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

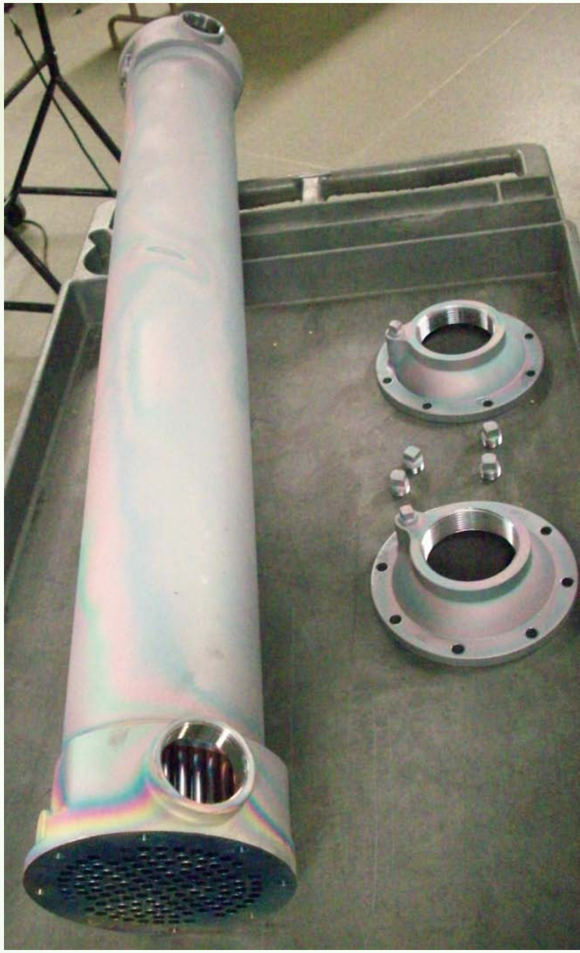
- Focus on silicon / functionalized silicon
  - Inert
  - Corrosion resistant
  - Diffusion barrier
  - Tailor properties (i.e. surface energy)

New Technology?

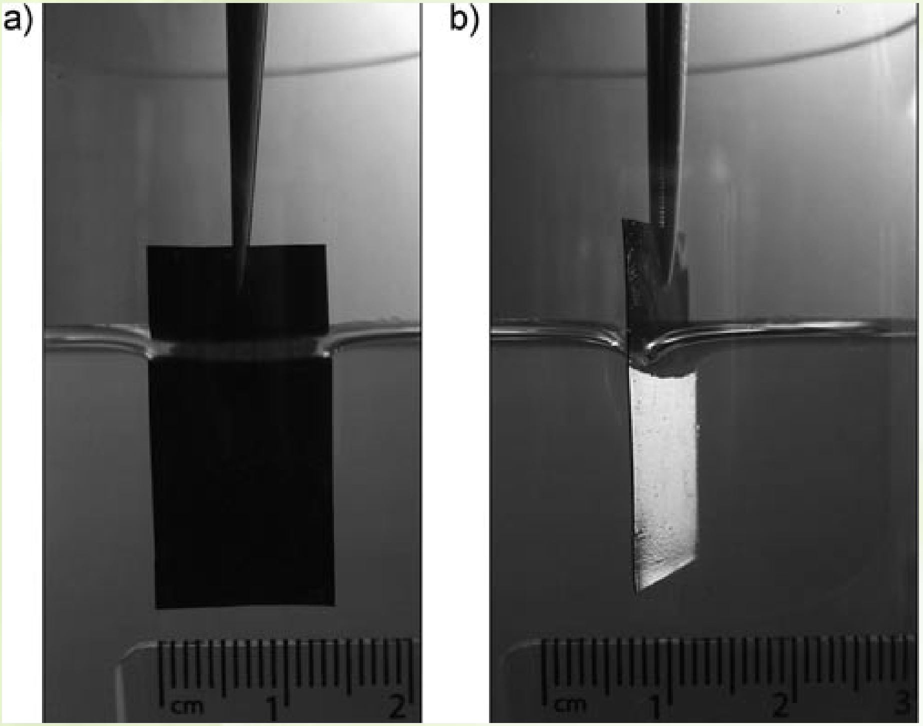
- Kipping – silicon materials in 1920's
  - Reductive coupling of silicon chlorides
  - Functional polysilanes – $[SiR_2]_n$
  - Functional polysilynes – $[SiR]_n$
  - Solubility issues
- Semiconductor industry (1960's)
  - High purity silicon depositions
  - Controlled doping, etching, implanting

Focus: Bulk surface modification

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



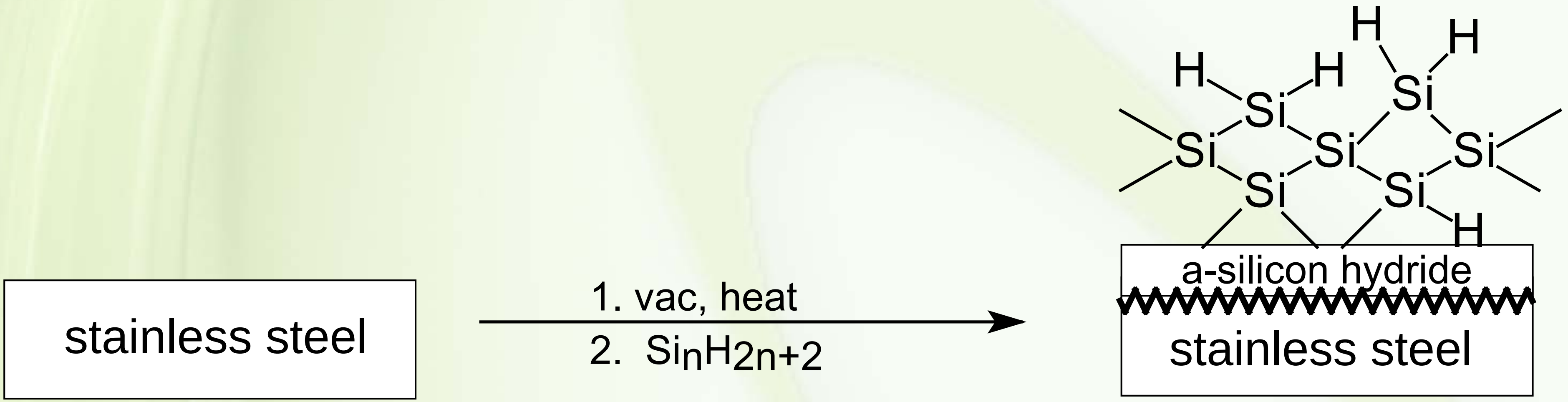
Why bother? Powerful Example…



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

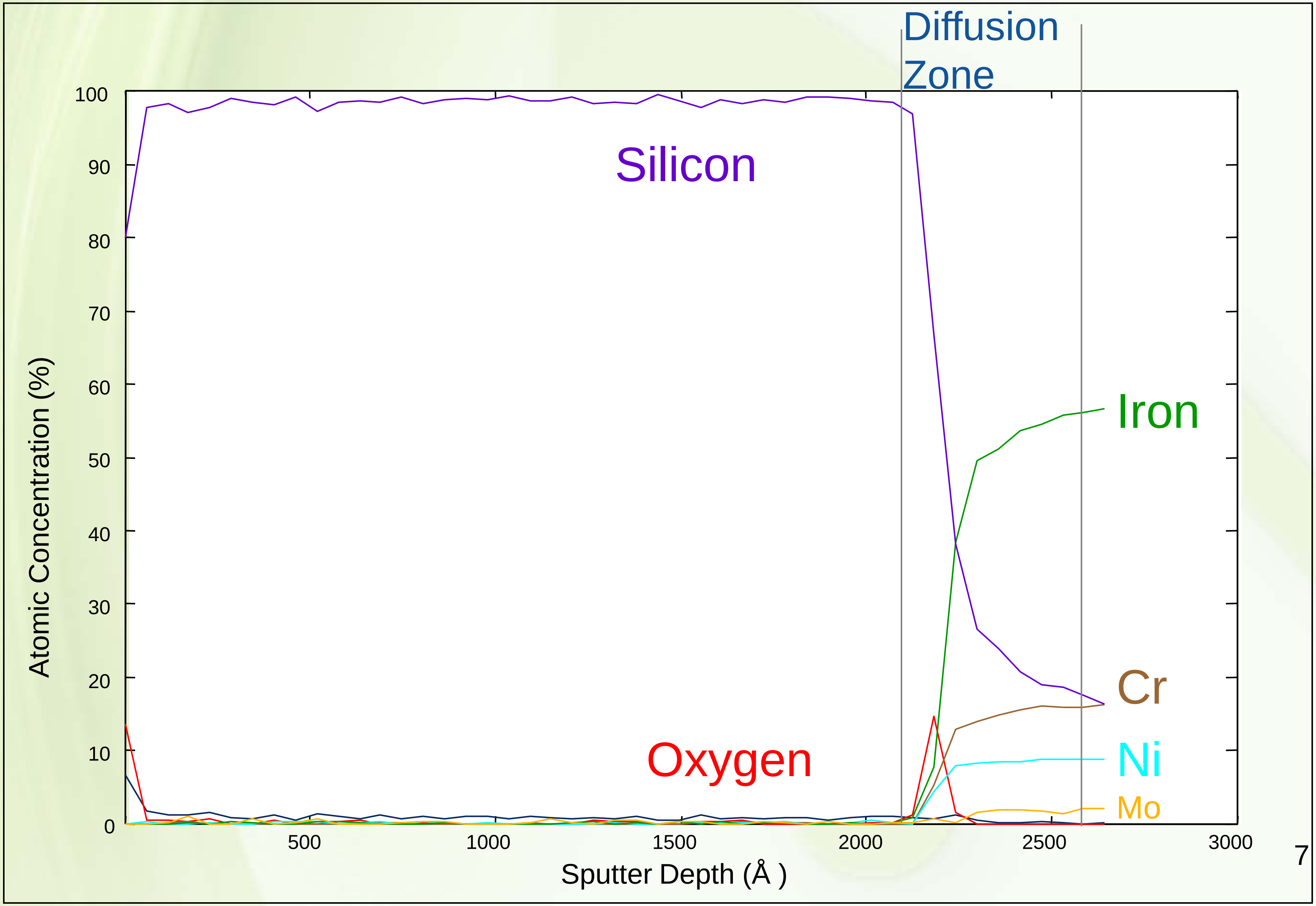
Larmour, I.A.; Bell, S.E.J; Saunders, G.C. *Angew. Chem. Int. Ed.* 2007, *46*, 1710-1712.

