Hot Filament Chemical Vapor Deposition of Organosilicon Composite Thin Films for Porous Dielectric Materials

April D. Ross

Department of Chemical Engineering

Massachusetts Institute of Technology

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Outline

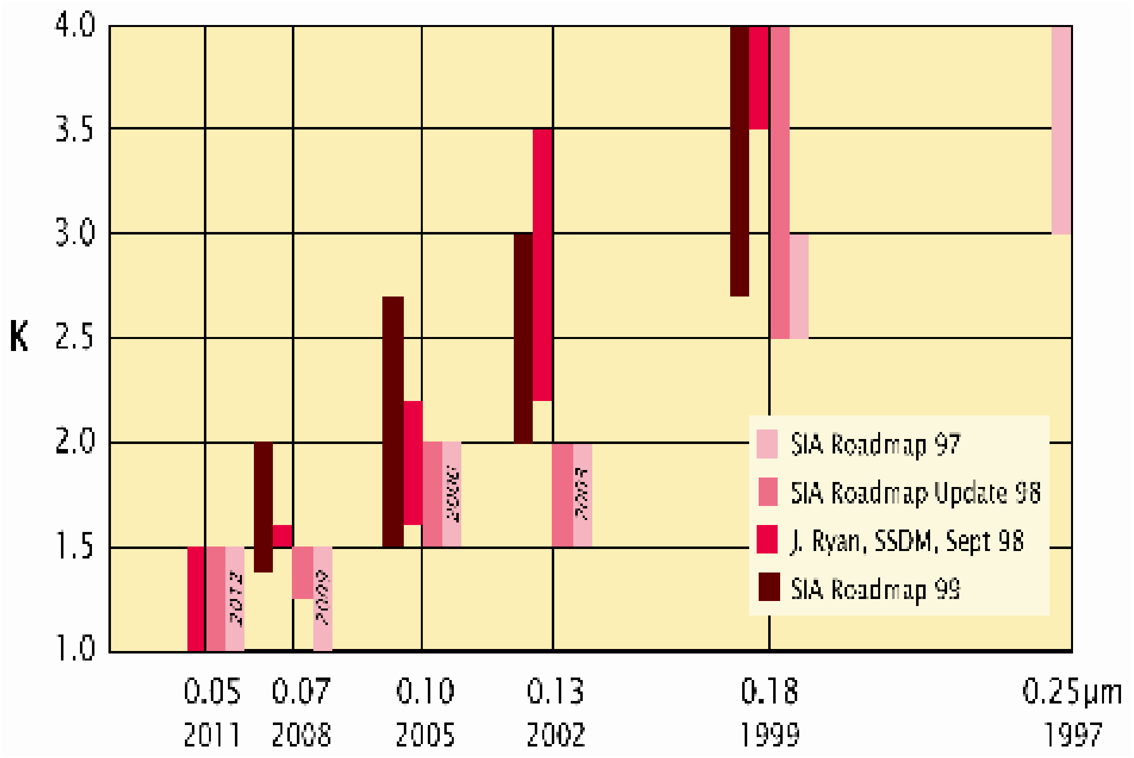
- Goals, Motivation
- CVD vs Spin-On
- Low-k
- Precursor Selection
- Experimental
  - CVD Types
  - Apparatus
  - Characterization Methods
- Preliminary Results
- Proposed Work

Goals

- Create a Porous Film by CVD
  - Rigid Organosilicon Matrix
  - Thermally Labile Porogen
  - Copolymerize by Hot Filament
- Evaluate Possibilities as a Porous Dielectric
  - Dielectric Properties
  - Mechanical Properties
  - Thermal Stability
  - Interface Morphology

Motivation

- Increasing Demand for High Speed Devices
  - Reducing Wire Resistance
  - Reducing Capacitance via the Dielectric Constant, κ



CVD vs Spin-On

- CVD
  - Thin, Conformal Coatings
  - Solventless
  - Ease of Integration
  - Potential for Nanoscale Porosity
  - Mechanical Properties
- Spin-On
  - Extendibility to Future Generations

AURORA™
CVD Process
κ=2.7

CORAL™
CVD Process
κ=2.7

Black Diamond™
CVD Process
κ=2.7

Flowfill™
CVD Process
κ=2.7

FLARE™
Spin-On Process
κ=2.8

SiLK™
Spin-On Process
κ=2.65

Solventless Low κ Dielectrics

A. Manufacturing Metrics (Effect on Performance, Yield, and Cost)

Replacing the silicon dioxide (SiO_2) interlevel dielectric layers in microprocessors with films of lower dielectric constant, κ, increases the speed, reduces the power consumption, and decreases the crosstalk between adjacent metal lines. The lowest dielectric constant leads to the fewest levels of interconnect, resulting in an economic and environmental "win-win". Spin-on process for low κ dielectrics such as SIlk (Dow) have the potential for high waste and solvent-related ESH concerns. Plasma CVD process are another possible candidate for the manufacture of low κ dielectrics.

