Role of Interfacial Contamination in Gate Dielectric Degradation

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PRESENTATION OUTLINE

- Motivation
- Results and discussion

  I. Organic contamination of ultra-thin SiO_2 gate dielectric

    a. Effect of processing conditions

    b. Mechanism of defect formation

  II. Contamination of high-k gate dielectric films

    a. Energetics and kinetics of trace-level H_2O and IPA on ZrO_2 and HfO_2

- Conclusions

ORGANIC CONTAMINANTS IN THE FAB

volatile solvents

process chemicals

polymer outgassing

Wafer carriers, storage boxes,

HEPA/ULPA filters

sealants, paints, tubings

SOURCES

IPA, acetone, NMP

siloxanes, amines

DBP, BHT, esters

sulfonamides, alcohols

organophosphates, DOP

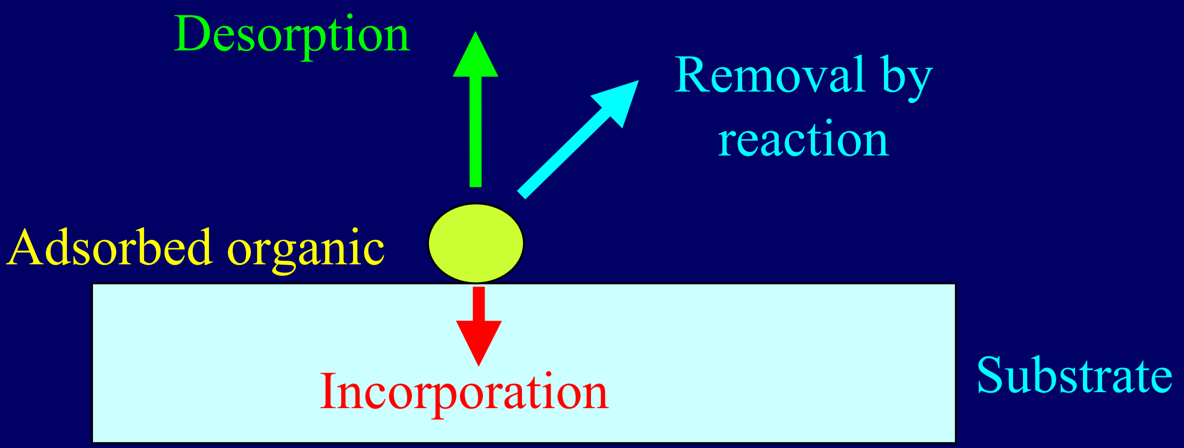
organosilicones

hydrocarbons

COMPOUNDS

www.balazs.com, JECS 146 (7) p. 2725 (1999), JECS 148 (7) p. G365 (2001)

FATE OF ADSORBED ORGANICS



- Competition between desorption, volatilization by reaction and incorporation governs the fate of adsorbed contaminants.
- Rapid thermal processes and inert process ambient highly susceptible to retention of organics.

EFFECTS OF ORGANIC CONTAMINATION

- Etch rate shifts due to incomplete wetting
- Contact corrosion
- Wafer and optics hazing
- Counter-doping
- Prevention of wafer bonding
- Delamination, non-uniform Cu seed deposition
- Malfunction of epitaxial growth
- Gate oxide degradation –

  SiC formation, local oxide thinning, positive charge in the bulk,

  ↑interface traps, threshold voltage shifts

  Hattori et. al., Appl. Phys. Lett. 71 (25), p. 3670 (1997), Kasi et. al., Appl. Phys. Lett. 59 (1), p. 108 (1991)

  Heyns. et. al., Jpn. J. Appl. Phys. – Pt. 1, 37 (9A), p. 4649, (1998), Jeon et. al., ECS- PV 99-6, p. 250 (1999

- ITRS recommendation for front-end surface preparation:

  @ 90 nm : Carbon $< 1.5 \times 10^{13}$ atoms/cm^2

ISSUES WITH NEW MATERIALS

- Incomplete desorption may lead to trapping of organics within the deposited films.

- Organic precursors can lead to carbon retention in the film.

  Mirica et. al., Applied Surface Science, 143 (1-4), p. 85 (1999)

- ALD – sequential film deposition

  contaminants can get dispersed throughout the deposited film.

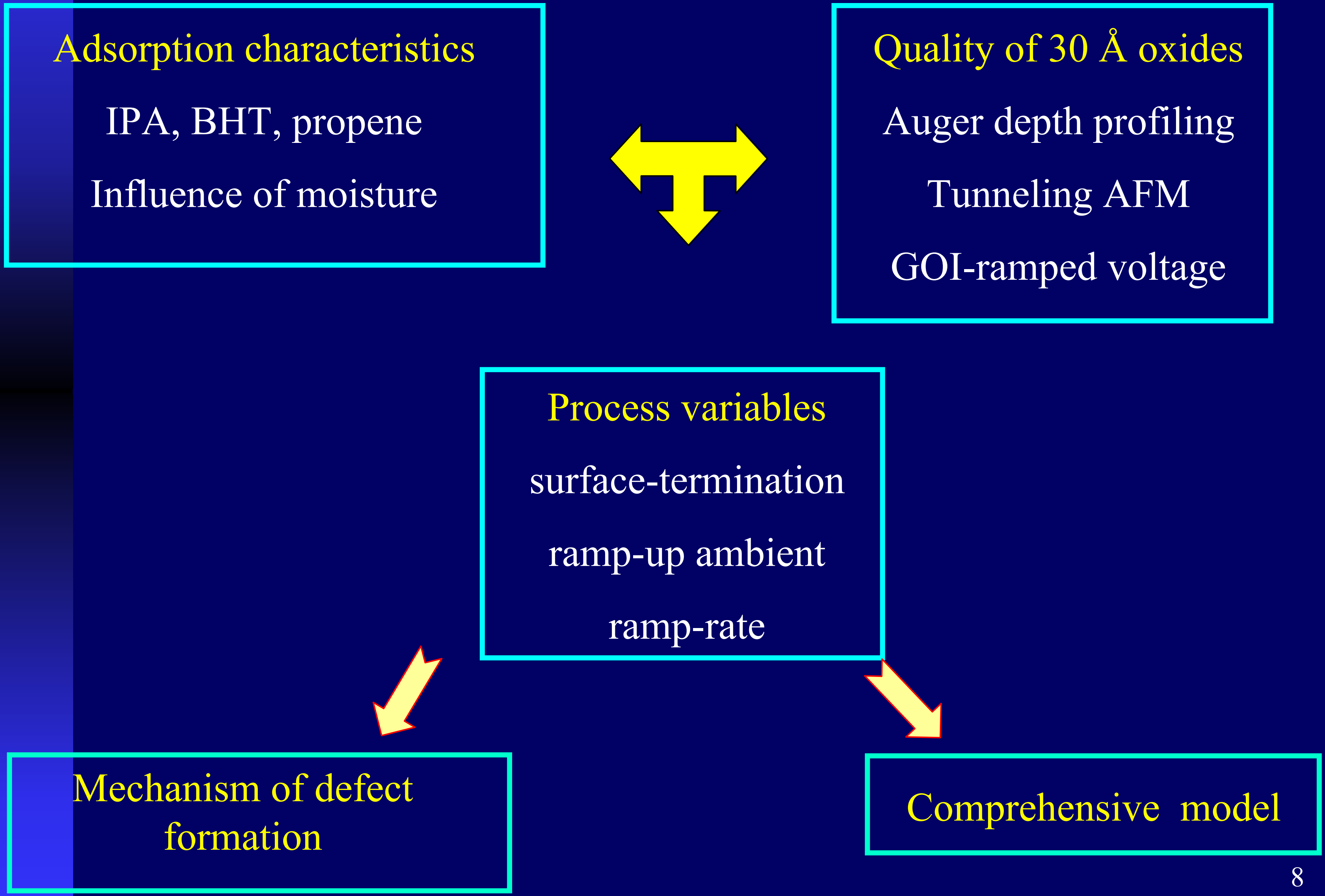
- Contamination on high-k film before poly deposition can be equally problematic.

- What is the sensitivity of high-k films to organic contamination ?

  Current ITRS numbers are applicable only for silicon.

BEHAVIOR OF ORGANICS DURING GATE OXIDE GROWTH BY THERMAL OXIDATION

METHOD OF APPROACH



Adsorption characteristics

IPA, BHT, propene

Influence of moisture

Quality of 30 Å oxides

Auger depth profiling

Tunneling AFM

GOI-ramped voltage

Process variables

surface-termination

ramp-up ambient

ramp-rate

Mechanism of defect formation

Comprehensive model

SCHEME OF EXPERIMENTS

- Contamination before oxidation
  Kinetics and extent
- Behavior during thermal oxidation
- Effect of processing conditions
  Type of cleaning
  Ramp-up ambient
  Ramp rate
- Understand mechanism of carbon incorporation

Objectives

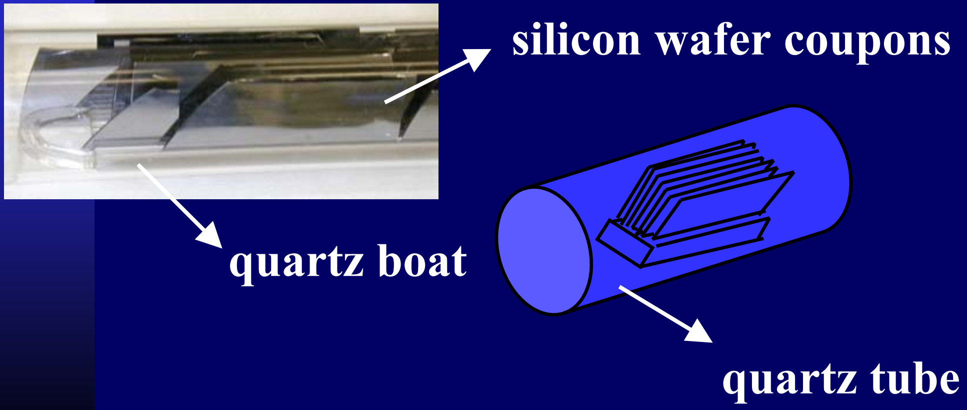
- Pre-gate oxidation cleaning
- Intentional organic contamination
- Desorption during oxidation
- Monitor outgassing of organics

Experimental strategy

Tracking real-time kinetics of organics during thermal processes is difficult:

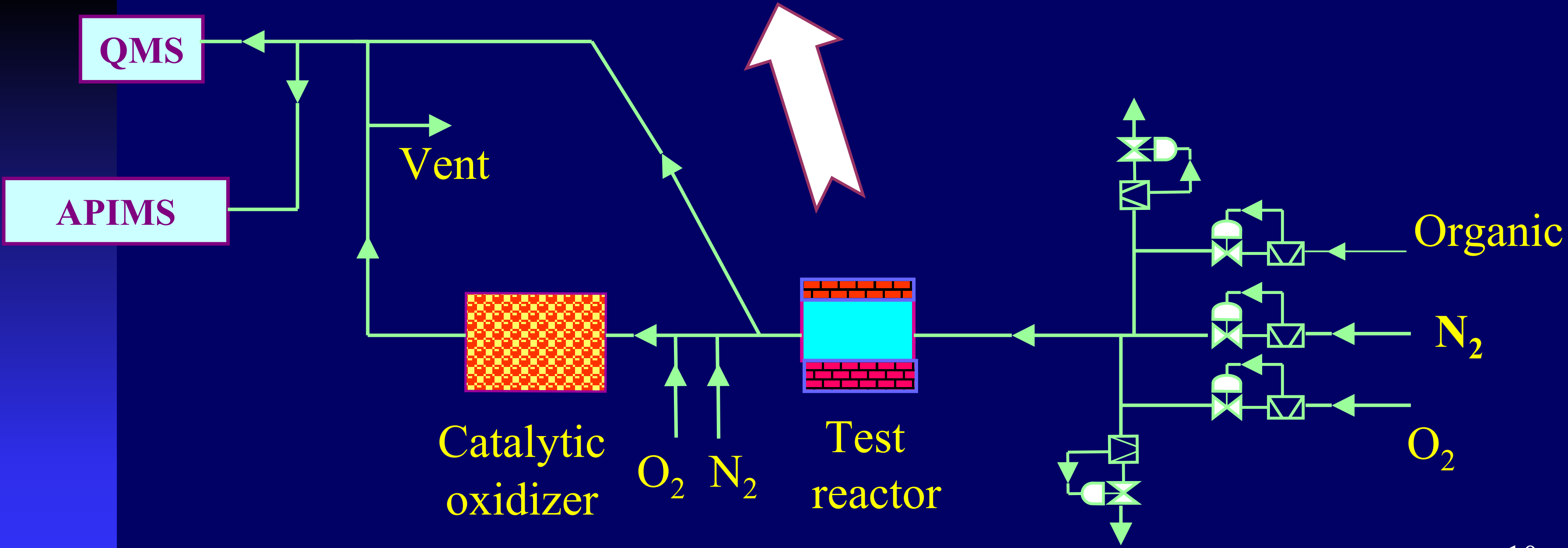
Catalytic oxidation - measure organics as Total Organic Carbon.

EXPERIMENTAL SETUP

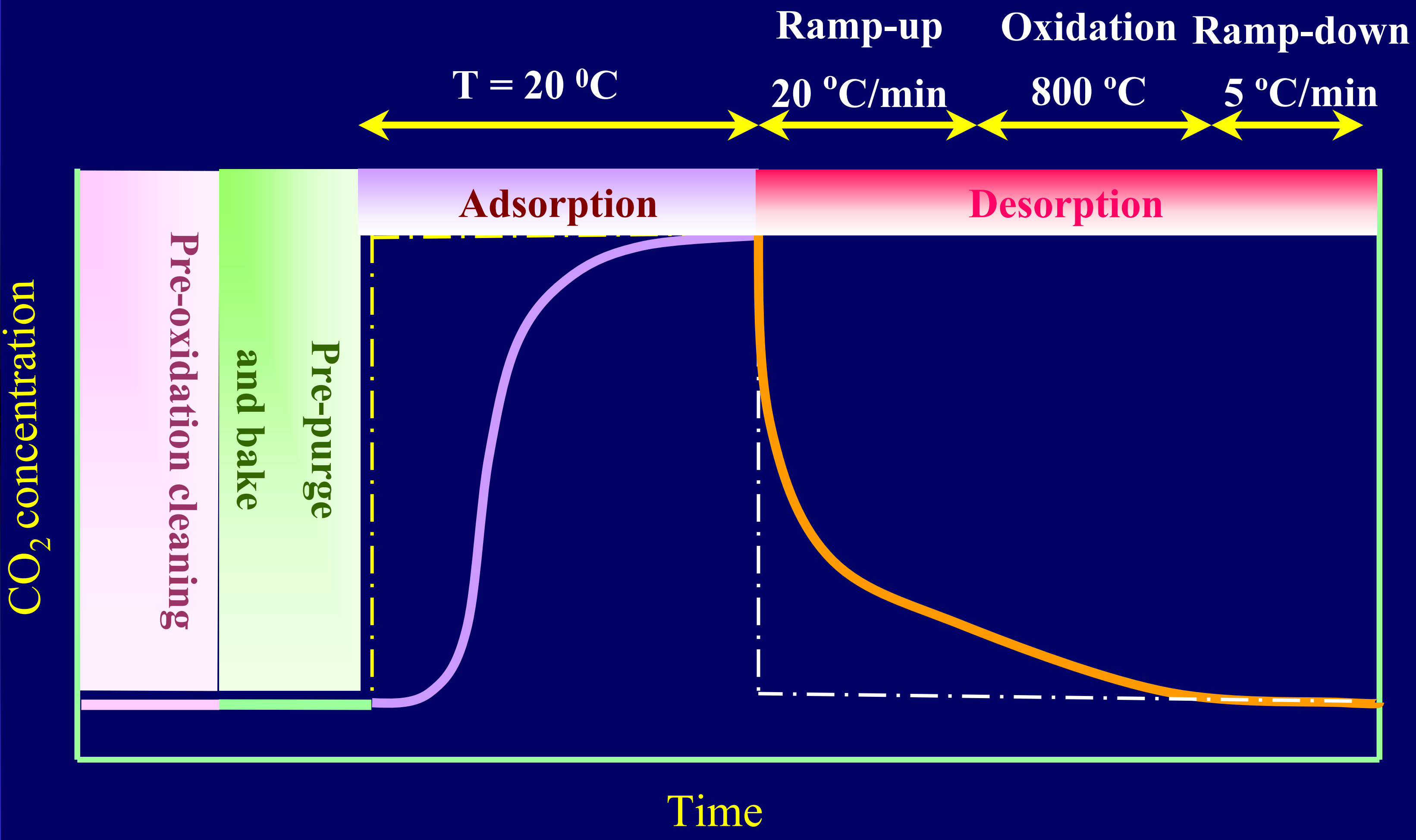


Salient features

- ❖ EPSS tubing
- ❖ all-metal MFCs
- ❖ certified gas mixtures
- ❖ ppm-ppt level detection

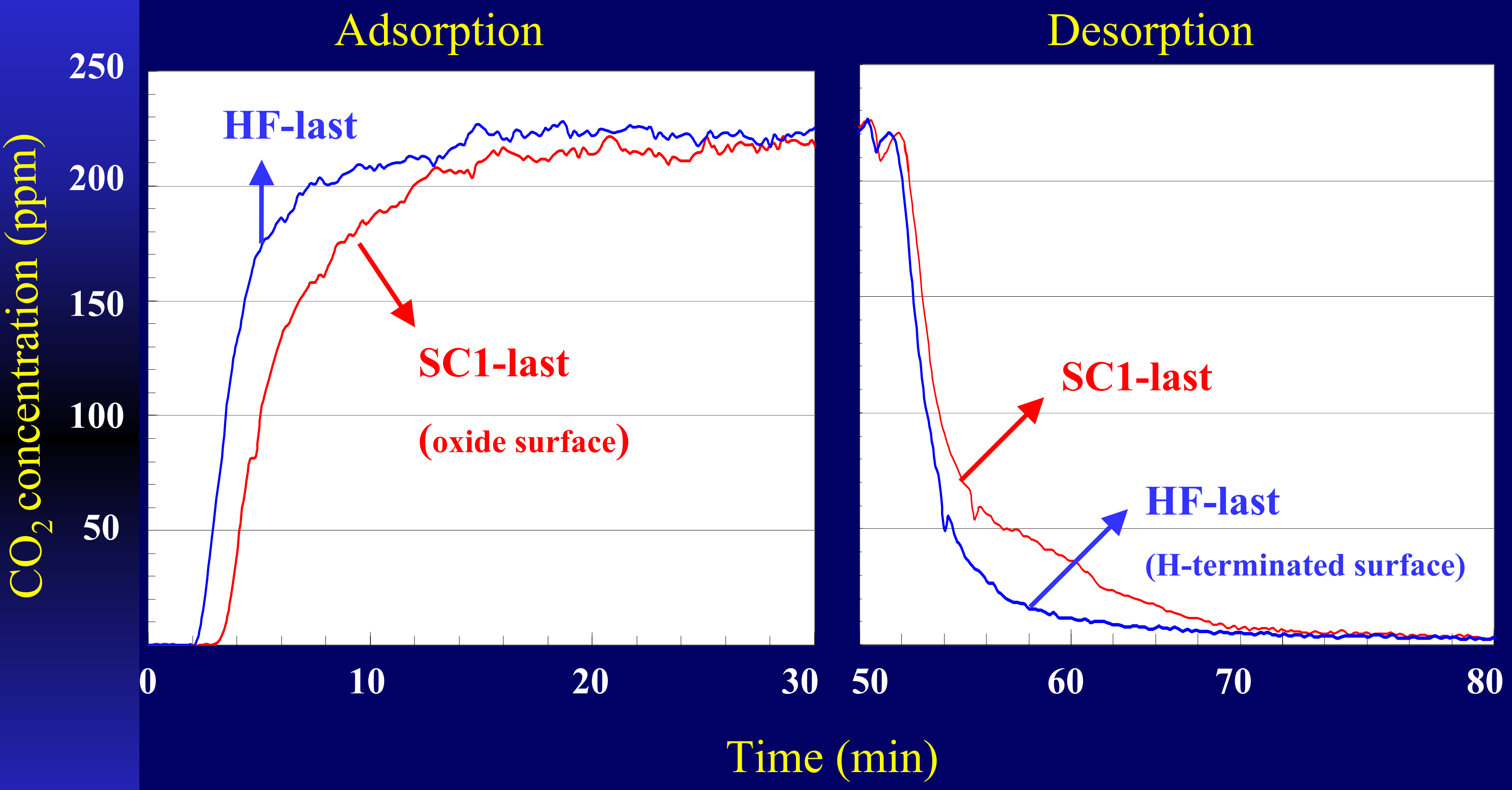


EXPERIMENTAL PROCEDURE



- **Desorption gas represents the ramp-up ambient in thermal oxidation – 100 % N_2 (inert ramp-up) or O_2 in N_2 (oxidizing ramp-up)**

