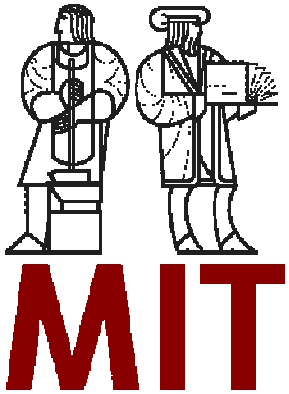


SRC/SEMATECH ERC for Environmentally Benign Semiconductor Manufacturing

Resist-Free Patterning of Low Dielectric Constant Polymer

December 13, 2007

Nathan J. Trujillo

Karen K. Gleason

Structure of This Talk

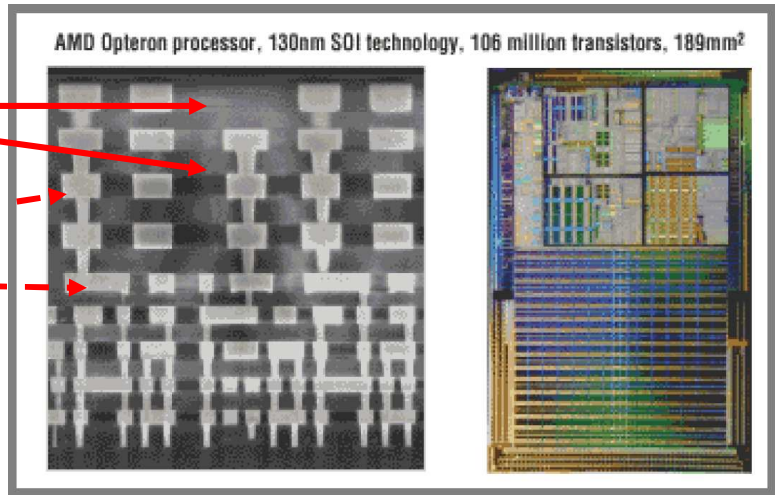
- Background on low-k materials
- The need for environmentally benign low-k processing
- New low-k precursor for iCVD
- Resistless patterning of low-k materials
  - Microcontact printing for additive polymer patterning
  - SAMs for patterned low-k
  - Resist-free photolithography

MIT

Anatomy of an Integrated Circuit

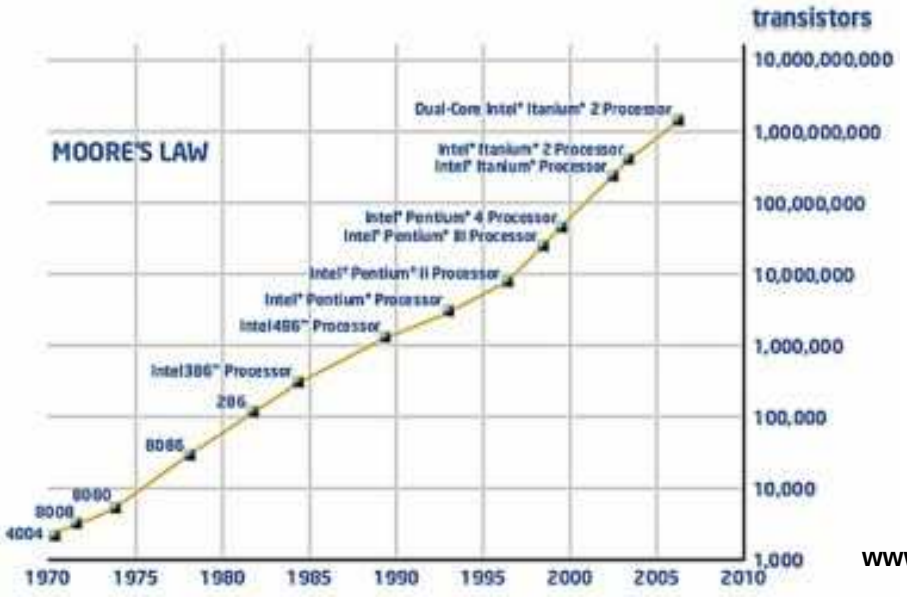
Low-k Dielectric (ILD)

Cu Interconnects



Increasing ILD feature size

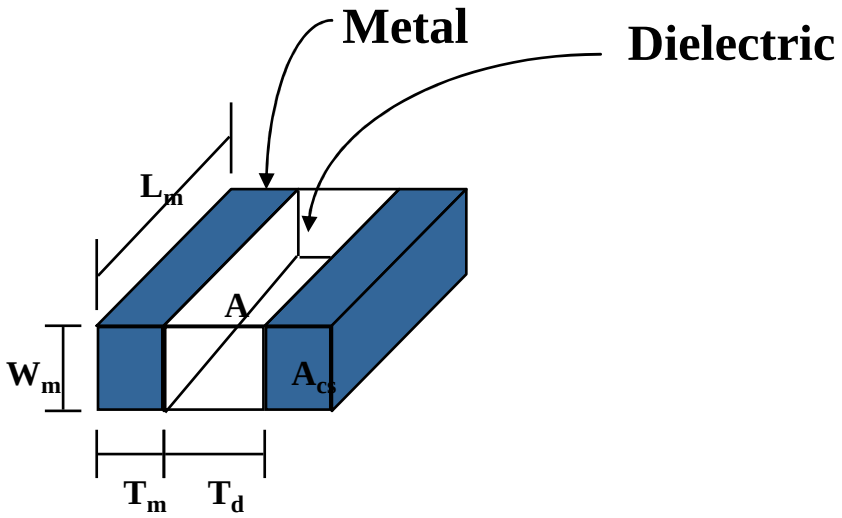
www.amd.com



Features are getting closer together!

www.intel.com

Why low-k?



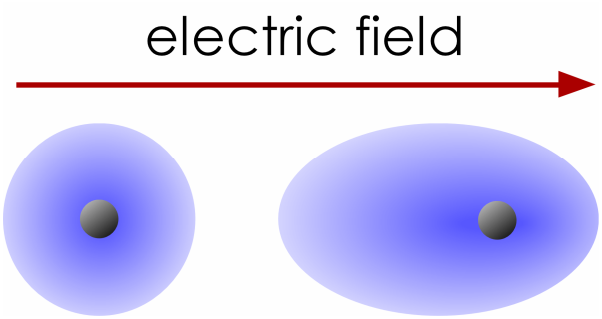
REDUCE:

- **RC Delay** $\tau \sim RC \sim \kappa\varepsilon_0\rho L_m^2/T_m T_d$ — *either metal or dielectric*
- **Power Consumption** $P \sim CV^2f$ — *dielectric only*
- **Cross Talk Noise** $N \sim C_{line\text{-}to\text{-}line}/C_{total}$ — *dielectric only*

MIT

Acquired electric dipole moment per unit volume: Polarization

electronic polarization
(induced dipole moment)



$$P = Zqd$$

P = polarization

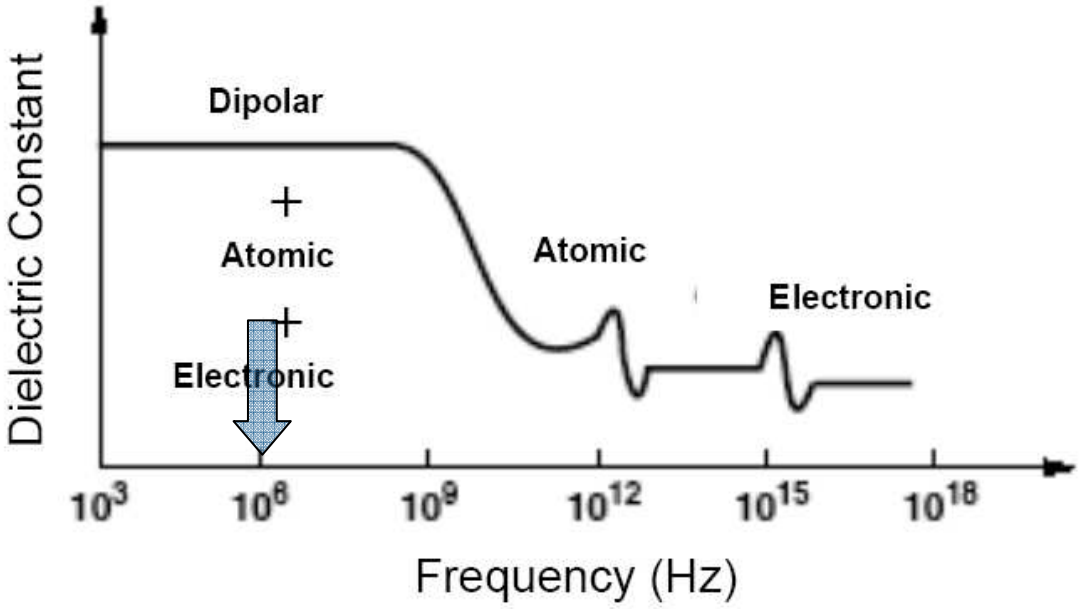
Z = number of charge centers per unit volume

q = electronic charge

d = displacement

} **qd** = induced dipole moment

How does P affect k?



relationship of dielectric constant & polarization

$$k = 1+4\pi P/E$$

relationship of dielectric constant & index of refraction

at low frequency : $k > n^2$

at high frequency: $k = n^2$ **(electronic polarization only)**

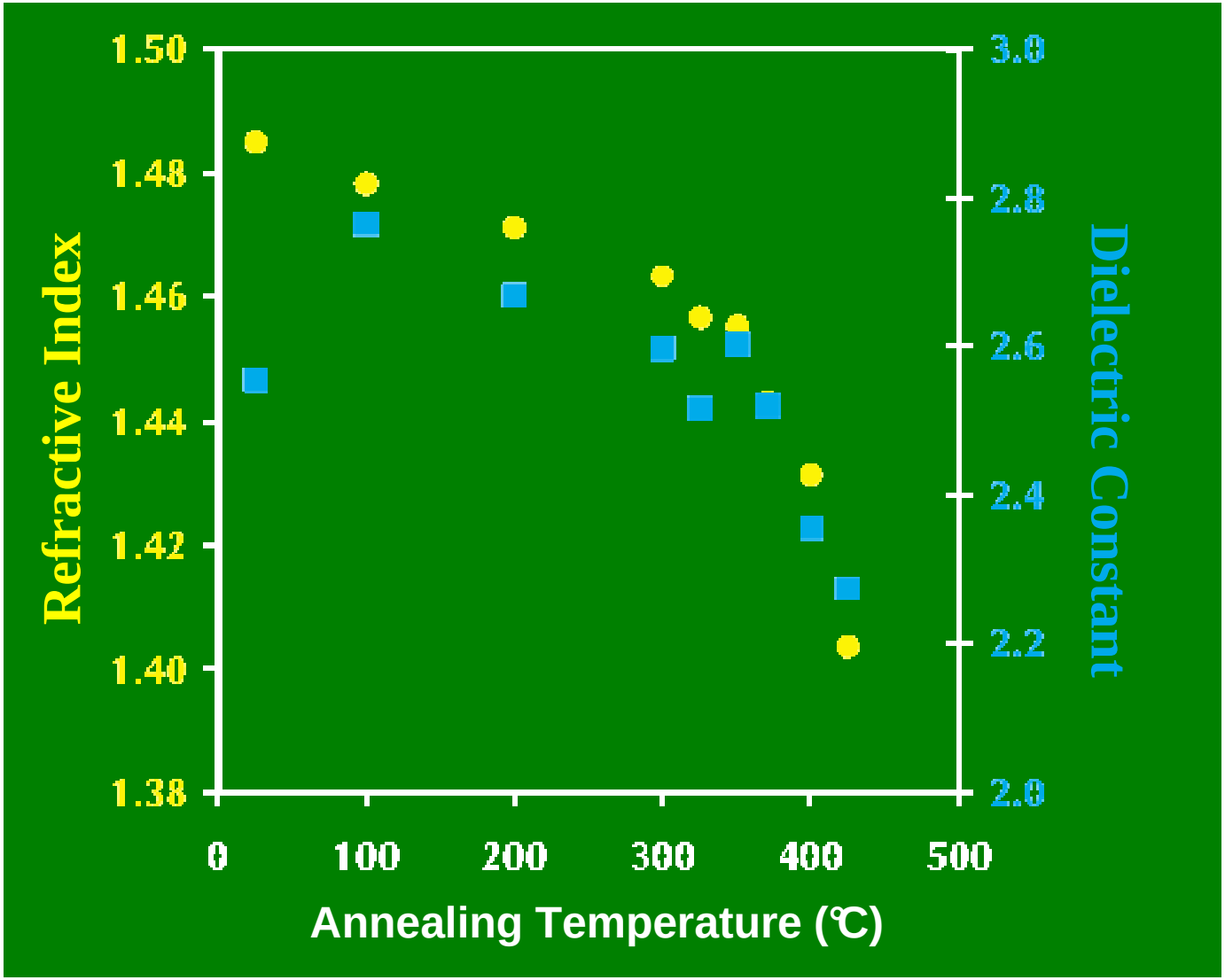
k: How low can you go?

