# Air Dielectric:
# CVD Sacrificial Materials
# (Task 425.001: ERC EBSM)

*Kelvin Chan* and Karen K. Gleason*
*Department of Chemical Engineering*
*Massachusetts Institute of Technology*

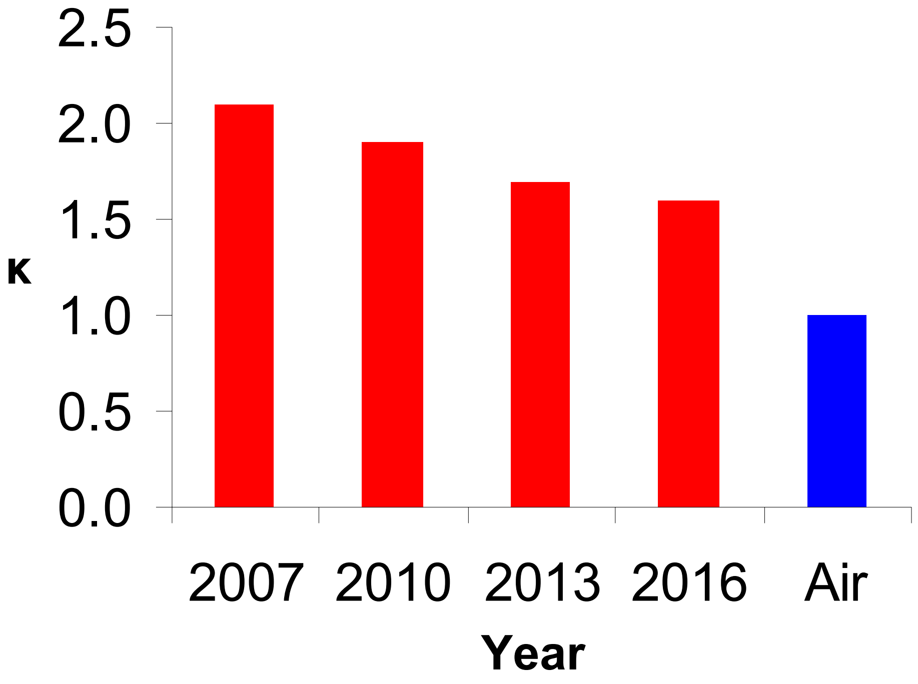
**defended PhD Aug 2005, joining Applied Materials*

# Motivation

- Air has the lowest possible dielectric constant of 1.0
  - reduced RC delay
  - lower power consumption
  - lower cross-talk noise

- Air has the lowest possible refractive index of 1.0
  - high index contrast in optical devices
    (e.g. thin-film optical filters)

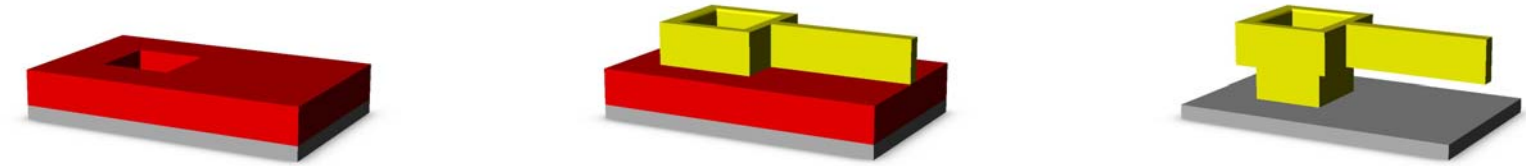
**Future Microprocessor Interconnect Technology Requirements***



*Source: International Technology Roadmap for Semiconductors 2001

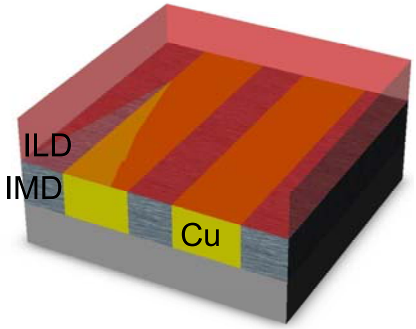
# Sacrificial Material

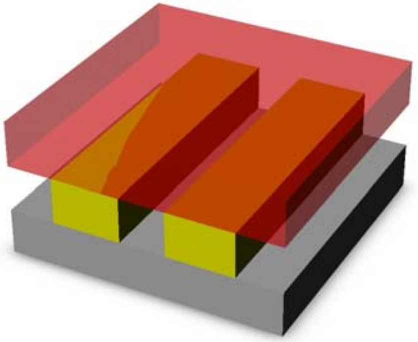
- **Frequent Use of Sacrificial Materials in <u>MEMS Fabrication</u>**
  - ☐ **Surface micromachining**



- **Use of Sacrificial Materials (or Porogens) for Low-Dielectric-Constant Integration**
  - ☐ **Air has the lowest k of 1.0 (reduce RC delay, power, noise)**

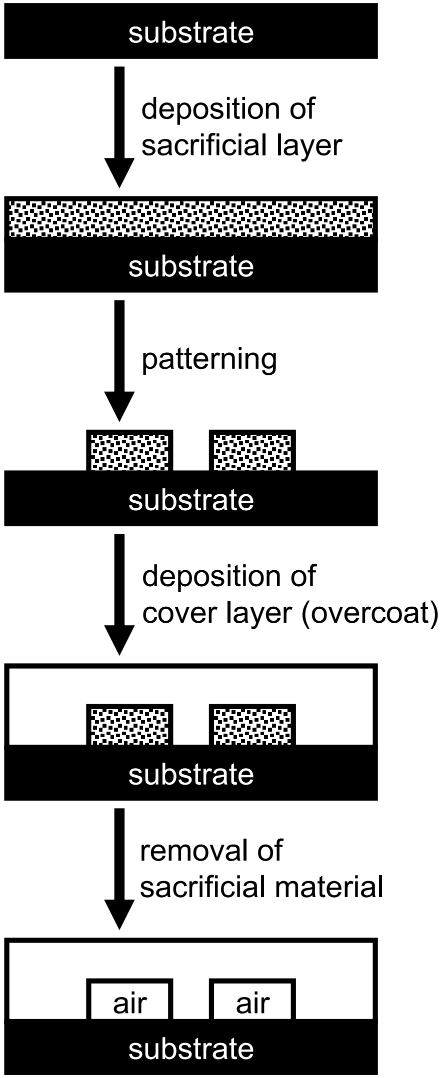
- **Complete or Partial Air Gaps as Inter-Metal Dielectric**





