SAND2006-5125C

Using Nanoparticles to Stabilize Thin Polymer Films

The 232nd ACS National Meeting, San Francisco, CA

Division of Polymeric Materials: Science & Engineering, Nanotechnology Applications in Coatings

Sunday, September 10, 2006

Melissa A. Holmes[1], Michael E. Mackay[1] and Rachel K. Giunta[2]

1) Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan

2) Organic Materials Department, Sandia National Laboratories, Albuquerque, New Mexico

National Nuclear Security Administration

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia National Laboratories

Acknowledgements

- **Sandia National Laboratories**
  - Microsystems and Engineering Sciences Applications
  - Center for Integrated Nanotechnologies
  - Laboratory Directed Research and Development
- **Argonne National Laboratory**
  - Intense Pulsed Neutron Source
    - This facility is funded by the U.S. Department of Energy, BES-Materials Science, under contract W-31-109-ENG-38 to the University of Chicago.
- **Michigan State University**

Presentation Outline

- Wetting/dewetting behavior of polymer films
- Addition of nanoparticles to polymer films, and the resulting wetting/dewetting behaviors
- Potential application for this technology – chemical sensors

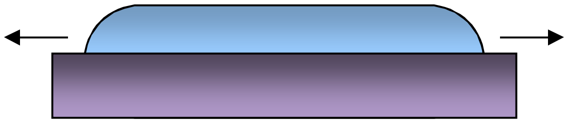
Thin Polymer Films

- Thin polymeric films are used in many new and emerging technologies:
  - Dielectric coatings
  - Fuel cells
  - Nanolithography resist layers
  - Chemical and biological sensors
- Films must be continuous, of uniform thickness and remain stable on a variety of substrates
- Often, however, the substrate is lower in energy than the polymer causing it to dewet under the appropriate conditions.

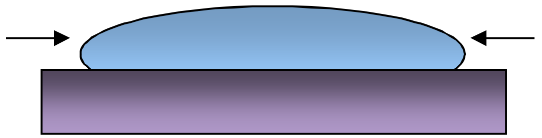
The Problem of Dewetting

- **When a liquid is spread out over a solid, the stability of the system depends upon the surface energy of the substrate (γ_S), the surface tension of the liquid (γ_L) and the interfacial energy between the two (γ_{LS})**
- **The spreading parameter (*S*) dictates if a liquid will wet the surface or not**

$$S = \gamma_S - \gamma_L - \gamma_{LS}$$



$S > 0$, wetting



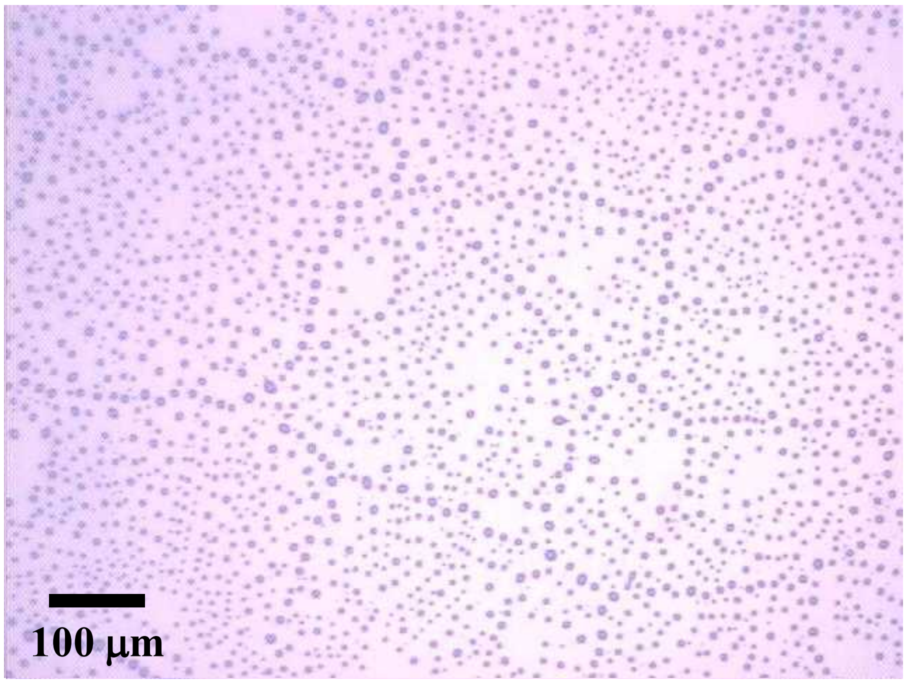
$S < 0$, dewetting

MICHIGAN STATE UNIVERSITY

Sandia National Laboratories

Dewetting of Polymer Films

Pure Polystyrene film (33 nm) annealed under a saturated toluene atmosphere



50 minutes

- **Glass Transition Temperature (T_g)**
  - Above this temperature, polymer is mobile
  - Induce dewetting
    - Heat the sample
    - Expose the sample to a plasticizing agent
- **Types of dewetting**
  - Spinodal
  - Nucleation and hole growth

Film Equilibrium

- **Bulk experiments were performed to determine the equilibrium concentration of solvent absorbed into the polymer**
  - **Polystyrene was weighed out and placed in a saturated toluene atmosphere**
  - **Sample was reweighed until there was no change to ensure equilibrium – one week**
  - **Final concentration of the sample was ~600 mg PS/ml solution**
- **For a thin film, the equilibration time is expected to be much shorter:**

$$\frac{D\tau}{\Delta^2} > 1$$

$D \sim 10^{-6}$ **cm²/s**, $\Delta = 30$ **nm →** $\tau \sim 10$ **μs**

•Bird, R. B.; Stewart, W. E.; Lightfoot, E. N., *Transport Phenomena*. J. Wiley: New York, 1960.

•Rauch, J.; Kohler, W., Collective and thermal diffusion in dilute, semidilute, and concentrated solutions of polystyrene in toluene. *Journal of Chemical Physics* **2003,** 119, (22), 11977-11988.

Film Viscosity

- **Using the Martin Equation we can estimate the viscosity of the film during annealing which will relate to the rate of dewetting:**

$$\frac{\eta_{sp}}{c[\eta]} = e^{k'[\eta]c}$$

η_0 **= 0.56 cP**

c **= 600 mg/ml**

$[\eta] \sim$ **38 ml/g**

$k' \sim$ **0.33**

→

η **= 23 Pa-s**

~ pure PS at 250 °C

•Gandhi, K. S.; Williams, M. C., Solvent Effects on Viscosity of Moderately Concentrated Polymer Solutions. *Journal of Polymer Science Part C-Polymer Symposium* **1971**, (35), 211.

•McCabe, W.; Smith, J.; Harriott, P., *Unit operations of chemical engineering*. McGraw-Hill: New York, 1993.

•Brandrup, J.; Immergut, E. H., *Polymer Handbook*. John Wiley & Sons: New York, 1989.

Effective Glass Transition Temperature

- **The Fox Equation can be used to determine the effective T_g of the film during annealing:**

$$\frac{1}{T_g} = \frac{w}{T_g^P} + \frac{1-w}{T_g^S}$$

Mass fraction of polymer, w = 0.60, T_g^P = 379 K, T_g^S = 117 K

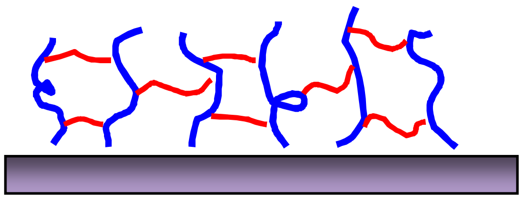
↳ **T_g = 200 K or -73 °C**

- **Therefore, rapid dewetting is expected at room temperature**

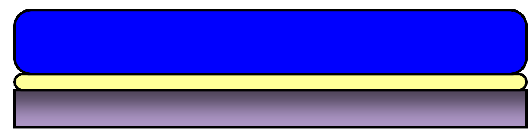
•Rauch, J.; Kohler, W., Collective and thermal diffusion in dilute, semidilute, and concentrated solutions of polystyrene in toluene. *Journal of Chemical Physics* **2003,** 119, (22), 11977-11988.

