Density Functional Theory (DFT) applied to the Chemical Vapor Deposition (CVD) of Low Dielectric Constant Materials

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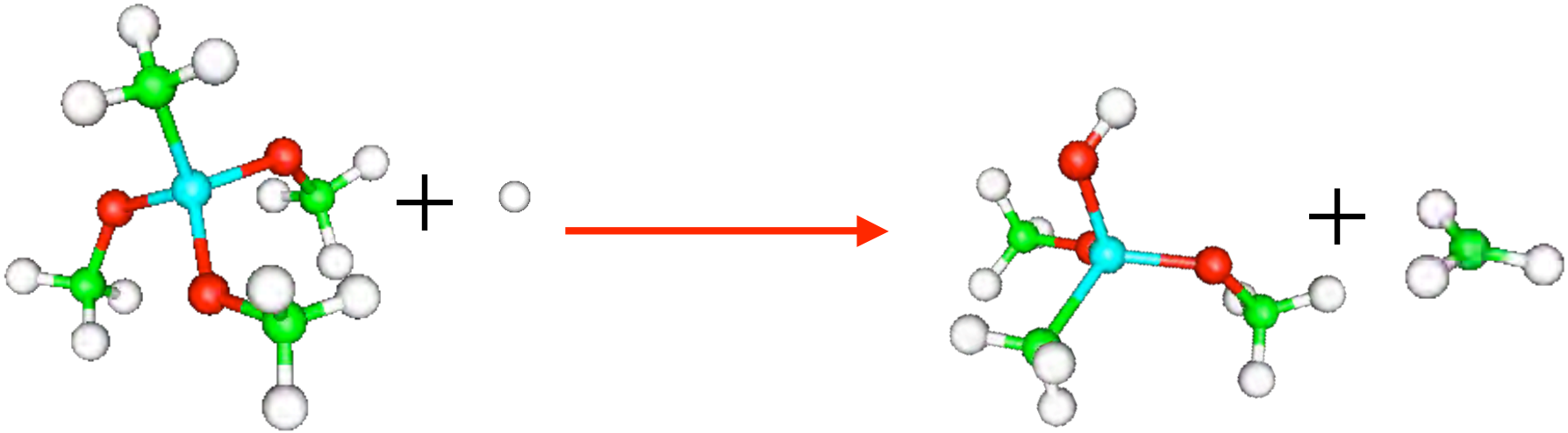
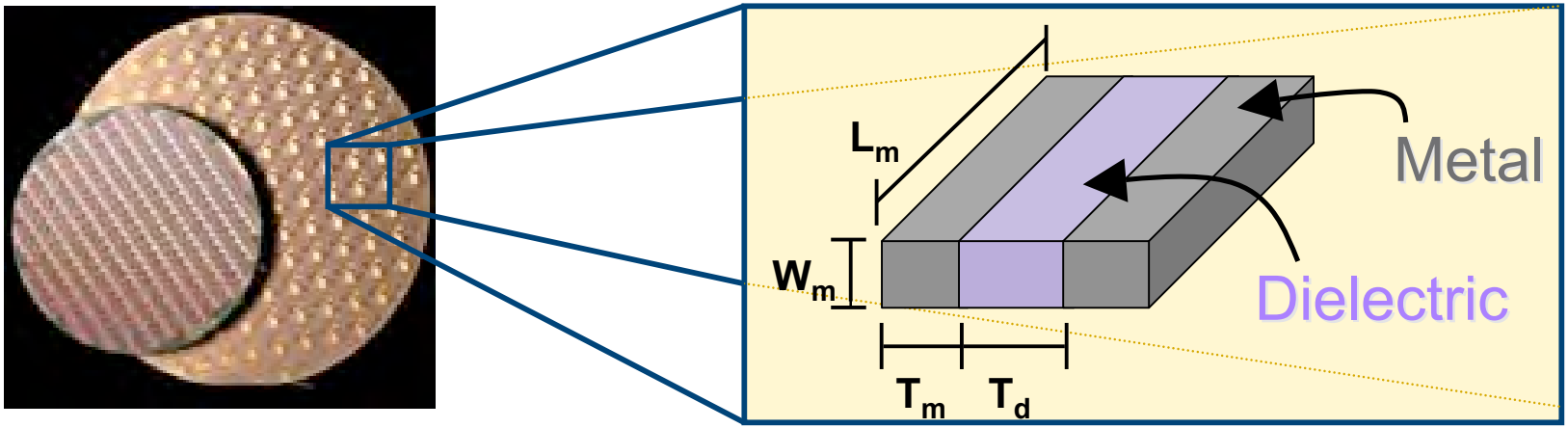


Dielectrics in Integrated Circuits



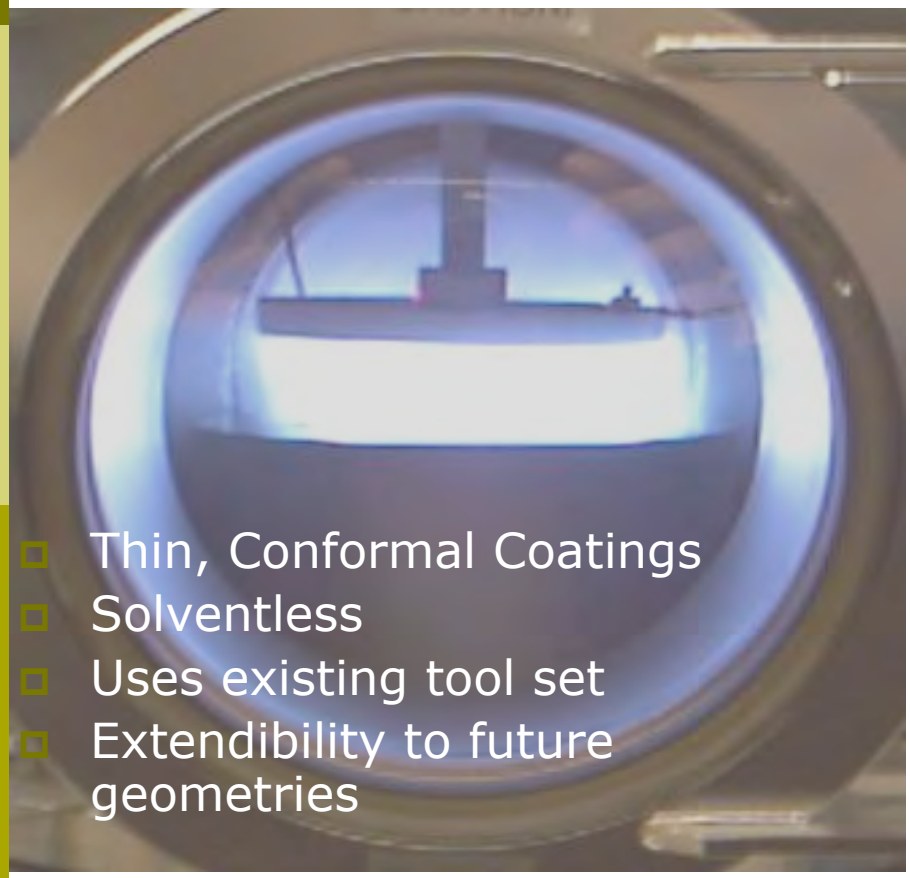
RC Delay: $\tau = RC = \left(\frac{\rho L_m}{W_m T_m}\right)\left(\frac{k\varepsilon_0 W_m L_m}{T_d}\right) = \frac{\rho k \varepsilon_0 (L_m)^2}{T_d T_m}$

Power Consumption: $P \sim CV^2 f$

Cross Talk Noise: $N \sim \frac{C_{line\text{-}to\text{-}line}}{C_{total}}$

Solventless Low-k Dielectrics

CVD vs Spin-On



- Thin, Conformal Coatings
- Solventless
- Uses existing tool set
- Extendibility to future geometries

- Large solvent use
  - Environmental and worker hazard
- Can not be used for complex geometries or multiple sacrificial layers

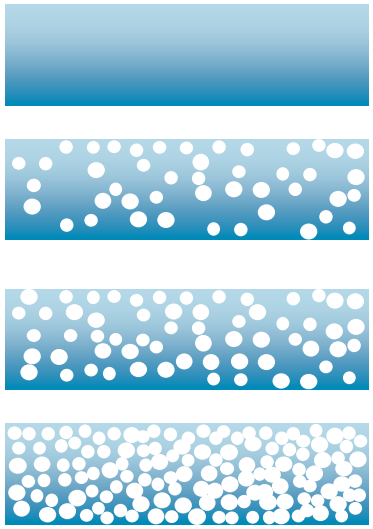
Semiconductor International, Sept 1998

Evolution of Dielectric Materials

- SiO_2 (k ~ 4.0)
- Fluorinated Silicate Glass (FSG), k ~ 3.7
- Organosilicate Glass (OSG), k ~ 2.7 – 3.6
- Porous OSG, k(*p*)
- Air Gap, k_{eff} ~ 1.4

Composition	Fully dense k
SiO_2	4.0
Si:O:C:H (Organosilicate Glass - OSG)	2.7-3.6

