SAND2014-3384C

Gold-Ceramic Thin Films: The New Gold Standard

for High Performance Electrical Sliding Contacts

Presented by Nicolas Argibay

Collaborators:

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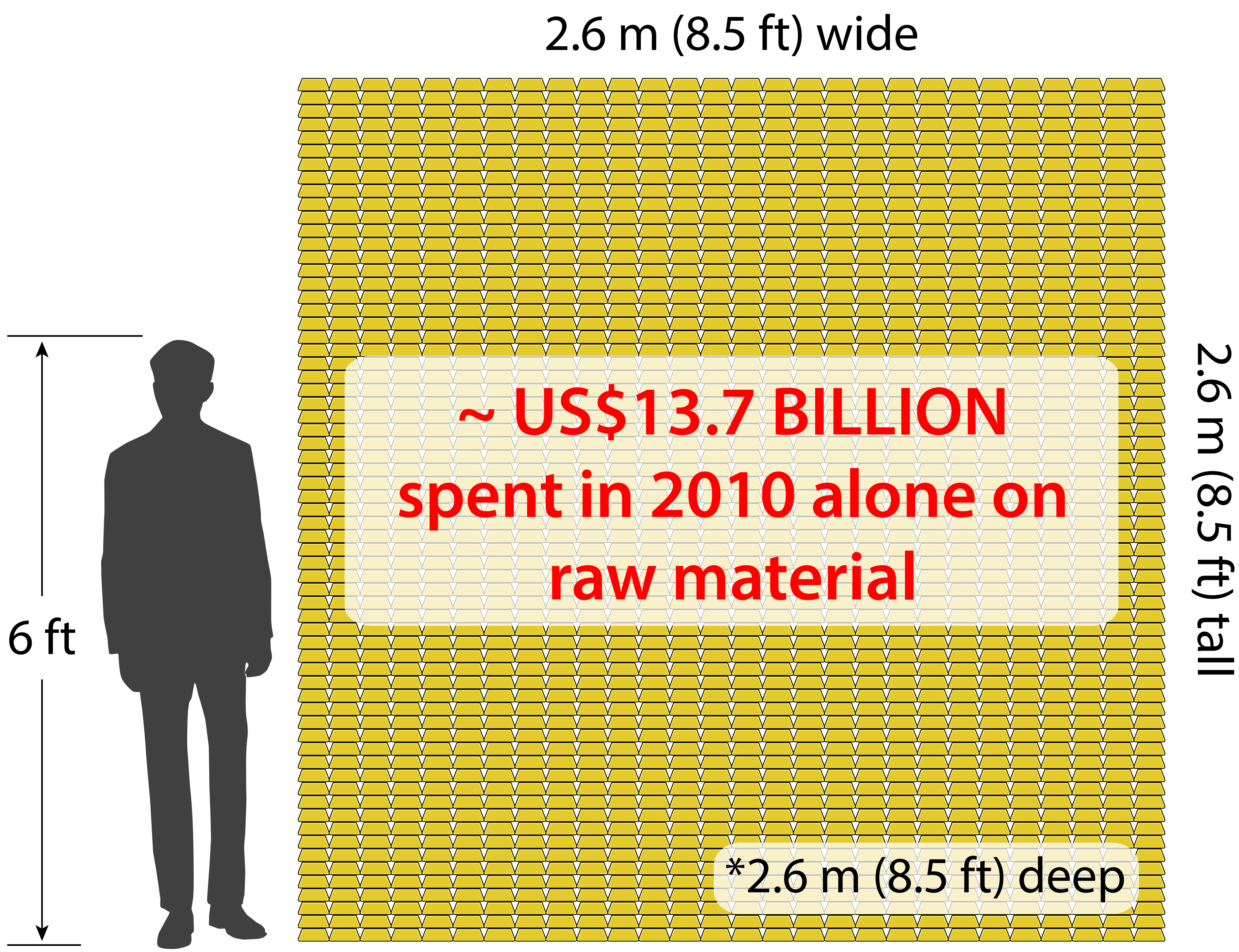
Brief aside: just how relevant is gold as a tribological coating?

An estimated 300 metric tons/year of gold used in electronics related applications, most of it in electroplated connectors and contacts (11% of yearly amount mined)

Equivalent to a cube comprised of ~25,000 standard gold bars (12 kg/26.4 lb each) ***per year***...



... or enough to clad the entire surface of the Eiffel Tower with pure gold 70 µm thick ***every year***

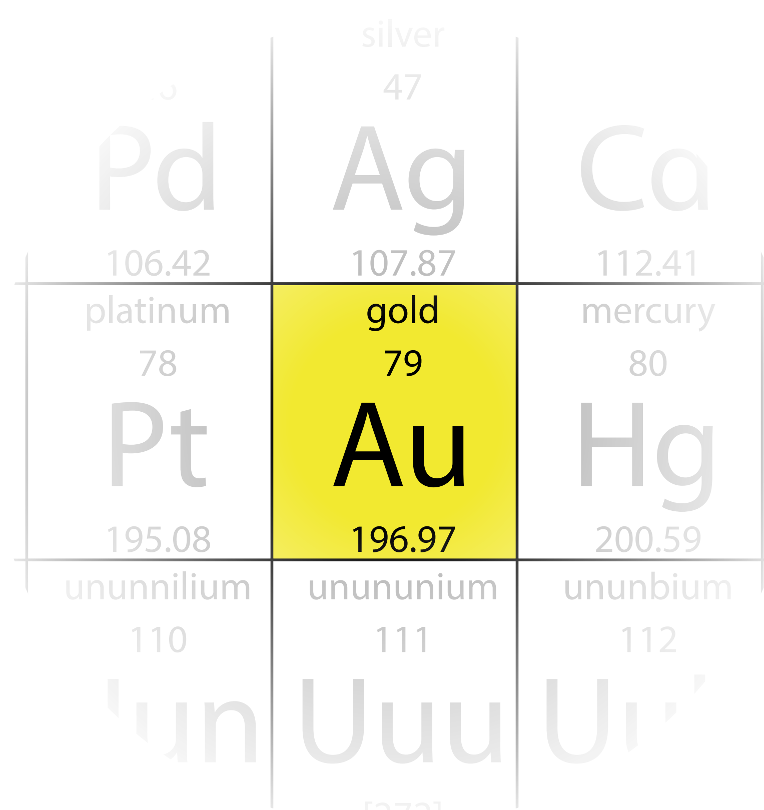
Reference: Gold Survey, Gold Fields Mineral Services Ltd., 2010

What is a common theme in the vast majority of electrical contacts?

MEMS: 1-2 µm thick gold and gold alloy films are typical

printed circuit boards (PCBs): 200 - 500 nm thick electroless gold films on soldered connections to prevent oxidation on PCBs

aerospace: 1 - 3 µm thick hard gold (ASTM/MilSpec) used to achieve predictable friction AND contact resistance over years or decades



What is electroplated "hard gold"?

Nominally gold with the addition of Ni/Co/Fe not exceeding 1 wt. %

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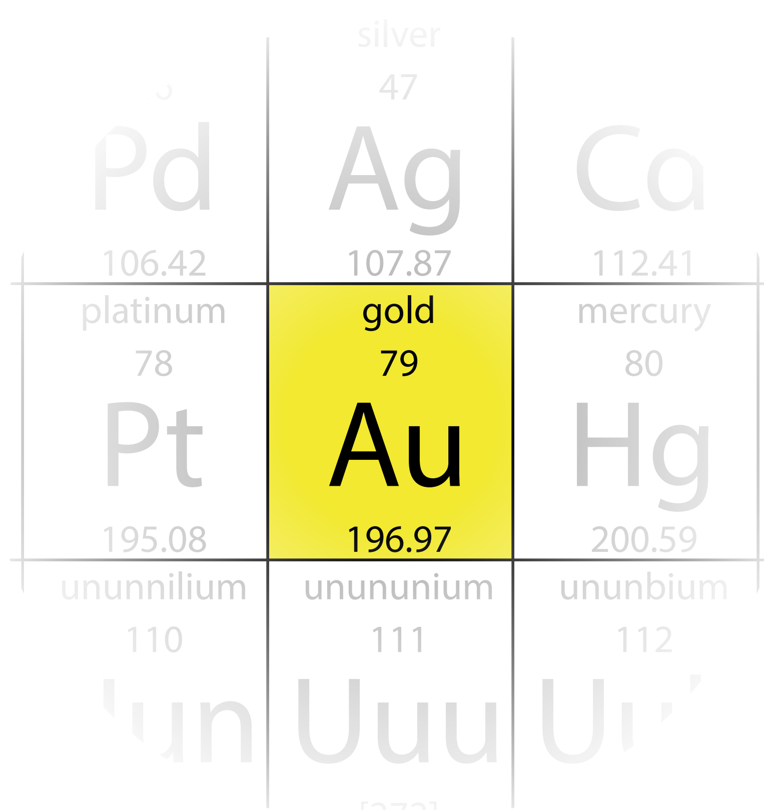


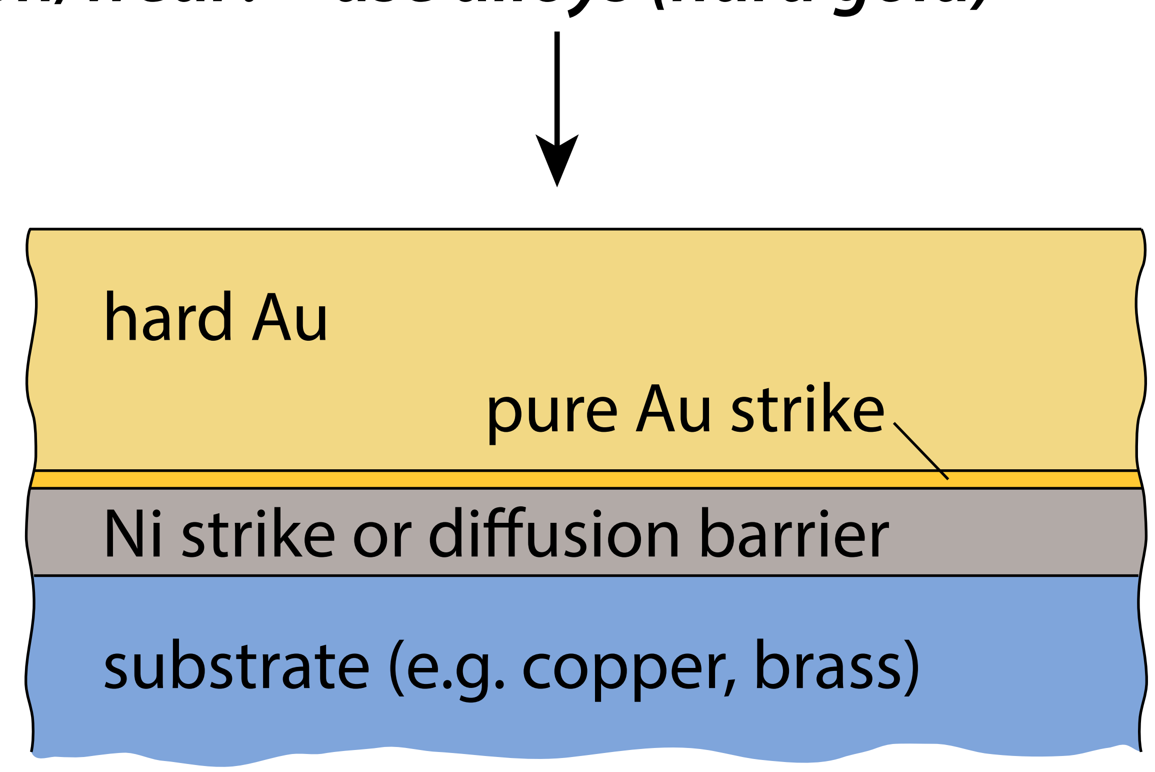
Why? Critical to performance are:

- oxidation resistance ***YES***

- ductility ***YES***

- electrical conductivity ***YES***

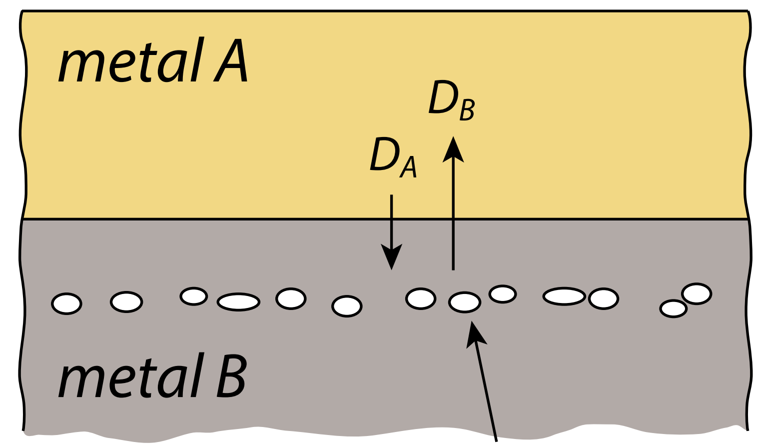
...but low friction/wear? ***use alloys (hard gold)***



What materials aging phenomena are relevant to tribological contacts?

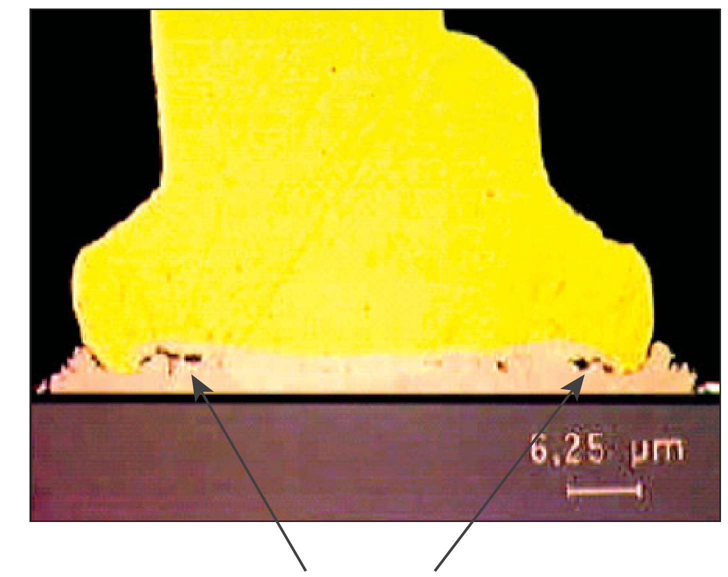
Kirkendall ***porosity*** (voiding) and the formation of ***intermetallics*** (embrittlement):

$D_A < D_B$ results in asymmetric flux of material



pore formation due to defect accumulation

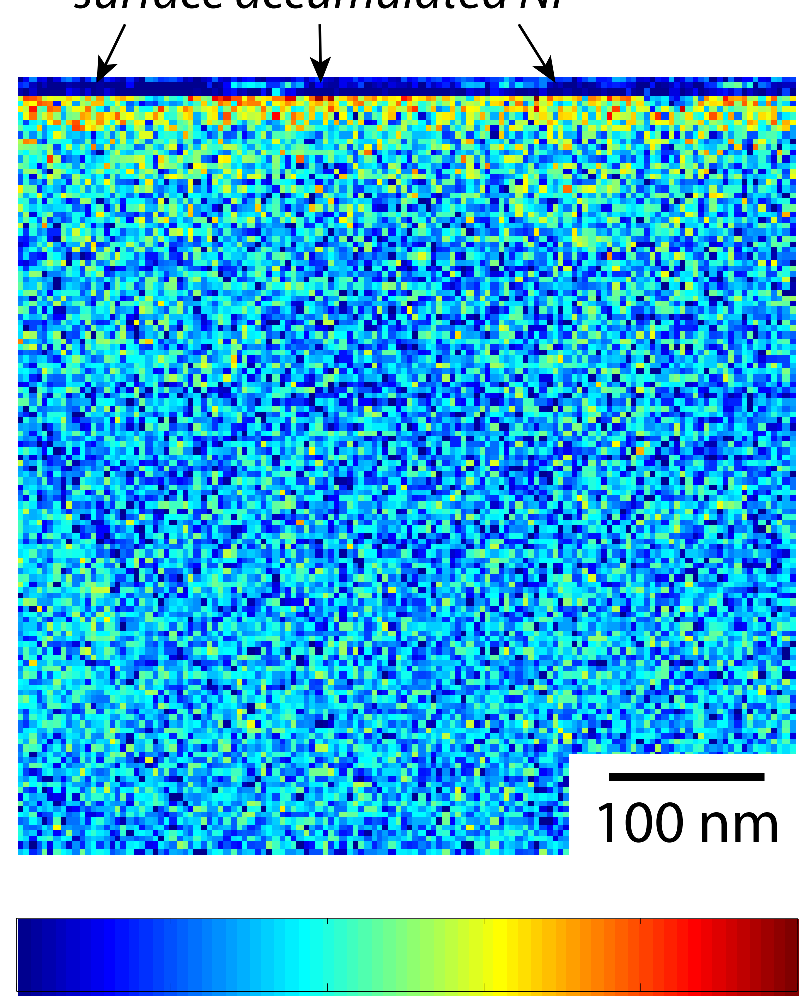
aged Au-Al ball bond used in flip chip bonding



formation of voids and interfacial fractures driven by formation of intermetallics

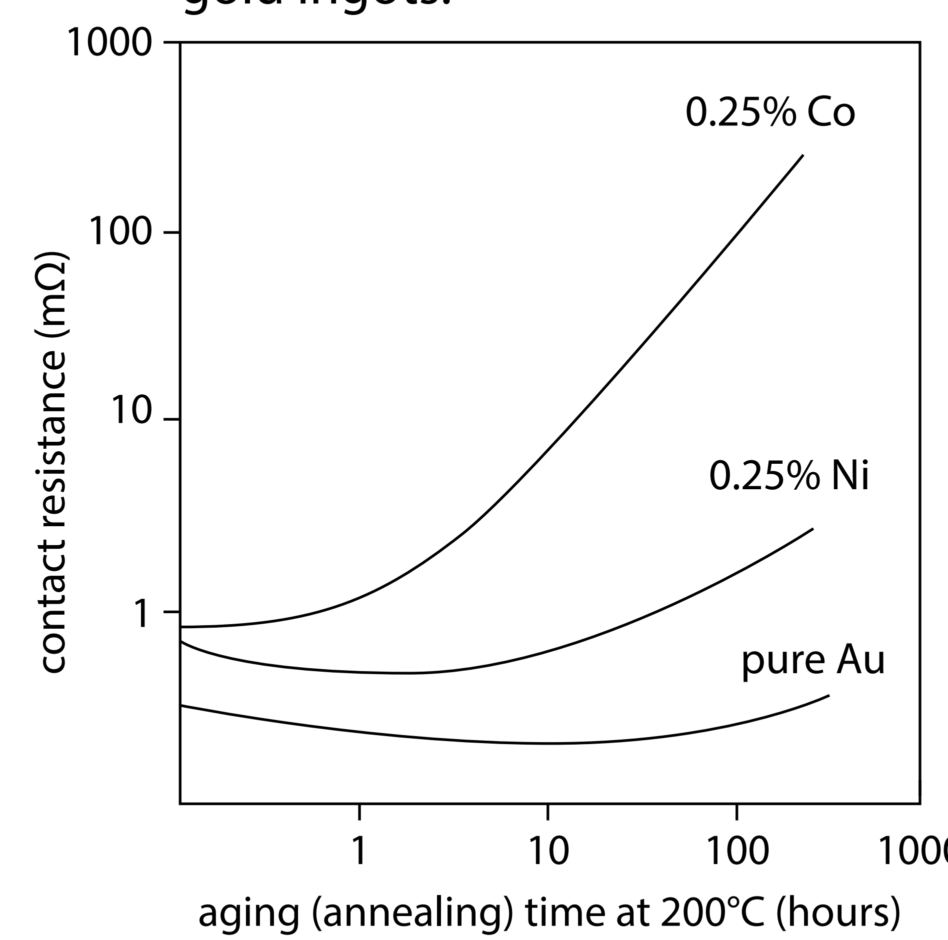
Surface accumulation of underlayer and codeposited species:

surface accumulated Ni



relative Ni concentration in a hard Au film aged at low temperature

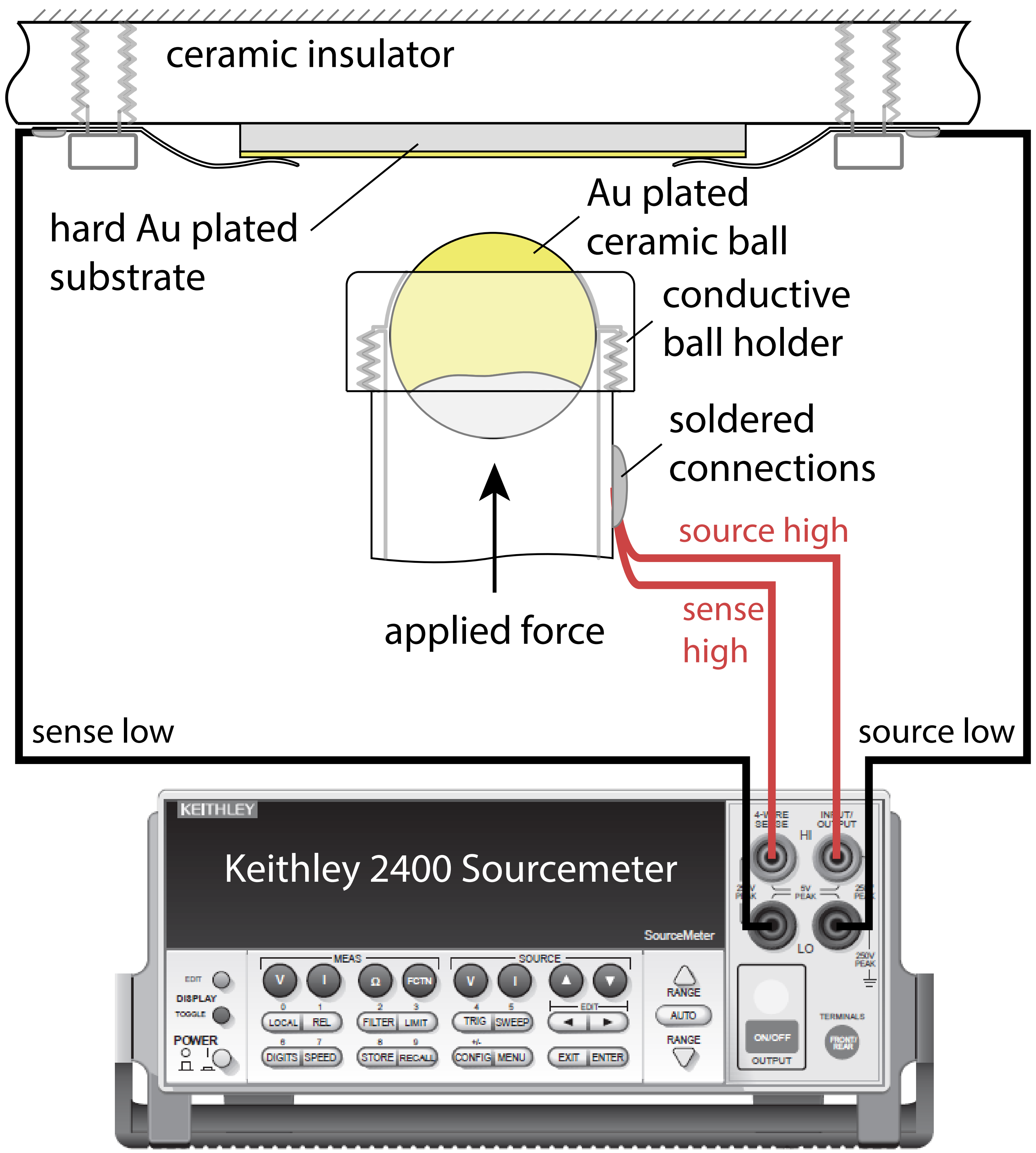
aging of **bulk** pure and alloyed gold ingots:

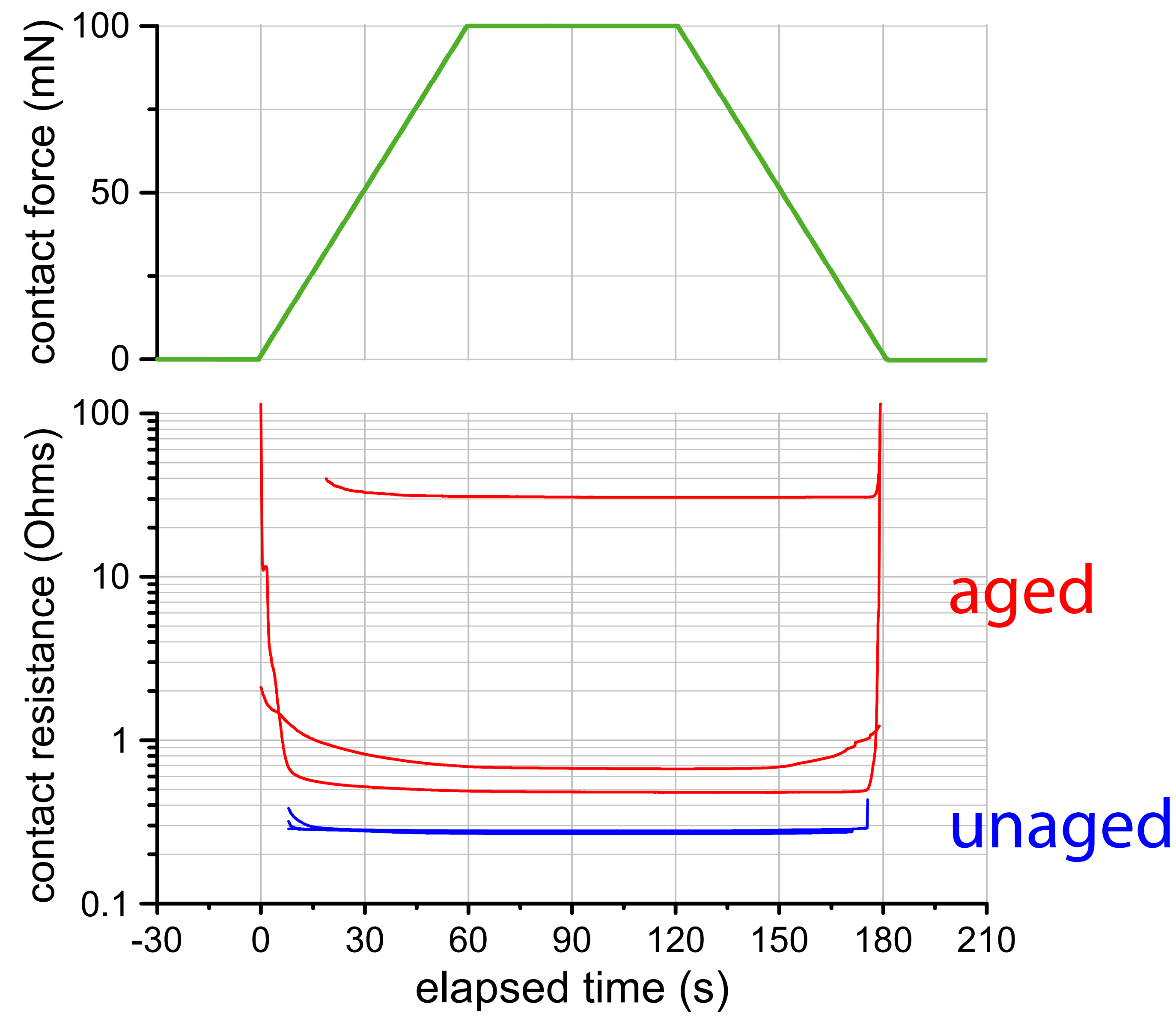


Reference: M. Antler, Plating and Surface Finishing, 1998

Surface accumulation and oxidation can significantly affect ECR

Electrical contact resistance of aged type I hard Au plated Fe-Ni substrate aged at 250°C for 42.5 hours in air:





- film thickness ~ 2 μm type I hard Au on a 5-7μm Ni strike
- 1 mA current
- ball radius : 1/32" (~ 0.79 mm)

several order of magnitude changes in contact resistance can occur quickly

New routes for mitigating aging in gold electrical contacts?