•Wiedersich, J.; Surovtsev, N. V.; Rossler, E., A comprehensive light scattering study of the glass former toluene. *Journal of Chemical Physics* **2000,** 113, (3), 1143-1153.

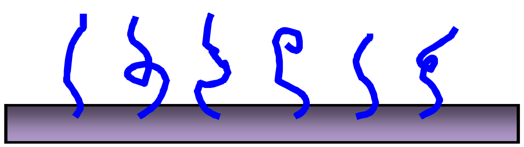
Ways to Stop Dewetting



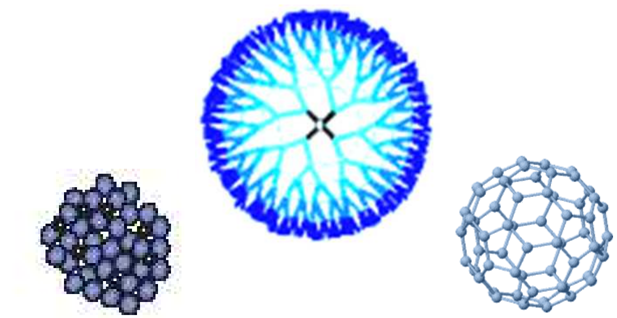
Crosslinking ✗



Surface Treatment ✗



Grafting ✗



Nanoparticles ✓

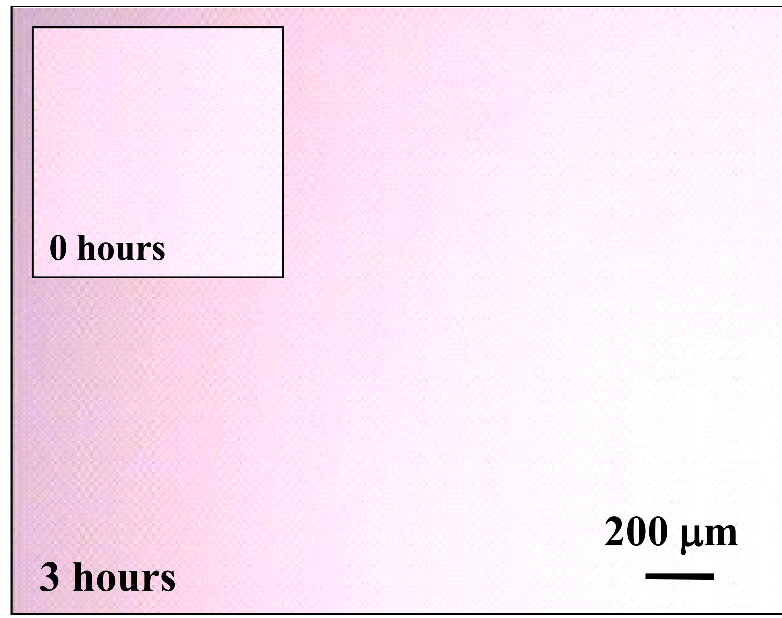
MICHIGAN STATE UNIVERSITY

Sandia National Laboratories

Addition of Fullerenes

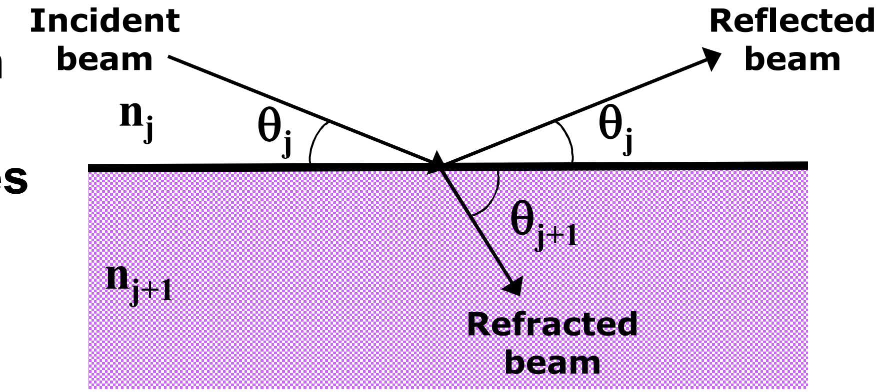
- A solution of PS with 3 wt% C_{60} was spin-coated on a piranha-cleaned wafer
  - Film thickness = 33 nm
- Sample was annealed for 3 hours under a saturated toluene atmosphere
  - No dewetting seen!
  - The fullerenes appear to eliminate dewetting just as they do for high temperature annealing
- Previous studies suggest that the elimination of dewetting is due to the location of the nanoparticles in the film
  - Neutron reflectivity

PS + 3 wt% C_{60} film (33 nm) annealed under a saturated toluene atmosphere



Neutron Reflection

- Neutron reflection is a technique that can be used to determine the depth-composition profile of thin planar samples
  - A beam of neutrons strike the sample surface at a glancing angle (θ)
  - The beam is either reflected or refracted
  - The angle of the refracted beam is dependent on the neutron refractive index of the material
- The neutron refractive index for a material is dependent on its scattering length density (ρ_z)
- By using materials with sufficient contrast in their scattering length densities, it is possible to determine their location in the sample

