

# Resist Technology for the Post-157nm Lithography Era: Issues and Perspectives

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## Outline

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- Introduction
  - Post-157nm lithography options
  - Resist technology options for post-157nm lithography
    - Conventional resist technology approaches
    - Emerging resist technology approaches
- Post-157nm lithography resist technology issues
  - Conventional resist technology issues
    - Limitations of chemical amplification reaction system in resists
      - Uncontrollable diffusion
      - Image spread and image blur
  - Ultrathin film imaging issues
    - Film instability & defects
    - Film thermophysical property changes
      - Enhanced acid transport
      - Enhanced sensitivity to contamination
      - Enhanced deprotection kinetics

## **Outline *cont'd***

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- Emerging resist technologies
- Environmental health and safety concerns
- Integrating conventional and emerging resist technologies
- Concluding remarks

# Post-157nm Lithography Technologies

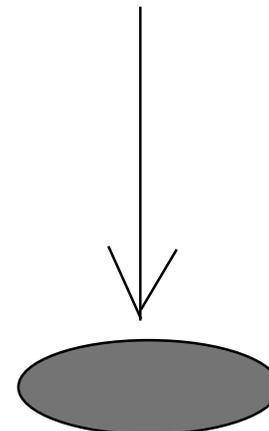
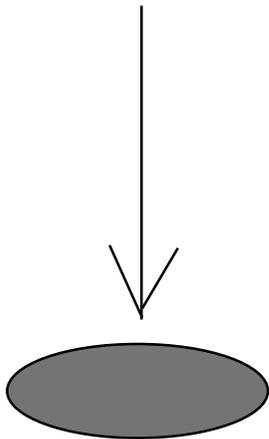


EUVL

EPL

$h\nu$   
( $\lambda=13.5$  nm)

$e^-$   
@ 100KV



Resist coated wafers

## Resist technology approaches for Post-157nm Lithography

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- Conventional techniques
  - Single Layer (SL) scheme
  - Thin Imaging Layer/Hardmask Scheme (TLI/HM)
  - Surface Silylation Scheme (SSS)
- Emerging techniques
  - Nanoimprinting Techniques “Soft Lithography”
  - Self-Assembly

# Conventional resist technology approaches for post-157nm lithography – issues & prospects



<b>Issue</b>	<b>SL</b>	<b>TLI/HM</b>	<b>SSS</b>
Transparency	Too opaque at nominal thickness	Good	Opacity is an advantage
Etch Resistance	Insufficient	Excellent Etch selectivity issues	Good (Thin SiO <sub>x</sub> good etch mask) Etch & silylation selectivity issues
Process	Simple	Imaging & processing separated (a plus)	Complex processing (Feature dependent silylation)
Process control	Not an issue	Not an issue	A serious issue

# Conventional resist technology approaches for post-157nm lithography – issues & prospects



<b>Issue</b>	<b>SL</b>	<b>TLI/HM</b>	<b>SSS</b>
LER	An issue	Problem	>10 nm
Resolution	Poor	High	Moderate
Sensitivity	Low (CA)	Low (CA)	Very low (CA)
Diffusion	Stability CD control issues	Problem	A serious problem
Defects	An issue	Not a serious issue	A serious problem

## Resist outgassing in vacuum

Sources of volatile organic materials include:

- protecting groups (majority contributor)
- photoacid generators
- solvent hydrolysis

Most resists (and neat polymers) show both an exposure-induced mass increase ( $E < 10 \text{ mJ/cm}^2$ ) and mass loss ( $E > 40 \text{ mJ/cm}^2$ )

Resist	Mass liberated per year (g)	QCM Results (molecules/cm <sup>2</sup> -sec)	GCMS Results (molecules/cm <sup>2</sup> -sec)	Thickness deposited (nm) $e=10^{-2}$
IBM V2.1	0.7	$3 \times 10^{12}$	$2 \times 10^{12}$	70
Shibley XP-7022	1	$4 \times 10^{12}$	$3 \times 10^{12}$	100
OMM RX-1	0.3	$< 1 \times 10^{12}$	$1 \times 10^{12}$	30
OMM bilayer	18	$4 \times 10^{13}$		1800
Sumitomo NEK-304	$< 0.3$	$< 1 \times 10^{12}$		$< 30$

Source: Kunz, R. *Personal Communications*, MIT Lincoln Labs, 1998

Summary of issues with conventional resist technology  
in post-157nm lithography



<b>Resist Parameter</b>	<b>EPL</b>	<b>EUVL</b>
Image distortion due to nonconducting resist film	A possibility	Not a problem
Outgassing	A problem (key to preventing charging effects due to contamination build-up in column)	A problem
Substrate & resist heating	A problem	Not a problem
Contrast requirement	>5 High contrast compensates for the backscattered e <sup>-</sup> that reduces the image contrast	Has to be high to improve LER

## Summary of issues with conventional resist technology in post-157nm lithography



<b>Resist Parameter</b>	<b>EPL</b>	<b>EUVL</b>
Tg	> max. temp rise due to e-beam heating, so as to prevent unwanted diffusion in the resist & loss of pattern fidelity	High enough to prevent dark reactions
Resolution loss due to Uncontrollable diffusion	A problem	A problem
Line edge roughness	A problem	A problem
Charging	A problem	Not a problem
Shot noise limit	A problem	A problem
Pattern collapse	A problem	A problem

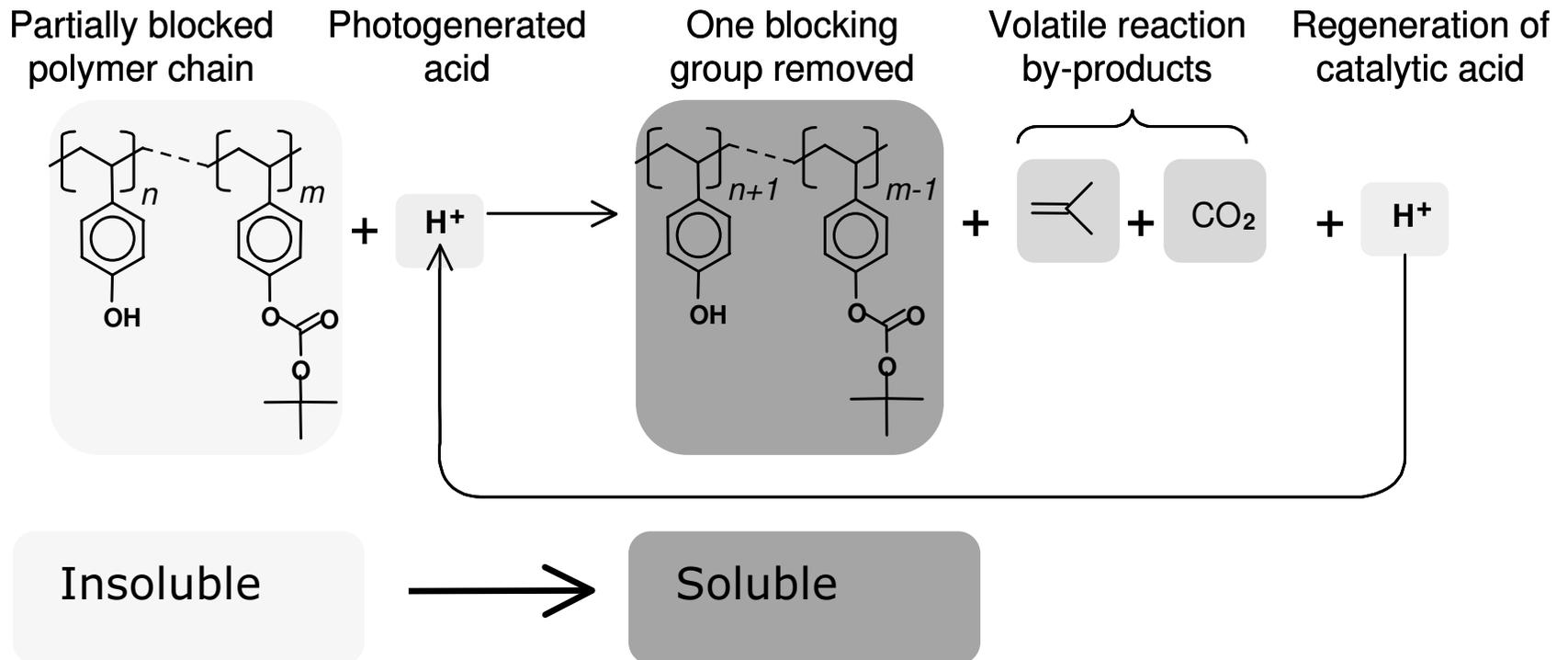
# Emerging resist technology options for post-157nm lithography



