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Title: SEM in-situ indentation fracture toughness of metal-ceramic nanolaminates

Author(s): William M. Mook, Rejin Koodakal, Damian Frey, Nan Li, Jon K. Bladwin, Johann Michler, Nathan A. Mara, Amit Misra

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Abstract, Text: U

SEM In-Situ Indentation Fracture Toughness of Metal-Ceramic Nanolaminates

William M. Mook[1,2], Rejin Raghavan[2], Damian Frey[2], Nan Li[1], Jon K. Baldwin[1], Johann Michler[2], Nathan A. Mara[1], Amit Misra[1]

[1] MPA-CINT: Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

[2] Laboratory for Mechanics of Materials and Nanostructures, Empa - Materials Science & Technology, Feuerwerkstrasse 39, 3602 Thun, Switzerland.

At the small length scales in micro- and nanotechnology the phenomenon of "smaller is stronger" is often observed. This increase in strength generally results in a corresponding decrease in toughness that can degrade the reliability of thin films, small structures and devices. Thus it is of critical importance to investigate material combinations and structures that increase toughness at the nanoscale while they simultaneously maintain strength. Recent work at LANL on nanolaminates composed of alternating layers of a metal with either a metallic glass or a ceramic have shown great promise along these lines. Indentation experiments conducted inside of an SEM are used here to quantify both hardness and indentation fracture toughness of the nanolaminates. Both pileup and crack growth is observed throughout the entire indentation cycle providing insight into the deformation and fracture mechanisms active in these nanolaminates during a contact event. The goals of this research are to study and understand the mechanisms that enable these disparate materials to co-deform and to produce a laminate with both high strength and high toughness at small length scales.

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SEM *In-Situ* Indentation Fracture Toughness of Metal-Ceramic Nanolaminates

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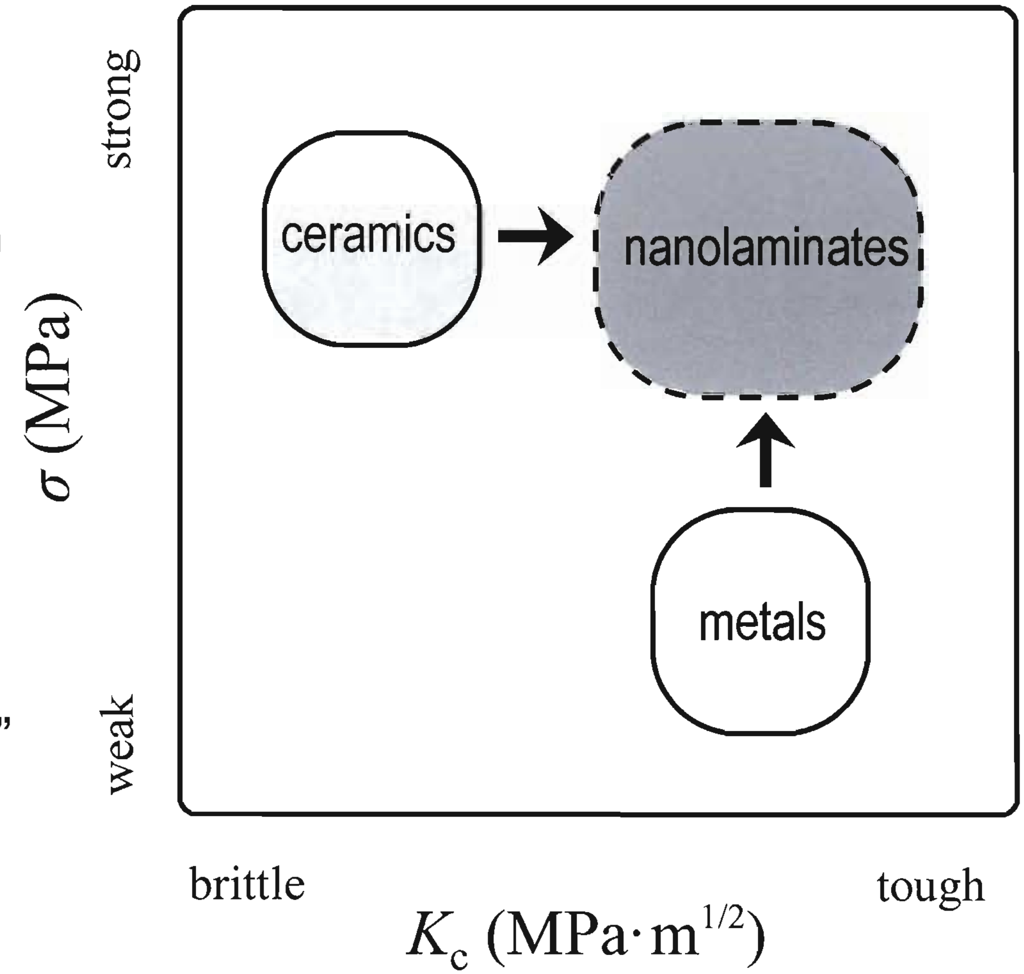
Challenge: To combine the toughness of a metal and the strength of a ceramic in a film.

- "Smaller is stronger"
  - Grain refinement = Hall-Petch
  - Thin films = Confined Layer Slip
  - Micropillars = Dislocation starvation
  - Nanoparticles = Surface/Volume
- "Smaller is tougher"
  - S.C. micropillars (Michler, et al., APL, 2007)
  - S.C. nanoparticles (Gerberich, et al., Phil. Mag., 2011)
- But a little larger than "smaller" is usually not both stronger + tougher.



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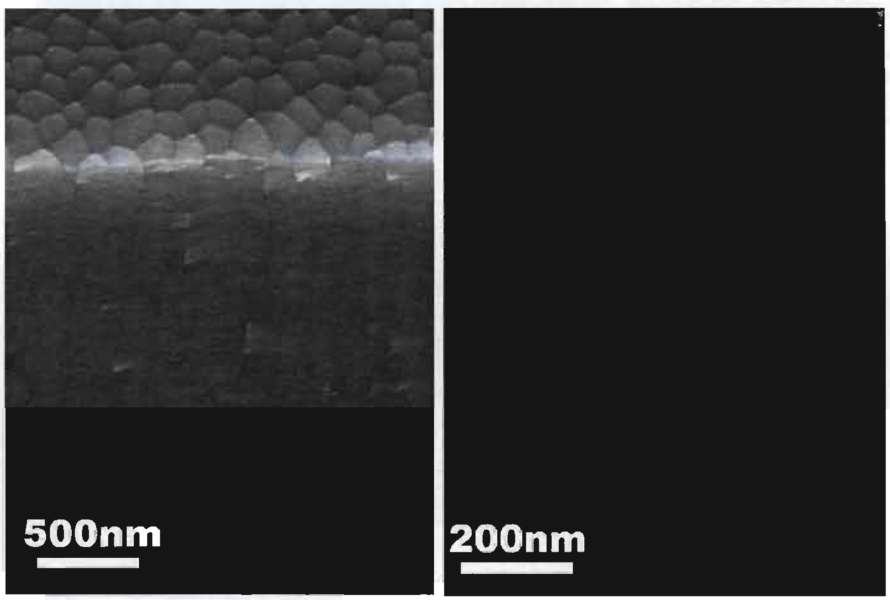
Background: Nanolaminate structure

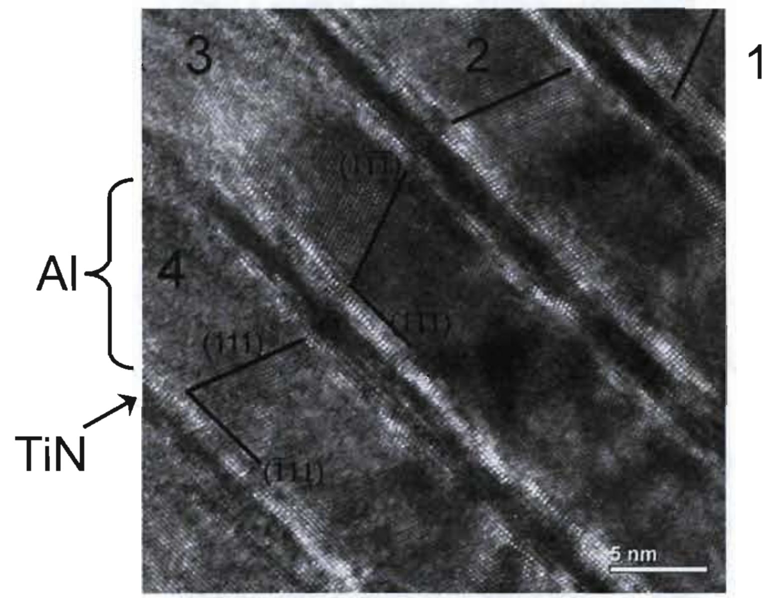
Columnar structure

Al-TiN (2nm-2nm)



Within column: twinned Al

Al-TiN (9nm-1nm)



Bhattacharyya, et al. *APL* **96** (2010) 093113.

