SAND2014-2800P

NM Tech, Graduate Seminar , April 4th, 2014

Synthesis and Thermal Stability of Gold-Zinc Oxide Nano-Composite Thin Films for Electrical Contacts

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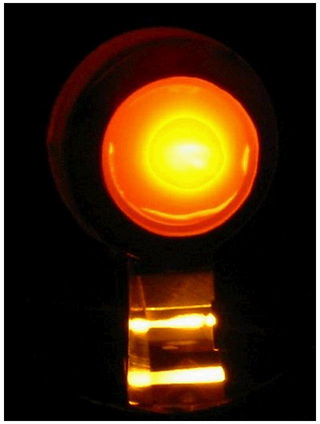

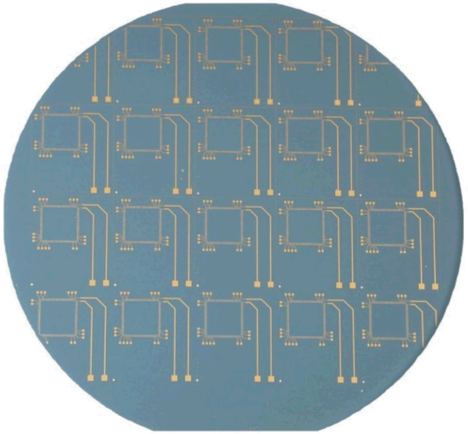

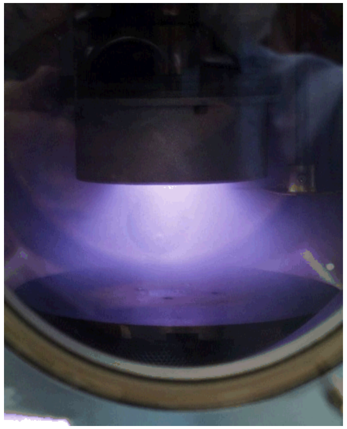

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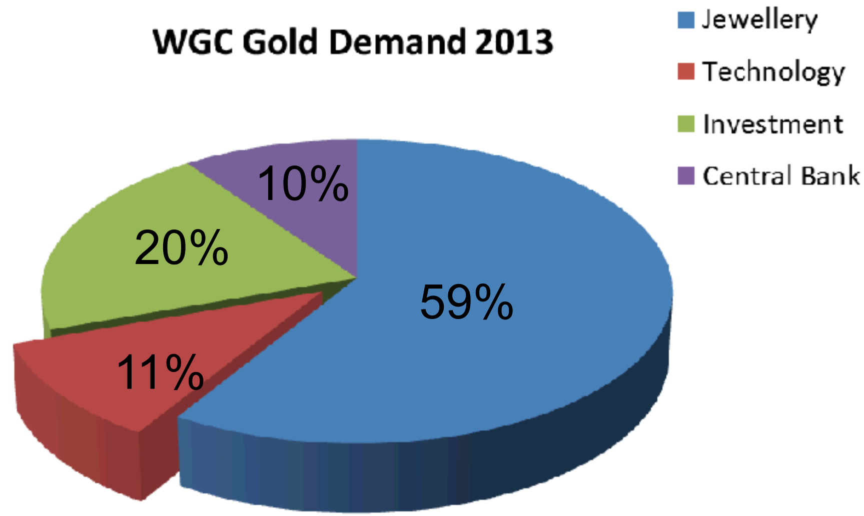
Outline

- **Technical Gold Usage Demand**
- **What is Hard Gold?**
- **Electroplating methods & problems**
- **Physical Vapor Deposition Methods**
- **Characterization of PVD Au-ZnO Thin Film**
- **Thermal Stability of Film**
  - DSC, Resistivity, In-situ TEM

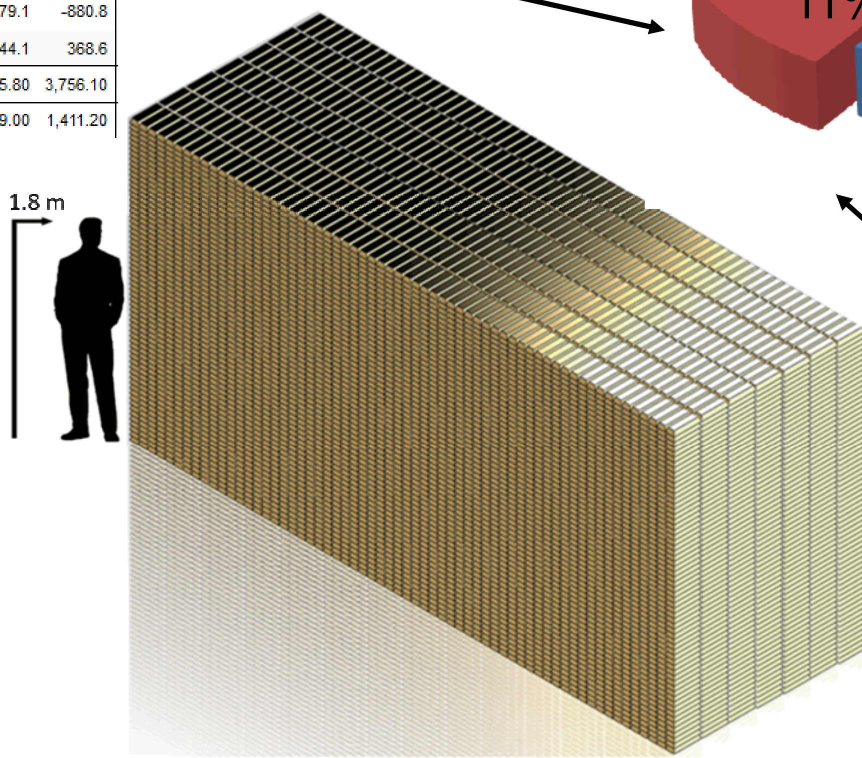
Gold Usage

World Gold Council, Gold Demand Report Feb. 2014

Tonnes	2012	2013[1]
Jewellery	1896.1	2,209.50
Technology	407.5	404.8
Electronics	284.5	282.4
Other Industrial	84.4	85
Dentistry	38.6	37.3
Investment	1,568.10	773.3
Total bar and coin demand	1,289.00	1,654.10
Physical Bar demand	962.7	1,266.90
Official Coin	213	283.4
Medals/Imitation Coin	113.4	103.8
ETFs & similar products[3]	279.1	-880.8
Central bank net purchases	544.1	368.6
Gold demand	4,415.80	3,756.10
London PM fix, US$/oz	1,669.00	1,411.20



8% Electronic Appl.
(300,000 kg / year)



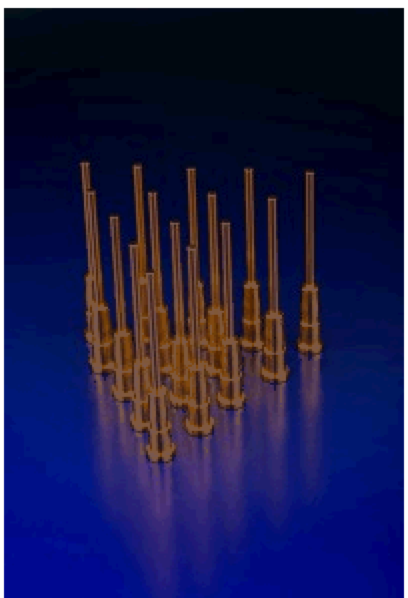
1% Dentistry
(included in Tech. usage)