Thermal CVD Process



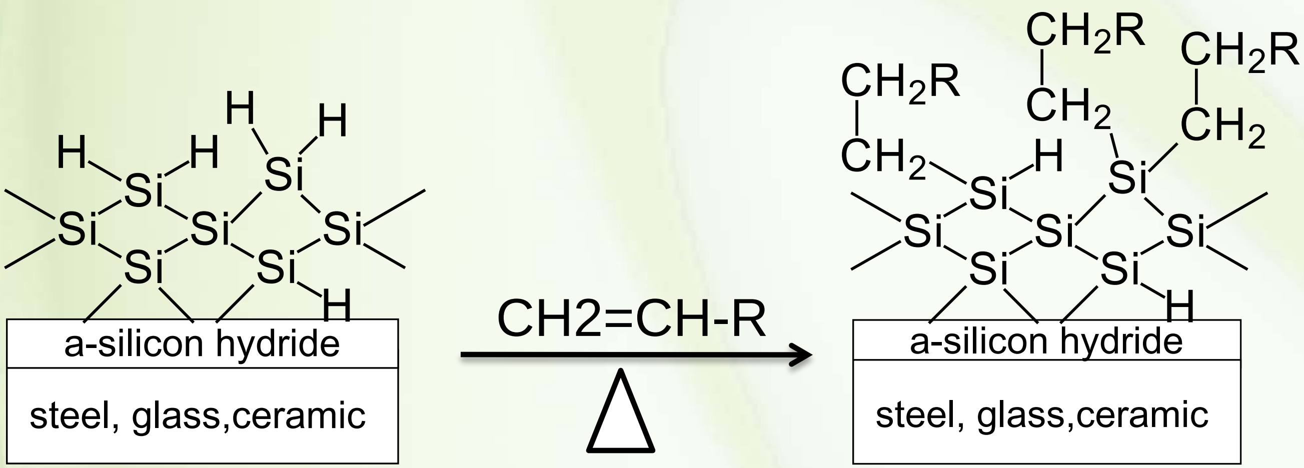
- Diffusion in to stainless lattice
- Native oxide formation on surface upon atmospheric exposure

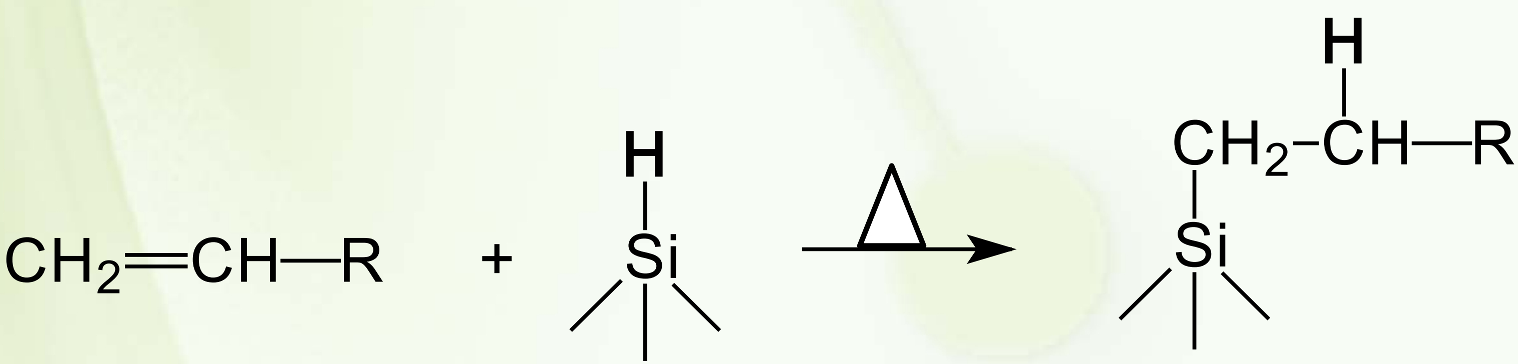
AES Depth Profile



In-Situ Surface Chemistry

- Functionalize via thermal hydrosilylation





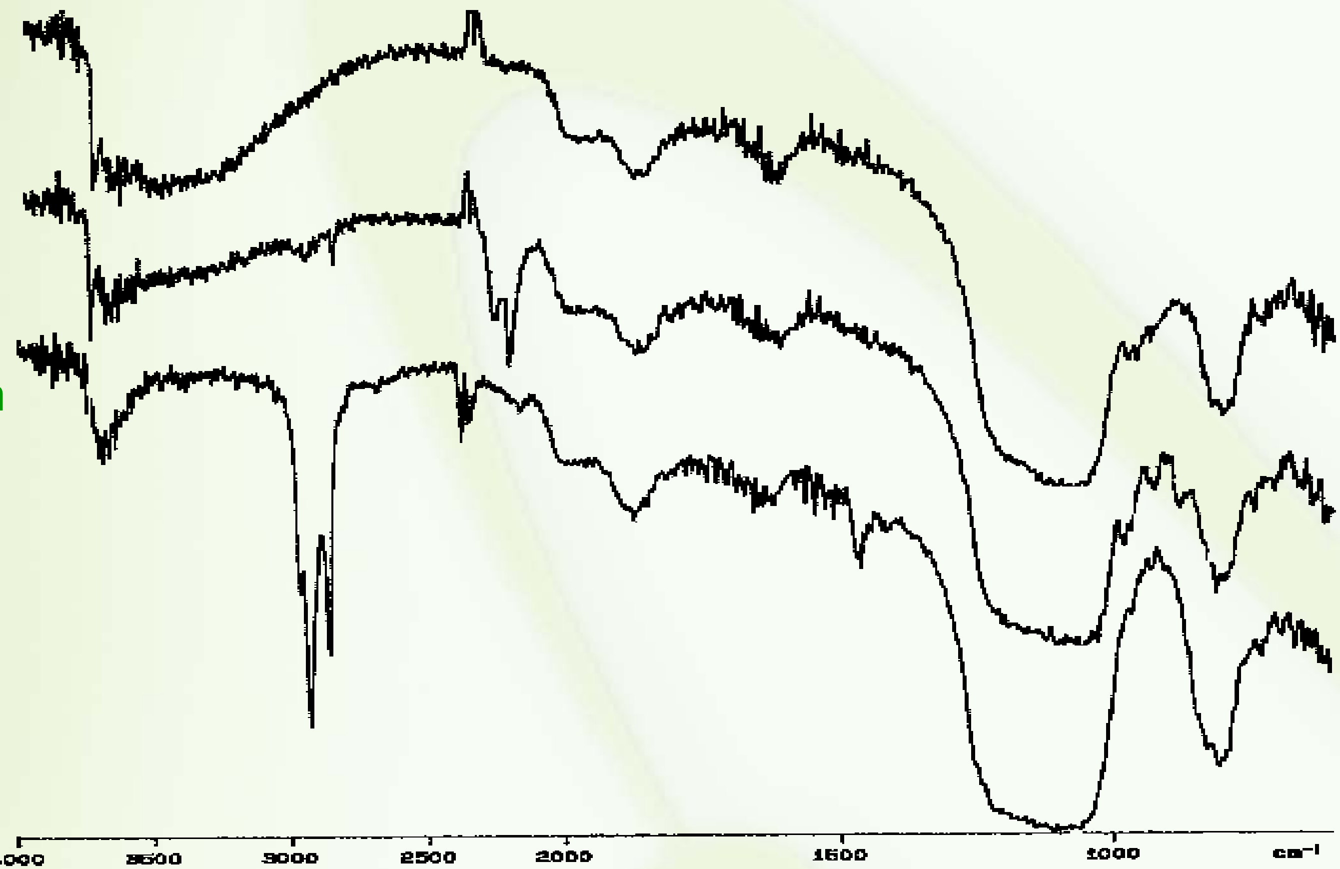
US Pat. #6,444,326

DRIFTS Illustration of Func.