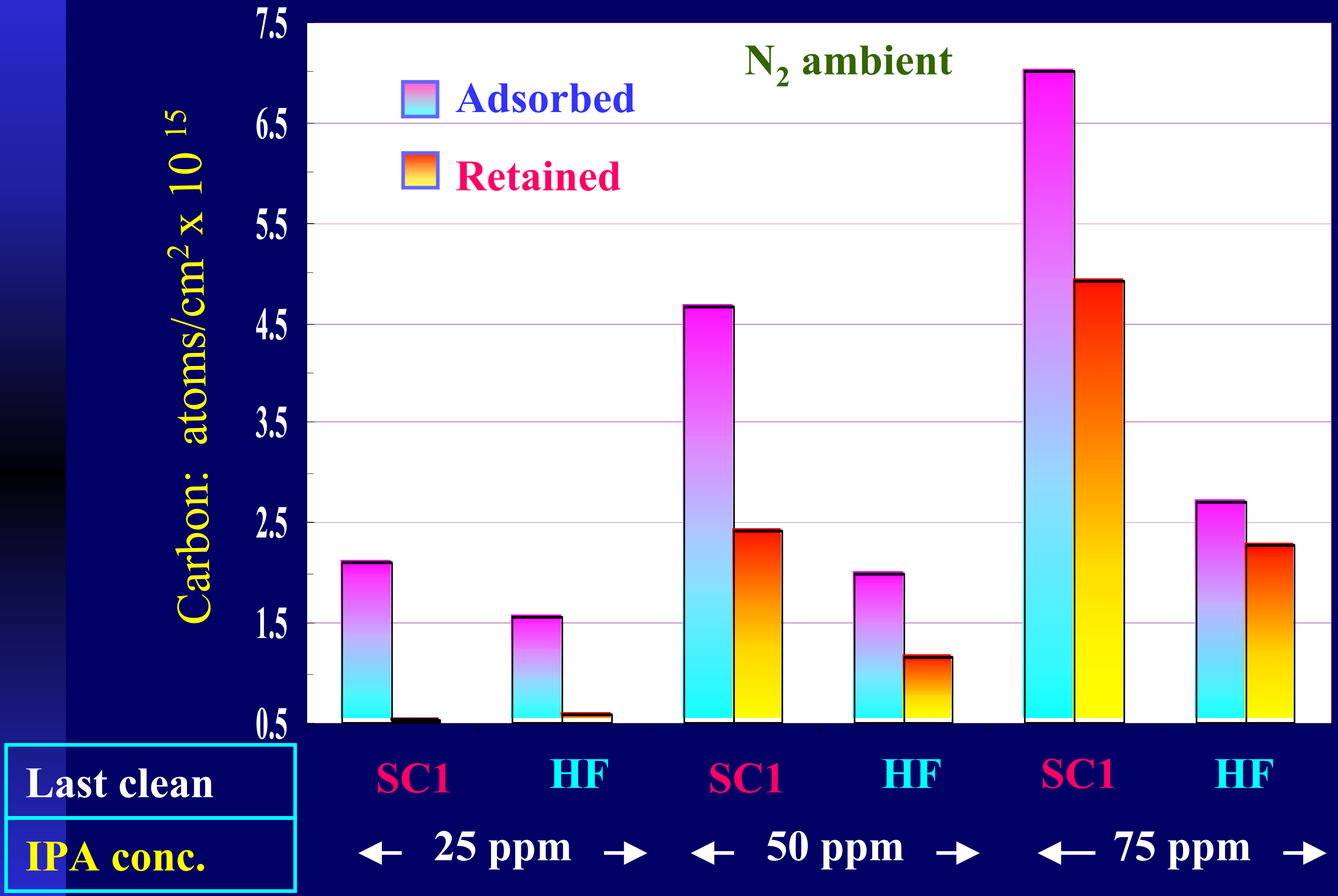
EXPERIMENTAL RESPONSE



75 ppm IPA challenge, ramp-up to 800 °C at 20 °C/min in N_2

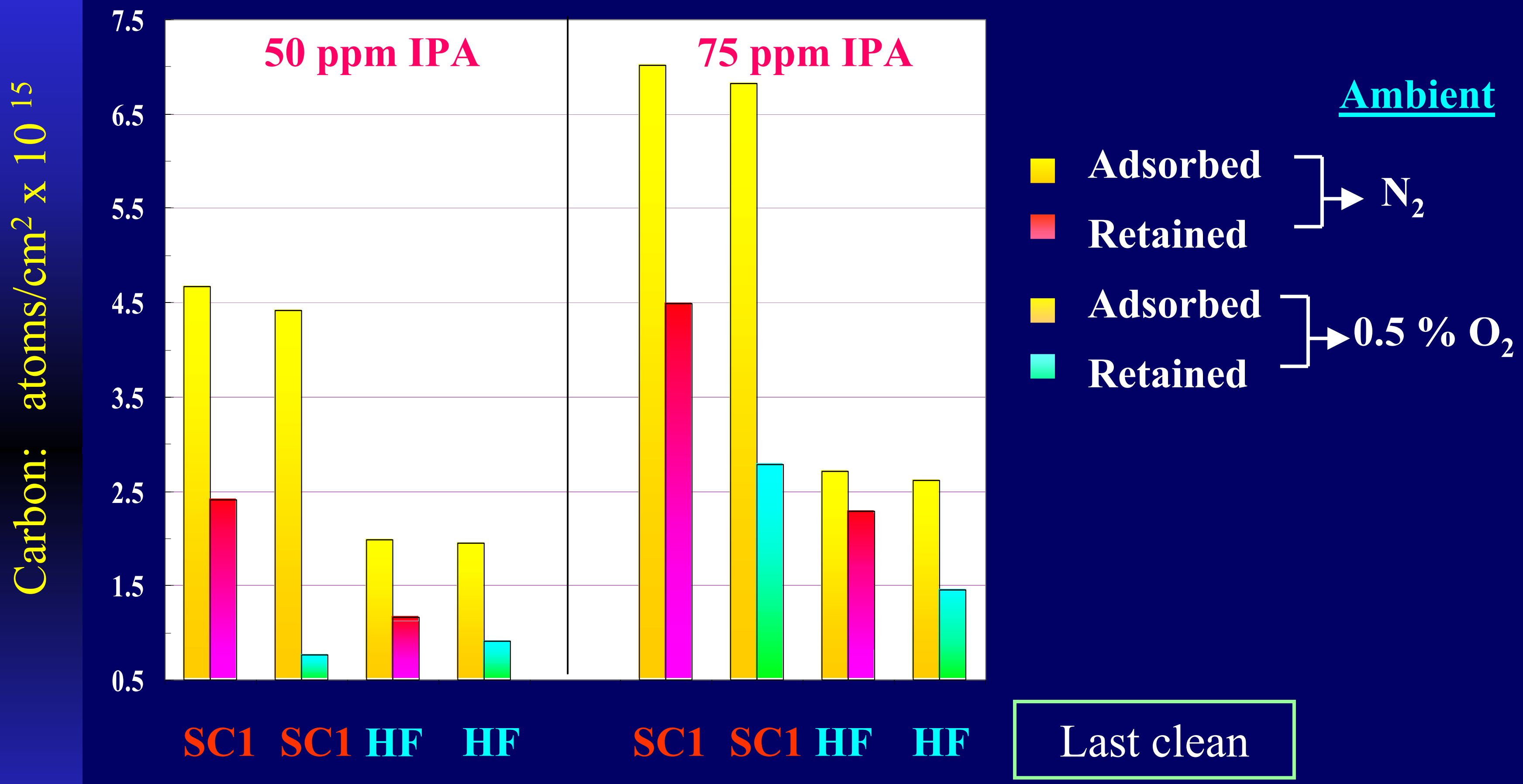
- SC1-last adsorbs more IPA than HF-last surface.

EFFECT OF CLEANS AND ORGANIC CONCENTRATION



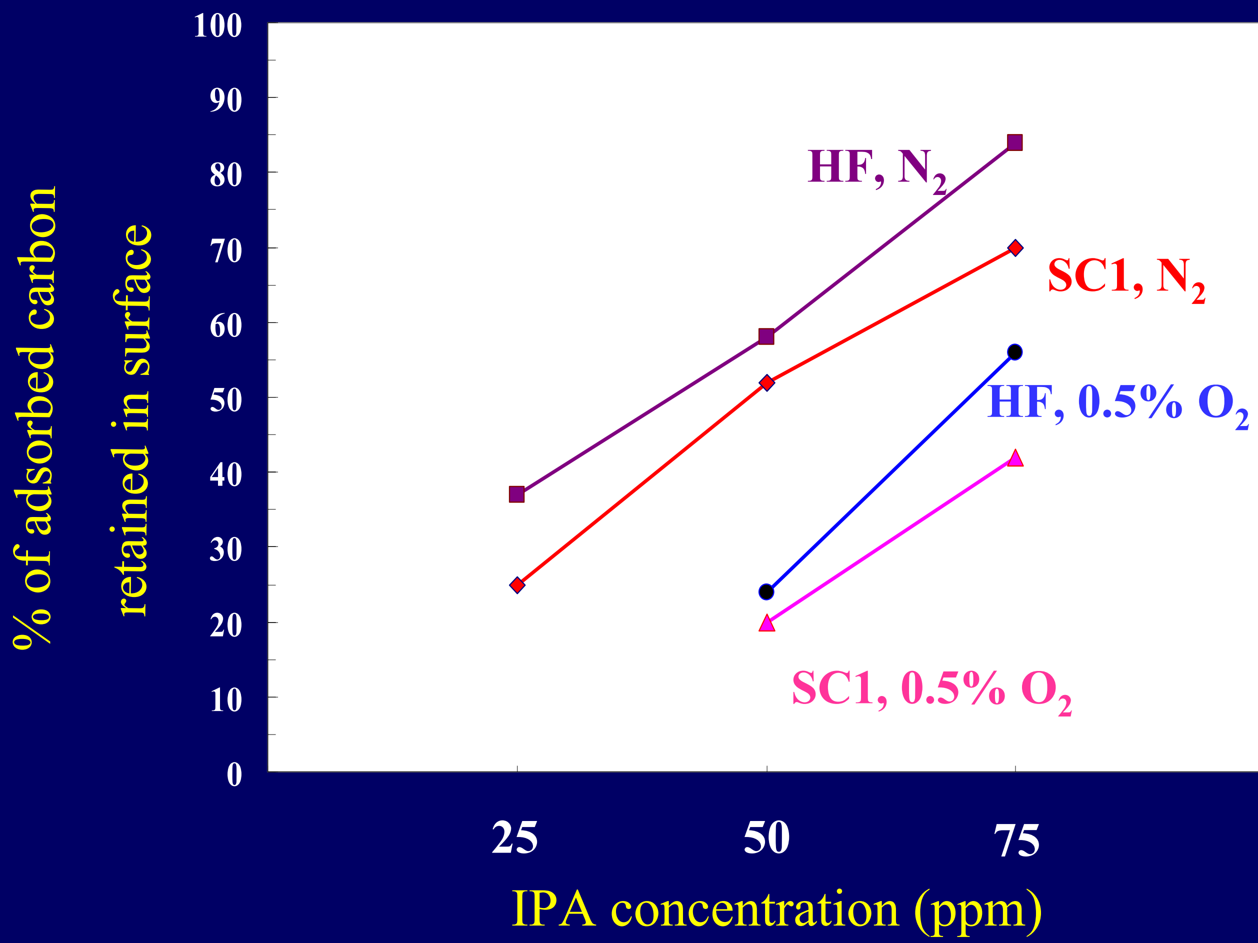
- Carbon adsorption proportional to ambient concentration.
- Greater carbon incorporation in SC1-last surfaces.