Technical Application

Electronic connectors and switches

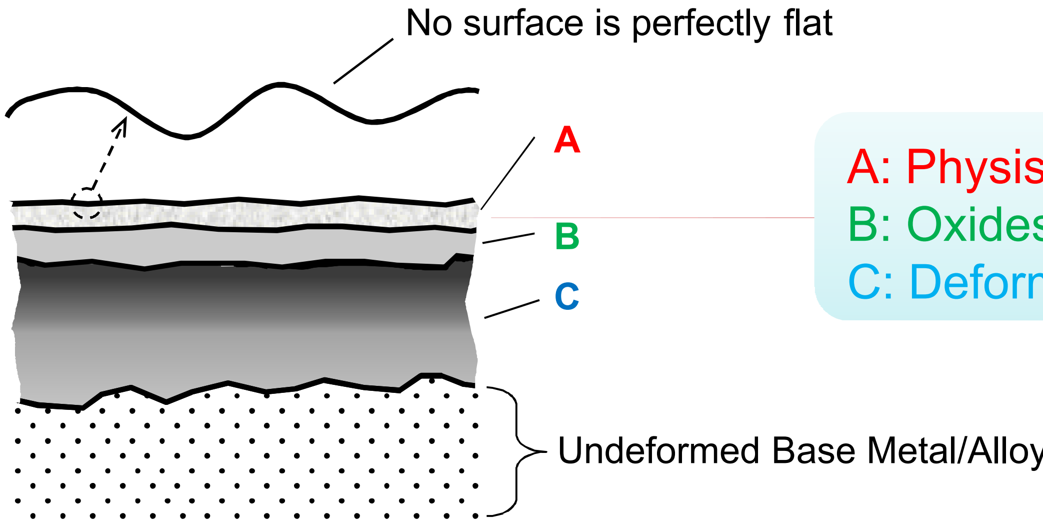
Electronics Applications: Connectors and contact pads on printed circuit boards

Chemically Inert and low electrical resistance

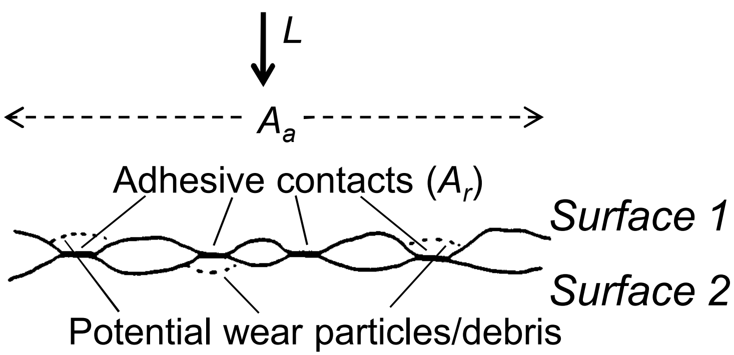


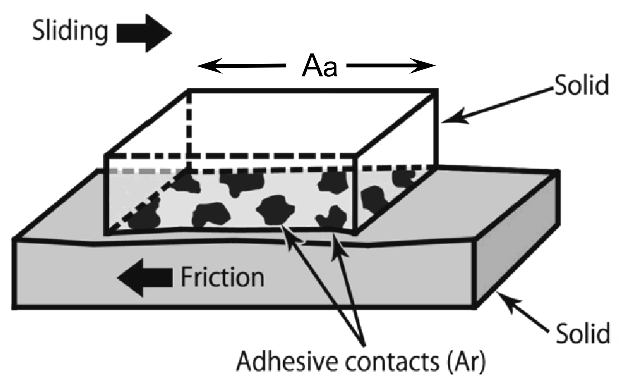
Nature of Metallic Surfaces

Sliding electrical contacts



A: Physisorbed/Chemisorbed
B: Oxides (Chemically Reacted)
C: Deformed layers





Real area of contact (A_r) to be minimized for low adhesion (Low Adhesive Wear)
Or maximized for reduced electrical contact resistance (ECR)

T.W. Scharf & S.V. Prasad, Journal of Material Science (2013) 48:511-531

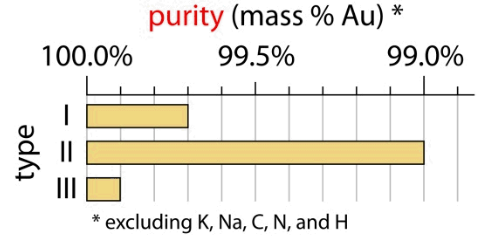
Hard Gold

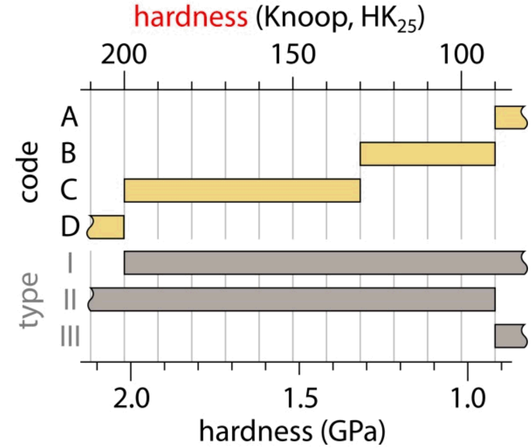
ASTM Types

From ASTM B488-11 / MIL-DTL-45204D:

	type	suggested applications (ASTM)
> 99.7% Au	I	general-purpose, high-reliability electrical contacts
(hardest) > 99.0% Au	II	general-purpose, wear resistance; low temperature only
(softest) > 99.9% Au	III	soldering; limits impact of oxidation of codeposited material
	IIIA	semiconductor components, nuclear eng., high temperature

- Pure gold is soft (low yield point) and has unacceptable amount of friction and wear
- Gold is typically hardened with minute alloying of Ni or Co (referred to as hard gold) to achieve the desired balance between friction, wear and ECR
- Current practice is to apply hard gold by electrodeposition
- *Nickel Underplating is used any time the substrate alloy contains Copper to prevent diffusion of Cu into Au coating.*





	minimum thickness	
class	µinch	µm
00	20	0.51
0	30	0.76
1	50	1.27
2	100	2.54
3	200	5.08
4	300	7.62
5	500	12.70
6	1500	38.10

Hall-Petch Strengthening

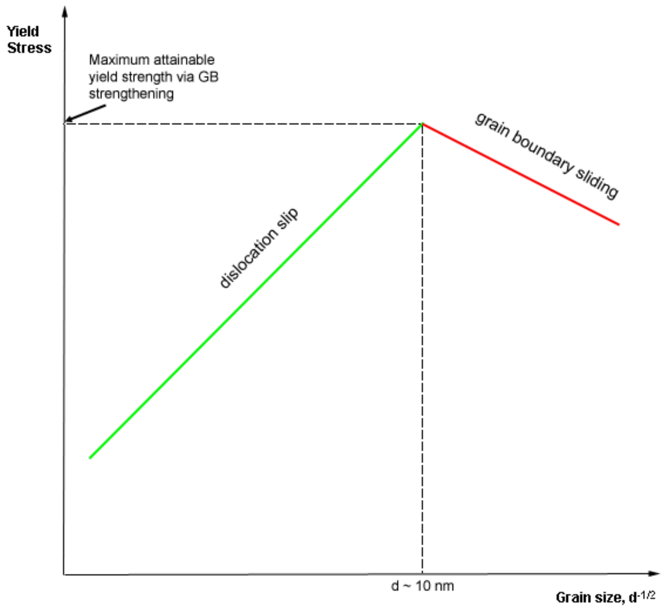
Grain Refinement

Hall-Petch relationship:

$$H = H_o + K_H d^{-1/2}$$

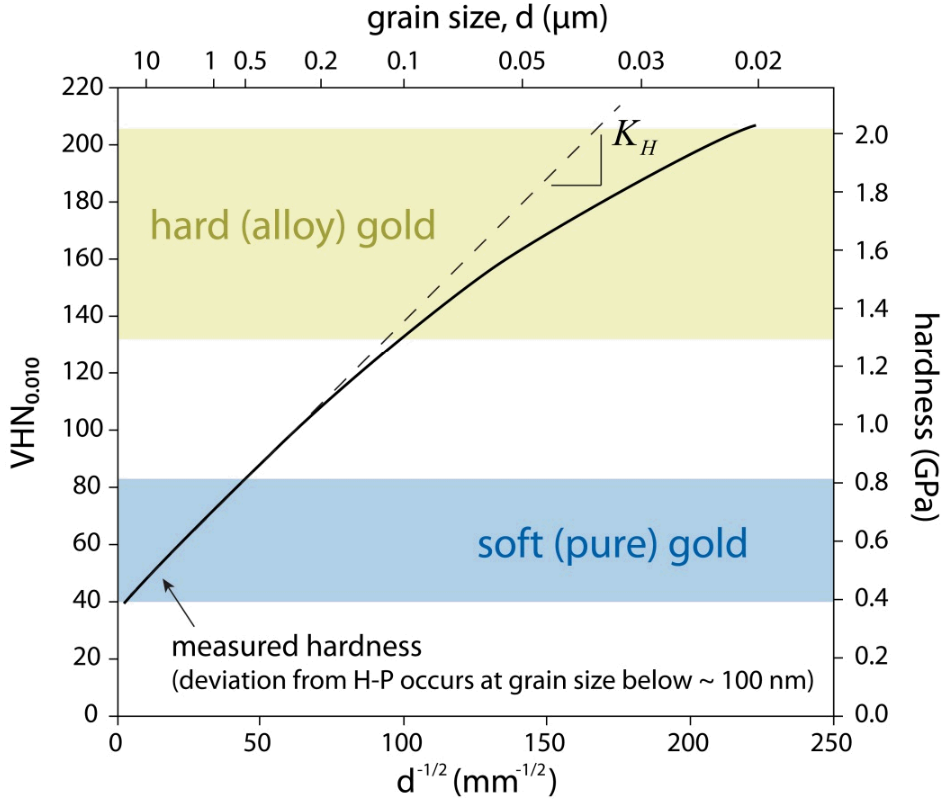
H - hardness
d - avg. grain diameter

Hall-Petch Strengthening Limit



Theoretical maximum strength at ~ 10nm

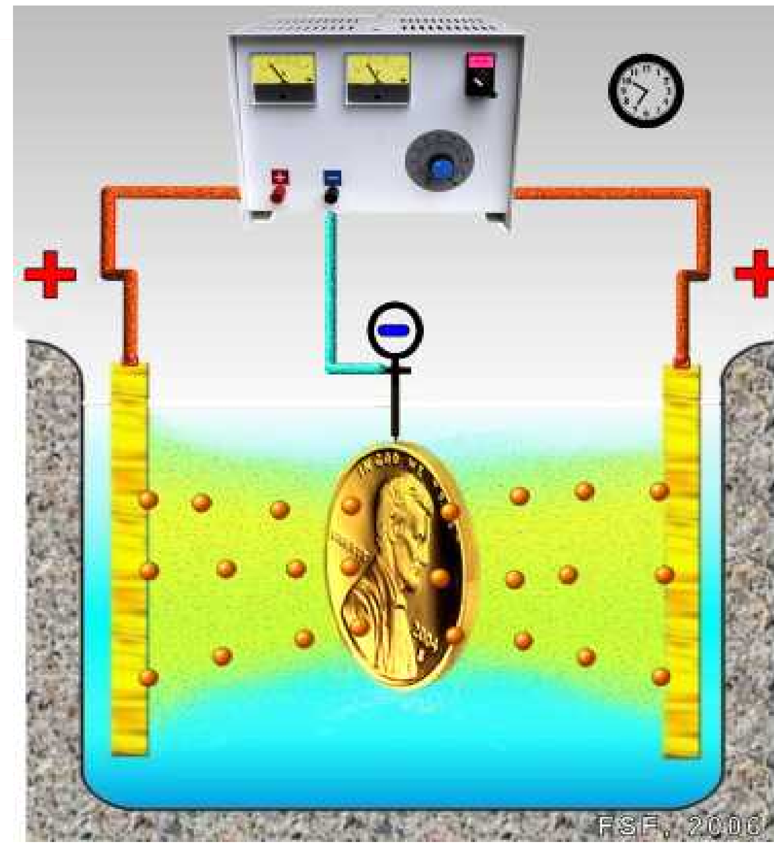
From: Lo, Augis, and Pinnel, JAP (1979)

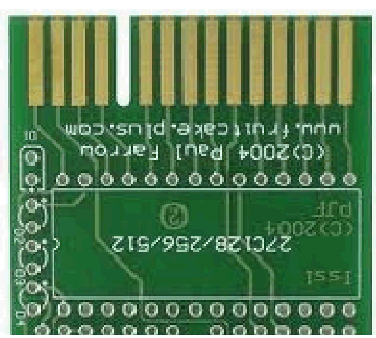


Electrochemical Deposition

Toxic plating baths

Hard Gold is typically plated from
cyanide solution $KAu(CN)_2$
a citrate buffer solution
modifiers of As, Cd or Tl,
a small amount of a hardening
agent such as Ni or Co
Nickel barrier layer applied first