Composition	Fully dense k
SiO_2	4.0
Si:O:F (FSG)	3.2–3.7
Si:O:C:H (OSG)	2.7–3.0
C:F	2.0–2.7

Air

k =1.0

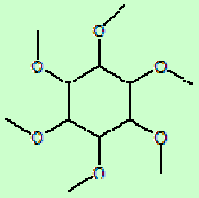
Air to get us there…



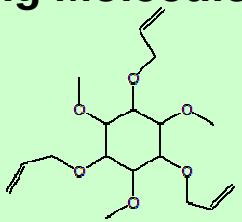
D.D. Burkey , K.K. Gleason, *J. Vac. Sci. Technol. A,* (2004) 22 (1)

Novel Porogens For Low-k

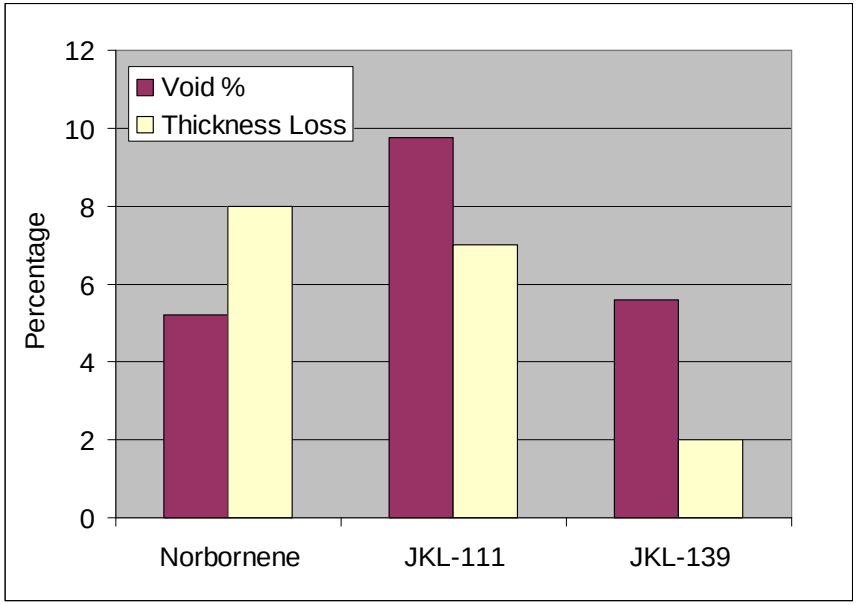
Novel Pore Generating Molecules



Hexamethyl ether of *myo*-inositol
JKL-111



JKL-139



- **Porogens provided by Chris Ober's group at Cornell**
- **Incorporated into V3D3 film through vinyl group and removed by annealing**
- **Film retention compares favorably to commercially available porogen, Norborene**

Source: Baxamusa, O'Shaughnessy, Gleason

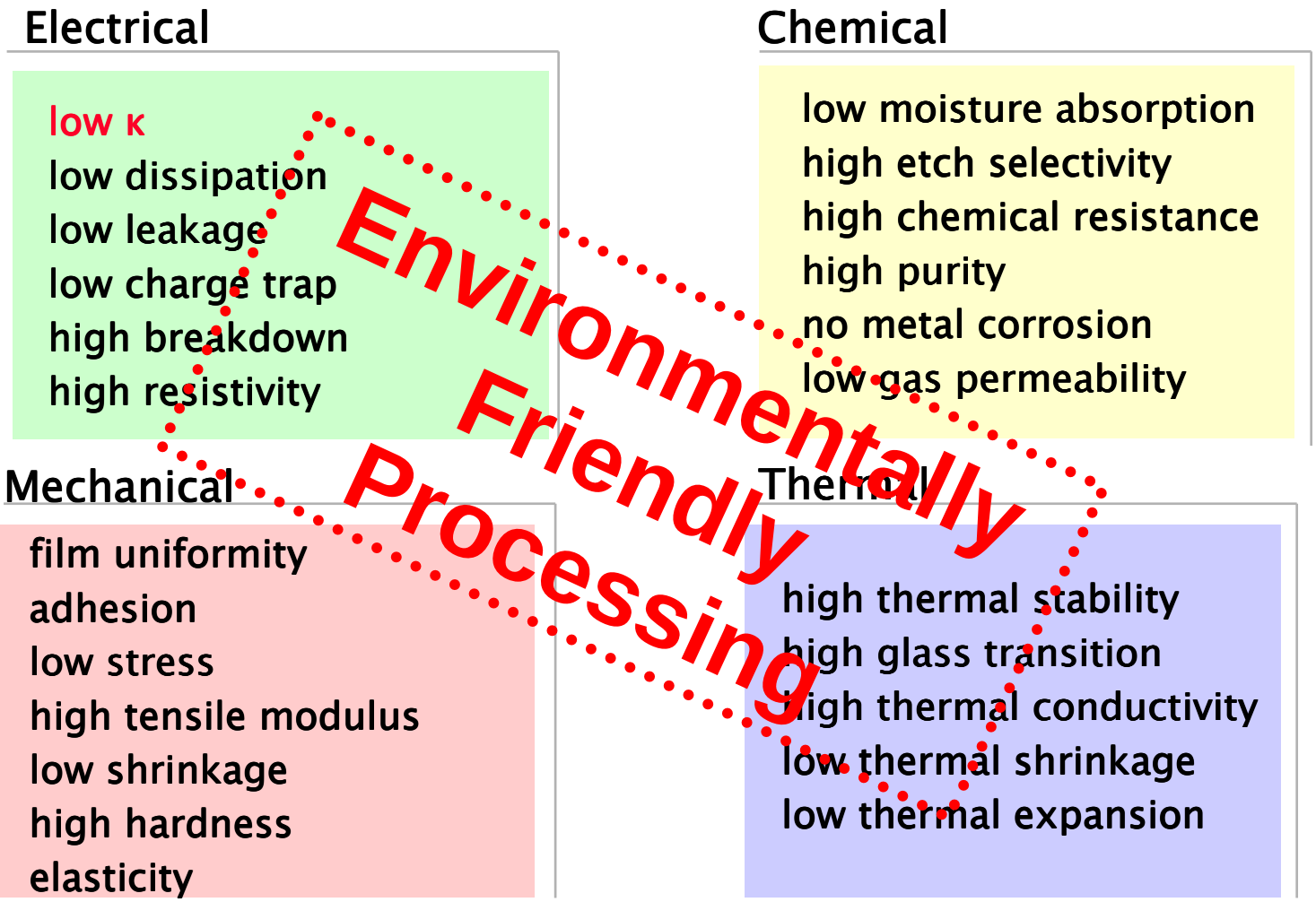
Need For Environmentally Friendly Low-k

	Year of Production	*2005*	*2006*	*2007*	*2008*	*2009*	*2010*	*2011*	*2012*	*2013*
	Technology Node (nm)	*80*	*70*	*65*	*57*	*50*	*45*	*40*	*36*	*32*
WAS	Interlevel metal insulator (minimum expected) – bulk dielectric constant (κ)	≤ 2.7	≤ 2.7	≤ 2.4	≤ 2.4	≤ 2.2	≤ 2.2	≤ 2.2	≤ 2.0	≤ 2.0
IS	Interlevel metal insulator – bulk dielectric constant (κ)	2.6-3.0	2.6-3.0	2.3-2.7	2.3-2.7	2.1-2.4	2.1-2.4	2.1-2.4	1.8-2.1	1.8-2.1
	Low-κ materials—spin-on and CVD	Minimum emission/waste processes			75% raw material (chemical) utilization			90% raw material (chemicals) utilization		

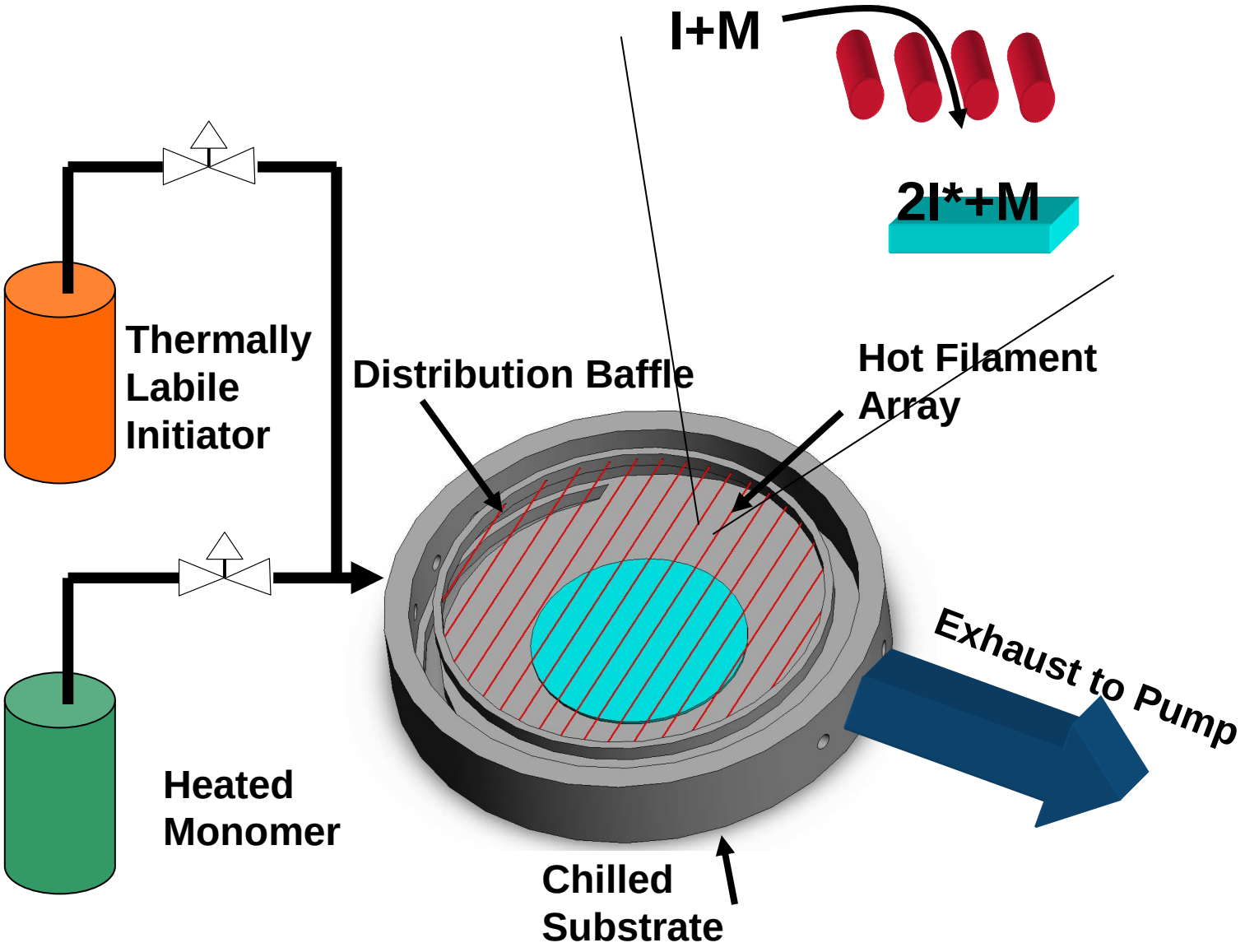
www.itrs.net 2006 ITRS Roadmap

In Short: Need k= 2.1 by 2012 and 90% chemical utilization by 2011!

