SIZE MATTERS

Mechanical Properties of Nano-sized Single Crystals

Julia R. Greer

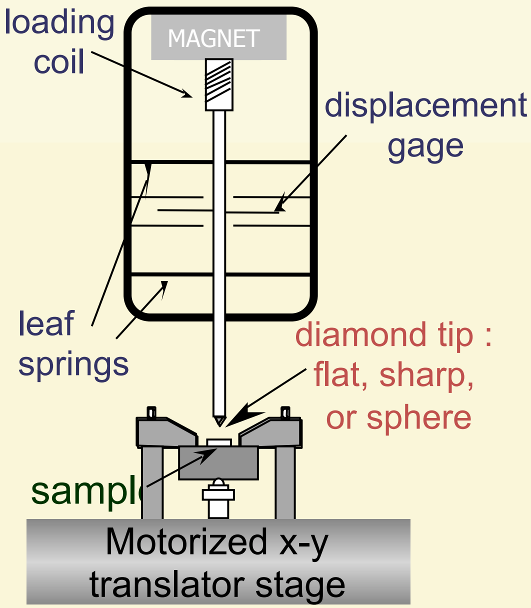
But really it's the work of
graduate student A.T. Jennings
and post-doc Ju-Young Kim

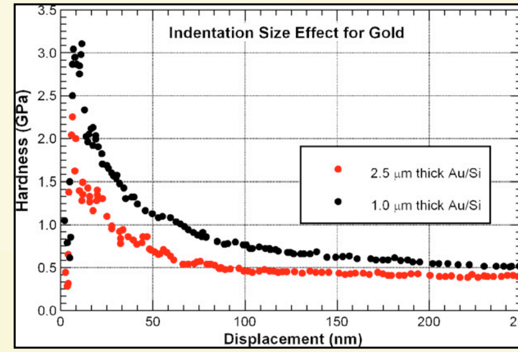
Division of Engineering and Applied Science
California Institute of Technology

Materials and Length Scales

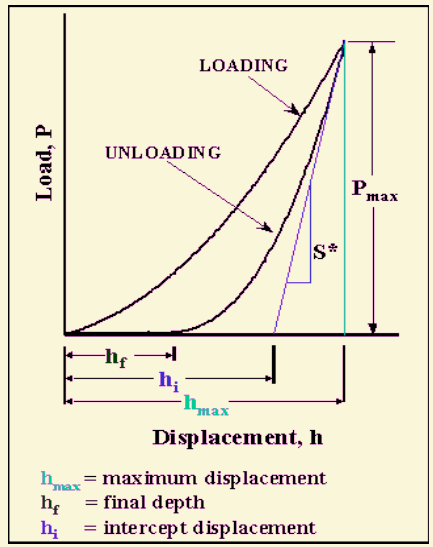
In nanocrystals (quantum dots, nanowires, nanotubes, etc.)
size modification tunes a variety of properties: optical, electronic, plasmonic, thermal, acoustic, etc. which
brings into question material structural integrity

Background: Nanoindentation

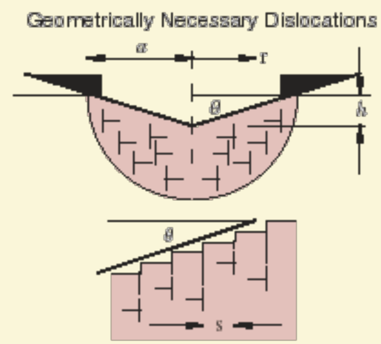




Nix, Feng, Greer, et al Thin Solid Films (2007)



VanLandingham, M.R. et al (2003)



$$\rho_{GND} = \frac{3\tan^2\theta}{2bh}$$

$$\therefore \left(\frac{H(h)}{H_0}\right)^2 = 1 + h^* \times \frac{1}{h}$$

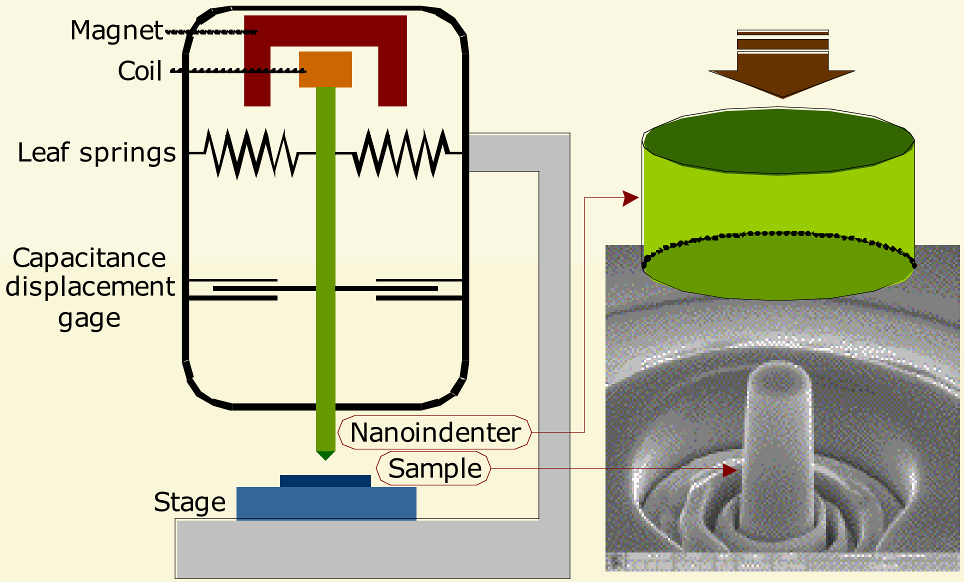
strain gradients drive hardness increase!

Disadvantages: Strain gradients, complex stress-strain calculations, limited plasticity information
Advantages: Elastic properties, hardness, deformation volume control

Great need for experimental techniques testing mechanical deformation at nano-scale *without* strain gradients!

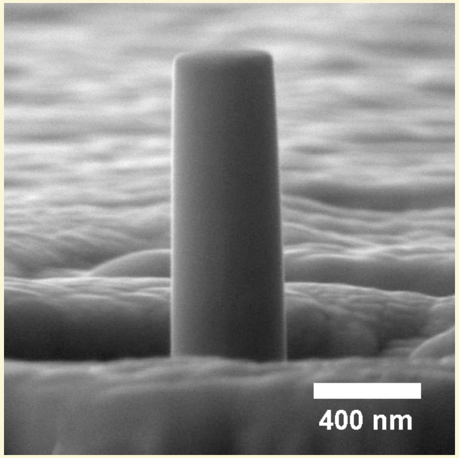
Micro-compression experimental setup

Nanoindenter
Agilent G200



- Flat punch indenter tip
- Constant displacement rate

Nano-pillar fabrication:
Mainly Focused Ion Beam (FIB)



- Diameter: 100 ~ 900 nm

Load-Displacement Data

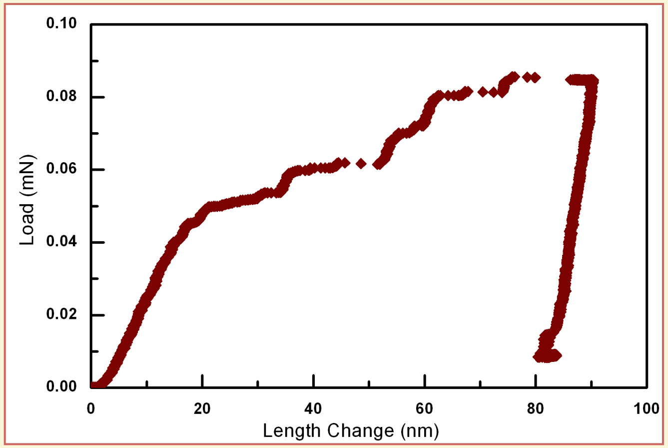
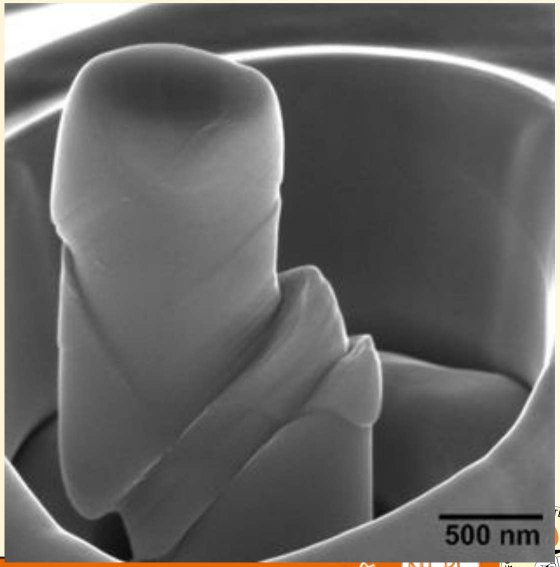
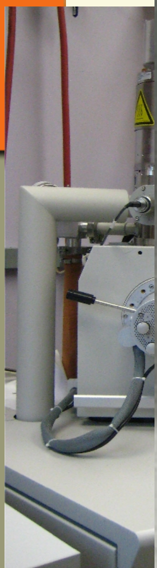
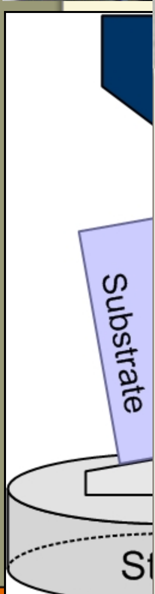
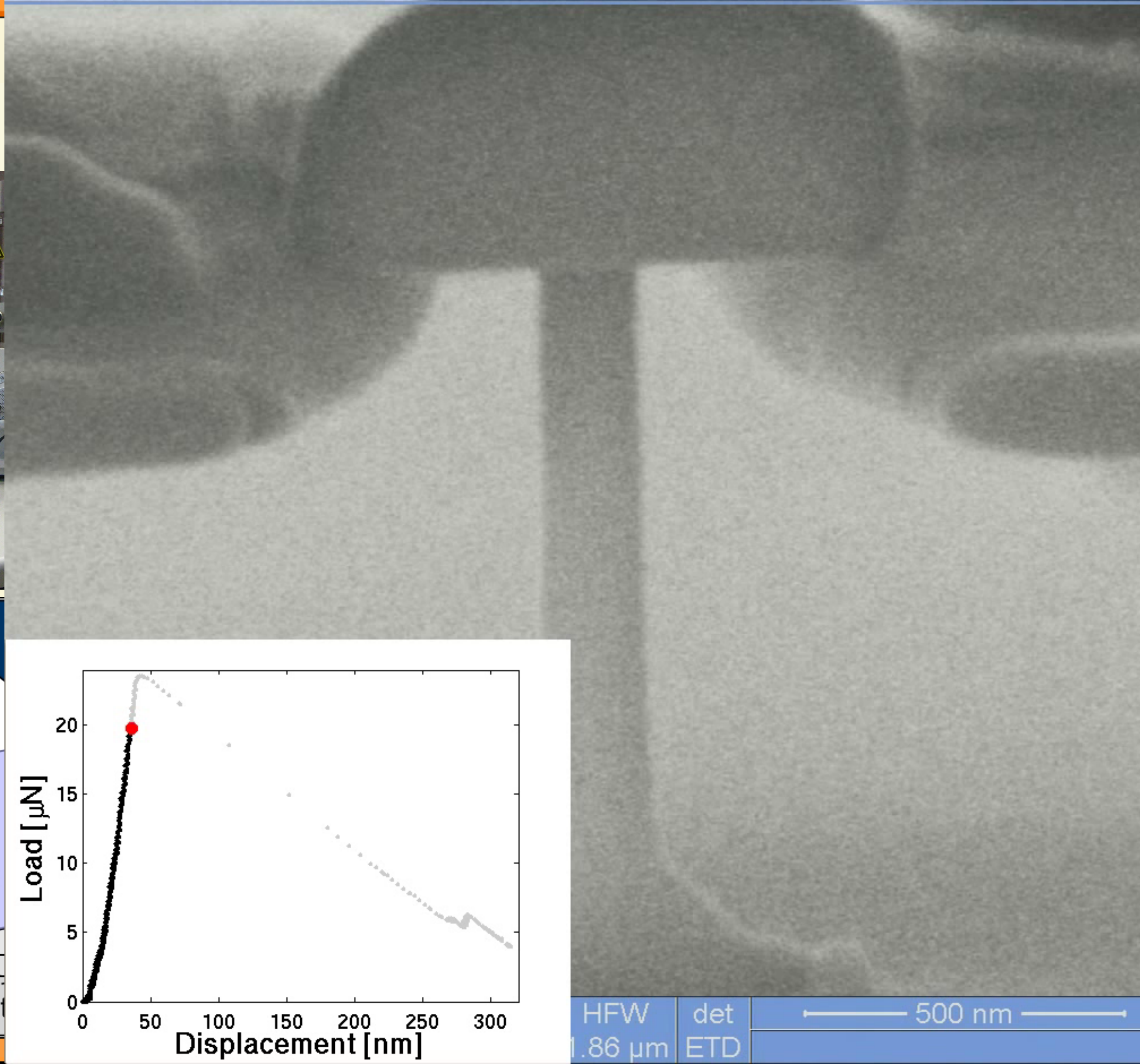


Image after compression





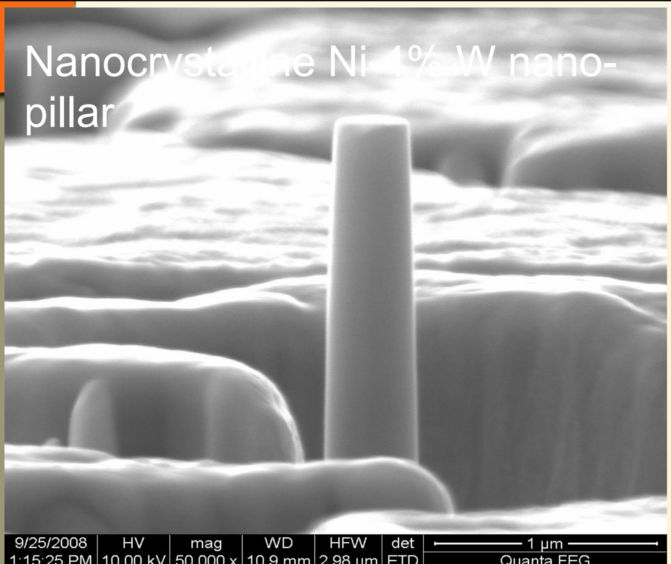

Substrate
St

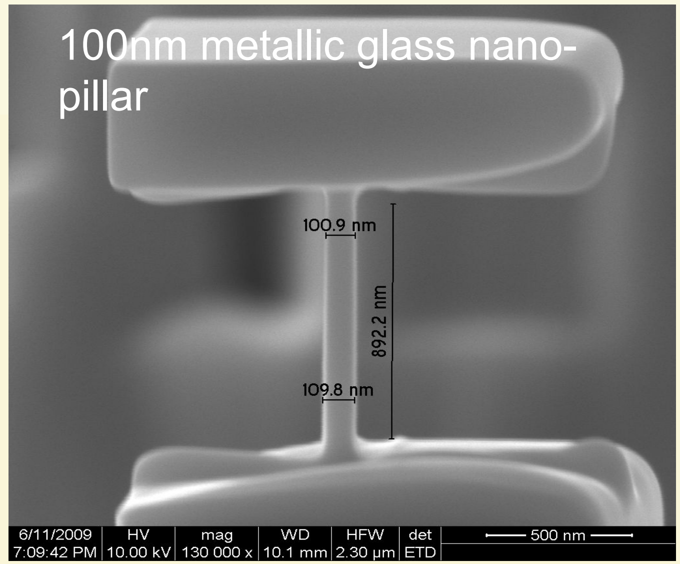

Load [μN]
Displacement [nm]
0
5
10
15
20
0
50
100
150
200
250
300
HFW
1.86 μm
det
ETD
500 nm

