Chemical Vapor Deposition of Organosilicon Composite Films for Porous Low-k Dielectrics

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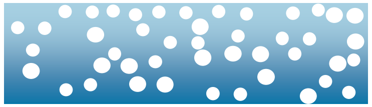
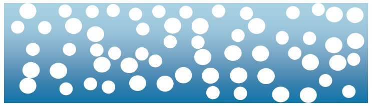
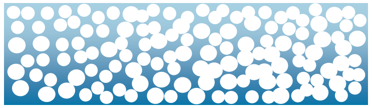
Goals

- Create a Porous, Low-κ Film by CVD
  - Rigid Organosilicon Matrix
  - Thermally Labile Porogen
  - Deposition by Pulsed Plasma Enhanced CVD

Composition	Fully dense κ
SiO_2	4.0
Si:O:C:H (Organosilicate Glass – OSG)	2.7–3.0

Air
κ =1.0

	% Porosity	**κ**
	0	2.7
	20	2.3
	50	1.75
	90	1.15

Technology Requirements - κ

Interconnect Technology Requirements - Near Term

Year of Production	2001	2002	2003	2004	2005	2006	2007
Interlevel metal insulator effective k-value	3.0-3.6	3.0-3.6	3.0-3.6	2.6-3.1	2.6-3.1	2.6-3.1	2.3-2.7
Interlevel metal insulator bulk k-value	<2.7	<2.7	<2.7	<2.4	<2.4	<2.4	<2.1

Interconnect Technology Requirements - Long Term

Year of Production	2010	2013	2016
Interlevel metal insulator effective k-value	2.1	1.9	1.8
Interlevel metal insulator bulk k-value	<1.9	<1.7	<1.6

Source: ITRS Roadmap for Semiconductors: 2001 Update - Interconnect - http://public.itrs.net

Industry Outlook

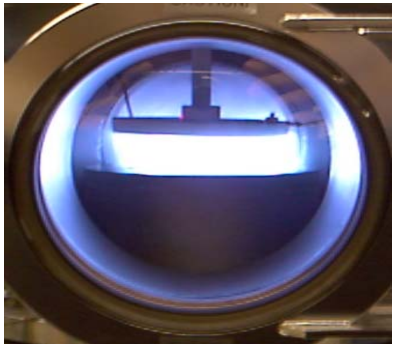
- The widely used ILD material for 0.13μm and older technologies are PECVD SiO_2 and SiOF

Materials/ Technology	0.13μm or 0.09μm	0.07μm	0.05μm
Organic	SiLκ™, Flare™, Paralyne-F(N), αFC, PAE,etc.	Porous SiLκ™, Porous Flare™, OXD, etc	Partial Air Gap, Complete Air Gap
Organosilicates	Carbon Doped Oxide, SOG, etc .	Porous CVD CDO, Porous SOD, CDO, etc.	Partial Air Gap, Complete Air Gap
Range of κ	2.8 to 3.0	1.9 to 2.6	1.0 T to 1.5

Dr. Eb Andideh, Intel Corporation (2003, MIT hosted ERC teleconference)

Solventless Low-κ Dielectrics

- Manufacturing Metrics: Lowering the dielectric constant of current ILDs leads to fewest levels of interconnect → economic and environmental "win-win"

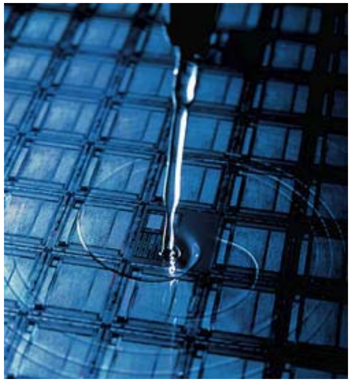


CVD

- Thin, Conformal Coatings
- Solventless
- Ease of Integration
- Mechanical Properties
- Unclear Strategy for porous materials

Spin-On

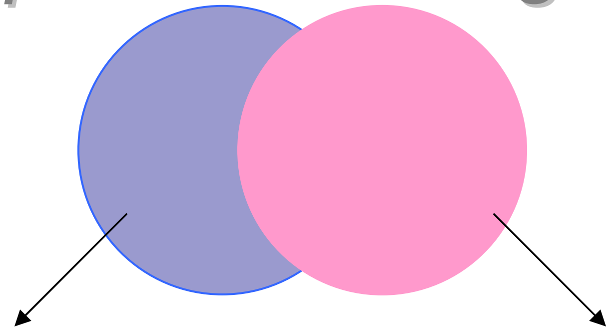
- Extendibility to Future Generations by adding pores



Goals/ Possibilities	Usage Reduction			Emission Reduction			
	Energy	Water	Chemicals	PFCx	VOCs	HAPs	Hazardous Wastes
Pulsed Plasma Enhanced CVD for k < 2.2	Data not available	NA	Order of magnitude greater consumption for spin-on (Hendricks)	Higher emissions for CVD due to chamber cleans	Great reduction vs Spin-on	Some reduction in acid vapors	Spin-on requires solids waste disposal

Composite Materials

Decouple Processing Windows

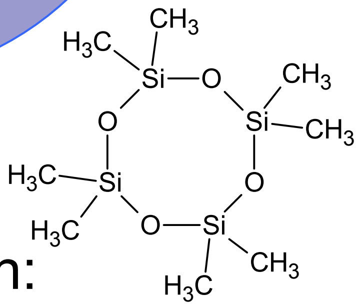


Matrix

Octamethyl-
cyclotetrasiloxane

Porogen

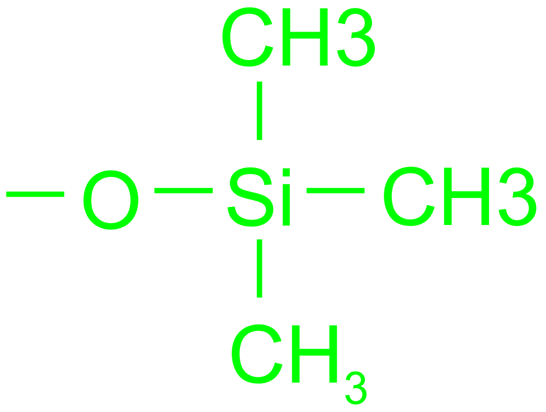
Polystyrene Beads
Cyclodextrin



- Primary Concern: Mechanical Integrity
  - Mechanical strength is reduced with porosity, p, by $(1\text{-}p)^3$

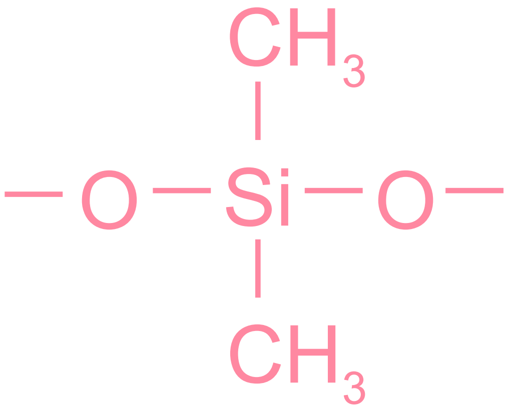
- Controlled Pore Size & Distribution
- No Covalent Bonding
- Decomposes under 400°C

OSG Mechanical Properties



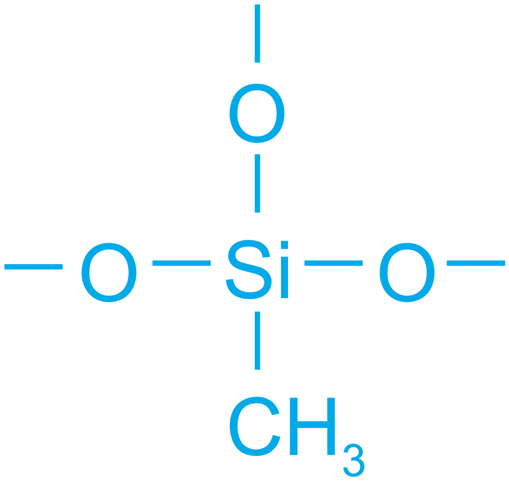
$$-\mathrm{O}-\overset{\mathrm{CH3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH3}$$