air as IMD

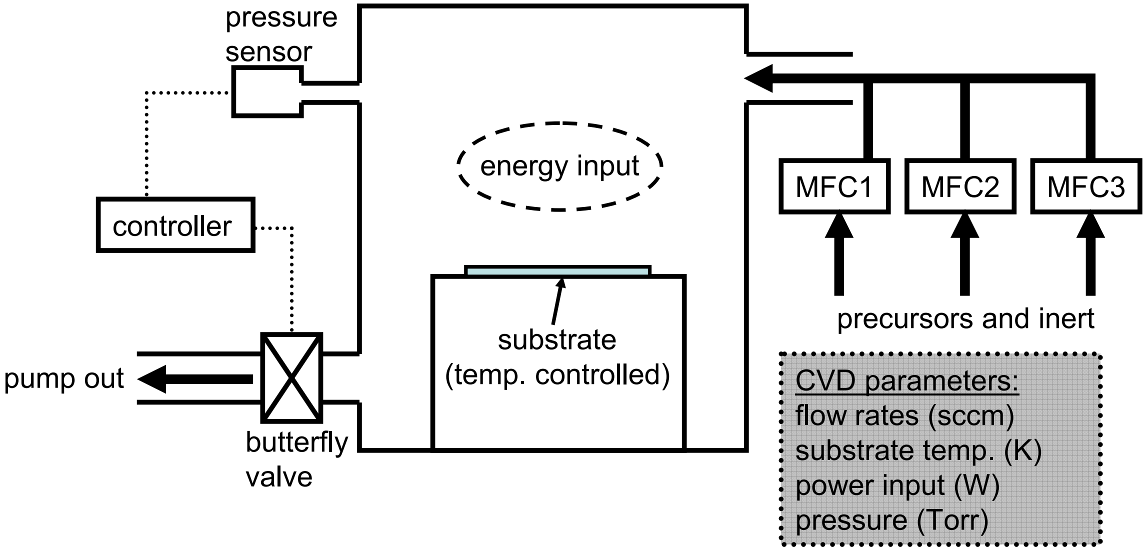
# Air-Gap Fabrication



- **Ordinary Sacrificial Materials**
  - ☐ **Require physical contact with etchant/solvent for selective removal**
  - ☐ **Surface-tension problems for wet processes**
- **Self-Decomposing Sacrificial Materials**
  - ☐ **Requires no agent for removal**
  - ☐ **Dry removal process (heat, UV, e-beam)**
  - ☐ **Allow fabrication of closed-cavity structures**

# CVD Polymers

- Polymer films synthesized *in situ* from their monomeric building blocks and involves no solvents in one step without curing
  - ☐ polymers need not be soluble
  - ☐ excellent thickness control
  - ☐ nanoscale thicknesses with macroscale uniformity
  - ☐ no surface tension and non-uniform wetting effects (complex geometries, 3D, soluble substrates)
  - ☐ no residual solvent

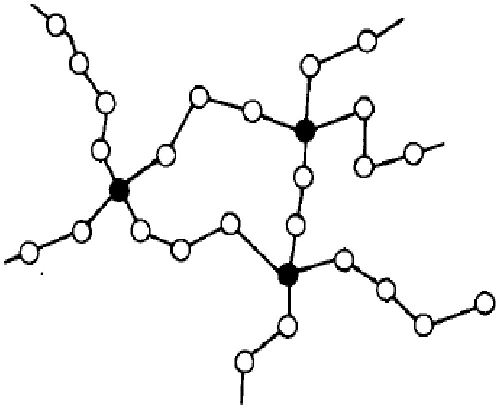


<u>CVD parameters:</u>
flow rates (sccm)
substrate temp. (K)
power input (W)
pressure (Torr)

# Energy Input for Polymer CVD

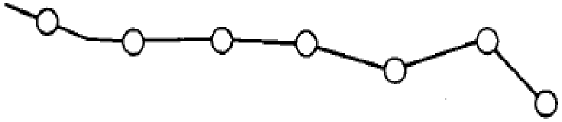
## Plasma Enhanced

- nonselective chemistry: char formation
- nonlinear polymers
- dangling bond defects



## Hot Filament

- selective thermal scission of bonds
- side-group retention
- linear polymers
- no dangling bonds or associated aging effects
- systematic control over composition using feed gas



# Initiated CVD (iCVD)

- iCVD of Poly(glycidyl methacrylate) (PGMA)
  - ☐ Mao Y; Gleason KK *Langmuir* **2004,** *20,* 2484
  - ☐ produced straight-chain, high-molecular-weight PGMA

Radical generation (gas phase/filament)

$I_2 \rightarrow 2\, I\cdot$

Initiation

$I\cdot + M \rightarrow IM\cdot$

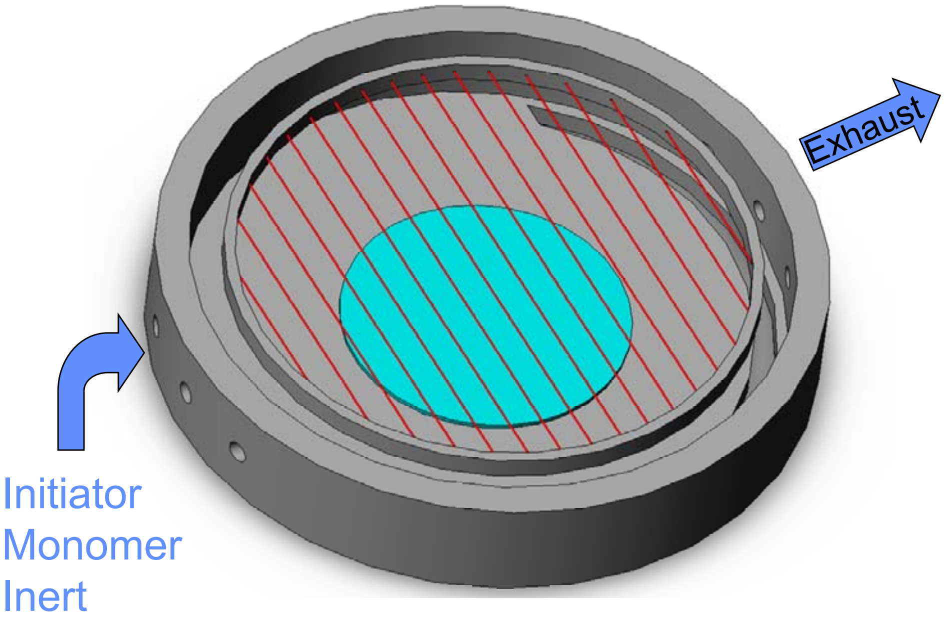
Propagation

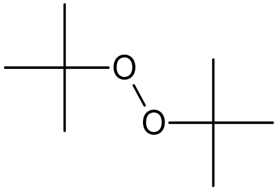
$IM_n\cdot + M \rightarrow IM_{n+1}\cdot$

Termination

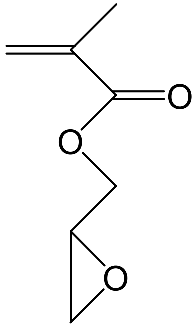
$IM_n\cdot + IM_p\cdot \rightarrow IM_{n+p}I$

$IM_n\cdot + IM_p\cdot \rightarrow IM_n + IM_p$





tert-butyl peroxide (TBPO)

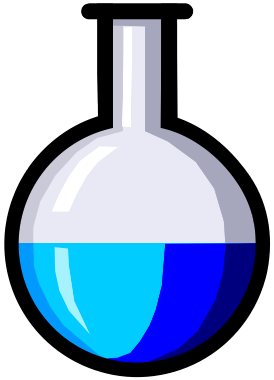


glycidyl methacrylate (GMA)