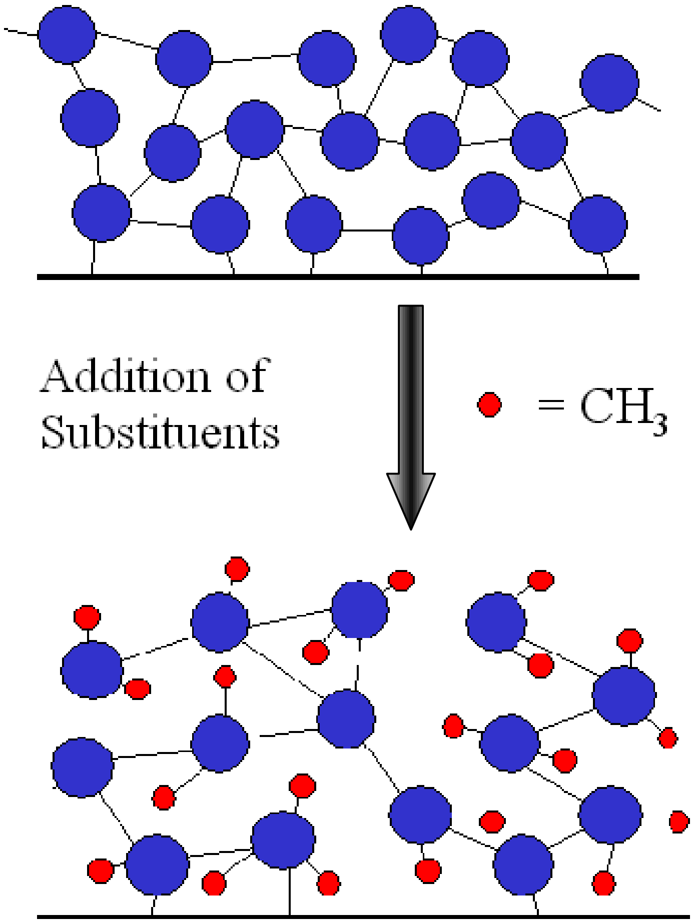
B. ESH Metrics

	Usage Reduction			Emission Reduction			
Goals / Possibilities	Energy	Water	Chemicals	PFCs	VOCs	HAPs	Other Hazardous Wastes
Hot Filament CVD for κ < 2.2	HFCVD uses 5-60% less power than plasma CVD	NA	2.2% utilization for HFCVD >> plasma CVD or spin on	TBD {reduction compared to plasma CVD (fewer chamber cleans may be required)}	Great reduction vs spin-on ~ same as plasma CVD	Some reduction in acid vapors	NA

