# Linking the challenges of materials technology with the opportunities in materials research - an academic perspective

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*Global R&D Trends – Implications for Materials Science*

Symposium Honoring Dr. Jeffrey Wadsworth
*2013 Acta Materialia Award in Materials and Society*

March 5, 2013



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# One R&D trend in materials science – in mechanical behavior

In addition to the long established problems in the discipline of structural materials:

Stiffer, Stronger, Tougher, Lighter…

We have now added:

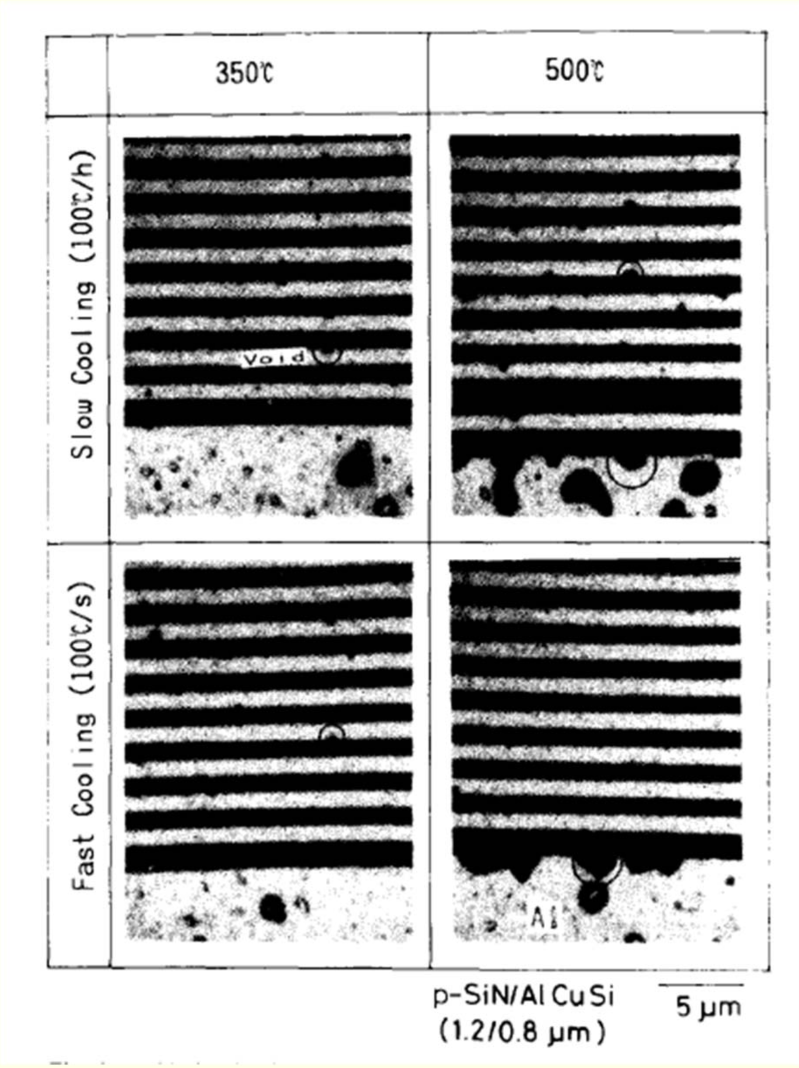
Smaller

•First motivated by needs from outside the discipline: microelectronics and functional materials

•Has led to new techniques and Ideas that now benefit a broad spectrum of science and technology

*I will call this a trend*

# Mechanical behavior problems in microelectronics ~ 1983




Craig Barrett, Intel

David Barnett, Stanford
Bill Nix, Stanford

Consulting about mechanical reliability in metal interconnects – metal cracking

Created need to understand stresses and mechanical properties of thin films – need for new techniques and concepts

*W.D. Nix, Wadsworth Symposium*

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# Nanoindenter – Pethica and Oliver - 1983

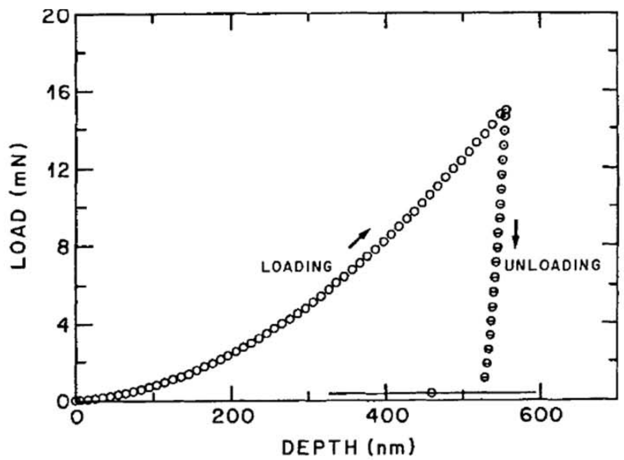
ASM meeting, Philadelphia, October 4,1983

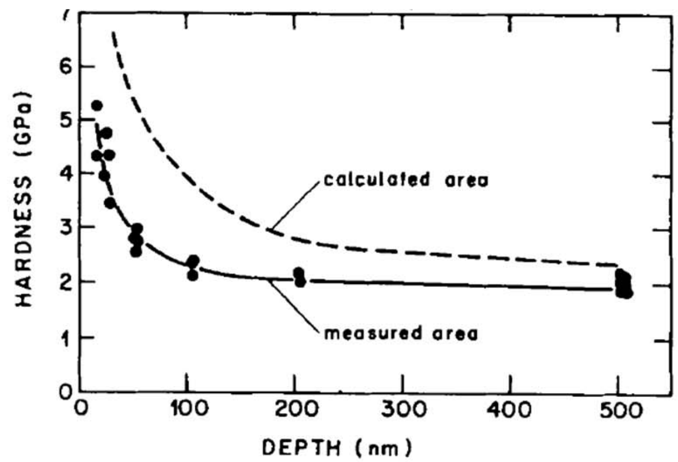
PHILOSOPHICAL MAGAZINE A, 1983, VOL. 48, NO. 4, 593–606

**Hardness measurement at penetration depths as small as 20 nm**

By J. B. PETHICA†, R. HUTCHINGS and W. C. OLIVER‡
Brown Boveri Research Center, CH-5405 Baden, Switzerland

[Received 18 April 1983 and accepted 1 May 1983]



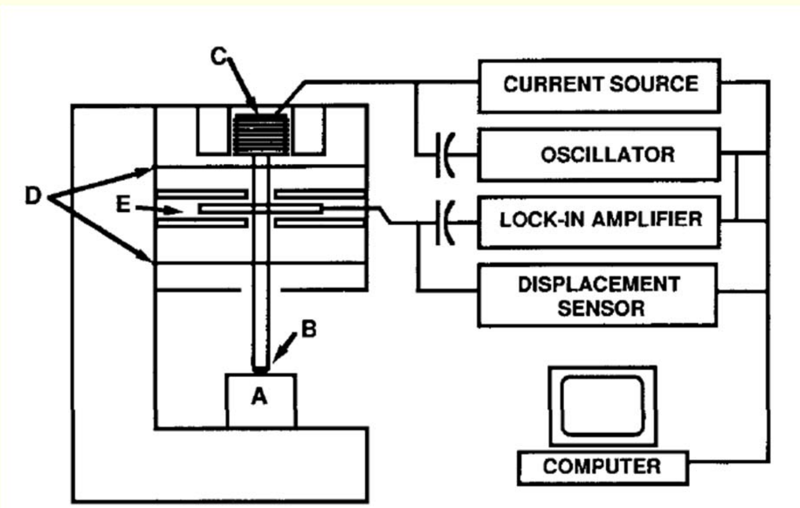
# Oliver & Pharr Method - 1992

An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments

J. Mater. Res., Vol. 7, No. 6, June 1992

W. C. Oliver
*Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6116*

G. M. Pharr
*Department of Materials Science, Rice University, P. O. Box 1982, Houston, Texas 77251*




Established the methodology for determining mechanical properties by nanoindentation

Google Scholar: 10,023 citations!

Most in field of Materials Science – by far!

*W.D. Nix, Wadsworth Symposium*

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# Application to Low-k Dielectric Films

