Effect Of Organic Contaminants
On
The Quality Of Ultra-Thin Silicon Oxide Films

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Presentation Outline

- Significance of Organic Contamination
- Research Objectives
- Experimental Approach
- Results and Discussion

  I a. BHT interactions at wafer and effect of moisture

  II Effect on Thin-Gate Oxidation

  a. Effect of Pre-Oxidation Cleans

  b. Effect of Organic Concentration

  c. Effect of Ramp Ambient

- Conclusions and Future work

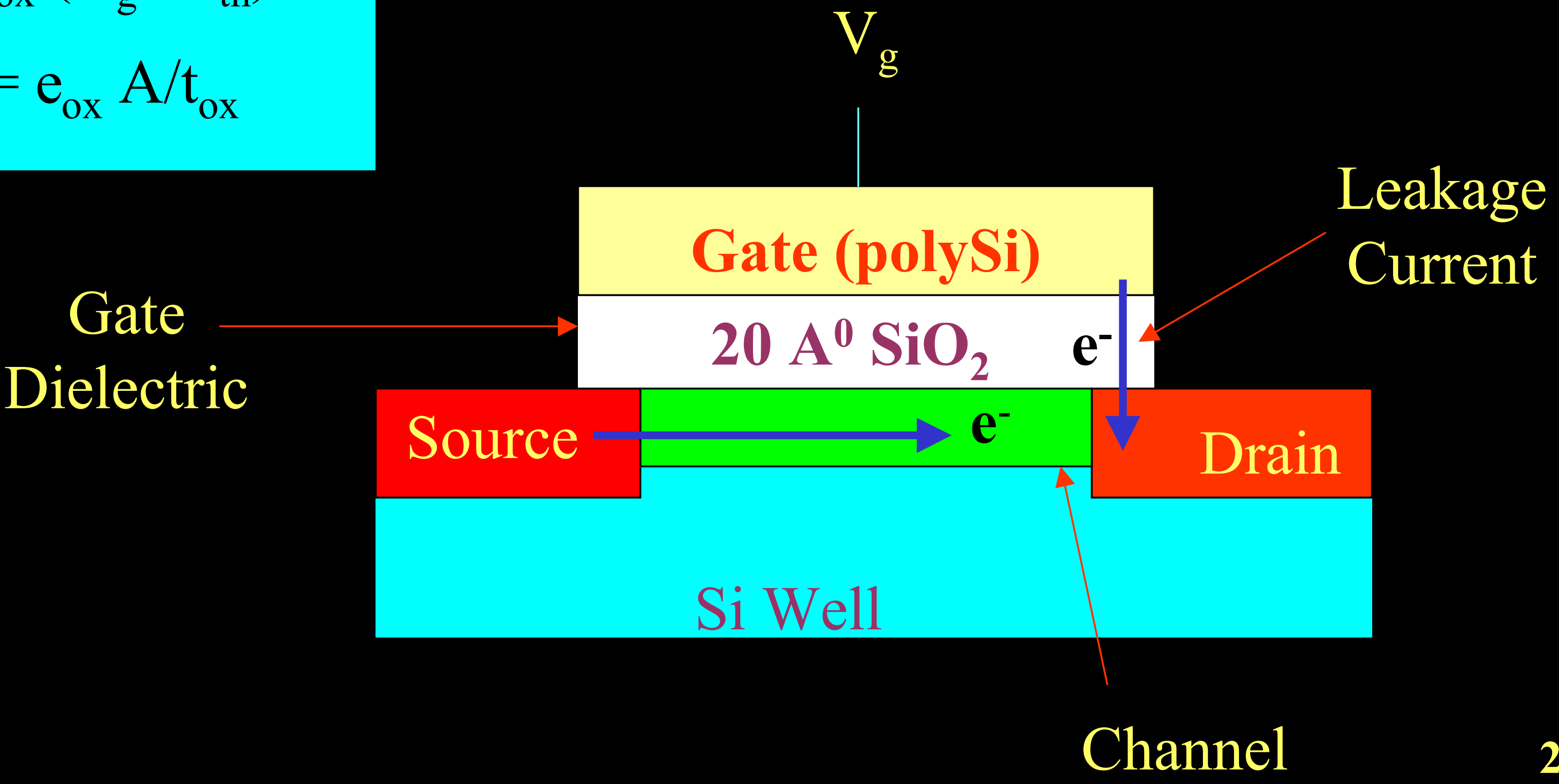
Ultra-Thin Oxides

Higher speed ⇒ Higher device density ⇒ Smaller structures

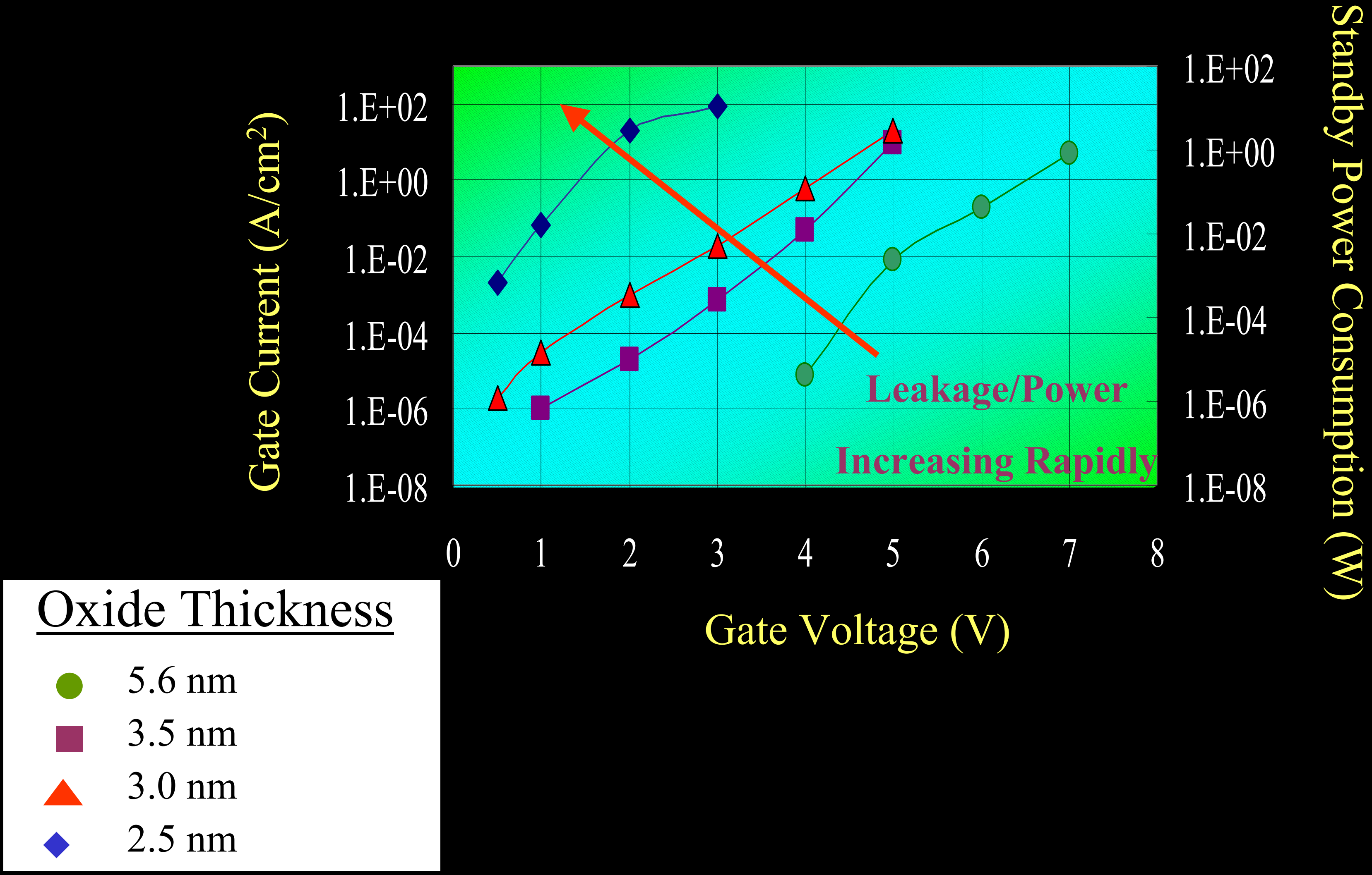
For transistors:

$I = C_{ox} (V_g - V_{th})^2$

$Cox = e_{ox} A/t_{ox}$



Effects at Low Dielectric Thicknesses

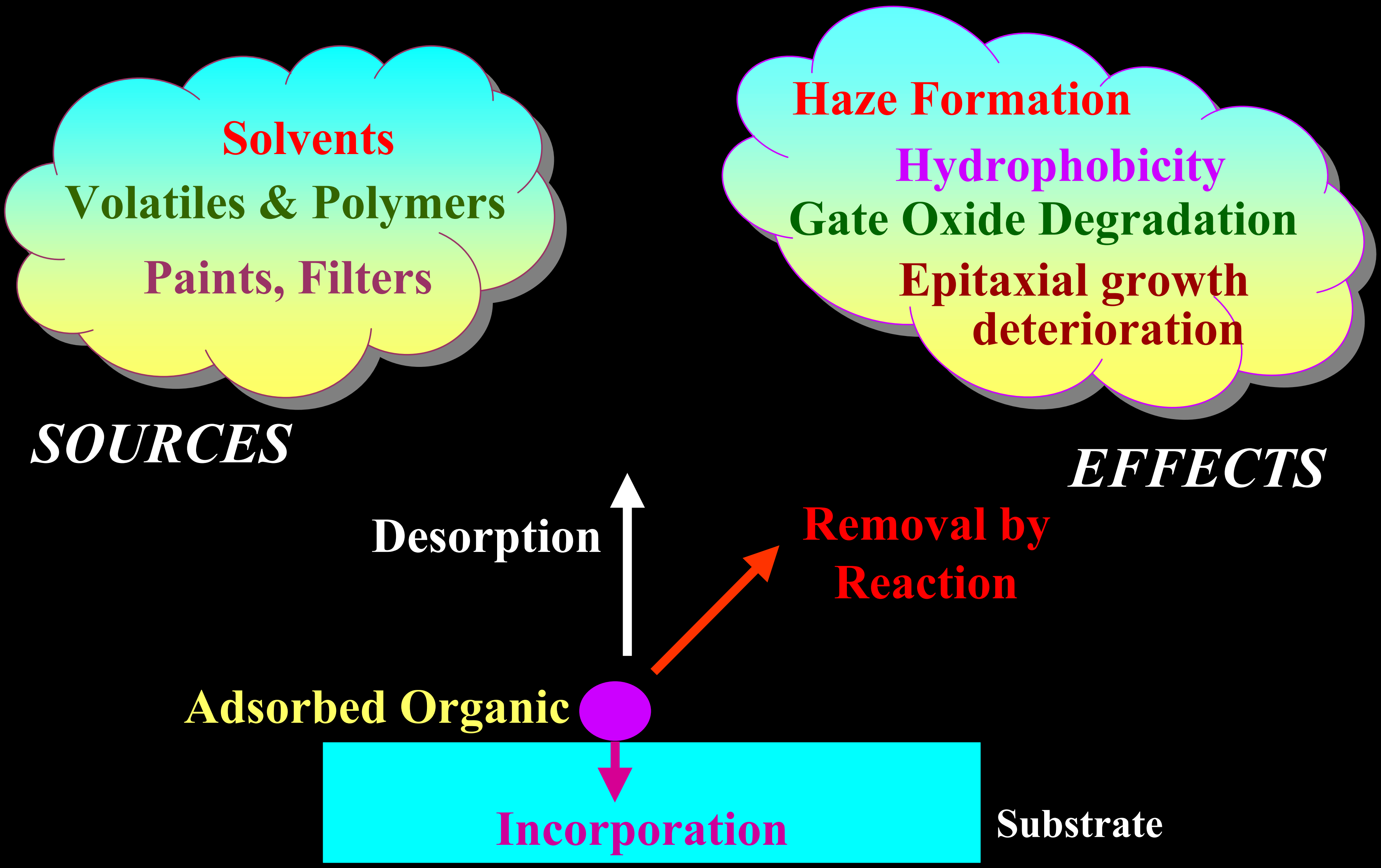


Leakage/Power Increasing Rapidly

Critical Contaminants

- Particles
- Metals
- Substrate Roughness
- Organics

Organics and their Consequences



Solvents
Volatiles & Polymers
Paints, Filters

SOURCES

Haze Formation
Hydrophobicity
Gate Oxide Degradation
Epitaxial growth deterioration

EFFECTS

Desorption

Removal by Reaction

Adsorbed Organic

Incorporation

Substrate

Typical Organics and their End-Effects

Compound Type	Probable Source	Potential Effect
Dibutyl Phthalate, Butyl Hydroxy Toluene, DOP	Polymeric materials, filters, paints, floor tiles	Gate oxide degradation
Amines, Amides	Cleaning solutions, CMP, humidity controllers, epoxies	Affect DUV lithography, increase linewidths
Organophosphates	HEPA/ULPA filters	Counter doping, voltage shifts
Silicones	Sealants, caulks	Hydrophobicity, particle formation
Cresols	Photoresists	Corrosion, hydrophobicity
Hydrocarbons	Polymers, tubes	Negative effect on wet and dry processes

Ref: www.balazs.com

Typical Organics on Wafer Surface

- Butyl Acetate
- Ethylene Glycol
- 2-Ethyl-hexanol
- 1-(1-Methylethoxy), 2- propanol
- 1,6- Hexanediol
- Caprolactam
- Dodecanoic ester
- Tris (2-chloroethyl) phosphate
- N-butyl benzene sulfonamide
- Dibutyl Phthalate

Trends :

- Low boiling organics adsorb immediately and decrease with time
- High boiling organics generally increase with time

Reported Literature On Organics

Kasi et al (IBM) : HF last surface prone to HC contamination, Annealing causes SiC formation and dielectric degradation.

Saga and Hattori (Sony) : Q_{bd} improves by O_2 addition. Residual F increases BHT and DBP uptake on HF last.

Guan, Gale and Bennett (Sematech) : C contamination at oxide-poly interface correlates with post-cleaning C on surface.

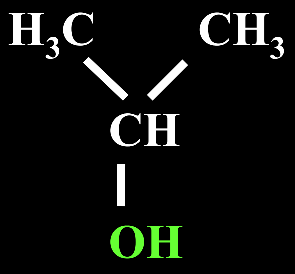
M.Verghese et al (U of Arizona): H_2O increases IPA uptake on silicon oxide and leads to chemisorption.

Research Objectives

Fundamental study of the fate and the effects of organic contamination

- How organics adhere to surface of wafer ?
- What happens to them in high temperature processes ?
- What are the consequences ?

Model Organics



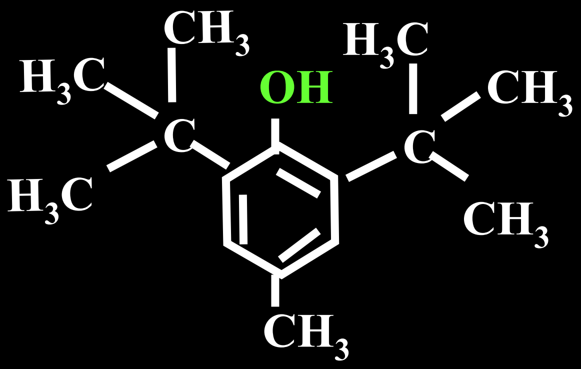
Iso Propyl Alcohol
(IPA)

Used as solvent, drying agent

M.Wt : 60.10

B.P : 83 ^{0}C

μ : 1.84 Debye



Butyl Hydroxy Toluene

(BHT)

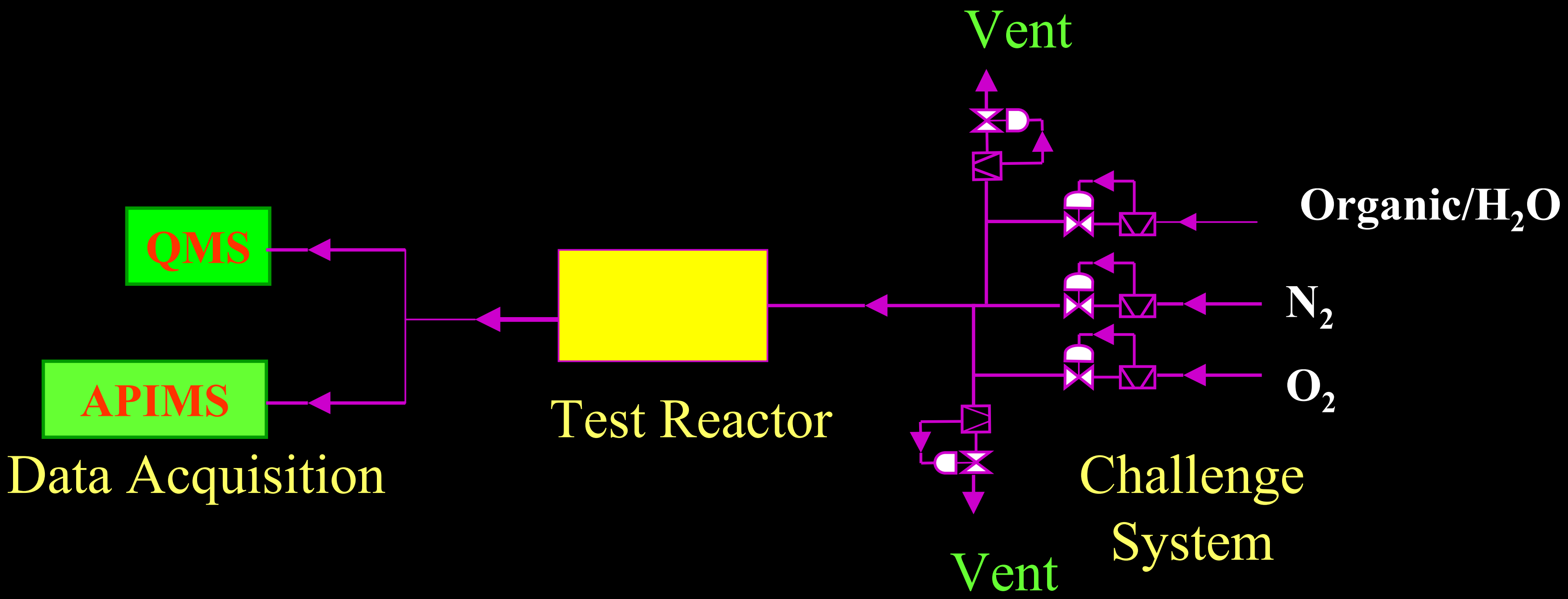
An antioxidant outgassing from polymeric materials such as plastic wafer carriers, storage boxes, bottles etc

