

# **Silicon-Based Surface Treatments for Improved Vacuum System Throughput, Inertness, and Corrosion Resistance**

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# Research Focus: Surface Modification

- Surface treatments to improve performance of ordinary materials
  - Stainless steels / carbon steels
  - Glass
  - High performance alloys
- Focus on silicon / functionalized silicon
  - Inert
  - Corrosion resistant
  - Diffusion barrier
  - Tailor properties (i.e. surface energy)

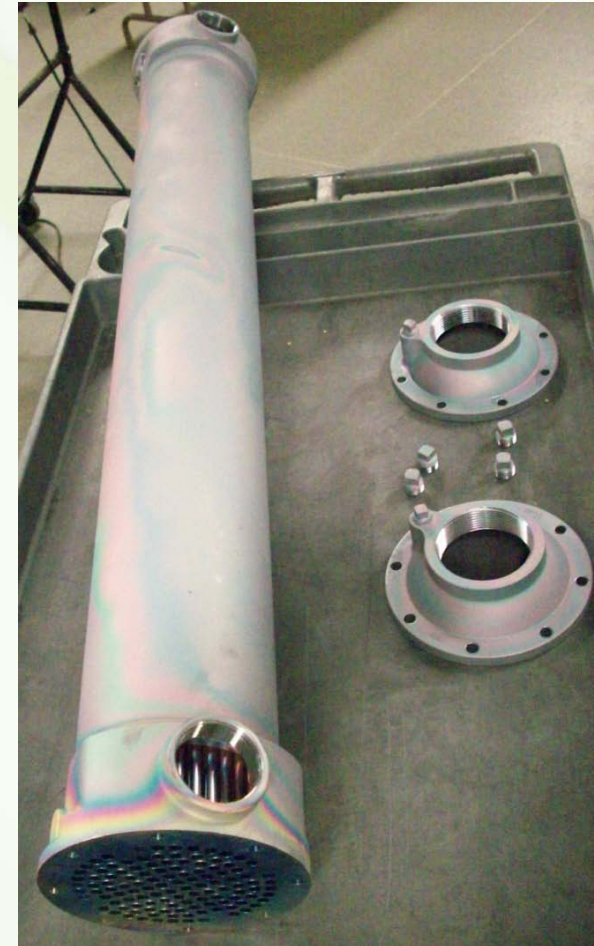


# New Technology?

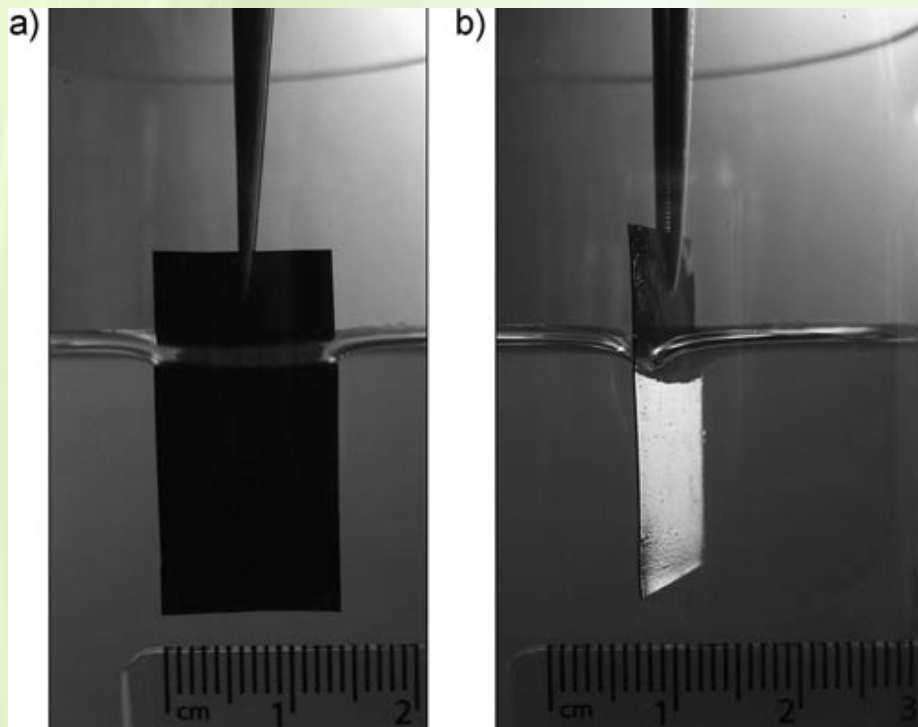
- Kipping – silicon materials in 1920's
  - Reductive coupling of silicon chlorides
  - Functional polysilanes –  $[\text{SiR}_2]_n$
  - Functional polysilynes –  $[\text{SiR}]_n$
  - Solubility issues
- Semiconductor industry (1960's)
  - High purity silicon depositions
  - Controlled doping, etching, implanting

# Focus: Bulk surface modification

- Regardless of
  - Configuration
    - 3D
    - Coiled tubing
  - Part count
  - Size (within reason...)
- Engineering surface performance beyond original design



# Why bother? Powerful Example...



- Silver texture on copper with heptadecafluoro -1-decanethiol coating
- Air layer between water and metal coupon
- Critical viewing angle =  $48.6^\circ$  (same as water/air reflection boundary);  $<1\%$  water in contact with surface ( $CA = 173^\circ$ )

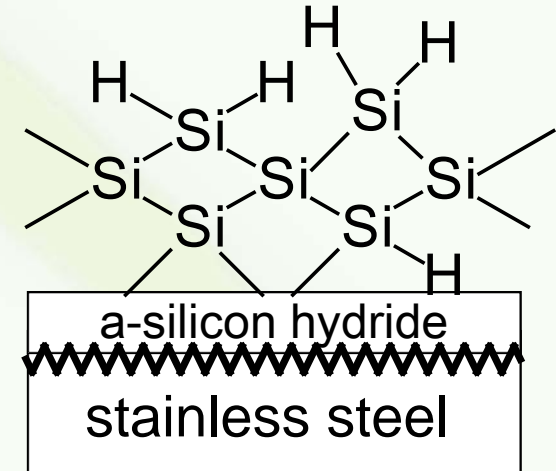
Larmour, I.A.; Bell, S.E.J; Saunders, G.C. *Angew. Chem. Int. Ed.* 2007, 46, 1710-1712.