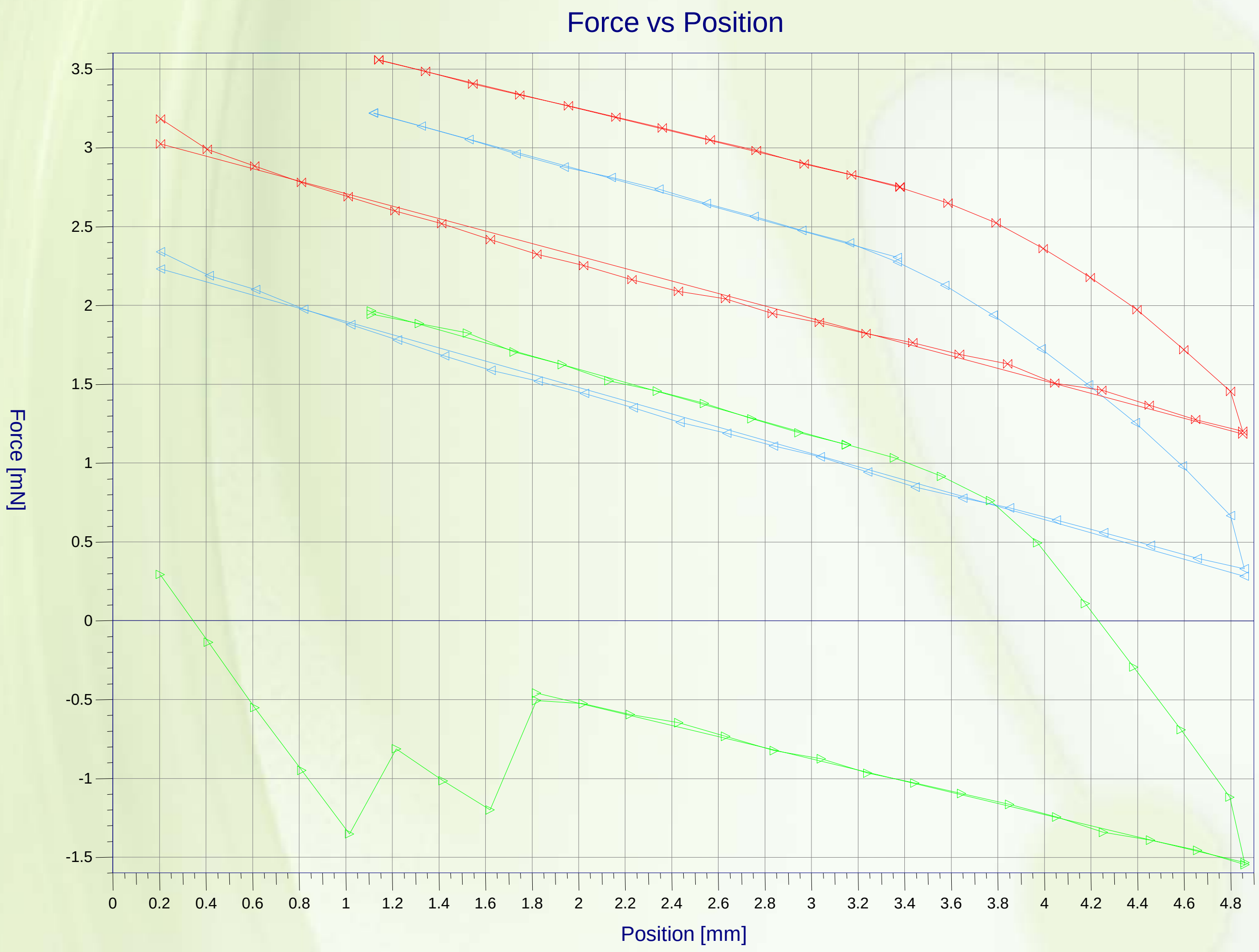
Raw 5um Silica

a-Si deposition
on Silica

Hydrocarbon
functionalization
on a-Si / silica



Surface Energy Measurements

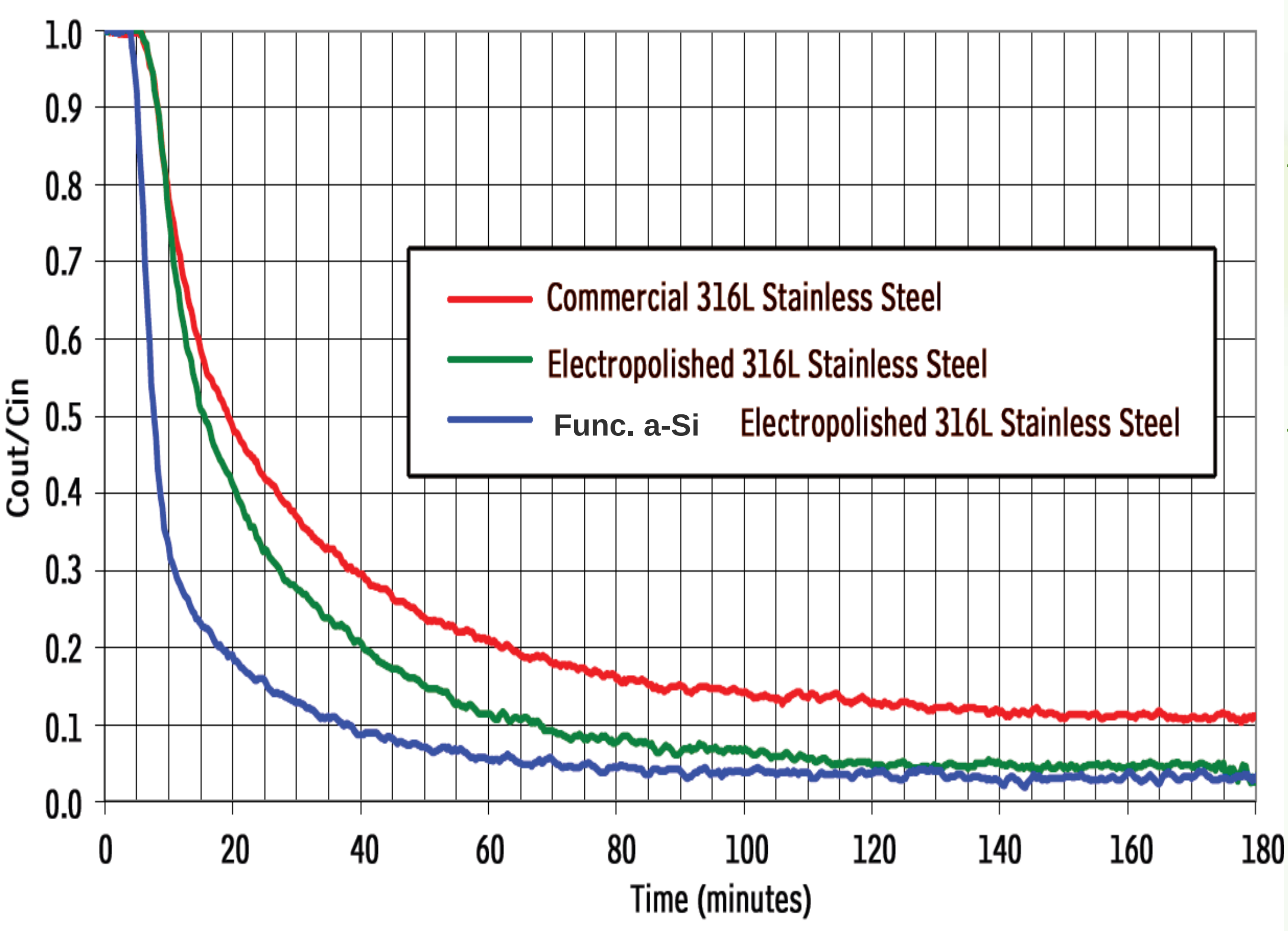


Bare 316ss
37.2° advancing
0° receding

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,

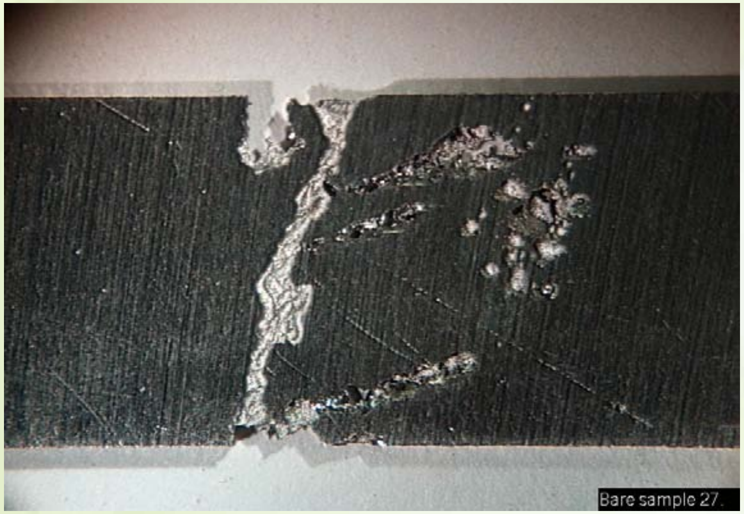
0.35 slpm, 22C

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

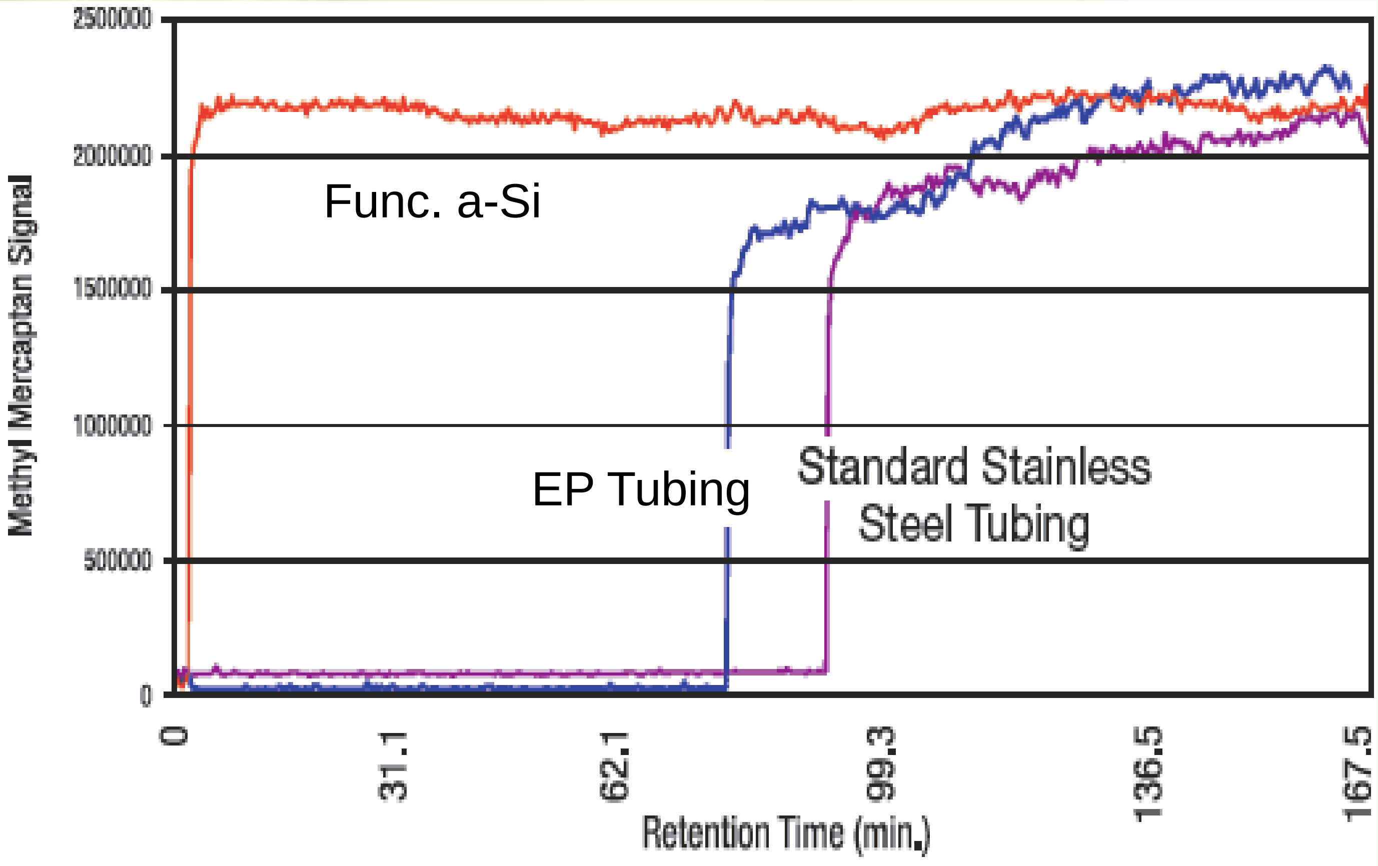
a-SiH coated 316 SS

ASTM G48 Method B: Pitting and Crevice Corrosion

6% Ferric Chloride solution, 72hrs, 20ºC, 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' = period of oscillation of molecule perp. surface, ca. 10^{-13} sec

