

MOLECULAR CONTAMINATION OF HIGH-k GATE DIELECTRIC SURFACES

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Presentation Outline

- Sources and effects of molecular contamination
- Research objectives
- Experimental approach
- Results and discussion
 - Adsorption loadings and kinetics on high-k materials
 - Modeling and simulation of adsorption
 - Impact of atmospheric molecular contamination (AMC) on ultrathin film thickness measurement
- Conclusions



Sources and Effects of Molecular Contamination

Moisture (H₂O)

EFFECTS

- Gate oxide deterioration
- Etch rate shifts due to incomplete wetting
- Wafer and optics hazing
- Counter-doping
- Delamination, non-uniform Cu-seed deposition
- Malfunction of epitaxial growth
- Photolithography

Organics from

Chemicals and Personnel

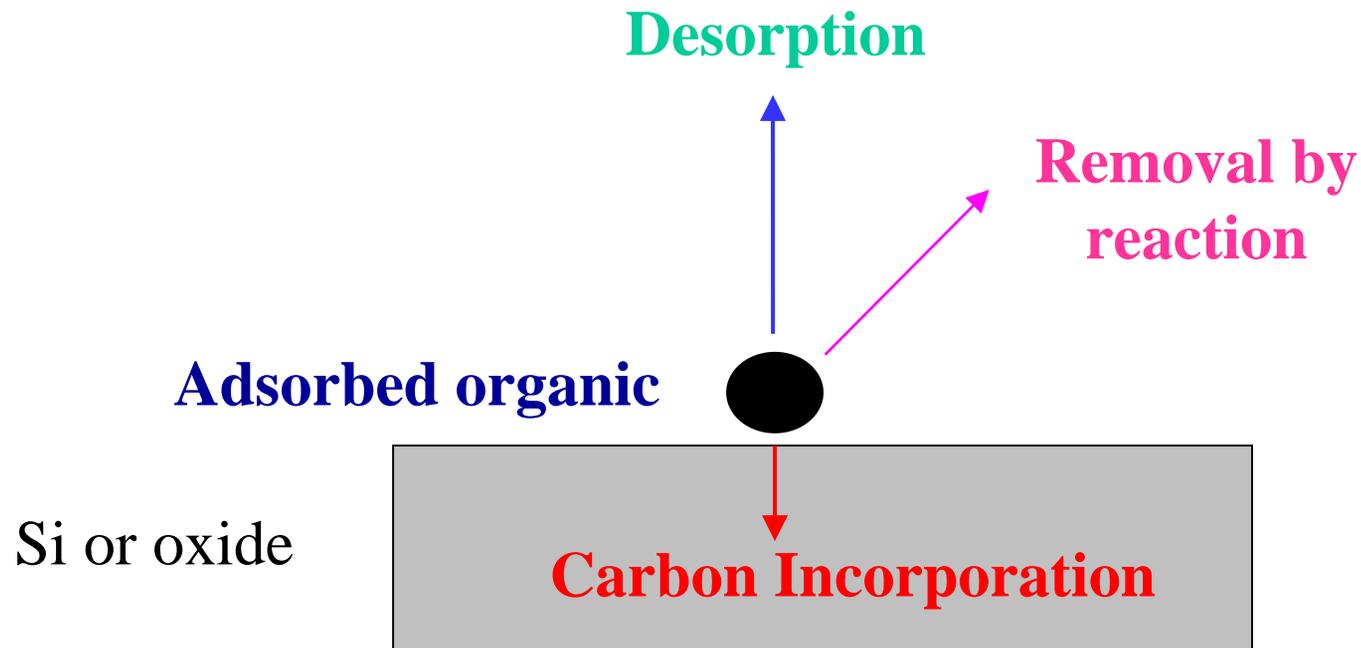
Paints and Filters

Wafer Boxes and Equipment

- ✓ Isopropanol (IPA)
- ✓ Butylated Hydroxy toluene (BHT)
- ✓ Dioctylphthalate (DOP)
- ✓ Amines



Gate Oxide Degradation



- Adsorbed organic can decompose and form carbide
- Defects cause increase in leakage current
- Amount of carbon incorporated depends on
 - temperature and temperature ramp-rate
 - concentration of organics in the gas-phase
 - energetics of the different processes shown above



Key Issues

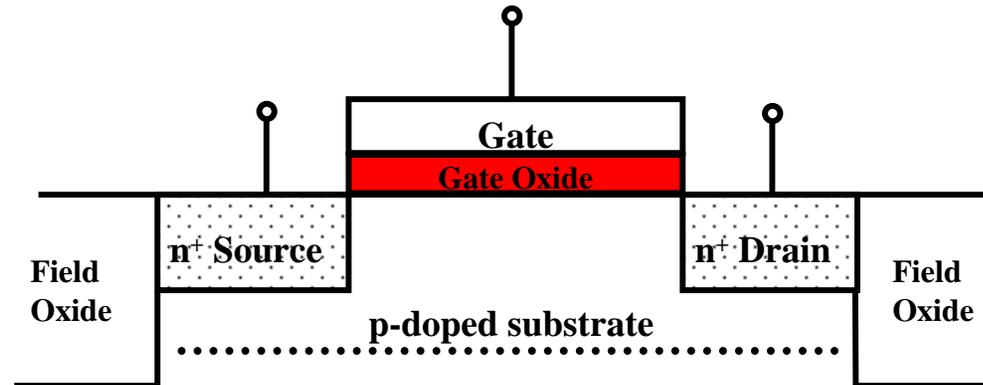
2002 ITRS Roadmap

Year	2001	2004	2008	2011
Technology	<i>130 nm</i>	<i>90 nm</i>	<i>60 nm</i>	<i>40 nm</i>
Organics C atoms / cm ²	2.6 x 10¹³	1.5 x 10¹³	0.7 x 10¹³	0.7 x 10¹³

- SiO₂ gate dielectric thickness in current MOS devices less than 20 Å
- Direct tunneling causes high leakage currents
- Ultrathin oxides highly sensitive to contamination



Limitations of SiO₂ as the Gate Dielectric



- Scaling of device dimensions calls for SiO₂ thinner than 12 Å for future MOS applications
- Key manufacturing related issues are:
 - » Thickness variation: within-wafer, wafer-to-wafer, run-to-run
 - » Penetration of impurities from gate into the dielectric
 - » Lifetime of devices
- Exponential increase in tunneling current with decreasing thickness is the fundamental limit to the scaling of SiO₂-based gate dielectrics



High-k Materials

Replace SiO₂ with a high-k material

Material	Dielectric constant	Bandgap (eV)
SiO ₂	3.9	8.9
Si ₃ N ₄	7	5.1
Al ₂ O ₃	9	8.7
Ta ₂ O ₅	26	4.5
TiO ₂	80	3.5
ZrO ₂	22-30	5.7
HfO ₂	22-35	7.8

- Si₃N₄ and Al₂O₃ are not long term solutions
- Ta₂O₅ and TiO₂ are not thermally stable on Si
- Zirconium and hafnium based materials look promising



Contamination Behavior of High-k Materials

- High-k gate dielectrics may be prone to molecular contamination in a manner similar to SiO_2
- Potential issues associated with molecular contamination of high-k materials:
 - surface roughness and adhesion of films during gate stack formation
 - reduction of overall dielectric constant
 - leakage current
- Characterization of adsorption behavior of new high-k films will assist in deciding their potential for successful integration in silicon MOS technology



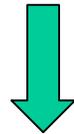
Research Objectives

- Study molecular contamination of high-k materials like HfO_2 and ZrO_2 and compare them with SiO_2
 - Adsorption loadings
 - Kinetics of adsorption/desorption
 - Mechanism of interactions of moisture and organics with wafer surfaces
- Develop fundamental models based on adsorption mechanism to simulate adsorption loading and surface concentration profiles



Method of Approach

Identification of molecular contaminants



Adsorption characteristics

Adsorption loading

Kinetics

Mechanism of interaction



Variables

Temperature

Concentration

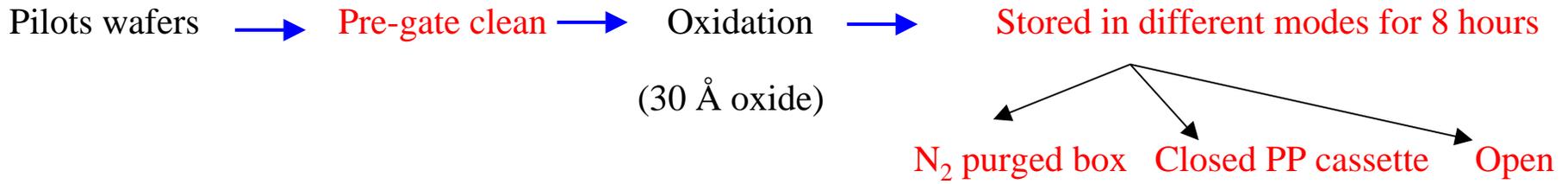


Effect on gate dielectric quality



Identification of Molecular Contaminants Adsorbed on SiO₂

Procedure



Surface Analysis Technique: ToF-SIMS

Contaminants:

Molecules	Peaks	Wafer type
H ₂ O	SiO _x H _y	All
IPA	C ₃ H ₇ O, SiCH ₃ O	All
PDMS	C ₅ H ₁₅ Si ₂ O	All
Amines	N containing species	Open
BHT		

- Storing wafers in N₂-purged boxes reduced contamination but not as much as that achieved by closed boxes
- Amount of molecular contaminants depended on location of wafer in the cassette
- Wafers stored near photolithography and wet benches had highest contamination



Model Contaminants

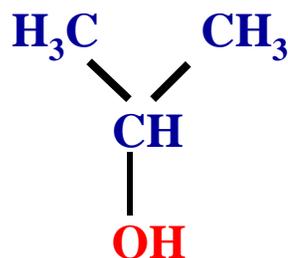
Moisture



Ubiquitous impurity

$\mu = 1.8 \text{ D}$

Isopropanol (IPA)