EFFECT OF OXYGEN IN RAMP-UP AMBIENT



- **0.5%** oxygen in ramp-up reduces carbon incorporation, but does not eliminate it.

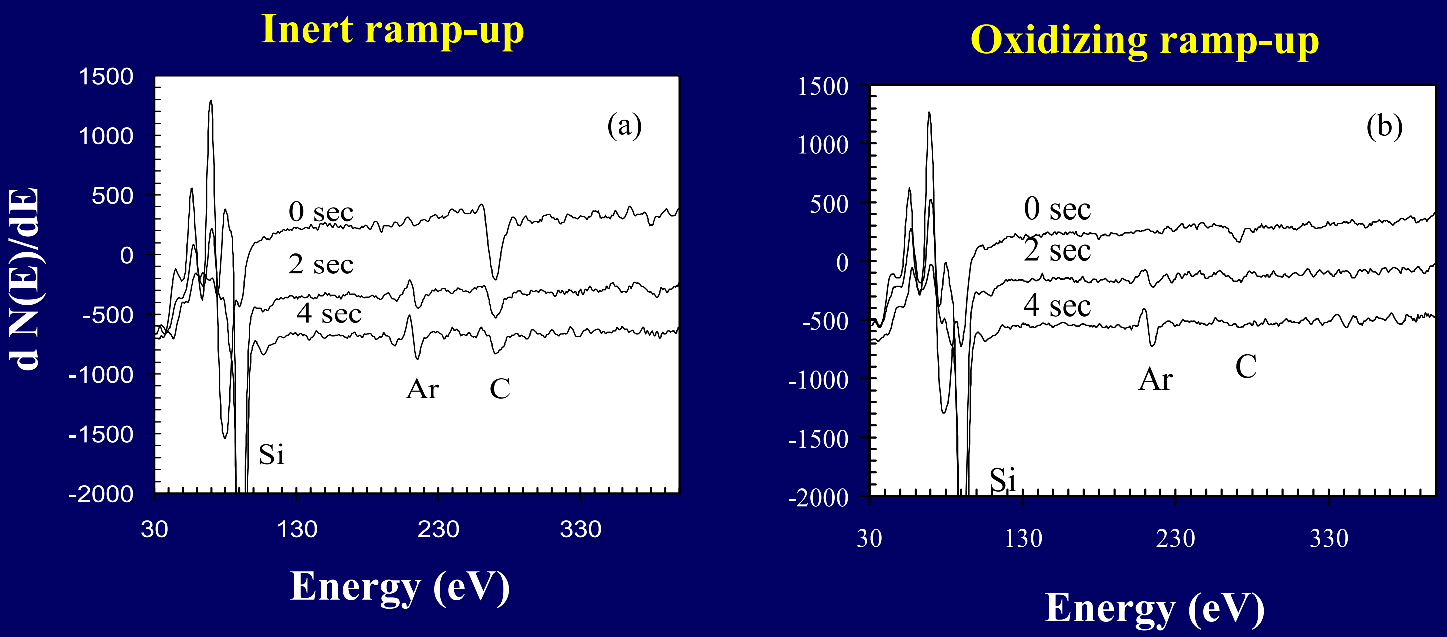
EXTENT OF CARBON INCORPORATION



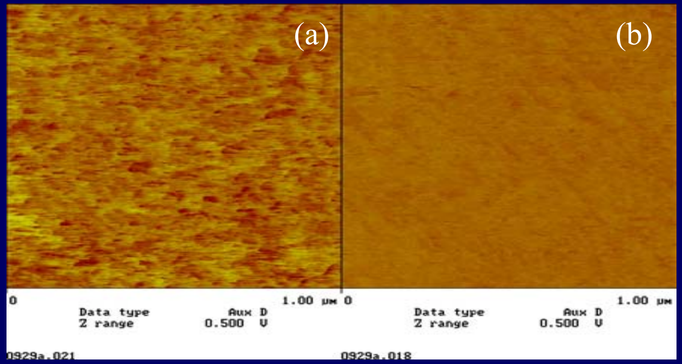
- Carbon incorporation proportional to concentration.
- Inspite of lower adsorption, HF-last retains a greater fraction of adsorbed carbon.

SURFACE AND ELECTRICAL ANALYSIS OF GATE OXIDES

Auger depth profile



TAFM



GOI defect density	> 20 cm^{-2}	0.26 cm^{-2}

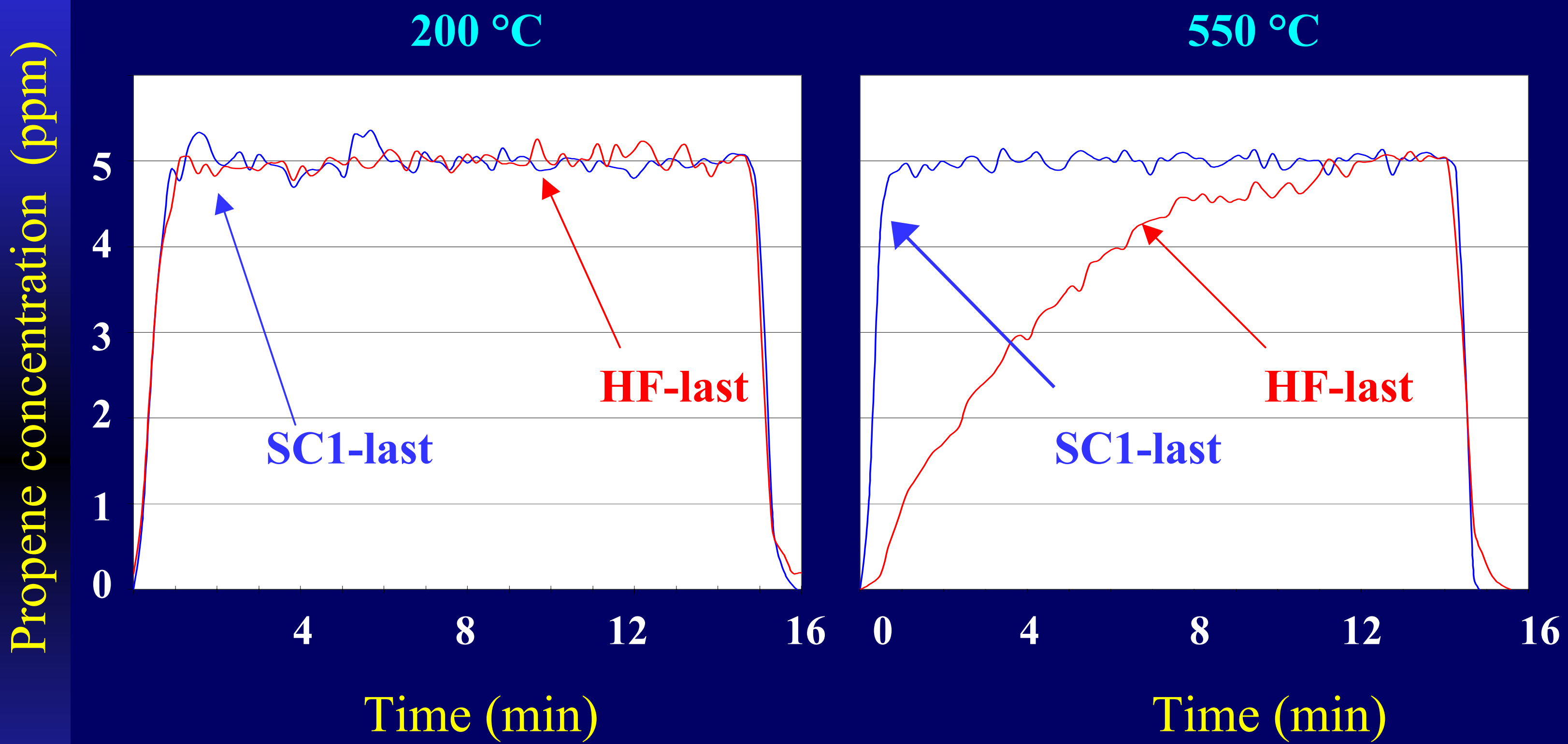
E_{bd} = 12 MV/cm

THERMAL DECOMPOSITION OF IPA

Why did HF-last wafers give bad oxides than SC1-last wafers?

- IPA decomposes above 400 °C.
- Primary product is propene + some acetone.
- Similar decomposition to unsaturated compounds or compounds with double bonds expected for other organics.

UNSATURATED COMPOUNDS AT HIGH TEMPERATURES

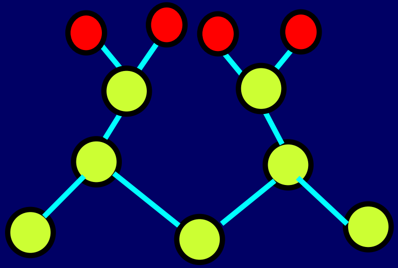


No adsorption

Chemisorption on HF-last!

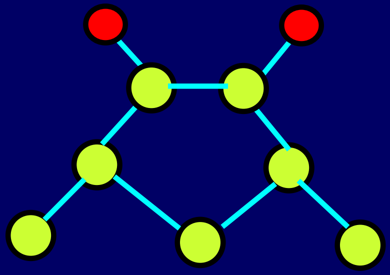
- HF-last adsorbs propene at higher temperatures, but SC1-last does not.

HYDROGEN TERMINATED SILICON AT HIGH TEMPERATURES



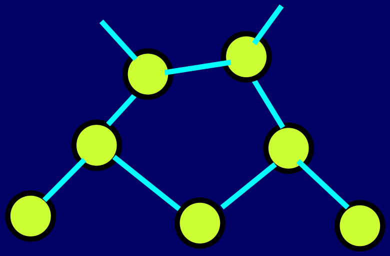
SiH_2 (1x1)

T < 410 ºC



SiH (2x1)

410 ºC < T < 530 ºC

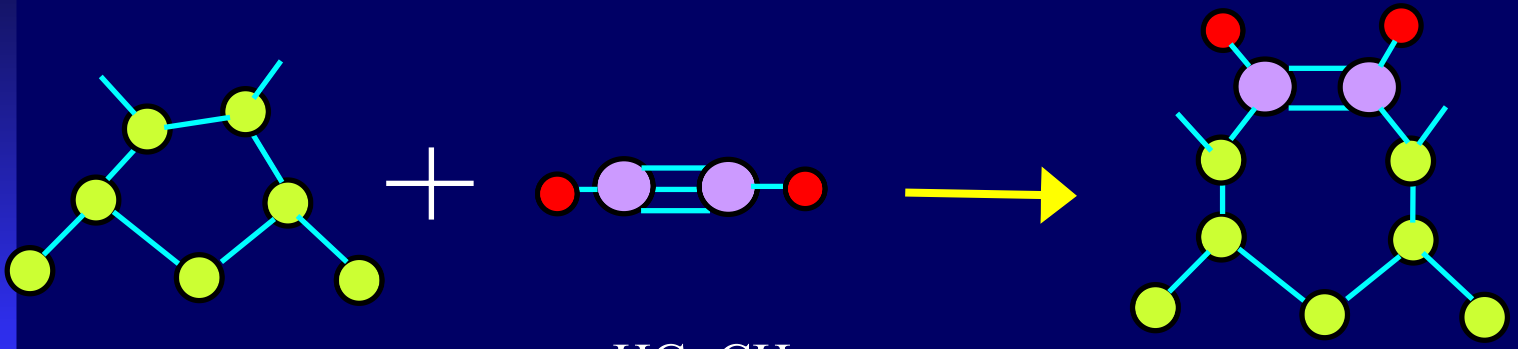


Si (2x1)

530 ºC < T

Si dimer with dangling bonds

Kasi et. al., Appl. Phys. Lett. 59 (1), p. 108 (1991).



