Correlation of Surface and Film Chemistry with Mechanical Properties in Interconnects

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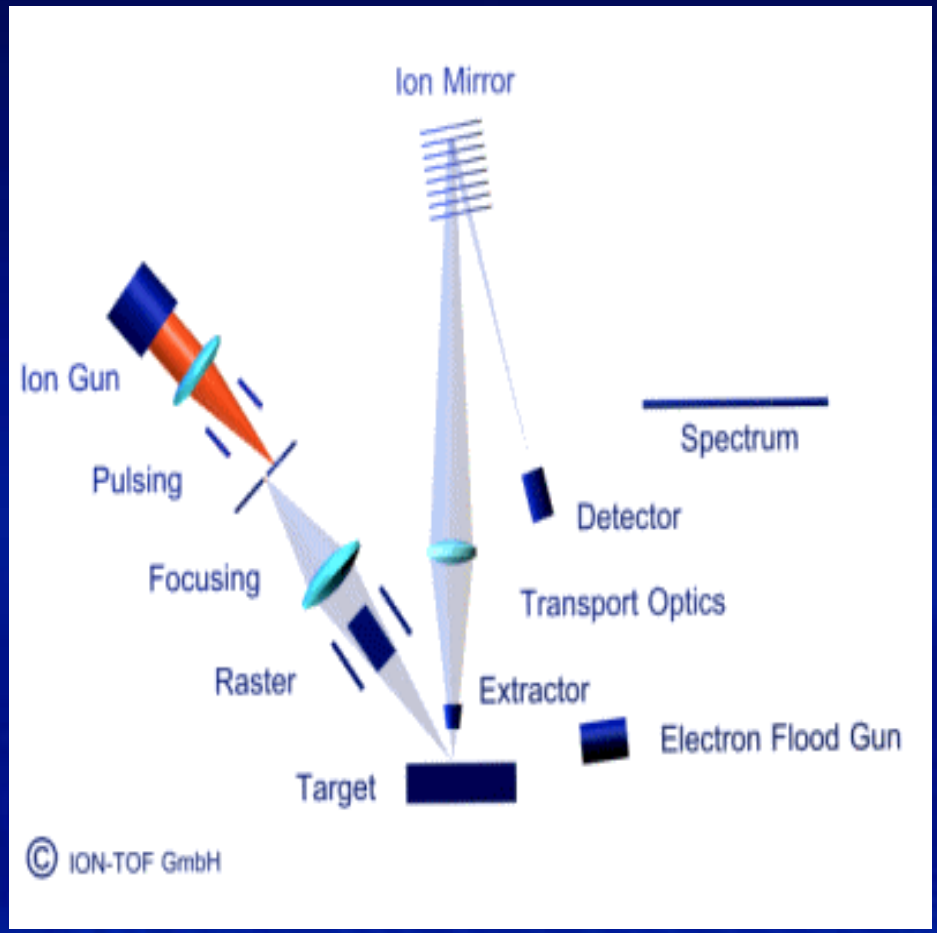
Outline

- Introduction
- Experimental
- ILD Surface Chemistry and ALD Activity
- ILD Surface Chemistry and Adhesion
- ILD Film Chemistry and k, Mechanical Properties
- Conclusions

Introduction

- To meet RC delay goals and minimize cross-talk, lower k dielectric films are required for 90 nm process technology and beyond.
- As the k is lowered, mechanical properties including elastic modulus, hardness, cohesive strength, and interfacial adhesion are generally reduced.
- Fundamental understanding of surface, interface and bulk chemistry and their relationship to electrical and mechanical properties are critical for material selection and integration.
- Close collaboration between disciplines is needed to make the learnings value added.

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)



- **Features**
  - Surface Sensitivity :Top 1nm, ppm level
  - Molecular Specificity
  - Sub-micron spatial resolution
  - Depth profiling with an additional sputtering ion beam

ILD Surface Chemistry Dictates TiN Atomic Layer Deposition(ALD) Activity

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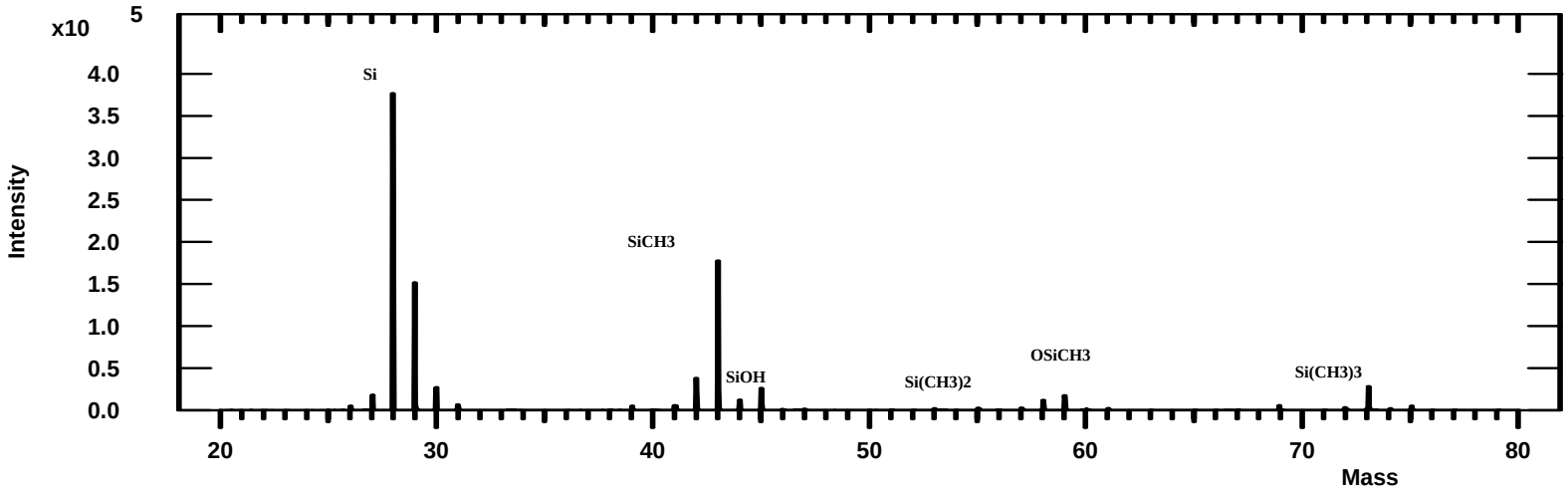
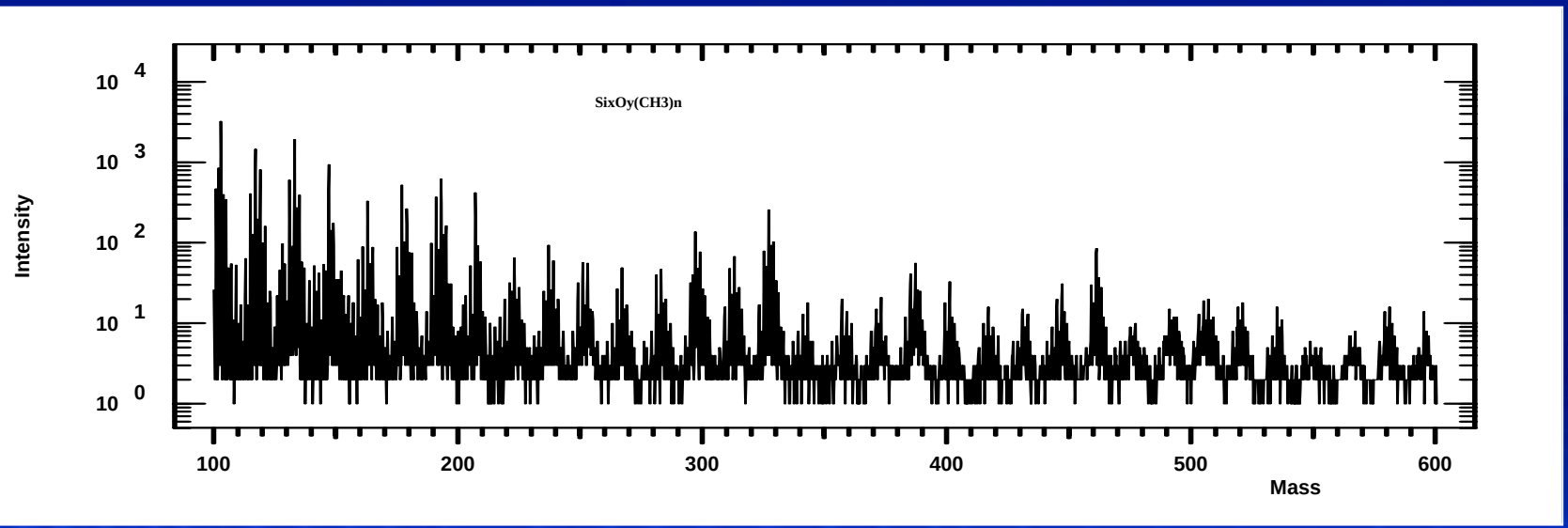
CVD Organosilicate --- Siloxane Structure