Nanonidentation compliant films

*W.C. Oliver & G.M. Pharr, MRS Bulletin (2010)*

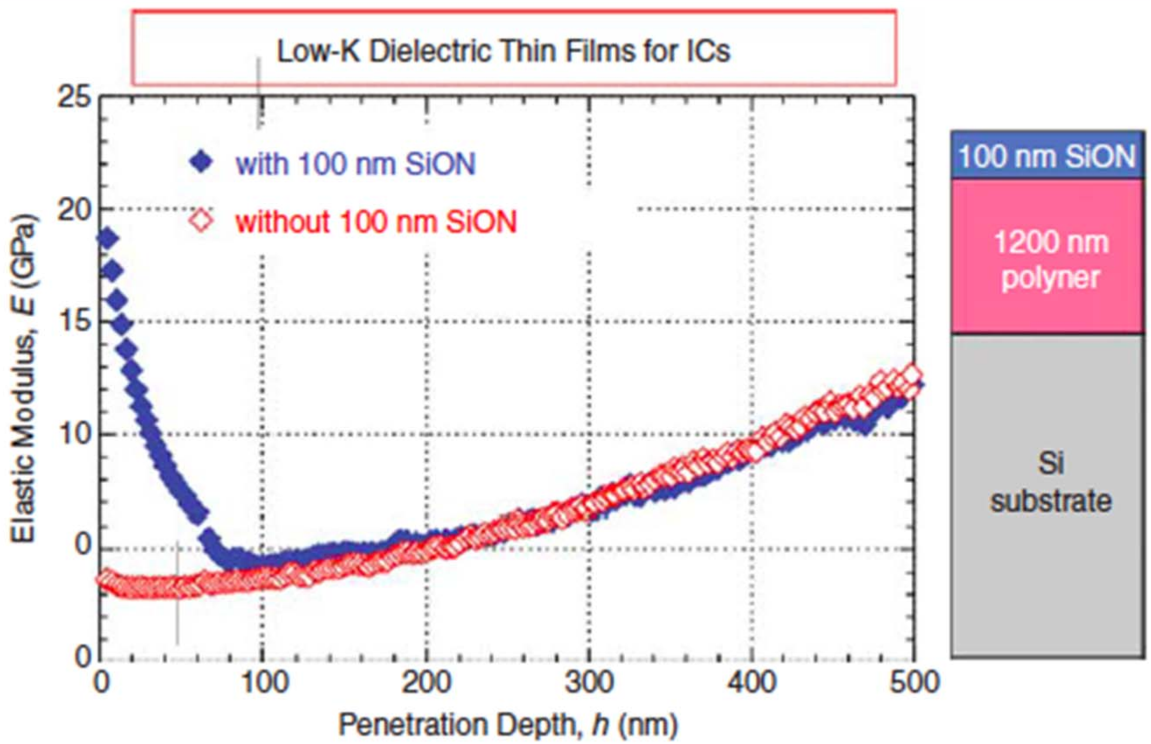


**Figure 8.** Nanoindentation measurement of the elastic modulus of layered structures used for integrated circuits (ICs) in the semiconductor industry. The results illustrate the utility of the continuous stiffness measurement technique (CSM), which allows continuous measurement of hardness and elastic modulus as the indenter penetrates the layers. The rapid increase in elastic modulus at small depths for the blue curve in comparison to the red curve indicates that the 100nm SiON layer is much stiffer than the underlying polymer.

# Application to Biology

Nanoindentation of plaques and hardening of the arteries

*W.C. Oliver & G.M. Pharr, MRS Bulletin (2010)*

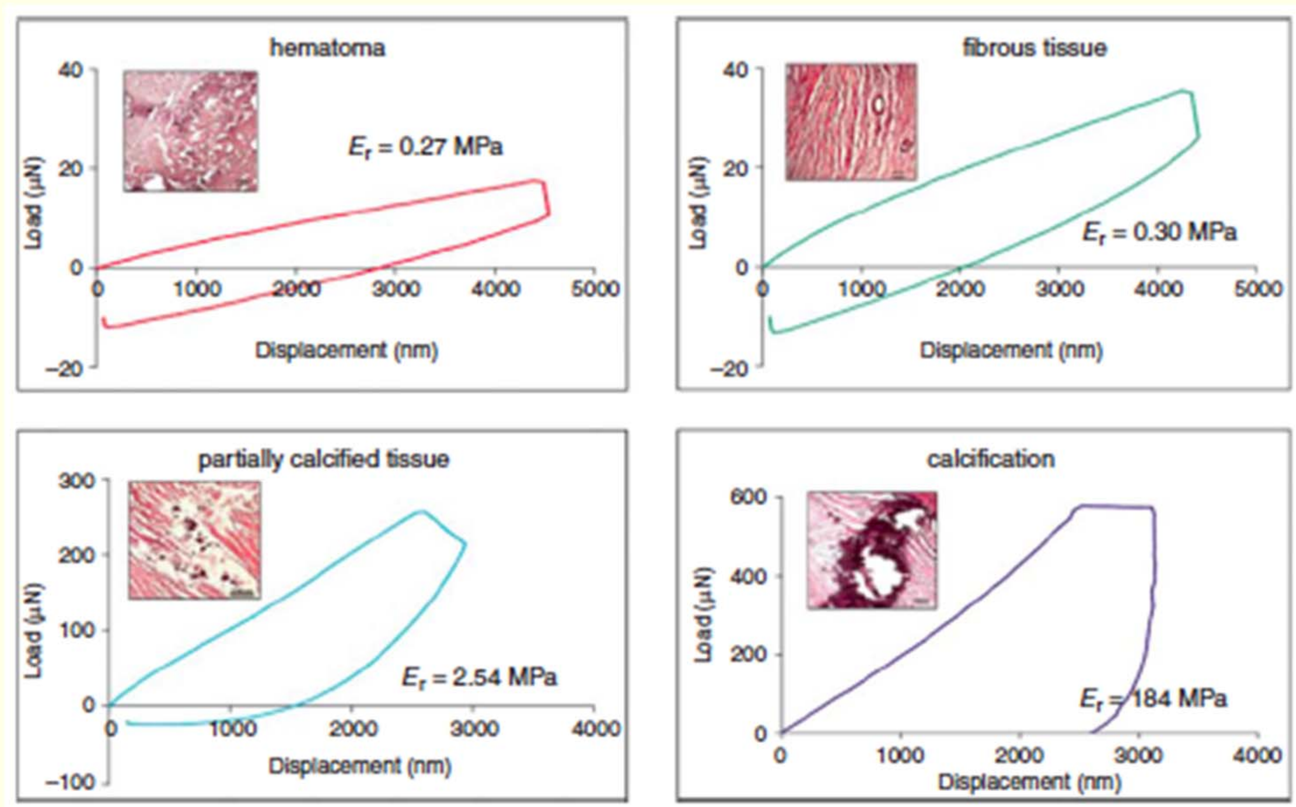


**Figure 10.** Nanoindentation load-displacement behavior of atherosclerotic plaques that cause hardening of the arteries. The series of curves shows how the elastic modulus of the plaques increases by nearly three orders of magnitude in the various stages of development. As the plaque becomes fully calcified in the later stages, it becomes hard and brittle, leading to serious medical problems when it breaks off and moves through the blood system. The negative loads observed during unloading indicate that the indenter had adhered to the surface and had to be pulled off.[13]

# MEMS Display Technology (QUALCOMM)

Flat, Deformable Mirrors as Pixels for Electronic Readers



Residual stresses and mechanical properties of the glass films are crucial



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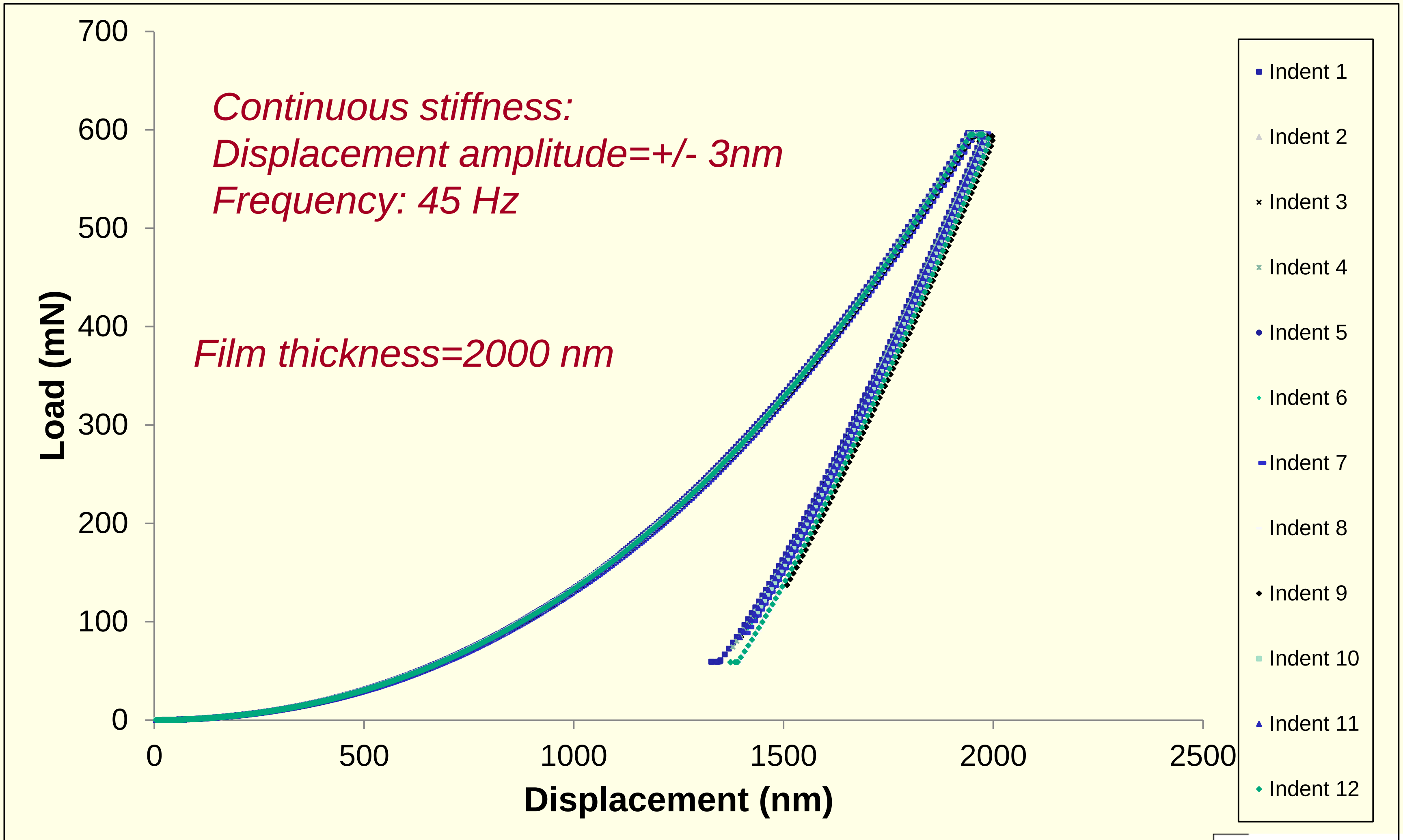
# Nanoindentation of a high quality glass film on Si (part of mirror-pixel structure)