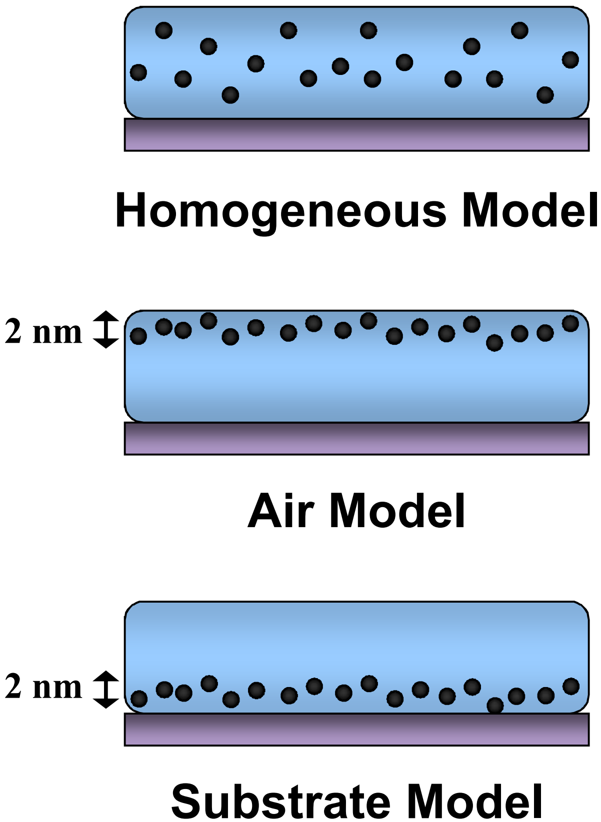


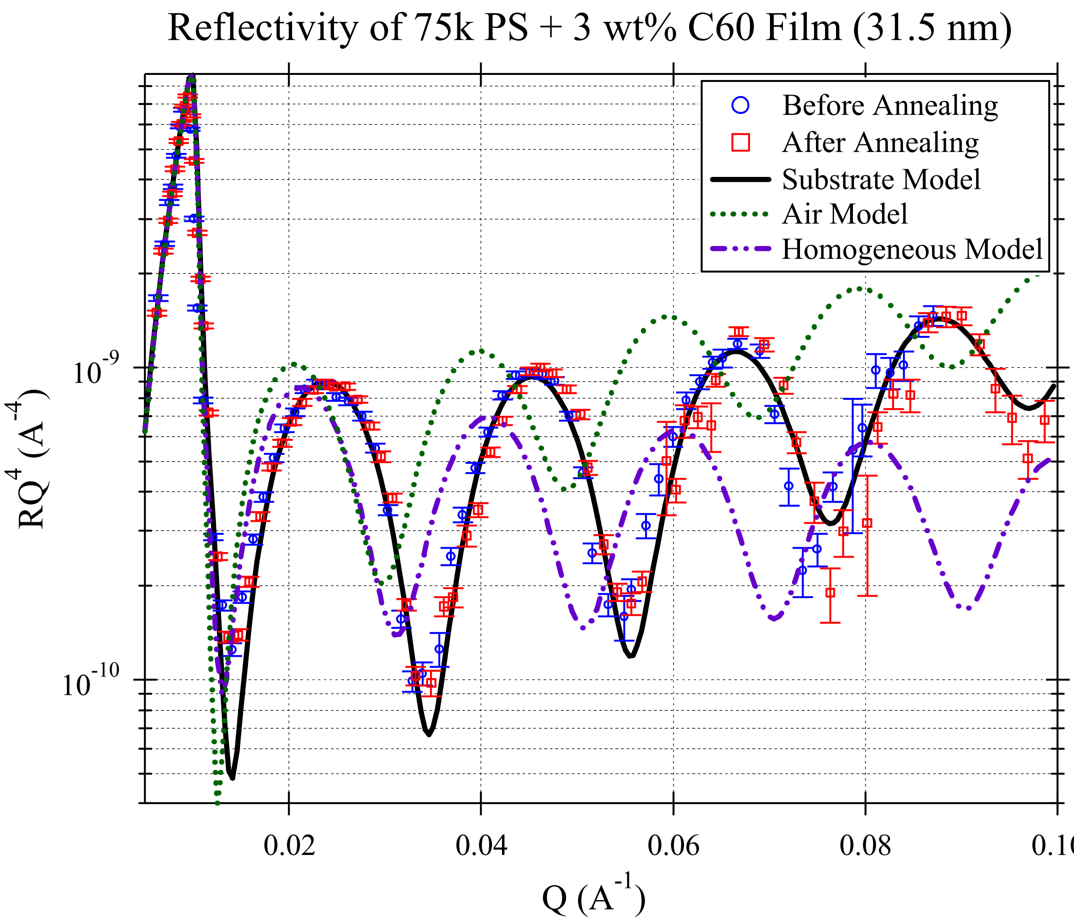
Snell's law: $n_j \cos\theta_j = n_{j+1} \cos\theta_{j+1}$

Scattering length densities for materials used in this work

Material	ρ_z (Å^{-2}) ×10^6
Silicon	2.07
C_{60}	5.73
PS	1.41
dPS	6.47

Reflectivity Data





Sample was annealed 3 hours under a saturated toluene atmosphere

Modeling Reflectivity Data

Model	Layer	Thickness (Å)	SLD (10^6 Å^{-2})
Substrate	1	295	1.41
	2	20	2.66
	wafer	-	2.07
Air	1	20	2.66
	2	295	1.41
	wafer	-	2.07
Homogeneous	1	315	1.49
	wafer	-	2.07

- From reflectivity model:

$$\phi_{C60,L} = \frac{\rho_L - \rho_{PS}}{\rho_{C60} - \rho_{PS}}$$

$$\phi_{C60,L} \sim 0.29$$

- 3 wt% → $\phi_{C60} = 0.018$
- From mass balance:

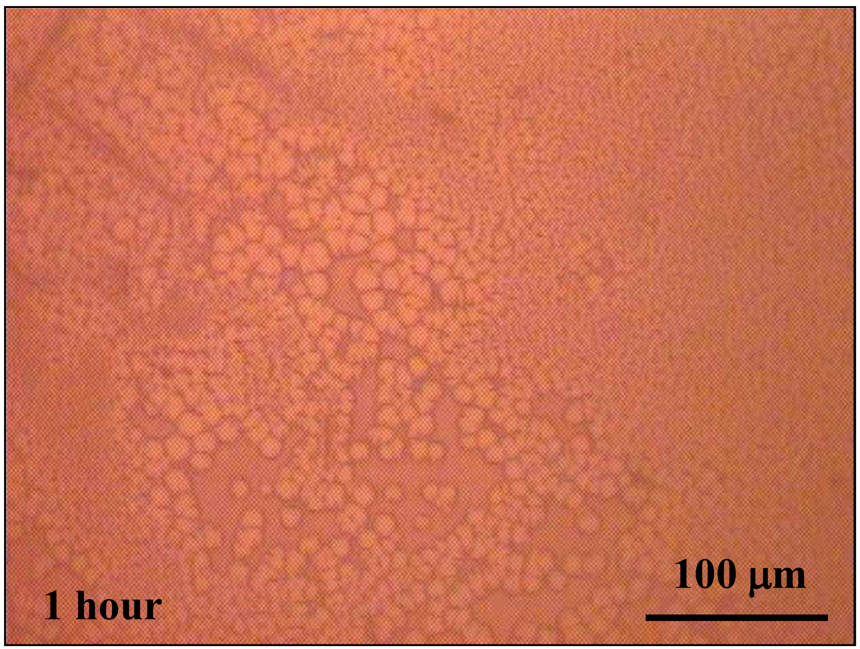
$$\phi_{C60,L} = \frac{\Delta}{\delta} \times \phi_{C60}$$

$$\phi_{C60,L} = 0.28$$

Good agreement!

Fullerenes First

PS film (30 nm) floated onto a fullerene layer and annealed under a saturated toluene atmosphere



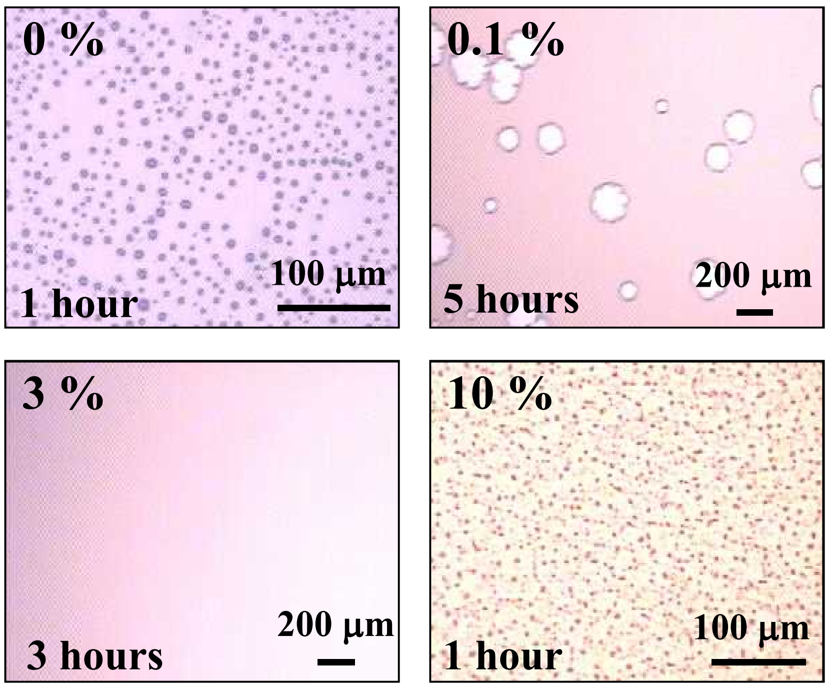
- A film was placed onto a fullerene layer and then solvent annealed
  - Dewetting of the film still occurred!
- Therefore can not attribute inhibition of dewetting solely to nanoroughness or a change in surface energy

How Dewetting is Inhibited

- From reflectivity, we know the fullerene-enriched layer at the substrate is ~2 nm thick, which is 2-3 fullerenes high
  - Layer forms during the spin-coating process due to phase separation from the poor solubility of fullerenes in the solvent
- The fullerenes create a gel-like network 2 nm thick that shields the adverse van der Waals forces emanating from the substrate

