NIST CENTENNIAL 1901-2001

High-throughput Approach for Polymer Thin Film Modulus Measurement

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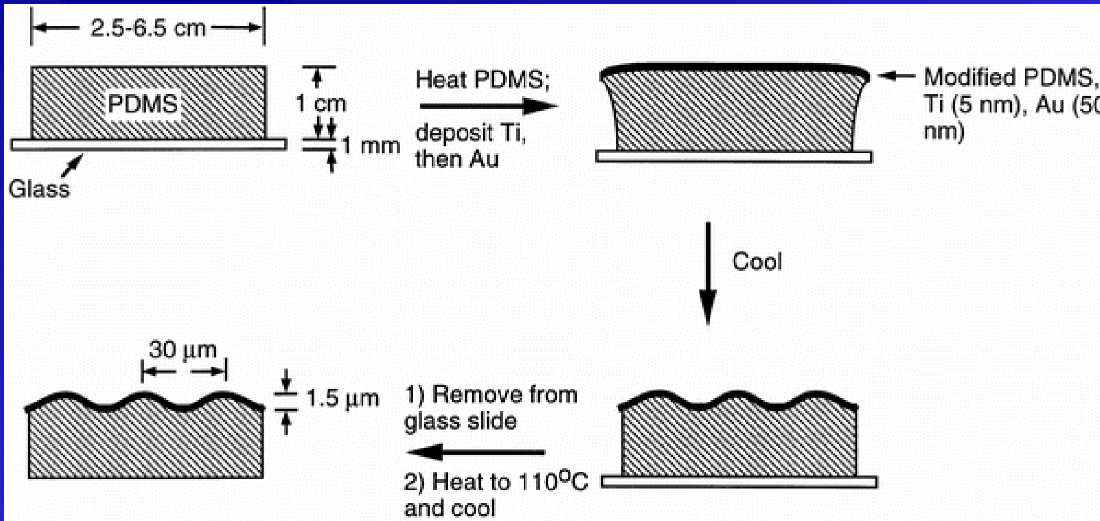
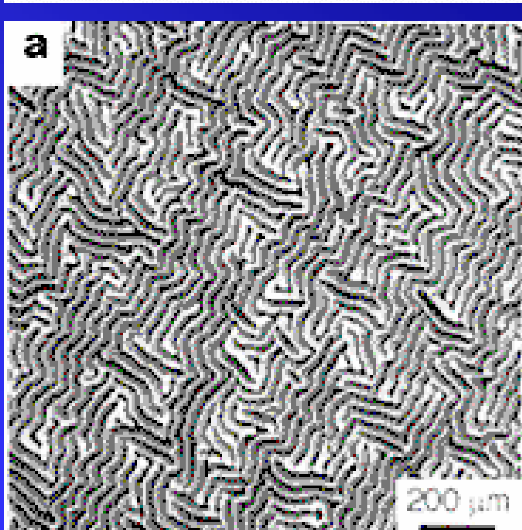
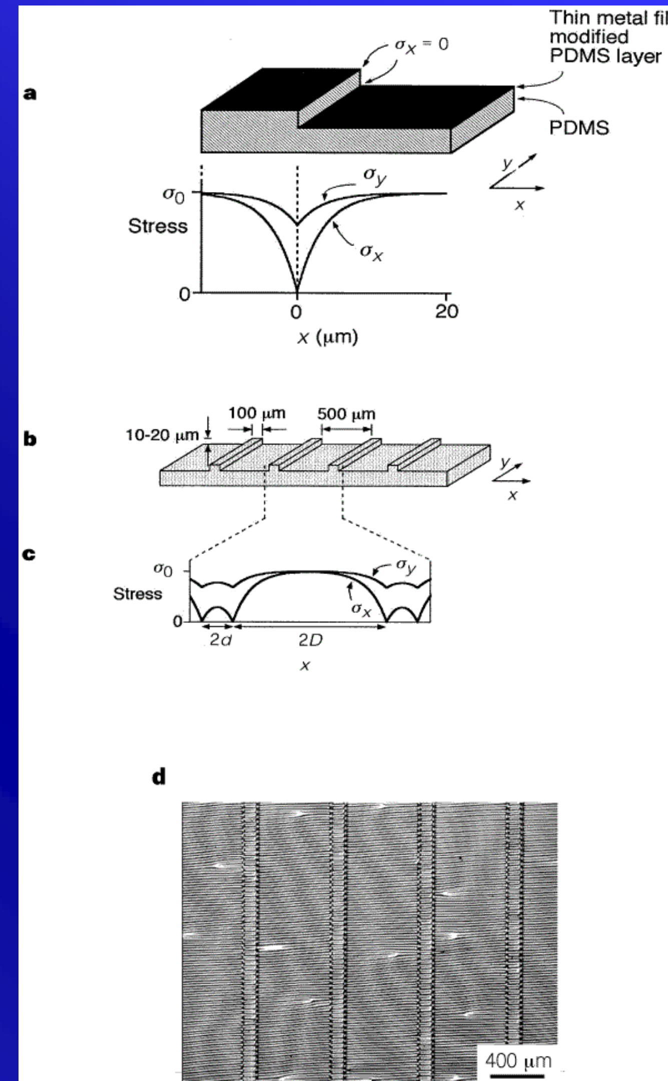
Technology Administration, U.S. Department of Commerce

Surface Buckling – Recent Studies







Bowden, Brittain, Evans, Hutchinson, & Whitesides. *Nature 393* (1998), 146.

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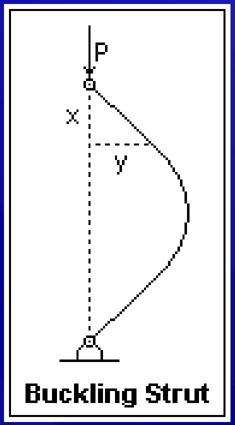
Surface Buckling - History

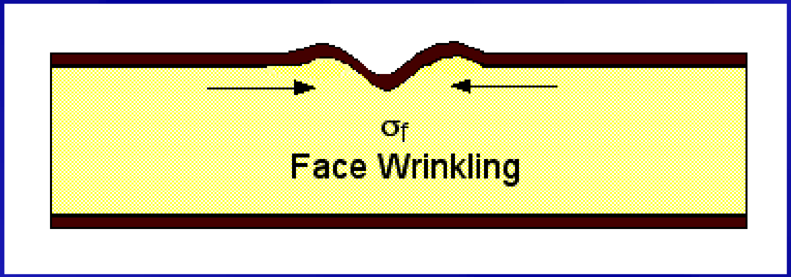
- **Euler : buckling of a beam or strut**

$$P_{CR} \approx \frac{EI}{L^2}$$



- **Five different modes of failure of a composite sandwich panel :**

1. **Yielding or fracture**
2. **Buckling or wrinkling**
3. **Core failure**
4. **Delamination**
5. **Indentation**



H.G.Allen, *Analysis and Design of Structural Sandwich Panels*, Pergamon Press, 1969.

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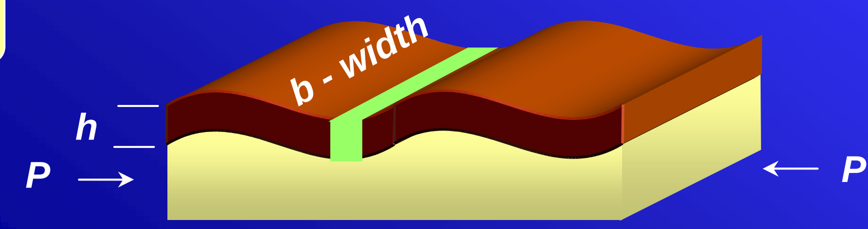
Buckling of a Structural Sandwich

Let's start with a beam bending equation:

$$E_p b h^3 \frac{\partial^4 w}{\partial x^4} + P \frac{\partial^2 w}{\partial x^2} \approx \sigma_z(x) b$$



w(x) **– local displacement in the z-axis**
P **– compressive load/force**
b **– width of a section**
h **– thickness of the rigid plate**
$\sigma_z(x)$ – shear stress

Now, let's assume the sandwich buckles sinusoidally:

$$w = w_m \sin \frac{2\pi}{d} x$$

d = wavelength of instability

w_m = amplitude of instability

And, the necessary stress required is:

$$\sigma_z \approx -\frac{E_m w_m}{d} \sin \frac{2\pi}{d} x$$

H.G.Allen, *Analysis and Design of Structural Sandwich Panels*, Pergamon Press, 1969

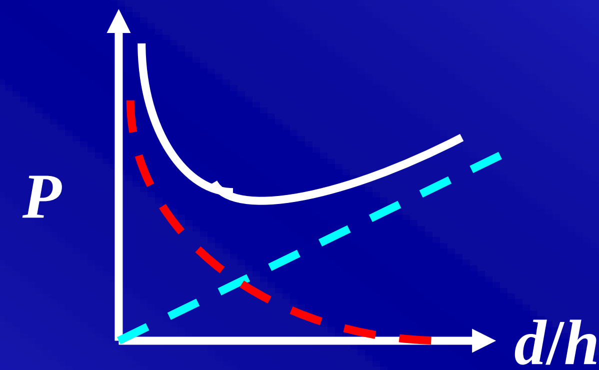
Buckling of a Structural Sandwich

Then, let's make all the necessary substitutions:

$$P \approx E_p\left(\frac{d}{h}\right)^{-2} + E_m\left(\frac{d}{h}\right)^{1}$$

What value of *d/h* will lead to a minimization of the lateral stress?

$$\frac{\partial P}{\partial\left(d/h\right)} = 0$$



The answer is:

$$d \sim h\left(\frac{E_p}{E_m}\right)^{1/3}$$

$$E_p = 12 \cdot E_m \cdot [(3-\upsilon)(1+\upsilon)]^{-1}(qh)^{-3}$$

H.G.Allen, *Analysis and Design of Structural Sandwich Panels*, Pergamon Press, 1969.

