Morphology and High-temperature Stability of Thin Alumina Coatings Deposited on Si, SiC, and Ni

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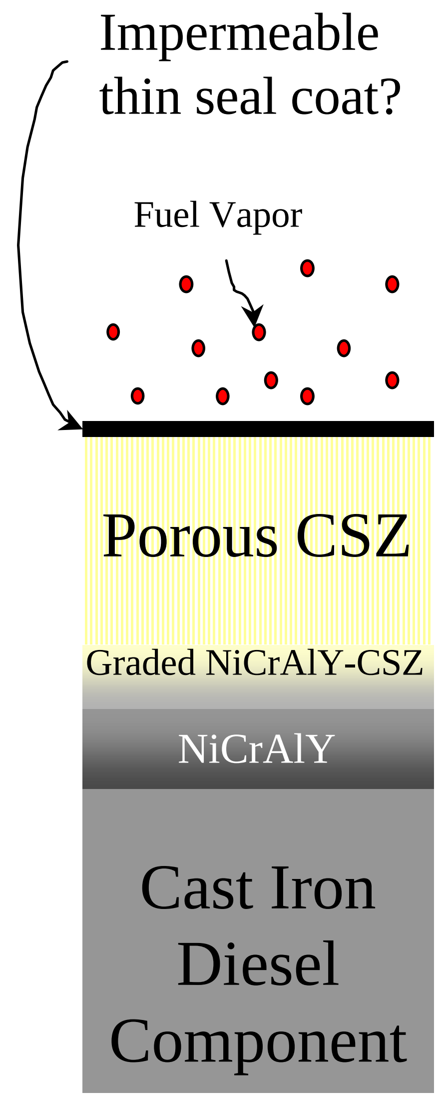
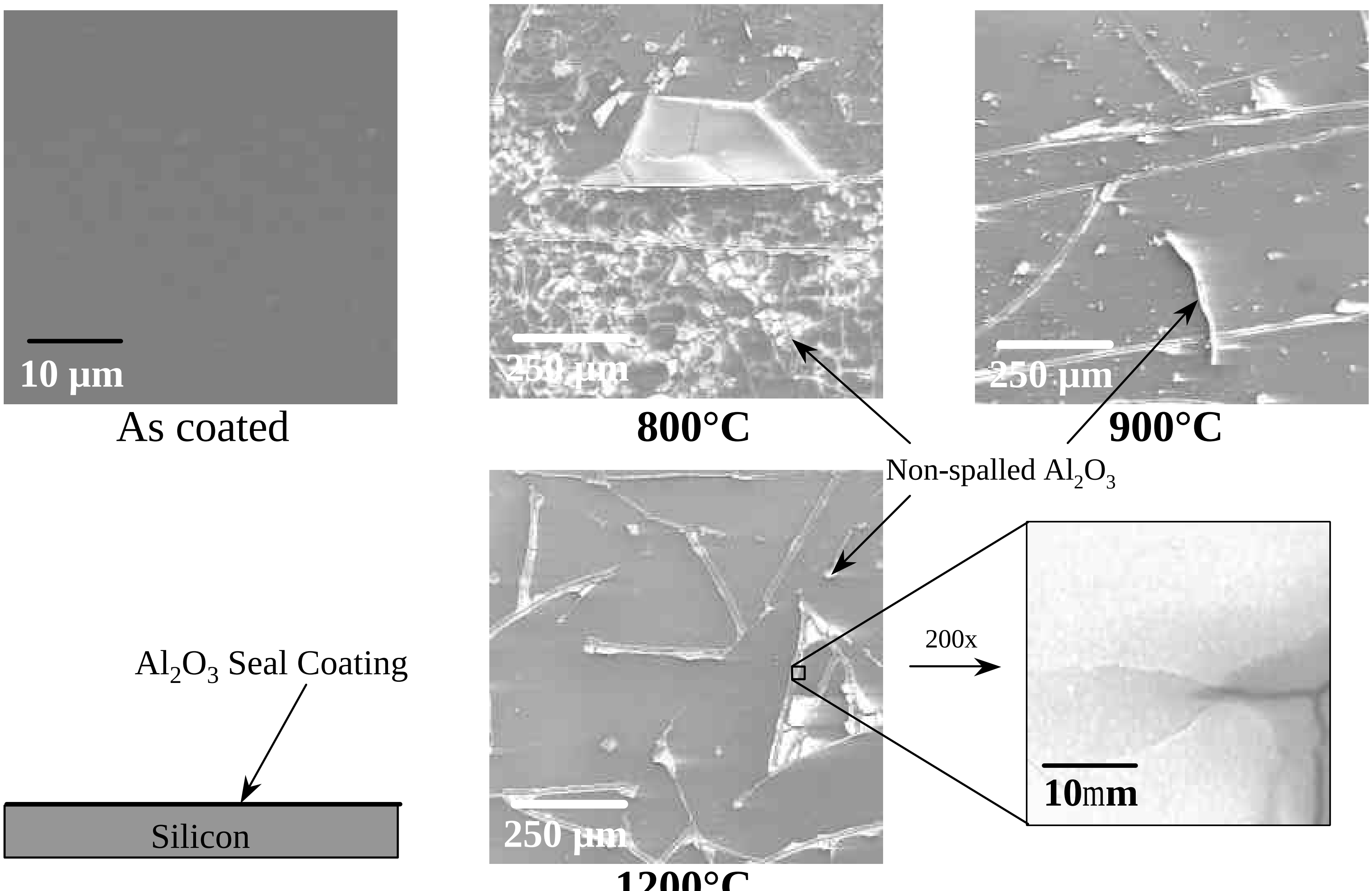
January 14, 1999