Air k=1.0

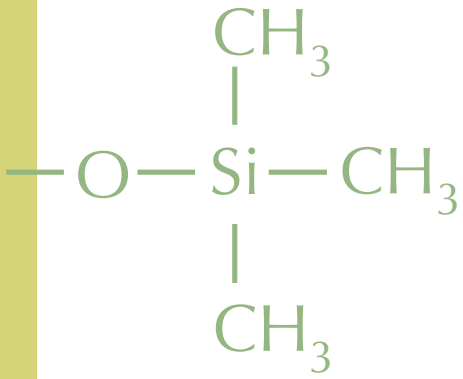


% Porosity	k
0	2.7
20	2.3
50	1.75
90	1.15

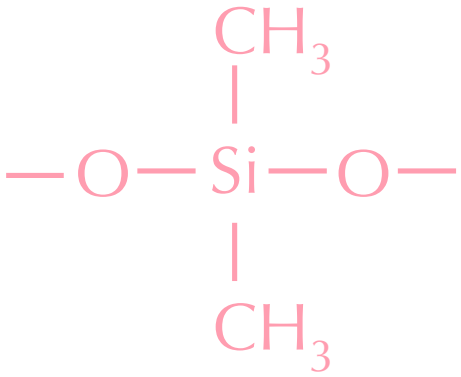
Precursor selection using Density Functional Theory (DFT)

- Large body of research for OSG deposition
  - Much is unpublished or non-specific to corporate intellectual property
- Perform experiments on the desktop first
  - Examine methoxymethylsilanes
  - Bond strengths – fragmentation patterns
  - Elementary reactions
- Utilize DFT to screen precursors
  - Save time, money, resources, reduces exposure risks

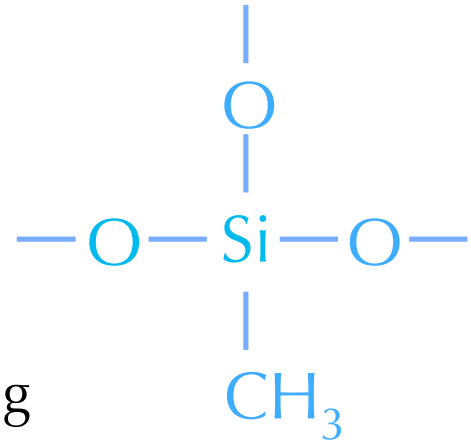
OSG Building Blocks



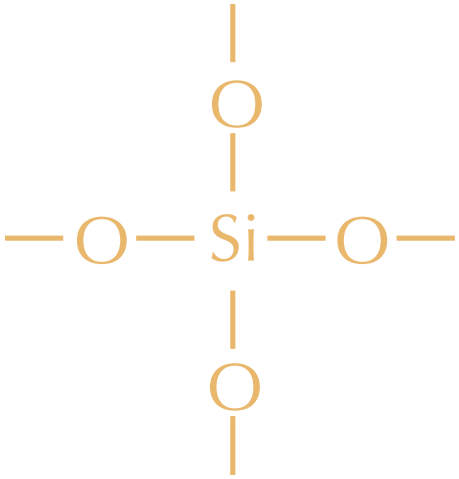
'M' Group
Chain Terminating



'D' Group
Chain Propagating



'T' Group
Chain Crosslinking



'Q' Group
Fully Crosslinked

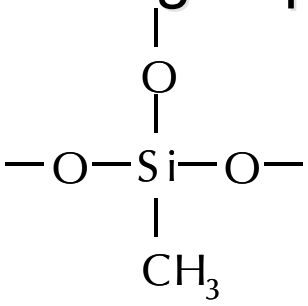
Higher Crosslinking → Harder Materials

Connectivity # : <r>

$$< r >= \frac{\#\ \text{Network Forming Bonds}}{\#\ \text{Network Forming Atoms}}$$

**To avoid double counting, each oxygen is counted as one half of an atom in the analysis.

For "T" group,



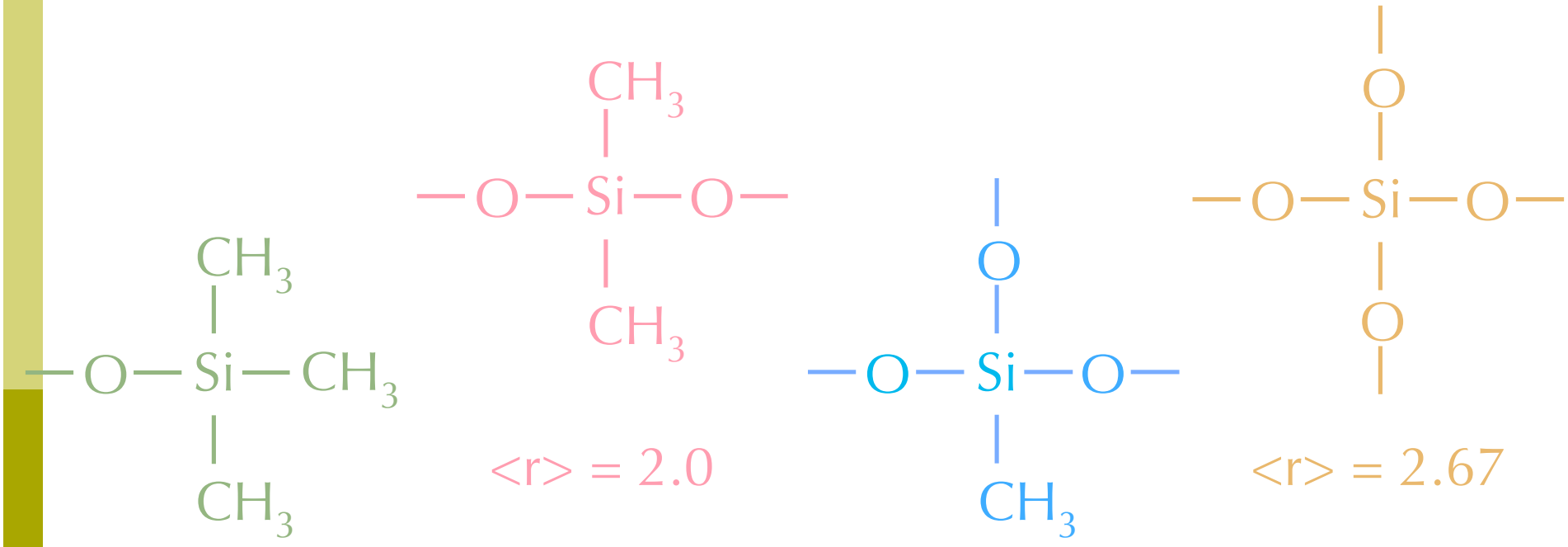
$$< r >= \frac{(1_{Si} \times 3_{bonds}) + \frac{1}{2}(3_O \times 2_{bonds})}{1_{Si} + \frac{1}{2}(3_O)} = 2.4$$

For $Si_xO_y(CH_3)_z$: $< r >= \dfrac{(4x - z) + \frac{(2y)}{2}}{x + \frac{y}{2}}$

A Theoretical Treatment

The Percolation of Rigidity

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



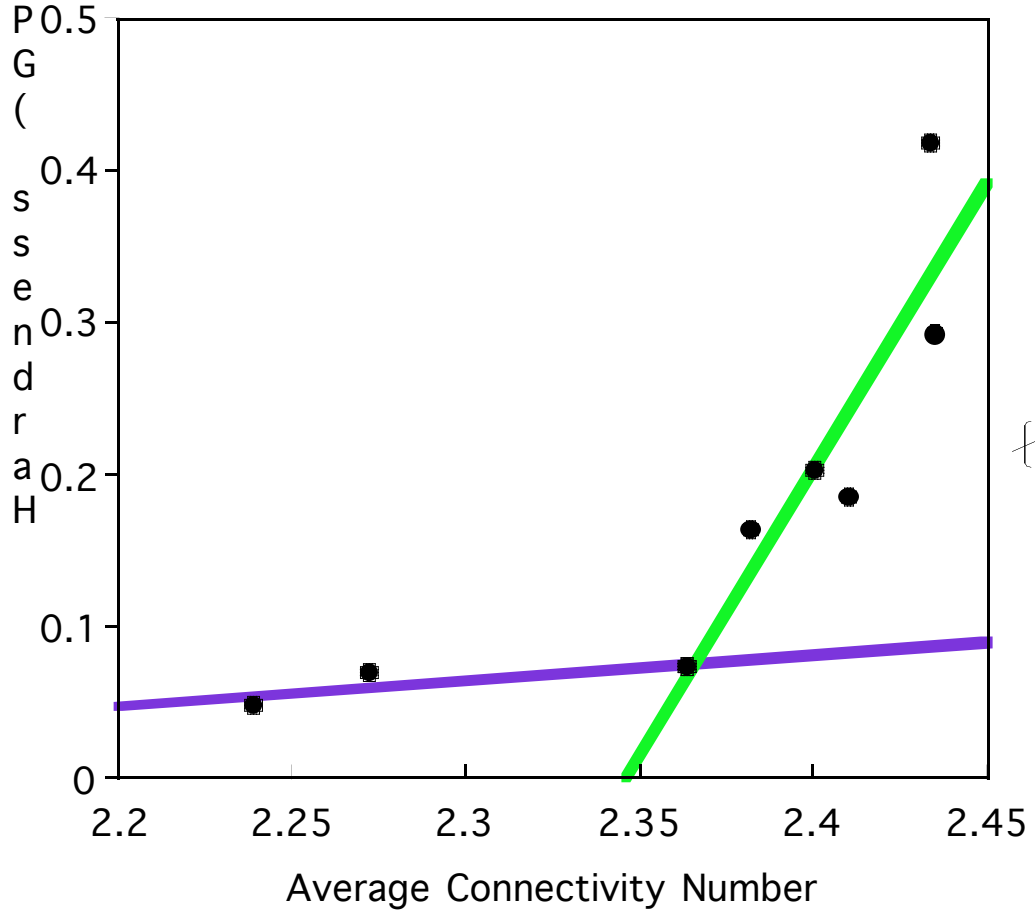
J. Phillips, *J. Non-Cryst. Solids* **34,** 153 (1979)
G.H. Dohler, R. Dandoloff, and H. Bilz, *J. Non-Cryst. Solids* **42,** 87 (1980)
S.J. Limb, K.K. Gleason, D.J. Edell, and E.F. Gleason, *J. Vac. Sci. Technol. A.* **15**(4),1814 (1997)
D.D. Burkey and K.K. Gleason, *J. Appl. Phys.* **93**, 5143 (2003)