‘M’ Group
Chain Terminating



$$-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-$$

‘D’ Group
Chain Propagating

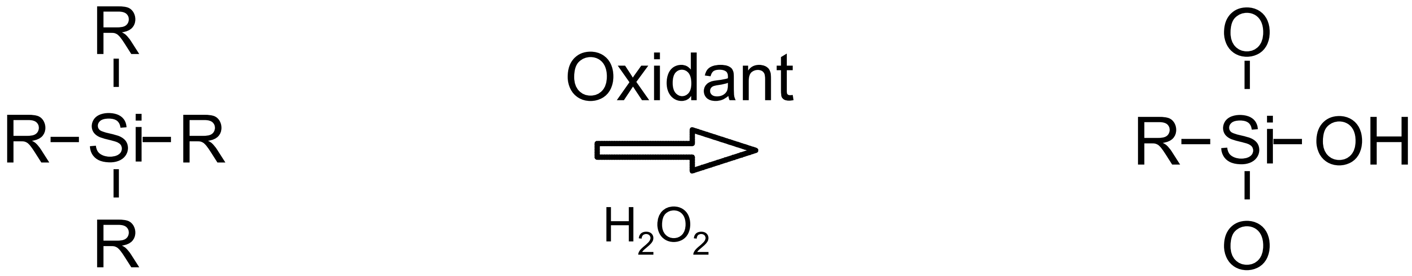


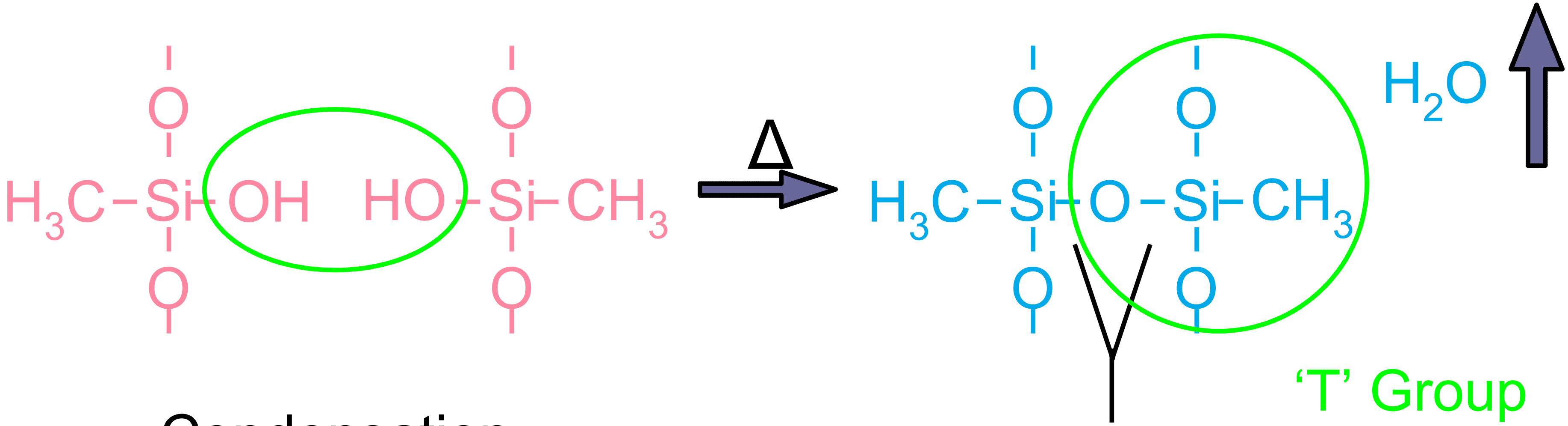
$$-\mathrm{O}-\overset{\overset{|}{\mathrm{O}}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-$$

‘T’ Group
Chain Crosslinking

Condensation Reactions

How can we make 'T' groups?