# Thermal CVD Process

stainless steel

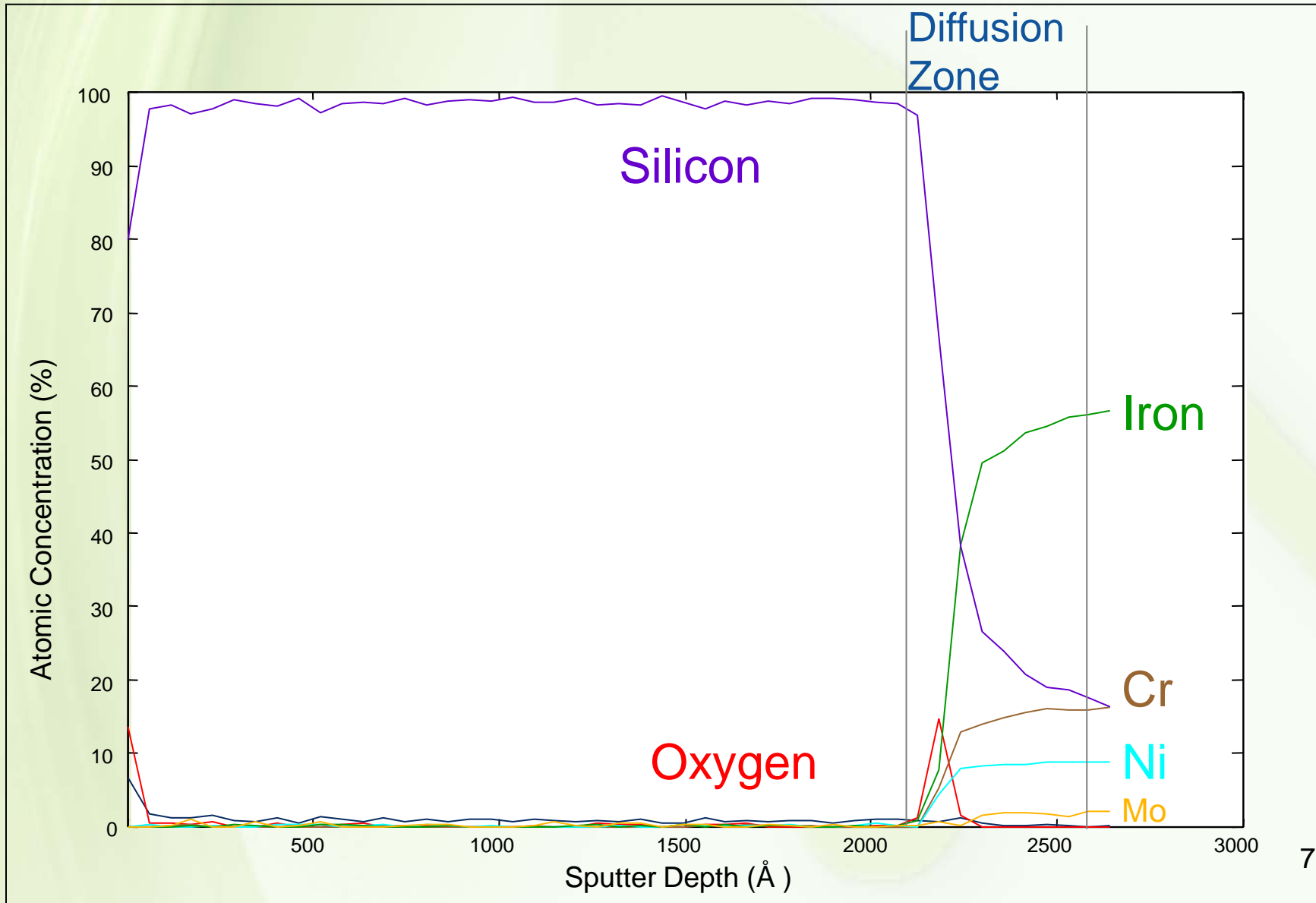
1. vac, heat

2.  $\text{Si}_n\text{H}_{2n+2}$



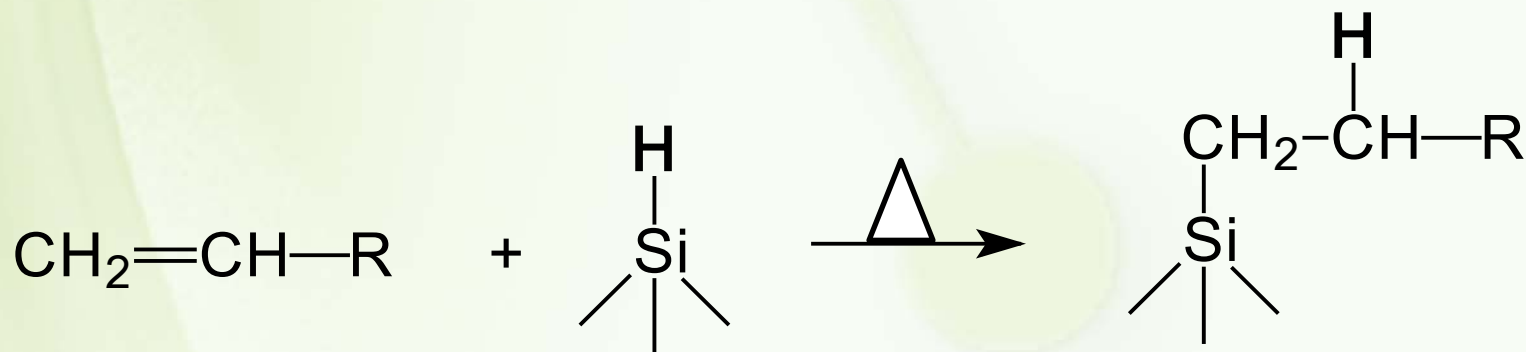
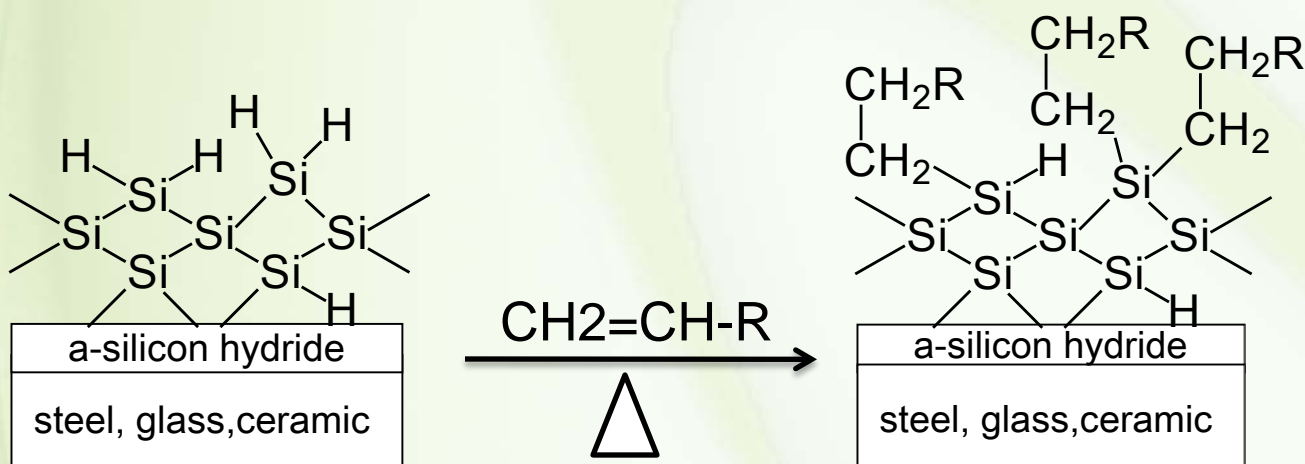
- Diffusion in to stainless lattice
- Native oxide formation on surface upon atmospheric exposure