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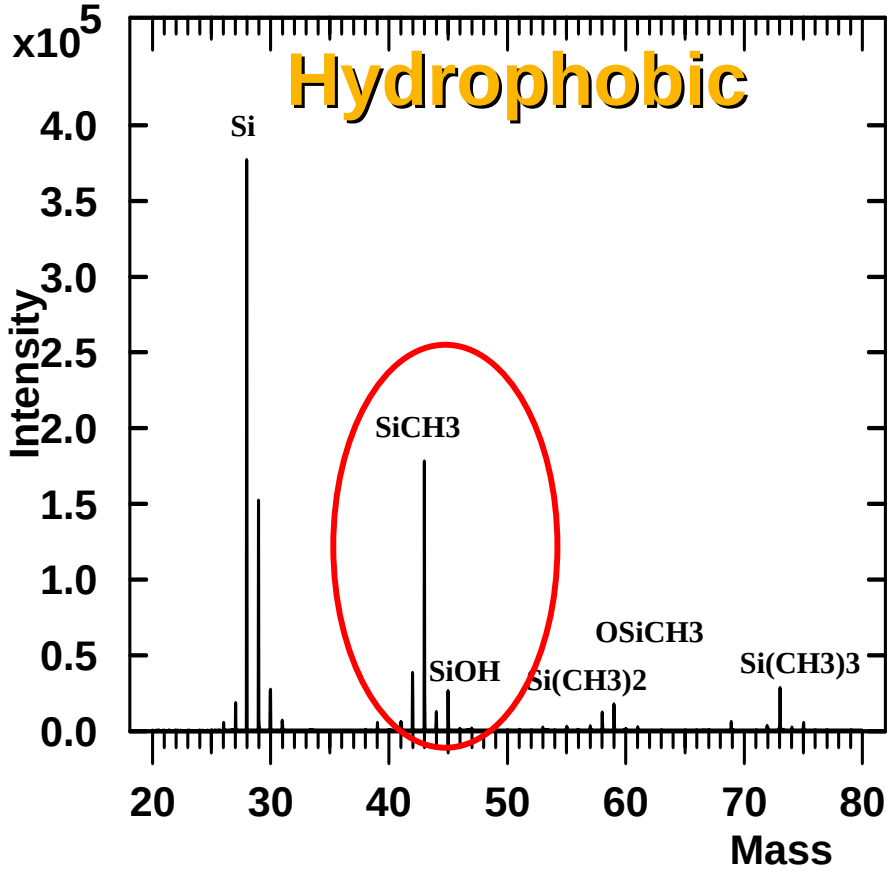
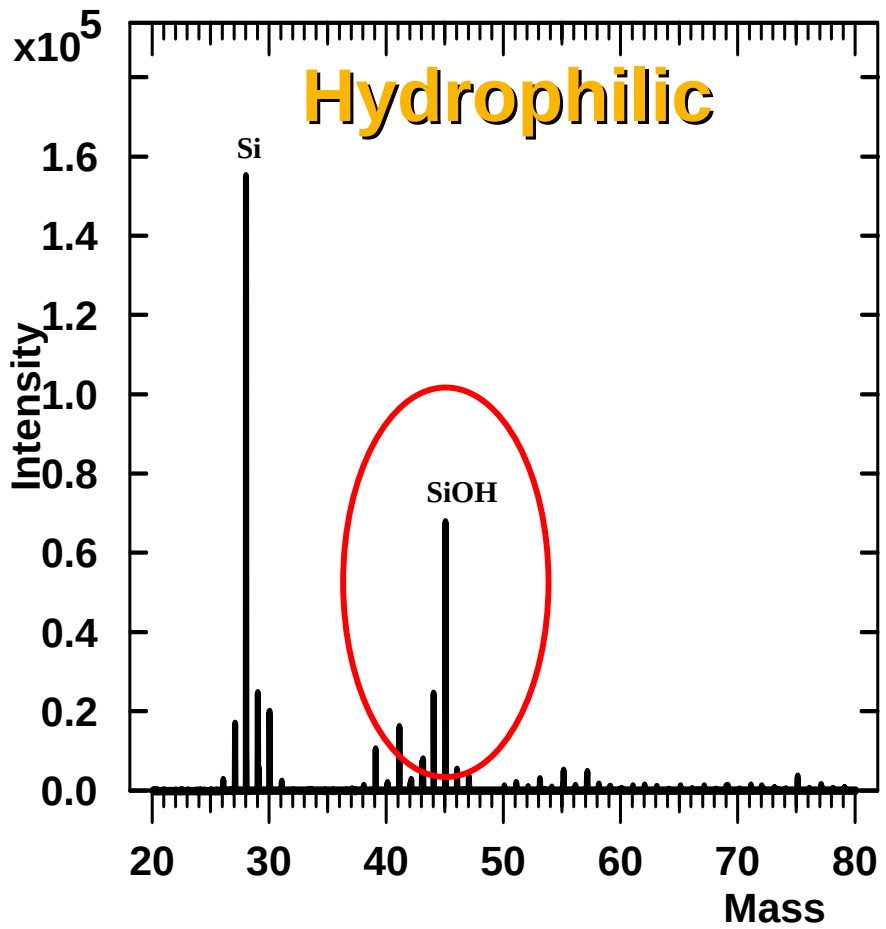
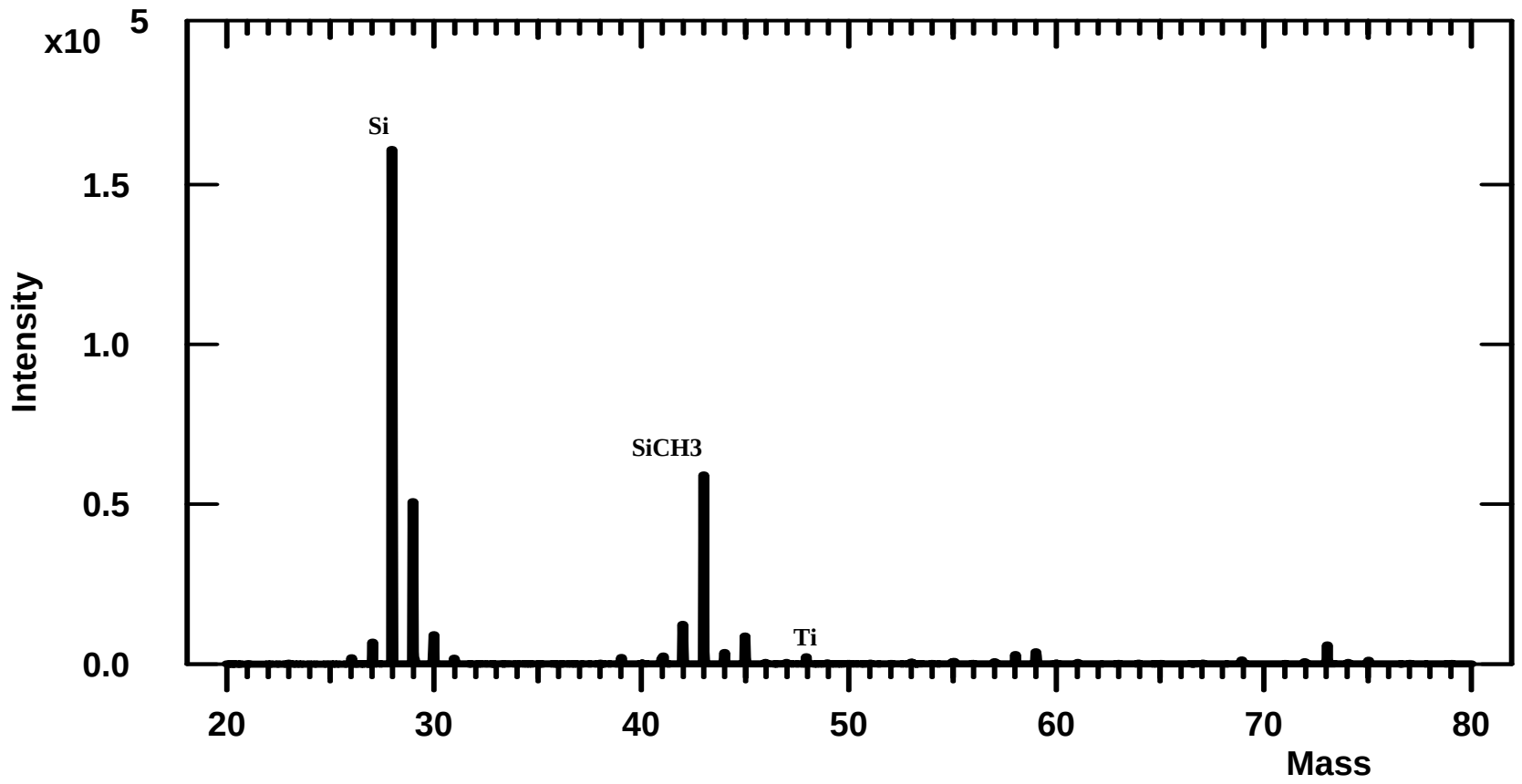
CVD Organosilicate (left): $SiCH_3$ Termination
Oxide (right): SiOH Termination