M.Wt :220.35

B.P : 265.2 ^{0}C

μ : 1.48 Debye

Experimental Setup - I



Vent

Organic/H_2O

QMS

N_2

APIMS

O_2

Data Acquisition

Test Reactor

Challenge System

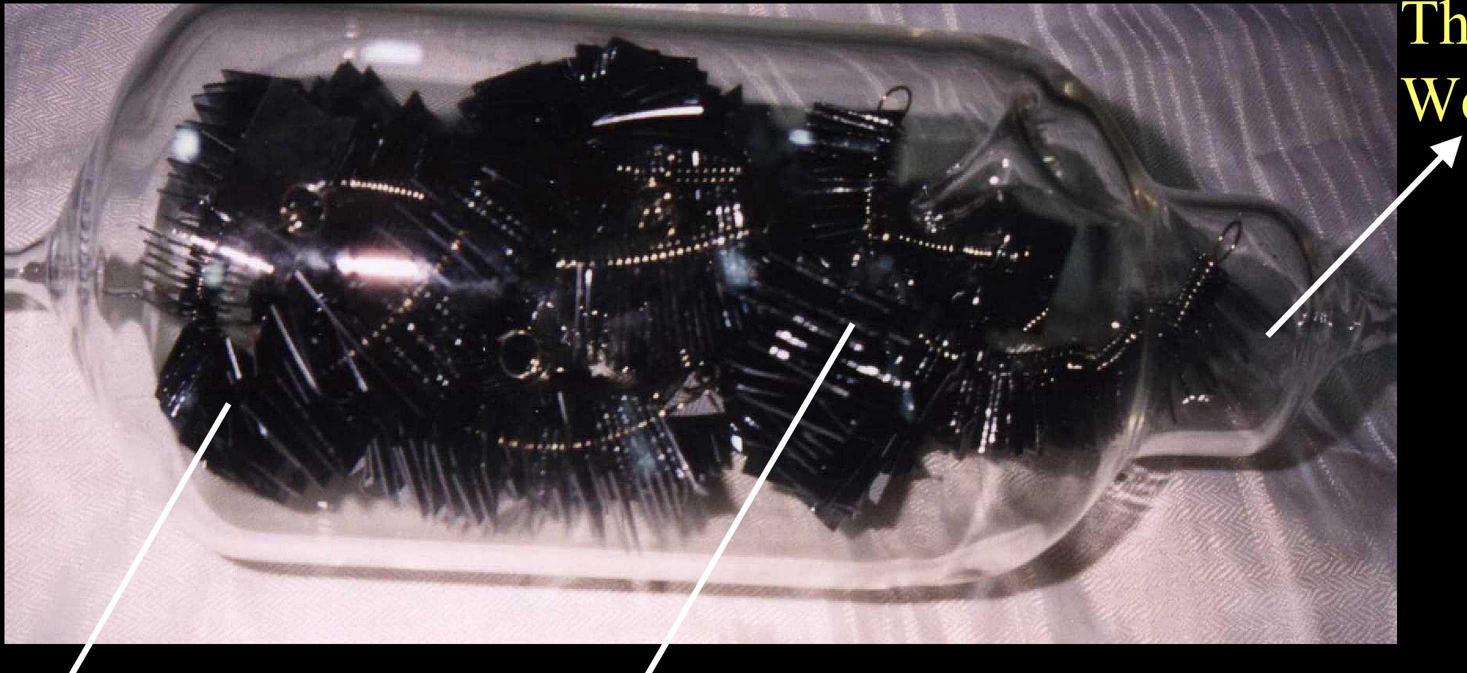
Vent

- All Metal MFCs
- EPSS Tubing, 7 RA
- No Dead Volumes
- Research Grade Gases
- Isotopic Labeling Studies

Detection Capabilities

- Single digit ppt levels !!
- Numerous dedicated analyzers
- Surface Analysis such as Auger