# AES Depth Profile



# In-Situ Surface Chemistry

- Functionalize via thermal hydrosilylation



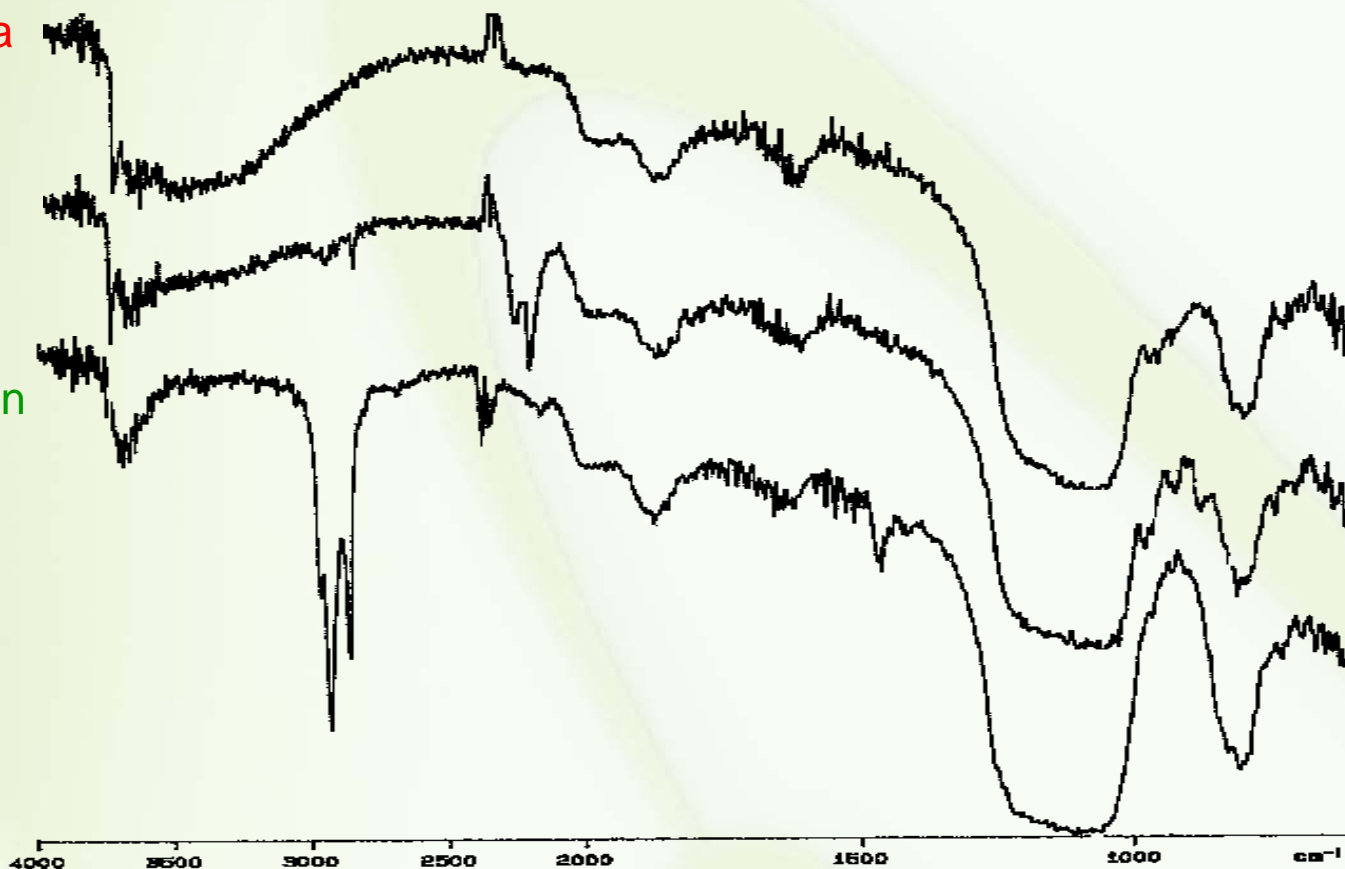


# DRIFTS Illustration of Func.

Raw 5um Silica

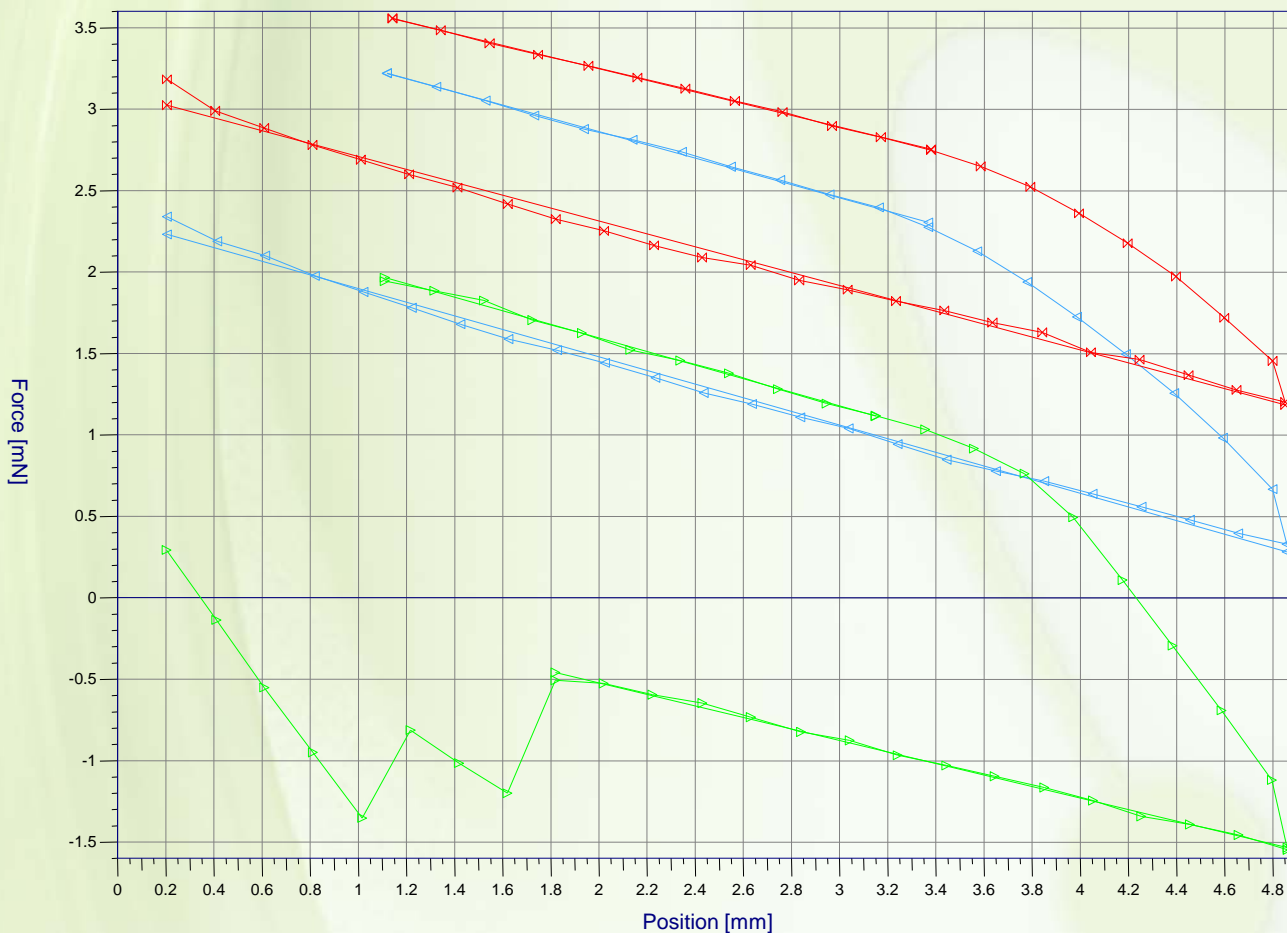
a-Si deposition  
on Silica

Hydrocarbon  
functionalization  
on a-Si / silica



# Surface Energy Measurements

Force vs Position

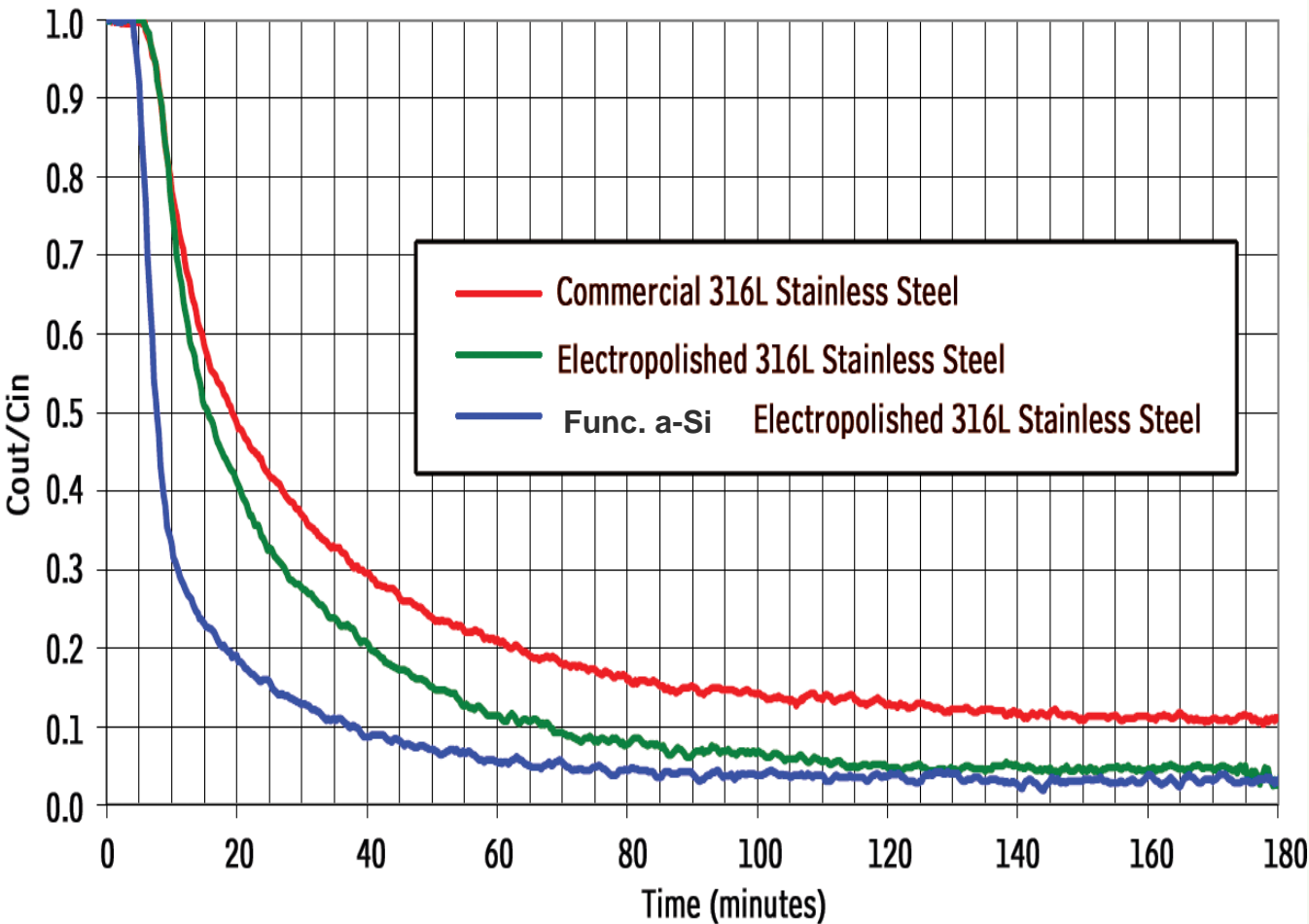


Bare 316ss  
 37.2° advancing  
 0° receding

a-Silicon coated  
 53.6° advancing  
 19.6° receding

Functionalized a-Si  
 87.3° advancing  
 51.5° receding

# Tubing Drydown Example



## Conditions:

100', ¼" tubing,  
0.35 slpm, 22C

## 1ppm Equilibration Time:

- Commercial seamless: 180 min. (96% DD)
- E-polished seamless: 60 min. (98% DD)
- Func. a-Si, e-polished seamless: 30 min. (98% DD)

Data courtesy of O'Brien Corporation, St. Louis, MO

# Anti-Corrosion Benefits Example



Untreated 316 SS



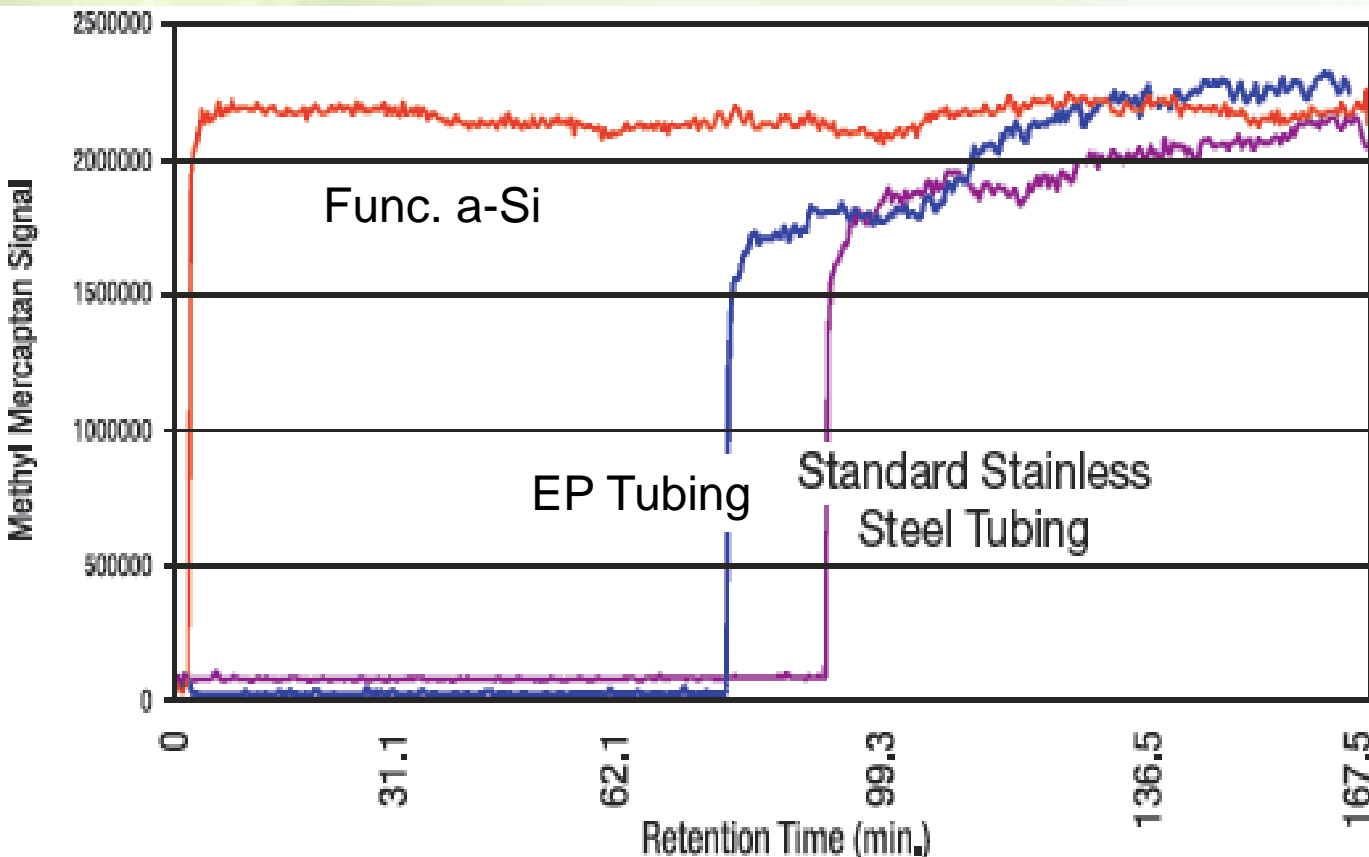
a-SiH coated 316 SS

ASTM G48 Method B: Pitting and Crevice Corrosion

6% Ferric Chloride solution, 72hrs, 20°C, Gasket wrap

~10X Improvement (weight loss)

