Ultra-thin Aerogel Films

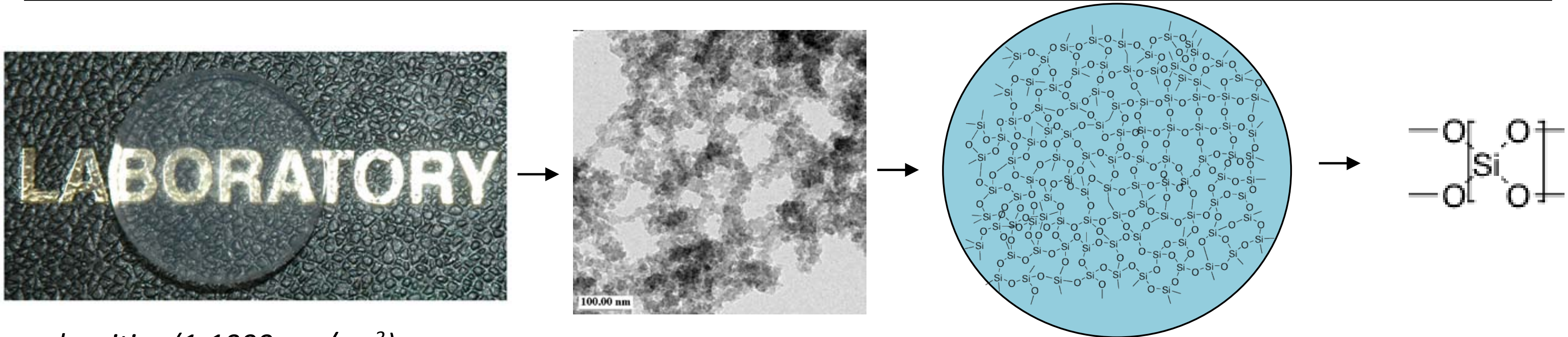
Los Alamos
NATIONAL LABORATORY
EST. 1943

Kimberly A.D. Obrey and Roland K. Schulze

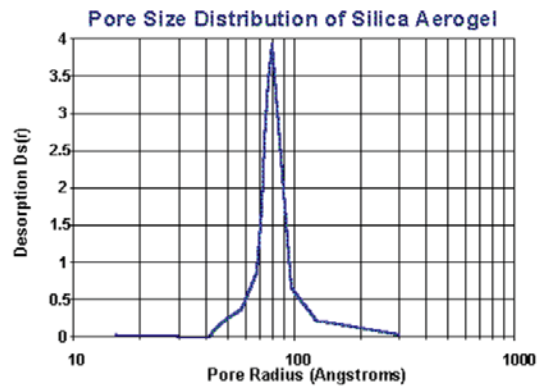
20th Target Fabrication Meeting
Santa Fe, NM
Tuesday, May 22, 2012

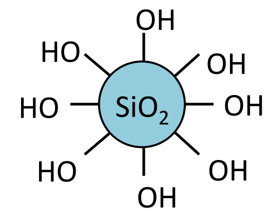
LA-UR 11-05466

Characteristics and select applications of silica aerogels

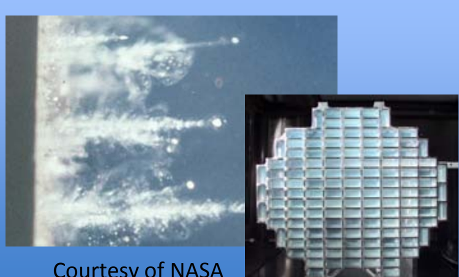


Low densities (1-1000 mg/cm^3)
Transparent
Composed of >95% air
High porosity (>95%)
Low thermal conductivity (0.012 W/ mK)
Large surface area (1600 m^2/g)
Mesoporous (20-2000 Å)
Open pore structure





Cometary dust collector



Courtesy of NASA

Thermal insulators

Courtesy of LBL

Unique insulating & structural uses

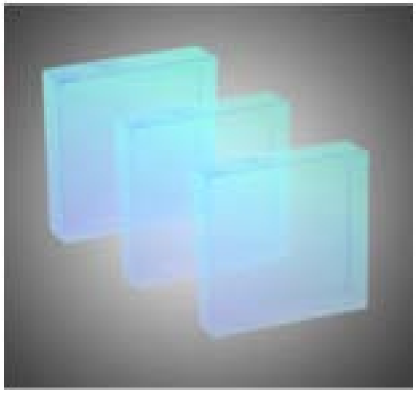
Courtesy of GZE and Dunlop

Chemical Sensors

Courtesy of LBL

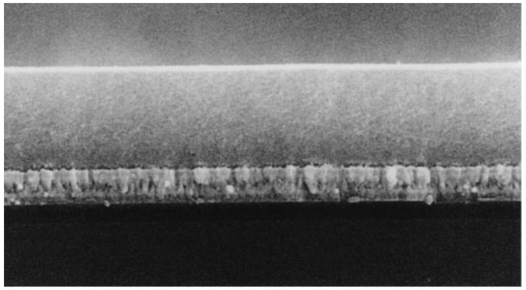
Silica aerogels can be synthesized in a variety of shapes

Monolithic



Courtesy of MarkeTech, Int.

Supported films



M.-H. Jo et al., Thin Solid Films 308–309 (1997) 490–494

Rolled

Courtesy of Aspen Aerogels

Spherical

K. A. D. Obrey-LANL

Powdered

Courtesy of Mineral & Metals

Complex

Courtesy of NeMe

General Silica Aerogel Synthesis

$Si(OCH_3)_4$
H_2O
Catalyst
Methanol

Add dopants to modify material properties

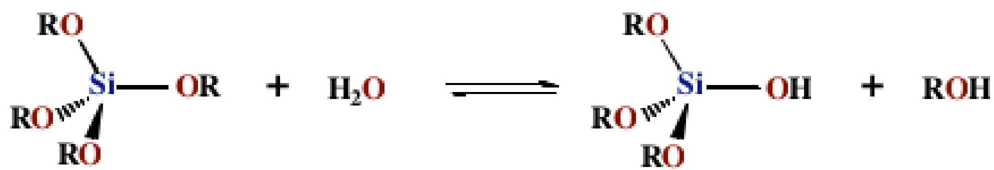
Dry the alcogel to either form aerogel or xerogel

Adjust reaction conditions to control surface area, density, porosity, and pore size

