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SRC/SEMATECH ERC for Environmentally Benign Semiconductor Manufacturing

# Depositing and Patterning a Robust and "Dense" Low-*k* Polymer by iCVD

December 11, 2008


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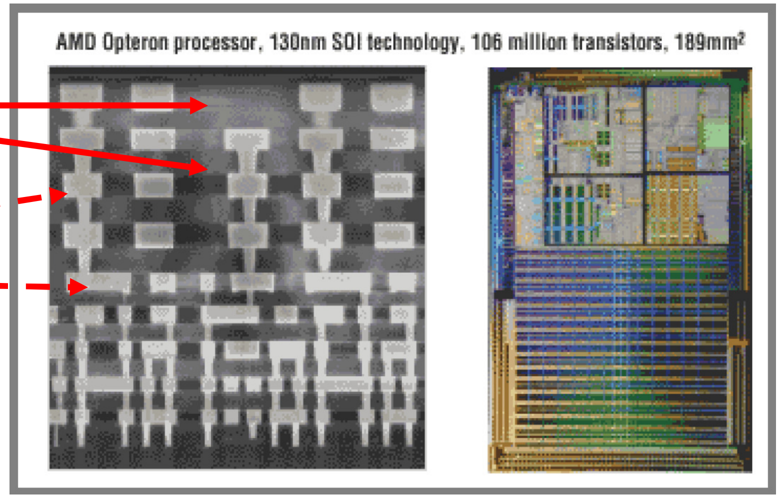
# Anatomy of an integrated circuit

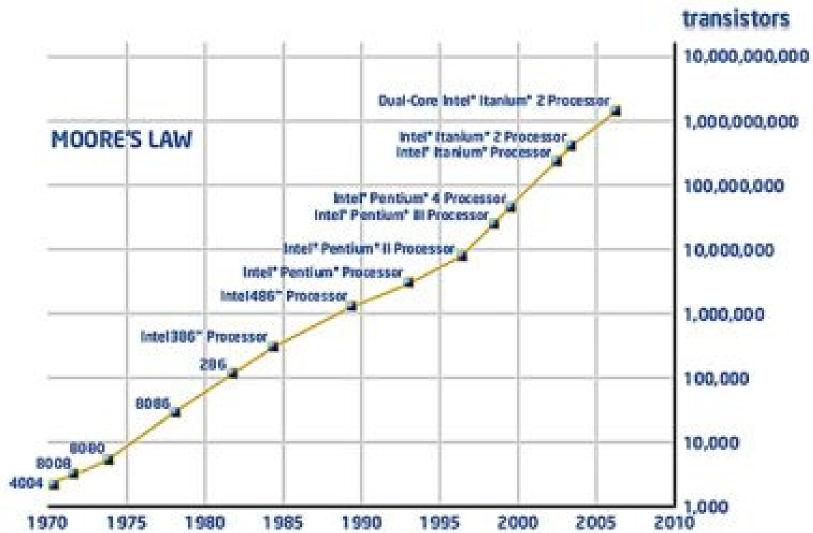
**Low-k Dielectric (ILD)**

**Cu Interconnects**




**Increasing ILD feature size**

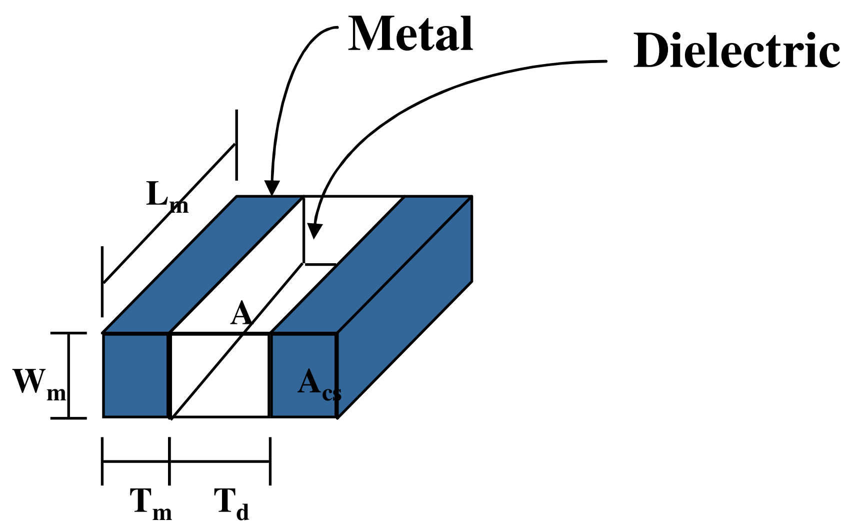
**www.amd.com**




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*

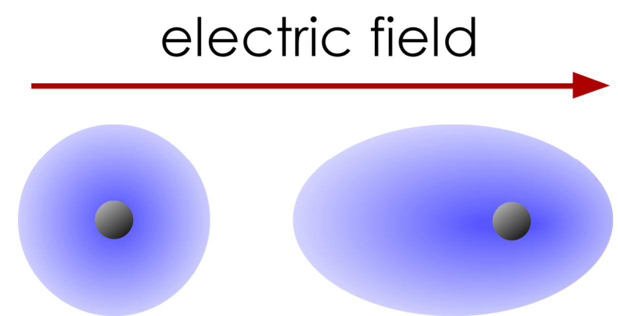
**•Power Consumption** $P \sim CV^2 f$

**•Cross Talk Noise** $N \sim C_{line\text{-}to\text{-}line}/C_{total}$

} *dielectric only*

# Acquired electric dipole moment per unit volume: Polarization

**electronic polarization (induced dipole moment)**




$$\mathbf{P = Zqd}$$

**P** = polarization

**Z** = number of charge centers per unit volume

**q** = electronic charge
**d** = displacement
} **qd** = induced dipole moment

**relationship of dielectric constant & polarization**

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

# *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 |

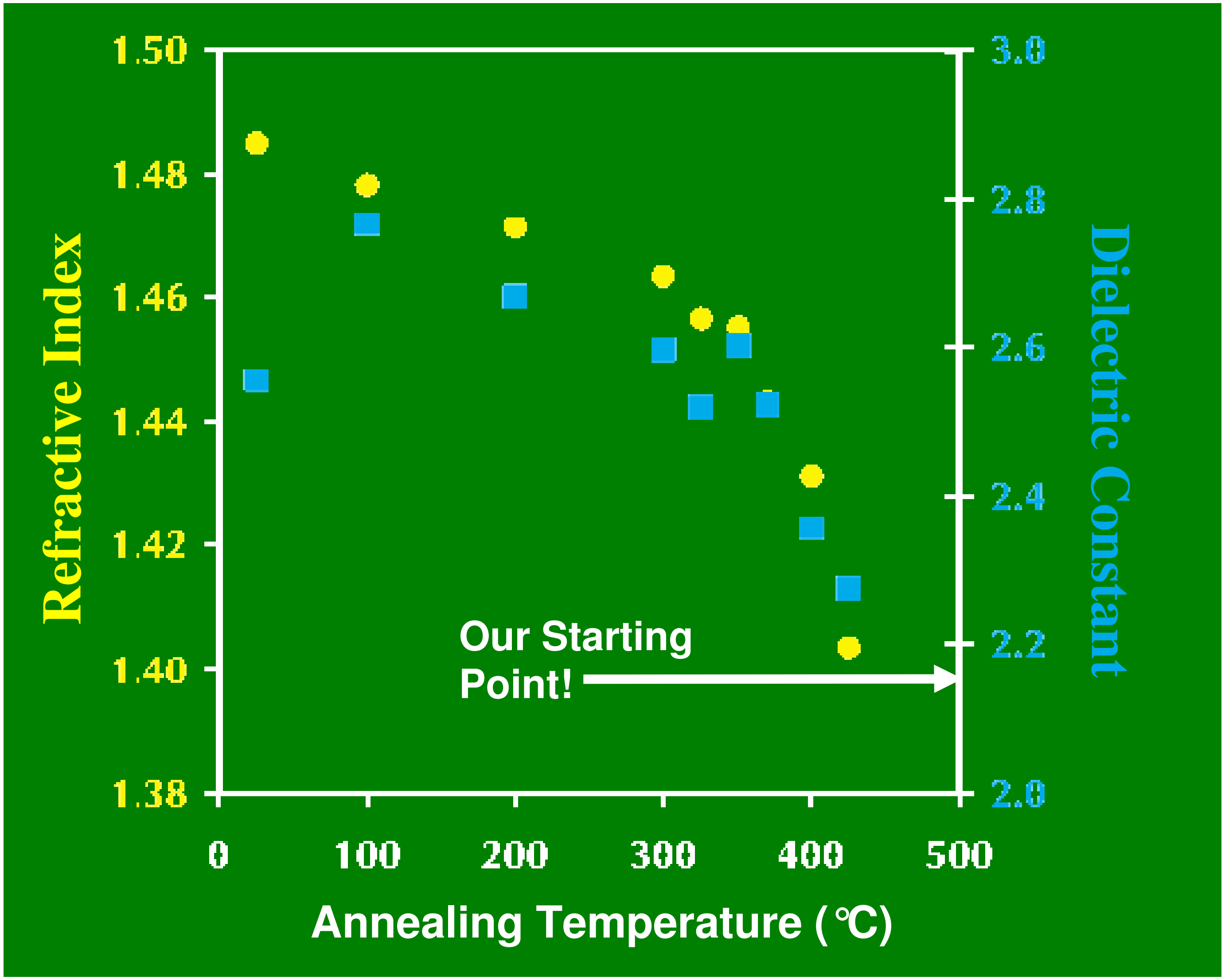
Air

k =1.0

# Air to get us there…

- Although *k* scales with porosity, mechanical properties of porous low-k typically scale as $(1\text{-}P)^3$