Attractive ILDs Have…

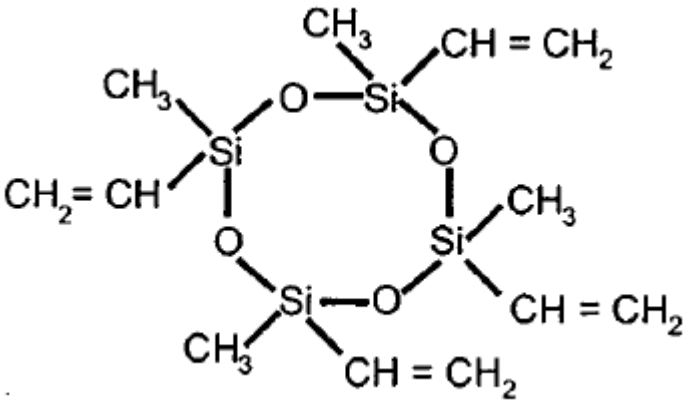


iCVD Summary

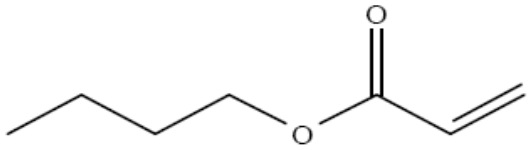


Low-k iCVD Precursor V4D4

- **Open siloxane ring for low-k**
- **Four vinyl groups make ideal for iCVD**
- **No need for cross linker**
- **3-D network from "puckered" ring**
- **Plasma polymerization gives k as low as 2.5**



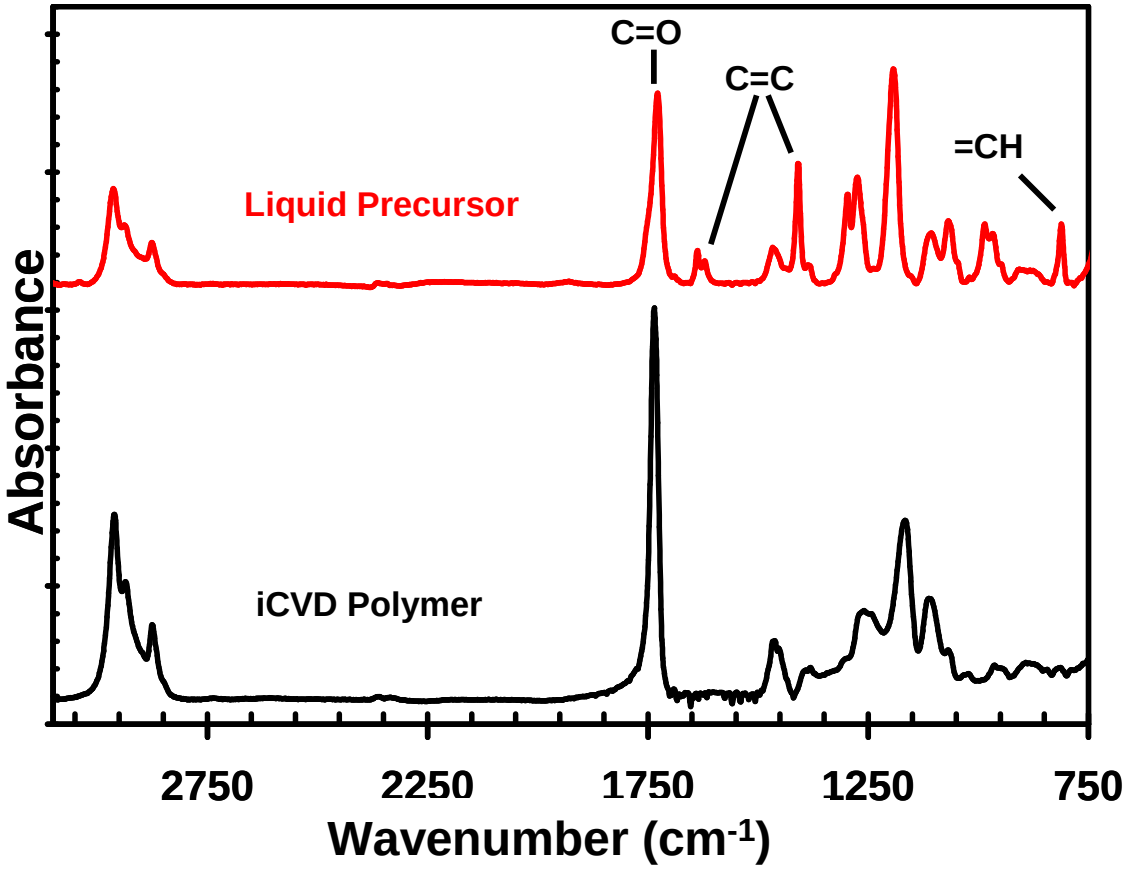
1,3,5,7-TETRAVINYLTETRAMETHYLCYCLOTETRASILOXANE