Si(100)- (2x1)

HC≡CH

di-σ bonded organic

Yates, Jr. et. al., J. Am. Chem. Soc., 114 (17), p. 6755 (1992).

MECHANISM FOR INTERACTION OF ORGANICS

SC1-last surface

Stable oxide film

Passivation loss: > 900 º C + highly inert

Polar organics can chemisorb

HF-last surface

H passivation lost around 525 º C

Si(100)-2x1 created with dangling bonds

Unsaturated molecules can cleave Si-Si bond to chemisorb

Thermal dissociation + loss of H-termination makes HTS more vulnerable

CONTAMINATION OF ALD DEPOSITED

ZrO_2 and HfO_2

HIGH-K GATE DIELECTRICS

HIGH-K GATE DIELECTRIC MATERIALS

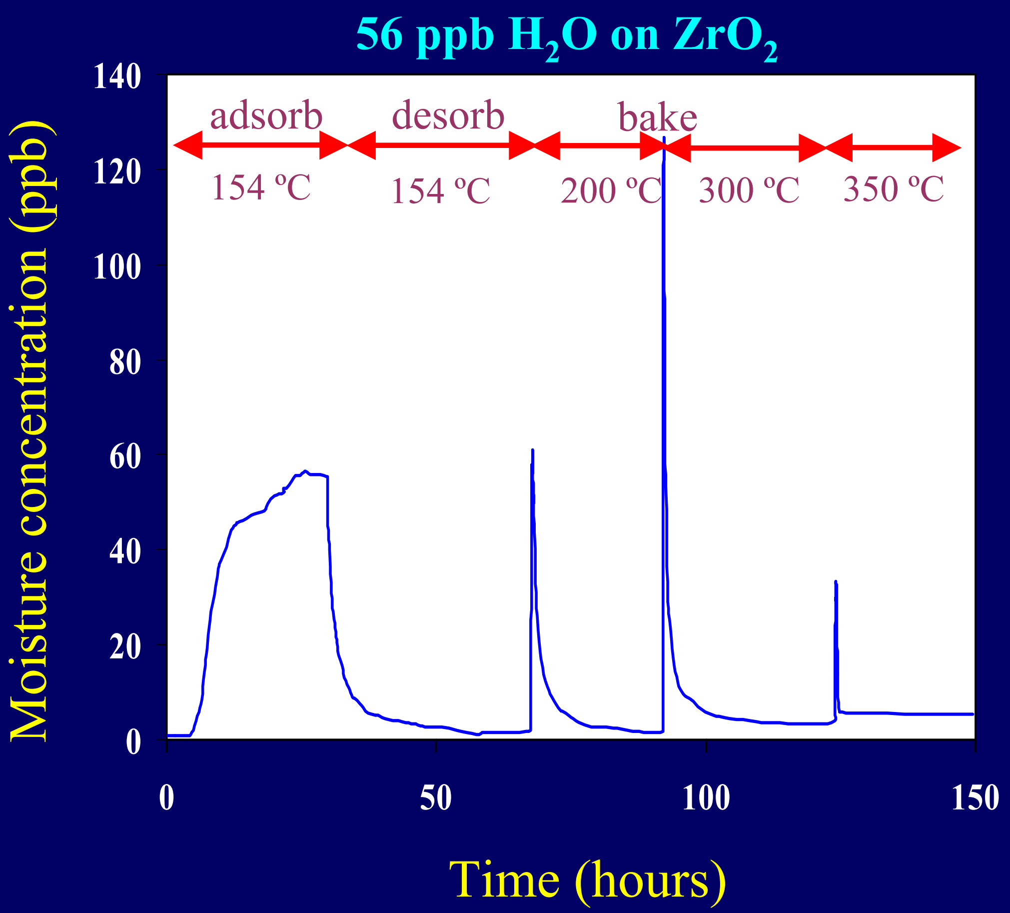
HfO_2 and ZrO_2 – leading high-k candidates for replacing SiO_2 as the gate dielectric.

Contamination problems

- Airborne contamination of moisture and organics before poly-deposition
- 50 Å films deposited by ALCVD^{TM} on double-polished Si wafers

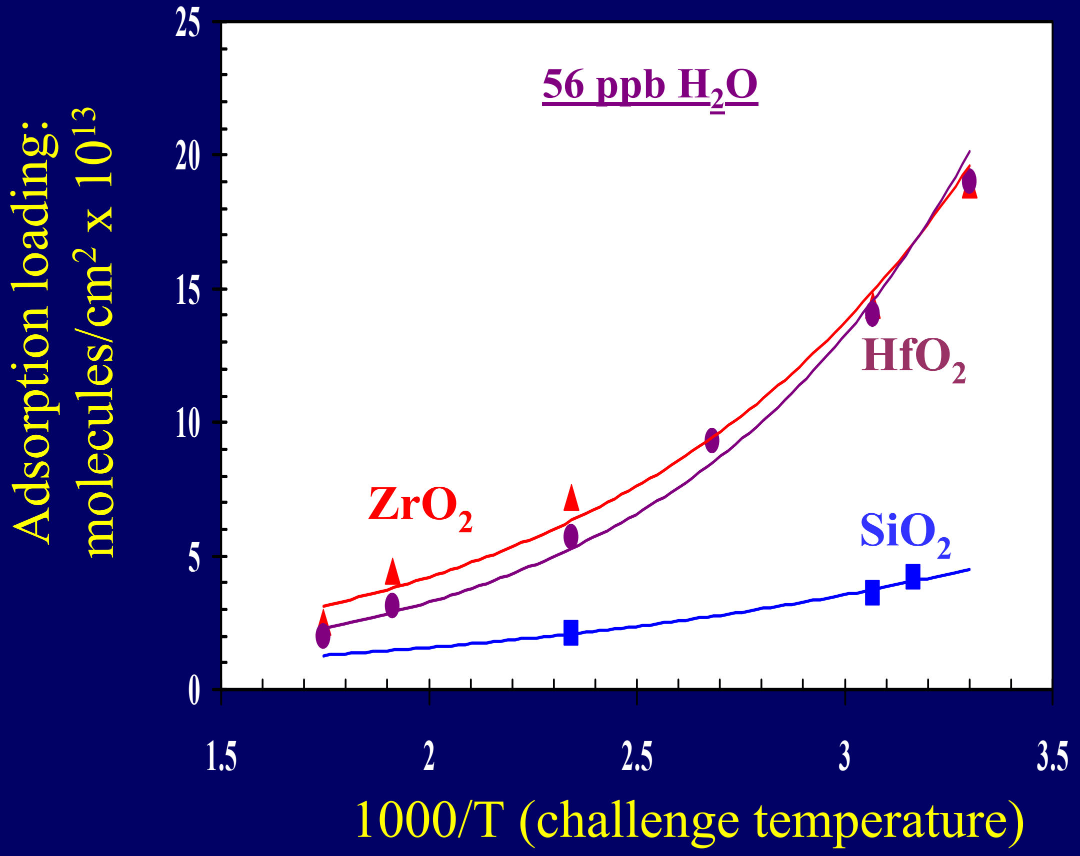
High surface area + efficient gas mixing !

EXPERIMENTAL PROCEDURE


56 ppb H_2O on ZrO_2

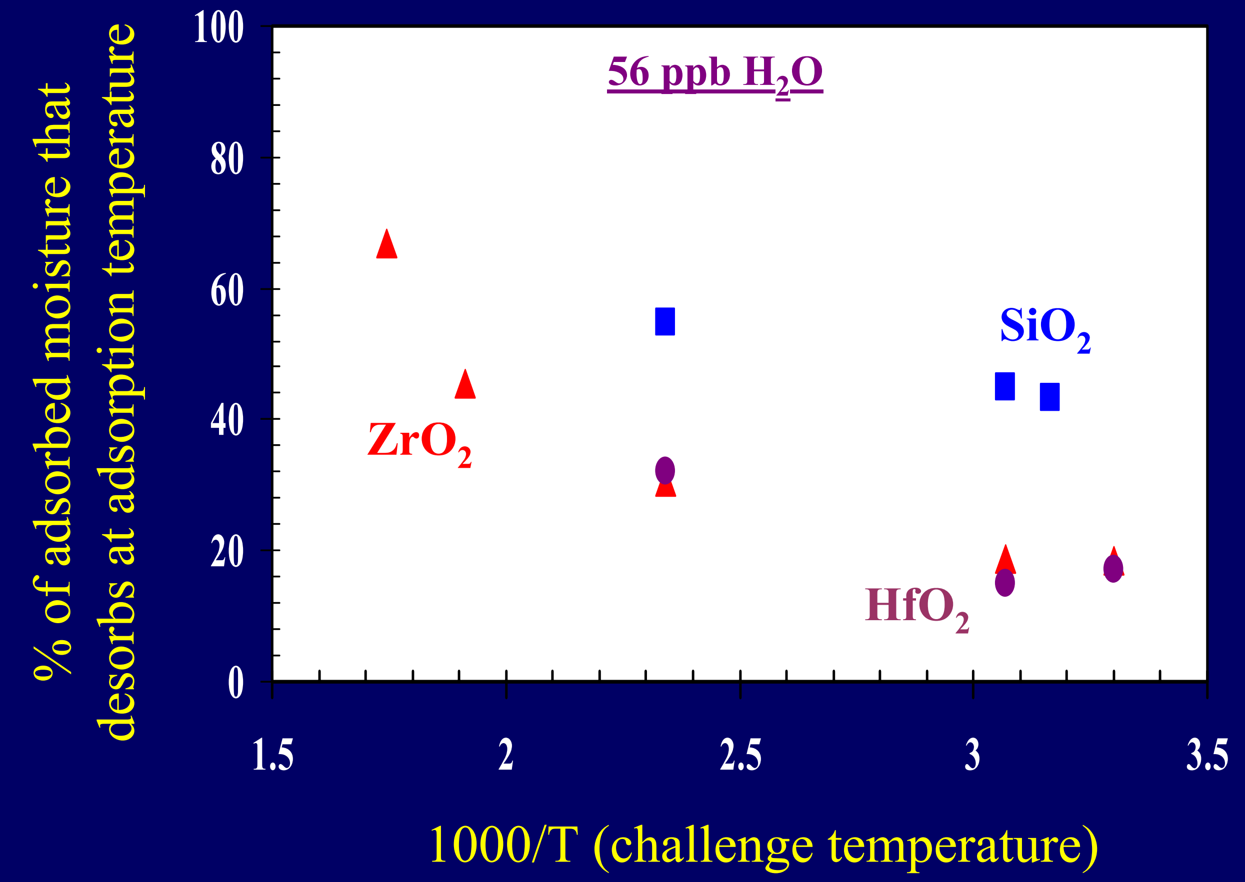
- Experiments performed on APIMS.
- Equilibrate contaminant at a given temperature, then desorb and bake upto 300 ºC.