Condensation Reaction

Crosslink formation

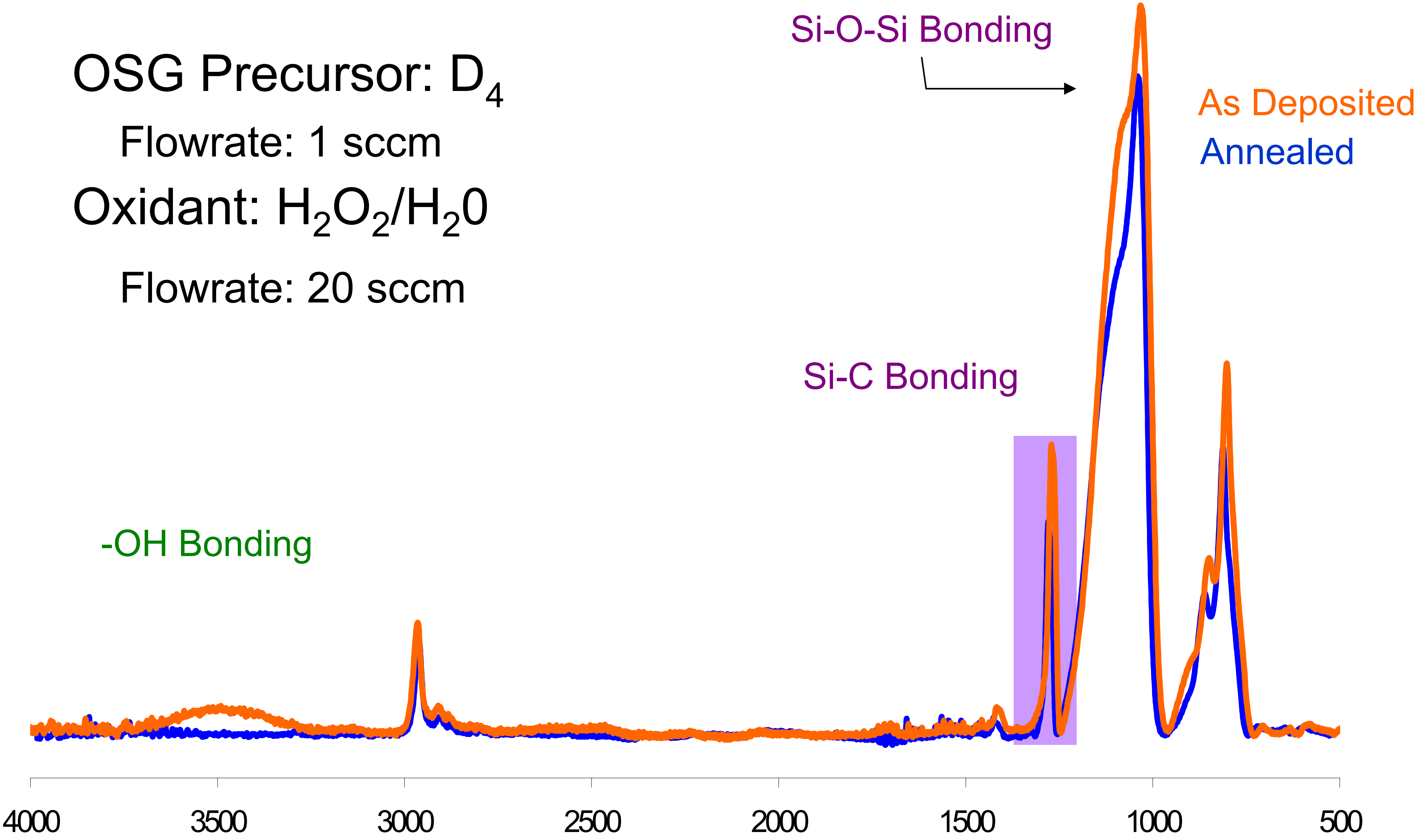
Monitoring Condensation

OSG Precursor: D_4

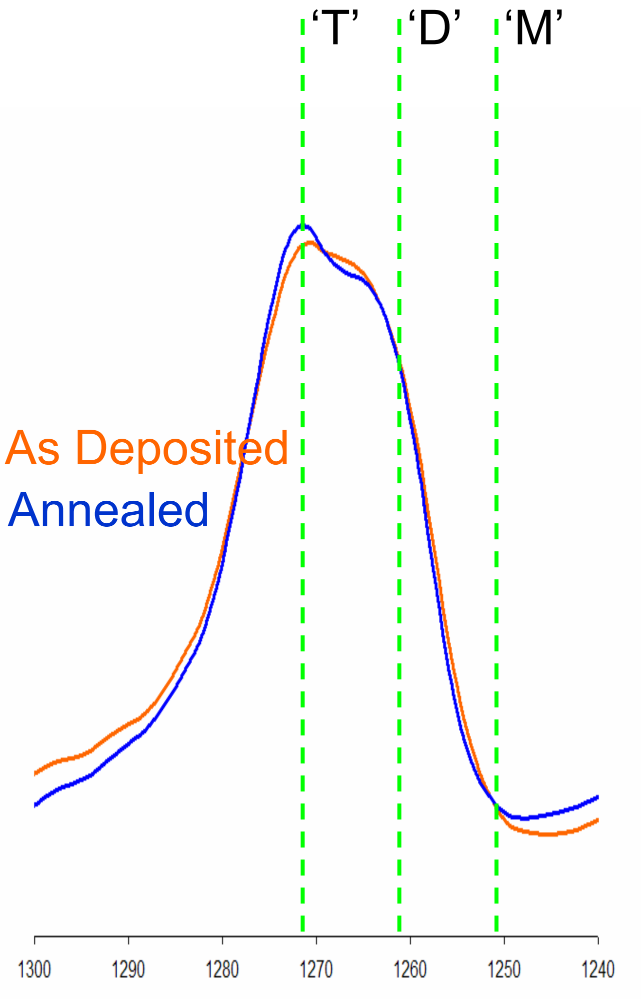
Flowrate: 1 sccm

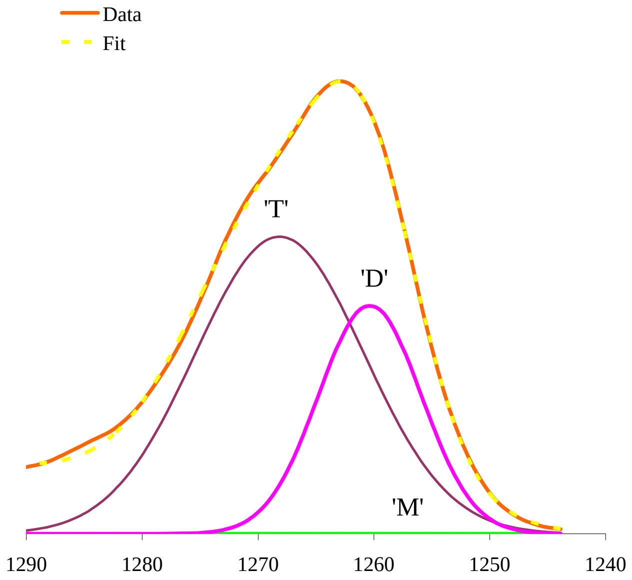
Oxidant: H_2O_2/H_20

Flowrate: 20 sccm



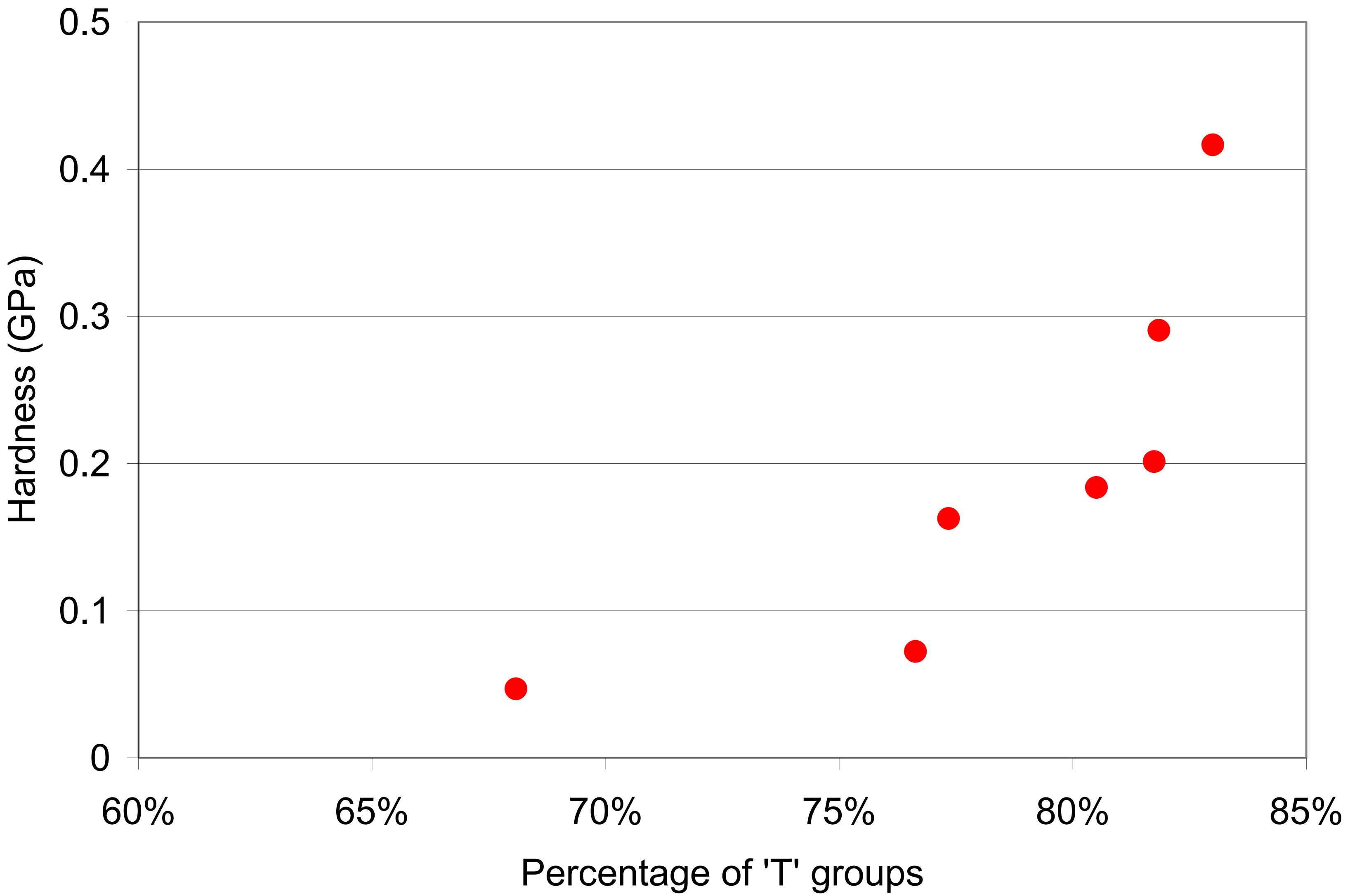
Quantifying Condensation





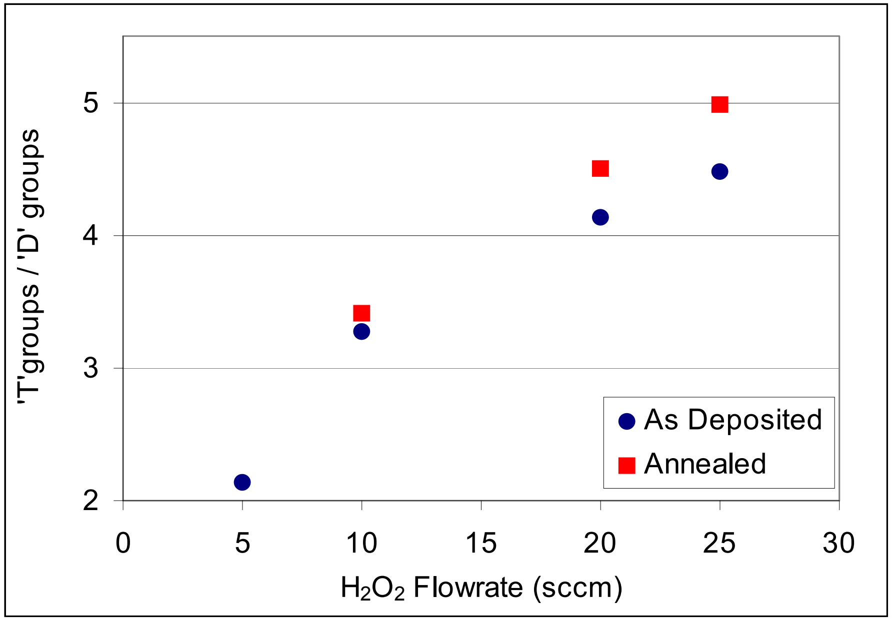
	D:T	Hardness (GPa)	Dielectric Constant (κ)
As Deposit	0.223	0.201	4.01
Annealed	0.200	0.417	2.91