- Advantageous to start from a dense film with a lower *k*




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

# Need for environmentally friendly low-*k*

| Year / Technology Node (nm) | 2001 / 130 | 2003 / 130 | 2004 / 90 | 2007 / 65 | 2010 / 45 | 2013 / 32 | 2017 / 20 |
|---|---|---|---|---|---|---|---|
| 2001 Roadmap | 3.0-3.6 | 3.0-3.6 | 2.6-3.1 | 2.3-2.7 | 2.1 | 1.9 | 1.8 |
| 2003 Roadmap | | 3.3-3.6 | 3.1-3.6 | 2.7-3.0 | 2.3-2.6 | 2.0-2.4 | 2.0 |
| 2006 Roadmap | | | | ≤2.4 | ≤ 2.2 | ≤ 2.0 | ≤ 1.8 |
| Updated 2006 Roadmap | | | | 2.3-2.7 | 2.1-2.4 | 1.8-2.1 | 1.6-1.9 |
| EHS for CVD and Spin-On | Minimum emissions/waste processes | | | | 75% Chemical Utilization | 90% Chemical Utilization | |

Manufacturable Solutions Known | Manufacturable Solutions Unknown

**To Summarize: Need *k* = 2.1 by 2012 and 90% raw chemical utilization by 2011!**

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# Attractive ILDs have…

**Electrical**

low κ
low dissipation
low leakage
low charge trap
high breakdown
high resistivity

**Chemical**

low moisture absorption
high etch selectivity
high chemical resistance
high purity
no metal corrosion
low gas permeability

**Mechanical**

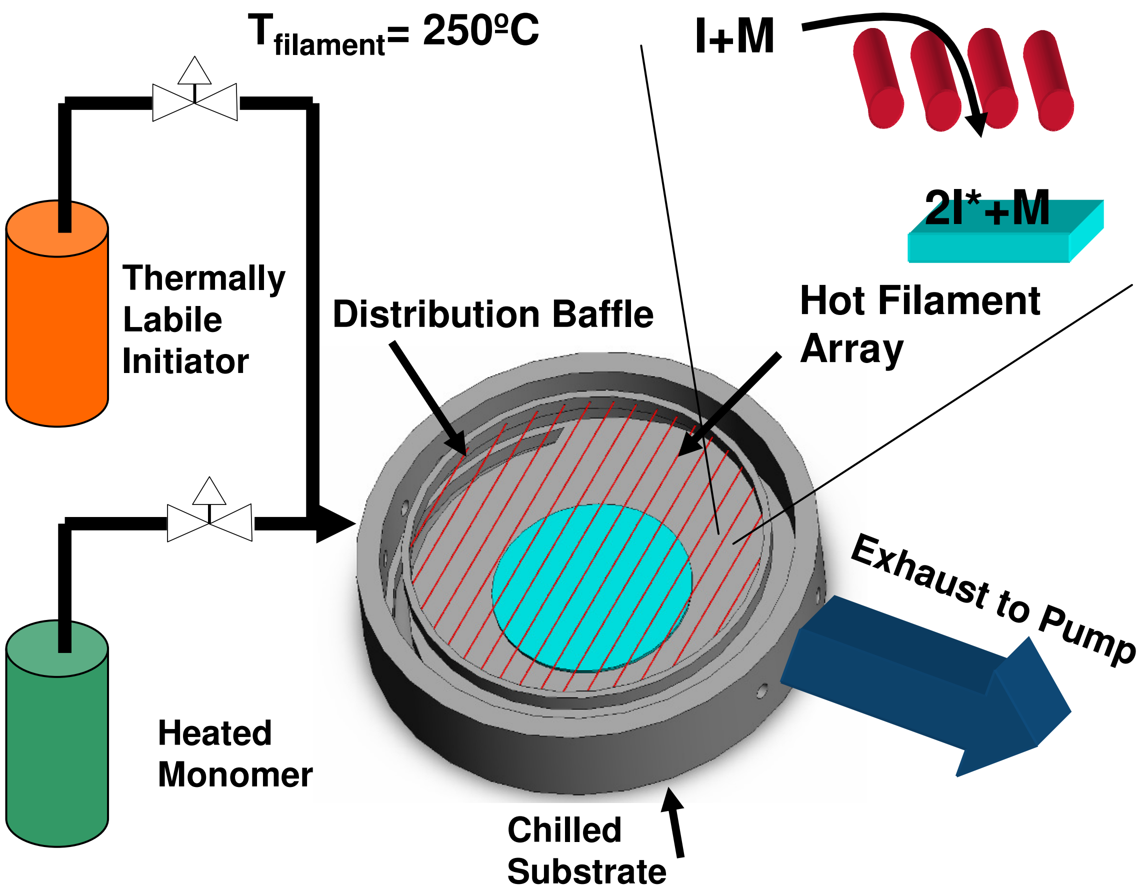
film uniformity
adhesion
low stress
high tensile modulus
low shrinkage
high hardness
elasticity

**Thermal**

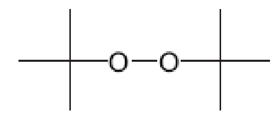
high thermal stability
high glass transition
high thermal conductivity
low thermal shrinkage
low thermal expansion

**Environmentally Friendly Processing**

# iCVD Process chemistry preserves functionality



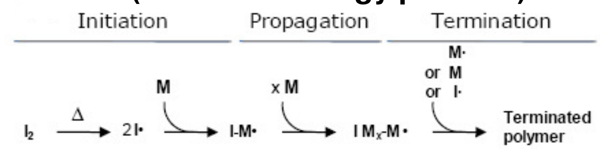

**Initiator**



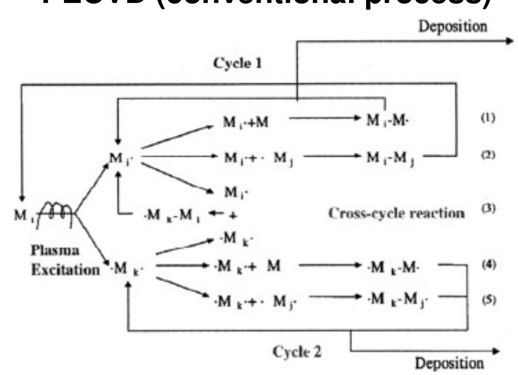

**tert-butyl peroxide**

**Proposed Polymerization Mechanisms**

**iCVD (novel low energy process)**



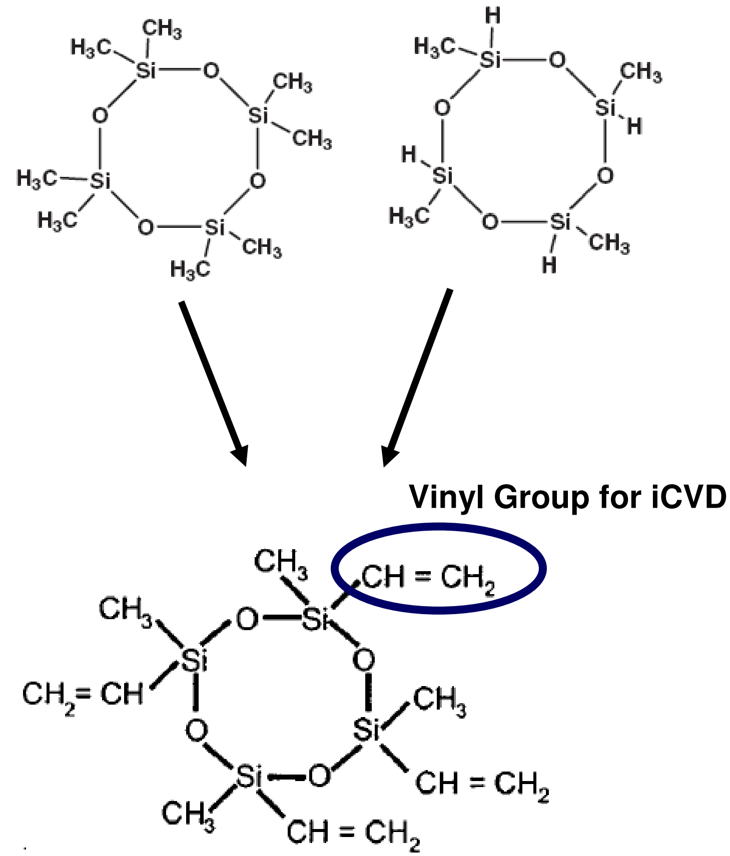

**PECVD (conventional process)**



# Low-*k* iCVD precursor: V4D4

- **Free volume of siloxane ring for low-*k***
- **Chemical structure analogous to commercially used low *k* organosilicate glass (OSG) precursors such as TOMCATS**
- **Four vinyl groups make ideal for free radical polymerization via iCVD**
- **No need for cross linker**
- **3-D network from "puckered" ring**

