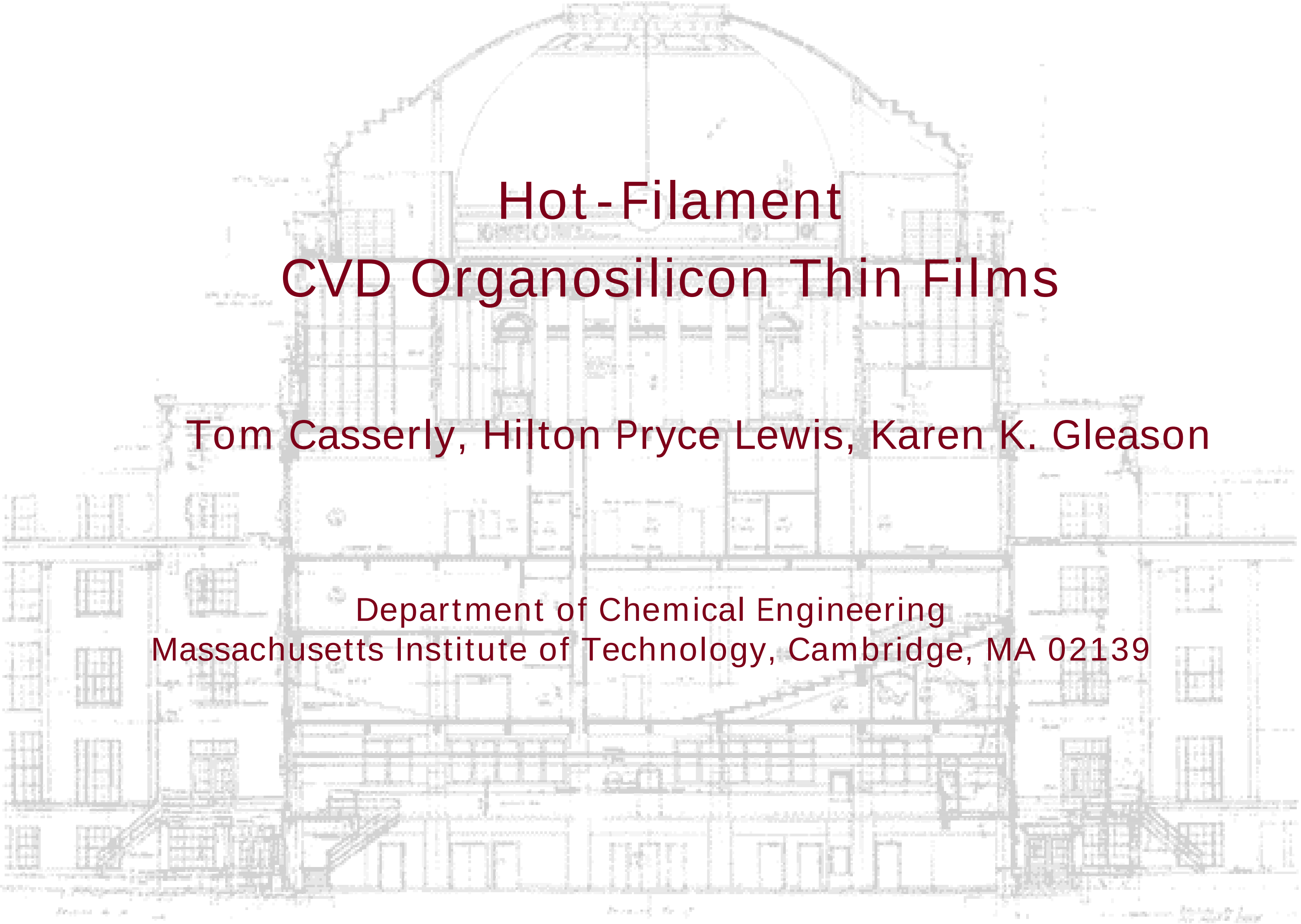

Hot-Filament
CVD Organosilicon Thin Films

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Motivation

- Current interlayer dielectrics reaching limits of practical use
    - SiO_2 has dielectric constant of 4.0-4.3
    - Capacitance is a function of dielectric constant: $C=\kappa A/d$
    - Capacitance effects RC time constant
- Alternative dielectrics: organosiloxane CVD thin films
    - Wide range of dielectric properties: k = 2.7~3.9
    - Good compatibility with silicon substrates
    - Ease of integration with current processing technique (evolutionary process)
    - Precursors readily available and generally non-toxic
    - Other names-organosilicate glasses (OSG), carbon-doped oxides, Si:O:C:H
- Porous CVD?
    - Void structure can lower dielectric constant < 2.7
    - Voids must be smaller than feature sizes (sub=100 nm)
    - Mechanical/Thermal issues are a concern

Commercial CVD OSG: $\kappa \sim 2.7$

MIT

Black Diamond™
PECVD Process

APPLIED MATERIALS®

CORAL™
PECVD Process

NOVELLUS

AURORA™
PECVD Process

ASM

FLOWFILL™
CVD Process

Trikon
TECHNOLOGIES

Low-κ Roadmap Updates

from Semiconductor International, June 2000

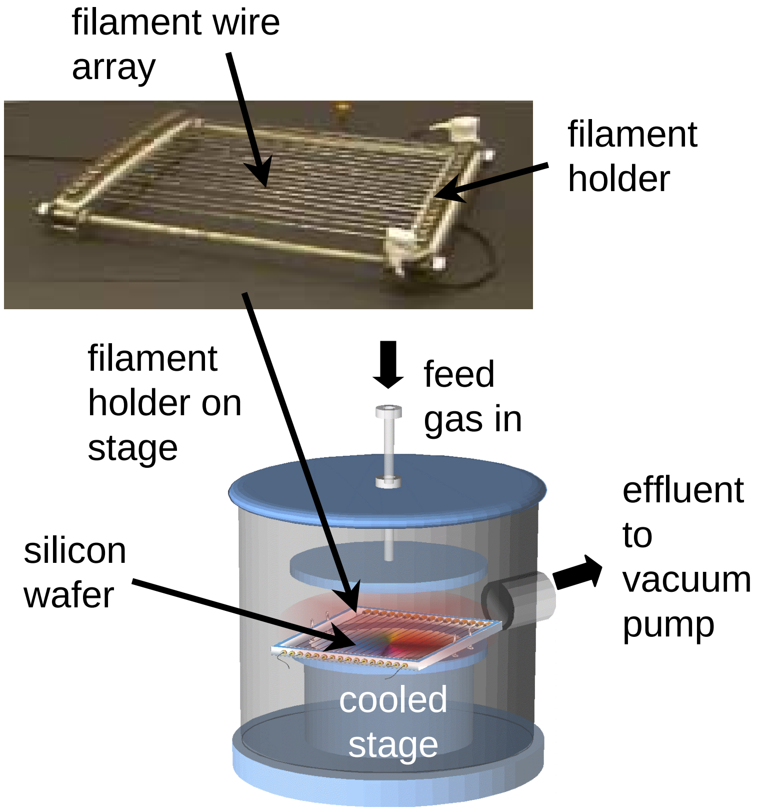
SIA Roadmap								
1997								
Year of first product	1997	1999	2001	2003	2006	2009	2012	
Shipment technology node	250 nm	180 nm	150 nm	130 nm	100 nm	70 nm	50 nm	
Interlevel metal insulator effective κ	3.0-4.1	2.5-3.0	2.0-2.5	1.5-2.0	1.5-2.0	<1.5	<1.5	
1999								
Year of first product		1999	2001	2002	2005	2008	2011	
Shipment technology node		180 nm	150 nm	130 nm	100 nm	70 nm	50 nm	
Interlevel metal insulator effective κ		3.5-4.0	2.7-3.5	2.7-3.5	1.6-2.2	<1.5	<1.5	
2000?								
Year of first product			2001	2003	2005	2007	2009	2011
Shipment technology node			180 nm	150 nm	130 nm	100 nm	70 nm	50 nm
Interlevel metal insulator effective κ			3.5-4.0	2.7-3.5	2.7-3.5	2.2-2.7	2.2-2.7	1.6-2.2

The effective dielectric constant required at each device generation was pushed out from 1997 to 1999. The 2000 edition could extend the use of k=2.4-3.3 (k_{eff} =2.7-3.5) materials due to integration challenges.