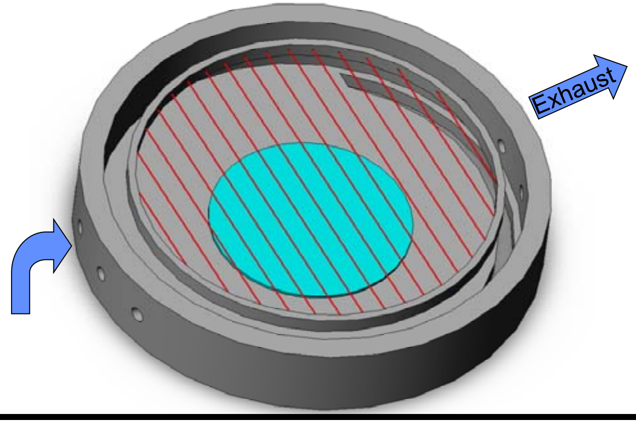
lowers filament temperatures
accelerates growth
allows molecular-weight control

# Transition From Wet to Dry

## solution free-radical polym.



## iCVD

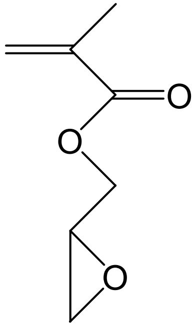


| Batch process | Continuous process |
|---|---|
| Single reaction medium | Two reaction media<br>- gas phase<br>- surface |
| Single temperature | Multiple Temperatures<br>- gas<br>- filament<br>- surface |
| All reactions occur at same temperature in one phase | Radical generation, initiation, propagation, and termination may occur in different phases |
| Concentrations of species depend on initial doses | Concentrations in gas phase depend on flow rates and total pressure<br>Concentrations on surface depend on adsorption equilibria, kinetics |

# Elements of Analyses

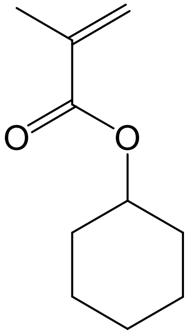
## Mechanistic Study

glycidyl methacrylate



GMA

cyclohexyl methacrylate

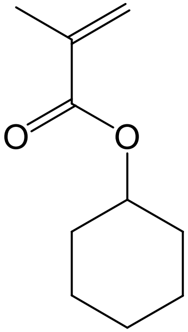


CHMA

-control of molecular weight
-control of deposition rate

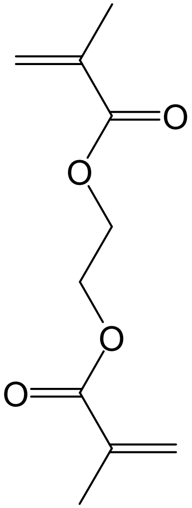
## Sacrificial Polymer

cyclohexyl methacrylate



CHMA

ethylene glycol dimethacrylate



EGDMA

-build-to-specification
 sacrificial polymer

# A Mechanistic Study of iCVD: Analyses of Deposition Rate and Molecular Weight

# Surface Propagation Hypothesis

Radical generation (gas phase/filament)

$I_2 \rightarrow 2\,I\cdot$

Initiation

$I\cdot + M \rightarrow IM\cdot$

Propagation

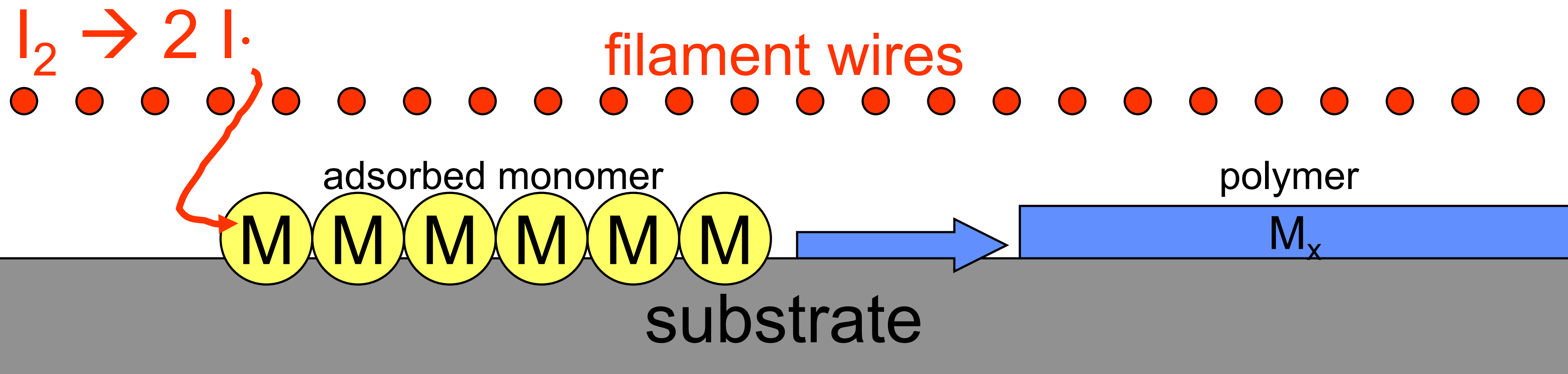
$IM_n\cdot + M \rightarrow IM_{n+1}\cdot$

Termination

$IM_n\cdot + IM_p\cdot \rightarrow IM_{n+p}I$

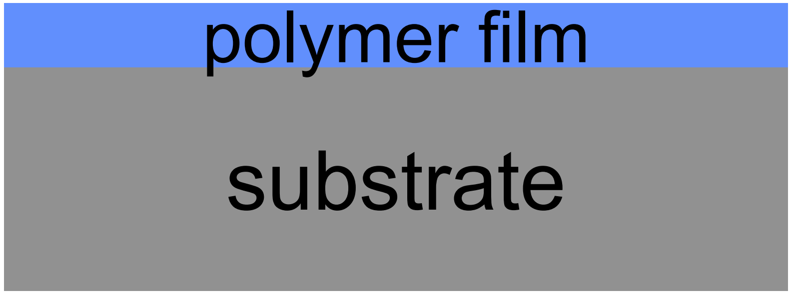
$IM_n\cdot + IM_p\cdot \rightarrow IM_n + IM_p$

- **Gas-phase concentration low**
  - **bimolecular reactions unlikely**
- **Volatility of dimer low**
  - **gas-phase propagation unlikely**
- **Surface concentration high**
  - **low vapor pressure monomer**



# Methodology

- Formulate model to predict rate of polymerization ($R_p$) and number-average molecular weight ($M_n$) based on surface propagation
- Experimentally measure $R_p$, $M_n$, and surface concentration ([M])
  - ☐ $R_p$ = thickness per time
  - ☐ measure $M_n$ by gel-permeation chromatography (GPC)
  - ☐ measure [M] by quartz-crystal microbalance (QCM)
- Manipulate [M] by changing surface temperature
  - ☐ gas, filament temperatures unaffected
  - ☐ gas-phase concentrations remain constant



# The Formulation for Surface Propagation

Radical generation (gas phase/filament)

$I_2 \xrightarrow[k_d]{} 2\,I\cdot$

Initiation (surface)