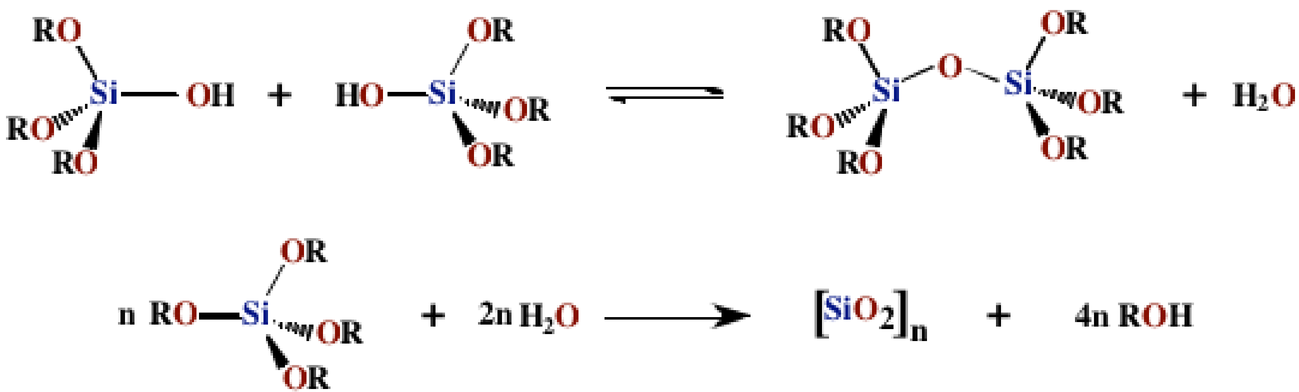
Adjust viscosity to prepare thin films

Alcogel

Hydrolysis

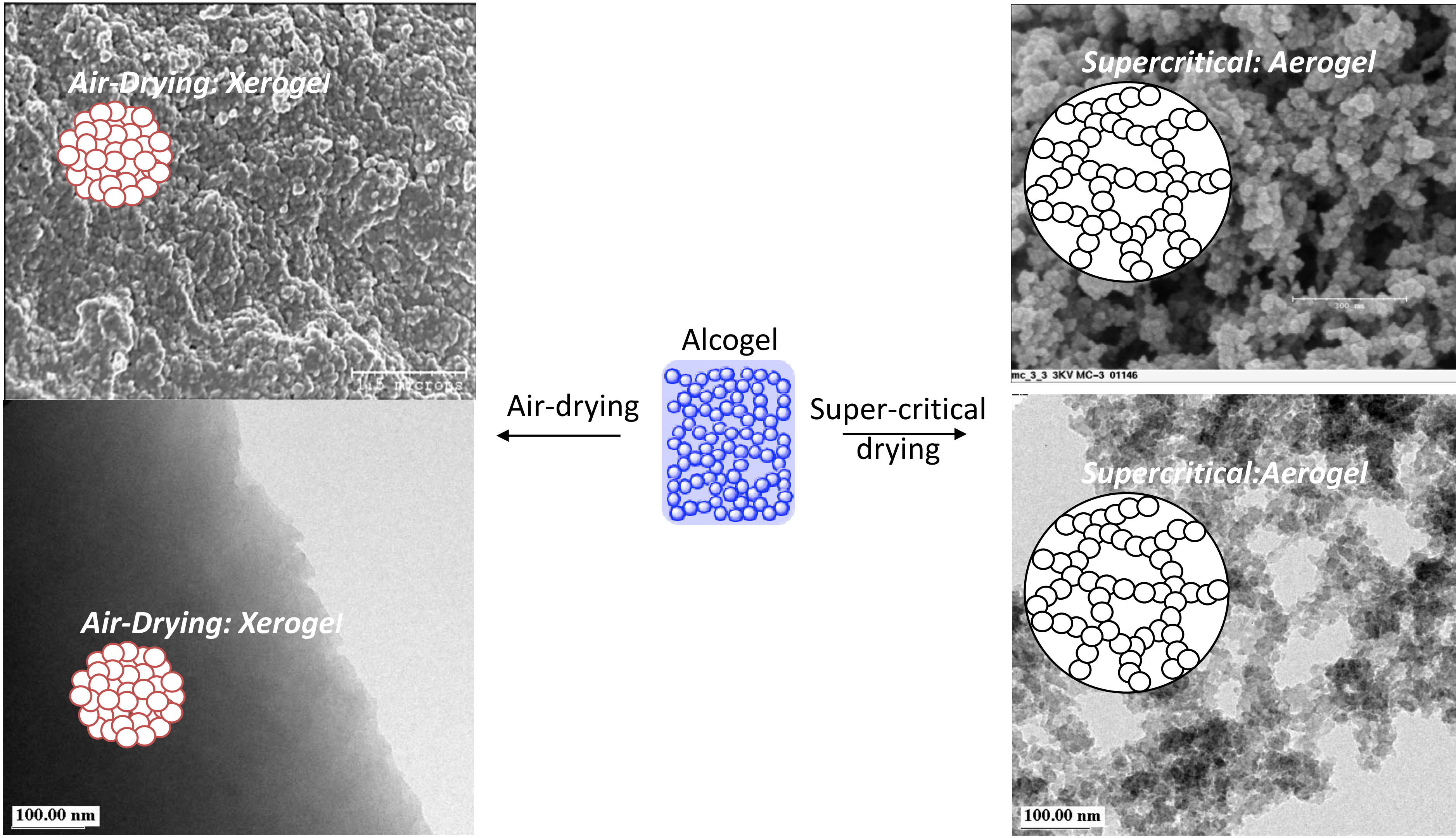


Condensation



Densities typically limited to ~1 – over 1000 mg/cm^3

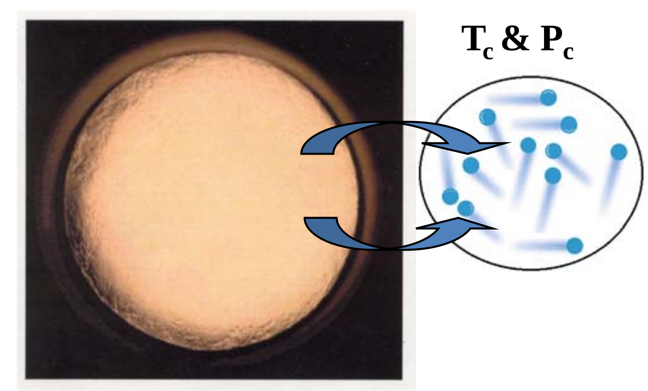
Comparison of Xerogel and Aerogel Structure

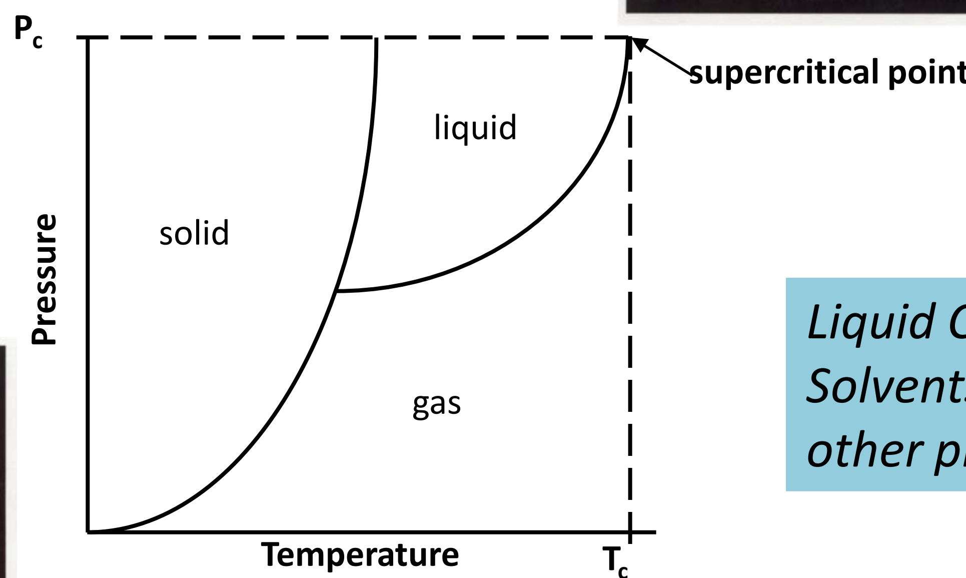


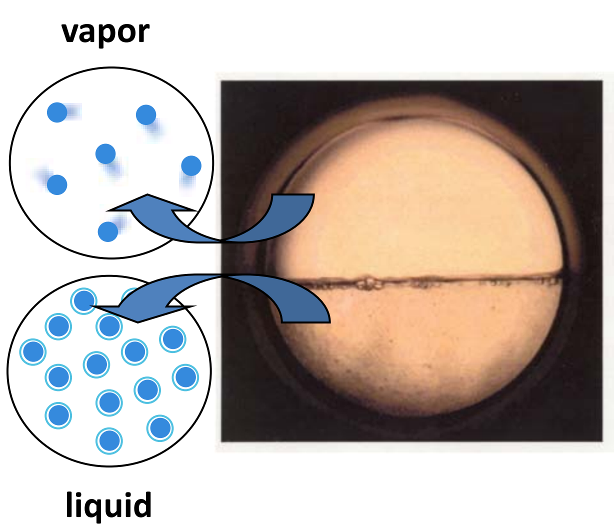
Loy, D. A.; Jamison, G. M.; Baugher, B. M.; Russick, E. M.; Assink, R. A.; Prabakar, S.; Shea, K. J. *J. Non-Cryst. Solids* **1995**, *186*, 44.