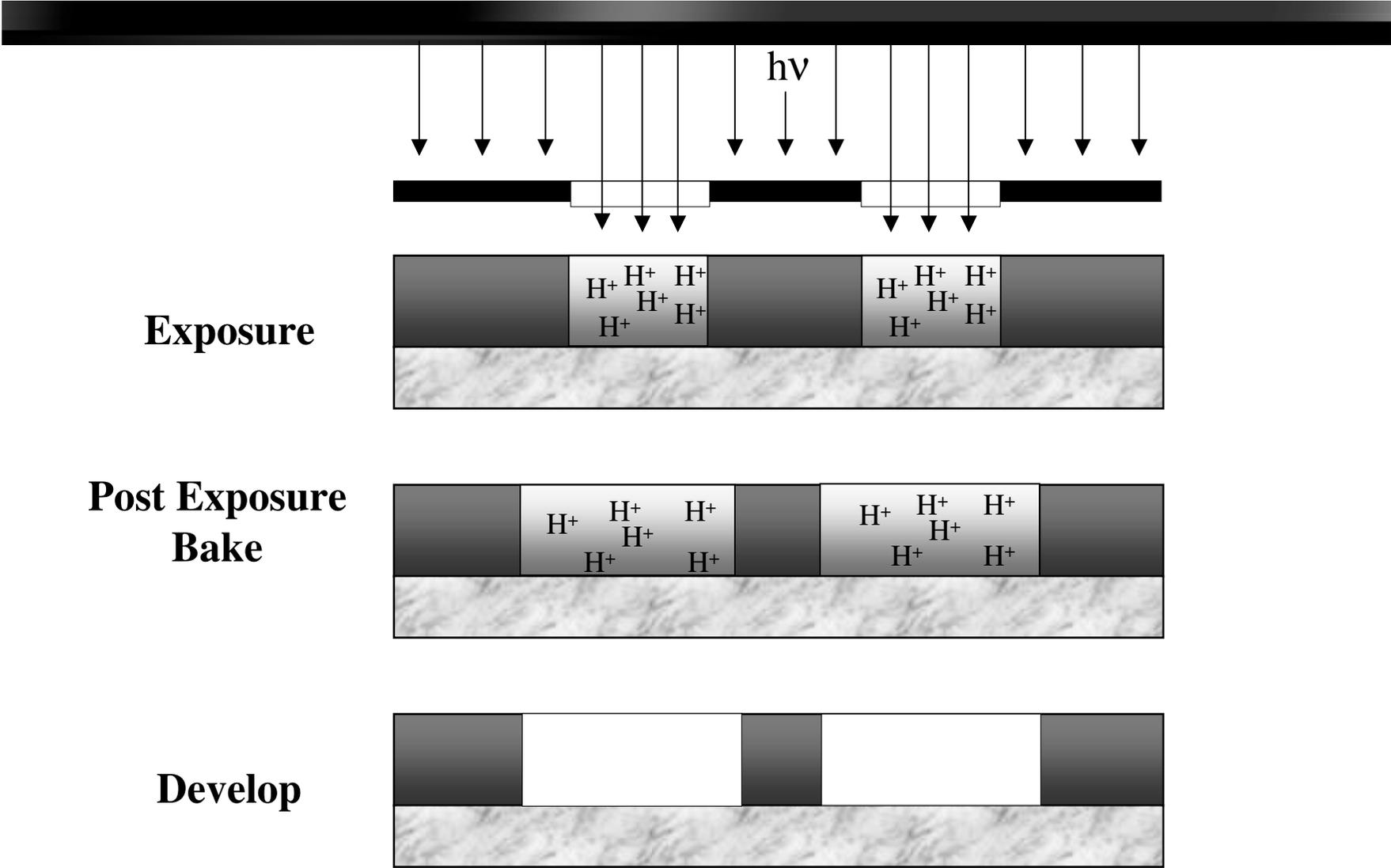
- Nano-imprint techniques “soft lithography”
- Self-assembly techniques
- Direct patterning techniques

# Principle of chemical amplification

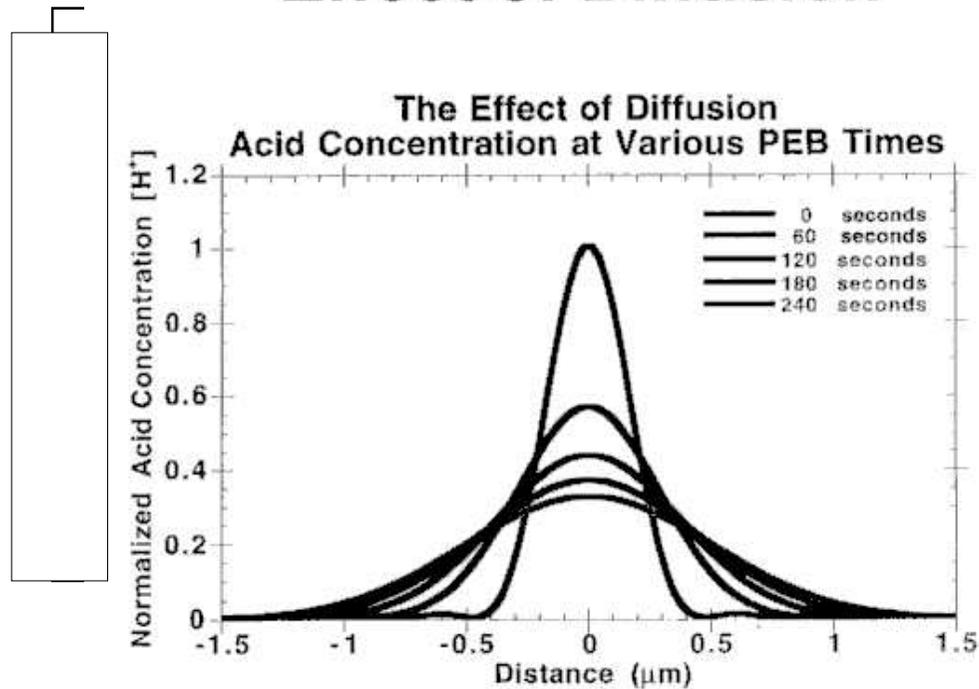
- Chemical amplification allows a single photoproduct to cause many solubility-switching reactions.



Achilles heel of chemical amplification resist system: **AMD**   
uncontrolled acid diffusion



## Effect of Diffusion



$$D = 5 \times 10^{-4} \mu\text{m}^2/\text{sec}$$

The initial acid concentration [H<sup>+</sup>] is defined by the aerial image.

Fedynyshyn, T.H., Szmanda, C. R., Blacksmith, R. F., Houck, W. E. *Proc. SPIE*, 1993, 1925, 2-13.

# Diffusion in Chemically amplified resist

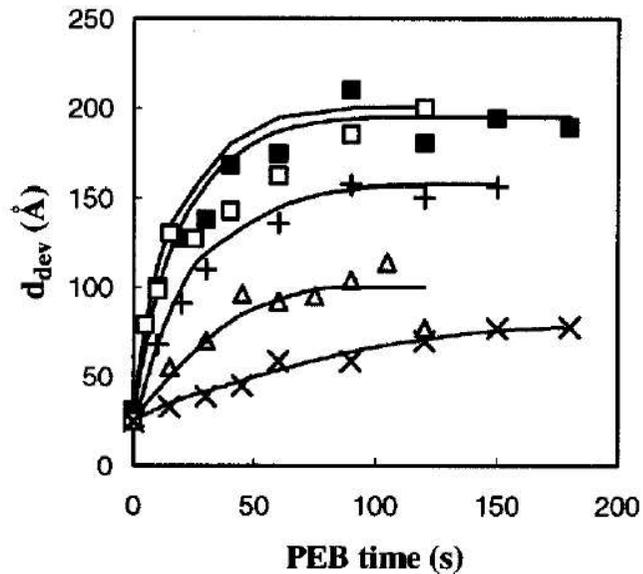


FIG. 1. Measured diffusional length ( $d_{dev}$ ) of perfluorooctanesulfonic acid (PFOS) in PBOCST at different temperatures: (×) 90 °C, (Δ) 100 °C, (+) 110 °C, (□) 120 °C, (■) 130 °C. Thickness: 1250 Å. The standard uncertainty in the  $d_{dev}$  measurement is  $\pm 10$  Å.