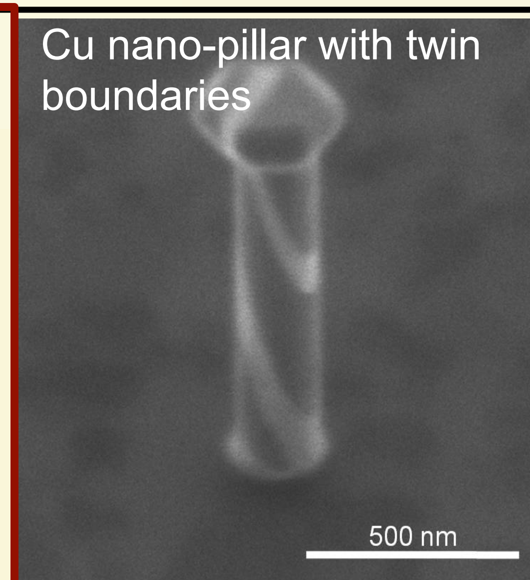
Nano-pillar Fabrication Methods

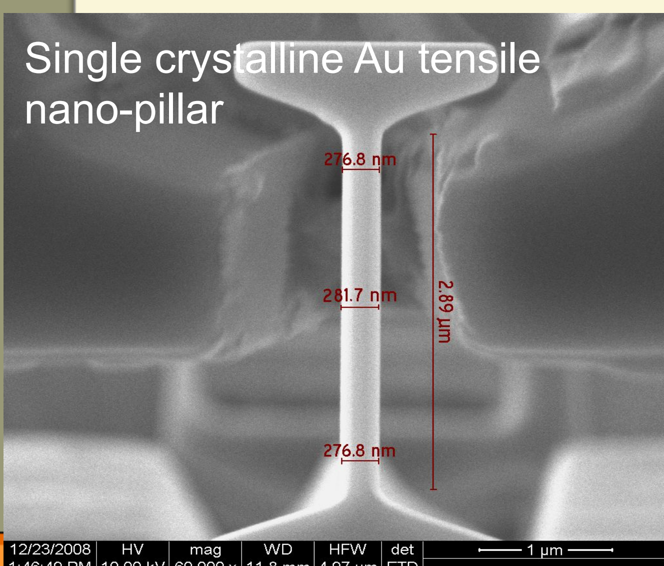
Focused Ion Beam

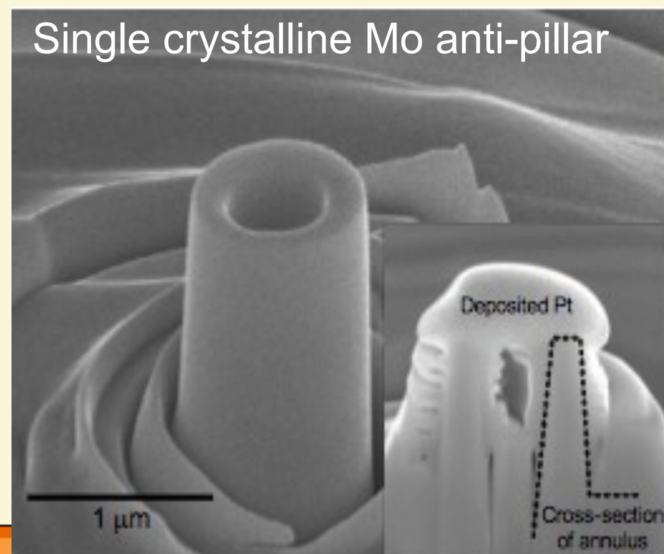
FIB-less

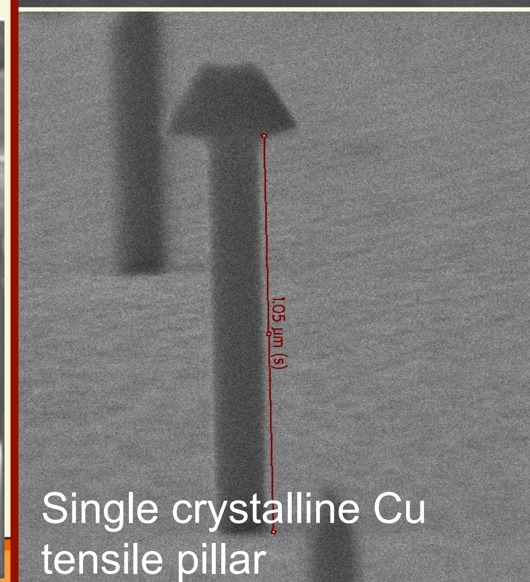




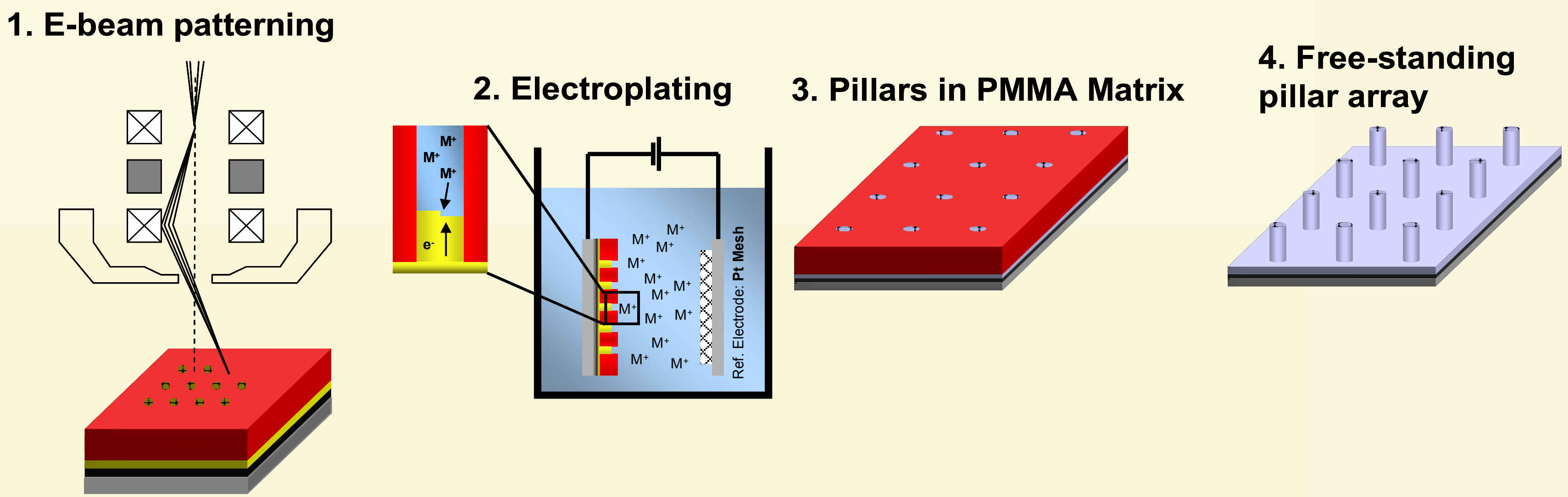


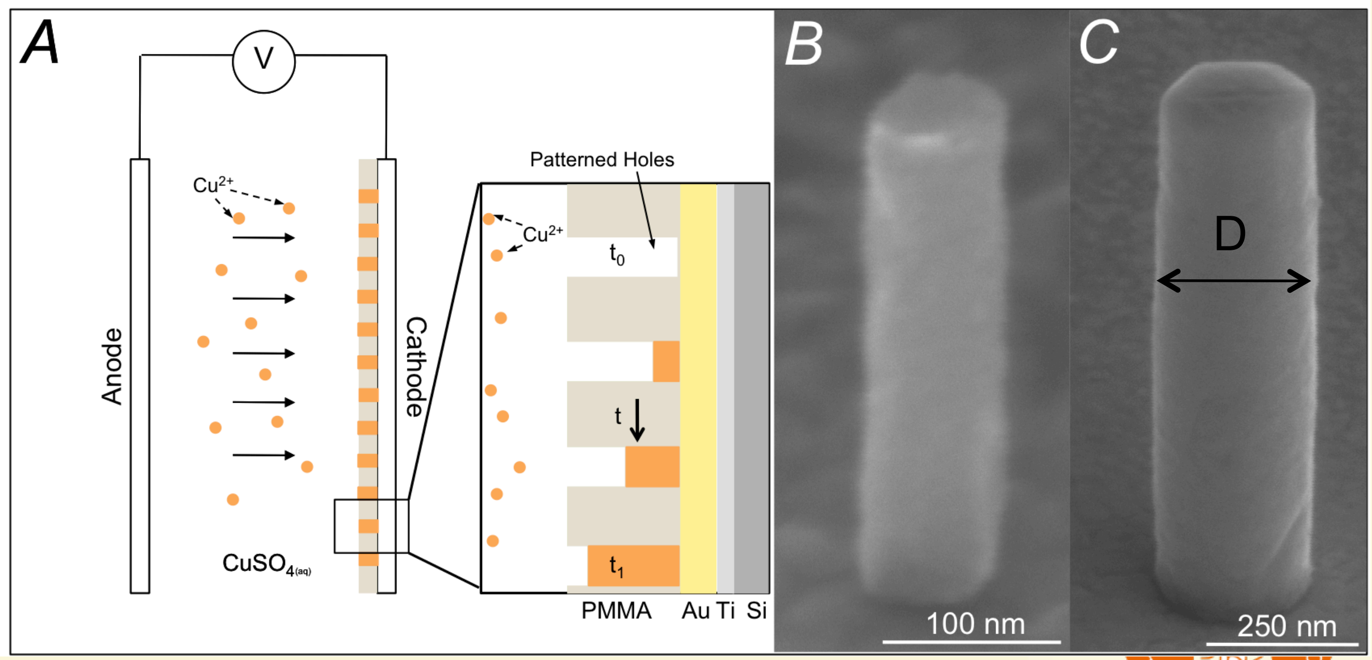






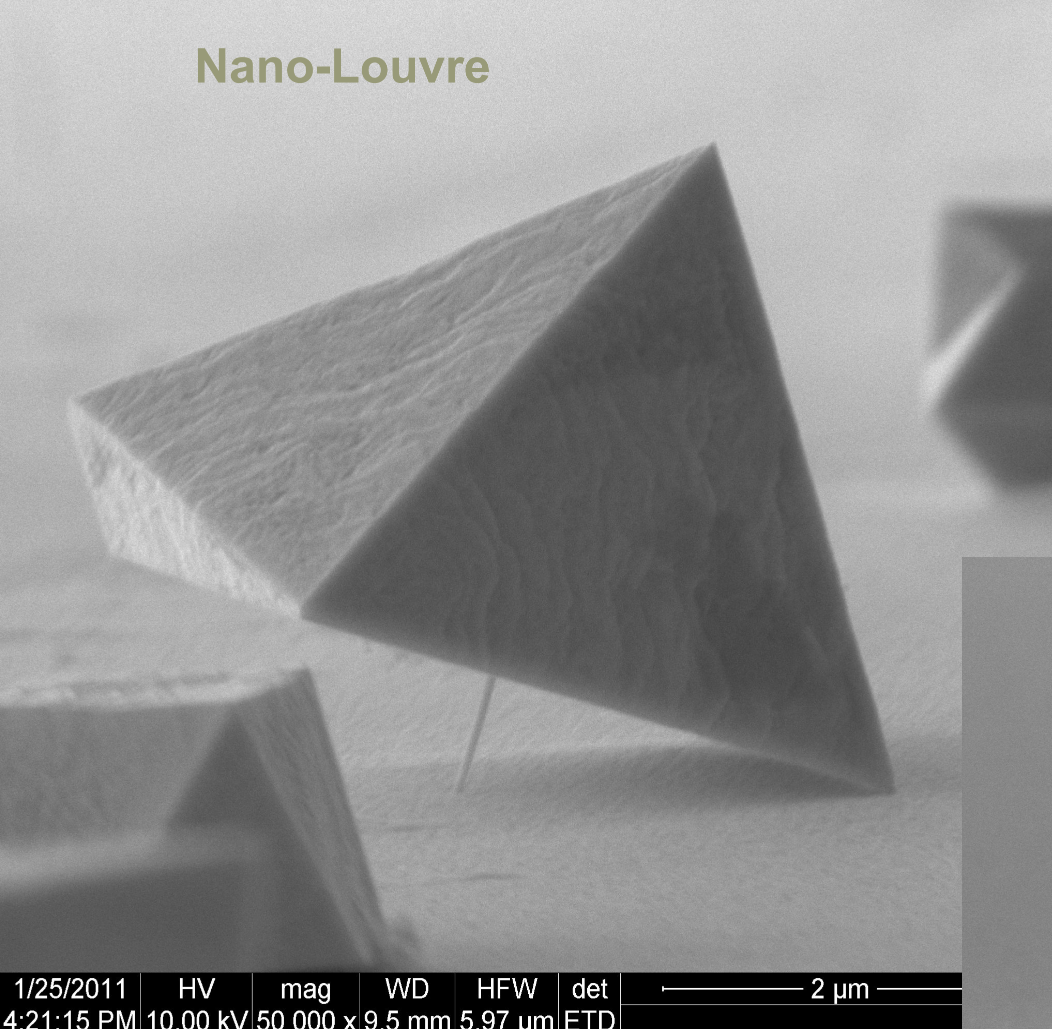
FIB-less fabrication: E-beam Litho => Electroplating

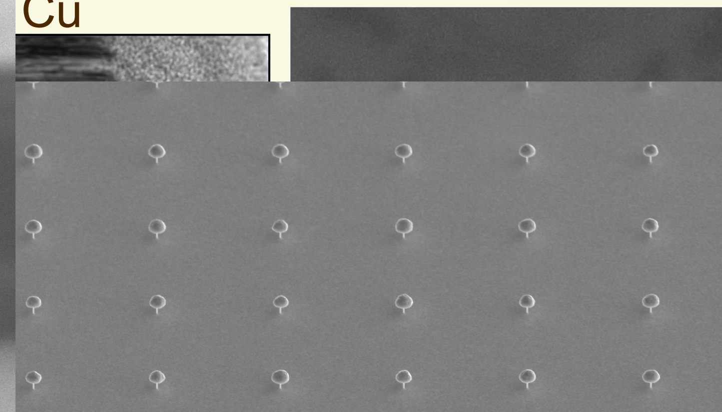


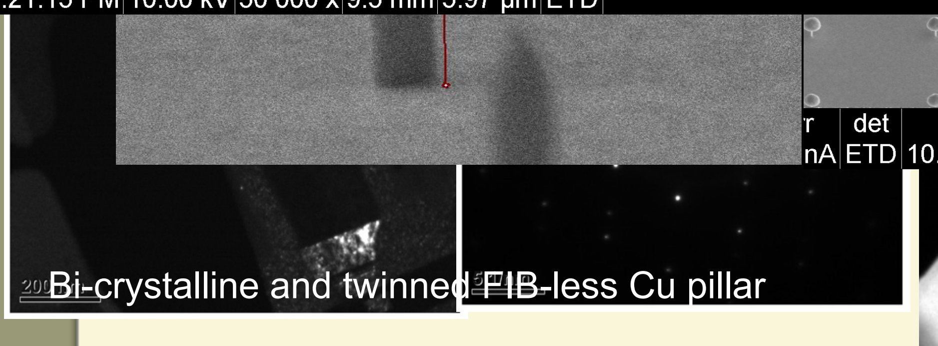


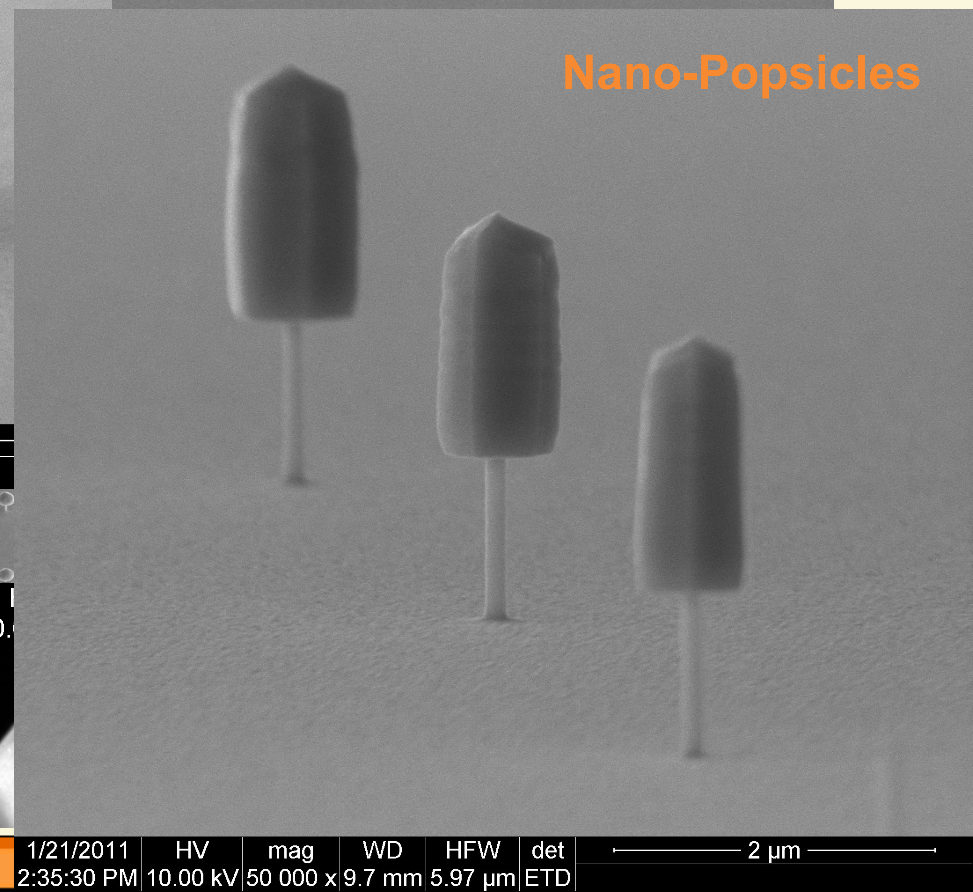
rough Novel Synthesis

Cu



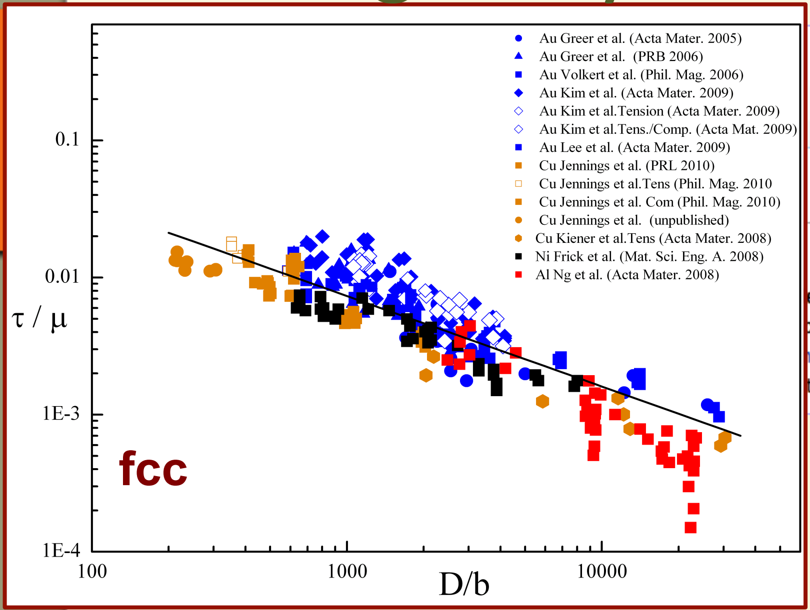


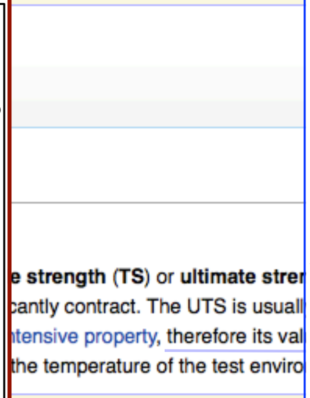




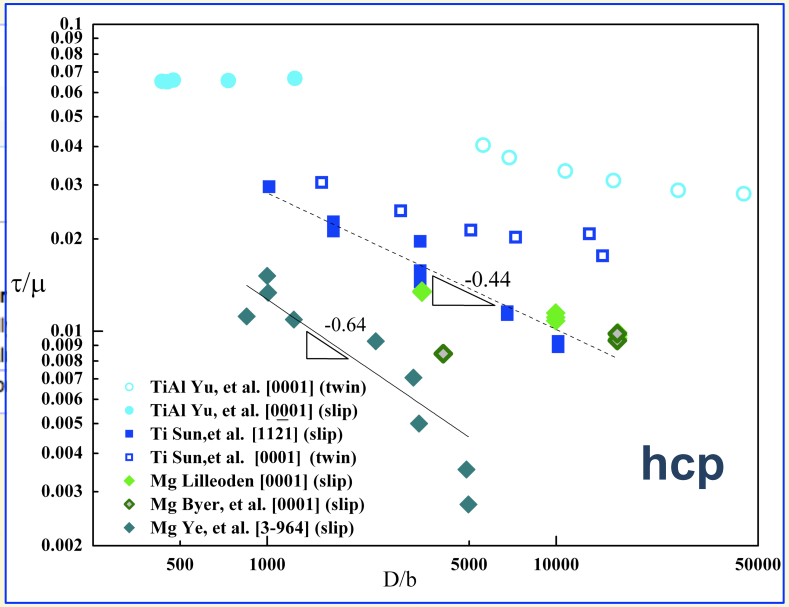
D. Jang, W. Cai, J.R. Greer *Nano Lett.* **11** (4) (2011)