Concentration Dependence

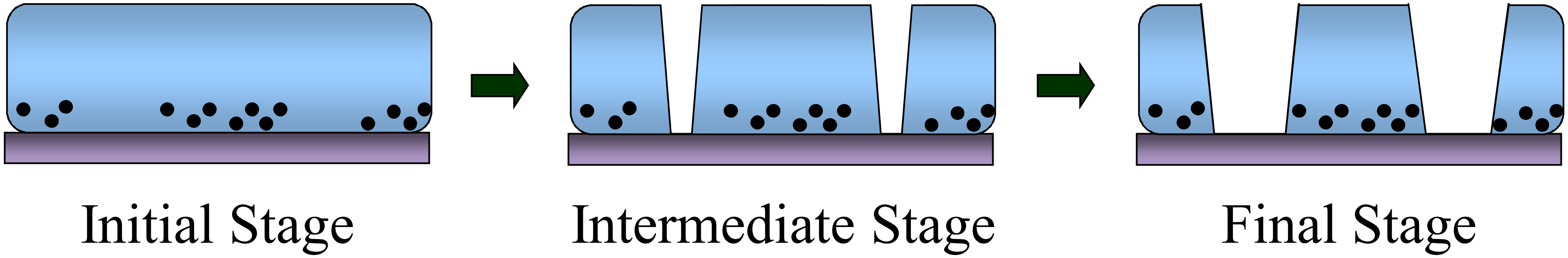
PS films with varying C_{60} concentrations (~30 nm) annealed under a saturated toluene atmosphere



- **The concentration of C_{60} dictates the ability of the film to resist dewetting**
- **There is an optimum concentration needed to fully retard dewetting**
  - **Below this concentration, holes form but eventually stop growing**
  - **Above this concentration, dewetting is seen again**

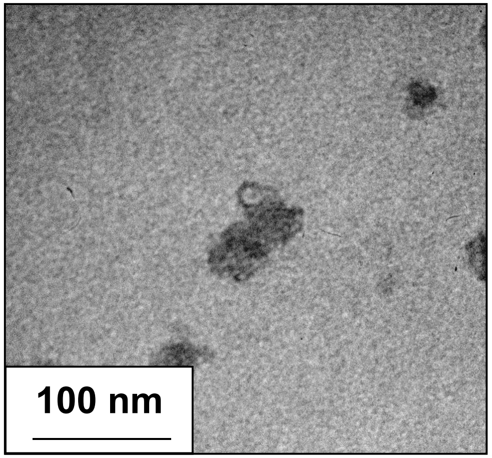
0.1 wt% C_{60} in 30 nm PS film

- **Partial dewetting occurs when the concentration of C_{60} is too low**
  - **Holes form where there are no or few nanoparticles**
  - **The holes grow until they reach an area where there are sufficient nanoparticles to inhibit dewetting**

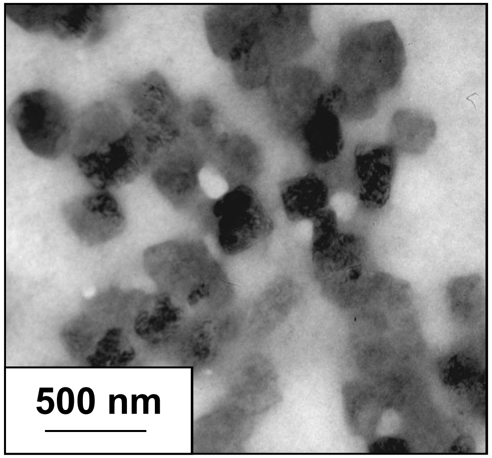


TEM for Comparison of 10 wt% Samples

- TEM was used to check for agglomeration of the fullerenes
  - Very few agglomerates were seen in the 3 wt% film
    - All agglomerates were <100 nm in size
  - Large clusters of agglomerates were seen throughout the 10 wt% film
    - Agglomerates were on the order of 200-300 nm in size, with micron sized clusters
- Particles of this size act as nucleating sites as seen in colloidal-sized particle systems



3 wt% C_{60}



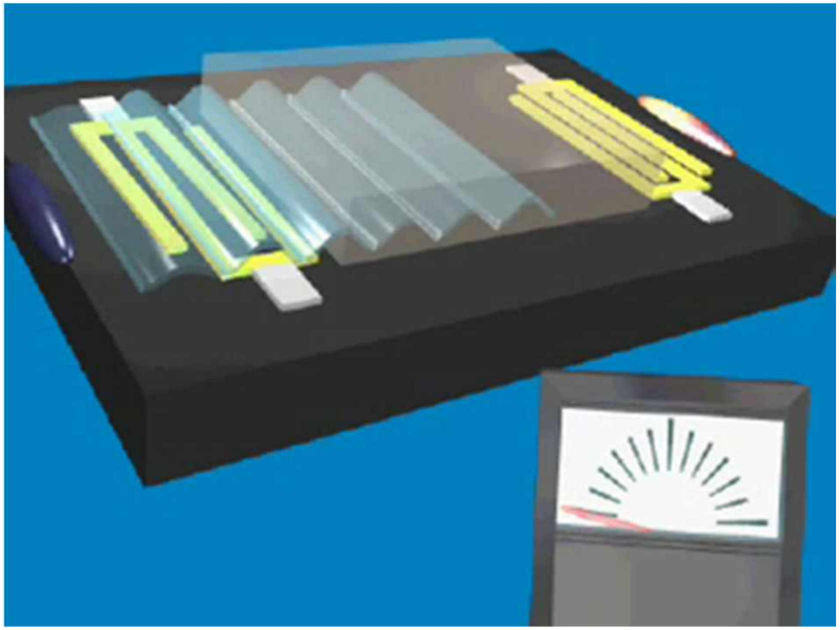
10 wt% C_{60}

MICHIGAN STATE UNIVERSITY

Sandia National Laboratories

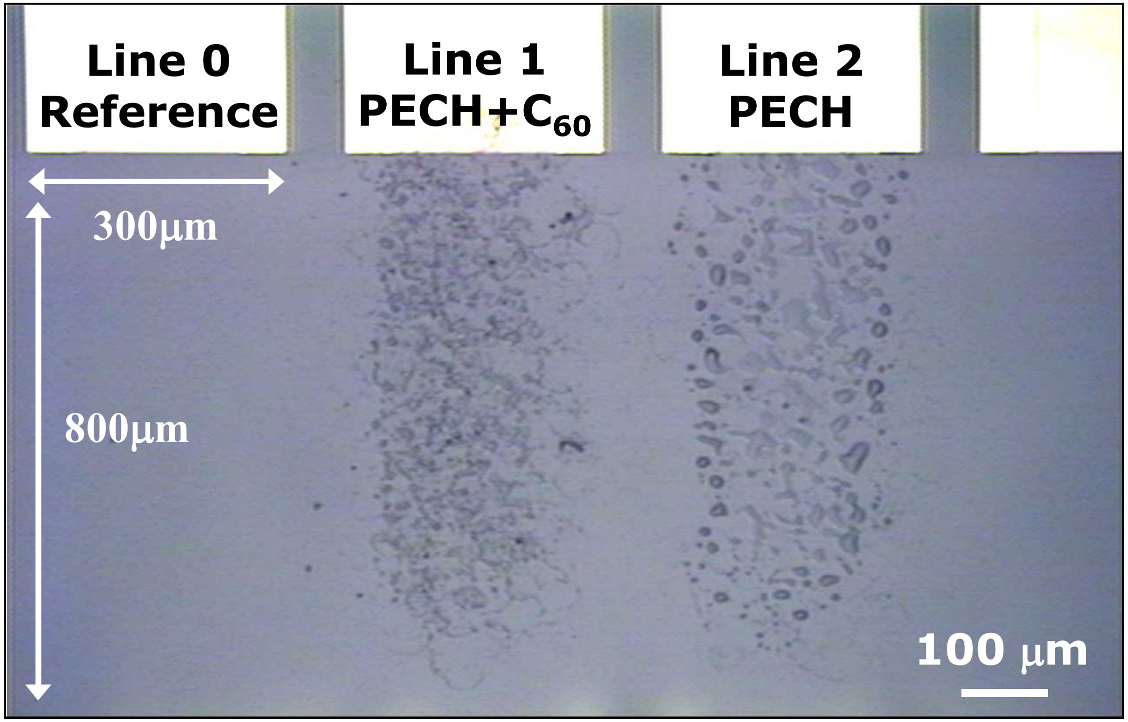
Application: Sandia's μChemLab – Detection Stage