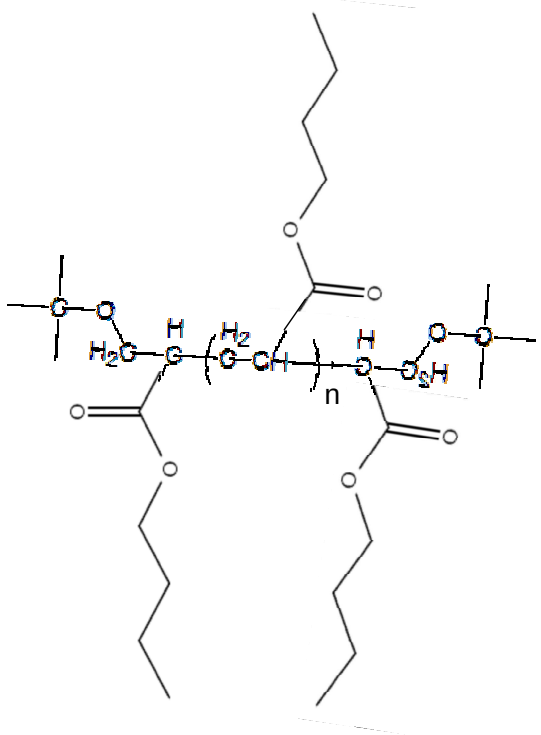


Proxy Monomer
n-Butyl Acrylate

MIT

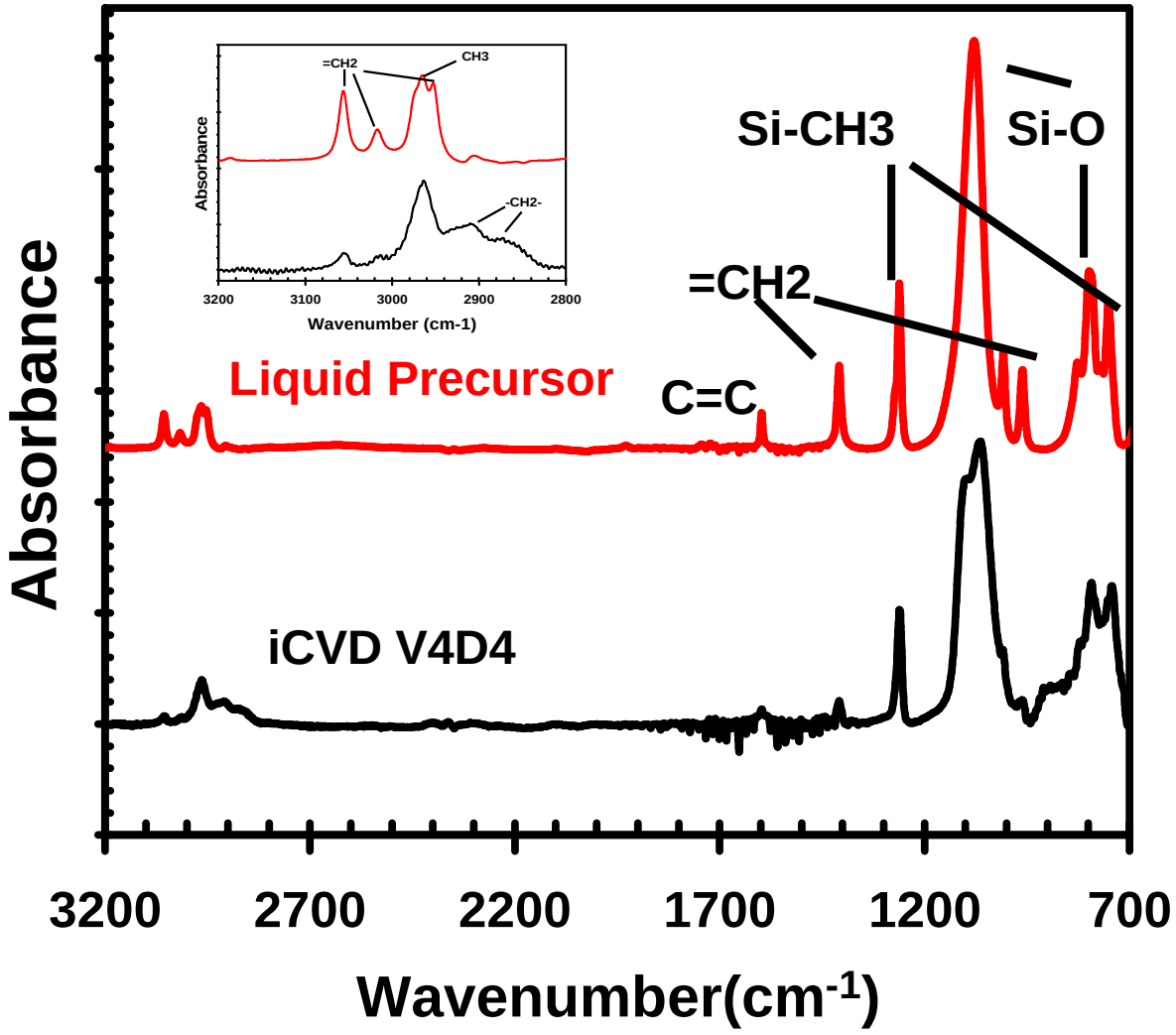
Poly(butyl acrylate) With TBP Initiator



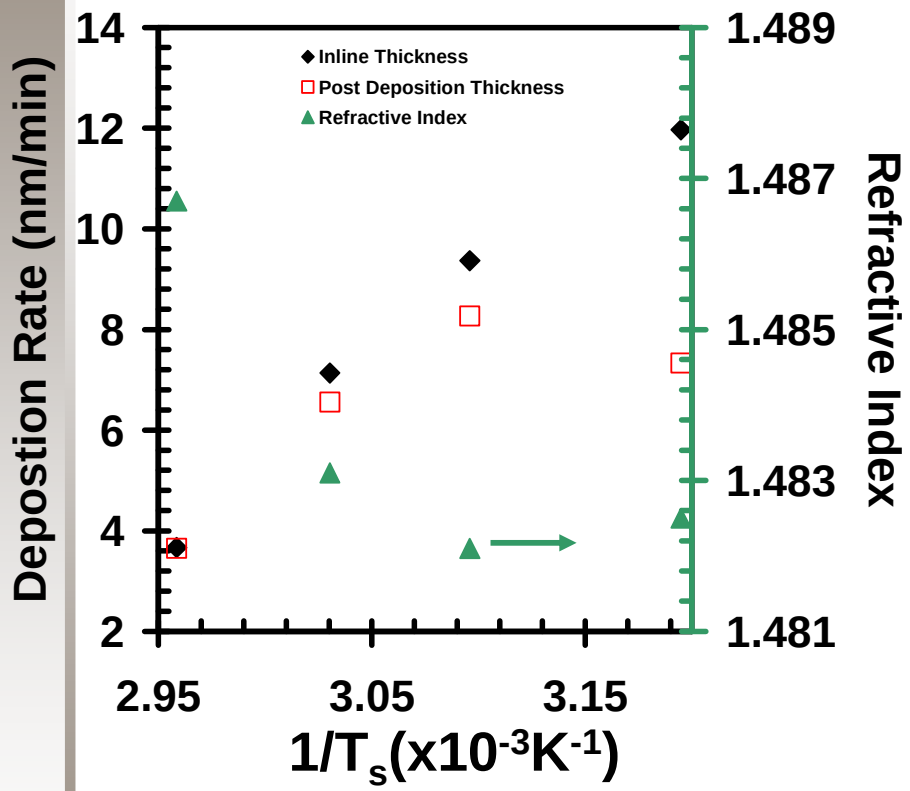


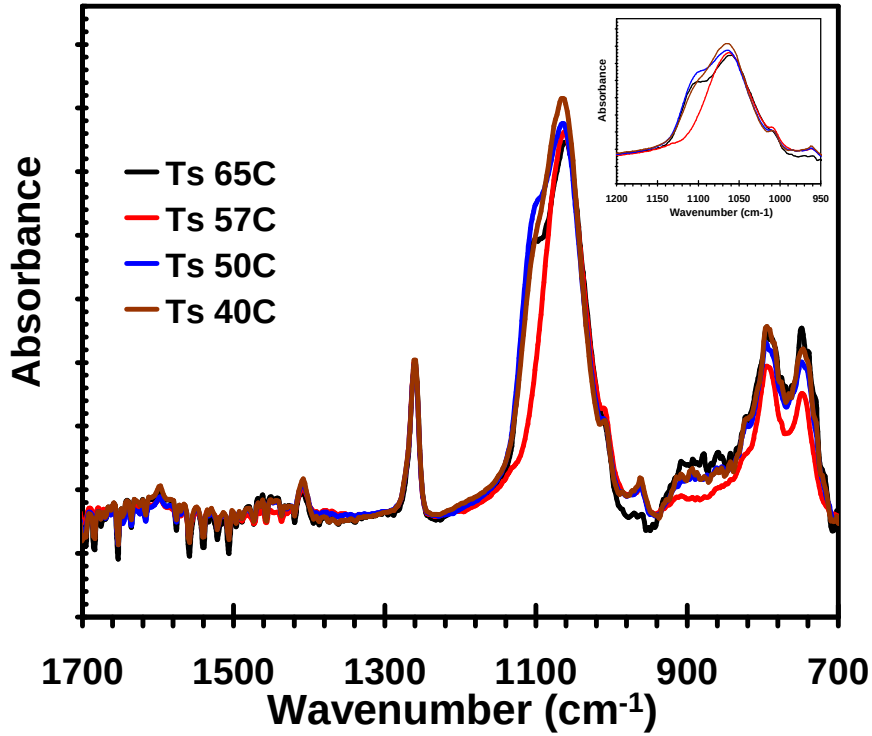
Deposition rates over 100 nm/min

V4D4 Successfully Polymerized Via iCVD



Substrate Temperature Study



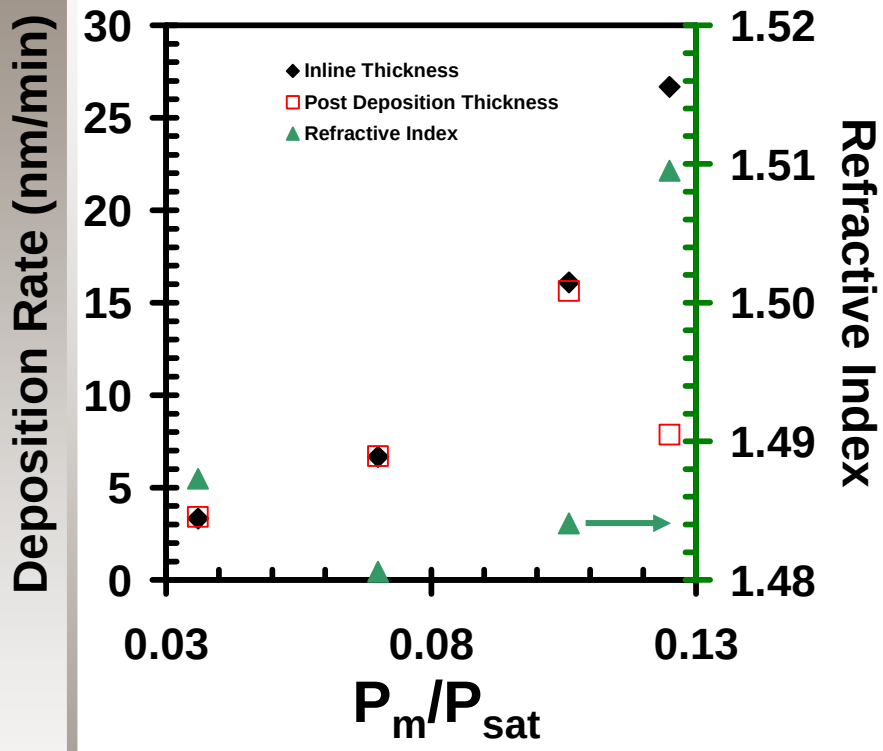


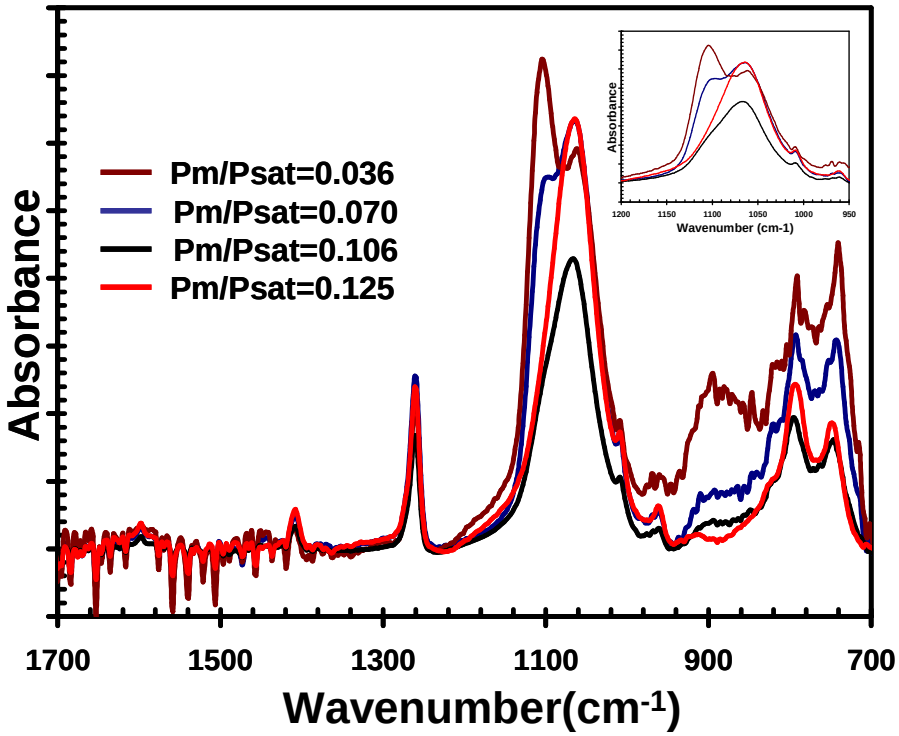
Negative activation energy indicates absorption limited process

Little apparent structural differences between most films

MIT

Pressure Effects on Structure





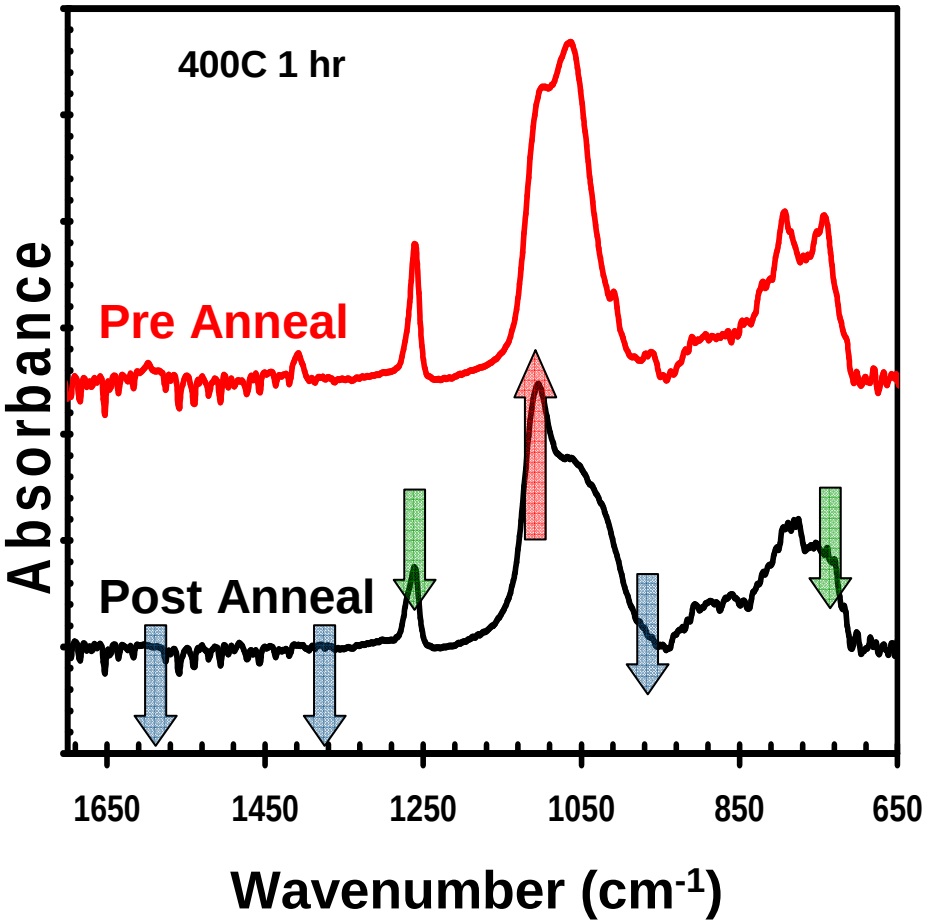
Same absorption trend indicates > monolayer absorption at high P

No condensation in reactor.

Significantly more Si-O cage structure at lower pressures.