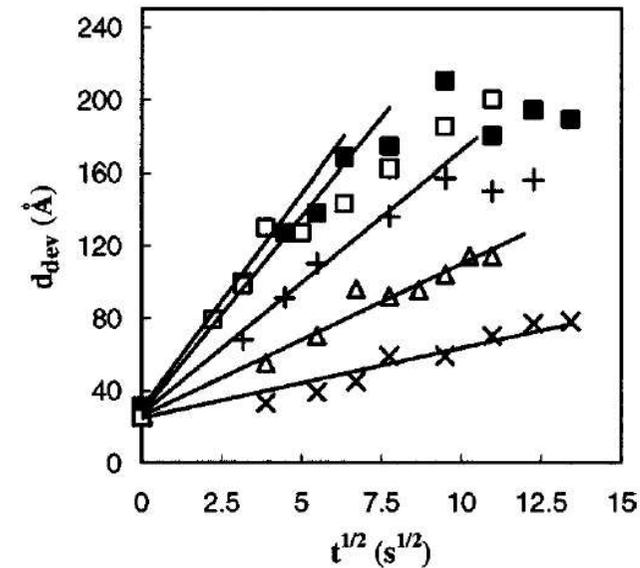
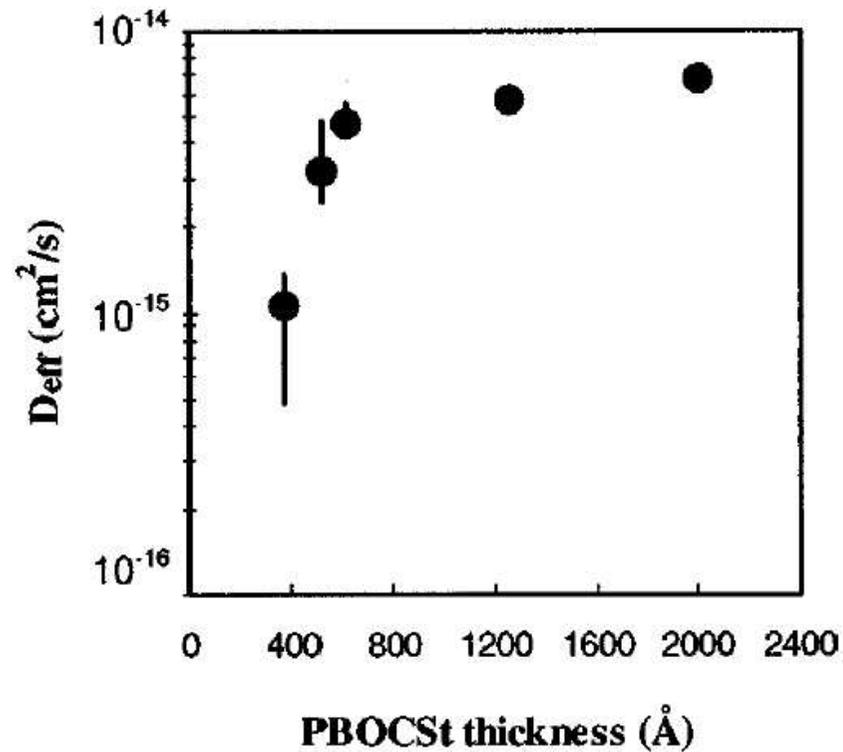


FIG. 2. Diffusion of PFOS into PBOCST at different temperatures. (×) 90 °C, (Δ) 100 °C, (+) 110 °C, (□) 120 °C, (■) 130 °C. Thickness: 1250 Å. The standard uncertainty in the  $d_{dev}$  measurement is  $\pm 10$  Å.

Goldfarb et al. *J.Vac.Sci. Tech. B* 19(6), 2699 (2001)

# Diffusion coefficient as a function of film thickness

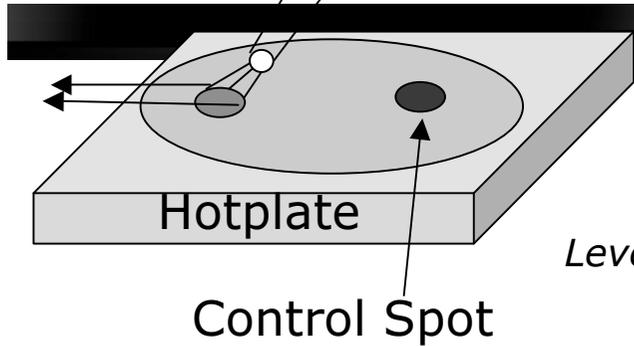


Profile shows asymptotic behavior at ~600Å, below which diffusion slows down remarkably, probably due to interfacial effects.

$D_{eff}$  as a function of film thickness for PFOS in PBOCST at 110 °C.

Goldfarb et al. *J.Vac.Sci. Tech. B* 19(6), 2699 (2001)

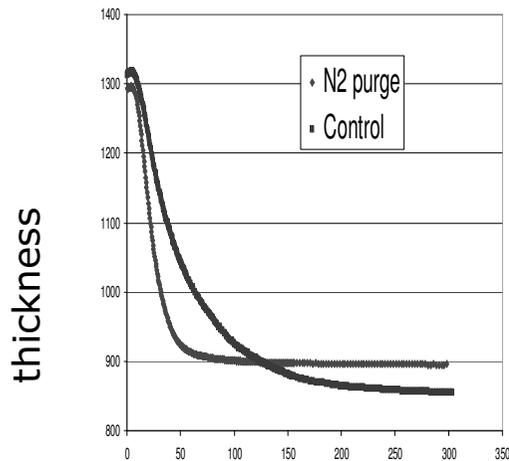
# Humidity Effects on Deprotection Kinetics



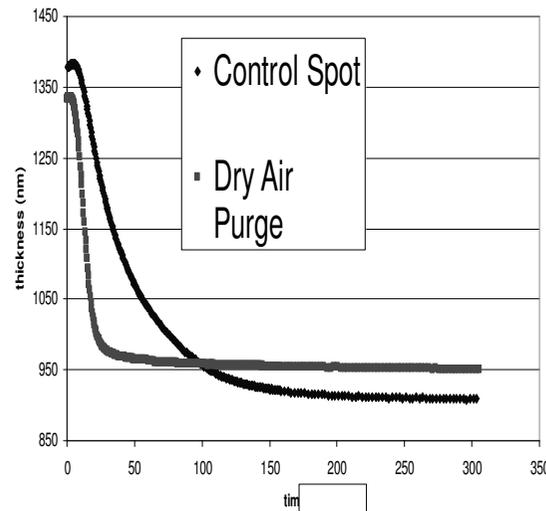
kinetics when the resist (TBOC) is purged with various gases (80°C PEB)

*Leveling effect of water -- implications for exposures in vacuum*

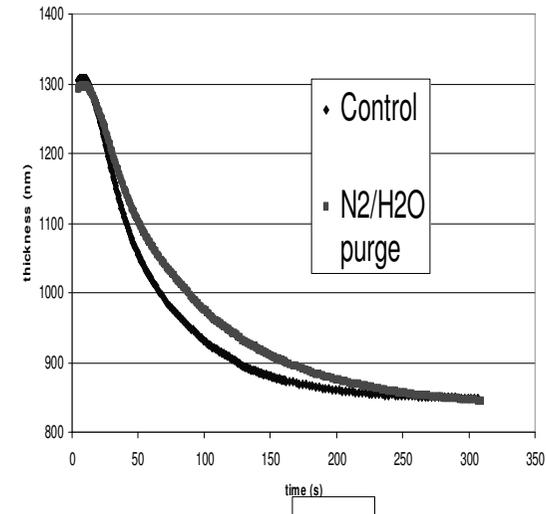
Nitrogen:



Dry Air

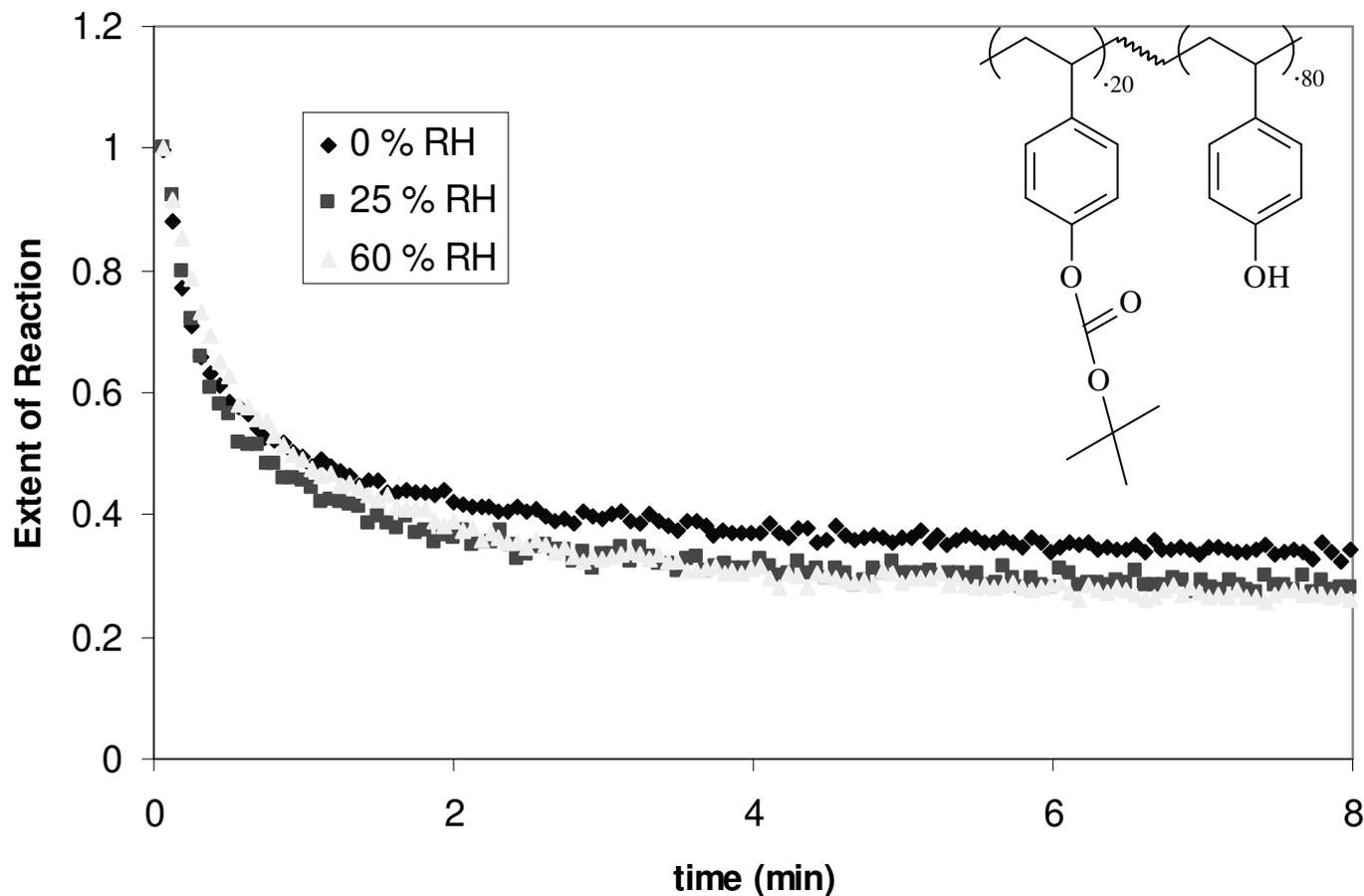


Nitrogen bubbled through H<sub>2</sub>O:



Sean Burns, UT-Austin (2002) – private communication

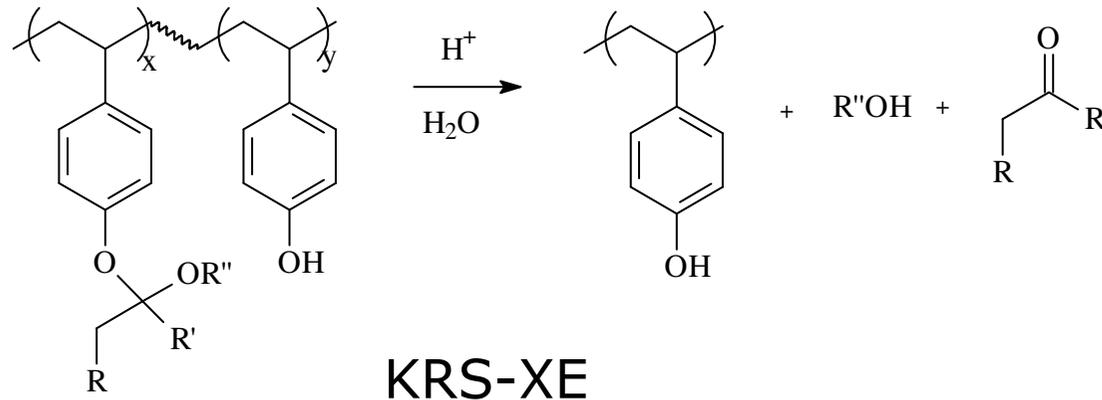
# The Effect of Humidity on TBOC/PHOST Copolymer Deprotection Kinetics



*Leveling effect of water -- implications for exposures in vacuum*

Sean Burns, UT-Austin (2002) – private communication

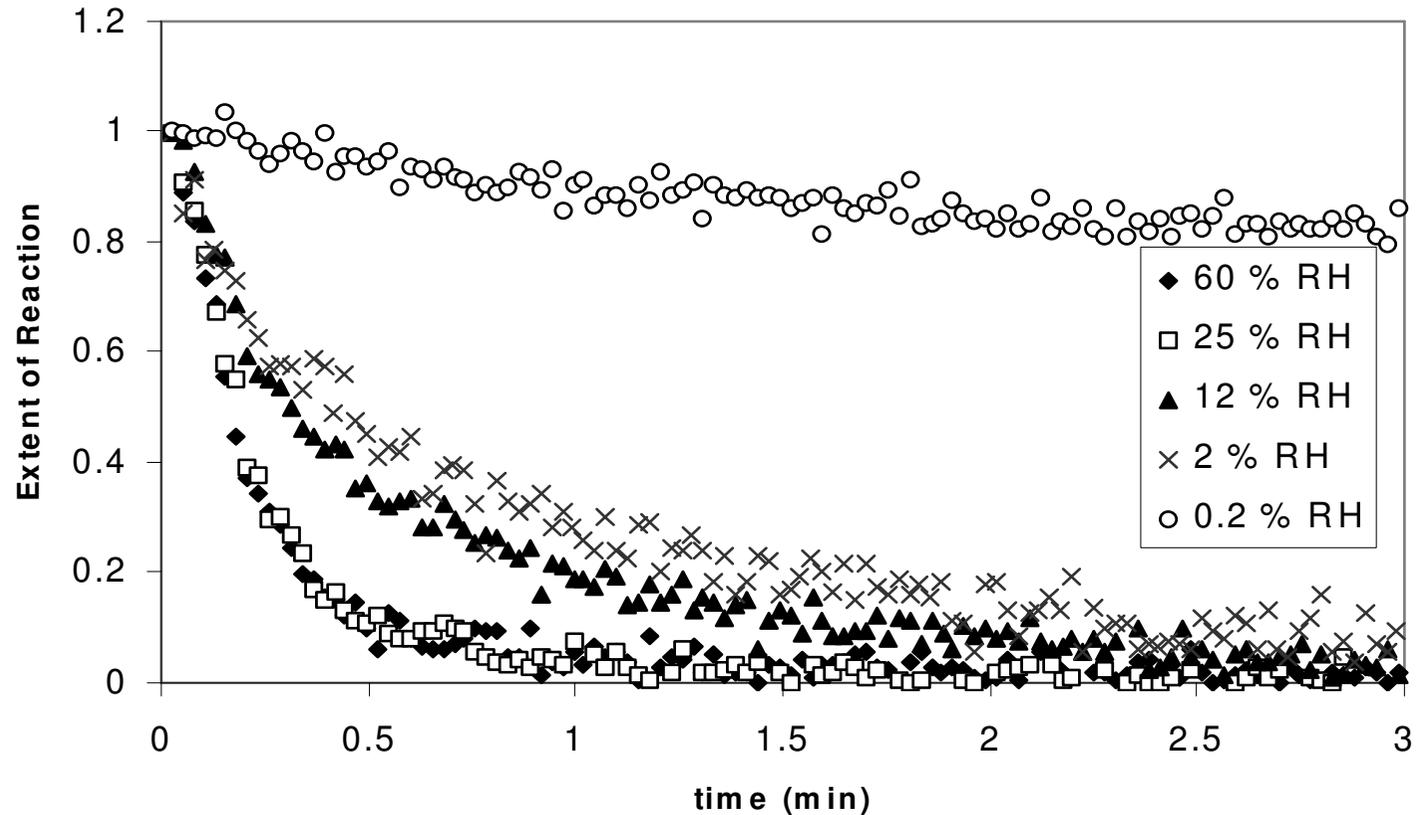
# Effect of humidity on low activation energy resists



- used primarily for e-beam photomask writing
- Insensitive to post exposure delays (reaction goes at room temp.)
- Insensitive to minor temperature fluctuations
- Requires water in order for deprotection to occur