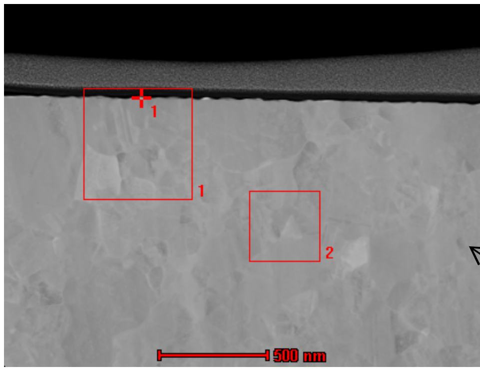


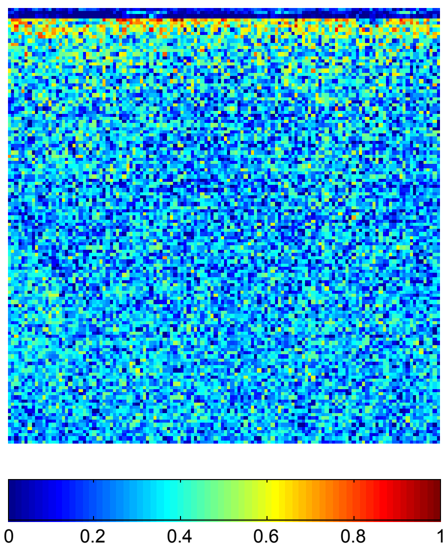


Issues With Electroplated hard Au

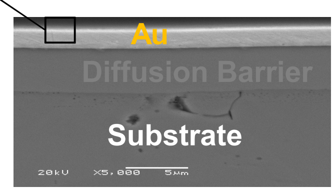
Surface oxide formation

Cross-sectional TEM and Spectral Imaging

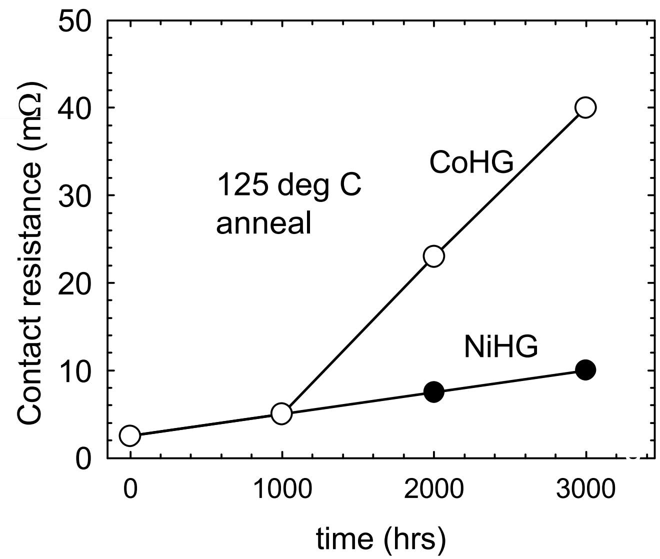




Relative Ni concentration After 35+ years



Ni or Co used for hardening Au may diffuse to the surface over time

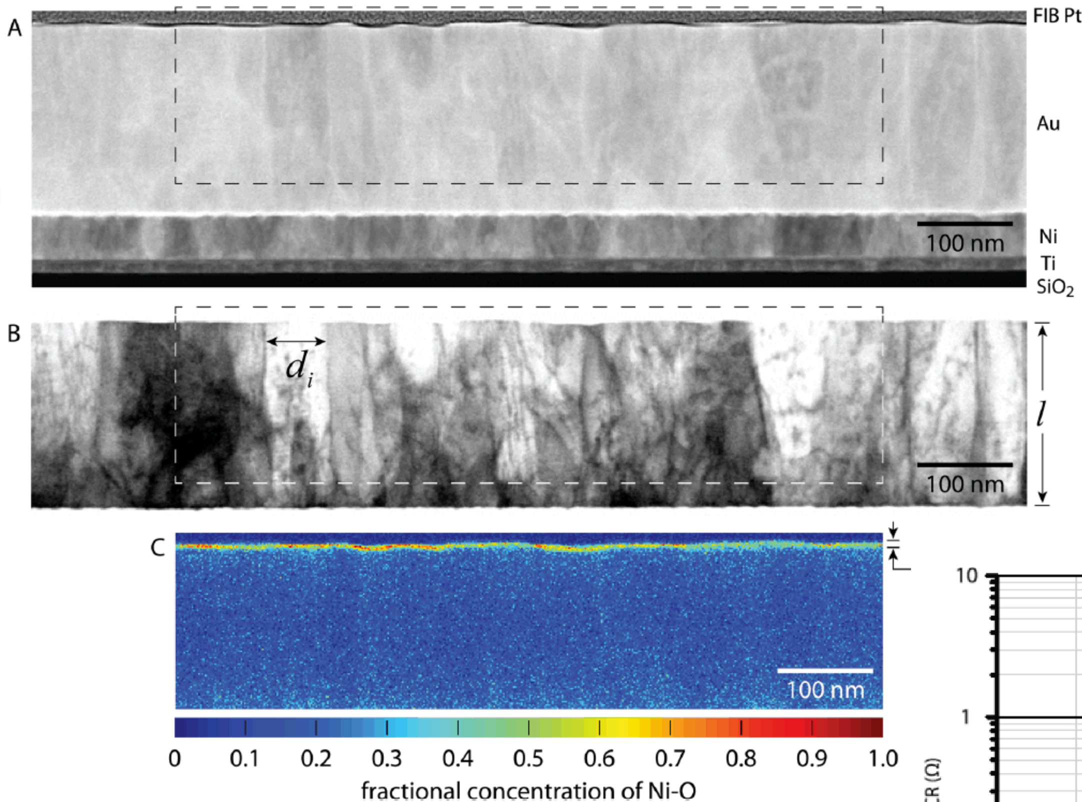


Y. Okinaka and M. Hoshino, Gold Bulletin, ***31****(1), 3 (1998).*

- Diffusion and segregation of hardeners and elements from “diffusion barriers” to the surface (ECR degradation)
- Limited electrochemistry (hardeners/diffusion barriers)
- Non-Technical issues…

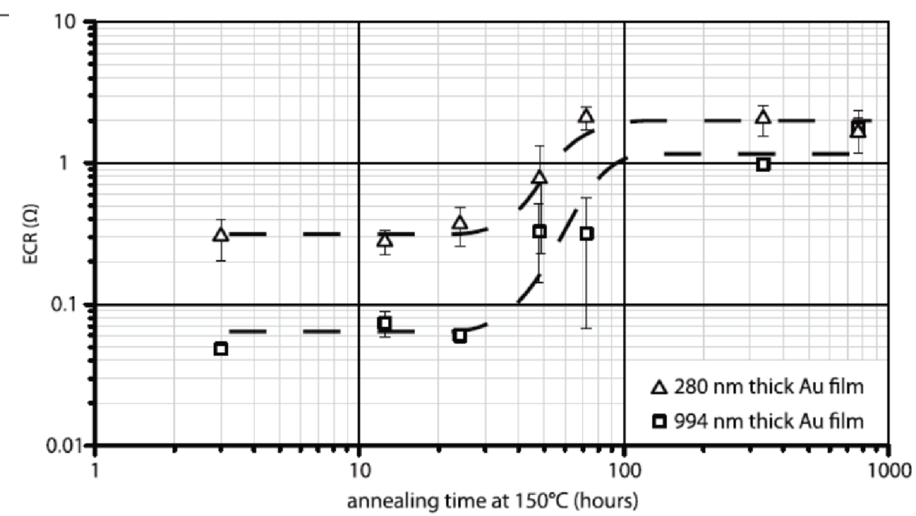
Surface Oxide Film

ECR degradation



Sputtered Au 280nm Film on Silicon w/Ti adhesion layer Ni Barrier layer

ECR degradation with time (diffusion through grain boundaries)



STEM EDS after 150°C and 32 days
NiO surface layer 1.5 – 4.5 nm thick

From Argibay, Brumbach, Dugger, Kotula JAP 2013

Novel Materials and Synthesis

Routes to Mitigate Diffusion

Novel routes: shut down solid diffusion of codeposited and underlayer materials via:

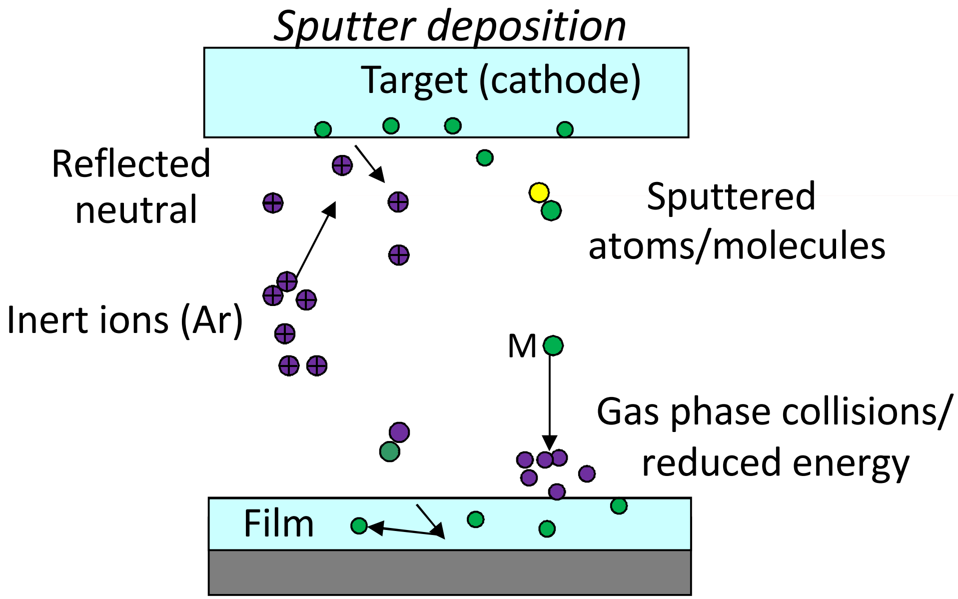
1. ceramics to harden Au in place of non-noble metals
2. introduce electron-tunneling-thin ceramic diffusion barrier layers (discussion of its effect on ECR)

These layers applied via Physical Vapor Deposition (PVD)