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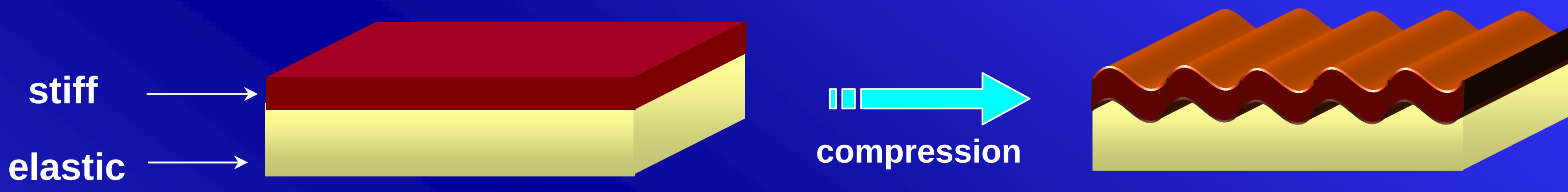
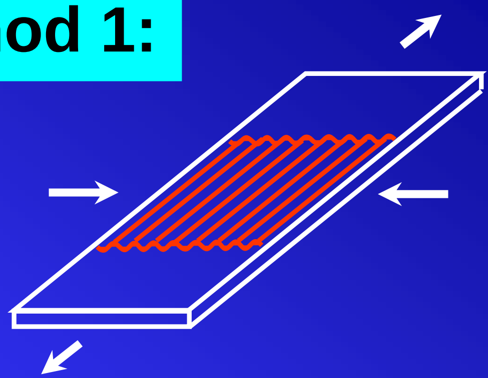
Strain Induced Elastomer Buckling Instability Measurement Method (SIEBIMM)



Method 1:

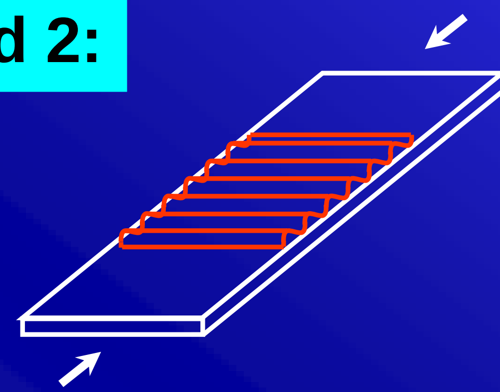


compression

$-\upsilon_m \varepsilon_y$

Strain ε_x

Method 2:



Compression ε_x

- Can be used to directly measure the Young's modulus **WITHOUT** modeling the material being investigated.
- Multiple gradient samples can be simultaneously measured

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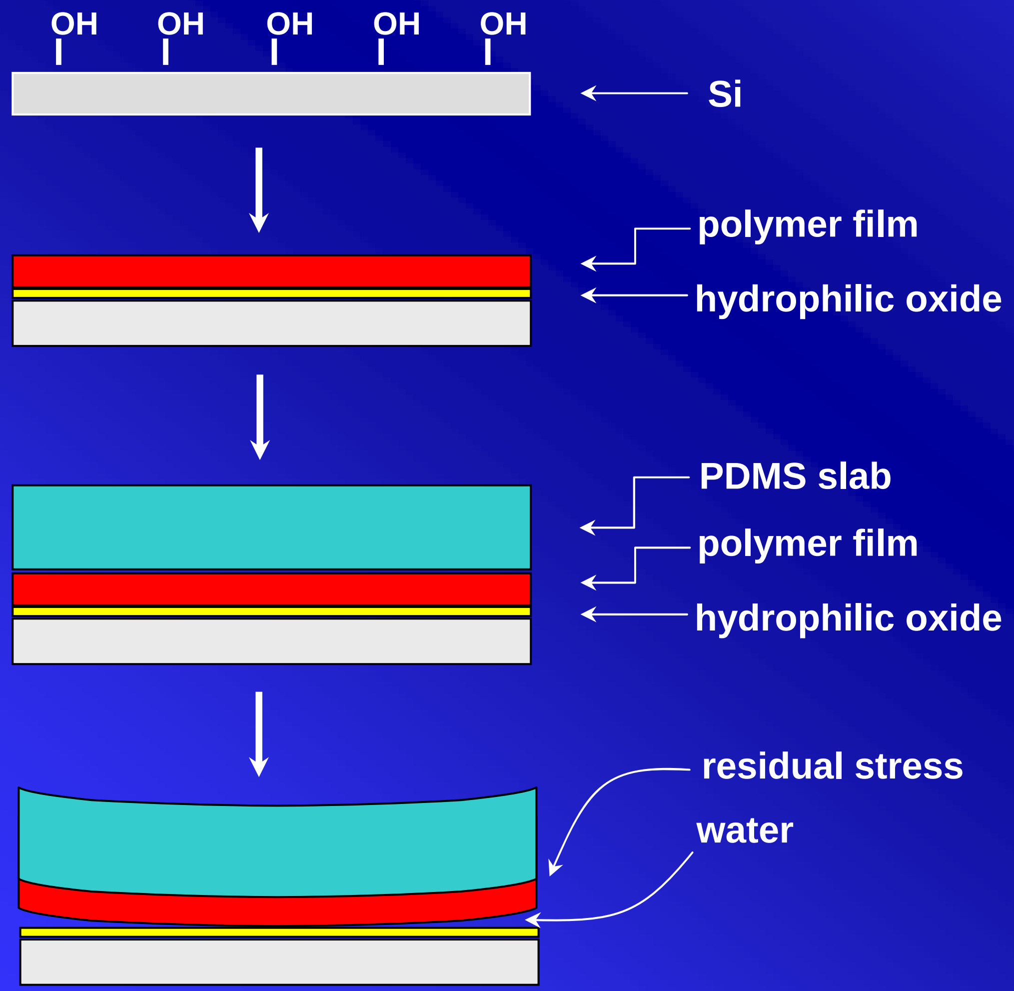
Bilayer Sample Preparation



Make surface of silicon oxide hydrophilic

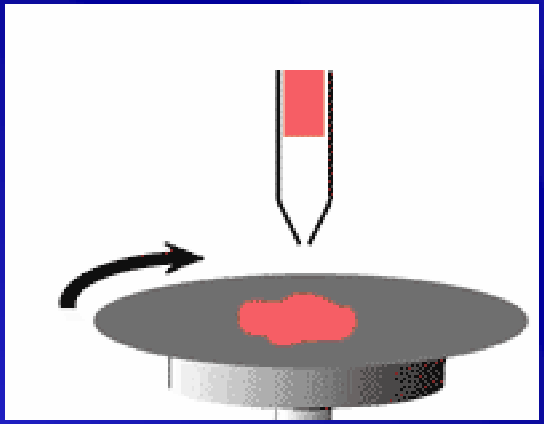
Prepare thin film by variety of techniques