*W.D. Nix, Wadsworth Symposium*

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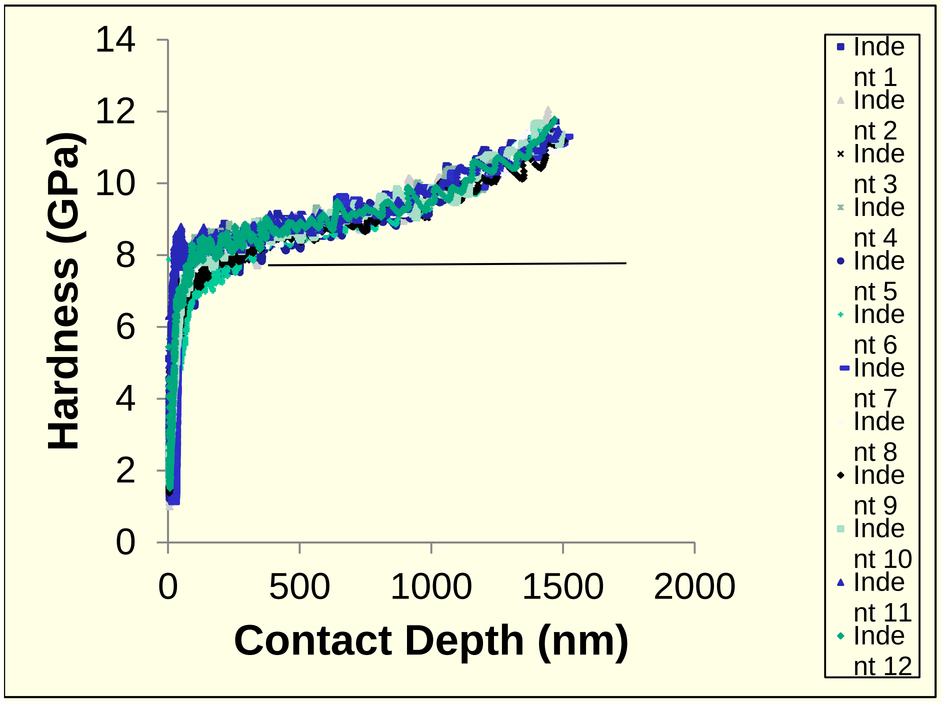
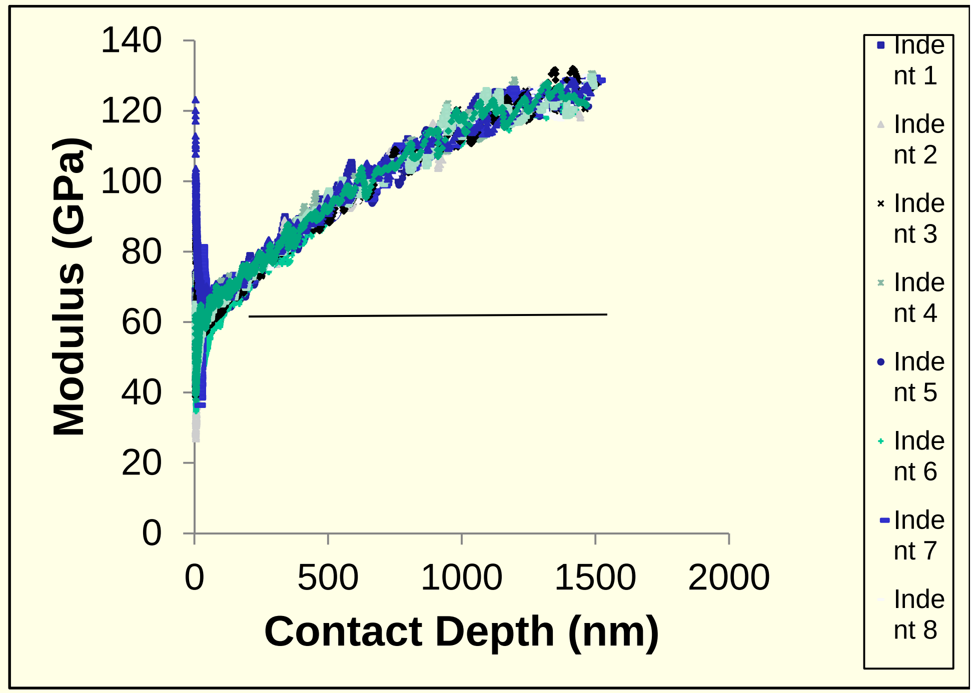
# Hardness and modulus of a high quality glass film on Si – substrate effect

*Continuous stiffness:*
*Displacement amplitude=+/- 3nm*
*Frequency: 45 Hz*

*Film thickness=2000 nm*
*Modulus of Si substrate is ~160 GPa*
*Poisson's Ratio=0.18*




*This characterization capability did not exist before 1983*

*W.D. Nix, Wadsworth Symposium*

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# Another newly developed technique based on an Intel-Stanford connection

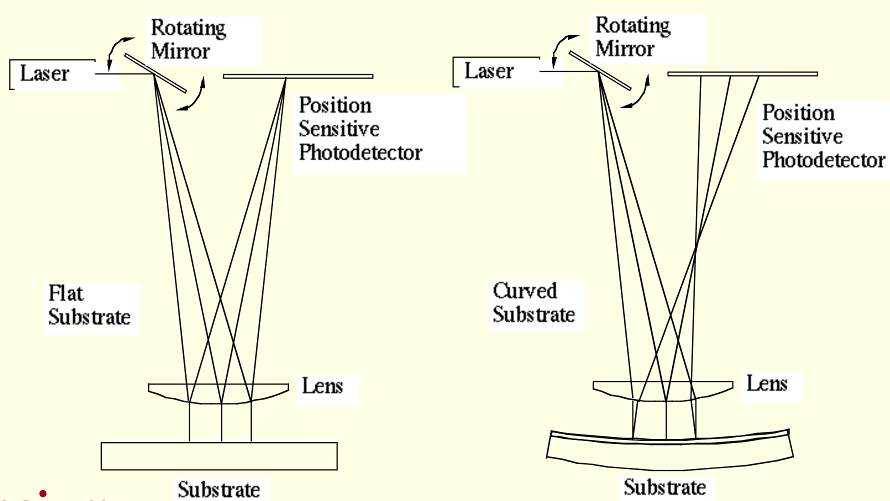
IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. ED-34, NO. 3, MARCH 1987

## Measurement and Interpretation of Stress in Aluminum-Based Metallization as a Function of Thermal History

PAUL A. FLINN, DONALD S. GARDNER, MEMBER, IEEE, AND WILLIAM D. NIX

Laser Scanning Technique for Measuring Substrate Curvature

Motion of Reflected Beam Indicates Substrate Curvature




*W.D. Nix, Wadsworth Symposium*

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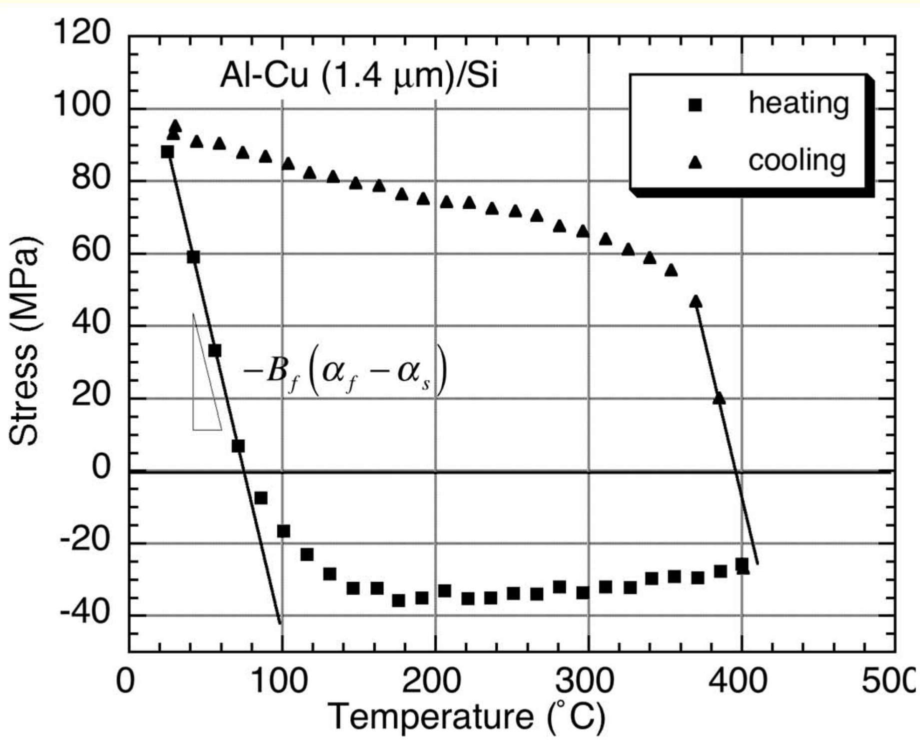
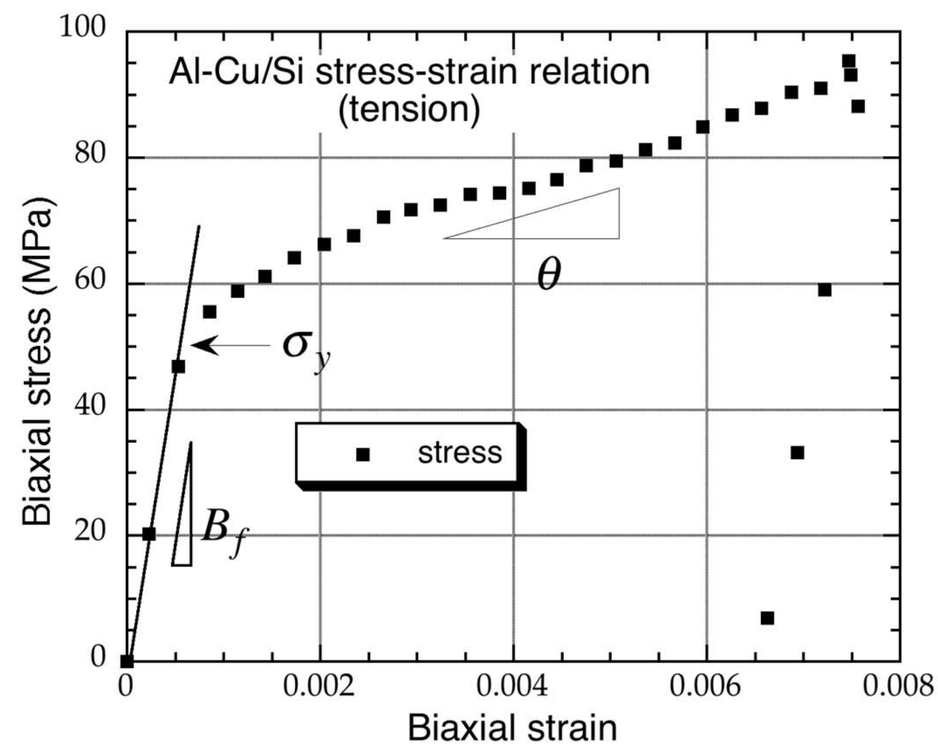
# Substrate curvature method for measuring elastic and plastic properties of thin films