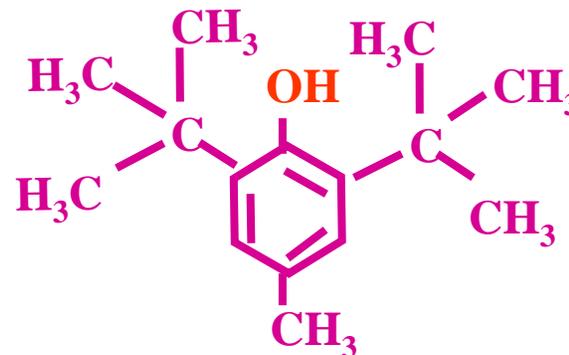
Used as solvent, drying agent

Mol.Wt : 60.10

B.P : 83°C

$\mu = 1.7 \text{ D}$

Butyl Hydroxy Toluene (BHT)



Used as antioxidant

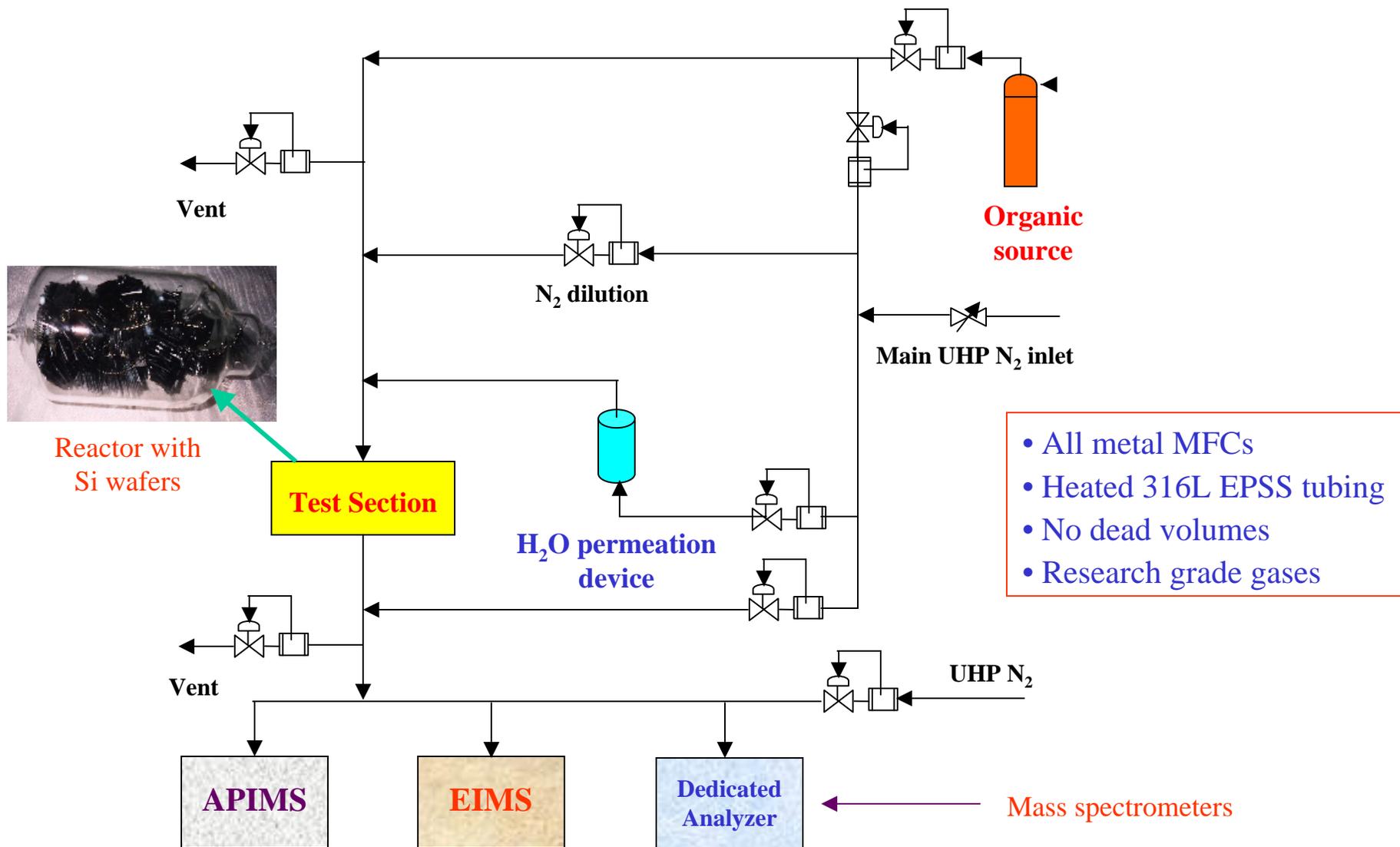
Mol.Wt : 220.35

B.P : 265.2°C

$\mu = 1.5 \text{ D}$

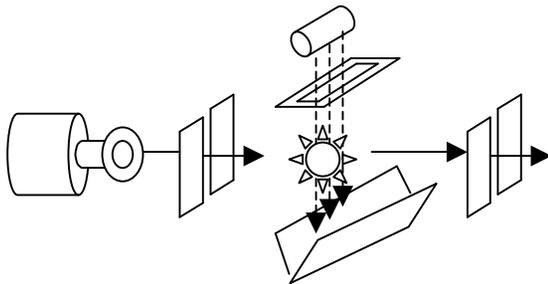


Experimental Setup



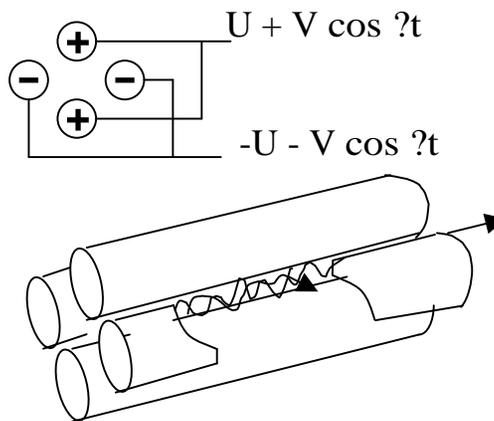
Atmospheric Pressure Ionization Mass Spectrometry (APIMS)

Ionization



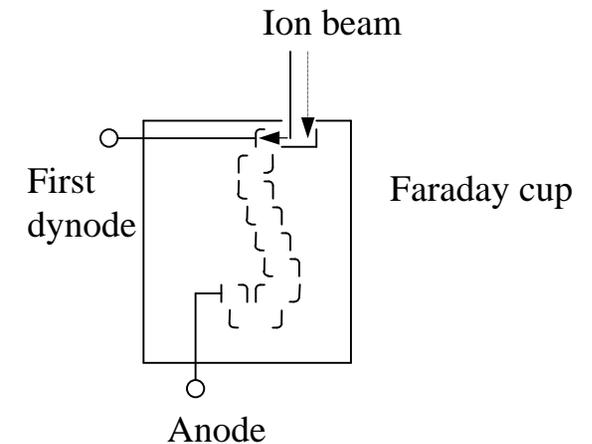
- Ionization by electron impact
- Atmospheric pressure
- High rate of ionization
- High sensitivity (ppt levels)

Separation



- Separation in a quadrupole
- Based on m/e ratio
- 3 quadrupoles enable analysis of peaks with overlapping m/e

Detection



- Electron multiplication by secondary electron emission



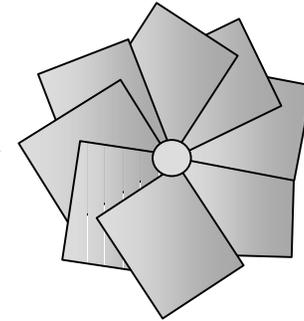
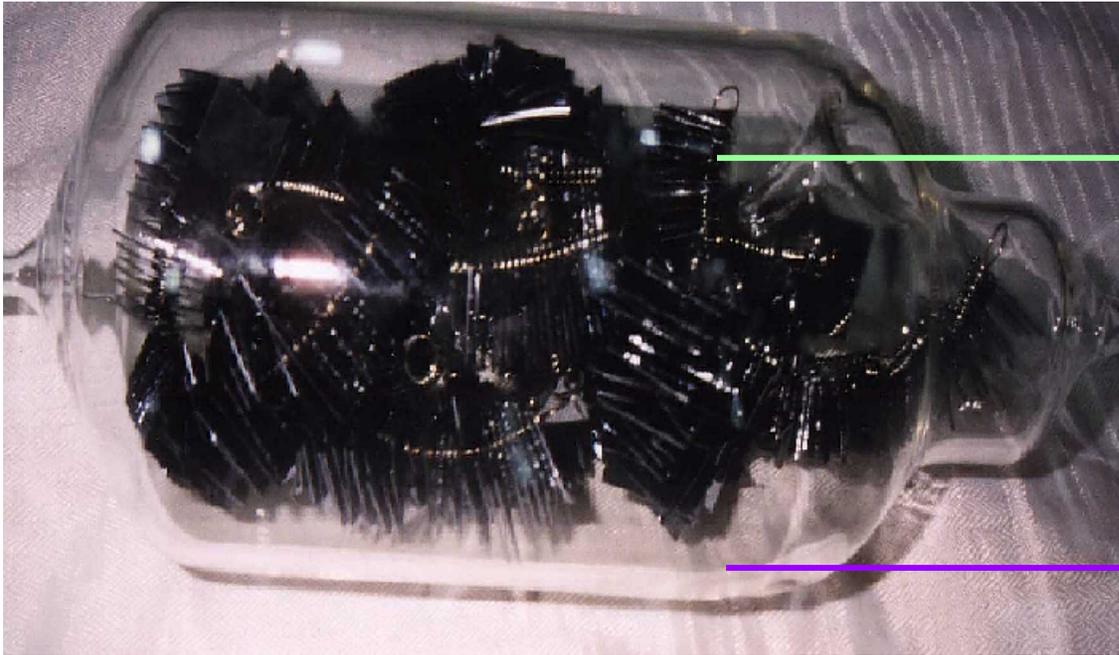
Sample Preparation