Single Crystals: Ubiquitous Size Effect

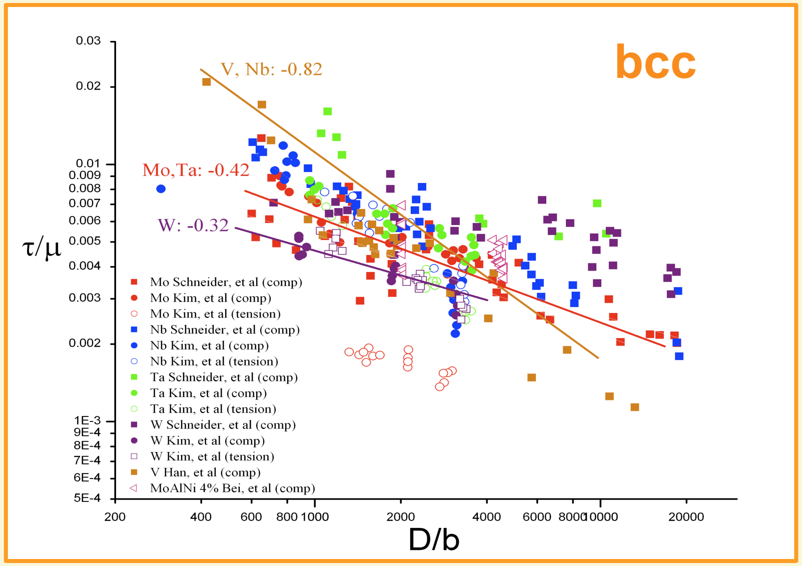




$$\sigma_f \propto D^{-n}$$

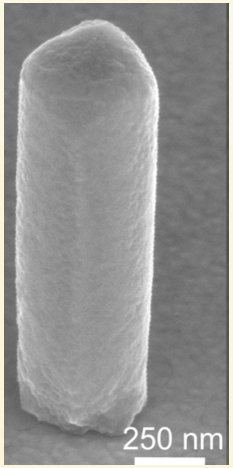


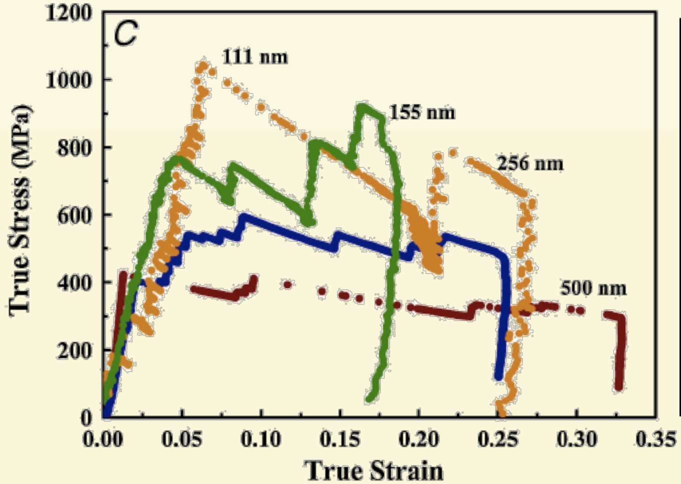
Dislocation Nucleation-controlled plasticity

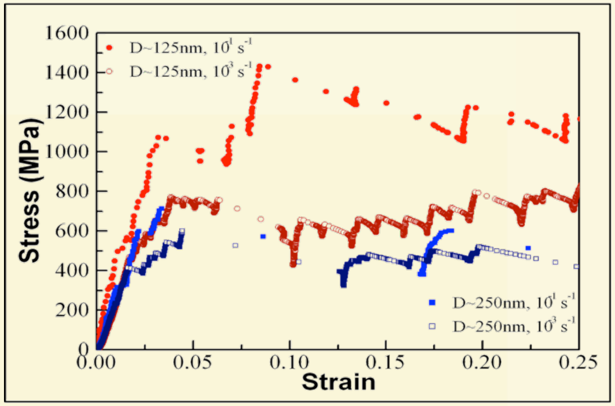


"Smaller is Stronger" and Strain Bursts

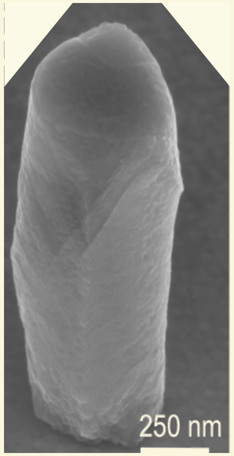
Pre-deformation



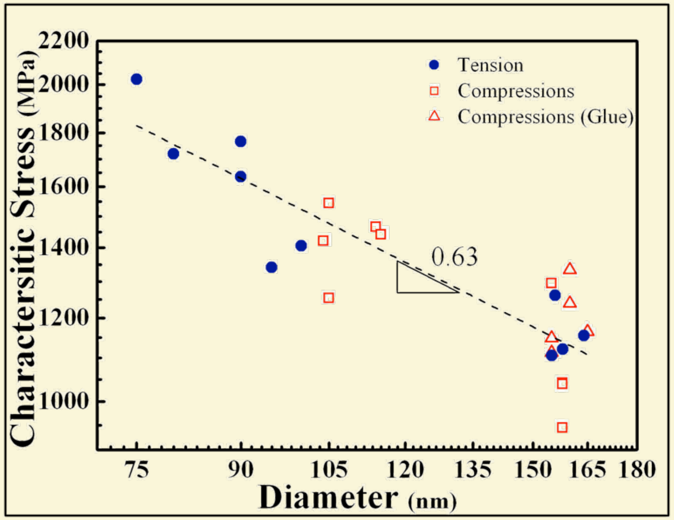


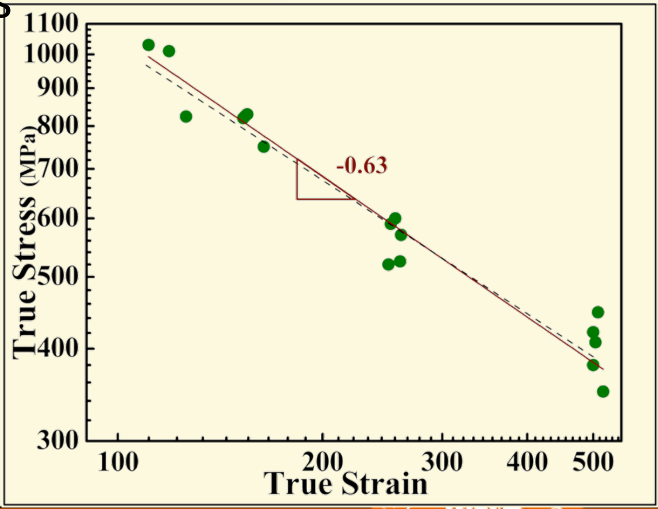


Post-deformation



Size effects with stochastic stress-strain signature and size effects are identical to FIB-fabricated pillars



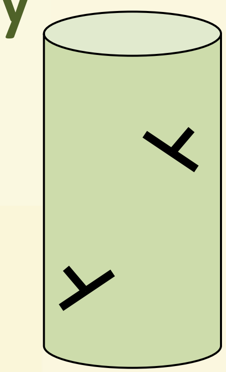


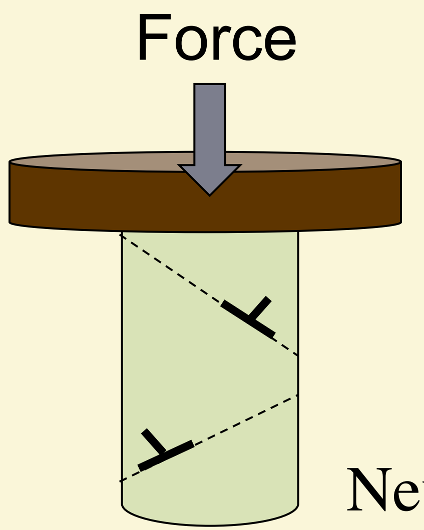
Jennings et al. *Phil Mag,* 91(7), 1108 (2010)

Jennings et al. *Phys Rev Lett,* 104, 135503 (2010)

Dislocation starvation and nucleation: source-controlled plasticity

In a nano-pillar (deeply in sub-micron regime) with non-zero initial dislocation density

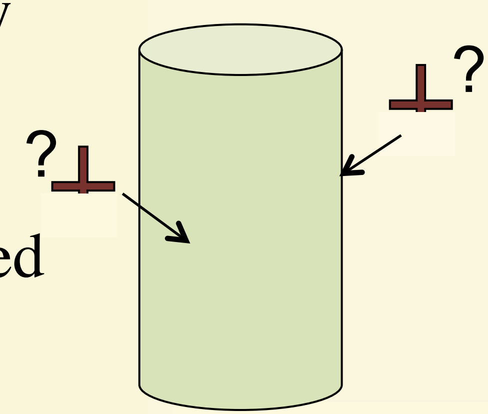




Under compression dislocations leave the crystal faster than they multiply

New dislocations have to be nucleated

WHERE?

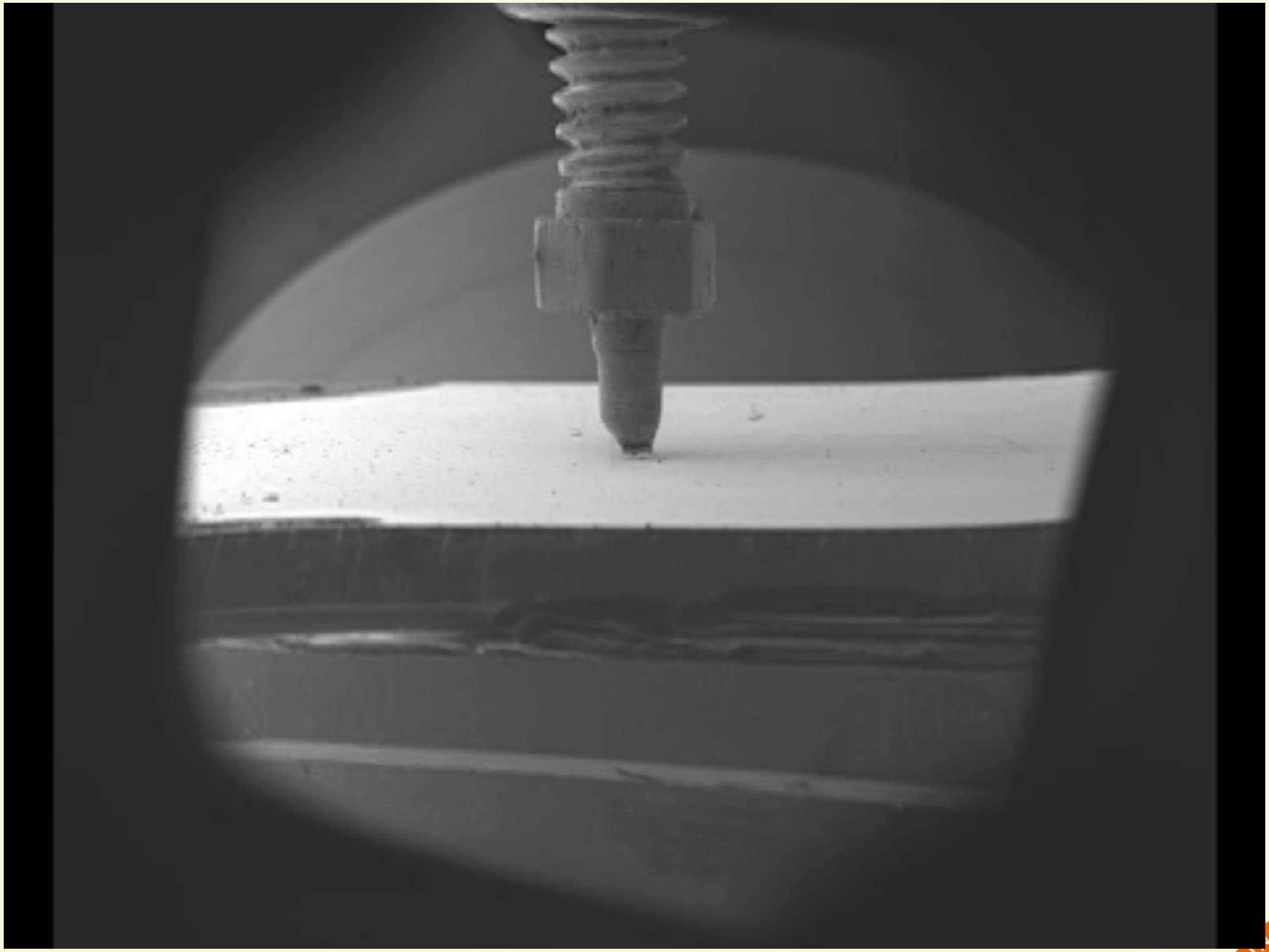


Coined hardening by dislocation starvation, occurs only in small volumes and not in bulk crystals.

Greer, J.R. and Nix, W.D. *Phys. Rev. B,* 73, 24 (2006)

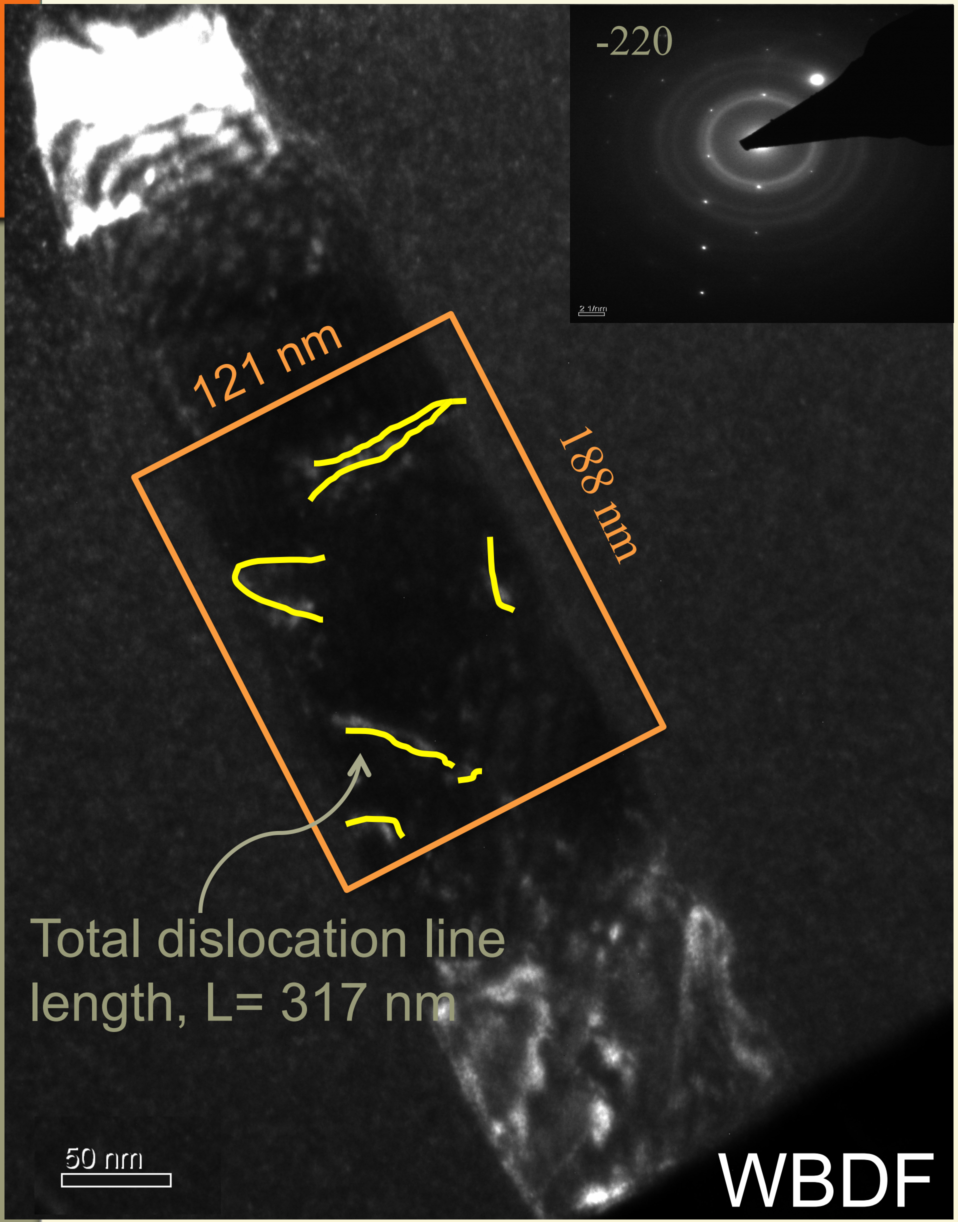
Insights into Deformation mechanisms: TEM

How do we TEM the same nano-pillars before and after deformation???



We test them directly on TEM grid!

Single Crystalline (FIB-less) Pillars are NOT dislocation-free



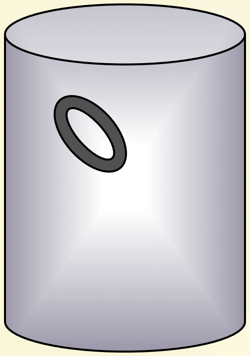
Dislocation Density:

$$\rho = L / \pi R^2 h$$

$\rho = 1.46 \times 10^{14}\ m^{-2}$

Relatively high!