# Tubing Inertness Example



## Sulfur Flow-Through Data:

- 100' 1/8" x .020" 316 SS tubing
- 0.5ppmv methyl mercaptan in He
- SCD detection

Data courtesy of Shell Research Technology Centre, Amsterdam

- What does this mean?
  - Activity at metallic interfaces can be minimized or avoided

# Vacuum System Issues

- Long evacuation times / poor base vacuum
  - ~~– Leaks~~
  - Volatile Contamination
    - Water vapor
      - Atmospheric
      - Gas lines
    - Organic
- Metallic / non-volatile contamination
  - Chamber material
  - Prior process remnants
- Root cause: Surface Interactions



# Seasoning

- Systems require time / dummy runs / process exposure before steady state is achieved
- Time and cost intensive
- Root cause: Surface Interactions



# Heat-Induced Outgassing

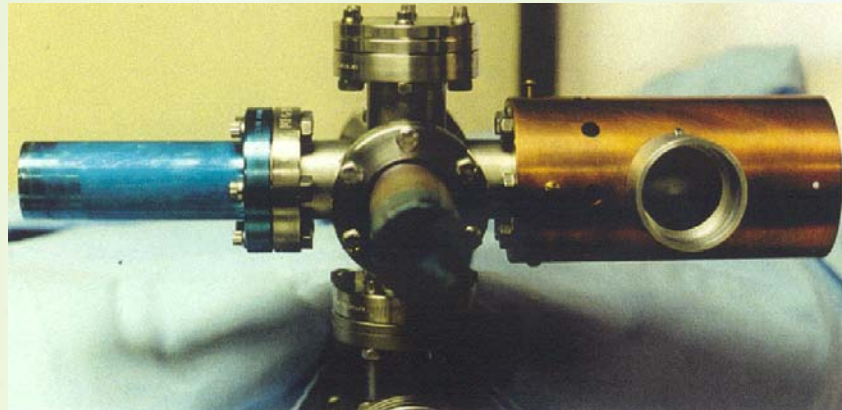
- How to measure a potential benefit?
- Outgassing rate (F) in monolayers per sec:  
$$F = [\exp (-E/RT)] / t'$$
$$t' = \text{period of oscillation of molecule perp. surface, ca. } 10^{-13} \text{ sec}$$
$$E = \text{energy of desorption (Kcal/g mol)}$$
$$R = \text{gas constant}$$

source: Roth, A. Vacuum Technology, Elsevier Science Publishers, Amsterdam, 2<sup>nd</sup> ed., p. 177.

- Slight elevation of sample temperature accelerates outgassing rate exponentially

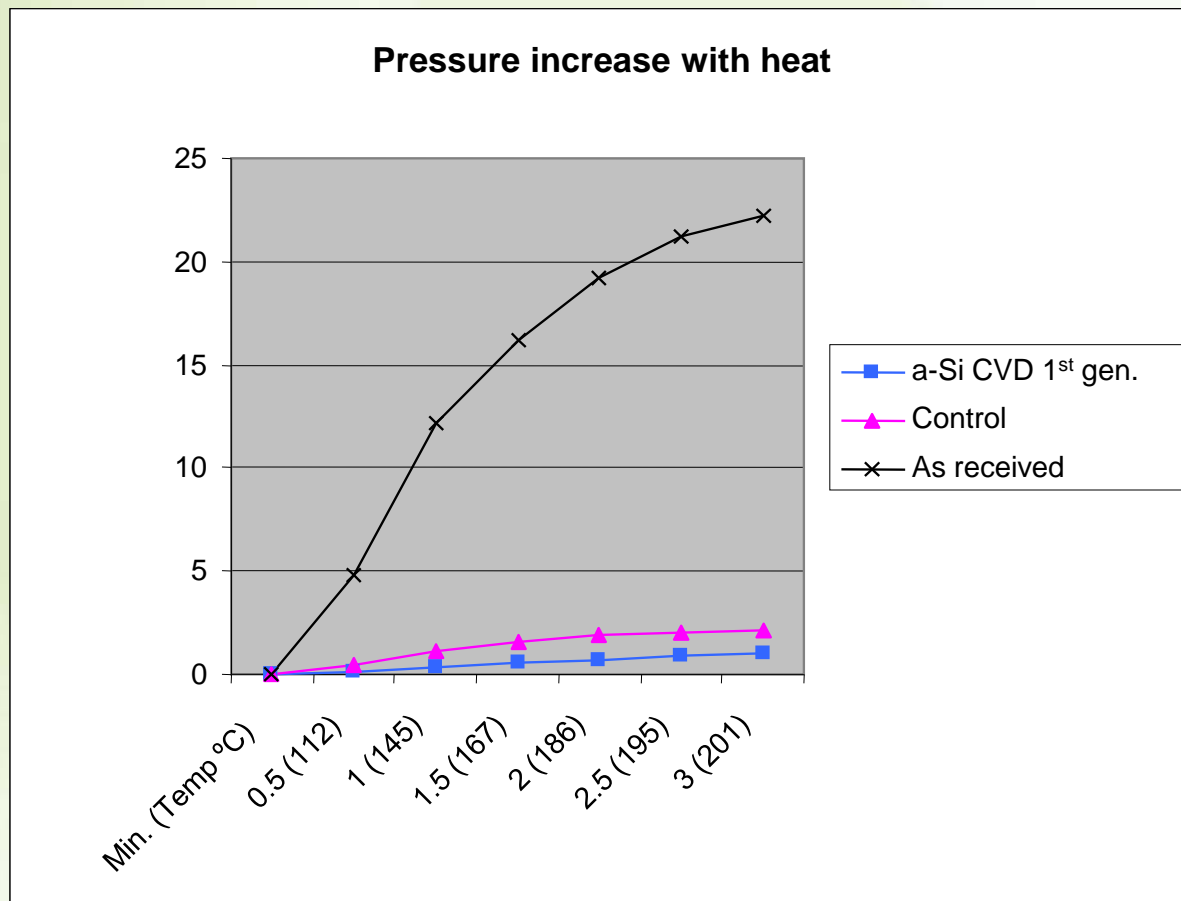


# Experimental Design: Heated Samples



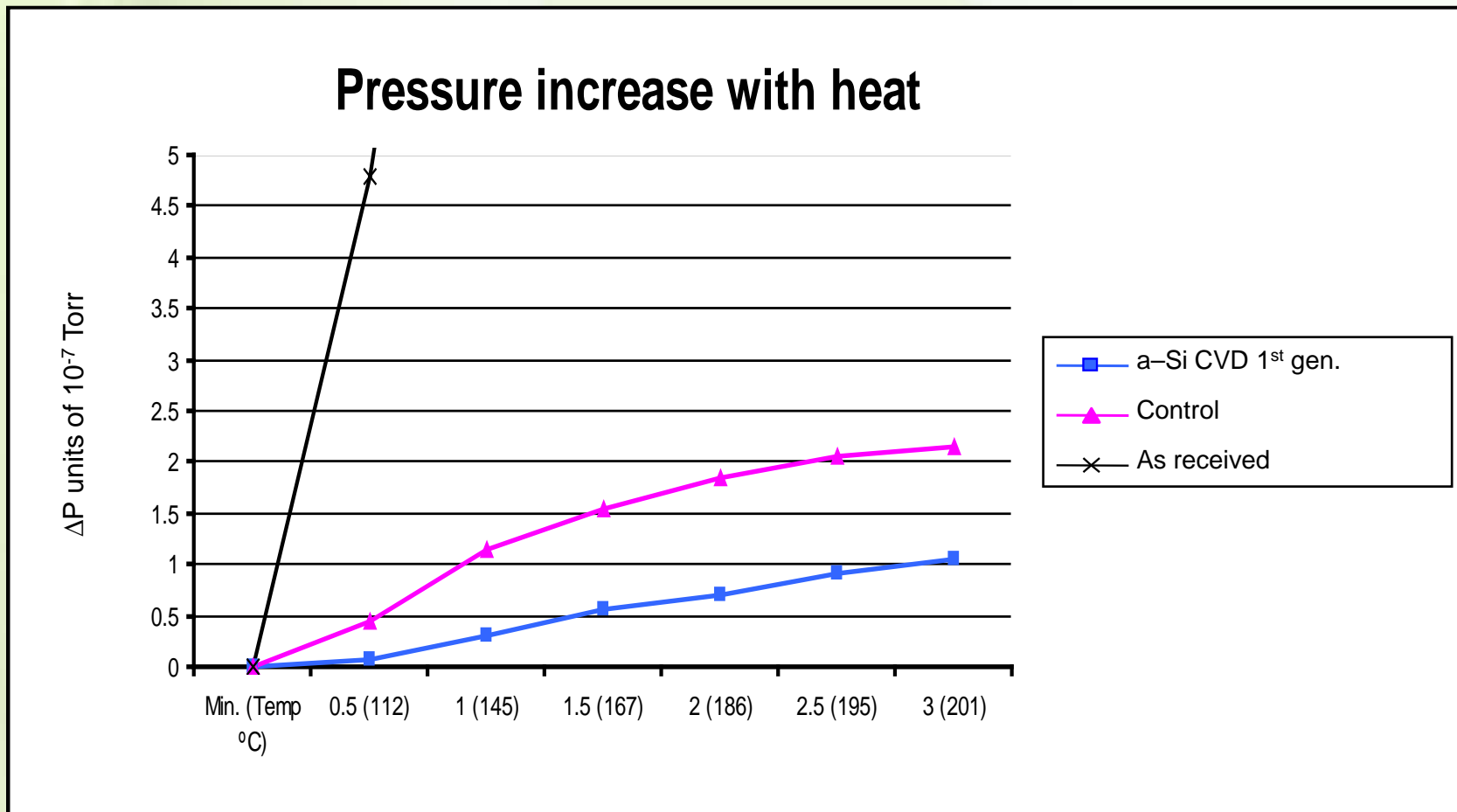
- Turbo pump for base pressures to  $10^{-8}$  Torr
  - pumping rate between gauge and pump: 12.5 l/sec (pump alone: 360 l/sec)
  - system vent with dry  $N_2$  between thermal cycles
- Ion pump for  $10^{-10}$  Torr (thermal cycles)
- Comparative evaluation parts
  - equally treated controls without deposition