$I\cdot + M \xrightarrow[k_i]{} IM\cdot$

Propagation (surface)

$IM_n\cdot + M \xrightarrow[k_p]{} IM_{n+1}\cdot$

Termination (surface)

$IM_n\cdot + IM_p\cdot \xrightarrow[k_t]{} IM_{n+p}I$

$IM_n\cdot + IM_p\cdot \xrightarrow[k_t]{} IM_n + IM_p$

Pseudo Steady State Hypothesis (PSSH)

$$\frac{d[I\cdot]}{dt} = \frac{k_c}{RT_\infty}\left(p_{I\cdot,\infty} - p_{I\cdot,0}\frac{T_\infty}{T_0}\right) - k_i[I\cdot][M]$$

$$= \frac{k_c}{RT_\infty}\left(p_{I\cdot,\infty} - \cancelto{0}{\frac{[I\cdot]}{K_{I\cdot}}}\frac{T_\infty}{T_0}\right) - k_i[I\cdot][M] = 0$$

$$\frac{d[IM_x\cdot]}{dt} = k_i[I\cdot][M] - 2k_t[IM_x\cdot]^2 = 0$$

polymerization rate

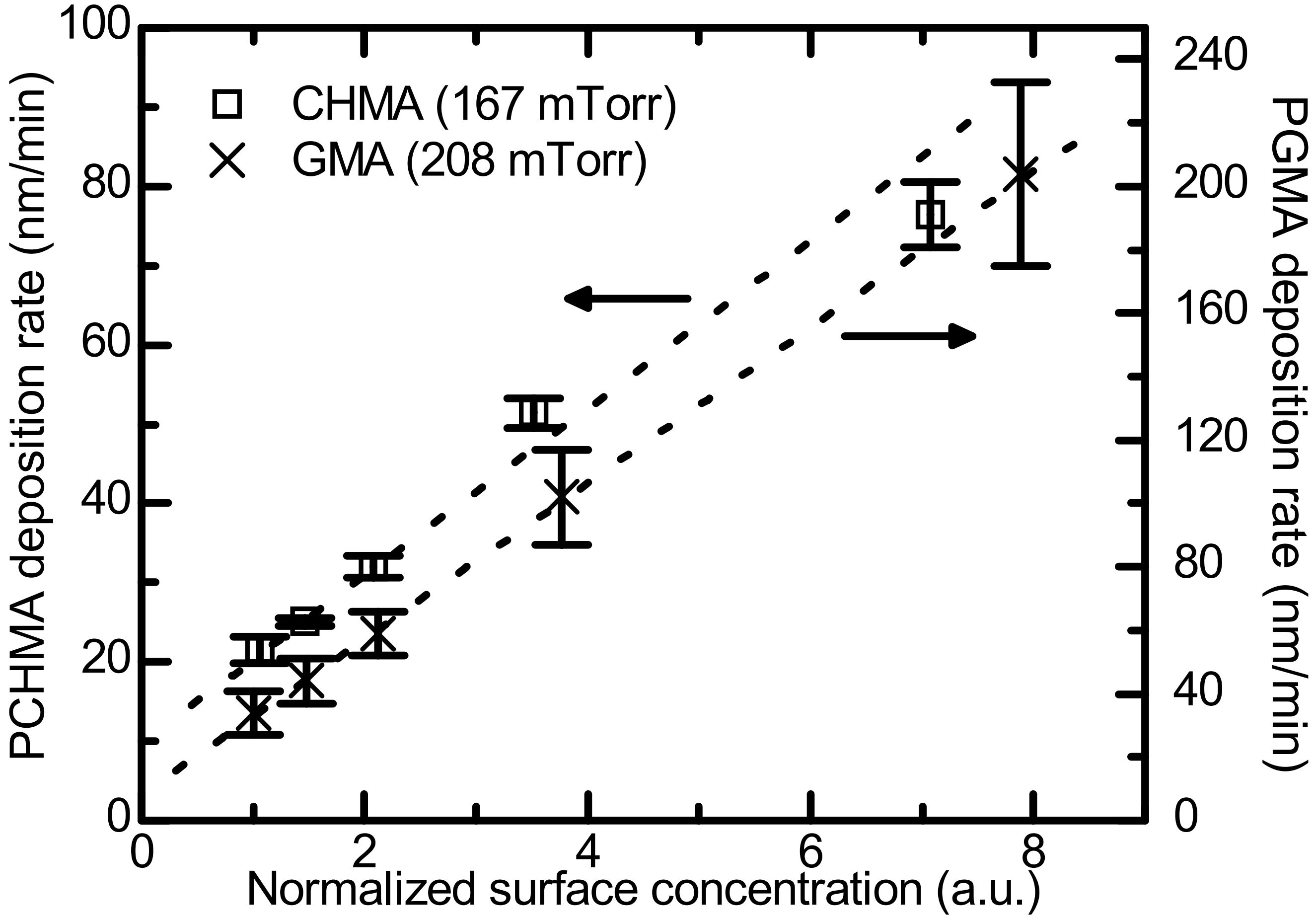
$$R_p = k_p[IM_x\cdot][M] = \left(\frac{k_p^2 k_c p_{I\cdot,\infty}}{2k_t RT_\infty}\right)^{0.5}[M]$$

kinetic chain length

$$\nu = \frac{R_p}{R_t} = \frac{k_p[M][IM\cdot]}{2k_t[IM\cdot]^2} = \frac{k_p[M]}{2k_t[IM\cdot]} = \left(\frac{k_p{}^2 RT_\infty}{2k_t k_c p_{I\cdot,\infty}}\right)^{0.5}[M]$$