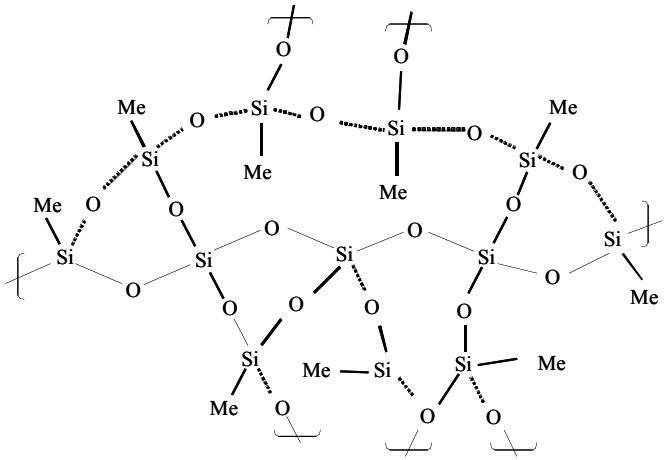
Connectivity # from FTIR

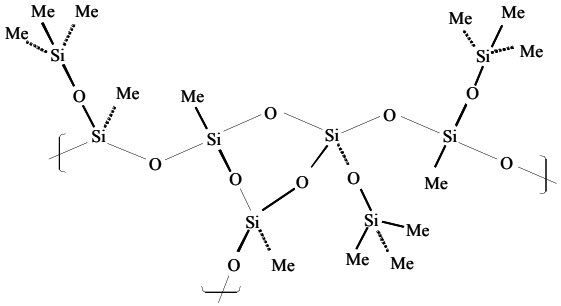
<r> = weighted contribution M, D, T, and Q groups

- Spectral curve fitting to find relative amounts of M, D and T groups within each spectra
- To find Q groups
  - Assumes same number Si atoms in each spectrum and each Si is bonded to either oxygen or carbon
  - Any differences in total combined area of M, D, and T attributed to Q groups
  - Calculates the minimum number of Q groups
- Selected conformation of FTIR data by solid-state magic angle spinning ^{29}Si NMR

The Percolation of Rigidity



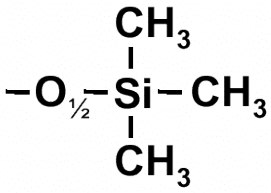




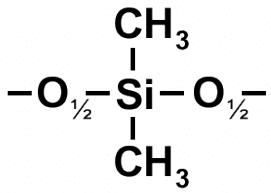
A.D. Ross and K.K. Gleason,
J. Appl. Phys. 97, 113707 (2005).

Design of Robust Overlying Dielectric

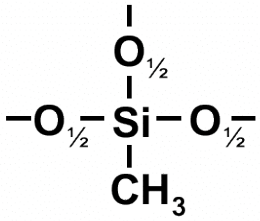
- Low-k OSG containing only T and Q groups
  - <r> greater than 2.4 → Harder films
  - Silicon oxygen bonds increase hardness and modulus
    - T groups ideal, retain carbon → lowering the dielectric constant
    - How can we intelligently choose precursors for hard OSG deposition?



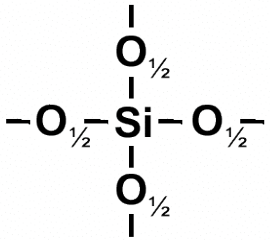
M



D



T



Q

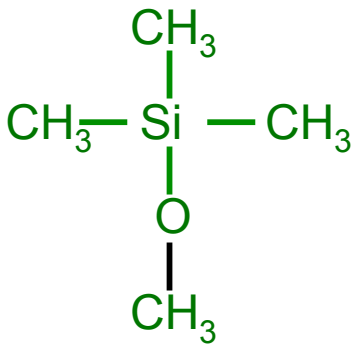
Methodology

- Examined two families of molecules
  - Methylsilanes $(CH_3)_nSiH_{4-n}$
  - Methoxymethylsilanes $(CH_3O)_nSi(CH_3)_{4-n}$
    - All fragments
    - All reaction products
  - 56 chemical species, radicals, ions
  - Over 100 reactions
- Using Gaussian®
  - Optimized Geometries
  - Performed Frequency Calculations
  - Single Point Energy Calculations

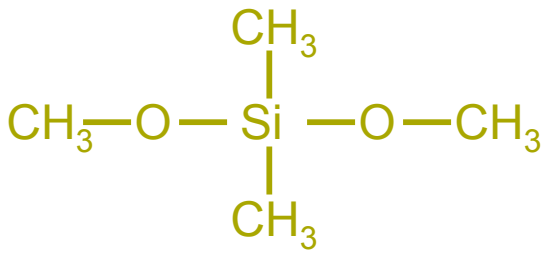
OSG Precursors

- Studied methylsilanes
- Examine a family of methoxymethylsilanes
  - Compute thermochemistry
  - PECVD depositions – Low Power to allow control over chemistry
  - Compare and interpret the results