Initial Seal Coating Work Reveals Volume Shrinkage Due to Crystallization: A Serious Obstacle

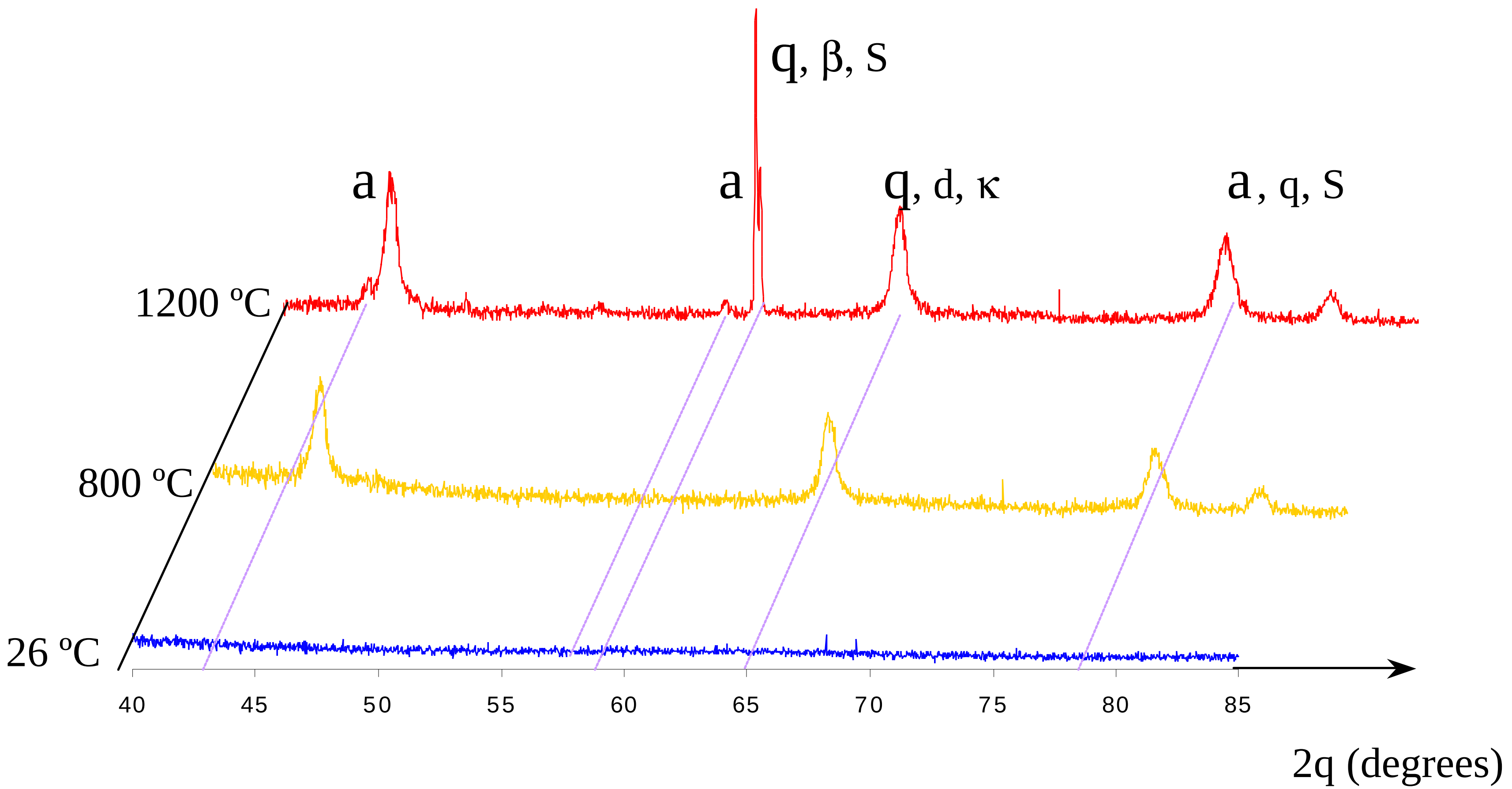
- Thermal Barrier Coatings (TBCs) are being considered to improve diesel engine efficiency
  - CeO_2-stabilized ZrO_2 (CSZ) prepared by air plasma spray (APS) is made porous for strain tolerance and enhanced thermal insulation
- Unexpectedly, testing at Caterpillar revealed a decrease in engine efficiency when components were coated with a TBC
  - One possible reason may be the porosity of the TBC, which is suspected to "entrain" fuel from the combustion chamber prior to ignition [B. Beardsley, 1990]
- Thick MOCVD Al_2O_3 coatings deposited on APS-CSZ adhered, but cracked significantly