# Deposition Rate vs. Surface Concentration

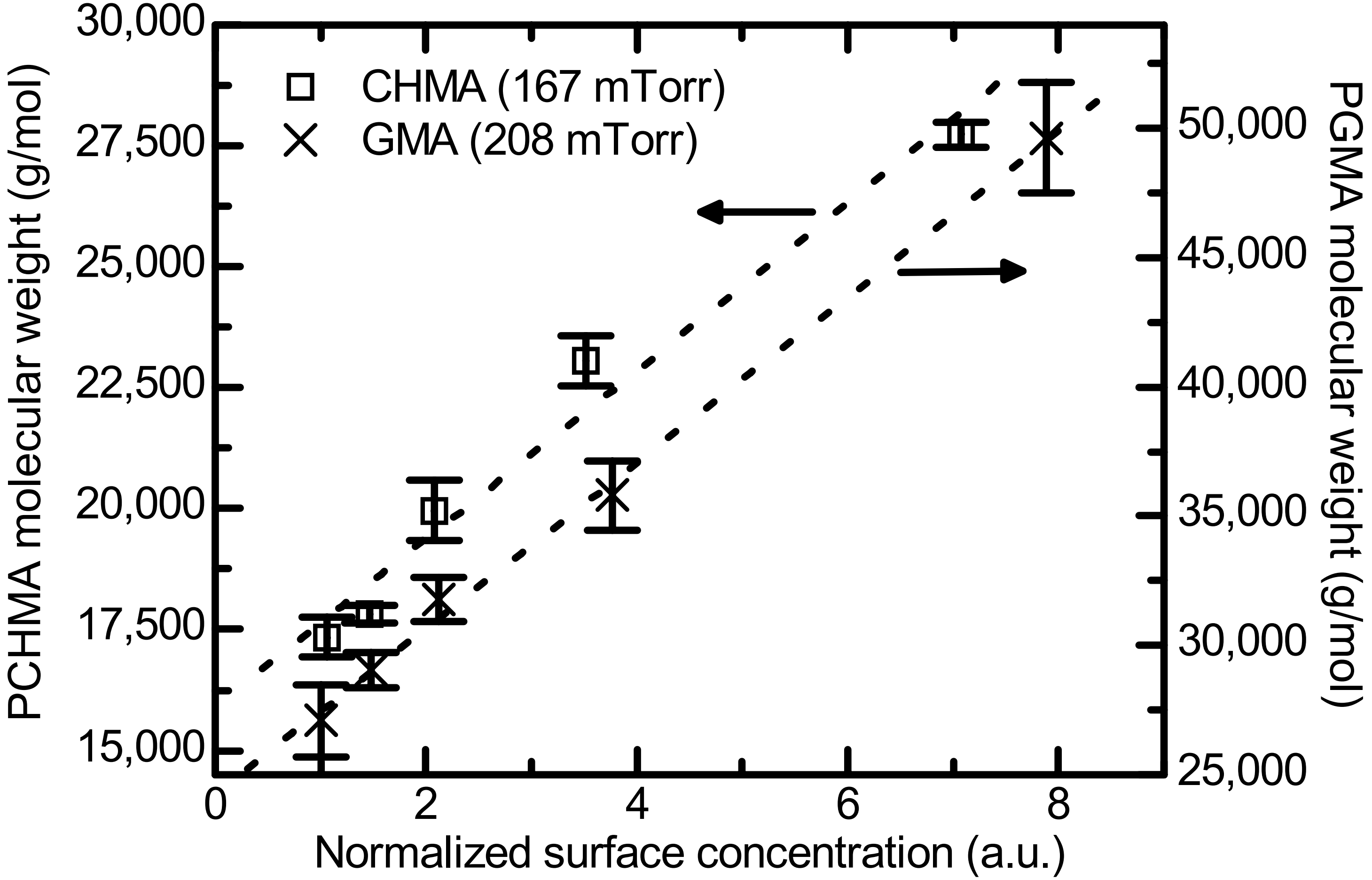
$$R_p = \left( \frac{k_p^2 k_c p_{I\cdot,\infty}}{2k_t RT_\infty} \right)^{0.5} [M]$$



Decreasing substrate temperature

# Molecular Weight vs. Surface Concentration

$$\nu = \left(\frac{k_p{}^2 R T_\infty}{2k_t k_c p_{I\cdot,\infty}}\right)^{0.5}[M]$$



→ Decreasing substrate temperature

# Mechanistic Study Conclusions

- Chain propagation occurs predominantly on surface
  - molecular weight increases with eq. surface concentration
  - deposition rate increases with eq. surface concentration
  - free-radical polymerization with adsorbed monomer initiated by incoming free radicals
- Surface concentration is at equilibrium during iCVD
  - monomer adsorption is not rate limiting
- Guideline for new monomers
  - high surface concentration
  - high $k_p^2/k_t$

$$\nu = \left( \frac{k_p^{\;2} R T_\infty}{2 k_t k_c \, p_{I\cdot,\infty}} \right)^{0.5} \left[ M \right]$$

# Air-Gap Fabrication using a Sacrificial Polymeric Thin Film Synthesized via iCVD

# Heat-Depolymerizing Polymers

- Heat-Depolymerizing Polymers
  - mechanical and thermal stability
  - decompose completely without residue

- Integration Issues
  - polymer dissolves in solvents
  - polymer etches slowly

- iCVD
  - to create as-deposited, cross-linked polymer that decomposes cleanly without leaving behind residue
    - insolubility
    - increased thermal stability
    - increased mechanical strength

# Self-Decomposing Sacrificial Materials

- Criteria for Success
  - High deposition rate
  - Good adhesion to substrate
  - Good adhesion to resist
  - Non-dissolving and non-swelling in solvents
  - High etch rate
  - Onset of decomposition temperature > 200 °C
  - Minimal amount of residue

- Bulk Organic Polymers
  - Poly(methyl methacrylate)
  - Polystyrene
  - Poly(α-methylstyrene)
  - Polyoxymethylene

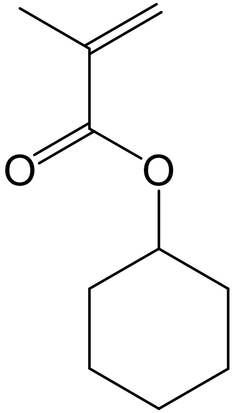
- Integration Issues
  - Polymer dissolves in solvents
  - Thin-film deposition difficult to achieve
    - PECVD unsuitable for the application
    - crystallization during spin-on deposition

# The Approach

- Initiated CVD (iCVD)
  - low energy input
  - low-temperature process
  - no ion bombardment or UV irradiation
  - selective polymerization with functionality retention

- Introduce Crosslinks in iCVD Intentionally
  - through use of a crosslinking agent which can depolymerize

# Monomers and Cross-linking Agent



Cyclohexyl Methacrylate
(CHMA)
168 g/mol
397 mT @ 35 °C
5 T @ 78 °C

MSDS excepts

Stable under normal temperatures and pressures.

Hazardous Decomposition Products: Carbon monoxide, carbon dioxide.

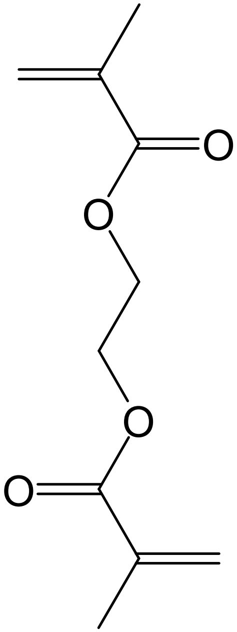
Hazardous Polymerization: Will not occur.

Potential Health Effects

Causes eye and skin irritation.

Carcinogenicity:

Not listed by ACGIH, IARC, NIOSH, NTP, or OSHA.



Ethylene Glycol Dimethacrylate
(EGDMA)
198 g/mol
27 mT @ 35 °C
5 T @ 89 °C

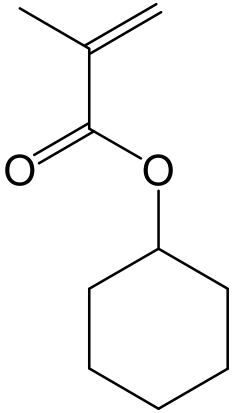
Irritating to respiratory system.

LD50/LC50: Oral, mouse: LD50 = 2 gm/kg; Oral, rat: LD50 = 3300 mg/kg.