- Surface Acoustic Wave (SAW) Sensor
  - Quartz substrate
  - IDTs
  - Polymer film
- Analyte absorbed into film
  - Small increase in mass results in a change in the velocity of the SAW
- Difficulty consistently depositing a stable polymer film on sensor surface
  - Addition of fullerenes gives a more stable response to challenges



Live SAW Sensor

- A live SAW sensor was sprayed with PECH (polyepichlorohydrin) and PECH + C_{60}
- The sensor was then challenged with various solvent vapors to test its response

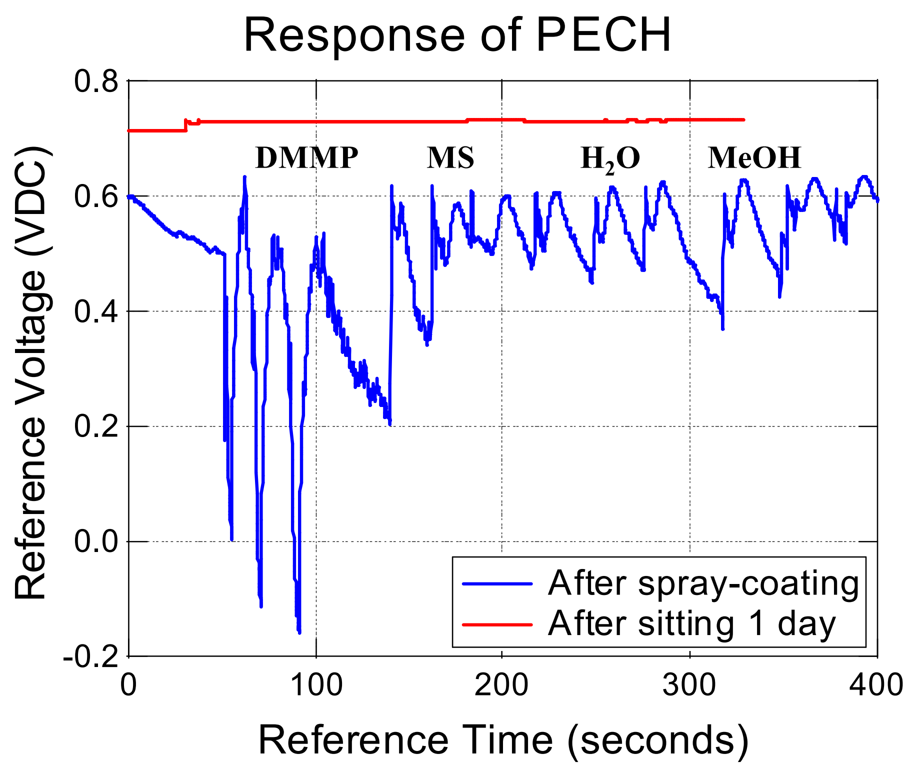


MICHIGAN STATE UNIVERSITY

Sandia National Laboratories

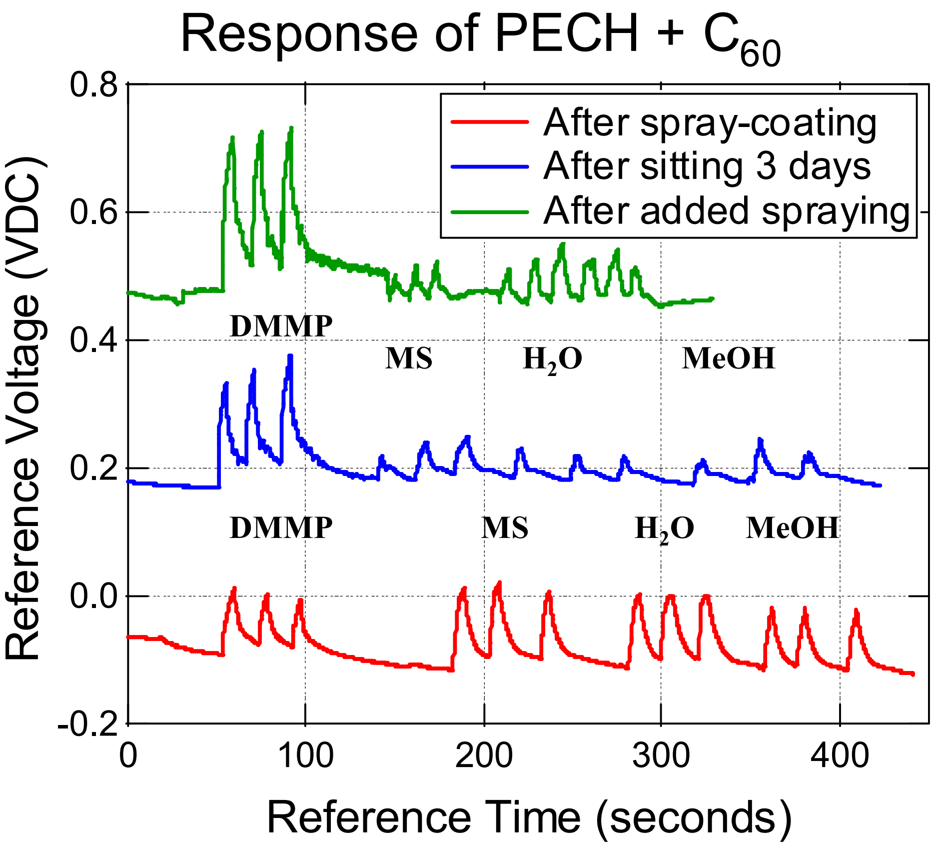
Sensor Response: PECH

- **The sensor response of pure PECH upon challenging is very erratic with an unstable baseline**
  - **Possible dewetting**
- **After one day, the sensor was challenged again giving no response**
  - **Sensor inoperable**



Sensor Response: PECH + C_{60}

- **Upon addition of fullerenes, the sensor gives a stable response with a stable baseline when challenged after spray-coating**
- **After several days and even the addition of more polymer, the sensor response remains stable**



MICHIGAN STATE UNIVERSITY

Sandia National Laboratories

Conclusion

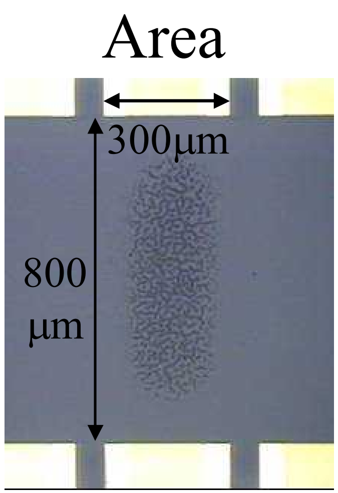
- Thin polystyrene films will dewet from a silicon substrate upon exposure to a saturated toluene atmosphere
- The addition of fullerenes to the polymer solution before spin-coating can inhibit dewetting of the film
- The inhibition of dewetting is caused by the fullerenes forming a gel-like layer at the substrate
- This technique is very appealing due to the fact that it does not alter the properties of the polymer or the substrate
- This technique can be used in sensor applications to manufacture more robust and reliable sensors.

Thank you!

Questions?

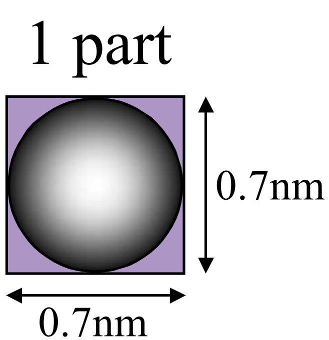
Why Fullerenes?