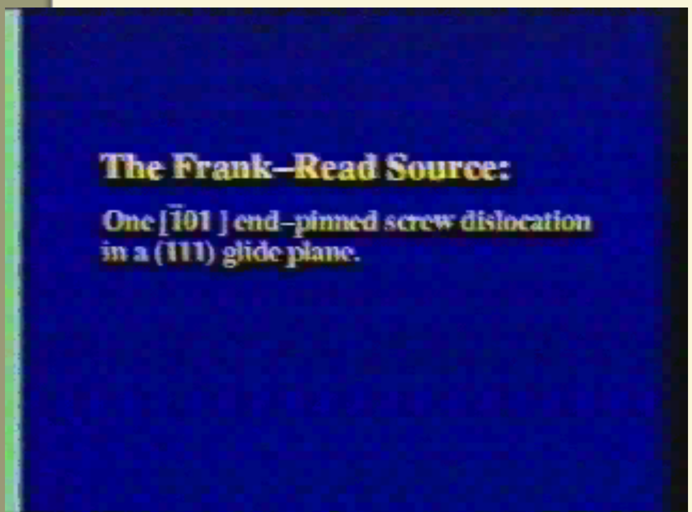
BUT important to recognize: the lowest attainable non-zero dislocation density is $1 \times 10^{12}\ m^{-2}$



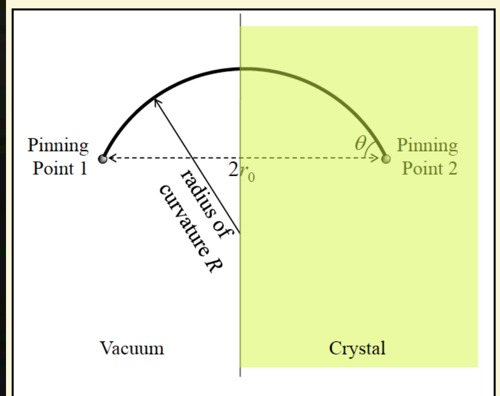
(corresponds to a 7-atom loop in 121nm x 188 nm cylindrical volume)

Dislocation Nucleation Sources

FRANK-READ Source
(a.k.a. conventional)
(Ω~100-1000b^3)

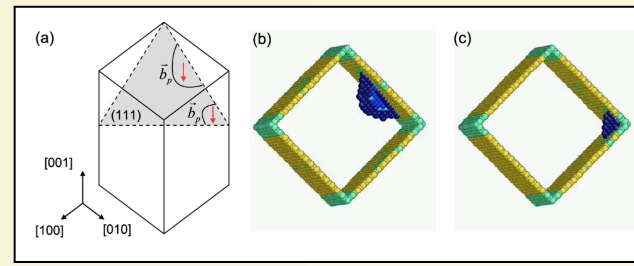


"Truncated" or
SINGLE ARM Source
(micron-sized pillars)
(Ω~50-500b^3)



Parthasarathy et al. *Scripta Mat* (2007)
Rao et al. *Acta Mat* (2008)
Tang et al *Phys Rev Lett* (2008)
Oh et al. *Nature Mat* (2009)
Weinberger et al. *Scripta Mat* (2010)

SURFACE Source
(Ω~1-10b^3)

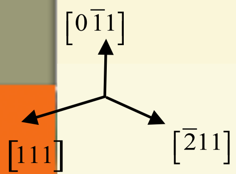


Gall et al *Nano Letters* (2004)
Diao et al *Acta Mat* (2006)
Zhu et al *Phys Rev Lett* (2008)
Lu et al *Nature Nano* (2010)

$$\Omega_{SAS} = \frac{\Omega_{F-R}}{2}$$

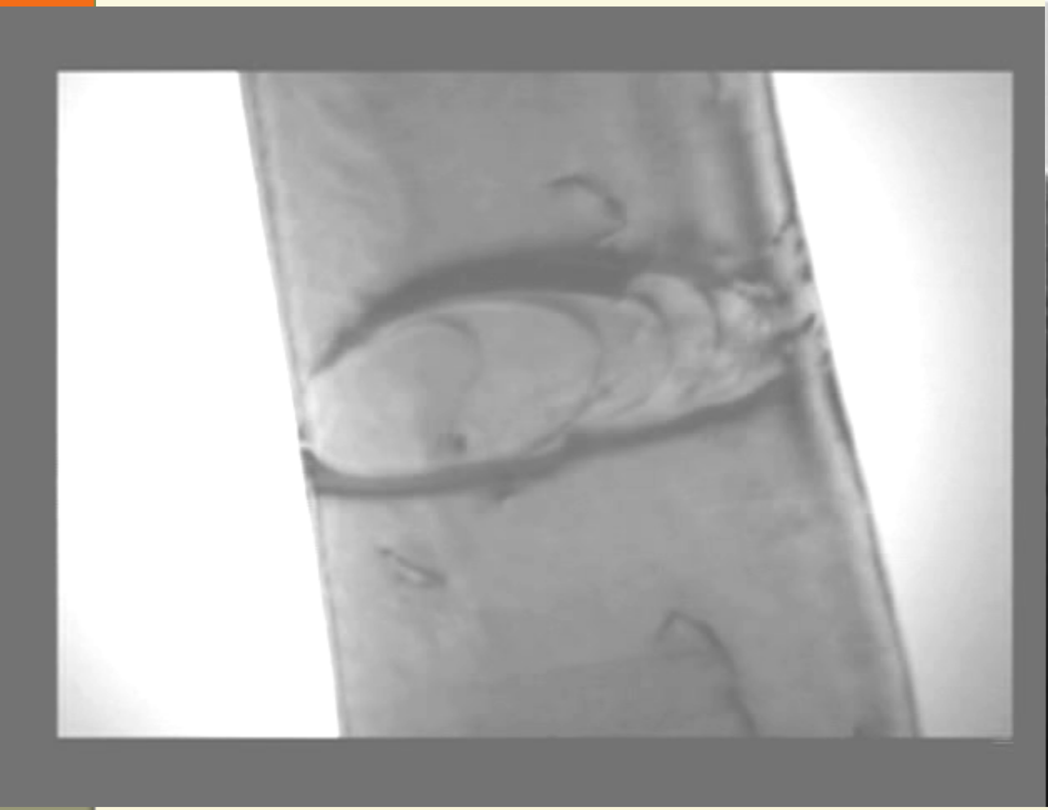
Activation volume can be experimentally determined by varying strain rate:

$$\Omega = k_B T \frac{\partial \ln(\dot{\gamma})}{\partial \tau}$$



Dislocation Nucleation Sources

Single-arm source



(SAS TEM movie courtesy M. Legros)

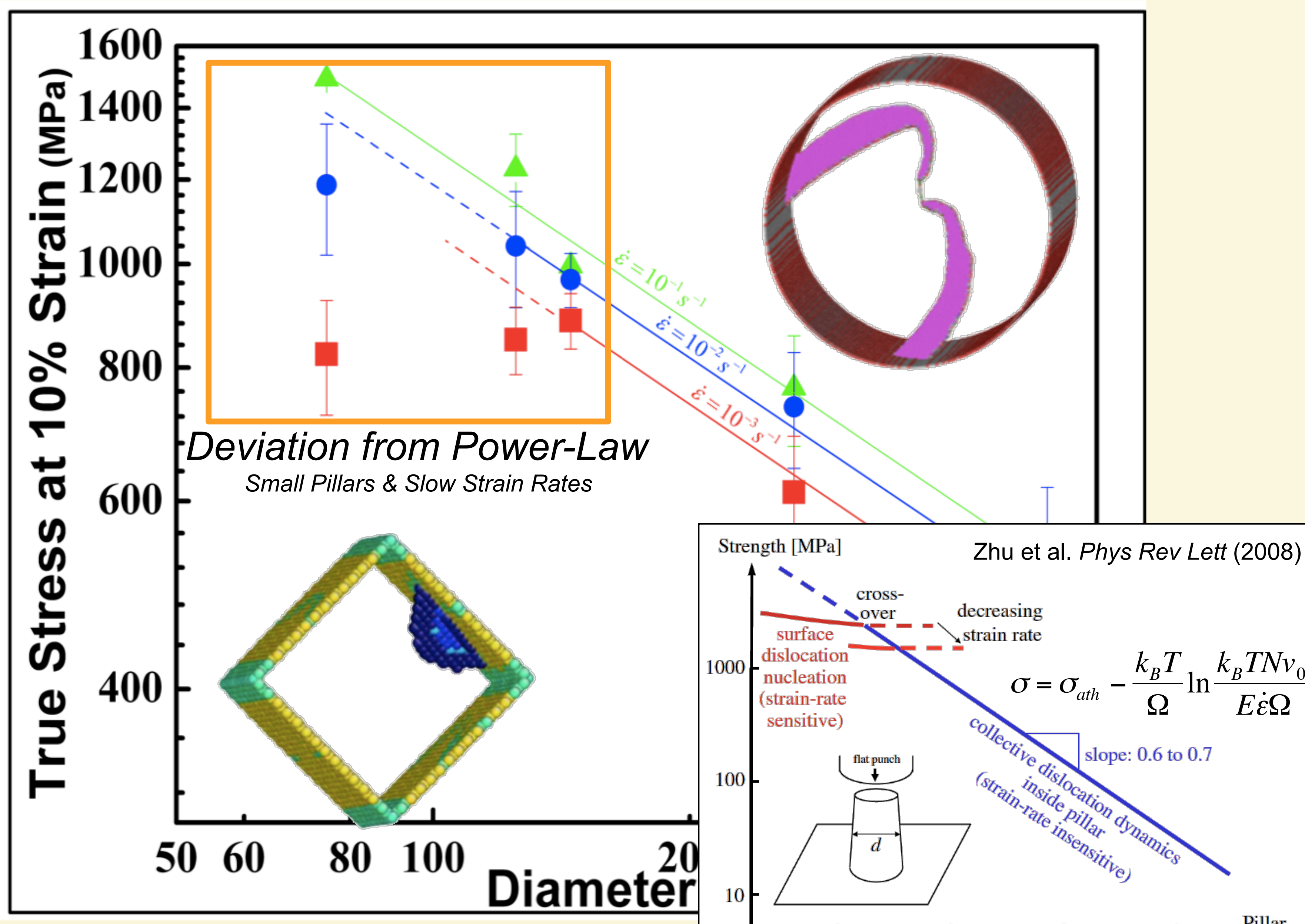
Surface source

MD movie courtesy of C. Weinberger

(SS TEM movie courtesy J. Huang)

Tang, Schwarz, Espinosa, *Phys. Rev. Lett.* (2007) Oh, S.H. et al, *Nature Mater.* (2009) Zheng, H. *et al.Nature Comm.* (2010)

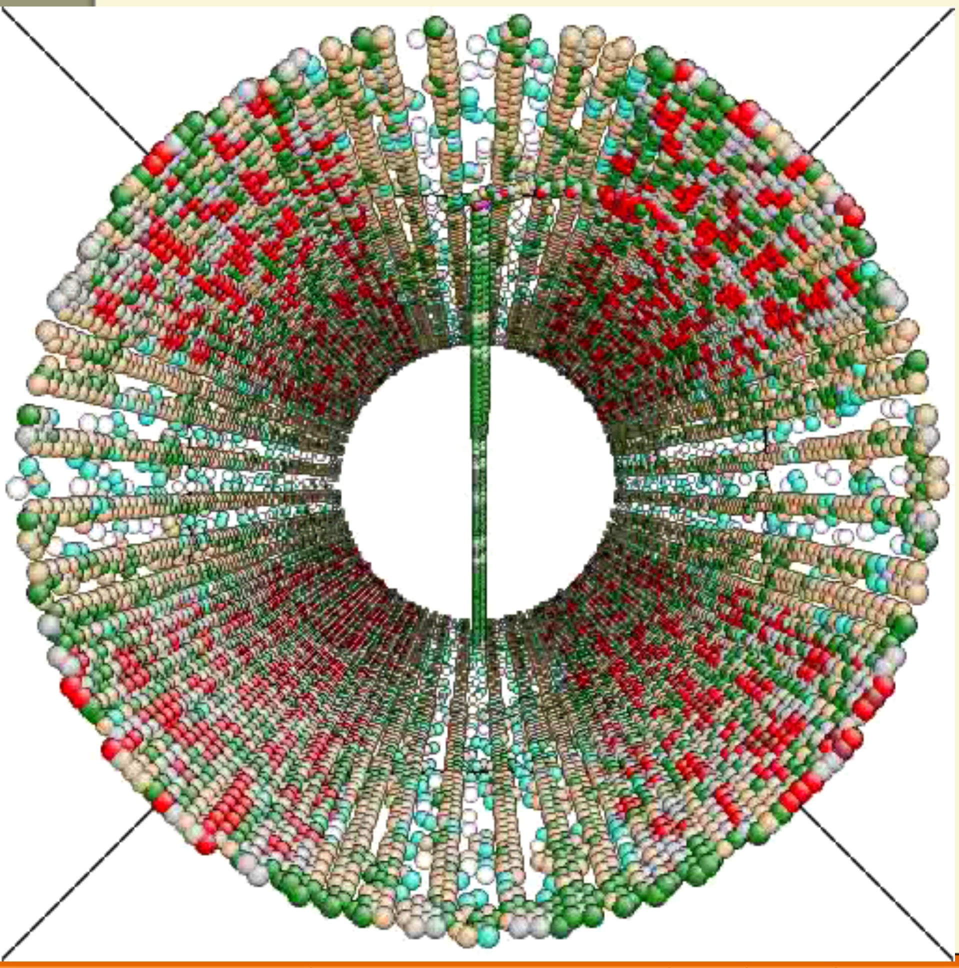
Surface vs. Single-Arm Sources



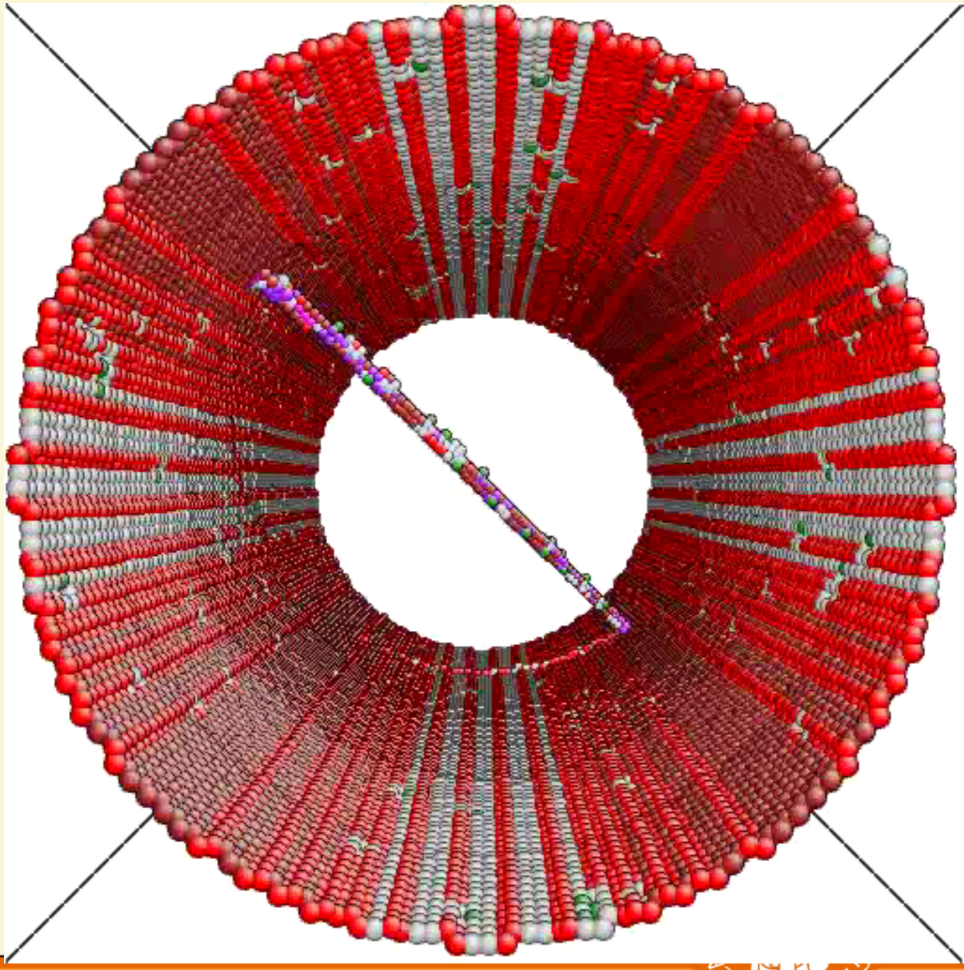
Jennings, A.T., Li, J., Greer, J.R. Acta Mater. (in press, 2011)

Atomistics of Dislocation Motion in Pillars: Molecular Dynamics Simulations

18nm-diameter Au pillar
Constant load = 500 MPa



24nm-diameter Mo pillar
Constant Load = 9 GPa



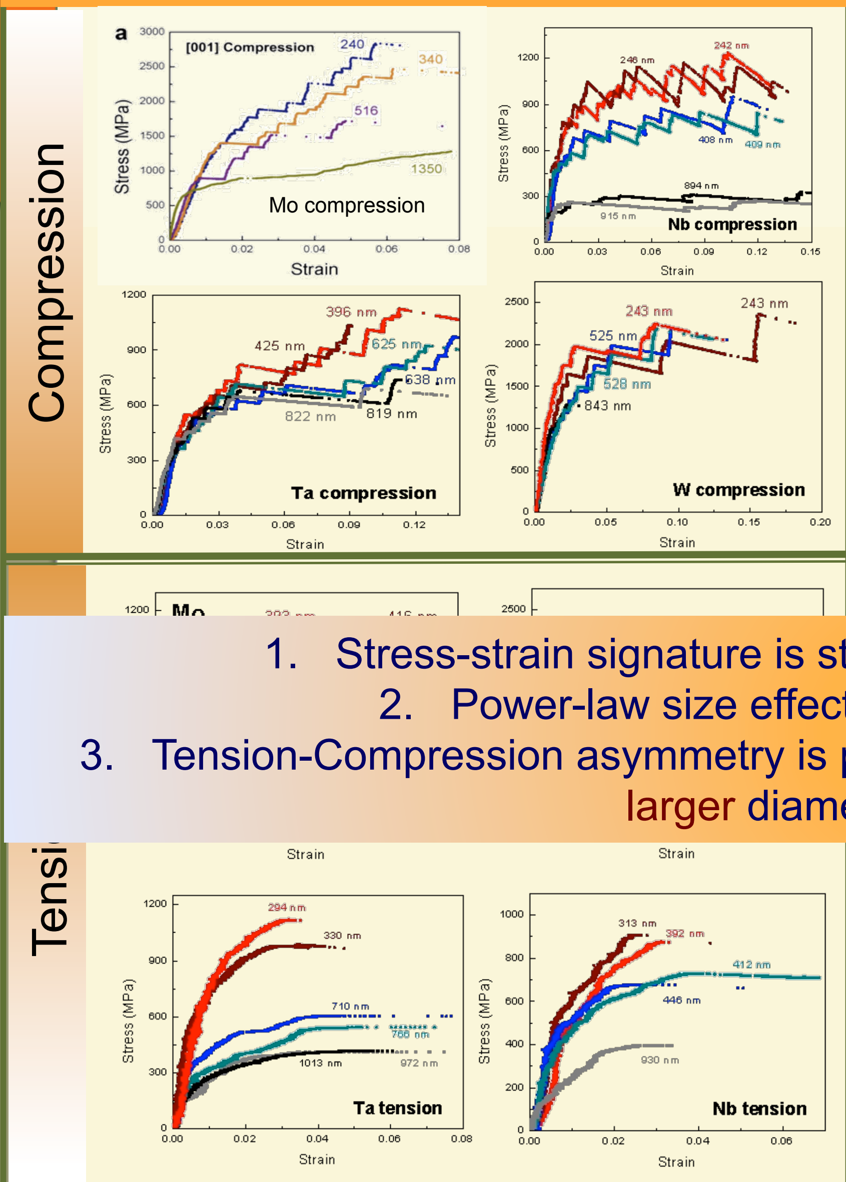
Weinberger and Cai, *Proc. Nat. Acad. Sci.* (2008)

Mechanical Properties of [001] bcc nano-pillars

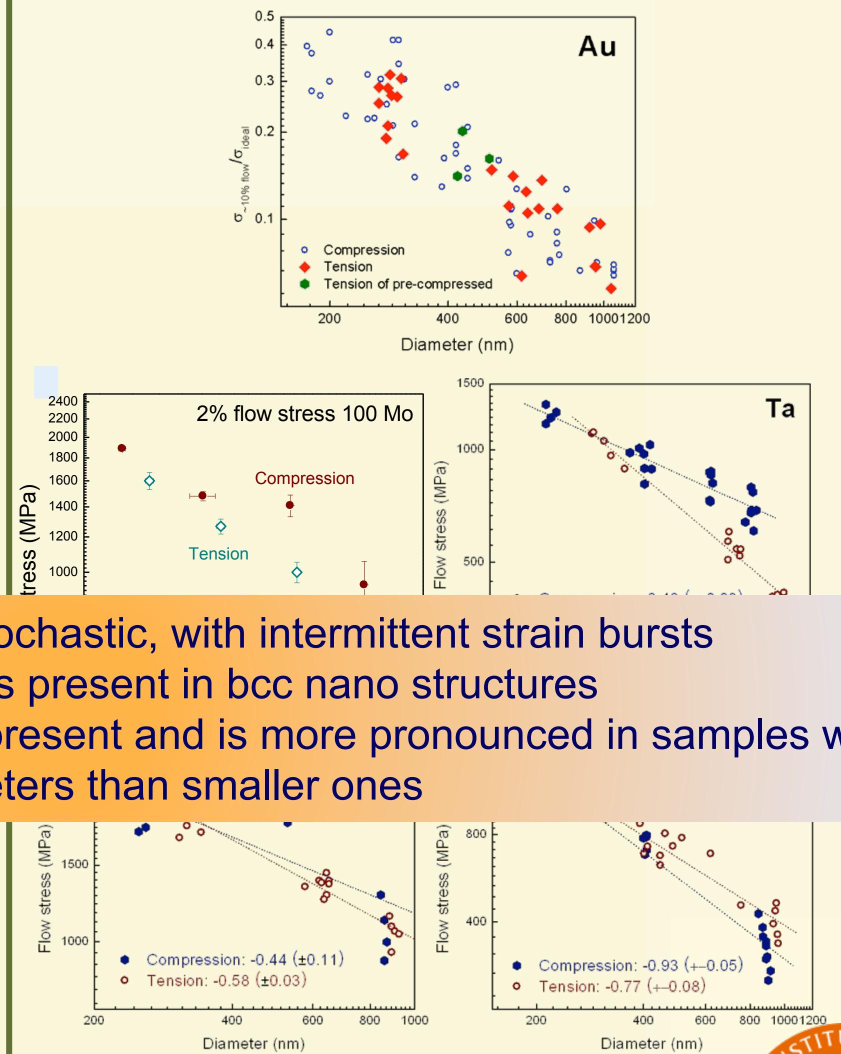
Stress-strain curves for Mo, Ta, Nb, and W