Cast PDMS sheet on top of substrate/film

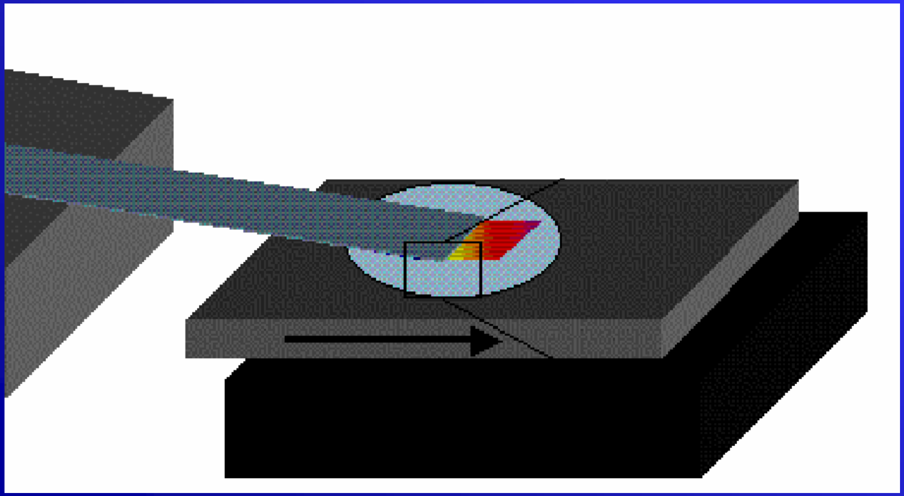
Release laminate by immersing in water

Thin Film Fabrication Techniques

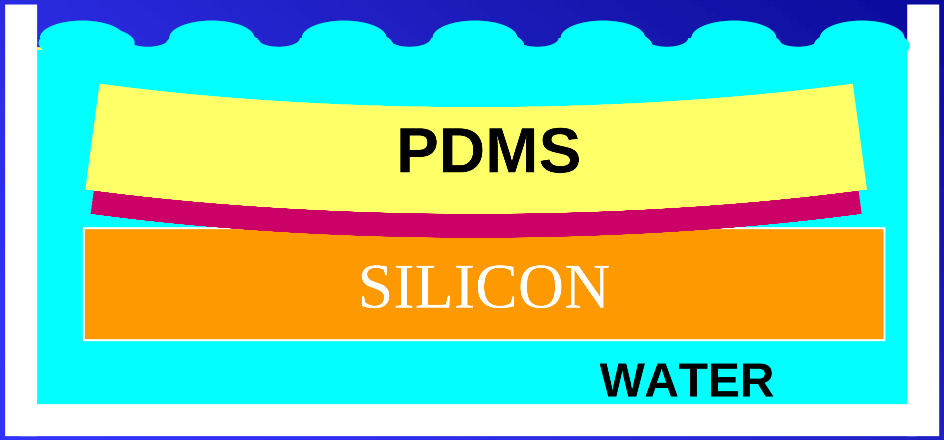
Spin Coating

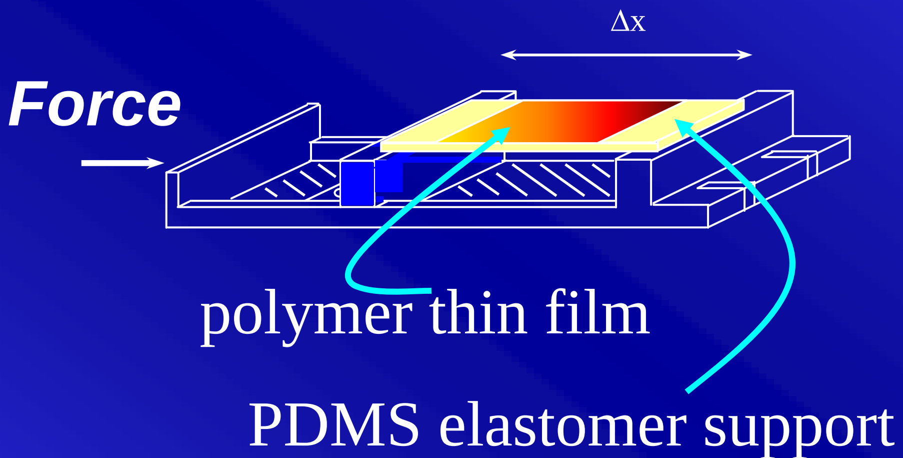


Flow Coating

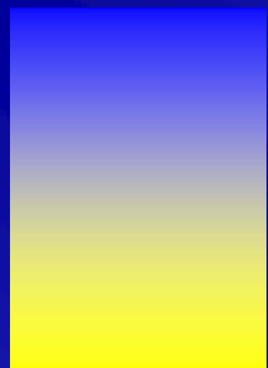


Lift-Off onto PDMS



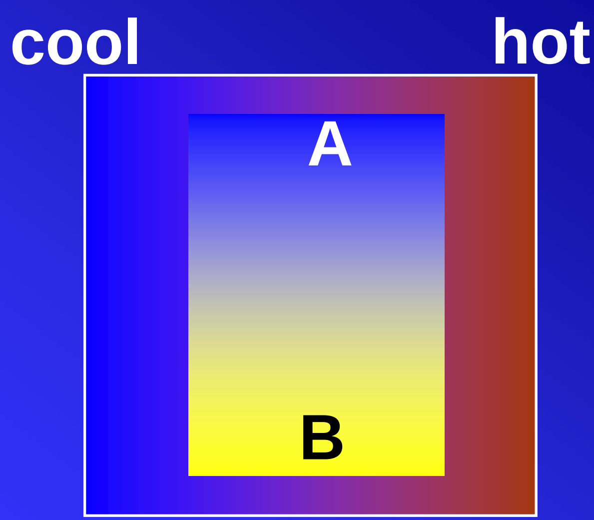


Gradient High-Throughput Approach



Gradient Specimen: **Gradually varies a property along one direction**

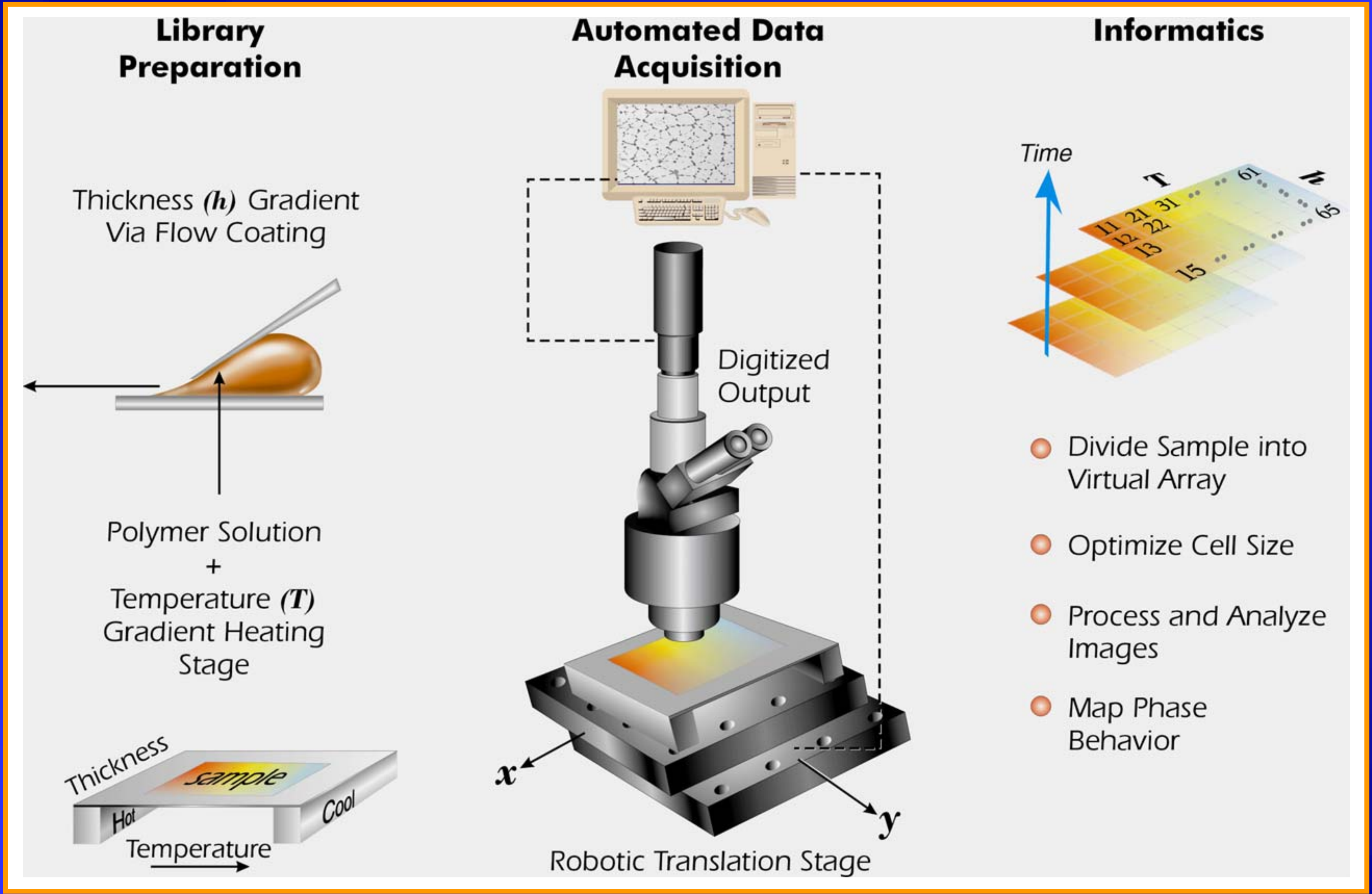
e.g. Composition, thickness, temperature



Crossed-Gradient Combinatorial Library:

- **Two orthogonal gradients**
- **Each point gives a different combination of (e.g) Temperature and Composition**
- **Every combination in range is covered**
- **Library can often “report” results by simple visual inspection**

Films and Coatings



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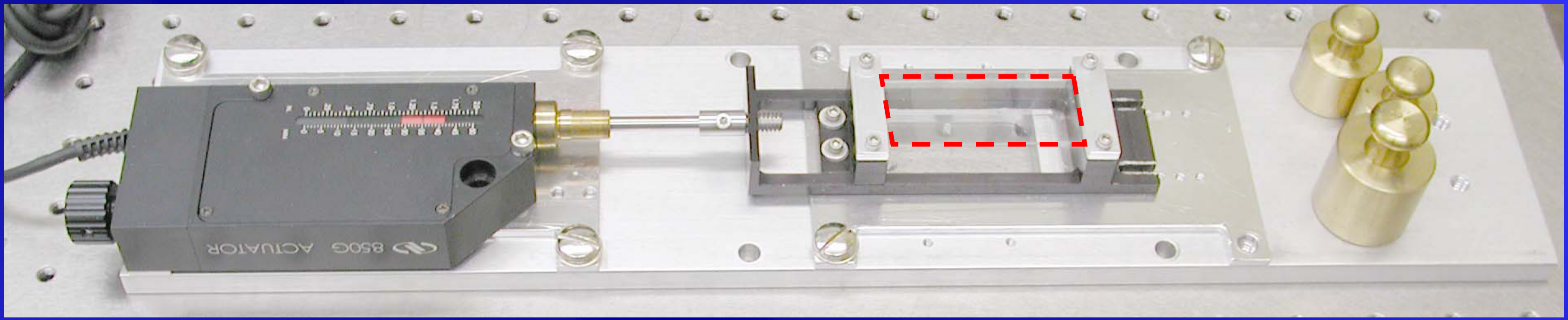
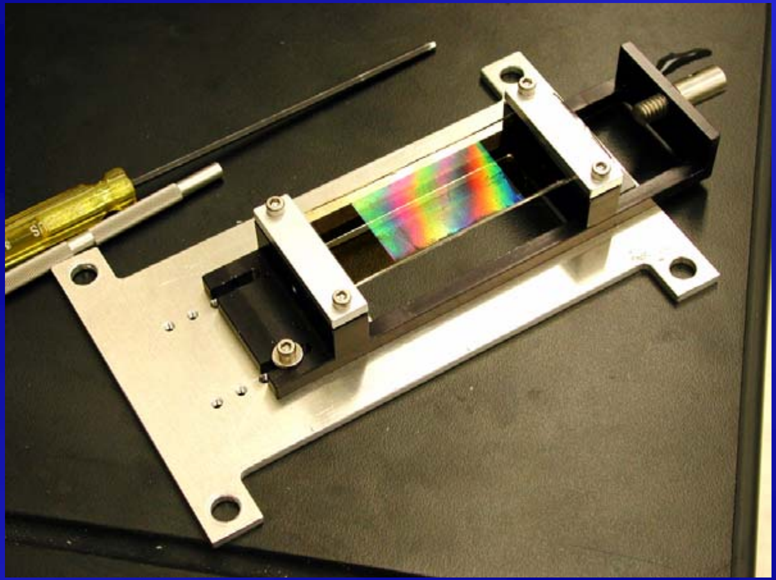
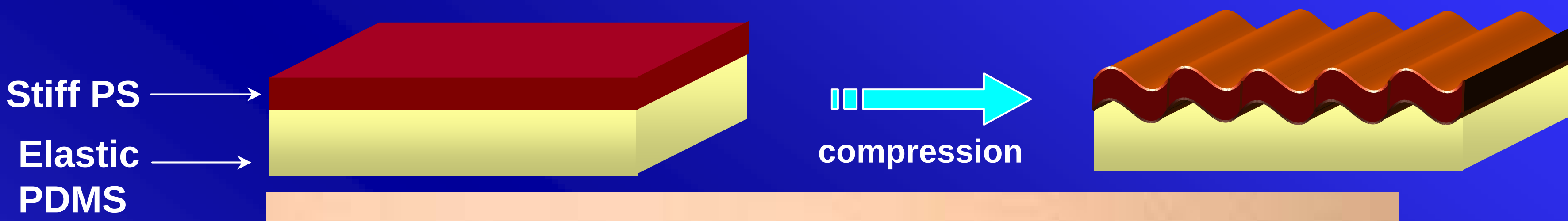
Gradient strain stage





SIEBIMM – Optical Microscopy (Method 2)