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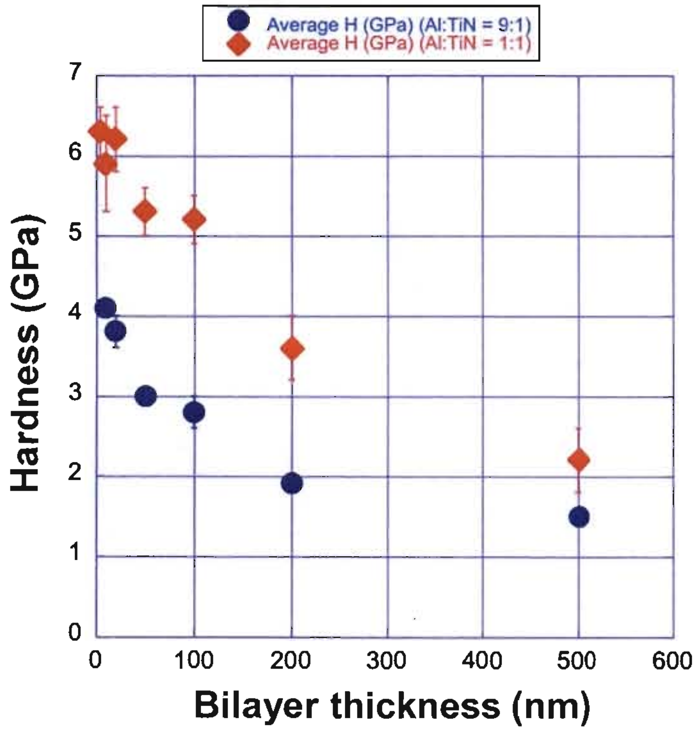
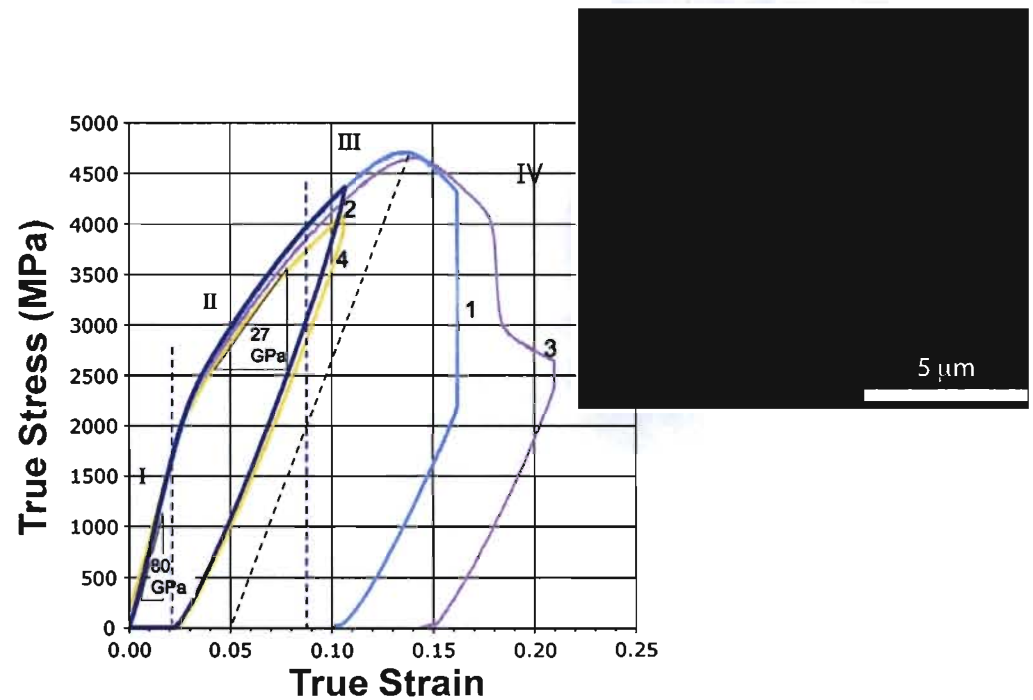
Background: Nanolaminate properties

Indentation



Pillar Compression



Bhattacharyya, et al. *Phil. Mag.* **90**, 13 (2010) 1711
Bhattacharyya, et al. *Acta Mater.* **59** (2011) 3804
Bhattacharyya, et al. *Scripta Mater.* **58** (2008) 981

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Background: Indentation Parameters

- Indention with cube corner to drive radial fracture.
- Load range: 1 μN to 1 N
- Indentation strain rate: 4 orders of magnitude

E.g., for a maximum load of 500 mN:

$\dot{\varepsilon} = 1.0$, loading 3 s

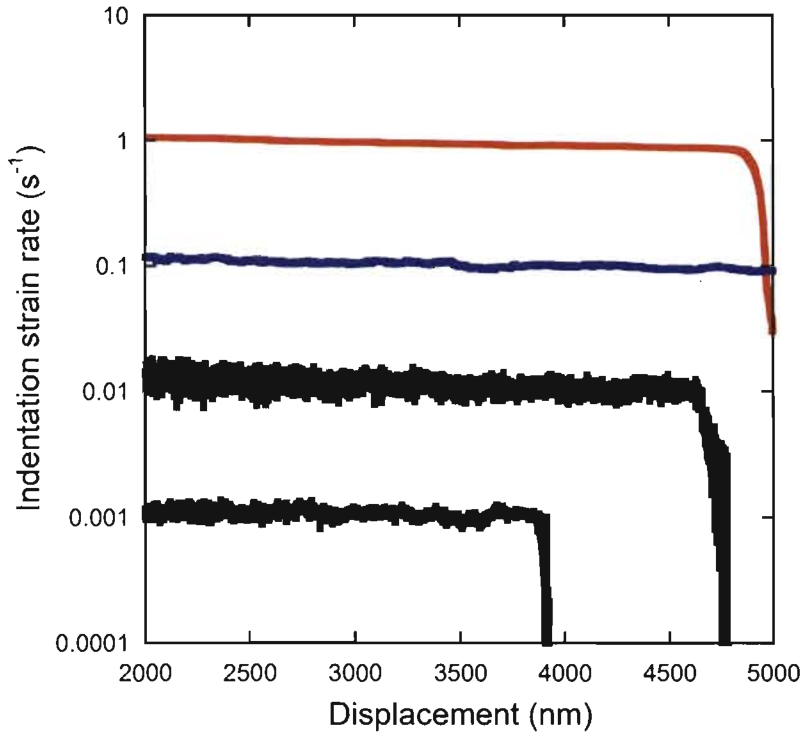
$\dot{\varepsilon} = 0.1$, loading 30 s

$\dot{\varepsilon} = 0.01$, loading 300 s

$\dot{\varepsilon} = 0.001$, loading 3000 s

$$\dot{\varepsilon} = \left(\frac{\dot{h}}{h}\right) = \frac{1}{2}\left(\frac{\dot{P}}{P}\right)$$

Lucas, Oiver, Pharr, Loubet, *MRS Proc.* **436** (1997) 233.



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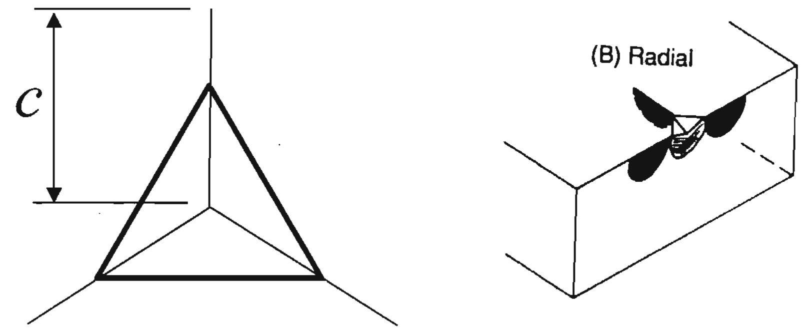
Background: Indentation Fracture Toughness

Lawn, Evans, Marshall, "Elastic-plastic indentation damage in ceramics: The median-radial crack system," *J. Am. Ceram. Soc.* 63, 9-10 (1980) 574.

$$K^{R} = \xi^{R}_{c.c.}\left(\frac{E}{H}\right)^{1/2}\left(\frac{P_{max}}{c^{3/2}}\right)$$



$K^R \equiv$ Residual stress intensity factor $(\mathrm{MPa}\sqrt{\mathrm{m}})$

$E \equiv$ Elastic Modulus (GPa)

$H \equiv$ Hardness (GPa)

$P_{max} \equiv$ Maximum Load (mN)

$c \equiv$ Crack length from center of indent μm

$\xi^{R}_{c.c.} \equiv$ Geometric constant $= 0.04^*$

*cube corner, Pharr, *MSEA* **A253** (1998) 151.