Thick (2.25μm) Al_2O_3 on Si Spalled upon Annealing



Crystallization of Al_2O_3 Occurs Relatively Rapidly (< 20 Hours) at 700°C to 1200°C



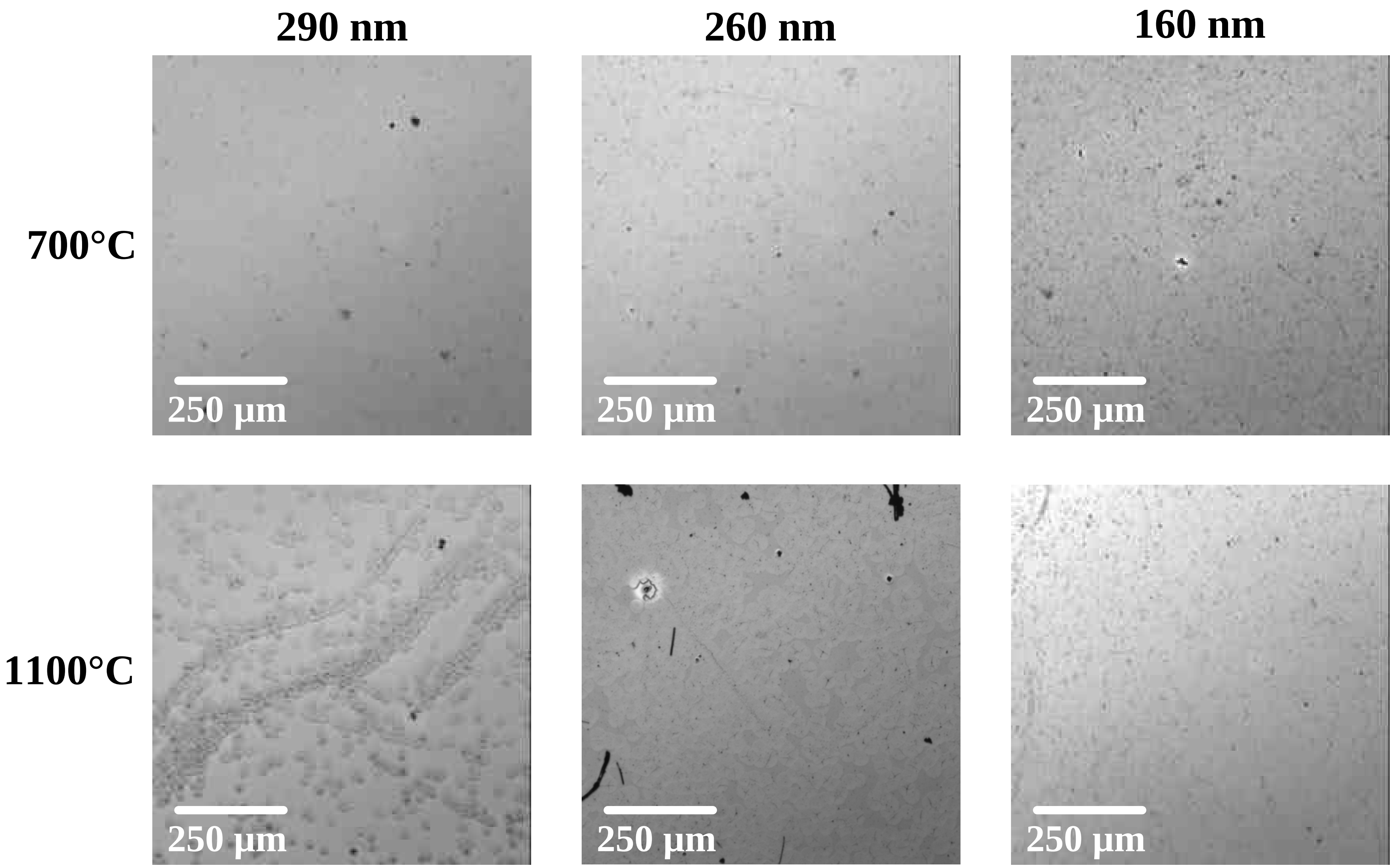
a: α-Al_2O_3 **S**: $Al_2Si_4O_{10}$

Not much Al_2O_3 remained on the substrate for XRD analysis

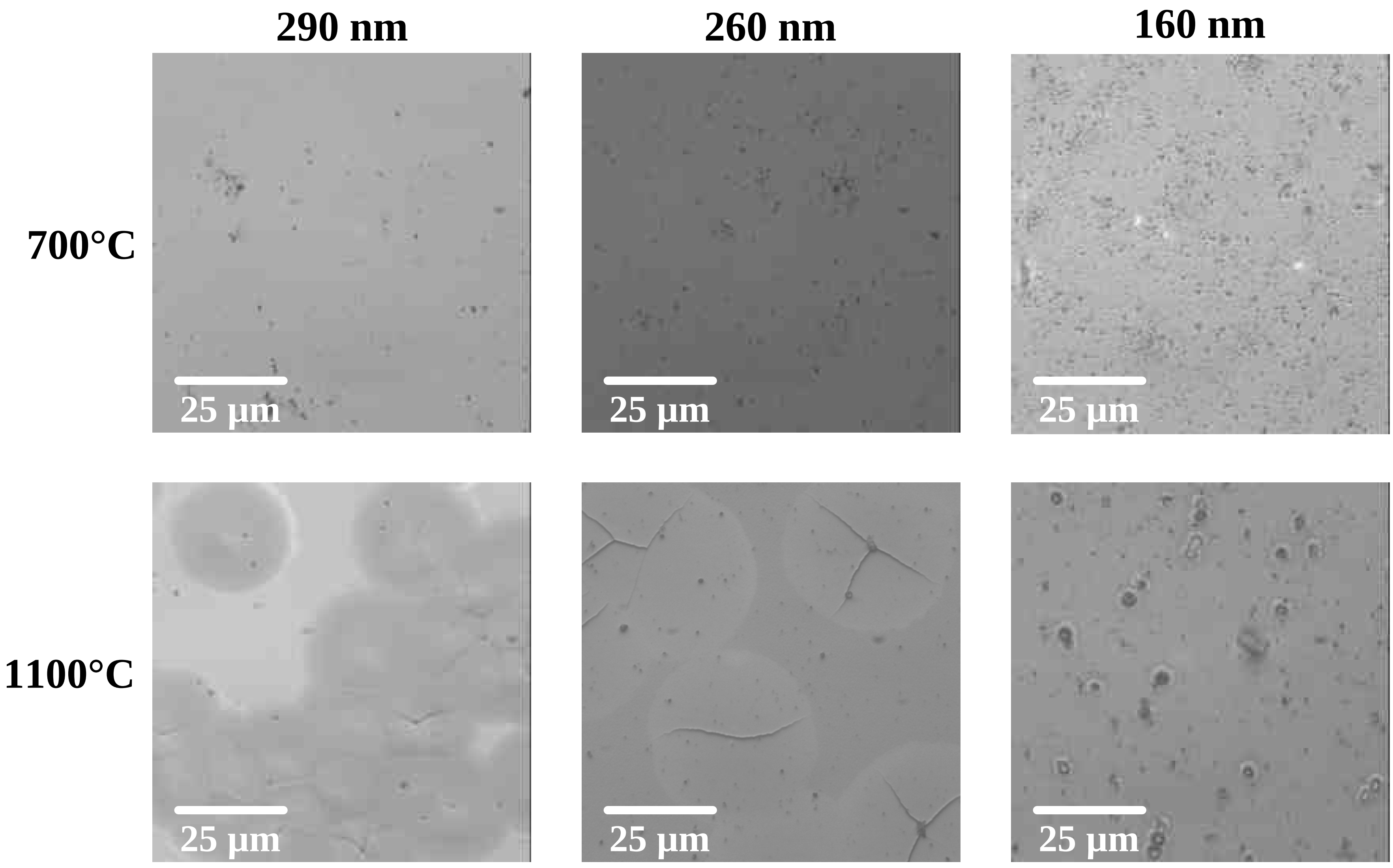
Spalling of Al_2O_3 Seal Coatings May Be Avoided by Reducing Coating Thickness

- Annealing of thick (2.25 µm) MOCVD Al_2O_3 coatings leads to inadequate adhesion and sealing
  - Considerable spallation on silicon due to:
    - CTE mismatch
    - Volume shrinkage due to crystallization
  - Adhered on CSZ, but coating cracked as crystallization occurred
    - Less CTE mismatch with CSZ than with Si
    - Better adhesion may be due to mechanical interlocking at CSZ/coating interface
    - Volume shrinkage still significant (~ 9%)
- Work by F.F. Lange stipulates that thin coatings (~100nm) are better able to contain tensile stress systems
  - crack propagation occurs only when free energy of any film would be reduced; strain energy depends on film thickness
  - There is a critical film thickness associated with a maximum internal energy