SIEBIMM - SALS

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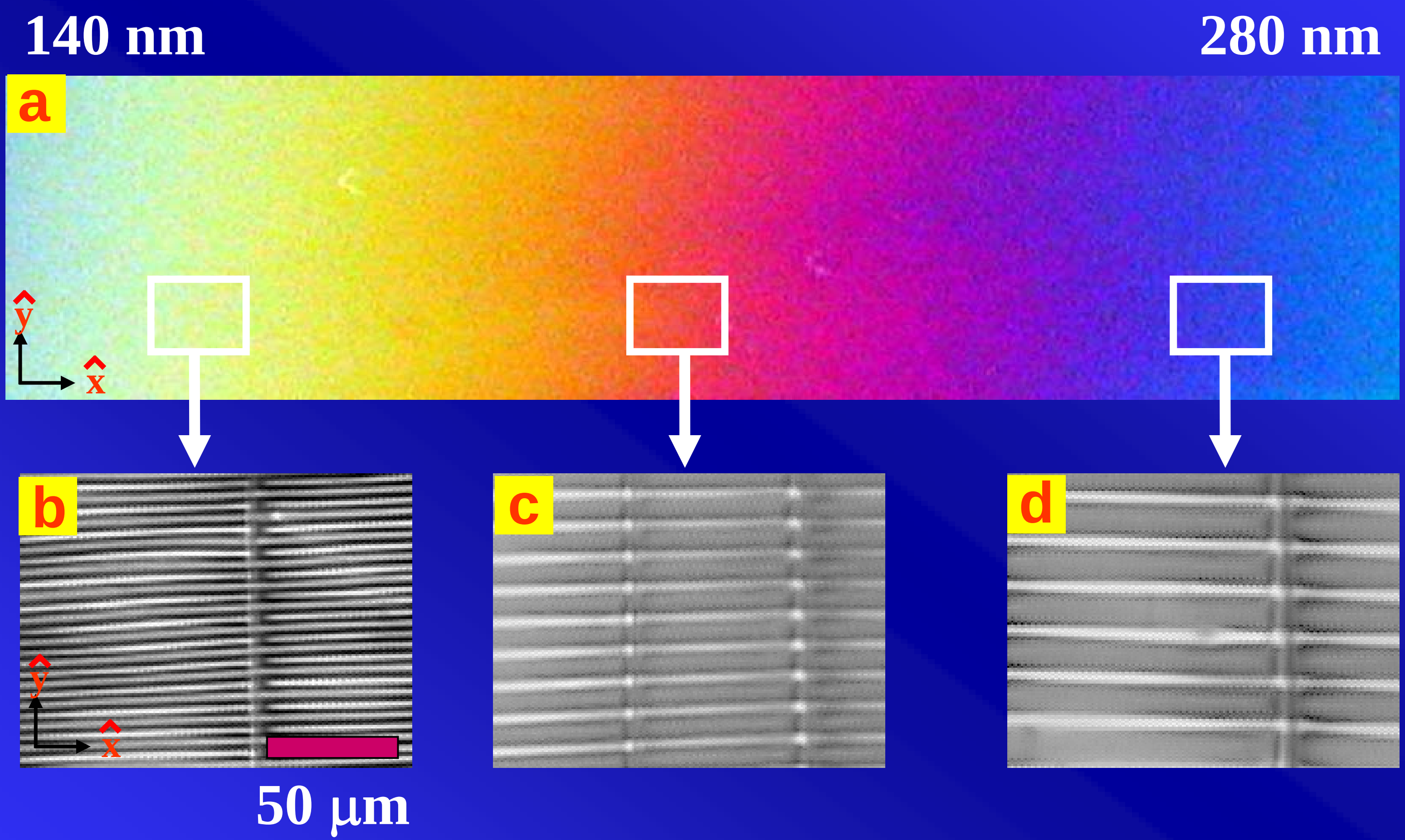
OM of Gradient-Thickness-PS Film / PDMS

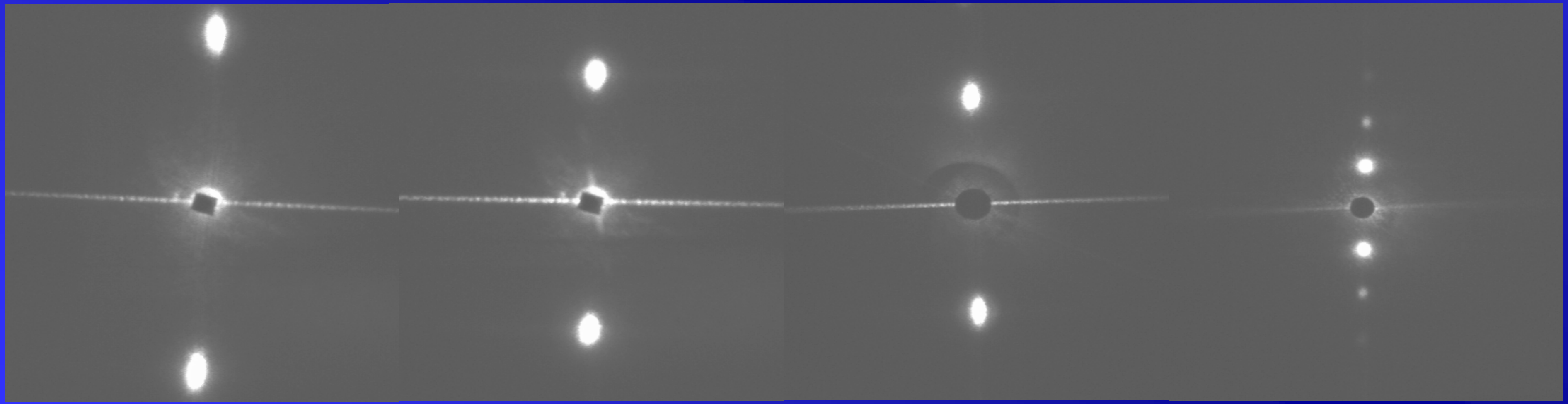


d=7 μm

d=10 μm

d=14 μm

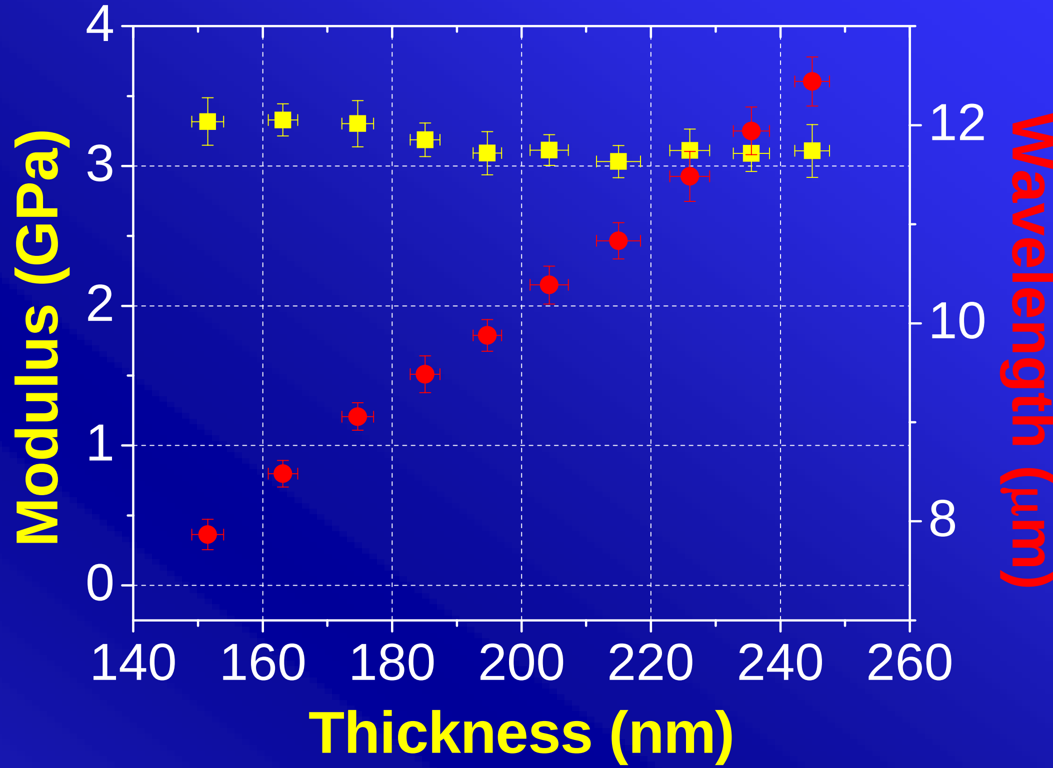
SALS on Gradient-Thickness-PS Film / PDMS



Rapidly map film modulus at different film thickness along gradient !

Gradient-Thickness-PS Film / PDMS

- **PS film with a thickness gradient.**
- **Buckling wavelength *d* increases linearly with thickness.**
- **SIEBIMM modulus:**
  3.17 GPa ±0.11 GPa
- **Flexural modulus:**
  3.22 GPa ± 0.05 GPa
  (Donald Hunston, NIST)



$$d \sim h\left(\frac{E_p}{E_m}\right)^{1/3}$$

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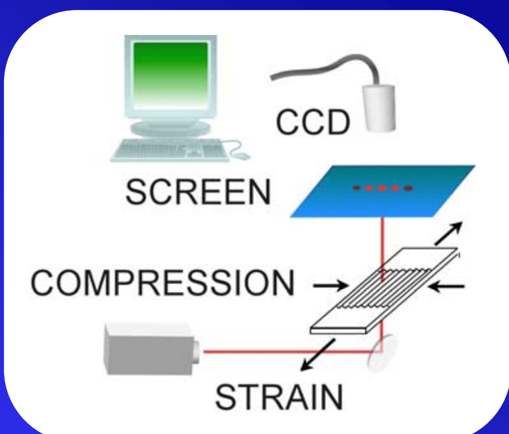
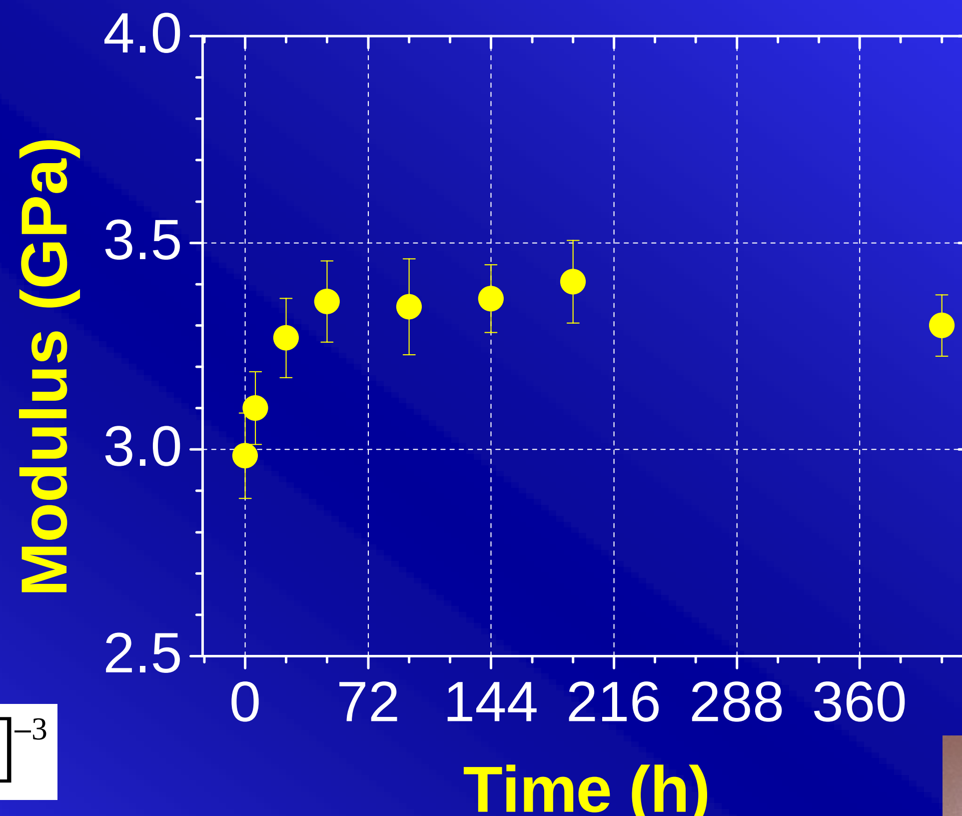
Film Aging Effect by SIEBIMM