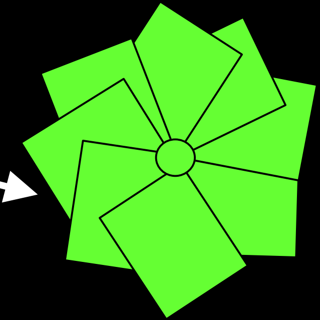
Reactor for Kinetic Studies



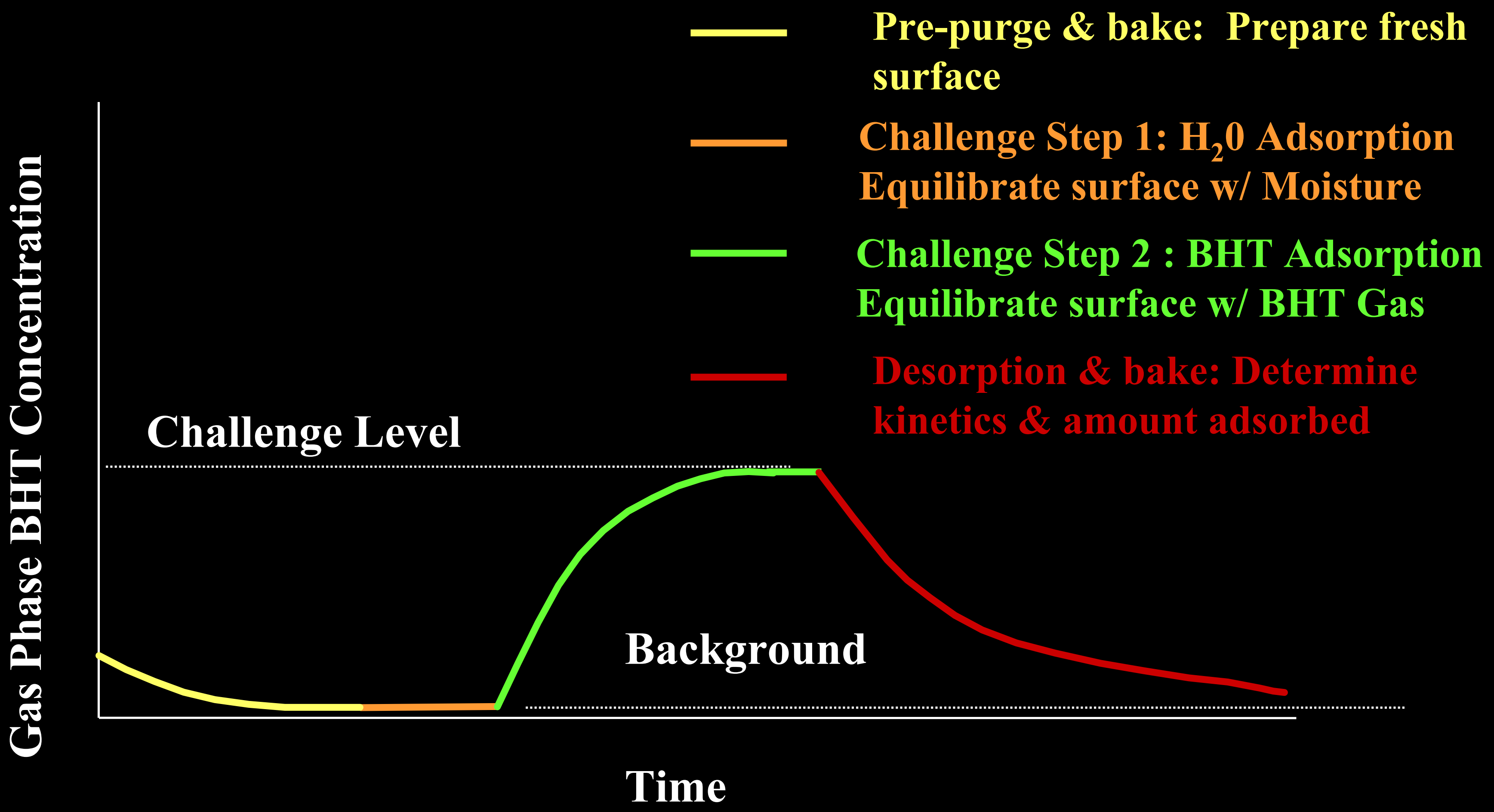
Thermal Well

Pyrex Reactor

Wafer Coupons



Experimental Procedure

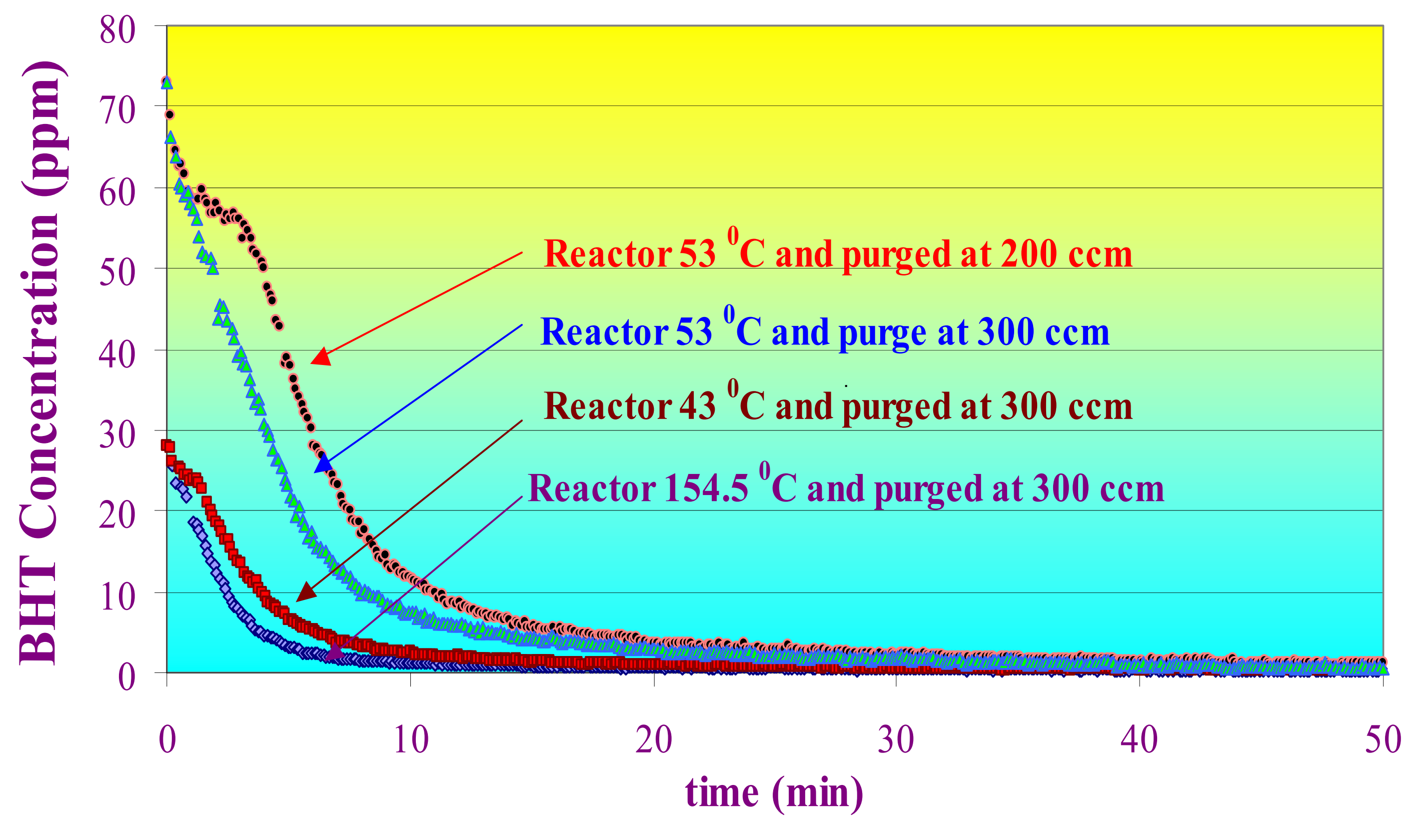

🟨 Pre-purge & bake: Prepare fresh surface

🟧 Challenge Step 1: $H_2$0 Adsorption Equilibrate surface w/ Moisture

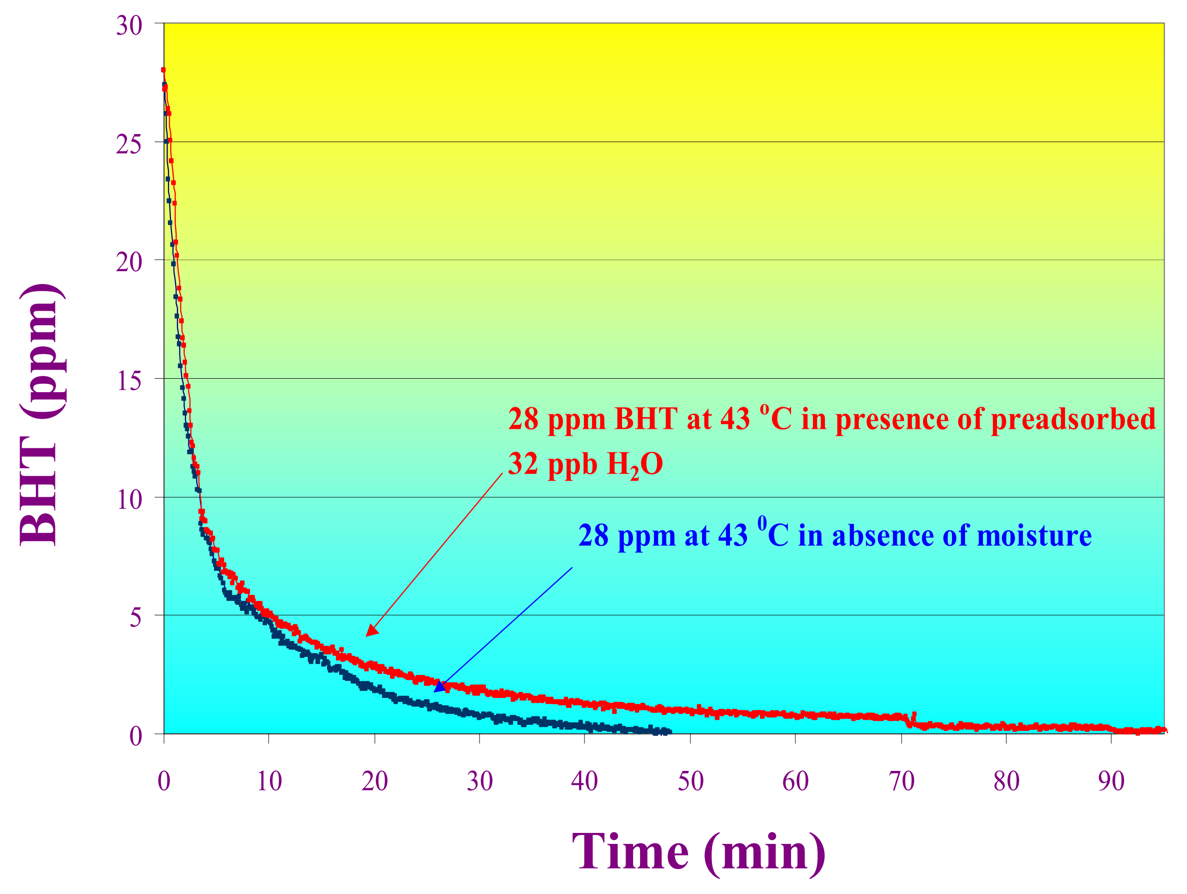
🟩 Challenge Step 2 : BHT Adsorption Equilibrate surface w/ BHT Gas