NO ALD TiN on the Organosilicate

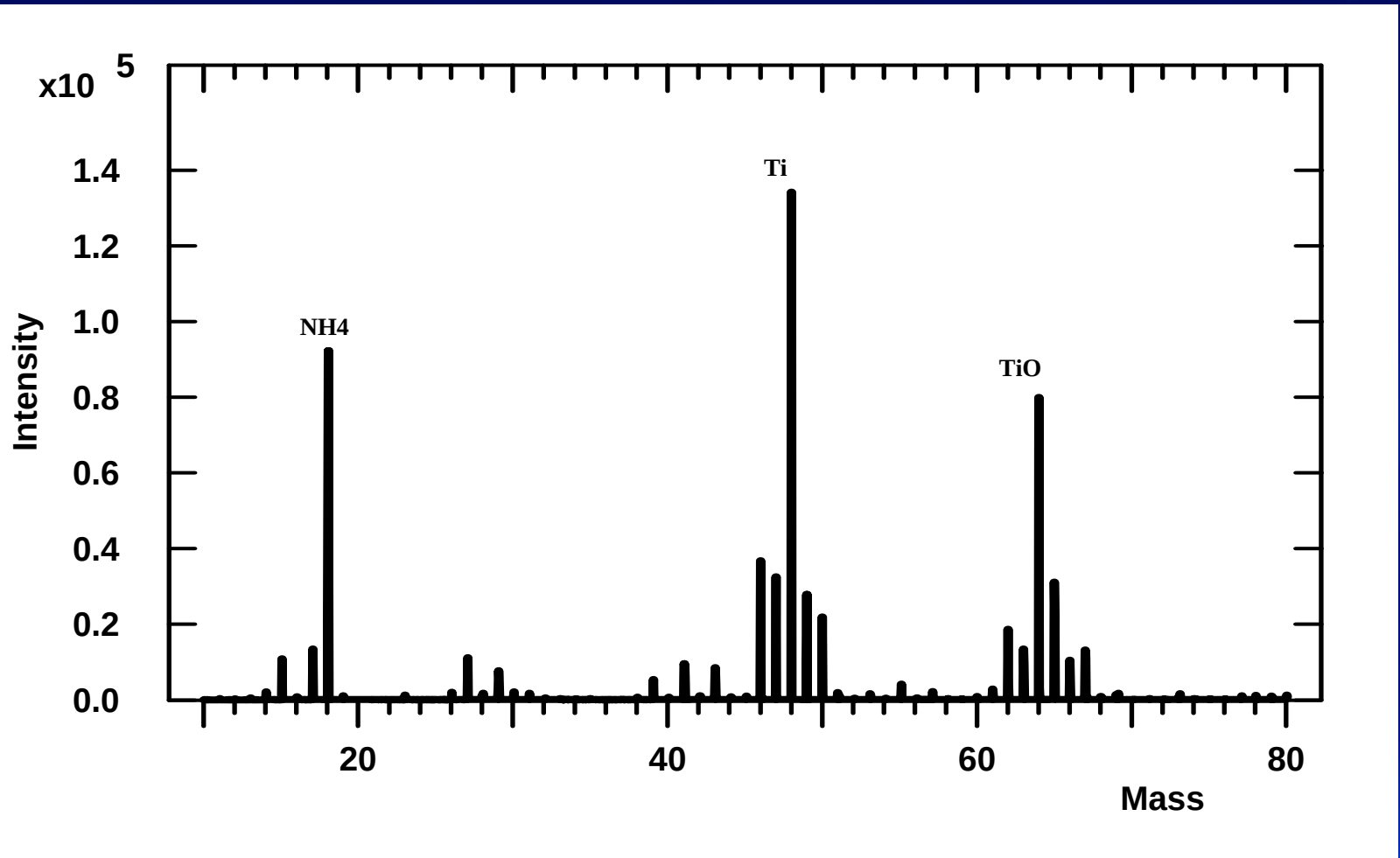
$TiCl_4$ + $Si\text{-}CH_3$ → No reaction