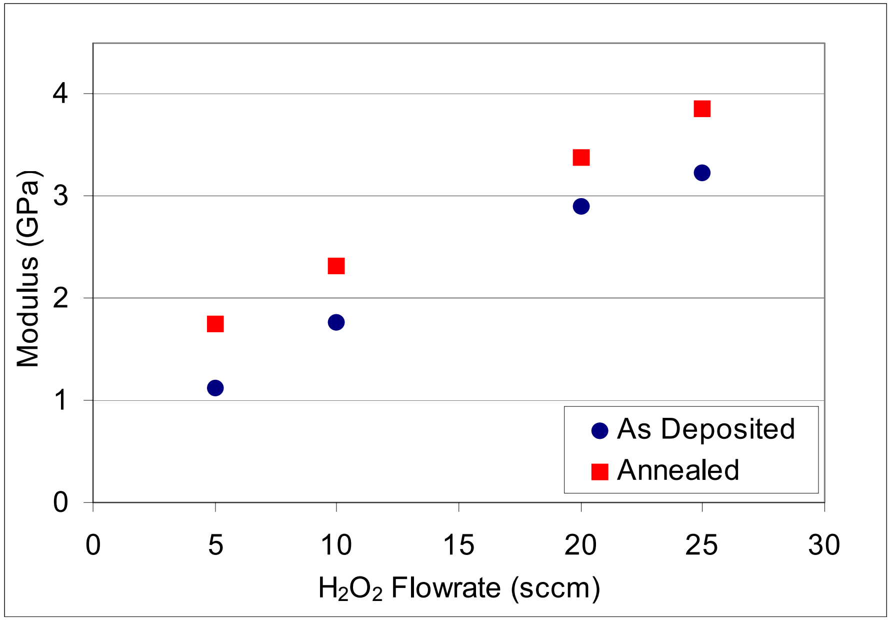
OSG Mechanical Properties



OSG Mechanical Properties

Increasing the H_2O_2 flowrate ….



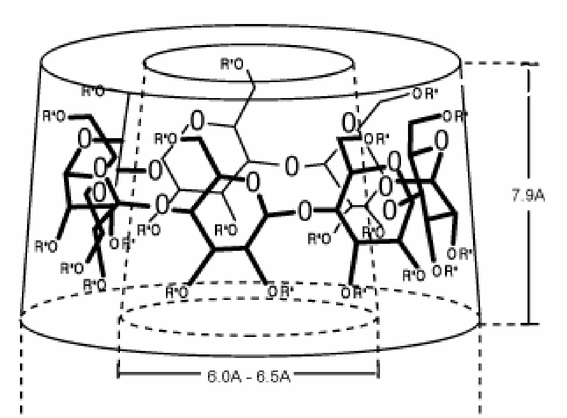


- Amount of 'T' groups relative to 'D' groups increases
- Both Modulus and Hardness increase
- Annealing increases percentage of T groups and Modulus

Composite Materials

- Polystyrene Beads
  - **Bead Diameters: 15nm (std = 3), 96nm (std = 9)**
  - **Health=0, Flammability=1, Reactivity=0**
  - **1% Styrene in Air: Health=1, Flammability=0, Reactivity=1**