➤ Films deposited in a Pulsar[®] 2000 reactor at **ASM America**, Tempe, AZ

Substrate	Czochralski (Cz) grown double-side polished Si-(100)
Deposition method	ALCVD [™] (Trademark of ASM)
Precursors	HfCl ₄ + H ₂ O ZrCl ₄ + H ₂ O
Temperature	300°C
Film thickness	50 Å
Post-deposition treatment	None
Crystallinity	HfO ₂ – amorphous ZrO ₂ – tetragonal polycrystalline



Experimental Reactor



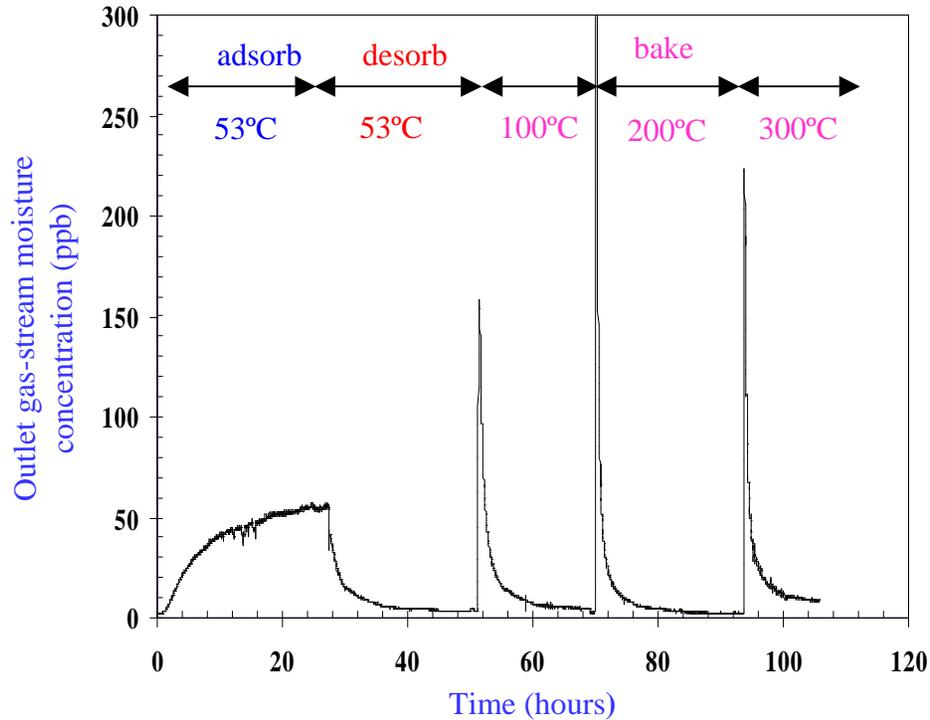
Wafer coupons
loaded on springs

Pyrex reactor

- Wafers diced into 1 cm x 2 cm coupons
- Coupons loaded on nickel coated steel springs and densely packed into a Pyrex[®] glass reactor
- Random orientation and reactor geometry results in good gas mixing
- High wafer to glass surface area ratio



Experimental Procedure



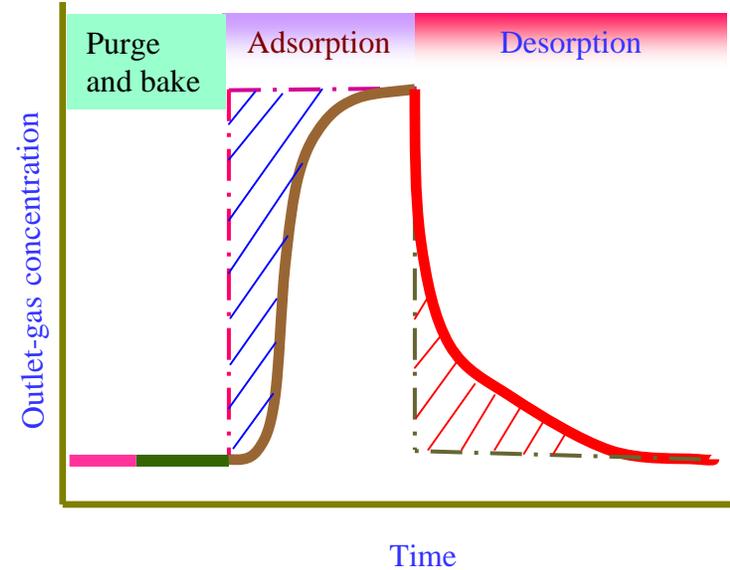
Typical impurity concentration profile at the reactor outlet as measured by mass spectrometer

Experimental procedure

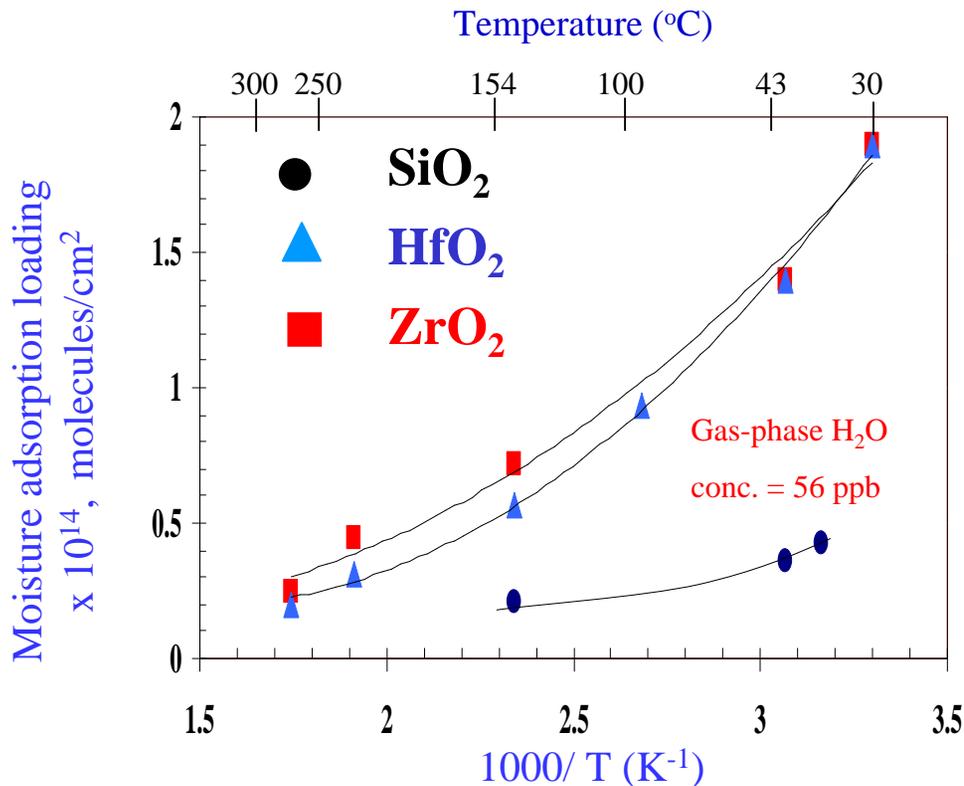
Adsorption at 53°C

Desorption at 53°C

Bake-out at 100, 200 & 300°C



Moisture Adsorption Loading

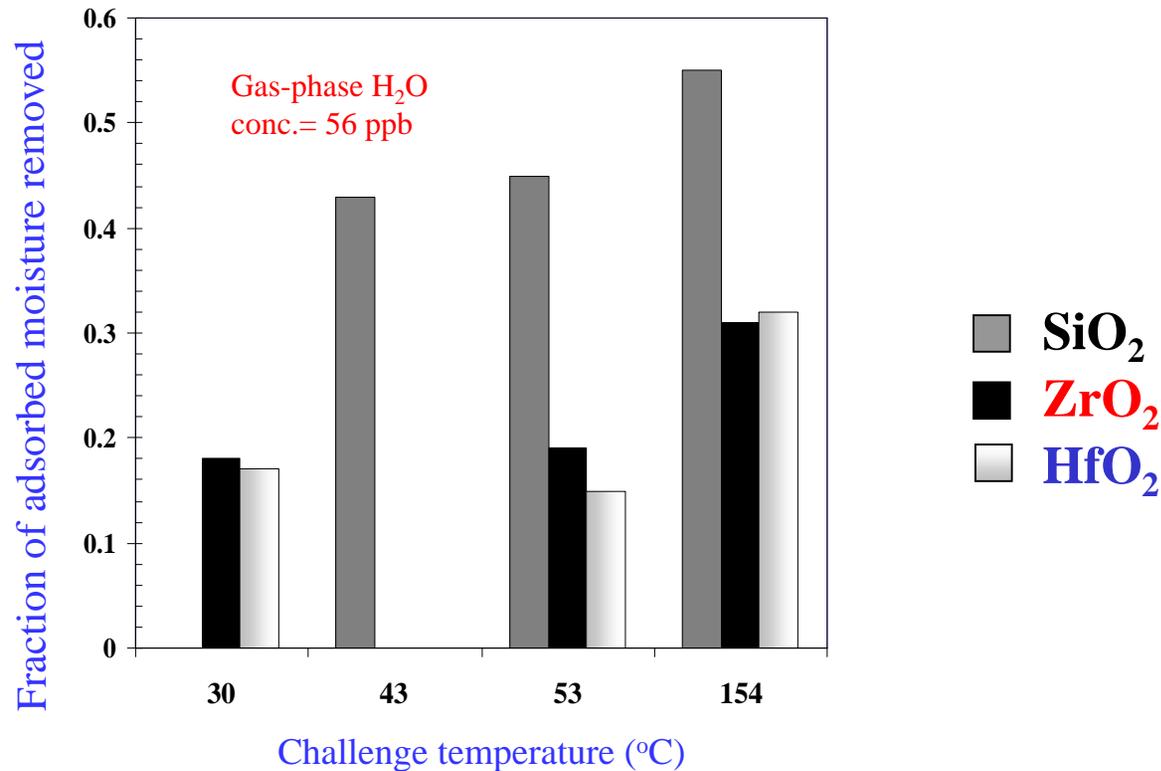


	Si-O	Hf-O/Zr-O
Δ Electronegativity	1.7	2.1
-OH site density (#/cm ²)	4.6×10^{14}	1.0×10^{15}