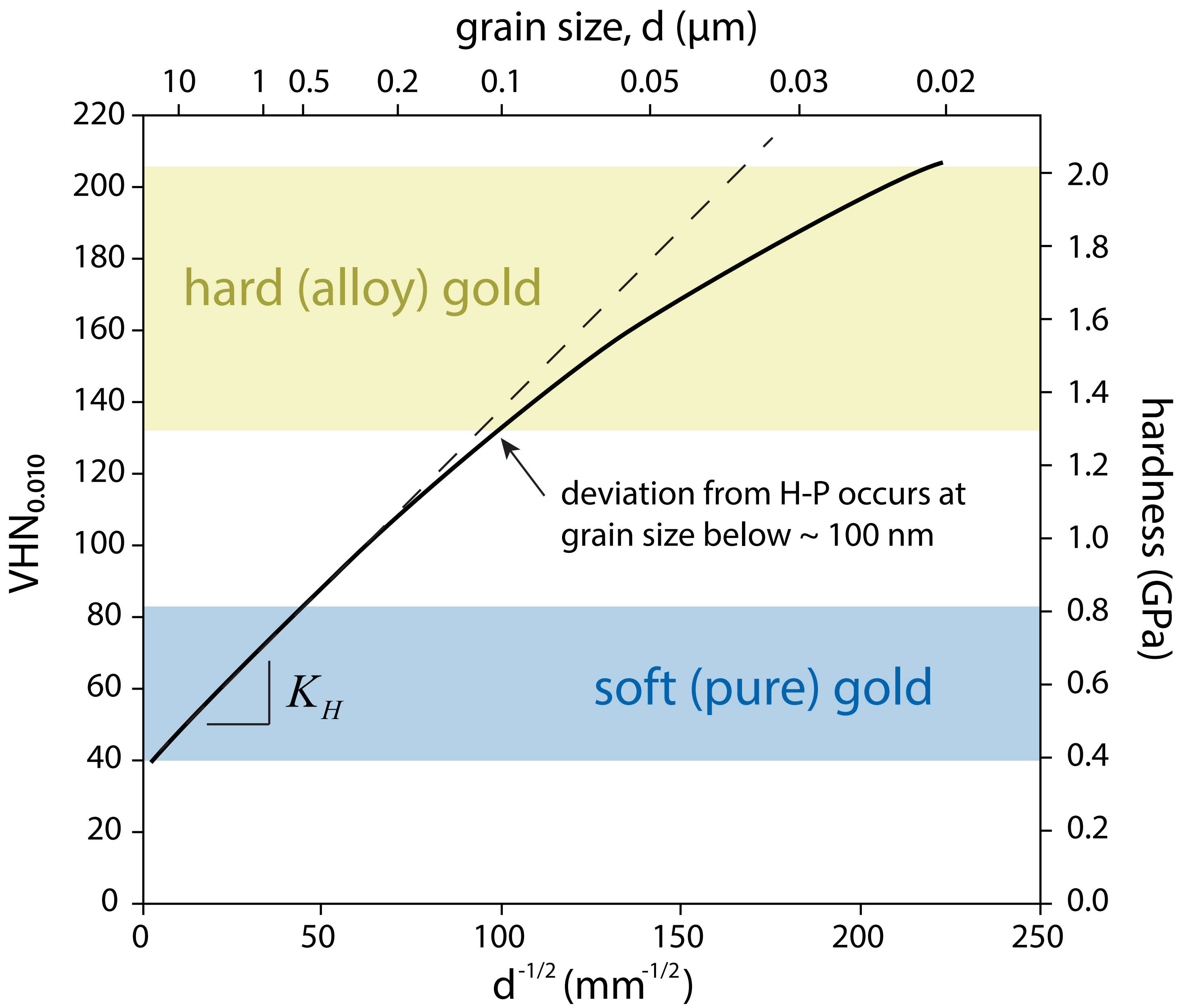
Traditionally: mitigate the aging phenomena, increase the service life of a contact by,

1. using sufficiently thick gold films
2. use an inert environment

Proposed: shut down solid diffusion of codeposited and underlayer materials via,

1. ceramics to harden Au in place of non-noble metals
2. introduce electron transparent ceramic diffusion barrier layers

Hard gold hardens primarily via Hall-Petch strengthening (grain refinement)

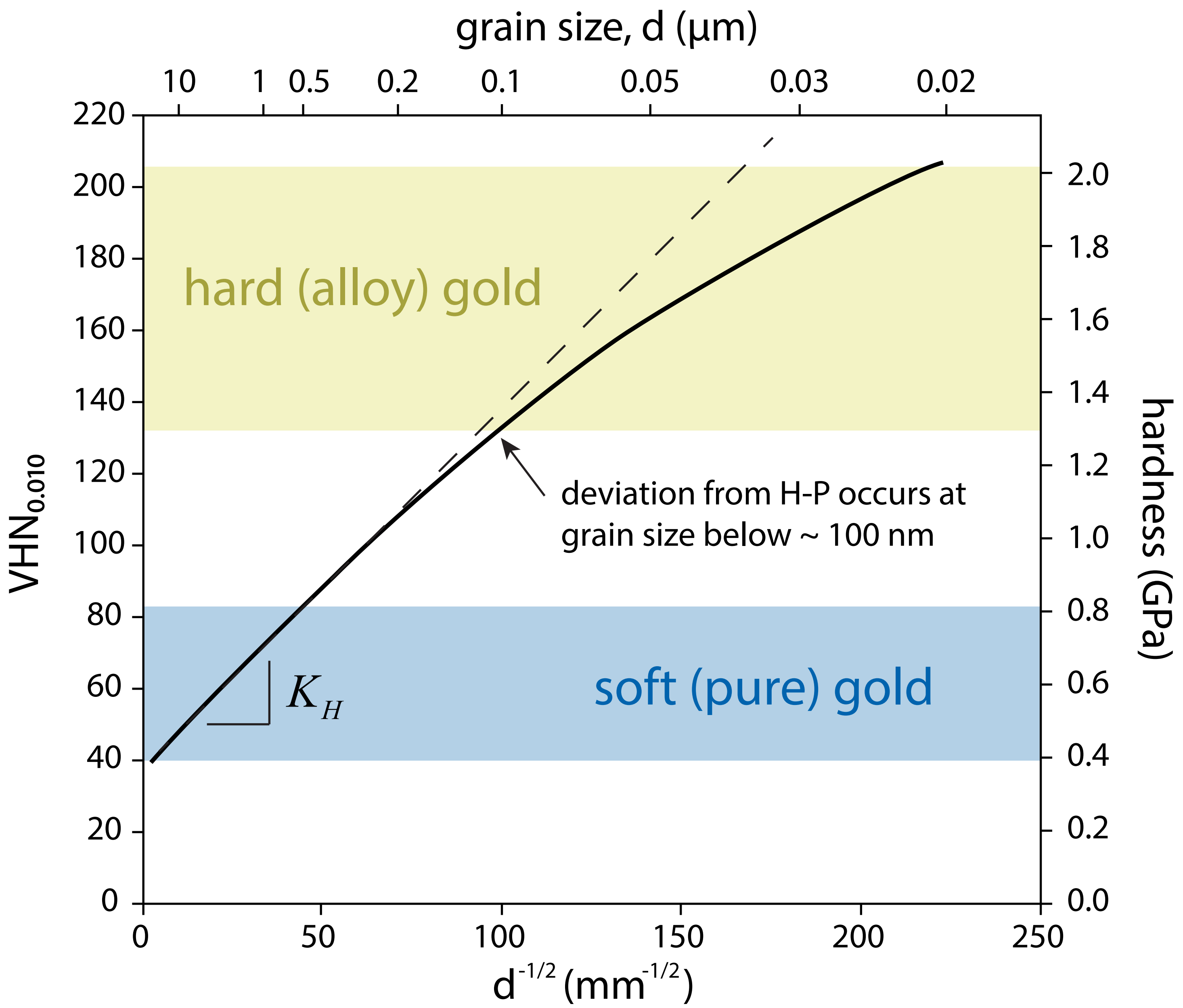


Reference: C. Lo, J. Augis, and M. Pinnel, JAP (1979)

Contact area to hardness relationship: $A_r \cong \frac{F_n}{H}$

Hall-Petch hardness to grain size relationship: $H = H_0 + K_H d^{-1/2}$

Zener pinning GB segregated second phase limits grain growth



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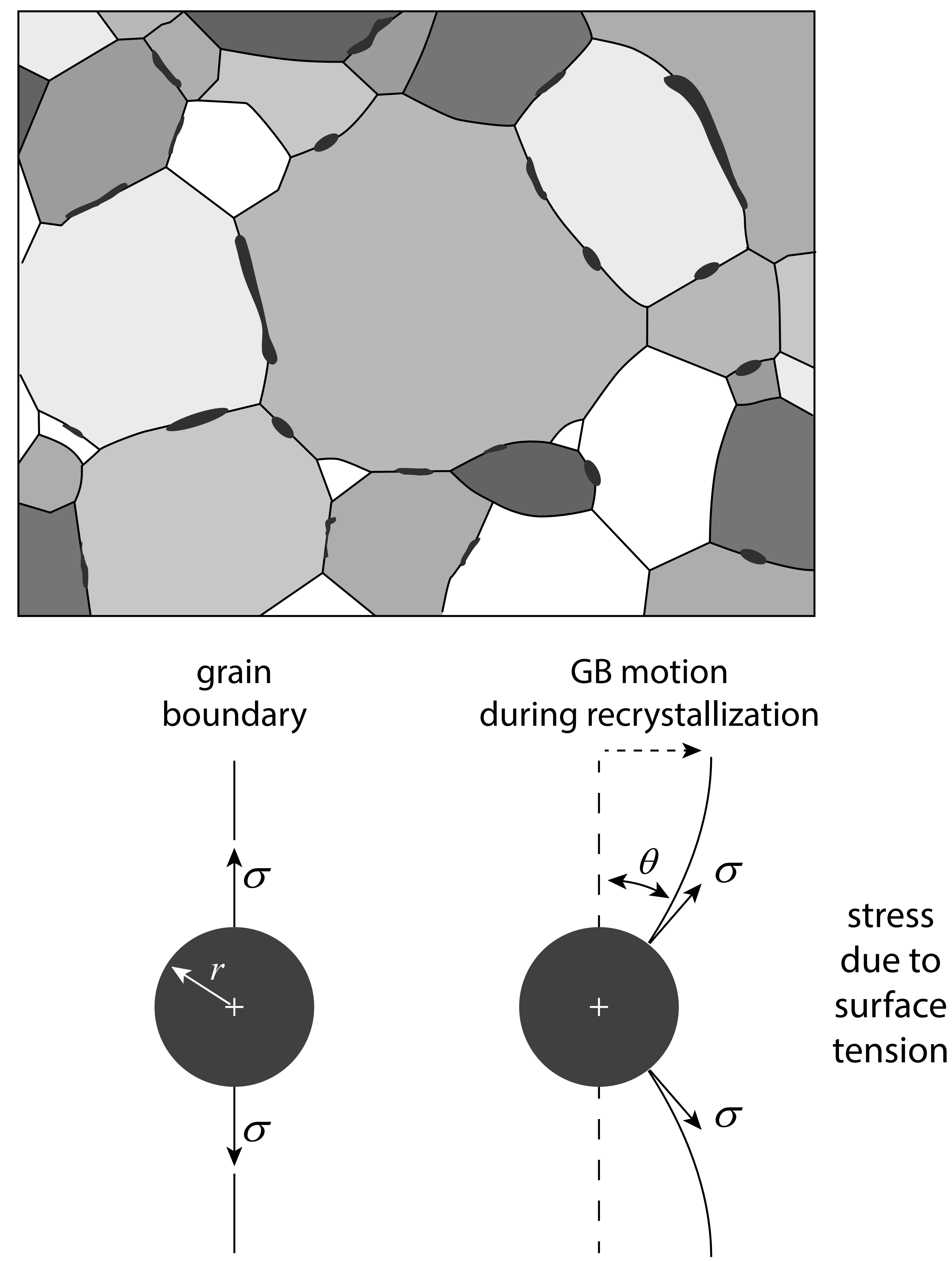
Contact area to hardness relationship: $A_r \cong \frac{F_n}{H}$

Hall-Petch hardness to grain size relationship: $H = H_0 + K_H d^{-1/2}$

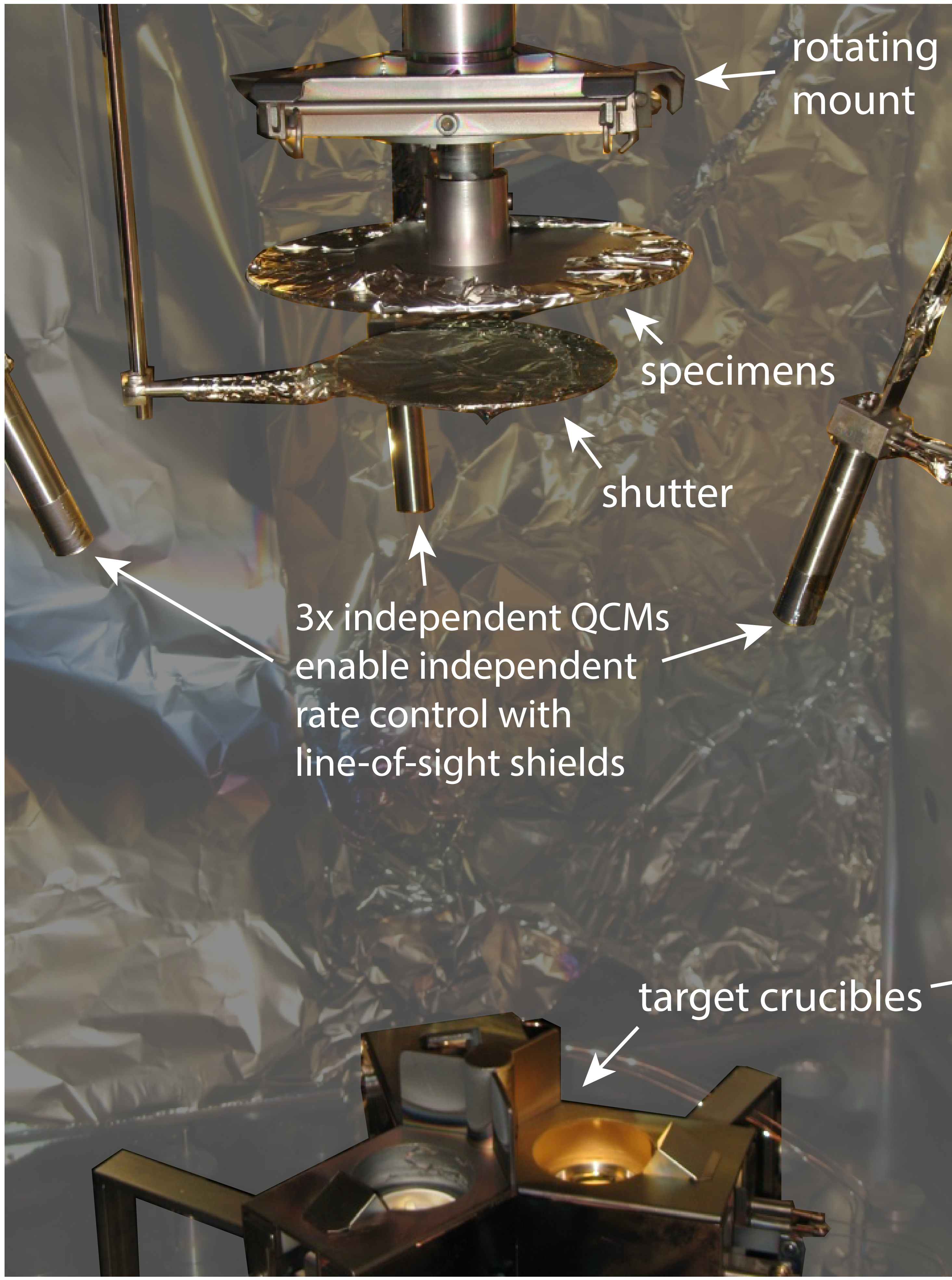
second-phase inclusions at GBs pin the boundaries and inhibit GB mobility (recrystallization)



drag force: $f_D = 2\pi r\sigma\cos\theta\sin\theta$

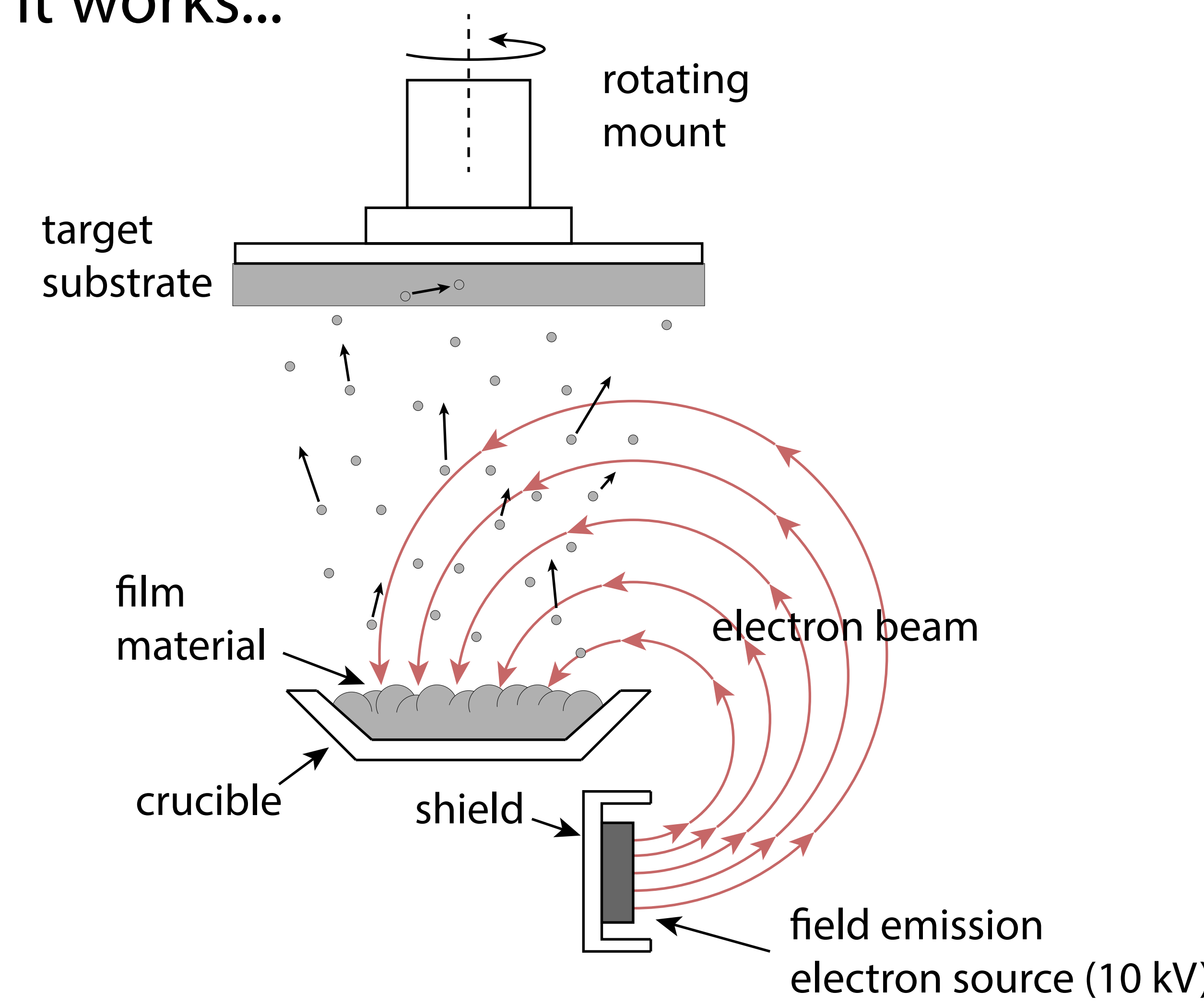
Electron beam deposition of metal-ceramic nanocomposite films

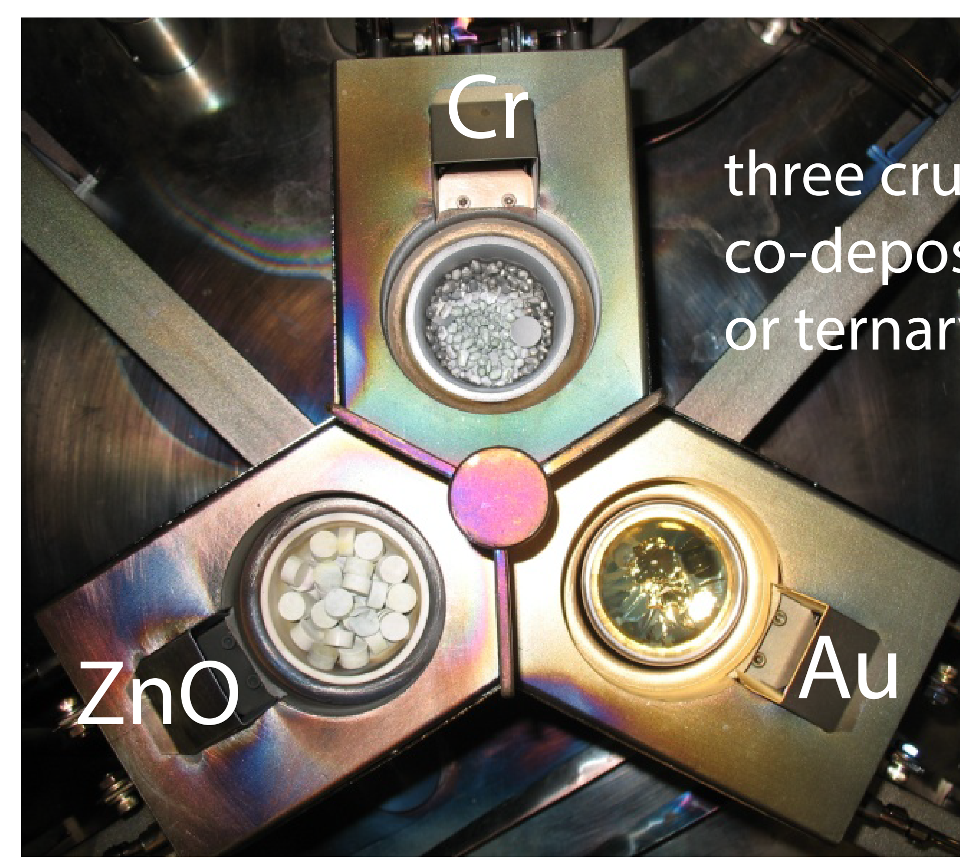
E-beam deposition chamber



Why e-beam? **ppm level composition control**

How it works...





three crucibles for co-deposition of binary or ternary alloy thin films

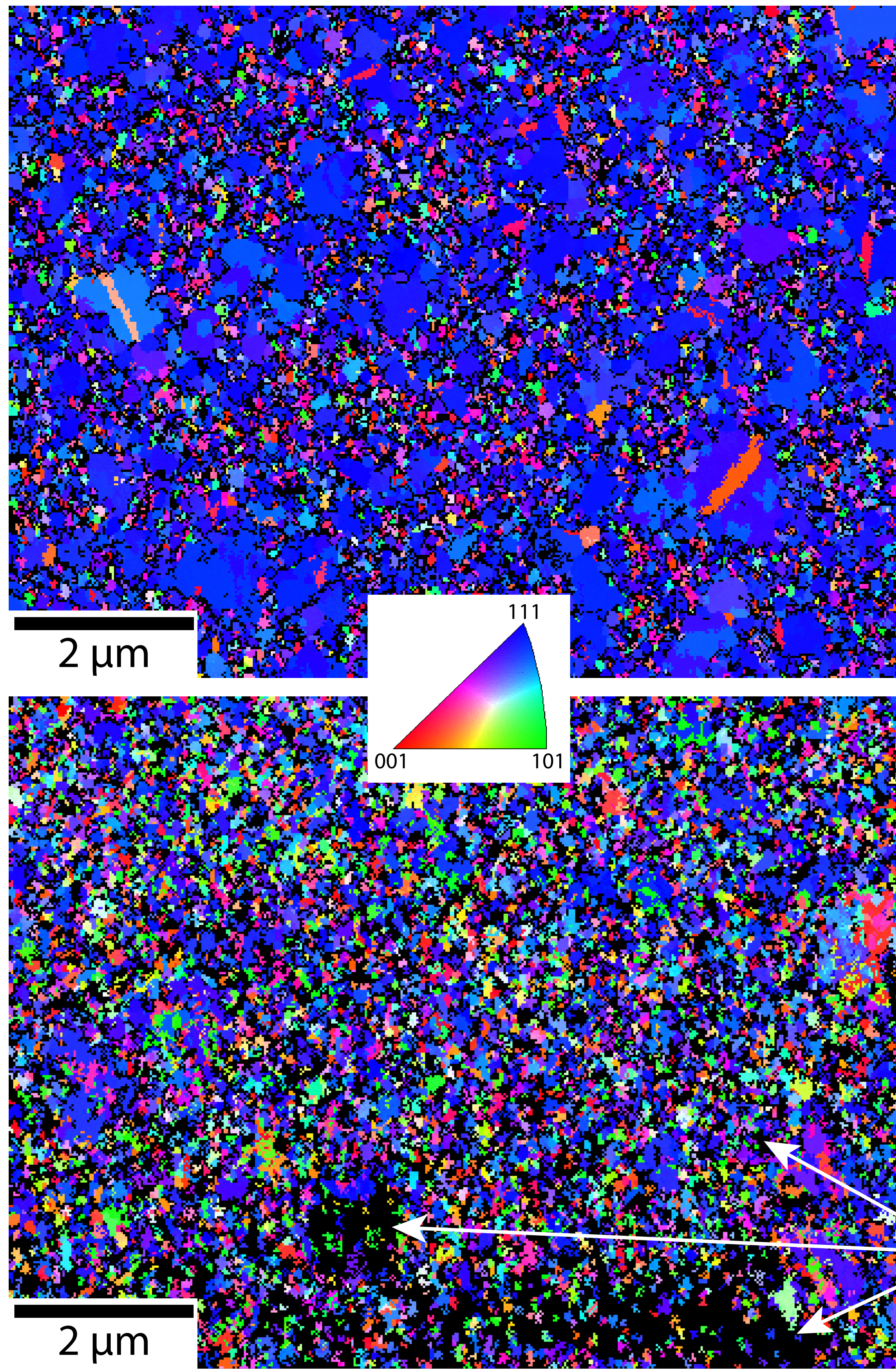
Electron backscatter diffraction maps showing grain refinement with alloying