Corresponds to less dense film

Thermal Stability: Sample T_{sub}= 50℃



Thickness Retention

84.7%

Refractive Index

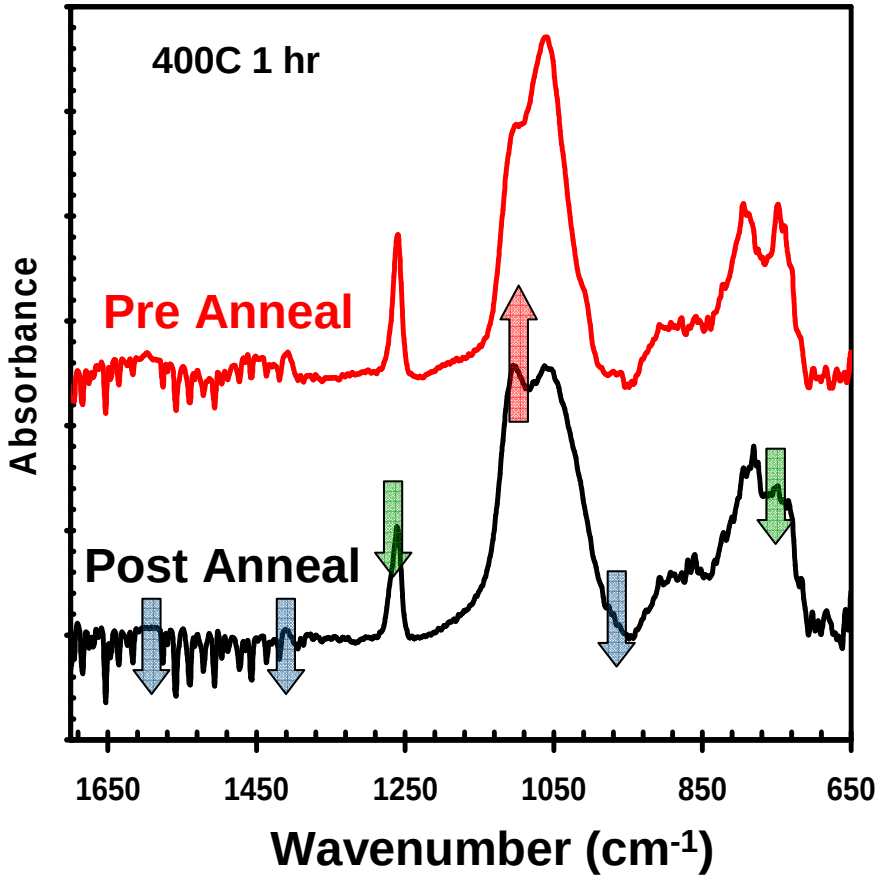
1.481 **1.451**

Dielectric Constant*

2.75 **2.55**

*Correlated from Burkey *J. Vac. Sci.* (2004) 22 (1)

Thermal Stability: Sample T_{sub}= 65℃



Thickness Retention

93.5%

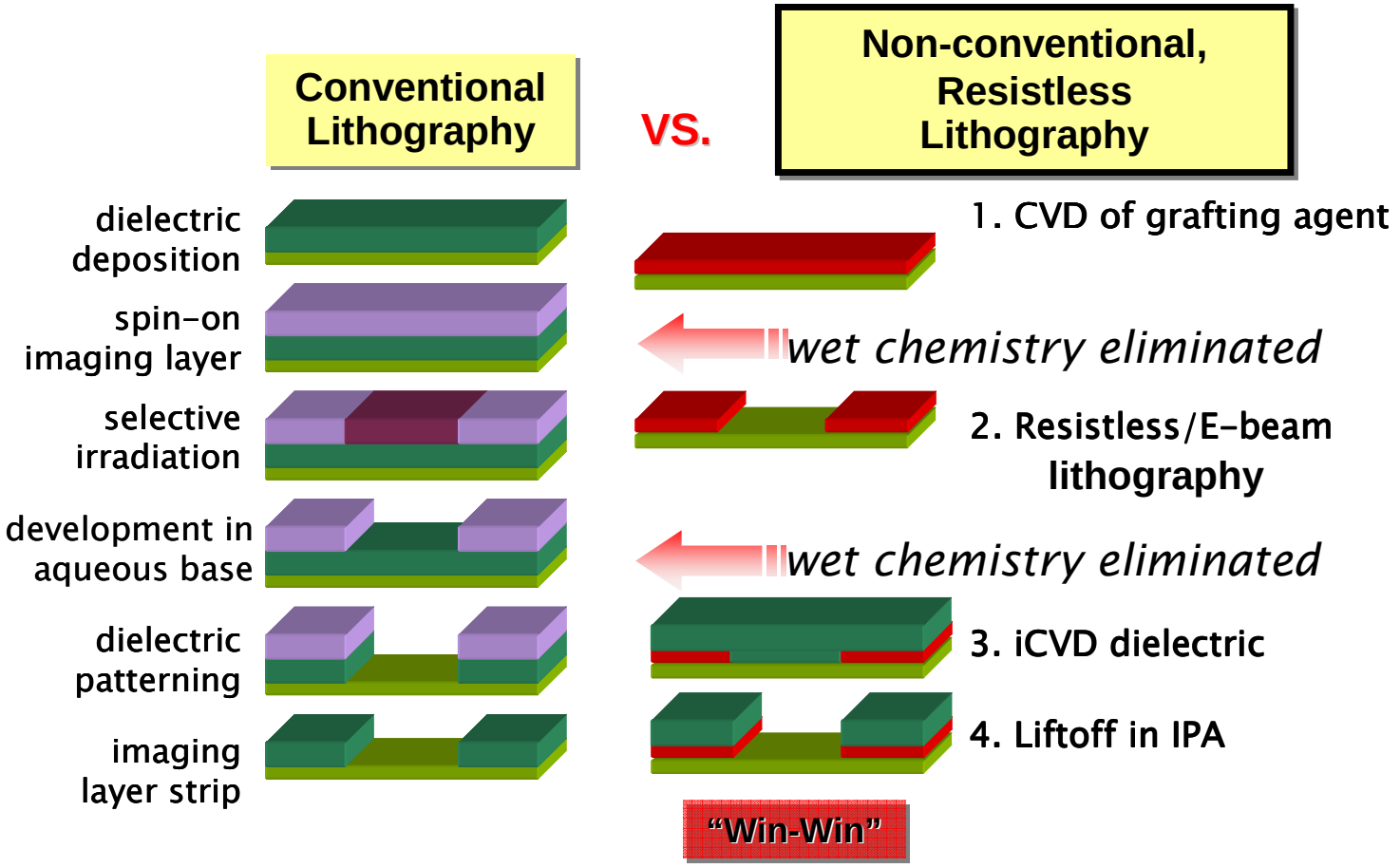
Refractive Index

1.493 **1.448**

***For plasma polymerized V4D4 n=1.45 corresponds to k=2.5!**

*Lubguban et al., *J. App. Phy.* (2002) 92 (2)

Resistless Patterning Prevents Waste

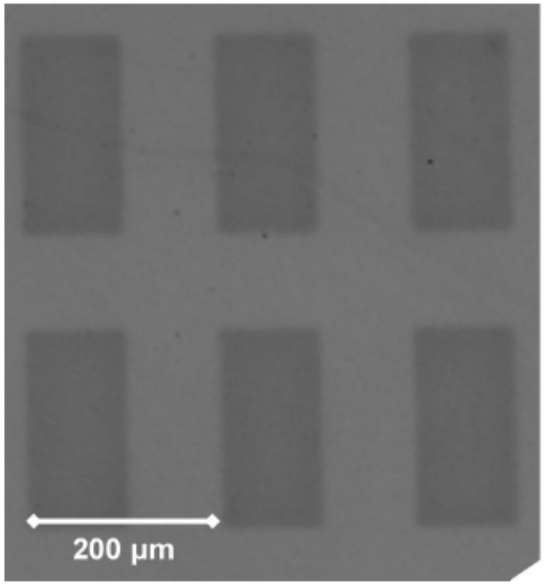


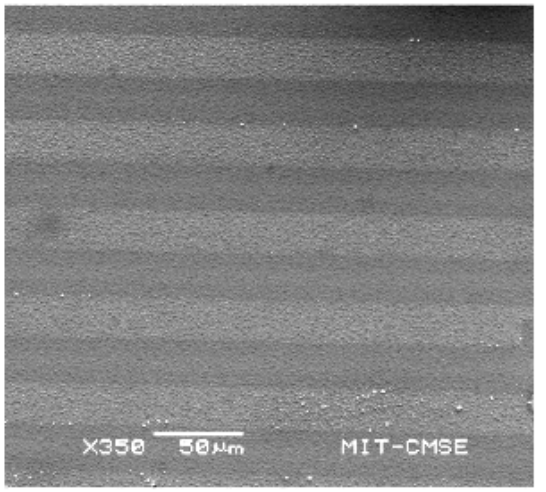
Simplify processing

Reduce ESH impact

Additively Patterned p(CHMA) Using piCVD

- **Micro contact printing to pattern photoinitiator, Michler's Ketone**
- **25 micron features 100nm thick in 45 min**
- **Room temperature deposition**
- **No autopolymerization with 365nm light**

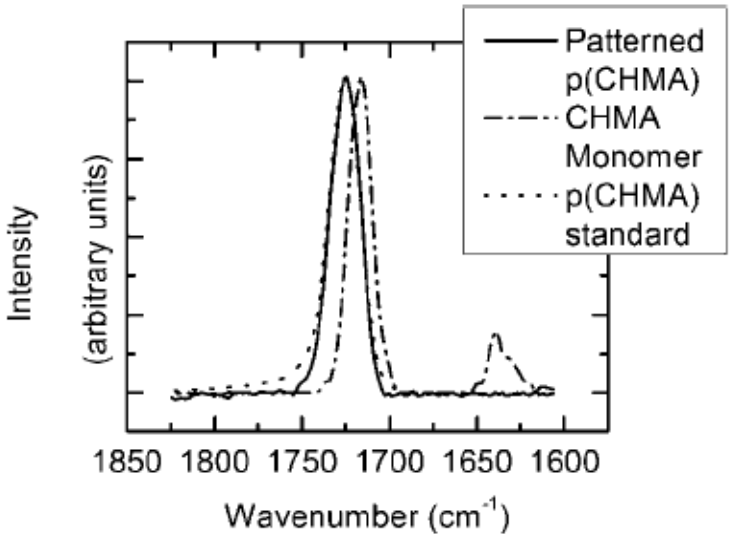


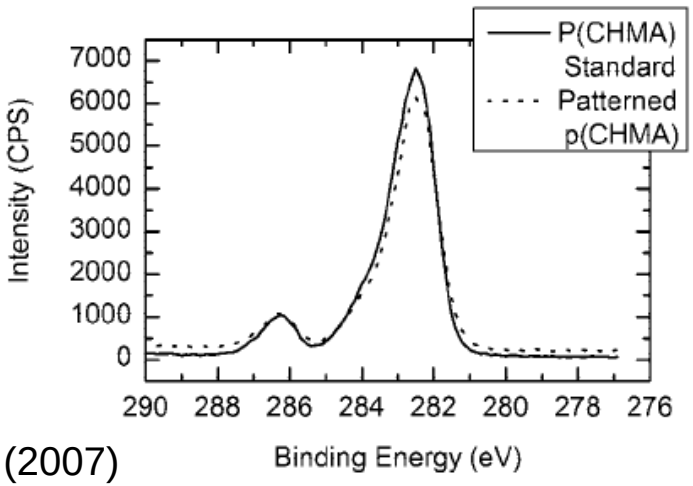


O'Shaughnessy, Baxamusa, Gleason, *Chem. Mater.,* (2007)

Additively Patterned p(CHMA) Using piCVD

- **FTIR confirms polymerization took place**
- **C1 s XPS matches carbonyl and methyl peaks**
- **Resolution determined by PDMS stamp**
- **No covalent adhesion to substrate**