Compression

Tensi



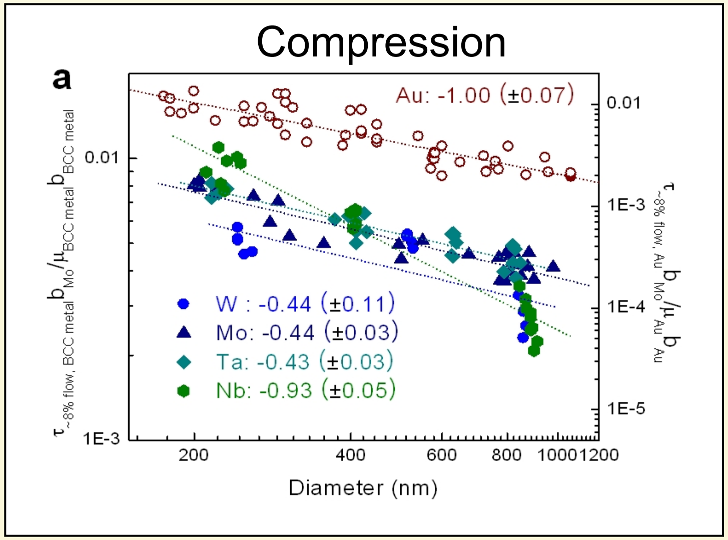
Tension vs. Compression

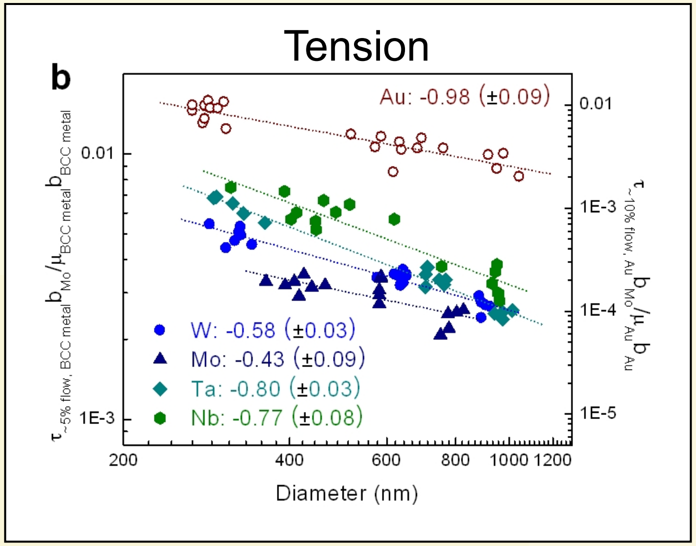


1. Stress-strain signature is stochastic, with intermittent strain bursts
2. Power-law size effects present in bcc nano structures
3. Tension-Compression asymmetry is present and is more pronounced in samples with larger diameters than smaller ones

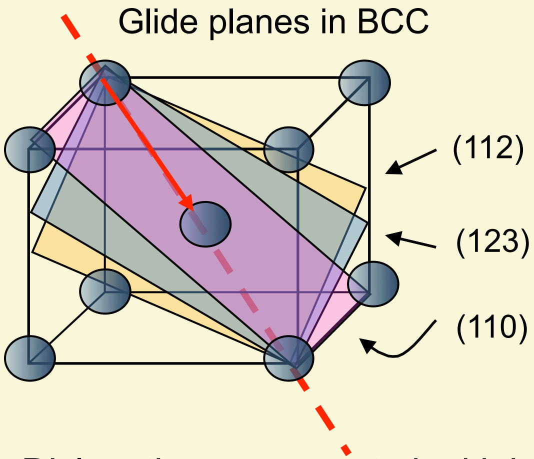
Kim, J.-Y., Jang, D., Greer, J.R. *Acta Mater.*, 58 2355-2363 (2010)

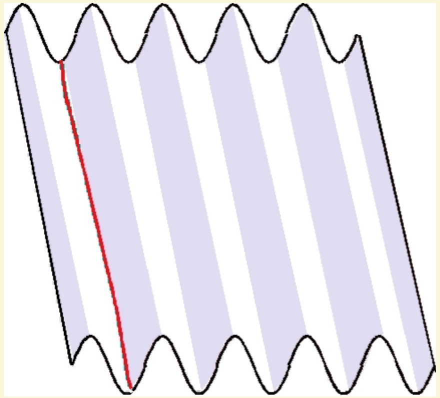
Origins of Different Size Effects





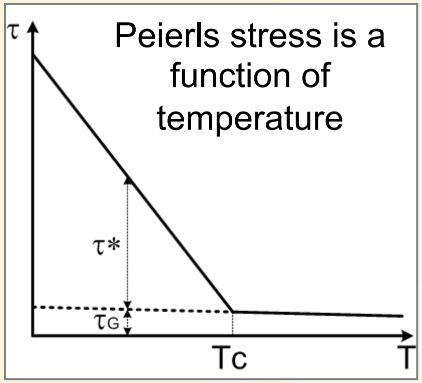
Overcoming Peierls potential is KEY in BCC Plasticity





Movie courtesy: S. Roberts

Critical temperature (K)



W: 760
Mo: 472
Ta: 440
Nb: 290

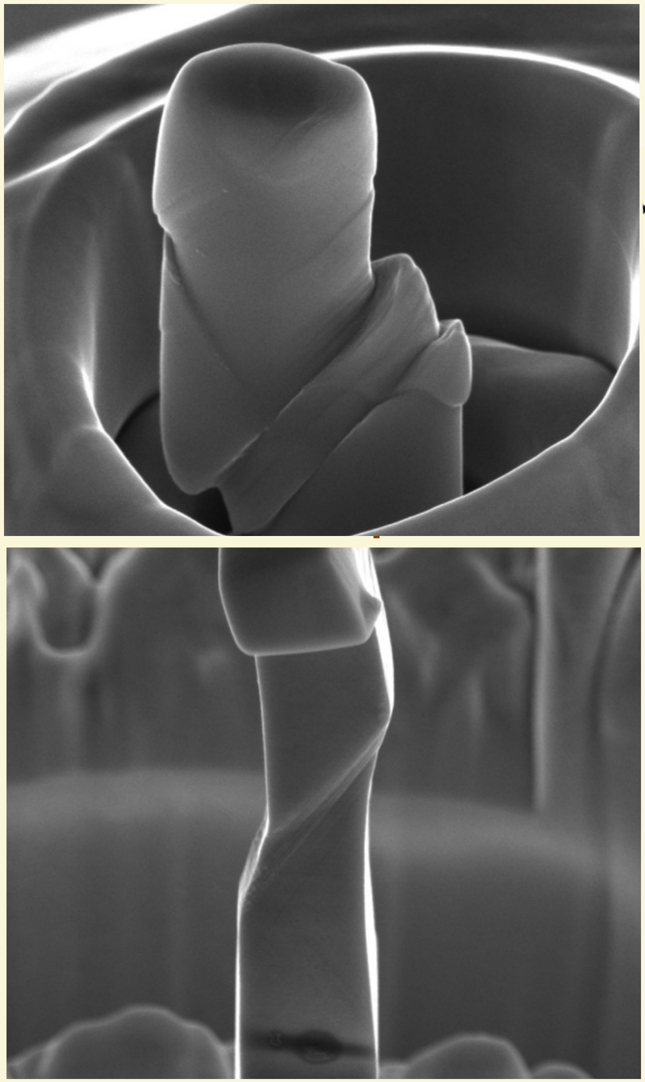
Au < Nb < Ta, Mo, W

- Dislocations propagate by kink-pair nucleation
- Must overcome Peierls potential → requires high stresses or T
- Screw dislocations are much slower than edge dislocations → dominate deformation below T_c

Kim, J.-Y., Jang, D., Greer, J.R. *Acta Mater.*, 58 2355-2363 (2010) Kim, J.-Y., Greer, J.R. *Appl. Phys. Lett.* (2008)

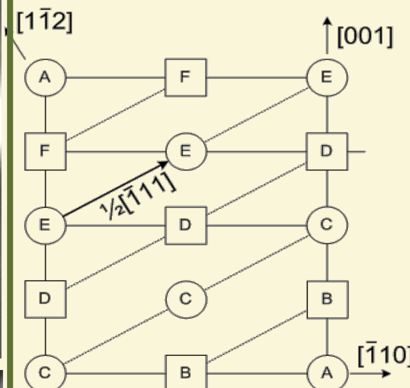
Origins of Tension-Compression Asymmetry

Different gripping constraints

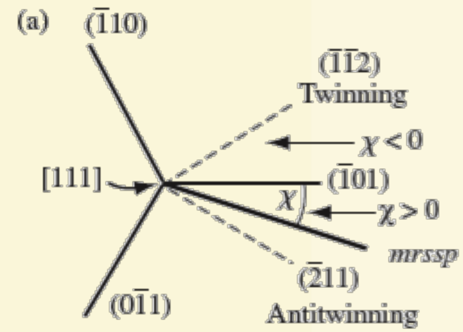


1. Intrinsic effect of BCC structure

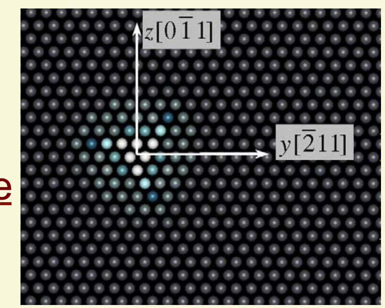
- Shear stresses in positive and negative <111> are not equivalent (except on {110} planes)
- Twinning vs. Anti-twinning on {112} planes (not mirror)



ABCDEFABCDEF



2. Extrinsic effect of BCC structure

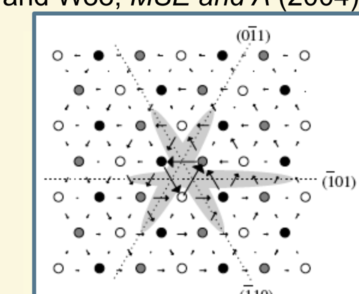


Tian and Woo, *MSE and A* (2004)

- Non-planar screw dislocation cores
- Non-Schmid behavior: Importance of shear stress components perpendicular to slip direction:

"+" for tension → τ_p ↓ → CRSS ↓

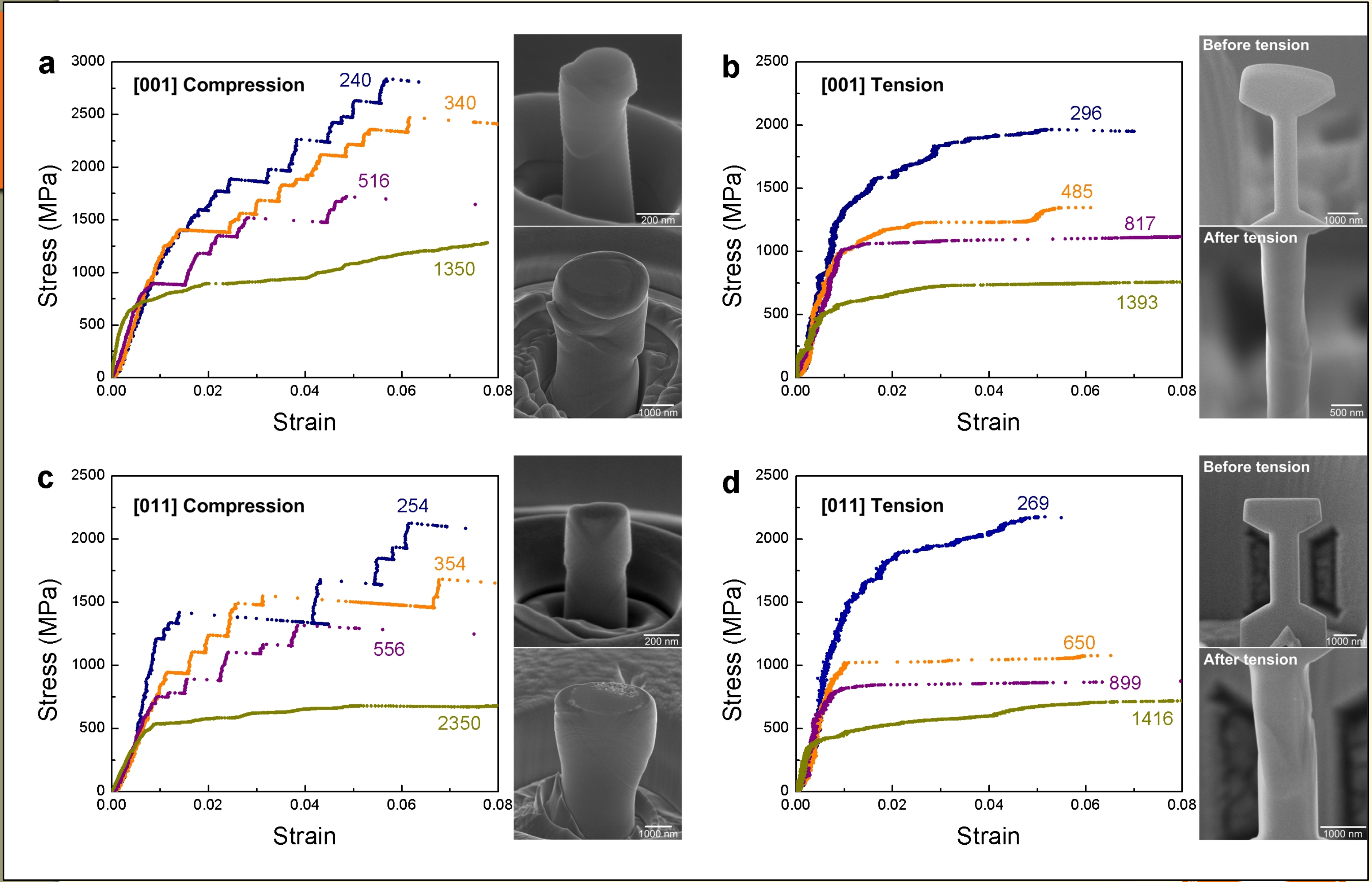
"-" for compression → τ_p ↑ → CRSS ↑



A.S. Argon "Strengthening Mechanisms in Crystal Plasticity" (2008)

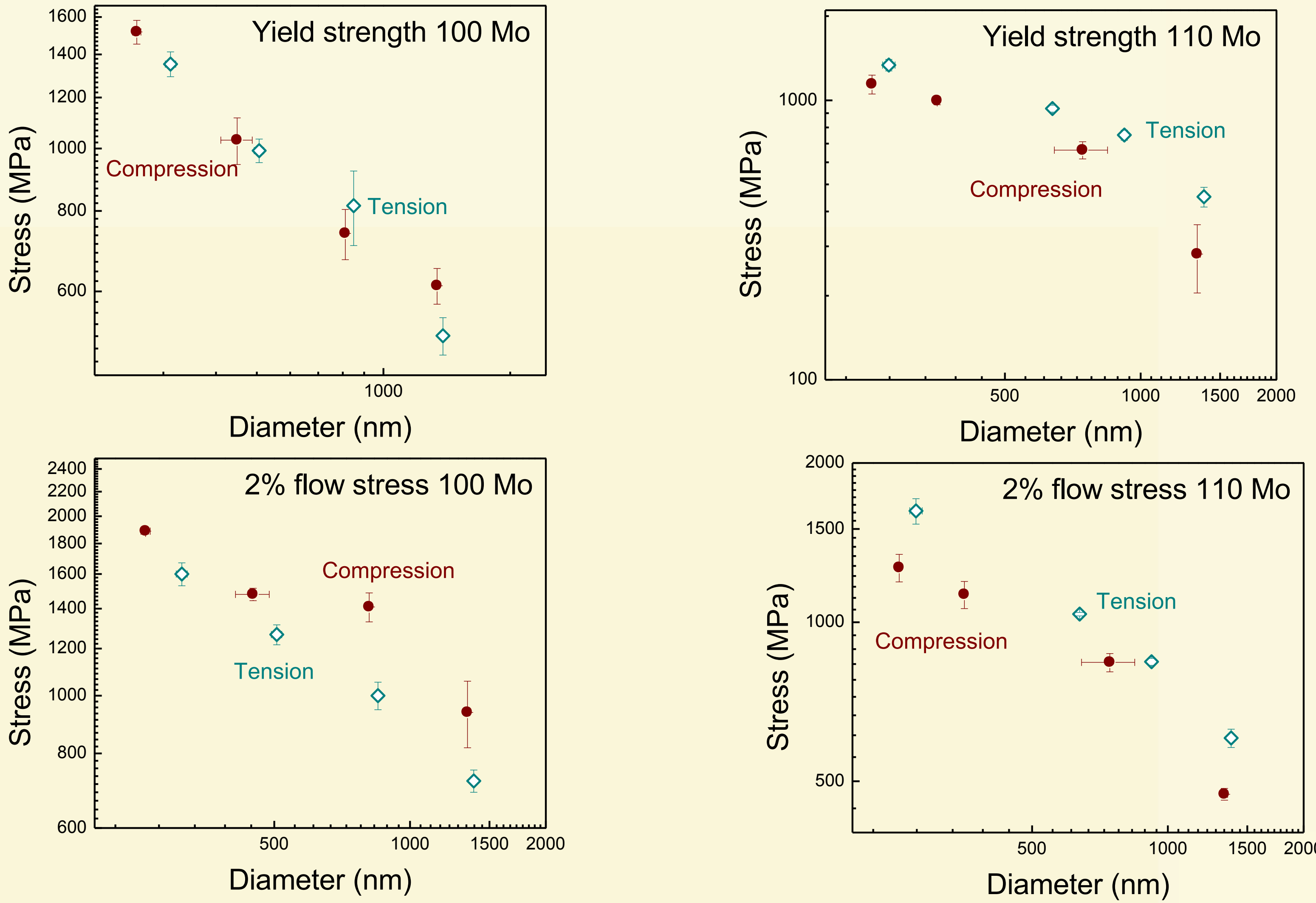
Groger and Vitek, *Acta Mater.* 56 (2008)