(e-beam deposited films)

surface normal orientation

2 µm thick
pure e-beam
gold film

grain size was bimodal
and textured,
avg. grain size > 500 nm

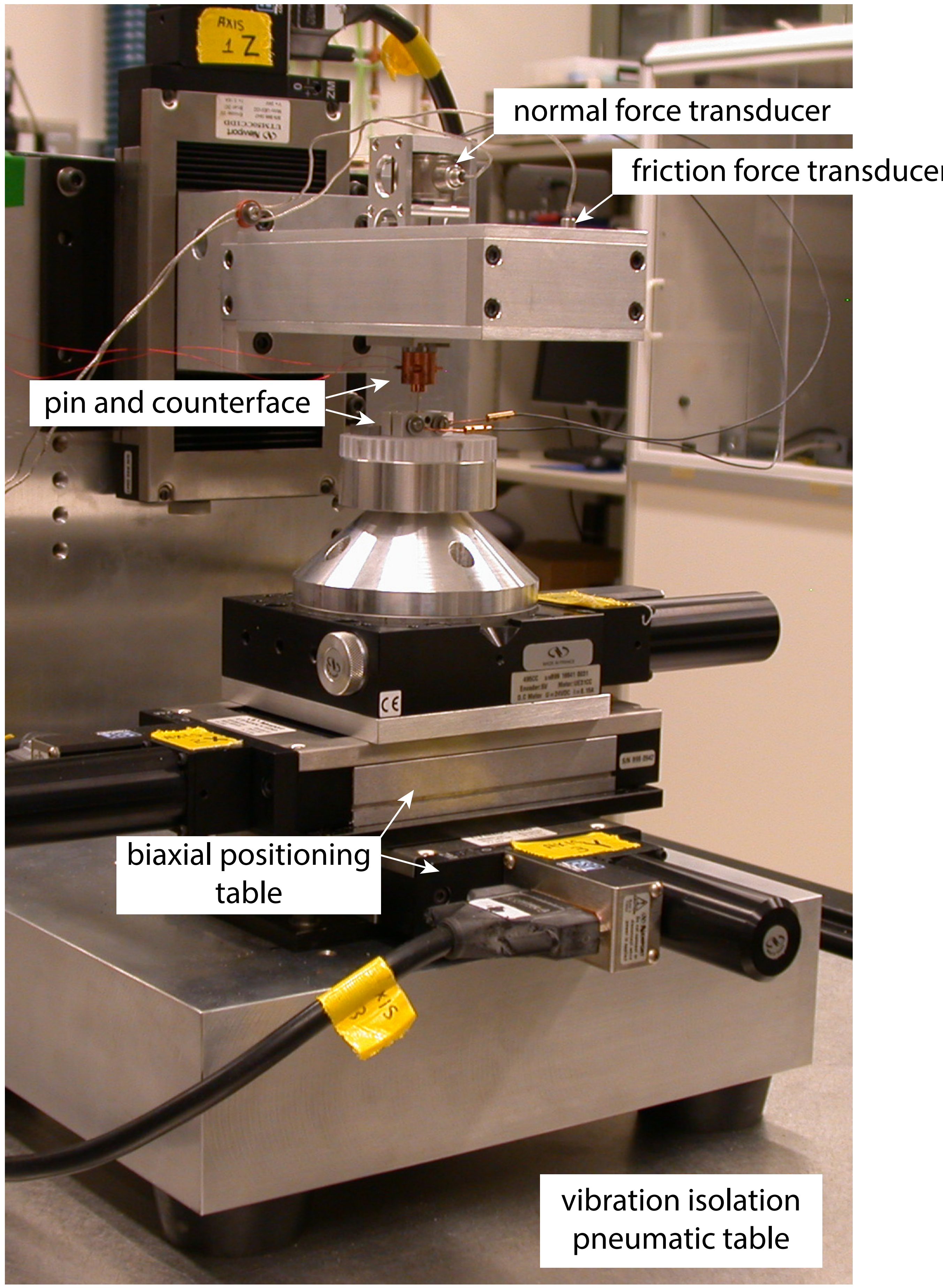


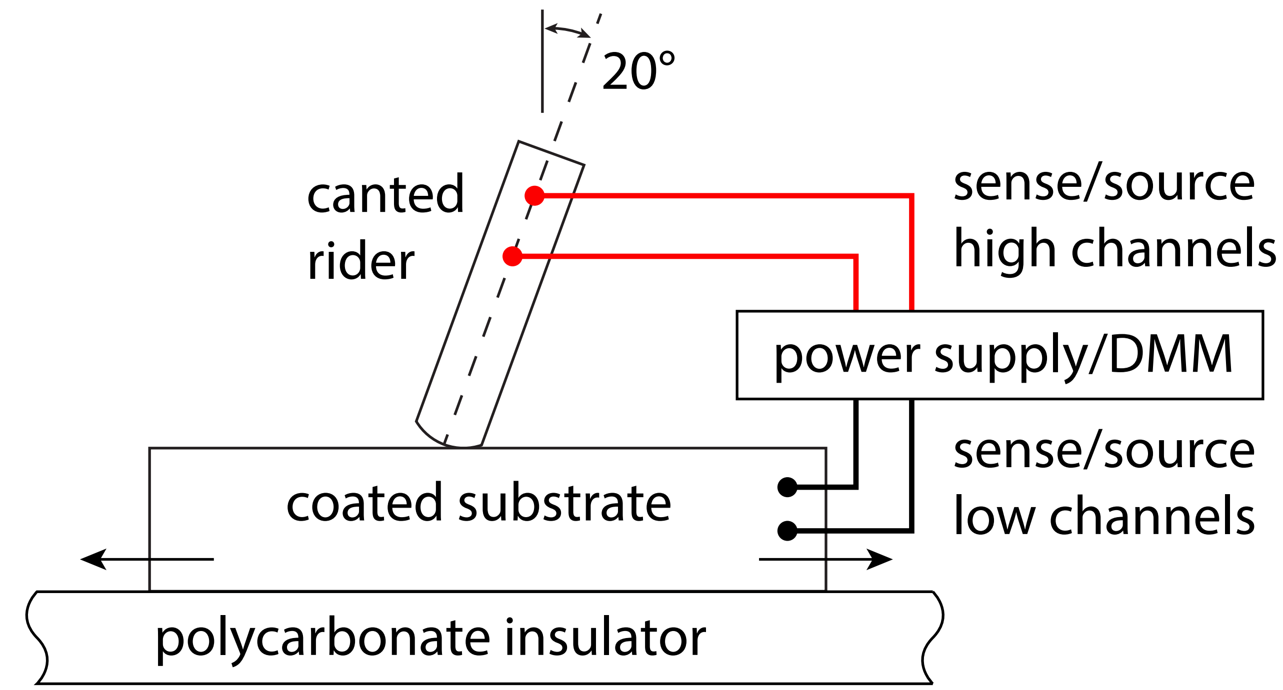
2 µm thick
0.1 vol. % ZnO
(0.03 wt. %)
gold film

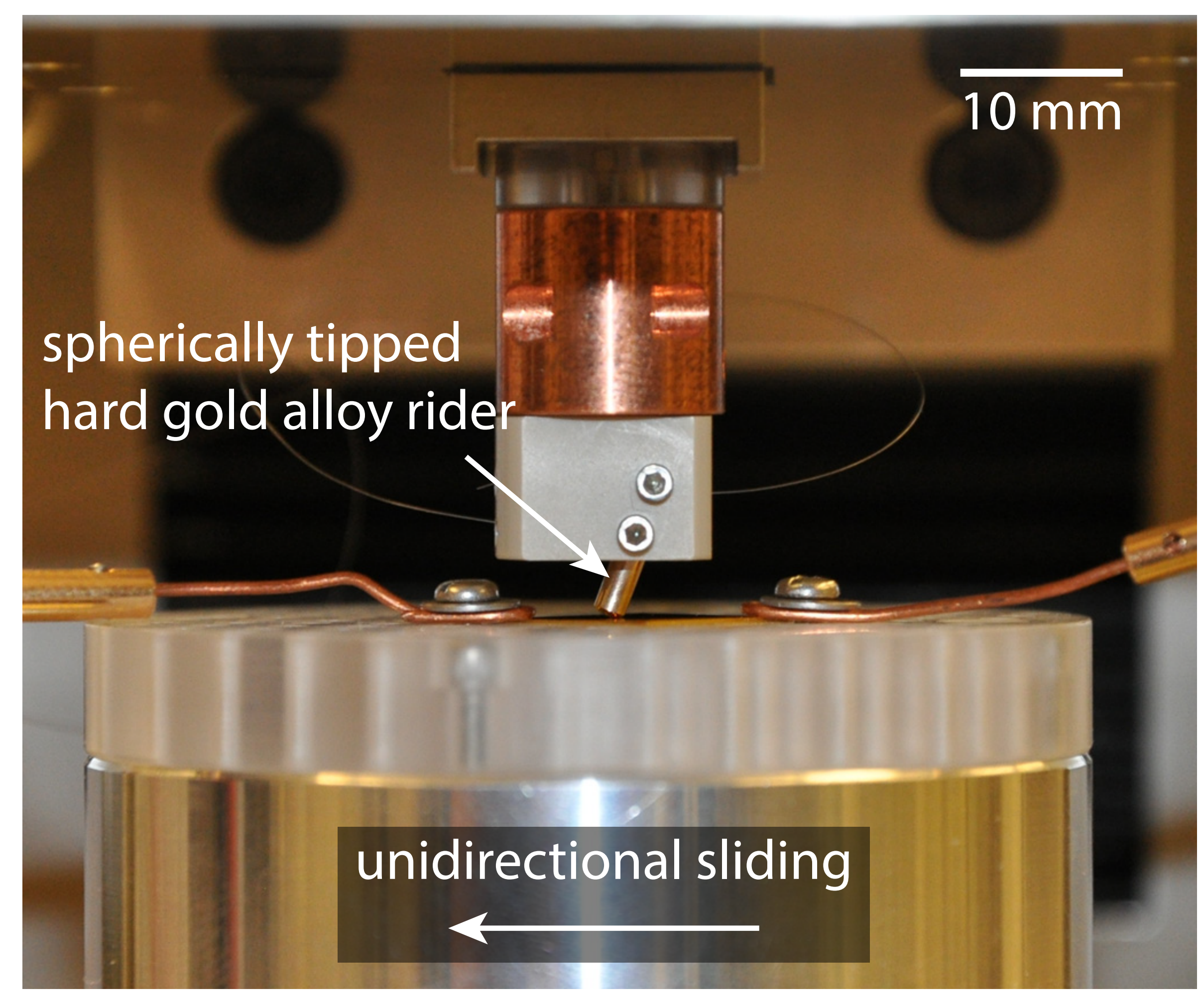
grains are equiaxed,
not textured,
avg. grain size ~ 100 nm

black pixels imply regions
with grain sizes < 50 nm

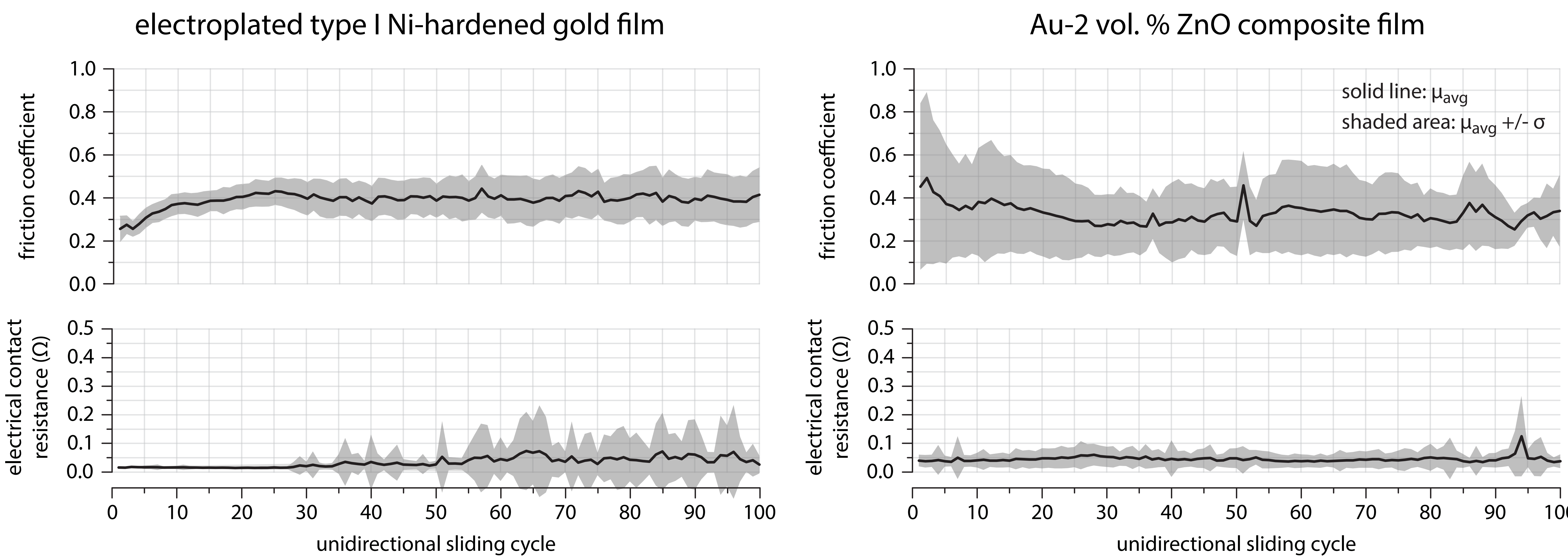
Sliding Electrical Contact Tester







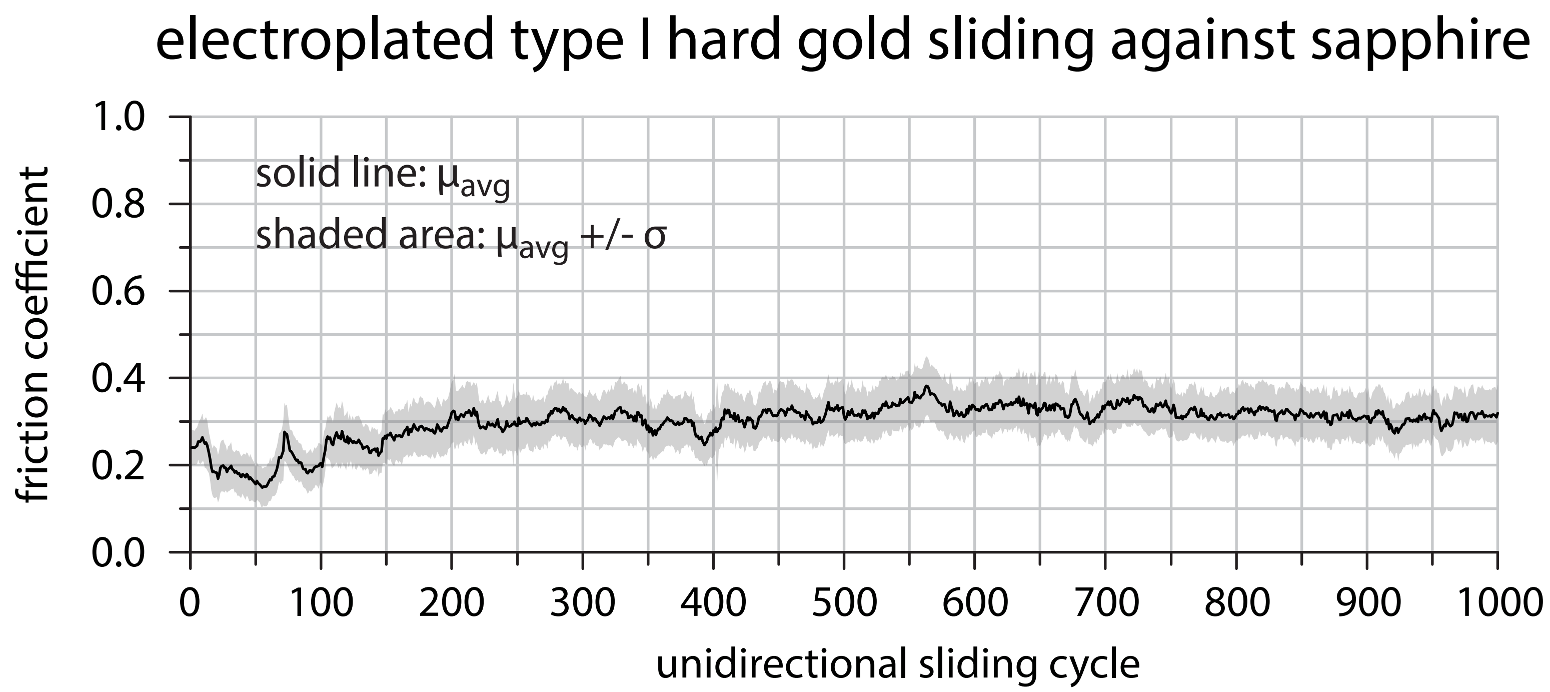
Au-ZnO shows similar tribological behavior to electroplated hard gold

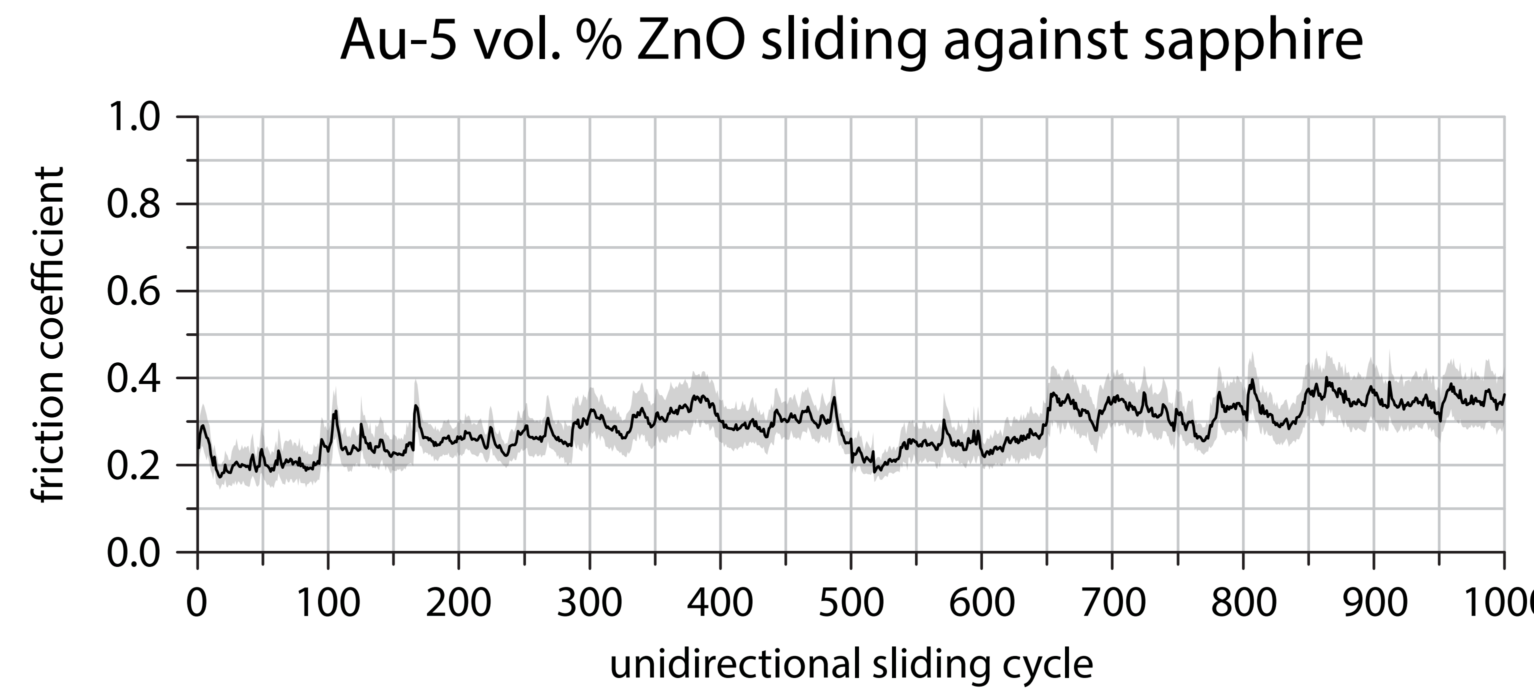


common testing parameters:

- sliding against a bulk hard gold alloy rider or pin (nominally 72-14-8-5-1 wt. % Au-Cu-Pt-Ag-Zn)
- rider tip radius was 3.175 mm
- contact force was 100 mN
- electrical probe current of 100 mA
- lab air at 21°C, sliding speed of 1 mm/s
- substrate material was alloy 52 (nominally 50/50 wt. % Fe/Ni)
- film thicknesses 2 - 5 μm; Ti/Pt bonding layers

Wear comparison of electroplated hard gold and Au-ZnO -- against sapphire

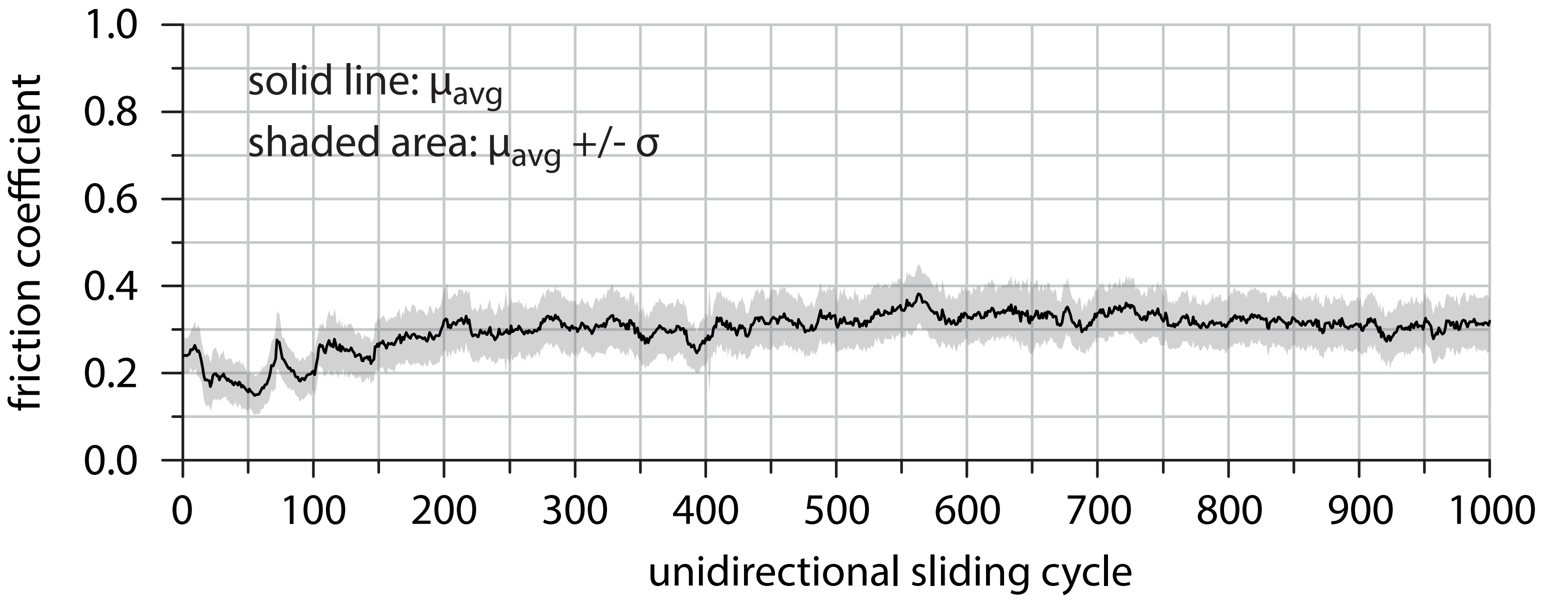




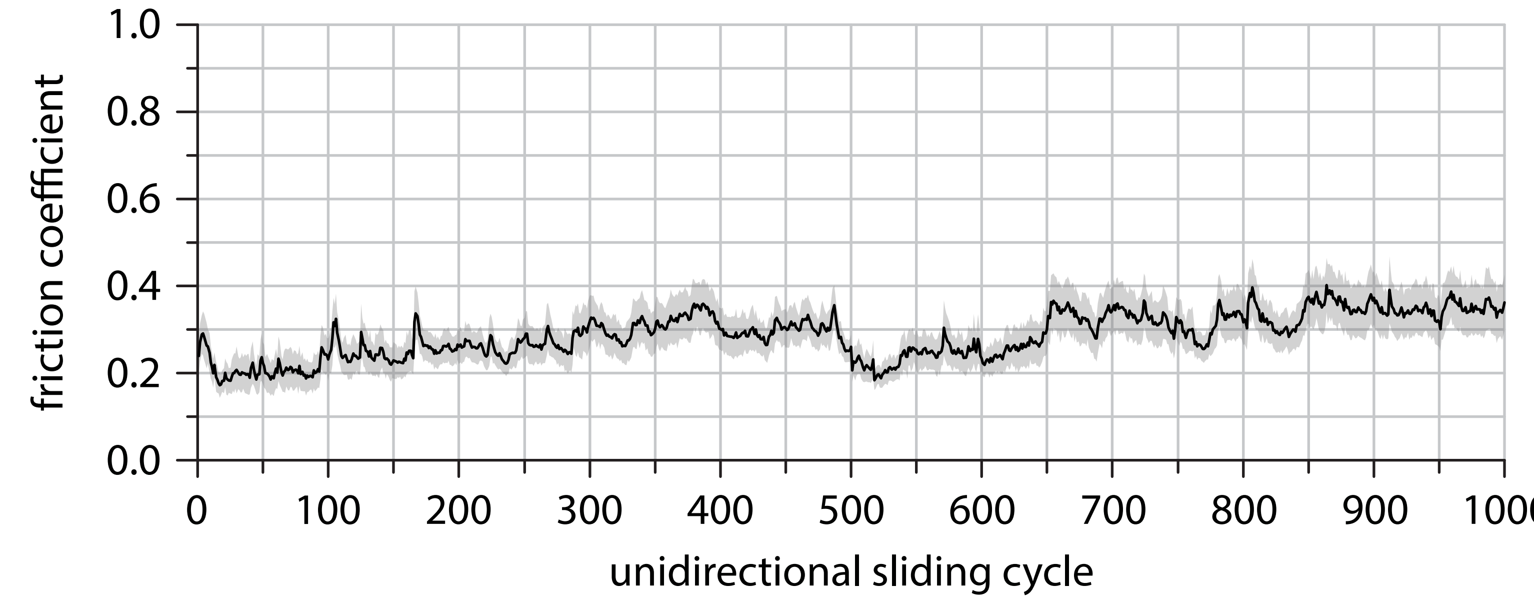
Now using 5 vol. % ZnO, sapphire ball radius of 1.59 mm, and contact force of 1N