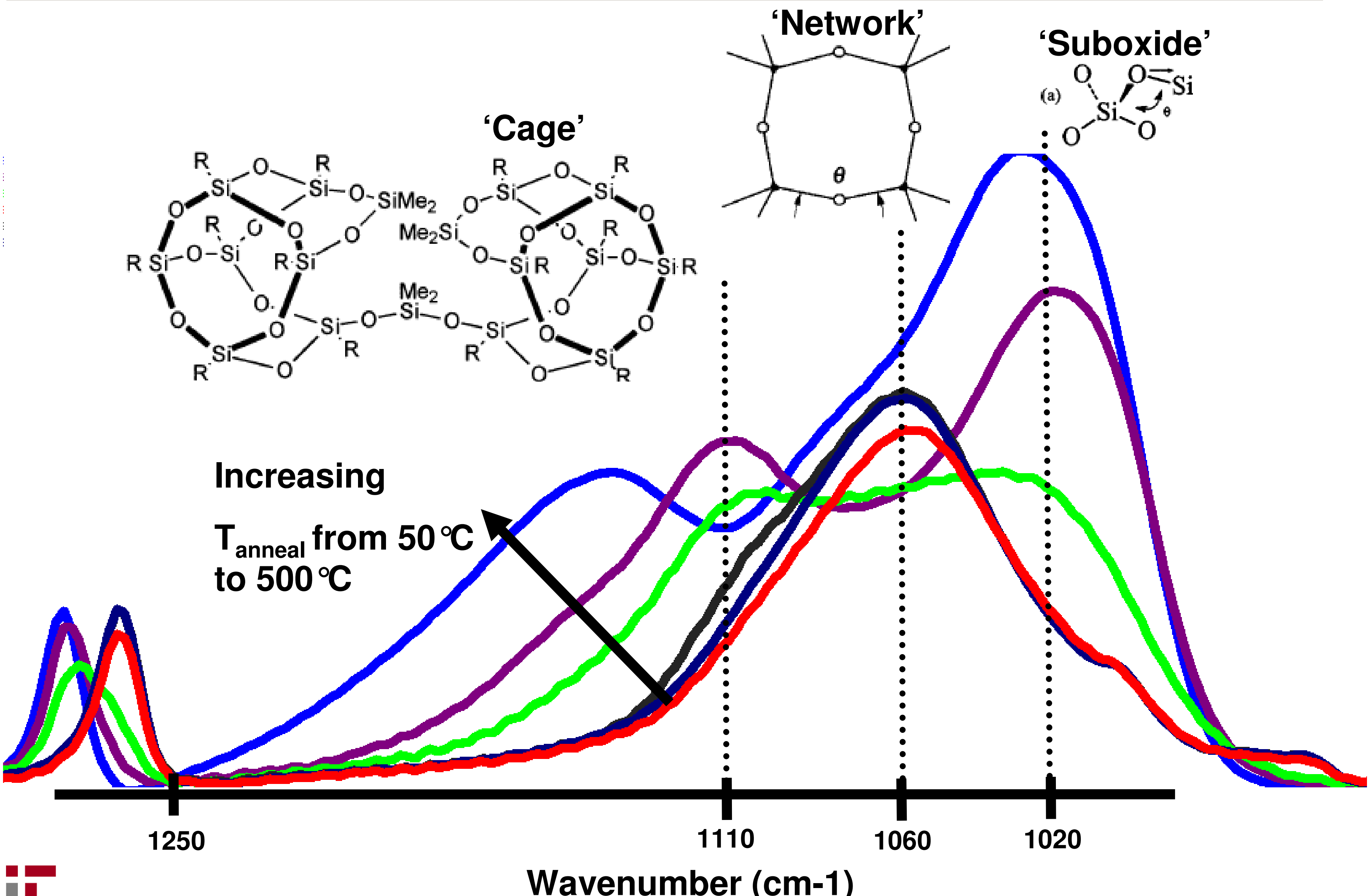
**Commercial PECVD Precursors for Low-*k***



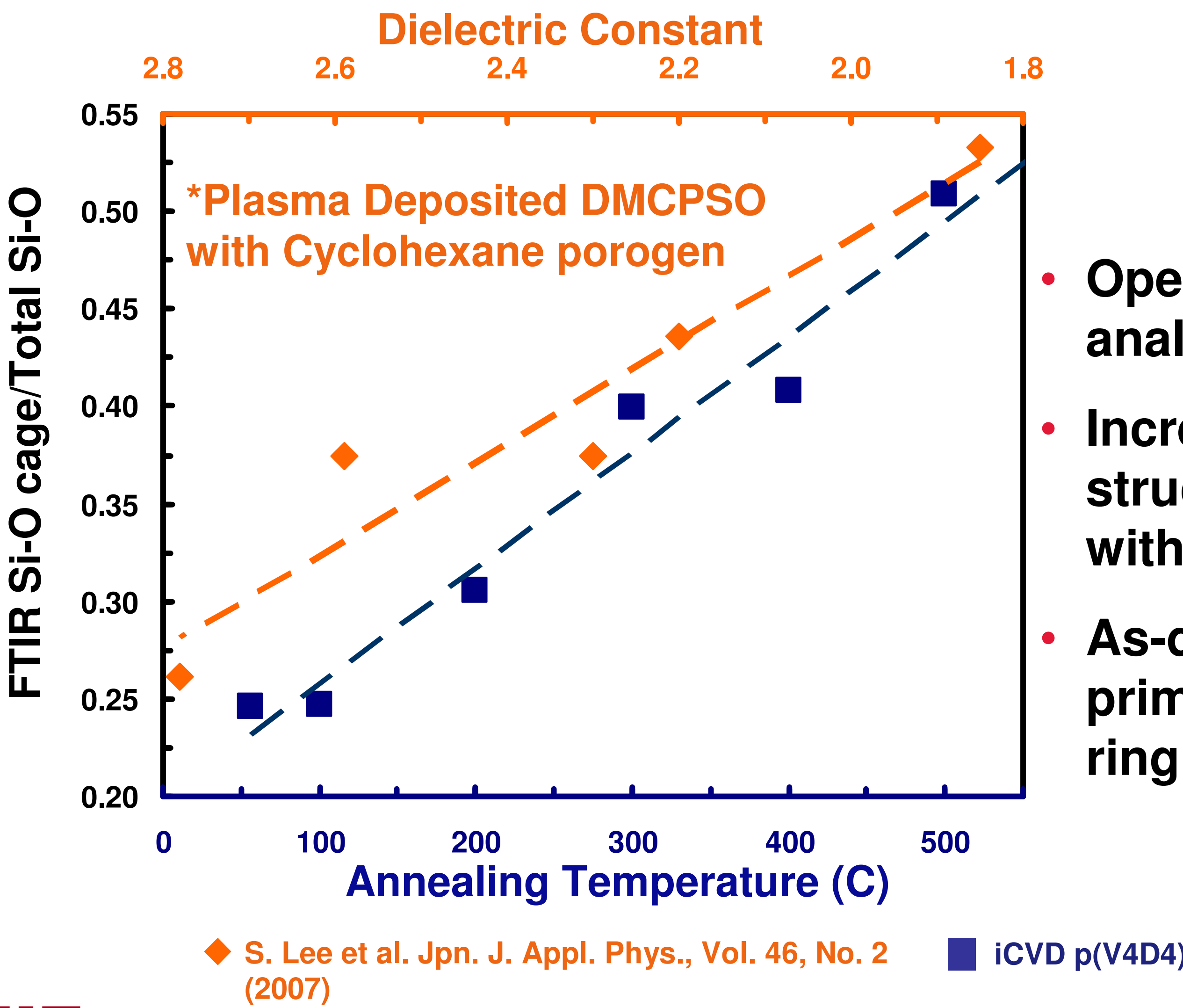

**1,3,5,7-TETRAVINYLTETRAMETHYLCYCLOTETRASILOXANE**

**Novel iCVD Precursor**

# Si-O-Si region deconvolution



# Annealing increases “cage-like” structure




- **Open structure analogous to MSQ**
- **Increasing cage structures associated with decreasing *k***
- **As-deposited structure primarily dominated by ring structure.**

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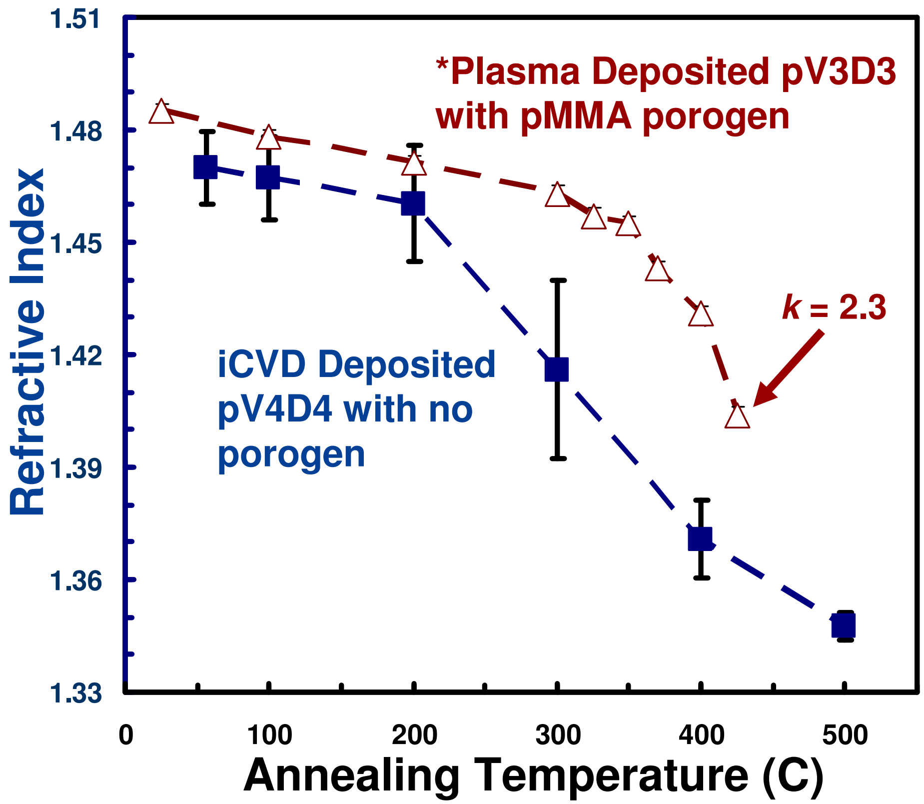
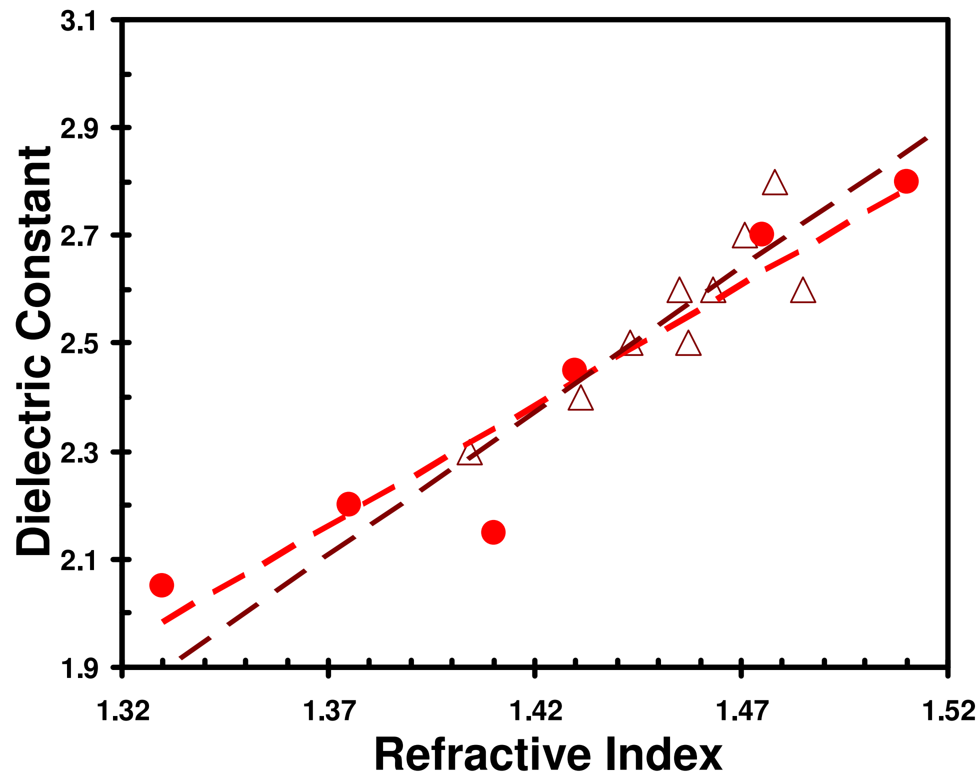
# Reduced film density with anneal