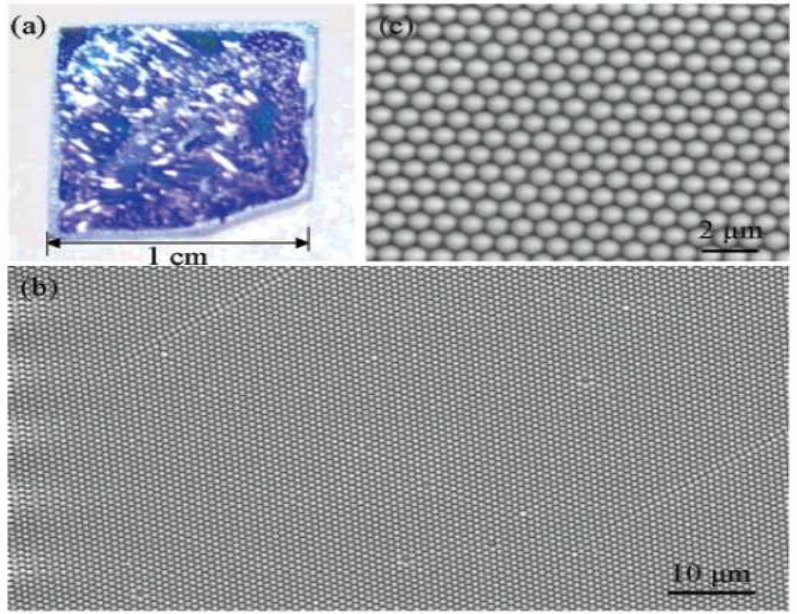


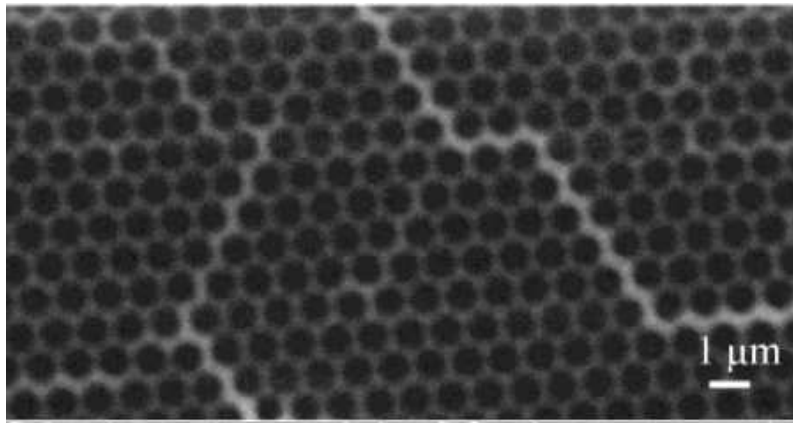


O'Shaughnessy, Baxamusa, Gleason, *Chem. Mater.*, (2007)

Self Assembly For Resist-Free Patterning

- PS monolayers self-assemble into HCP configuration
- Many publications report methods for creating SAM
- Sputtering usually used for pattering
- Large well-ordered arrays from inexpensive non-conventional lithography

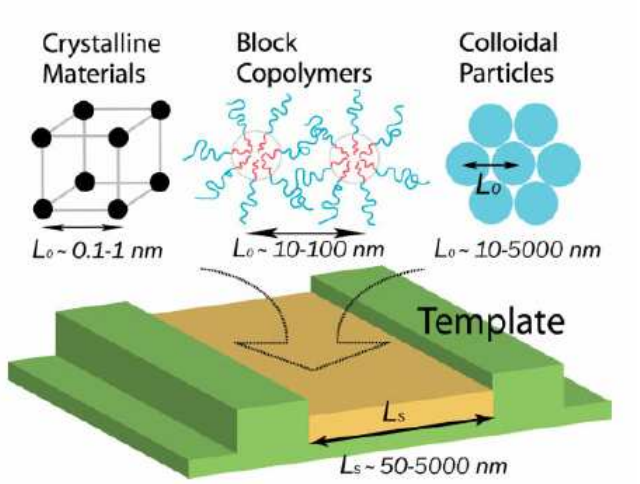


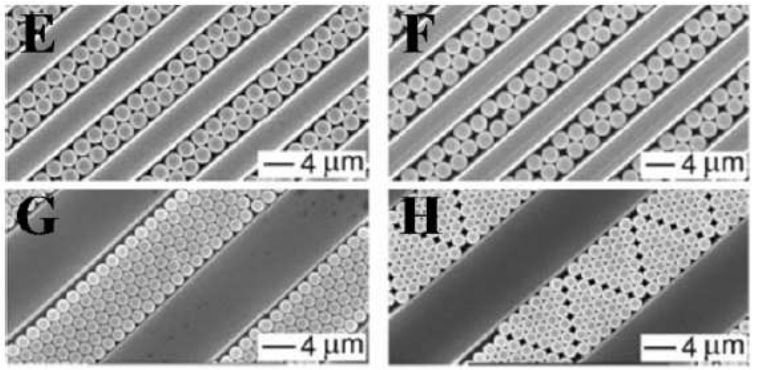


Wang et al.,*Nano Lett.,* (2004),4, (3)

Top Down Helping Bottom Up

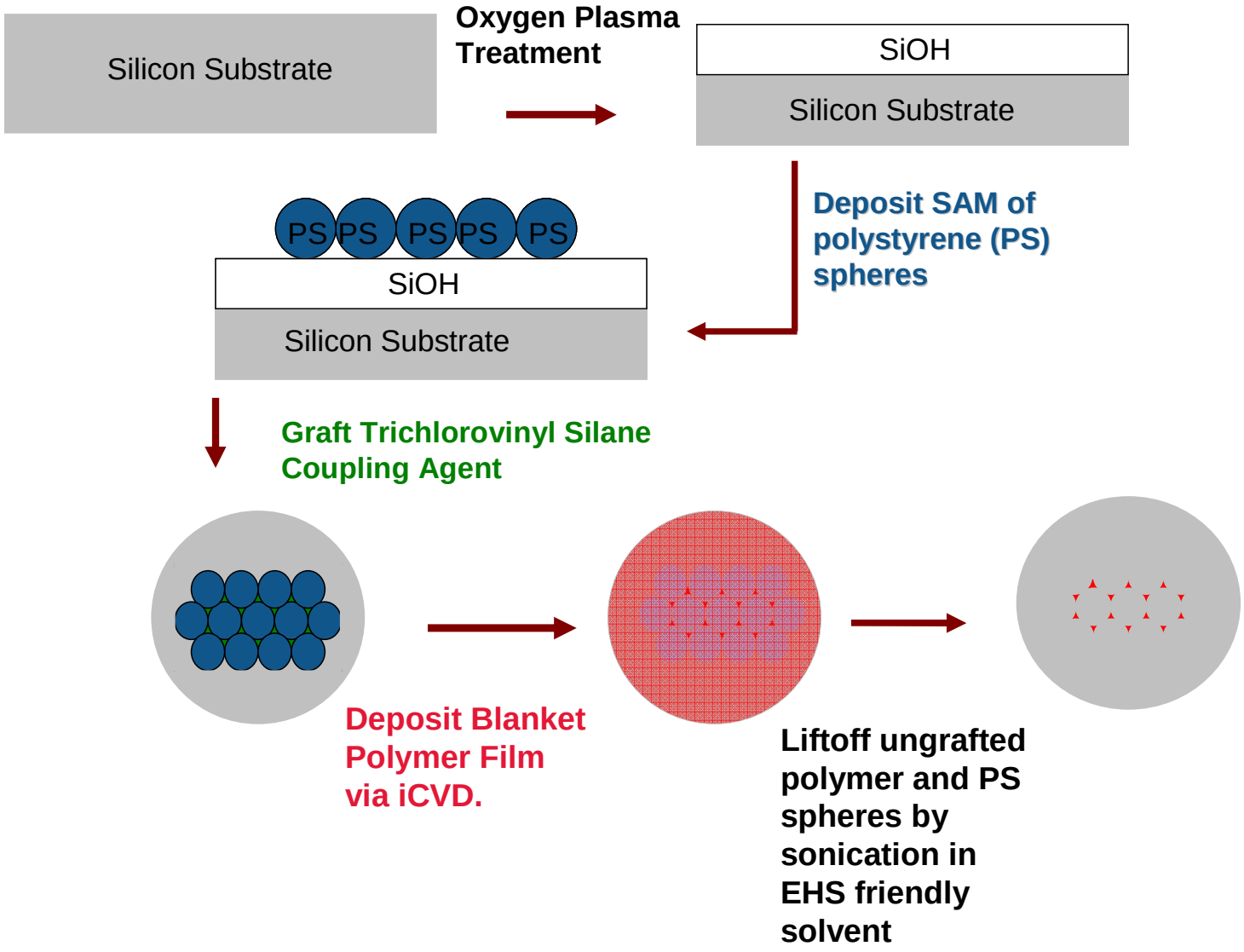
- **Use of conventional lithography to create large scale orientation**
- **Eliminates large scale defects**
- **Drives rational design for hierarchical structures with periodic features**
- **Can work with various forms of self-assembly**





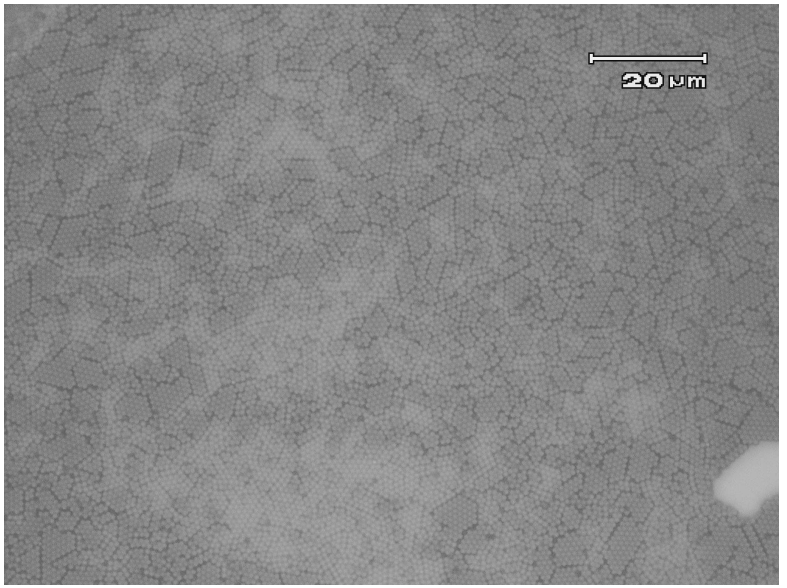
Cheng et al., *Adv. Mater.* (2006), *18*

Additive Polymer Patterning Using Self Assembled Monolayer(SAM) as Mask



Resistless Patterned poly(butyl acrylate)