# Outgassing Data – Heated Samples at HV



- Turbopump,  $1 \times 10^{-7}$  Torr base pressure
- 10hr under vacuum

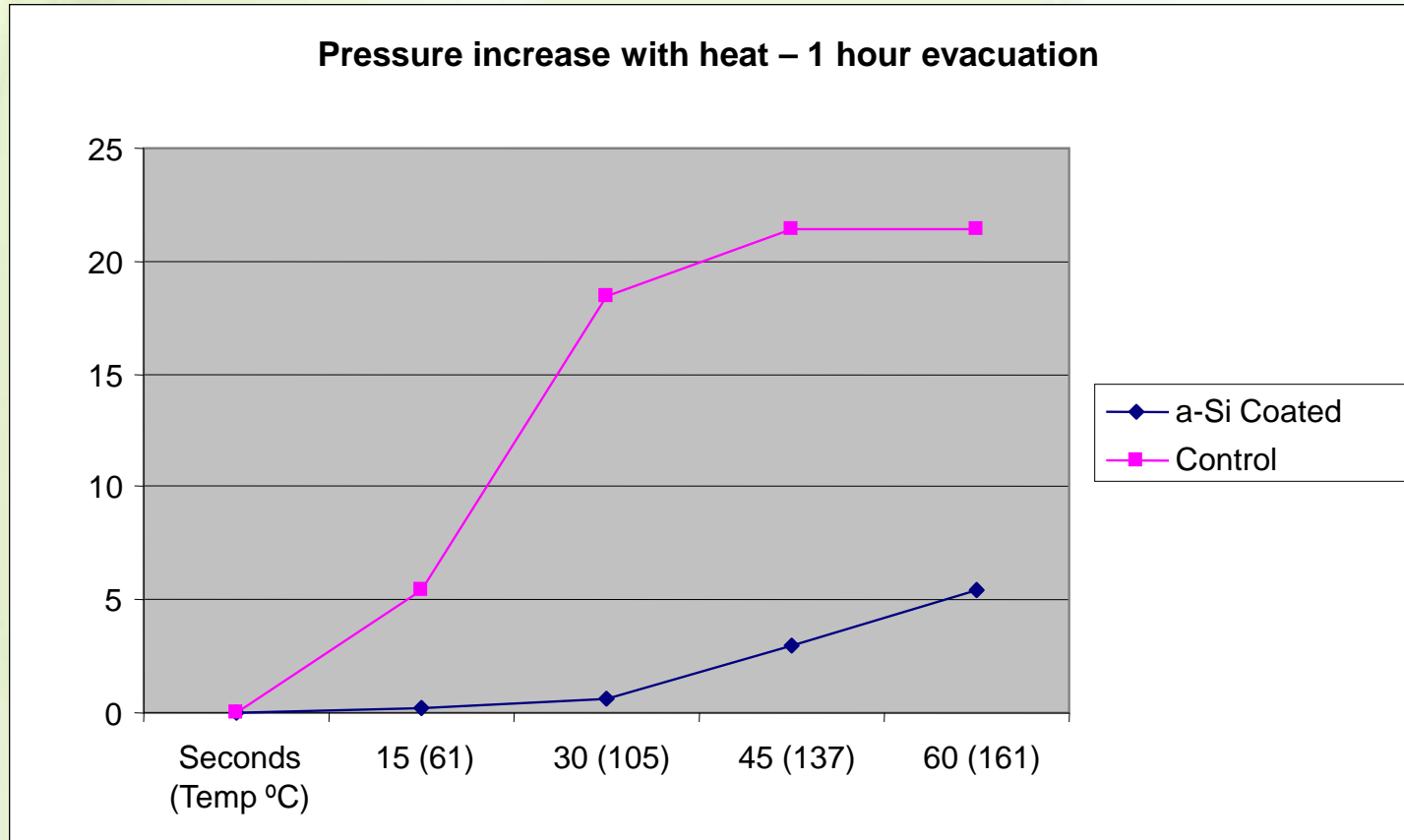
# Outgassing Data – HV Heated Samples



- 7.5 fold improvement at 112°C

# Outgassing Data – HV

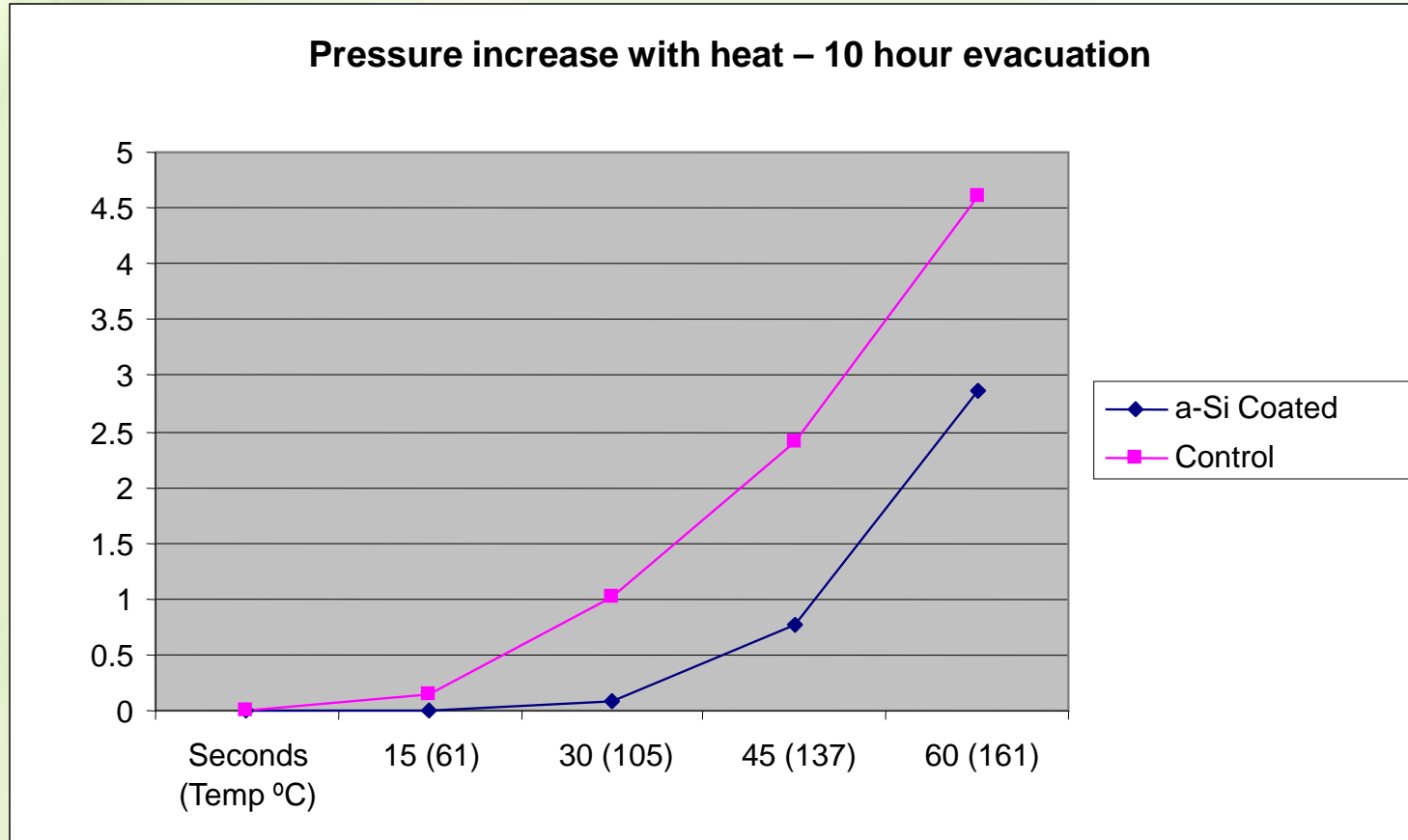
## Realistic Evacuation Times



- Turbopump,  $4.6 \times 10^{-7}$  Torr base pressure
- 1hr under vacuum ( $\Delta P1$ )