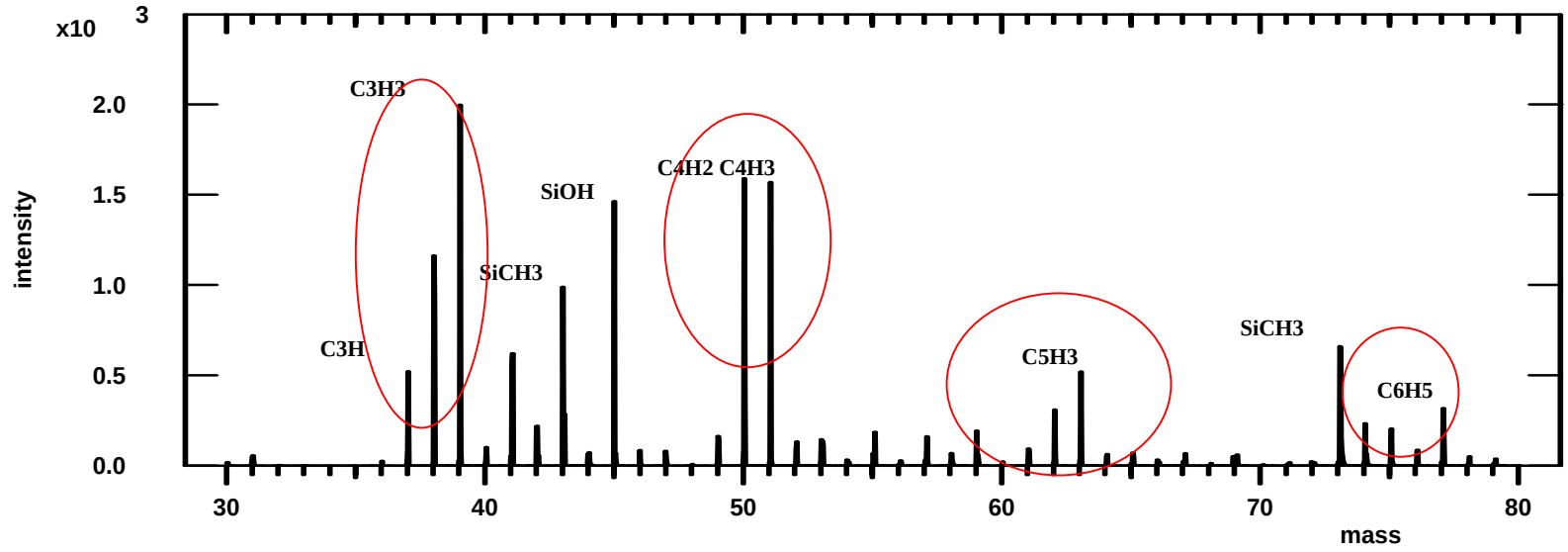
Thick ALD TiN on Oxide

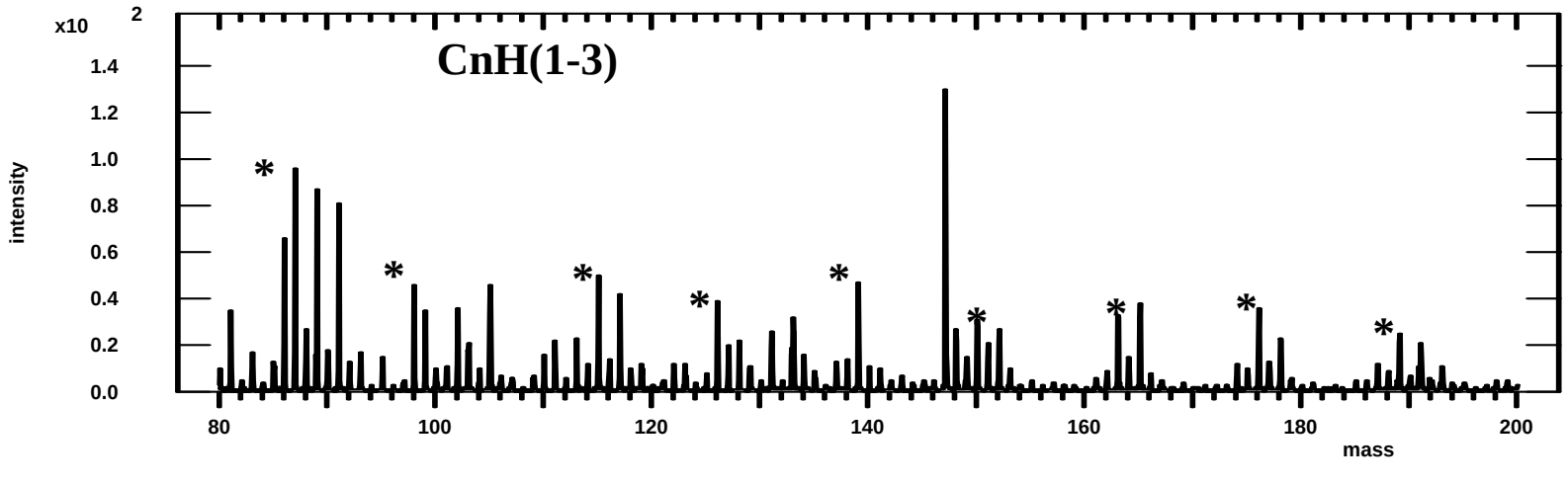
$TiCl_4$ + Si-O-H → ClxTi-O-Si + HCl

ClxTi-O-Si + NH_3 → NHyClzTi-O-Si + HCl



Mass Spectrum of a Polymer ILD: Aromatics