Wear comparison of electroplated hard gold and Au-ZnO -- against sapphire

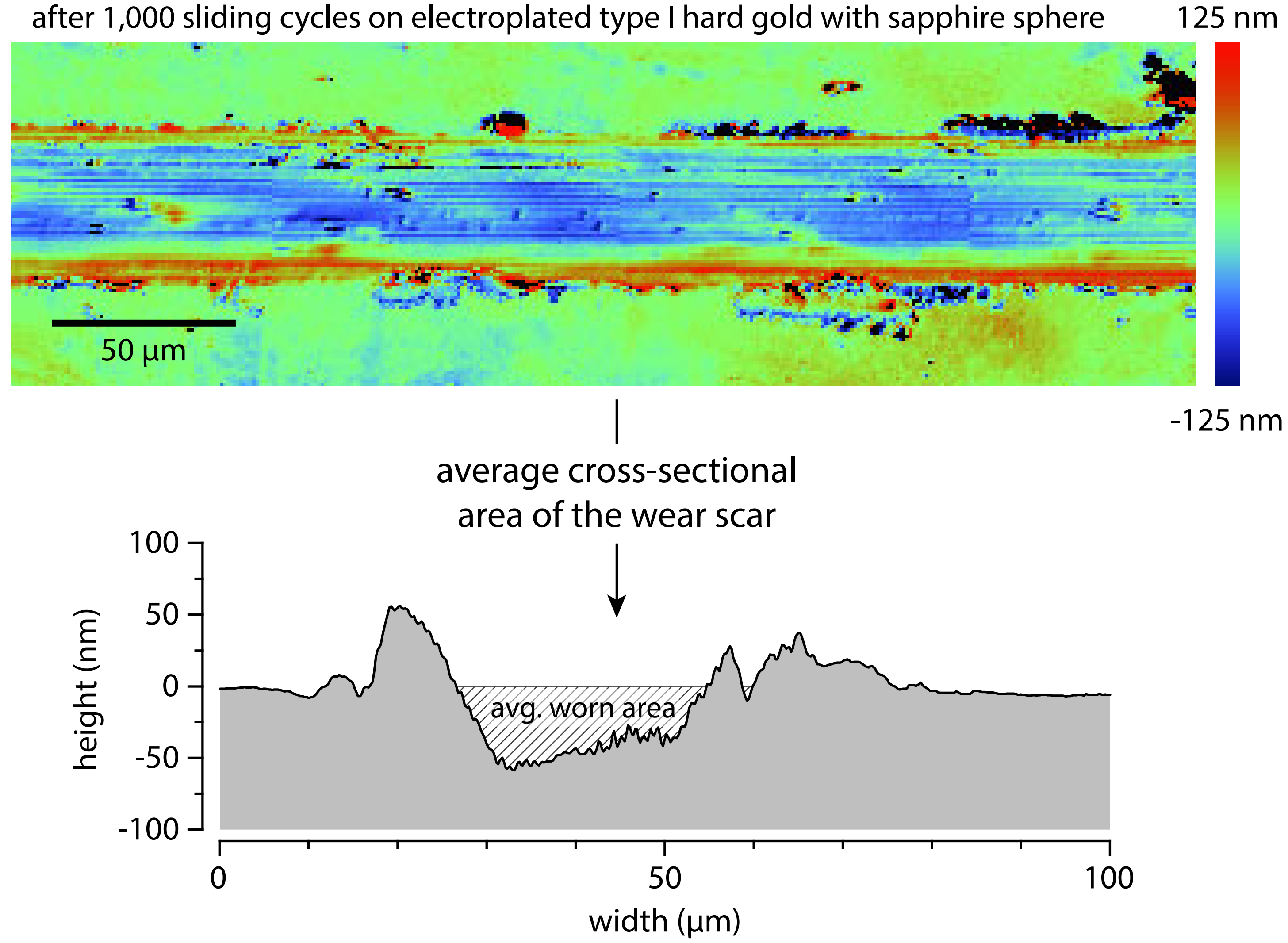
electroplated type I hard gold sliding against sapphire



Au-5 vol. % ZnO sliding against sapphire



after 1,000 sliding cycles on electroplated type I hard gold with sapphire sphere



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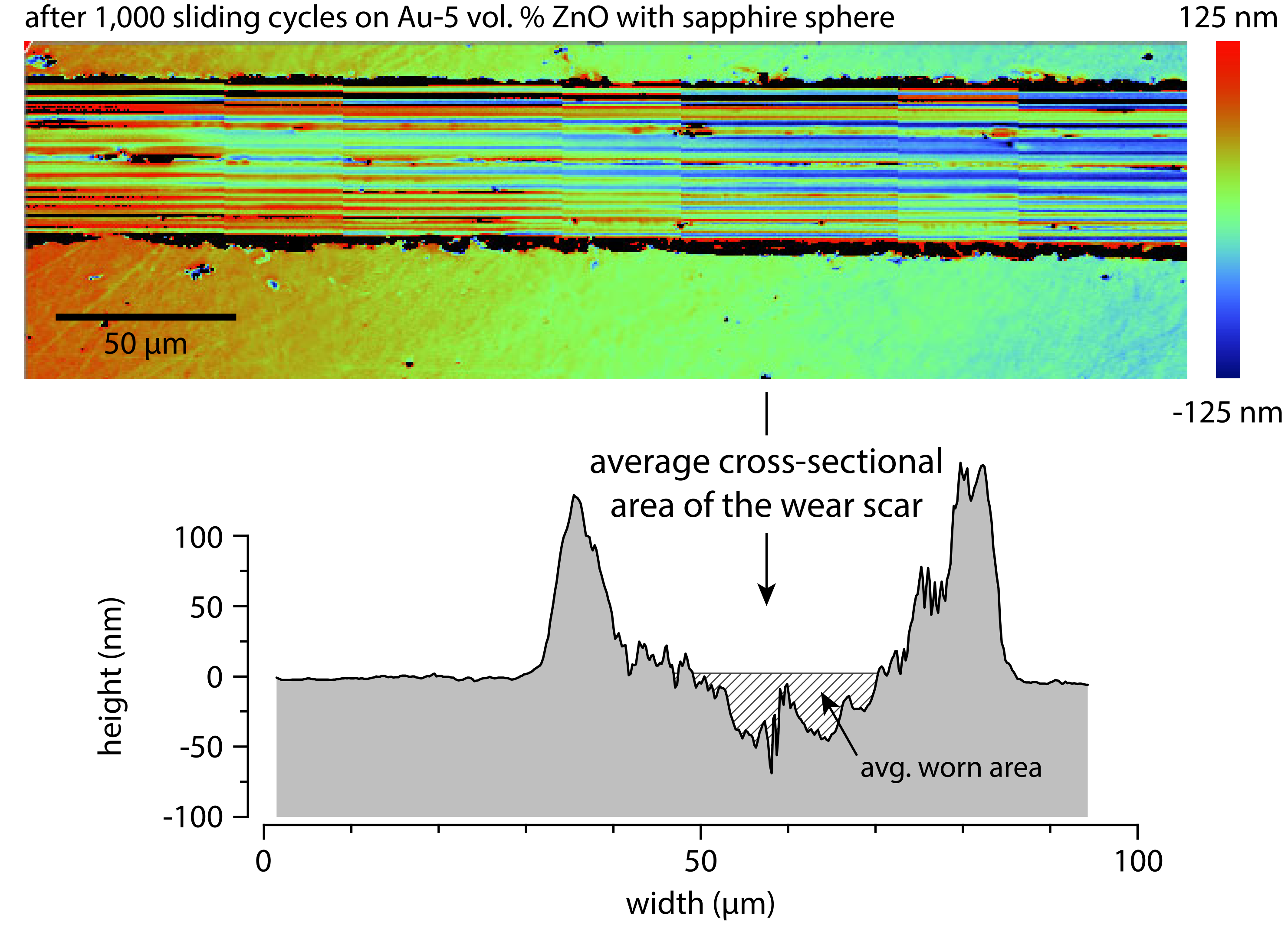
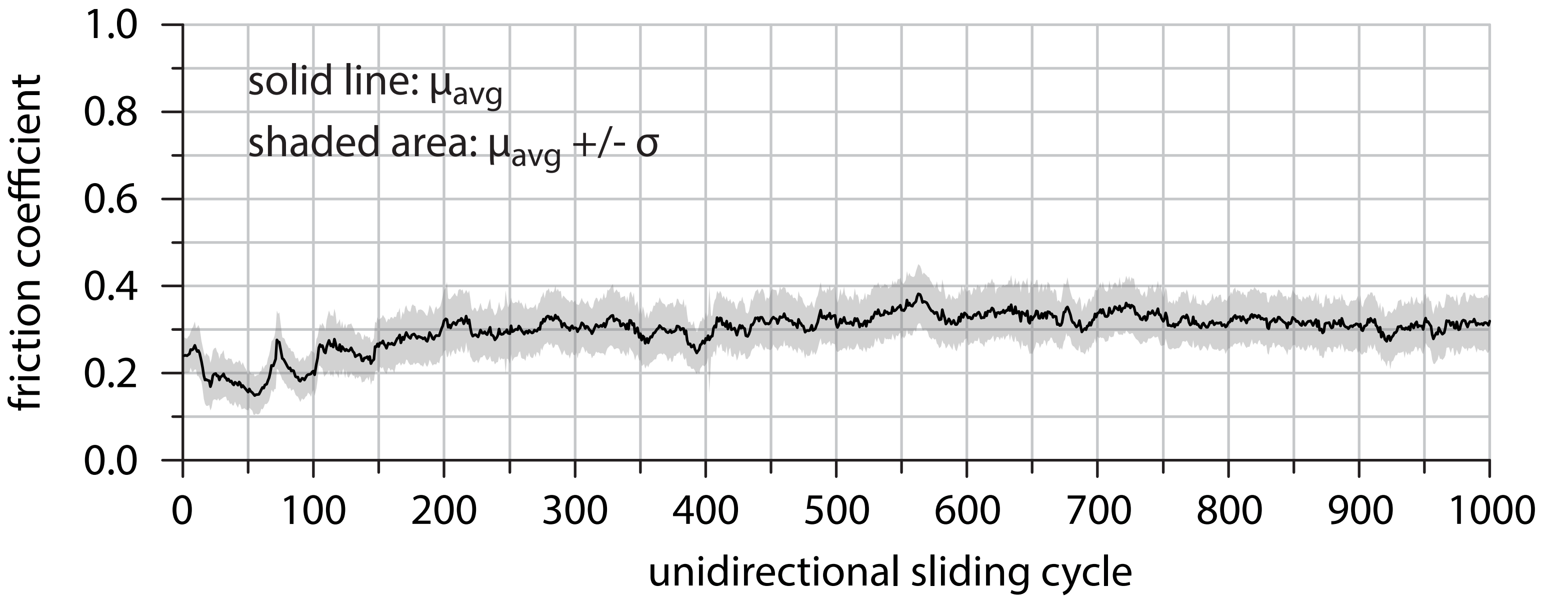


Au-ZnO nanocomposite shows similar wear behavior to electroplated hard Au

electroplated type I hard gold sliding against sapphire



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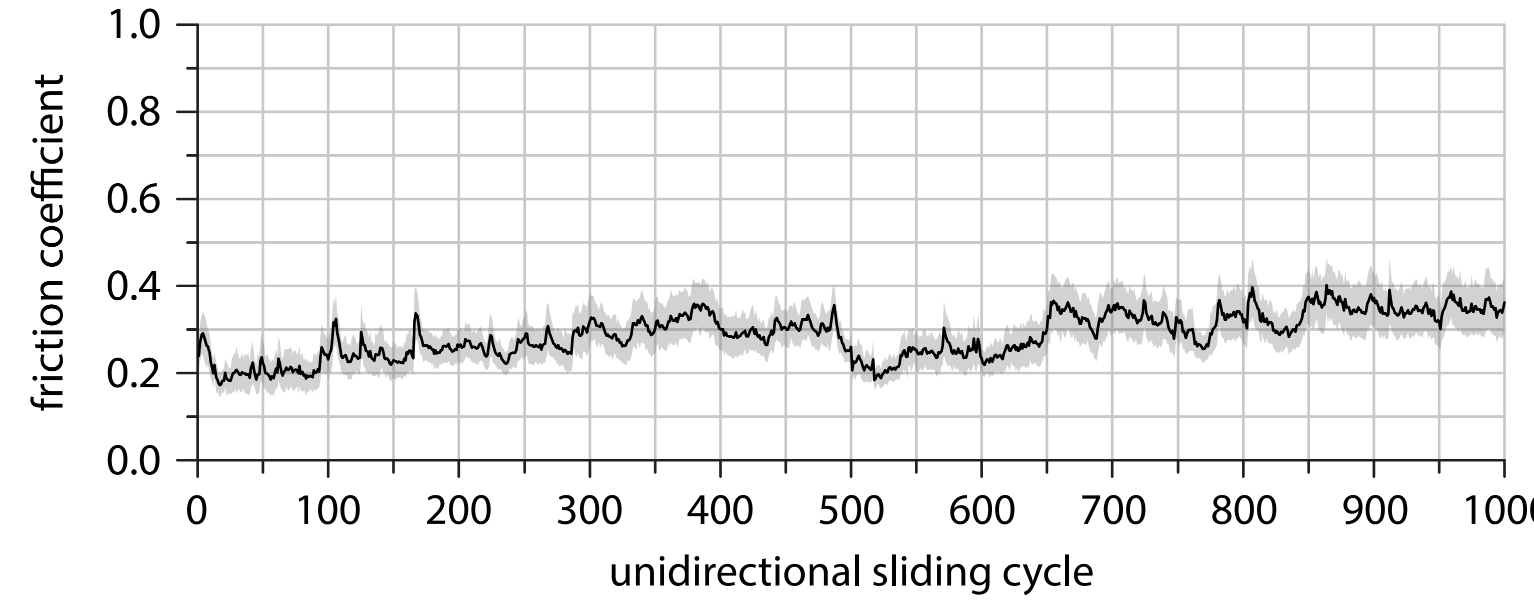
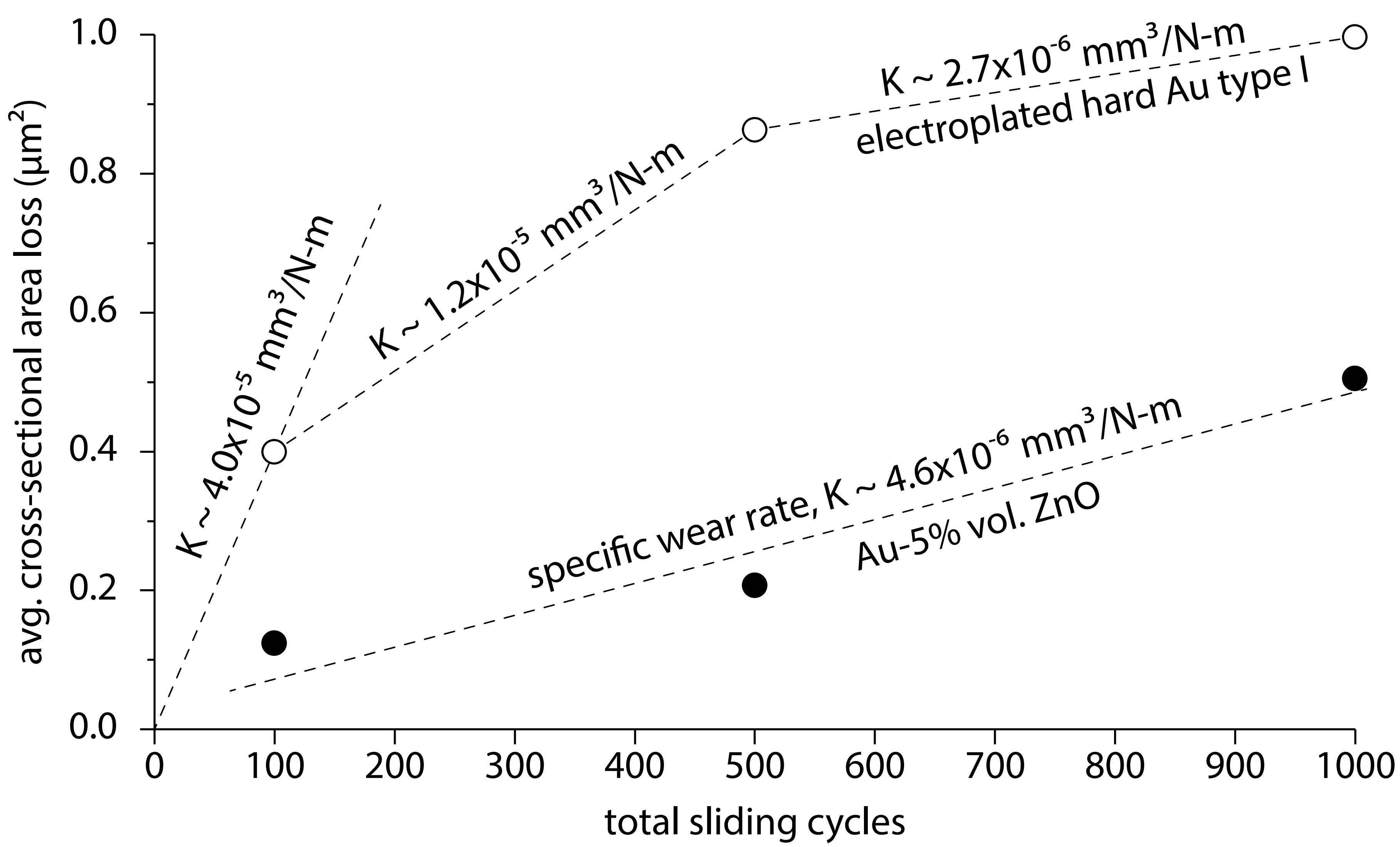
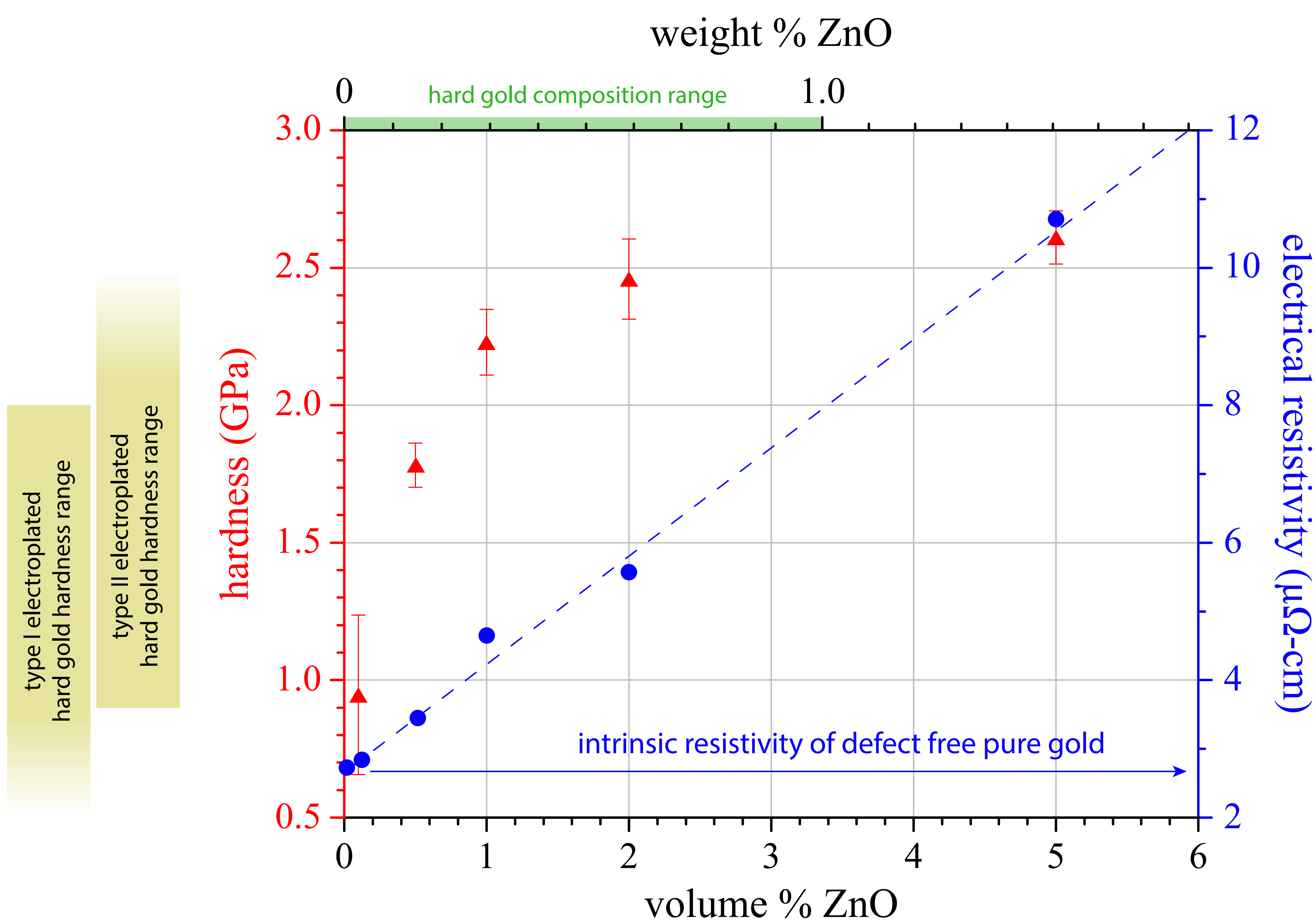
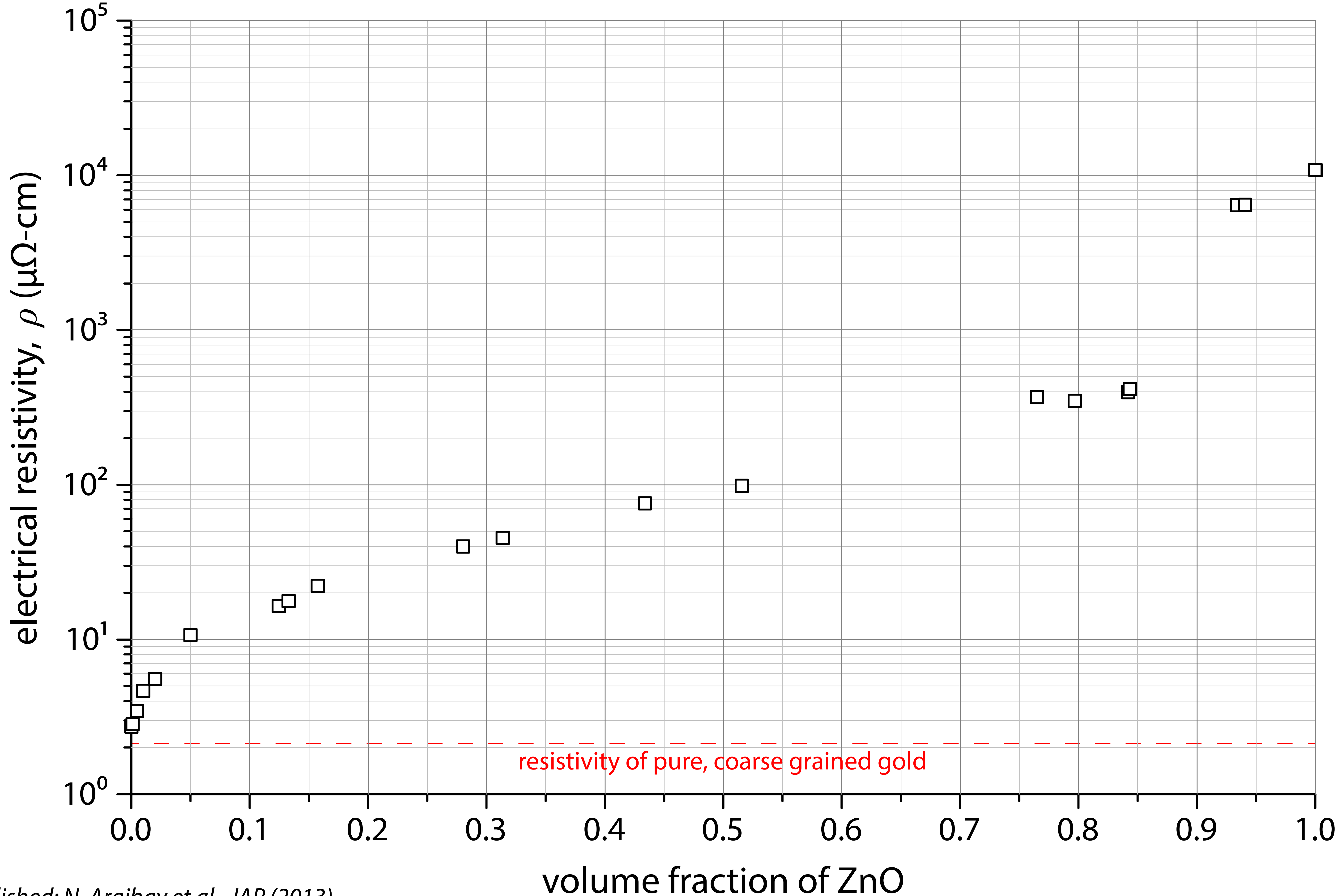




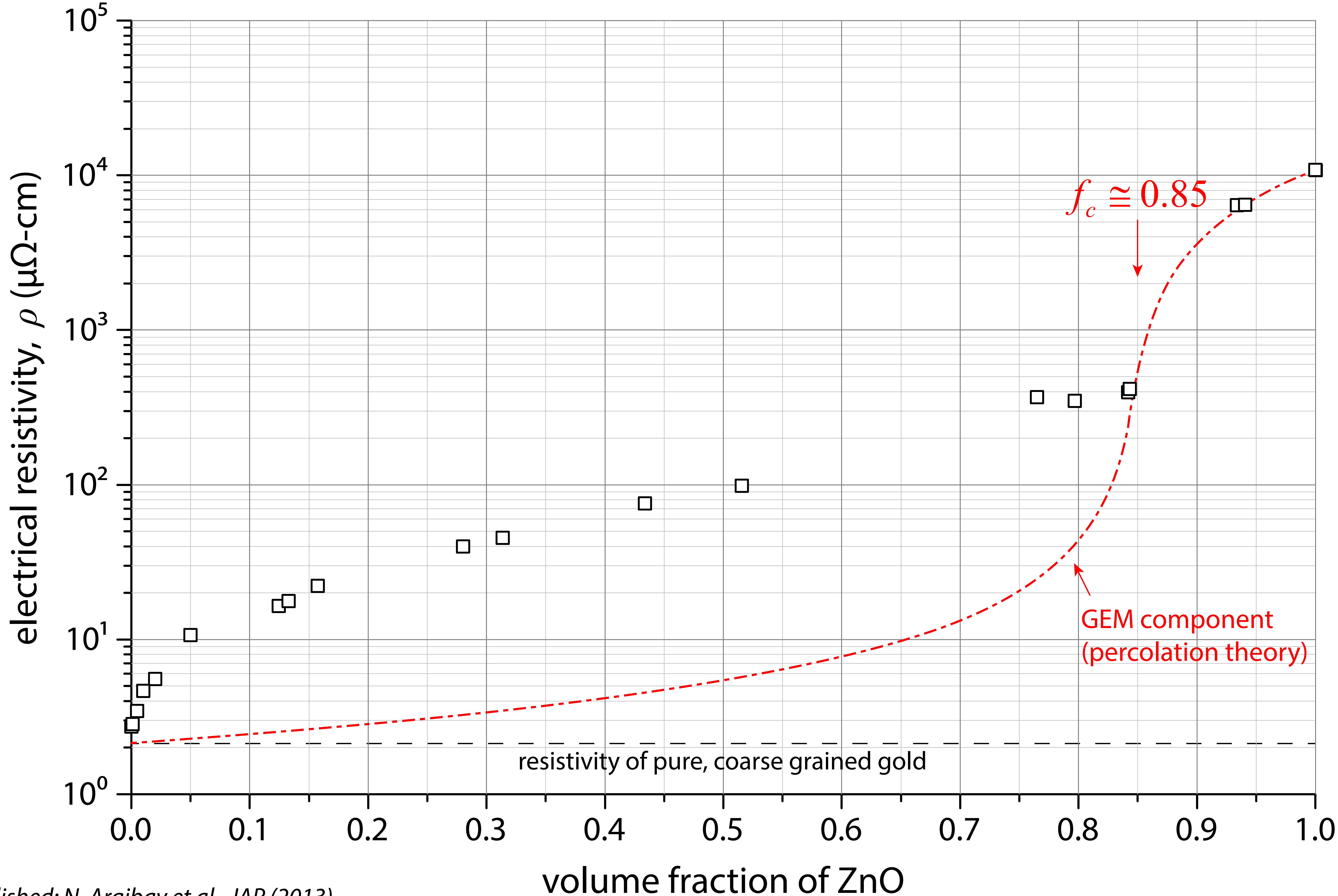
Hardness and electrical resistivity increase as function of composition