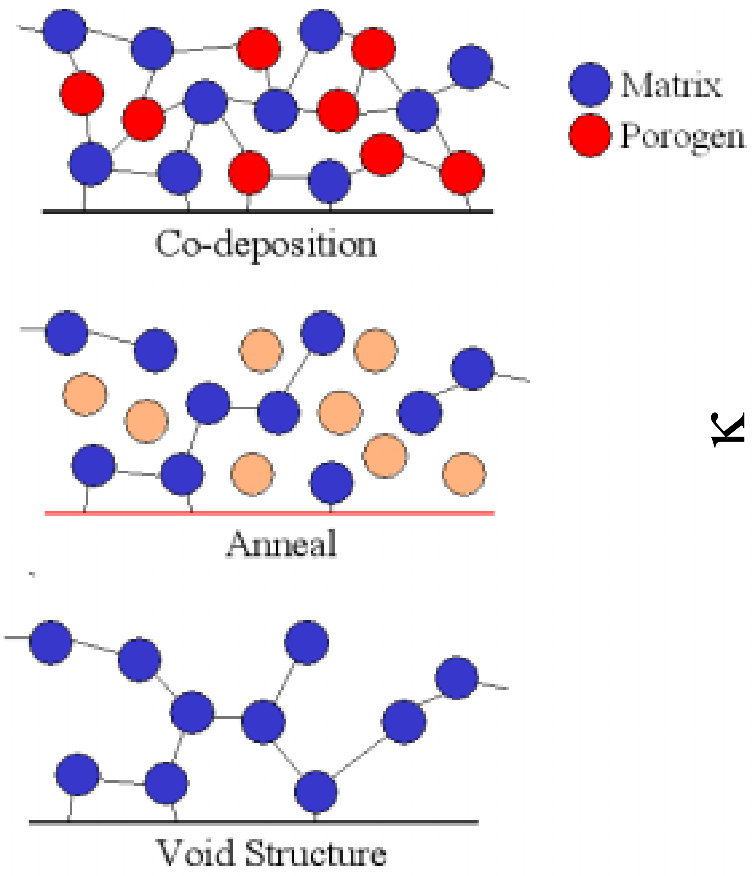
Low-k

- Incorporate Atoms with Lower Polarizability

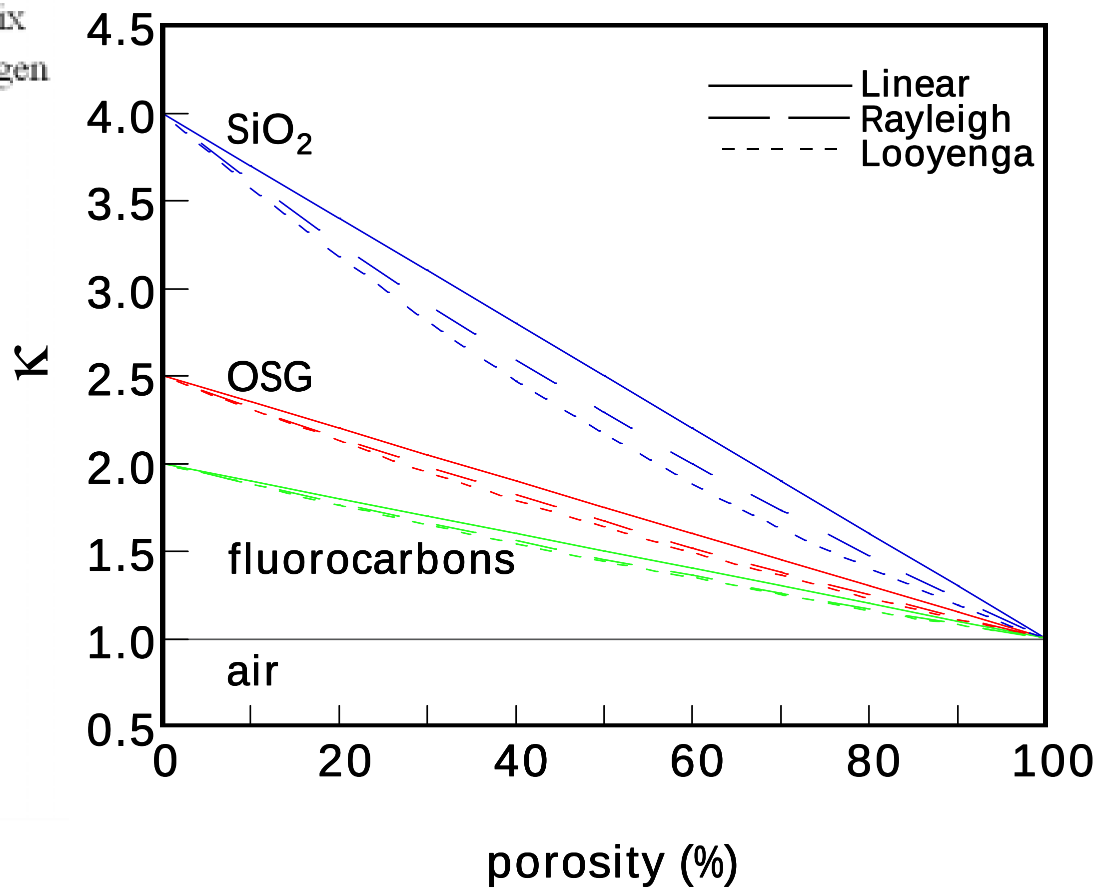
- Decrease Density of Material



Porous Low-k



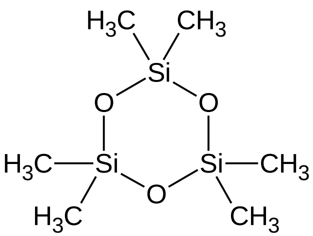
Matrix
Porogen
Co-deposition
Anneal
Void Structure



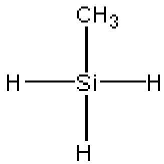
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
κ
0
20
40
60
80
100
porosity (%)
Linear
Rayleigh
Looyenga
SiO2
OSG
fluorocarbons
air

Precursor Selection: Matrix

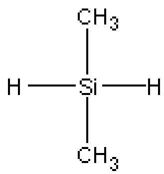
- Mechanical Strength
- Thermal Stability



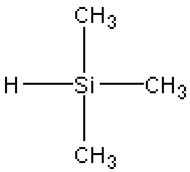
Hexamethylcyclotrisiloxane
(D_3)



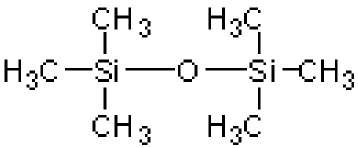
Methylsilane
(1MS)



Dimethylsilane
(2MS)

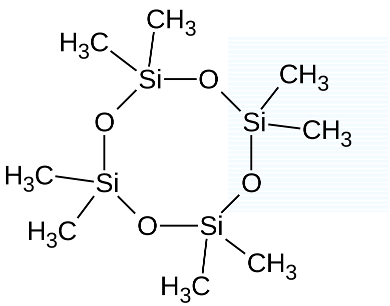


Trimethylsilane
(3MS)



"D" unit

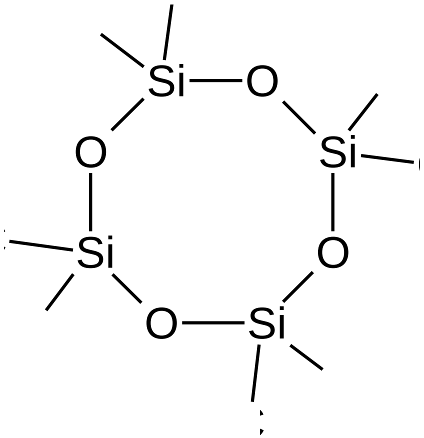
Hexamethyldisiloxane
(HMDSO)



Octamethylcyclotetrasiloxane
(D_4)

The Percolation of Rigidity

"For solids in which all atoms are able to form two or more bonds, the percolation of ridigity occurs at a connectivity number of 2.4*"



D_4 has a connectivity number of 8:

There are two possibly network forming bonds per silicon atom

For a rigid film, replace (on average) 2.4 silicon bonds with connections to other film structures

*S.J. Limb, K.K. Gleason, D.J. Edell, and E.F. Gleason *J. Vac. Sci. Technol. A*. **15**(4), 1814-1818 (1997)

D_4 Toxicology and Immunology

Klykken PC, et al; Dow Corning Corp

"Toxicology and humoral immunity assessment of octamethylcyclotetrasilane (D-4) following a 28-day whole body vapor inhalation exposure in Fischer 344 rats"

Drug and Chemical Toxicology, 22 (4) 655-677 1999

- 28 day study at 0 (room air), 7, 20, 60, 180, and 540 ppm D_4 for 6 hours/day, 5 days/week
- Parameters studied: body and organ weights, gross pathology, histopathology, serum chemistries, urinalysis, and the ability of the D_4 exposed animals to mount an IgM antibody response

RESULTS:

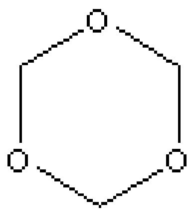
- No adverse effects on body weight, food consumption, or urinalysis
- No exposure related histopathological alterations at any site for any exposure group
- A statistically significant increase in liver weight and liver to body weight ratio was observed in both male (180-540ppm) and female (20-540ppm) rats, which was not observed in the 14-day recovery animals
- No other significant organ weight changes
- No alterations noted in immune system function at any of the D_4 exposure levels

Cost & ESH Data

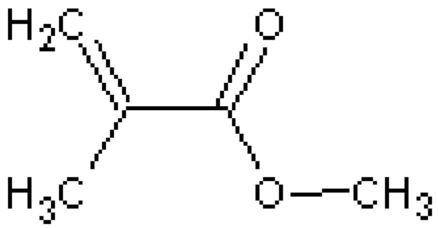
Name	D3	D4	4MS	3MS	2MS	MS
CAS-NO	541-05-9	556-67-2	75-76-3	993-07-7	1111-74-6	992-94-9
MW	222.46	296.62	88.225	74.198	60.171	46.144
Melting Point	64°C	17.4°C	-99°C	-135.9°C	-150°C	-157°C
Boiling Point	134°C	175°C	26.6°C	6.7°C	-20°C	-57°C
Flash Point	35°C	51°C	-27°C	<-20°C	<-40°C	<-40°C
Cost per 100g	$15-30	$4.67	$49	$195	$320	$950
Cost per mol	$32-64	$13.85	$43.23	$144.69	$192.55	$438.37
HMIS Codes						
- Health	1	1	1	2	3	3
- Flammability	3	3	4	4	4	4
- Reactivity	0	0	0	1	1	3

Precursor Selection: Porogen

- Thermally Degrade in the Absence of Oxygen Below 400°C
- Short Decomposition Time
- Leave Negligible Residue

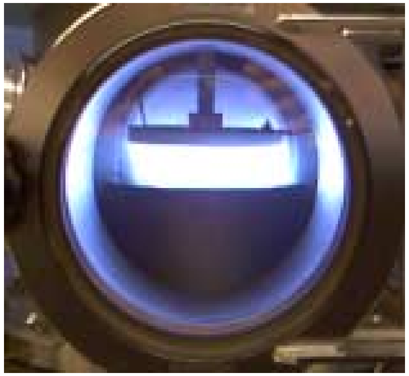


Trioxane



Methyl Methacrylate

Chemical Vapor Deposition

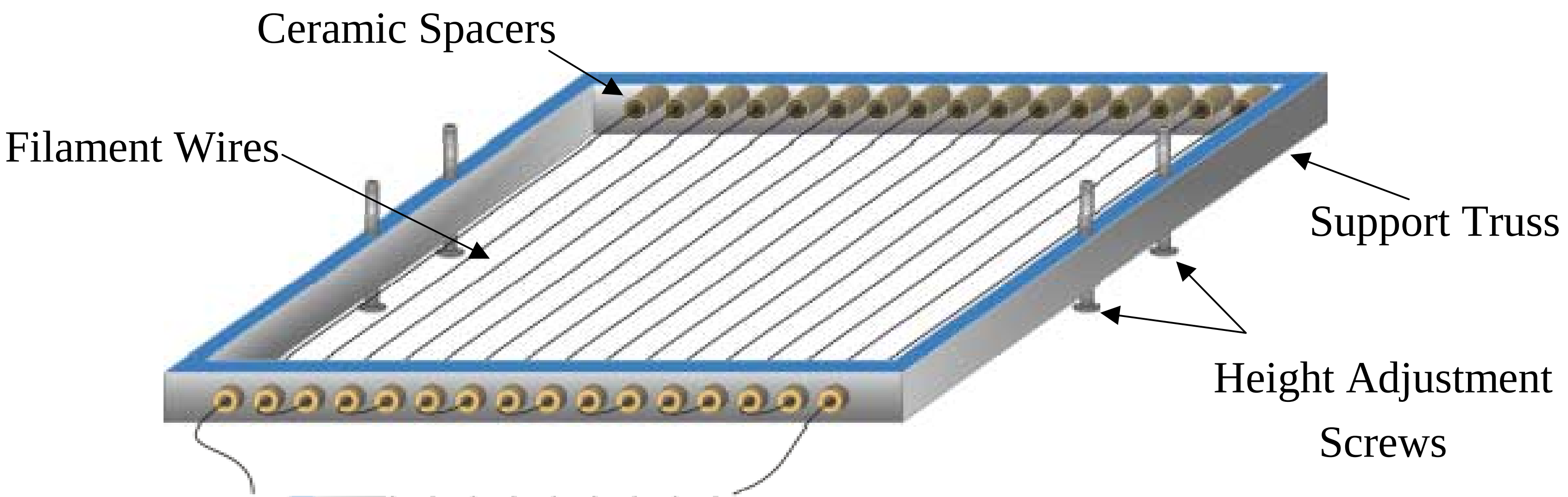


- Plasma Enhanced
  - Decomposes higher variety of chemicals
  - Show aging effects upon exposure to the atmosphere
  - High degree of crosslinking
  - High number of dangling bonds