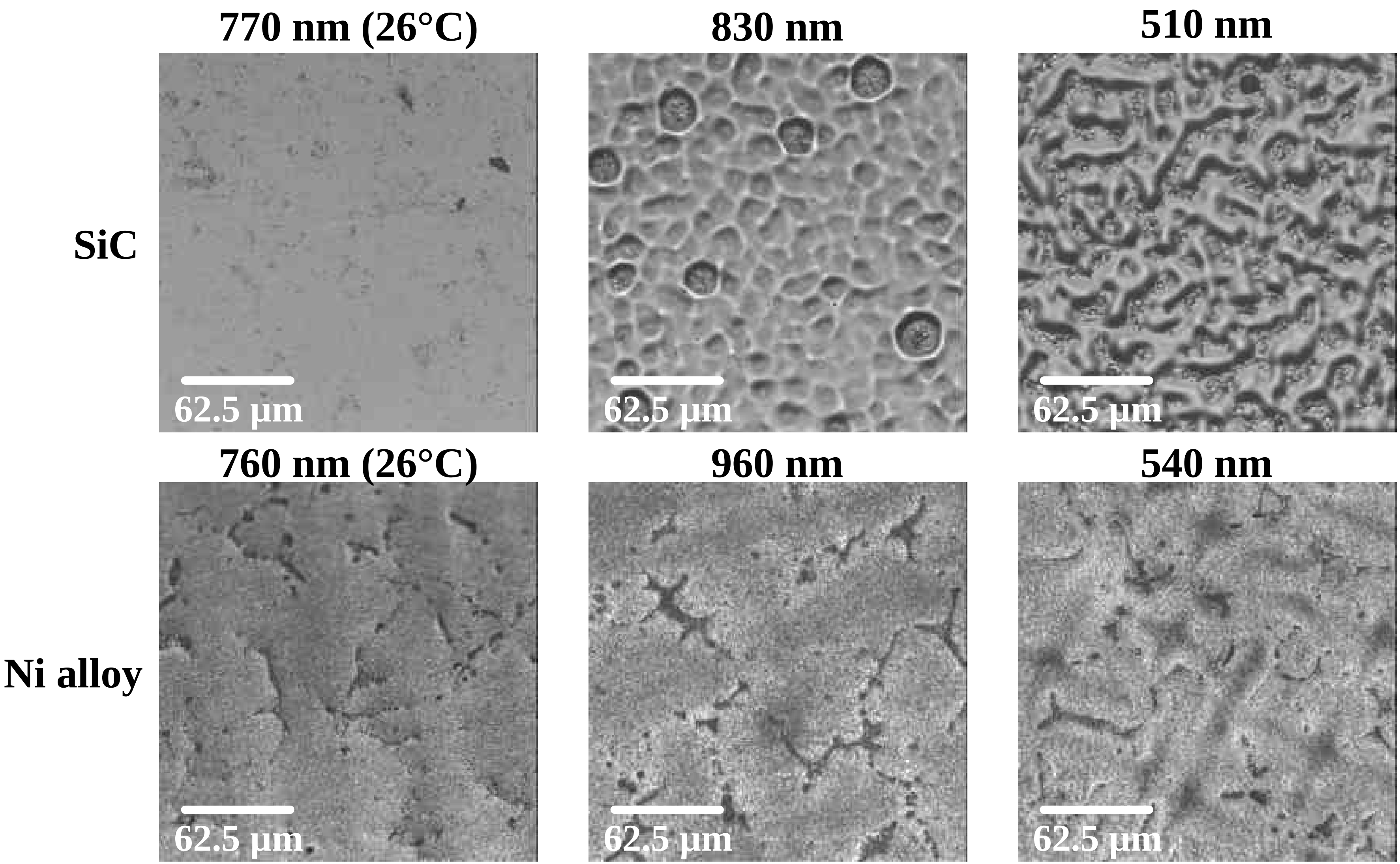
Sub-micron Coatings Exhibited Slight Cracking



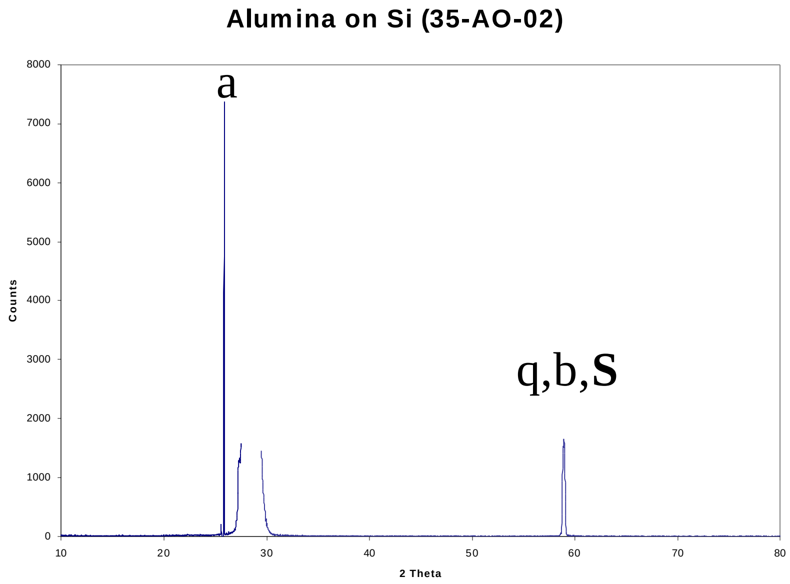
Micro-Cracking Falls With Coating Thickness