- **Next Process Node: 150nm $\xrightarrow{2003}$ κ = 2.7-3.5**

  Must move to porous films to achieve lower κ values

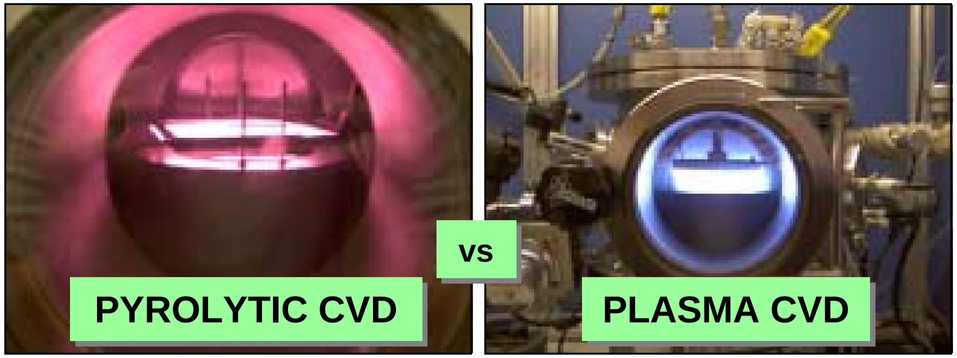
Hot-Filament Chemical Vapor Deposition



operating parameters

pressure	*0.1 - 5.0 Torr*
filament temp.	*500 - 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.
- More homogeneous, less crosslinked structure than plasma CVD.
    - no ion or electron bombardment
    - no UV irradiation
    - limited reaction pathways



Precursor selection

Cyclic Siloxanes

- Benefits:
  - Built in structure - no need for a both a Si and O precursor
  - potential for higher carbon incorporation
  - potential for free volume
  - low cost
  - minimal environmental impact
  - minimal health and safety risks**
  - Organosiloxanes are generally non-reactive and stable at ambient conditions
  - Good Adhesion to Si

- Possible Drawbacks
  - Liquid and solid precursors with moderate to poor vapor pressures requiring continuous heating to volatlize: Solution - donated MKS 1153 - Low Vapor Pressure Mass Flow Controller
  - Potentially Flammable: Store in fireproof locker
  - Potential Irritant: Proper gloves/eyewear at all times

D4 Toxicology and Immunology Study

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 D4 for 6 hours/day, 5 days/week
- Parameters studied: body and organ weights, gross pathology, histopathology, serum chemistries, urinalysis, and the ability of the D4 exposed animals to mount an IgM antibody response

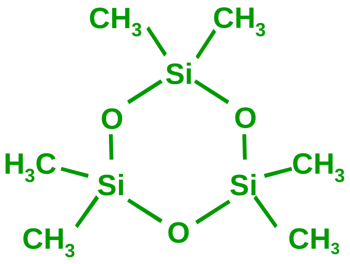
RESULTS:

- 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 D4 exposure levels

CVD Organosilicon Films

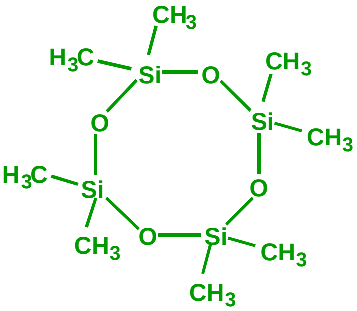
- Use cyclic precursors
  - ring strain => more reactive
  - higher vapor pressures