# Outgassing Data – HV

## Realistic Evacuation Times

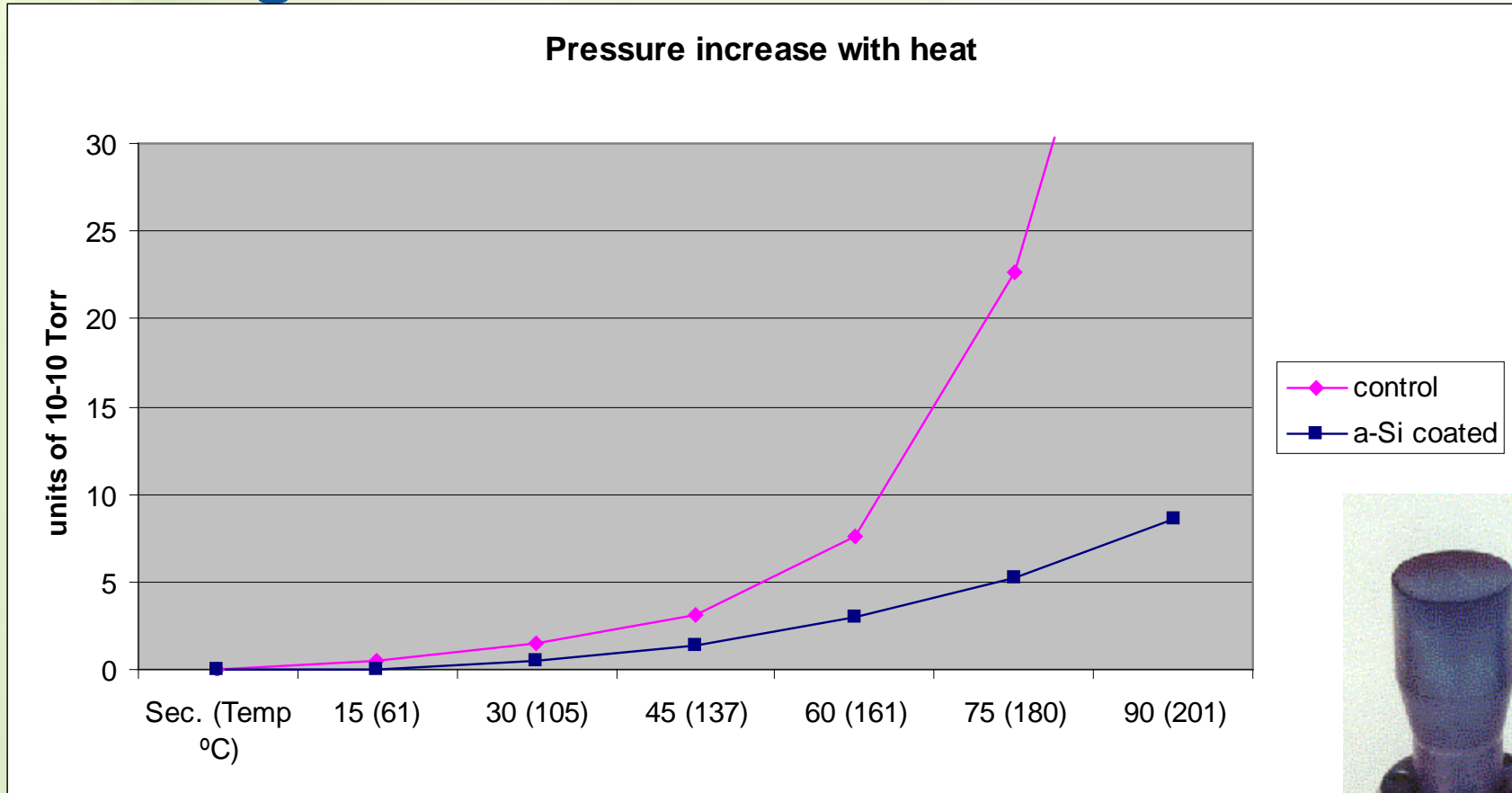


- Turbopump,  $7.5 \times 10^{-8}$  Torr base pressure
- 10hr under vacuum ( $\Delta P2$ )

# Outgassing Calculations

- For the system ( $P_A$ ), sample area = 125cm<sup>2</sup>,  
conductance = 12.5 l/sec;  
therefore,  $\Delta Q = \Delta P(12.5/125) = \Delta P/10$
- At 1 hour, 61°C:  
 $\Delta Q_1$  (control) =  $5.4 \times 10^{-8}$  Torr l sec<sup>-1</sup> cm<sup>-2</sup>;  
 $\Delta Q_1$  (a-silicon) =  $0.2 \times 10^{-8}$  Torr l sec<sup>-1</sup> cm<sup>-2</sup>  
27x improvement
- At 10 hours, 61°C:  
 $\Delta Q_{10}$  (control) =  $0.14 \times 10^{-8}$  Torr l sec<sup>-1</sup> cm<sup>-2</sup>;  
 $\Delta Q_{10}$  (a-silicon) =  $0.01 \times 10^{-8}$  Torr l sec<sup>-1</sup> cm<sup>-2</sup>  
14x improvement

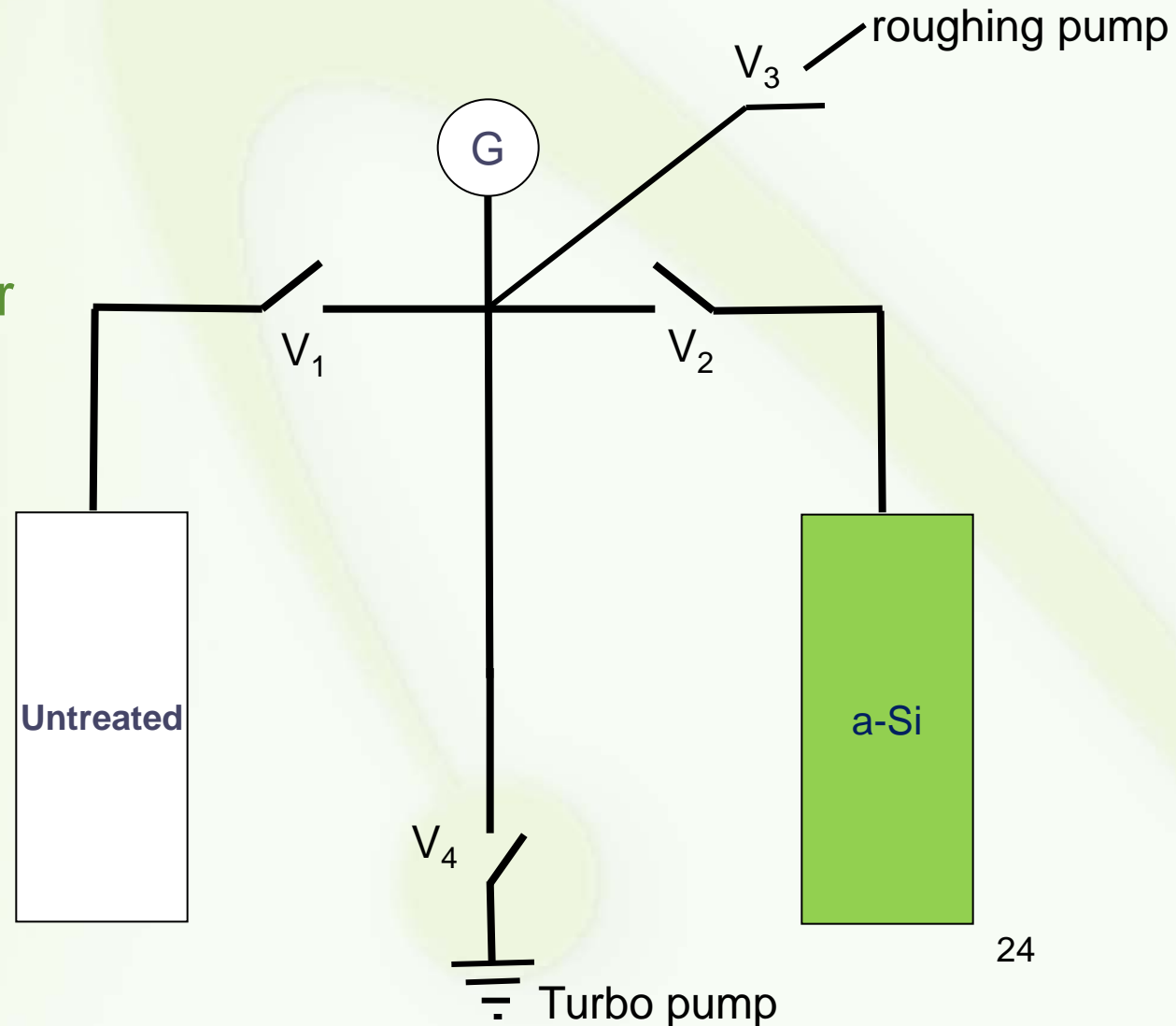
# UHV comparison – B/A ion gauge housings



- Ion pump,  $1.2 \times 10^{-10}$  Torr base pressure
- 156 days under vacuum (5th baking cycle)
- 3.3-fold improvement at 105°C  
(no measurable  $\Delta P$  for a-Si at 61°C,  $7.0 \times 10^{-12}$  Torr  $\Delta P$  at 105°C)

# Chamber Comparison; No Heat

- Common pumping line
- Valve isolation
- Alternating chamber measurements
- Roughing pump for first 44 min.