Supercritical Drying

- *Behaves as a gas (no surface tension) and liquid (density)*
- *Higher diffusivity than traditional solvents*
- *Absence of liquid-vapor interface*
- *No capillary pressure*
- *Minimize collapse & shrinkage during drying*
- *Porous, low-density structure*



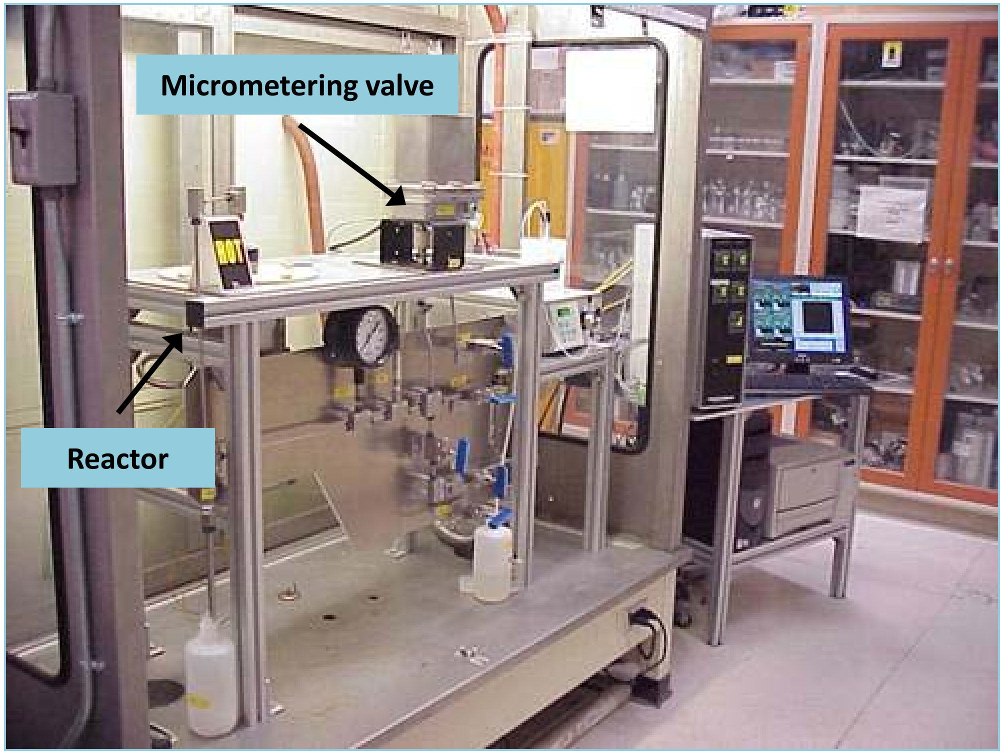




Liquid CO_2 or Solvents…used in other processes too

Supercritical solvent drying to achieve lower density aerogels

Supercritical Solvent Extraction Apparatus



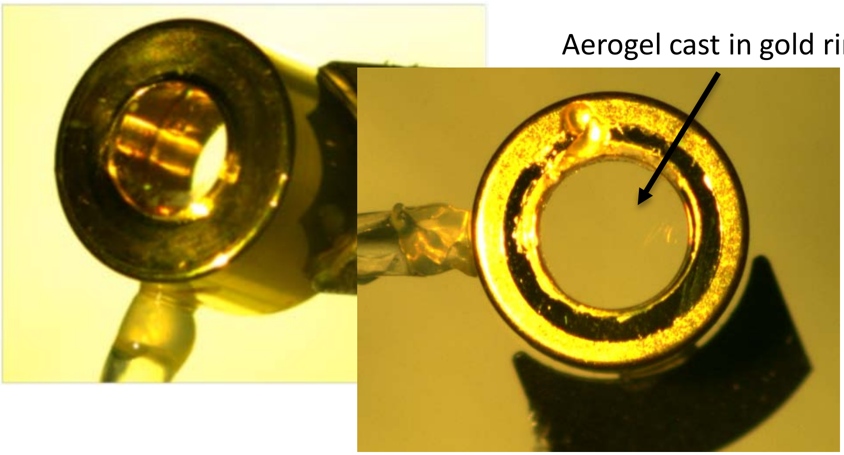
Various organic solvents may be used: methanol, ethanol, acetone
Typically use methanol: 2000 psi and 330°C
2 day operation

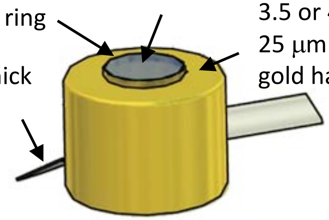
sample molds

Gel is poured and molded into specific shape.
Density is determined from a sample mold.
Typically synthesize densities from 5-60mg/cm^3

Most targets requiring aerogel at LANL are monolithic produced by casting and/or machining

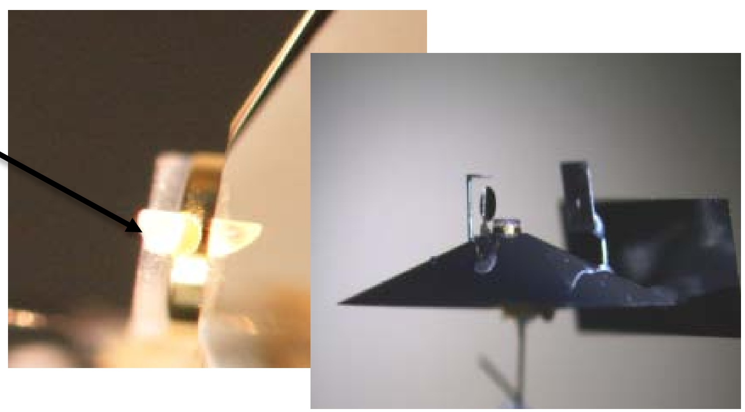
Pleiades: NIF



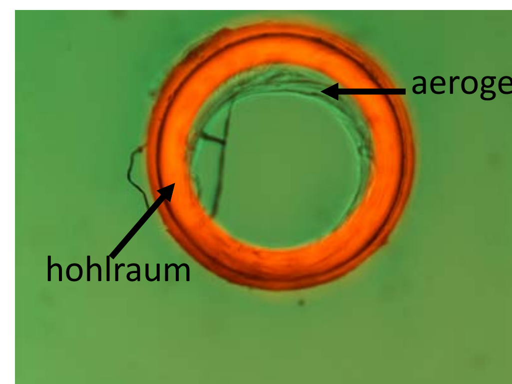


Blastwave: Z

DP-EOS: Omega



Hohlraum lined with 5.4 mg/cm^3 silica aerogel



Recently, a program at LANL required ultra-thin aerogel films.