*Technique did not exist before the mid-1980s – led to new wave of science on the strength and plasticity of thin film materials*

***W.D. Nix, Wadsworth Symposium***

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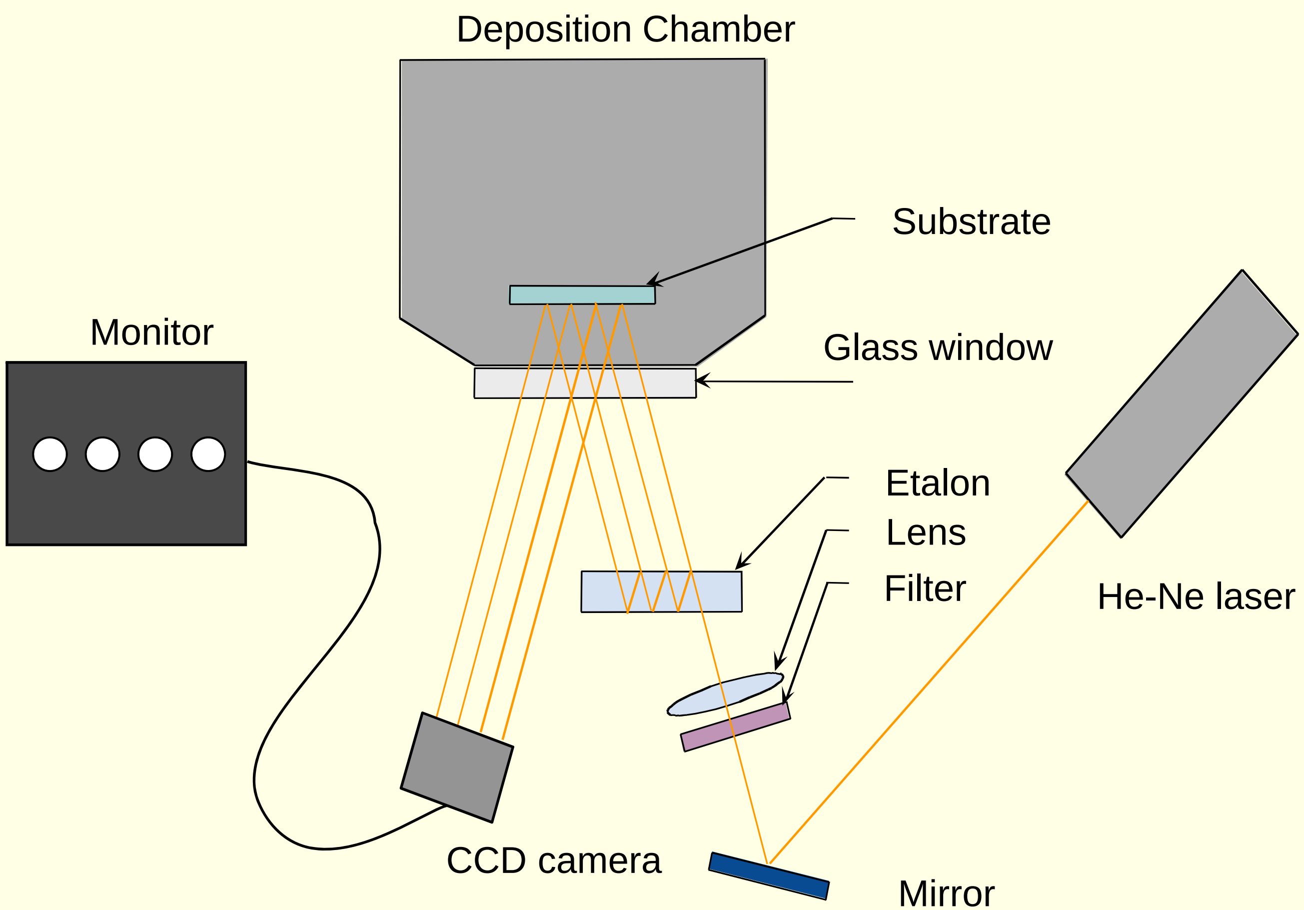
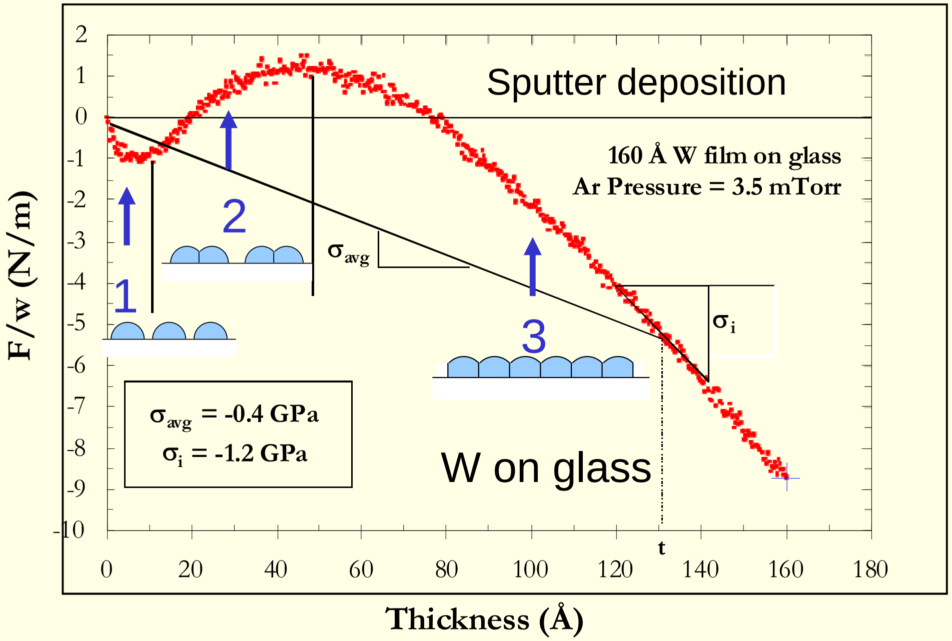
# Interest in stress measurement led to new in-situ techniques




*J.A. Floro, E. Chason and S.R. Lee, MRS Symposium, Fall 1995*

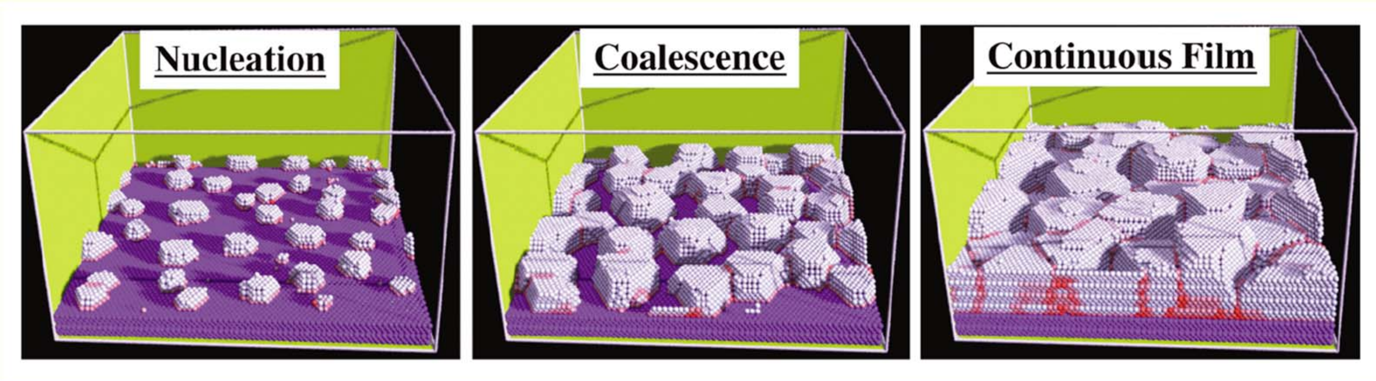
# Stress Evolution in Deposited Thin Films