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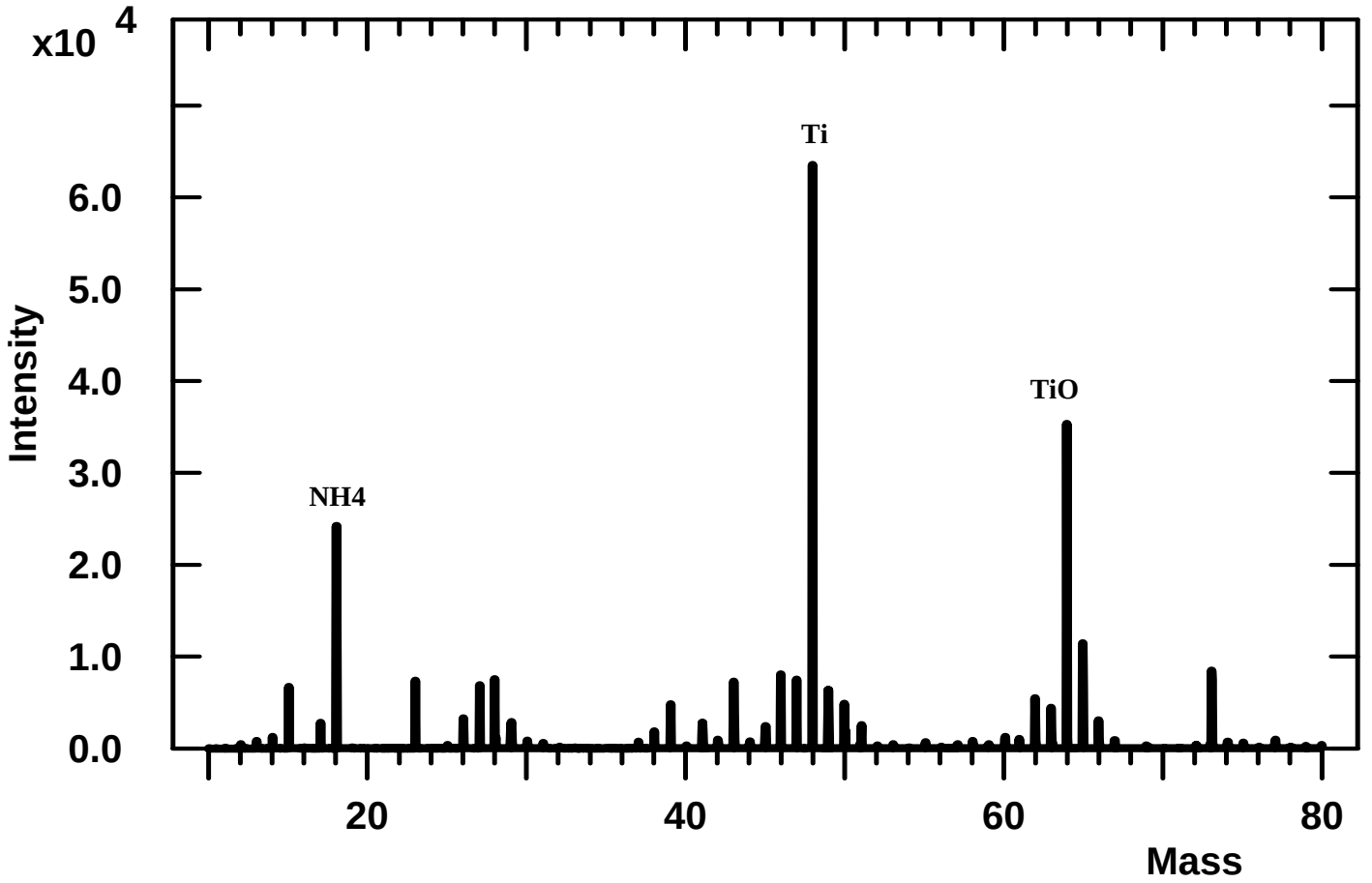
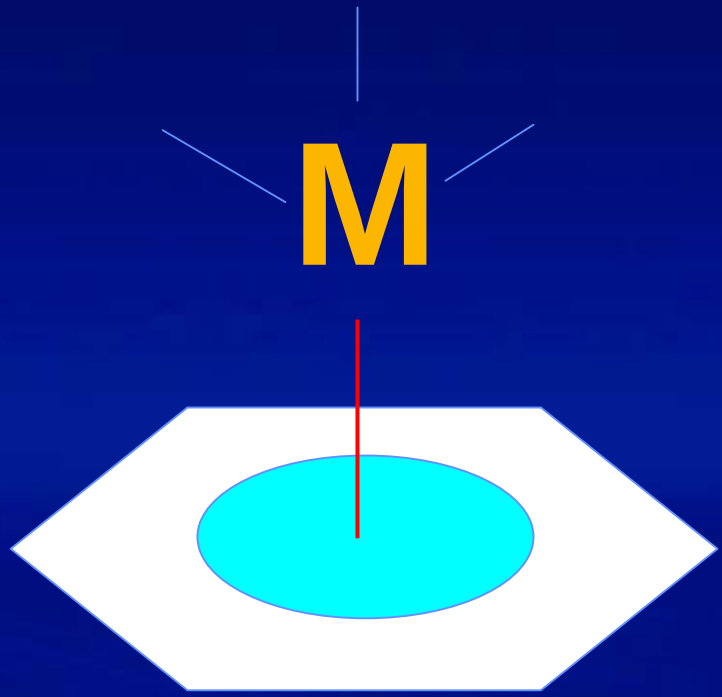
Thick ALD TiN on the Polymer



A Possible Bonding Configuration of Ti to the Aromatics: Coordination with π Electrons