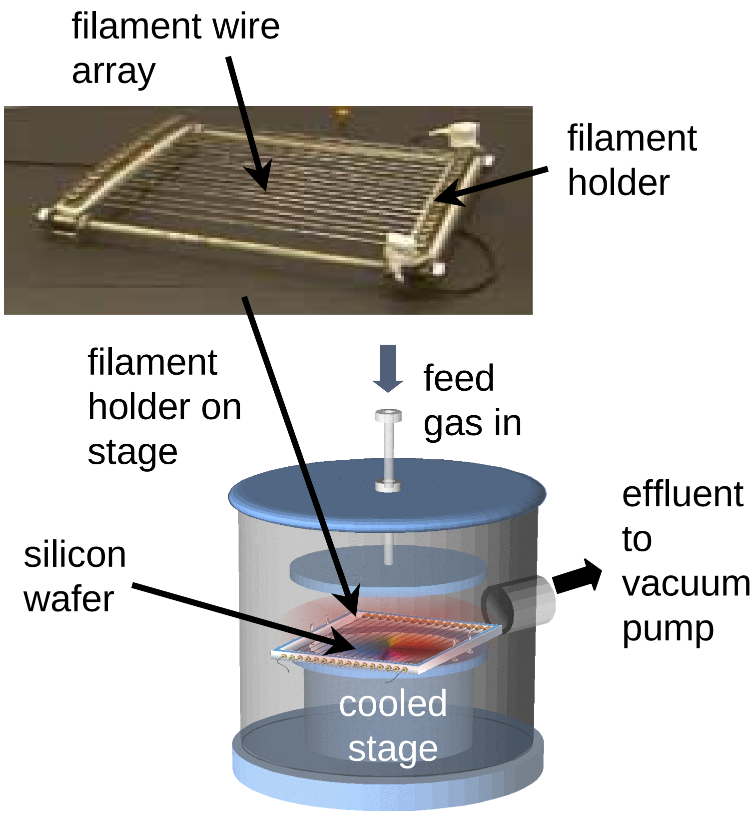
- Hot Filament
  - Greater control of precursor fragmentation & reaction pathways
  - Less crosslinking, dangling bonds
  - Film Hardness

Hot Filament Variables

- Filament Temperature
- Filament Spacing
- Filament Wire
- Diluent Gas Ratio
- Pressure



Apparatus



operating parameters

• pressure	*0.1 - 5.0 Torr*
• filament temp.	*600 - 1200°C*
• substrate temp.	*cooling water*
• precursor flow rate	*5 - 30 sccm*
• filament-wafer spacing	*0.5 - 5.0 cm*
• power	0.1 - 1.5 kW

- Thermal generation of growth precursors at hot filament.
- Substrate cooled to improve adsorption of film-growing species.

Characterization Methods

- Fourier-Transform Infrared Spectroscopy, Raman
  - Qualitative information on functional groups
- X-Ray Photoelectron Spectroscopy
  - Quantitative information on atomic composition and oxidation states
- Solid State Nuclear Magnetic Resonance
  - Quantitative information on atomic structure, bonding environments

- Atomic Force Microscopy
  - Surface topography, roughness
- Electron Microscopy
  - Cross-sectional morphology, defects
- Profilometry
  - Film thickness

- Laser Interferometry
  - In-situ film thickness, real-time growth rates
- Mass Spectrometry
  - In-situ identification of ionic and neutral species in the gas-phase

Characterization Methods

- Spectroscopic Ellipsometry
  - Film thickness, refractive index
  - Porosity
- Mercury Probe
  - Capacitance-voltage measurements for dielectric constant
  - Leakage current
- Interferometry for Thermal Stability
- Nano-indentation for Mechanical Strength

Proposed Work

Deposit Porogens
- Determine Deposition Conditions
- Determine Film Characteristics

Deposit Matrix
- Determine Deposition Conditions
- Determine Film Characteristics