*V. Ramaswamy & B.M. Clemens, (2001)*




A new line of research on the origins of stresses in thin films

*J.A. Floro, E. Chason, R.C. Cammarata, D.J. Srolovitz, MRS Bulletin (2002)*



# What are the lessons learned?

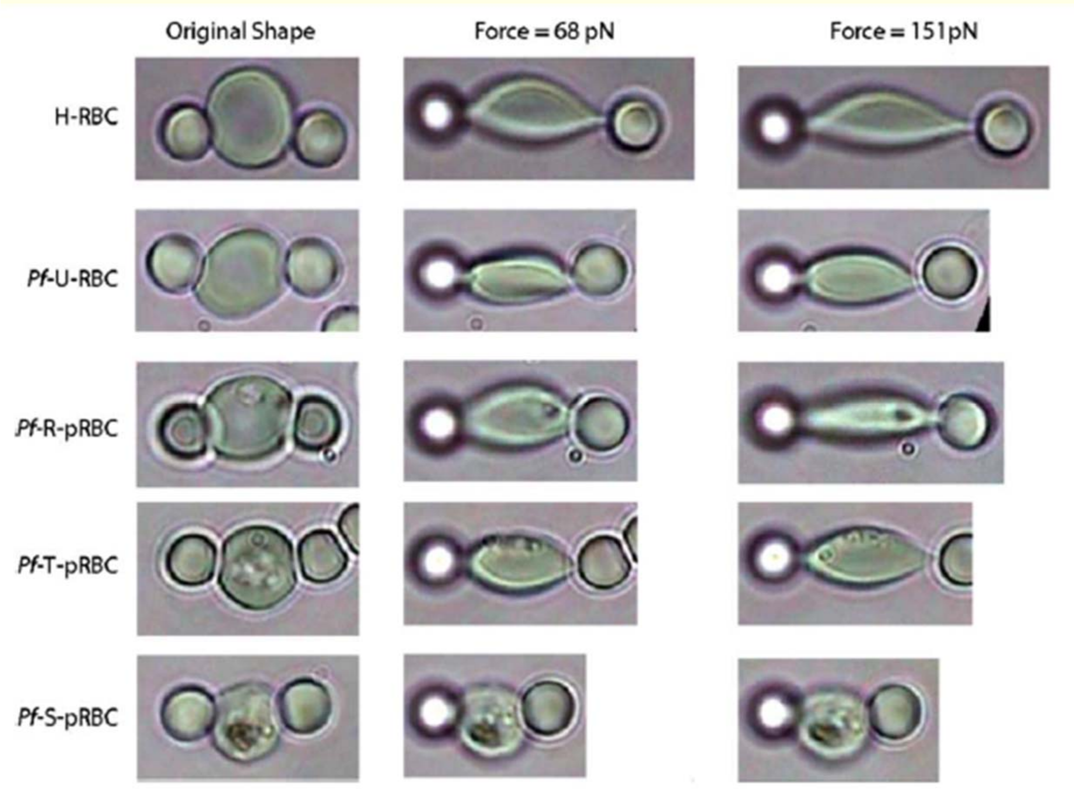
- Useful to consider problems outside your own discipline or specialty (microelectronics, functional materials)
- Useful to look for new techniques or methods that can be used to address the new problems
  - Nanoindentation
  - Substrate curvature techniques
- Connecting the new techniques to the new problems leads to new lines of research that both contribute to the solution of important problems and advance the discipline (mechanical behavior)

# Subra Suresh's work on Malaria

Acta Biomaterialia 1 (2005) 15–30

Connections between single-cell biomechanics and human disease states: gastrointestinal cancer and malaria

S. Suresh [a,b,*], J. Spatz [c], J.P. Mills [a], A. Micoulet [c], M. Dao [a], C.T. Lim [d], M. Beil [e], T. Seufferlein [e]




*Huge change in elastic rigidity*

From research on metal fatigue and thin film mechanical properties to research on malaria!

Problem: Malaria induced by P. falciparum in red blood cells; most widespread parasitic disease in humans

Technique: Optical tweezers *S. Henon S et al. J. Biophys (1999)*

*W.D. Nix, Wadsworth Symposium*

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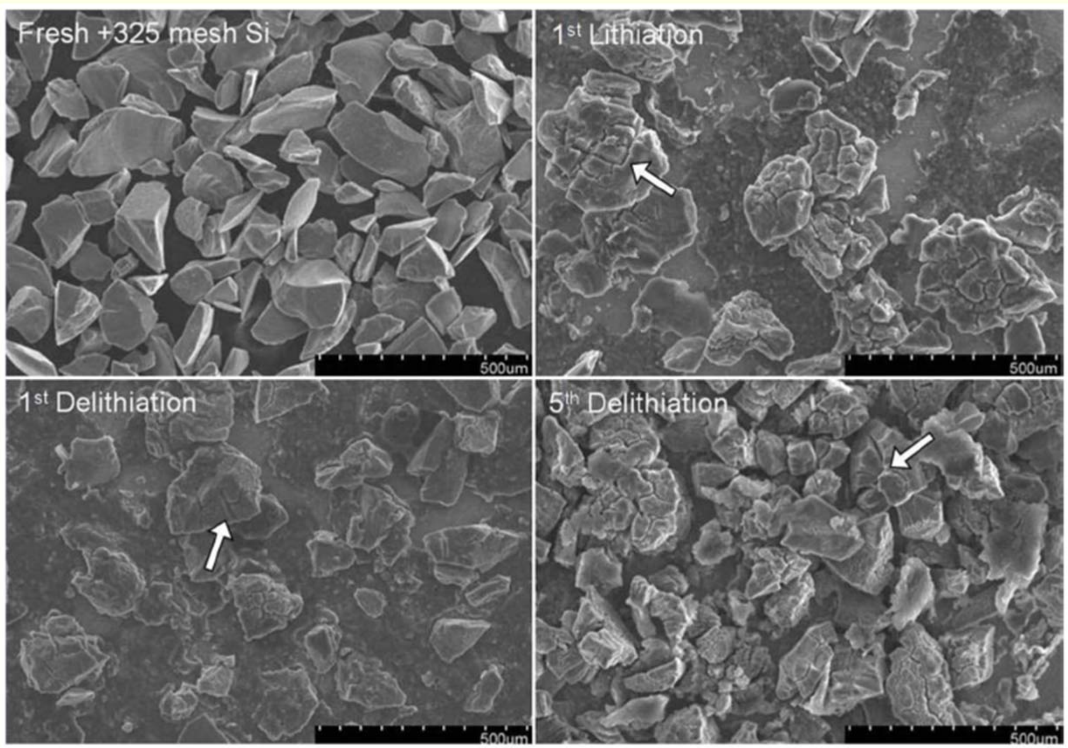
# A new problem in the field of lithium ion batteries - decrepitation

**Decrepitation Model For Capacity Loss During Cycling of Alloys in Rechargeable Electrochemical Systems**

**R.A. Huggins* and W.D. Nix****

Ionics, Vol. 6, 57-63 (2000)




Smaller particles resist fracture – understood in terms of fracture mechanics

But problem did not attract attention until….

Nanowire electrodes synthesized!

*K. Rhodes et al. Journal ECS (2010)*



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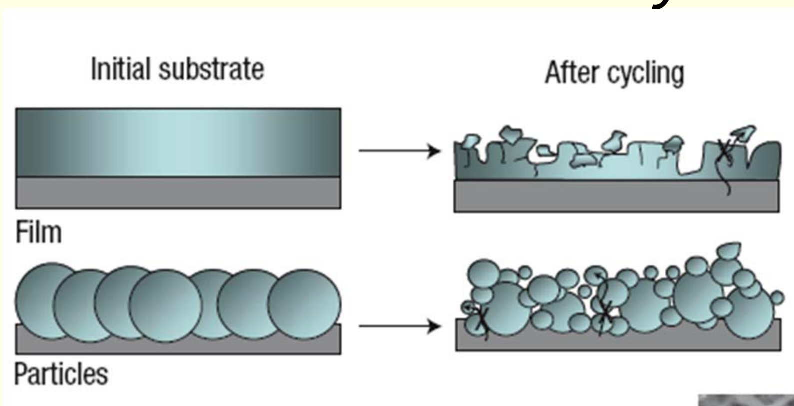
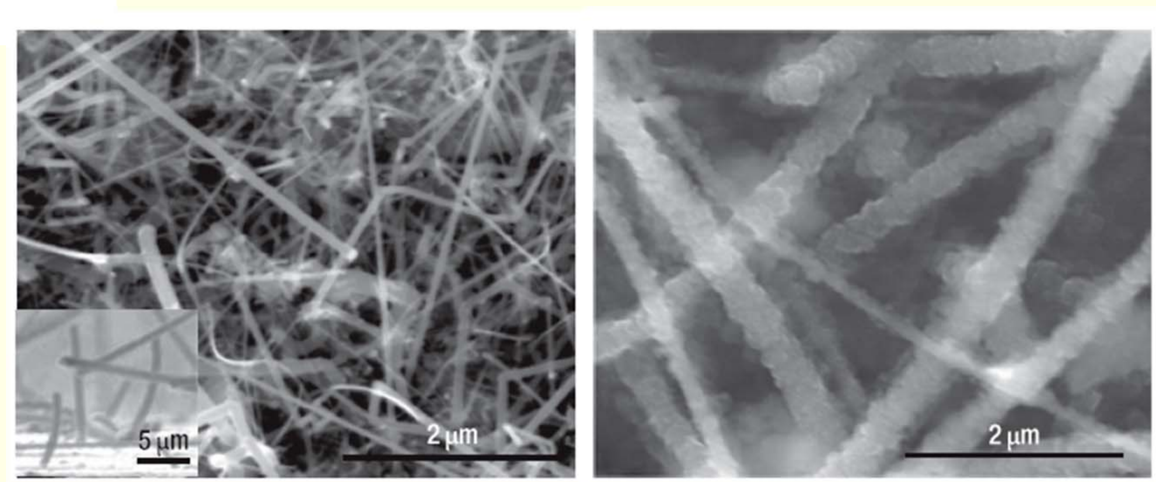
# The decrepitation problem and a nanowire solution