- Cyclodextrin
  - 1.54nm diameter

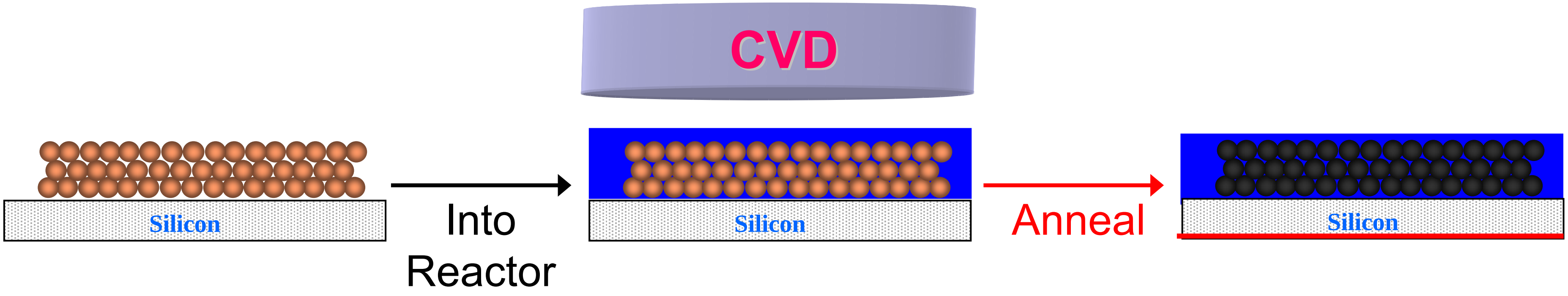


CTD, Inc

Spin On: Jin-Heong Yim, et al. 2003

Composite Materials

- Polystyrene Beads



CVD

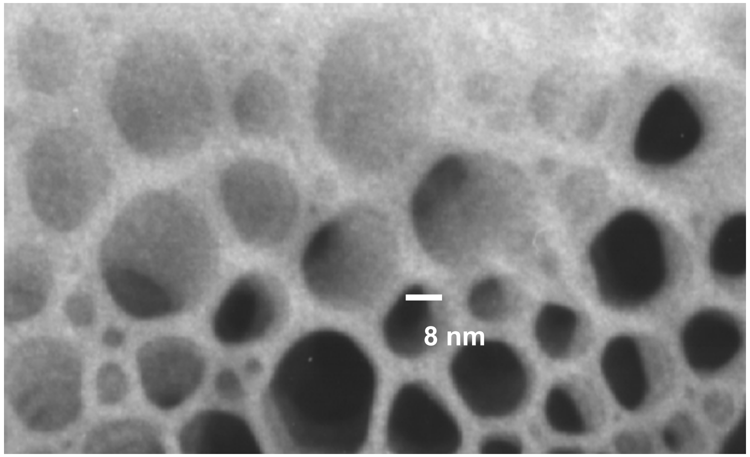
Silicon

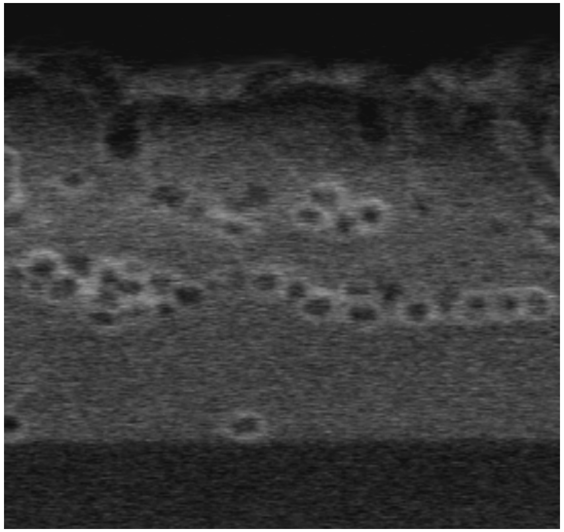
Into Reactor

Silicon

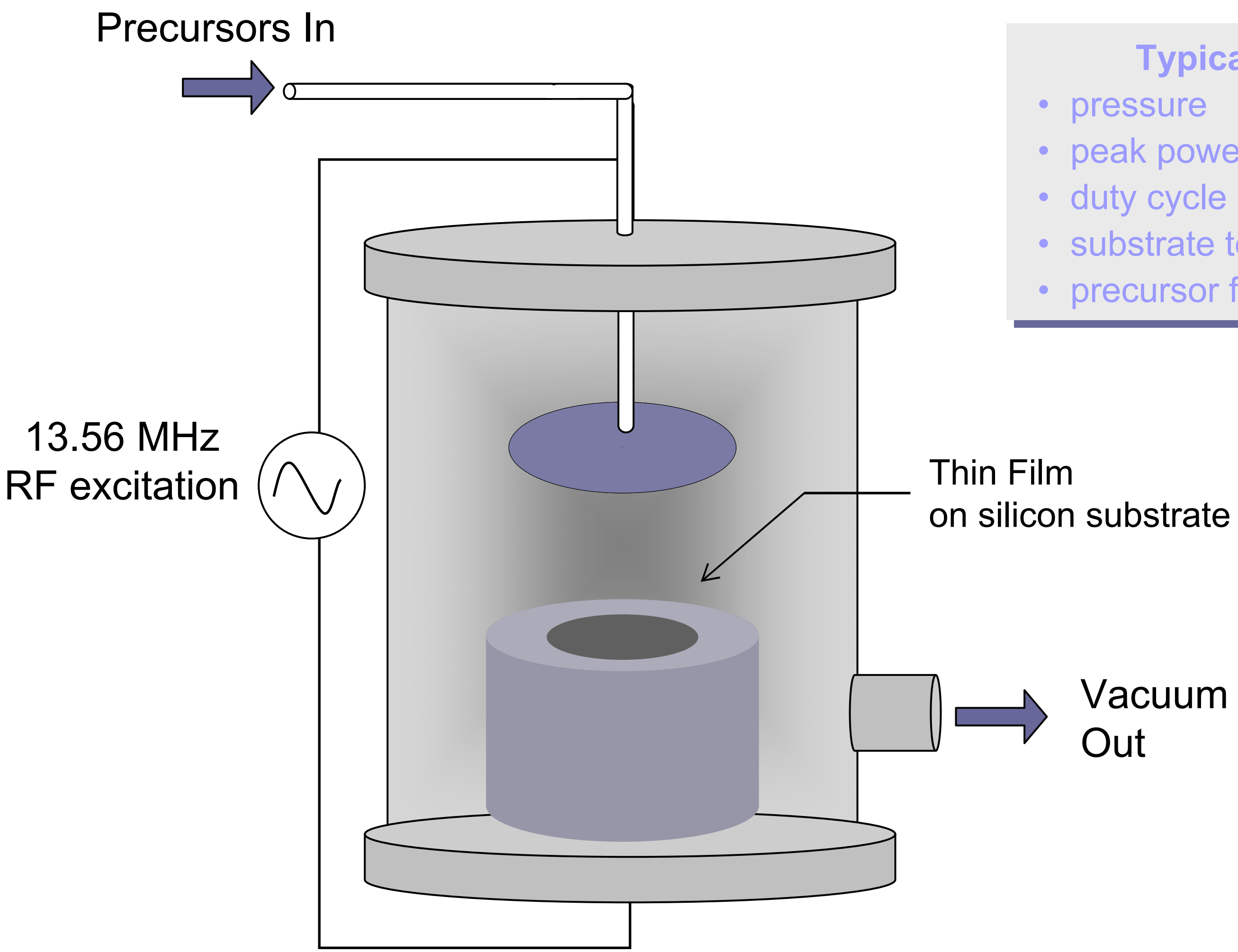
Anneal

Silicon





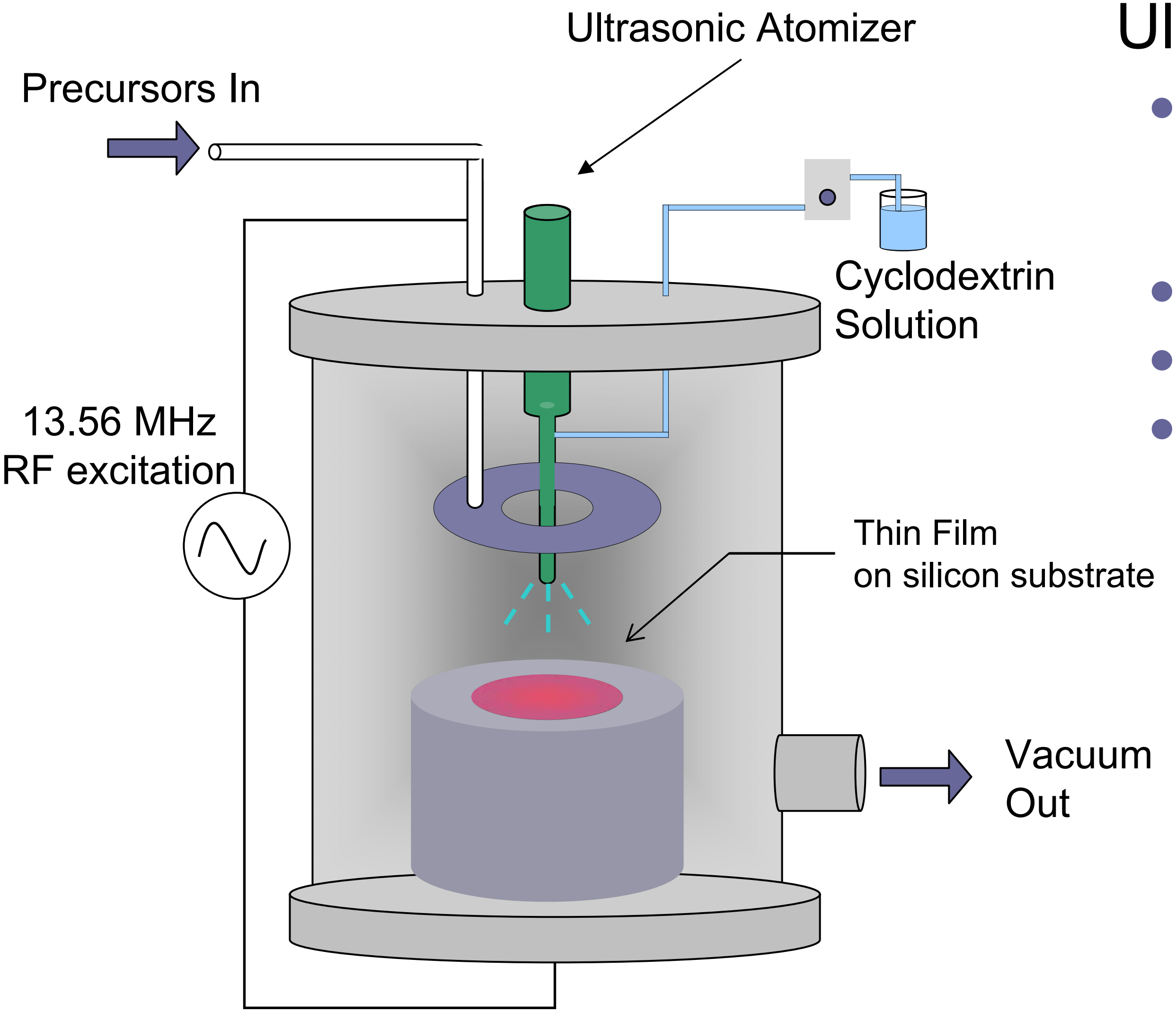
Reactor Configuration



Typical Operating Parameters

pressure	*300 mTorr*
peak power	*100-300 W*
duty cycle	10-25%
substrate temp	*cooling water*
precursor flow rate	*0 - 20 sccm*