Sean Burns, UT-Austin (2002) – private communication

# Kinetics of KRS-XE deprotection under various % RH

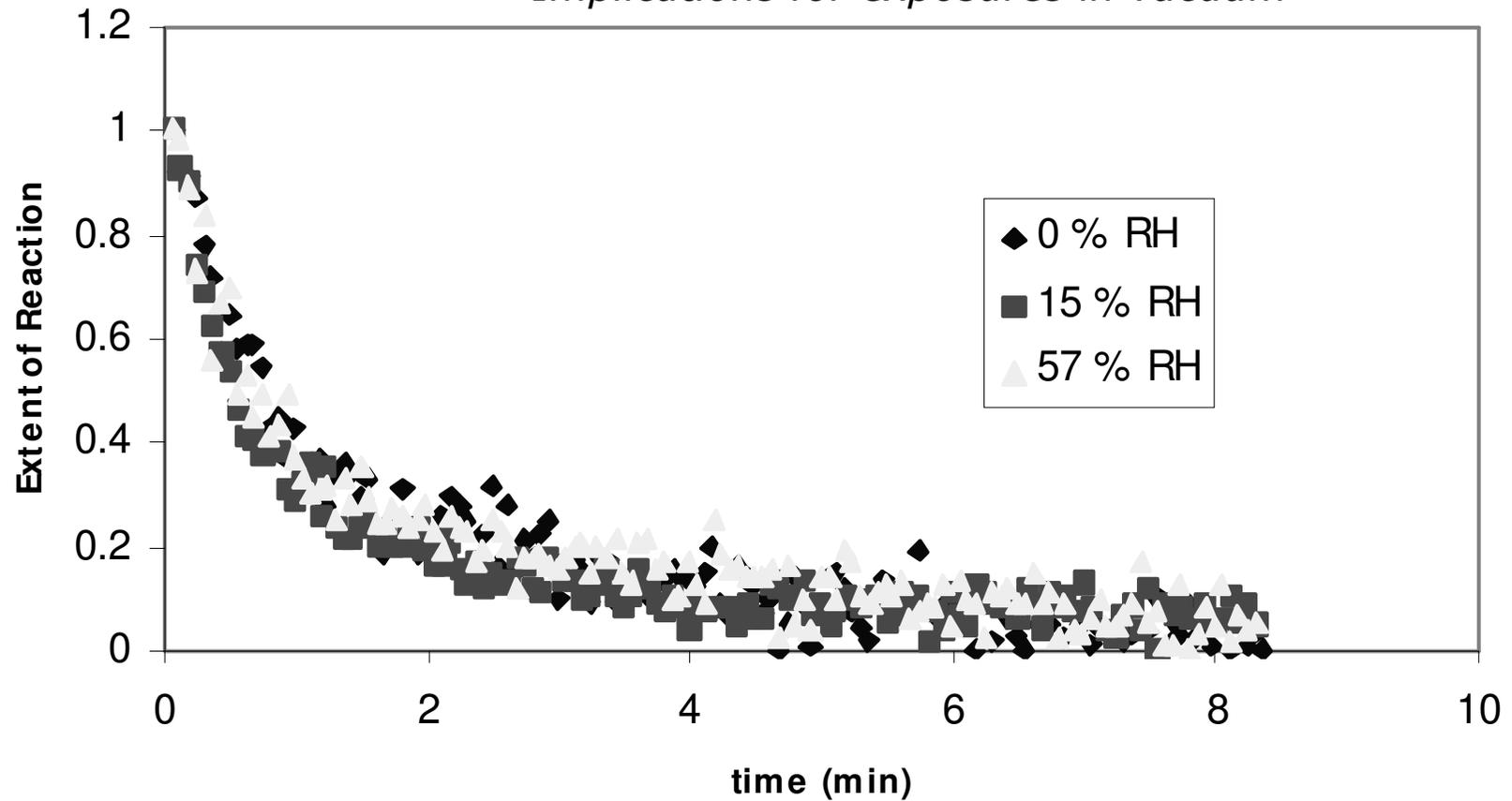


*Leveling effect of water -- implications for exposures in vacuum*  
Sean Burns, UT-Austin (2002) – private communication

# Effect of Humidity on Deprotection Kinetics of UV6

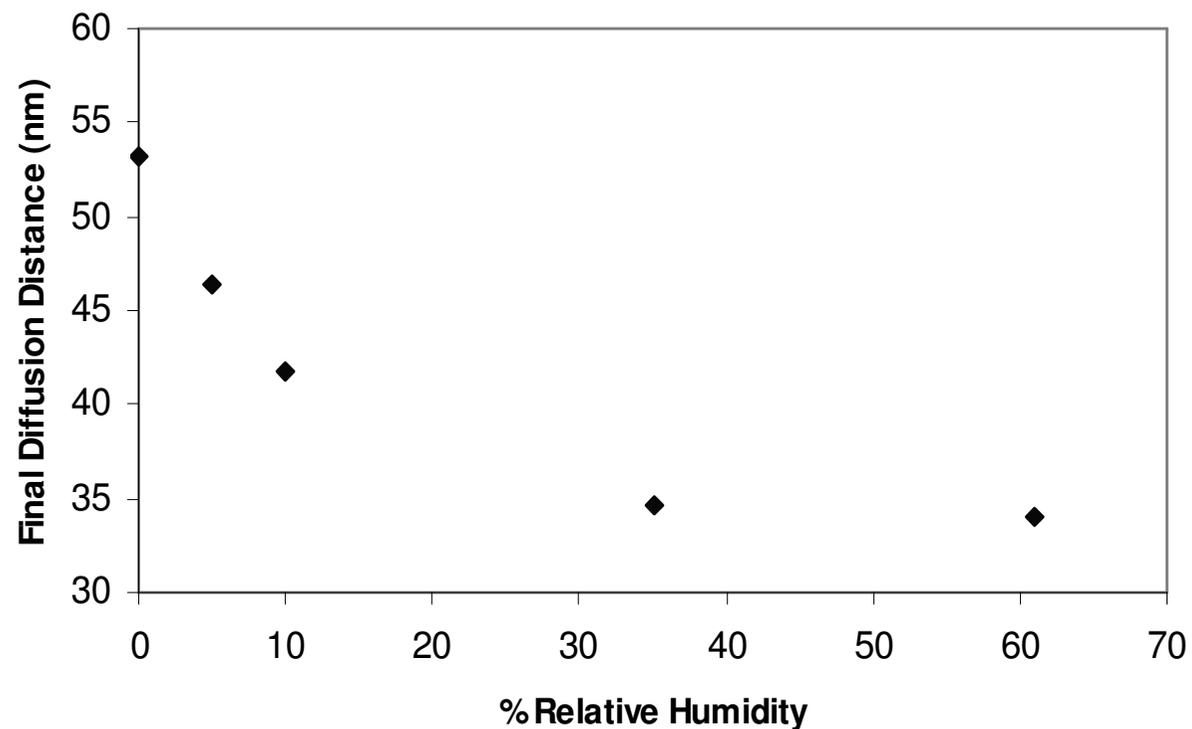


*Implications for exposures in vacuum*



Sean Burns, UT-Austin (2002) – private communication

## Final Acid Diffusion Distance vs. % RH

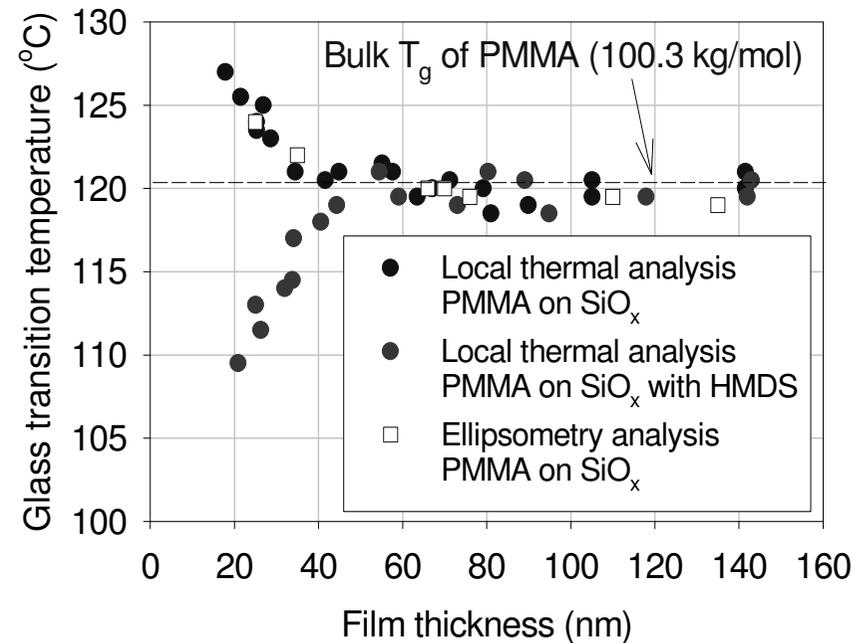
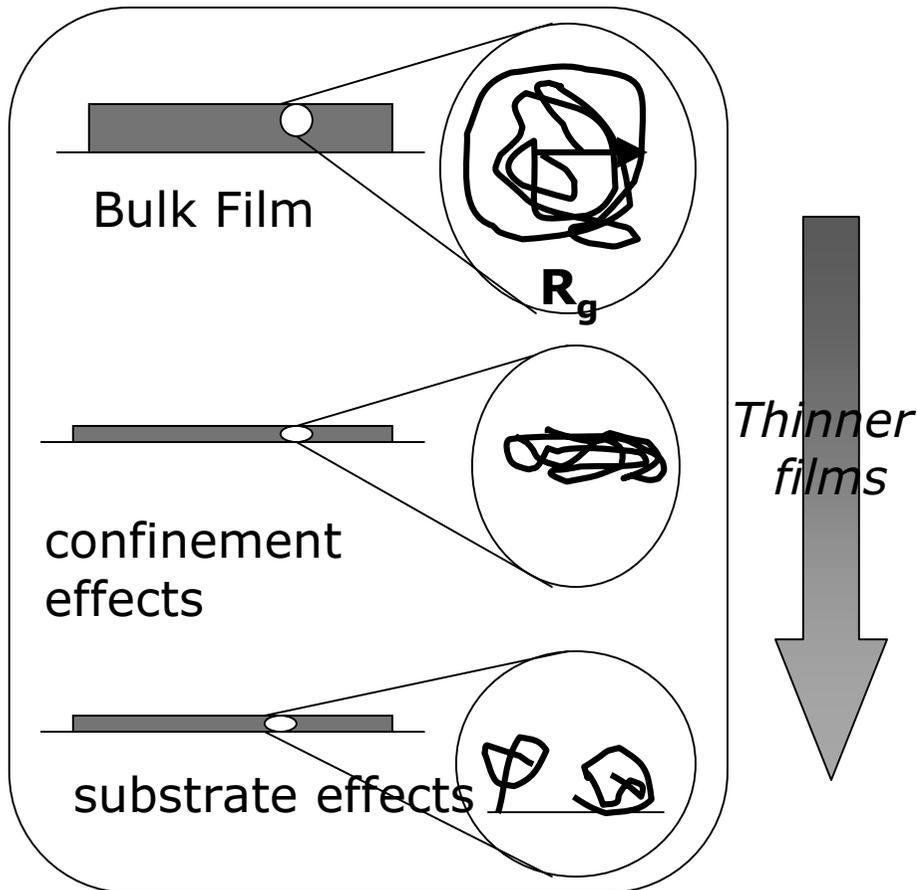