ENERGETICS OF MOISTURE ADSORPTION



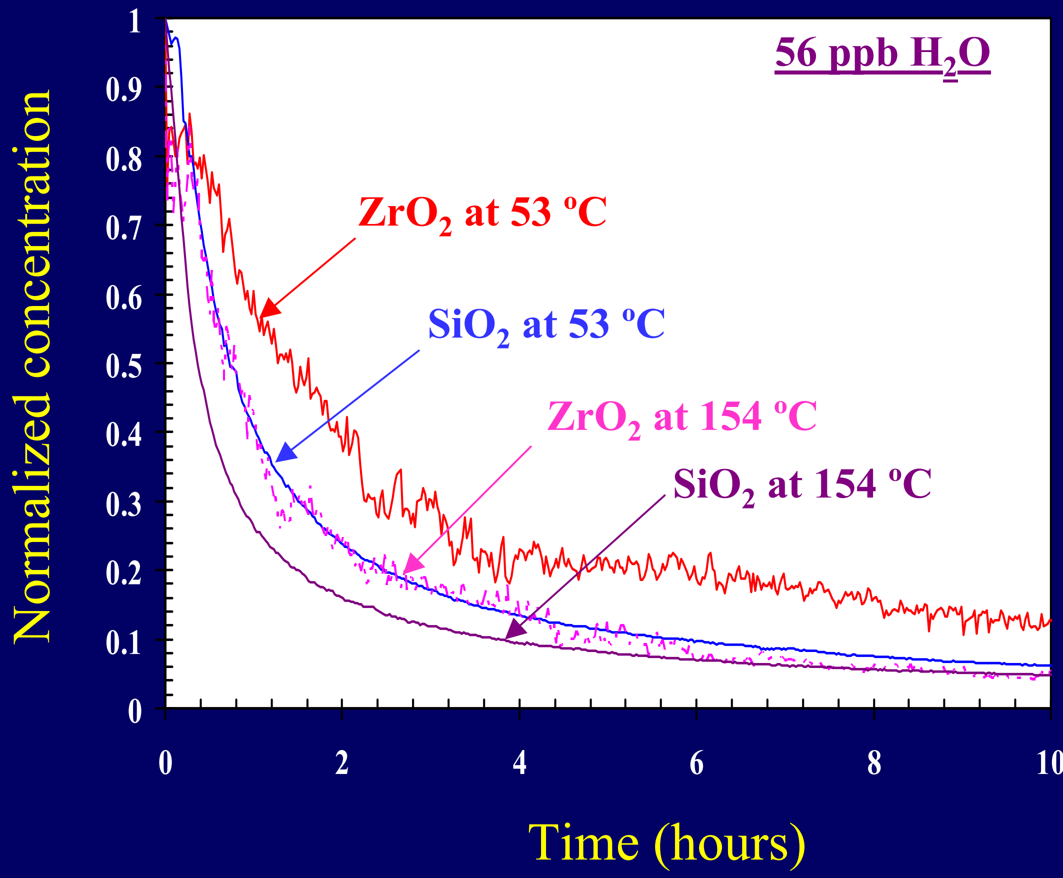
- Higher moisture adsorption on ZrO_2 and HfO_2 than on SiO_2.
- Adsorption on ZrO_2 and HfO_2 is more temperature sensitive: more energetic !

RELATIVE EASE OF MOISTURE DESORPTION



- Much more difficult to desorb moisture from ZrO_2 and HfO_2 at a given temperature.

MOISTURE DESORPTION KINETICS



- Desorption of moisture is slower from ZrO_2 as compared to **SiO_2.**

FUNDAMENTALS OF MOISTURE ADSORPTION

- Dissociative chemisorption on both SiO_2 and ZrO_2

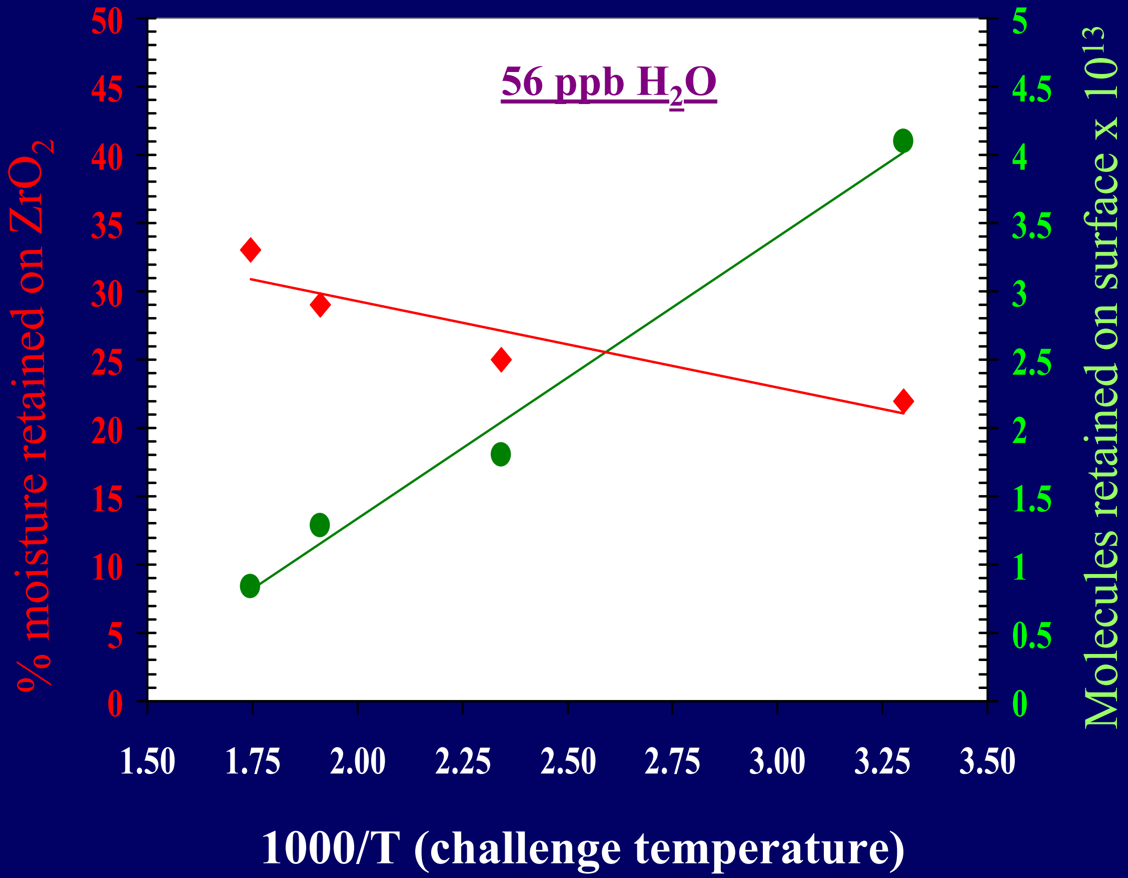
	SiO_2	ZrO_2
Δ Electronegativity	1.7	2.1
-OH site density	4.6×10^{14} cm^{-2}	1.5×10^{15} cm^{-2} (monoclinic)

- Compare fractional surface coverage L

$$L/ (1-L)^2 \alpha \quad K_{eqm}$$

L indeed higher for ZrO_2 : more favorable adsorption

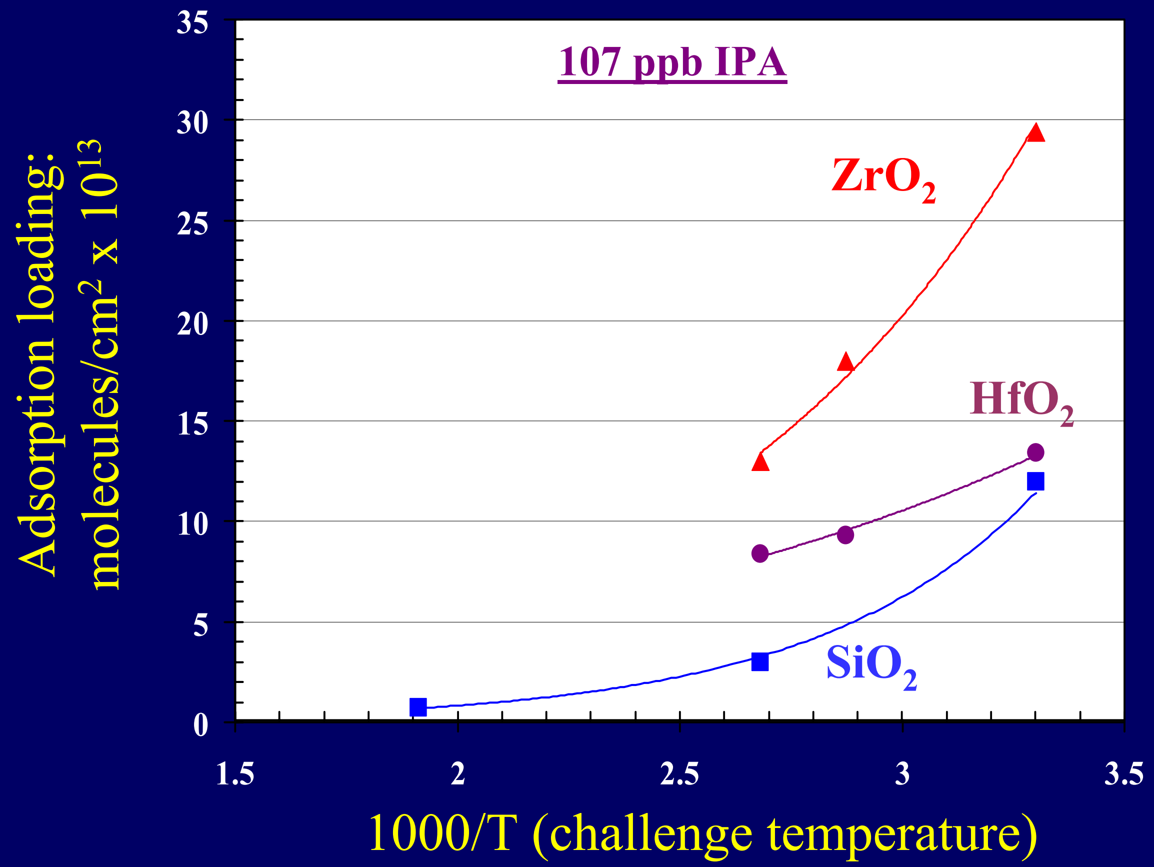
MOISTURE RETENTION ON ZrO_2



- Moisture retention is negligible on SiO_2 and HfO_2 but not so on ZrO_2.
- Does moisture desorb from ZrO_2 above 350 ºC ?