Published: N. Argibay et al., JAP (2013)

Au-ZnO Resistivity: combination of electron scattering at GBs and percolation theory



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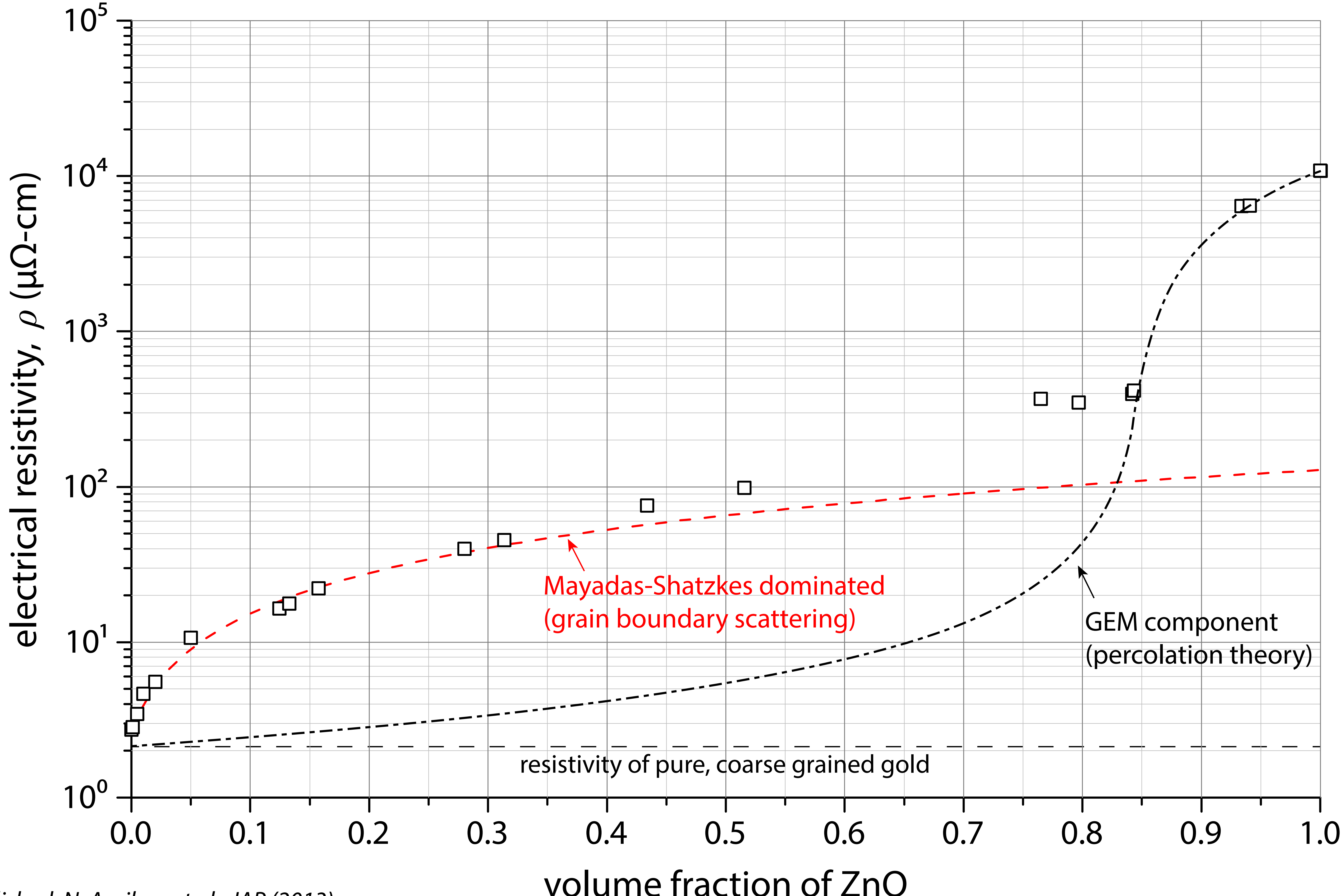

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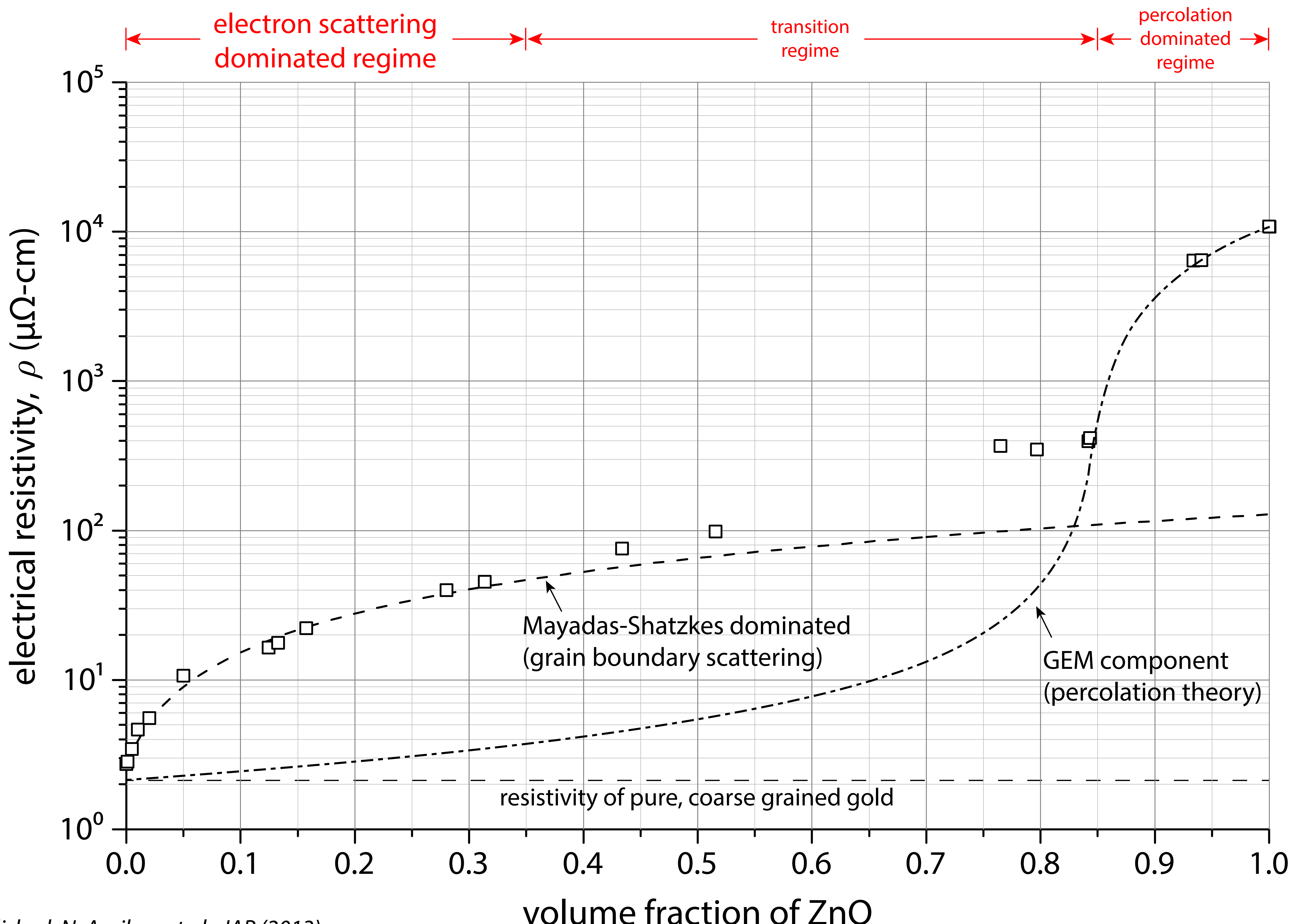

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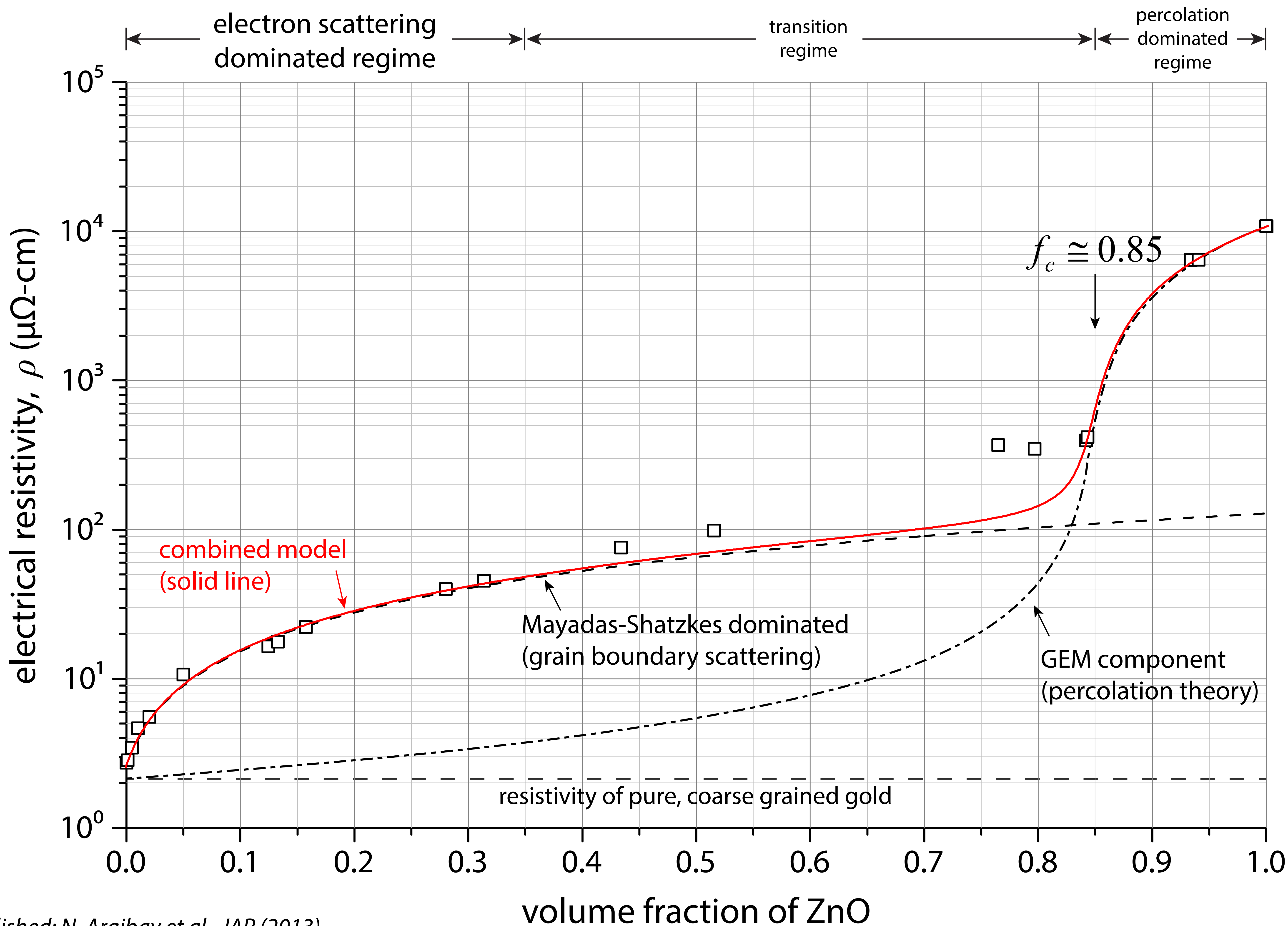

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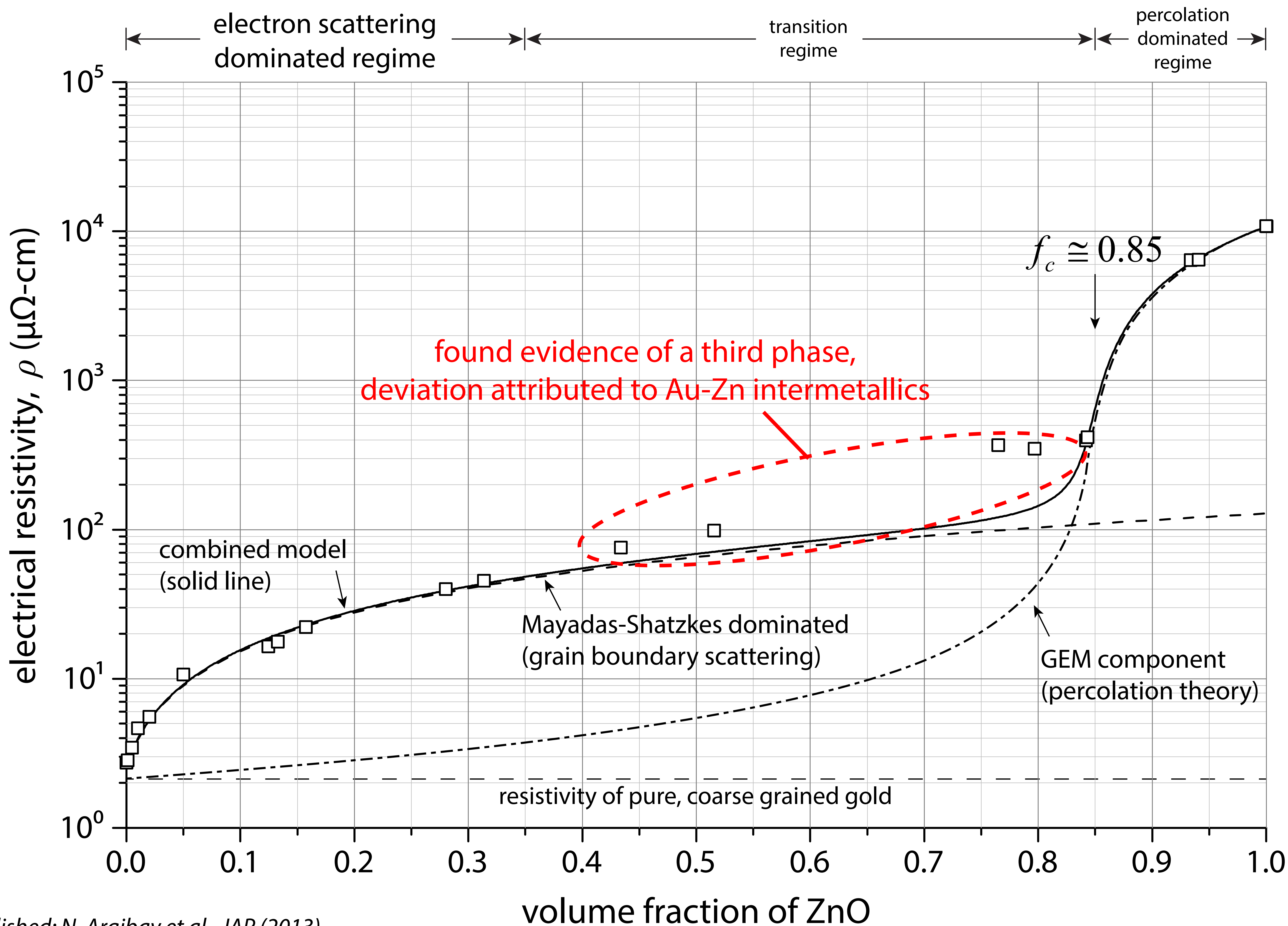

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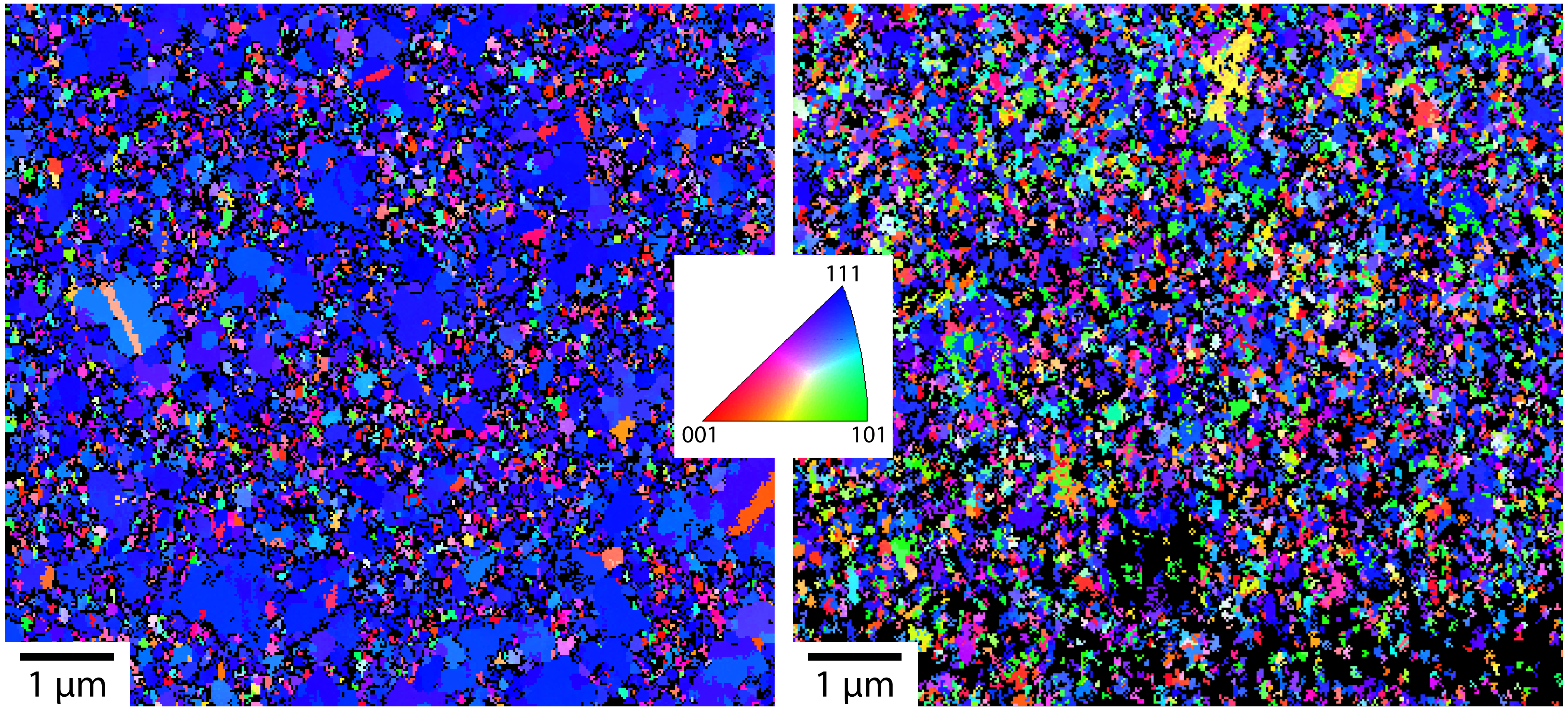
Determination of grain size with varying composition via microscopy

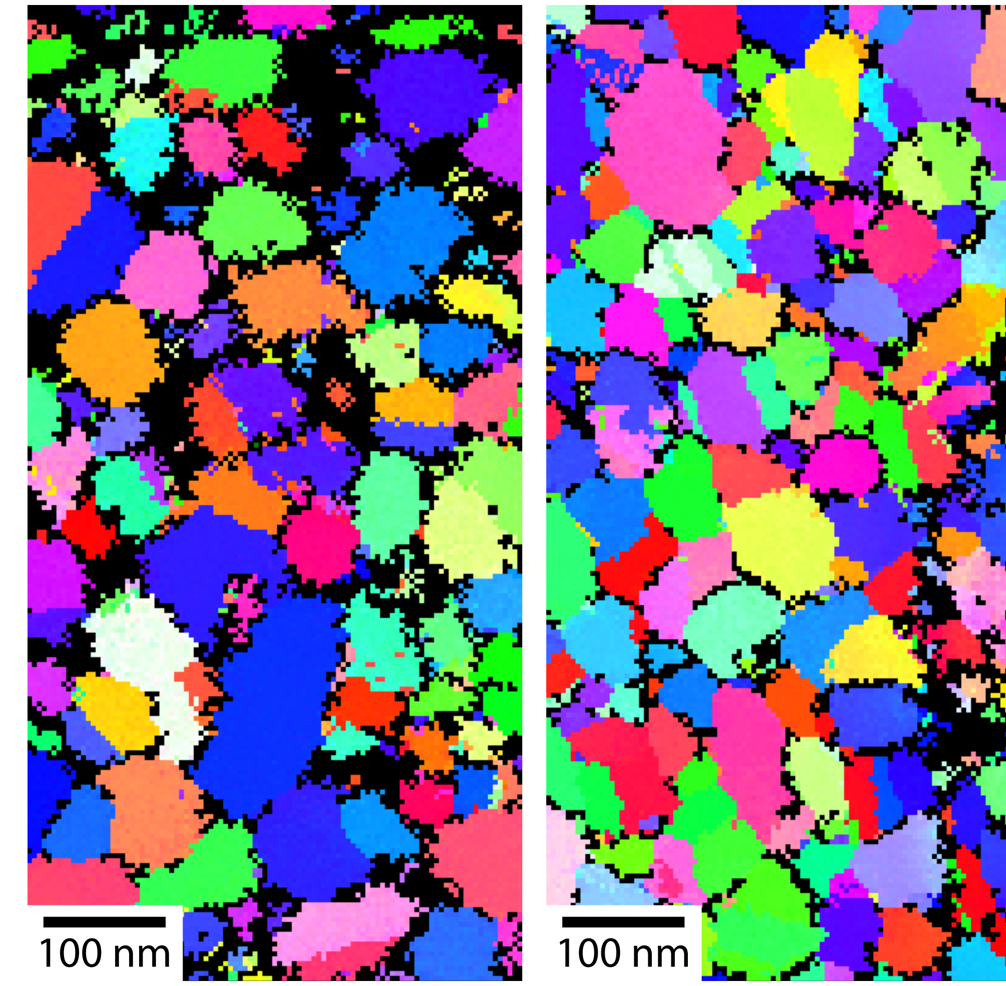
Film surface-normal EBSD mapping:

pure Au film | 0.1 vol. % ZnO film



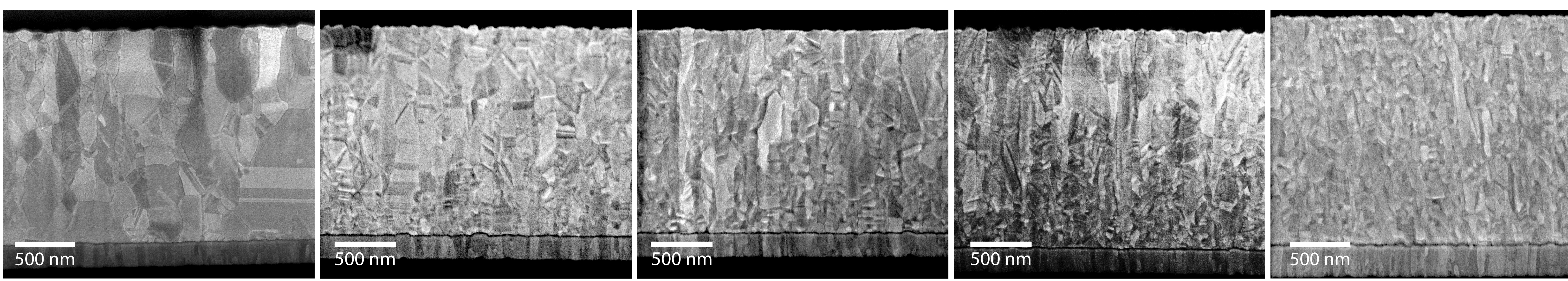
Transmission Kikuchi diffraction:

1.0 vol. % ZnO film | 2.0 vol. % ZnO film



SEM of FIB milled and etched cross-sectional views:

Increasing ZnO concentration →



0.1 vol. % ZnO film | 0.5 vol. % ZnO film | 1.0 vol. % ZnO film | 2.0 vol. % ZnO film | 5.0 vol. % ZnO film

(XRD was inconclusive)

Mayadas-Shatzkes model (electron scattering at GBs):

$$\frac{\rho}{\rho_o} = \left[1 - \frac{3}{2}\alpha + 3\alpha^2 - 3\alpha^3 \ln\left(1 + \frac{1}{\alpha}\right)\right]^{-1}$$

Scattering parameter:

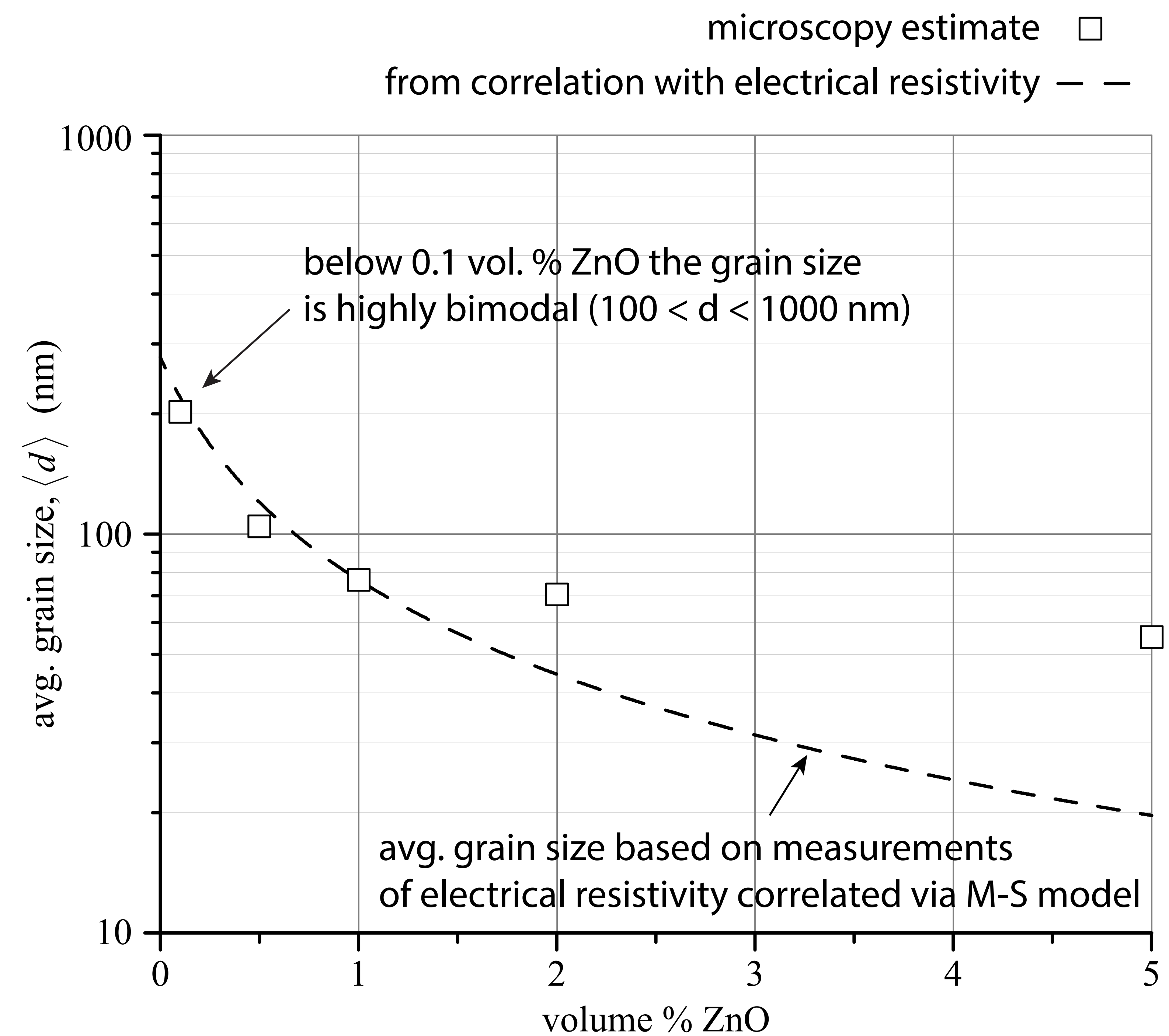
$$\alpha = \frac{\lambda}{d}\frac{R}{1-R}$$