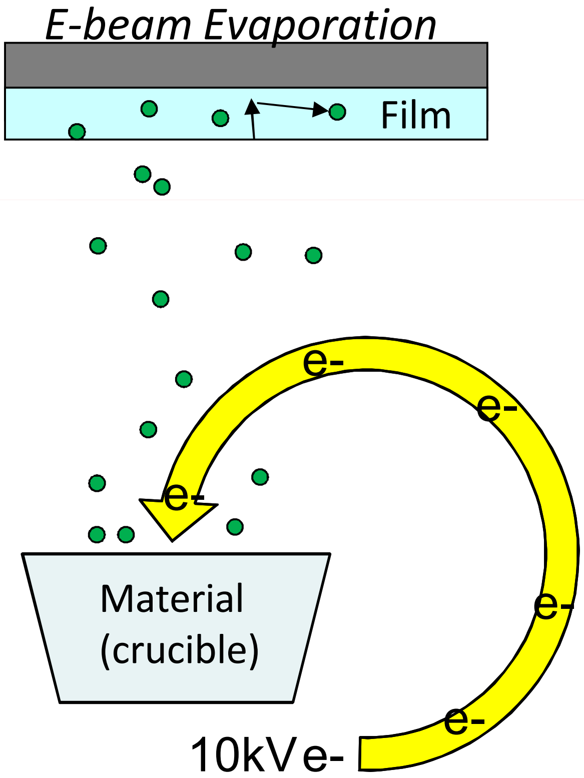
- *Au-ZnO codeposition by E-beam evaporation*
- *Ion implantation of noble gasses into the PVD Au*
- *Novel ceramic diffusion barrier layers (not possible by electrochemical techniques)*

Physical Vapor Deposition (PVD)

Sputtering vs E-beam Evaporation



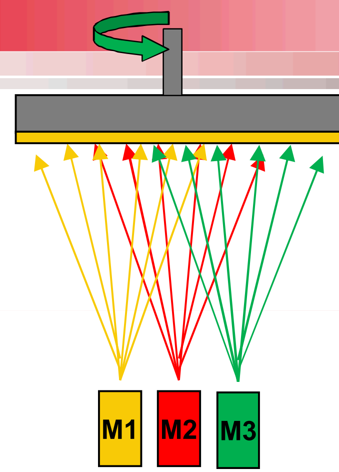
- Target material removed by kinetic energy of inert ions
- Requires plasma ignition for ionization of sputter gas (Ar)
- Minimum energy for ignition limits deposition rate ratio ~ 50:1 (2%)
- Good control over film properties (pressure, power, biasing, temperature)



- Target material vaporized by thermal energy from electron beam
- Terrific rate control with feedback from QCM
- Can deposit at extremely slow rates (ppm level composition control)

Co-Deposition (PVD)

Thin Film Capabilities

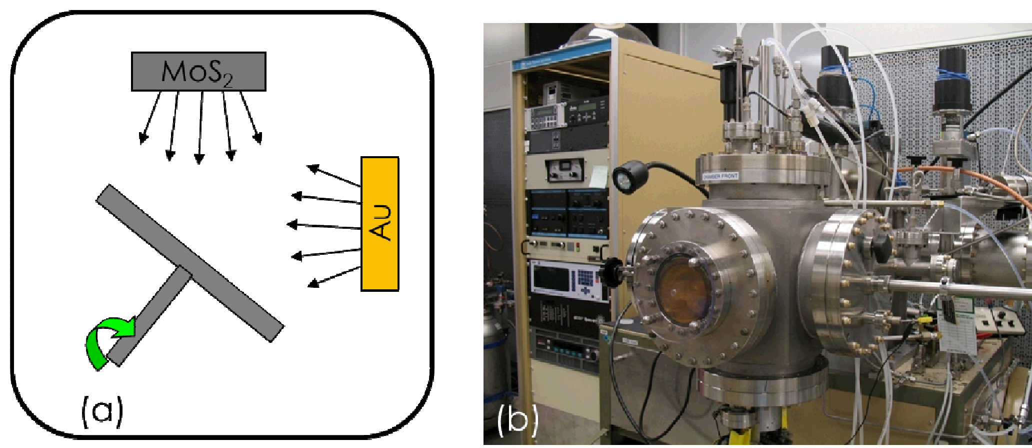


Evaporation:

- Triad e-beam evaporation of ternary alloy thin films
- Shutter in front of substrate for consistent composition, graded or layered films
- Independent QCM control of material deposition rate
- Compositional control to < 0.1%

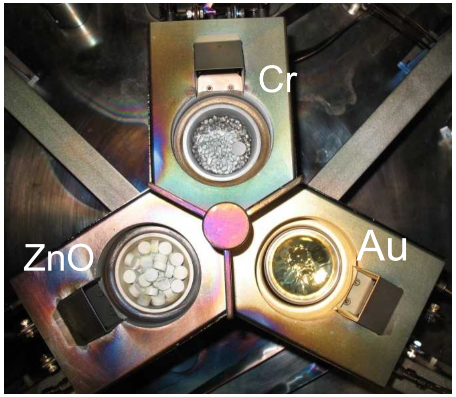
Sputtering:

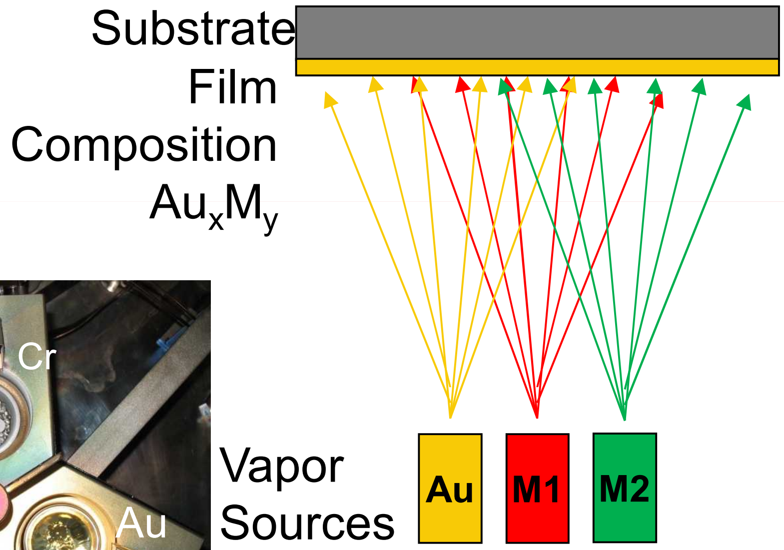
- Co-deposition of elements, alloys and compounds
- Composition control to ~1%



Triad E-Beam Deposition

E-beam approach chosen for compositional control

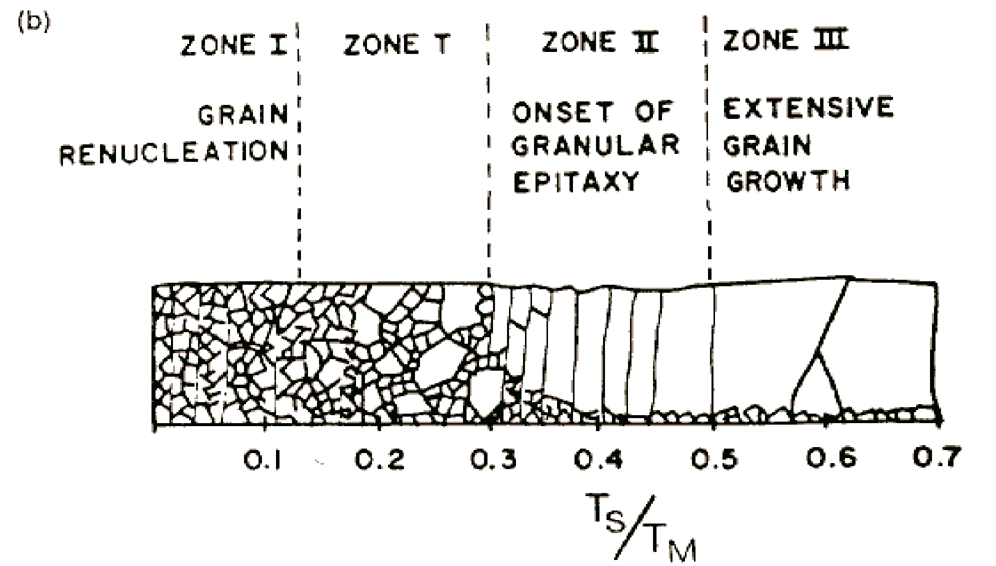




- Triad electron gun for E-beam evaporation
- Co-deposition of ternary alloy thin films
- Shutter in front of substrate for consistent composition
- Substrate rotation for improved uniformity
- Line of sight shields on QCMs eliminate cross-talk