- HfO₂ and ZrO₂ have higher adsorption loading than SiO₂
- ZrO₂ has higher adsorption capacity than HfO₂ since it is polycrystalline
- Adsorption of moisture on HfO₂ and ZrO₂ is more energetic



Moisture Retention after Isothermal N₂ Purge

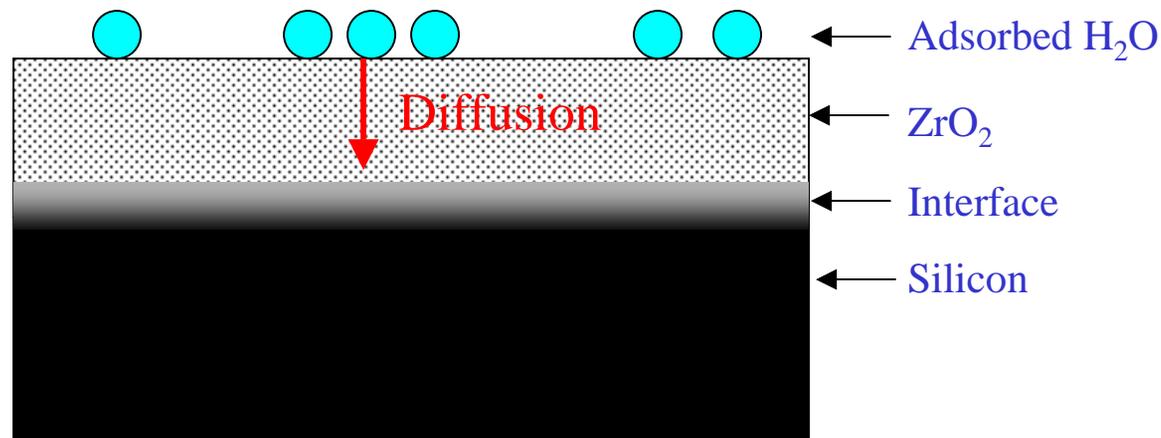


- 45-50 % of adsorbed moisture removed from SiO₂ during isothermal N₂ purge
- Only 20-30 % of adsorbed moisture removed from HfO₂ and ZrO₂



Moisture Retention after Thermal Bake

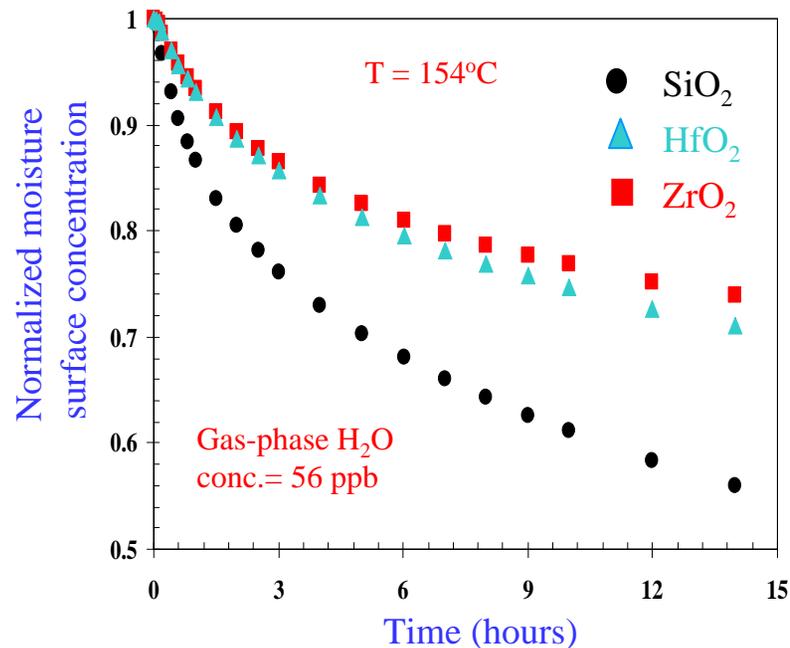
- Reactor baked sequentially to facilitate moisture removal
- Mass balance calculations indicate that 100% of the adsorbed moisture desorbs from SiO_2 & HfO_2 after 300°C bake; whereas
- ZrO_2 surfaces retains some moisture even after 300°C bake; this is detrimental to the gate dielectric quality



- Potential issues associated with moisture contamination of ZrO_2 films:
 - Lowering of dielectric constant during subsequent processing
 - Increase in leakage current



Moisture Desorption Kinetics

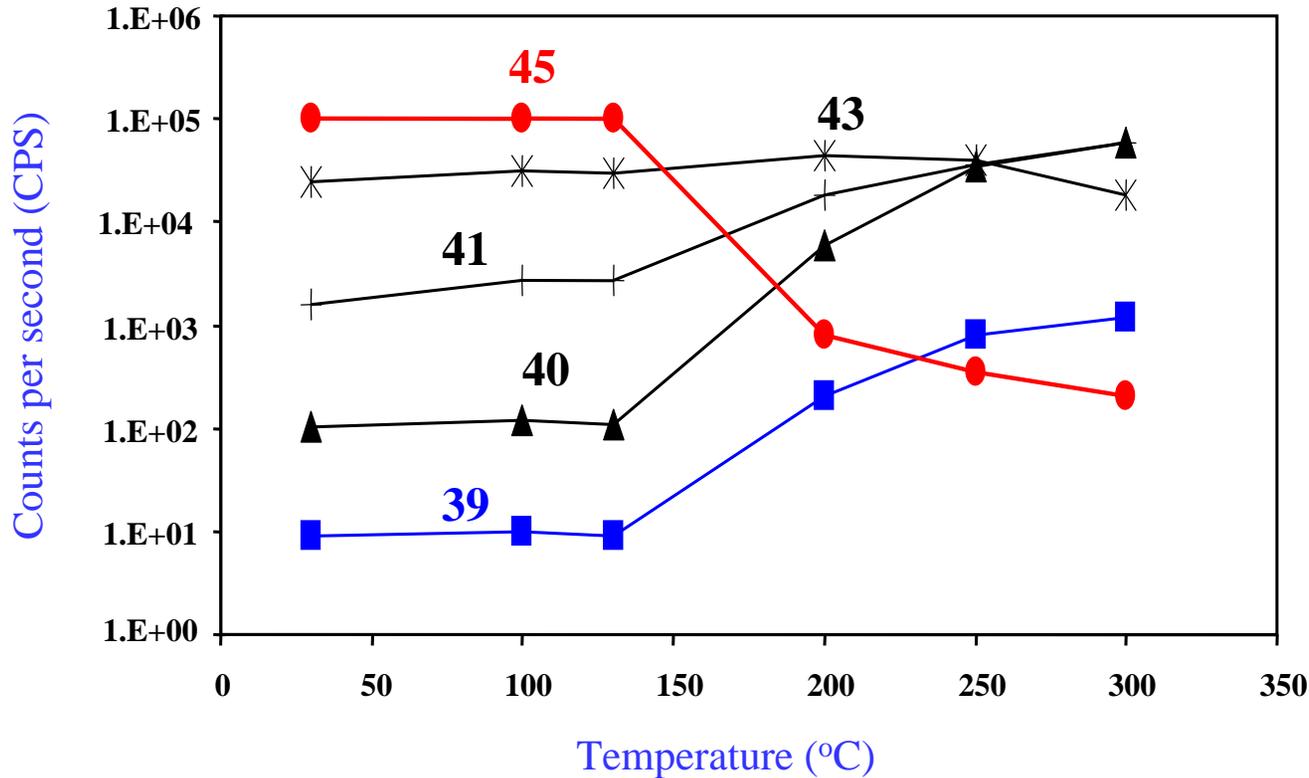


- H_2O desorption kinetics on HfO_2 and ZrO_2 **slower** than on SiO_2
- This highlights the difficulty in removal of H_2O from the new high-k materials
- **Higher bake temperatures** and **longer bake times** would be required to desorb H_2O from HfO_2 and ZrO_2
- Moisture contamination of HfO_2 and ZrO_2 is a serious issue



Decomposition of Isopropanol (IPA)