- **Cheap and readily available!**



$$Area = 300\,\mu m \times 800\,\mu m = 2.4 \times 10^{11}\, nm^2$$

$$\frac{1\,part}{(0.7\,nm)^2} \times \frac{3 \times 10^{-22}\, g}{1\,part} = 6.1 \times 10^{-22}\, g/nm^2$$



$$\left(2.4 \times 10^{11}\, nm^2\right) \times \left(6.1 \times 10^{-22}\, g/nm^2\right) = 1.5 \times 10^{-10}\, g$$

$$\left(1.5 \times 10^{-10}\, g\right) \times \left(\$250/g\right) = \text{n\$37.5/sensor}$$

Neutron Reflection

- By using materials with sufficient contrast in their scattering length densities, it is possible to determine their location in the sample

$$\rho_z = \frac{\left(\sum b_i\right) D N_A}{M_m}$$

$$n_m = 1 - \frac{\lambda \rho_z}{2\pi}$$

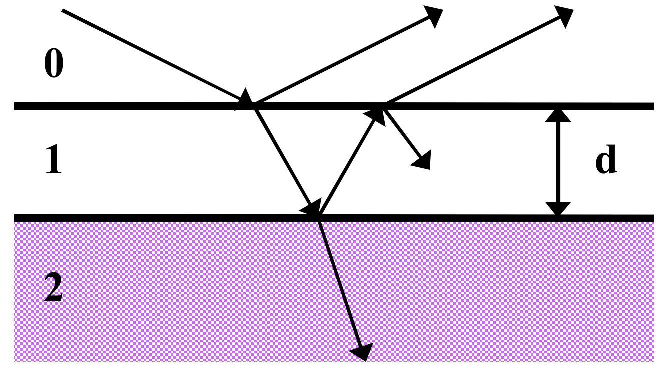
- The specular reflection (R) is measured as a function of the neutron wave vector transfer (Q)

$$Q = \frac{4\pi}{\lambda}\sin\theta$$

$$R(Q) = \frac{I_{ref}(Q)}{I_{inc}(Q)}$$

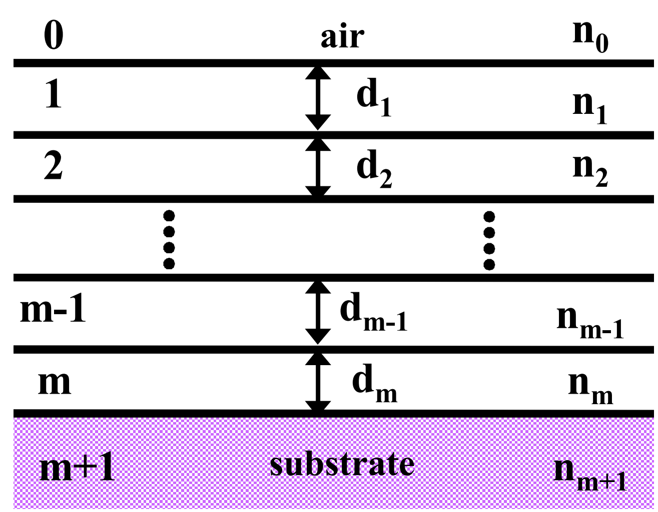
Reflectivity

- The reflectivity data can then be modeled using layers of different scattering length densities to determine the depth-composition profile



$$r_{m,m+1} = \frac{n_m \sin\theta_m - n_{m+1}\sin\theta_{m+1}}{n_m \sin\theta_m + n_{m+1}\sin\theta_{m+1}}$$

$$R = r_{m,m+1}^2$$

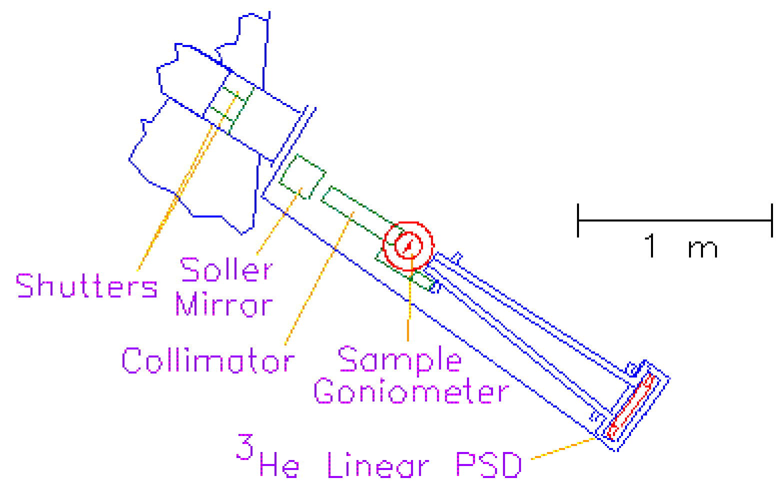


MICHIGAN STATE UNIVERSITY

Sandia National Laboratories

POSY2

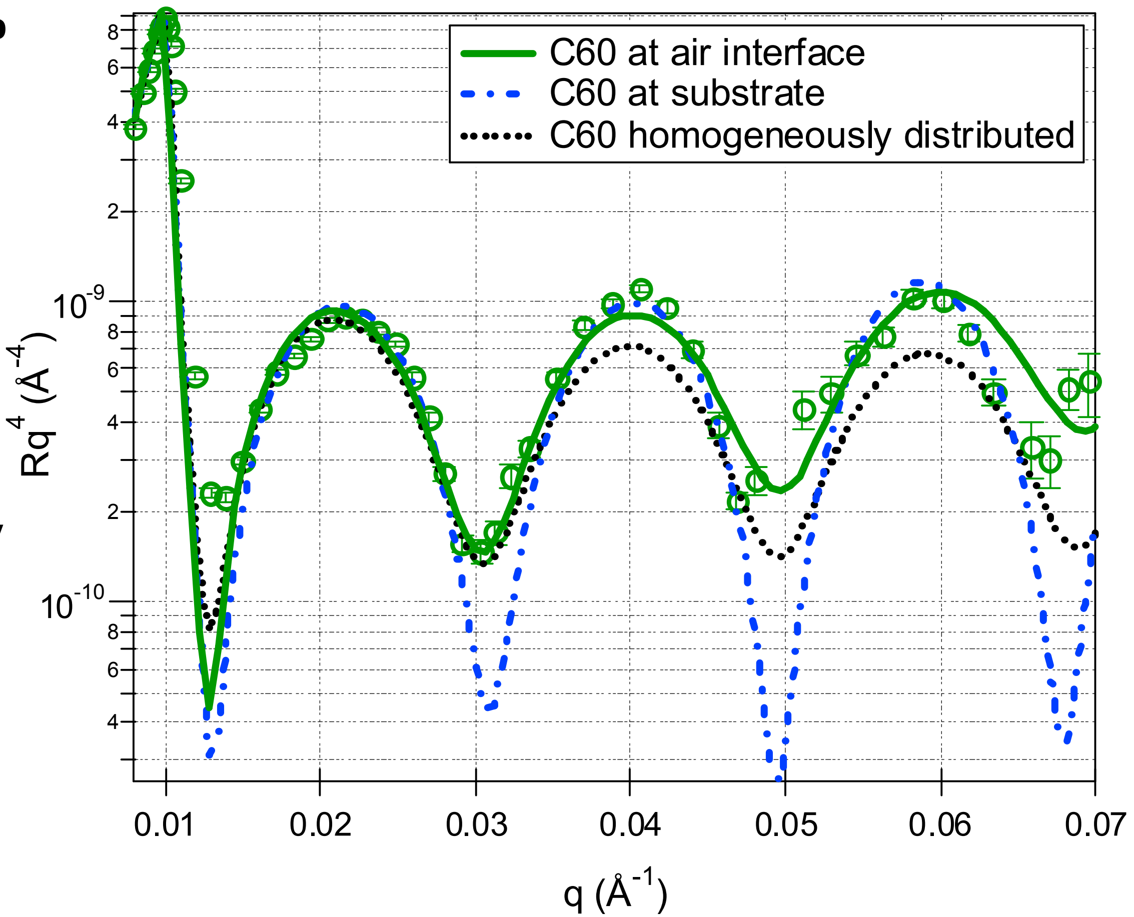
- **The primary pulsed beam contains all wavelengths in the spectrum moderated to 20 K by a solid methane moderator. The intensity reflected at one angle *q* is measured as a function of the wavelength. The reflectivity is calculated by normalizing the intensities reflected to those of the direct beam. This measurements covers a range of *q*'s defined by the largest and the shortest wavelengths available. To extend the range of *q* measurements are taken at different angles. Reflectivity curves taken at different angles are spliced together by fitting the data in the partially overlapping *q* ranges. The data are put on an absolute basis by assuming that at the lowest *q* part of the *q* range covers the region of total reflection (*R*=1). The procedure assumes that the resolution function Δ*q*/*q* is constant.**