Surface Chemistry Impacts Barrier/ILD Adhesion

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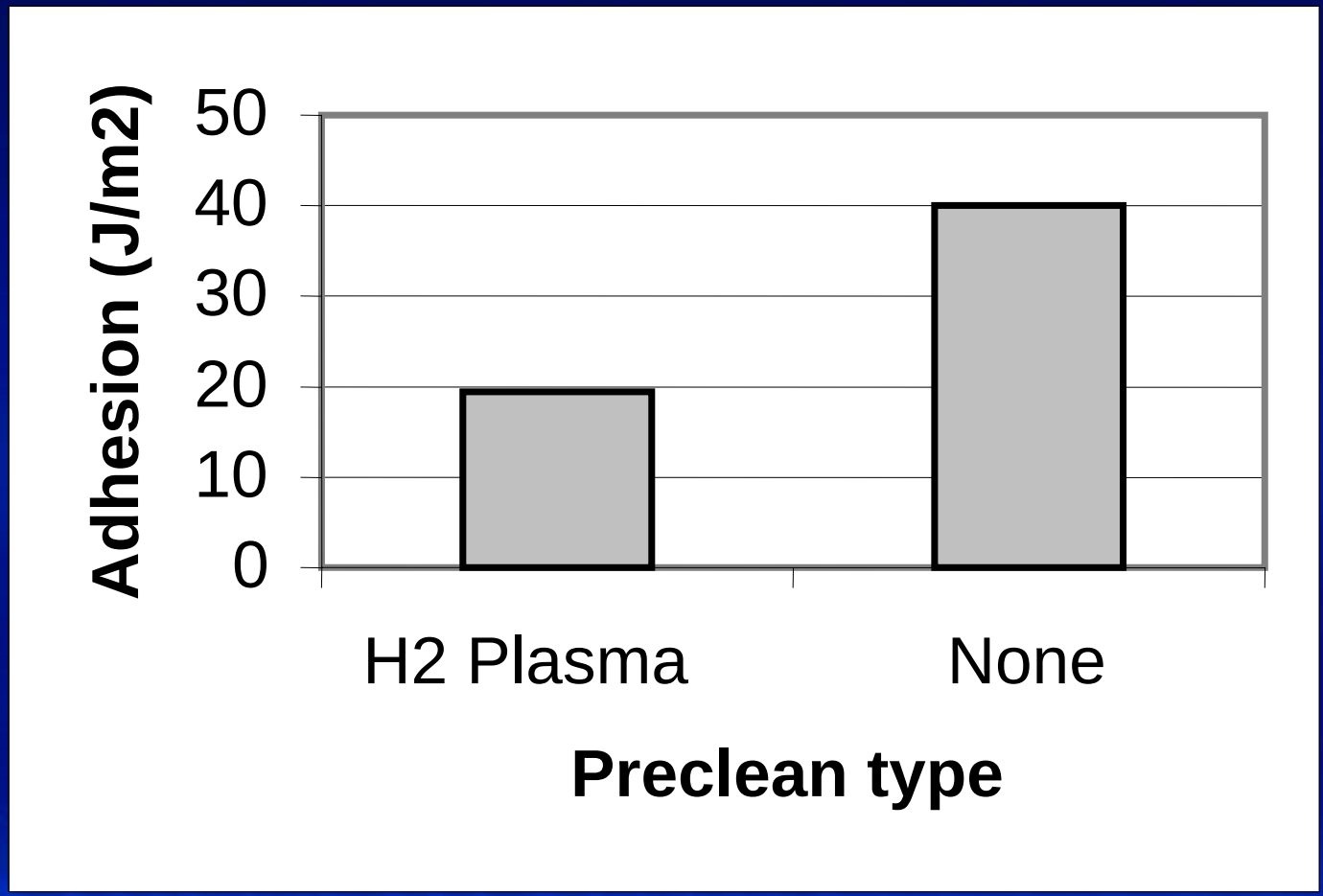
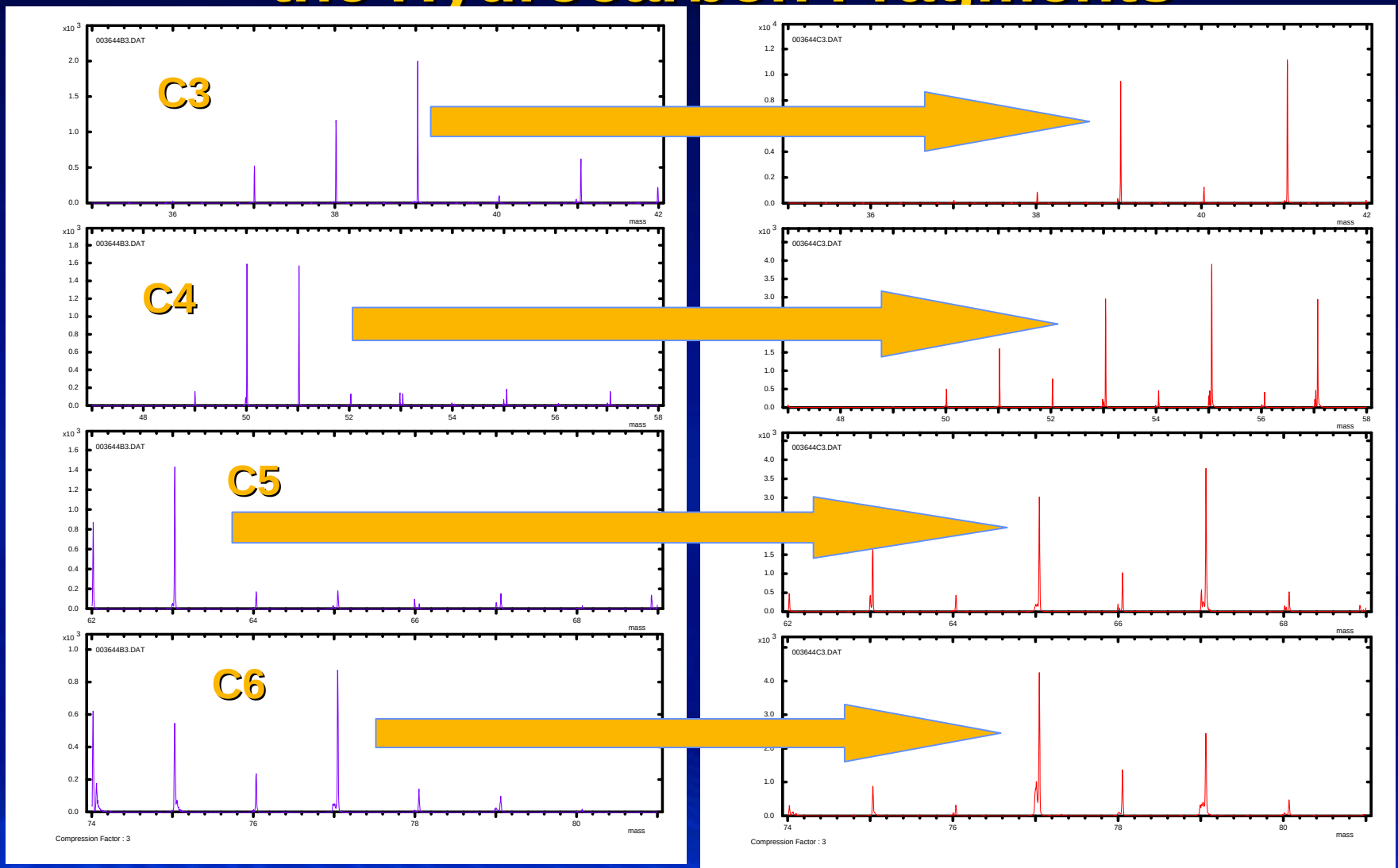
Strong Adhesion between a CVD Ti Based Barrier and the Polymer ILD
H_2 Plasma Pretreatment Degrades Adhesion