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

● A. Grill, J. Appl. Phys., Vol. 93, No. 3, 1 February 2003

■ iCVD p(V4D4)

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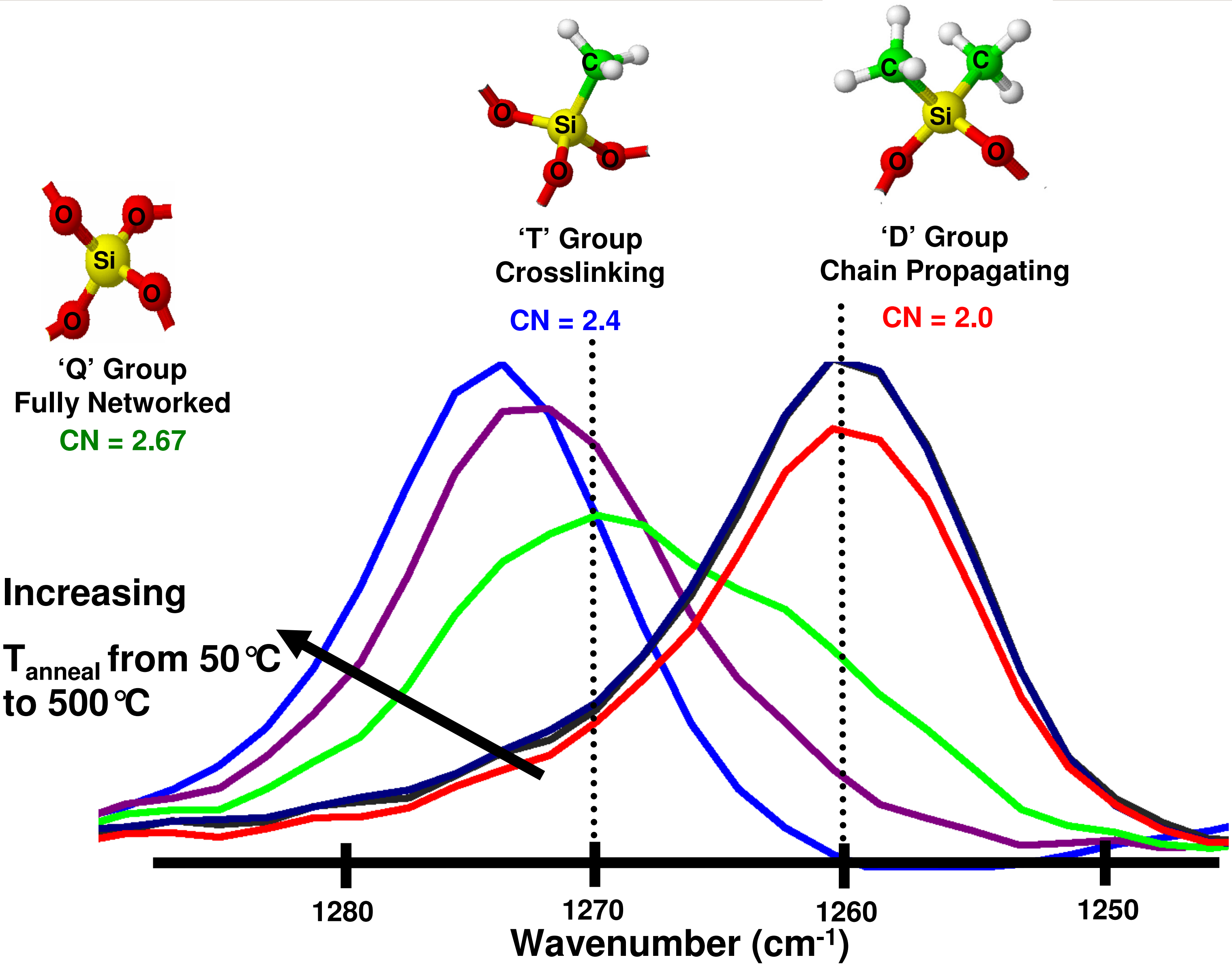
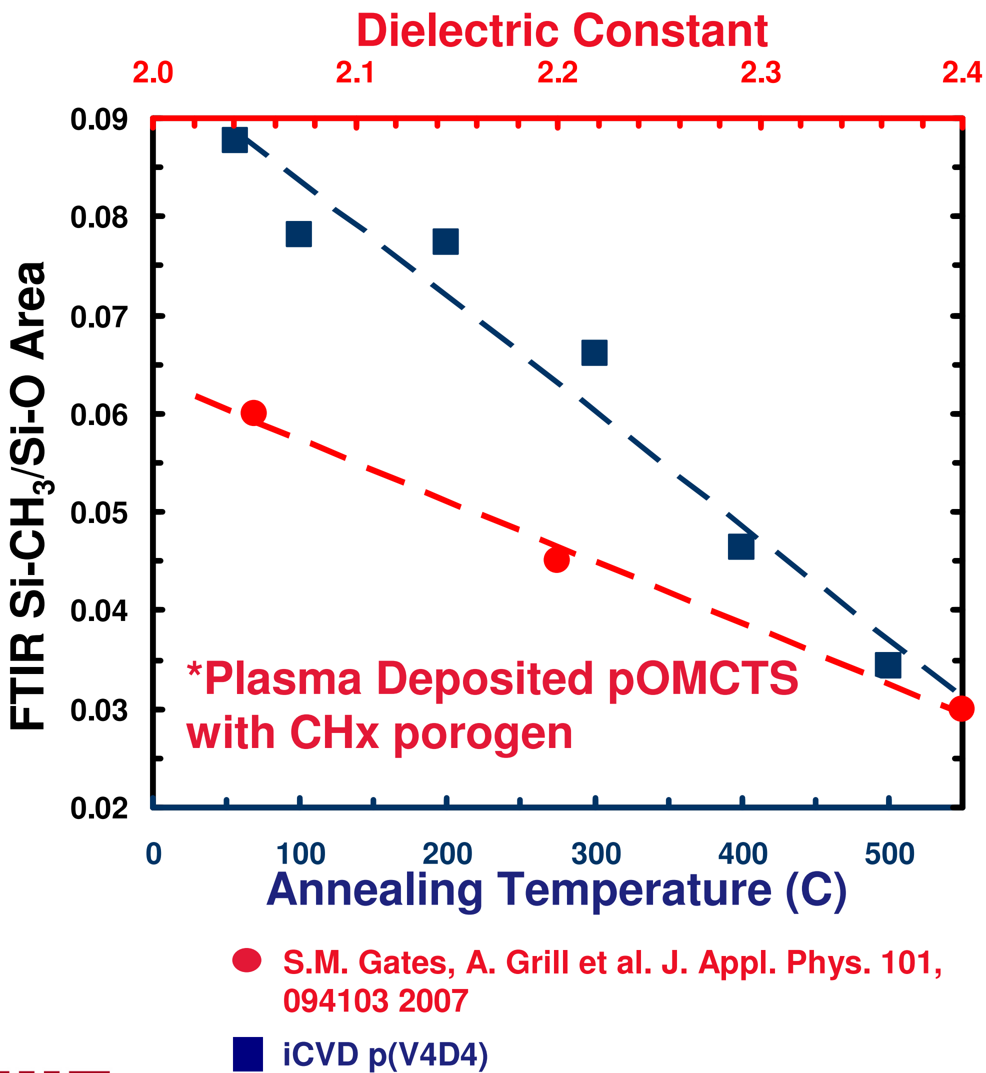
# Increased crosslinking with –CH3 removal