Beam Size	Neutrons/pulse	Δq/q	θ range	λ range
5×0.3 cm	100	3-5%	0-3º	1-16 Å

Reflectivity of "Flipped" Films

- **A polystyrene with 3 wt% fullerenes was spin-coated onto freshly cleaved mica and "flipped" onto a Sigmacote silanized wafer**
  - **Expect fullerene enriched layer to initially be at air interface**
- **Was not able to perform reflectivity on annealed film because dewetting occurred!**



MICHIGAN STATE UNIVERSITY

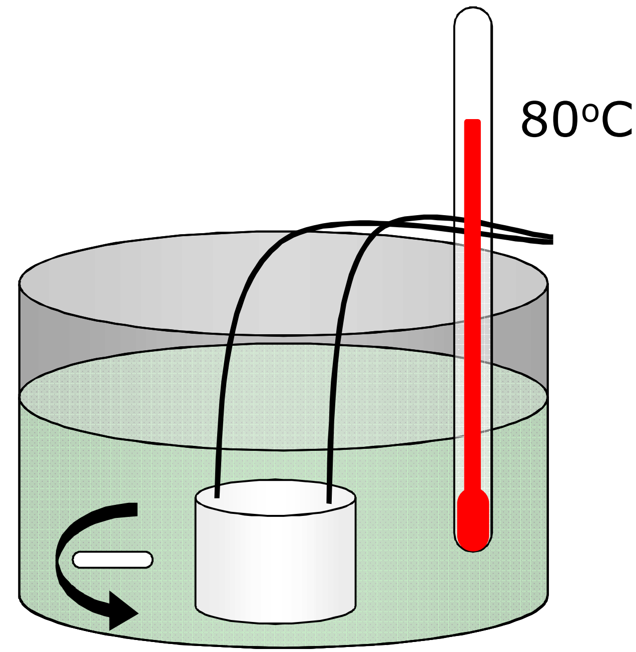
Sandia National Laboratories

Piranha Cleaning

- **Wafers are placed in a Teflon holder and placed in a beaker with 70% H_2SO_4 and 30% H_2O_2 by volume**
- **The solution is stirred continuously and kept at 80°C for 1 hour**

$$H_2SO_4 + H_2O_2 \Rightarrow H_2SO_5 + H_2O$$

- **The piranha oxidizes the organic contaminants making them soluble in the solution so they may be washed away**
- **The wafers are then rinsed in filtered DI water and used immediately**

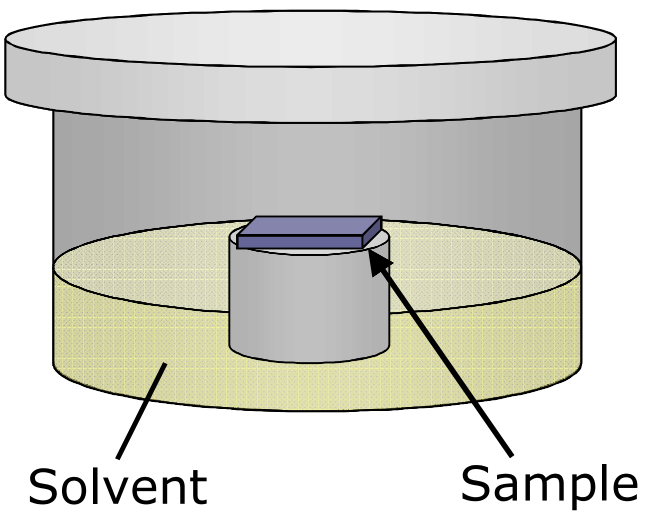


$$\gamma_S^d \approx 34.8\frac{mN}{m};\gamma_S^p \approx 35.8\frac{mN}{m}$$

$$\Rightarrow \gamma_S \approx 70.6\frac{mN}{m}$$

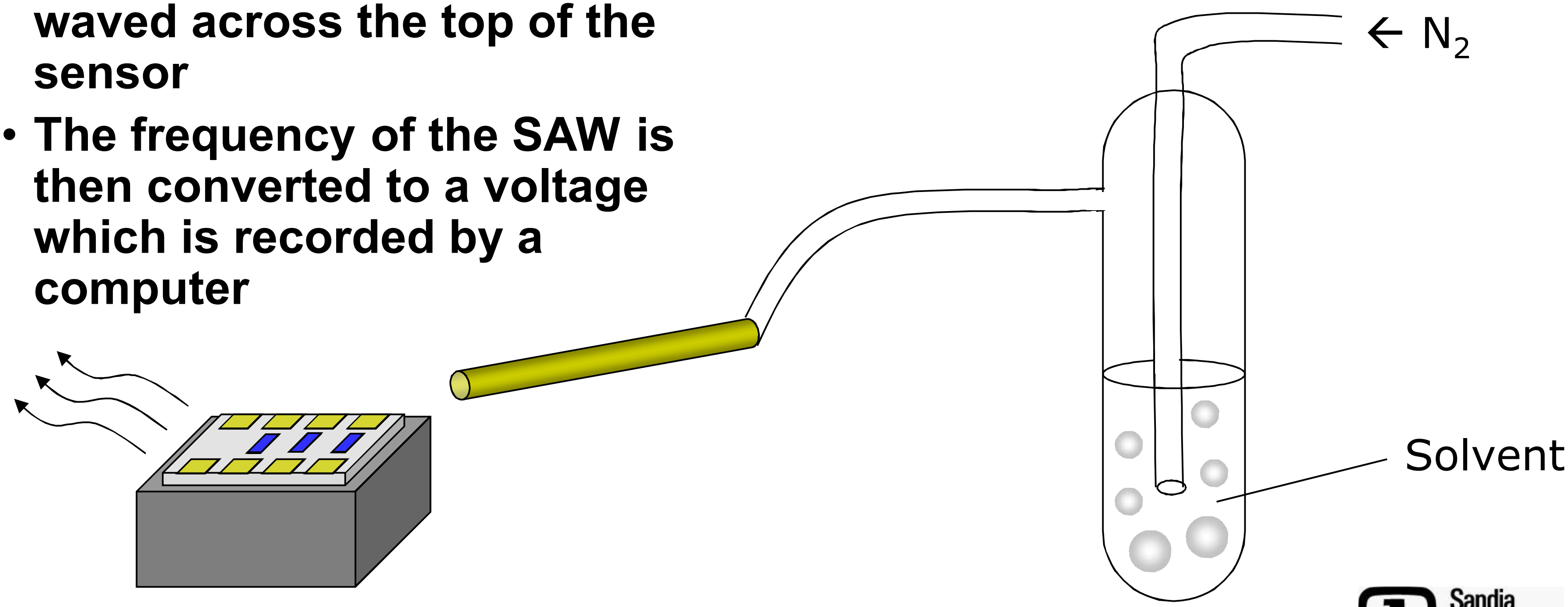
Solvent Annealing

- Sample is suspended above the solvent in a tightly sealed container
- Solvent and its vapor reach equilibrium and also the solvent is absorbed into the film reaching equilibrium