H_2 Plasma Treatment Increases H Content in the Hydrocarbon Fragments



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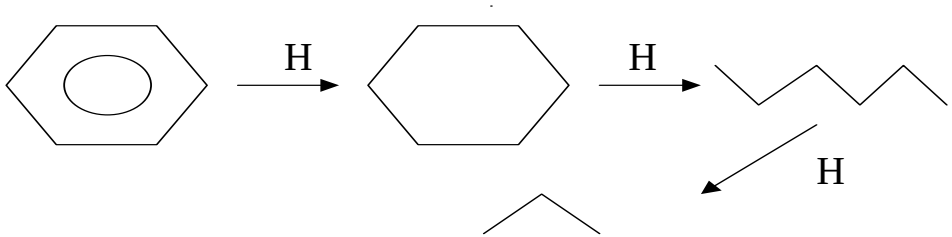
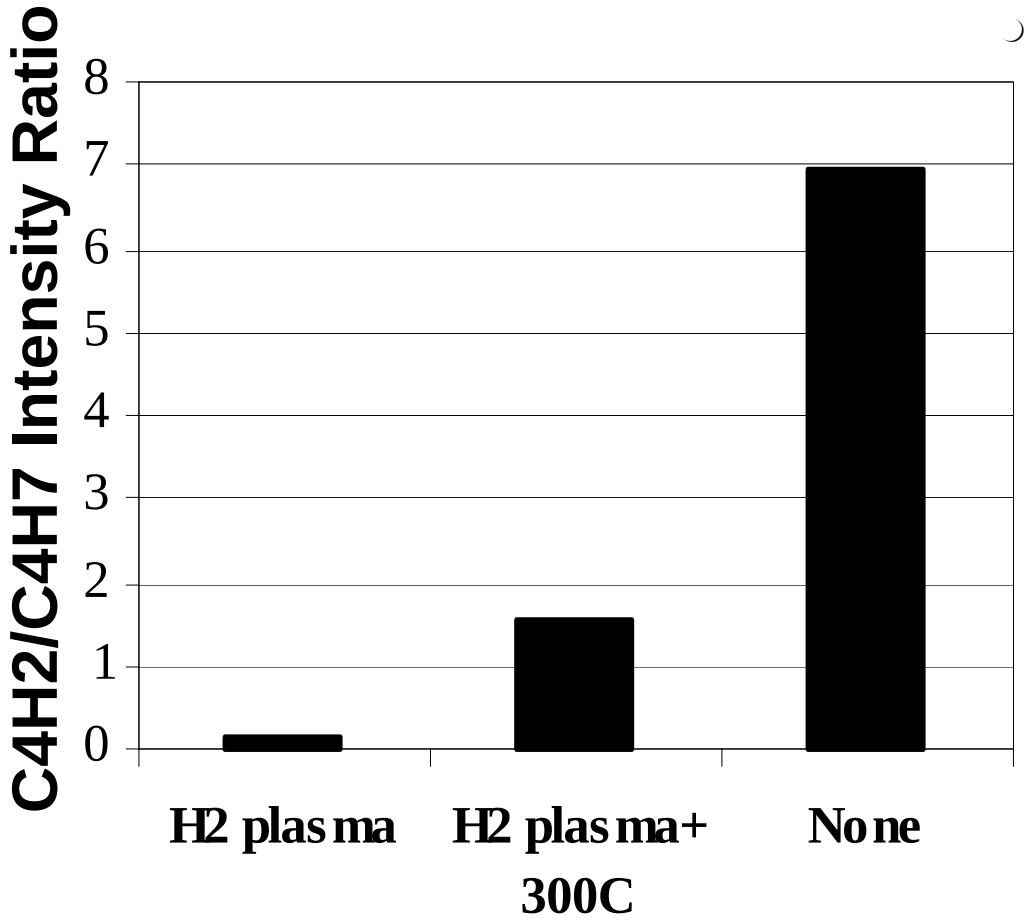
Hydrogenation Pathways
(1) Decrease the Density of π Electrons --Less Bonding between Ti and the Polymer
(2) Reduce Crosslinkng in the Film



Hydrogenated Products are Less Thermally Stable

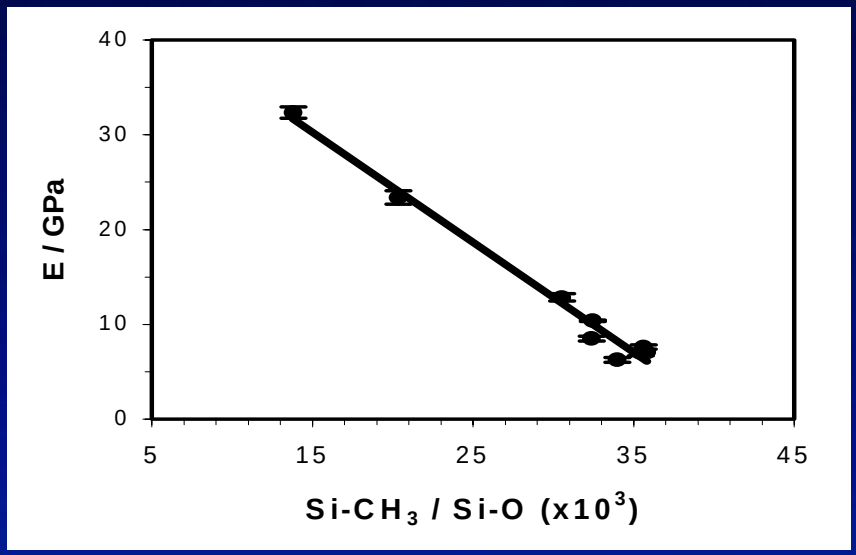


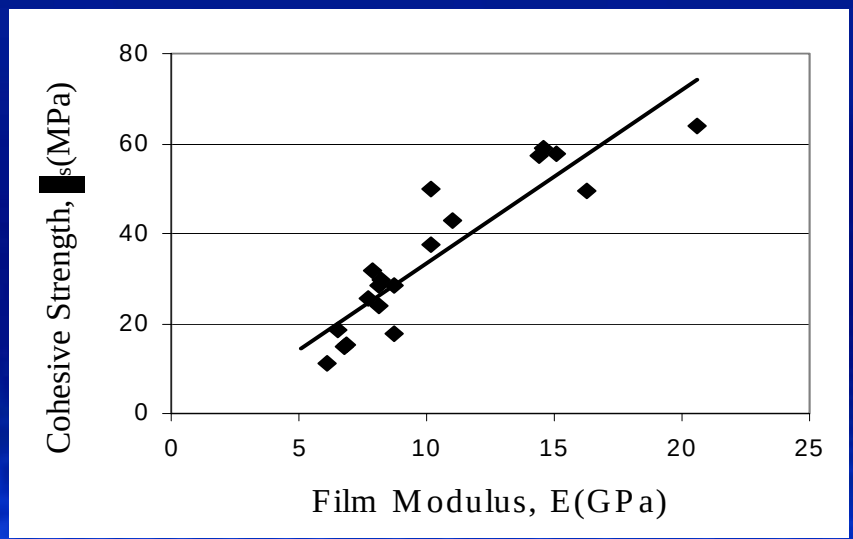
Explains

- Delamnation of the barrier on H_2 treated film upon thermal treatment;
- Reduction/elimination of delamination by 200-400C anneal of H_2 treated film prior to barrier deposition

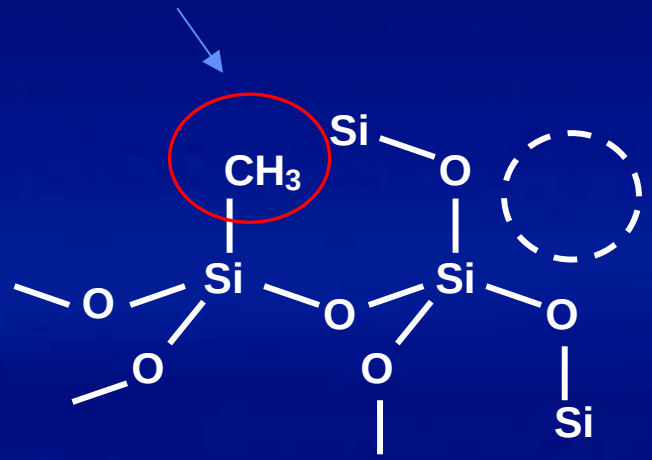
Film Chemistry of the CVD Organosilicate and Mechanical Properties