Effects of Crystallographic Orientation: [001] vs. [011]



J.Y. Kim, D. Jang, and J.R. Greer *Int J Plasticity* (in press, 2011)

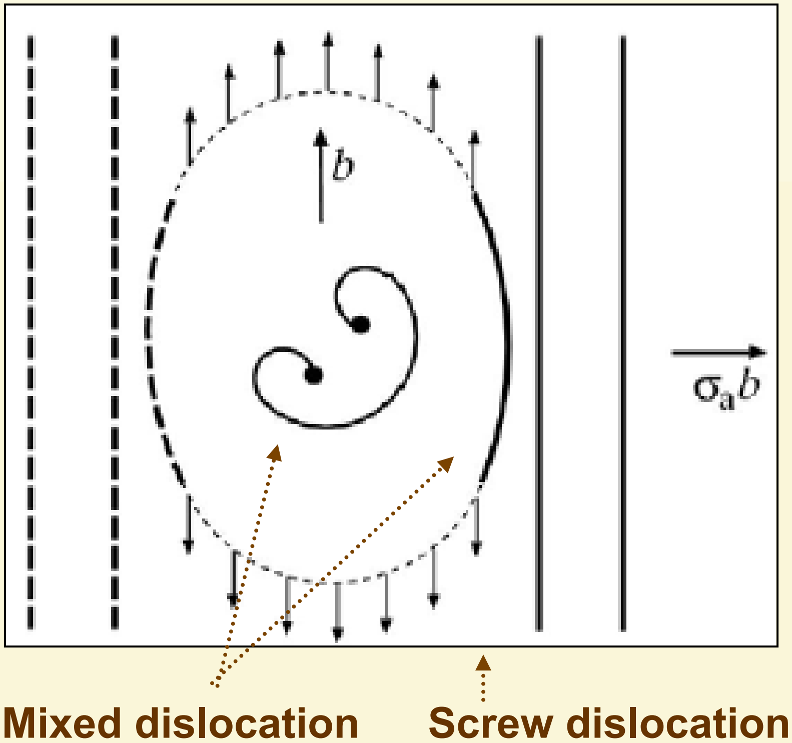
Effect of Orientation: [001] vs. [011]

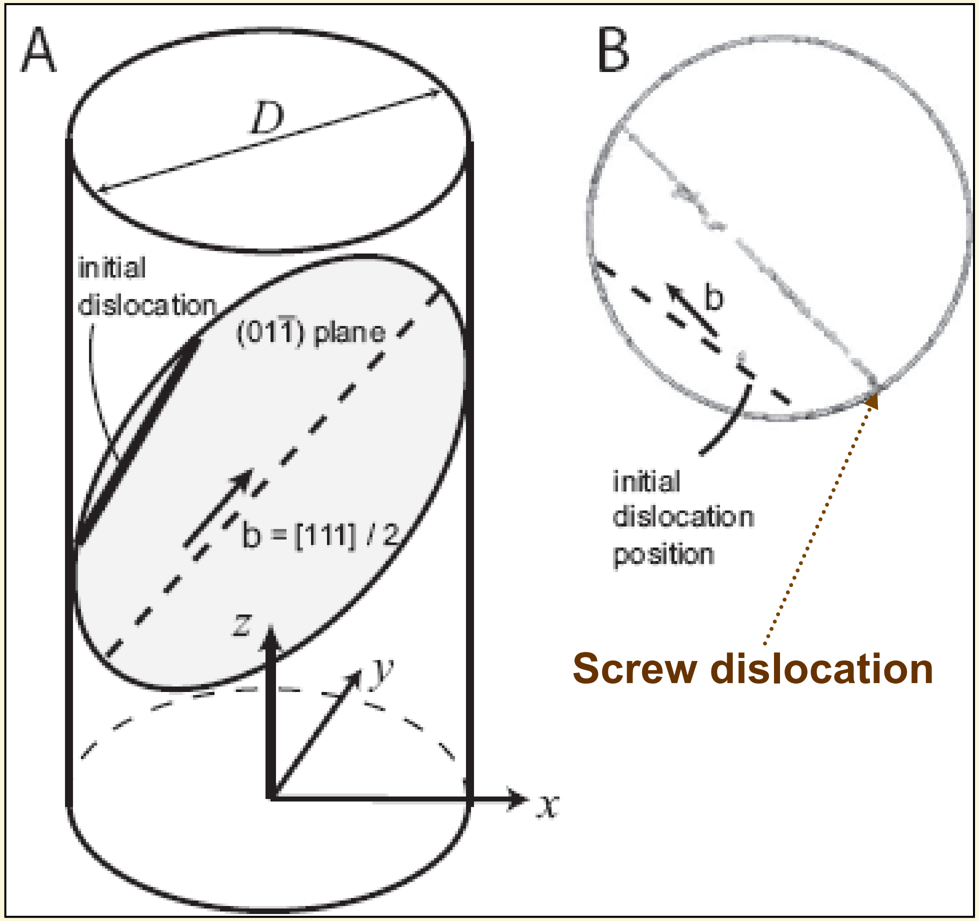


Tension-compression asymmetry is more pronounced in flow stress (rather than in yield strength) and in samples with larger diameters (rather than smaller ones)

J.Y. Kim, D. Jang, and J.R. Greer *Int J Plasticity* (in press, 2011)

Diminishing effects of screw dislocations with smaller size



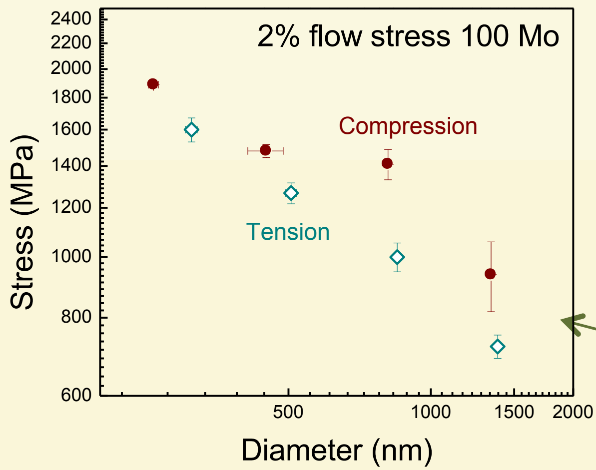


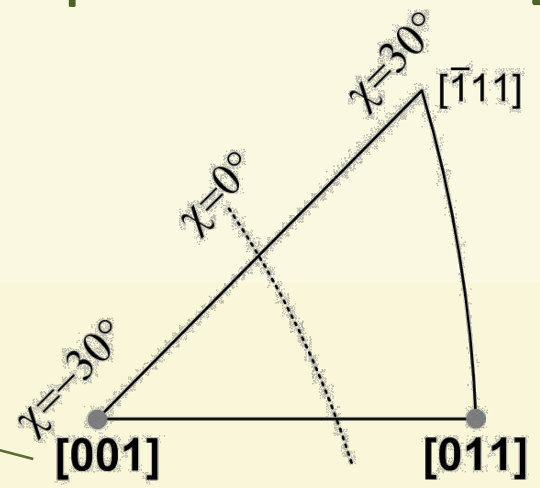
Screw dislocations appear to play a more important role in flow stress (rather than yield stress) and in larger (rather than smaller) pillars

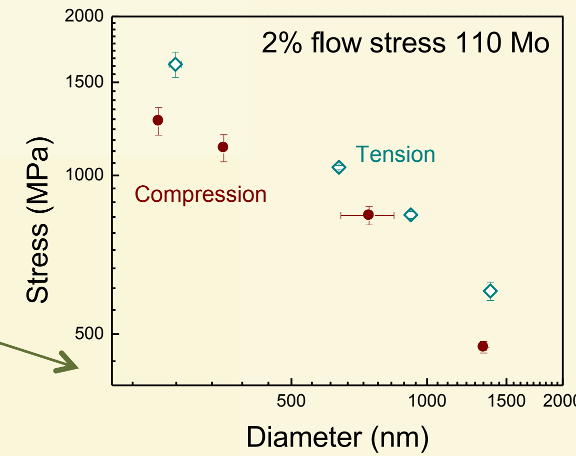
Groger and Vitek, *Phil. Mag. Lett.* (2007)

Weinberger and Cai, *PNAS* (2008)

Tension vs. Compression and [001] vs. [011]







Orientation Factor	Slip System	Schmid
	(1 01)[111]	0.41
[001]	(-211)[111]	0.24
	(-1-12)[111]	0.47
[011]	(-211)[111]	0.47
	(-1-12)[111]	0.24

Opposite χ for $(\bar{1}\,\bar{1}\,2)$ and $(\bar{2}11)$ planes => diametrically opposite twinning-antitwinning slip

- [001] orientation: $(\bar{1}\,\bar{1}\,2)$ shears in the twinning sense => Compression >Tension
- [011] orientation: $(\bar{2}11)$ shears in the antitwinning sense => Tension > Compression

Compression >Tension for [100] Mo while
Tension >Compression for [110] Mo

J.Y. Kim, D. Jang, and J.R. Greer *Int J Plasticity* (in press, 2011)

Deformation Mechanisms and Size Effects

Plasticity carriers:
Dislocations

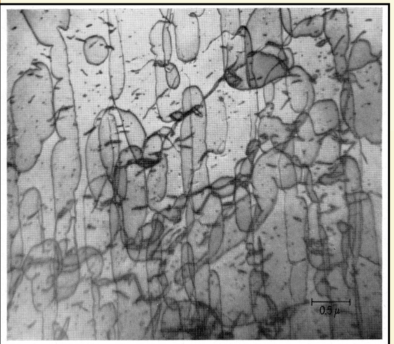


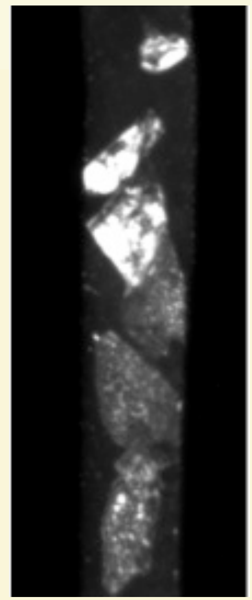
Fig. 12. Exceptionally strong area-contrast effect in areas enclosed by dislocation lines. Plane of foil is (011). (Reflection not determined.) × 37,500

Low and Trial, *Acta Met*. (1962)
Fe-3% Si

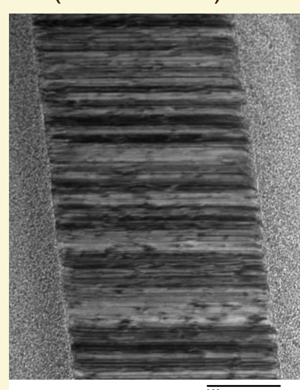
Single Crystals
(Au, Mo, Nb, etc.)

Plasticity carriers:
Dislocations + grain/twin boundaries

Bi-Crystals (Al)
See poster by A. Kunz
(Room 31B)

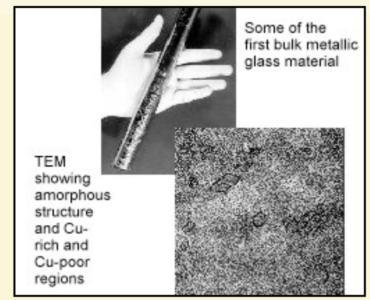


Nanocrystalline
Metals (Ni)



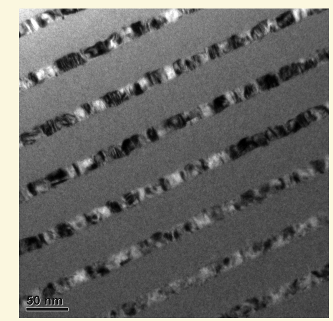
Nano-twinned
Metals (Cu)

Plasticity carriers:
Shear Transformation Zones (STZs)



Metallic glasses
See talk by D. Jang
on Thursday at 2pm
(Bulk Metallic Glasses VIII)

Plasticity carriers:
STZs + dislocations



Amorphous/
Nanocrystalline
Nanolaminates
See talk by J.-Y. Kim
on Thursday at 2:20pm
(1-D Mechanics)

Increasing disorder (introducing boundaries and amorphous-ness)

Summary and Acknowledgements

- Single crystalline Cu (fcc) nano-pillars fabricated without FIB yet with similar dislocation densities exhibit an identical size effect and stochastic intermittent flow as FIB-produced ones
- Dislocation starvation followed by surface source nucleation likely dominates plasticity at sizes below ~125nm
- Dislocation multiplication through single-arm source operation likely governs plasticity in pillars above ~125nm diameters
- Single crystalline Cu nano-pillars exhibit significant strain rate sensitivity at very small sizes, possibly corresponding to activation of surface sources
- Body-centered (bcc) nano-pillars also exhibit stochastic behavior, but much more complex size effects and tension-compression asymmetry

Helpful discussions:
C. Weinberger (Sandia NL)
J. Li (U Penn)

DARPA DSO
DARPA Young Faculty Award

CSEM Center for the Science & Engineering of Materials
National Science Foundation MRSEC California Institute of Technology
DMR-0520565

ONR OFFICE OF NAVAL RESEARCH
Award No: N000140910883

National Science Foundation WHERE DISCOVERIES BEGIN
NSF Career Grant DMR-0748267

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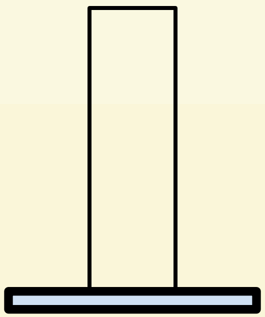
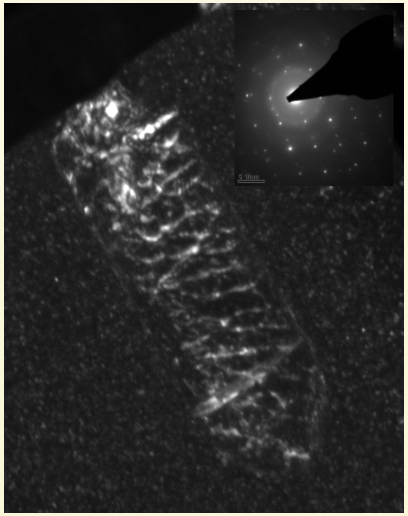
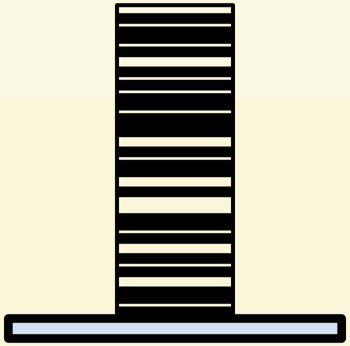
Introducing multiple boundaries