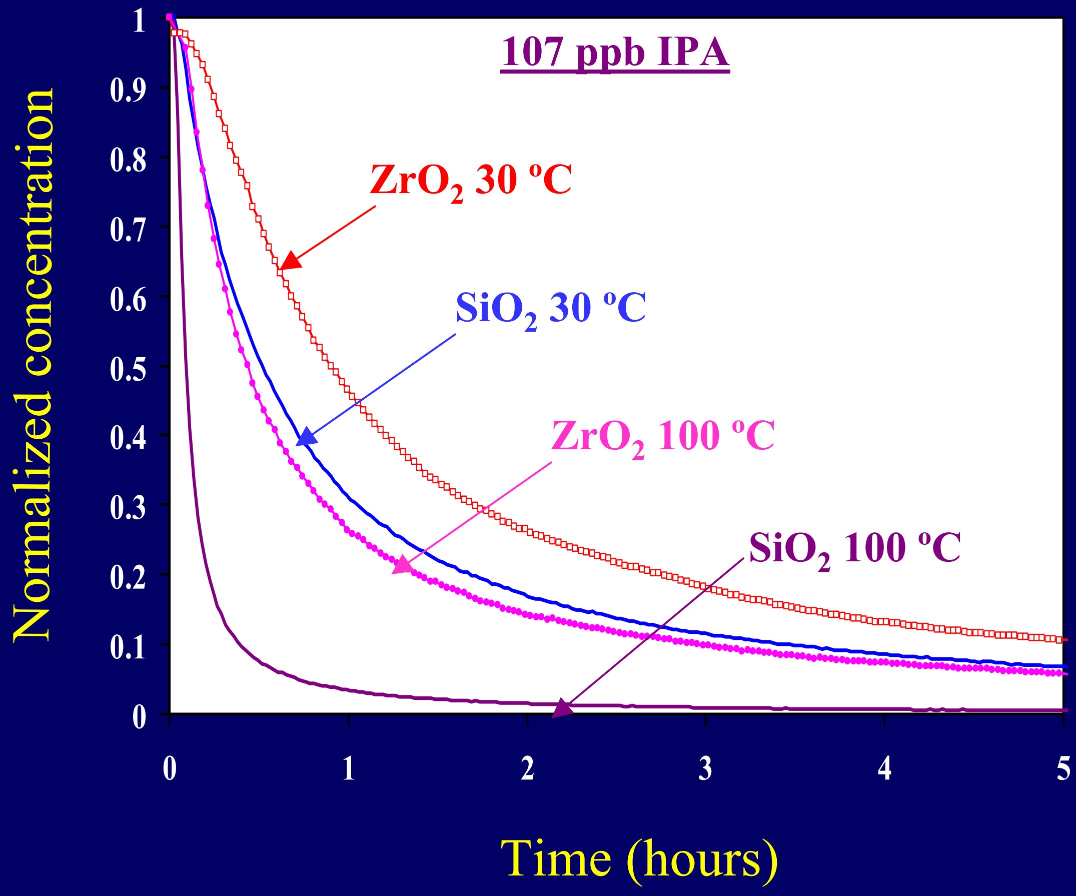
-could form interfacial oxide by diffusion at poly-deposition temperatures

IPA ADSORPTION ON ZrO_2, HfO_2 AND SiO_2



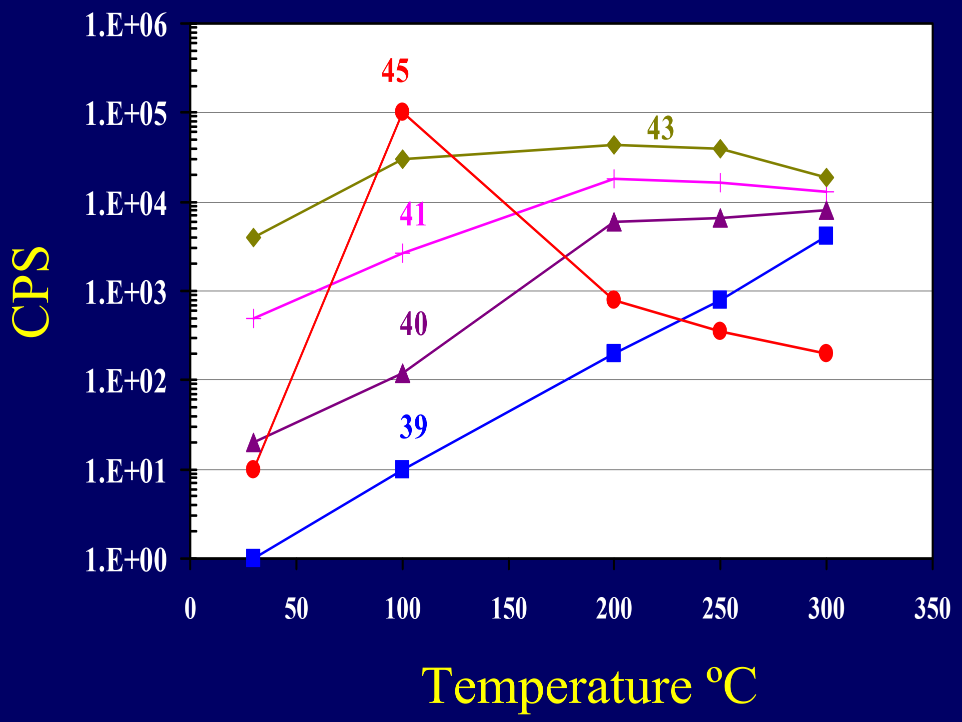
- Adsorption of IPA is highest on ZrO_2.
- ITRS calls for 2.8 x 10^{13} atoms/ cm^2 of carbon for the 60 nm node
- ppb level organics enough to adsorb carbon above acceptable levels!

IPA DESORPTION KINETICS



- Like moisture, desorption of IPA is slower from ZrO_2.

THERMAL CONVERSION OF IPA ON ZrO_2 AND HfO_2

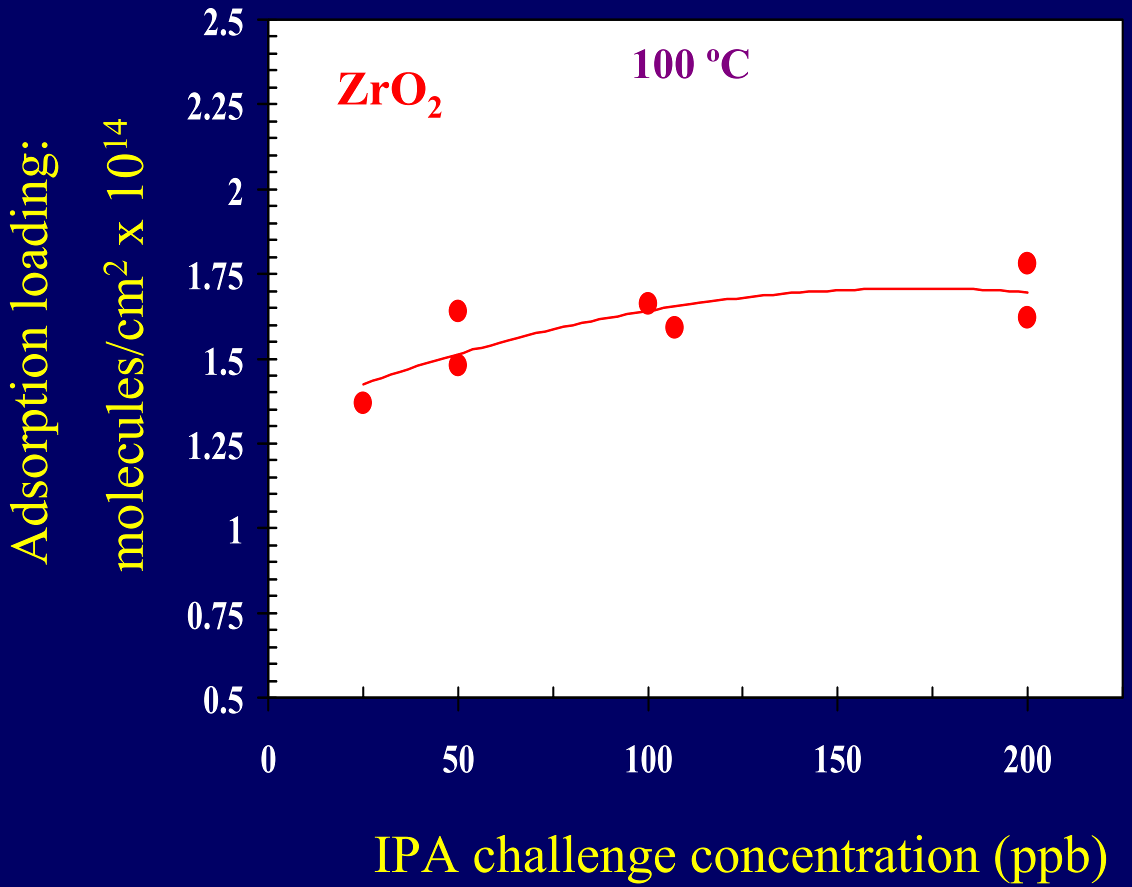


Note: counts at 30 ºC are for zero-gas.