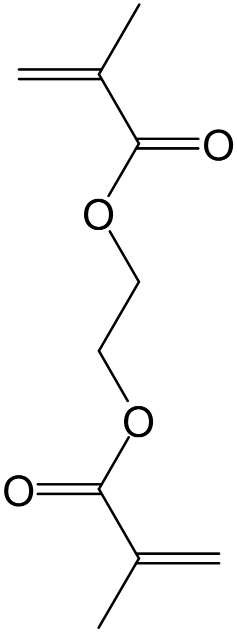
Carcinogenicity: Not listed by ACGIH, IARC, NIOSH, NTP, or :

Stable under normal temperatures and pressures.

# FTIR of crosslinked copolymer

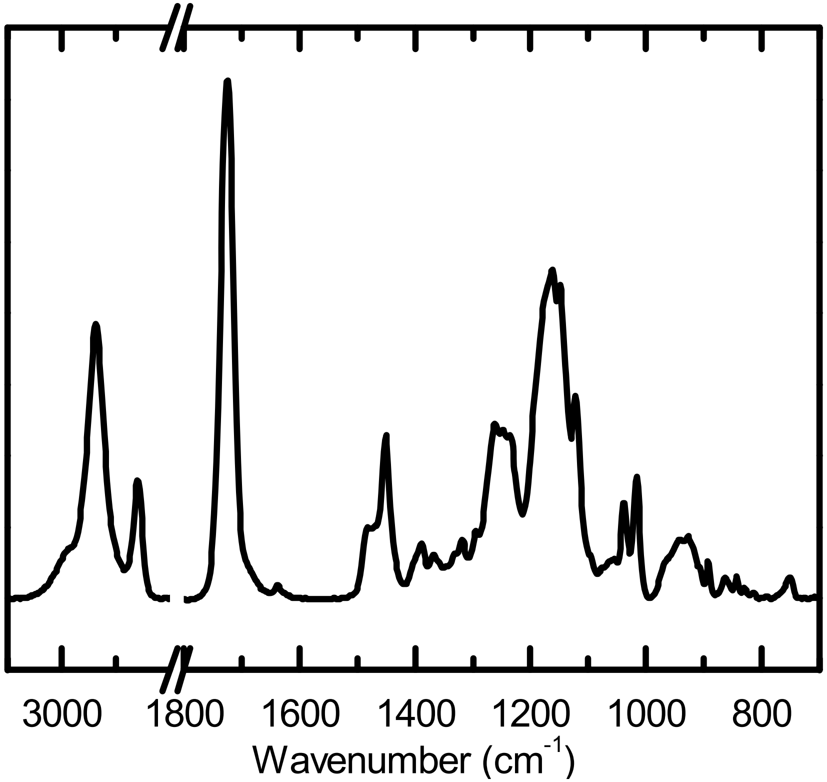


Cyclohexyl Methacrylate
(CHMA)

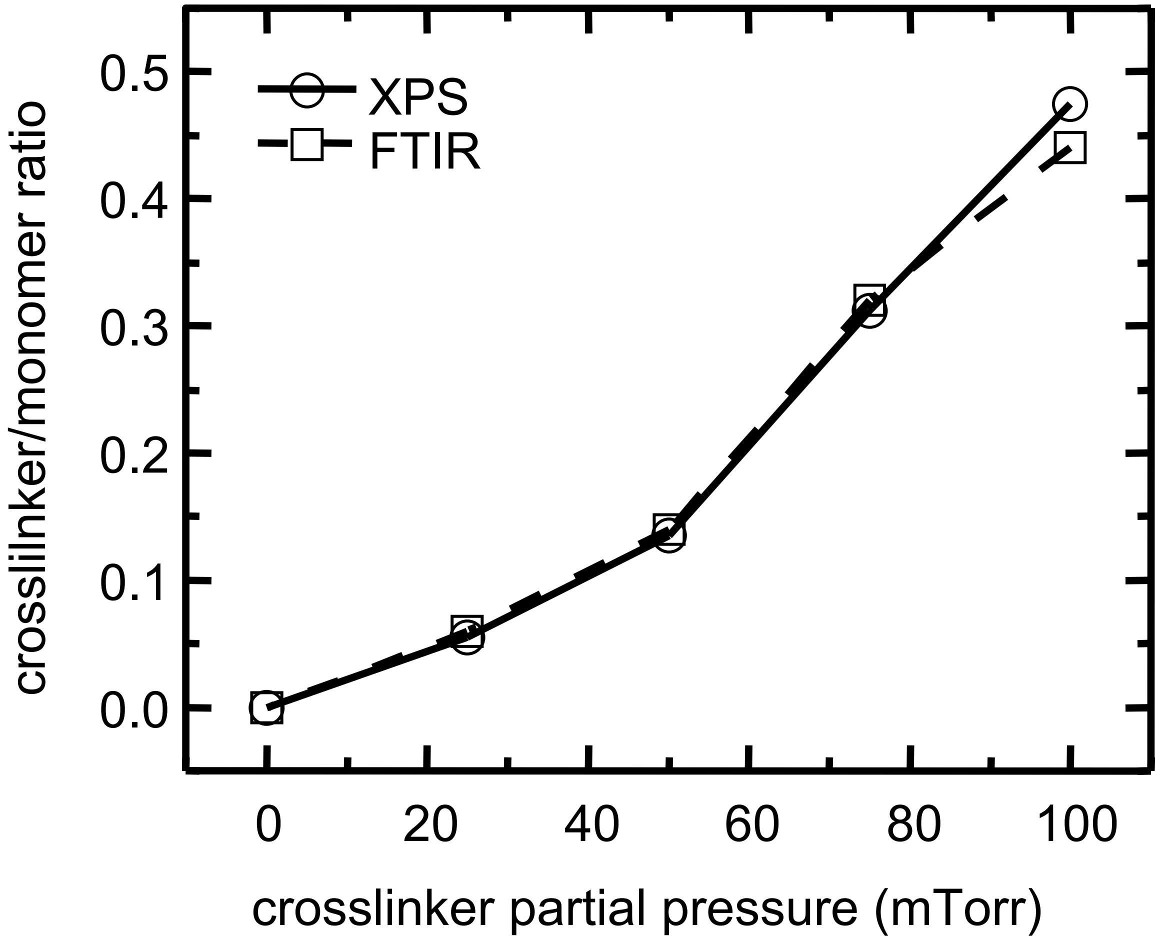


Ethylene Glycol Dimethacrylate
(EGDMA)