Film Morphology ZT

Transitional Zone



<u>Nucleation and subsequent recombination lead to the final film microstructure.</u>
Morphology is influenced by: Substrate temperature, deposition rate, bulk and surface diffusion

Zone I : All grain boundaries are immobile

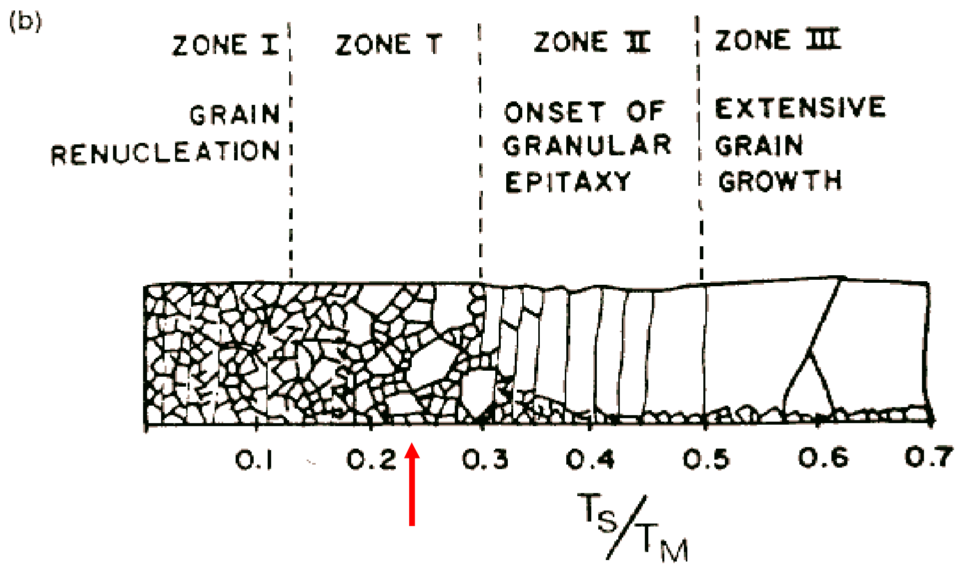
Zone T: small diameter columns with poor crystallinity. High dislocation density

Zone II: Surface diffusion is becoming dominant. Grain boundaries are mobile. Growth of columns with tight grain boundaries. Voids are filled by surface diffusion. Fewer defects.

Hentzell, JVST-A 1984

Zone Model for Evaporated Films

Substrate Temperature



Fraction of T_m	Au Temp (ºC)	Au Temp (K)	ZnO Temp (ºC)	ZnO Temp (K)
T_m	1064	1337	2248	2521
0.5 T_m	396	669	988	1261
0.4 T_m	262	535	735	1008
0.3 T_m	128	401	483	756
0.22 T_m	25	298	281	554

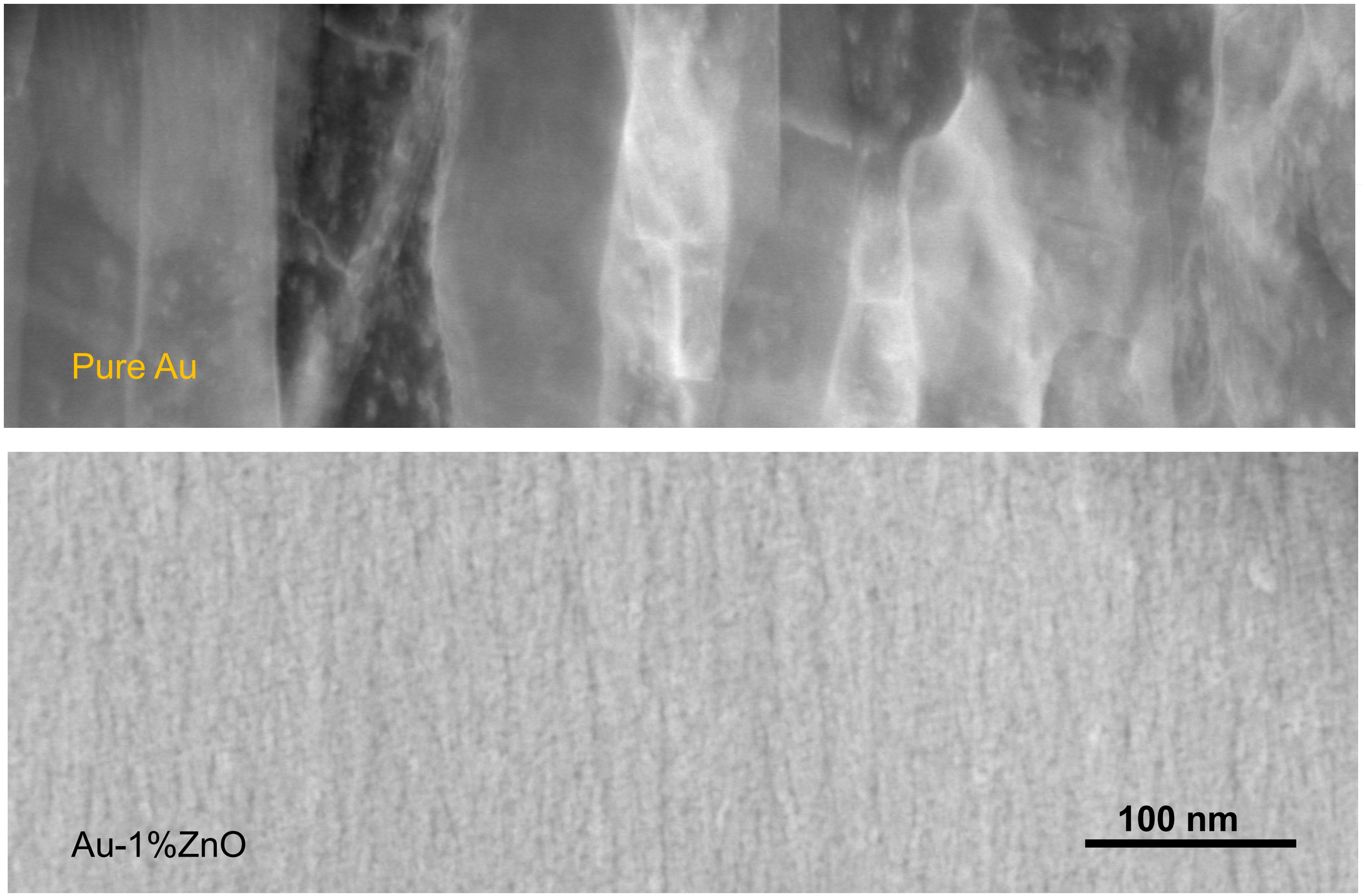
Hentzell, JVST-A 1984

Thin Film Characterization

- Electron backscatter detection (EBSD) in SEM
- X-Ray Florescence XRF & Electron Microprobe
- Aberration corrected scanning transmission electron microscopy (AC-STEM)
- TEM EDS Spectral imaging
- ECR-Tribology
    - Friction and wear analysis
- Nano-indentation
- 4-Point probe
- Differential Scanning Calorimetry DSC

Cross-Sectional TEM

(TEM Specimens prepared by FIB)