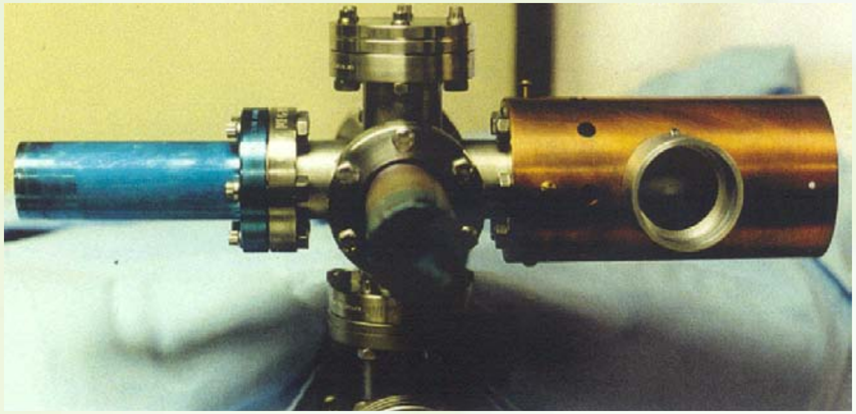
  E = energy of desorption (Kcal/g mol)

  R = gas constant

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

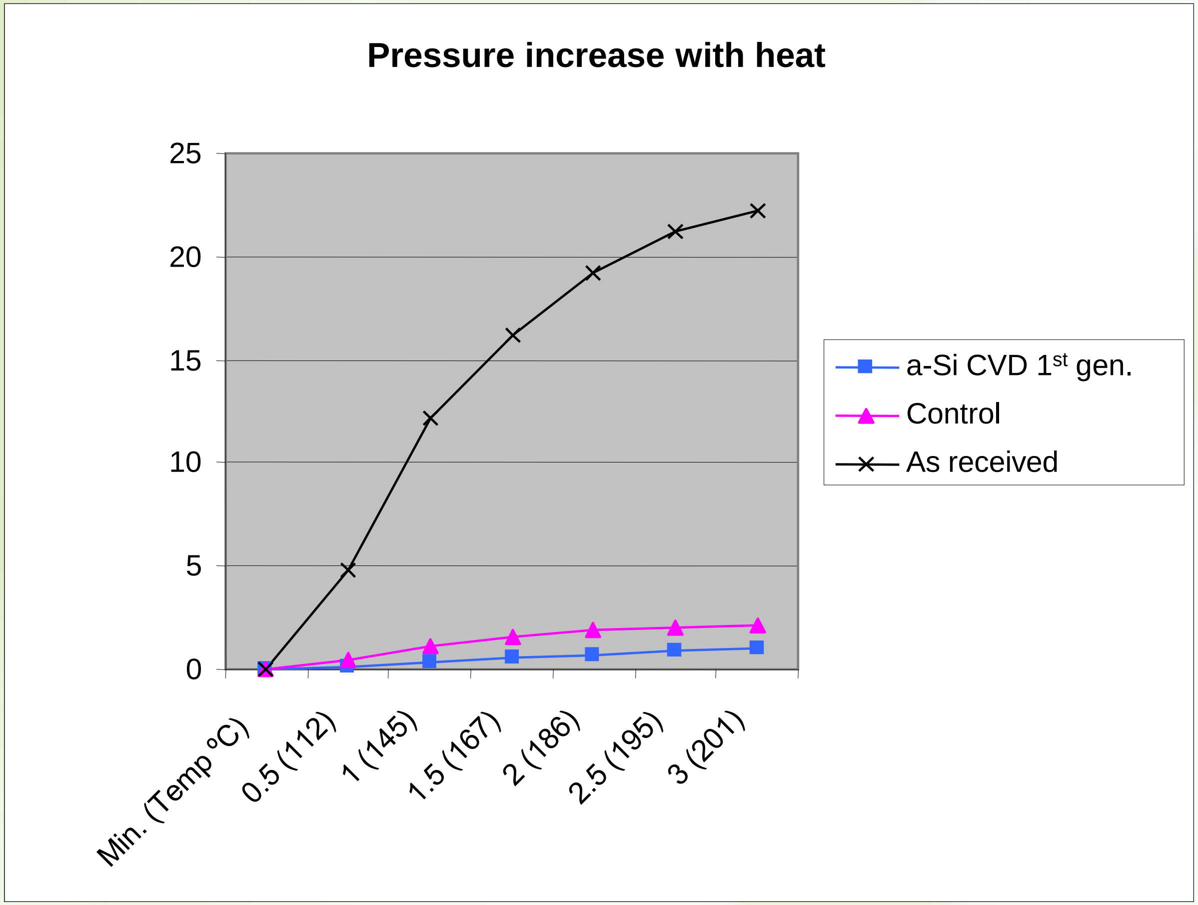
- Slight elevation of sample temperature accelerates outgassing rate exponentially

Experimental Design: Heated Samples



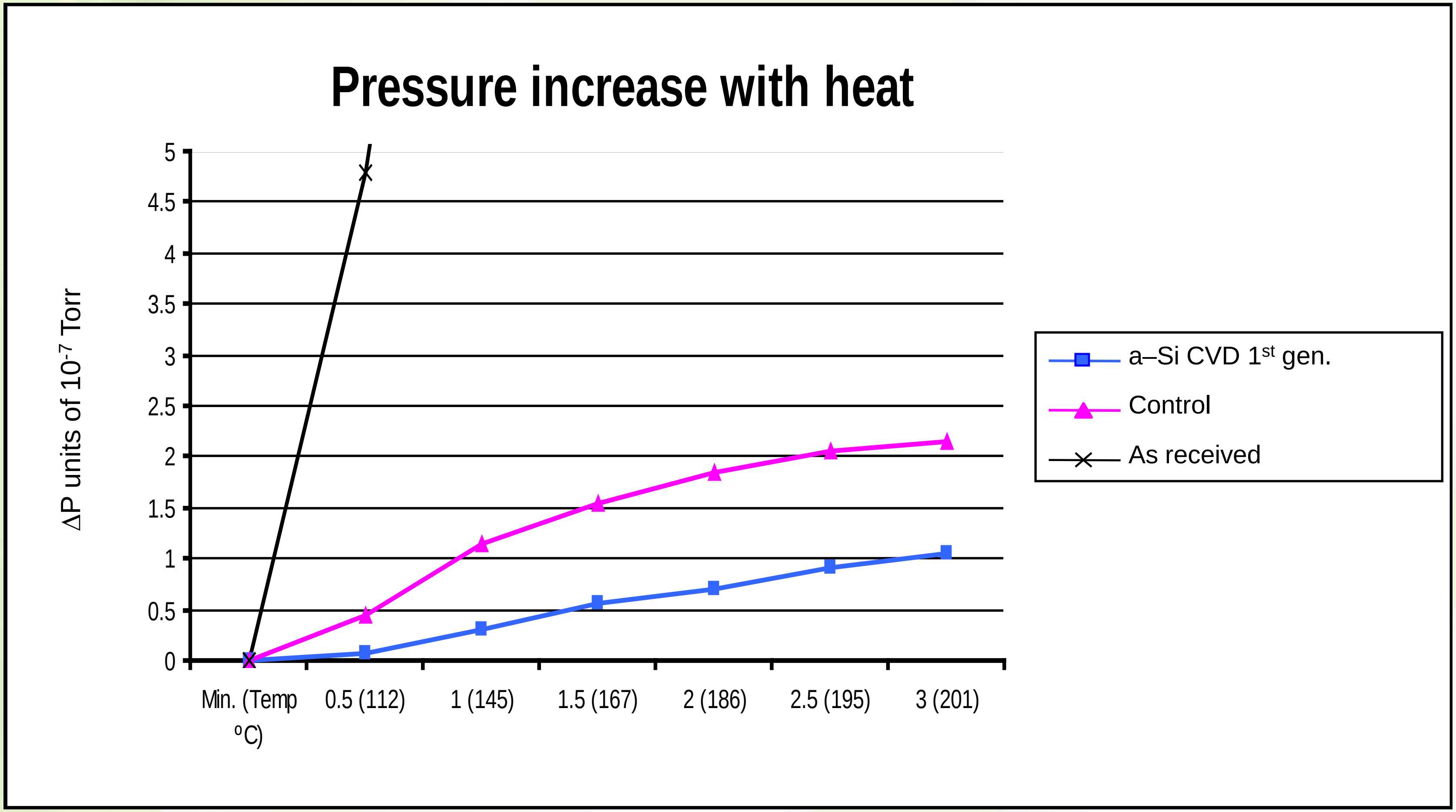
- Turbo pump for base pressures to 10^{-8} Torr
  - pumping rate between gauge and pump: 12.5 l/sec (pump alone: 360 l/sec)
  - system vent with dry N_2 between thermal cycles
- Ion pump for 10^{-10} Torr (thermal cycles)
- Comparative evaluation parts
  - equally treated controls without deposition