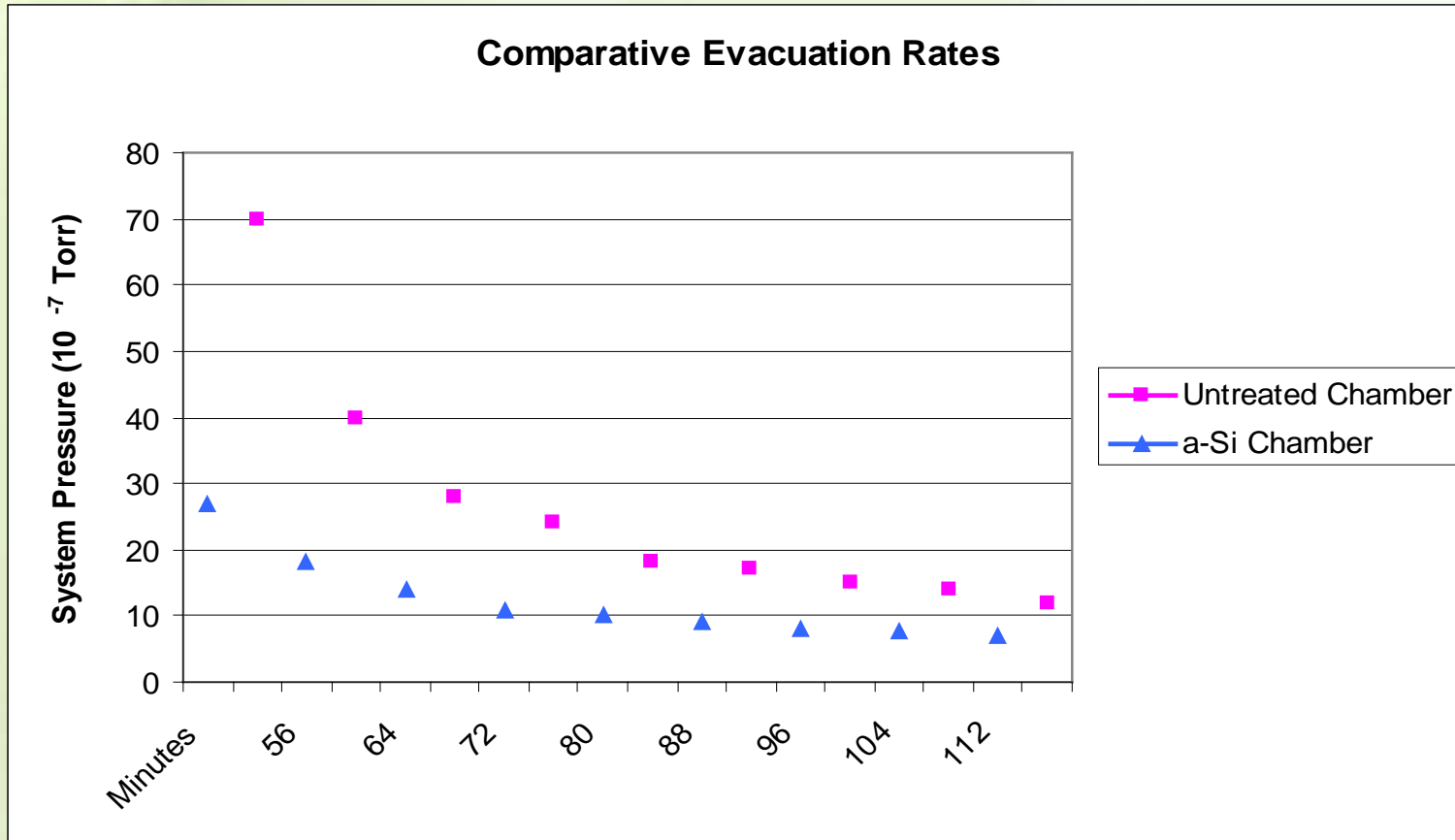


# Chamber Comparisons; No Heat



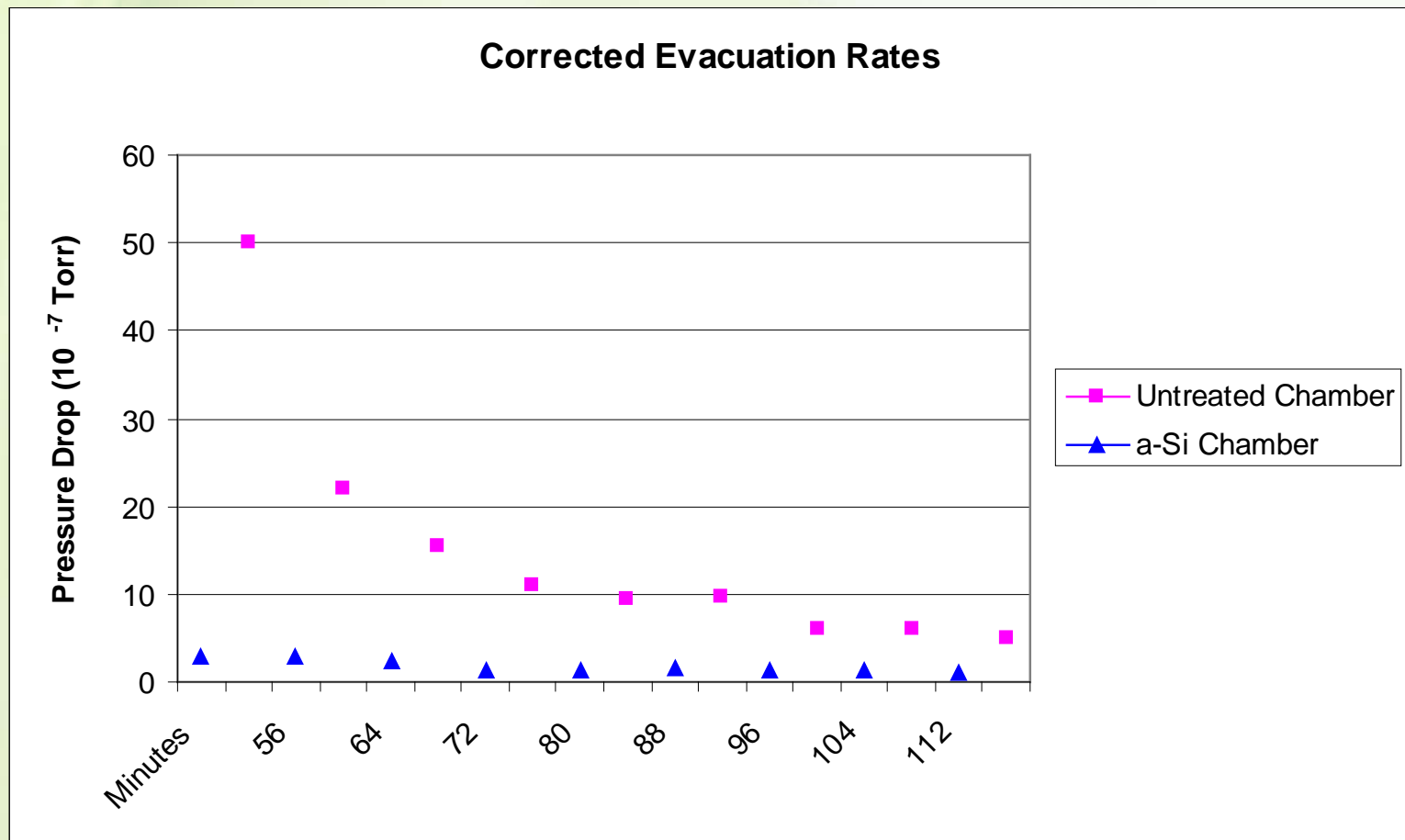
- System conductance: 7.4 l/sec
- 360 l/sec turbomolecular pump
- Cold cathode gauge

# Chamber Comparisons; No Heat



- Alternate-pumpdown system pressures
- 80-84 minute range: 2.4-fold improvement

# Corrected Comparison

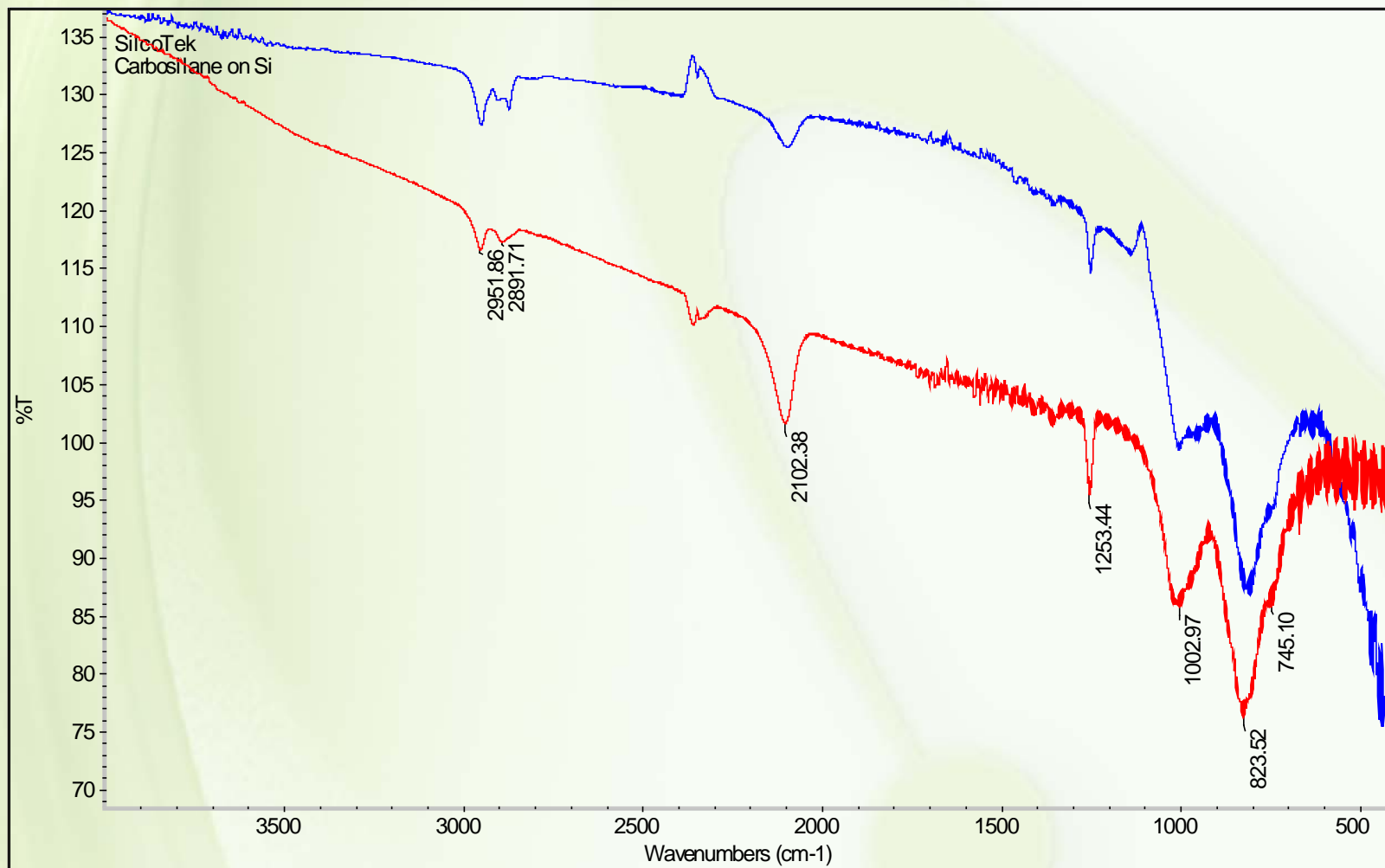


- Alternate pressure drop system measurements (true outgassing of isolated chambers)
- 80-84 minute range: 9.1-fold improvement