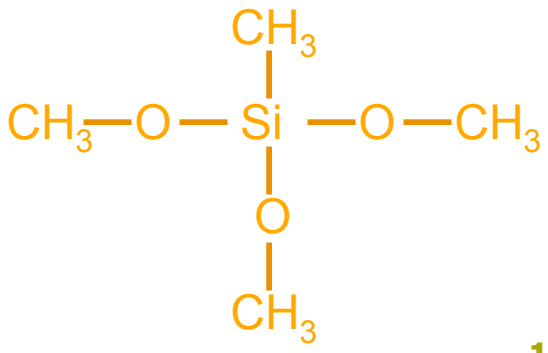
Methoxytrimethylsilane
MO3MS



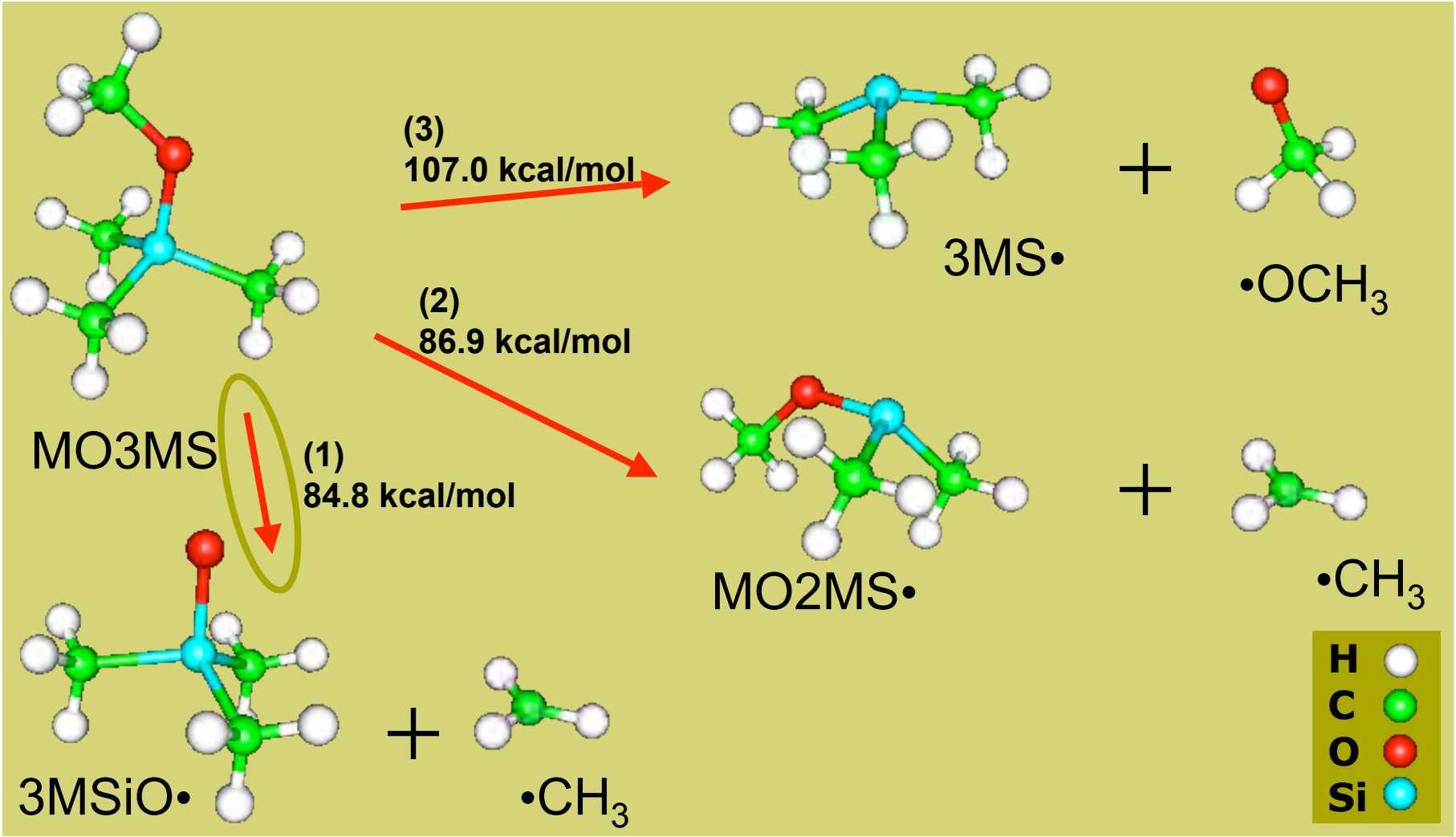
Dimethoxydimethylsilane
2MO2MS



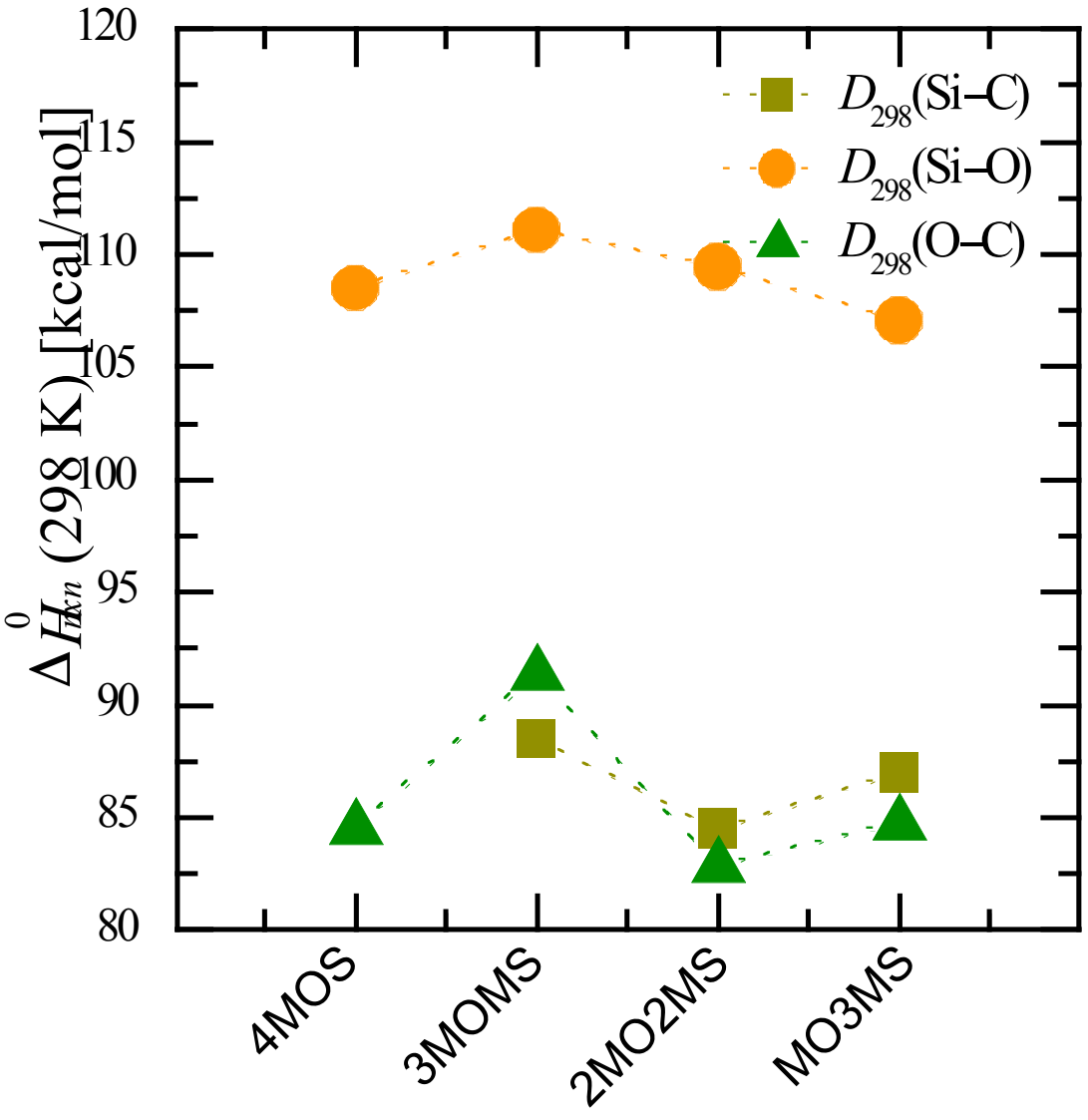
Trimethoxymethylsilane
3MOMS



Fragmentation of Methoxytrimethylsilane (MO3MS)

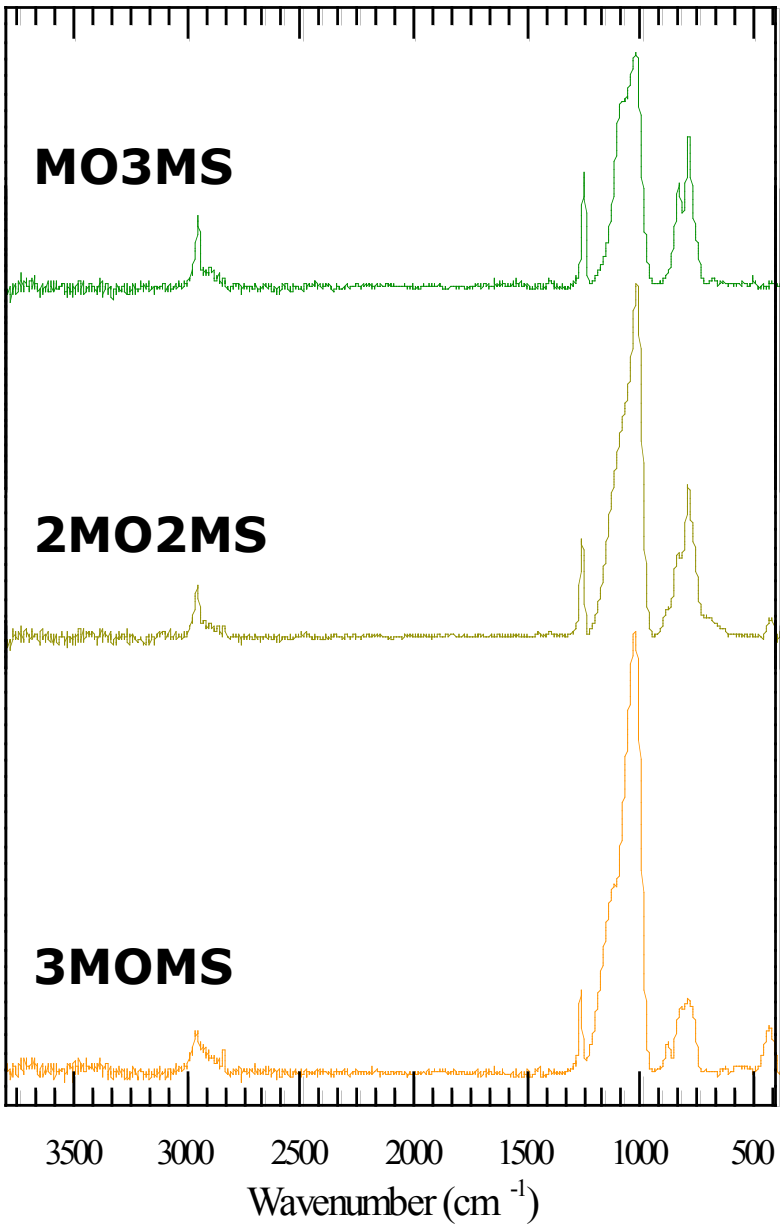


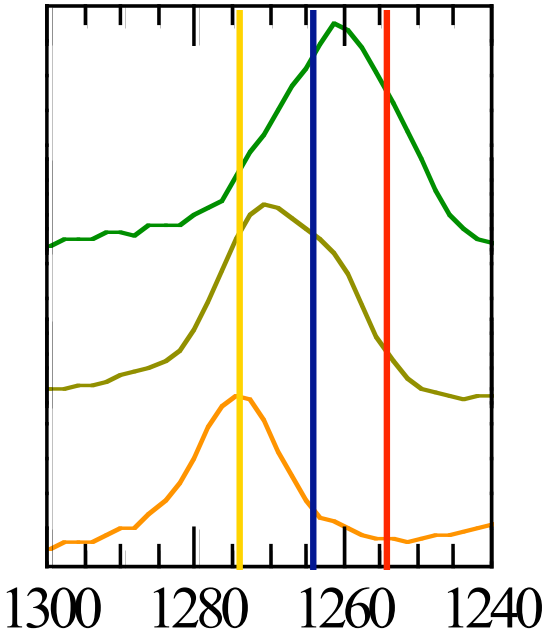
Bond Dissociation Energies



- Si-O bond is strongest (likely preserved)
- Si-C and O-C bonds have similar bond strengths
  - No selectivity
  - Likely loss of Si-C bonding
- Expectations
  - MO3MS – M
  - 2MO2MS – D
  - 3MOMS – T