🟥 Desorption & bake: Determine kinetics & amount adsorbed

BHT Desorption Profiles



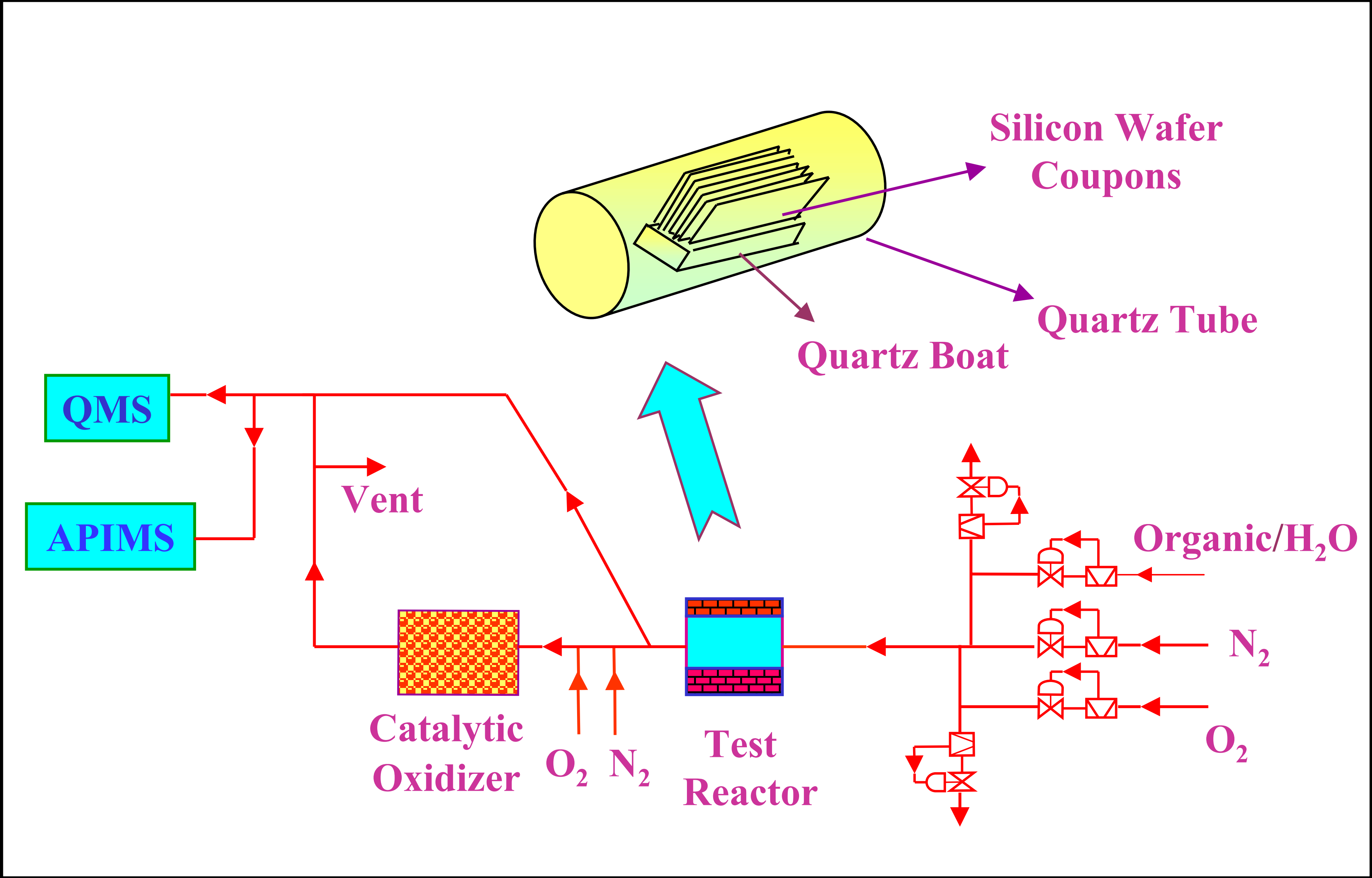
Effect of Moisture on BHT adsorption



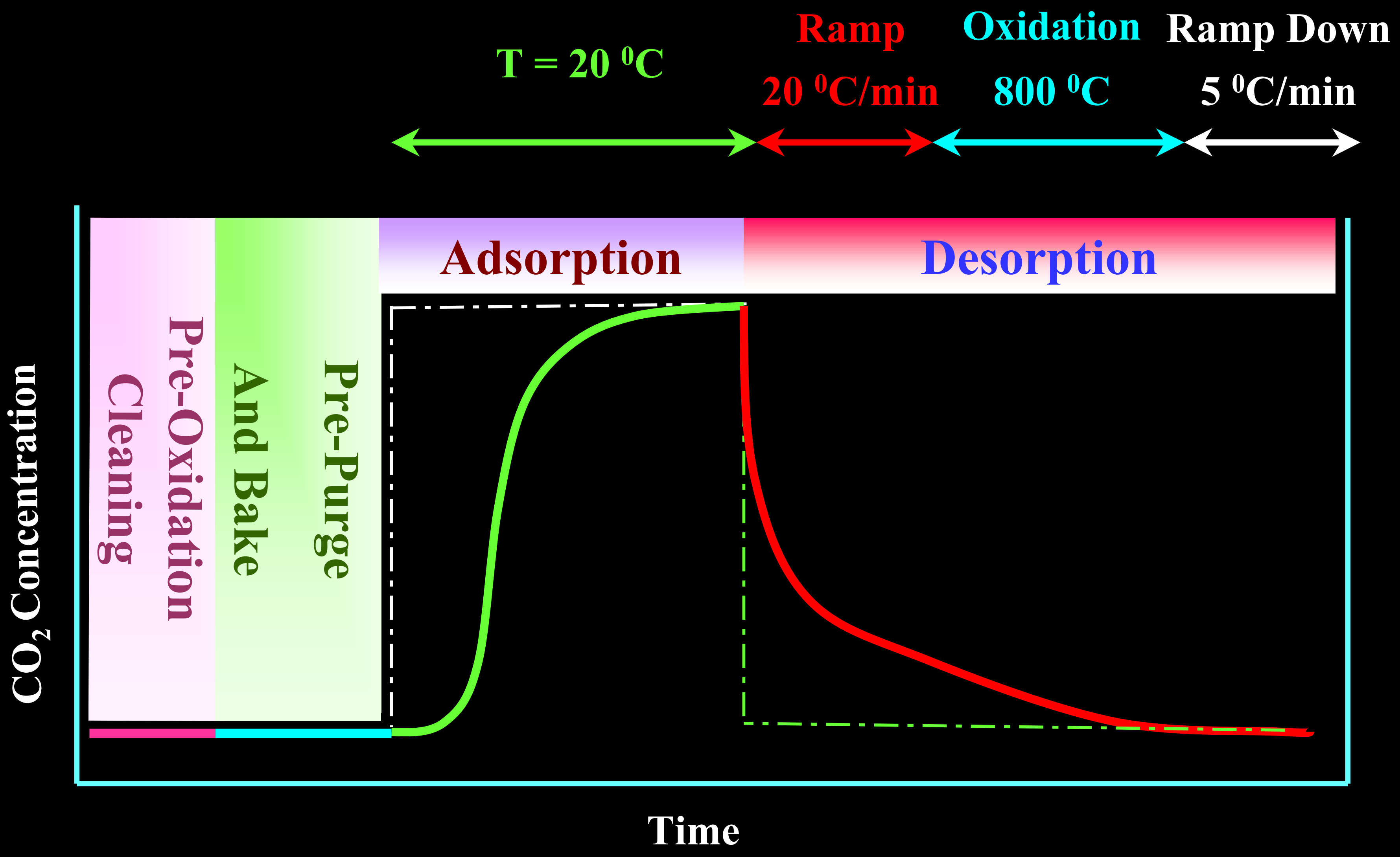
Organic Loading on Surface

BHT ppm	H_2O ppb	Temp. ^0C	# BHT $/cm^2$	# H_2O $/cm^2$	# BHT per H_2O
28	0	43	3.4 E14		
28	32	43	5.0 E14	3.5 E13	2.3
28	0	105	2.5 E14		
28	32	105	3.7 E14	2.5 E13	2.3
28	0	150	2.1E14		
28	32	150	3.0 E14	2.1 E13	2.1