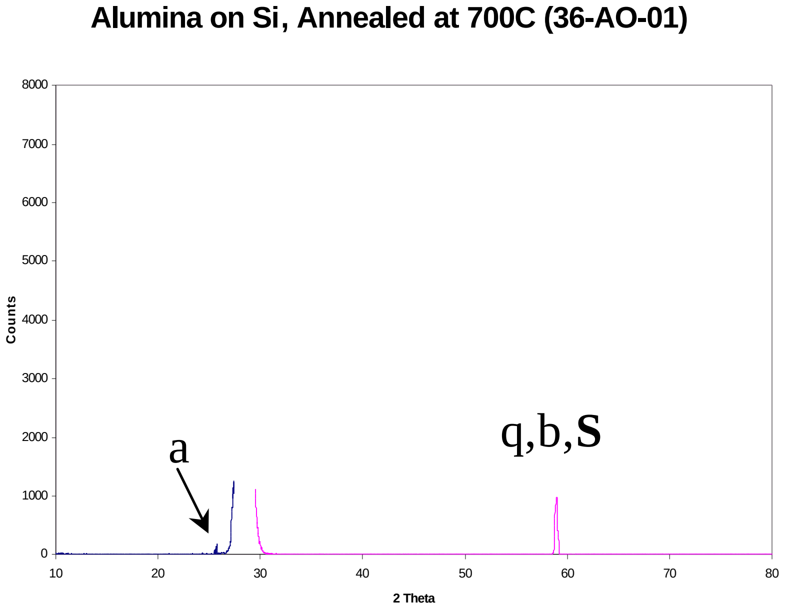


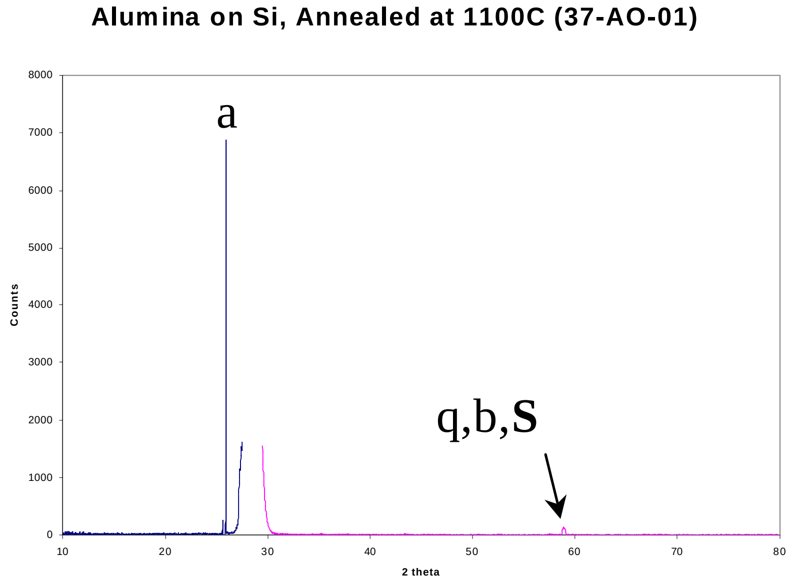
Silicon Carbide & Nickel Alloy Substrates at 1100°C