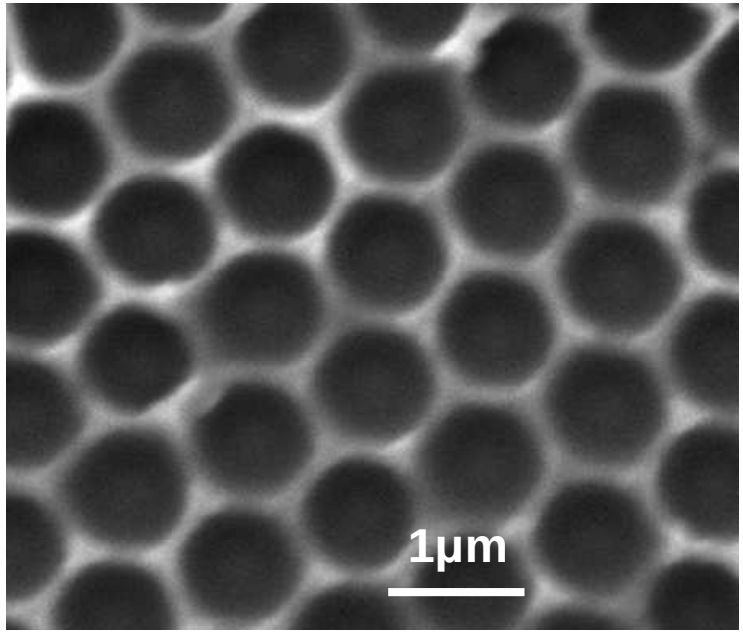
- Solution cast 1 µm spheres in TritonX/Methanol
- Trichlorovinylsilane used as coupling agent
- Deposited 1µm film of poly(butyl acrylate)
- Sonication in THF overnight

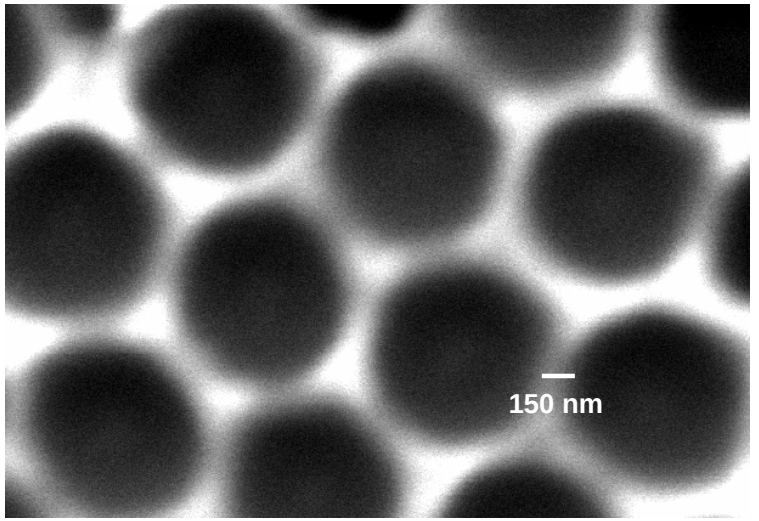


MIT

3…2…1……Lift-off!

- SEM images show complete lift-off
- Large honeycomb pattern observed
- Feature sizes as small as 150nm
- Withstand repeated solvent rinse

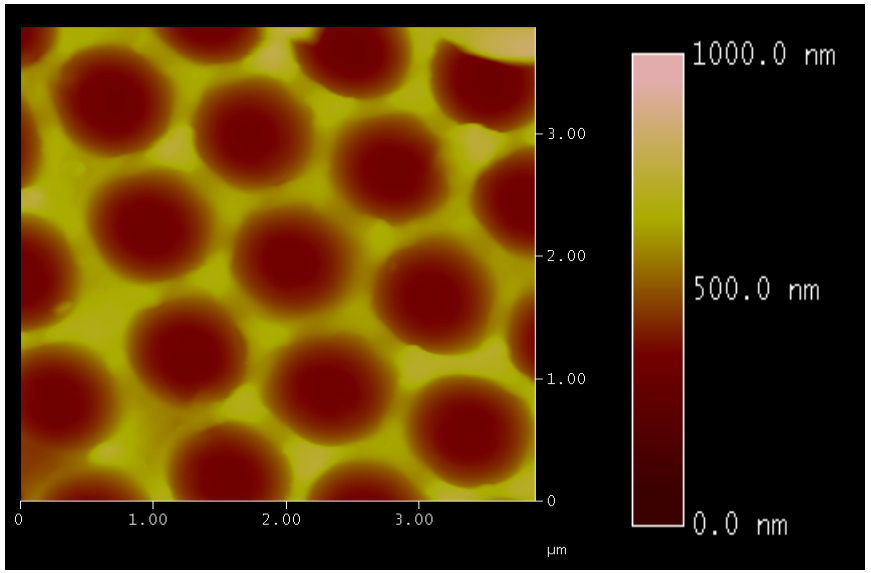




MIT

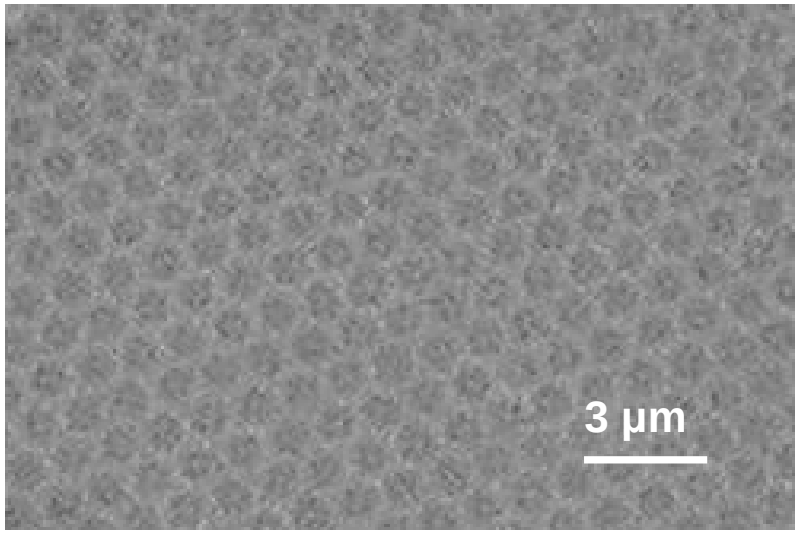
AFM Image of Grafted Pattern

- Very high aspect ratio features
- Height up to 700 nm
- Could not obtain thick grafted film without particles.
- Knudsen diffusion leads to different reaction scheme within SAM domains



Low-k Lift-Off With IPA

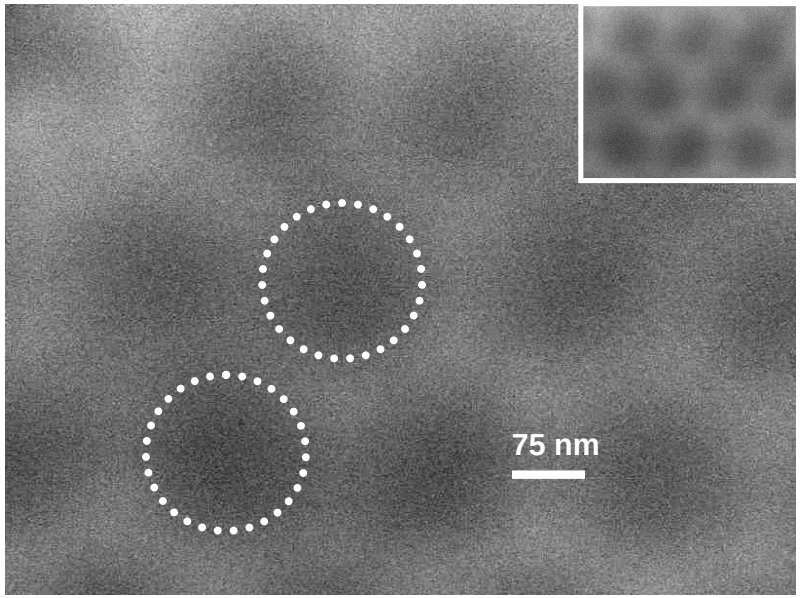
- V4D4 Pattern with 1 µm spheres
- Very well-ordered patterns achieved
- Lift-off after sonicating in IPA for 1 hr
- Achieved full lift-off with environmentally friendly solvent



MIT

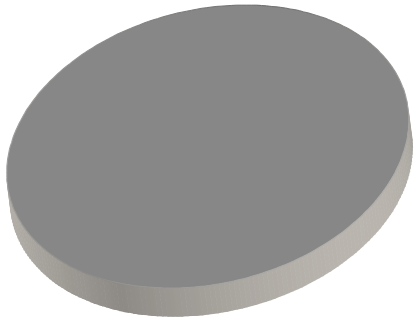
Environmentally Friendly 75 nm Low-k Pattern

- Used 200nm spheres for pattern
- Very well ordered patterns achieved from IPA lift-off
- Smallest features about 75nm wide and about 100nm in height
- Excellent substrate adhesion:10 minute sonication in THF



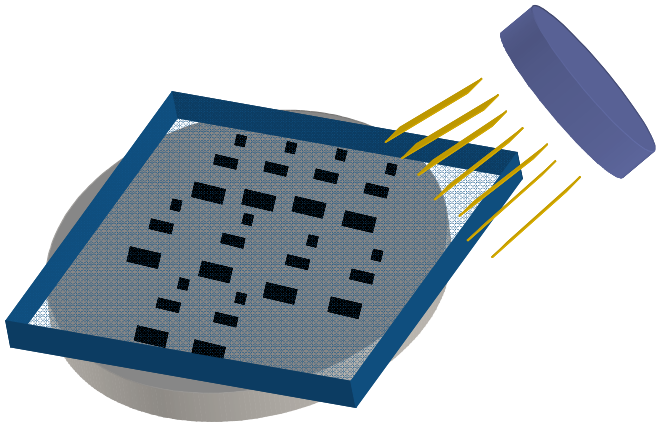
MIT

Resist-Free Photo Lithography

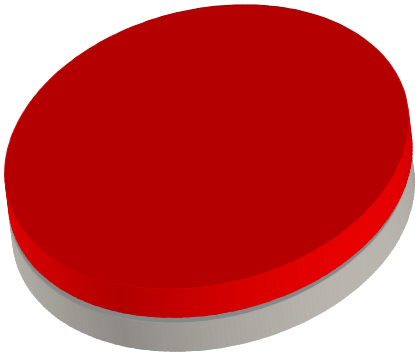


Vinyl Silane Treated Wafer

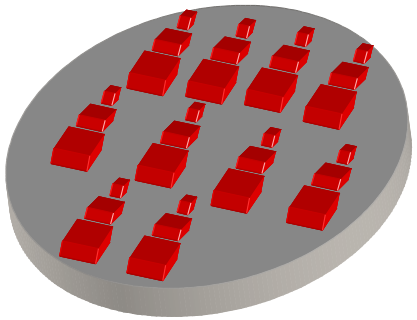
Quartz Shadow
Mask and Deep UV
Light Exposure