Approach: Study time dependence of modulus measurement w/ SIEBIMM



$$E_p = 12E_m\left[(3-\nu_m)(1+\nu_m)\right]^{-1}\left[qh\right]^{-3}$$



No discernable film thickness change with aging

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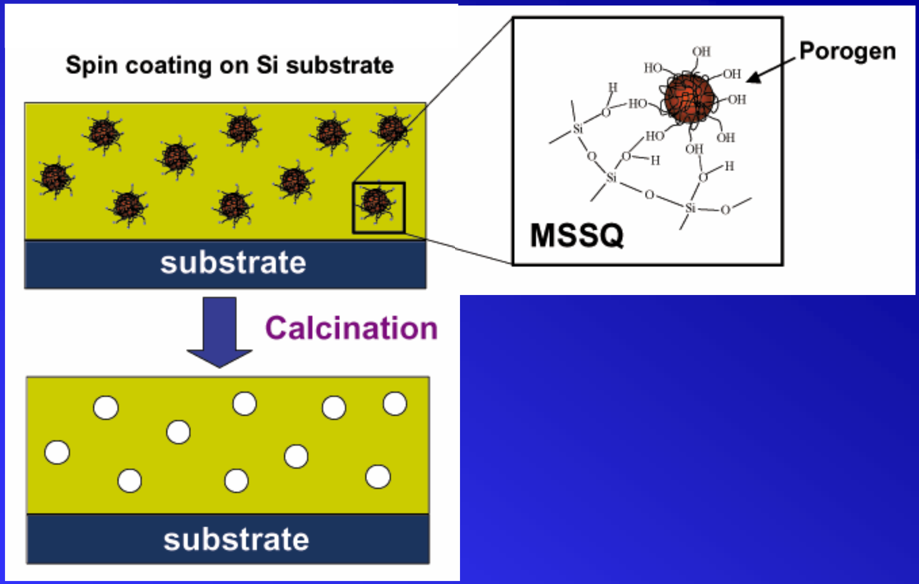
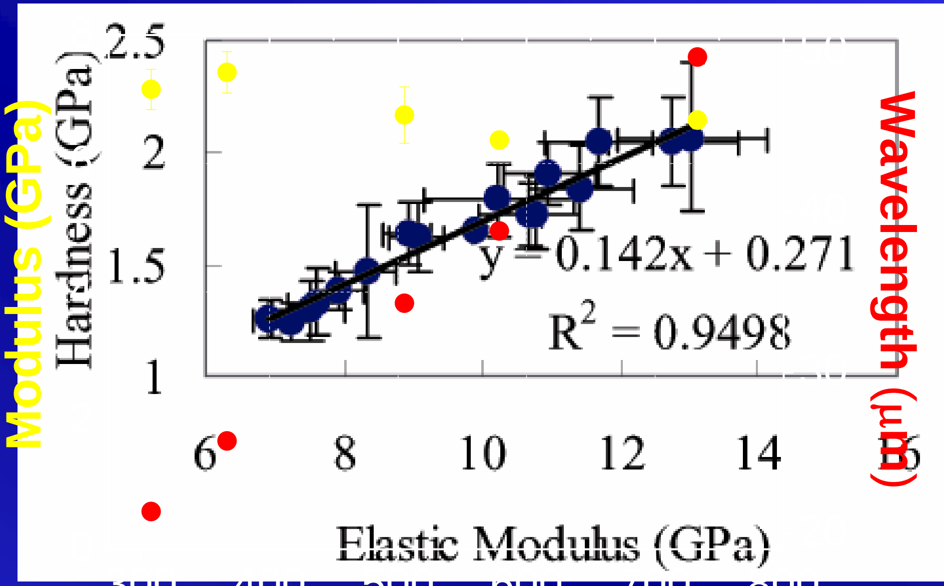
Nanoporous Films

- Nanoporous (low-k) films are a critical technology for sub-100 nm semiconductor applications.
- The mechanical properties (modulus, hardness, etc) are integral to the resilience of these films to CMP/planarization



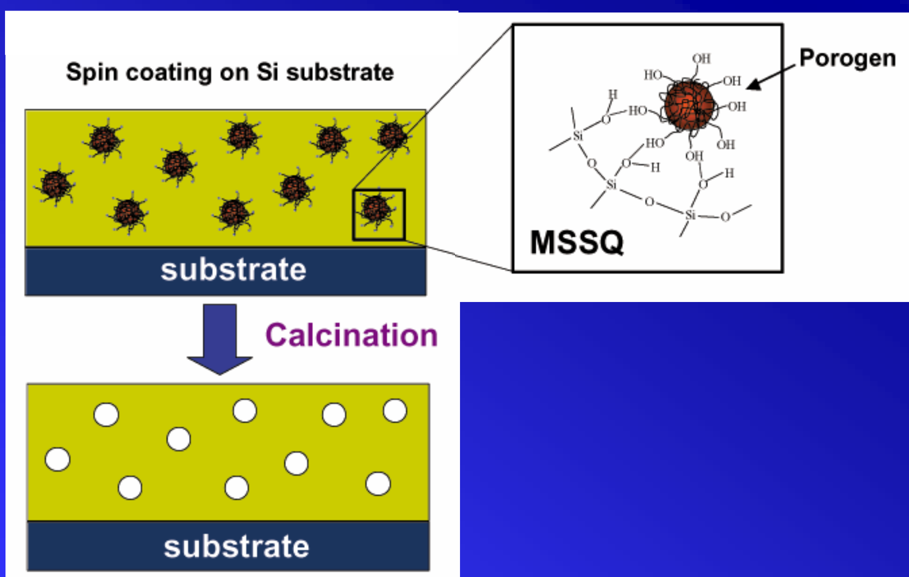
*Samples supplied by Dr. Kim, IBM Almaden