Mass spectrometer response for HfO₂ exposed to 107 ppb IPA

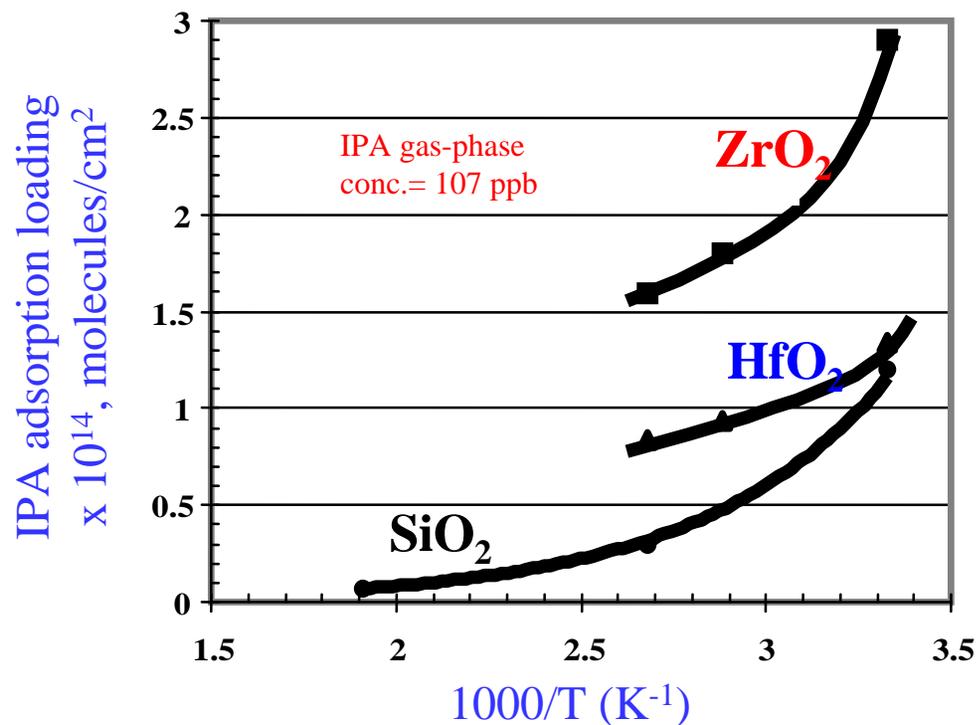


m/e	Fragment
39	C ₃ H ₃ ⁺ (Propene)
40	C ₃ H ₄ ⁺
41	C ₃ H ₅ ⁺
43	C ₃ H ₇ ⁺ , CH ₃ CO ⁺ , N ₃ ⁺
45	C ₂ H ₅ O ⁺ (IPA)

- Count rate of IPA (@ m/e = 45) drop steadily as temperature increases beyond 130°C
- Count rate of propene (@ m/e = 39, 41) increases simultaneously



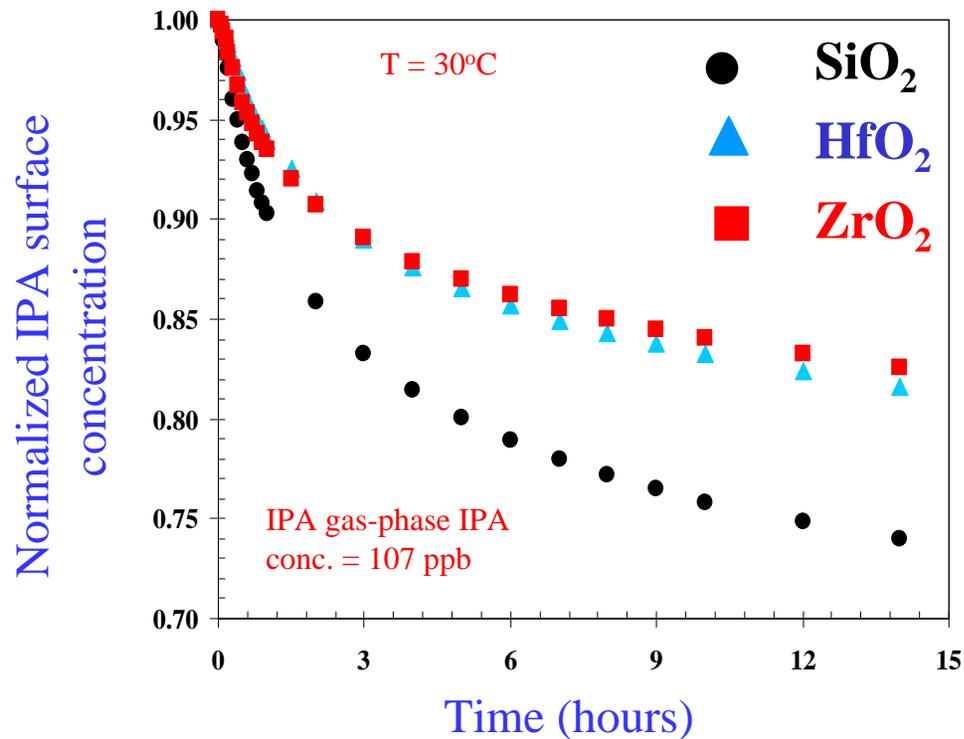
IPA Adsorption Loading



- HfO₂ and ZrO₂ have higher IPA adsorption loading than SiO₂
- IPA loading order: ZrO₂ > HfO₂ > SiO₂
- Same trend was observed over a wide range of concentrations



IPA Desorption Kinetics



- Desorption of IPA is **slower** on HfO₂ and ZrO₂
- Difference in IPA desorption kinetics between HfO₂ and ZrO₂ is relatively smaller than that between HfO₂ and SiO₂ or ZrO₂ and SiO₂
- Removal of IPA from HfO₂ and ZrO₂ films take longer time
- Behavior of other **polar organics** like BHT and DOP can be expected to be similar to that of IPA

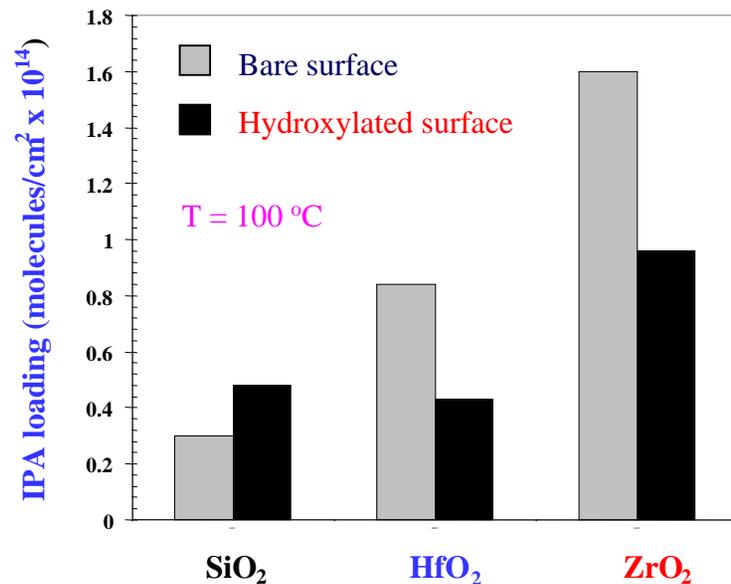


Effect of Pre-Adsorbed Moisture on IPA Loading

Experimental Procedure

Step 1. Moisture challenge (conc: 56 ppb)

Step 2. IPA challenge (conc: 107 ppb)

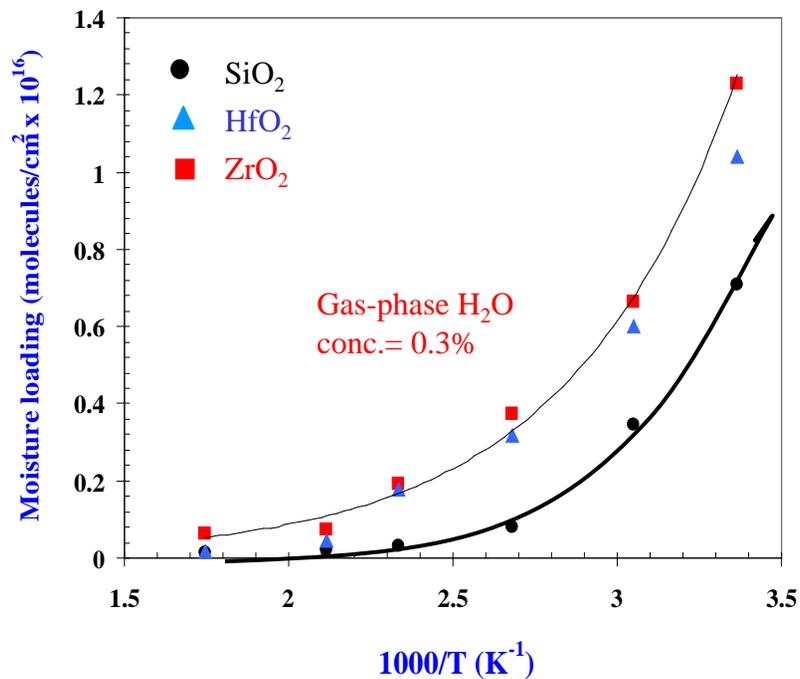


- Presence of one contaminant can affect adsorption/desorption characteristics of other
- Moisture hydroxylates oxide surfaces; the hydroxyl groups **change the nature** of the surface
- Pre-adsorbed moisture **enhances** IPA adsorption on **SiO₂**, but **reduces** IPA adsorption on **HfO₂** and **ZrO₂**
- IPA is more attracted to bare HfO₂ and ZrO₂ surfaces than to hydroxylated surfaces. Presence of H₂O reduces their affinity for IPA



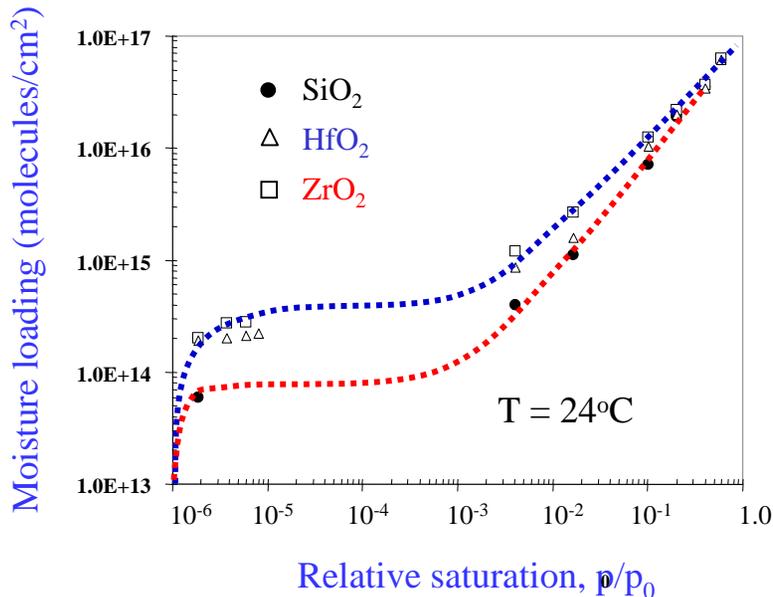
High Concentration Moisture Contamination