Deposit Blanket
Polymer Film Via iCVD



Rinse/Sonicate With
EHS Friendly
Solvent



MIT

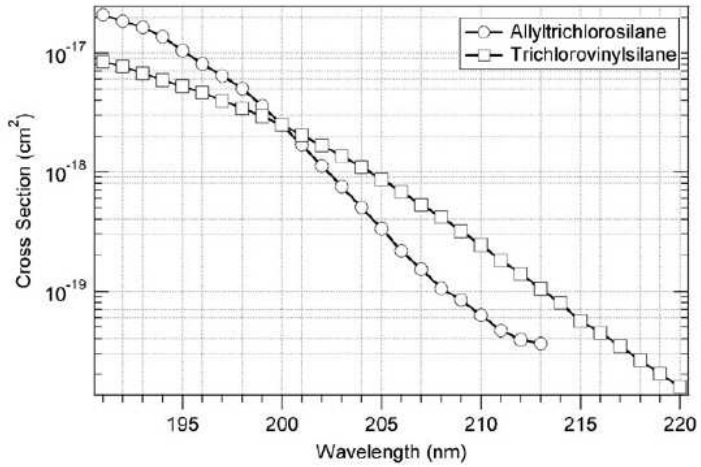
Photolysis of Trichlorovinylsilane

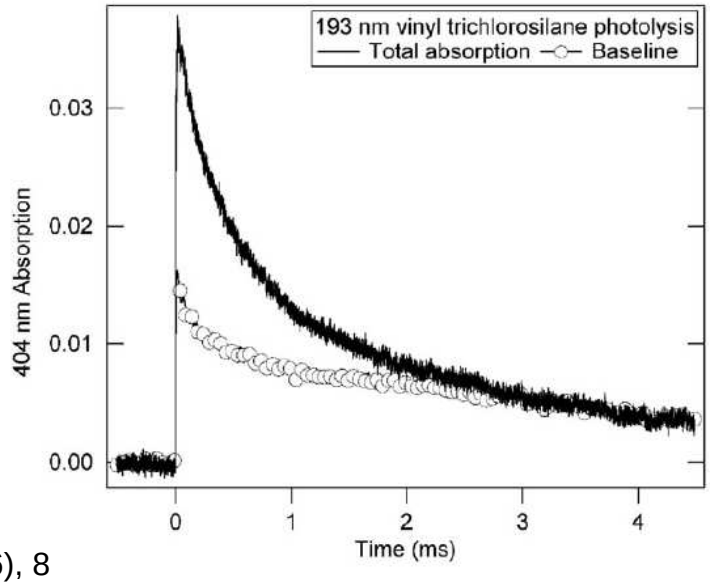
$$RSiCl_3 \xrightarrow{193\ nm} RSiCl_2 + Cl$$

$$RSiCl_3 \xrightarrow{193\ nm} R + SiCl_3$$

$$RSiCl_3 \xrightarrow{193\ nm} RCl + SiCl_2$$

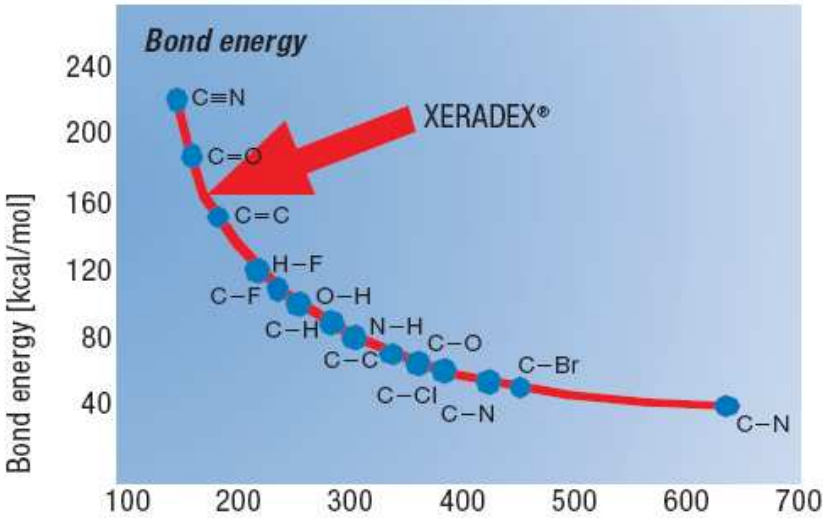
$$RSiCl_3 \xrightarrow{193\ nm} RSiCl + Cl_2$$



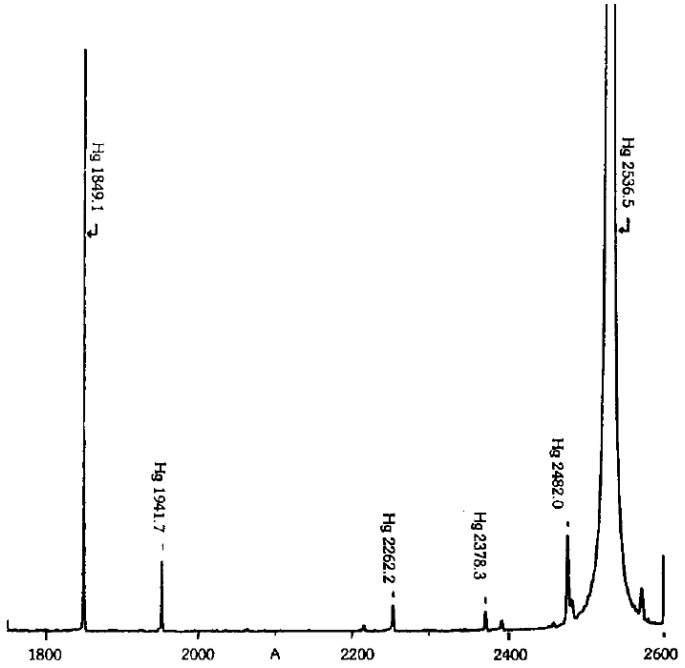


DeSain et al., *Phys. Chem. Chem. Phys,* (2006), 8

Hg Lamp: The Cheap Alternative



www.Hitechlamaps.com



www.Uvp.com

$8,000 for XERADEX®

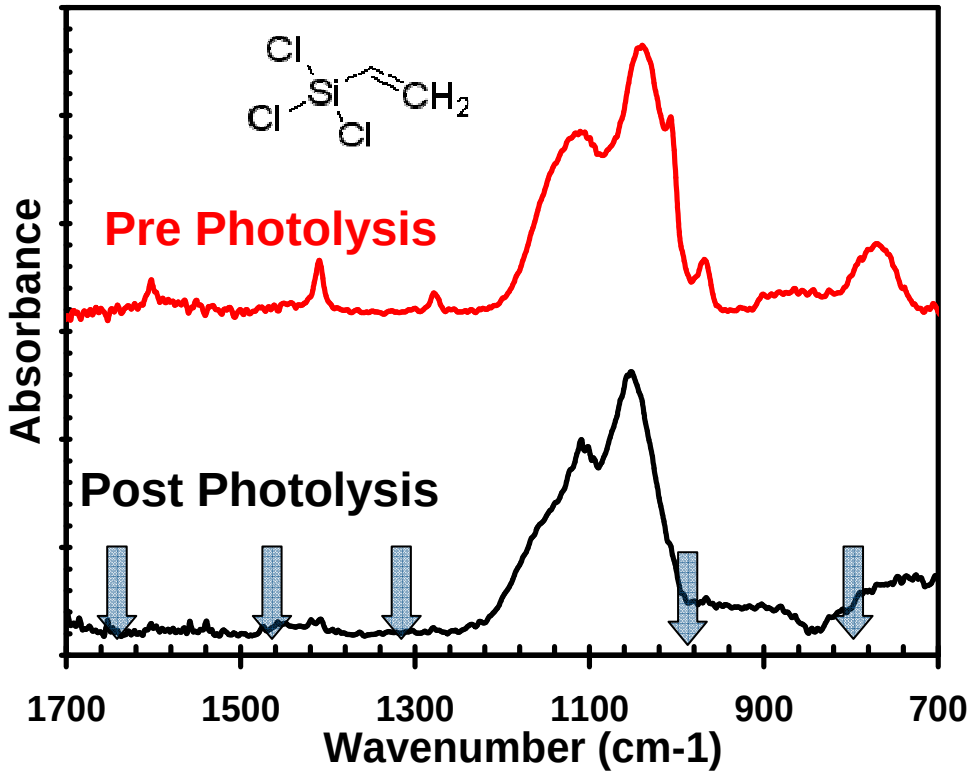
UHV Lamp, 40 W VUV radiation

Hg lamp in house= Free

Less than 1W output in range of interest

MIT

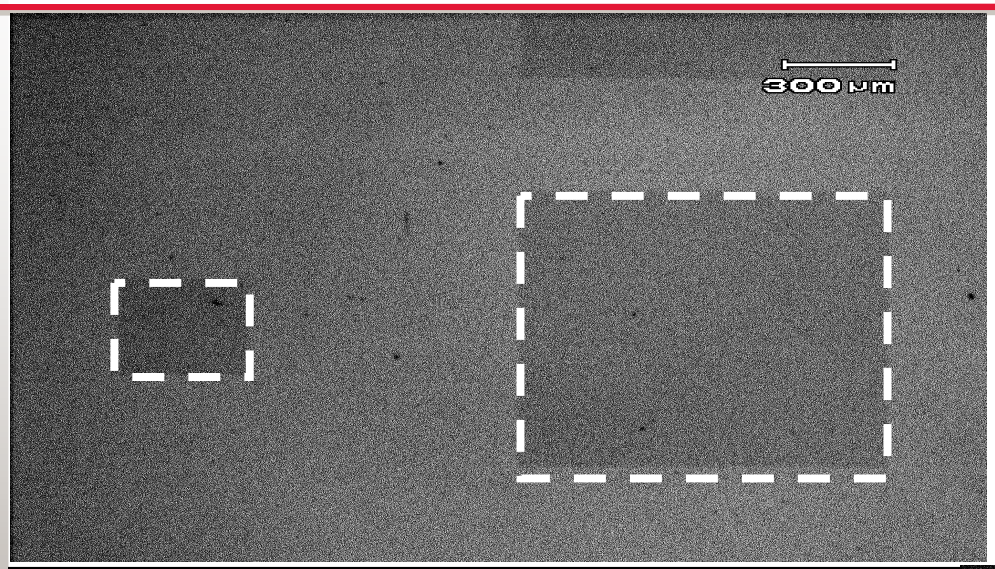
Grafting and Photolysis



Thickness 28nm	Contact Angle 97º
Thickness 26nm	Contact Angle 50º

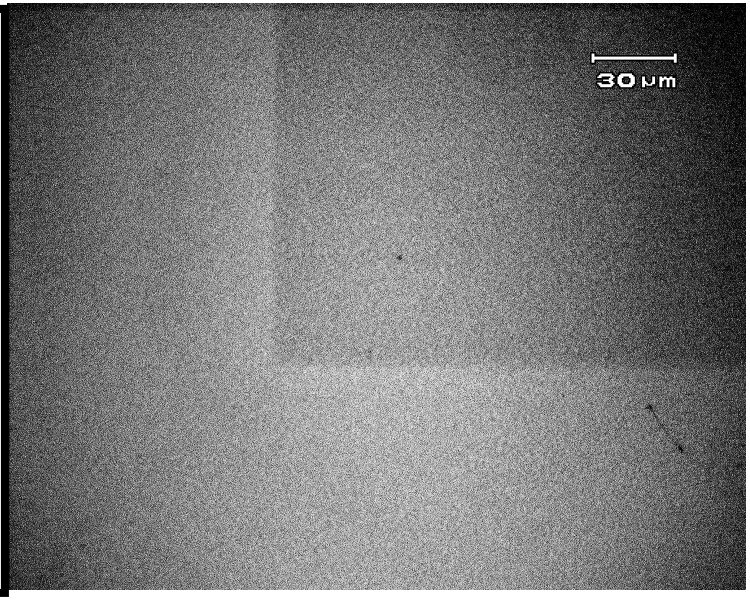
Loss of organic moieties and hydrophilic contact angle indicate destruction of vinyl

Environmentally Friendly Photolithography of poly(butyl acrylate)



Pre Deposition
Thickness 35 nm
Contact Angle 68º

Post Deposition
Thickness 53 nm
Contact Angle 105º



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Conclusion

- Low-k poly(V4D4) successfully deposited via iCVD
- Critical substrate temperature and Pm/Psat at which deposition rate declines
- Low reactor pressure yields highest Si-O cage structure in polymer
- V4D4 films are thermally stable at 400ºC
- Dielectric constant below 2.5 possible without porogen
- Additive patterning achieved through microcontact printing
- 75 nm low-k pattern produced by environmentally friendly process
- Resist free photolithography possible using 193 nm light

MIT

Future Work

- Build test structures to measure k
- Mechanical Characterization of V4D4 blanket film
- Introduce porogens as done with V3D3 in collaboration with Cornell
- Resistless photolithography with smaller features
- Extend to e-beam patterned wafers from Cornell for high resolution features
- Deposit thicker polymer via resistless photolithography patterning (may require crosslinker)

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