Goal: Synthesize free-standing, low density, ultra-thin silica aerogel films

<u>Silica aerogel film specifications</u>

- Density: 20 mg/cm^3
- Film Thickness: 100-200 nm
- Orientation: "free-standing" defined as some area where both front and back of aerogel is exposed

- First reported silica aerogel thin film was in 1989 (N. Mulders), studying He uptake in porous films. These were sub-cm in size and were cut to shape.
- Since then, more than 400 publications on aerogel films have been written.
- Previous work has been focused on supported aerogel structures.
- The films are usually deposited via spin-coating, dip-coating, or spray-coating the alcogel
- Most aerogel films are 1um or more in thickness.

Traditional Synthesis Methodologies to make aerogel films

Spin-coating:

- Film thicknesses are typically less than 2 um
- This process used to spin glass coatings for electronic applications
- Typical substrates are Pyrex glass slides and silicon wafers up to 3" diameter.
- The procedure for forming films is to deposit droplet of precursor solution onto the spinning substrate while its spin rate is increasing up to a desired spin speed and a solvent saturated atmosphere.
- Typically, the gel will form within a few minutes, after which the substrate is removed from the coater and immersed in solvent. The substrates with films are stored submersed in solvent until ready for supercritical drying.

Dip coating:

- Dip coating is the simplest of the coating processes, but it is used only when all surfaces of a substrate material are to be coated.
- Film thicknesses less than a few micrometers are obtainable depending on the viscosity of the precursor and the withdraw rate.

Spray coating:

- This process has been used to put thicker single layer coatings on substrates like glass and silicon wafers.
- Films as thick as 80 um have been achieved by this method.
- An aspirator is used to spray the precursor solution directly onto the substrate.
- Excess solution drains by gravity, leaving a thick film which gels within a few minutes.
- These films have a varying thickness due to the draining, but the surface of the gel is smooth and continuous.
- After gel has formed, the substrate is manually immersed in solvent until ready for supercritical drying.

Spin coating offers best success in achieving film thickness of 200 nm.

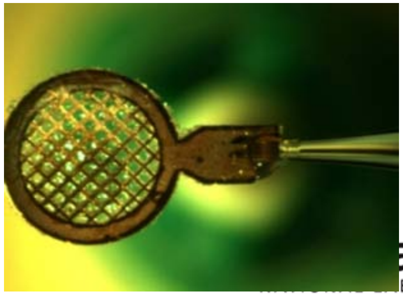
Spin-Coating Specifications:

- Alcogel solution of corresponding density was used
- Deposit alcogel at various gel-times to ensure optimal film thickness and smoothness
- Spin speeds (500-3000 rpm)
- Immerse coatings in solvent before super-critical drying process to prevent films from drying out.

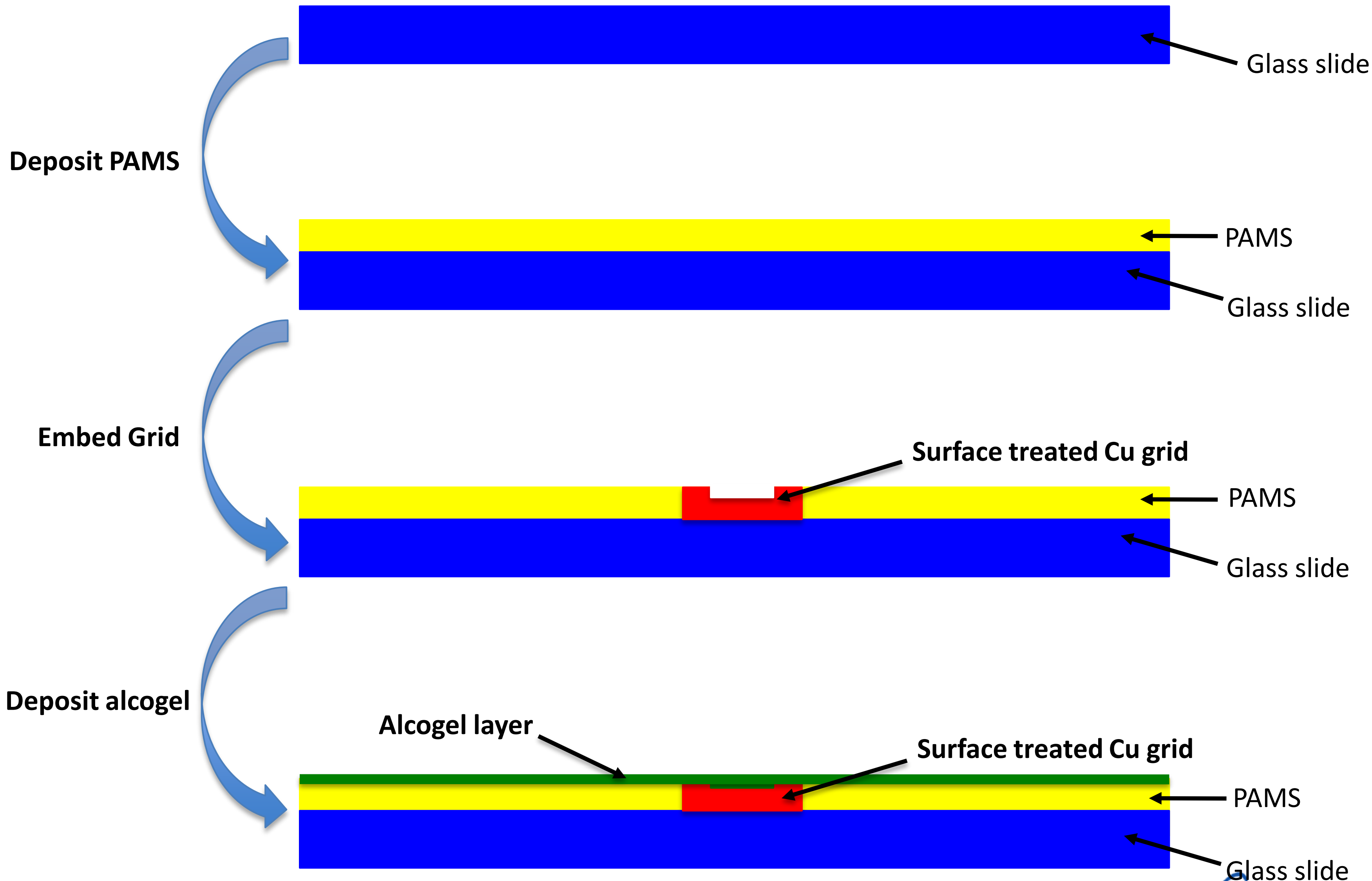
Two types of films were produced:

1) Supported films:
   - alcogel is spin-coated onto glass slides
   - film thickness and flatness was measured using prolifometry of supported aerogel films

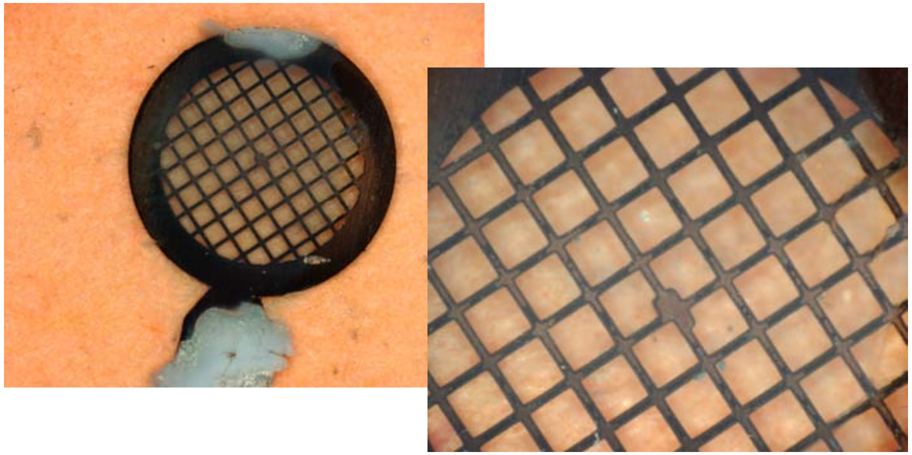
2) Free-standing films:
   - TEM grids were used as structural supports
   - Copper TEM grids were surface treated with warm (~50C) NaOH and methanol prior to use
   - Mount grids to do spin coating by using polymer interface