Experimental Setup - II

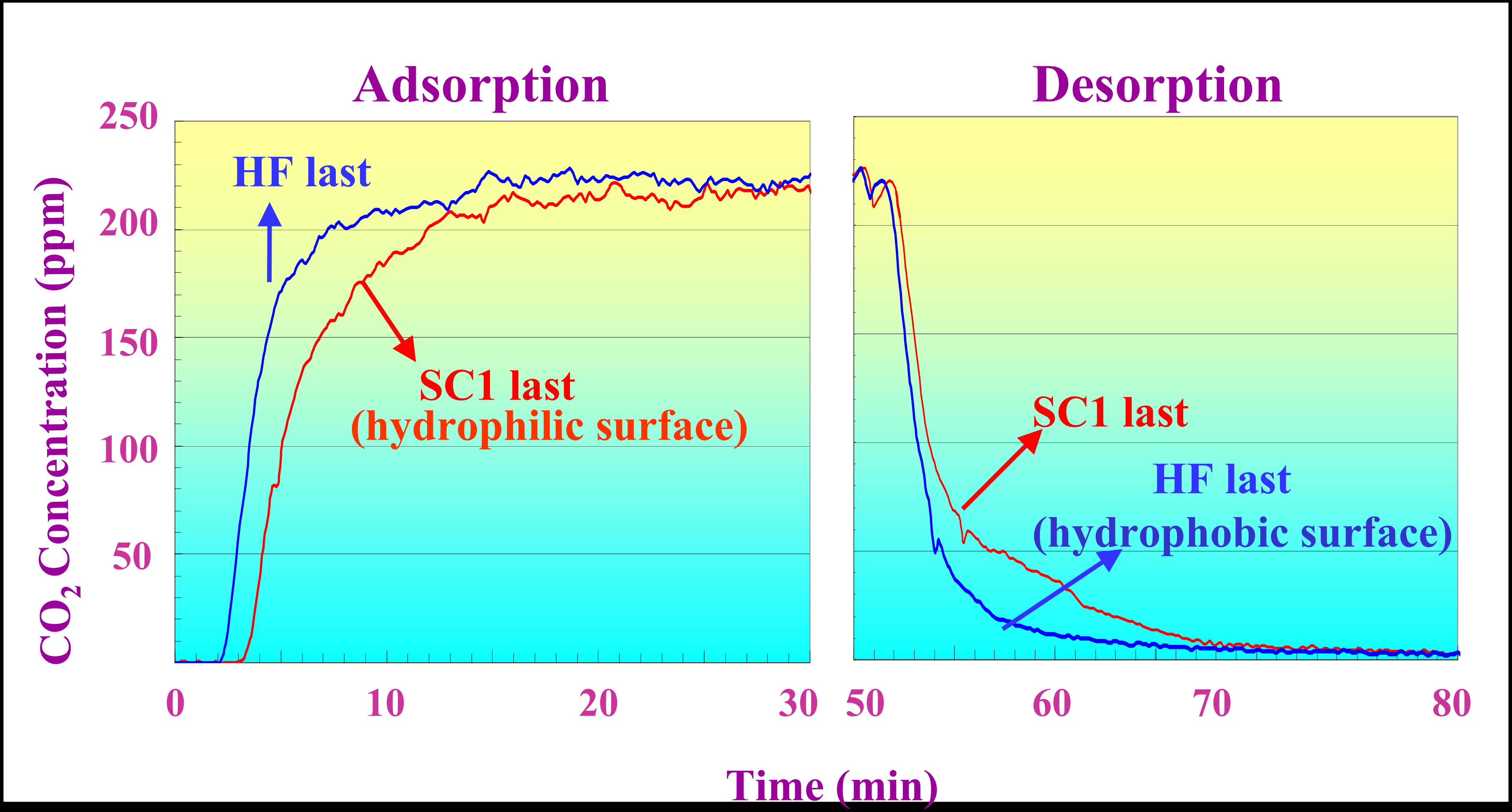


Experimental Procedure

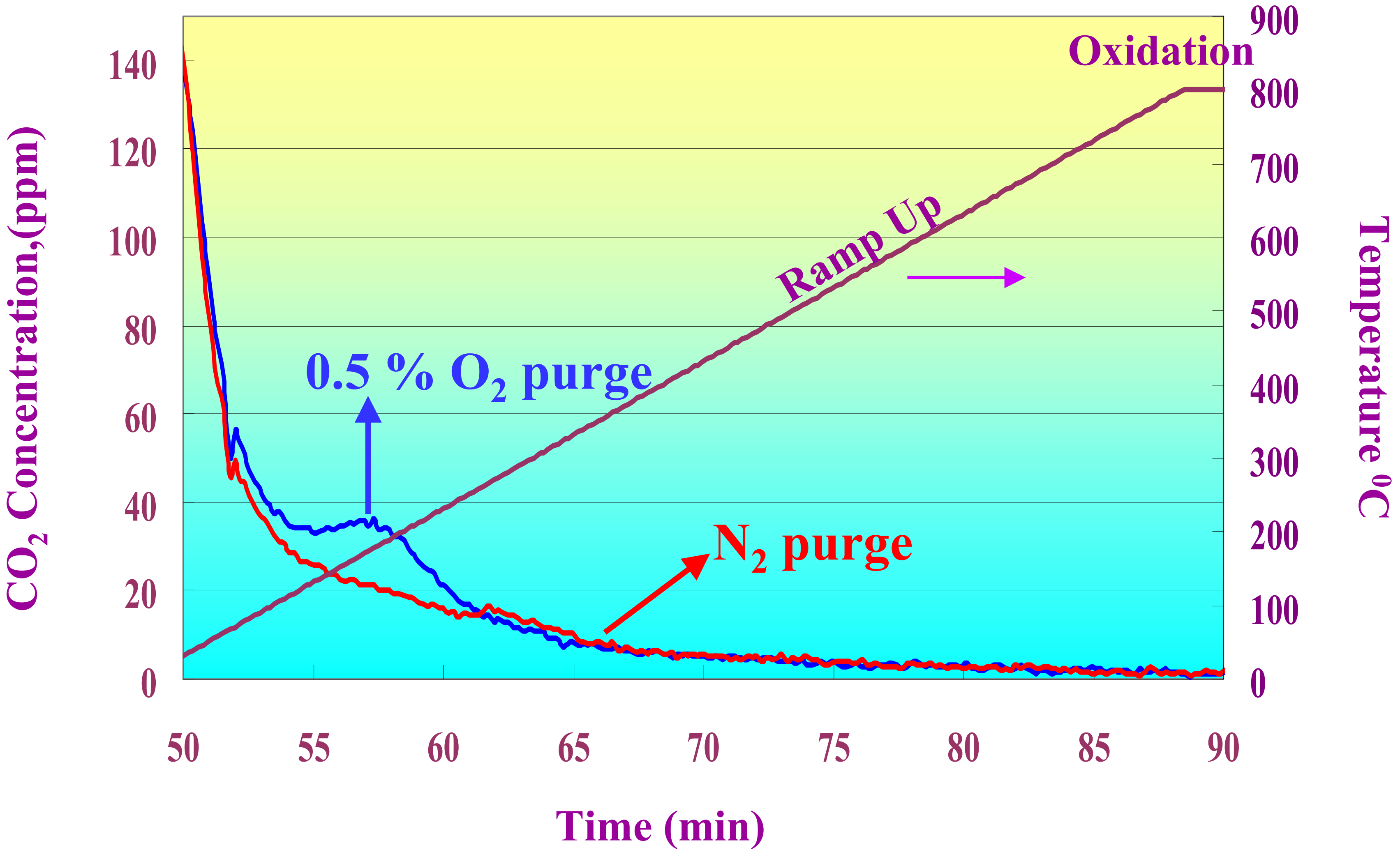


Experimental Response

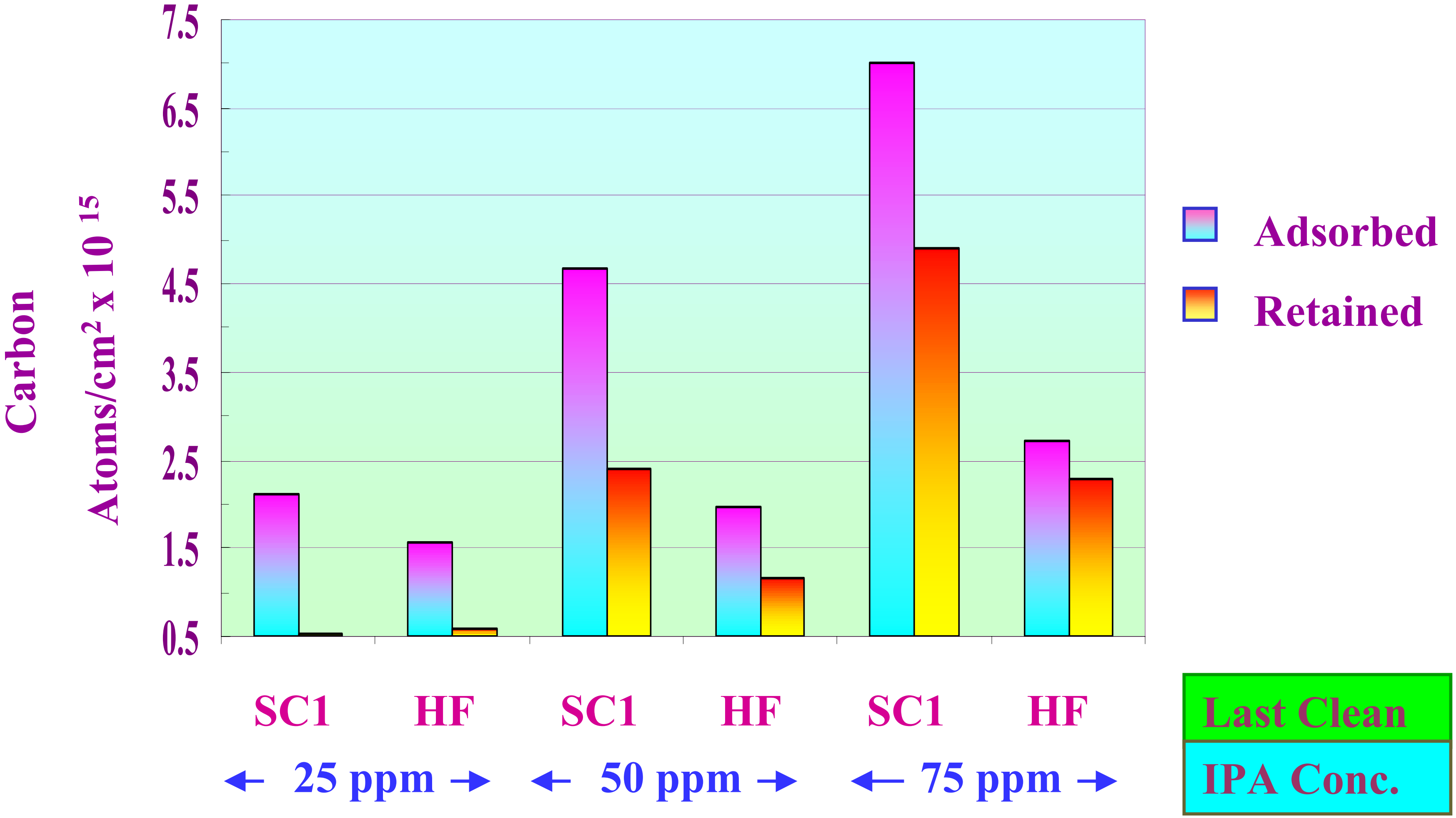
75 ppm IPA challenge, Ramp up to 800 ^{0}C at 20 ^{0}C/min in N_2