Al layer thickness (nm)	TiN layer thickness (nm)	Bilayer thickness (nm)	Average E_r (GPa)	Average H (GPa)
450	50	500	116.0	1.6
180	20	200	141.3	2.0
→ 90	10	100	112.0	2.8
45	5	50	133.9	3.1
18	2	20	100.0	4.0
→ 9	1	10	135.9	4.1
250	250	500	215.3	2.3
100	100	200	175.2	3.5
50	50	100	179.2	5.2
25	25	50	150.3	5.4
10	10	20	145.3	6.3
→ 5	5	10	129.5	5.7
→ 2	2	4	148.1	6.3

Bhattacharyya, et al. *Phil. Mag.* **90**, 13 (2010) 1711

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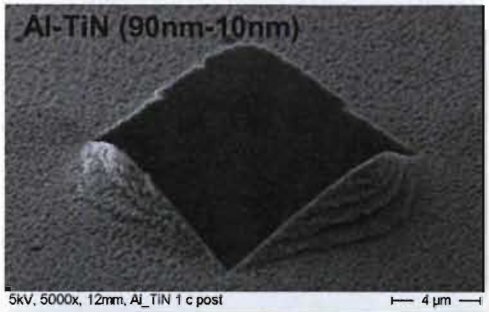
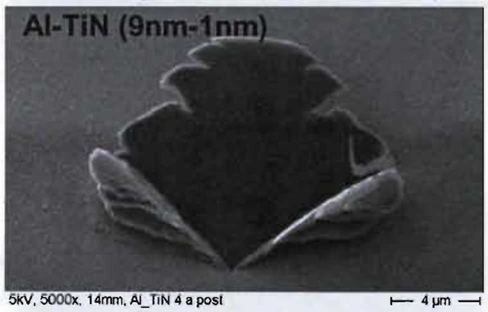
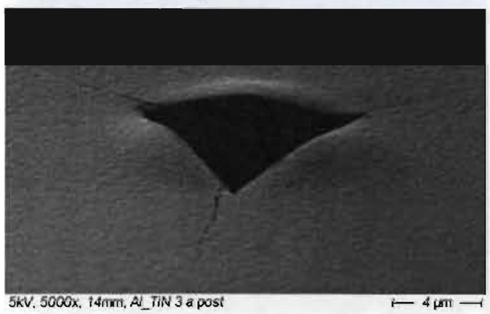
SEM-Indentation Observations







- **Radial surface cracks in Al-TiN**
  - **90 nm – 10 nm**
    - **NO** surface cracks at any rate ($0.001 < \varepsilon < 20$)
    - Consecutive shear band formation
  - **9 nm – 1 nm**
    - Indentation rate effect
      - $\varepsilon \ll 0.001 \rightarrow$ no radial surface cracks
      - $\varepsilon \cong 0.001 \rightarrow$ cracking > 170mN
      - $\varepsilon > 0.05 \rightarrow$ cracking < 90mN
    - **NO** growth during unloading
    - Both intra- and intercolumnar
    - Consecutive shear band formation
  - **5 nm – 5 nm**
    - **NO** observable effect of indentation rate
    - **NO** growth during unloading
    - Mainly intercolumnar
  - **2 nm – 2 nm**
    - **NO** observable effect of indentation rate
    - **Possible growth** during unloading
    - Intracolumnar cracks

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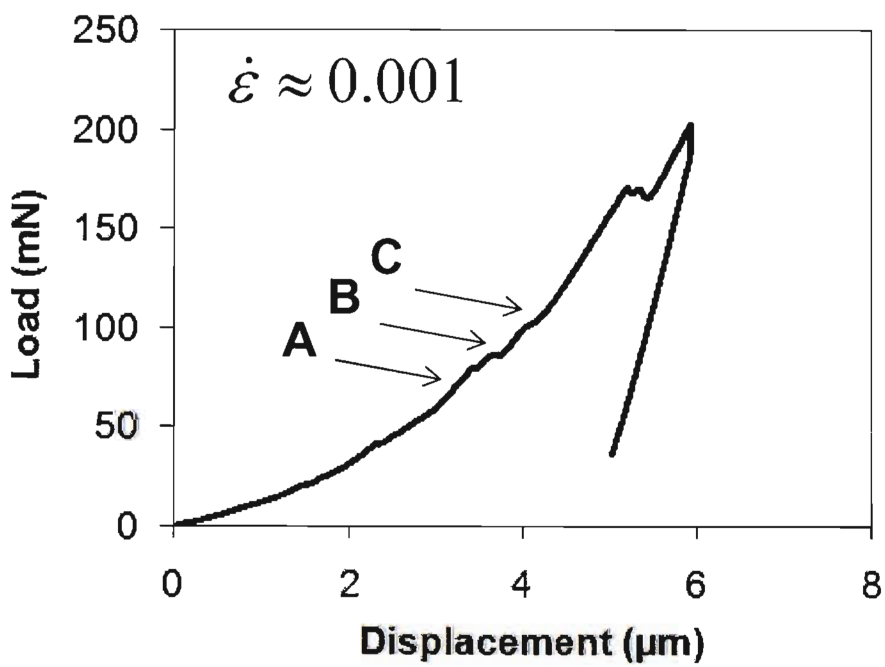
Toughening mechanism: Indentation rate effect

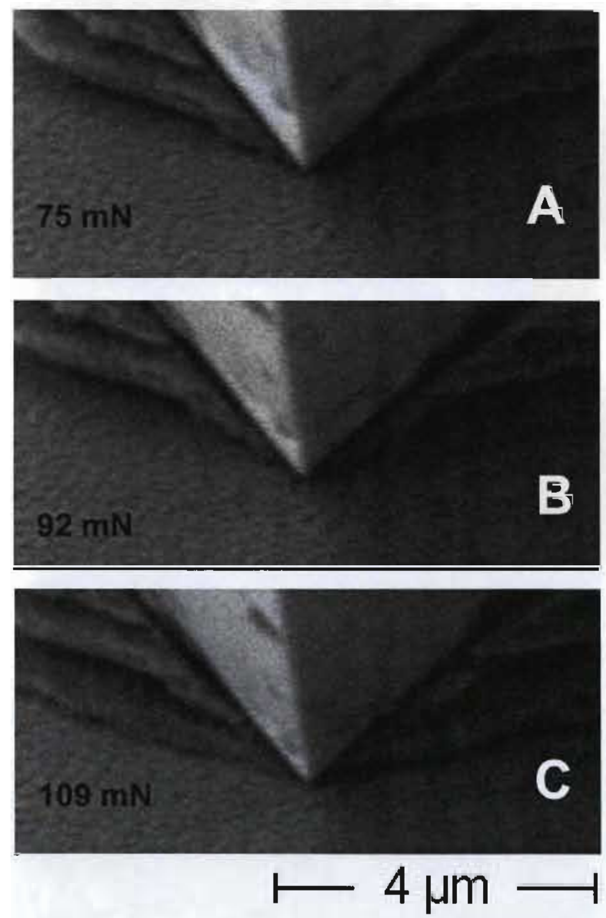


Al-TiN (9nm-1nm) indentation: shear bands consume radial cracks

No crack

Embryonic radial crack

No crack



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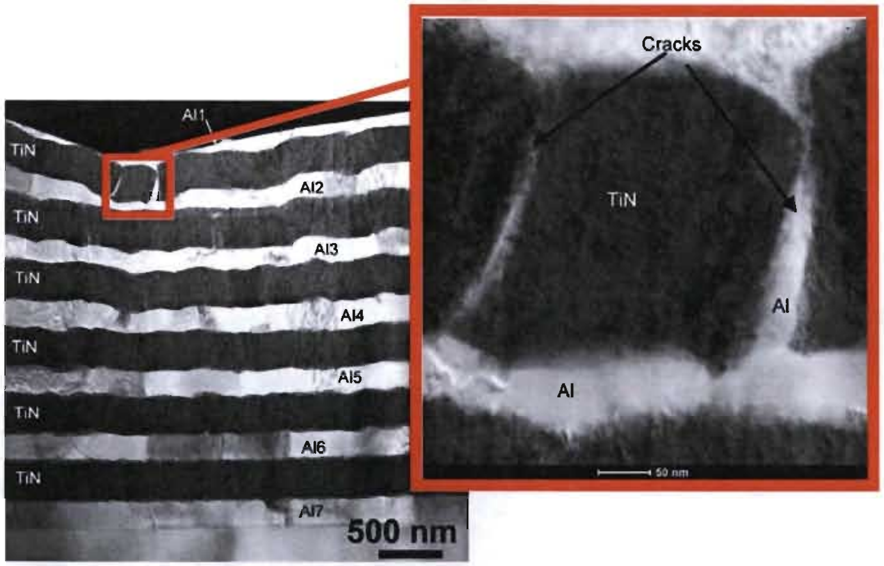
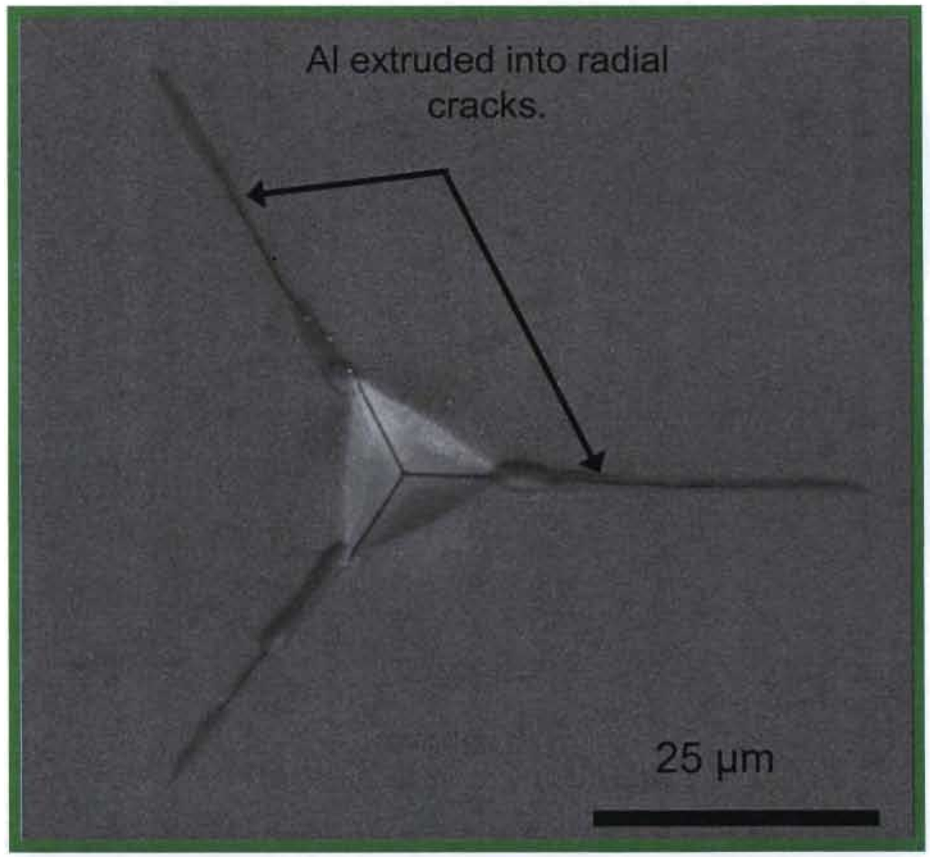
Toughening mechanism: Flow of Al blunts crack tips