*Leveling effect of water -- implications for exposures in vacuum*

Sean Burns, UT-Austin (2002) – private communication

# Film thermophysical property changes with thickness

*Thermal Probe Measurements of  $T_g$  in UTF*

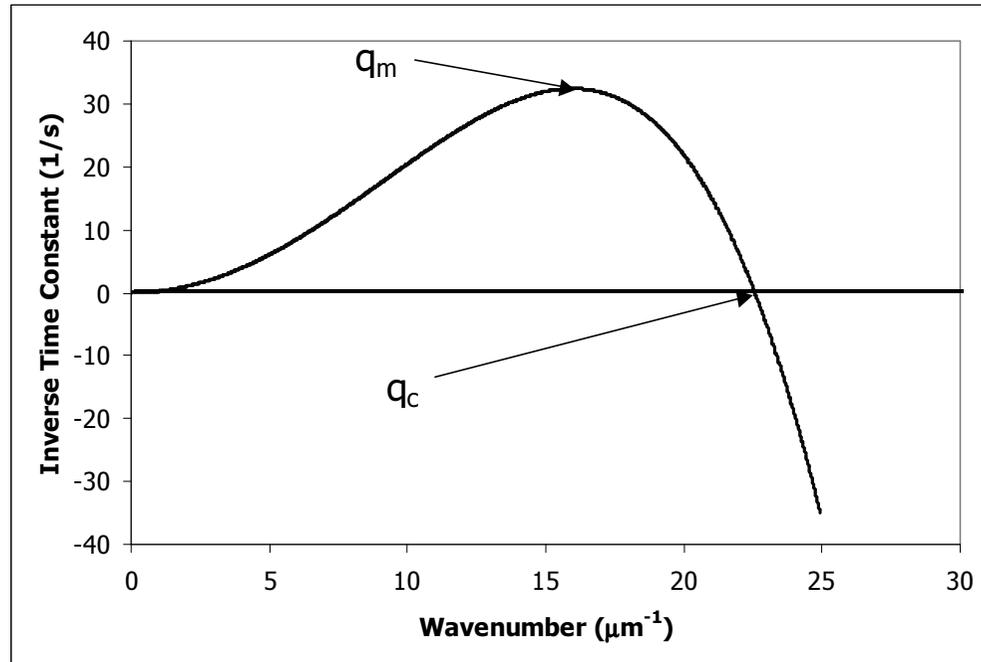


D.Fryer, P.Nealey and J.de Pablo.  
*Macromol.* **33**, 6439 (2000)

# UTR film issue: thin film stability dispersion curve of polystyrene film



$$(A = 8 \times 10^{-20} \text{ J}, \gamma = 40 \times 10^{-3} \text{ J/m}^2)$$



$$s = \frac{q^2}{\eta} \left[ -\gamma q^2 h_o^3 + \frac{A}{2\pi h_o} \right]$$

$$\tau_{\min} = \frac{4^2 \pi^2 \eta h_o^5 \gamma}{A^2}$$

$$q_c = \frac{1}{h_o^2} \sqrt{\frac{A}{2\pi\gamma}}$$

Critical wave# increases like  $1/h_o^2$  as the film thickness  $h_o$  decreases  
 >> increasing region of frequency space will be susceptible to film instabilities.

$q < q_c$ , ( $A/2\pi h_o > \gamma q^2 h_o^3$ ),  $\tau$  is positive and surface disturbances are amplified exponentially, eventually reaching the substrate and nucleating a hole.

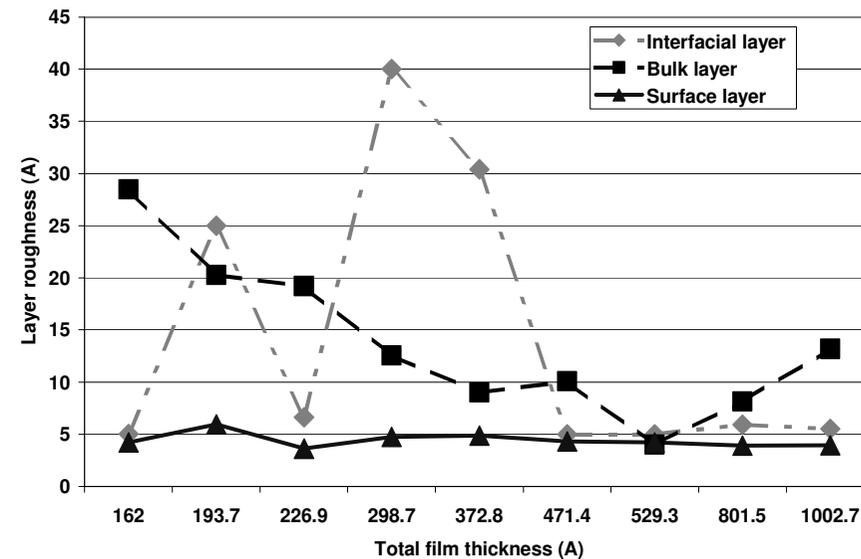
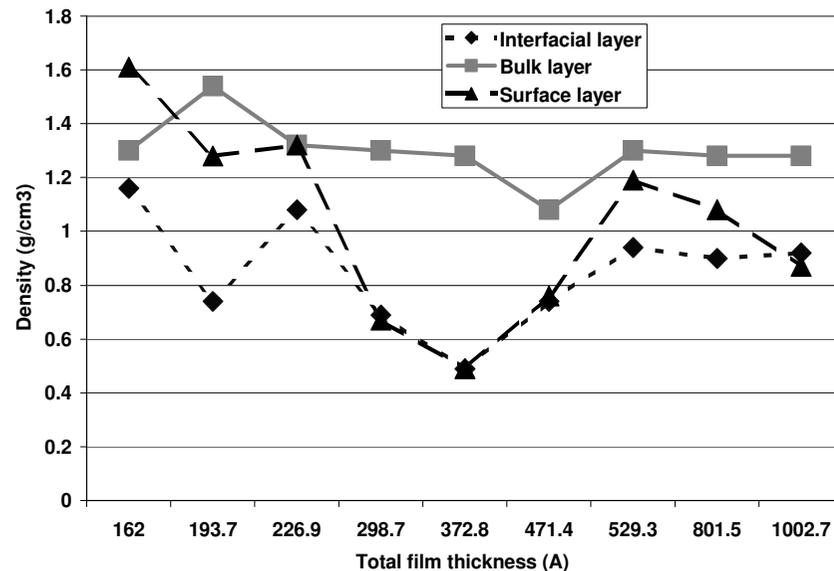
If  $\tau_{\min} \ll$  time required for resist spinning, drying and curing, then disturbances will continue to grow exponentially and will eventually rupture the film before it has a chance to solidify.