FTIR of PECVD OSG films





M & D

D & T

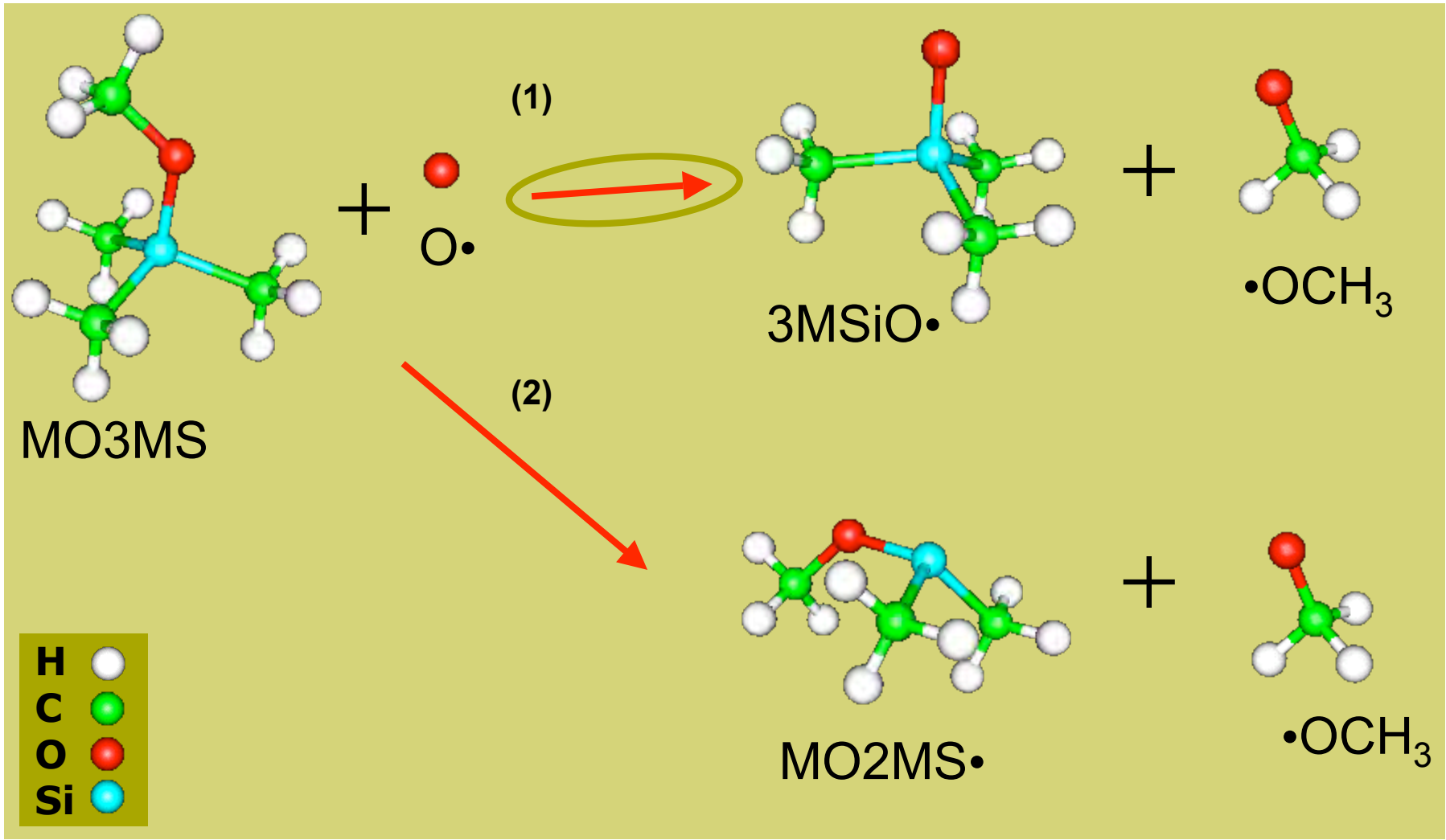
Mostly T

- Si–O–Si stretching mode
  - Increases with increased precursor oxygenation
  - Intensity of ordered peak increases
- Dielectric constants after a 1 hour anneal at 400°C
  - From MO3MS – 2.78
  - From 2MO2MS – 2.85
  - From 3MOMS – 3.20

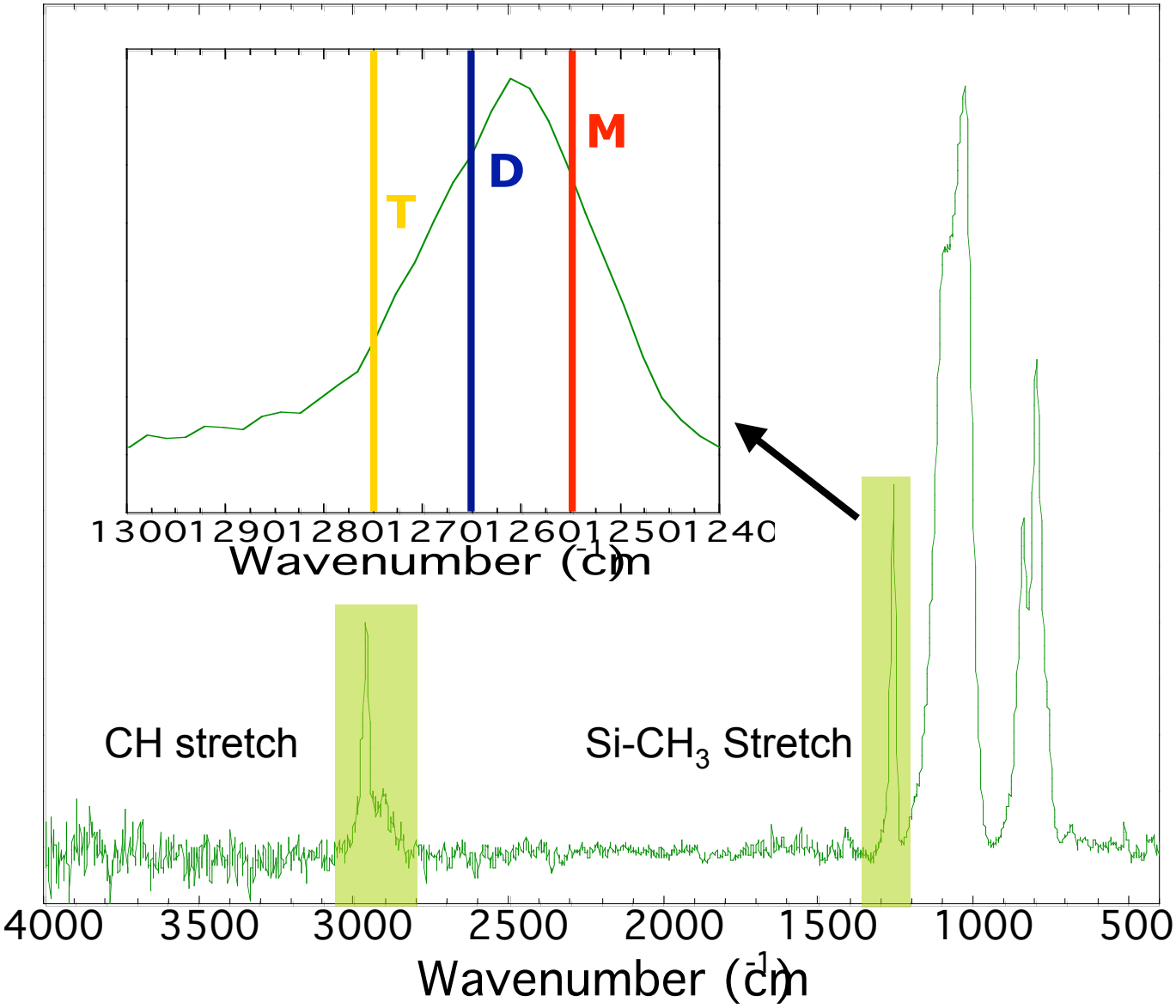
Strategy to increase T groups

- Examine pathways in presence of O atom
  - Use precursor with most Si-C bonding
    - Retain more Si-C bonding
    - Lower k
- Compute thermochemistry on desktop
- PECVD depositions on the bench
- Compare results