Outgassing Data – Heated Samples at HV



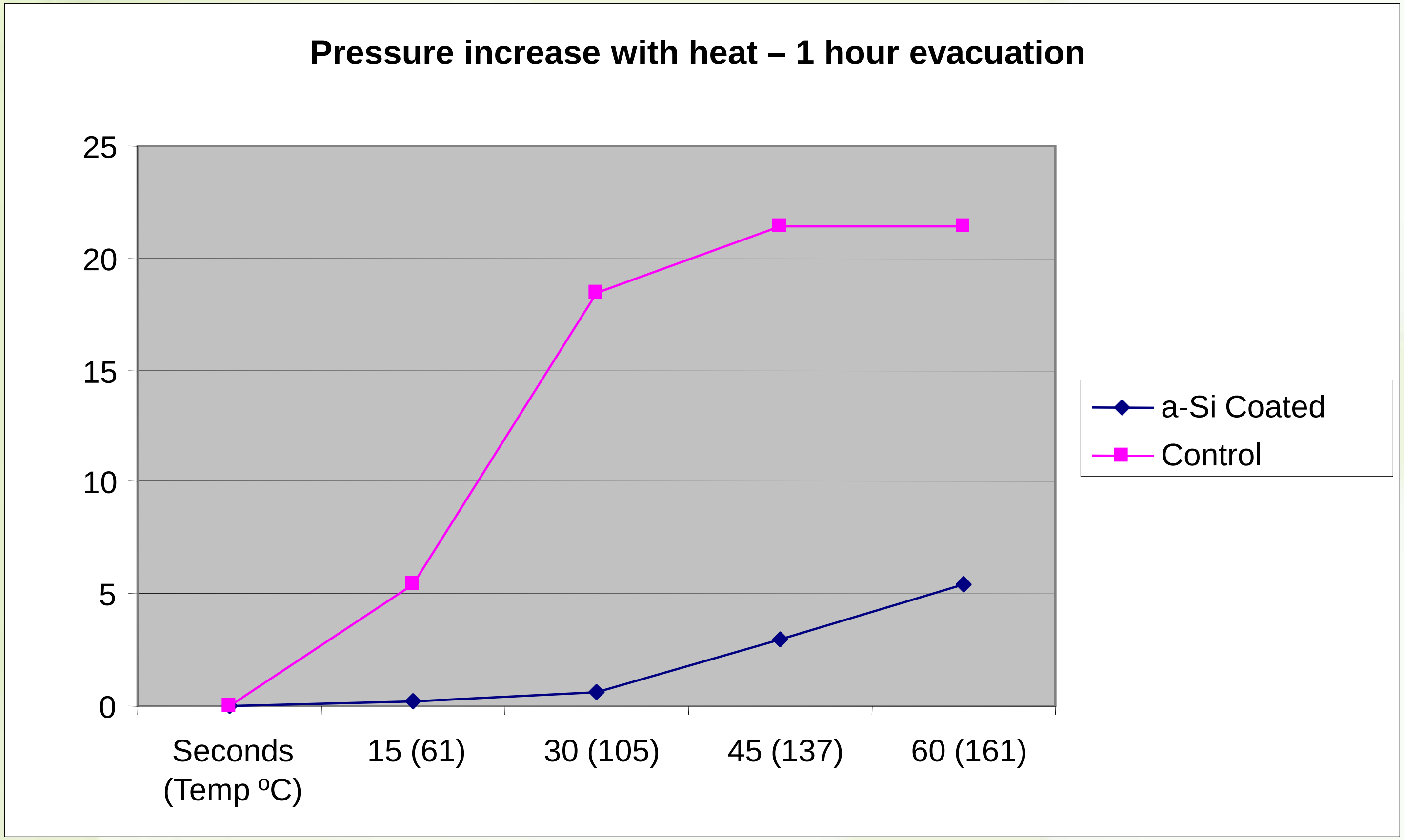
- Turbopump, 1 x 10^{-7} Torr base pressure
- 10hr under vacuum

Outgassing Data – HV Heated Samples



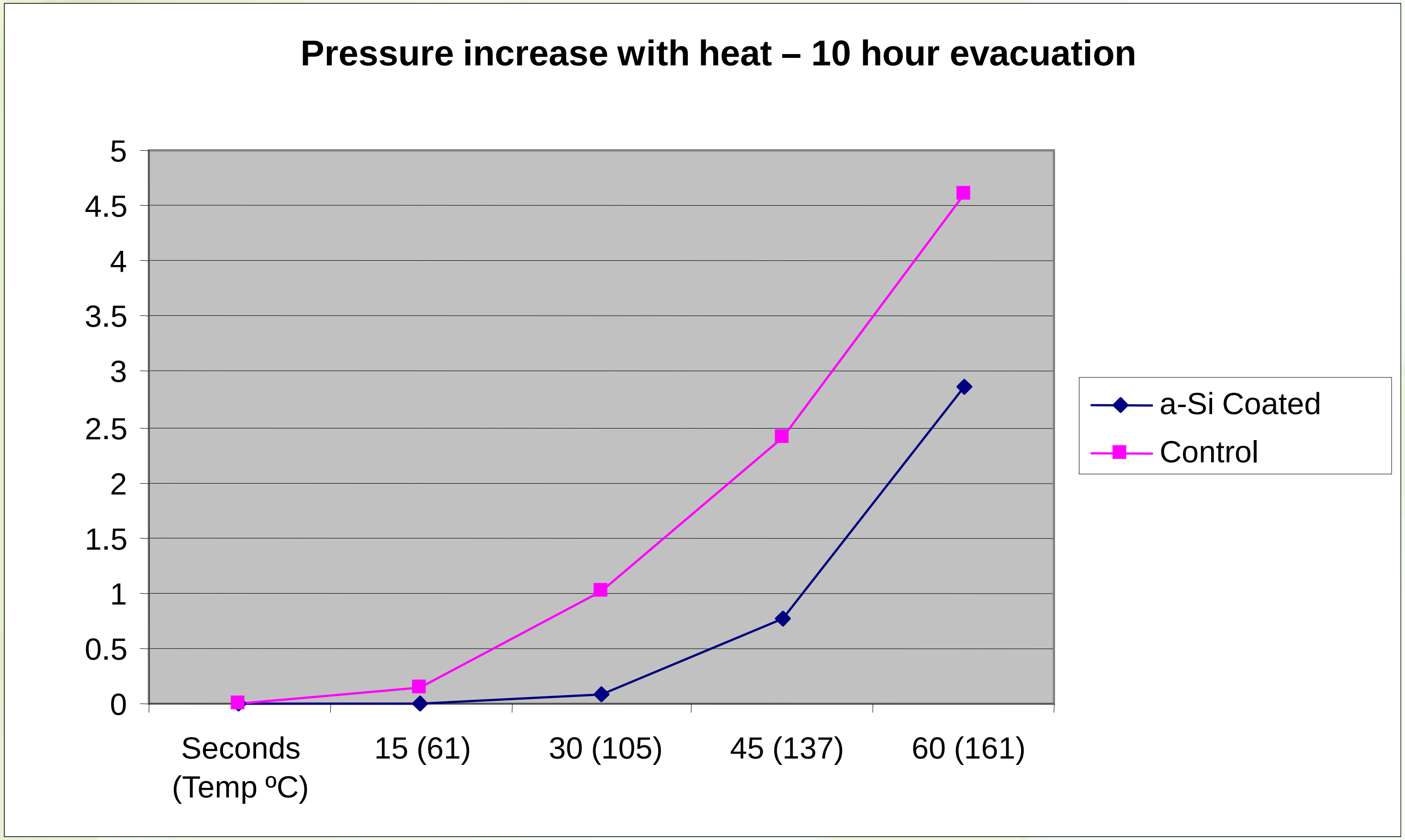
- 7.5 fold improvement at 112ºC

Outgassing Data – HV Realistic Evacuation Times



- Turbopump, 4.6 x 10^{-7} Torr base pressure
- 1hr under vacuum (ΔP1)

Outgassing Data – HV Realistic Evacuation Times



- Turbopump, 7.5 x 10^{-8} Torr base pressure
- 10hr under vacuum (ΔP2)

Outgassing Calculations

- For the system (P_A), sample area = 125cm^2, conductance = 12.5 l/sec;

  therefore, $\Delta Q = \Delta P(12.5/125) = \Delta P/10$

- At 1 hour, 61ºC:

  ΔQ_1 (control) = 5.4 x 10^{-8} Torr l sec^{-1} cm^{-2};

  ΔQ_1 (a-silicon) = 0.2 x 10^{-8} Torr l sec^{-1} cm^{-2}

  <u>27x improvement</u>

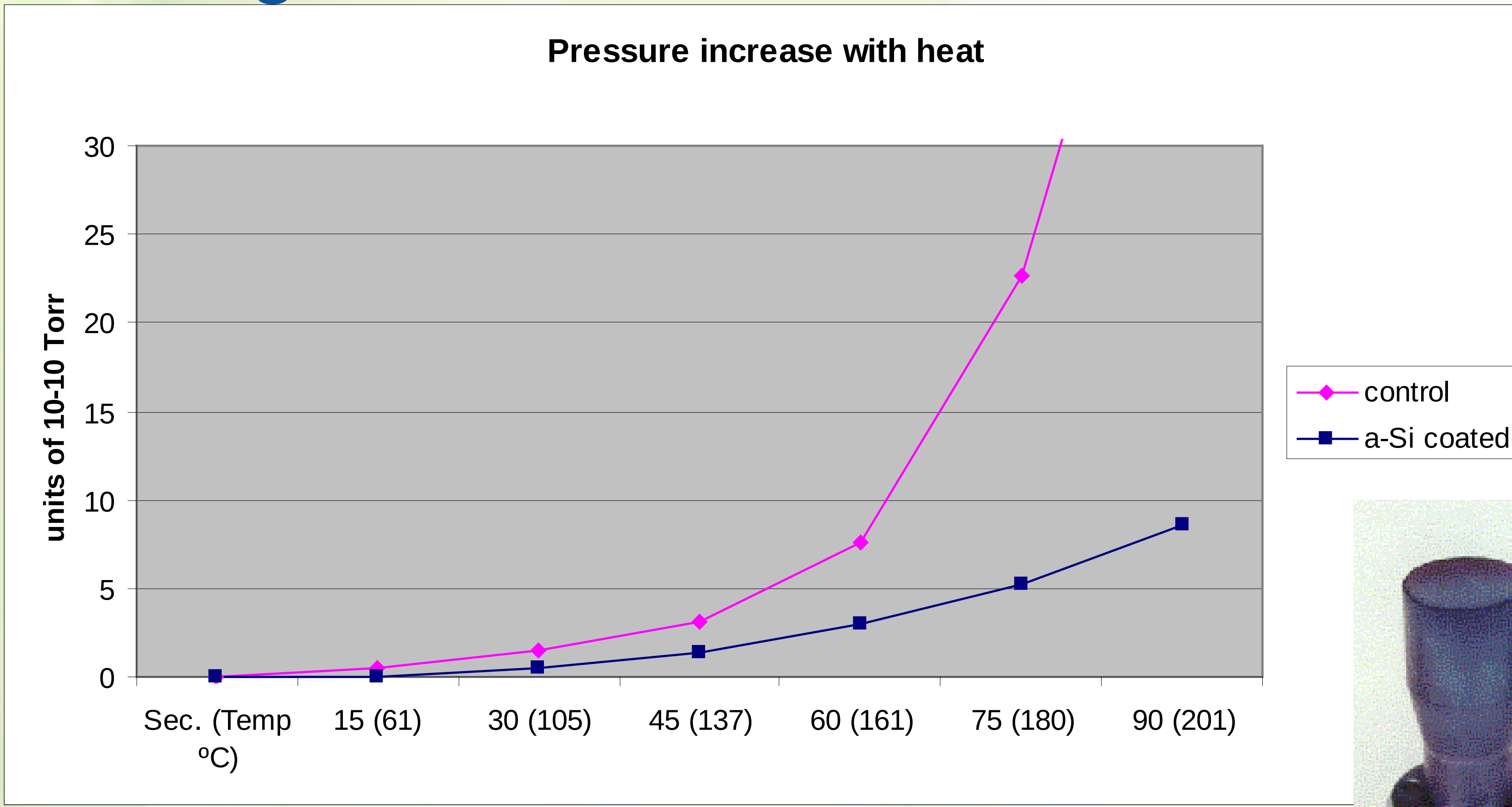
- At 10 hours, 61ºC:

  ΔQ_{10} (control) = 0.14 x 10^{-8} Torr l sec^{-1} cm^{-2};

  ΔQ_{10} (a-silicon) = 0.01 x 10^{-8} Torr l sec^{-1} cm^{-2}

  <u>14x improvement</u>

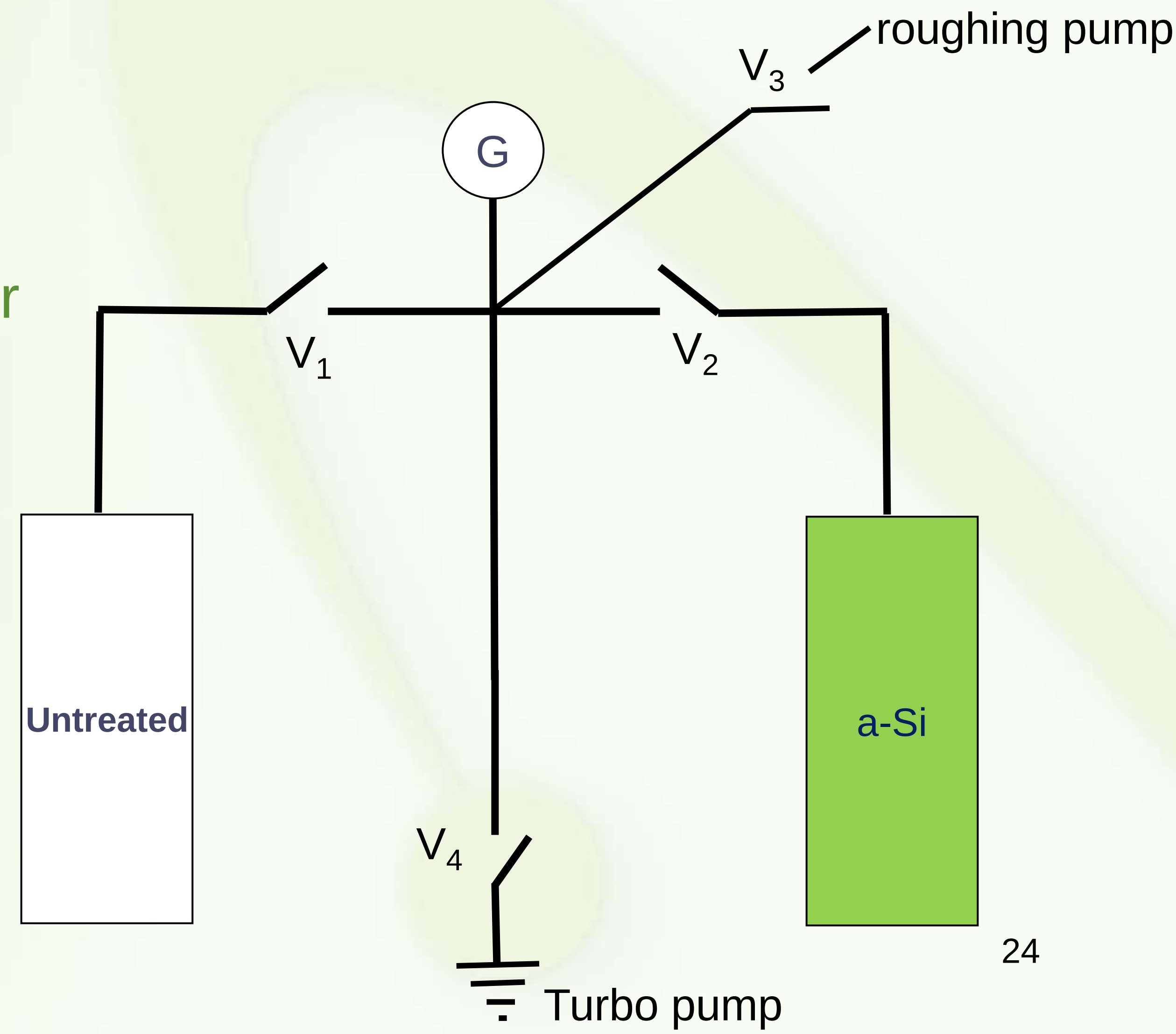
UHV comparison – B/A ion gauge housings



- Ion pump, 1.2 x 10^{-10} Torr base pressure
- 156 days under vacuum (5th baking cycle)
- 3.3-fold improvement at 105ºC
  (no measurable ΔP for a-Si at 61ºC, 7.0 x 10^{-12} Torr ΔP at 105ºC)