Modulus and Cohesive Strength Decrease with Higher Si-CH_3 in the Film





Does not contribute to bonding between Si



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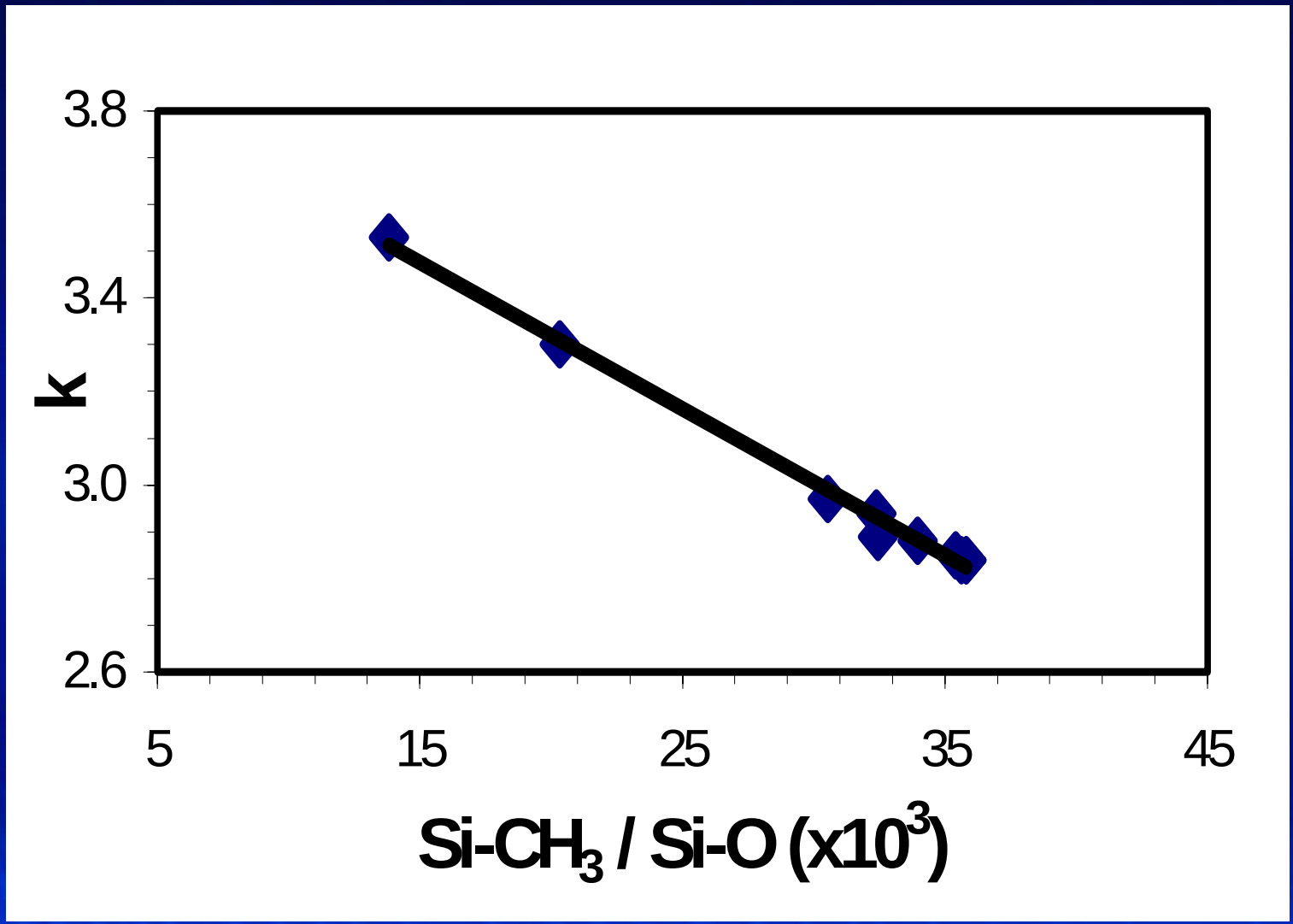
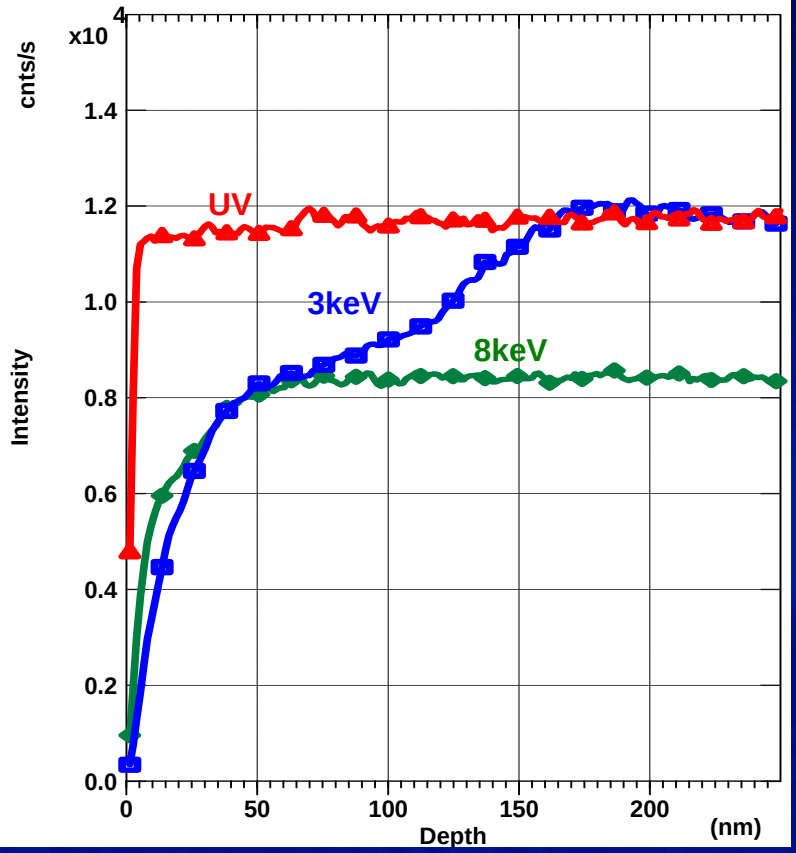
Corresponding with Lower k



E-beam Treatment Reduces Si-CH_3 and Increases Modulus and Hardness



Treatment Conditions	Elastic Modulus (GPa)	Hardness (GPa)
Untreated	9.9 ± 0.1	1.8 ± 0.1
UV-treated	8.5 ± 0.9	1.7 ± 0.1
e-beam treated 8 keV	22.8 ± 0.4	3.1 ± 0.1
e-beam treated 3 keV	12.8 ± 0.4	1.9 ± 0.1

Conclusions

- Surface functional groups of the ILDs dictate the TiN nucleation during ALD process
  - methyl silane groups on organosilicate surface are not active; silanols are needed;
  - Aromatics on polymers active
- Surface hydrogenation of the polymer degrades the barrier/polymer adhesion and thermal stability
  - Less Ti-C coordination
  - Decreased polymer crosslinking
- $SiCH_3$ in the film modulates the film elastic modulus, hardness, cohesive strength as well as dielectric constant.
- Fundamental understanding of chemistry of Cu-Low K interconnect interfaces is critical to technology development.