D_3



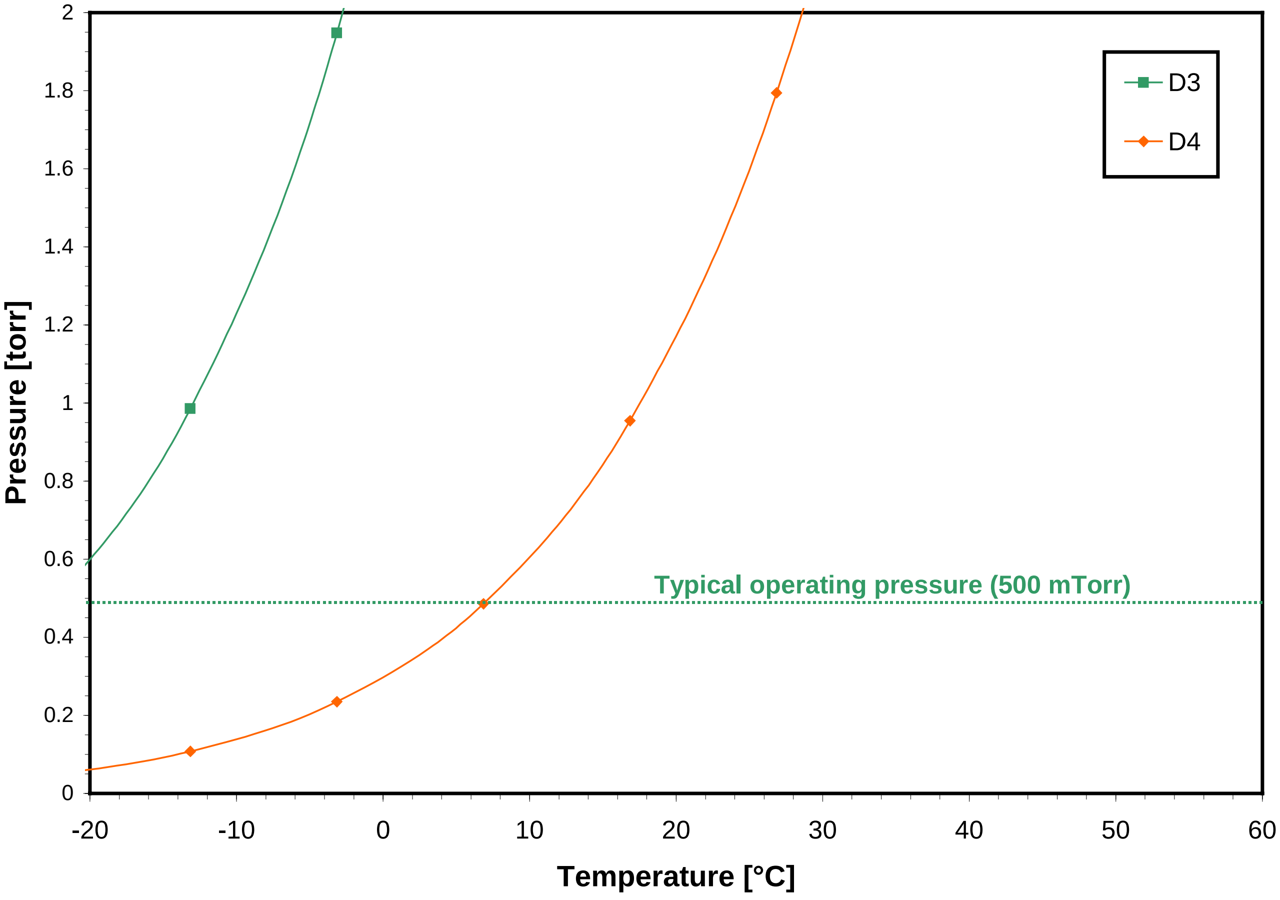
ring strain = 2.5 kcal/mol

D_4



ring strain = 0.24 kcal/mol

Silicone Vapour Pressure Curves for Operation



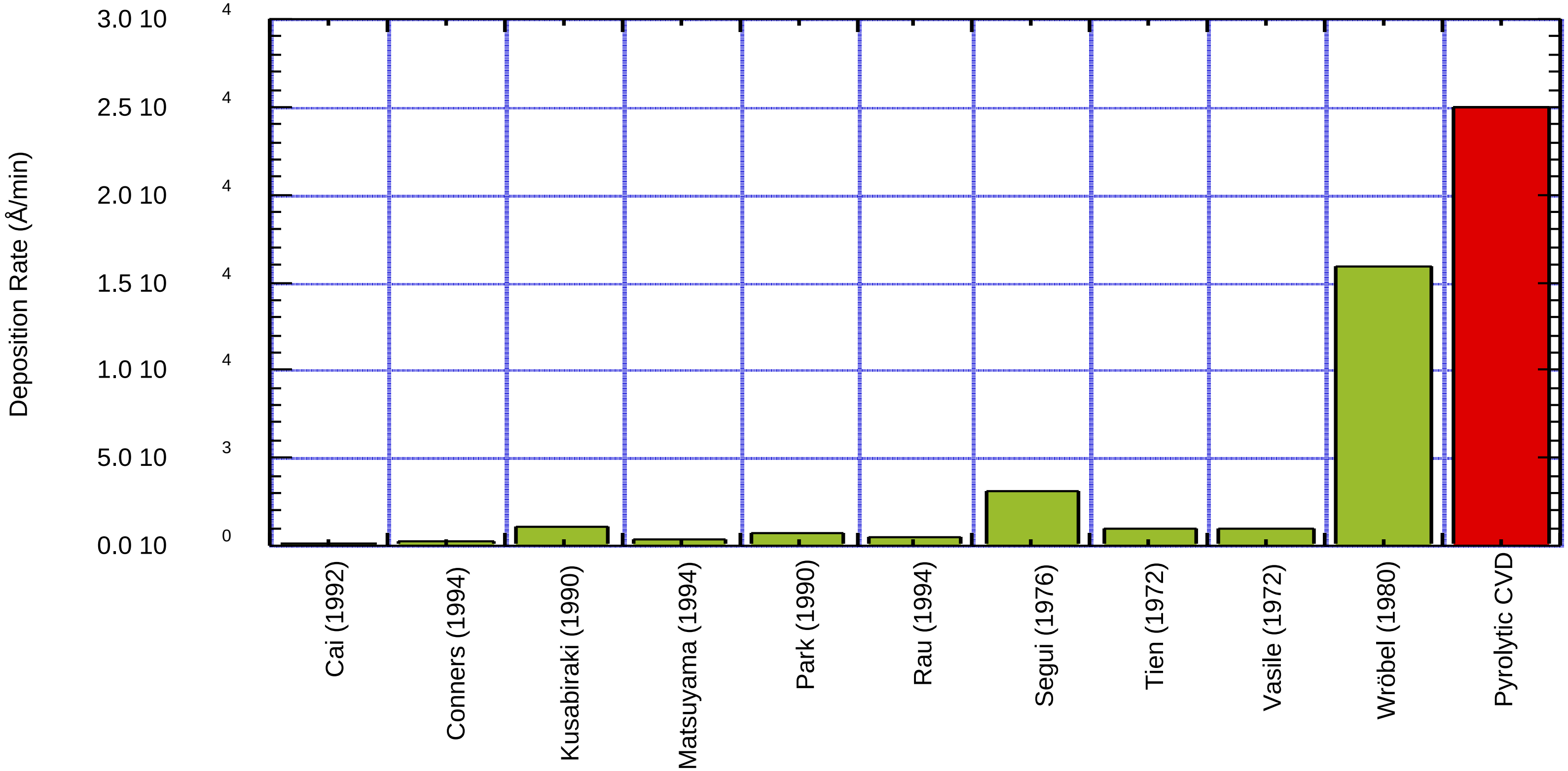
$$d\ln\frac{P}{P_0} = \frac{\Delta_{vap}H}{RT^2}dT$$

Cost & ESH of D3 & D4 vs 4MS, 3MS, 2MS & 1MS

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
Autoignition Temp	n/a	400°C	450°C	310°C	230°C	130°C

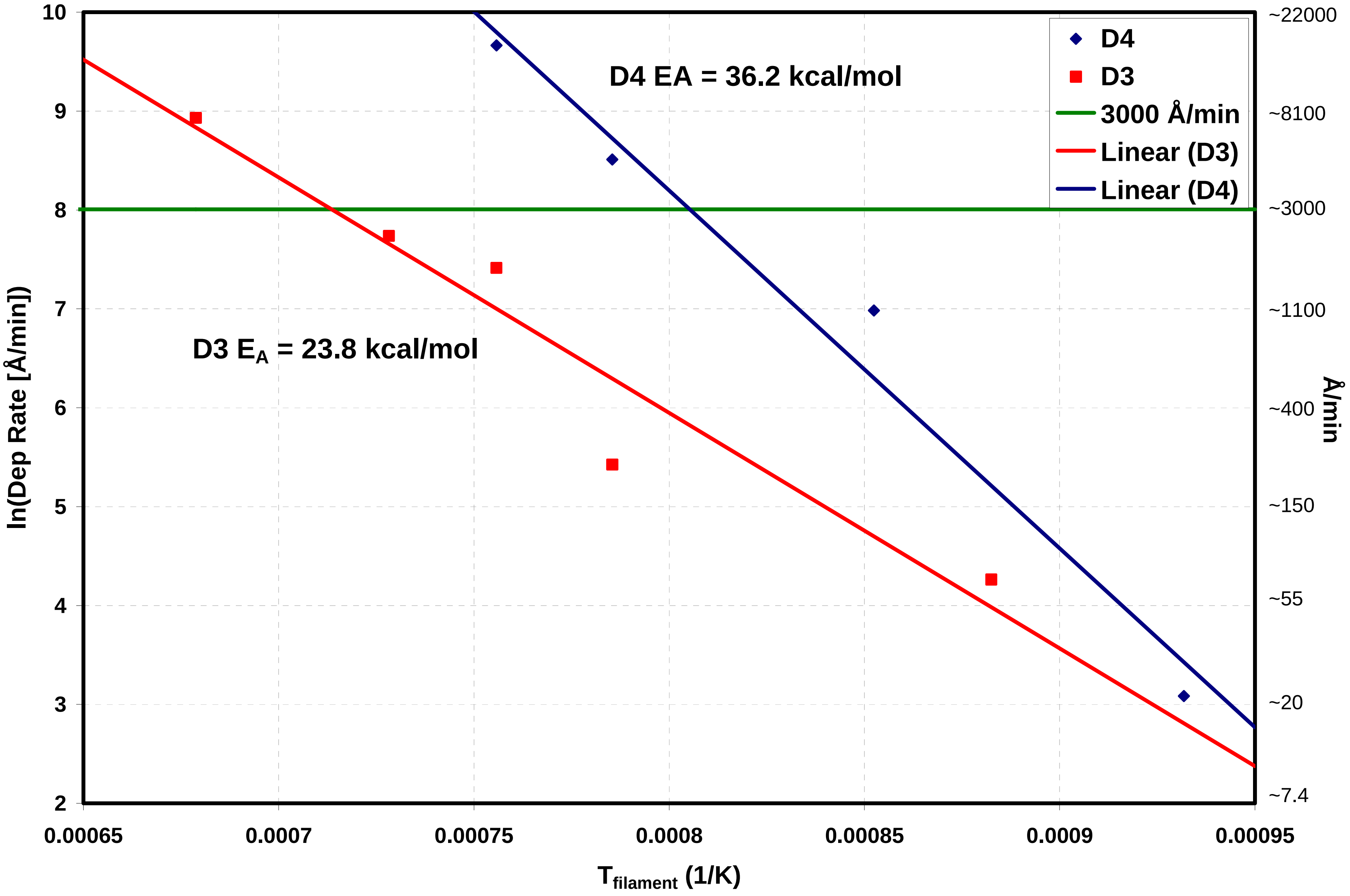
Comparison of Growth Rates

- Compare with growth rates of hexamethyl-disiloxane (HMDS) PECVD films:

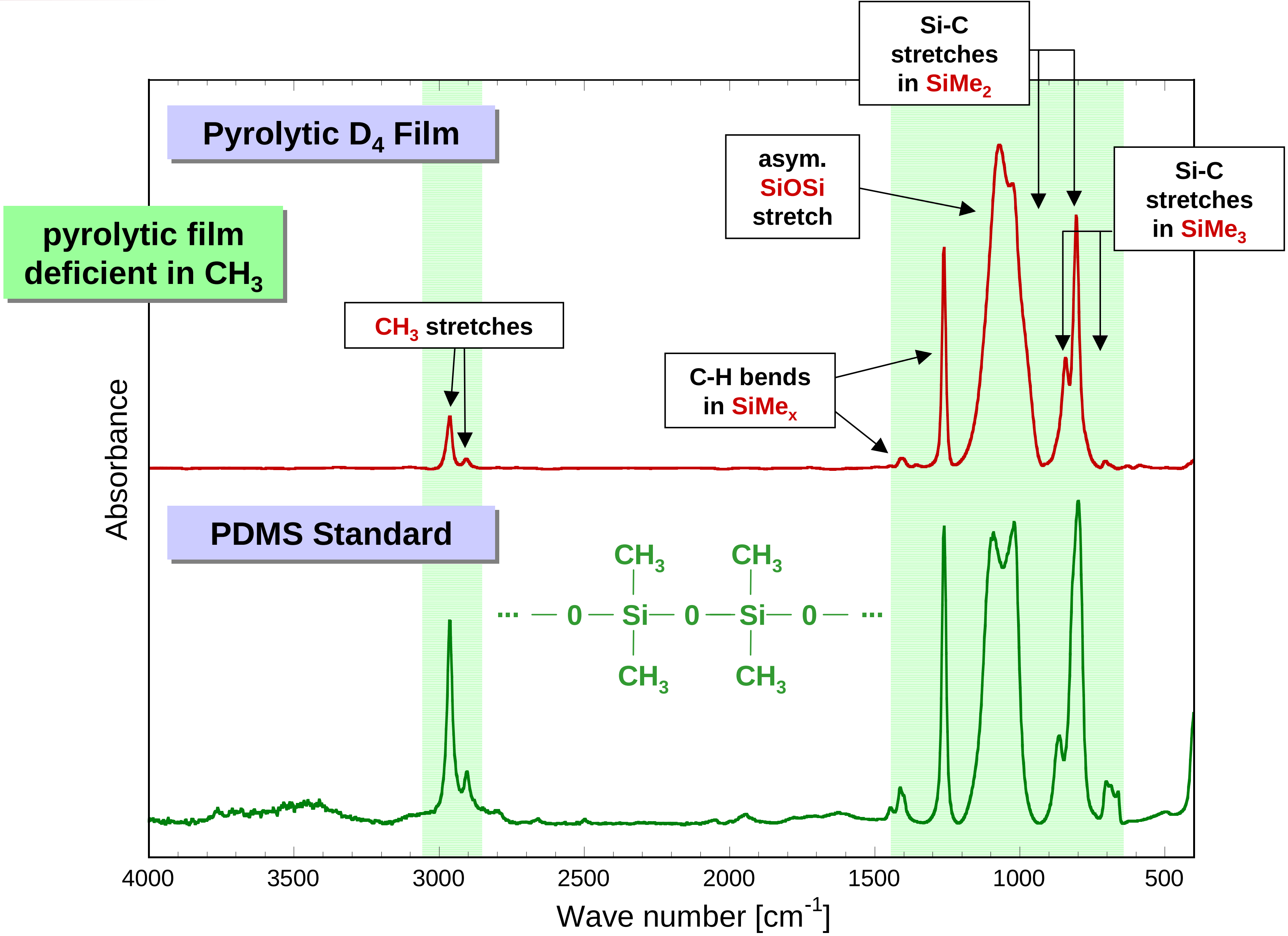


- Max pyrolytic/HFCVD rate: *2.5x10^{4} Å/min*
- Max PECVD rate for HMDS: *1.6x10^{4} Å/min*
  (microwave discharge)