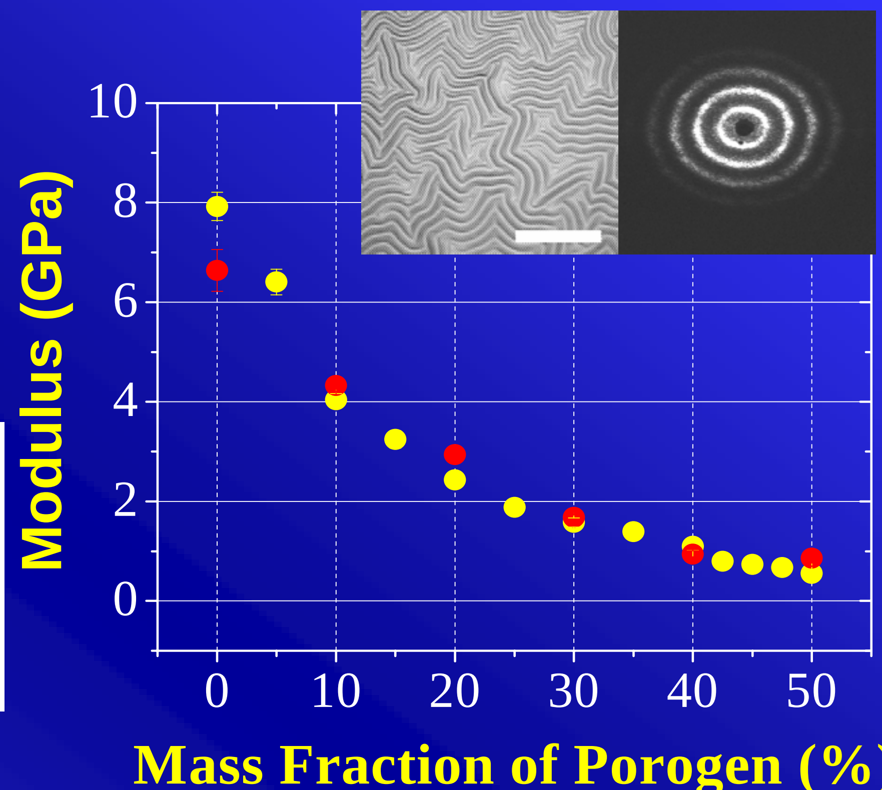


Vella et al., *Mat. Res. Soc. Symp. Proc.* 716 B12.13

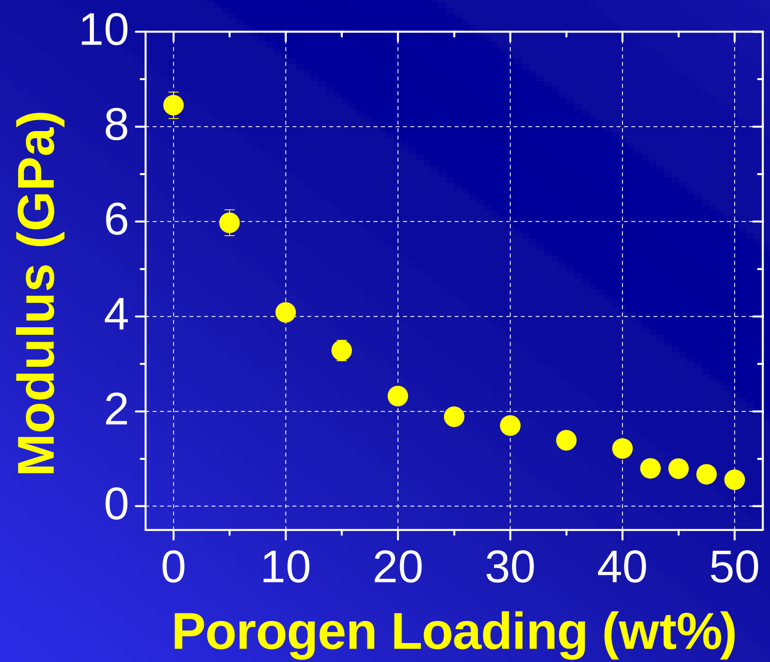
Nanoporous Films

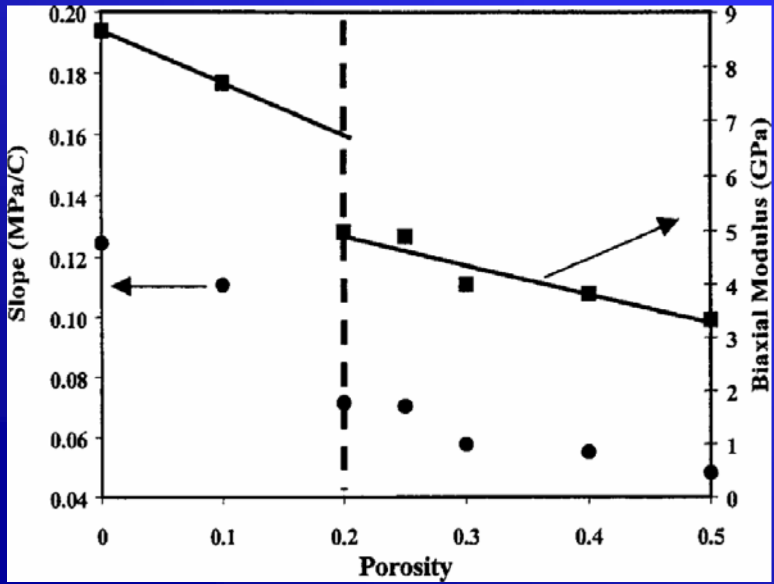
- Collaboration w/ IBM Alamden
- Launched collaboration w/
  J. Watkins (UMass Amherst)





Nanoporous Films





Liu *et al., Appl. Phys. Lett.* 81 4180 (2002).

- Modulus decreases monotonically with increasing porosity.
- No abrupt transitions observed (percolation point).
- Highest loading leads to < 1 GPa modulus.

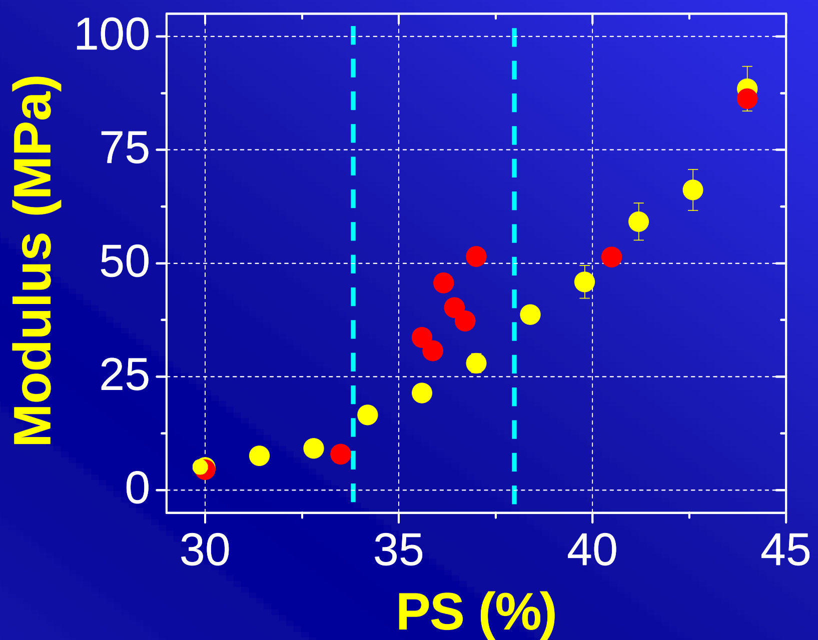
**Samples supplied by Dr. Kim, IBM Almaden*

Tunable Block Copolymer Blends (Soft Systems)

- Modulus of the film is tuned by ratio of two P(S-I-S) triblock copolymers:

Vector 4215 (30% PS, more rubbery)
Vector 4411 (44% PS, more glassy)

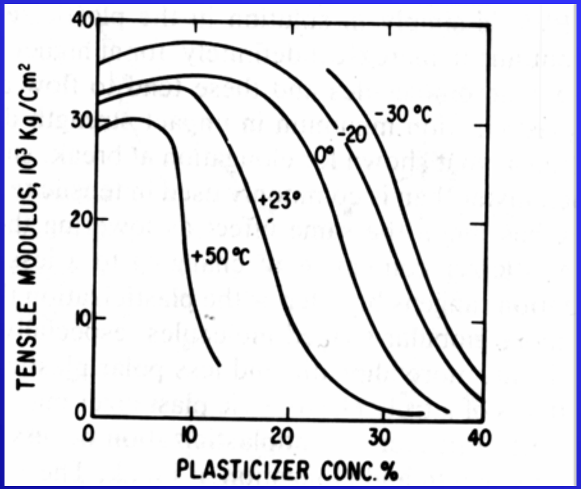
- Optically clear, miscible system
- Morphological transitions observed by SAXS
- We can span the range of polymeric E: GPa → MPa

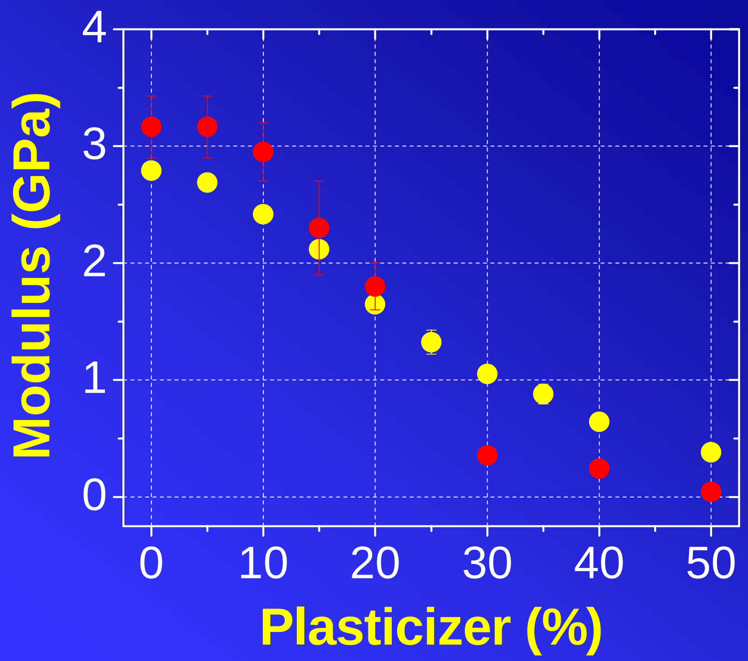


● K. Heffner, senior thesis, Princeton University. (Traditional Instron tests)

Plasticized Polymer Films

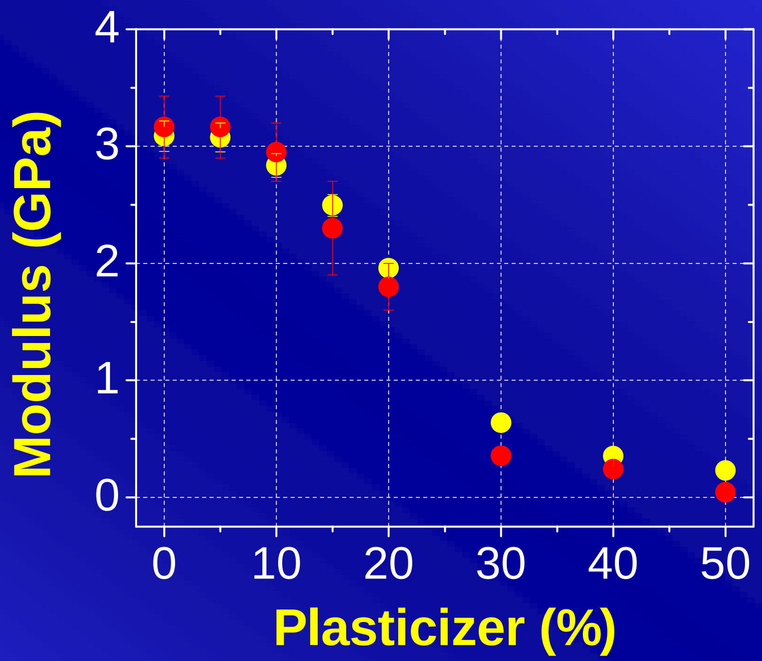
- Modulus measurement of plasticized polystyrene (dioctyl phthalate blend).
- SIEBIMM successfully follows decrease in modulus with plasticizer.
- Nanoindentation (red) agrees well with SIEBIMM. (Mark VanLandingham, NIST)



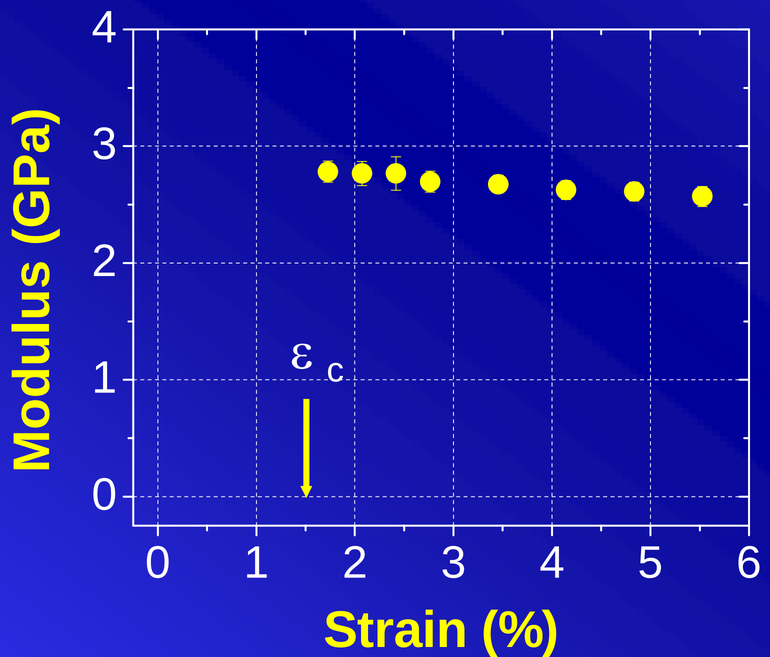


age

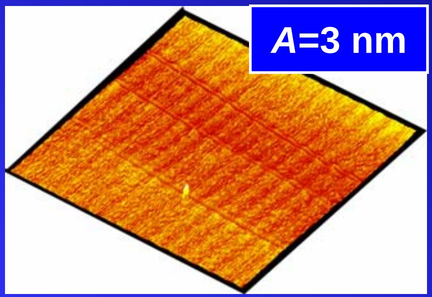
1d



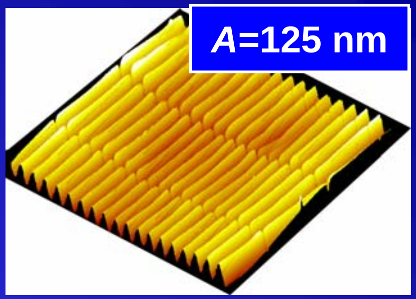
Effects of Strain



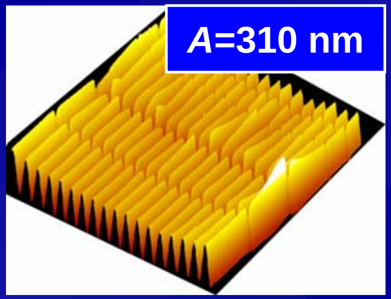
- Even for glassy/brittle polystyrene, modulus measurement relatively insensitive to strain (for strain < 5%)
- ε_c needed to induce buckling
- Measurements typically made at lowest strain that triggers instability