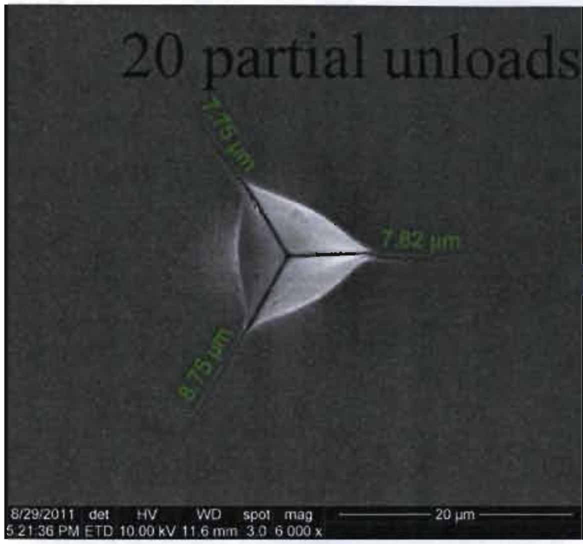
Al-TiN (250nm-250nm) indent where Al flowed into cracks.

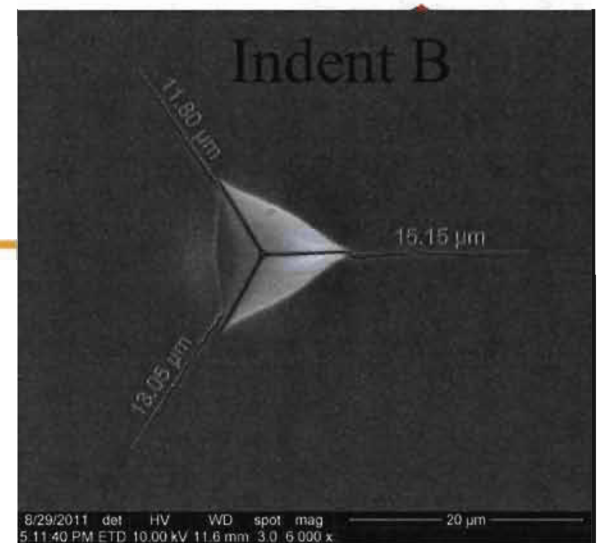


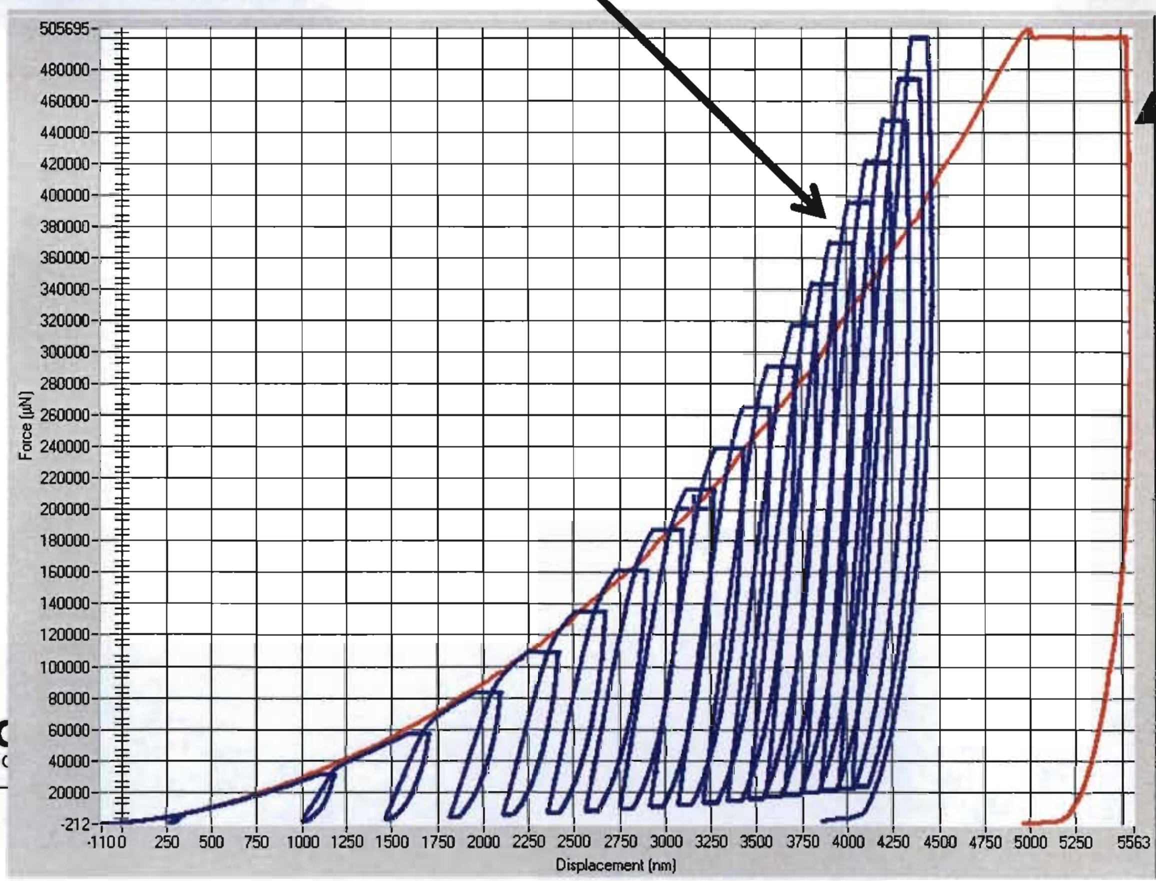
Bhattacharyya, et al. *Phil. Mag.* **90**, 13 (2010) 1711

Al-TiN (5nm-5nm) indent to 1N followed by reloading.




20 partial unloads
7.75 µm
7.82 µm
8.75 µm
8/29/2011 det HV WD spot mag
5:21:36 PM ETD 10.00 kV 11.6 mm 3.0 6 000 x
20 µm


Indent B
11.80 µm
15.15 µm
13.05 µm
8/29/2011 det HV WD spot mag
5:11:40 PM ETD 10.00 kV 11.6 mm 3.0 6 000 x
20 µm


Force (µN)
505695
480000
460000
440000
420000
400000
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
-212
-1100 250 500 750 1000 1250 1500 1750 2000 2250 2500 2750 3000 3250 3500 3750 4000 4250 4500 4750 5000 5250 5563
Displacement (nm)

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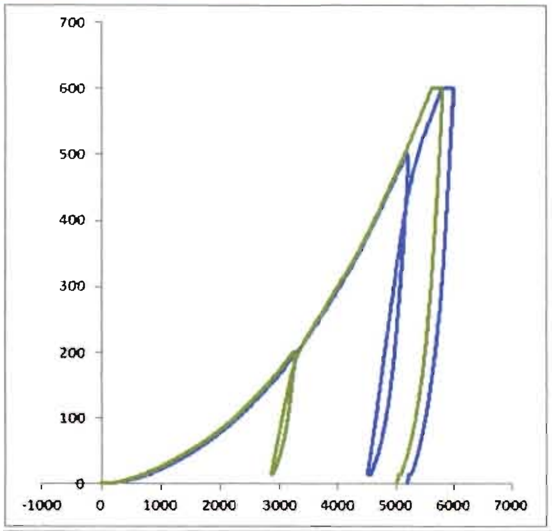
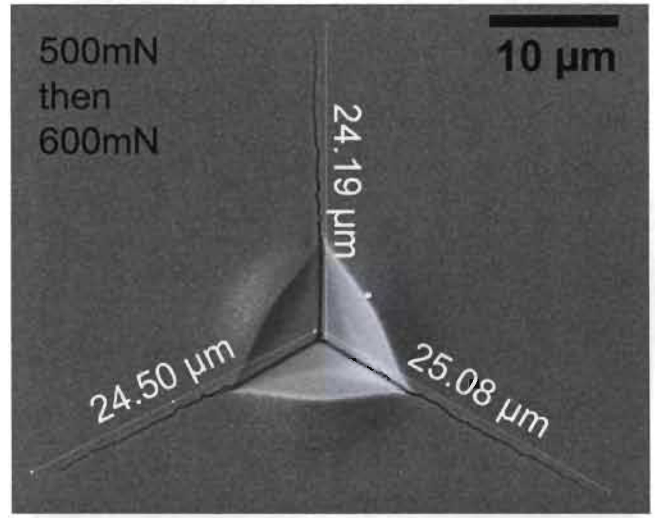
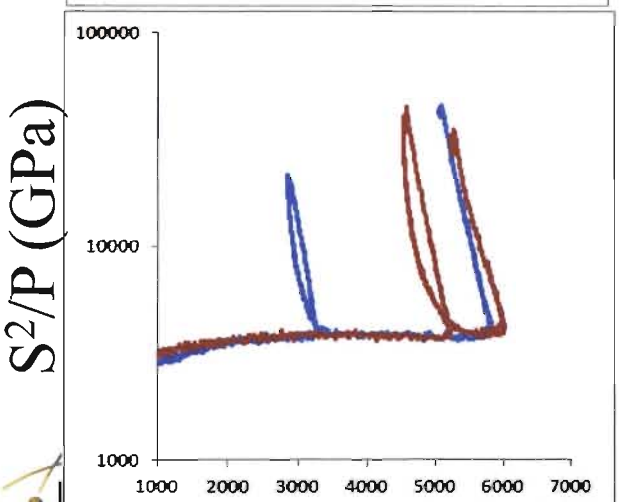
Can CSM detect when cracking begins, its extent and any flow of Al?