- Moisture source: Gas bubbler
- Data acquisition: Electron Impact Mass Spectrometer (EIMS)
- Moisture levels in cleanroom air: High ppm to percentage levels
- H₂O loading order: ZrO₂ > HfO₂ > SiO₂
- Loading values indicate that multiple layers formed

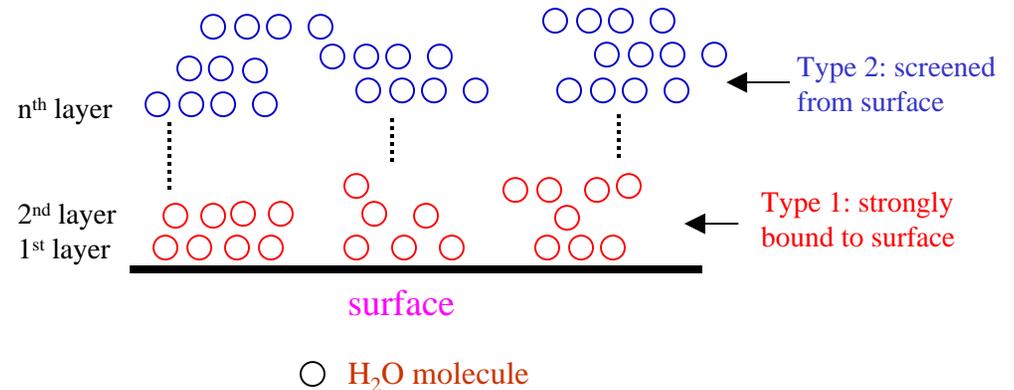


Effect of Concentration on Moisture Loading

Typical BET adsorption isotherm



Schematic illustration of multilayer adsorption



- Adsorption loading first saturates at a particular level and then again increases indefinitely, **similar to BET**
- Loading values indicate formation of **multiple layers**
- Difference in loading between $\text{HfO}_2/\text{ZrO}_2$ and SiO_2 is **higher initially at low surface coverage**, but decreases gradually
- As the surface gets covered with multiple layers, the **subsequent molecules get screened** from the surface

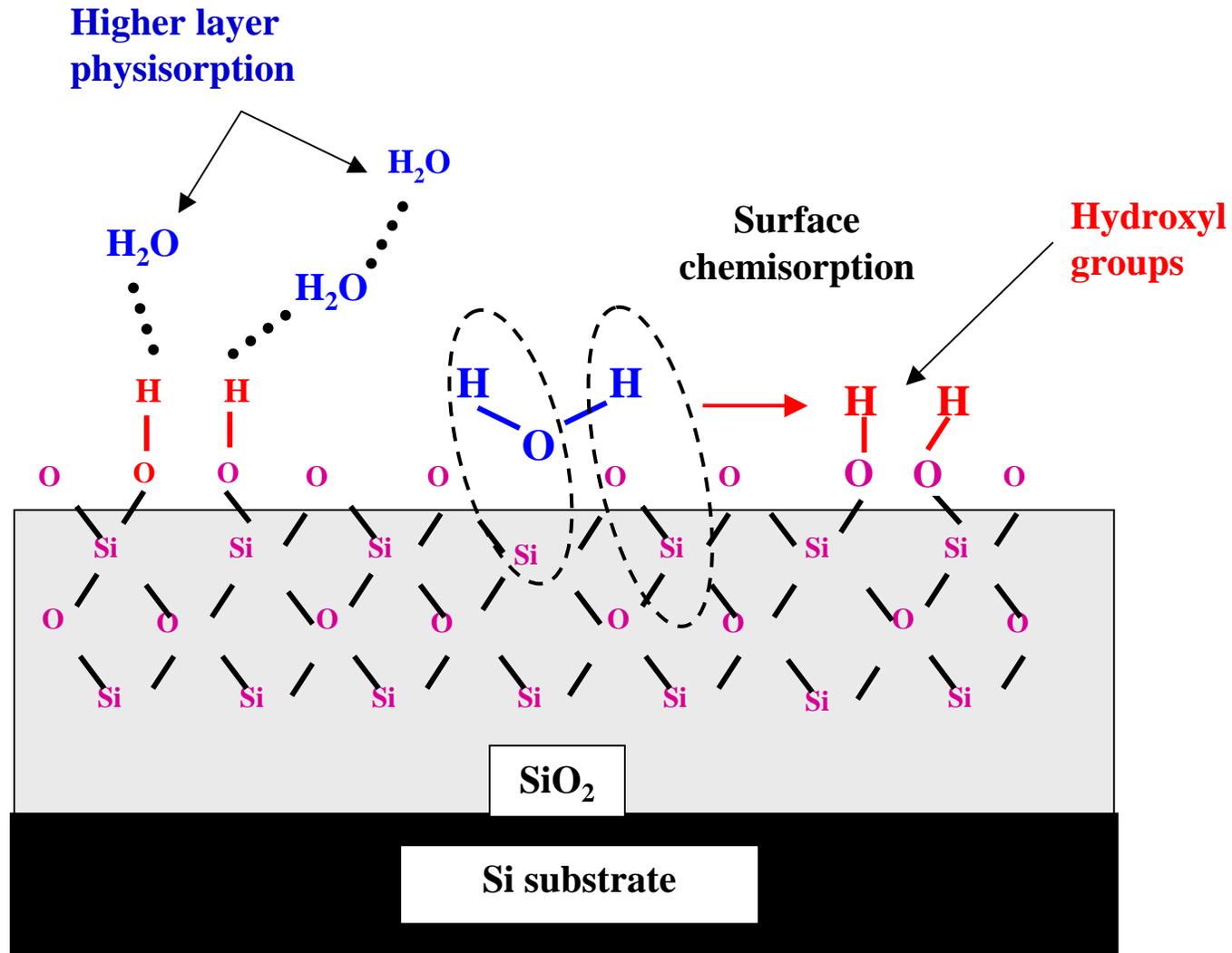


Simulation of Adsorption/Desorption Profiles

- Study mechanism of adsorption/desorption
- Develop rate expressions based on the mechanism
- Validate the model by fitting it to experimental data
- Estimate rate parameters (rate constants and activation energies)
- Use model to simulate concentration profiles and adsorption loading
- Application: Optimization of process conditions to reduce effect of molecular contamination



Mechanism of Multilayer Adsorption of Moisture



Development of Adsorption Model

Type	Reaction	Species balance equations
Chemisorption	$H_2O + 2X \xrightleftharpoons[kd0]{ka0} 2X - OH$	$\frac{d[XOH]}{dt} = 2 * ka0 * C_g * [X]^2 - 2 * kd0 * [XOH]$
Physisorption	$H_2O + X - OH \xrightleftharpoons[kd1]{ka1} S$	$\frac{d[S]}{dt} = ka1 * C_g * (1 - [X]) - kd1 * [S]$
		$[X] + [XOH] = 1$

CSTR (Mixed Reactor) Model



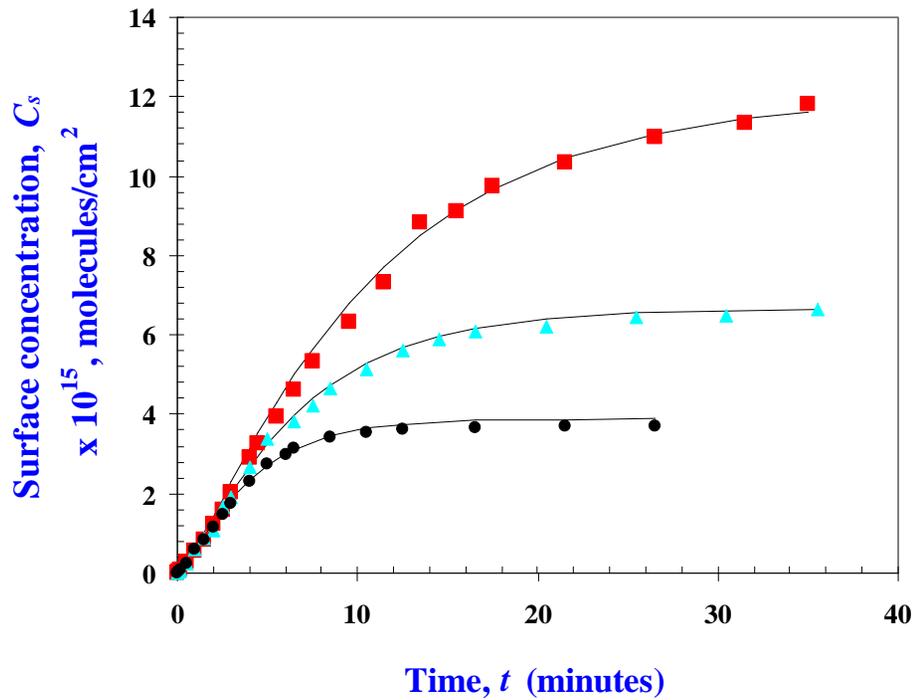
$$\frac{dC_g}{dt} = \frac{Q}{V} (C_{gin} - C_g) - \frac{A}{V} \cdot r$$

- Q = Volumetric flow rate
- C_g = Gas-phase concentration
(moisture or organic)
- C_{gin} = Inlet-gas concentration
- V = Reactor volume
- r = Net rate of adsorption