Challenging the Sensor

- Nitrogen is fed to a bubbler which is filled with the solvent
- It bubbles through and creates a saturated vapor stream which is fed through a nozzle and waved across the top of the sensor
- The frequency of the SAW is then converted to a voltage which is recorded by a computer

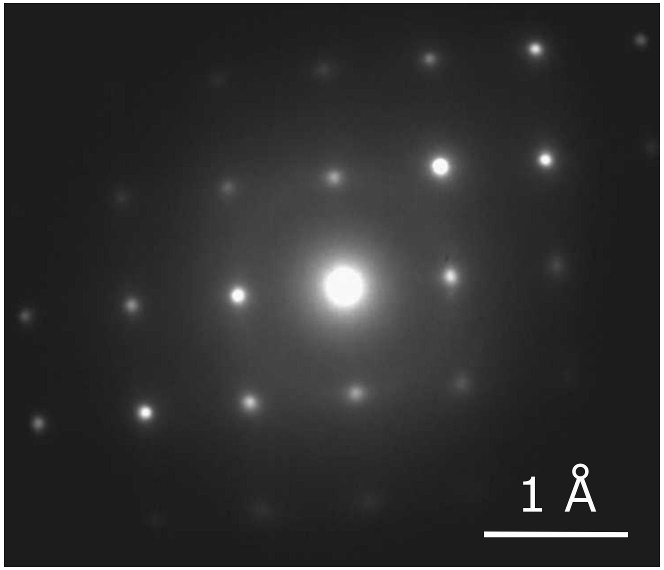


MICHIGAN STATE UNIVERSITY

Sandia National Laboratories

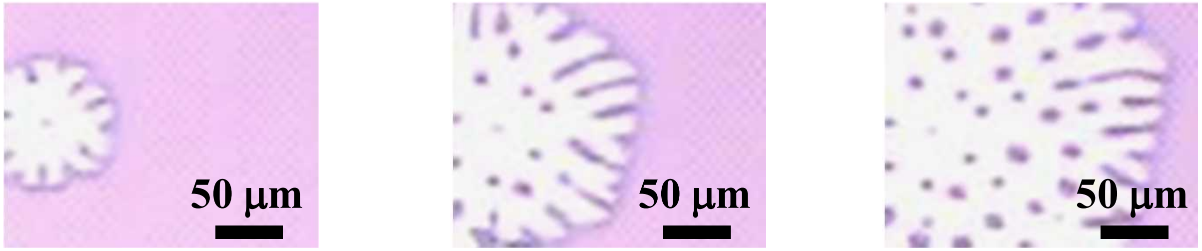
TEM Diffraction

- Diffraction was done on a fullerene agglomeration
- Diffraction pattern shows crystalline structure of the fullerenes
- More experiments would need to be done tilting the sample in different orientations to determine the exact structure



Fingering Instability

- Similar to patterns seen in Hele-Shaw flow where a lower viscosity fluid is forced into a region of higher viscosity fluid
- Fingers form and eventually break off into droplets through Rayleigh instabilities
- Other explanation is from dewetting of water on mica
  - due to viscosity the water collects in the rim at a thickness higher than the equilibrium thickness which is sensitive to longitudinal periodic fluctuations leading to finger creation



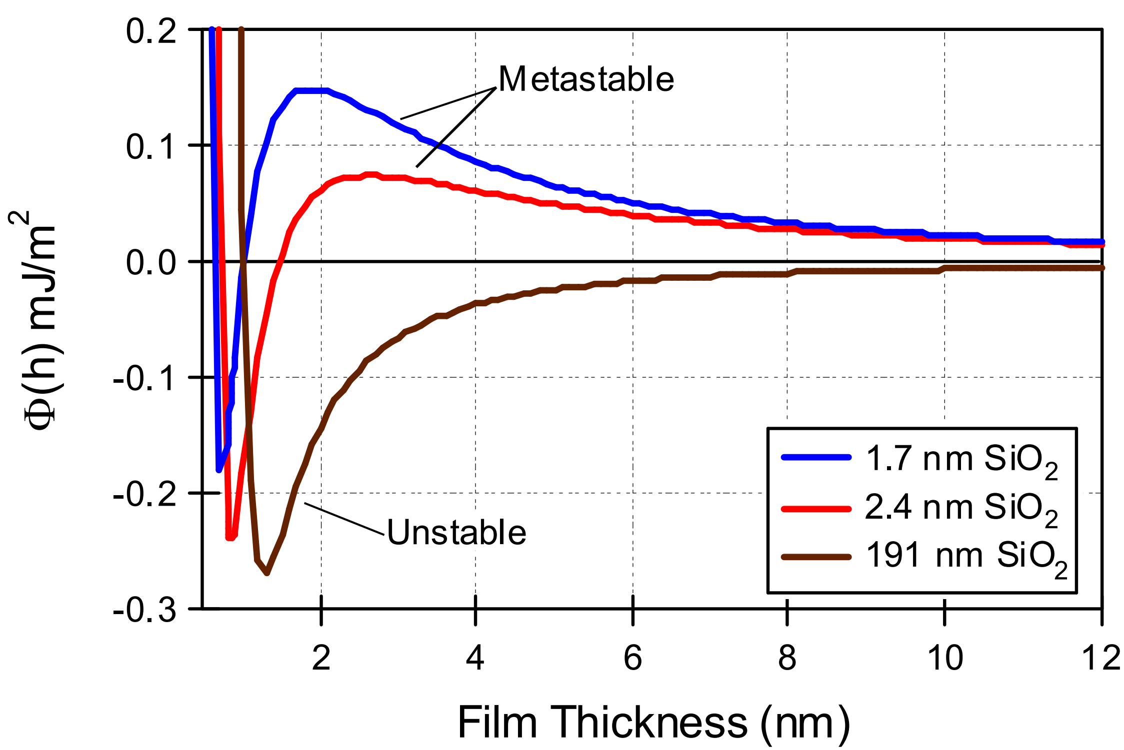
10 minutes 15 minutes 20 minutes

Interfacial Potential

$$\phi_{vdW}(h) = \frac{c}{h^8} - \frac{A_{SiO}}{12\pi h^2} + \frac{A_{SiO} - A_{Si}}{12\pi (h+d)^2}$$

$A_{SiO} = 1.8(3)E^{-20}$ J

$A_{Si} = -2.2(5)E^{-20}$ J

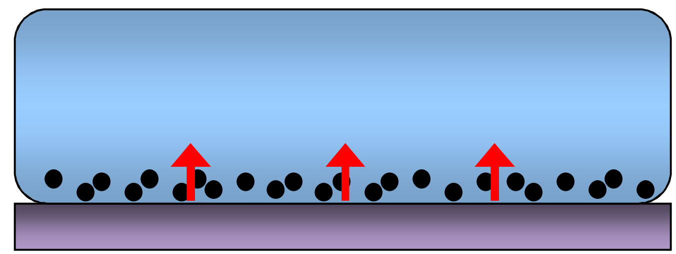


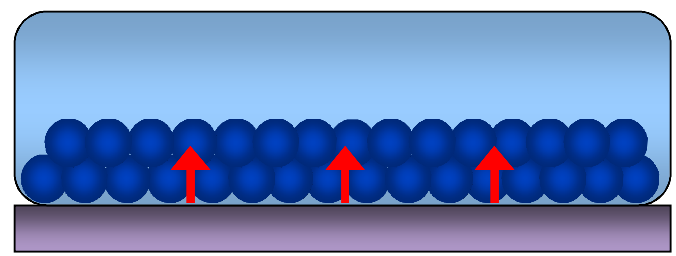
MICHIGAN STATE UNIVERSITY

Sandia National Laboratories

Surface Energy: Fullerenes vs. PSNPs

- **Stronger forces due to the lower surface energy of the substrate**
  - **2 nm fullerene layer not thick enough to retard forces**
  - **PSNPs are larger in diameter and it is possible to have more than a monolayer at the substrate**





MICHIGAN STATE UNIVERSITY

Sandia National Laboratories