Chamber Comparison; No Heat

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

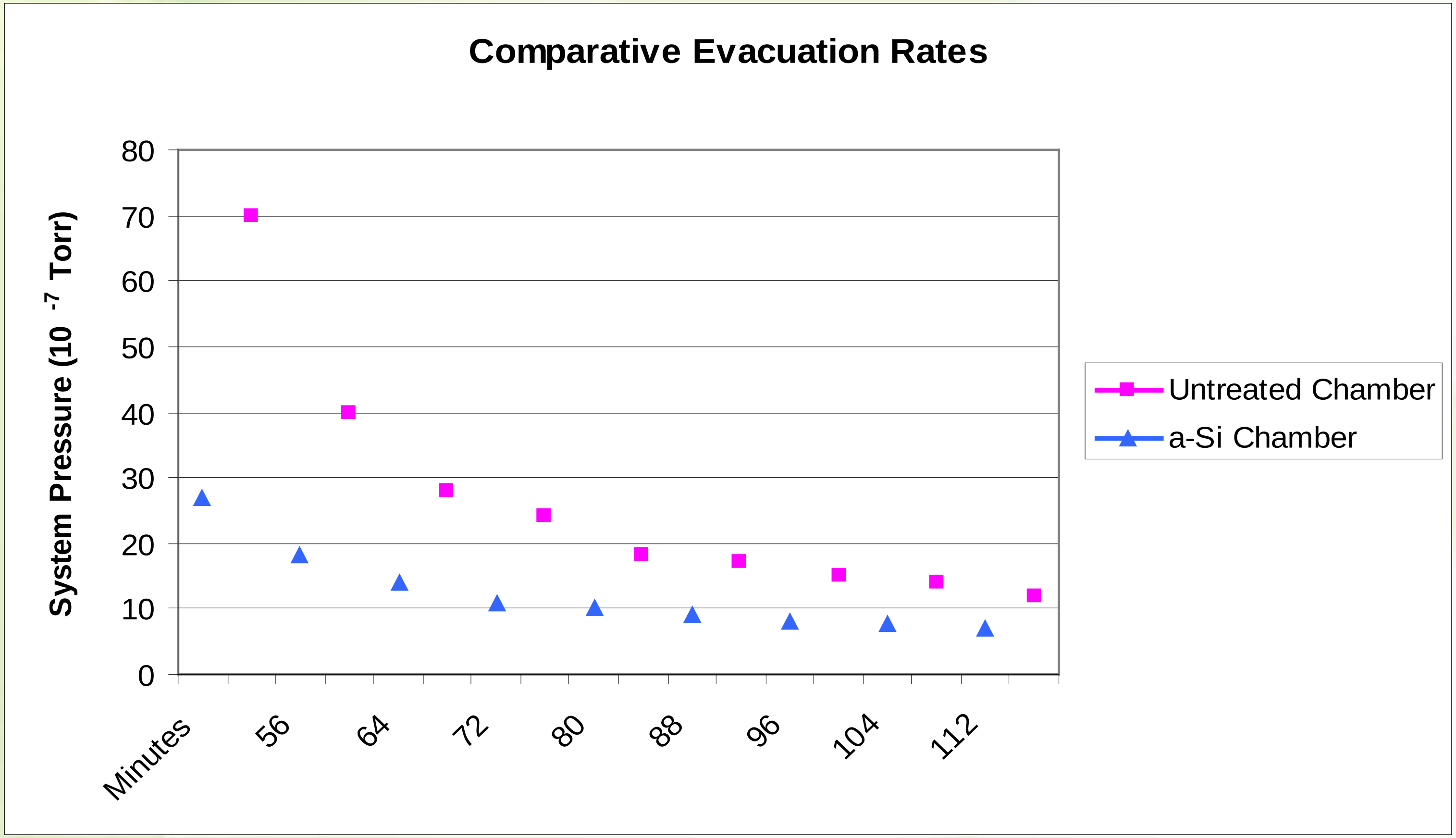


SilcoTek™ Driving Innovation

Chamber Comparisons; No Heat

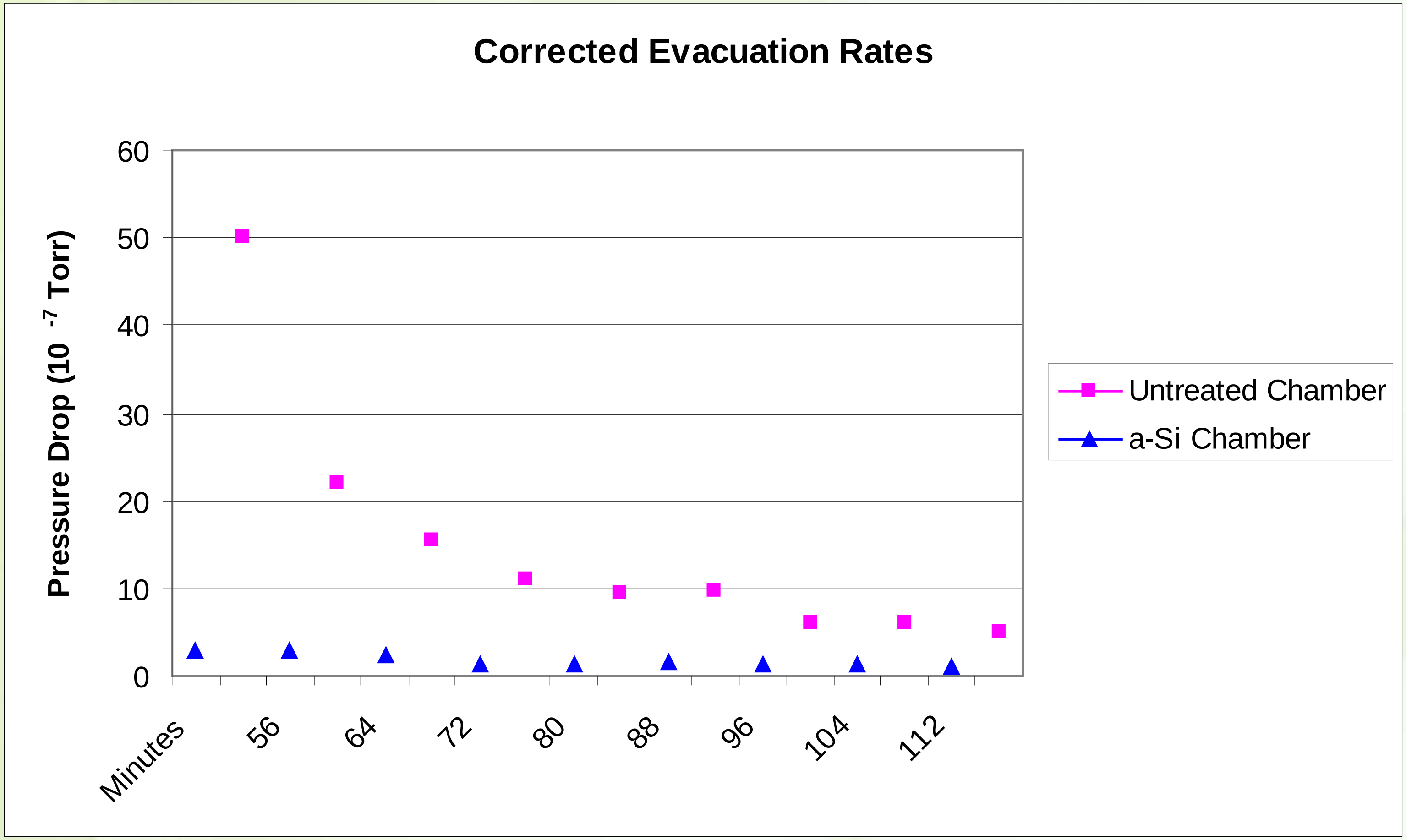
- System conductance: 7.4 l/sec
- 360 l/sec turbomolecular pump
- Cold cathode gauge

Chamber Comparisons; No Heat



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

Corrected Comparison

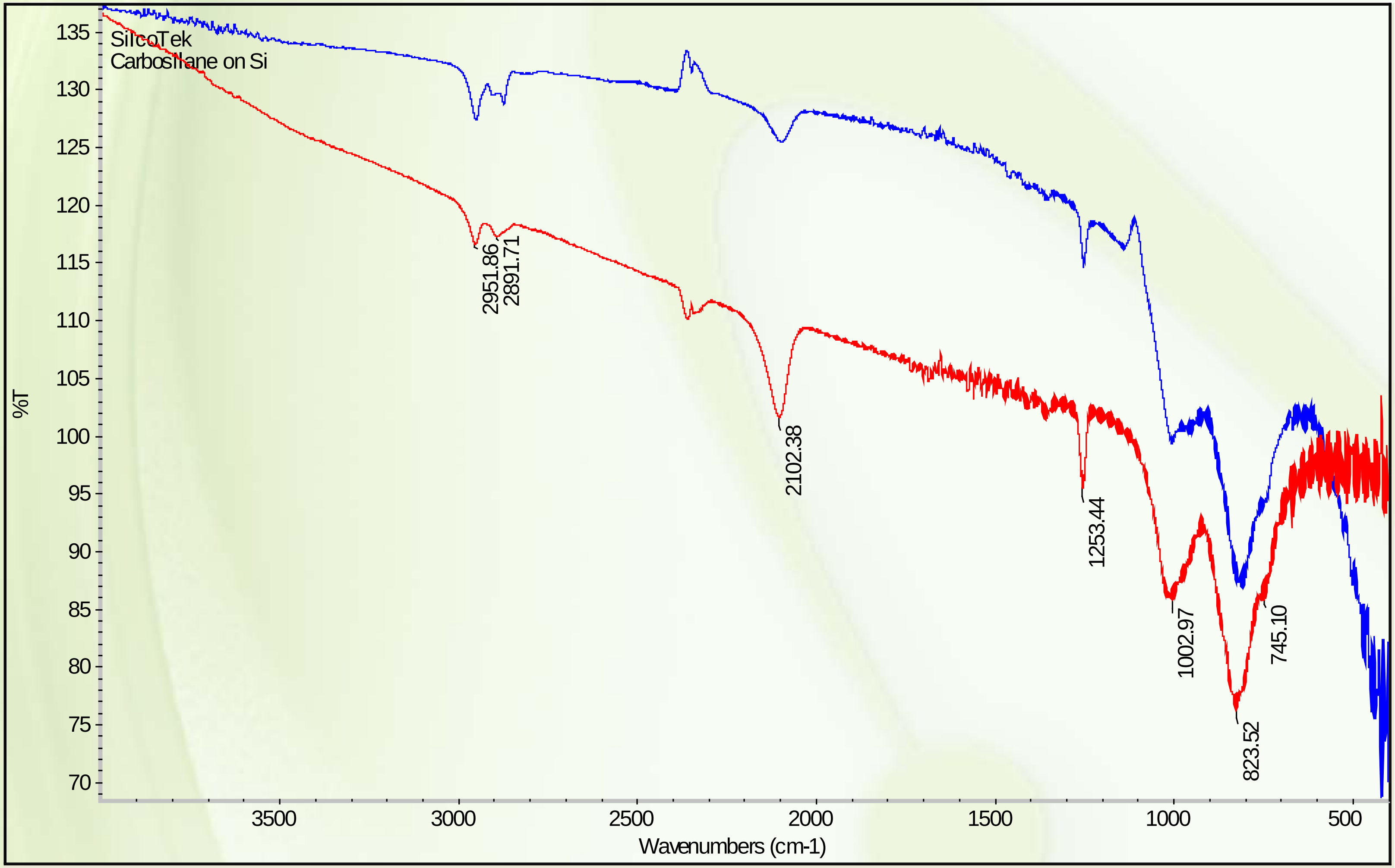


- Alternate pressure drop system measurements (true outgassing of isolated chambers)
- 80-84 minute range: 9.1-fold improvement