Step-by-step Process for making Free-standing Films



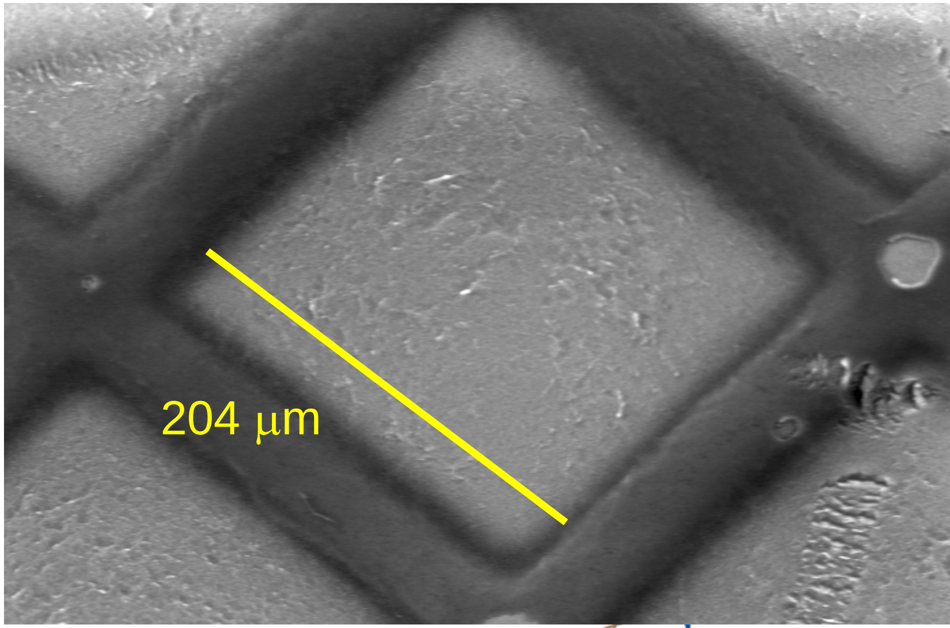
Free-standing nanometer thick aerogel films



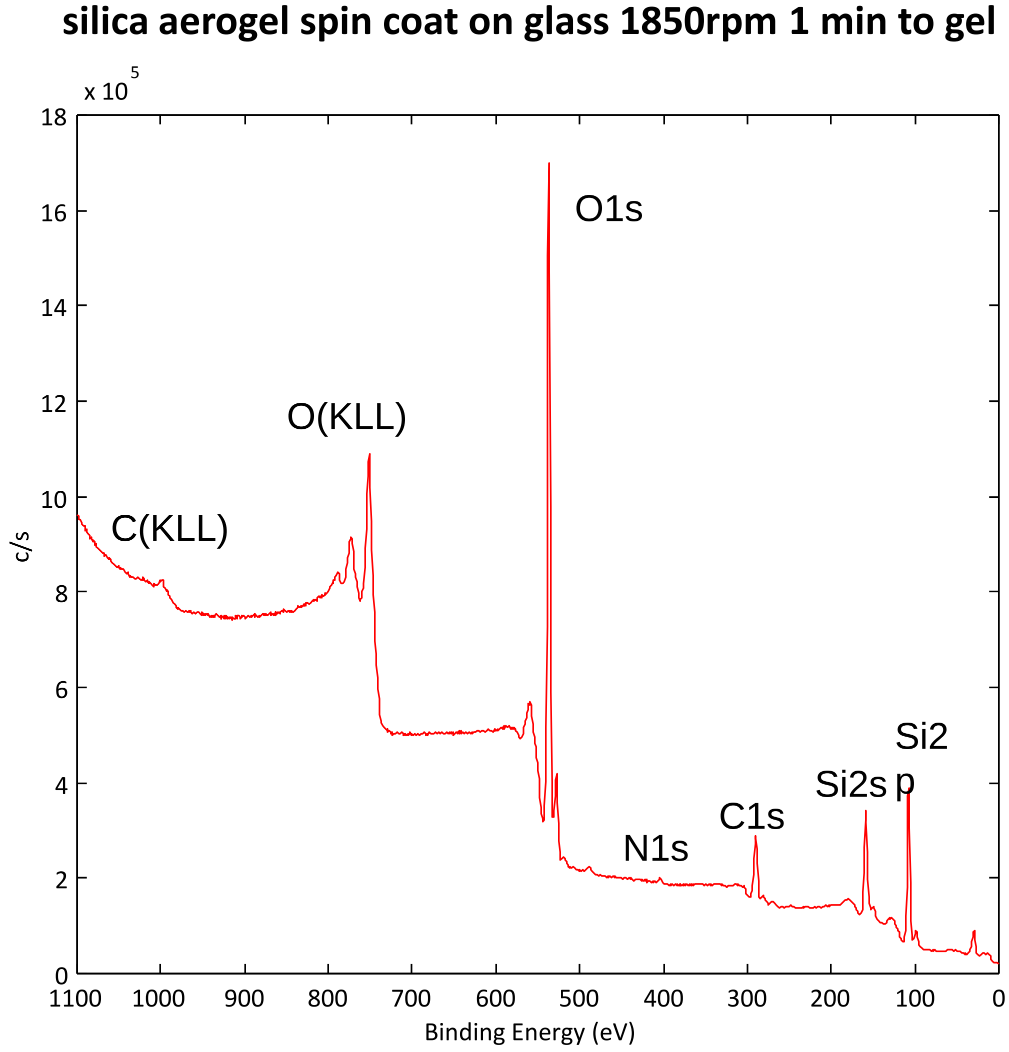
- Optical microscopy shows uniform distribution of aerogel through the grid