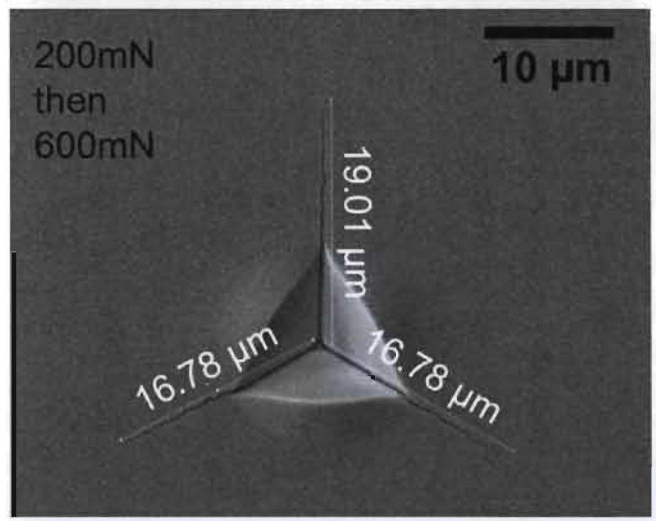


5nm5nm 600mN-500mN e=0.01 1s hold





5nm5nm 600mN-200mN e=0.01 1s hold



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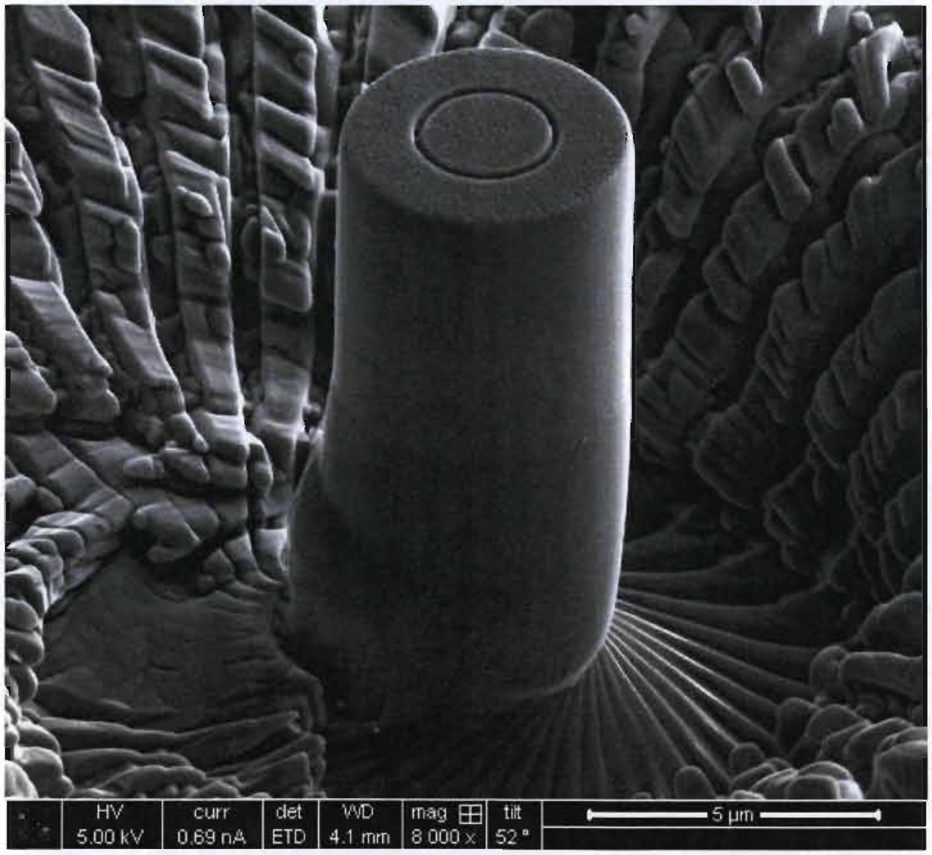
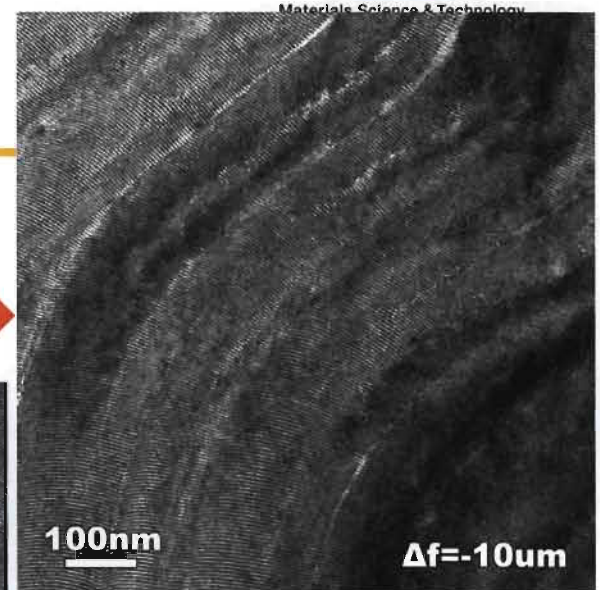
Co-deformation of Al-TiN (2nm-2nm) layers