Methoxytrimethylsilane (MO3MS) reactions with Oxygen ($^3P_2$) atom

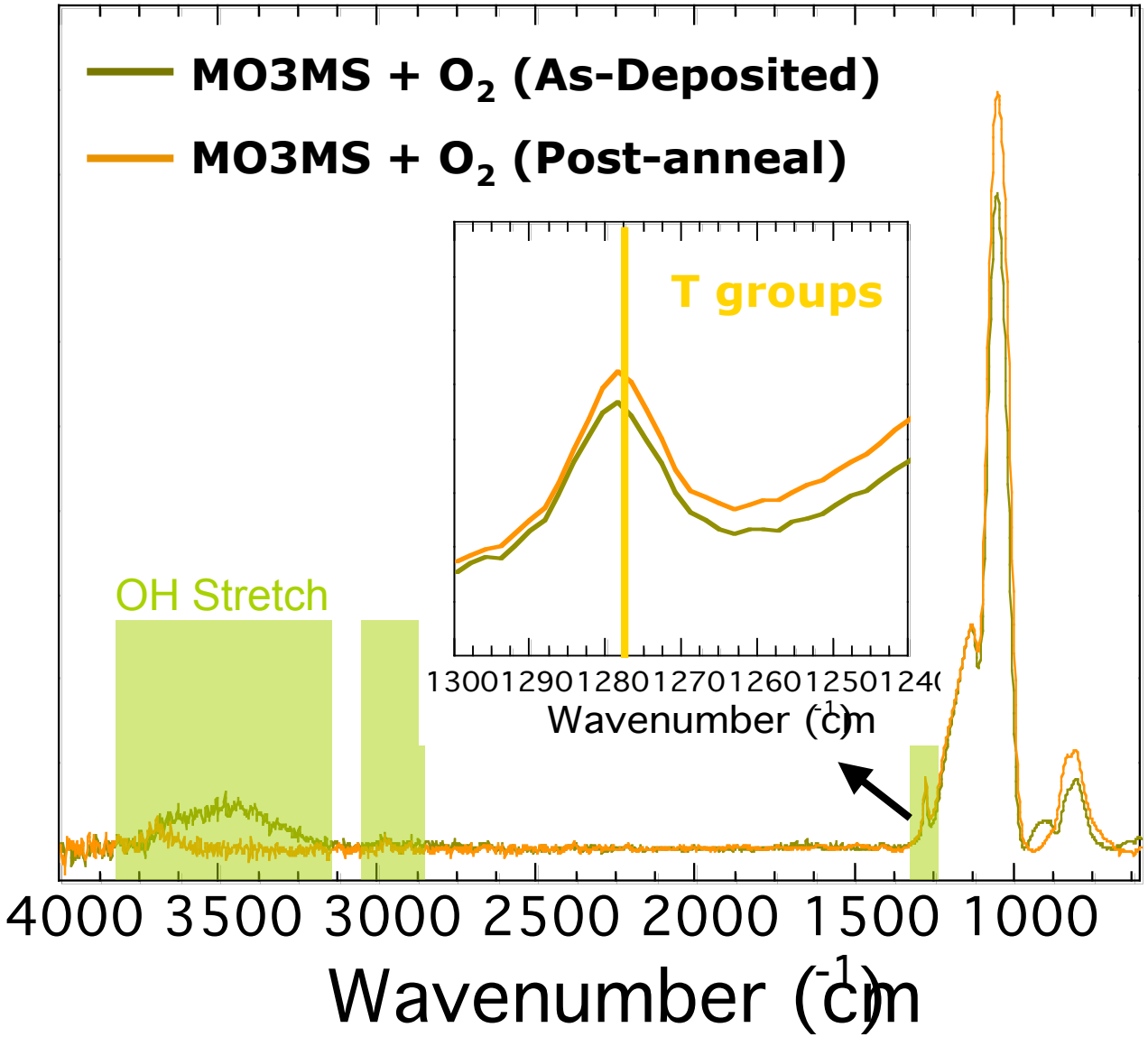


FTIR of PECVD film from MO3MS



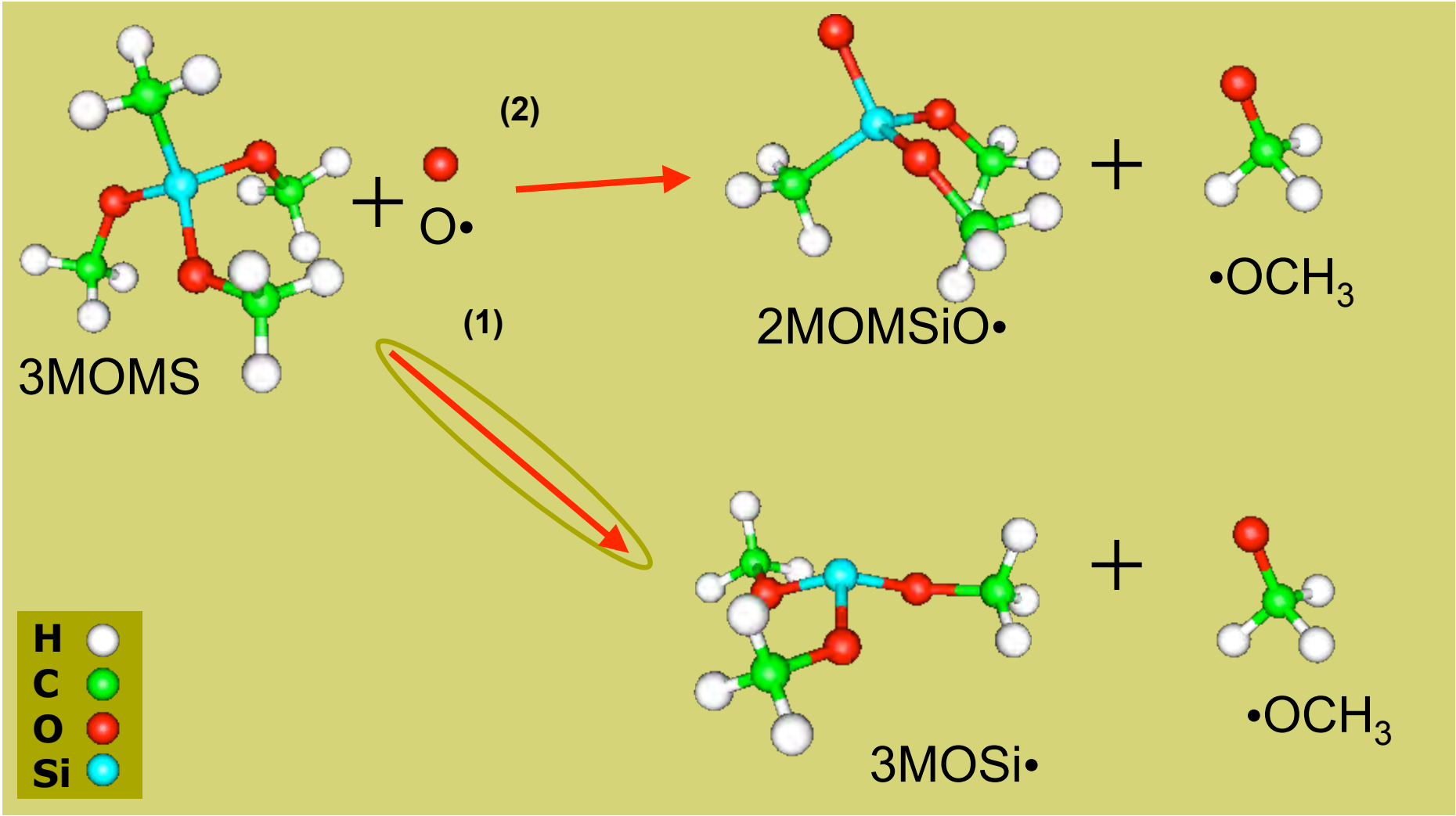
- Results match expectation
  - Lots of CH
  - Mostly M & D groups
- k ~ 2.78
- Below percolation of rigidity