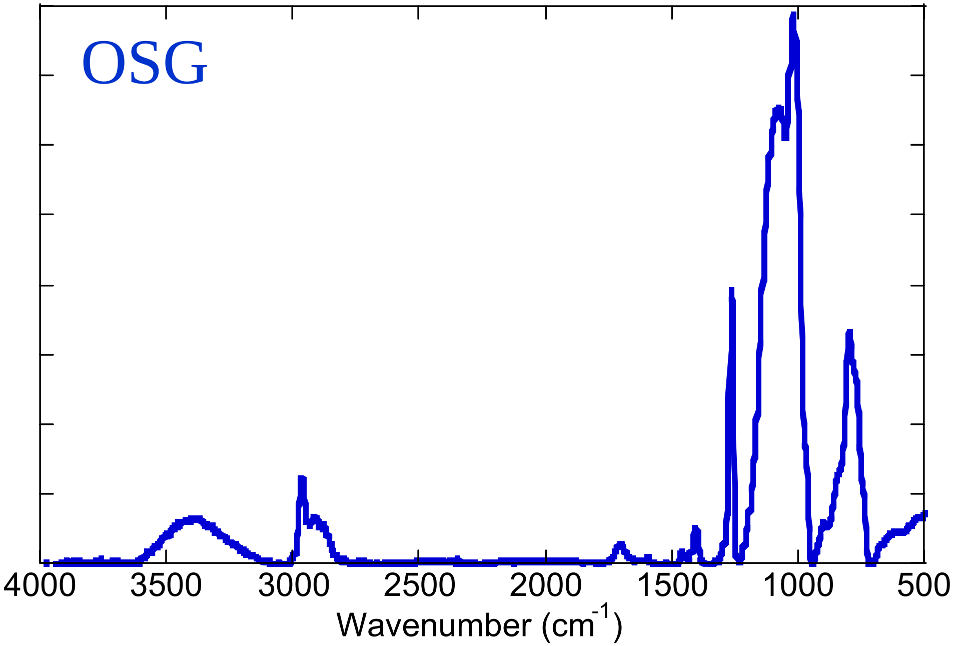
Reactor Configuration



Ultrasonic Atomization

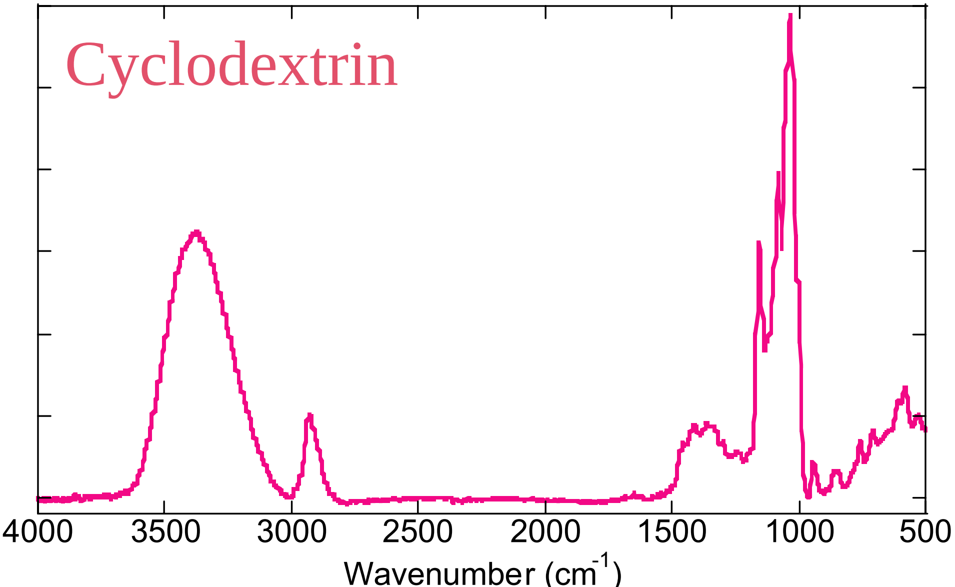
- Uses low ultrasonic vibrational energy for atomization
- Dispenses microliters/min
- Pressureless atomization
- Can handle up to 30% solids

Atomized Delivery of Water and Porogen



- Deposited with 0.2 ml/min of water atomization
- Deposition Rate:

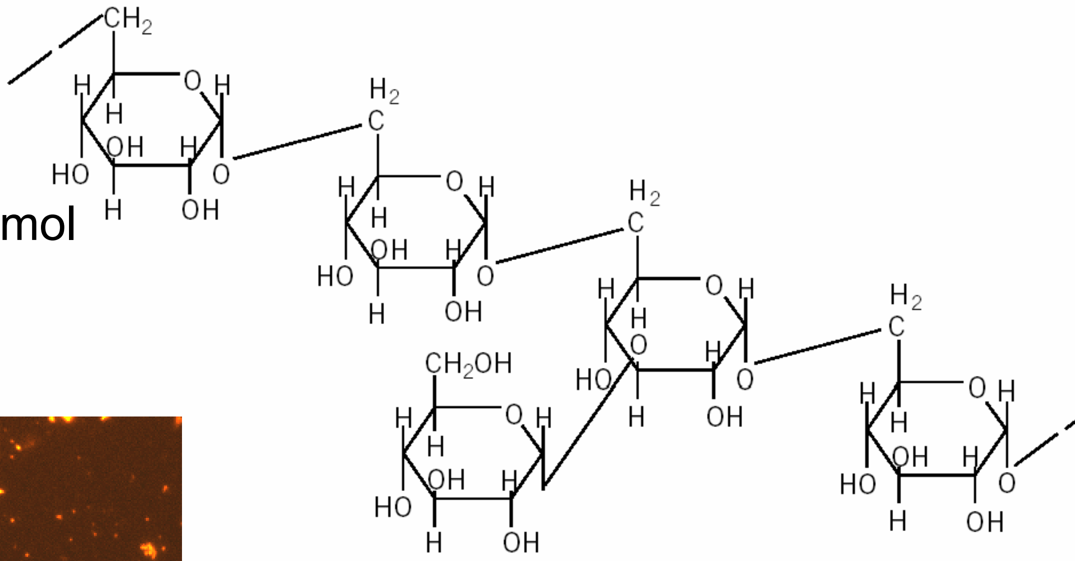
  up to 4.0 μm/min

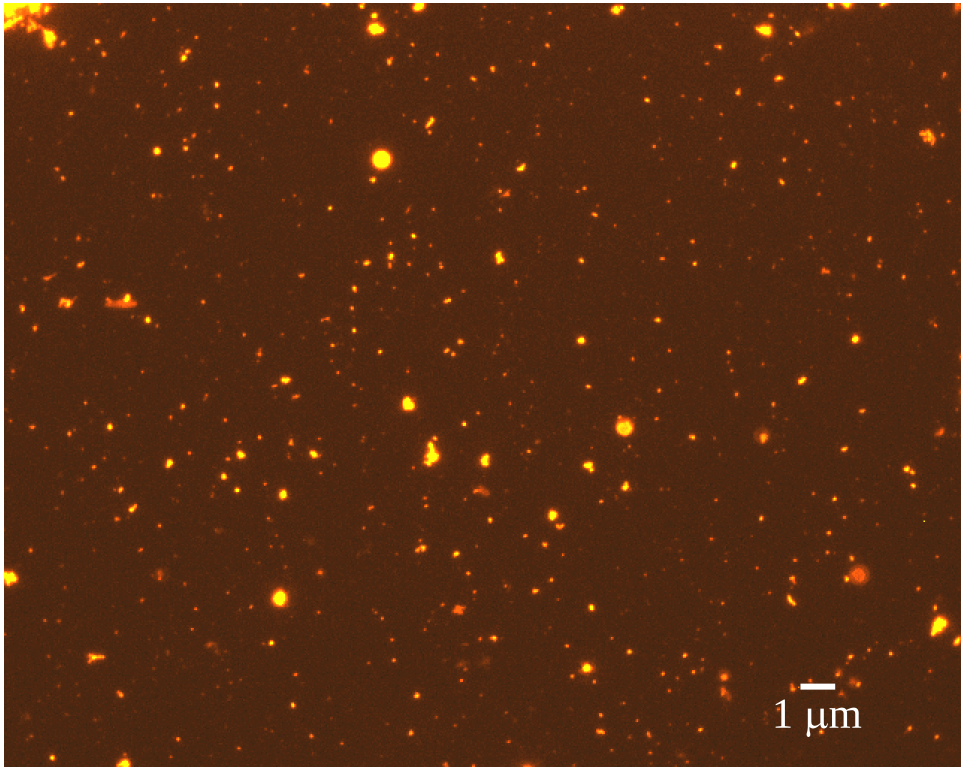


- Deposited using ultrasonic atomization under vacuum conditions

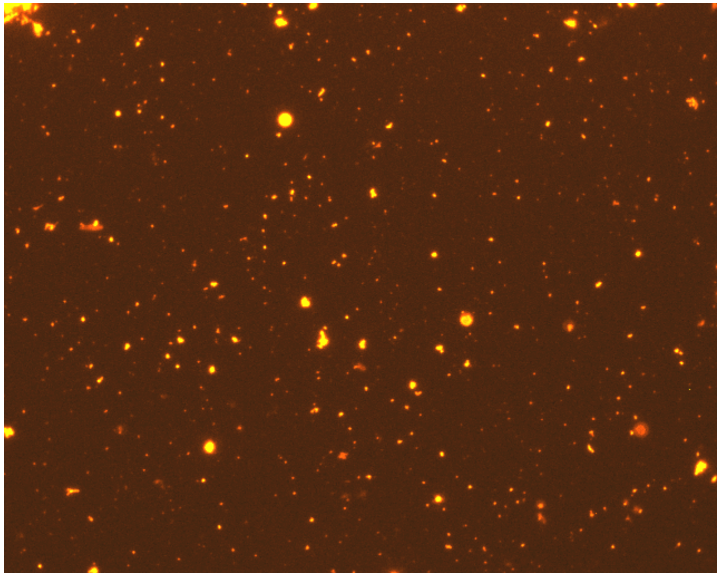
Porogen Detection

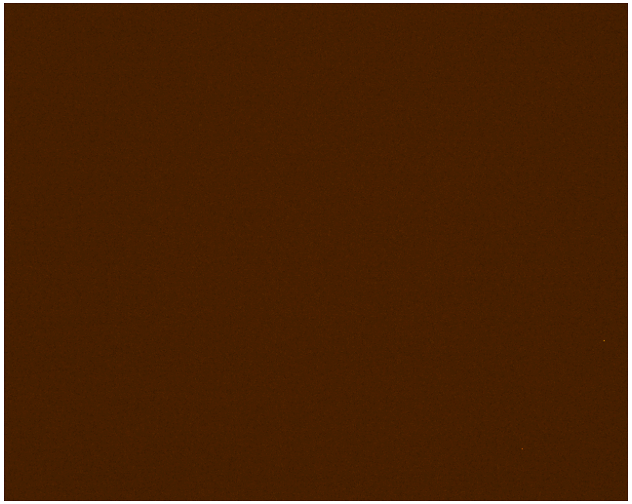
- Dextran
  - Molecular Weight: 3000 g/mol
  - Texas Red® labeling

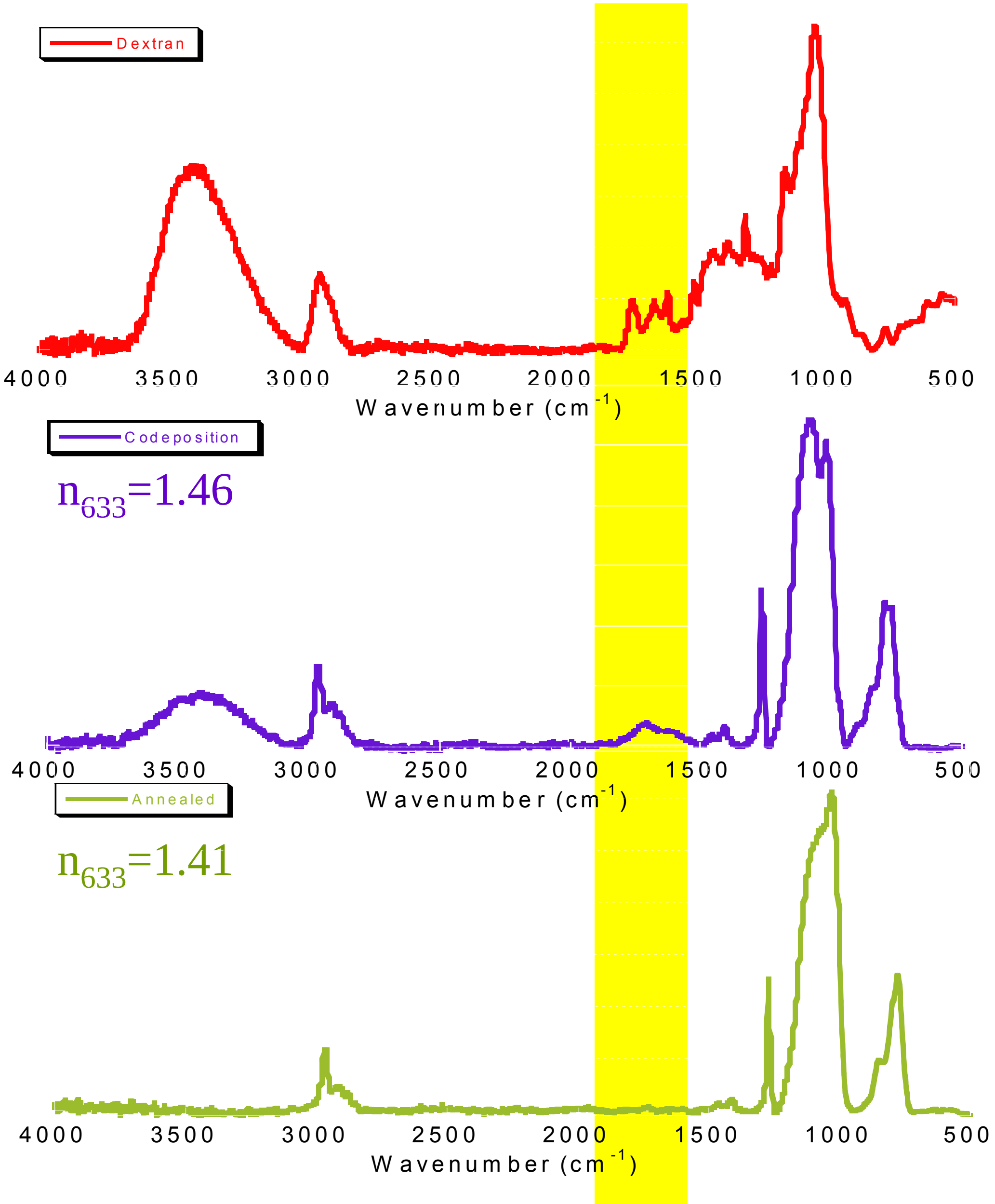




Dextran & OSG FTIR Analysis







$n_{633}=1.46$

$n_{633}=1.41$

Conclusions for Porogens

- Porogen Delivery
  - Ultrasonic atomization used to deposit porogen under vacuum conditions
  - Dextran co-deposited with OSG matrix
  - Removal of dextran through annealing

- Pulsed Plasma Enhanced CVD process for depositing OSG films
  - OSG thin films were deposited using D_4
  - H_2O_2 used as oxidant to promote –OH bonding
  - Condensation reaction improves hardness
  - Film properties linked to structure through FTIR

Air Gaps

Either increasing fragile porous low k materials must be integrated

or

A robust sacrificial layer must be integrated which can form air in the final step
(sacrificial layer = 100% porogen)

- **Havemann and Jeng (TI), US Patent 5461003, 1995.**

- **Anand *et al., IEEE*, 1997.**

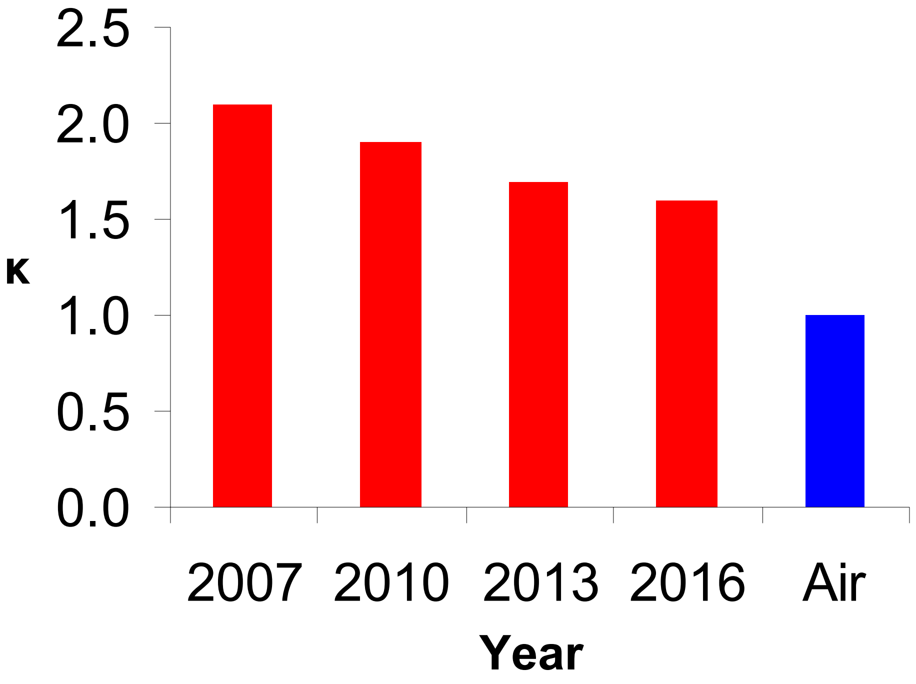
Gleason Group Research by Tom Casserly and Kelvin Chan