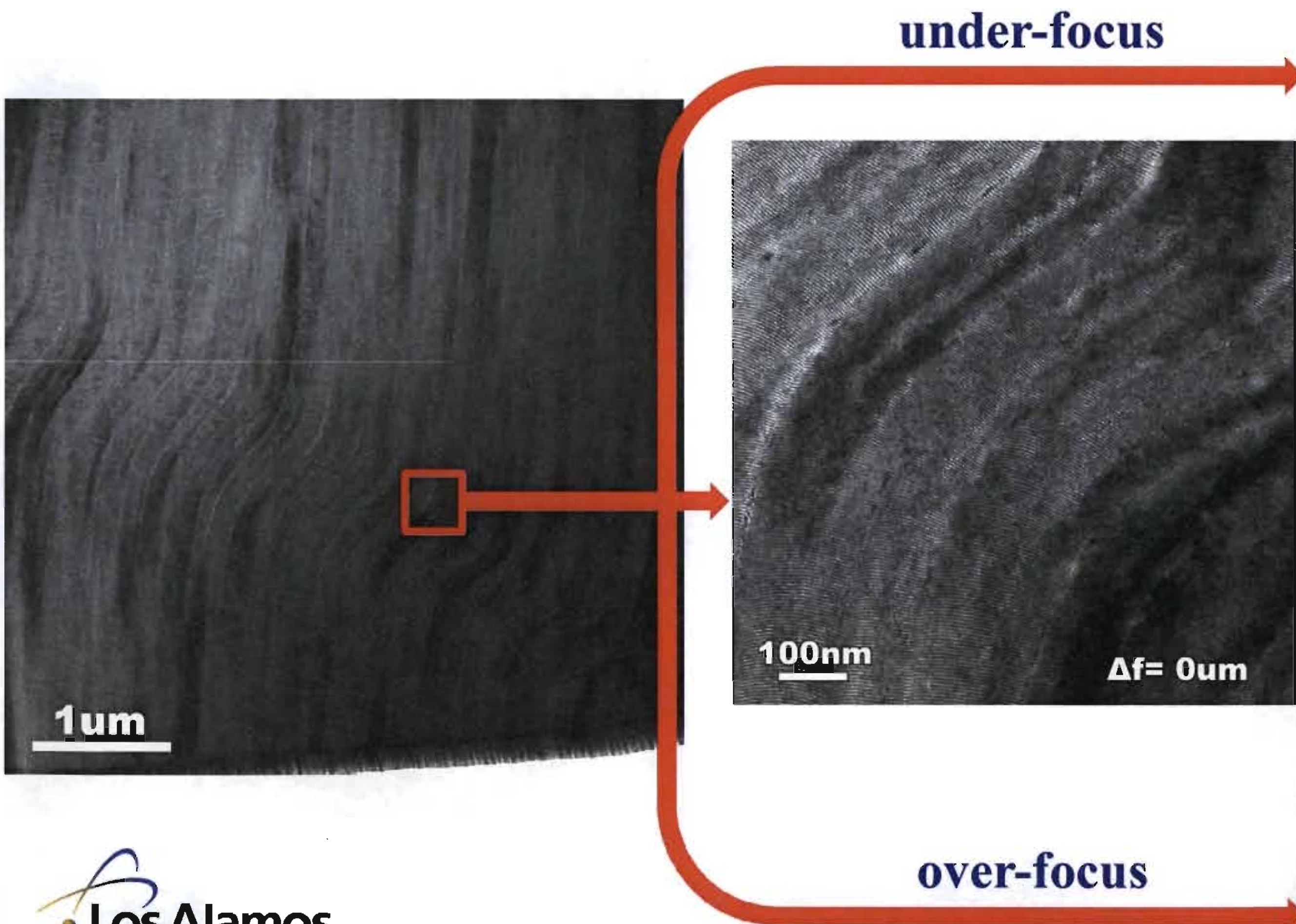
Compressed pillar

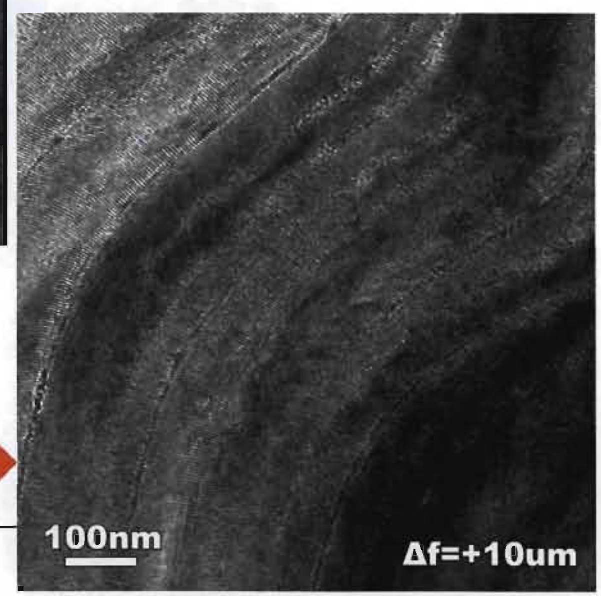


TEM foil

Micro-voids are generated between columns after compression







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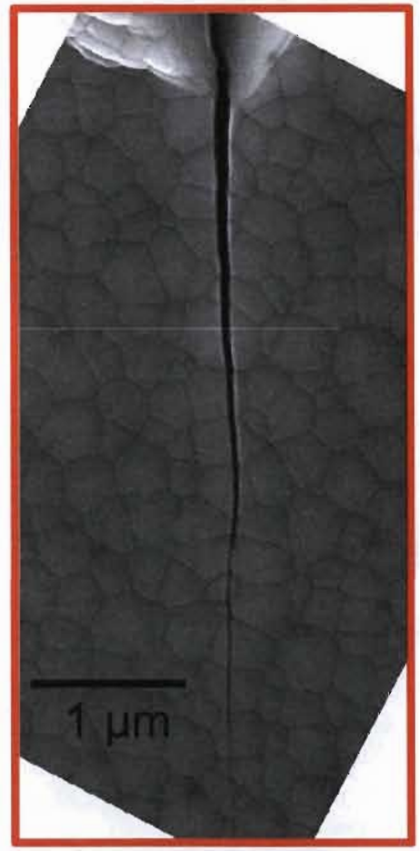
Intra- vs. intercolumnar radial fracture

Al-TiN (9nm-1nm)

Al-TiN (2nm-2nm)



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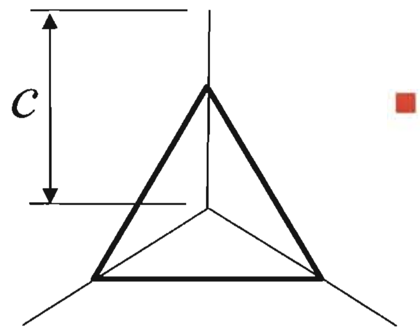
Nanolaminate Indentation Fracture Toughness



$$K^{R} = \xi^{R}_{c.c.}\left(\frac{E}{H}\right)^{1/2}\left(\frac{P_{max}}{c^{3/2}}\right)$$

- **Possible toughening mechanisms** — $K^{R}\left(\mathrm{MPa}\cdot\sqrt{\mathrm{m}}\right)$
  - **Flow of Al into cracks (?)**
    - **5 nm – 5 nm**
      - Monotonic loading : 1.2
      - 2 cycles : 1.3
      - 10 cycles : 1.4
      - 20 cycles : 1.5
    - **2 nm – 2 nm**
      - Monotonic loading : 1.4
      - 2 cycles : 2.8
  - **Rate effect, low rate favors shear band formation at expense of radial cracking.**
    - **9 nm – 1 nm**
      - ε = 1.0 : 1.2
      - ε = 0.001 : 1.5

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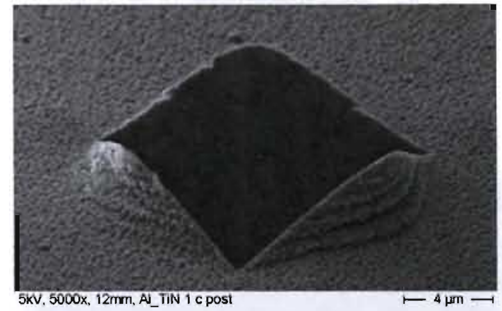
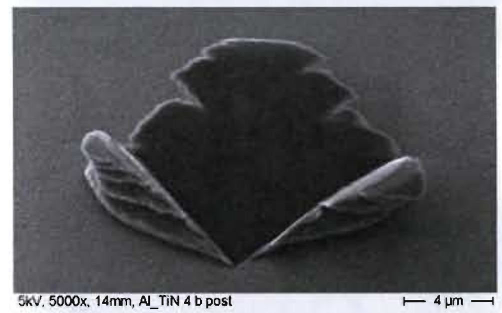
How to define this complex deformation?

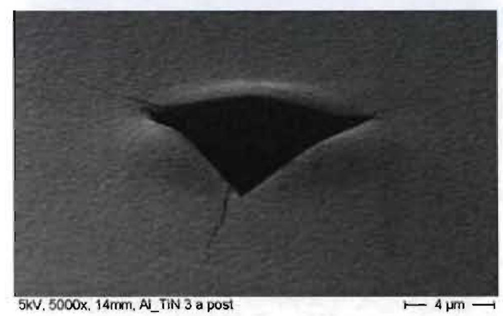
- Al-TiN (90nm-10nm), 7 µm deep c.c. indent
  - Smooth load-displacement curve
  - Smooth pileup formation
  - Consecutive shear band formation
- Al-TiN (9nm-1nm), 7 µm deep c.c. indent
  - Serrated load-displacement curve
  - Serrated pileup formation
  - Individual shear bands form along one face of the indenter at a time and consume embryonic surface cracks when indentation rate is 5nm/s or below (see movie).
- Al-TiN (5nm-5nm), 6 µm deep c.c. indent
  - Smooth load-displacement curve
  - Minimal pile-up
  - Either zero or one shear band formed beneath indent on each indenter face.



15 nm/s



2 nm/s



10 nm/s

Nanolaminate deformation beneath and around indents is similar to geological structures.

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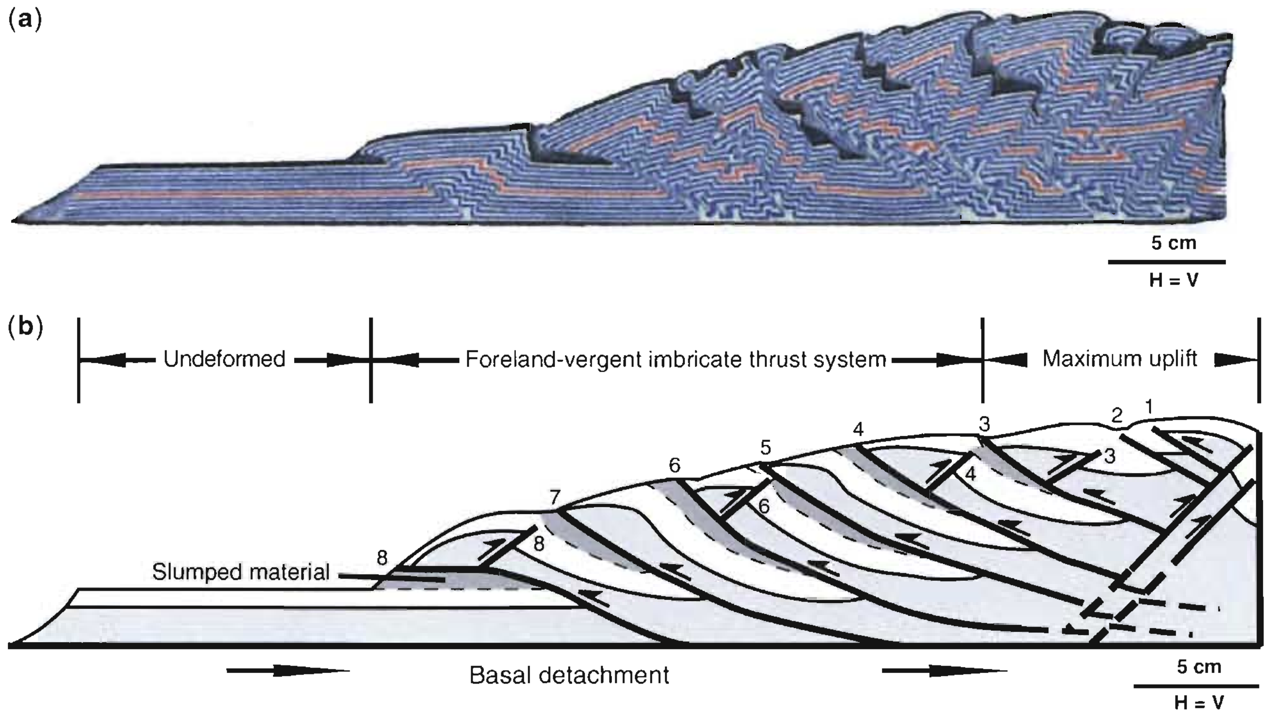
In compression rocks either fold (ductile) or fault (brittle) and many complex structures have been defined beginning in the 17th century.