3% strain

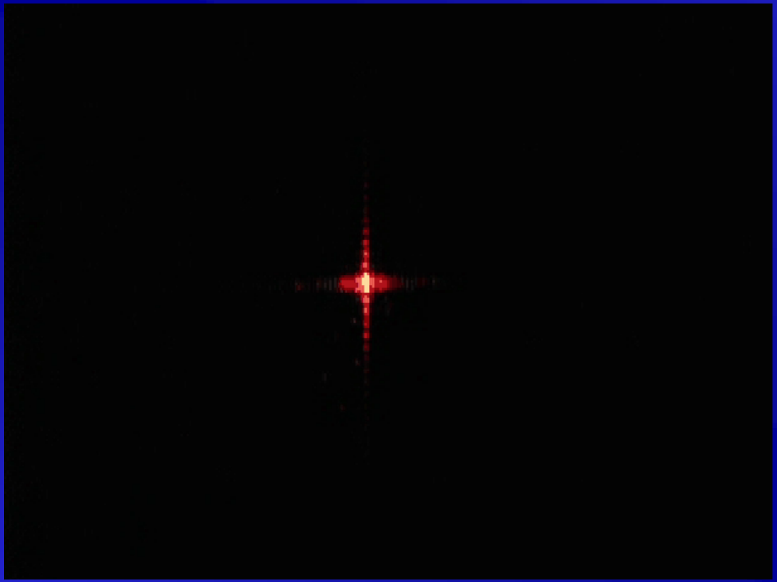


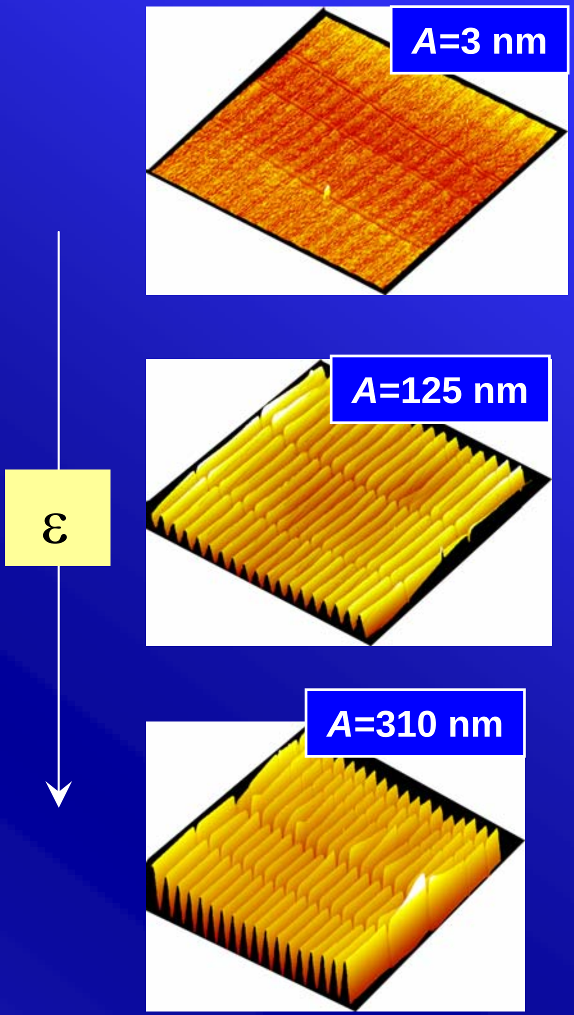
7% strain

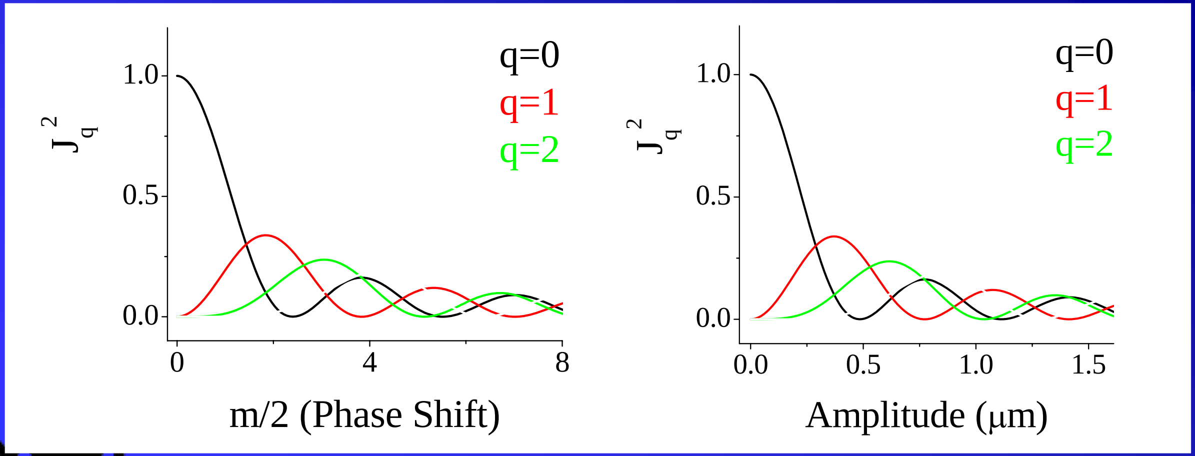


10% strain

Sinusoidal Phase Gratings



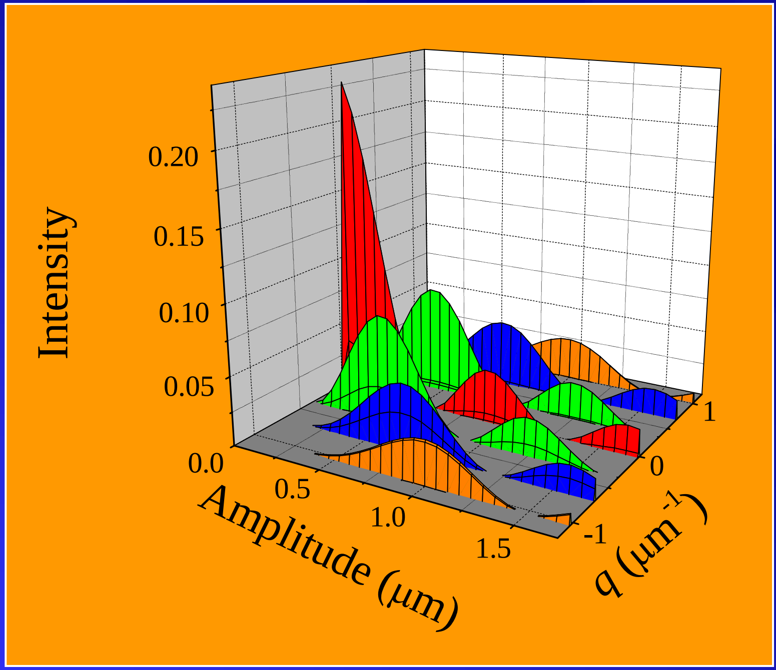




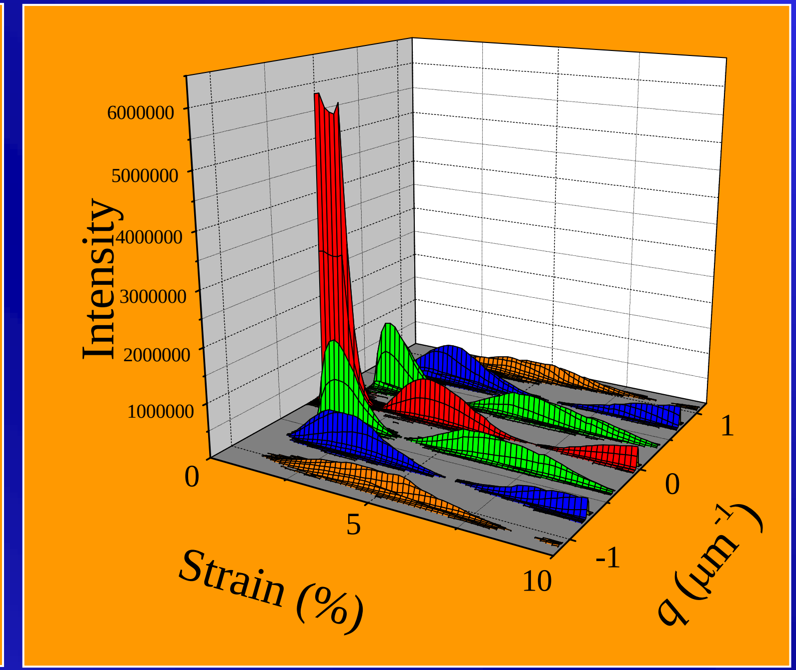
Stafford, Harrison

Mechanical Properties of Nanoscale Thin Films by LS

Issue: conversion from strain to amplitude in SIEBIMM
Approach: high-resolution light scattering as a function of strain