All other temperatures are for 100 ppb IPA

- ZrO_2 has a catalytic effect on IPA – same is true for HfO_2
- Thermal decomposition at temperatures as low as 130 ºC
- Main products: propene and acetone
- Above 250 ºC, further fragmentation occurs

EFFECT OF CONCENTRATION ON IPA ADSORPTION LOADING



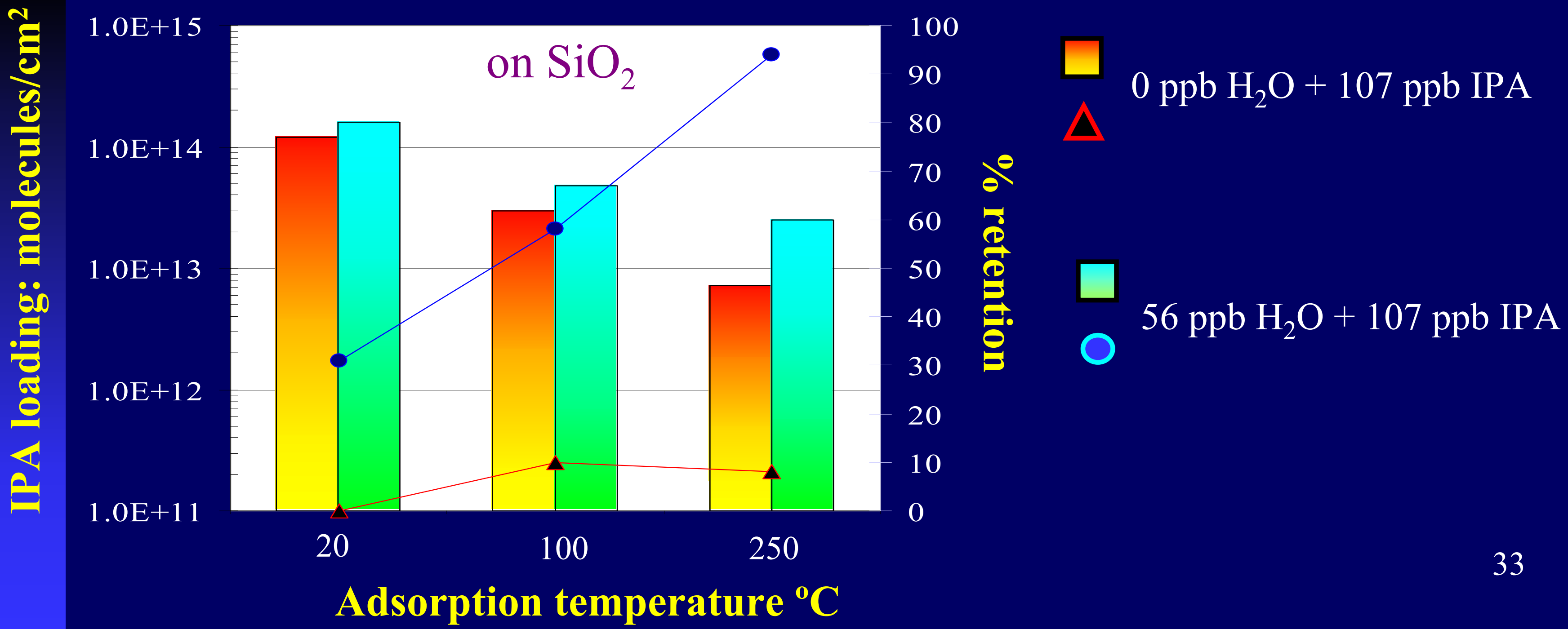
- Amount of contamination is insensitive to IPA concentration.
- ZrO_2 surface appears to have a saturation limit for IPA in ppb range.

ROLE OF MOISTURE IN ATTRACTING ORGANICS

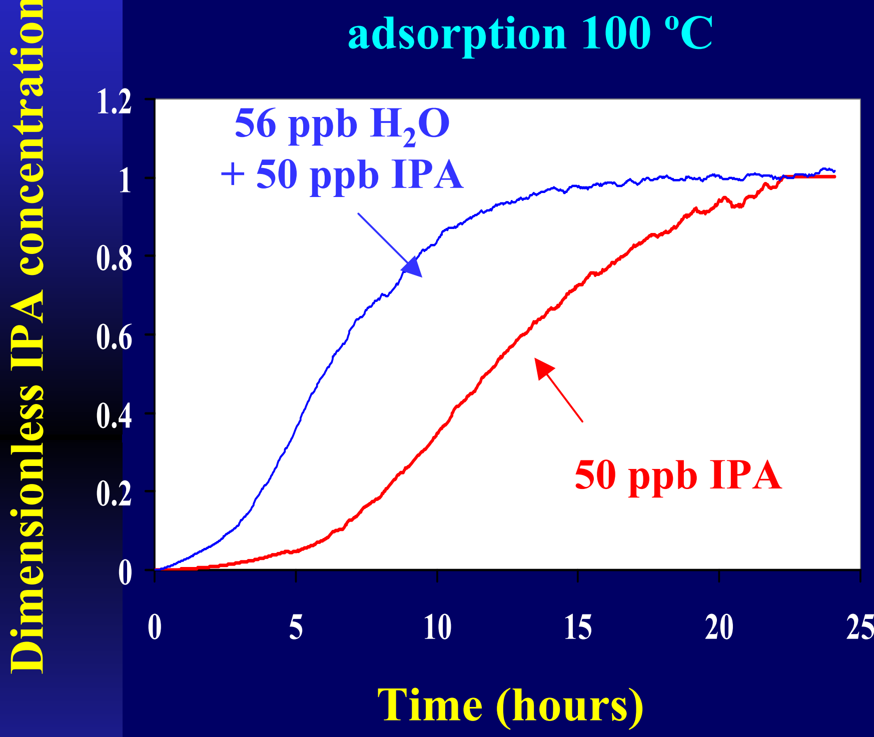
- Moisture acts as a glue in attracting polar organics such as IPA, BHT, DOP on SiO_2 through hydrogen bonding.

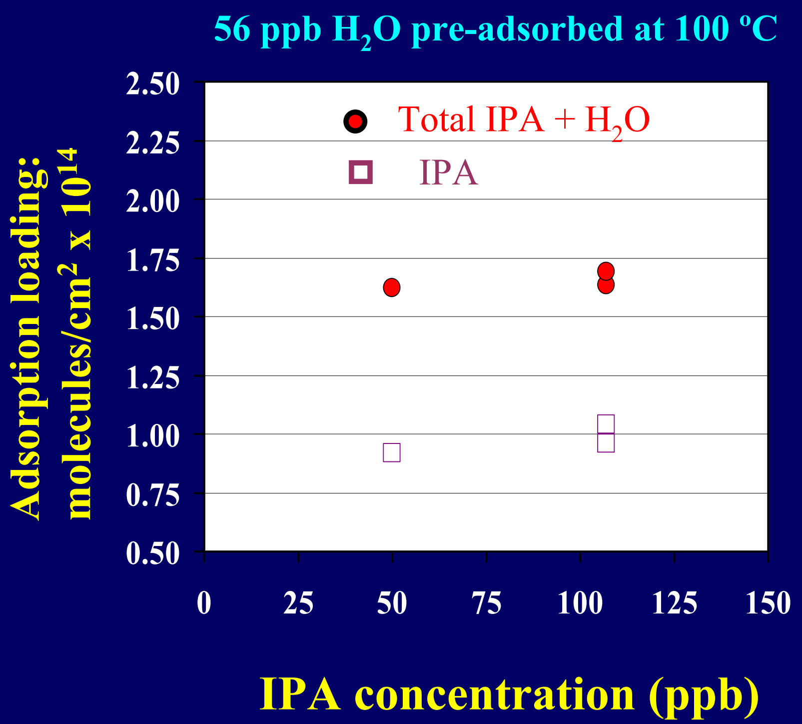
  N. Kagi et. al., IEST proceedings, p. 569 (1998).

- It leads to chemisorption of IPA at high temperatures through alkoxy formation. Verghese et. al., ECS proceedings, PV 98-6, p. 112 (1999).



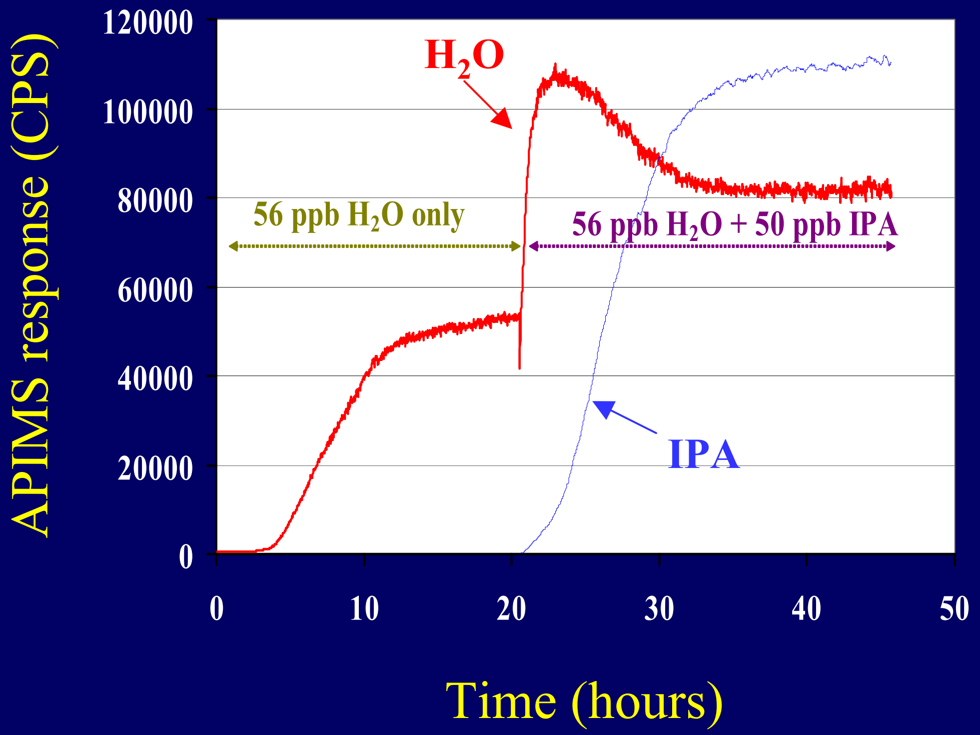
EFFECT OF HYDROXYLATION ON IPA ADSORPTION ON ZrO_2


adsorption 100 °C


56 ppb H_2O pre-adsorbed at 100 °C

- Hydroxylation by pre-adsorbed moisture reduces IPA adsorption on ZrO_2 vs. an increase in IPA adsorption on SiO_2 !
- Total coverage of H_2O + IPA tends to reach the saturation limit.

IPA ADSORPTION ON HYDROXYLATED ZrO_2



- Moisture gets released upon IPA challenge.
- This could be water formed through either alkoxy formation or competitive adsorption of IPA and water.

FUTURE WORK

ZrO_2 and HfO_2

- High concentration H_2O and organics exposure
- Can moisture be removed from ZrO_2 above 400 ºC ?
- Effect of contamination on electrical performance of high-k films

CONCLUSIONS

- Interfacial contamination due to organics can be detrimental to ultra-thin gate dielectrics.
- Processing conditions play an important role in oxidation/ incorporation of organics in silicon.
- A mechanism for organic retention in silicon oxide was proposed.
- Moisture and IPA contamination of high-k candidates ZrO_2 and HfO_2 is more severe than that on SiO_2.
- Upto 350 ºC, moisture does not completely desorb from ZrO_2 – can be problematic.
- ZrO_2 and HfO_2 have a catalytic role in dissociation of IPA.
- Moisture pre-adsorption enhances adsorption of polar organics on SiO_2, studies with other organics are required to establish the effect on ZrO_2.

ACKNOWLEDGEMENTS

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