FTIR PECVD film from MO3MS + O_2

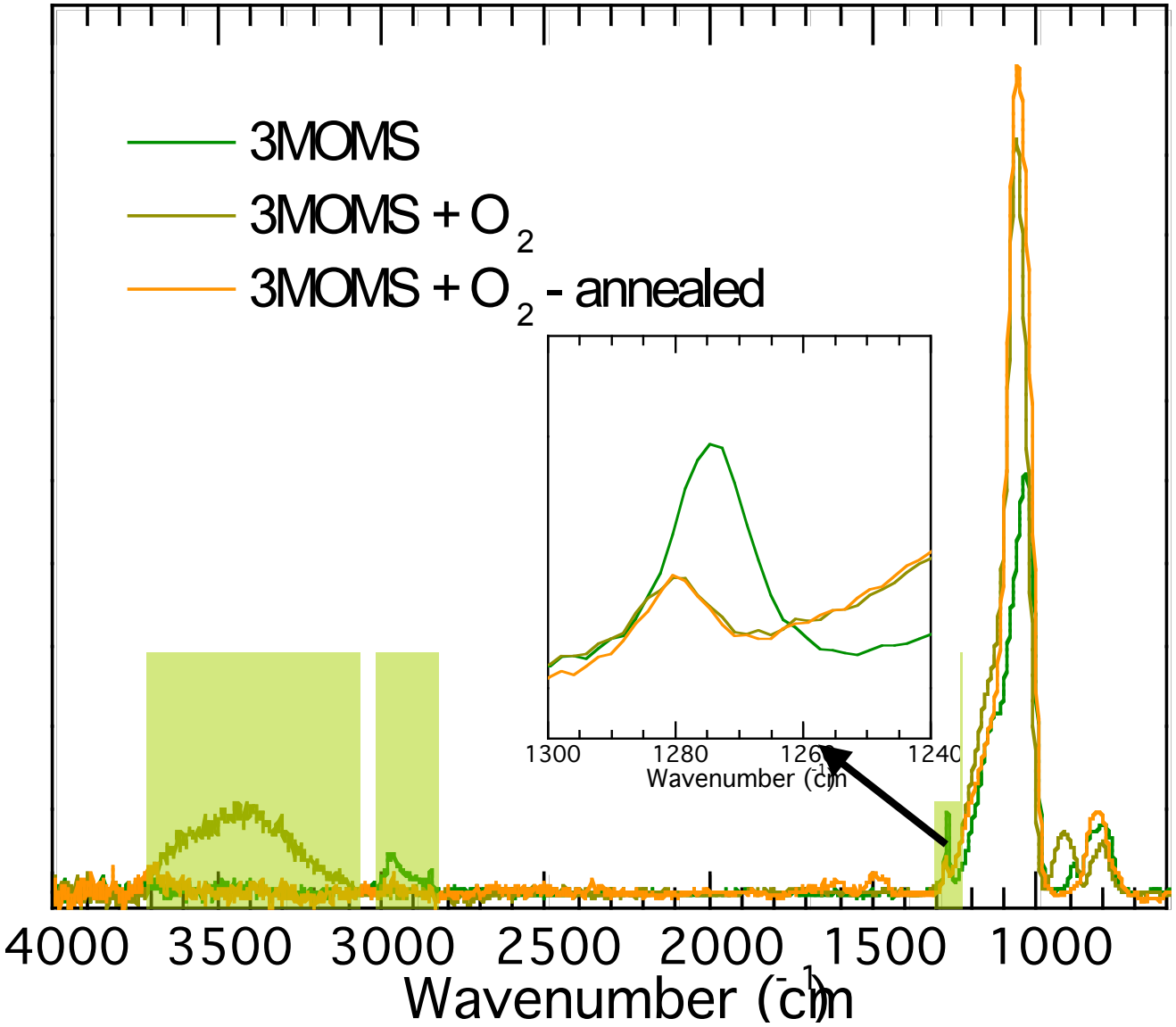


- OH present in film
  - Removed upon annealing
  - Increased Si-O-Si band
- Very little CH
- Only T & Q groups
- k ~ 5.94 (as-dep)
- k ~ 4.06 (post-anneal)

Trimethoxymethylsilane (3MOMS) reaction with Oxygen ($^3P_2$) atom



FTIR of PECVD films from 3MOMS + O_2

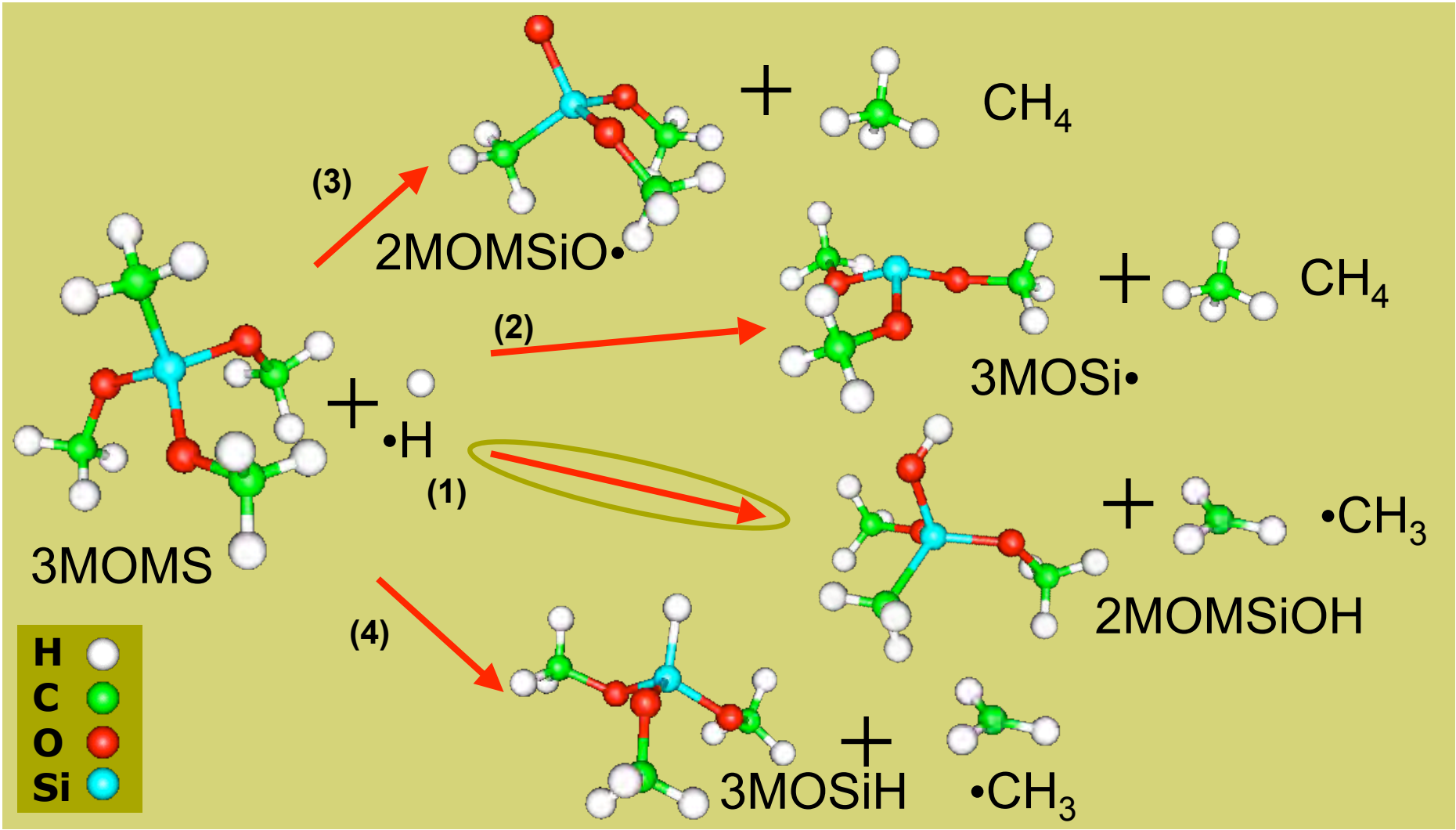


- Loss of selectivity
- All T & Q groups
- Little CH remaining
- Increased Si–O–Si
- Damage to film
  - OH content
  - k ~ 4.29
  - Compared to k ~ 3.20

Summary to this point

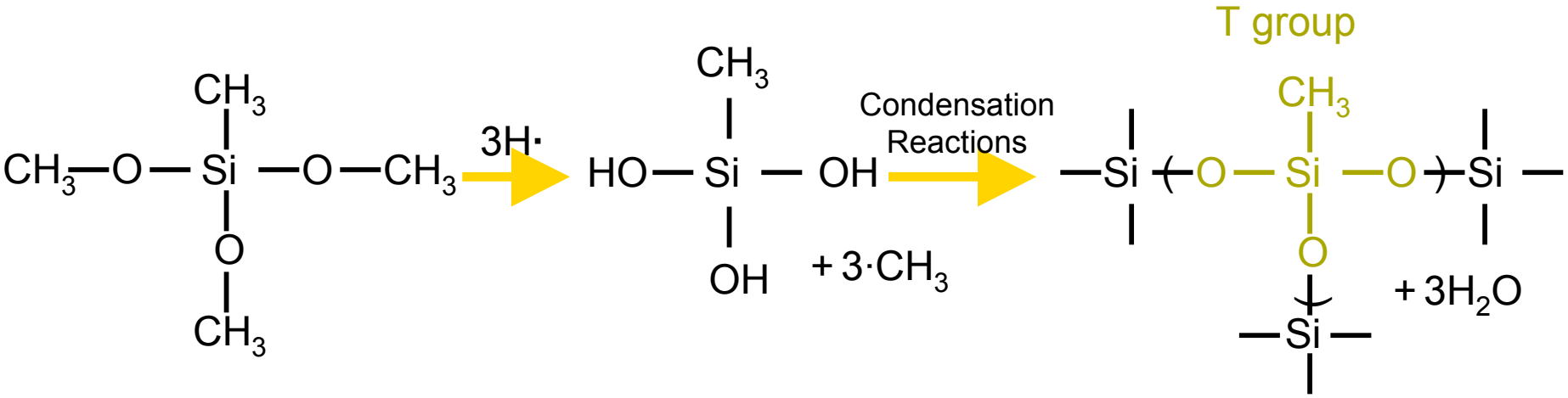
- Films from monomer only
  - dielectric constants <3 obtained
  - Not enough T groups to get <r> above percolation of rigidity
- Films from monomer plus O_2
  - Loss of selectivity
  - Damage to film – SiOH in resulting film
  - Dielectric constants are high
- Consider reducing chemistry
  - Examine reactions with hydrogen atom