Arrhenius Plot of Growth Rate



Structure of Pyrolytic Organosilicon Films



Pyrolytic D_4 Film

pyrolytic film deficient in CH_3

PDMS Standard

CH_3 stretches

C-H bends in $SiMe_x$

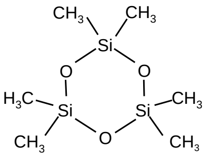
asym. SiOSi stretch

Si-C stretches in $SiMe_2$

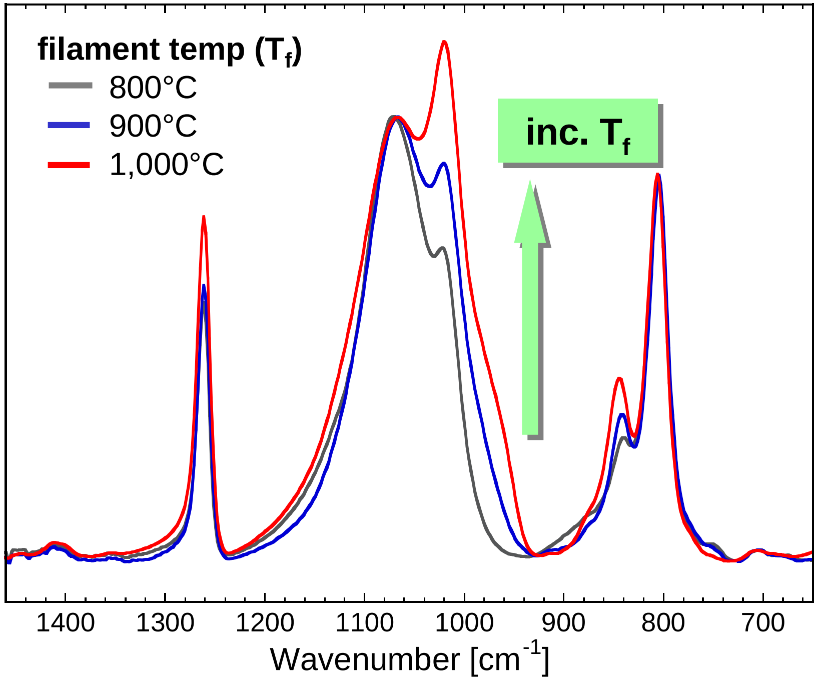
Si-C stretches in $SiMe_3$

Structural Control of Pyrolytic Films

D$_3$

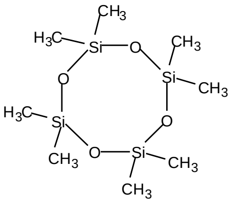


ring strain = 2.5 kcal/mol

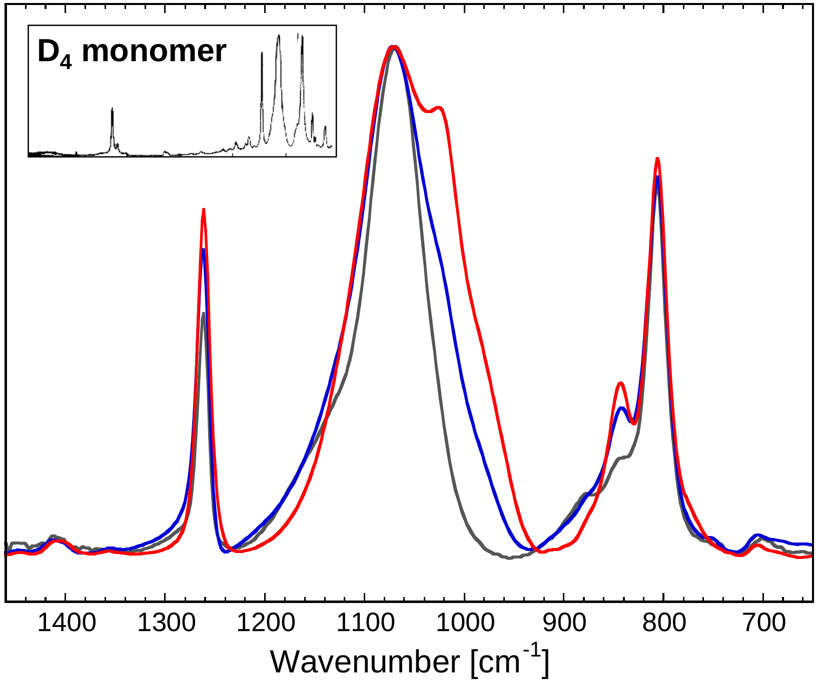


T$_f$ important control parameter

D$_4$

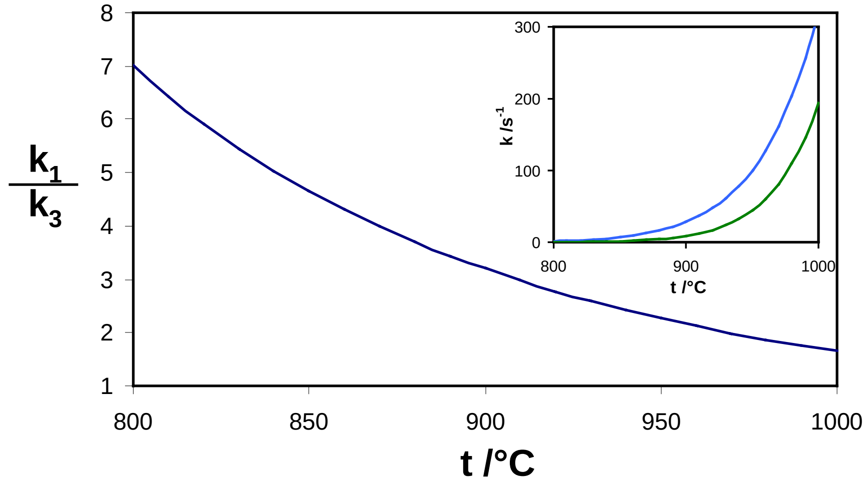


ring strain = 0.24 kcal/mol



D$_4$ film retains monomeric structure at low T$_f$

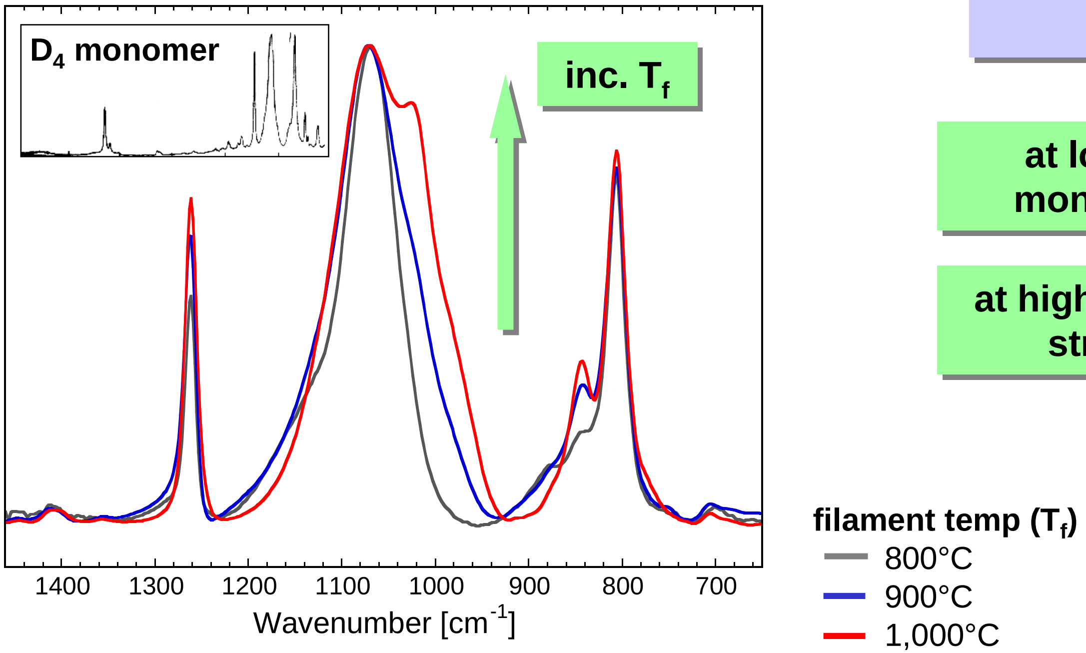
Chemistry of Organosilicon Films



kinetics

reaction 1	$D_4 \overset{k_1}{\longleftrightarrow}$	D_3 +	D_1
reaction 3	$D_3 \xrightarrow{k_3}$	Me• +	$Me_5O_3Si_3$•

FTIR spectra of pyrolytic film from D_4



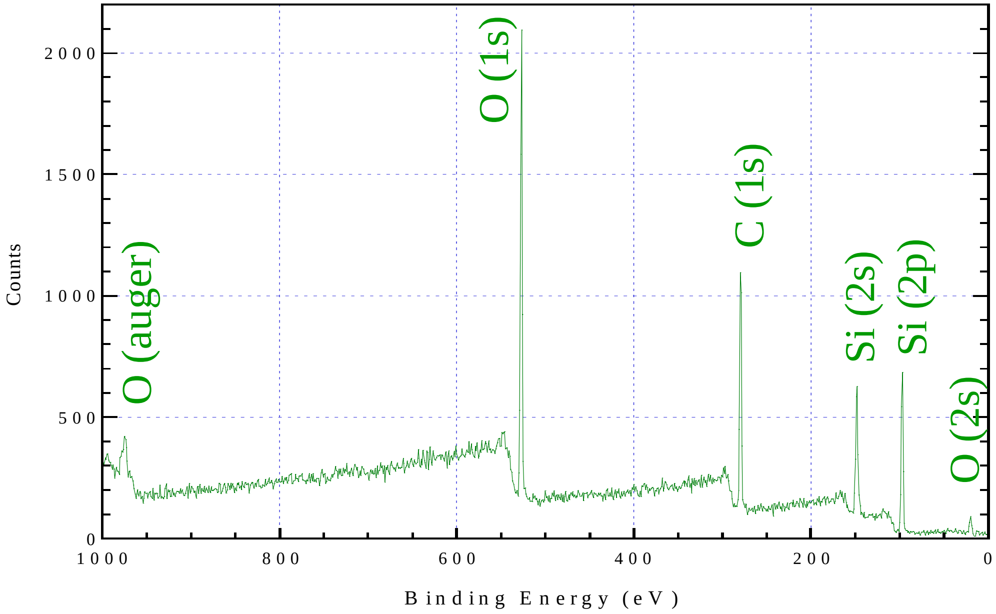
film structure

at lower T_f, film retains monomeric D_4 structure

at high T_f, film approximates structure of D_3 films

X-Ray Photoelectron Spectroscopy (XPS)

- Survey scan of pyrolytic D4 film shows only C, O & Si



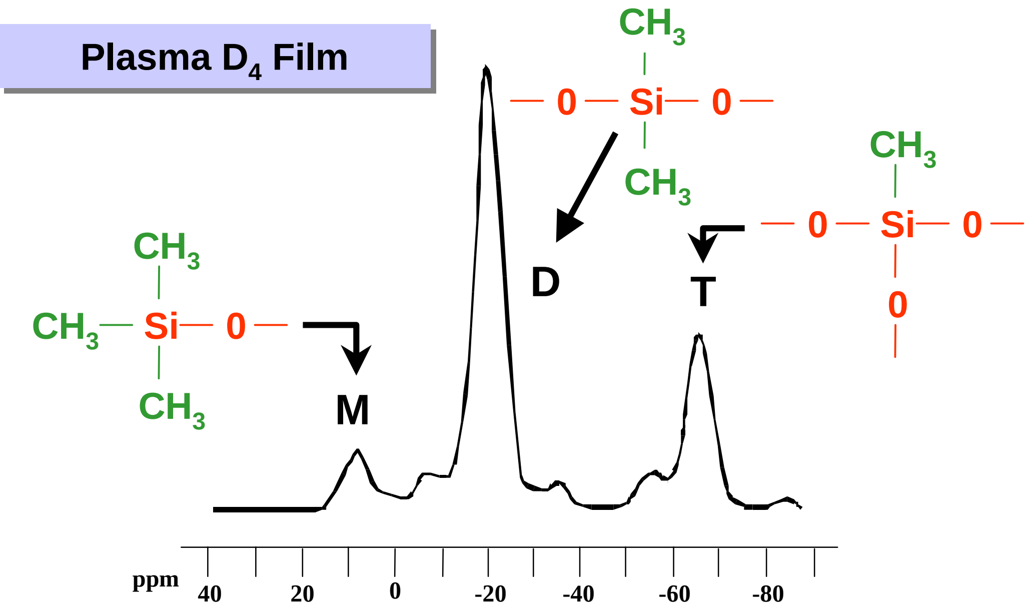
- Elemental analysis indicates loss of methyl groups
  - Corresponds to loss of 1.8 $-CH_3$ groups per D_4 molecule

Film	**O:Si**	**C:Si**
PDMS secondary standard	1	2
Average of four pyrolytic films	1.03 ± 0.02	1.54 ± 0.08

  - High-resolution Si (2p) spectra cannot differentiate oxidation states other than Si^{2+}