*Si anode in $Li^+$ battery*




*Silicon is a promising anodic material*

*Experiences huge volume expansion and decrepitation*

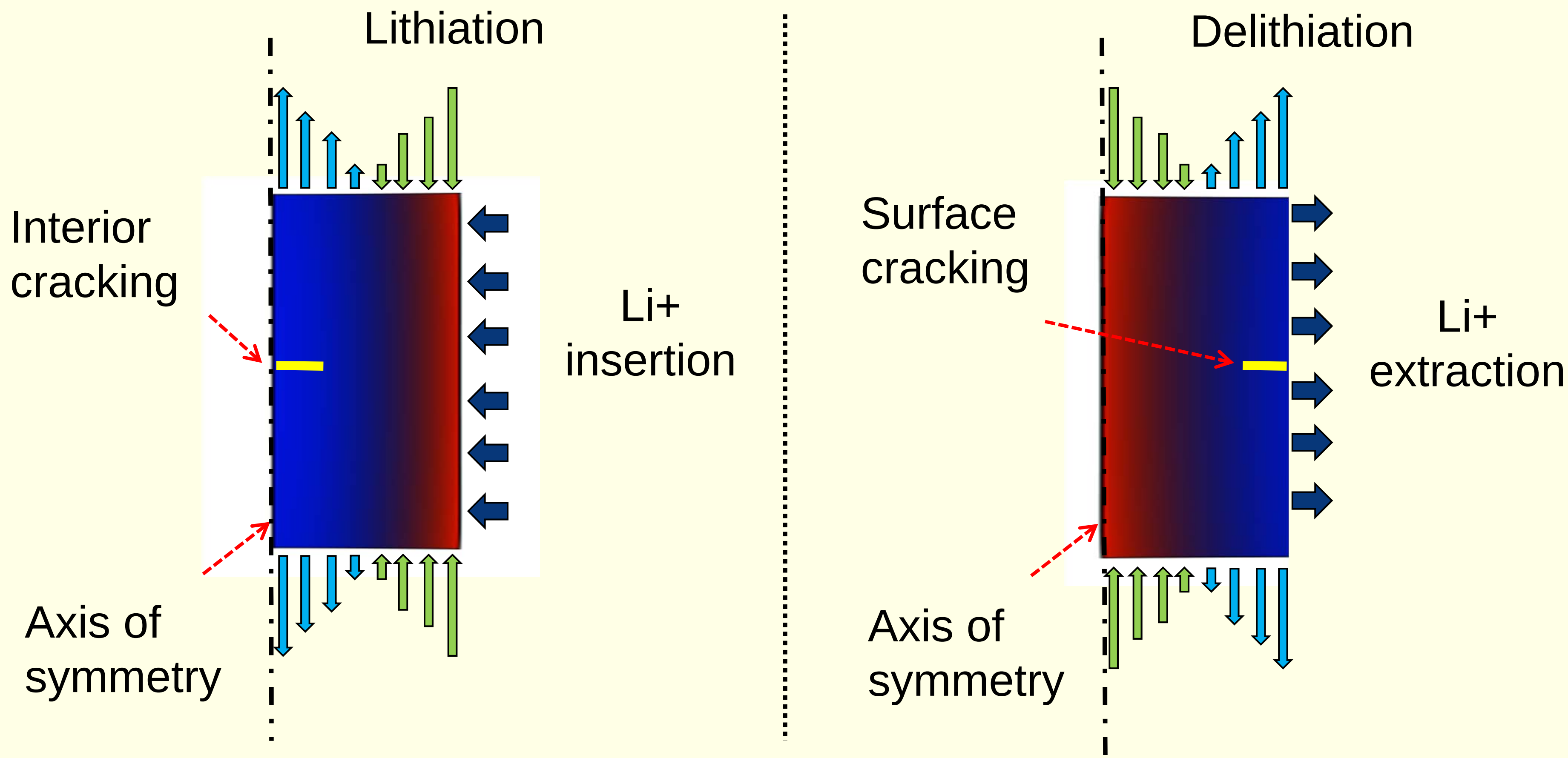



*Nanowire electrodes more tolerant*

*C. K. Chan et. al. Nature Nanotech. (2008)*

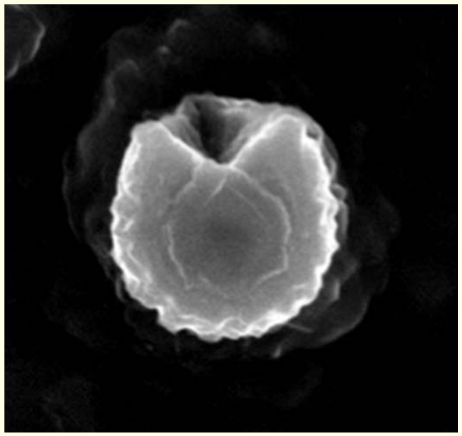
*Is there a critical size?*

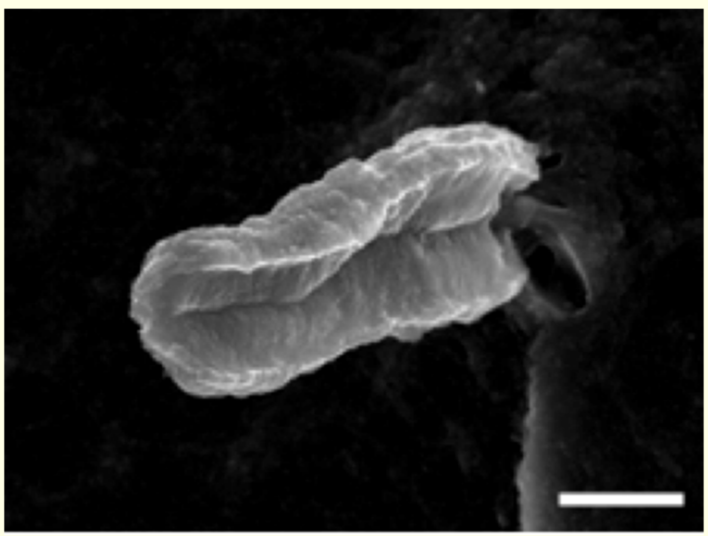
# Modeling fracture using the electrochemical shock – thermal shock analogy

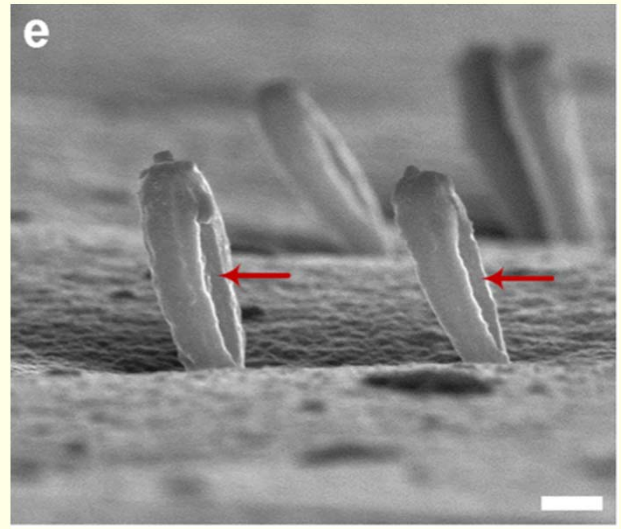


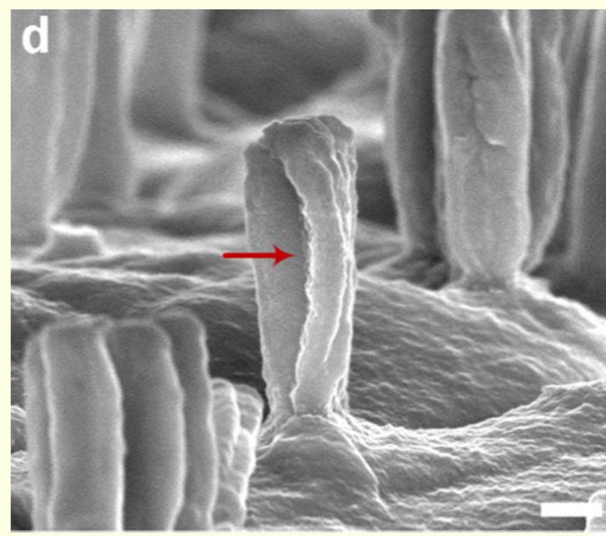

*I. Ryu et. al., JMPS, 2011*

# But surface cracking of crystalline Si is observed during lithiation!








*W.D. Nix, Wadsworth Symposium*

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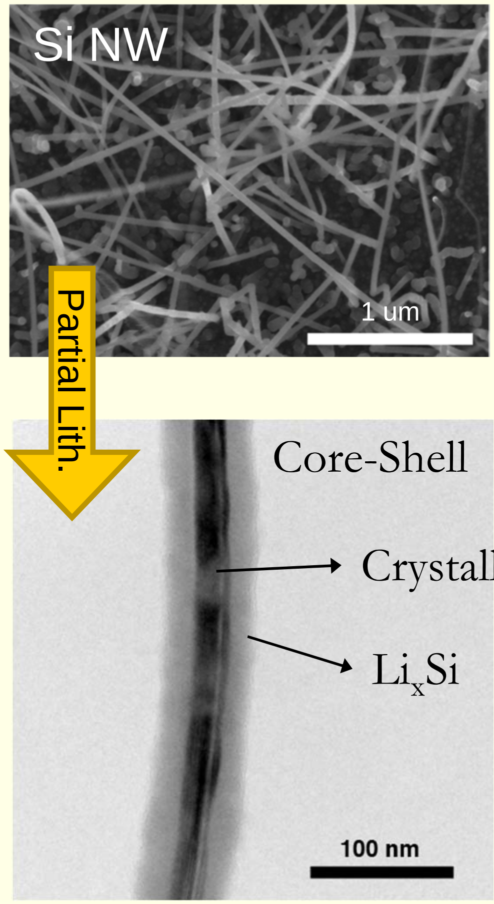
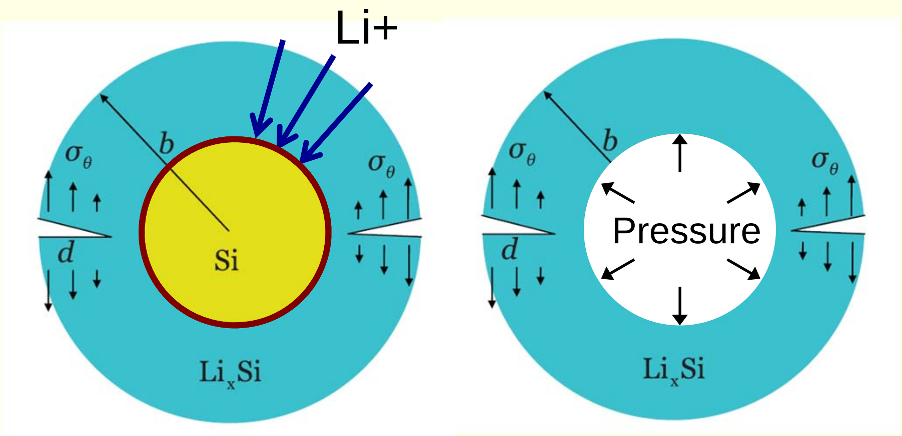
# Core-shell lithiation of Si NWs