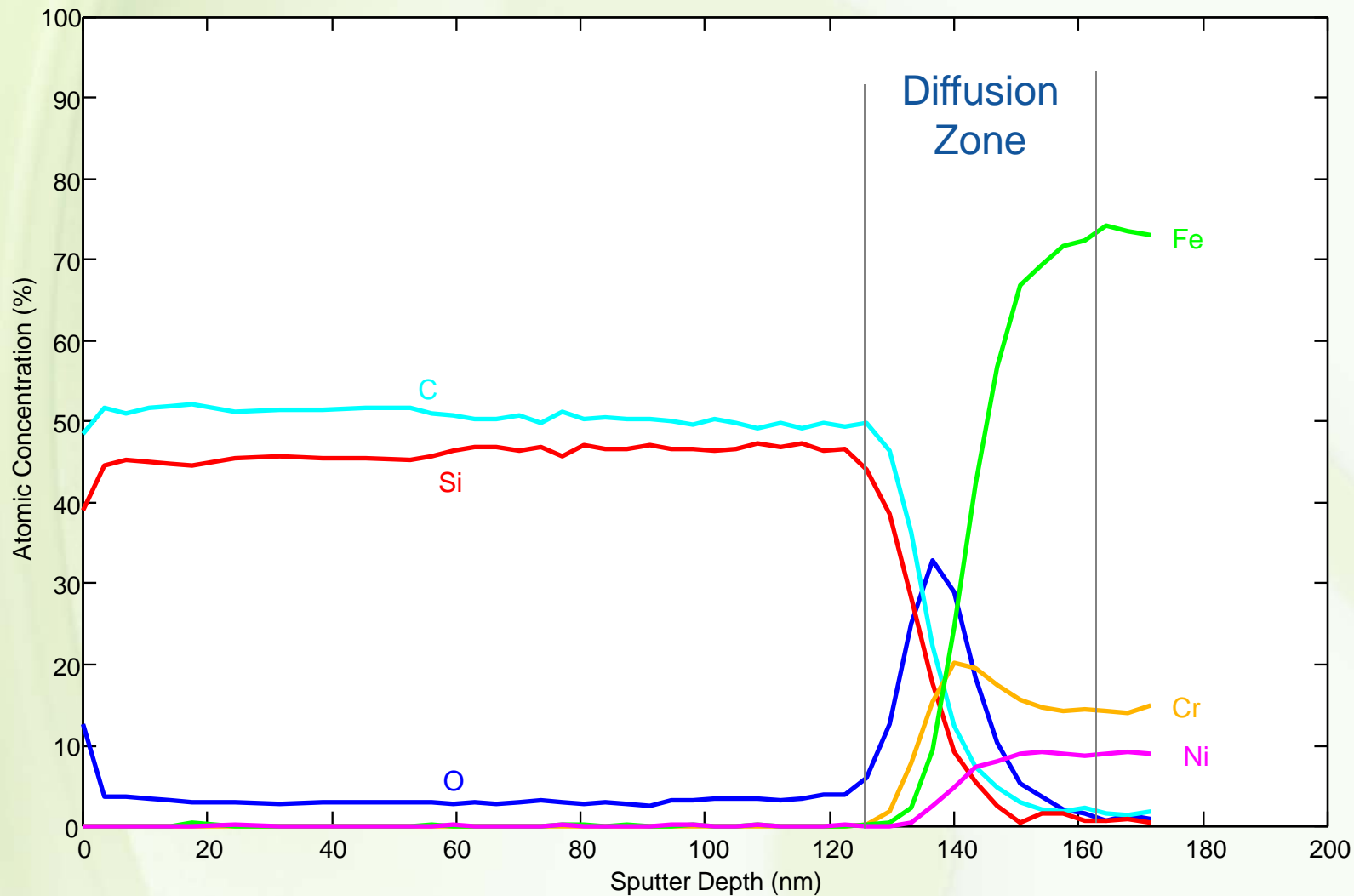
# Current Research: Carbosilane Materials

- C, Si, H in CVD-deposited matrix
- Excellent inertness
- Improved corrosion resistance
- High hydrophobicity
- Si-H functionality for additional chemistry

# Carbosilane FT-IR



# AES Depth Profile



# Acid / Base Resistance

- ASTM G31 screening:
  - 6M HCl, 24 hrs, 316 SS coupons, 22° C

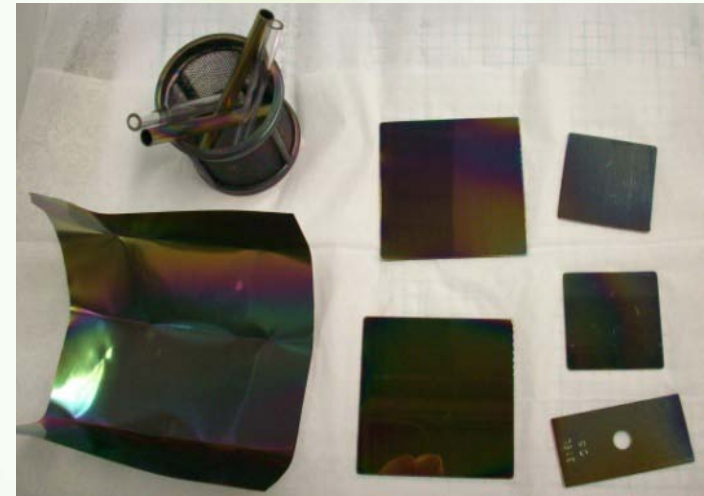
Surface	mpy	Enhancement
316 SS control	91.90	----
a-Si corr. res.	18.43	5.0 X
carbosilane	3.29	27.9 X

- High pH Inertness
  - 18% KOH, 19 hrs, 316 SS sample cylinder, 22° C
  - No weight loss – need further assessment
  - Inert to 10ppmv H<sub>2</sub>S static storage over 48 hrs.



# Hydrophobicity / Appearance

Surface	Advancing / Receding
a-Silicon	53.6 / 19.6
Funct. a-Silicon (HC)	87.3 / 51.5
carbosilane	100.5 / 63.5
Funct. Carbosilane (HC)	104.7 / 90.1
Funct. Carbosilane (F)	110.5 / 94.8



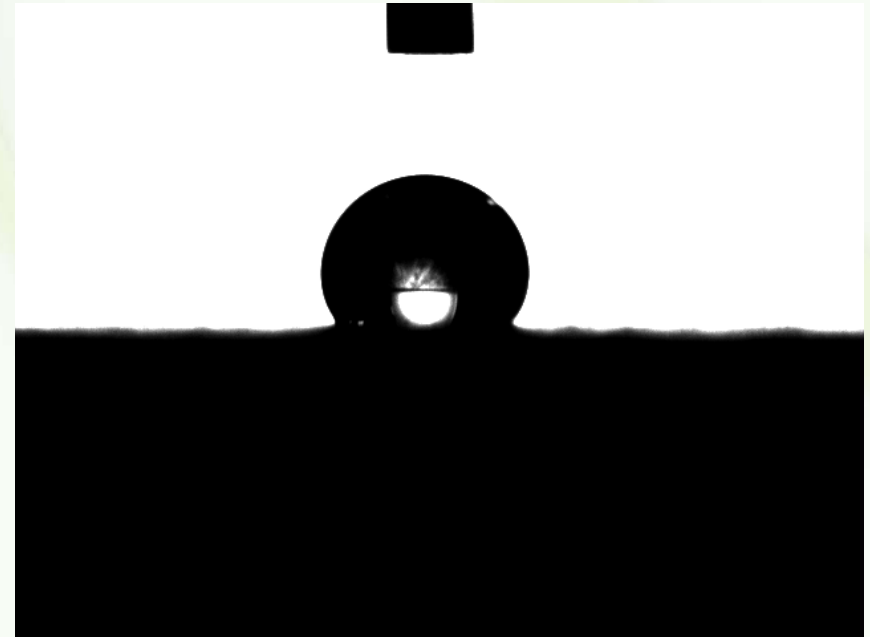
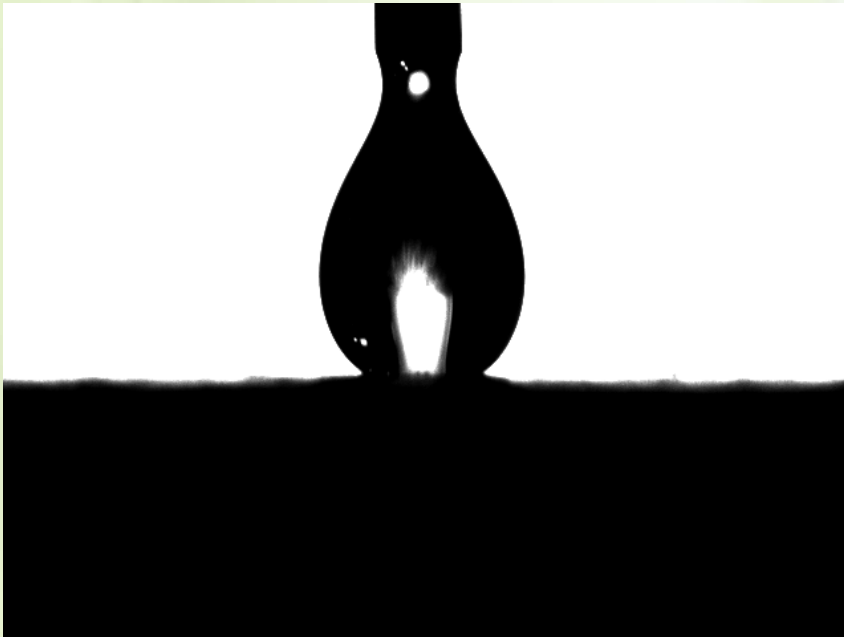
-narrowing the hysteresis gap  
to Cassie-Baxter state



# Contact Angle Illustration

Close to Release...

- DI water CA:  $127^\circ$
- On 304 stainless corrosion coupon; no topography modification



# Conclusions / Future

- Continuing research in to bulk surface modifications for the vacuum science and semiconductor industries
- Focus on silicon and carbosilane materials
  - Outgassing control
  - Inertness
  - Contaminant control
  - Anti-corrosion