Analytical Predictions

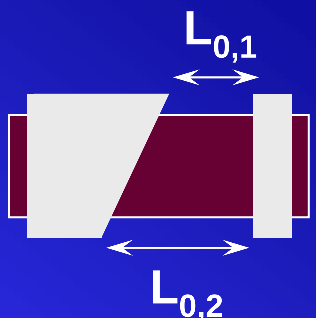


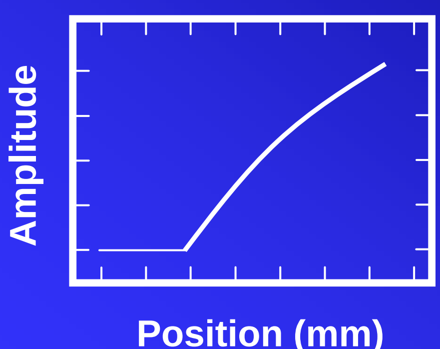
Experimental Results

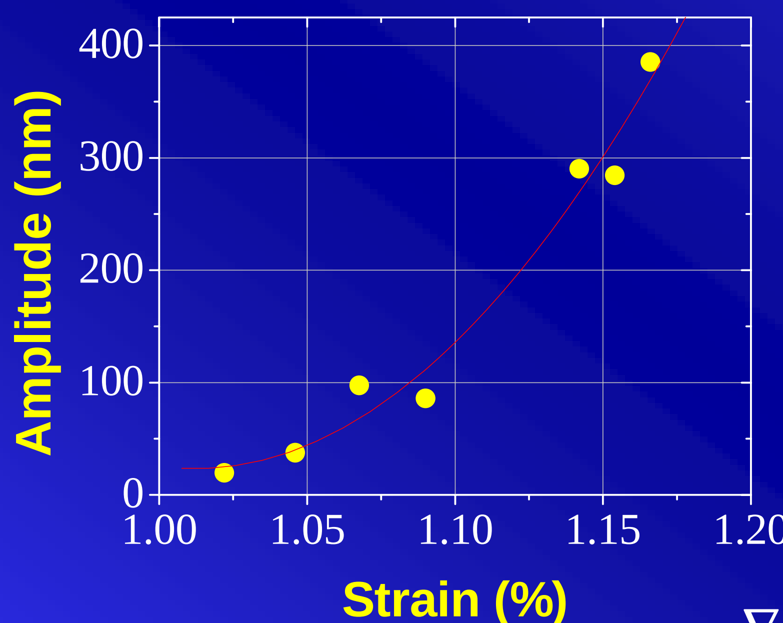
Could yield insight into the residual stress in nanoporous films

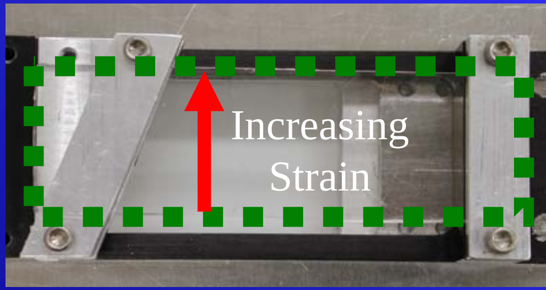
Exploring Strain Gradients with SIEBIMM

Issue: Can we make controlled topography?
strain gradient = amplitude gradient (roughness)
Approach: Gradient mechanical strain stage

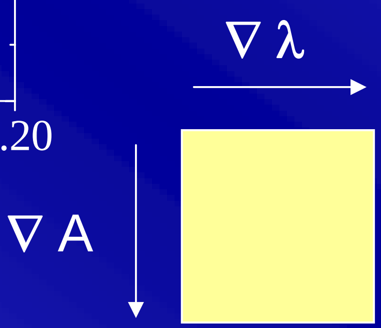








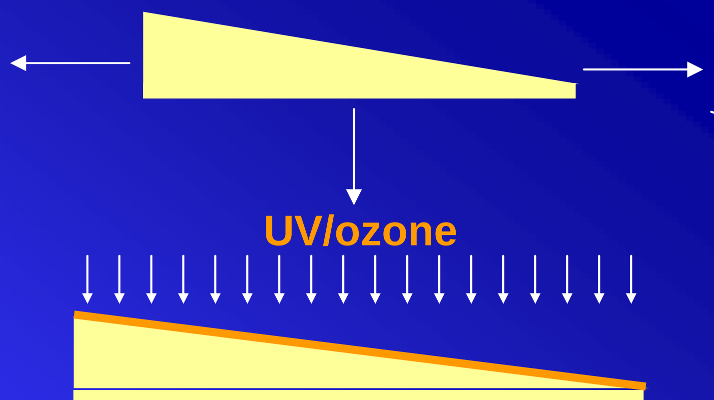
M.Aaron



Exploring Strain Gradients with SIEBIMM

Issue: Can we make controlled topography?

Gradient thickness = wavelength gradient $\nabla \lambda$

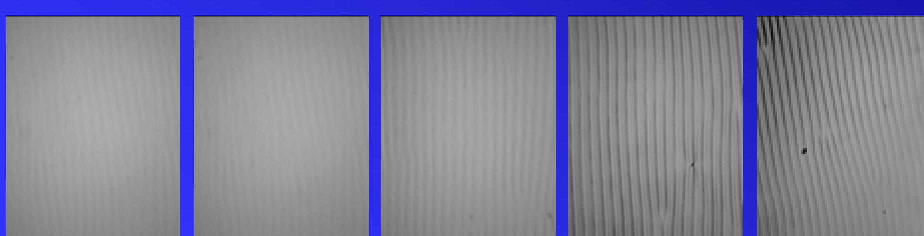


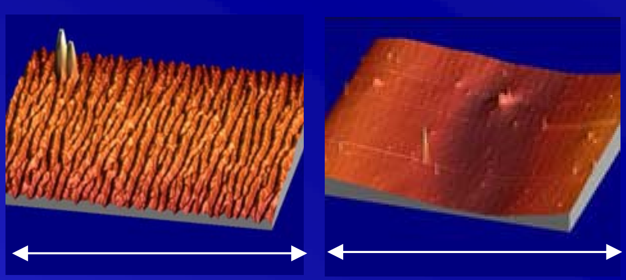
σ = F/A

$\varepsilon = \sigma$/E

$\longrightarrow$ $\varepsilon \sim$ 1/h

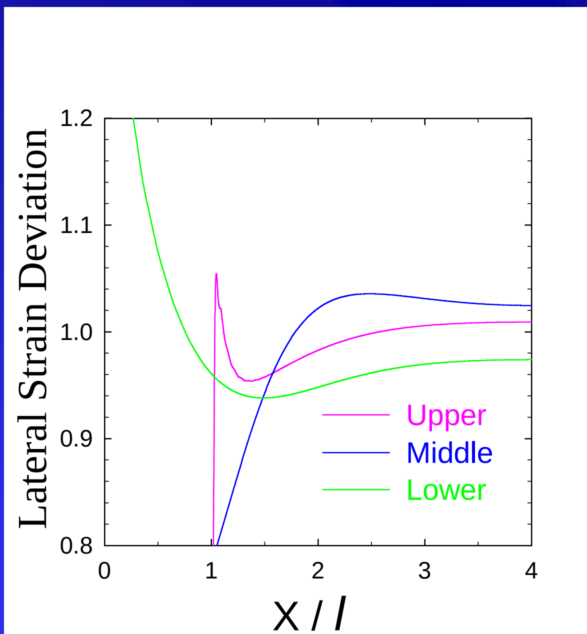
polymer film

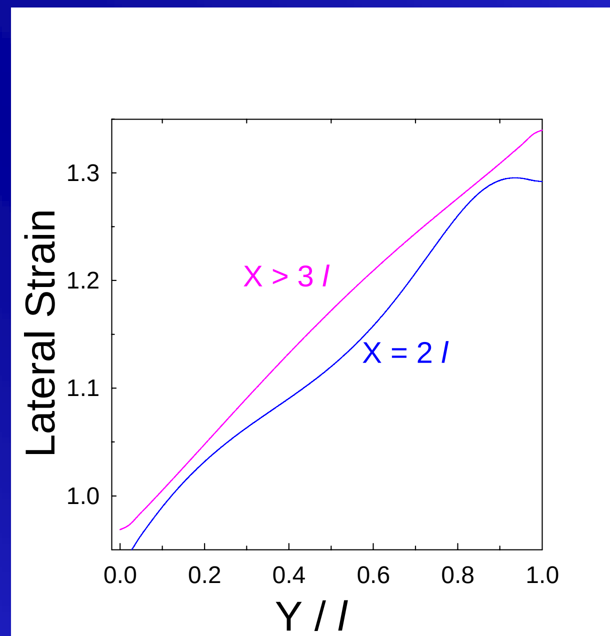


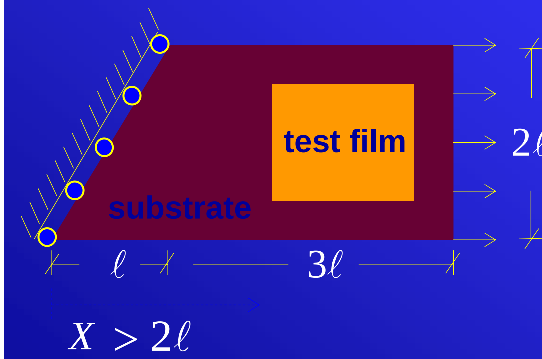


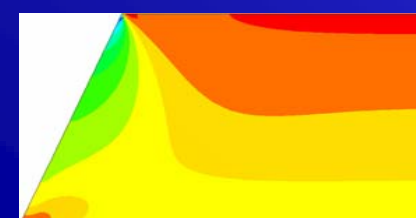
2 μm **100 μm**

Finite Element Analysis of Gradient Strain Stage









Yields direct relationship between angle and area of uniformity.
Defines window of opportunity for strain gradient.

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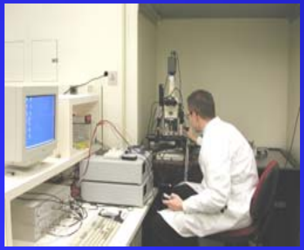
Acknowledgements

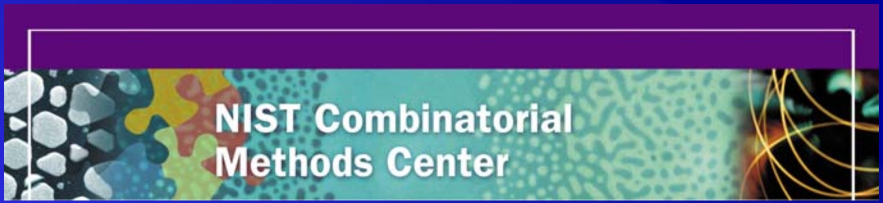
Team SIEBIMM:

- Eric J. Amis
- Don Hunston
- Sheng Lin-Gibson
- Mark VanLandingham

- National Research Council

- Craig Hawker





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