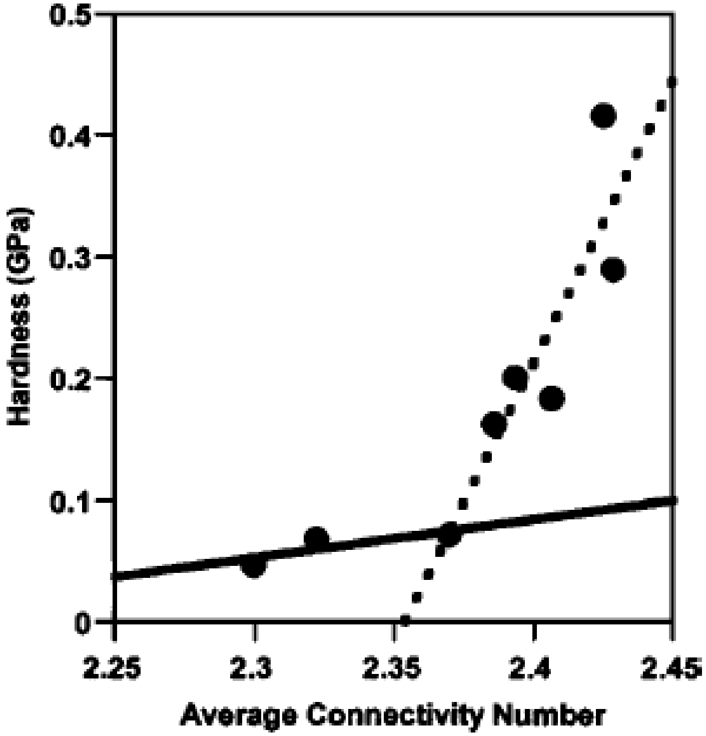


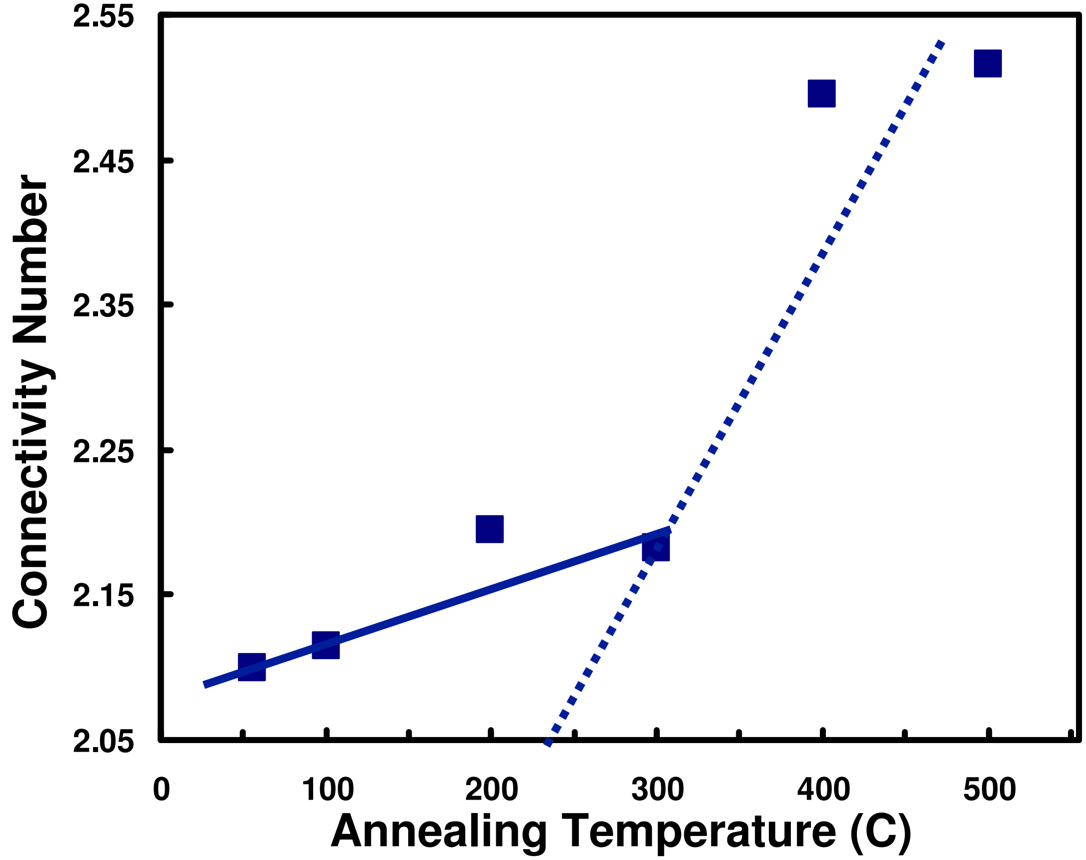
# Remaining methyl groups indicate an open film structure




***Loss of –CH3 improves mechanical properties, yet sufficient groups remain to help keep k low***

# High connectivity at higher temperatures




● A. Ross, K.K. Gleason, J. Appl. Phys. 97, 113707 (2005)

■ iCVD p(V4D4)

***Percolation threshold at CN = 2.4. Above threshold, film is amorphous and rigid!***

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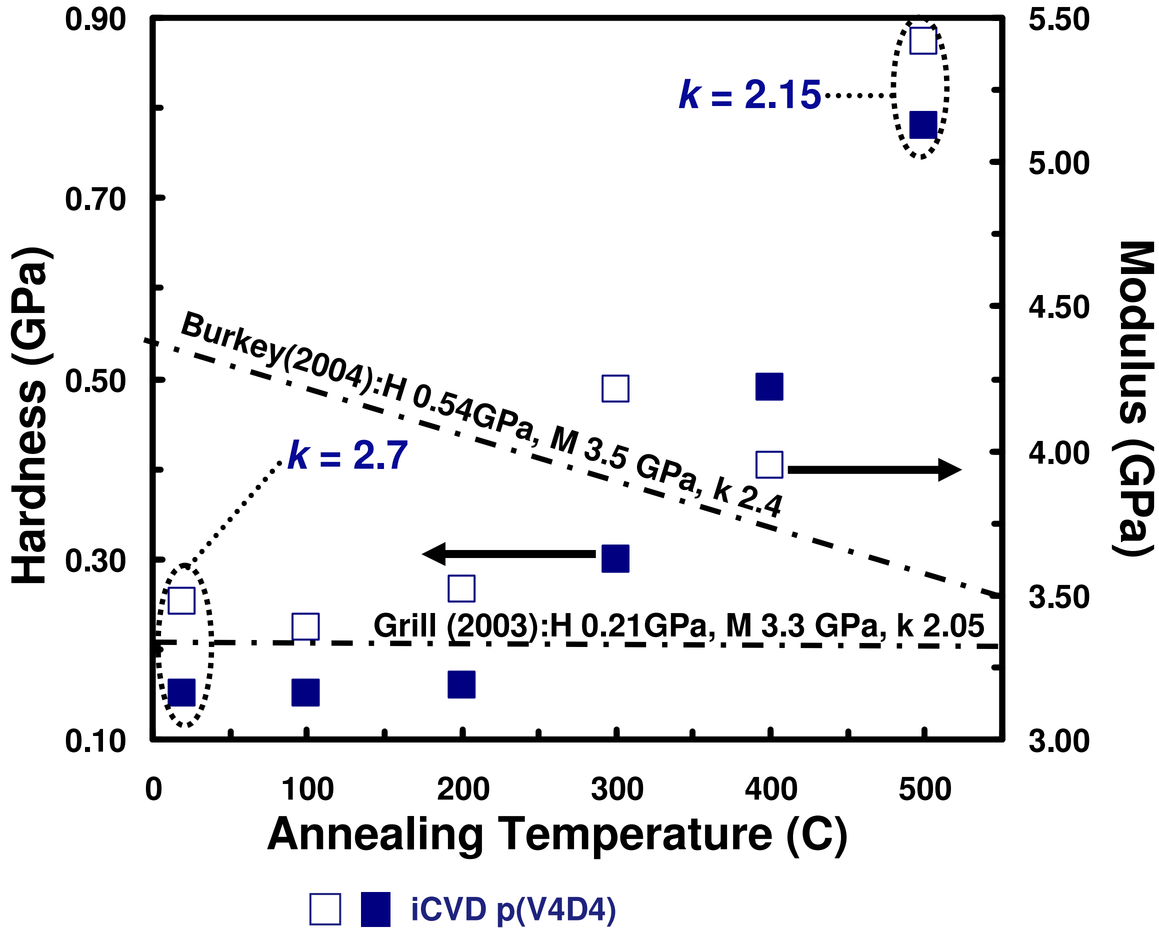
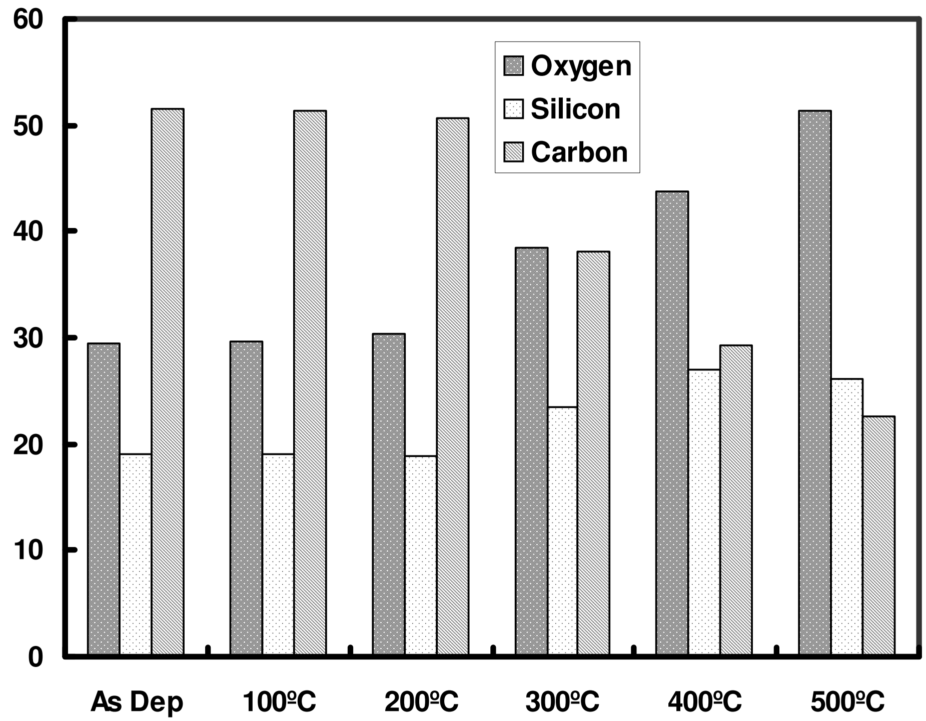
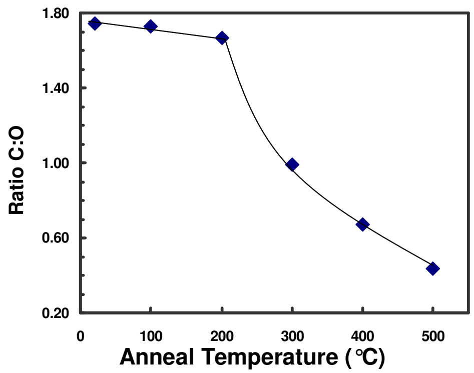
# Mechanical enhancement

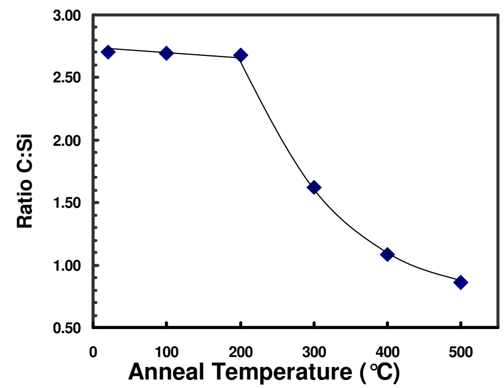
- Enhanced mechanical properties ≥ 200℃ suggests bond rearrangement
- Greater than 0.5 GPa hardness above percolation threshold
- Hardest film associated with lowest dielectric constant. No trade-off between *k* and H.