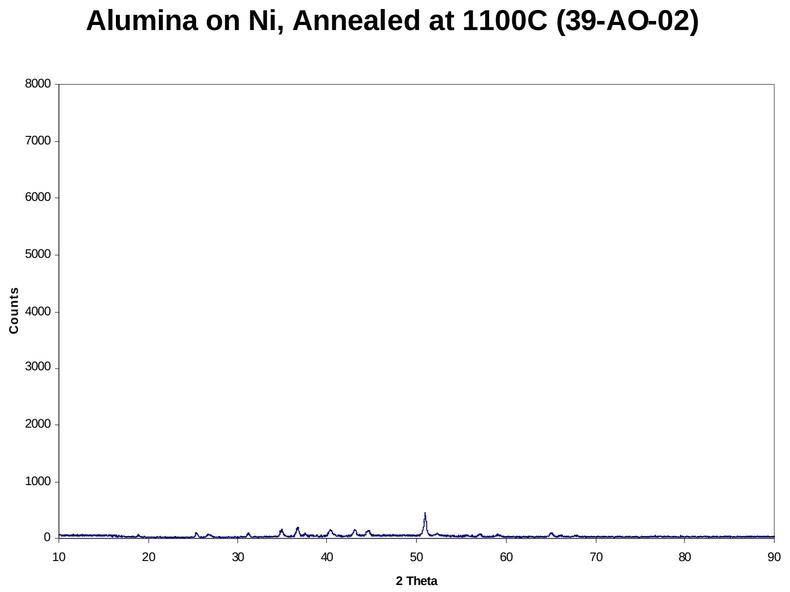


XRD Demonstrates Only Minimal Transformation







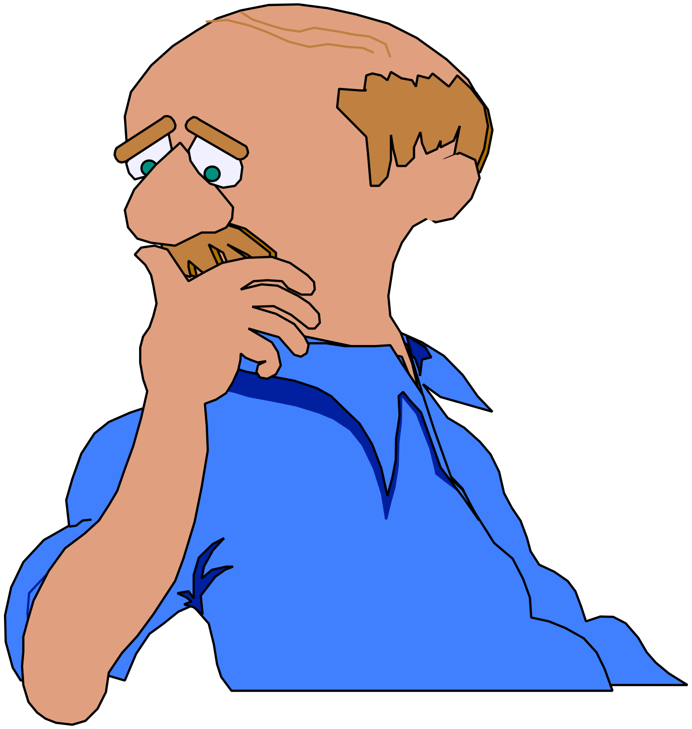


Annealing of Al_2O_3 Coatings at 1100°C for 20 Hours Showed Several Thickness-based Trends

- Thinner coatings on silicon appear to maintain a lower distribution of crack-initiating "pores"
- Despite this, transformation is not evident in XRD patterns, requiring additional effort to confirm Al_2O_3 crystallization
- Coatings on silicon carbide appear to "coagulate" more easily as thickness drops, especially in center of samples
- Coatings on nickel alloy substrates demonstrate increased leveling as thickness decreases
- With confirmation of crystallinity, sub-100nm coatings can be analyzed for micro-cracks

Substrate Heating Issues Considered

- Atmospheric plasma processing
  - High energy, very low substrate temperature
  - High reaction area/volume inherent to process

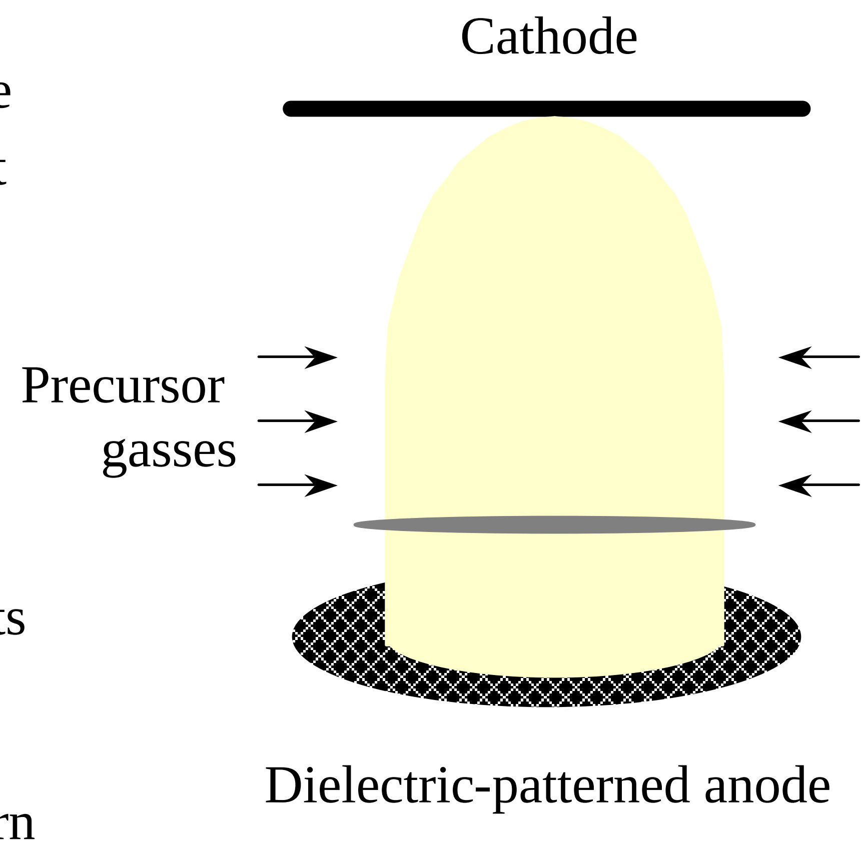


- Flat, resistive element heater
  - Increased substrate temperature, expensive
  - Low maximum temperature
- Optical heating methods
  - esoteric and complex