NMR: Plasma vs. Pyrolytic Organosilicon Films

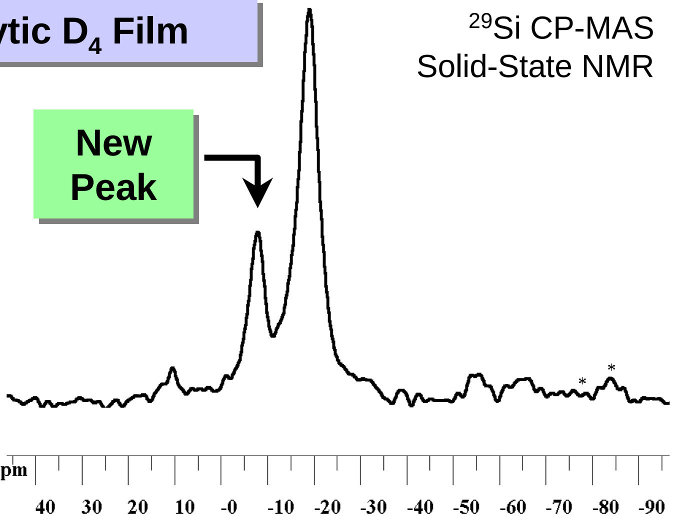
Plasma D_4 Film



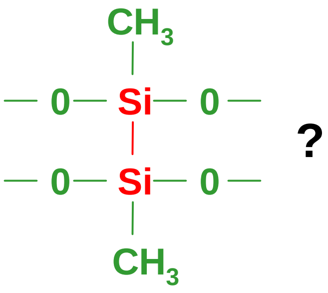
Adapted from Tajima and Yamamoto,
J. Polym. Sci., Pt. A Polym. Chem.,**25**, 1737 (1987)

Pyrolytic D_4 Film

^{29}Si CP-MAS
Solid-State NMR



- New peak observed

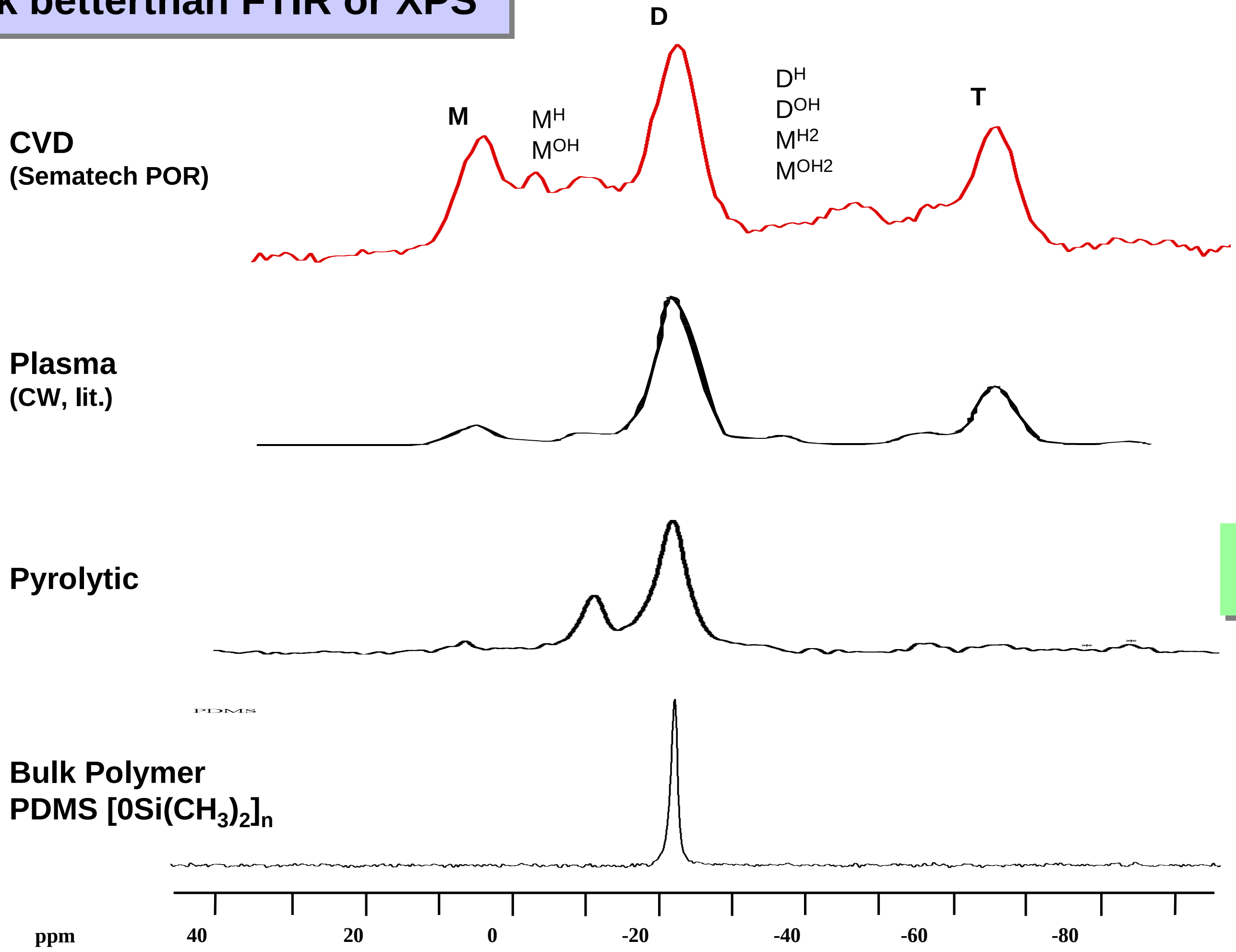


- Consistent with
  - Crosslinking suggested by film hardness and insolubility in organic solvents
  - methyl loss in FTIR and XPS
  - existence of only Si(II) in XPS
  - C:Si ratio of ~1.6 consistent with XPS and NMR; O:Si ratio of 1.0