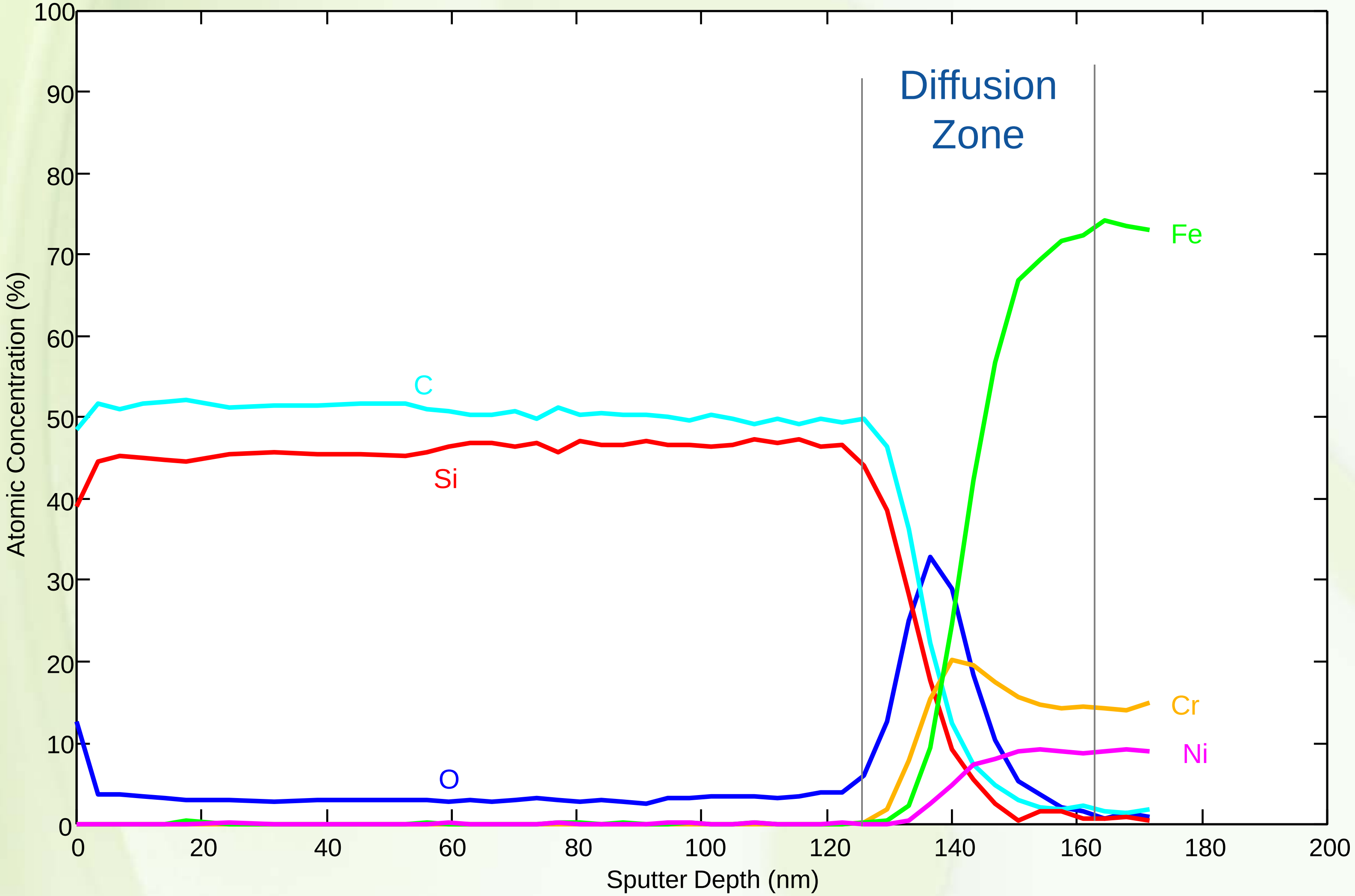
Current Research: Carbosilane Materials

- 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

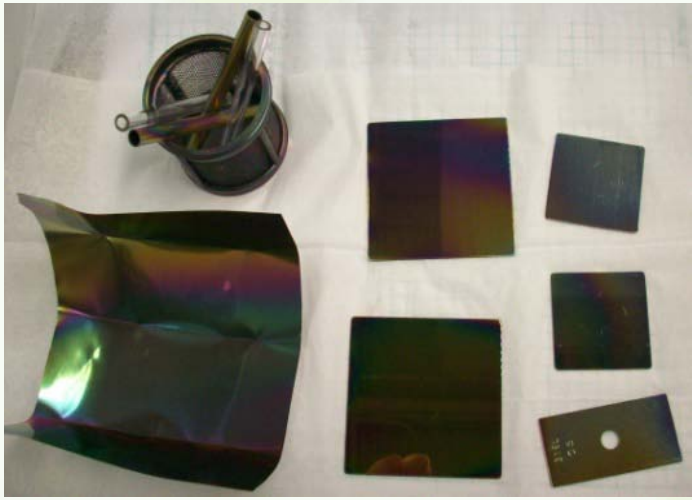
- ASTM G31 screening:
  - 6M HCl, 24 hrs, 316 SS coupons, 22° C

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_2S 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

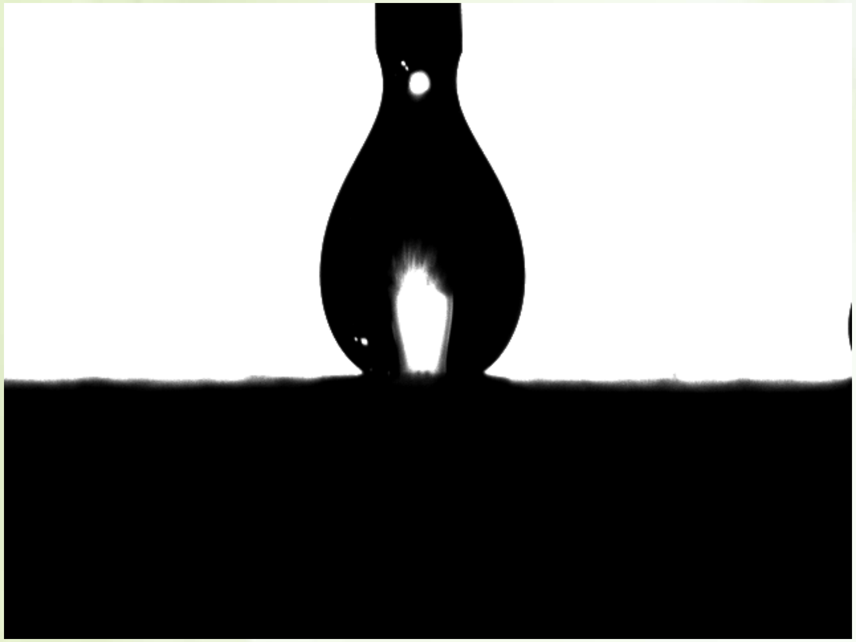


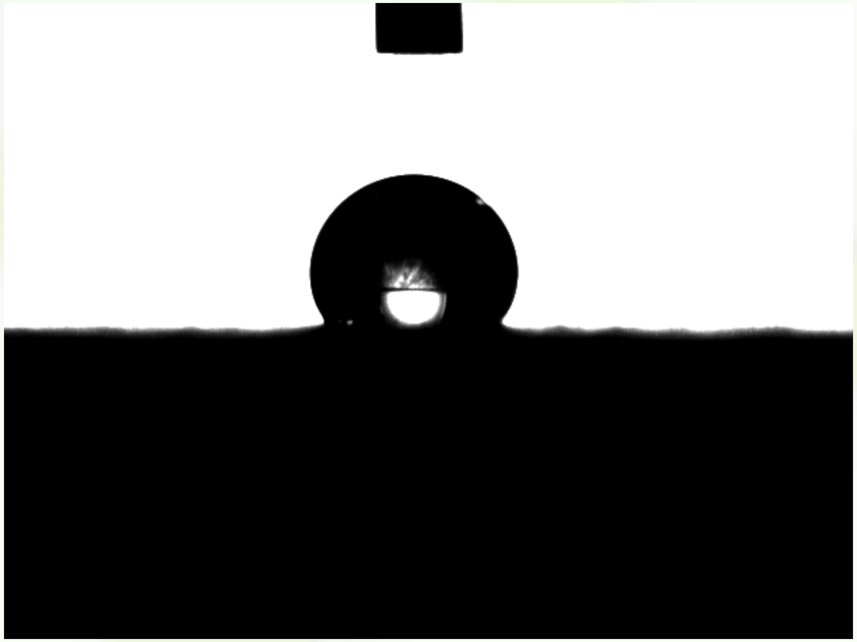
-narrowing the hysteresis gap to Cassie-Baxter state

Contact Angle Illustration

Close to Release…

- DI water CA: 127°
- 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