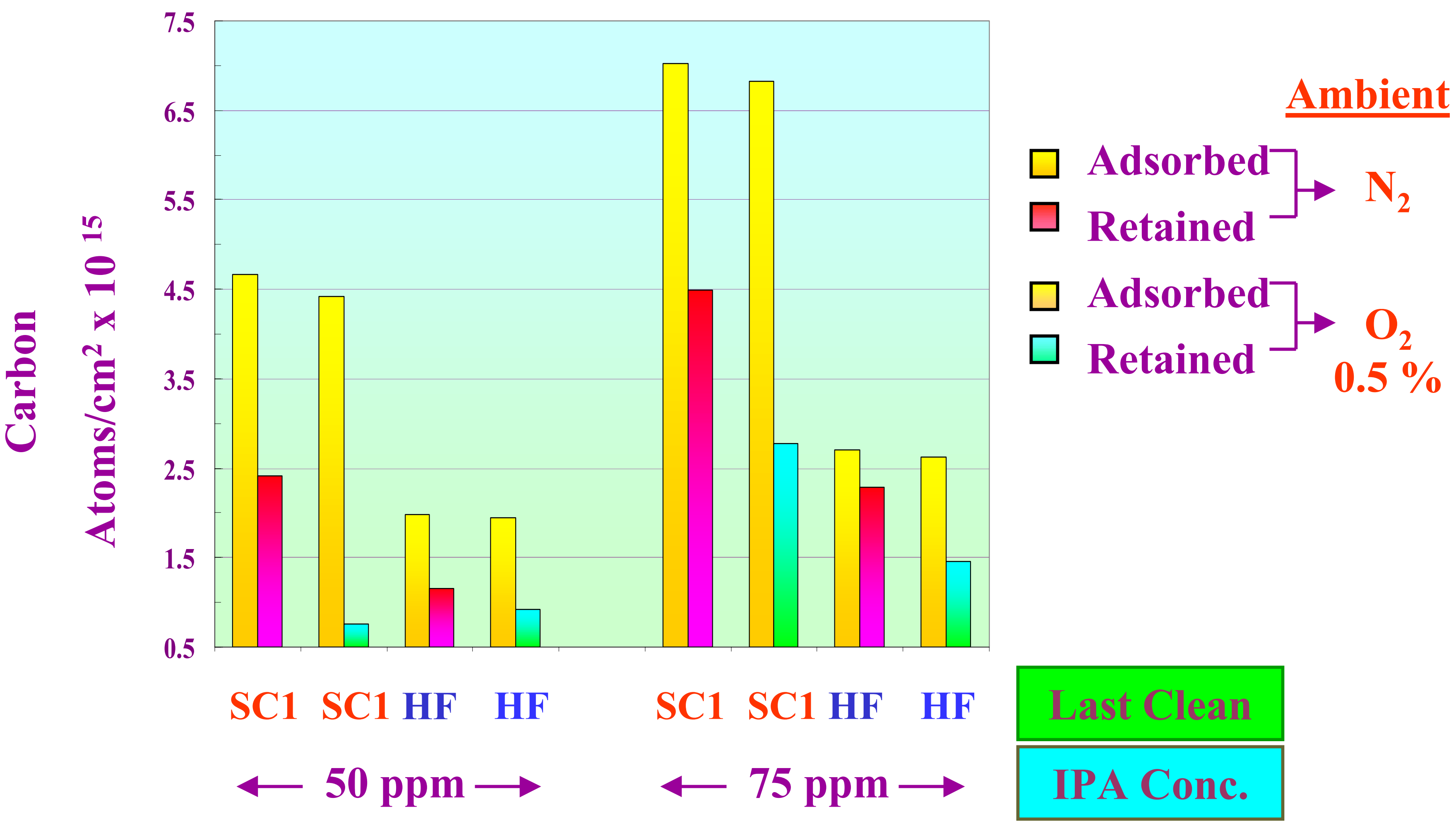
50 ppm IPA Challenge on SC1 last wafers



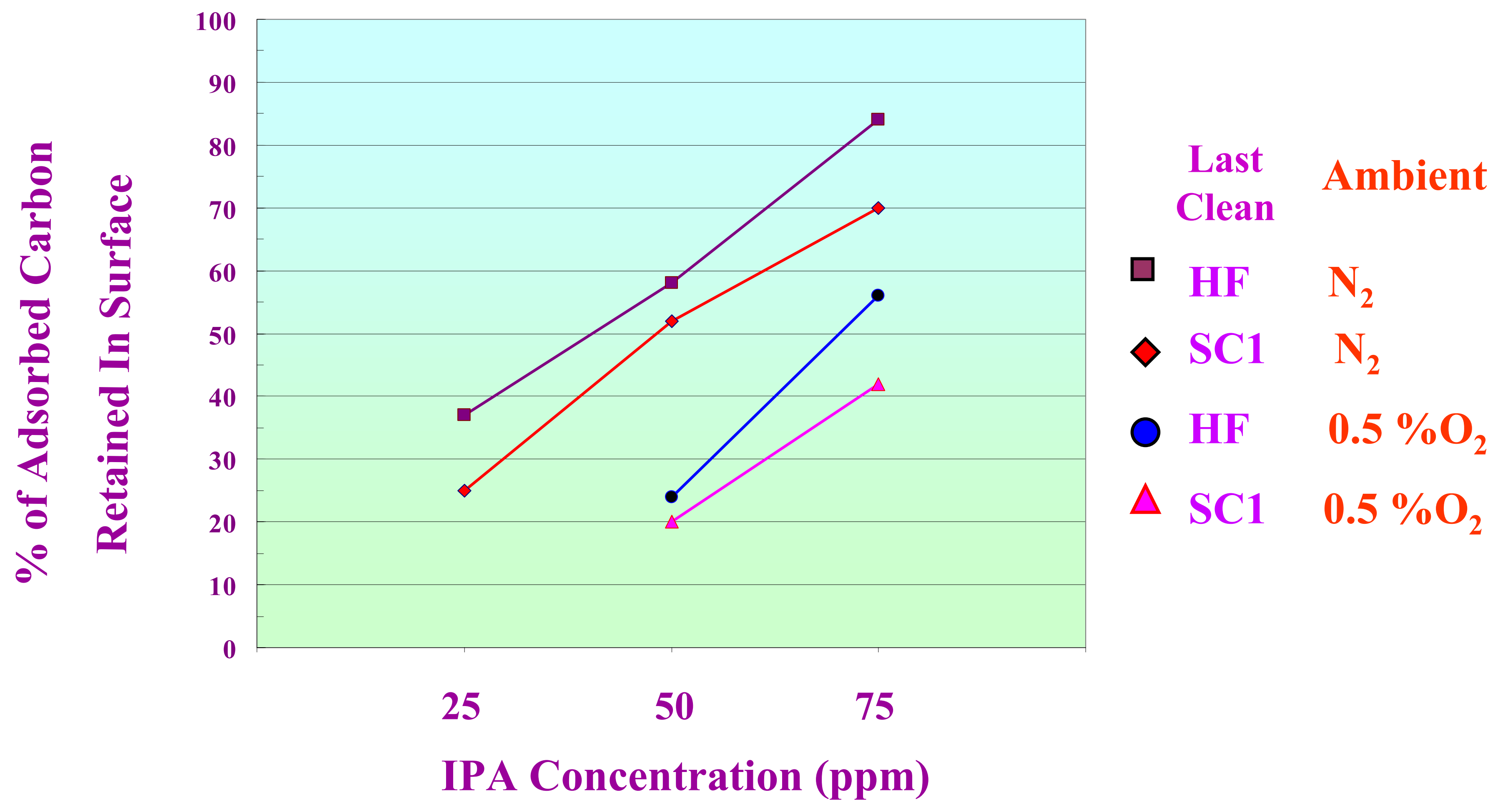
Effect of Cleans and Organic Concentration