Match Deposition Temperatures

Copolymerize
- Determine Film Characteristics

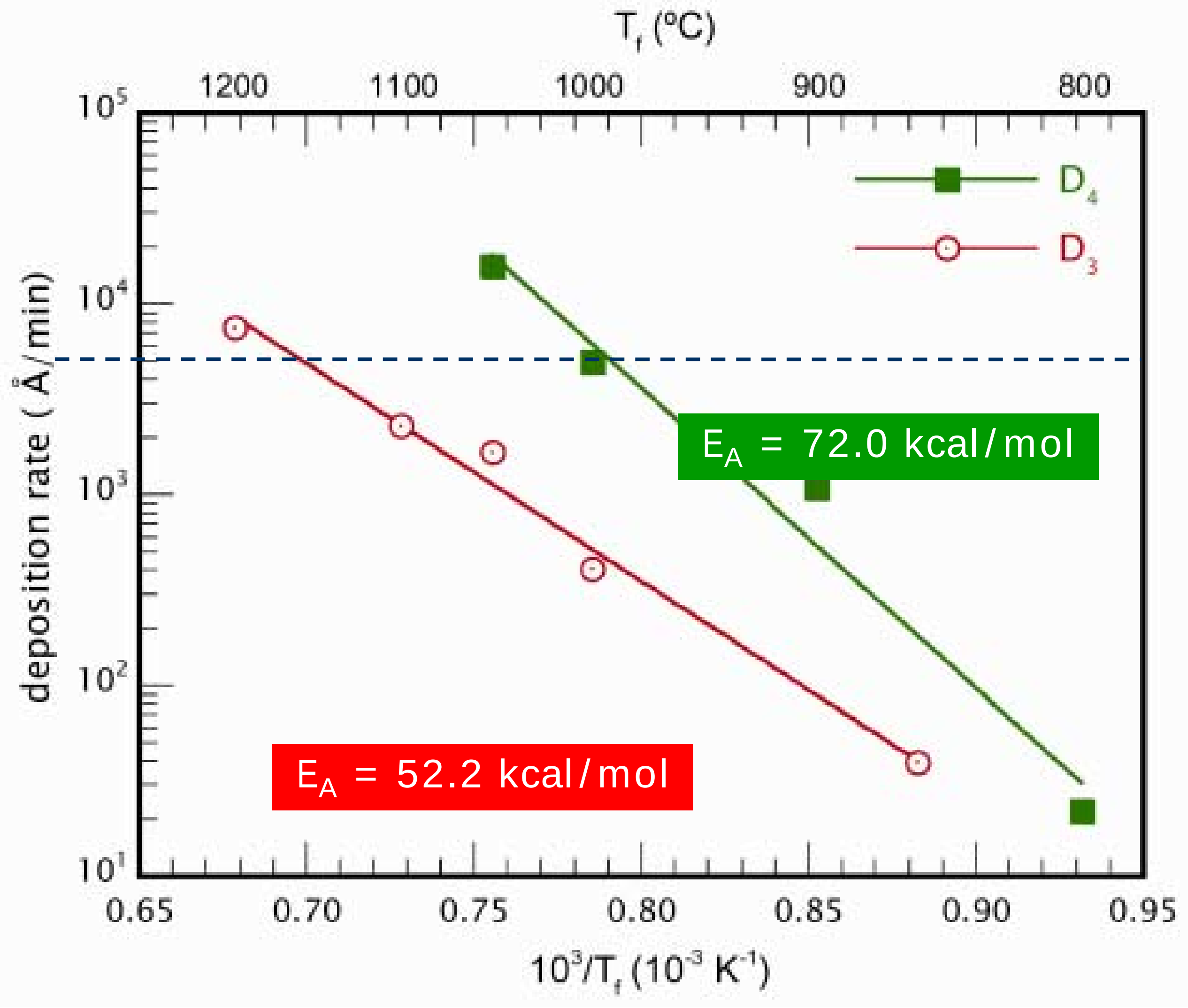
Goals
- Control Degree of Porosity
- Homogeneous, Small Pores
- Correlation of Properties with Porosity

HFCVD Deposition Kinetics

High deposition rates.

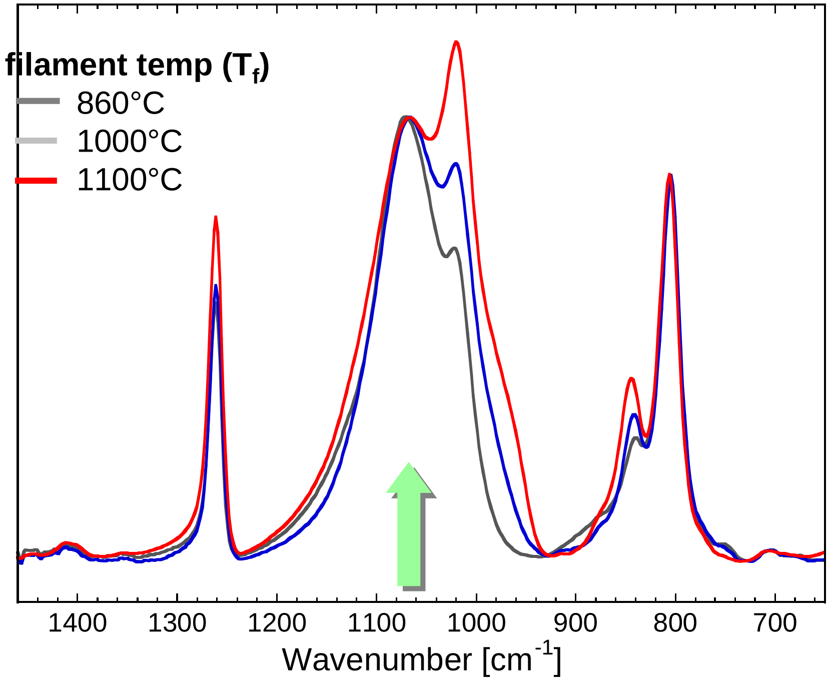
1.0 μm/min

Efficient Energy & Chemical Utilization

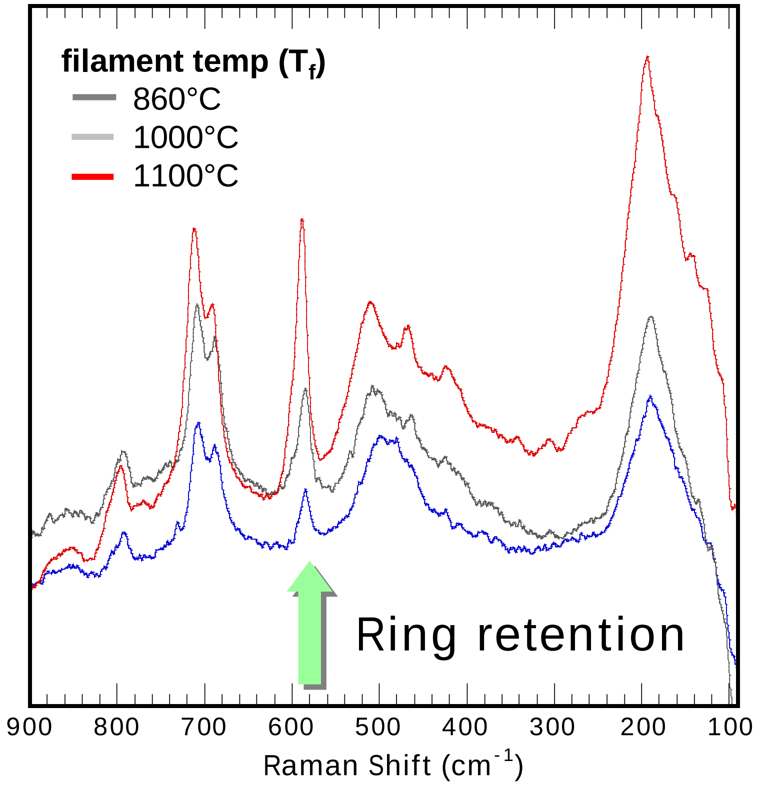


Structure of HFCVD Organosilicon Films from D_3

Fourier Transform Infrared Spectroscopy (FTIR)