*Two phase core-shell*

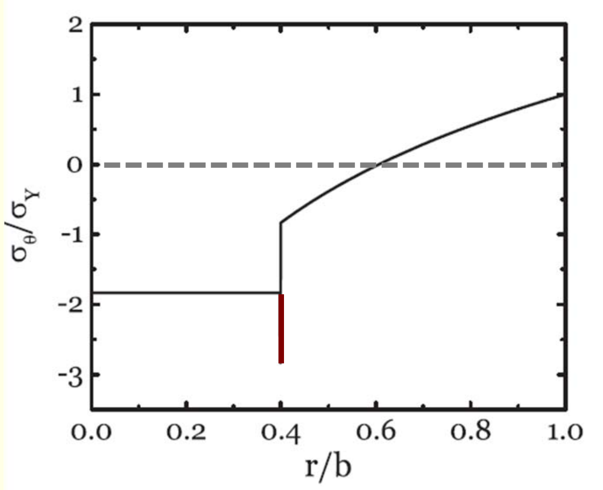



*K. Zhao, .. Z. Suo, et al., ECS, (2012)*

Interface reaction controlled




$$\sigma_\theta = \sigma_Y(1 - \ln(b/r))$$




Tension
at surface

*W.D. Nix, Wadsworth Symposium*

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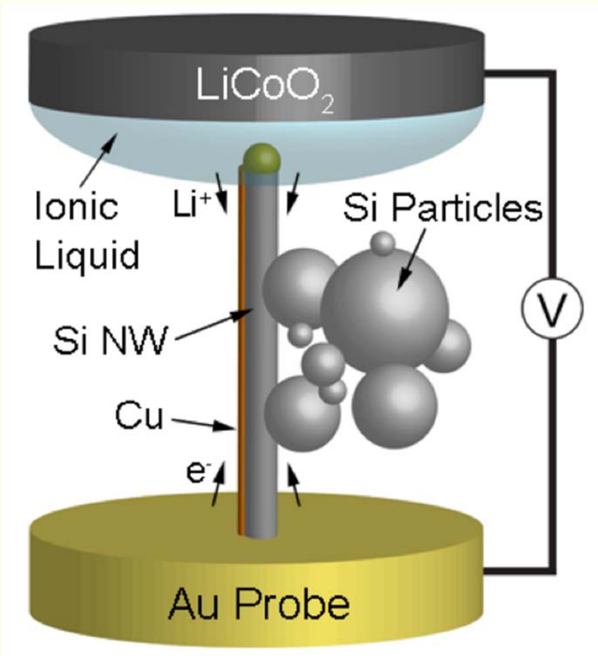
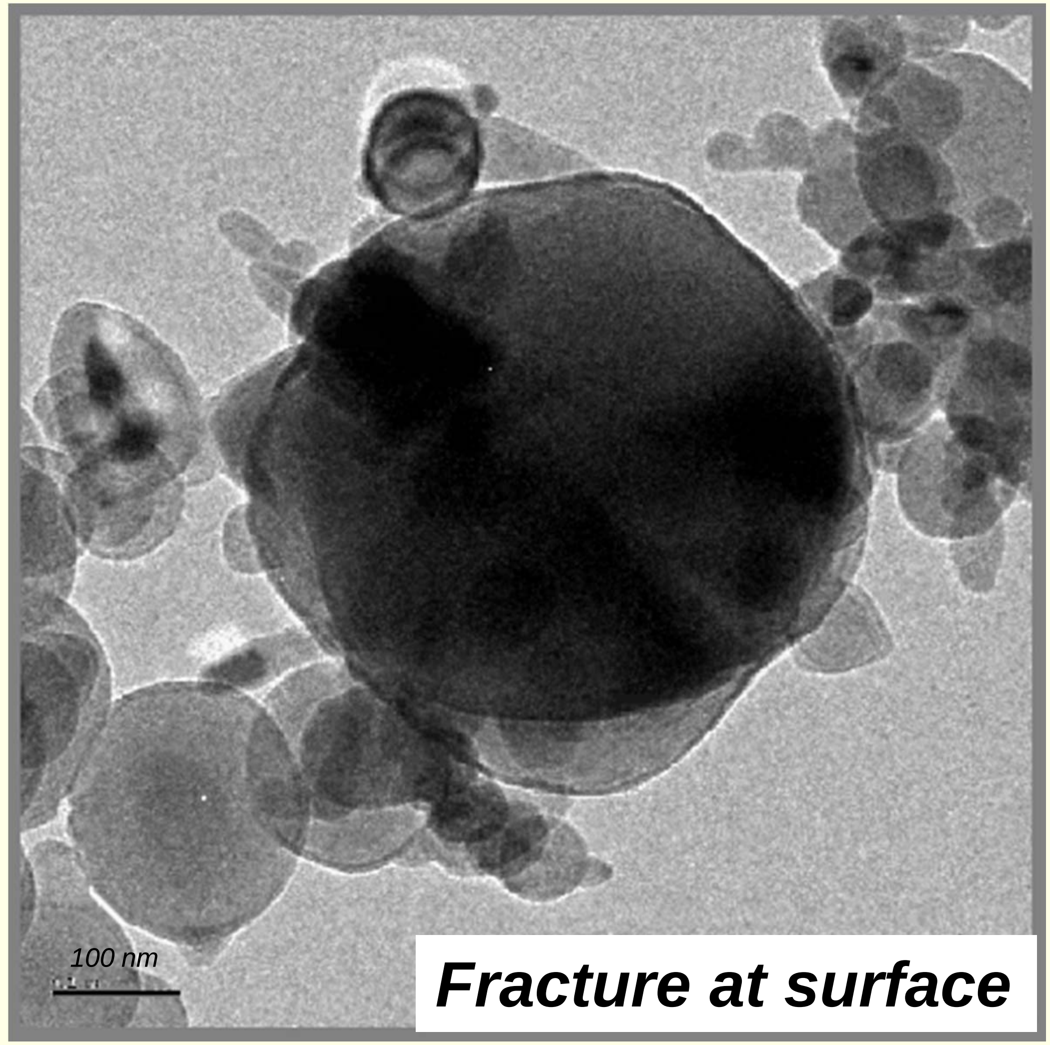
# In-situ TEM of Si nanoparticles during lithiation