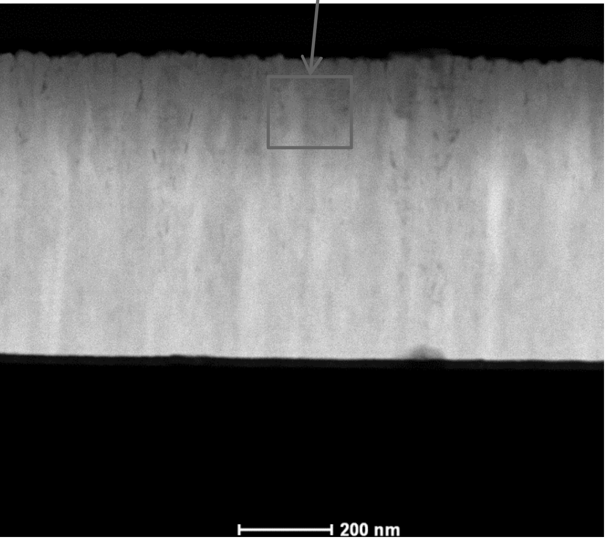


Columnar grain structure is clearly observed with a significant reduction in grain size in the columnar grain diameter in Au-(1%)ZnO

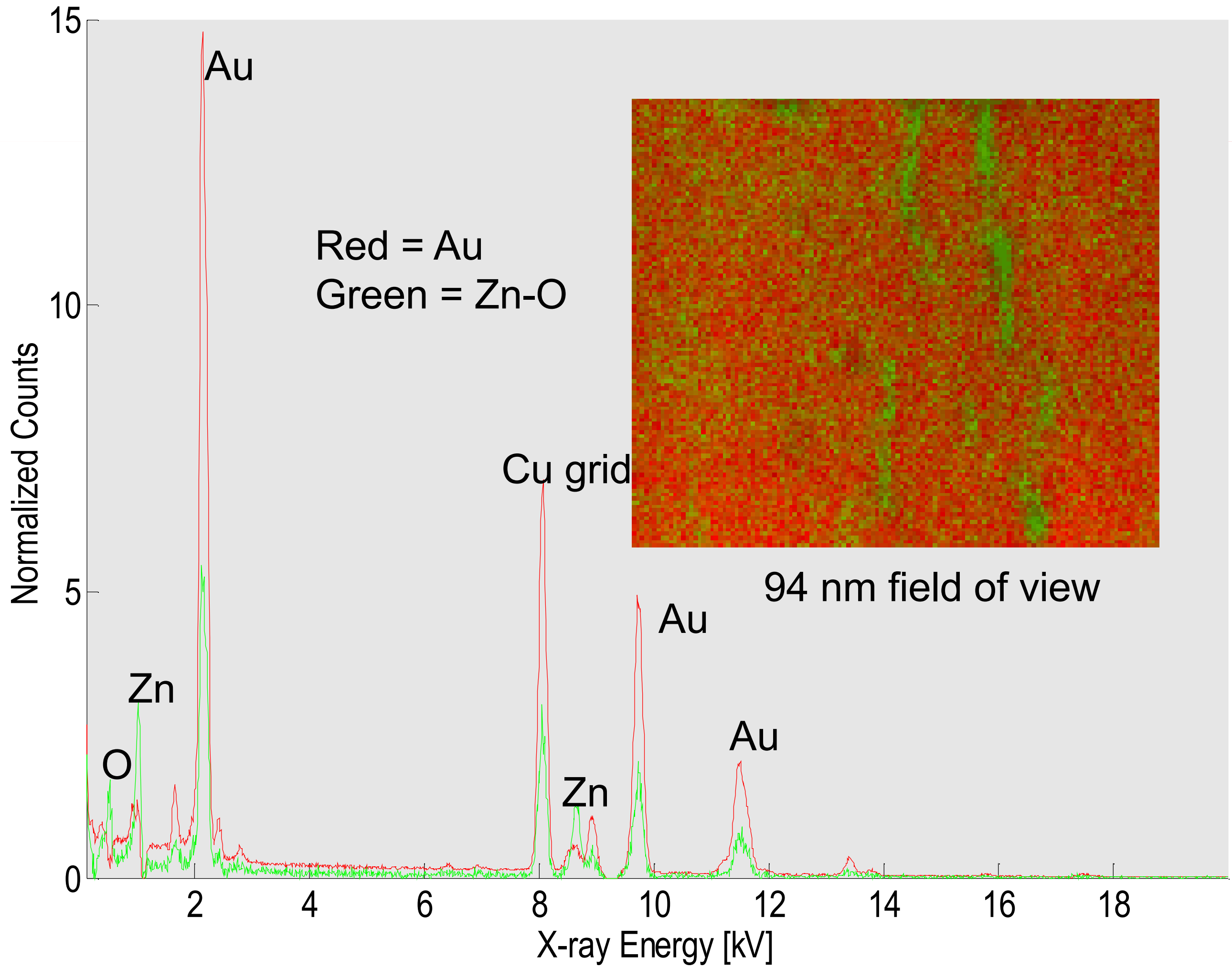
Spectral Analysis

Distribution of ZnO (Green)