Extreme Properties

- 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

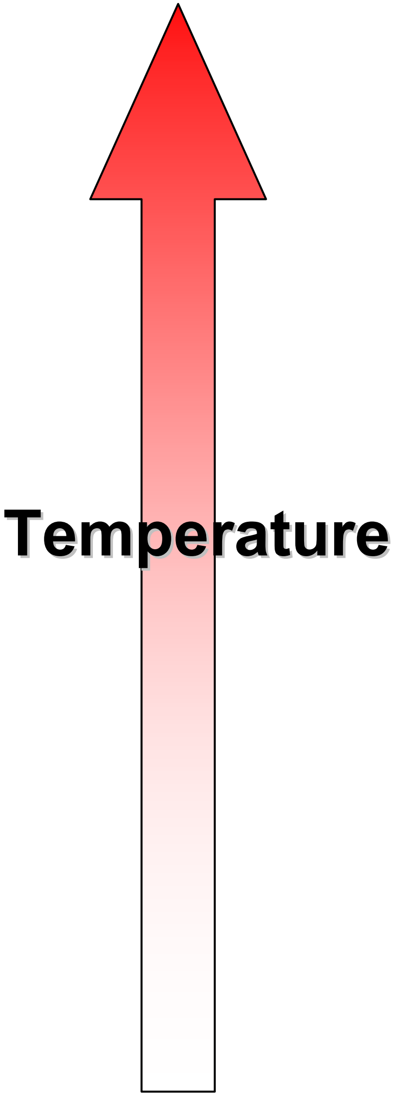
    (e.g. thin-film optical filters)



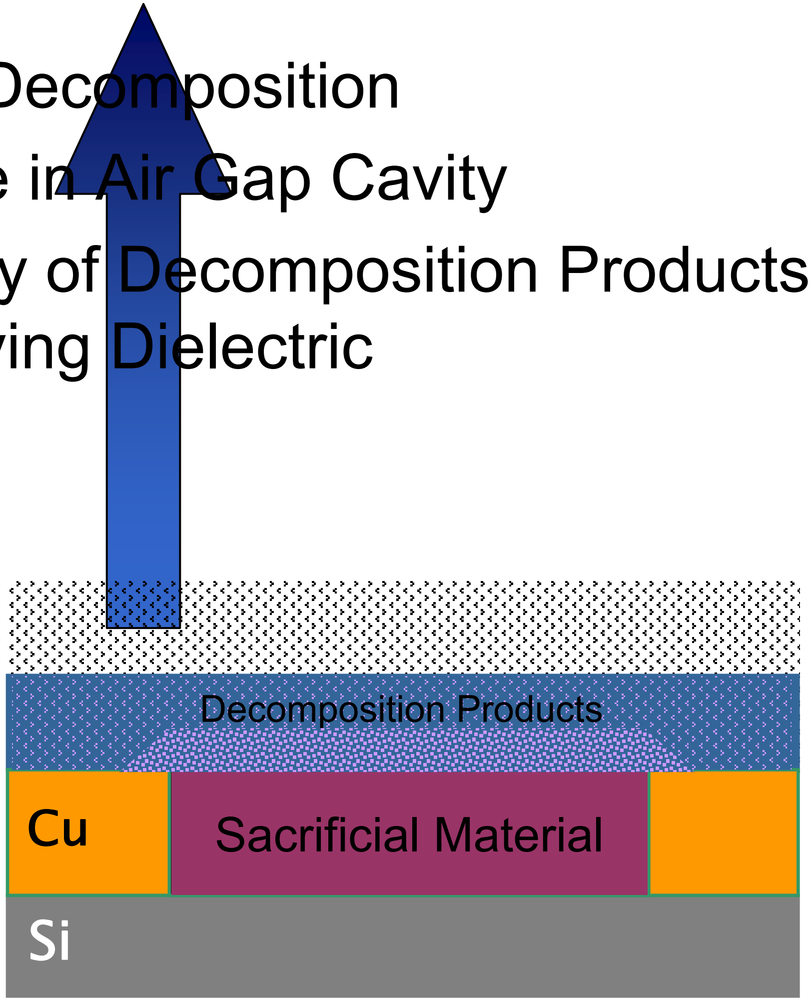
Future Microprocessor Interconnect Technology Requirements*

*Source: International Technology Roadmap for Semiconductors 2001

Sacrificial Layers in Air Gap Formation

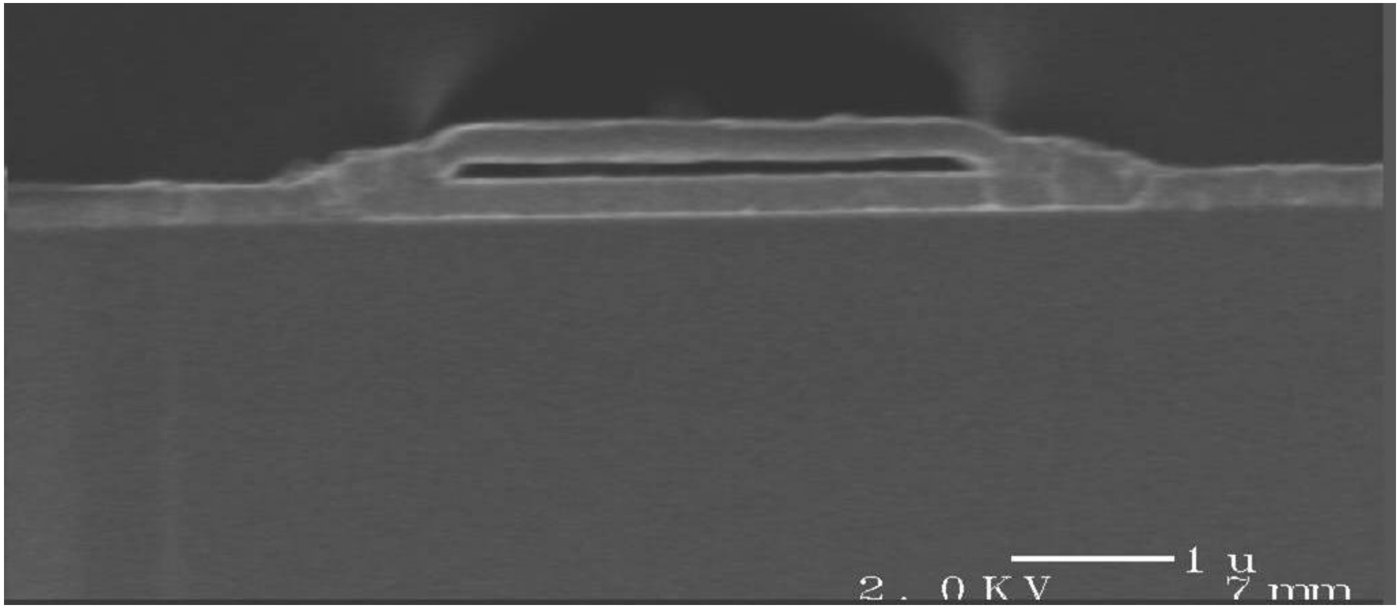


- Rate of Decomposition
- Pressure in Air Gap Cavity
- Diffusivity of Decomposition Products in Overlying Dielectric



Closed Cavity Air Gap

Single-Level Structure



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