Empirical relationship between scattering parameter and composition is linear:

$$\alpha = 43.19 f + 0.165$$

Between 0 and 30 vol. % ZnO, M-S seems to fit well, corresponding to a range:

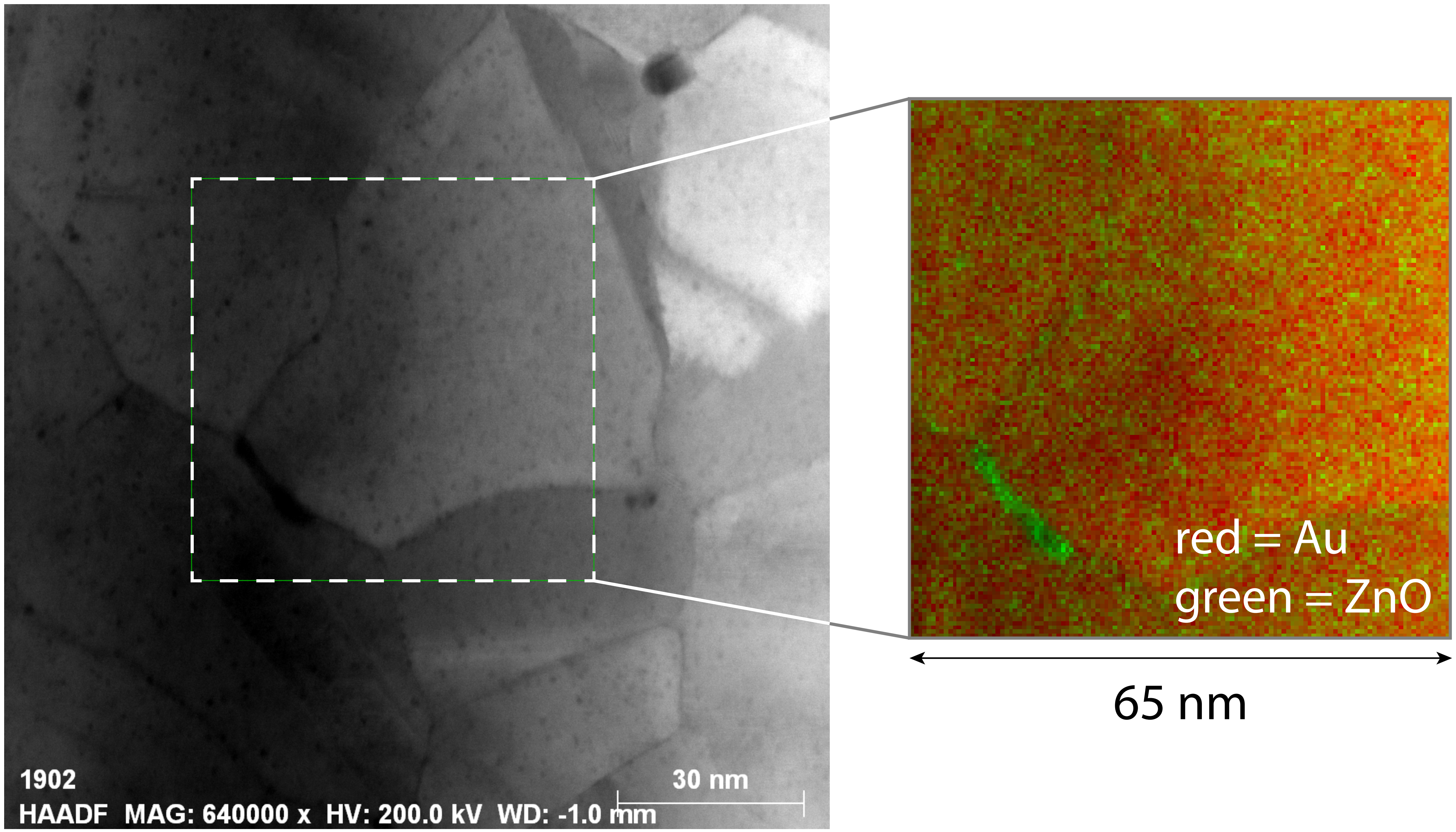
$$0.1 < \alpha < 10$$



Is it possible to confidently correlate grain size to resistivity via scattering parameter?

Film Surface-Planar STEM Composition Mapping -- Confirms GB Segregation

Cross-sectional composition map of a Au- 5 vol. % ZnO
film showing grain boundary segregated ZnO in a Au matrix



Zener pinning GB segregated second phase limits grain growth

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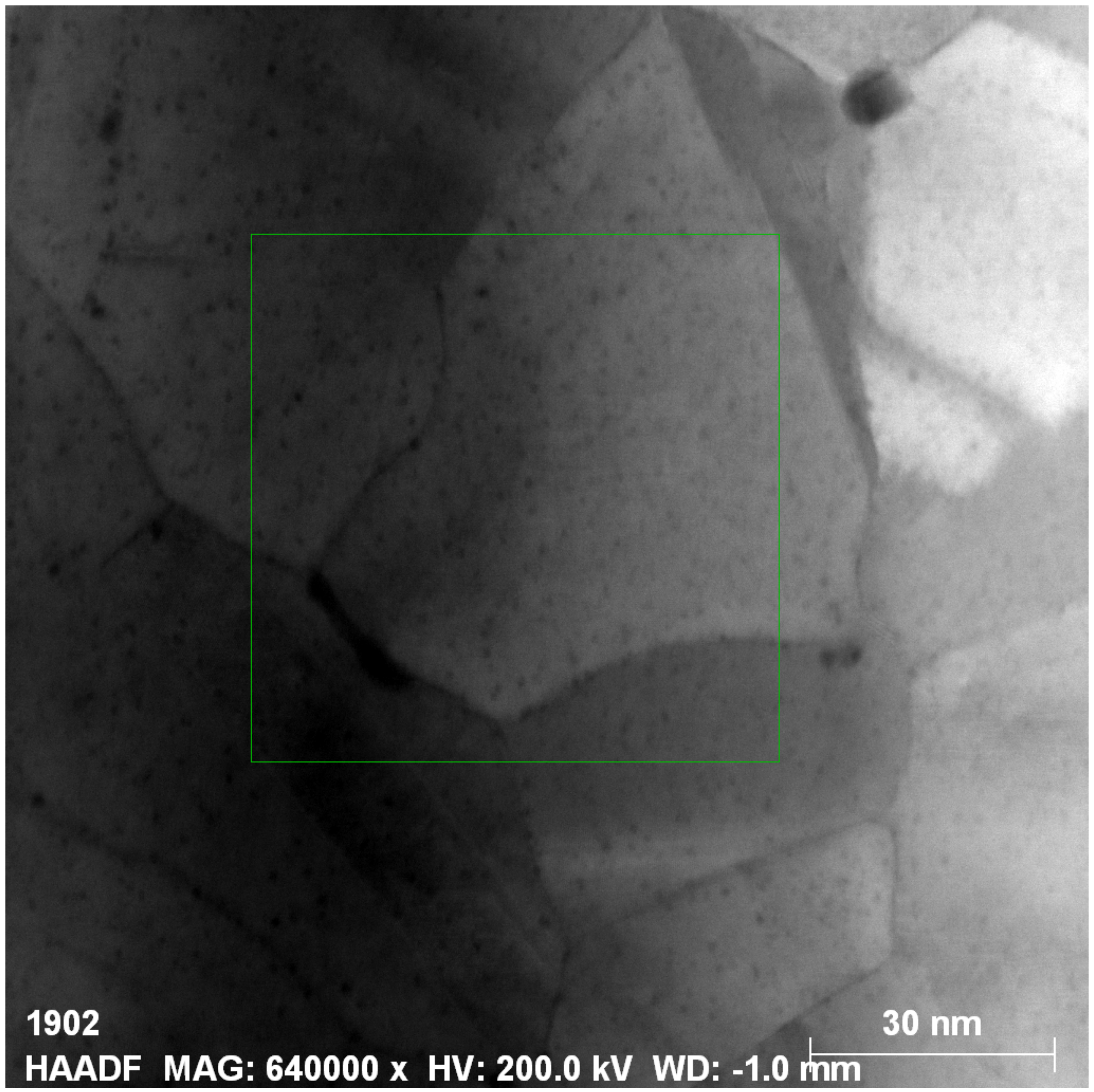
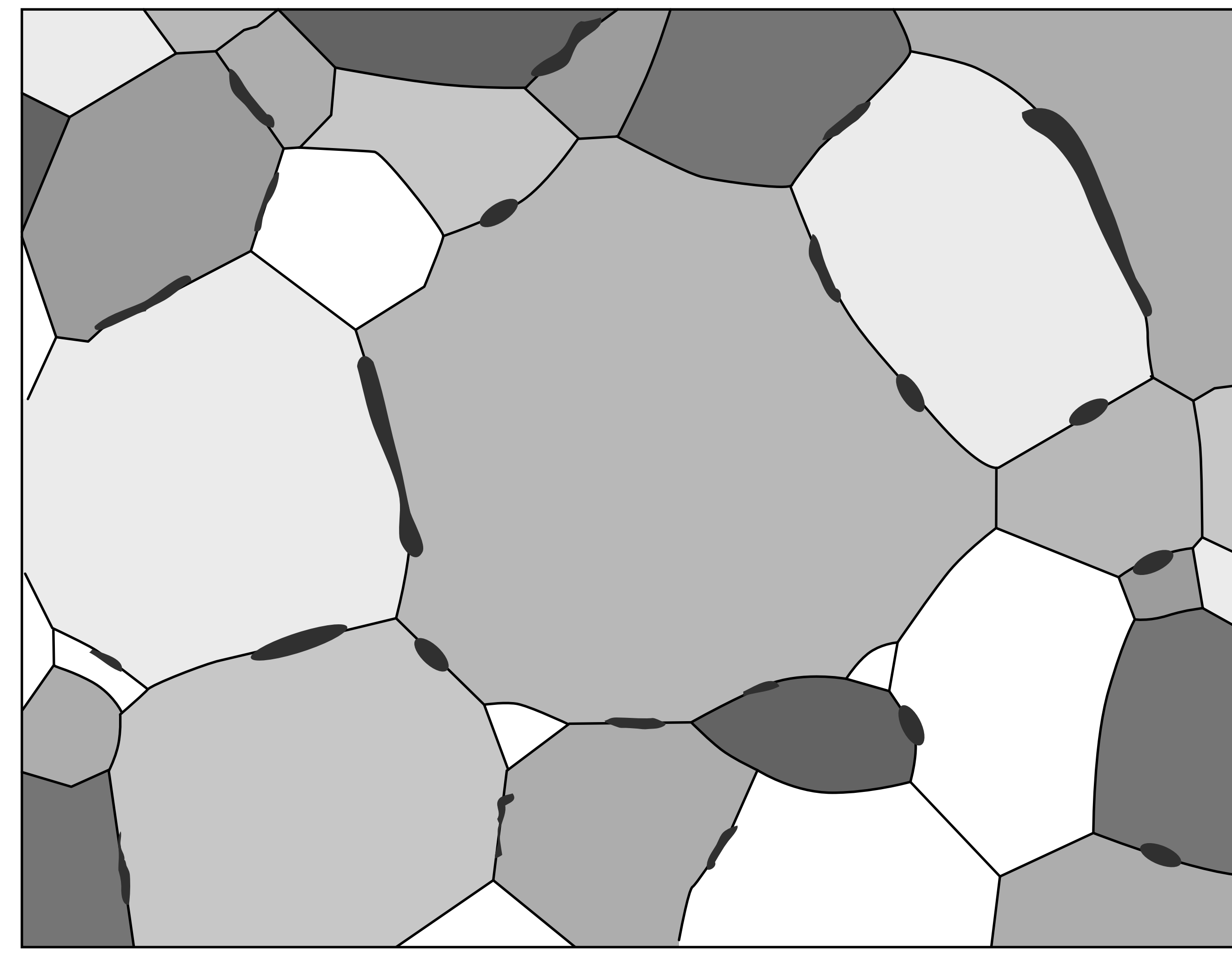
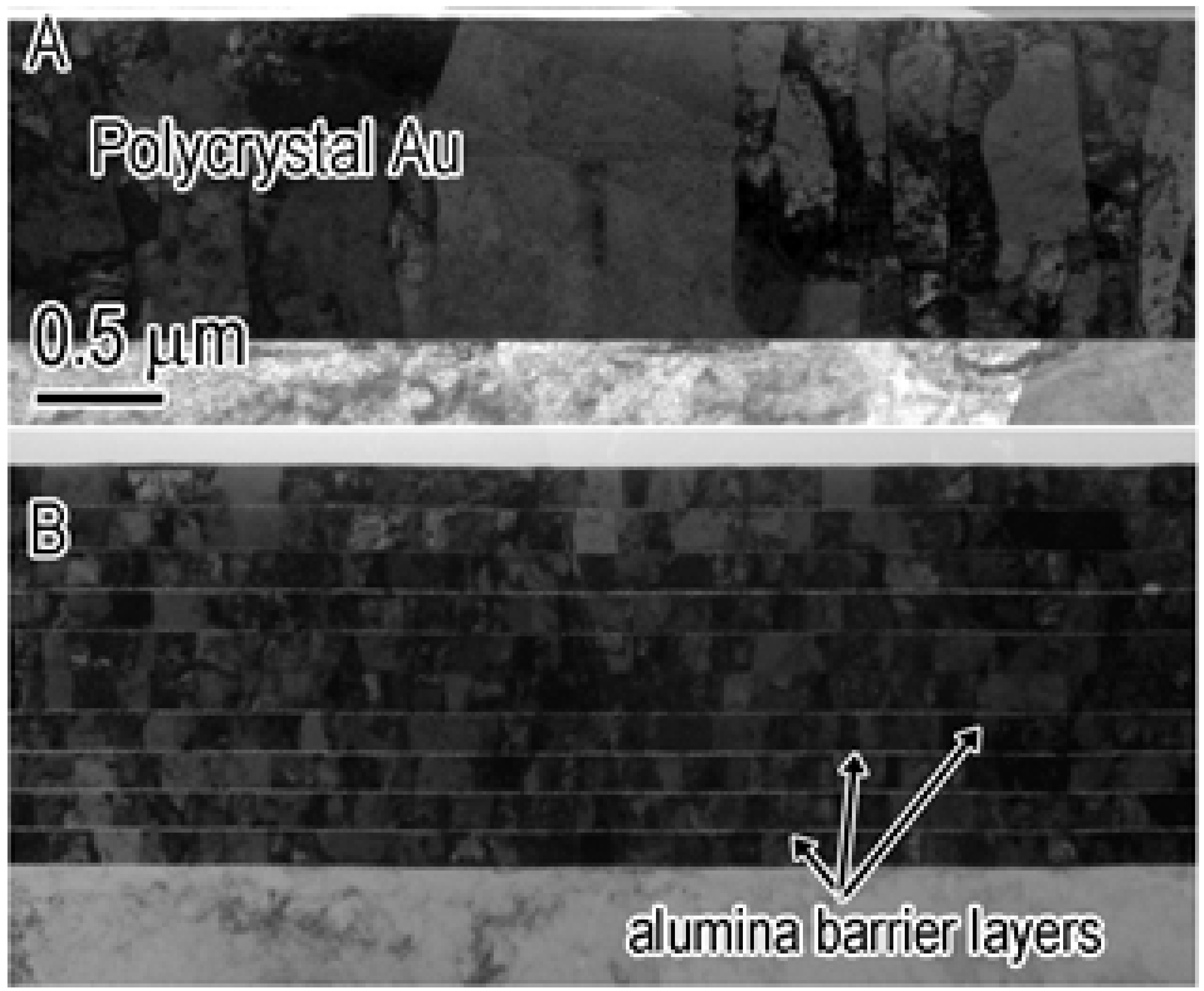




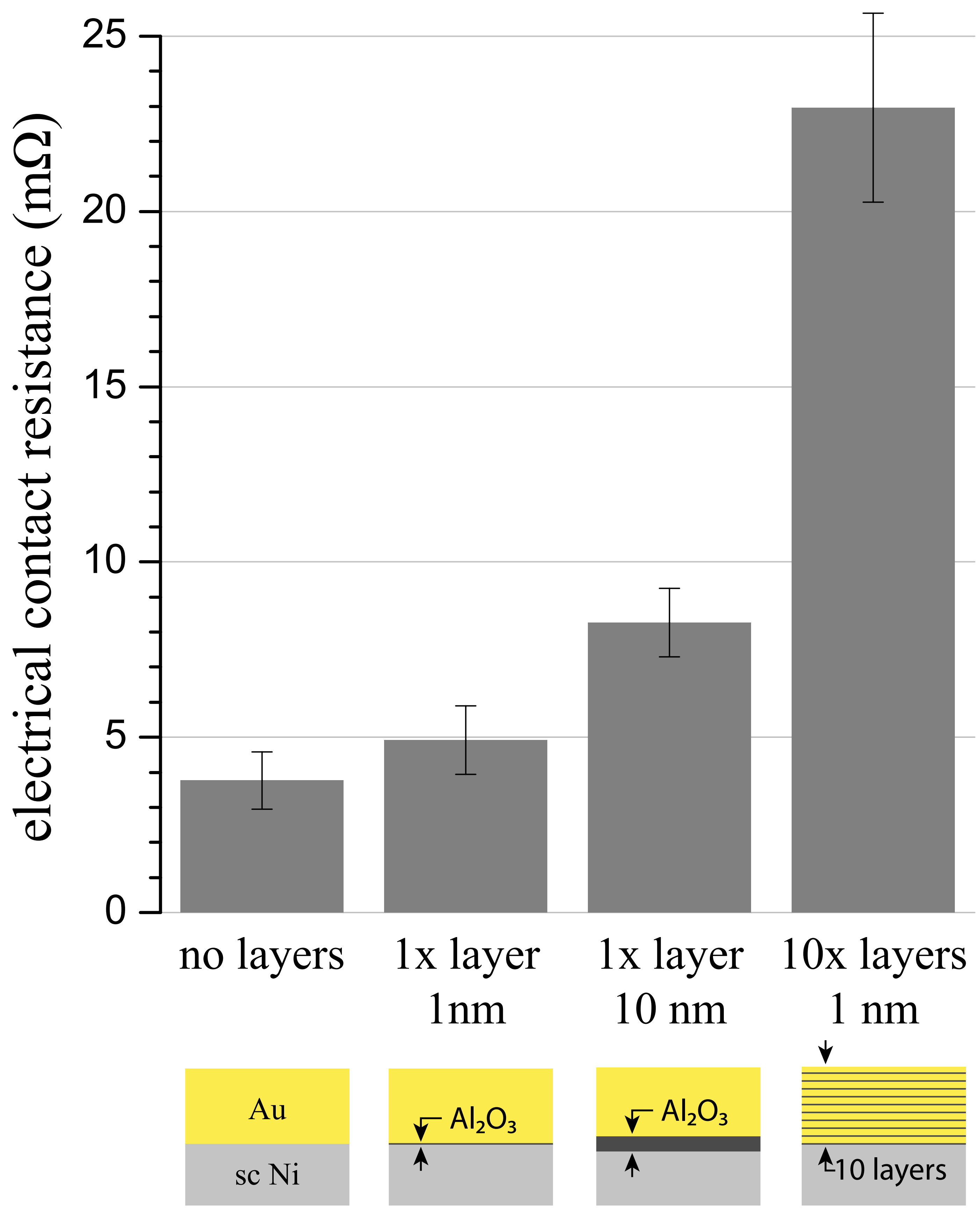
Investigation of ceramic diffusion barriers via pulsed laser deposition (PLD)

Au and Au/Al_2O_3 single and multi-layer films on PLD deposited onto single crystal nickel substrate



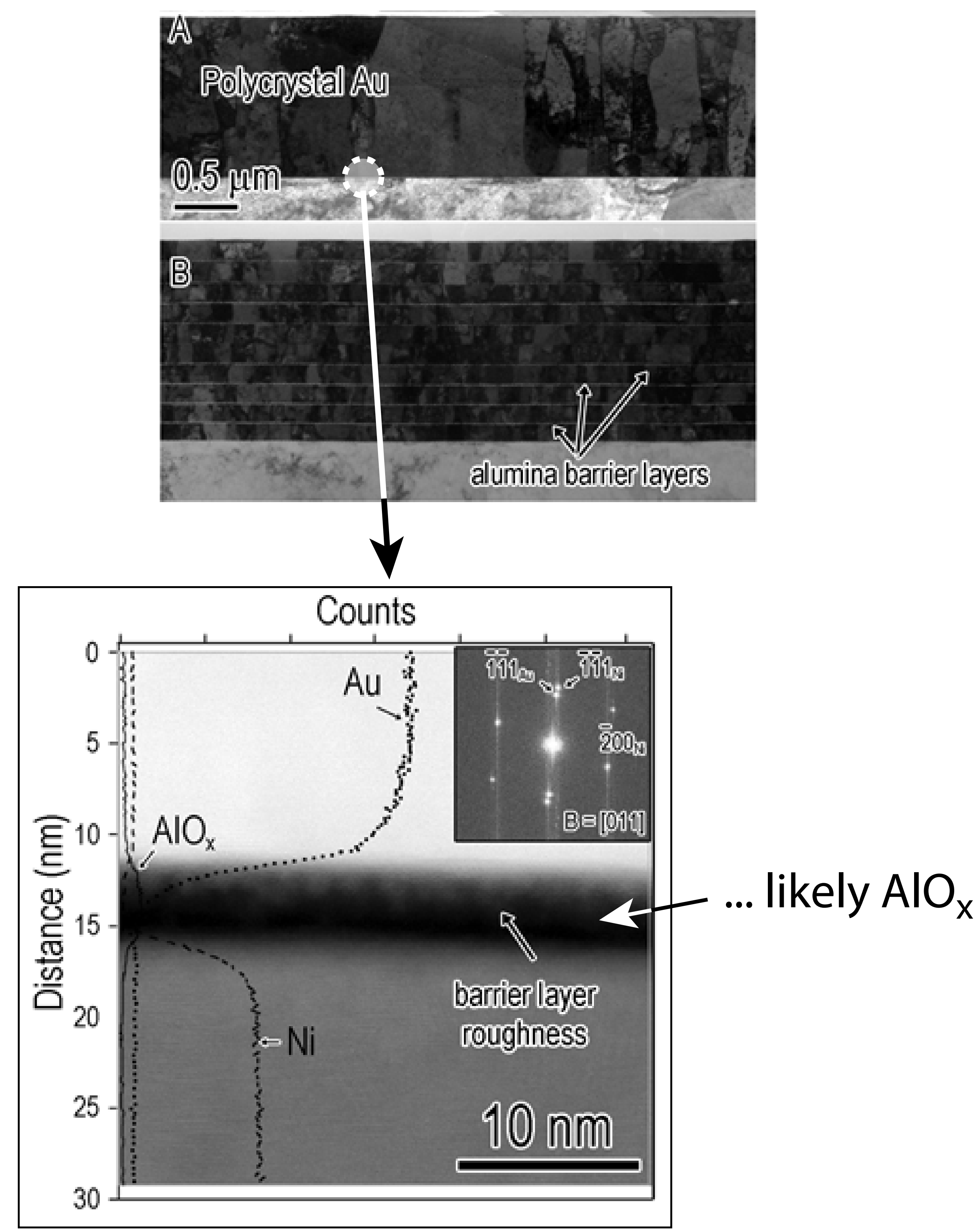
The ECR increase with oxide barrier (Al_2O_3) film was low

experimental data: contact resistance



measured with: 1.6 mm radius annealed Au tip at 100 mN

Au and Au/Al_2O_3 single and multi-layer films on PLD deposited onto single crystal nickel substrate



STEM image of Au/Al_xO_y/Ni interface

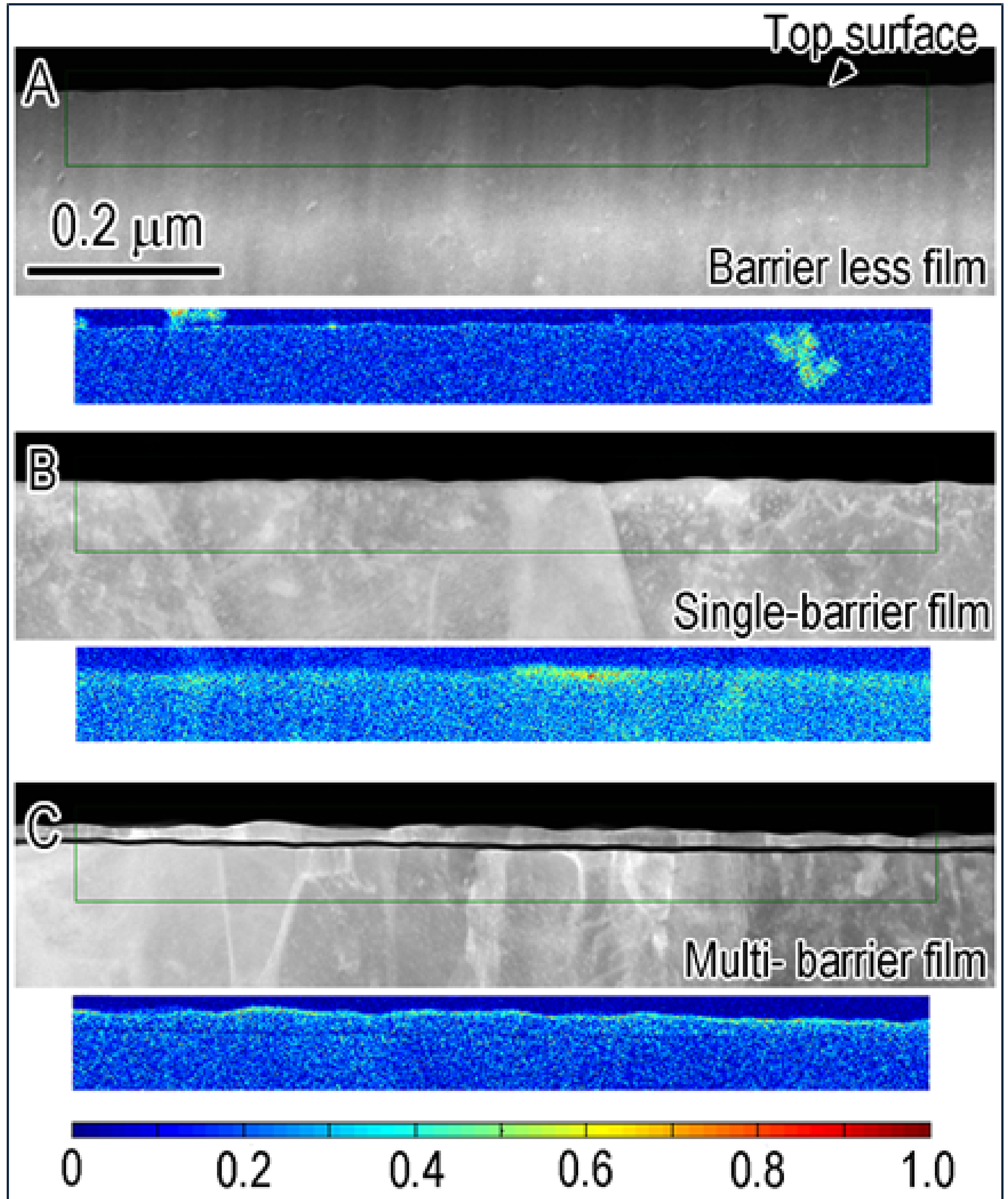
Surface accumulation of Ni reduced with alumina diffusion barrier layers

cross-section TEM of films after 5 day anneal at 250°C:

no barrier layer film, but <u>single crystal gold</u> (templated) top layer on single crystal nickel substrate