Trimethoxymethylsilane (3MOMS) reaction with Hydrogen ($^2S_{1/2}$) atom

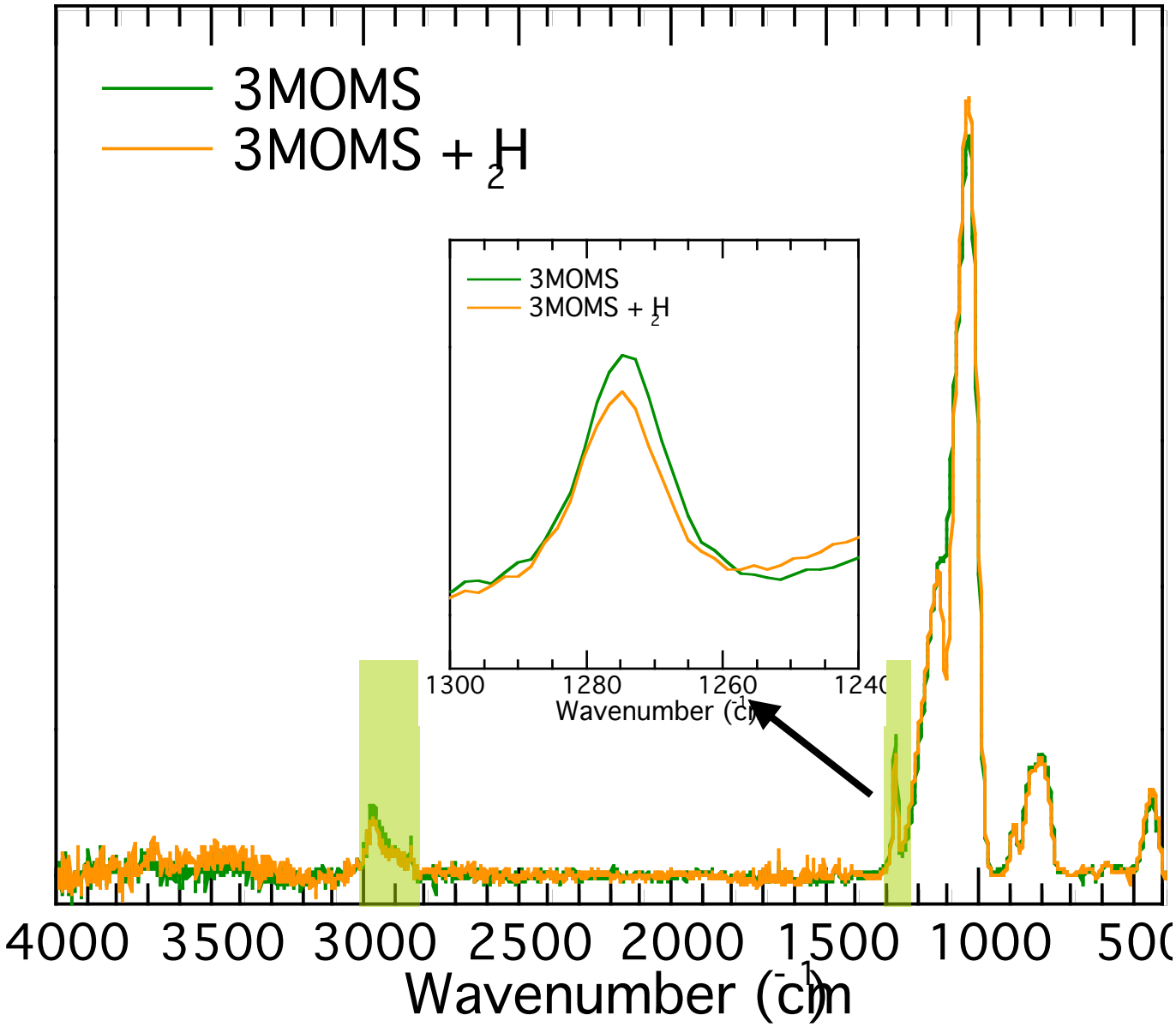


Silanol Formation and reactions

- Conversion of methoxy to silanol is greatly thermodynamically favored over silane formation by removing a methyl group
- If all methoxy groups can be converted to silanol groups . . .
  - Control the ratios of M, D, T, and Q groups by varying the precursor flow rates of MO3MS, 2MO2MS, 3MOMS, 4MOS respectively



FTIR of PECVD films from 3MOMS + H_2

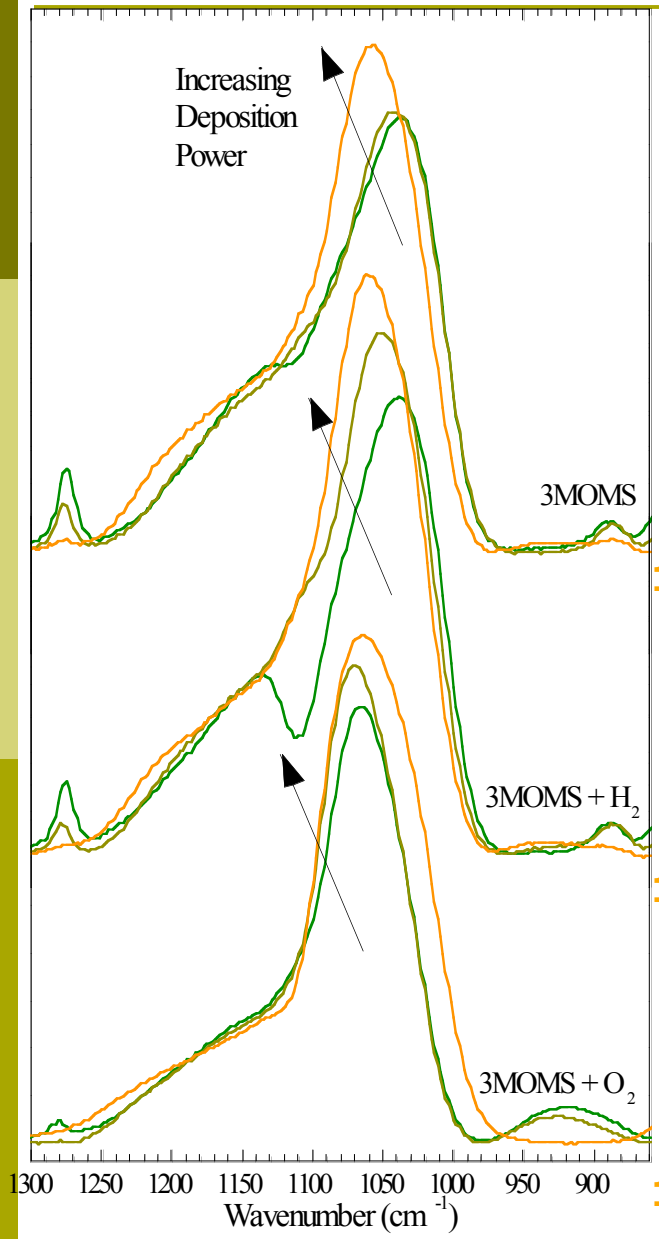


- T groups only
- Less CH due to conversion of OCH_3
- k ~ 3.18

Other approaches to increase hardness

- Increase Power
  - Higher crosslinking
  - More dense film
  - What happens for us?
- Expectations
  - Loss of selectivity
  - Tend toward random assembly of radical species

3MOMS at varied plasma powers



20W - k ~ 3.20
40W - k ~ 3.53
100W - k ~ 4.54

20W - k ~ 3.18
40W - k ~ 4.15
100W - k ~ 4.92

20W - k ~ 4.29
40W - k ~ 5.02
100W - k ~ 4.57

- Loss of chemical selectivity
  - Loss of $Si–CH_3$
  - Complete conversion to Q, or Q and Si-Si bonding
  - Dielectric constants increase with increased power
  - Same effect is seen with pulsed plasma using 200W peak power

Methoxymethylsilane Summary

- Able to use DFT to predict CVD chemistry for low power systems
- Low-k films from precursors only but not above percolation of rigidity
- Addition of oxygen
  - Get only T and Q groups
  - k is high (>4)
- Creation of T groups with 3MOMS in reducing environment
  - Dielectric constant ~3
  - Stay above percolation of rigidity → harder films
- At high power, lose selectivity and increase k
- Operating at low power allows for as much control over the chemistry as possible in a plasma system

Conclusions

- DFT applied to CVD system
  - Screen precursors for intelligent material design
    - Discover fragmentation patterns
    - Study primary reactions
    - Apply for low power systems
- PECVD of low-k OSG
  - Low power depositions correspond with predicted chemistry
  - Novel use of reducing environment – designed from DFT

Acknowledgements

- SRC/Novellus Fellowship
- NSF/SRC ERC for EBSM

for more detail

T.B. Casserly and K.K. Gleason, "Enthalpies of Formation and Reaction for Primary Reactions of Methyl- and Methylmethoxysilanes from Density Functional Theory", *Plasma Processes and Polymers*, 2(9), 669-678 (2005).

T.B. Casserly and K.K. Gleason, "Chemical Vapor Deposition of Organosilicon Thin Films from Methoxysilane", Plasma Processes and Polymers 2(9), 679-698 (2005).

T.B. Casserly and K.K. Gleason, " Density functional theory calculation of Si-29 NMR chemical shifts of organosiloxanes", J. Phys. Chem. B 109 (28): 13605-13610 (2005).

A.D. Ross and K.K. Gleason, "Effects of condensation reactions on the structural, mechanical, and electrical properties of plasma-deposited organosilicon thin films from octamethylcyclotetrasiloxane", J. Appl. Phys. 97 (11): 113707 (2005).

A.D. Ross and K.K. Gleason, "Enhancement of mechanical properties of organosilicon thin films deposited from diethylsilane" J. Vac. Sci. Technol. A 23 (3): 465-469 (2005).