U. Okoroanyanwu, *J. Vac. Sci. Technol.* **B 18(6)**, 3381 (2000)

U. Okoroanyanwu, *Future Fab International*, **vol 10**, 157 (2001)

# Ultrathin film imaging issue: thin film instabilities

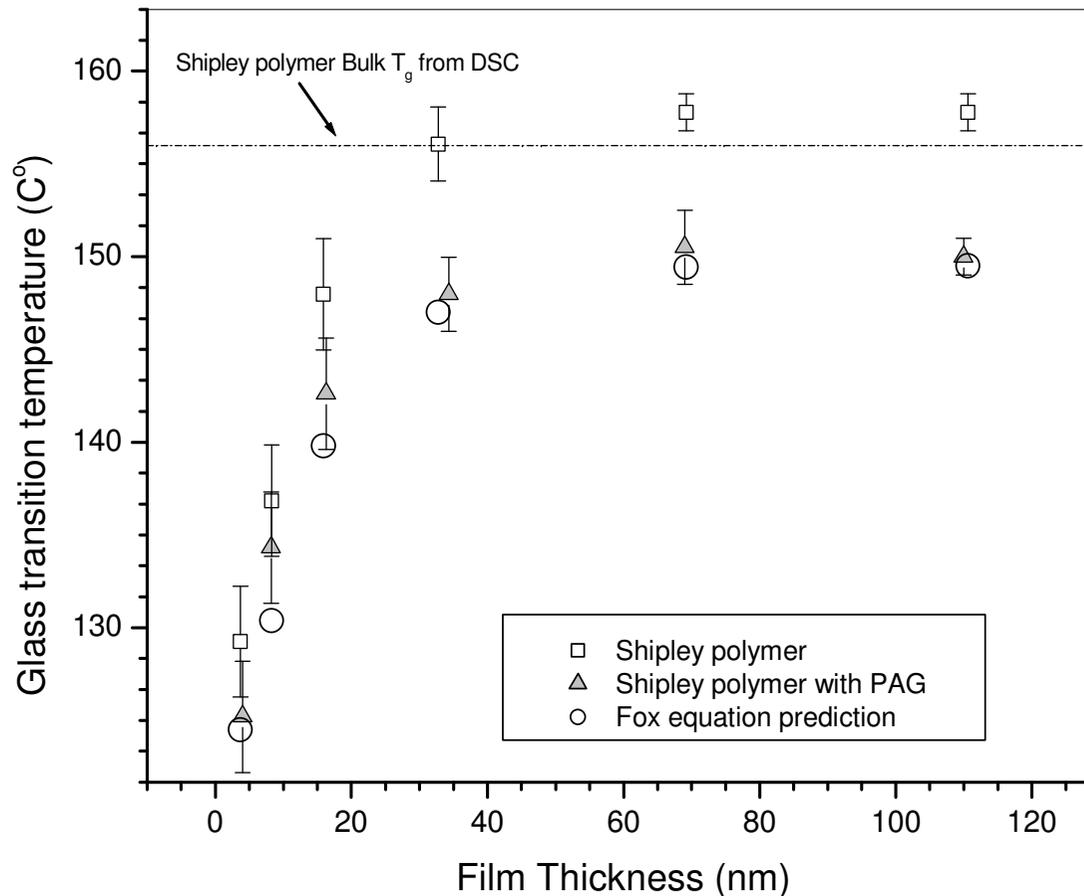
Film layer density and roughness as a function of Shipley XP-98248 (phenolic ESCAP polymer based resist) of thickness . Film was spincoated on Si wafer. X-ray reflectivity measurements.



Onset of film instability ~ <53nm

U. Okoroanyanwu, *J. Vac. Sci. Technol.* **B 18(6)**, 3381 (2000)  
 U. Okoroanyanwu, *Future Fab International*, **vol 10**, 157 (2001)

# Ultrathin film imaging issue: T<sub>g</sub> depression with film thickness



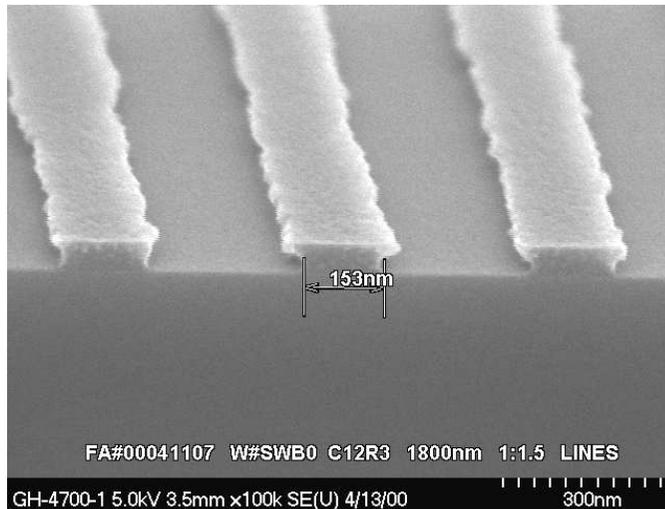
## Fox Equation

$$\frac{1}{T_g} = \frac{M_1}{T_{g1}} + \frac{M_2}{T_{g2}}$$

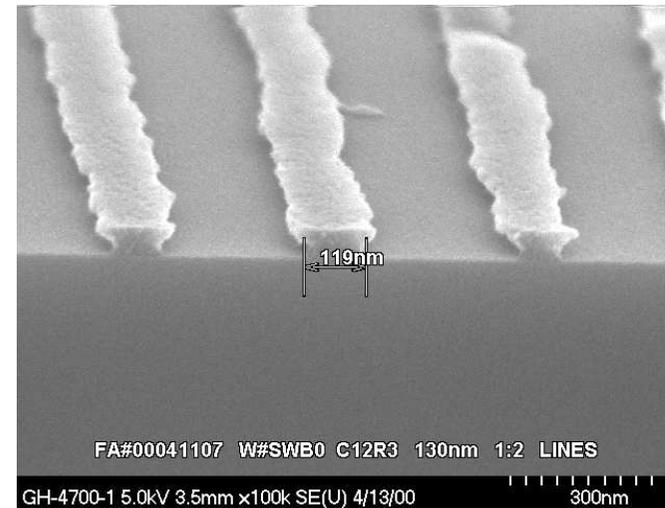
Depression of T<sub>g</sub> with Film thickness.

J. D'Amour, C.W. Frank, U. Okoroanyanwu, *Proc. SPIE*, vol. **4690**, 936 (2002)

# Ultrathin film imaging issue: enhanced environmental sensitivity of UTR films



**180nm 1:1.5 Features**



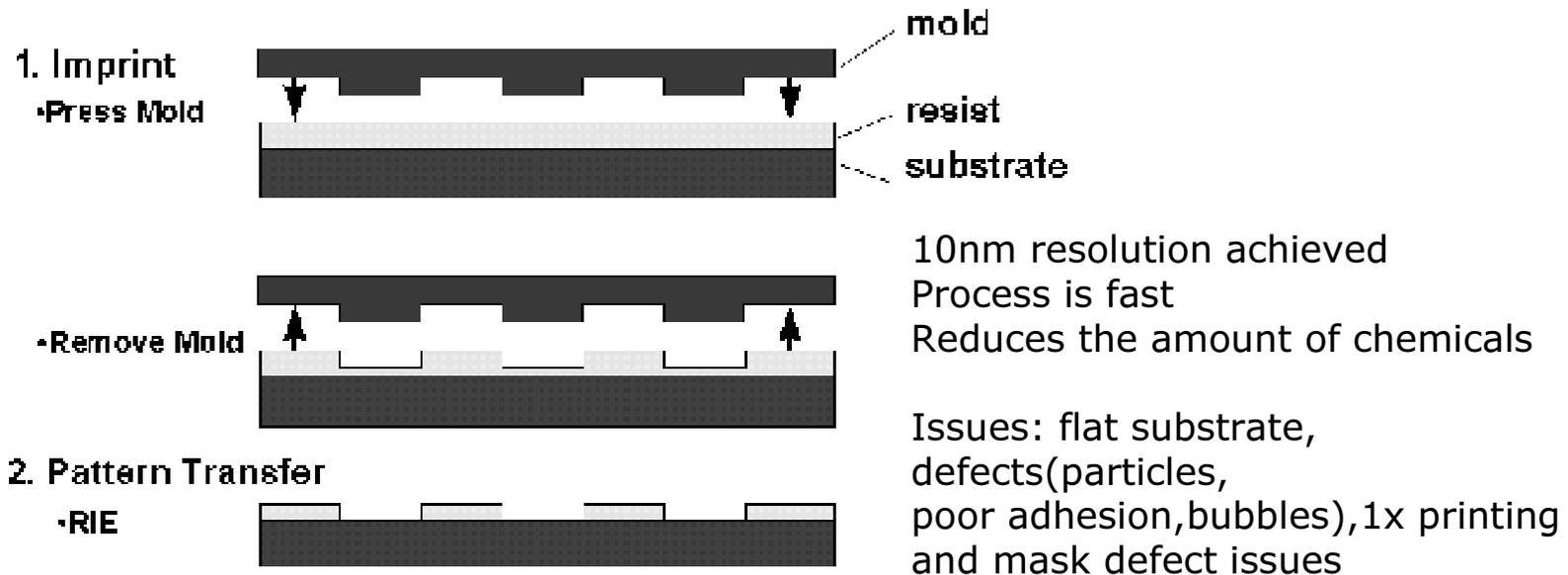
**130nm 1:2 Features**

SEM images of line and space patterns printed with ~60 nm thick Shipley XP-98248 (phenolic ESCAP polymer based) resist on bare silicon and exposed at 157-nm.