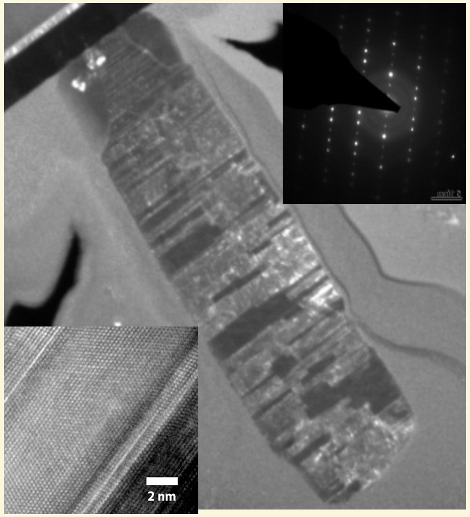
Single Crystals



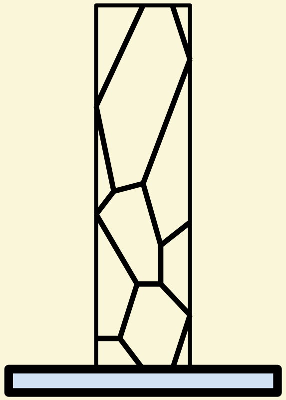


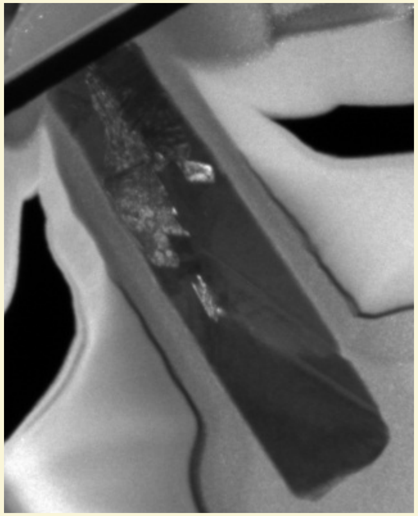
Nano-twinned



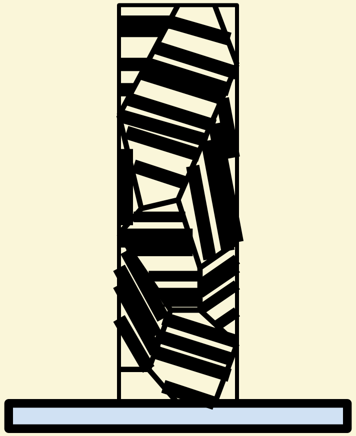


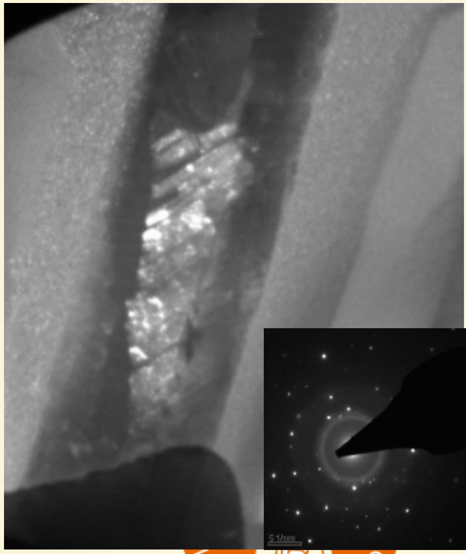
Nanocrystalline





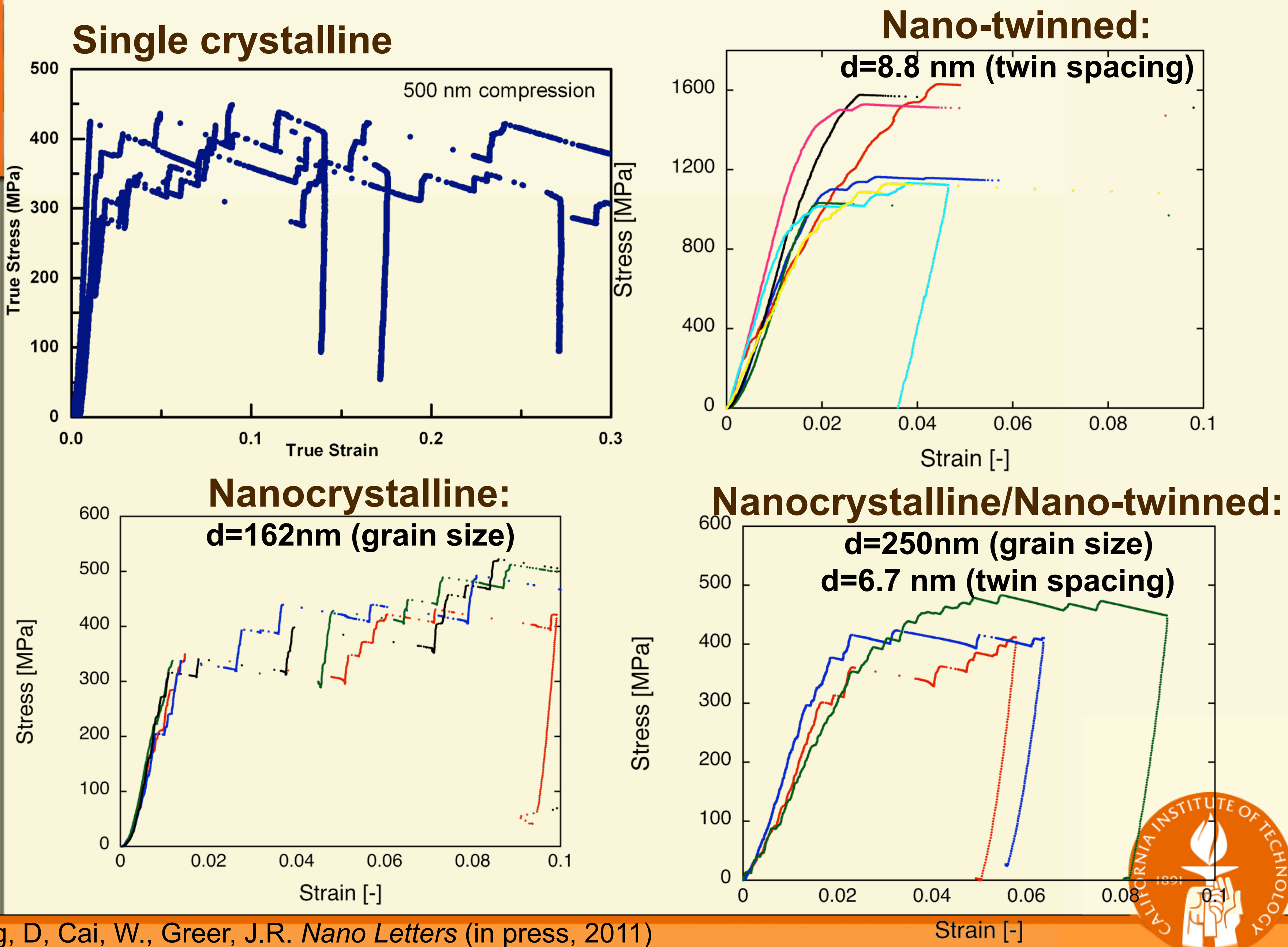
Nanocrystalline + Nano-twinned





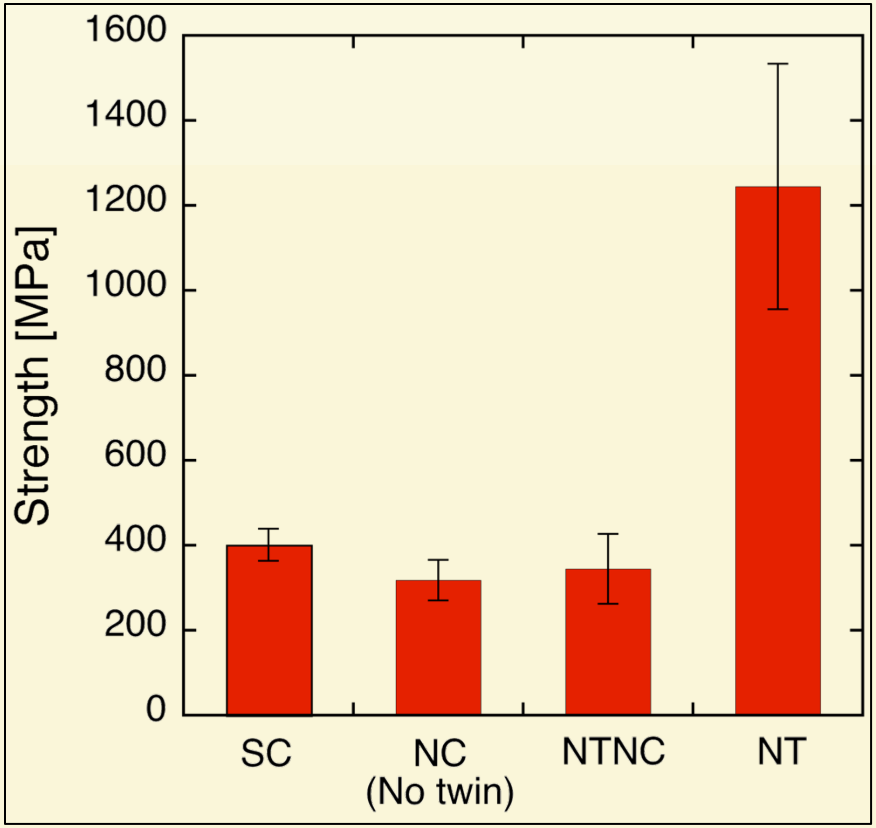
Jang, D, Cai, W., Greer, J.R. *Nano Letters* (in press, 2011)

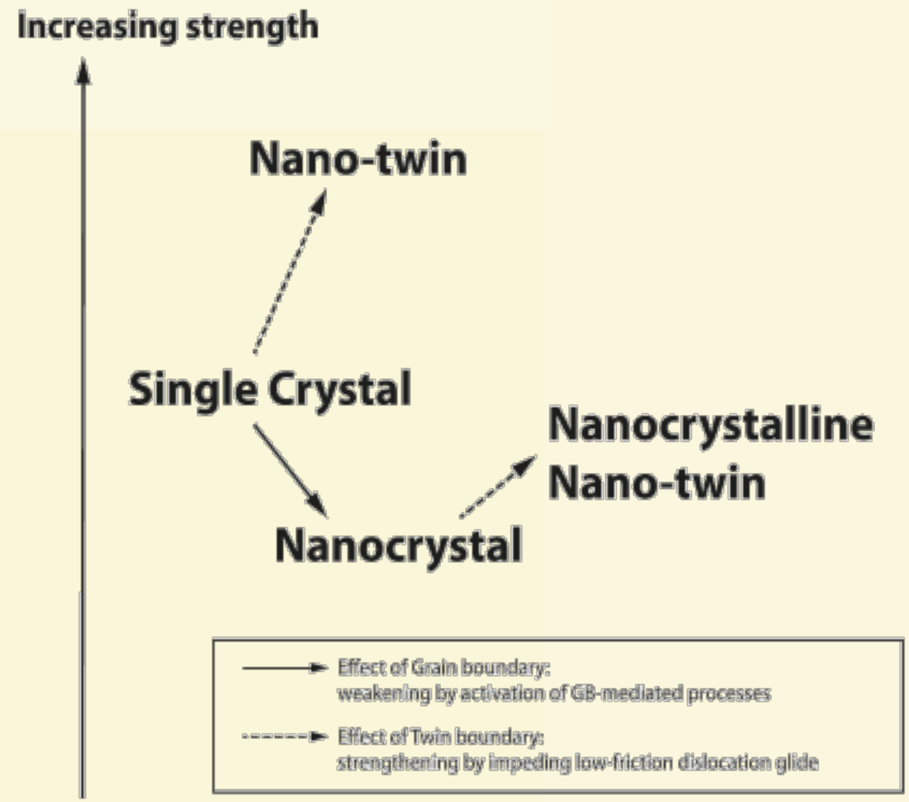
Stress vs. strain for each microstructure (D=500nm)



Jang, D, Cai, W., Greer, J.R. *Nano Letters* (in press, 2011)

Strength: Intrinsic (d) vs. Extrinsic (D)

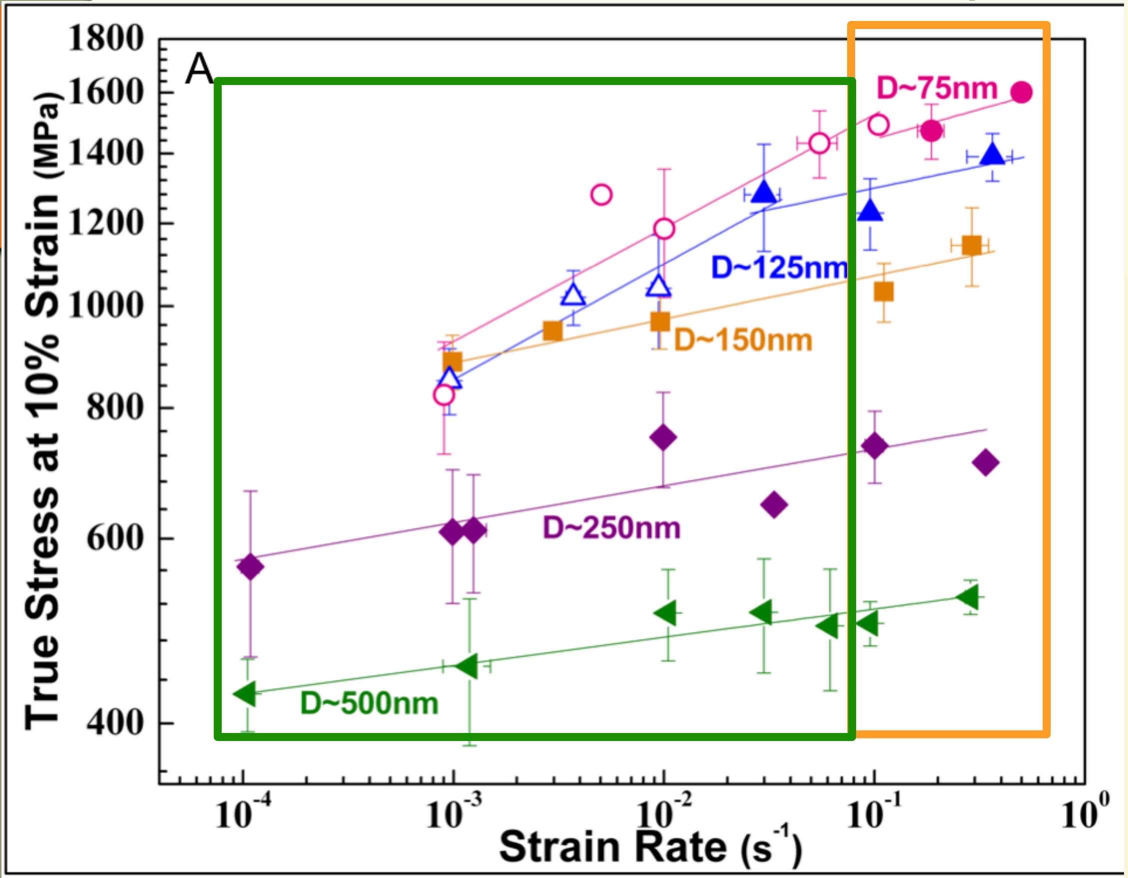




Introducing **twin** boundaries increases strength
Introducing **grain** boundaries decreases strength

Jang, D, Cai, W., Greer, J.R. *Nano Letters* (in press, 2011)

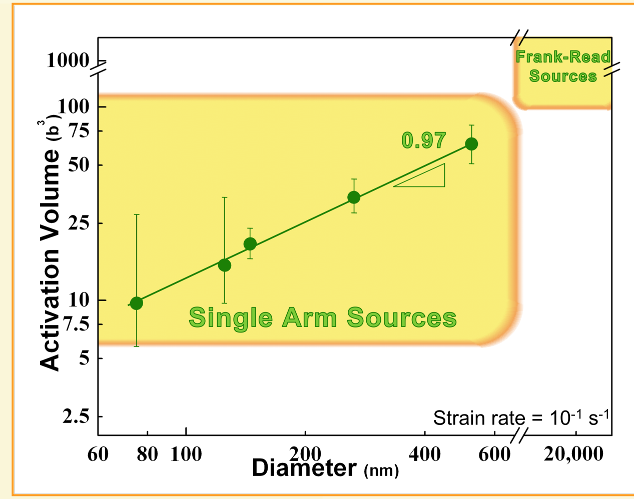
Strain Rate Sensitivity => Activation Volume



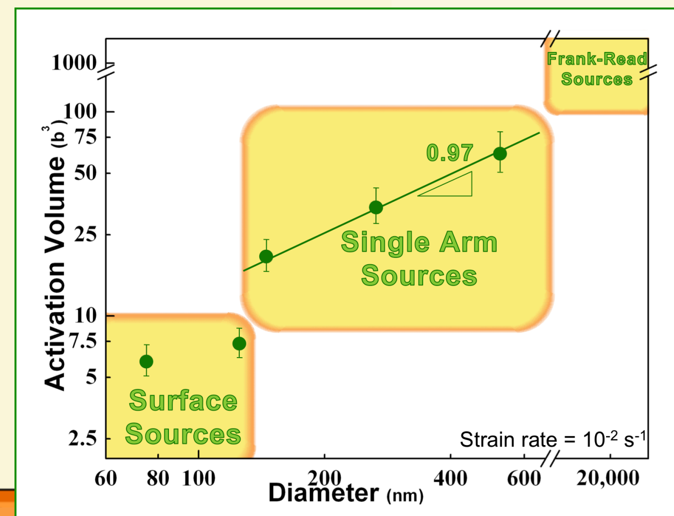
$$\sigma = \sigma_o \dot{\varepsilon}^m$$

$$\Omega = k_B T \frac{\partial \ln(\dot{\gamma})}{\partial \tau}$$

$$\tau = M\sigma$$
$$\dot{\gamma} = M\dot{\varepsilon}$$



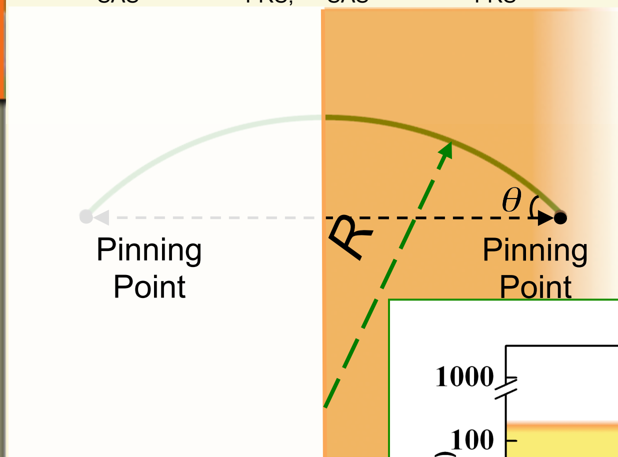
Transition to surface source operation may be manifested as deviation from the "athermal" size effect



Jennings, A.T., Li, J., Greer, J.R. (submitted, 2011)

Activation Volume for a Single-Arm Source

1/2 of Frank-Read Source:
$Q_{SAS} = 1/2\, Q_{FRS};\ \Omega_{SAS} = 1/2\, \Omega_{FRS}$

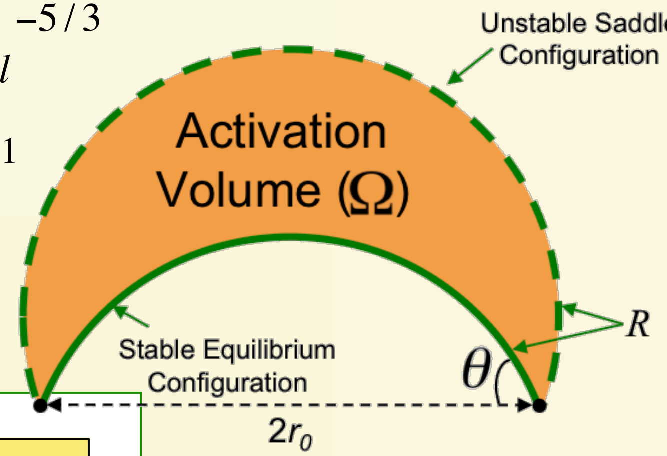


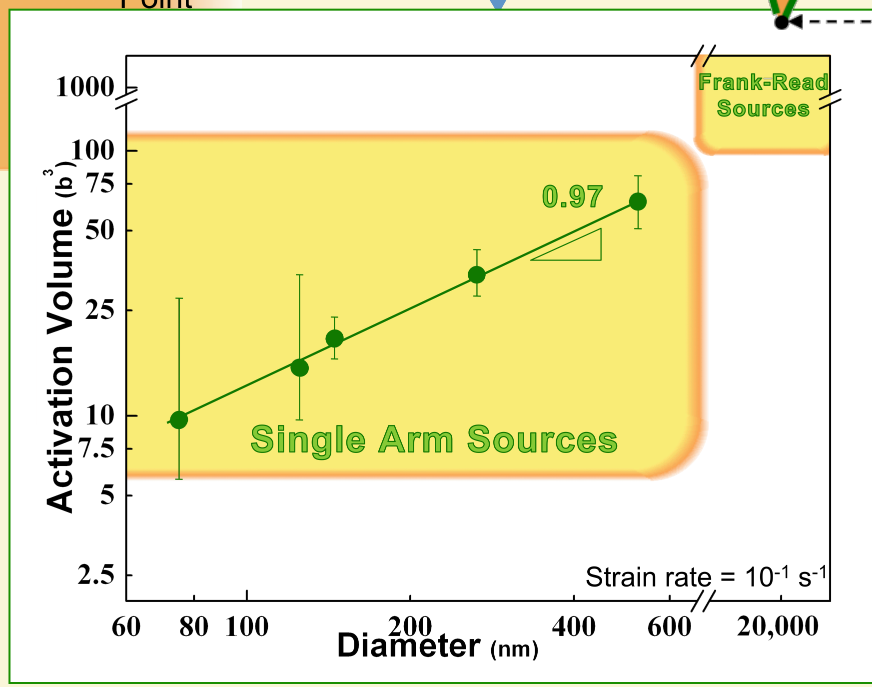
$$\Omega(\tau_{athermal}) \propto \tau_{athermal}^{-5/3}$$

$$\downarrow \quad \frac{\tau_{athermal} - \tau}{\tau_{athermal}} << 1$$

$$\tau_{athermal} \propto \boxed{D}^{-n}$$

$\downarrow$





$$= b\left(A^* - 2A_i\right) = b r_0^{\,2} f(\theta)$$

$\downarrow$

$$\tau_{athermal} = \frac{\mu b}{2 r_0} \qquad R \geq r_0$$

$$\frac{\tau_{athermal} - \tau}{\tau_{athermal}} << 1$$

$$Q \propto \frac{\left(\tau_{athermal} - \tau\right)^{3/2}}{\tau_{athermal}^{\,1/2}} \cong 0.7eV$$