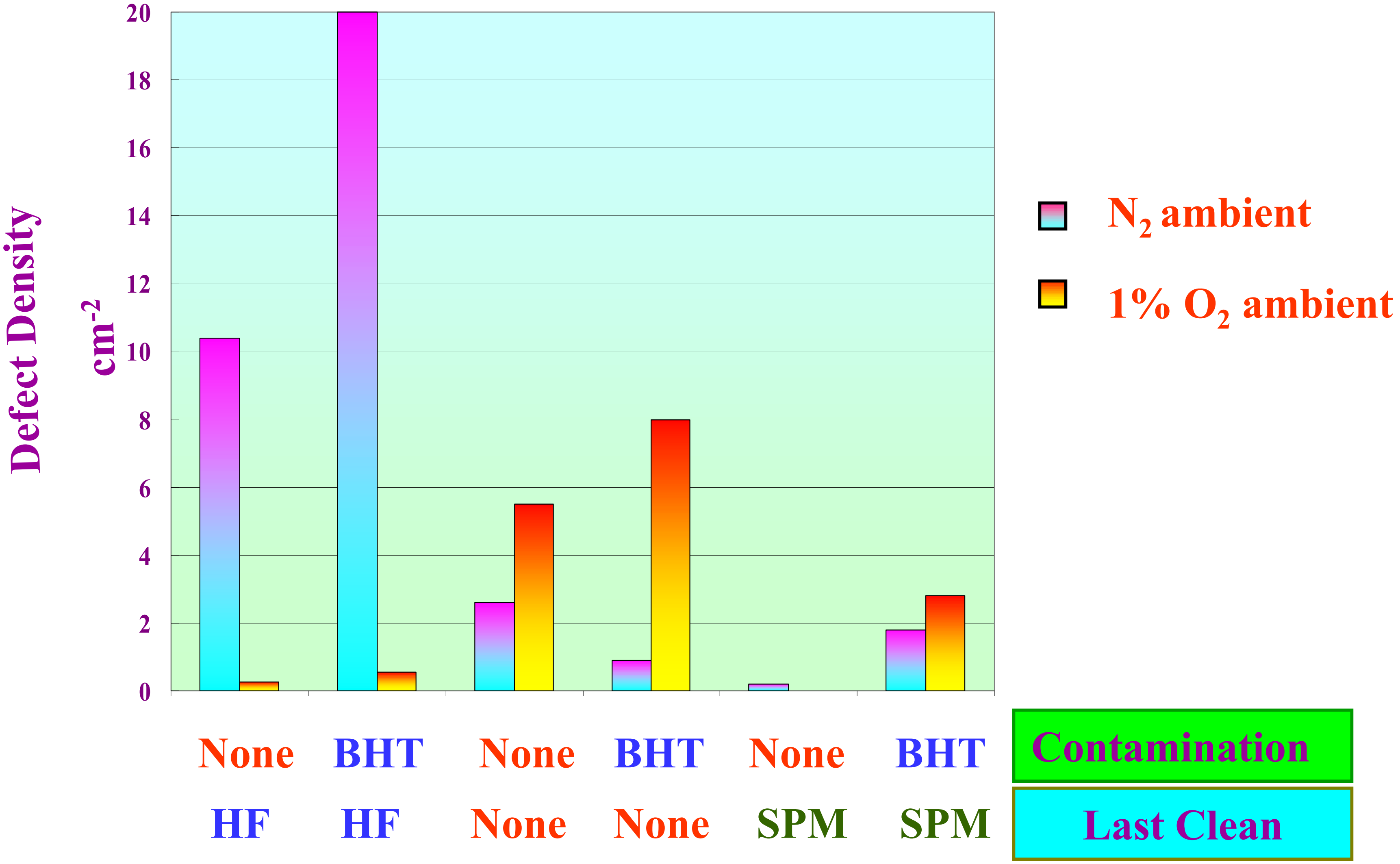
Effect of Oxygen during Ramp-Up



Carbon Incorporation in Substrate



Effect on Gate Oxide Integrity



Model for Oxidation/Incorporation of Organics

Species

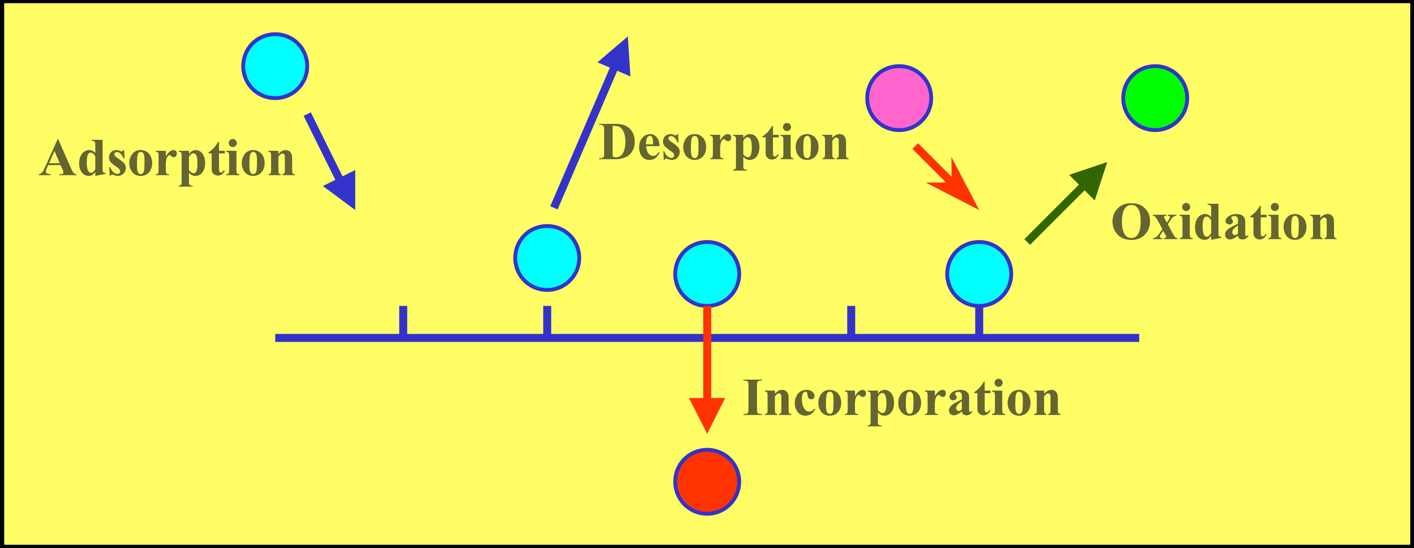
- ● Gas Phase Organic (C_{org})
- ● Adsorbed Organic (R)
- ● Oxygen (O_2)
- ● Oxidation Product (P)
- ● Incorporated Carbon (I)

Reactions

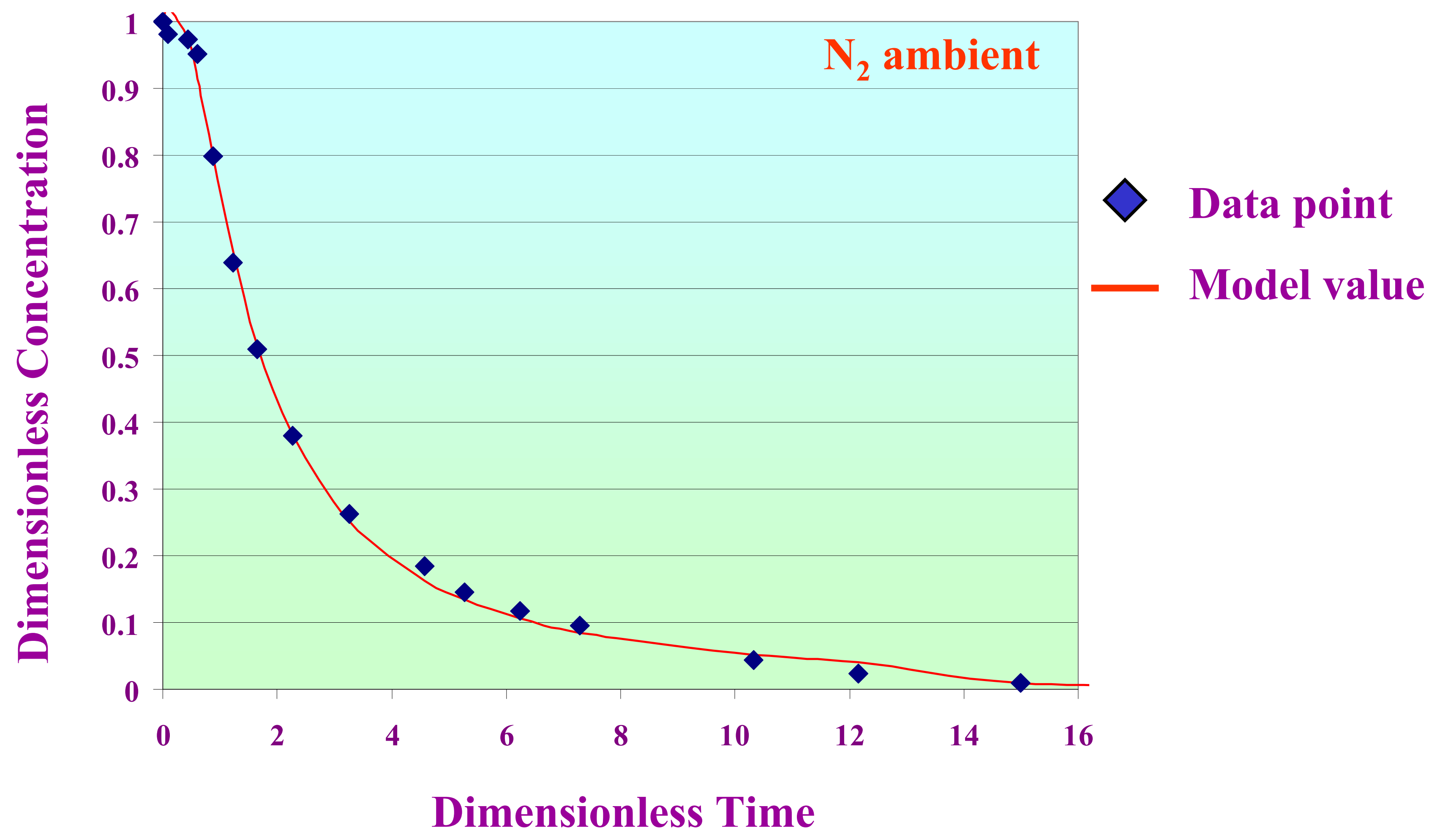
$$C_{org} + X \underset{k_d}{\overset{k_a}{\longleftrightarrow}} R$$

$$R + O_2 \xrightarrow{k_{ox}} P + X$$

$$R \xrightarrow{k_{inc}} I$$



Fit of Model to Data



Typical Model Parameters

Process	Parameter	Symbol	N_2 ambient Ramp	O_2 ambient Ramp
Adsorption	Rate constant @ 20°C	k_a (cm/min)	5.8E-02	3.7E-03
	Activation energy	E_a (kJ/mol)	18.9	18.9
Desorption	Rate constant @ 20°C	k_d (min^{-1})	1.5E-01	1.7E-02
	Activation energy	E_d (kJ/mol)	6.2	6.2
Incorporation	Rate constant @ 700°C	k_{inc} (min^{-1})	4.4E-02	1.5E-02
	Activation energy	E_{inc} (kJ/mol)	77.9	77.9
Surface oxidation	Rate constant @ 20°C	k_s (cm/min)		1.2E-14
	Activation energy	E_s (kJ/mol)		88.4

CONCLUSIONS

- Organic contamination affects interfacial and thin film properties in gate oxidation and epitaxial growth.

- Moisture enhances adsorption of polar organics such as BHT, IPA and forms chemisorbed species at high temperatures.

- A novel method is developed to detect the kinetics and mechanism of the removal/retention of trace organic contamination.

- SC1 last (hydrophilic) surface adsorbs greater amounts of IPA compared with HF last (hydrophobic) surface. However, a greater fraction of the adsorbed organic gets incorporated in the hydrophobic surface.

CONCLUSIONS (cont.)

- As IPA concentration increases, carbon incorporation in the substrate increases.

- Oxygen in ramp-up decreases the amount of carbon incorporation and the resulting defects; however, it appears to cause other defects, possibly due to immobilization of certain inorganic impurities.

- A model is developed and validated to simulate the simultaneous removal and incorporation of organic impurities during desorption or thermal oxidation.

Future Work

- Study other factors in oxidation
- Complete experiments with BHT
- Investigate effects of DOP
- Continue refining the models
- Organics on promising Alternate Gate Dielectrics