- SEM indicated uniform distribution
- Some areas are cracked and pitted

SEM images of 40 mg/cm^3 aerogel on 100 mesh Cu grid

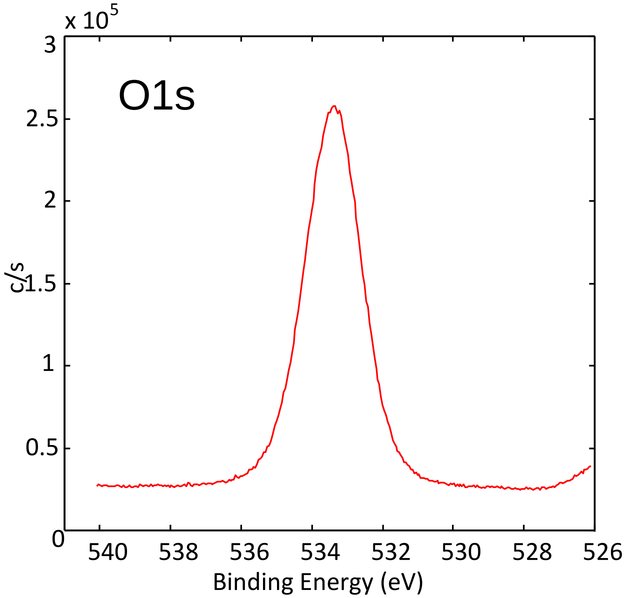


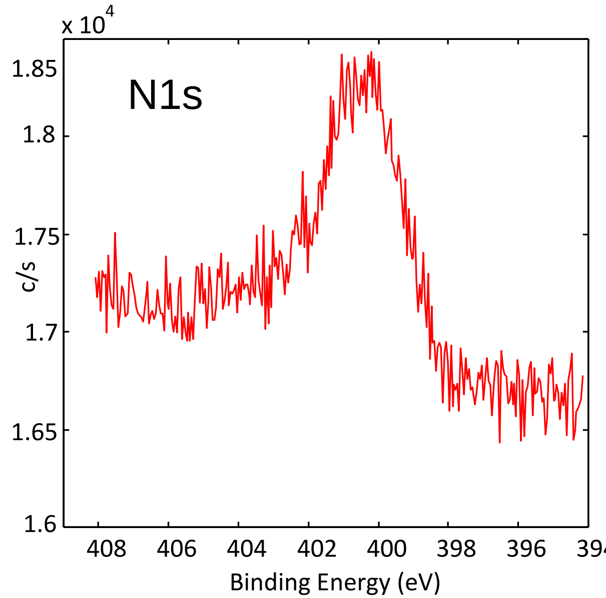
XPS of aerogel thin film

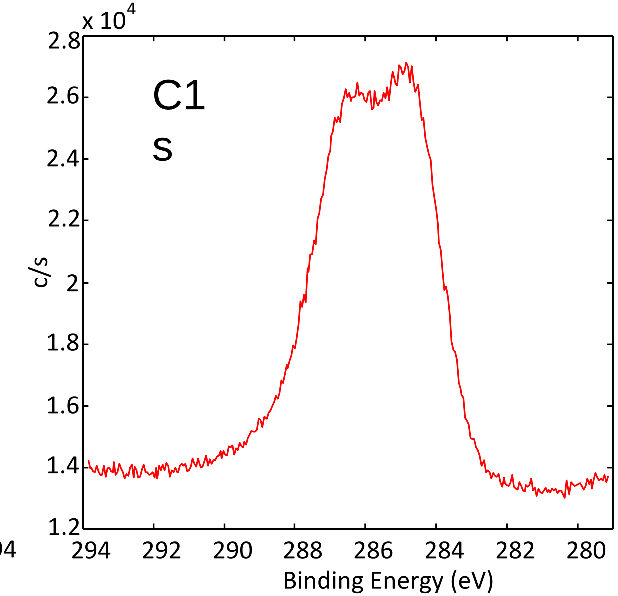


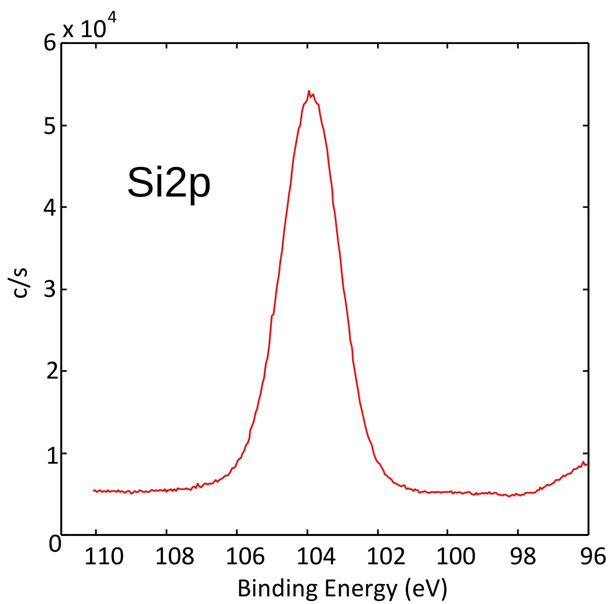
Soft x-ray exposure (1256 eV) causes damage to aerogel film or carbon present in/on film - film turns brown