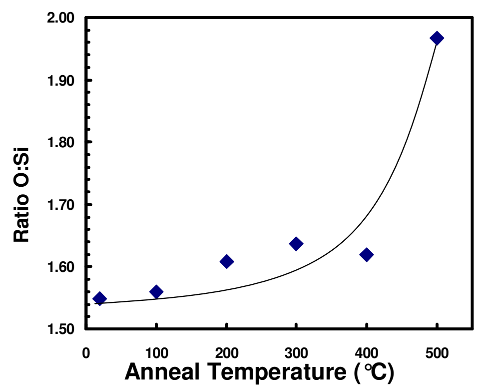


# Atomic composition by X-ray Photoelectron Spectroscopy (XPS)



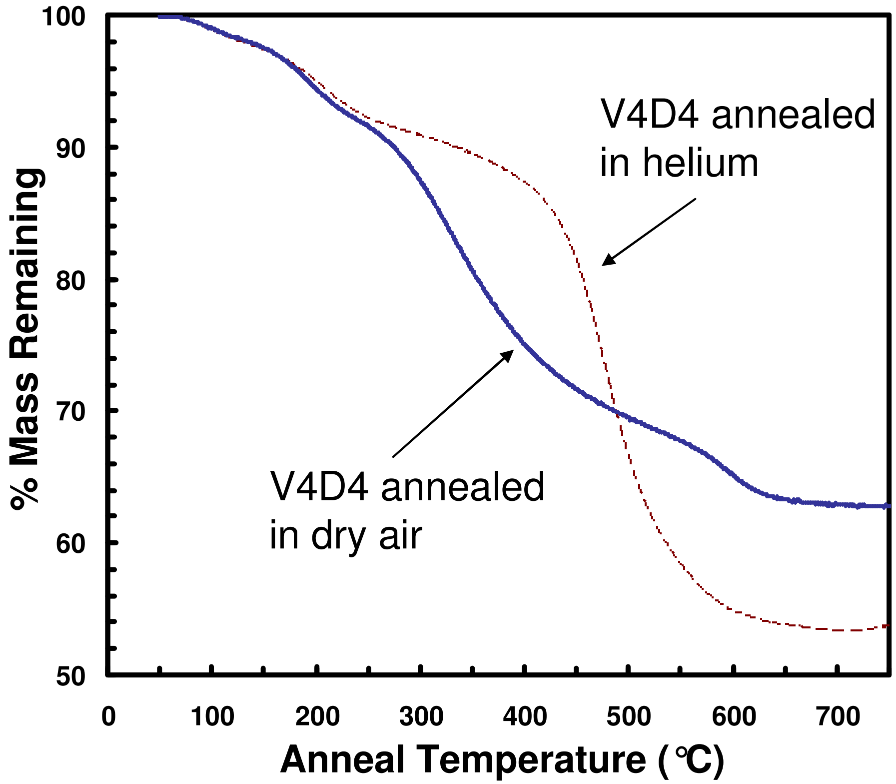



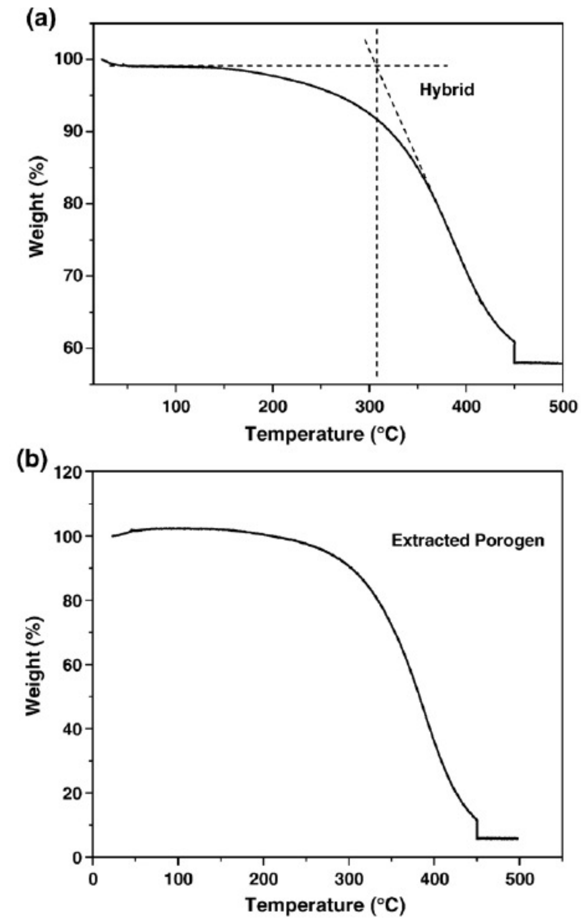




- **Constant composition ≤ 200℃ suggests bond rearrangement**
- **Increased 'Q' groups from oxygen injection at high temperatures responsible for improved H and M**
- **Between 200℃ to 400℃, constant Si:O with decreased Si:C indicates Si-Si bond formation**

# Thermo Gravimetric Analysis (TGA): decomposition and reaction in several stages




- Staged decomposition, compared to porous-MSQ
- Enhanced reactivity in air, not just thermal dissociation
- Stable mass retention is larger, suggests oxygen incorporation