Non-equilibrium, Atmospheric Plasma Processing

(Luis Amorer & Prof. Kunhardt)

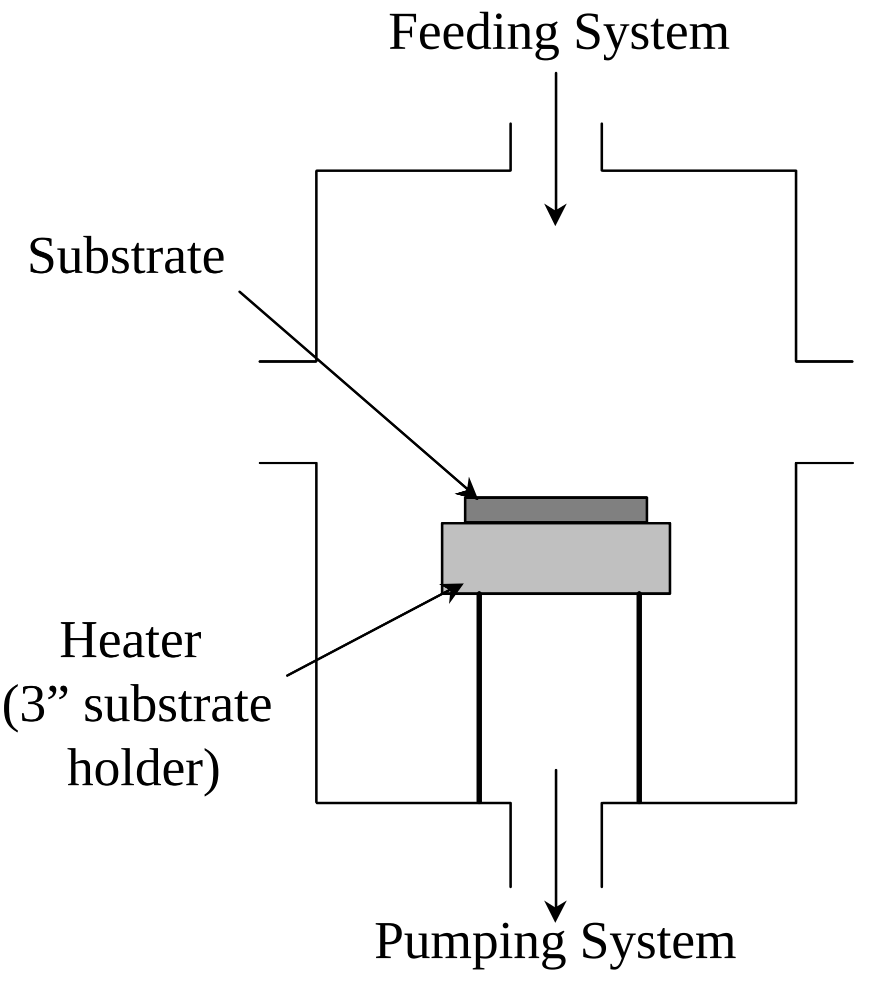
- Advantages
  - Processing at atmospheric pressure
  - Minimal substrate heating (can put hand in plasma)
  - High T_e ~0.2 - 0.3 keV >> T_i~T_n
  - Large processing area/volume
- Obstacles
  - Plasma only just beginning to be characterized (no conclusive results of any nature, yet)
  - Anodes are fabricated using by depositing a highly-complex pattern of a high-dielectric material on the base anode material



Flat High-temperature Resistive Heater May Be to Expensive

(Bell Labs / US, Inc. Thin Film Products)

- Advantages
  - Excellent temperature stability (±2°C) and uniformity (±8°C)
  - Short ramp time of 20 minutes (for 3” diameter heater)
  - Oxidation resistant
  - Geometrically compatible with current reactor
- Disadvantages
  - Maximum rated temperature of 950°C
  - High cost: \$3,500 - \$3,800 for 3” diameter heater



Optical Heating Methods Tend to Be Esoteric and Complex

- No information found on companies who manufacture focused UV or IR radiation heaters was found
- In one RTCVD (rapid thermal) setup, tungsten coil lamps are used in conjunction with mirrors lining the chamber to focus stray light on the substrate
- fast heating applications
  - requires fairly high angle of incidence to avoid requiring mirrors to maintain reasonable efficiency