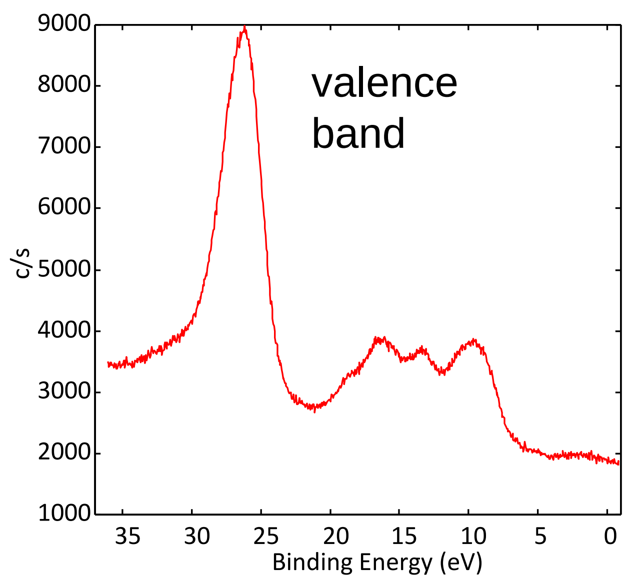
XPS verifies aerogel SiO_2 in thin film









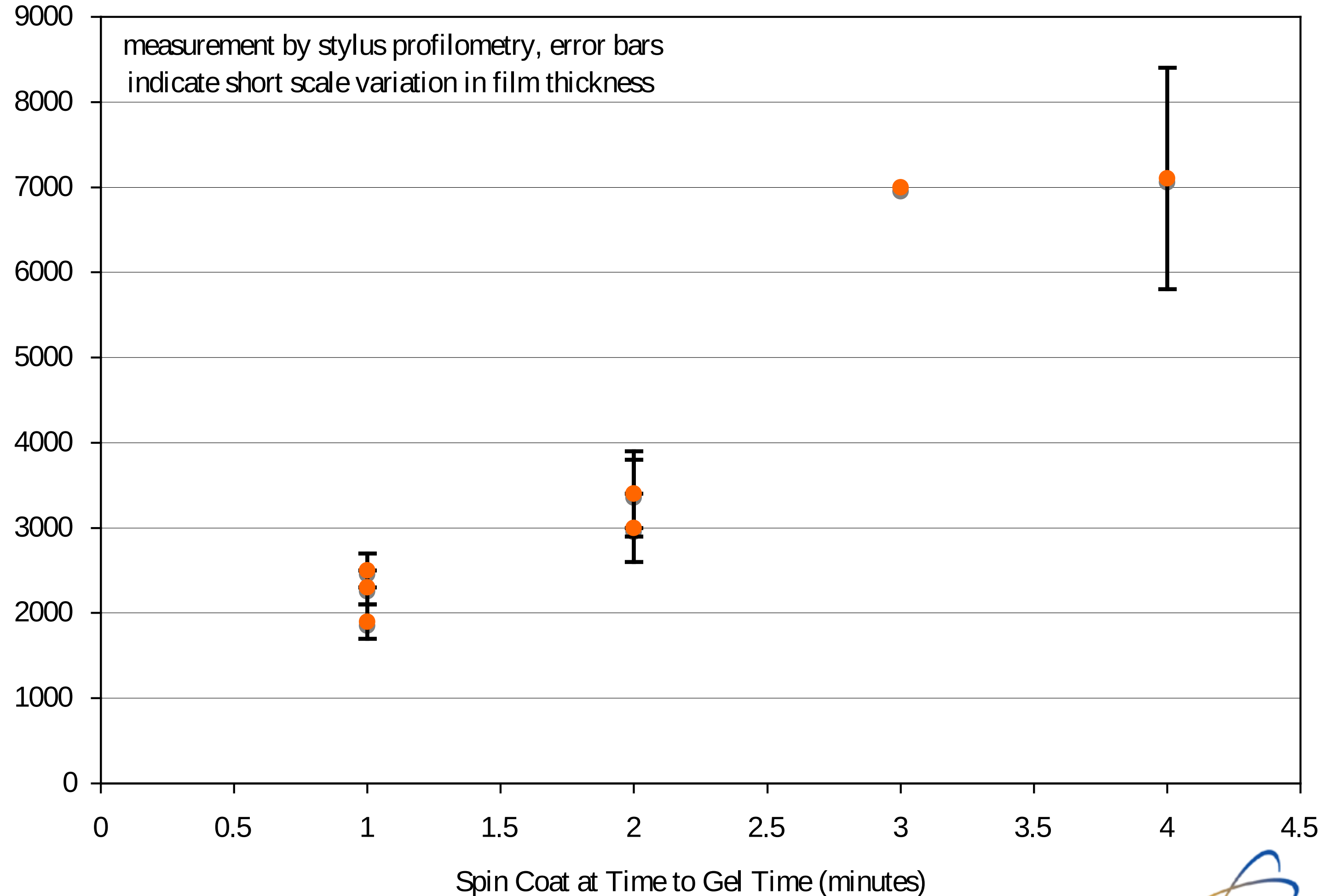


- 2 chemical forms of C – hydrocarbon and some oxy-carbon
- Typical valence band spectra of SiO_2 structure.
- Si in form of SiO_2
- some N present
- atomic concentration %
  - Si 27%
  - O 57%
  - N 1%
  - C 16%

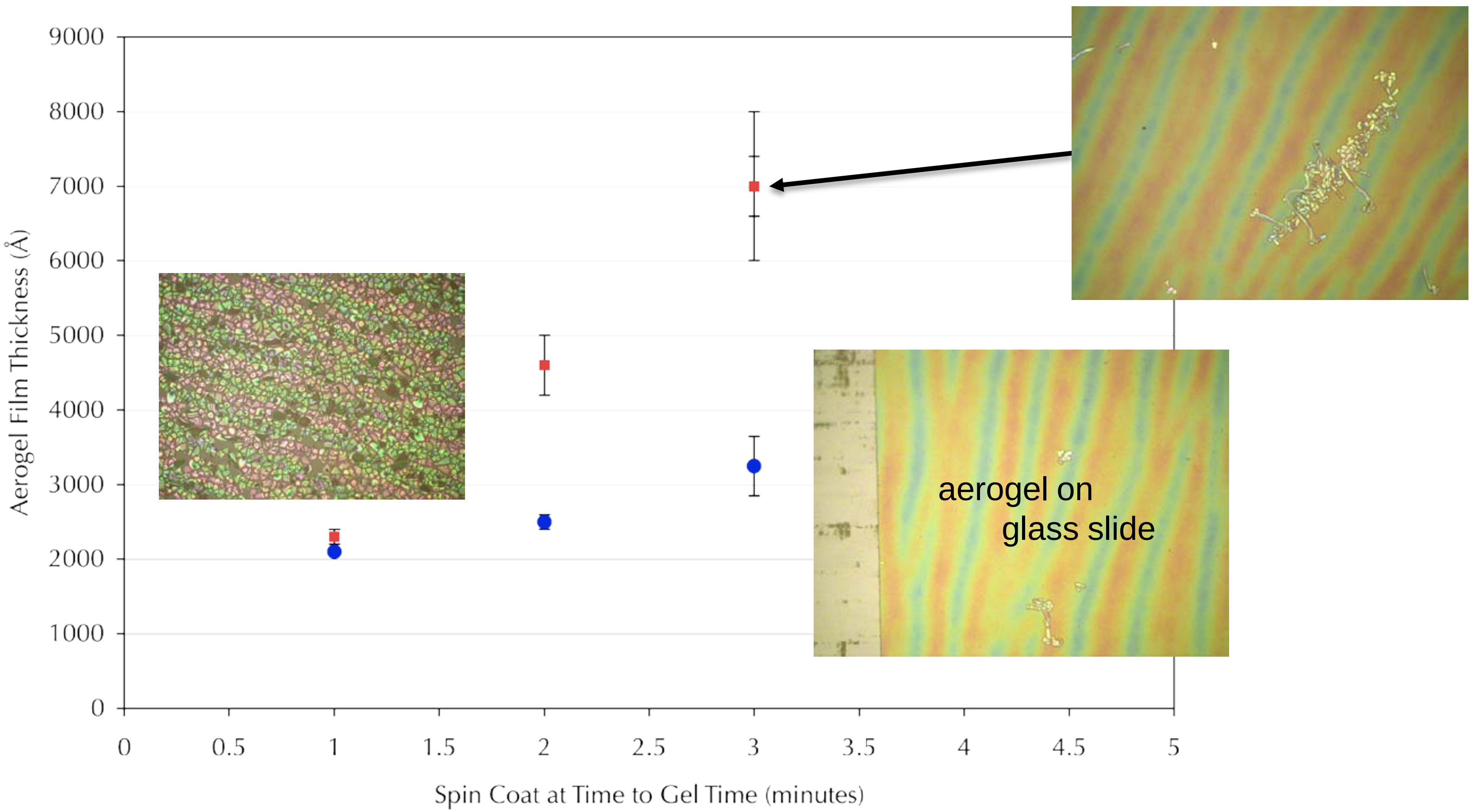
Los Alamos NATIONAL LABORATORY EST. 1943

Investigating how aerogel film thickness corresponds to spin coating at specific gel-times

Aerogel thin films created by spin coating 60 mg/cm^3 alcogel solution onto glass slides with subsequent super-critical treatment to form silica aerogel