U. Okoroanyanwu, *J. Vac. Sci. Technol.* **B 18(6)**, 3381 (2000)

U. Okoroanyanwu, *Future Fab International*, **vol 10**, 157 (2001)

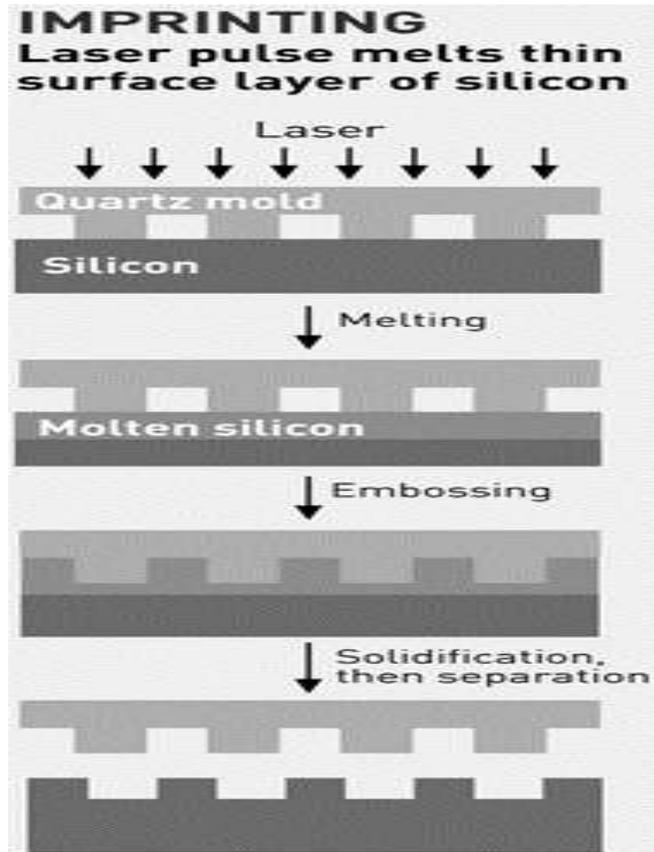
# Emerging resist technology options for post-157nm lithography: nano-imprinting



Patterning is by deforming the coated polymer (polydimethylsiloxane) shape through embossing (with a mold), rather than by altering resist through radiation (with particle beams). Following imprinting, anisotropic etch is used to remove resist residues in the compressed area to expose the underneath substrate.

S.Y. Chou, P.R. Krauss, P.J. Renstrom, *Science* **272**, 88 (1996)  
Xia et al. *Adv. Mater.* **9**, 147 (1997)

# Emerging resist technology options for post-157nm lithography: Direct patterning technique (Laser-Assisted Direct Imprint (LADI))



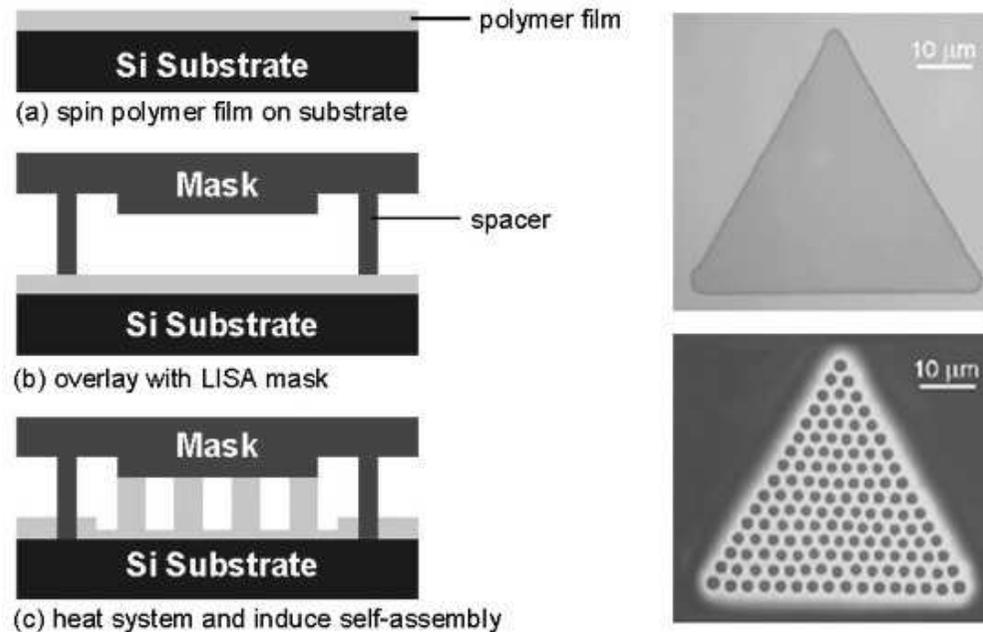
XeCl “excimer” laser with 20ns pulse, a transparent patterned quartz mold to mechanically imprint the molten surface of a silicon wafer. Surface quickly solidifies and, because there is no adhesion between the quartz and silicon, the mold can be removed without damage.

- Extremely high resolution
- Process is fast
- No chemicals!
- No pattern collapse issue

Issues: flat substrate  
1x printing and mask  
defect issues

Chou et al. *Nature* **417**, 835 (2002)

# Emerging resist technology options for post-157nm lithography: Lithographically Induced Self-Assembly (LISA)

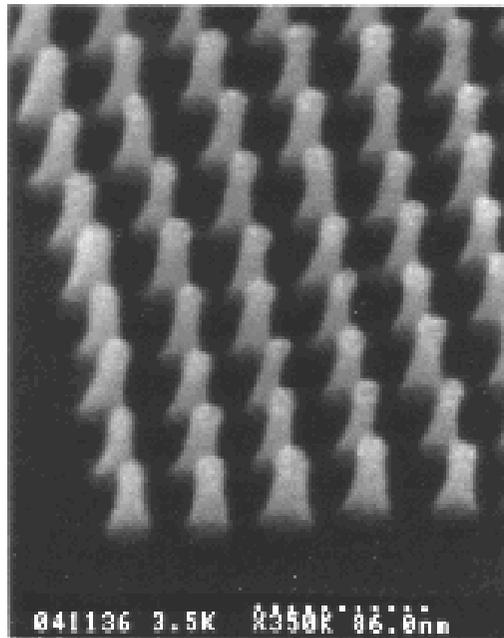


Advantages:  
It is simple.  
Environmentally friendly  
(Eliminates the need  
chemicals used in  
conventional lithography).

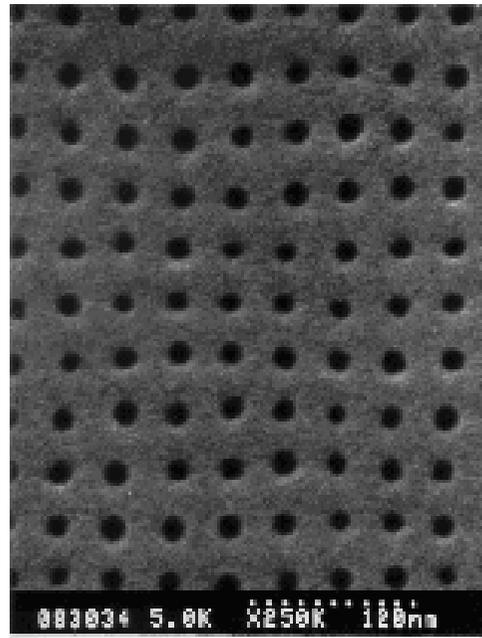
Mask is held apart from the polymer surface by spacers. The system is heated above the  $T_g$  of the polymer, such that the polymer rises up against the forces of gravity and surface Tension, forming periodic structures that are aligned to any pattern on the mask.

- 1). S.Y. Chou and L. Zhuang, J. Vac. Sci. Technol. B **17**, 3197 (1999).
- 2). S.Y. Chou, L. Zhuang, and L.J. Guo, Appl. Phys. Lett. **75**, 1004 (1999).
- 3). P. Deshpande and S.Y. Chou, Appl. Phys. Lett. **79**, 1688 (2001).
- 4). P. Deshpande and S.Y. Chou, J. Vac. Sci. Technol. B **19**, 2741 (2001).
- 5). S.Y. Chou. MRS Bulletin **26**, 512 (2001).

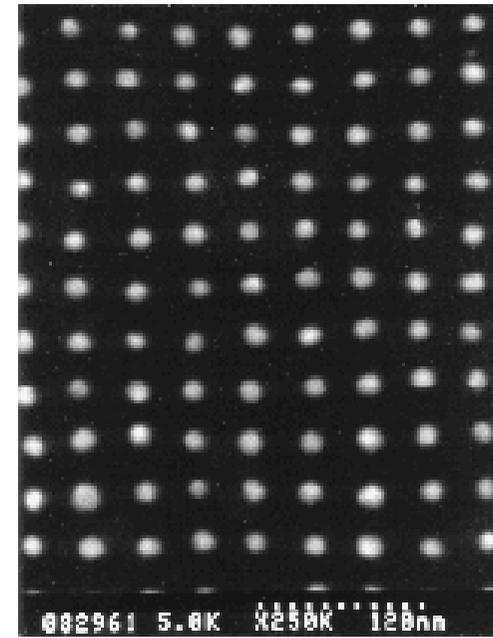
# LADI results



Imprint mold with  
10nm diameter pillars



10nm diameter holes  
imprinted in PMMA



10nm diameter metal  
dots fabricated by NIL

Chou et al. *Nature* **417**, 835 (2002)

## Summary

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- Conventional resist technology will be resolution limited at post-157nm lithography era design rules
  - Chemical amplification chemistry runs into “diffusional limits”
  - Thin film instabilities and degradation of thermophysical properties will become significant.
- Nanoimprinting and self-assembly techniques appear promising, but challenges remain.
  - High resolution with high throughput potential
  - Environmentally friendly
  - Defects remain a concern
- Integrating the best attributes of conventional lithography with those of emerging techniques are feasible and appear promising.
  - Laser-assisted direct imprint & lithographically-induced self assembly are steps in the right direction



## Acknowledgments

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**Monique Erckens (IMEC)  
IMEC Teleconference facilities Dept.**