$\downarrow$

$$f(\theta) \propto r_0^{-1/3}$$

$\downarrow$

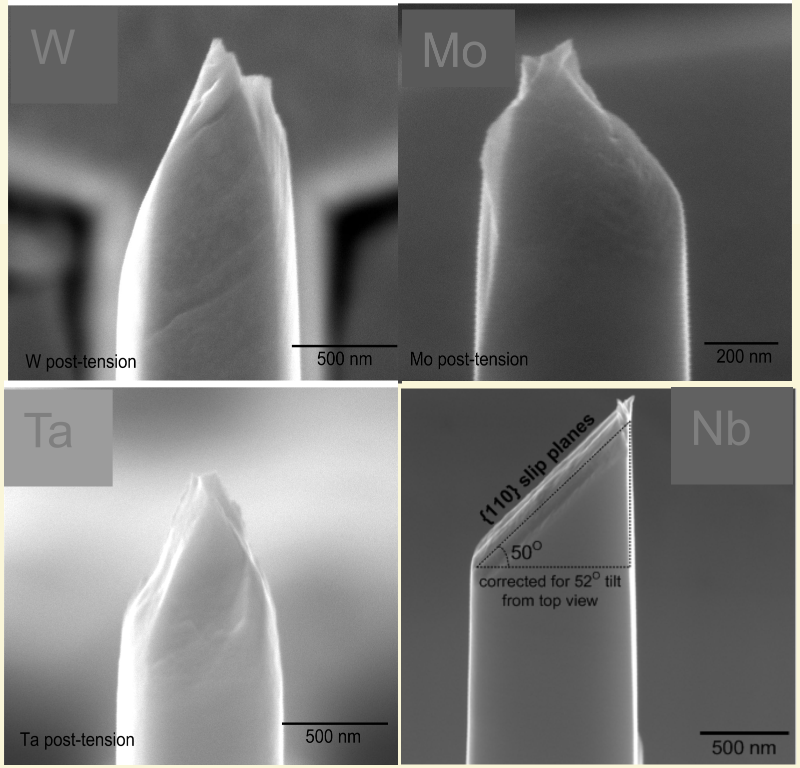
$$\Omega_{F-R} \propto r_0^{5/3}$$

Nabarro (1989)
Shemenski (1965)
Estrin et al (2007)
Zhu et al (2010)

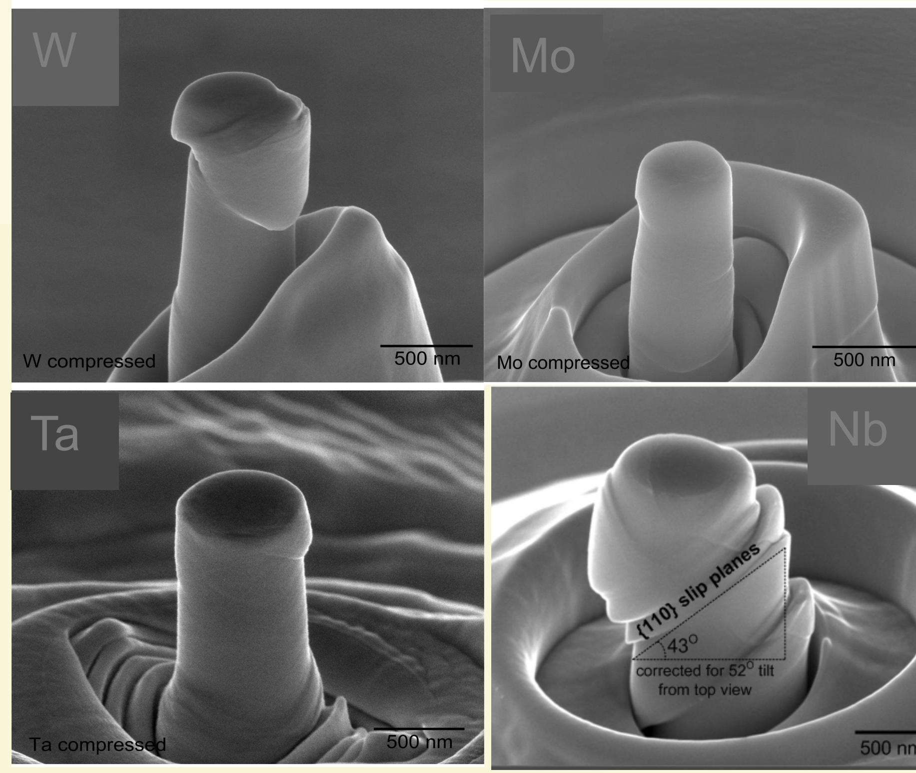
Jennings, A.T., Li, J., Greer, J.R. (submitted, 2011)

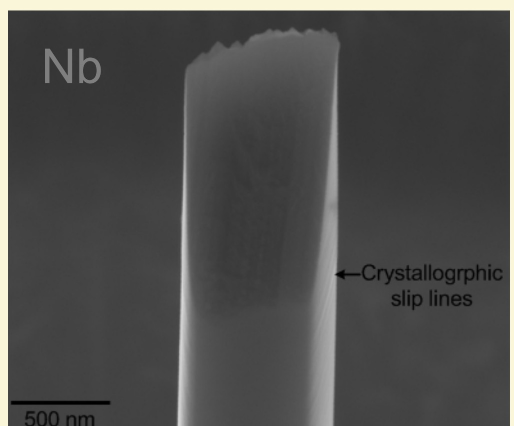
Moving onto BCC metals: Post-testing morphology

Pronounced shearing-off in tension



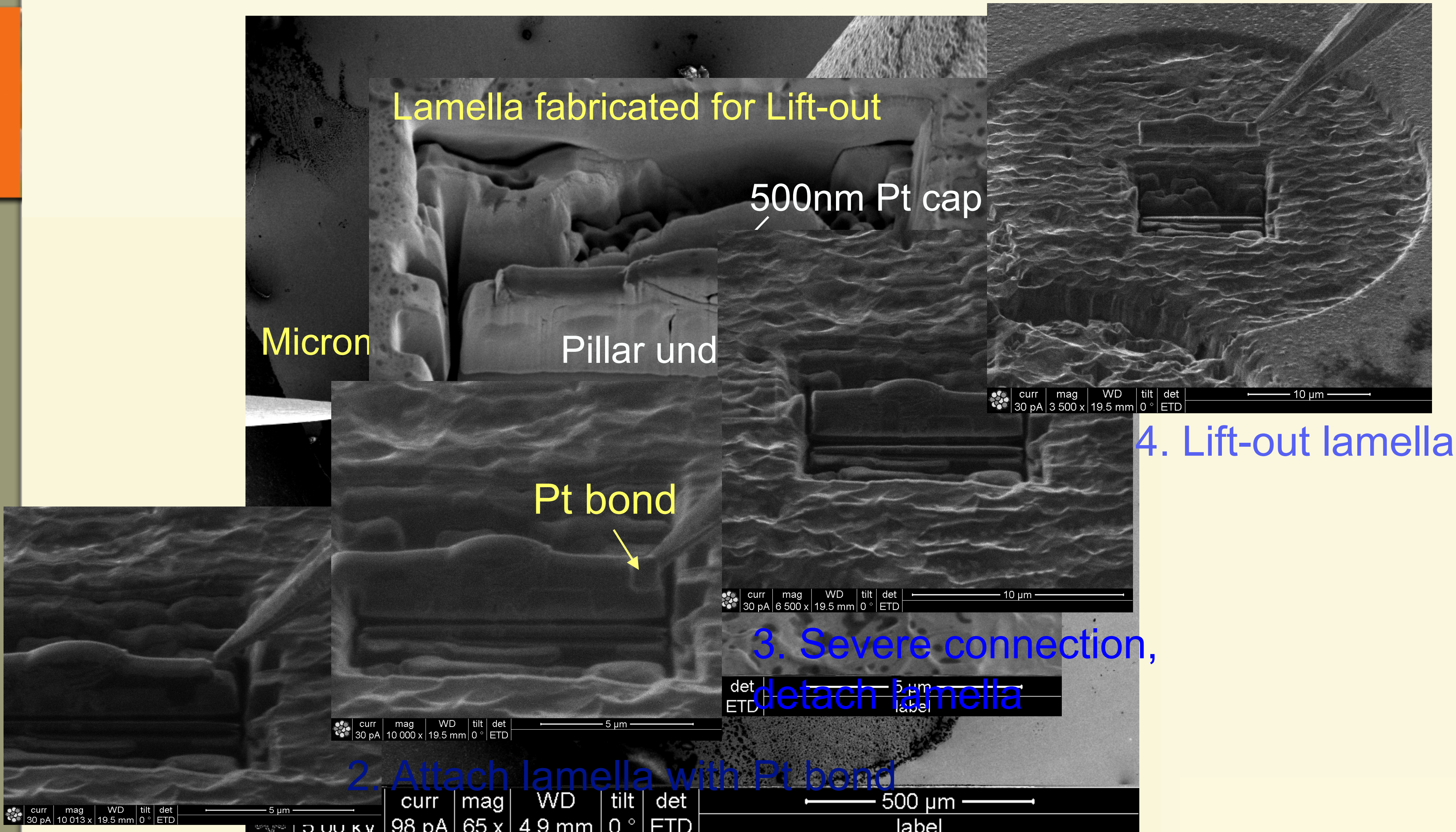
Crystallographic slip in compression





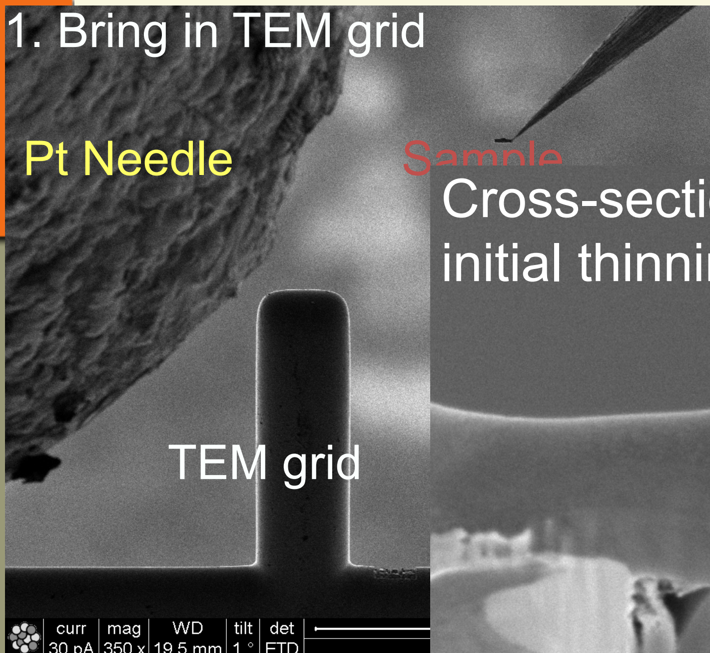
Kim, J.-Y., Jang, D., Greer, J.R. *Acta Mater.*, 58 2355-2363 (2010)
Kim, J.-Y., et al. *Scripta Mater.* 61, 3 (2009)

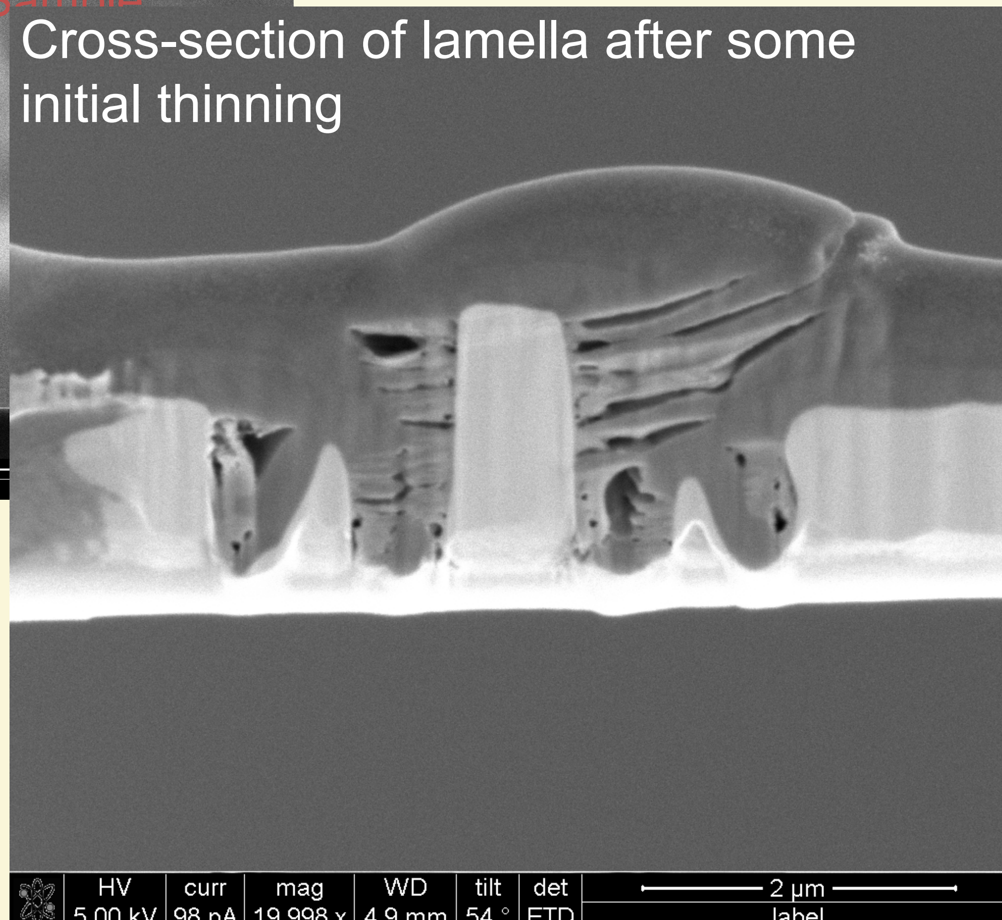
TEM Sample Preparation: Phase 1

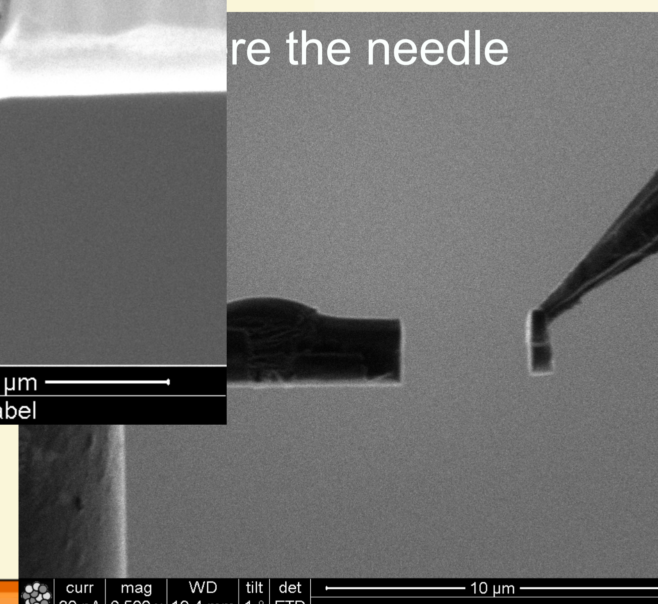


1. Bring Micromanipulator almost in contact with lamella

TEM Sample Preparation: Phase 2

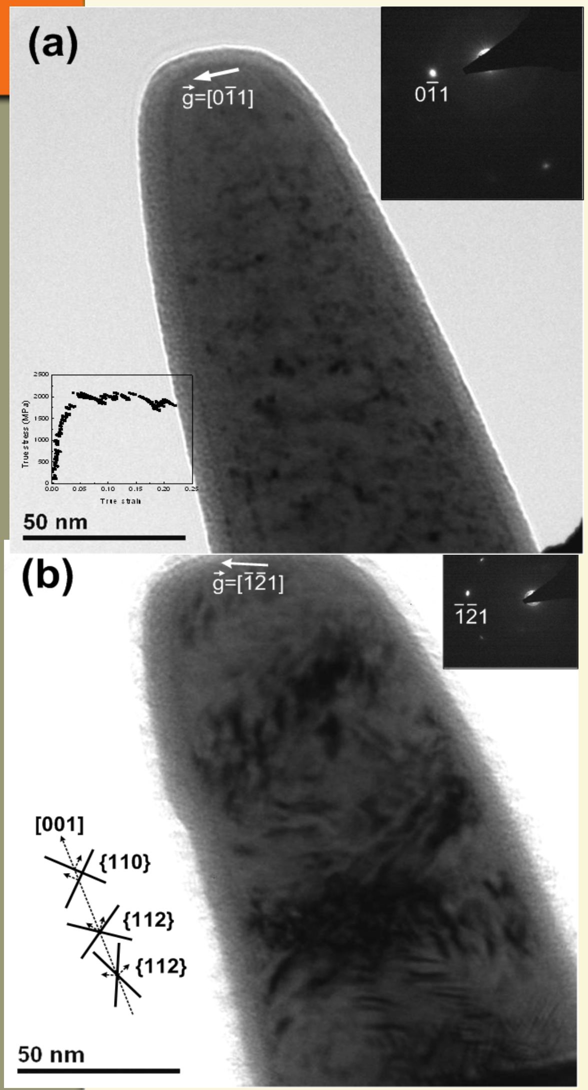






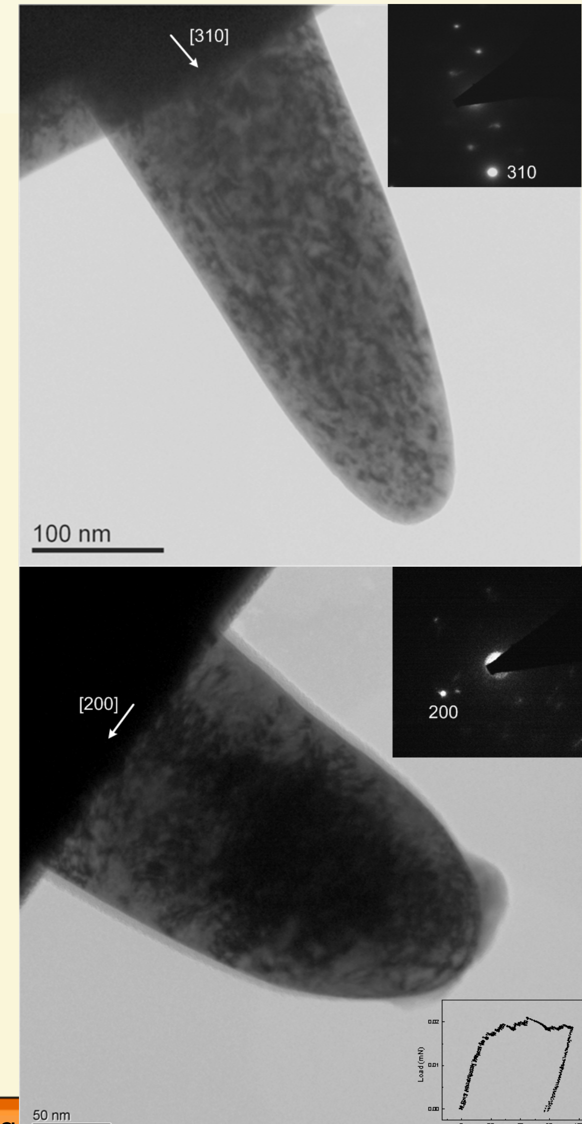
TEM Analysis of deformed pillars

Nb



- ⇒ Complex dislocation networks formed in Nb and Mo after compression
- ⇒ Partial dislocations generated on {110}, {112}, and {123} planes in Nb
- ⇒ Dislocation segments are straight (rather than wavy) in Nb implying rare cross-slip
- ⇒ Dislocation density increases in Nb and Mo after compression

Mo



Kim, J.-Y., Jang, D., Greer, J.R. *Scripta Mater*. 61, 3 (2009). TEM images by Dongchan Jang