Resulting Polymer

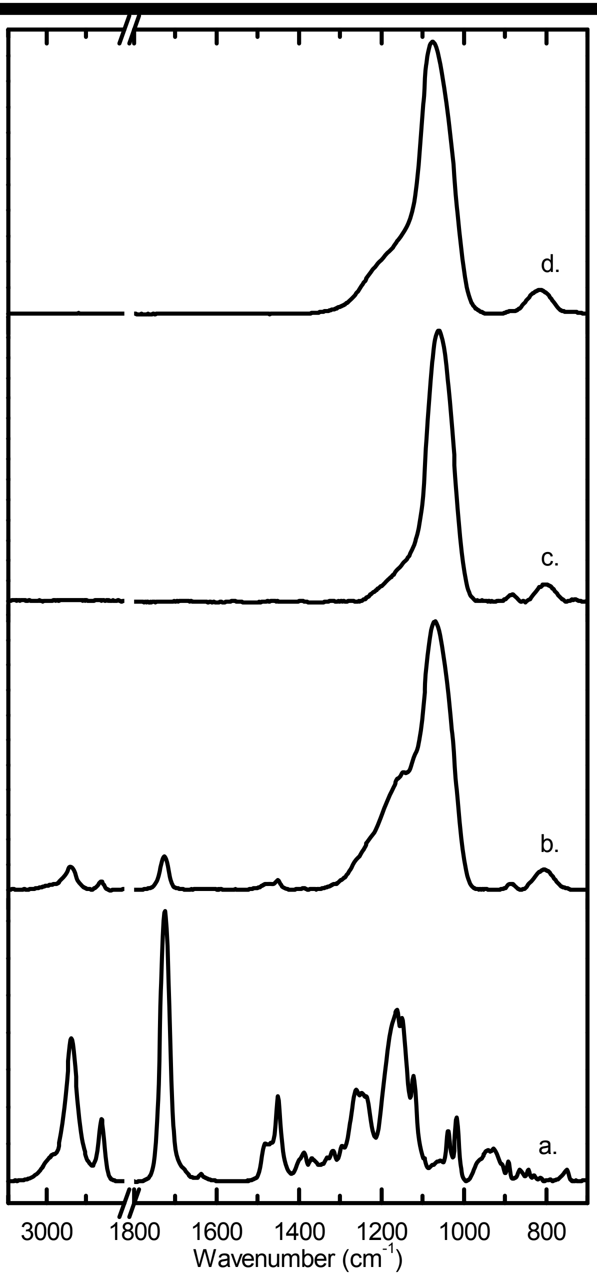


# Cross-link Density (FTIR & XPS)



two independent methods confirm systematic control of crosslink incorporation in the film

# FTIR



After Annealing

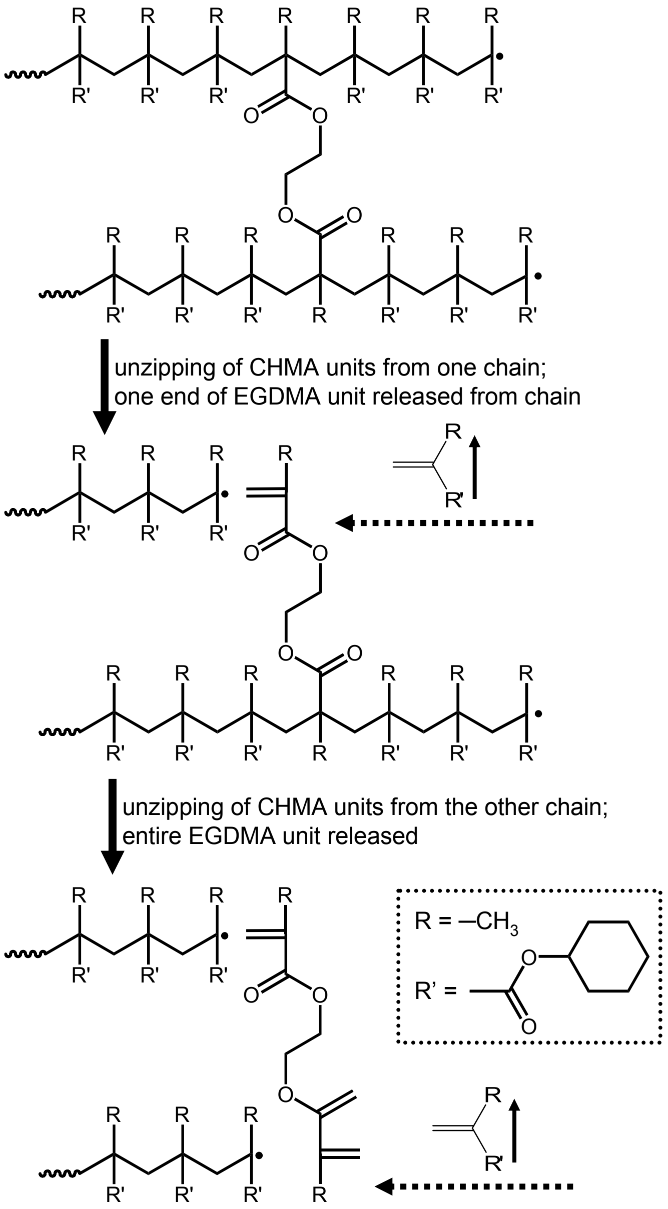
PECVD $SiO_2$

Before Annealing

iCVD Crosslinked PCHMA

# Film Properties

- **Does not dissolve in any commonly used solvents**
- **Decomposition > 99.7% by thickness (VASE)**
- **Onset temperature of decomp. ~ 270 °C (ITS)**
- **Good adhesion to substrate and photoresist**
- **High etch rate in oxygen RIE (0.35 µm/min)**



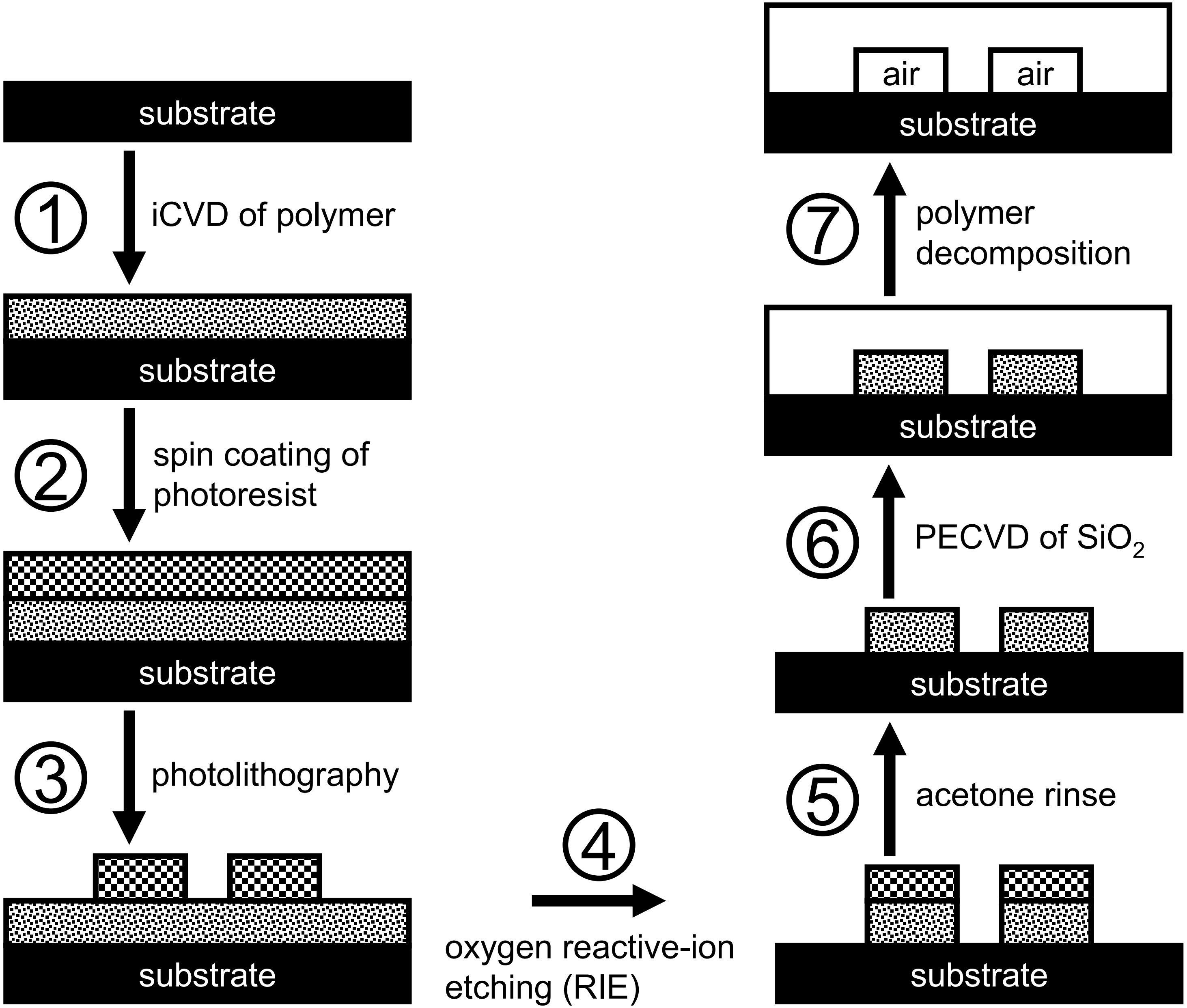
unzipping of CHMA units from one chain;
one end of EGDMA unit released from chain