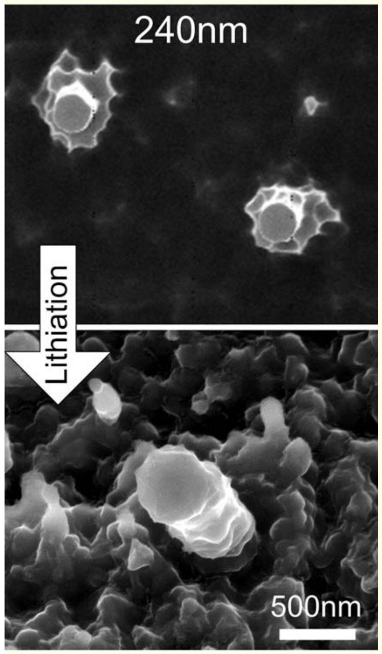


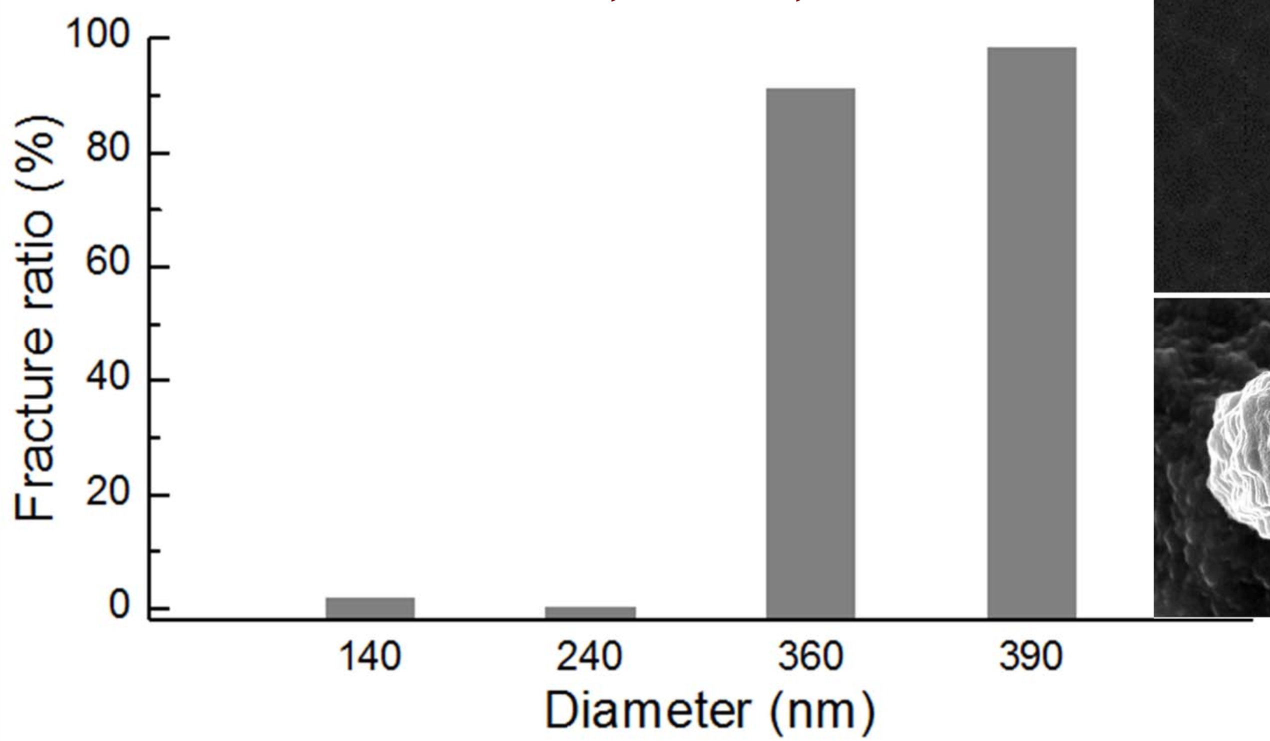



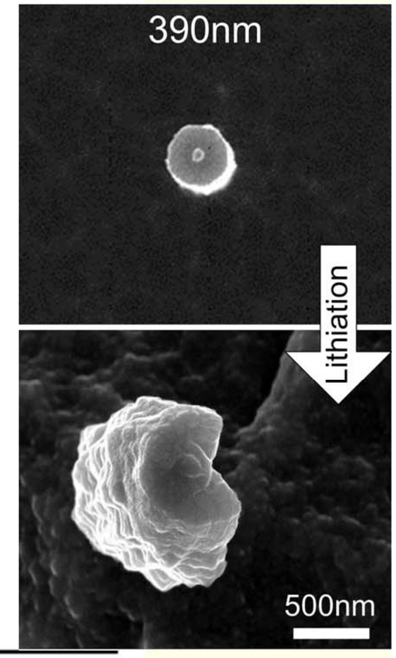

*M.T. McDowell, I. Ryu, S. W. Lee et al., Advanced Materials, 2012*

# Size dependence of fracture <111> Si nanopillars

*S. W. Lee et al., PNAS, 2012*



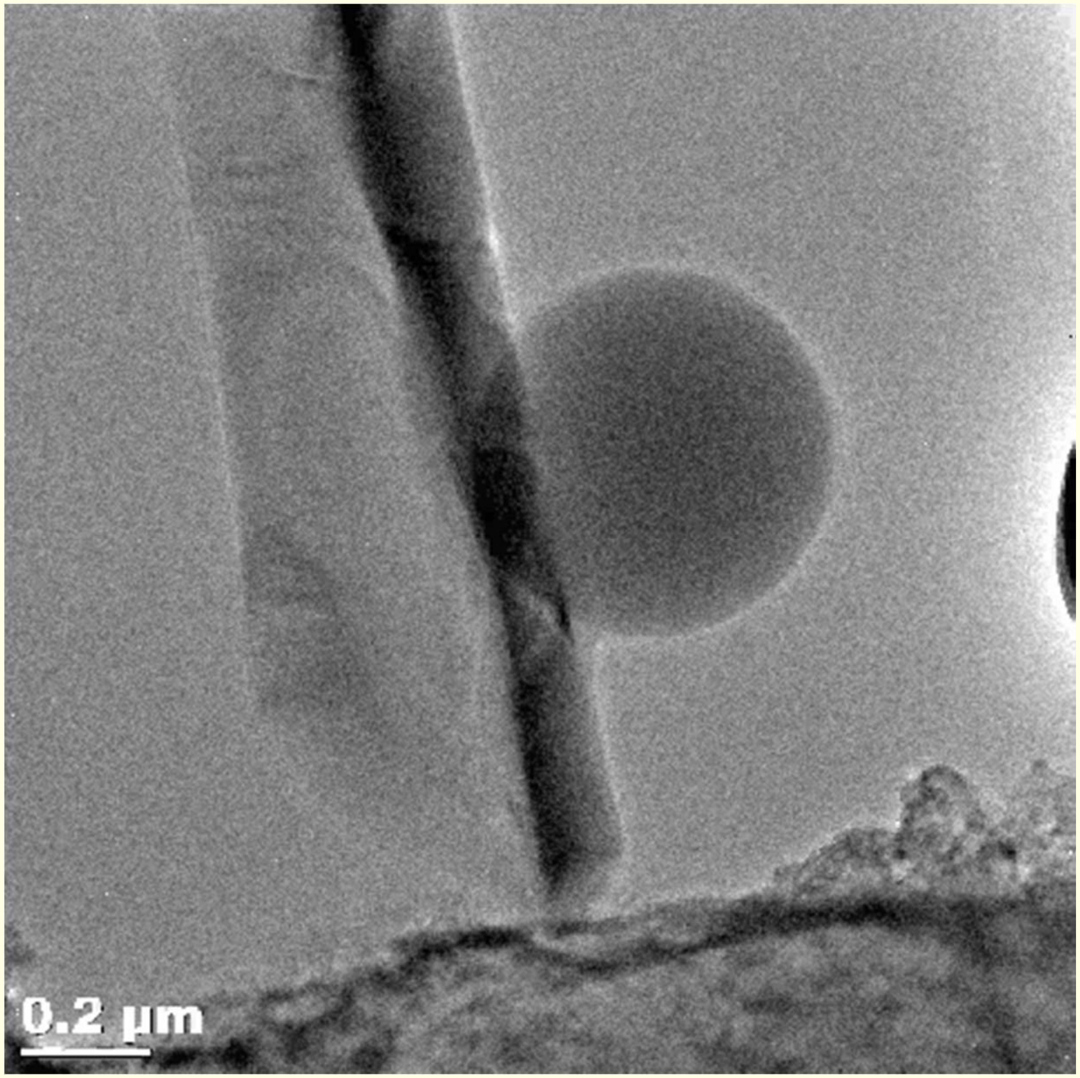




Smaller size and slow reaction prevent fracture

~300 nm is critical diameter of fracture

*W.D. Nix, Wadsworth Symposium*

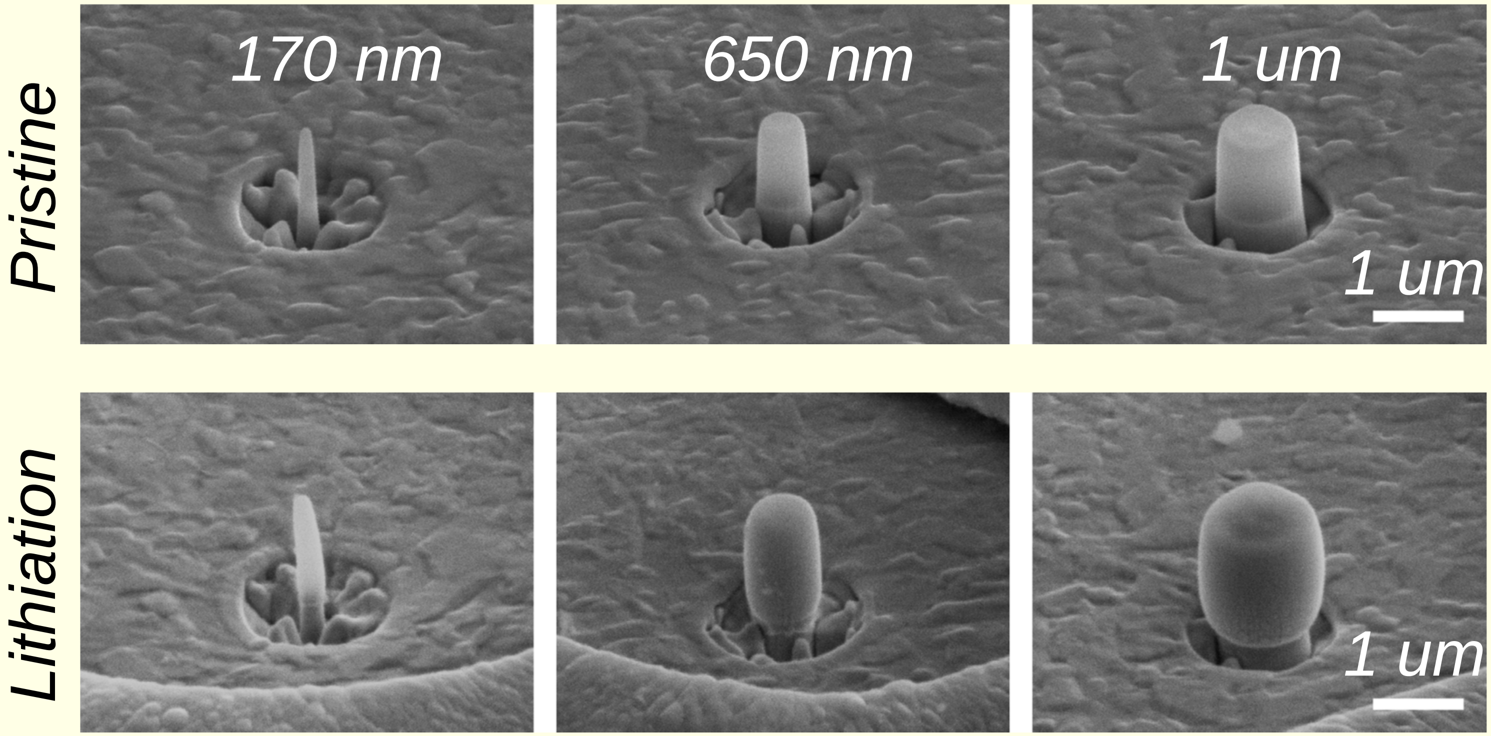
# Lithiation of an amorphous Si nanoparticle




*M.T. McDowell et al, Nano Letters (2013)*

No Fracture!

# Lithiation of amorphous Si nanopillars




*No fracture observed for diameters up to a few micrometers*

*L.A. Berla et al., in preparation, 2013*

# What are the lessons learned?

- Useful to consider problems outside your own discipline or specialty (electrochemistry and batteries)
- Useful to look for new techniques or methods that can be used to address the new problems
  Nanowires
  Nanopillars
- Connecting the new techniques to the new problems leads to new lines of research that both contribute to the solution of important problems and advance the discipline (mechanical behavior)

# Conclusions

- Useful to consider problems outside your own discipline or specialty – beware of learning more and more about less and less
- Useful to look for new techniques or methods that can be used to address the new problems – they need not be "invented here"
- Connecting the new techniques to the new problems leads to new lines of research that both contribute to the solution of important problems and advance the discipline
- This style of research has become a trend in recent decades

**Thank you for your interest and attention**

*and congratulations to Jeff*