pyrolytic films different from plasma films

CVD for Control of Film Composition

NMR details variation in film network betterthan FTIR or XPS



more C

lower κ

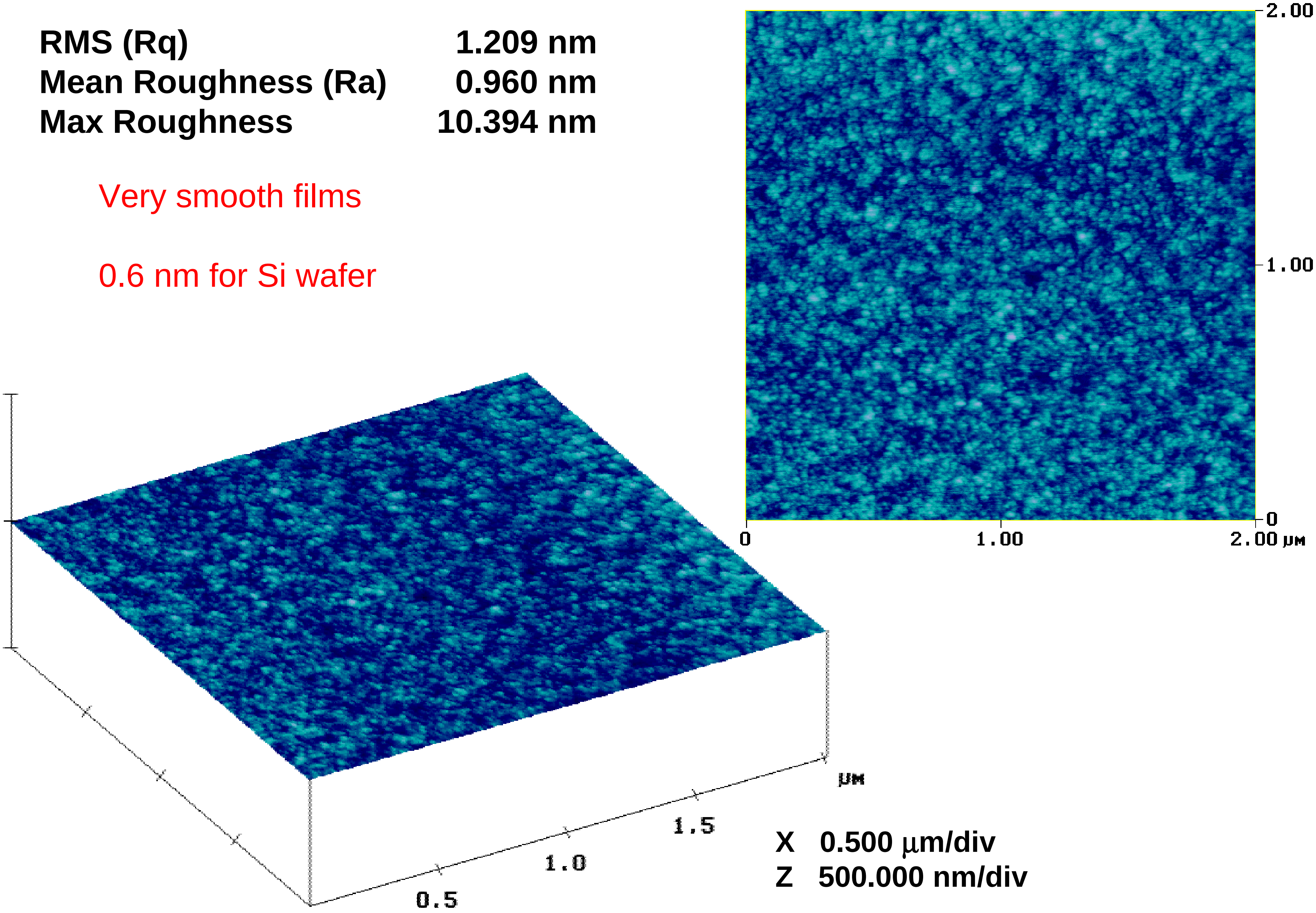
^{29}Si NMR of Organosilicon Films

AFM of HFCVD SiOCH Film from D4 @ 900°C

RMS (Rq)	**1.209 nm**
Mean Roughness (Ra)	**0.960 nm**
Max Roughness	**10.394 nm**