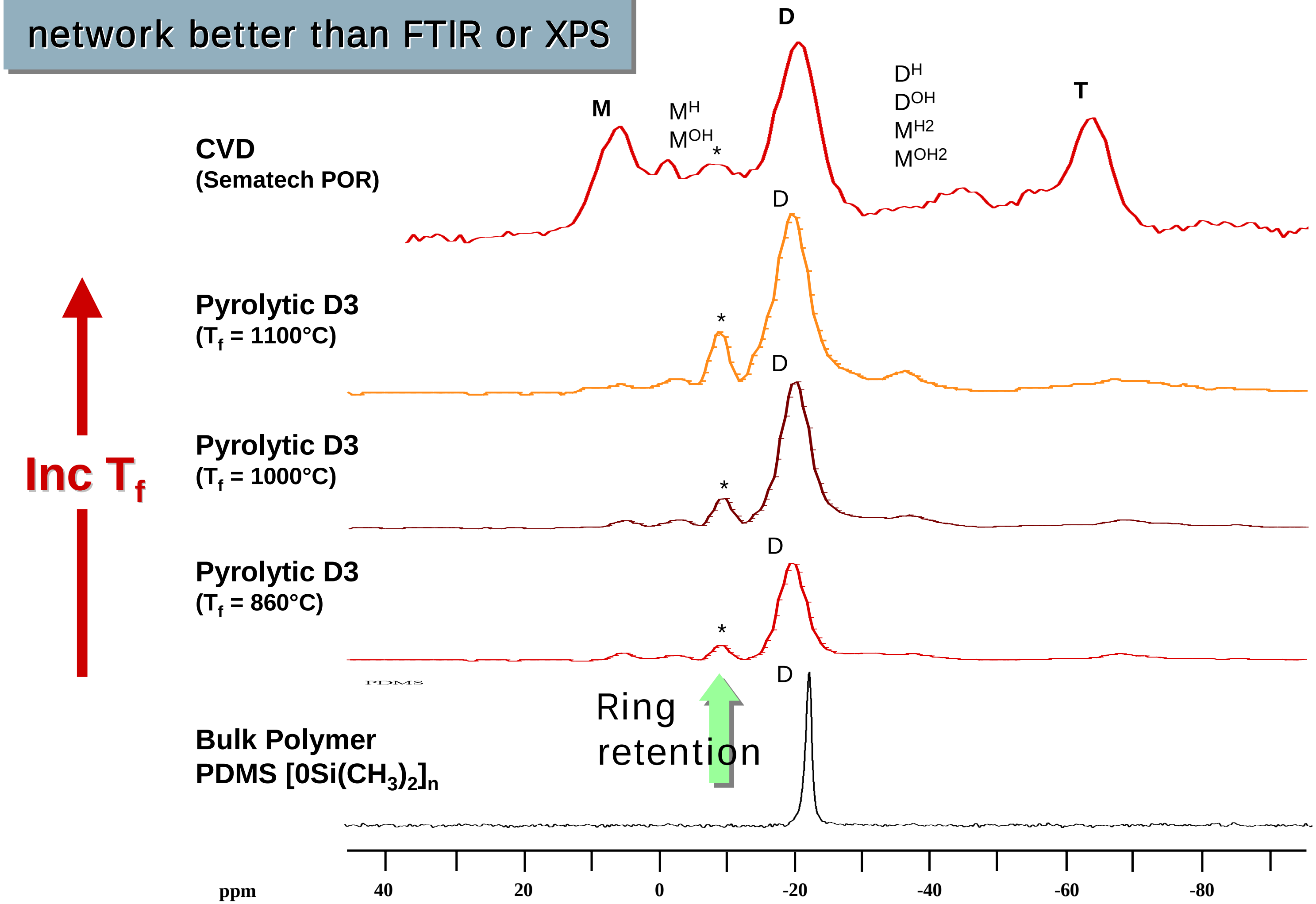
Raman Spectroscopy

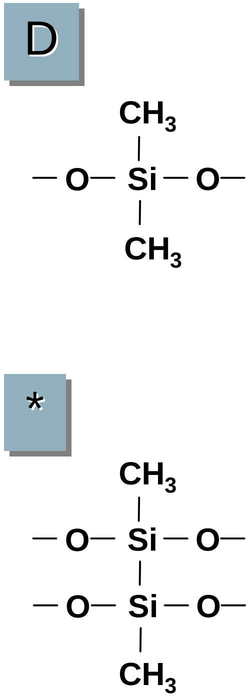


Filament temperature important control parameter

CVD for Control of Film Composition

NMR details variation in film network better than FTIR or XPS

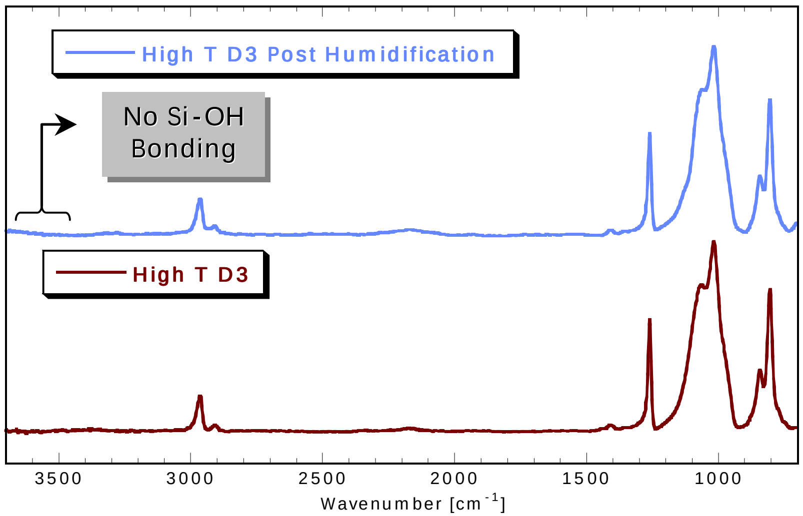


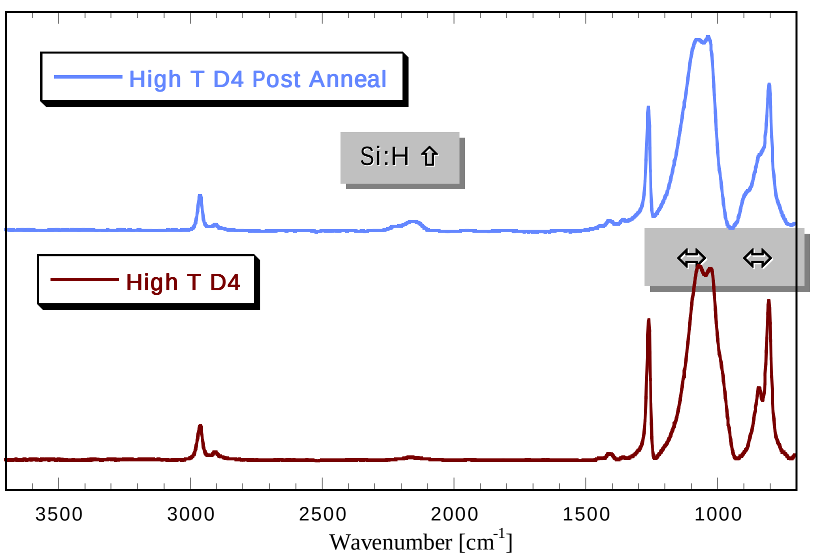


^{29}Si NMR of Organosilicon Films

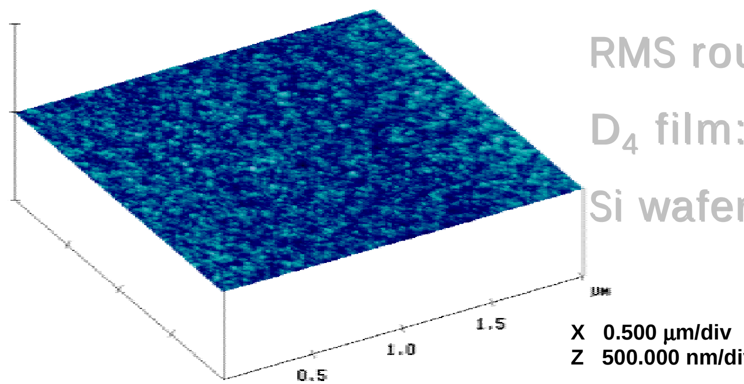
Humidification, Thermal Stability & Roughness Anaylsis

85% RH for 24 hrs: no water uptake





AFM of HFCVD D_4 film @ 900°C



RMS roughness

D_4 film: 1.209 nm

Si wafer: 0.60 nm

Anneal: Ramp to 375°C for 1 hr with rapid cool down

	$T_{filament}$ [°C]	Thickness [Å] Initial	Post Anneal	% Change
D3	860	1401	1378	-2%
	1000	2626	2687	2%
	1100	4811	4530	-6%
D4	800	2238	2035	-9%
	900	5551	5054	-9%
	1000	7801	7380	-5%

The post anneal FTIR shows little change:
- Si-H peak increases
- peaks below 1200 cm^{-1} broaden

Concerns

- Will Structure Collapse?
- Will Porogen Exit Too Fast?
- Will Defects Be Left Behind?
  - Passivation Chemistry

Conclusions

- New HFCVD process developed for depositing thin organosilicon films
  - Low cost, low ESH impact precursors
  - High growth rates (~16,000 Å/min) for efficient energy and chemical utilization
  - Deposition at ambient substrate temperature
  - Film contains long chains and/or large rings of PDMS-like structure
  - Films retain ring structure and differ from plasma CVD film
  - Filament temperature systematically controls film structure
  - Films are thermally stable and resistant to water uptake
- New characterization tools for OSG films
  - ^{29}Si Nuclear Magnetic Resonance (NMR)
  - Raman Spectroscopy

Future Work

- Use porogens to create porosity in OSG HFCVD films with κ<2.2
  - Requires low temperature deposition
  - Requires lack of film densification
  - Requires ~20% porosity
- Collaborate with Rafael Reif's group on etching and ESH for OSG
- Collaborate with Thrust D to determine 157nm photosensitivity for OSG

Acknowledgements

- The Gleason Group
- The Sawin Lab
- Center for Materials Research and Engineering
- My Thesis Committee