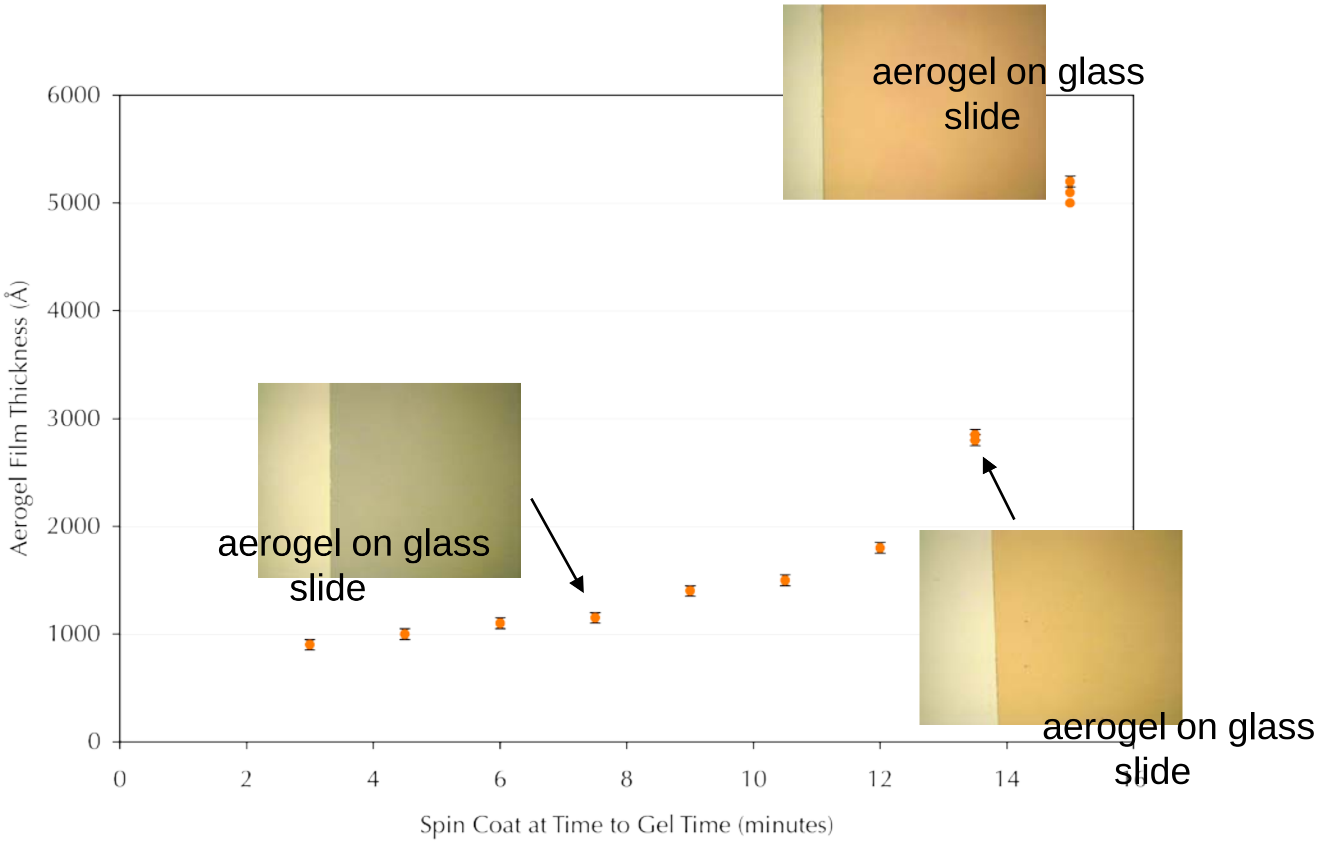


Surface roughness at corresponding film thickness of 60 mg/cm³ aerogel



- Two data sets of 60 mg/cm³ aerogel film. The **blue circle** is higher spin-speed compared to the **red square**.
- Film variations can be as small as 200Å
- Film variations more commonly about 800Å
- In general, film thickness variations are smaller at lower time-to-gel time
- Higher time-to-gel samples (3-4 minutes) tend to have an increased variation in film thickness (0.5 mm)

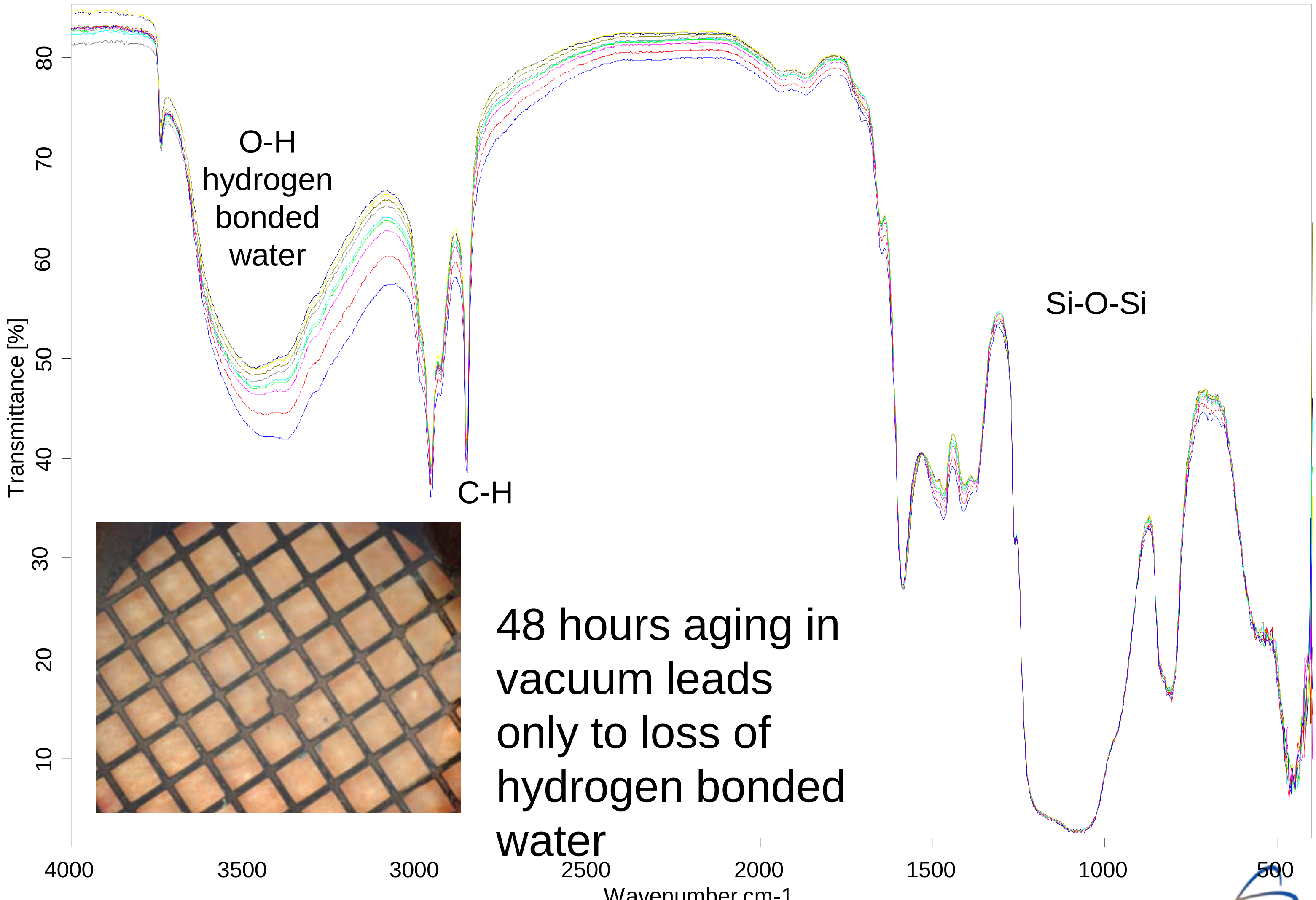
Low density aerogel films: 20 mg/cm^3



Details:

- lower concentration solution (for lower density aerogel) yields smoother films
- films are very smooth and very uniform over large are (color)
- film variation (roughness) for 40 mg/cm^3 aerogel is typically <100Å
- film variation (roughness) for 20 mg/cm^3 aerogel is typically <~50Å
- longer times (after mix - up to about 2/3 gel time) generally yield smoother films

40 mg/cm³ aerogel on 100 mesh Cu grid - FTIR analysis / vacuum stability



48 hours aging in vacuum leads only to loss of hydrogen bonded water

Conclusions

- We are able to produce free-standing low-density (20 mg/cm^3) silica aerogel films with thicknesses of 100nm
- Film thickness increases with gel-time: increase in viscosity
- Film thickness increases with density: increase in material concentration
- Higher spin speeds yields thinner films: greater ability to spread material
- 60 mg/cm^3 films are relatively smooth (~200Å variation):
- 40 mg/cm^3 and 20 mg/cm^3 yield lower variations in film thickness (<100Å and <50Å respectively)
- Smaller variation in thickness as density decreases: lower material content allows better mixing
- At higher gel-times times (>~70% of gel time) the thickness increases rapidly

Two possibilities:

1) At lower times less methanol is retained during spin coating and film ends up being thinner with probably less free volume - can we measure this? At higher times, higher solution viscosity from crosslink reaction causes more methanol to be retained, yielding thicker films and resulting in higher free volume in aerogel.

2) Methanol is retained in the spin coated gel to the same extent for all times and film thickness variation is just due to solution viscosity and surface tension at time of spin coat - resulting in consistent free volume aerogel for all times.