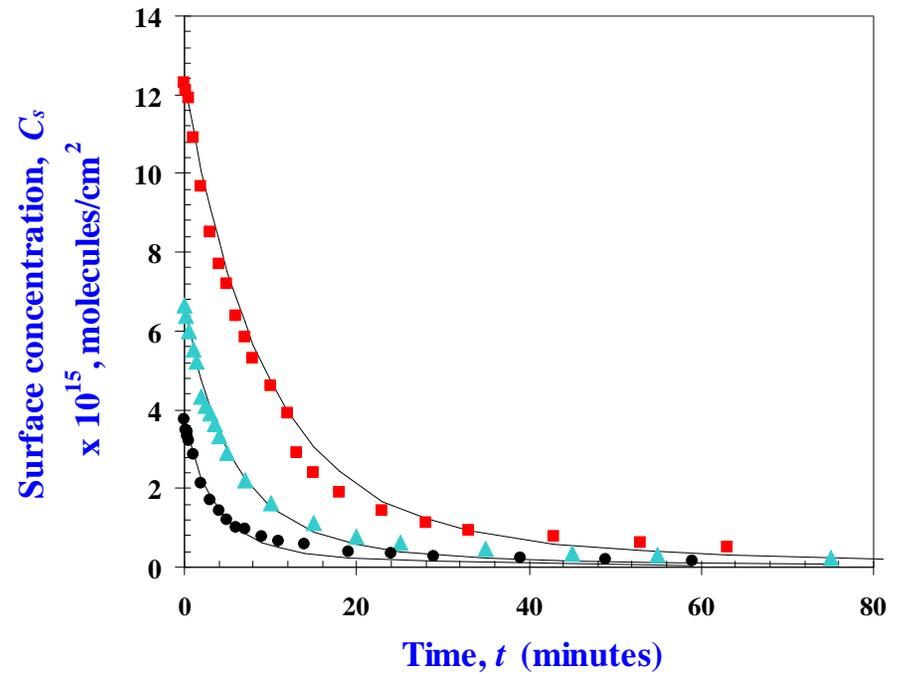


Validation of Model

- Model
- 24 °C experimental data on ZrO₂
- ▲ 55 °C experimental data on ZrO₂
- 100 °C experimental data on ZrO₂



Adsorption

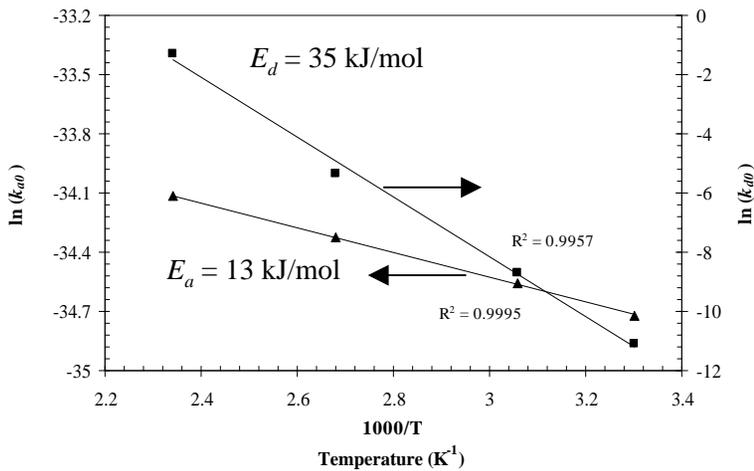


Desorption

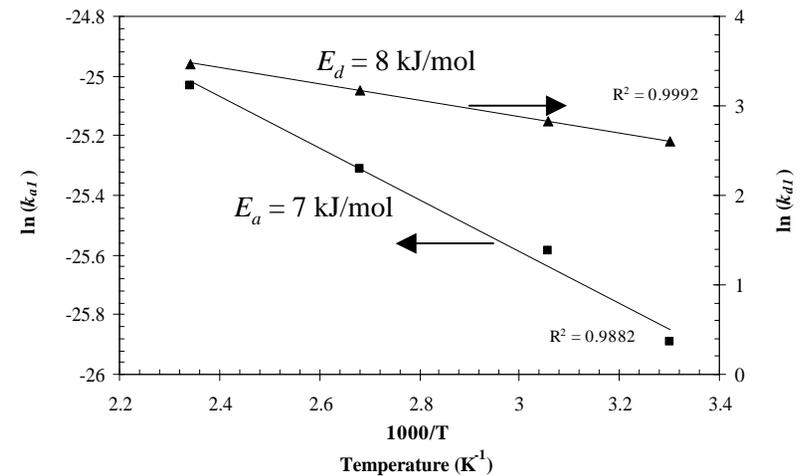


Rate Parameters for Adsorption of Moisture

Process	Symbols	Units	SiO ₂ @ 30 °C	HfO ₂ @ 30 °C	ZrO ₂ @ 30 °C	Order
Surface chemisorption	K_{a0}	cm ³ /min	5.0 x 10 ⁻¹⁶	7.2 x 10 ⁻¹⁶	6.8 x 10 ⁻¹⁶	HfO ₂ , ZrO ₂ > SiO ₂
	K_{d0}	1/min	0.04	0.00004	0.00003	HfO ₂ , ZrO ₂ < SiO ₂
Higher layer physisorption	K_{a1}	cm ³ /min	1.2 x 10 ⁻¹⁴	5.7 x 10 ⁻¹²	6.1 x 10 ⁻¹²	HfO ₂ , ZrO ₂ > SiO ₂
	K_{d1}	1/min	13.6	13.4	14	HfO ₂ , ZrO ₂ ~ SiO ₂



Arrhenius plots



Energetics of Adsorption of Moisture

Process	Symbols	Units	SiO ₂	HfO ₂	ZrO ₂	Order
Surface chemisorption	E_{a0}	kJ/mol	21	13	11	HfO ₂ , ZrO ₂ < SiO ₂
	E_{d0}	kJ/mol	29	35	40	HfO ₂ , ZrO ₂ > SiO ₂
Higher layer physisorption	E_{a1}	kJ/mol	6	7	7	HfO ₂ , ZrO ₂ ~ SiO ₂
	E_{d1}	kJ/mol	11	8	8	HfO ₂ , ZrO ₂ ~ SiO ₂

- Activation energy of surface chemisorption on HfO₂ and ZrO₂ is **lower** than that on SiO₂
- Activation energy of desorption of chemisorbed moisture from HfO₂ and ZrO₂ is **higher** than that from SiO₂
- ZrO₂ forms the **strongest** metal-hydroxyl (M-OH) bond
- Energetics of moisture physisorption on higher layers are the **same** for all 3 oxides since it is not influenced by the nature of the surface



Energetics of Adsorption of IPA

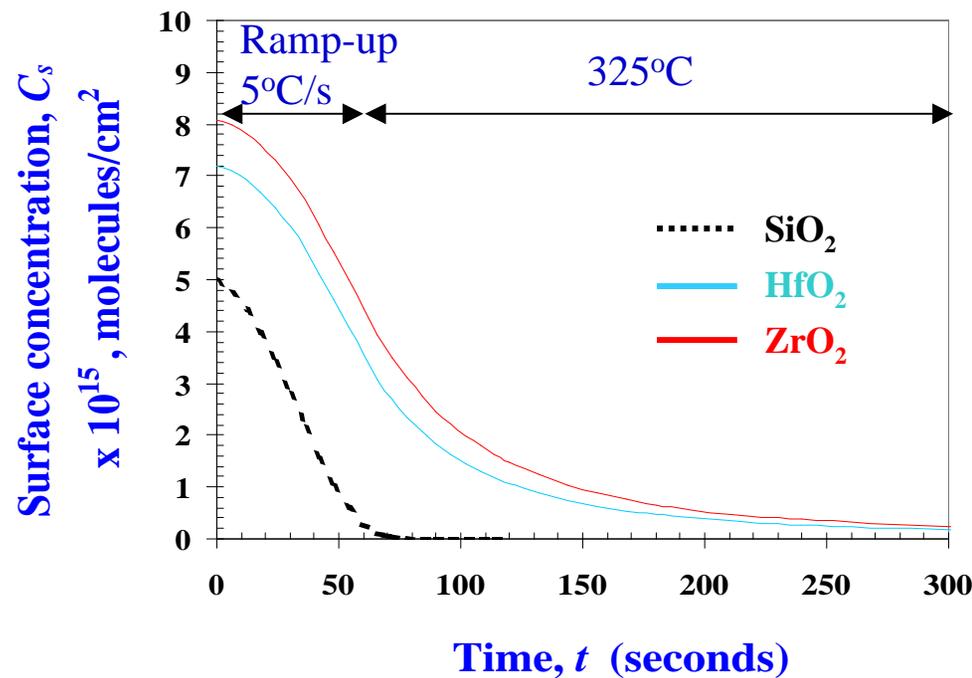
Process	Symbols	Units	SiO ₂	HfO ₂	ZrO ₂	Order
Surface adsorption	E_{a0}	kJ/mol	3	9	17	HfO ₂ , ZrO ₂ > SiO ₂
	E_{d0}	kJ/mol	11	14	19	HfO ₂ , ZrO ₂ > SiO ₂
Higher layer adsorption	E_{a1}	kJ/mol	6	7	7	HfO ₂ , ZrO ₂ ~ SiO ₂
	E_{d1}	kJ/mol	8	9	11	HfO ₂ , ZrO ₂ ~ SiO ₂

- Activation energies of adsorption of IPA on SiO₂, HfO₂ and ZrO₂ follow the same trend as that for H₂O
- Values of activation energy of surface adsorption indicate that IPA only **physisorbs** on bare oxide surfaces



Practical Applications of Model

- Model describes actual processes and explains experimental results
- It is a practical tool for
 - estimation of surface contamination and
 - optimization of process conditions to minimize effects of molecular contamination