<u>1 nm thick AlOx</u> barrier layer, polycrystal Au top layer

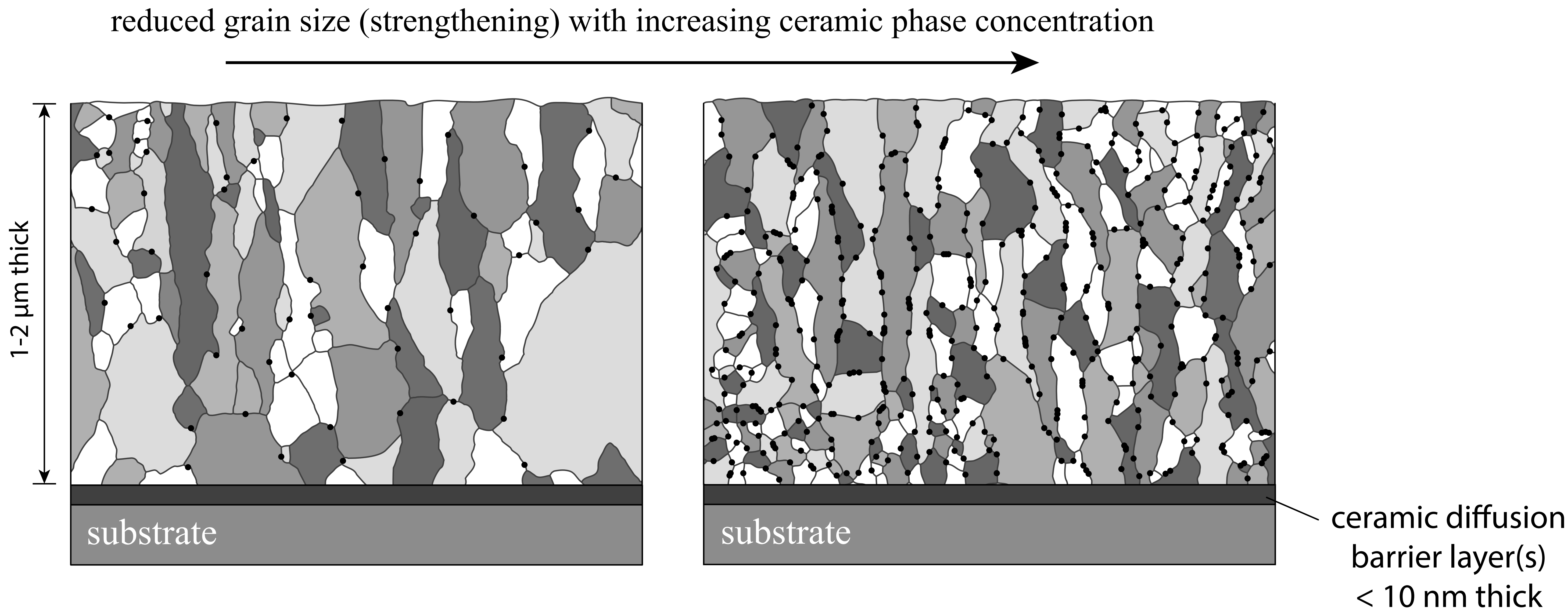
<u>ten 1 nm thick AlOx</u> barrier layers, polycrystal Au top layer



fractional concentration of Ni-O

Summary: E-beam codeposited Au-ceramic films and graded/layered structures

Nanocrystalline noble metal tribofilms strengthened via GB segregated codeposited ceramic phase(s)



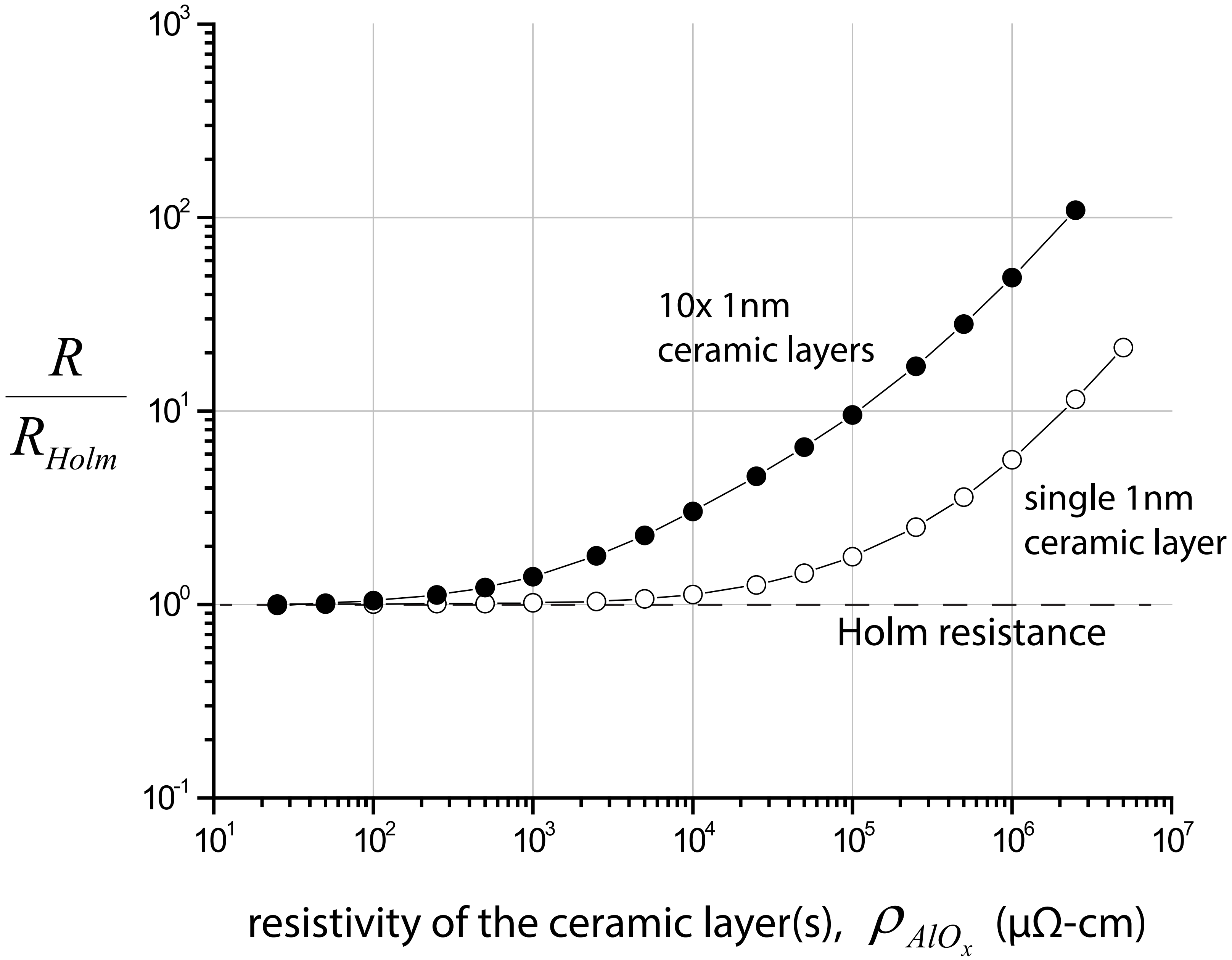
Acknowledgments

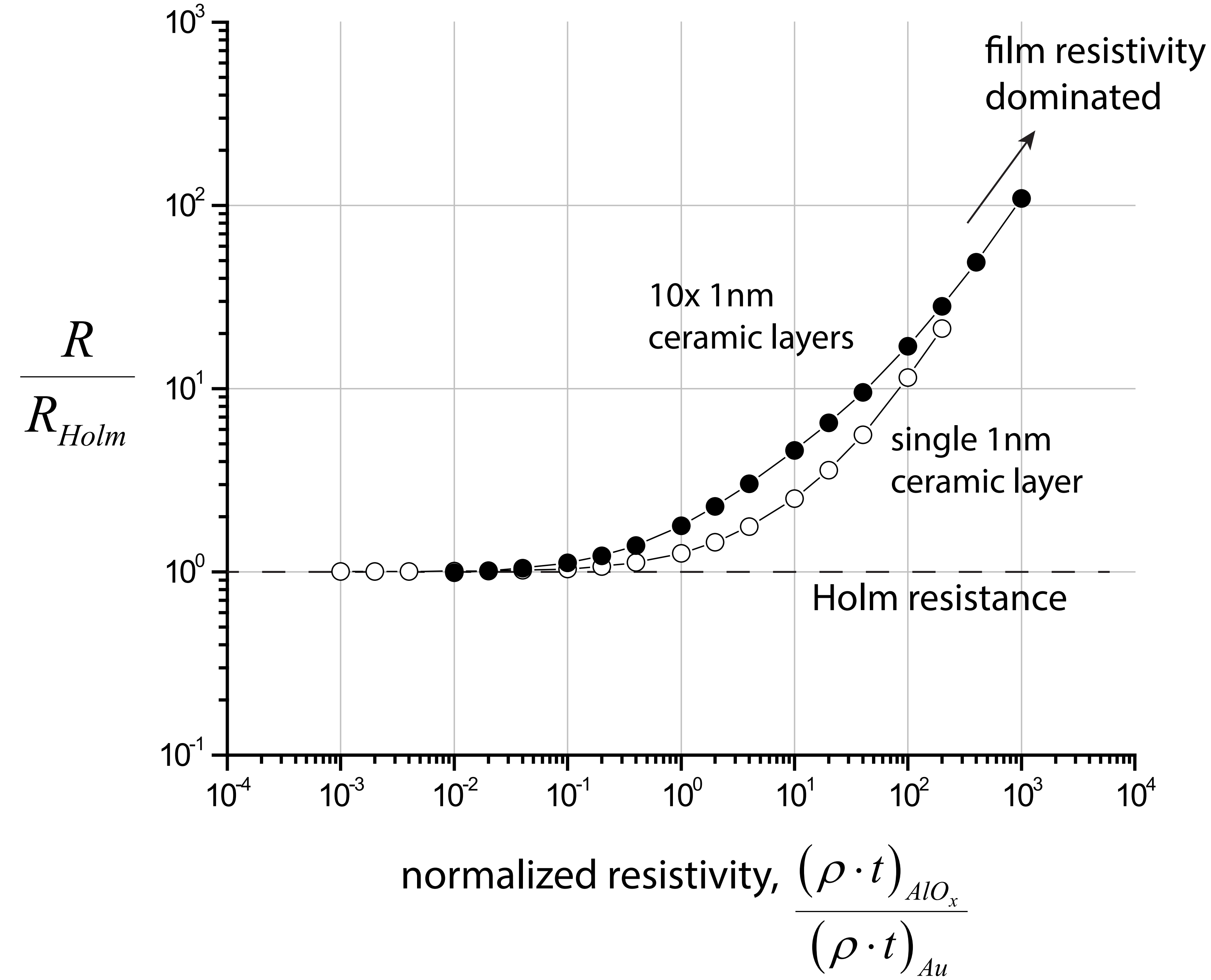
Rand Garfield for tribological test specimen preparation

Bonnie McKenzie for SEM-EDS imaging

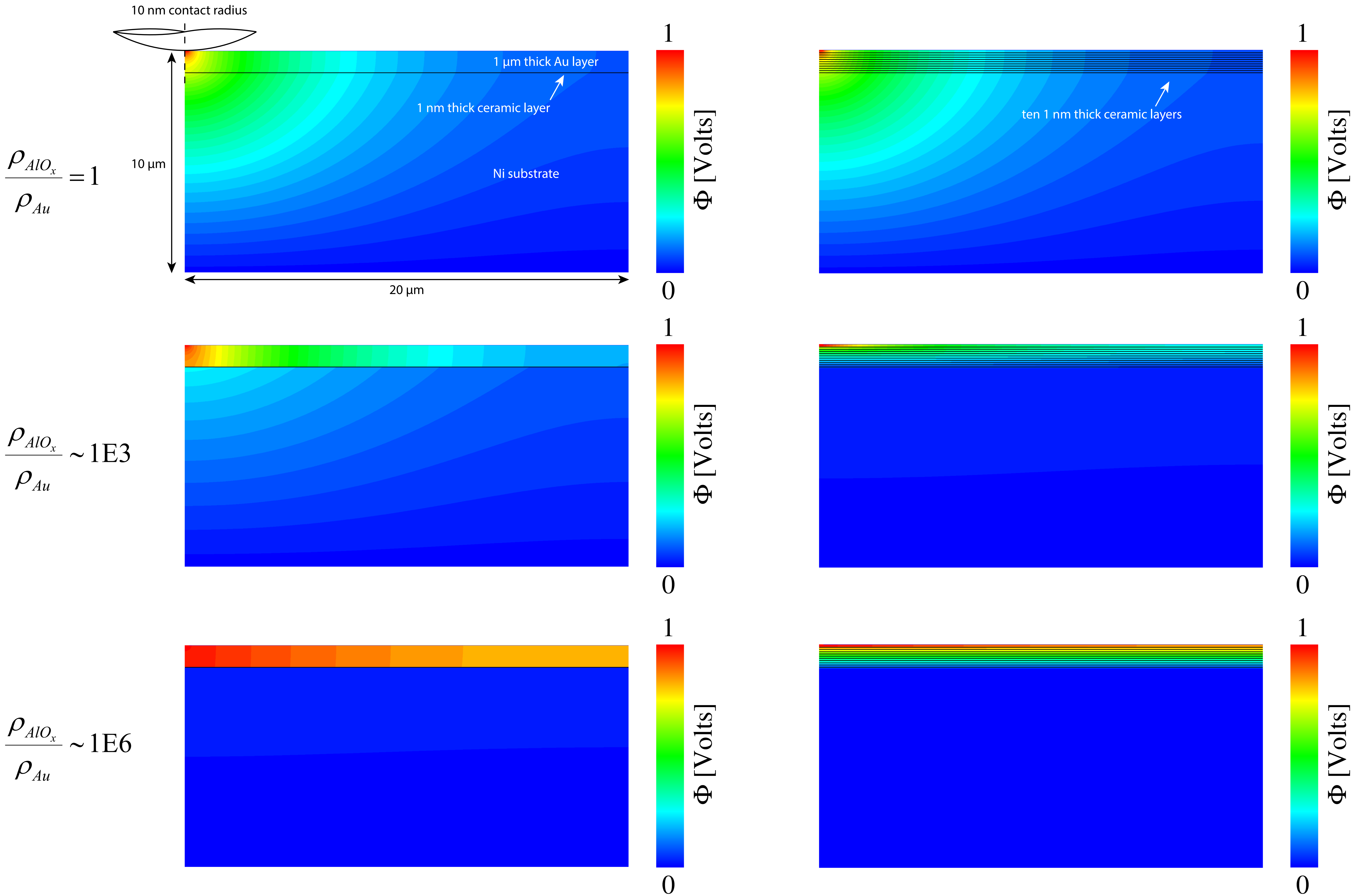
Michael Rye for diffraction composition mapping

Finite element modeling prediction of resistivity



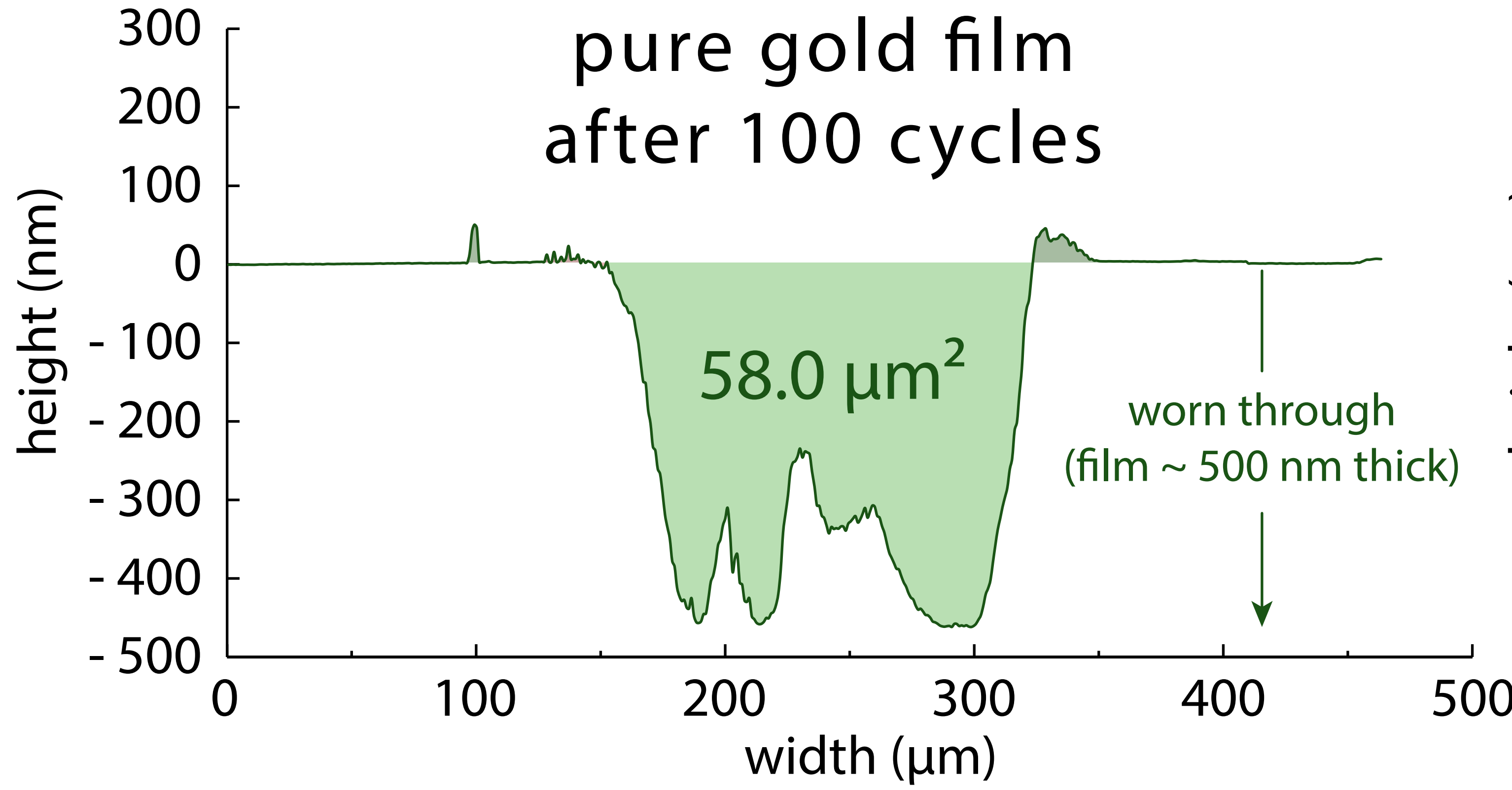


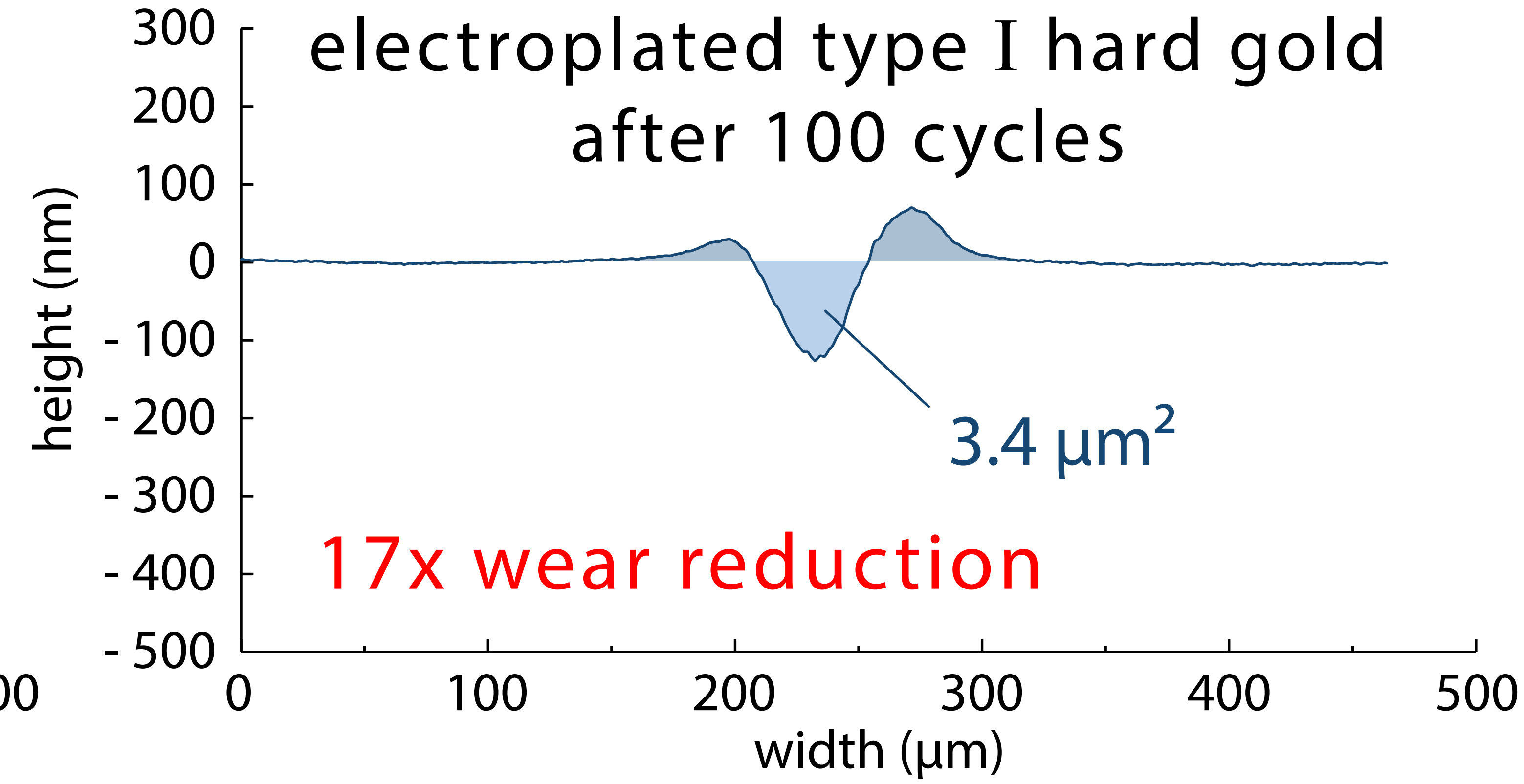
FEM isopotential maps



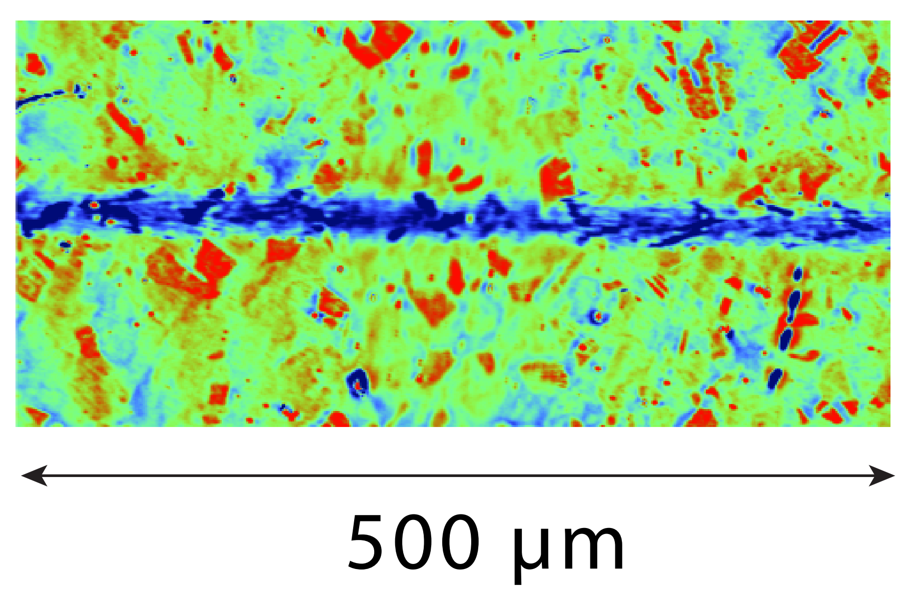
Hard gold is also highly wear resistant

average wear track cross-section in same sliding conditions against Neyoro G rider:



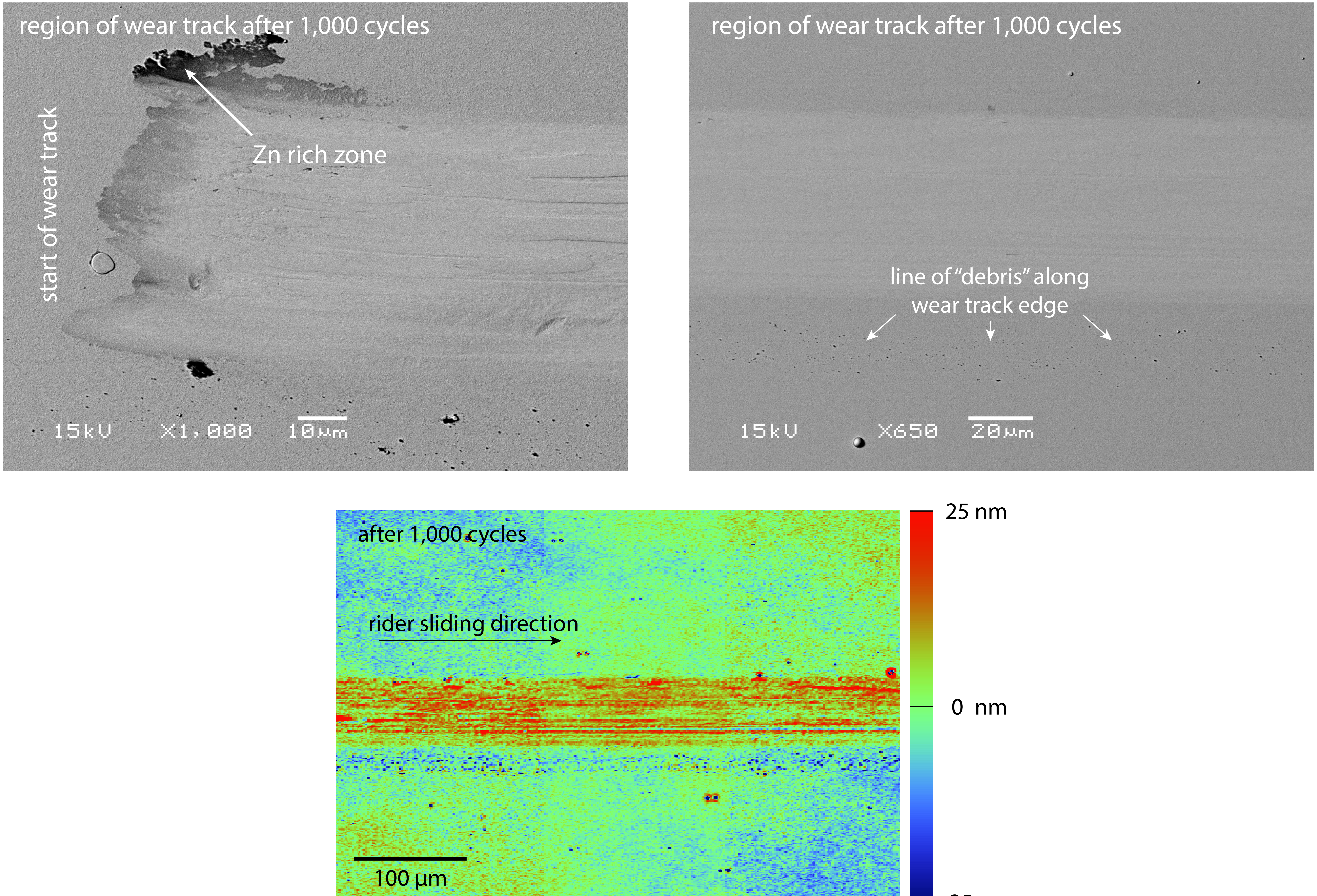


(example of topographical map)



average linescans over
50% of wear track length

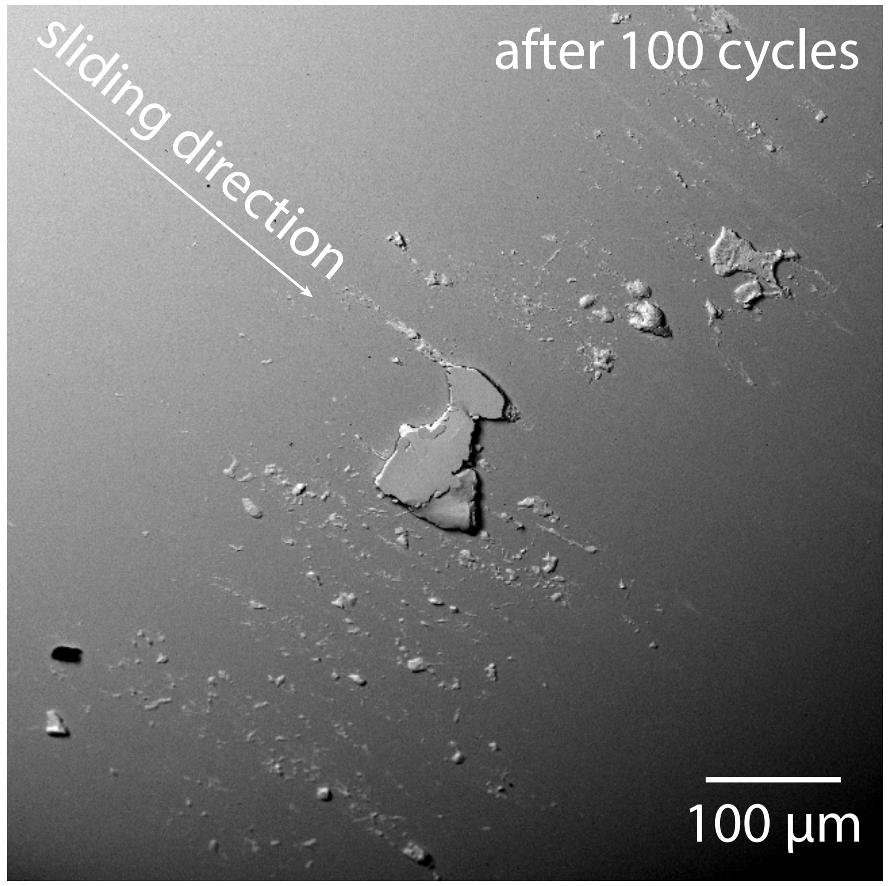
Effectively zero wear of the 2% ZnO gold nanocomposite

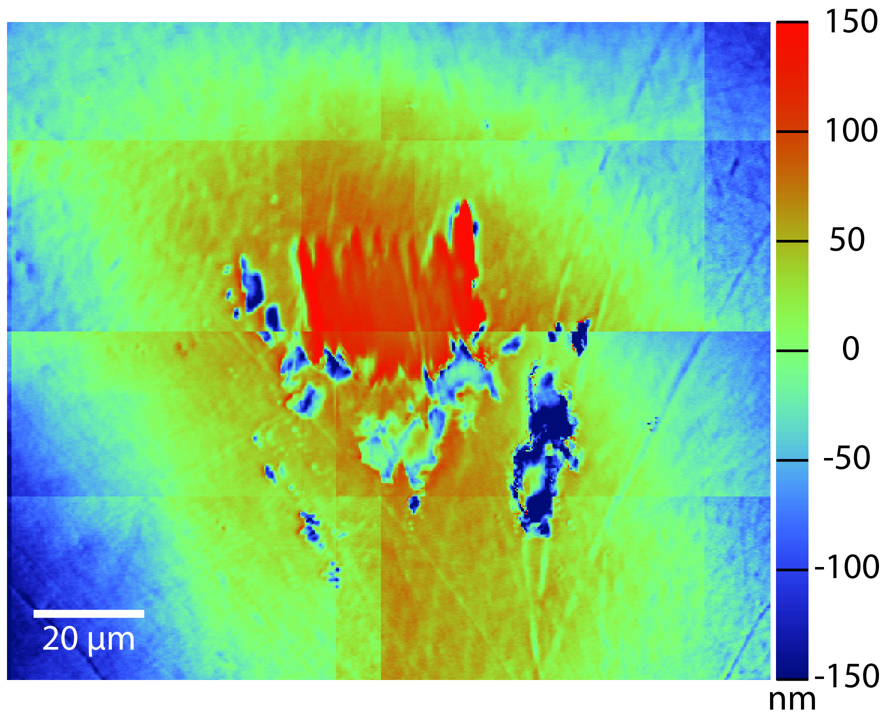


The 2% ZnO gold film wore the (hard!) Neyoro G pin

SEM of rider surface

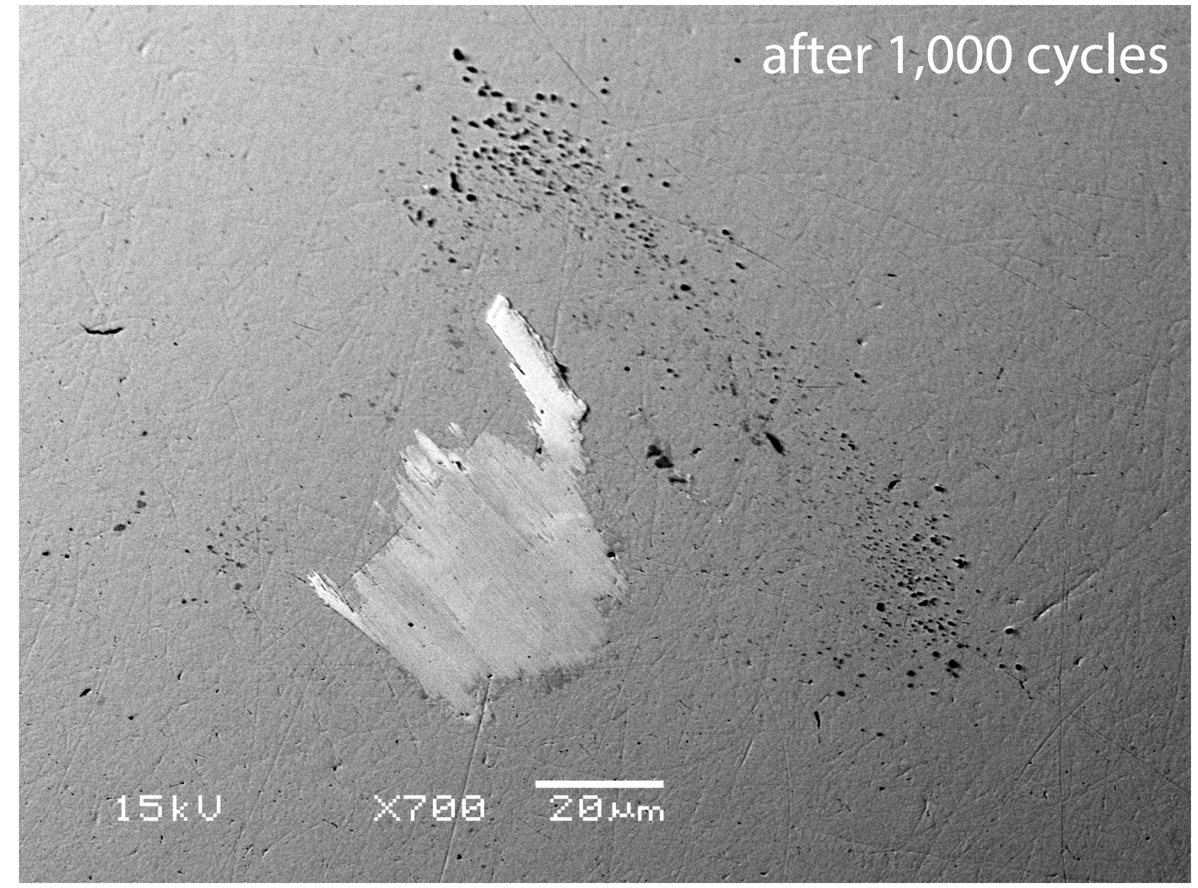
sliding against pure Au

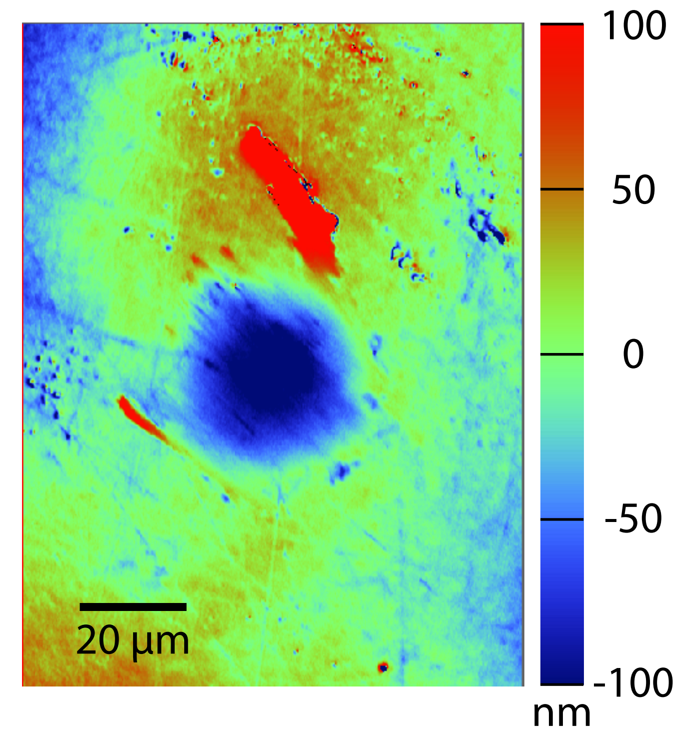




SEM of rider surface

sliding against 2 % ZnO-Au





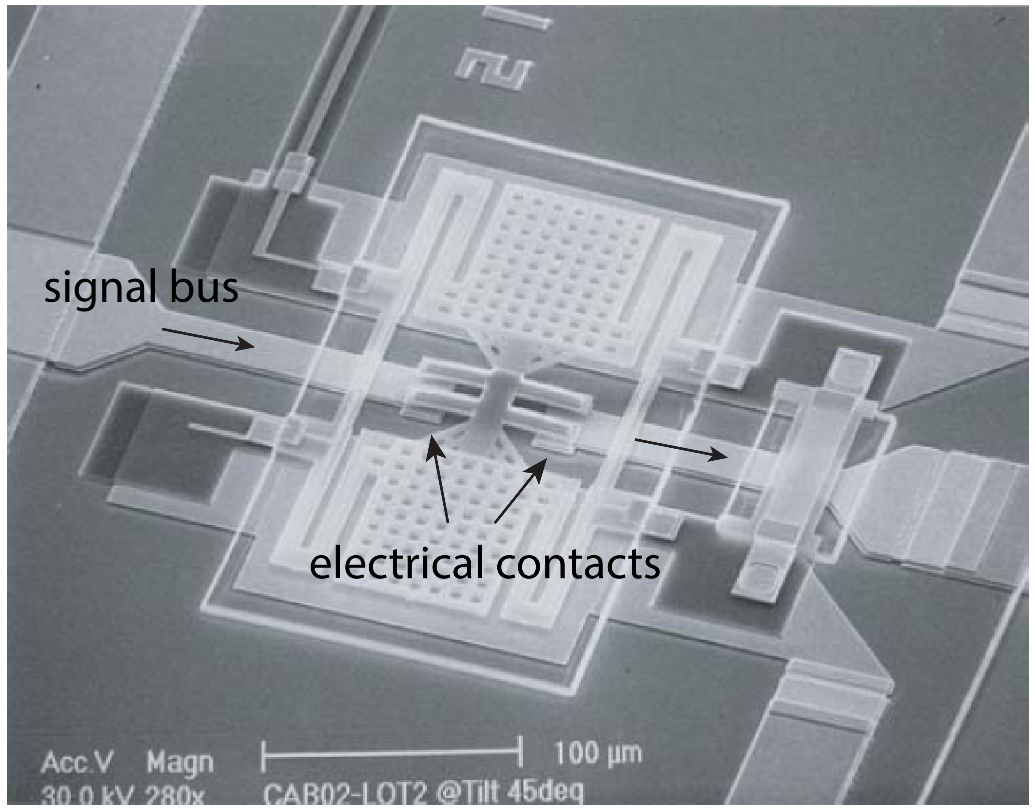
Neyoro G rider is HARD (~ 250 Knoop, or ~ 2.5 GPa)

reference: the hardest "hard gold" is in the 2.0 to 2.5 GPa range

preliminary result via nanoindentatoin, 0.1% strain : 1% ZnO-Au hardness ~ 2.6 GPa

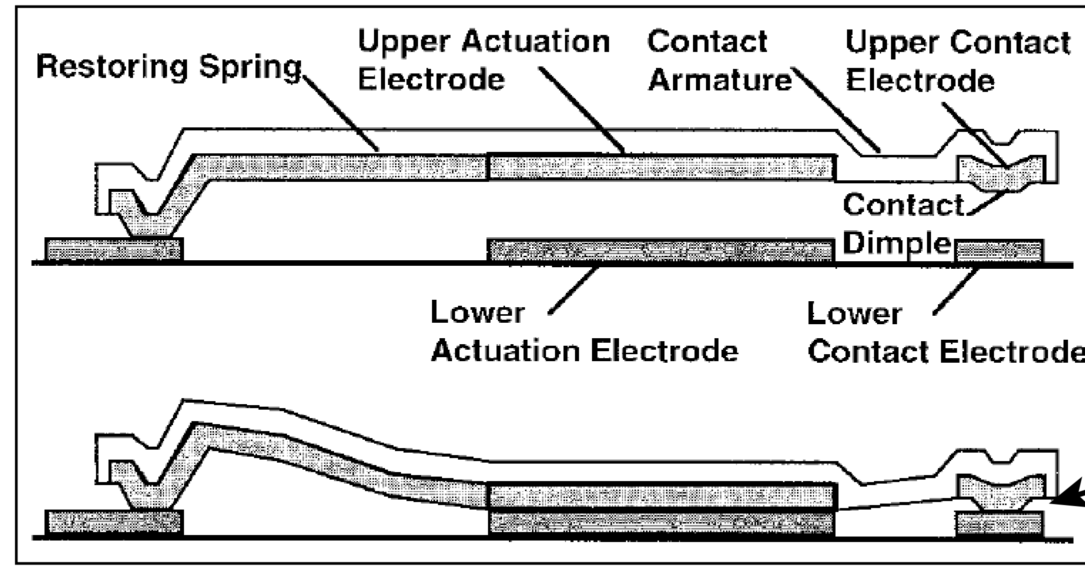
What are some examples of mechanical-electrical contacts?

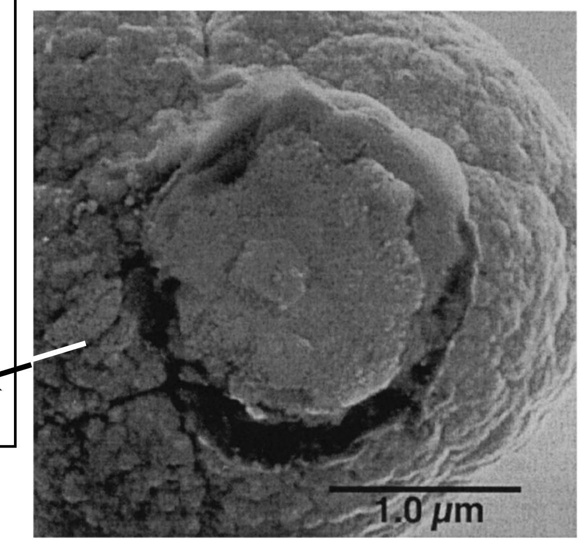
MEMS



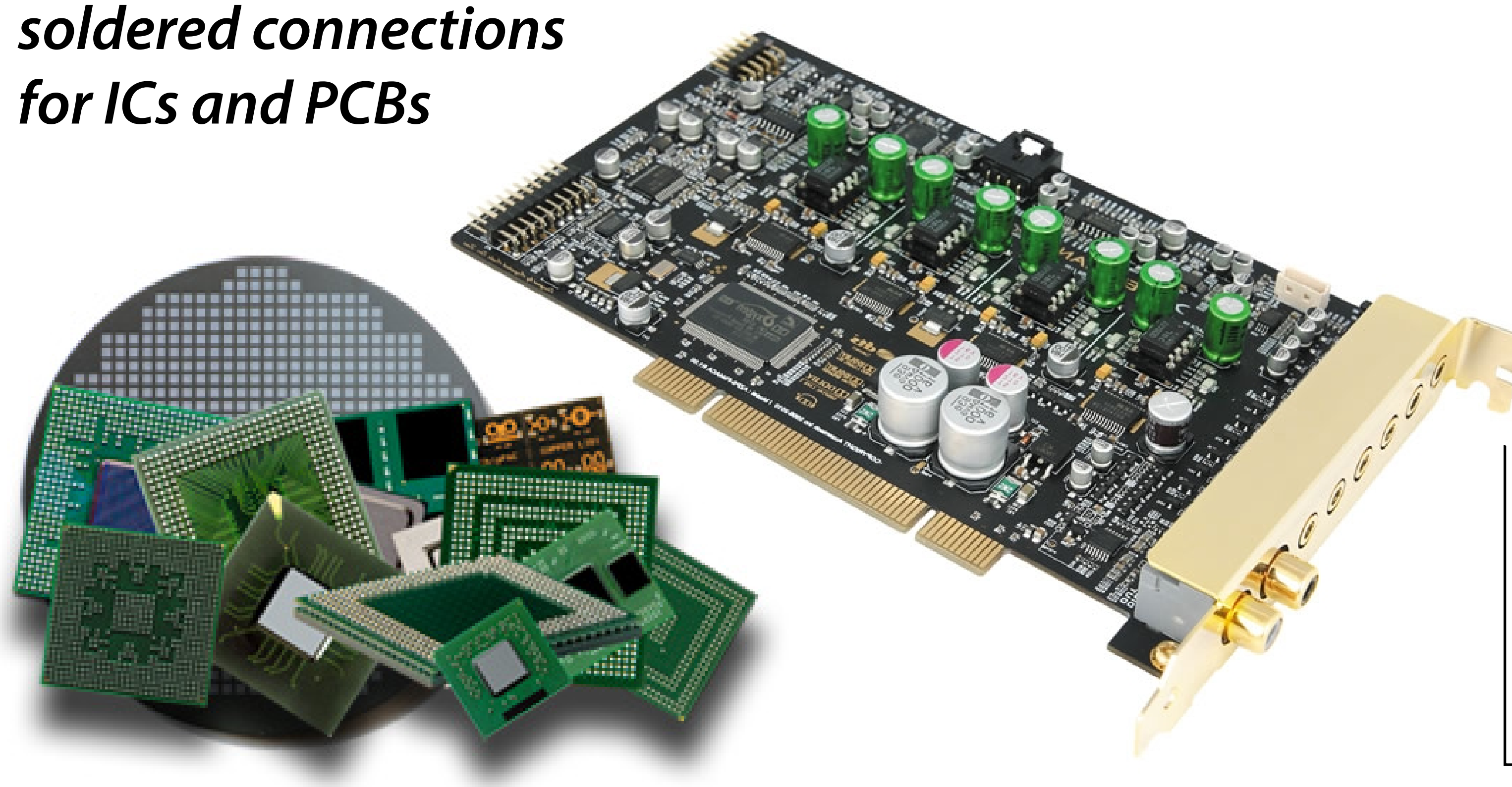
Rockwell Scientific metal-metal switch

switching GHz signals

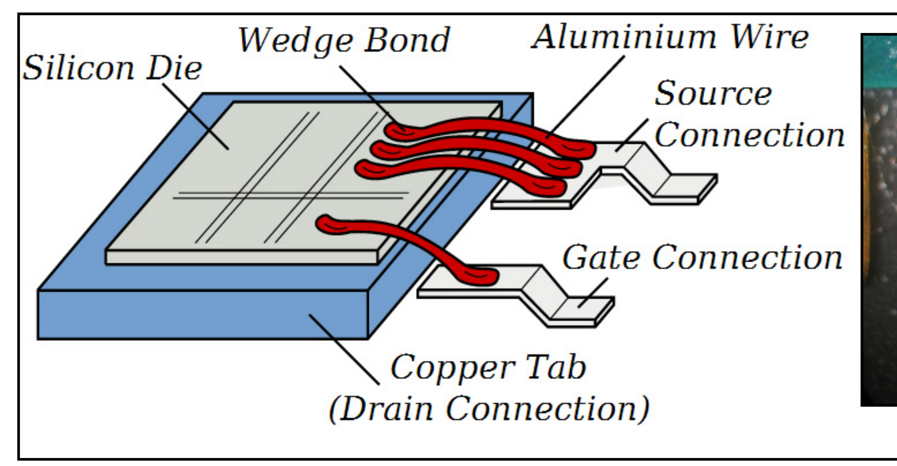


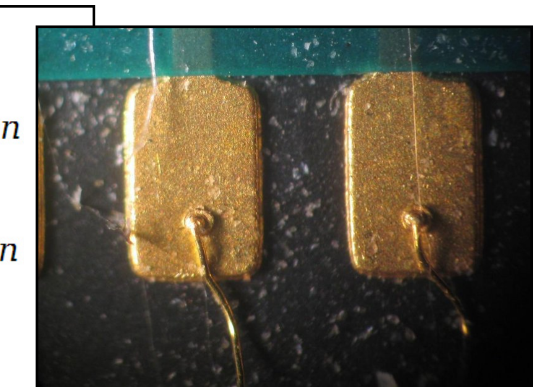


soldered connections for ICs and PCBs

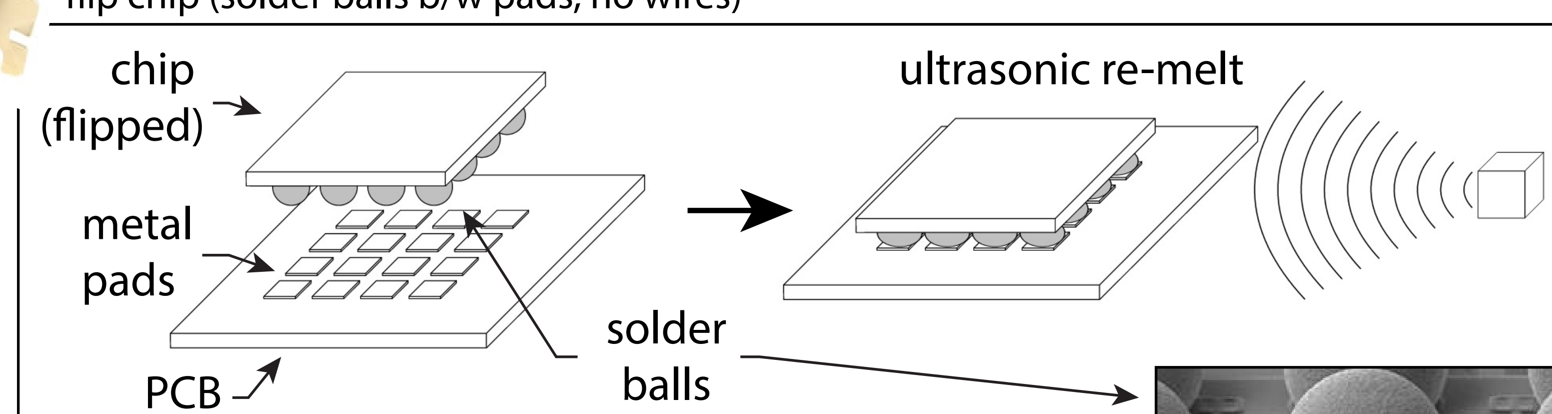


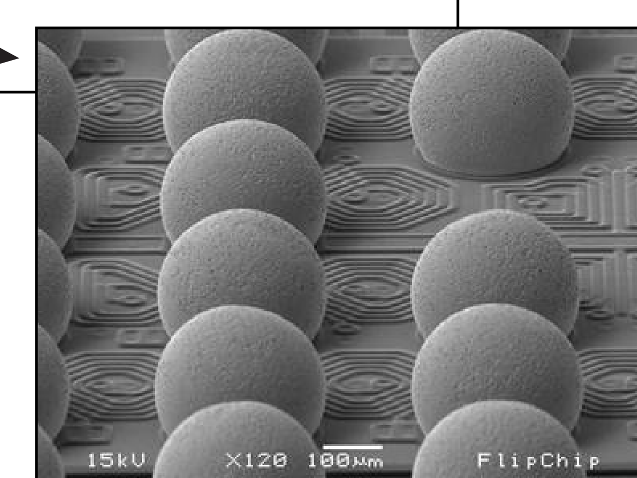
wire bonding of ICs





flip chip (solder balls b/w pads, no wires)





When electricity is required to pass through a contact, the surfaces are <u>metallic</u> (conductivity!)