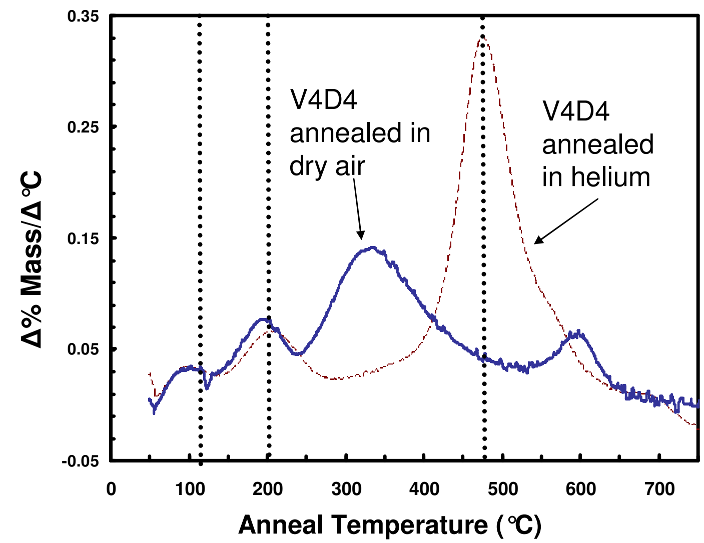


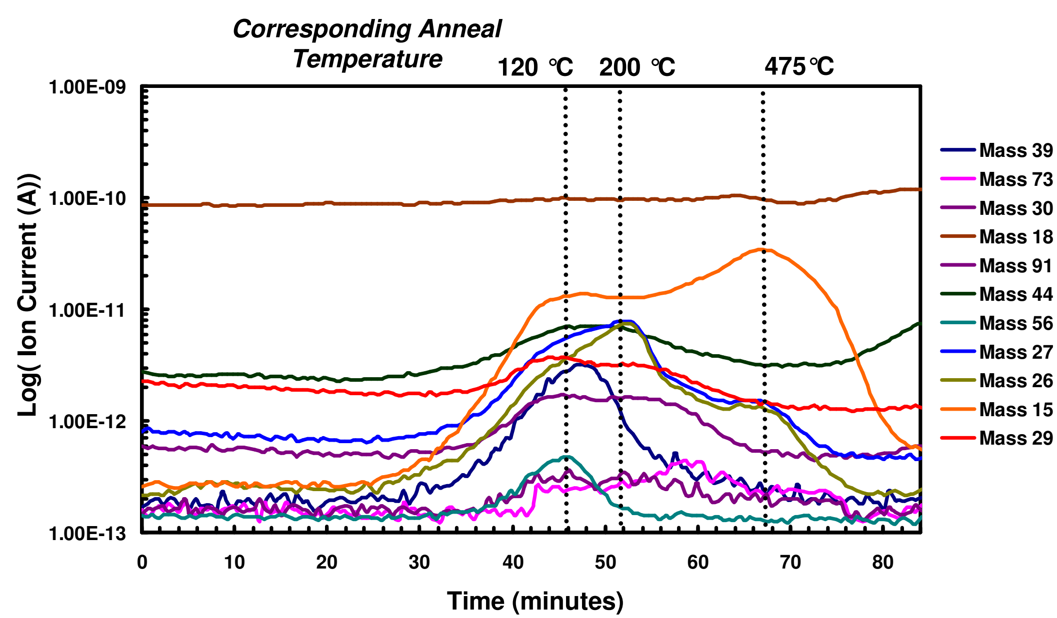

**Spin-On MSQ precursor with 38% porogen loading**

**A. Zenasni et al. Thin Solid Films 516 (2008) 1097–1103**

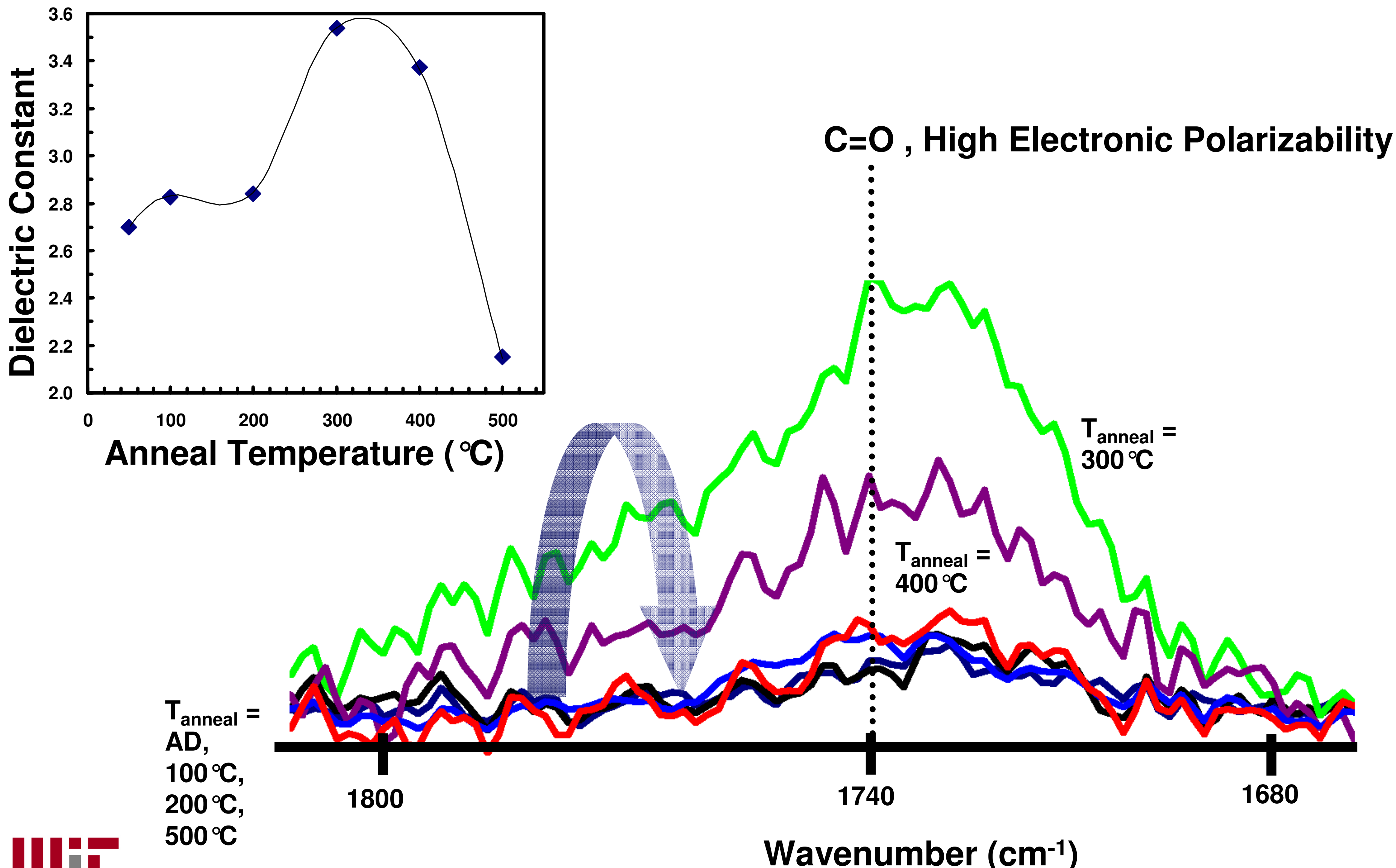
# Several chemistries indicated by Residual Gas Analyzer (RGA)

- Major decomposition events occur at lower temperatures for films annealed in air
- Over 60 potential species tracked by TGA/RGA system
- No water detected in as-deposited film
- Most species evolve during first two events.
- The third event mainly represents -CH3 decomposition



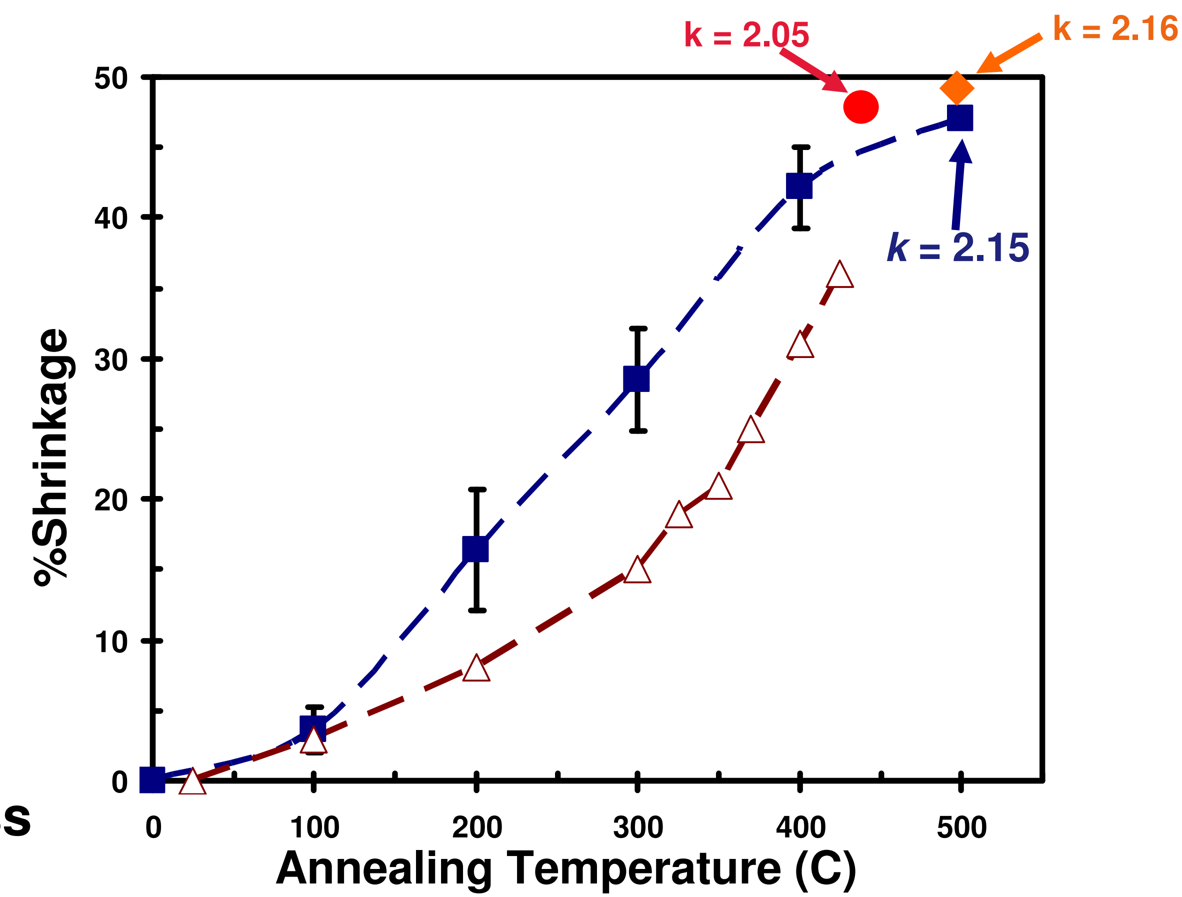



# Reduced polarizability results in lower *k*



# Curing behavior for annealed films

- Annealed films would be most attractive for application
- In subsequent thermal cycles, annealed films, > 400℃, stable thickness within 1%
- No water uptake in cured film, as evidenced by FTIR
- Film loss in curing process comparable to literature




◆ S. Lee et al. Jpn. J. Appl. Phys., Vol. 46, No. 2 (2007)

● S.M. Gates, A. Grill et al. J. Appl. Phys. 101, 094103 2007

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

■ iCVD p(V4D4)

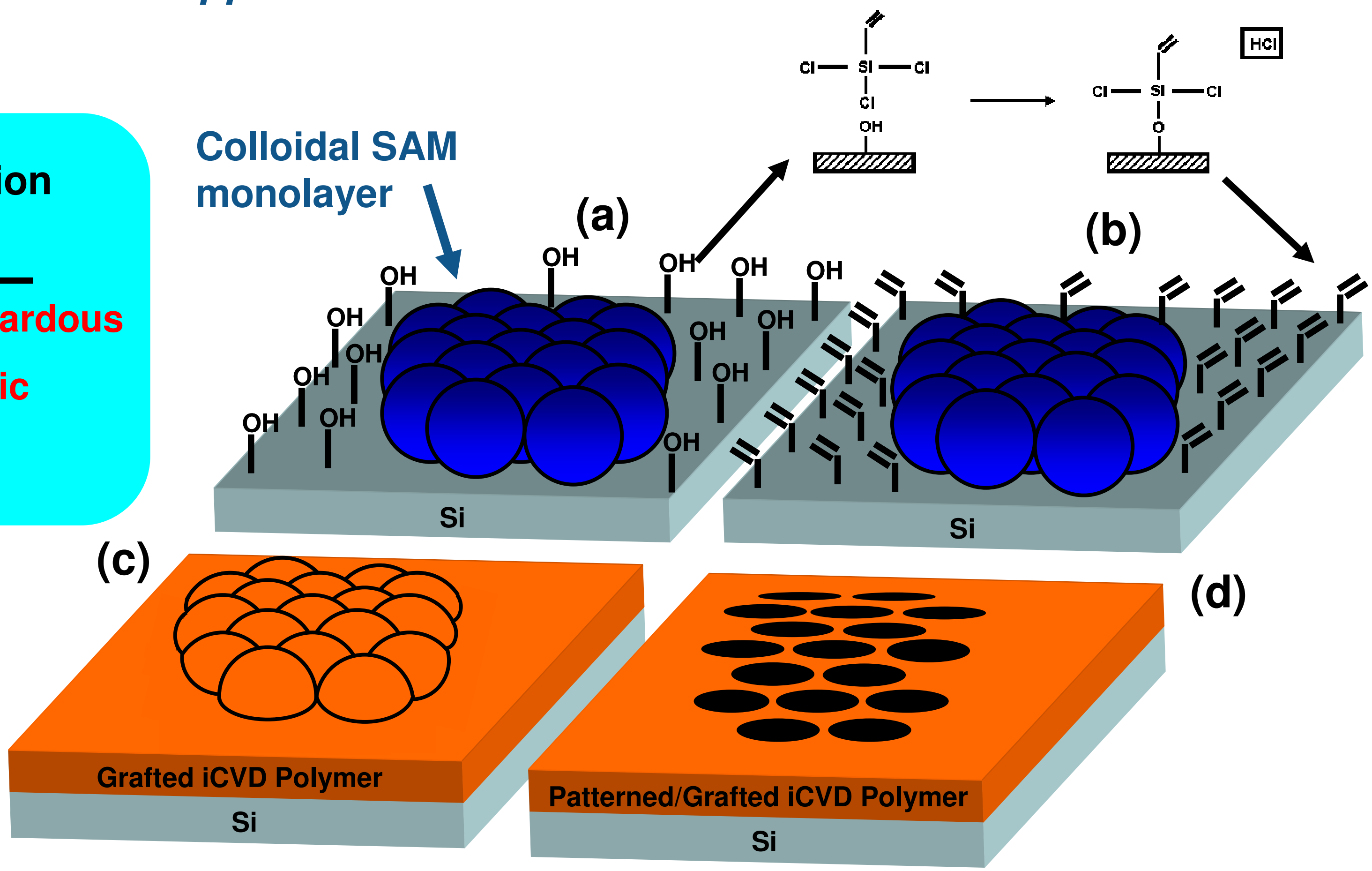
# Additive polymer patterning using self-assembled mask (no traditional lithography)