unzipping of CHMA units from the other chain;
entire EGDMA unit released

R = $-CH_3$

R' =

# The Fabrication



substrate

① iCVD of polymer

substrate

② spin coating of photoresist

substrate

③ photolithography

substrate

④ oxygen reactive-ion etching (RIE)

substrate

⑤ acetone rinse

substrate

⑥ PECVD of $SiO_2$

substrate

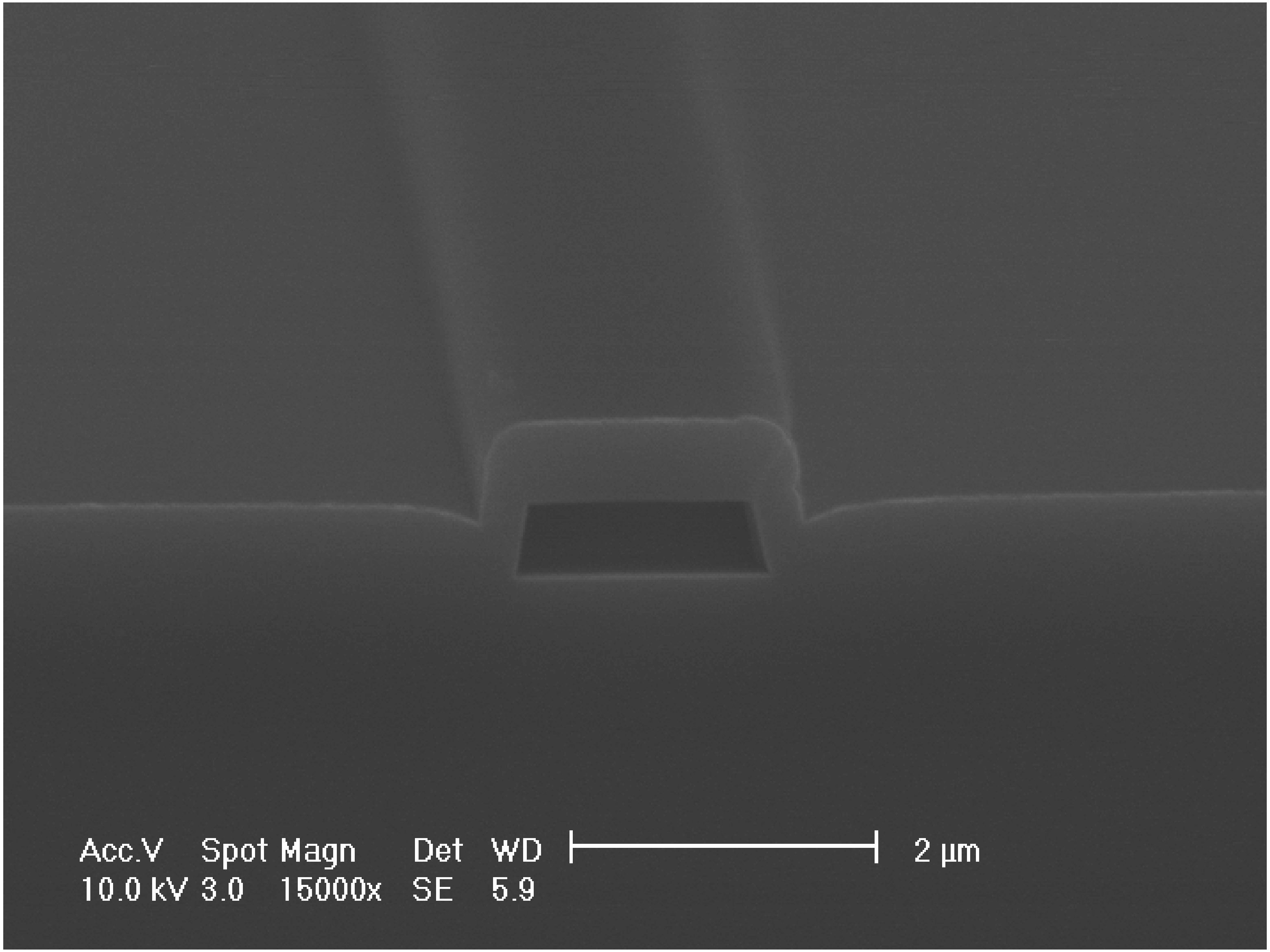
⑦ polymer decomposition

air

air

substrate

# The Resulting Structure



# PCHMA iCVD Conclusions

- Cross-linked PCHMA made in situ on the surface of a substrate in one step by iCVD without using any solvents. Not possible to spin cast this insoluble material.
- Networked polymer completely decomposes cleanly
  - maximum of 0.3% residue
  - crosslinking via the dimethacrylate monomer is key
  - degree of crosslinking can be systematically adjusted
- Cross-linking renders the polymer stable in practically all solvents: photoresist can be removed by dissolution instead of ashing.
- The high etch rate (0.35 μm/min) in oxygen reactive-ion etching in addition to the stability in solvents eliminates the need of a hard mask during etching. Eliminating the hard mask represents an improvement over previously-reported spin-on sacrificial materials.
- The onset of thermal decomposition is 270 °C, meaning that the polymer can survive other high-temperature processing steps.
- Fabrication using conventional lithographic, etching, and deposition techniques resulted in void structures having feature sizes of a minimum of 1.5 μm. With better lithography, smaller feature sizes can be fabricated.

# Acknowledgments

- SRC International Fellowship
- NSF/SRC ERC for EBSM
- MRSEC Shared Facilities
- Kurt Broderick, MT