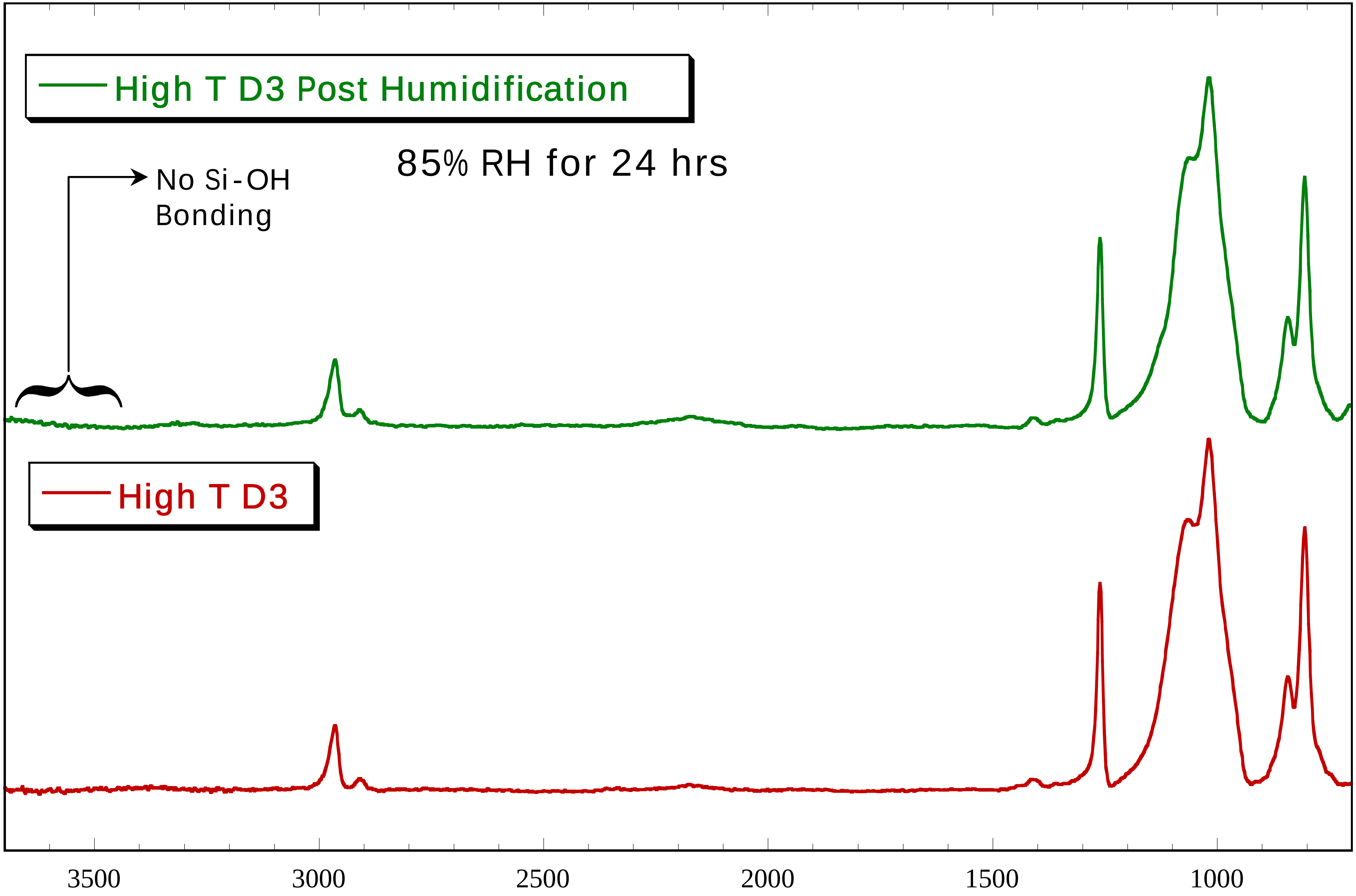
Very smooth films

0.6 nm for Si wafer



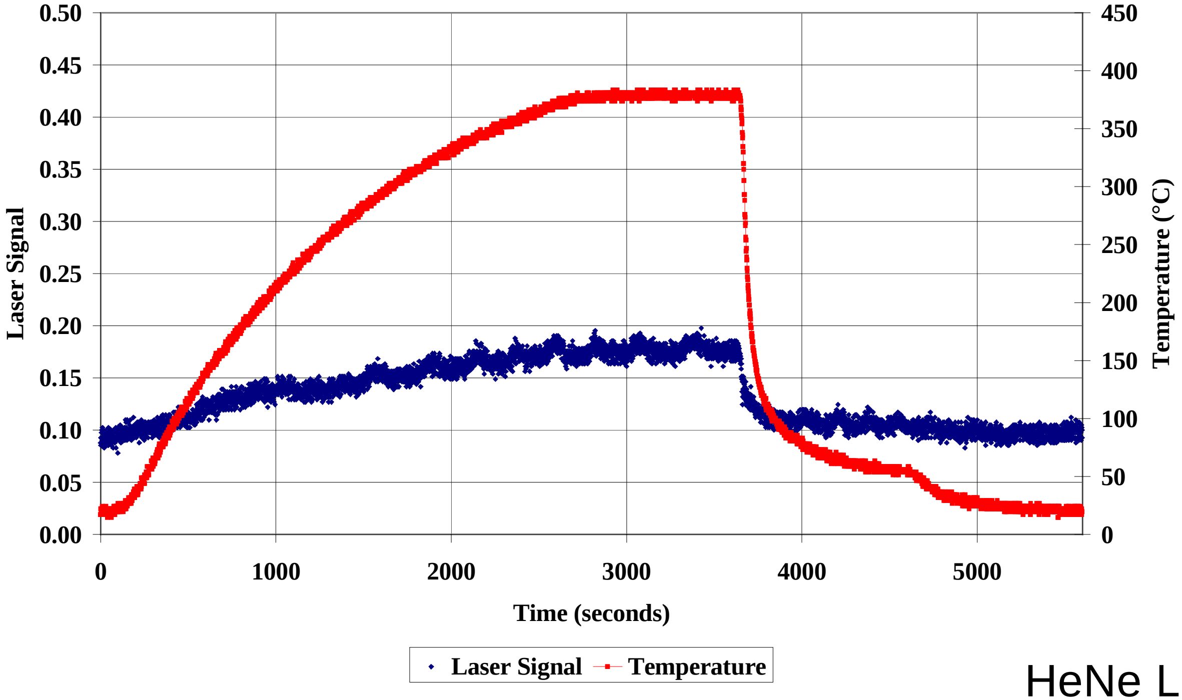
X 0.500 μm/div
Z 500.000 nm/div

FTIR Pre- and Post-Humidification



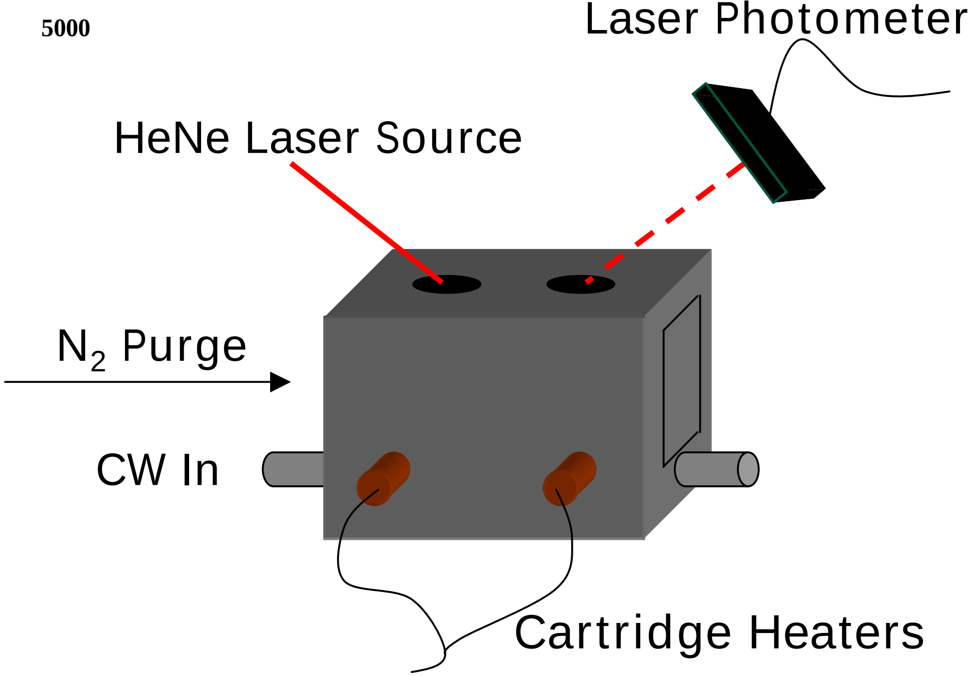
Thanks to INTEL for donating the Relative Humidity Chamber

Thermal Stability



- Ramp to 375°C for 1 hr
- Rapid Cooldown
- Thermal Cycling

	$T_{filament}$ [°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%



Laser Photometer

HeNe Laser Source

N_2 Purge

CW In

Cartridge Heaters

I.T.S. – Interferometry for Thermal Stability

Conclusions

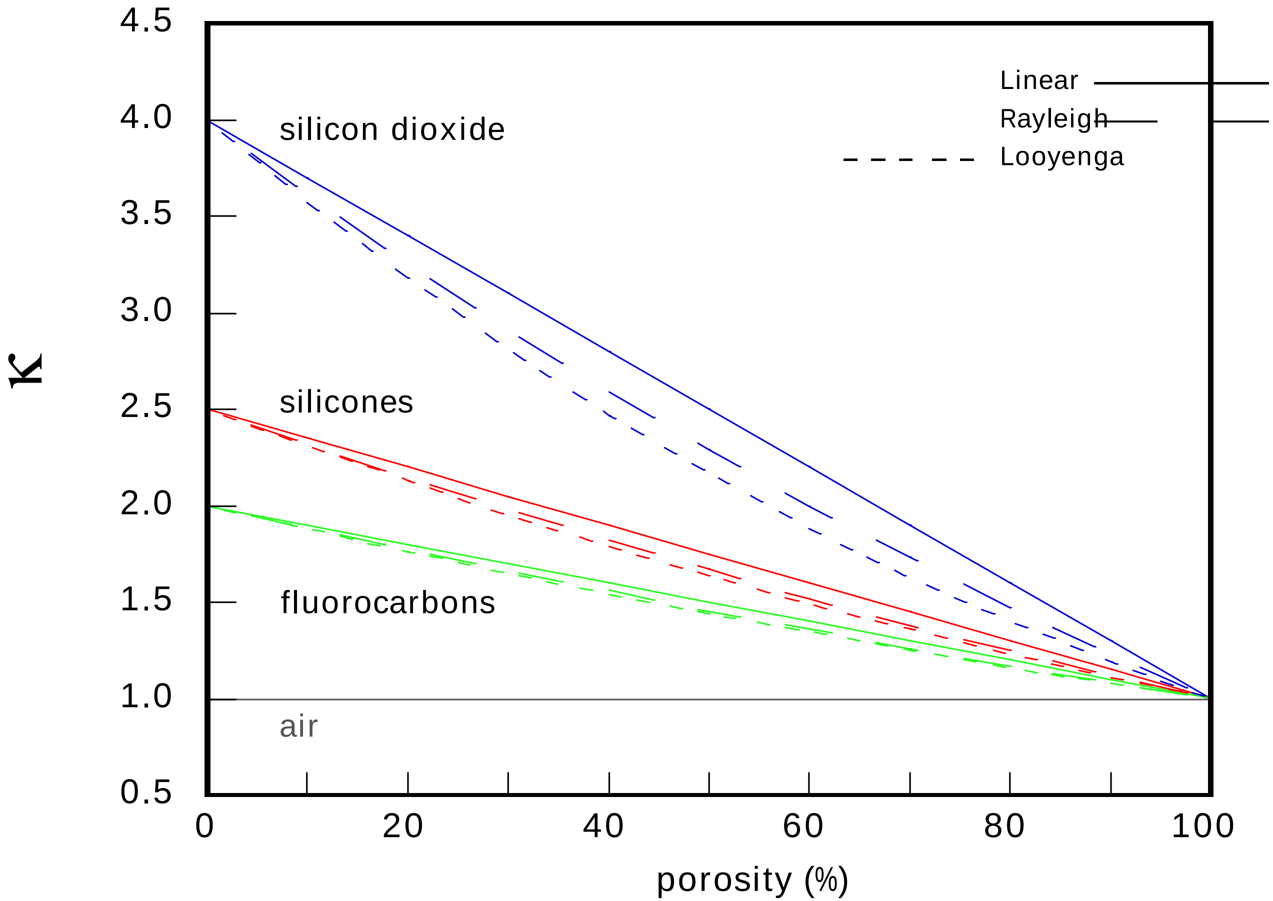
- New pyrolytic CVD process developed for depositing thin organosilicon films
- Advantages:
  - High growth rates
  - Deposition possible under medium vacuum

    and at ambient substrate temperature
  - Thermally stable and resistant to water uptake
  - Film contains long chains and/or large rings of PDMS-like structure
  - Control of film structure possible by varying deposition conditions
  - Film structure different from plasma polymerized film
- Other potential applications
  - Dry resists for deep UV photolithography at 157nm

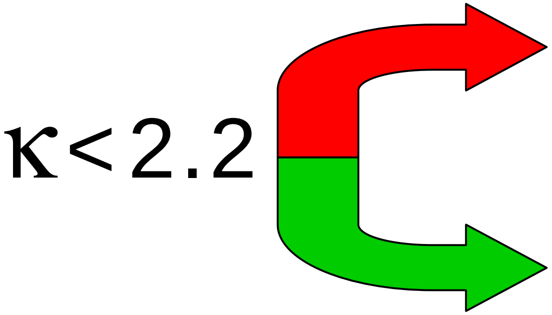
Acknowledgements

- **Dan Burkey, Jose Mendez Del-Rio, Laura Merz, Mike Kwan**
- **NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Research (NSF/SRC ERC EBSM)**
- **Center for Materials Science and Engineering, MIT: NSF supported MRSEC Shared Facilities**
- **Intel Corp: Relative Humidity Chamber**
- **MKS: Low Vapor Pressure Mass Flow Controller and Orion Mass Spectrometer**

κ vs. Porosity



- Voids can lower dielectric constant
- All voids must be much smaller than feature sizes
- Mechanical / Thermal issues are a concern



κ<2.2

SiO_2 ~ 65-70% porous

Silicones ~ 20% porous