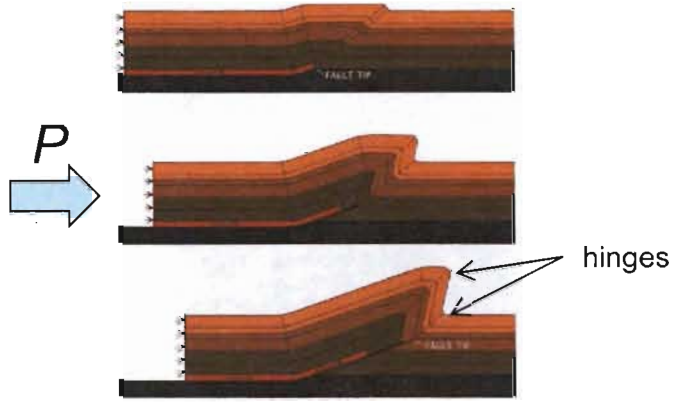


Poblet & Lisle, “Kinematic evolution and structural styles of fold-and-thrust belts,” *Geological Society, London, Special Publications* 349 (2011) 1.

Thanks to Dr. Xavier Maeder now @ U. of Lausanne.

Nanolaminate Deformation Structures: Analogues to Geology

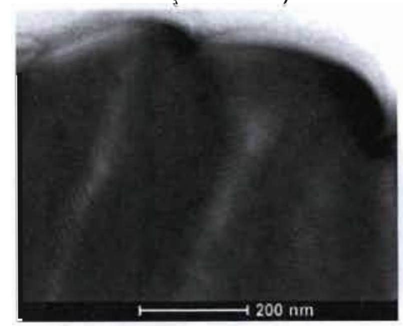
Fault-propagation folds yield at hinges.



Storti, et al. "Growth stratal architectures associated to decollement folds and fault-propagation folds. Inferences on fold kinematics," *Tectonophysics* 282 (1997) 353.

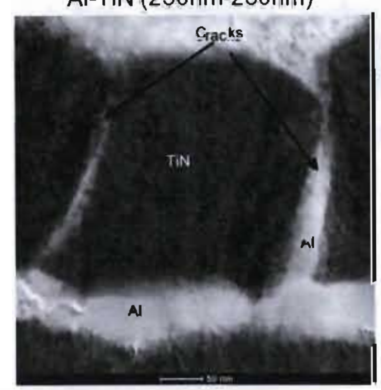
Bhattacharyya, et al. *Phil. Mag.* (2010).

Al-TiN (9nm-1nm)



Boudinage: geological term for structures formed when a rigid body fractures and is embedded in a ductile layer due to plastic flow of ductile layer from hydrostatic pressure.

Al-TiN (250nm-250nm)



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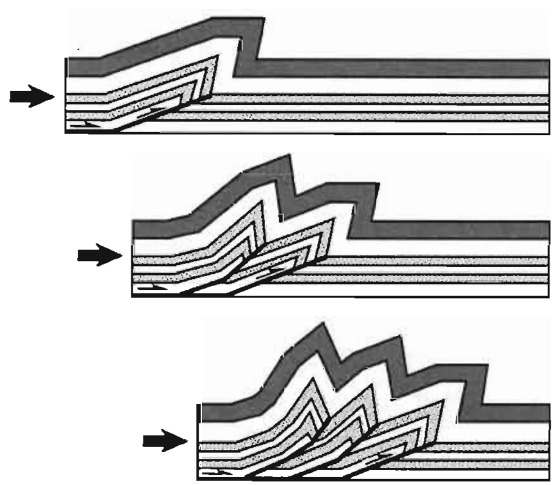
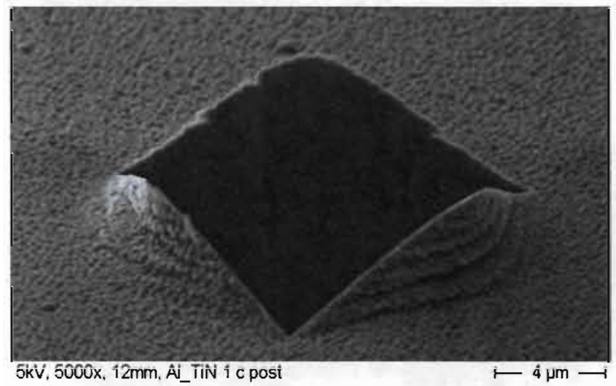
Nanolaminate Deformation Structures: Analogues to Geology

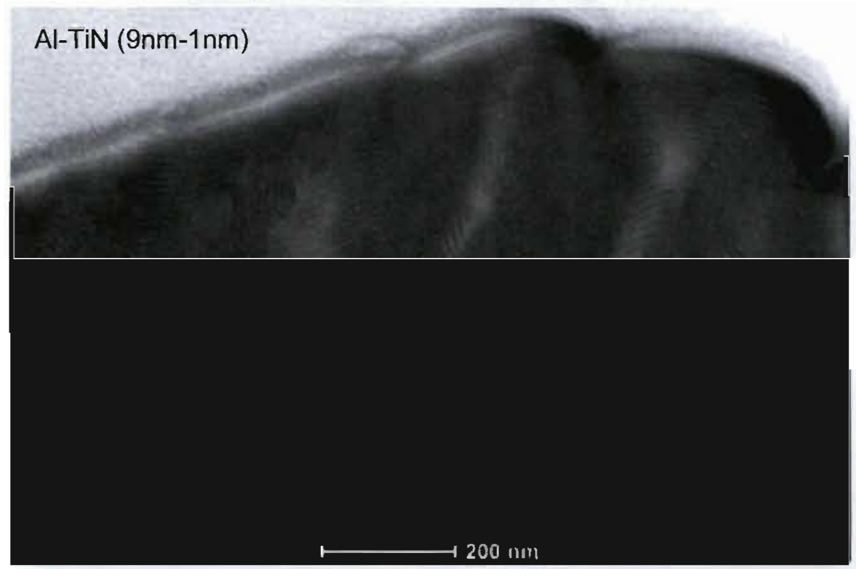
"Development of an imbricate thrust system and related fault-propagation folds following a break-forward sequence and steepening of the earliest (hinterlandward) thrusts."



Poblet & Lisle, "Kinematic evolution and structural styles of fold-and-thrust belts," *Geological Society, London, Special Publications* 349 (2011) 1.

Al-TiN (90nm-10nm)





Bhattacharyya, et al. *Phil. Mag.* (2010).

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Nanolaminate Deformation Structures: Analogues to Geology

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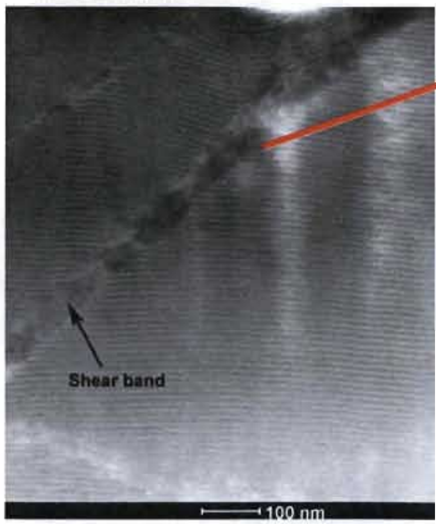
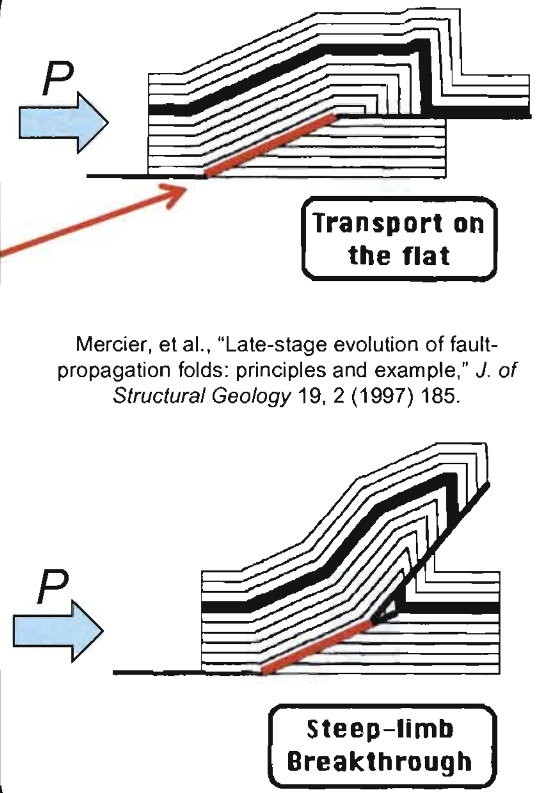
Post-blockage evolution of a fault propagation fold can show either 'steep-limb breakthrough' or 'transport on the flat.'