- *Non-Conventional lithography offers: Cost-saving alternative to conventional photolithography.*
- *No need for expensive steppers*

**Solvent Substitution**

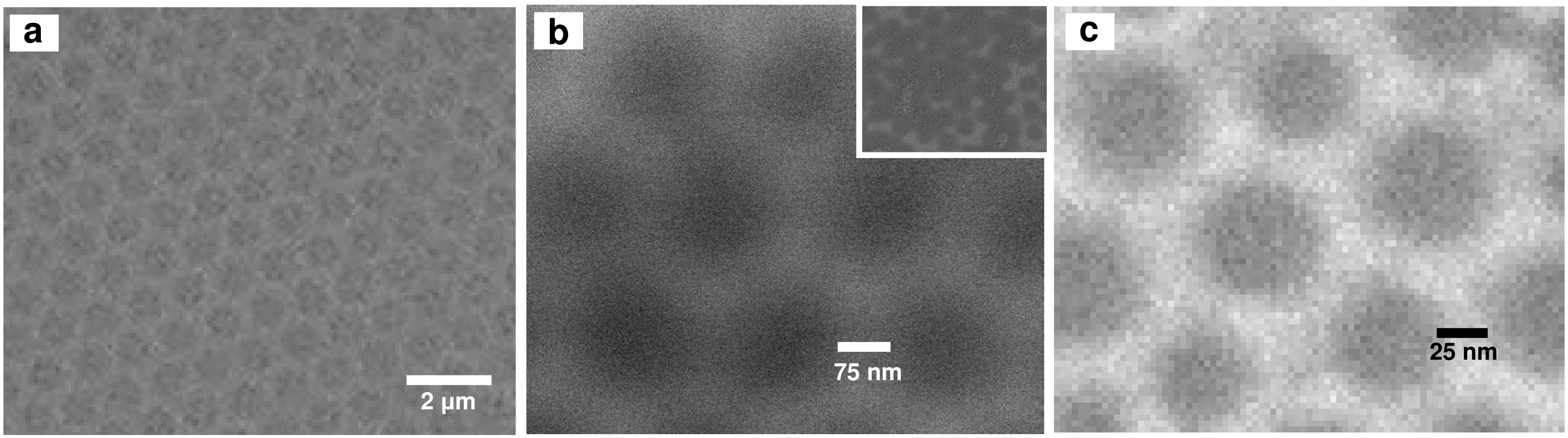
**IPA vs. TMAH**

| IPA | TMAH |
|---|---|
| •Non-hazardous | •Hazardous |
| •Biodegradable | •Toxic |
| •Non-toxic | |

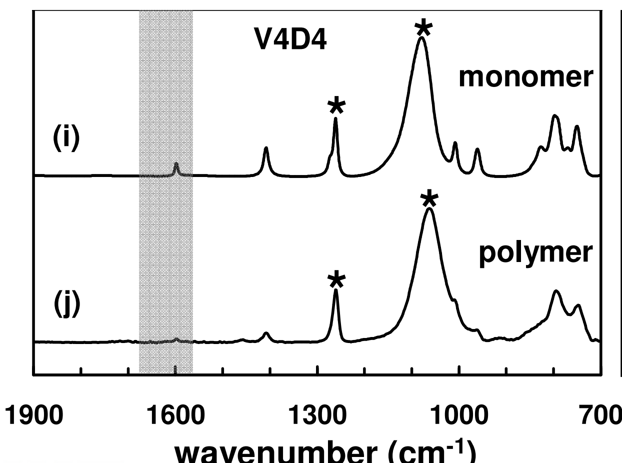


# Low-*k* iCVD p(V4D4) Patterns: 25 nm features & no traditional lithography

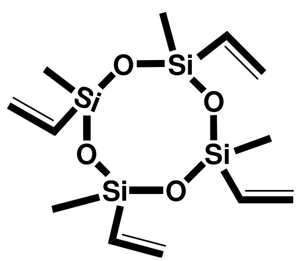
**1 µm Template** | **200 nm Template** | **25 nm Template**




***Decreasing Template Diameter***




**Utility: Low dielectric constant polymer for integrated circuits**

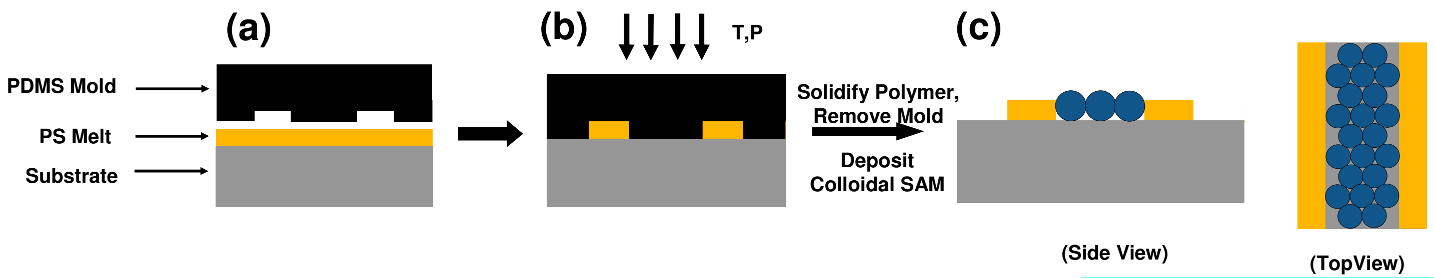


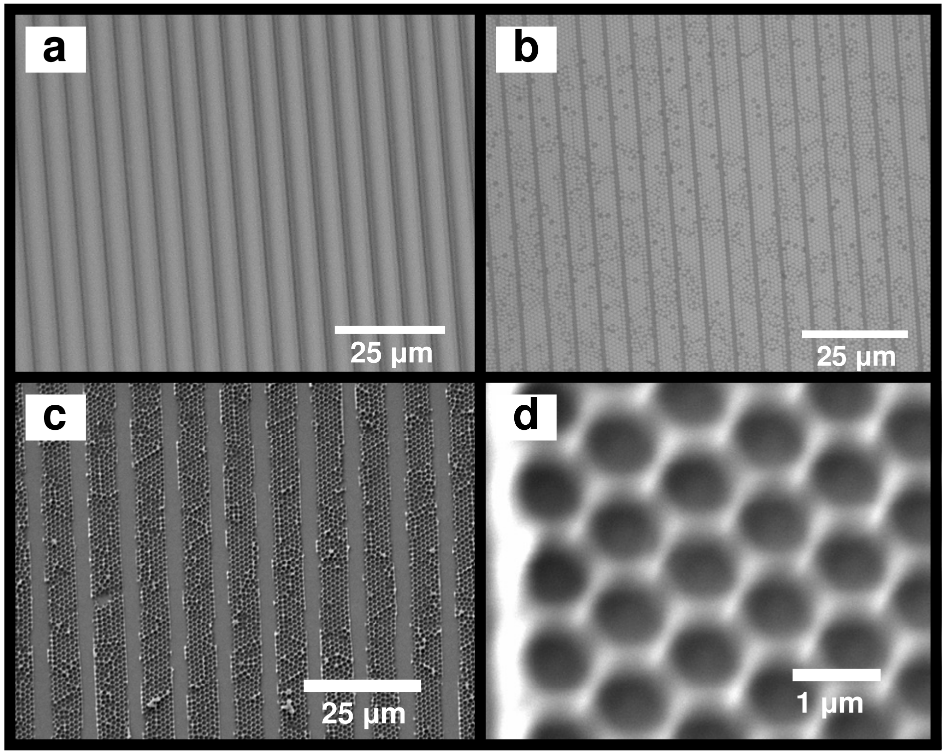

***k* ~ 2.7**

*Eliminates need for etching of low-k, a problematic step*

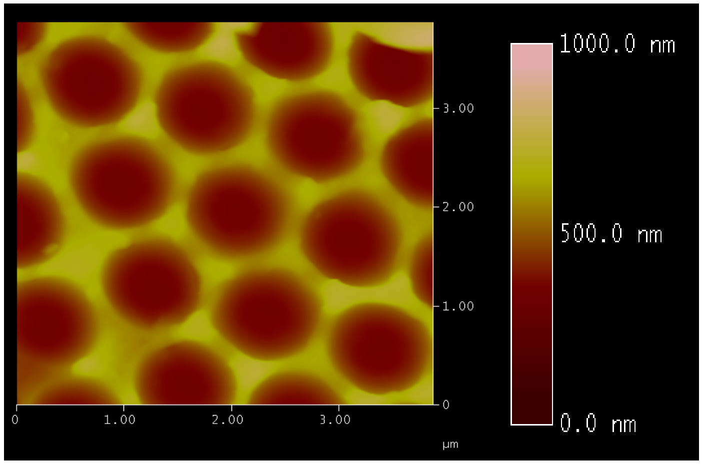
# Multi-scale patterned low-*k* by template assisted assembly

## "Top Down" helps "bottom-up": Capillary Force Lithography Template




- *Multi-scale low-k features that are spatially addressable.*
- *No Conventional Lithography!*



# In summary

- iCVD is a low-energy process for depositing a novel low-*k* precursor V4D4
- The high degree of organic content in the as-deposited films affords the ability to systematically tune the film properties by annealing.
- The incorporation of atmospheric oxygen, at high temperatures, enhances the mechanical and electrical properties of the films.
- These “dense” annealed films provide favorable mechanical and electrical properties for incorporating thermally sensitive porogen molecules
- Multi-scale features were patterned for the dielectric constant polymer, down to 25 nm, without the need for environmentally harmful solvents or expensive lithography tools