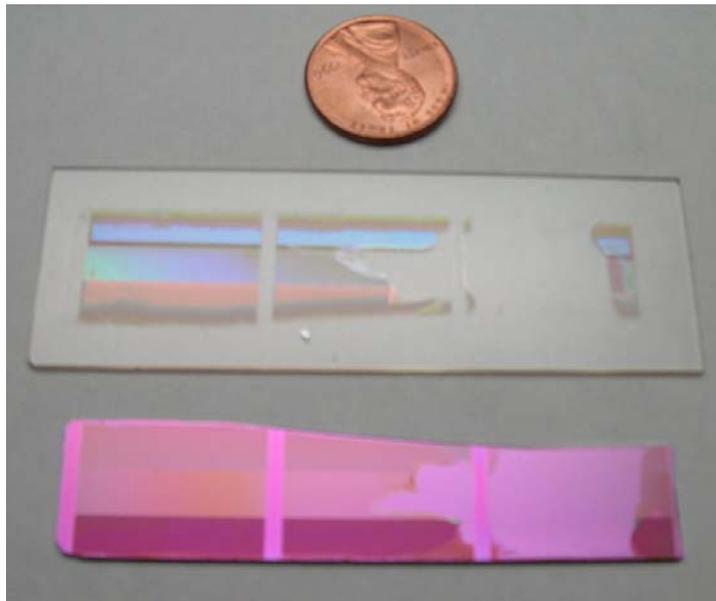


Surface Energy Gradient #2

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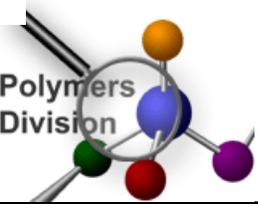
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- Gradient is steep (low-resolution)
- Failure occurs in Zone 4 ($\sim \theta_A = 100$)

- Repeat experiment
- Again, failure occurs in \sim Zone 4

Smaller pitch size (higher surface area) fails sooner.



Conclusions

- Adhesion & release in UV-NIL is highly dependent on surface chemistry
- C&HT methods can accelerate R&D as well as provide operation windows for QC
- Simple inspection yields qualitative measure of adhesion & release

Future Work

- Conduct more high-resolution surface energy gradients ($\theta_A \approx 150-100$)
- Modify γ_{r-s} using methacryloxypropyl-type silane coupling agents
- Use wedge test to quantify adhesion energy (G_c) (SURF 2006).

Acknowledgments

- Brian Berry - UVO treatments
- Kate Hollabaugh - SURF student
- Susan Barnes - digital pictures