Al-TiN (9nm-1nm)

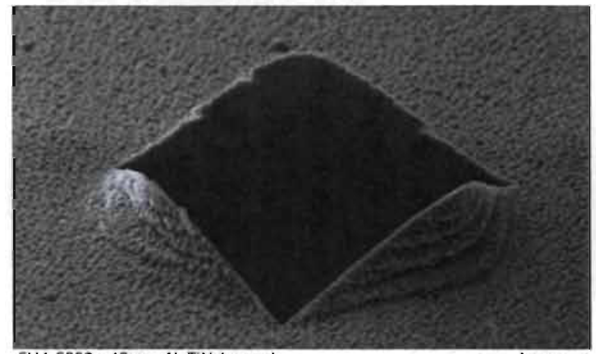


Bhattacharyya, et al. *Phil. Mag.* (2010).



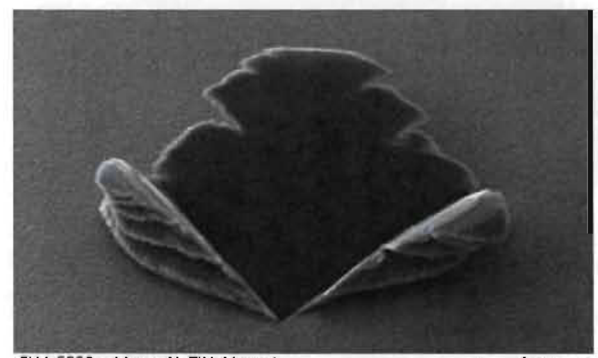
Mercier, et al., "Late-stage evolution of fault-propagation folds: principles and example," *J. of Structural Geology* 19, 2 (1997) 185.

Al-TiN (90nm-10nm)



5kV, 5000x, 12mm, Al_TiN 1 c post — 4 µm

Al-TiN (9nm-1nm)



5kV, 5000x, 14mm, Al_TiN 4 b post — 4 µm

Chevron Folds

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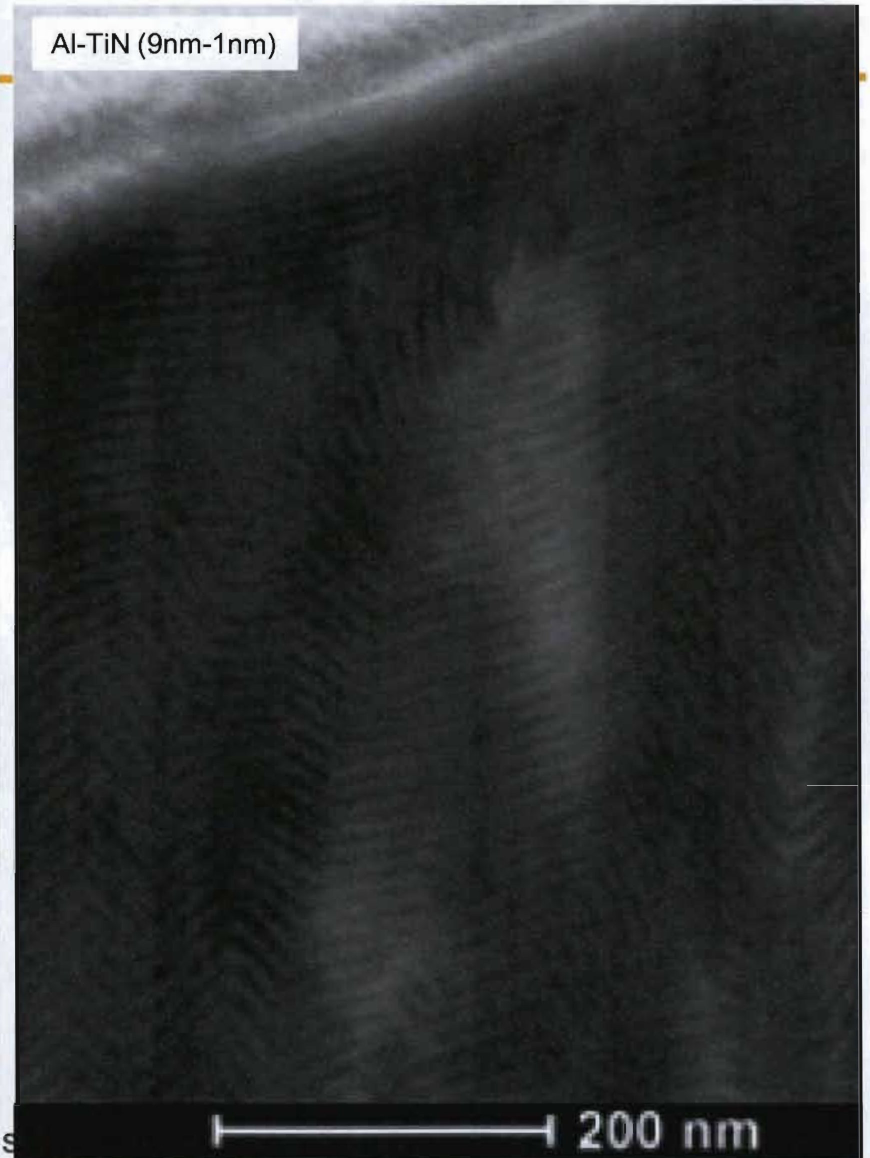
Ramsay, "Development of Chevron Folds," *Geological Soc. of America Bulletin* 85 (1974) 1741.



Bhattacharyya, et al. *Phil. Mag.* (2010).

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Summary

- SEM in-situ indentation insights
  - No radial crack growth during unloading.
  - Shear bands form at expense of radial cracks.

Al (nm)	TiN (nm)	Pile up	Shear bands	Radial cracks	Unload growth	Rate effect	Al flow	TiN flow	K^R (MPa m$^{1/2}$)
90	10	Yes	Yes	No	-	-	Yes	No	-
9	1	Yes	Yes	Yes	No	Yes	Yes	No	1.5
5	5	No	No	Yes	No	No	Yes	No	1.5
2	2	No	No	Yes	?	No	?	?	2.8

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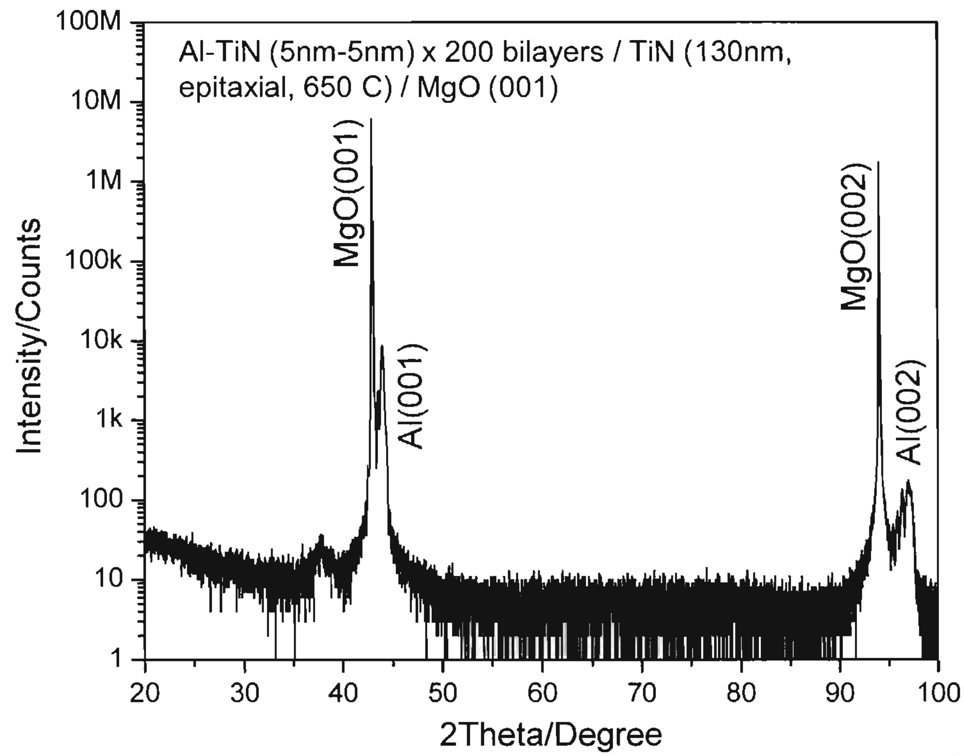
Future work and Acknowledgements

- Optimize deposition parameters
  - High temp deposition = superlattices
  - MgO (001) & (111); Si (001) & (111) creates different interface structures
- Toughening mechanisms
- Critical metal and ceramic length scales



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