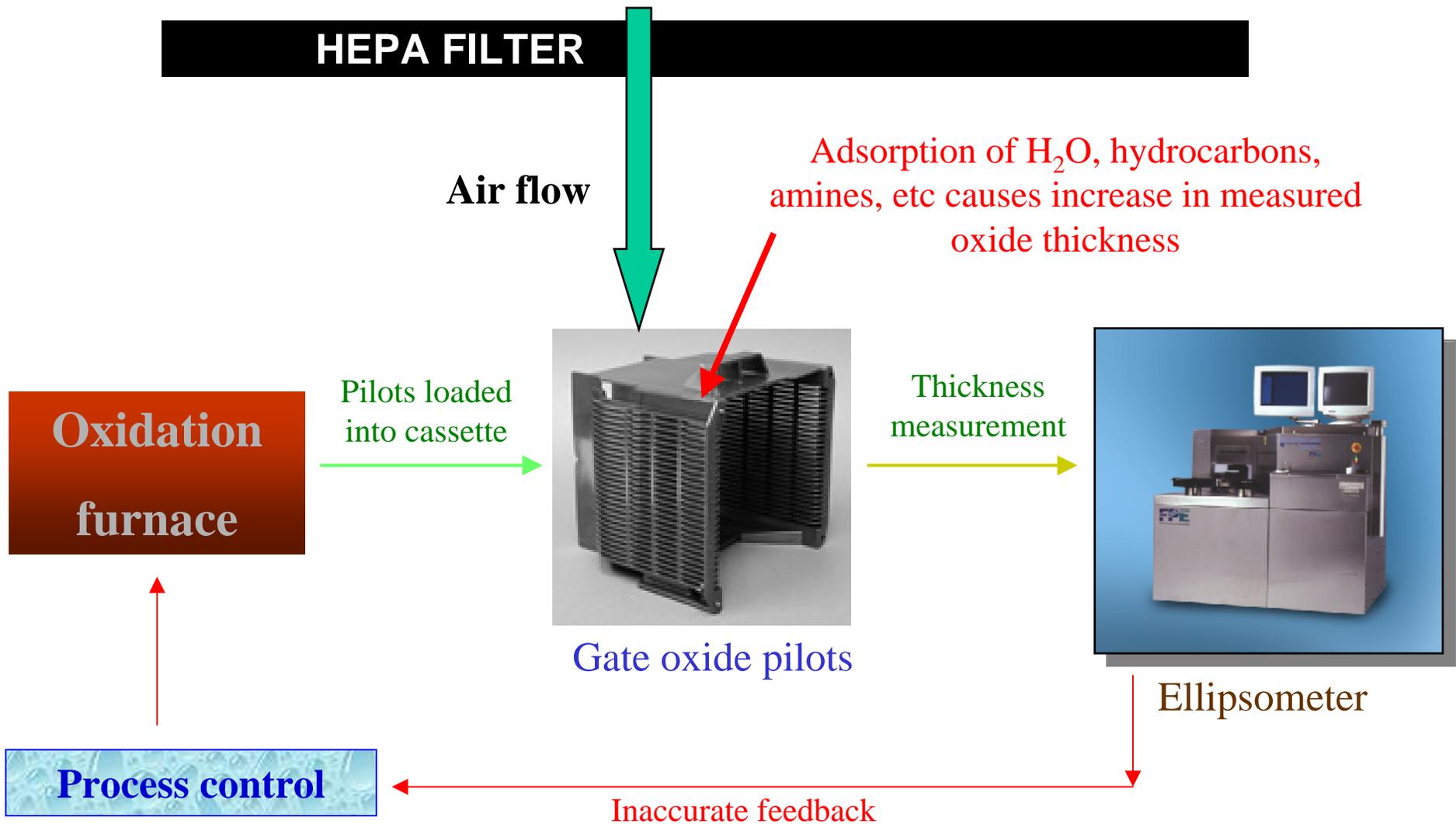


Gas-phase H_2O concentration = 0.2 %

Adsorption temperature = 24°C

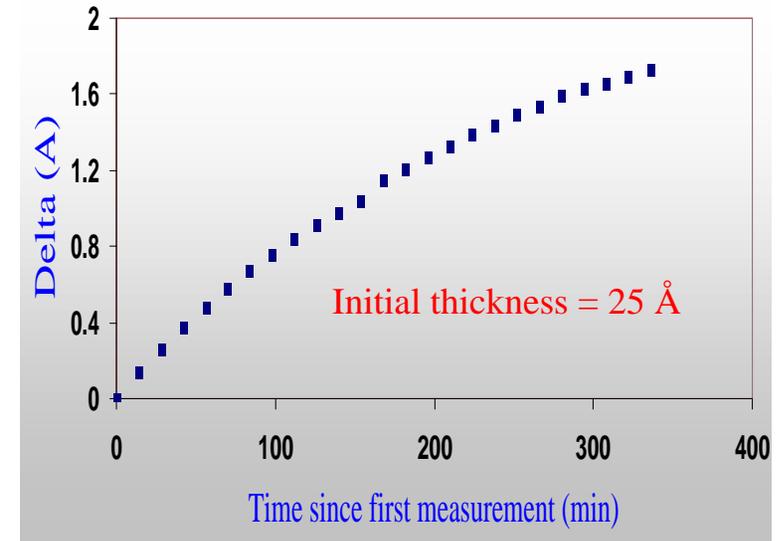


Impact of Molecular Contamination on Optical Thickness Measurement of Gate Oxide Pilot Wafers



Apparent Increase in Thickness Measurement of Gate Oxide Pilot Wafers due to Molecular Contamination

- Inevitable delay time between gate oxidation and pilot thickness measurement
- Adsorption of molecules from the cleanroom air results in the formation of the so-called “environmental film” (EF)
- Results in an **apparent increase** in optical thickness measurement
- Adsorption of contaminants is **not uniform** across the wafer
- Thickness measured apparently has **higher standard deviation (s)**
- The apparent change in thickness varies from wafer-to-wafer and run-to-run; this results in an **incorrect feedback** to the process controller

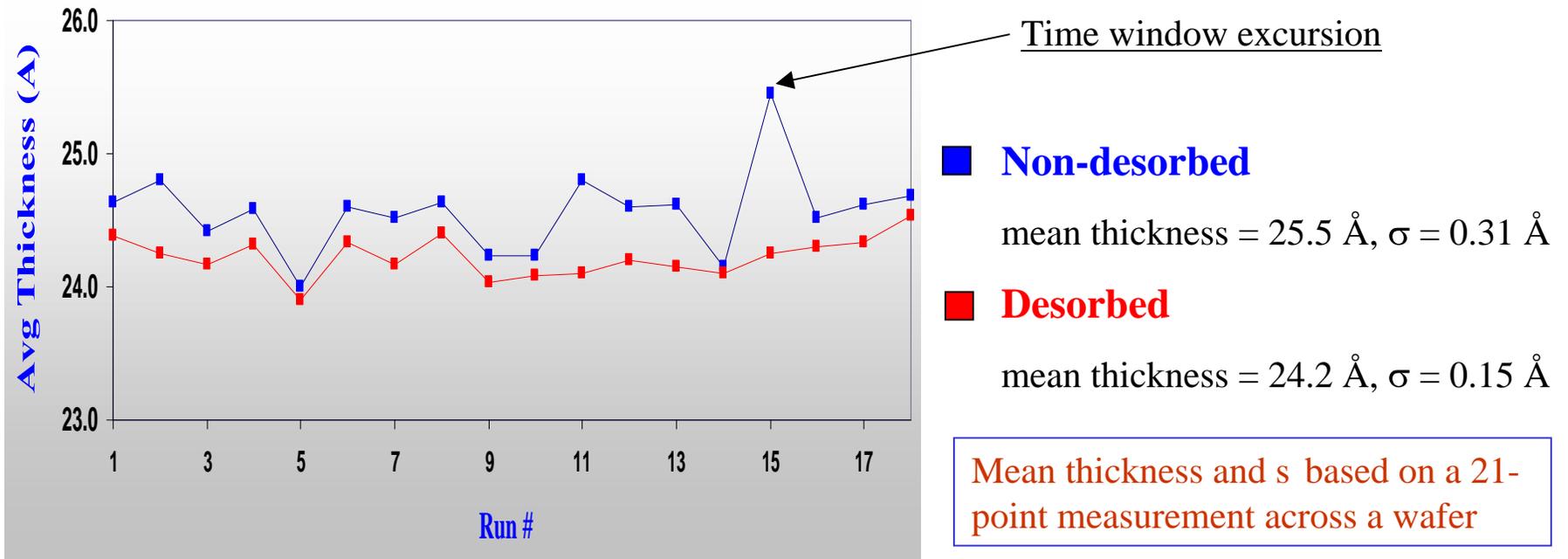


Delta = difference between first and subsequent measurements

Initial environmental film growth rate (as measured optically) = 0.015 \AA/min



Improvement in Thickness Measurement by Thermal Desorption



- Oxide pilots subjected to thermal desorption in a “Desorber” just prior to thickness measurement
- The post-desorption thickness data truly represents process or tool performance
- Thermal desorption improves uniformity: within-wafer, wafer-to-wafer, run-to-run
- Results in tighter process control



Conclusions

- HfO_2 and ZrO_2 dielectric surfaces adsorb higher amounts of moisture and IPA than SiO_2 . Therefore, HfO_2 and ZrO_2 dielectrics are more prone to molecular contamination than SiO_2
- ZrO_2 films retain some moisture even after a 300°C bake-out; this can be detrimental to the gate oxide quality
- ZrO_2 was shown to form the strongest metal-hydroxyl (M-OH) bond and adsorb IPA stronger than SiO_2 and HfO_2
- ZrO_2 should not be the material of choice from the standpoint of molecular contamination
- But the actual extent of gate dielectric deterioration can be determined only after electrical tests are performed
- Molecular contamination deteriorates precision performance of ellipsometers; thermal desorption of contaminants prior to thickness measurement significantly improves gate oxidation process control



Future Work

- Can residual moisture be removed from ZrO_2 beyond 350°C?
- Development of models to simulate competitive adsorption / desorption profiles of multiple molecular contaminants



Acknowledgements

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Texas Instruments

Dr. Rick Wise

External Research

Dr. Paul Tiner

Manager, Diffusion

ERC/SRC

Engineering Research Center for Environmentally
Benign Semiconductor Manufacturing

CMC

Center for Microcontamination Control



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