Region of spectral analysis

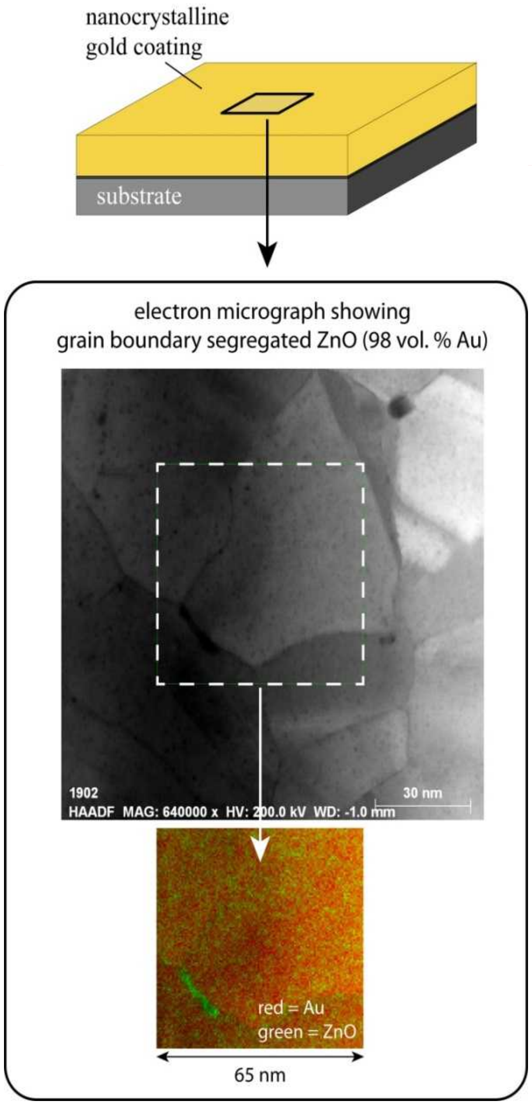


STEM cross-section of Au-(5%)ZnO



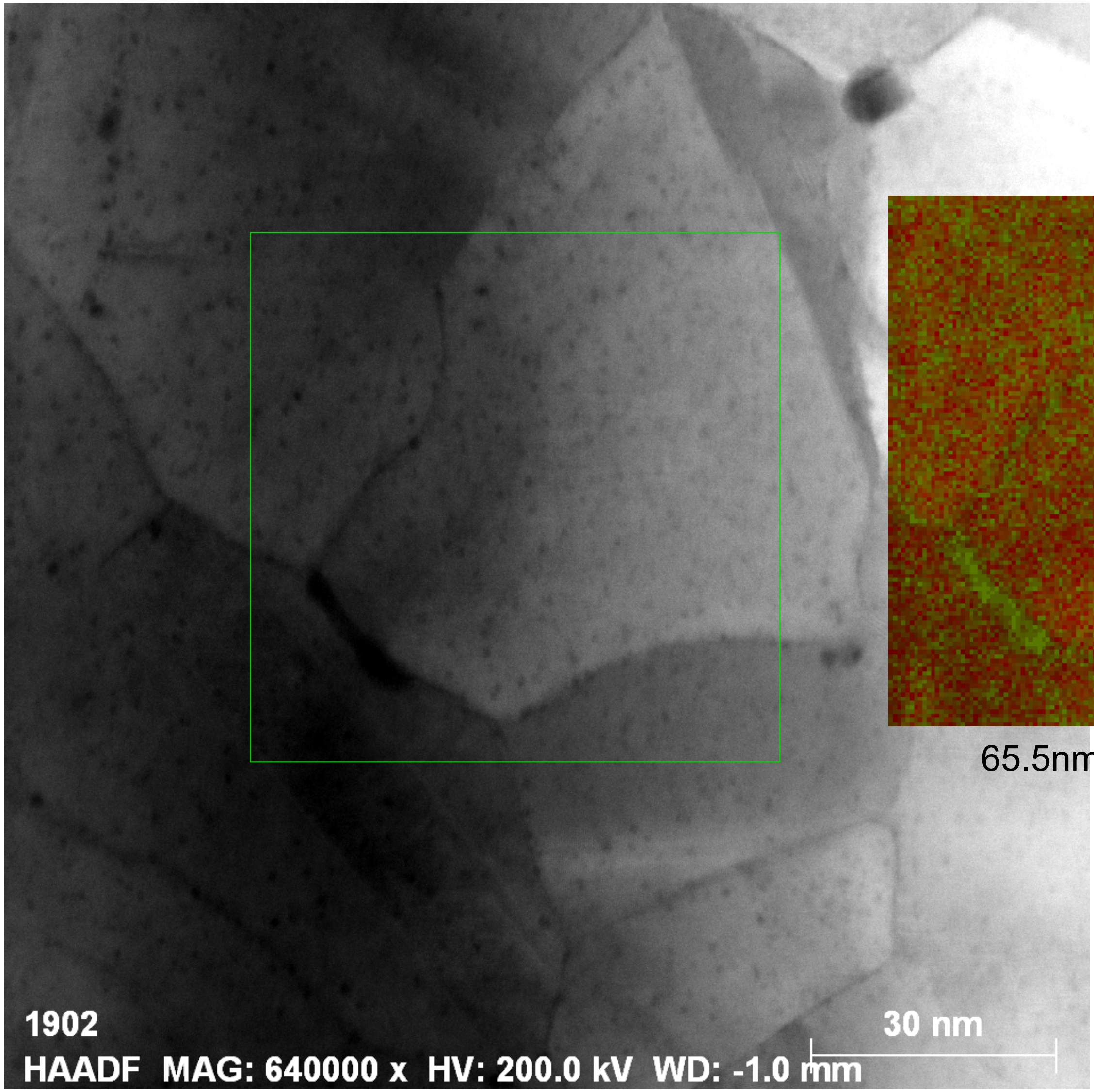
Titan STEM

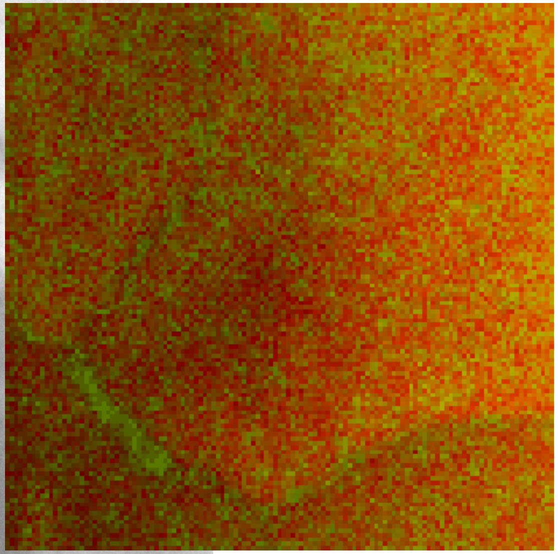
Real time EDS while scanning



AC-TEM

Au + 2% ZnO

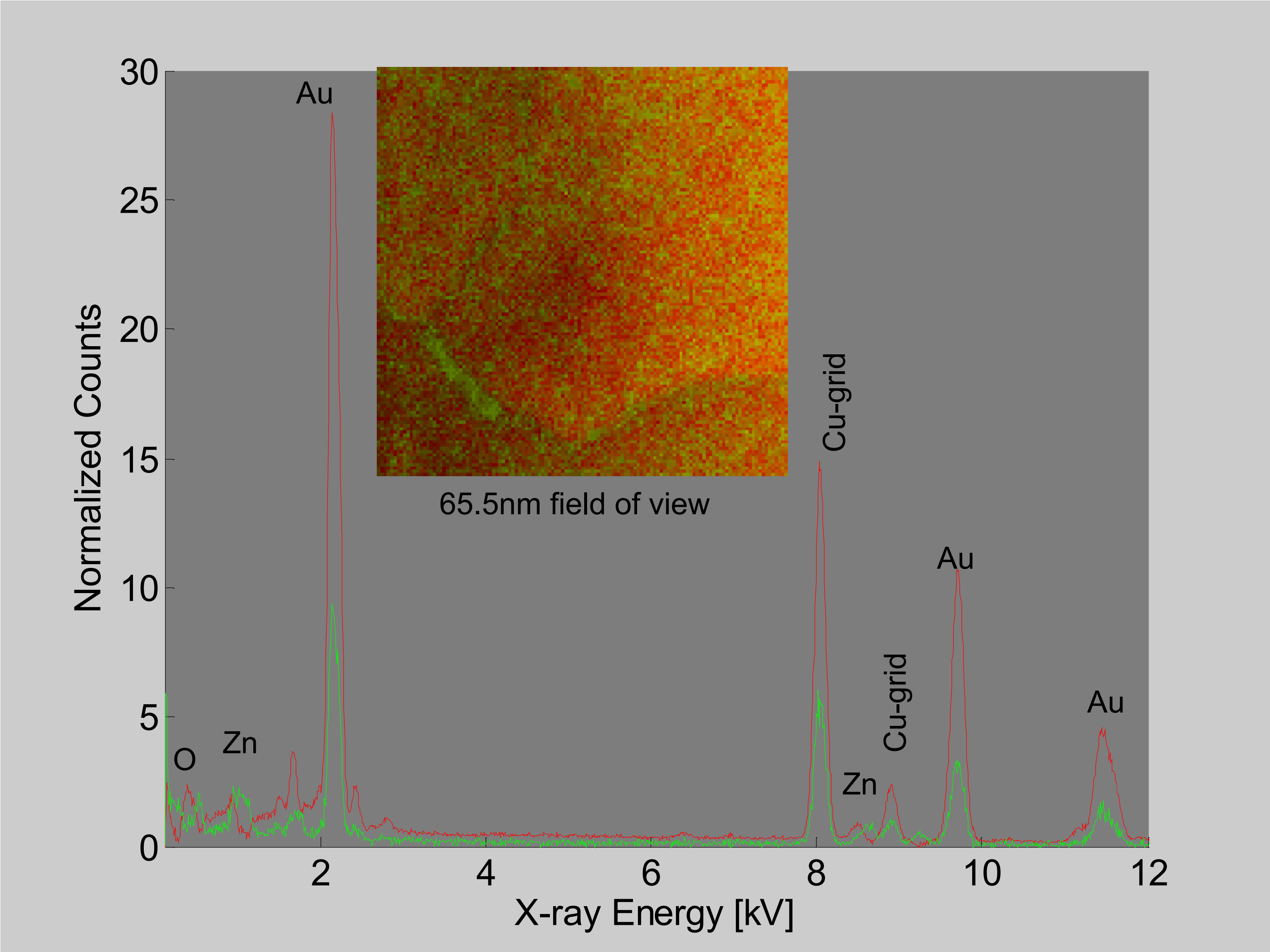




65.5nm field of view

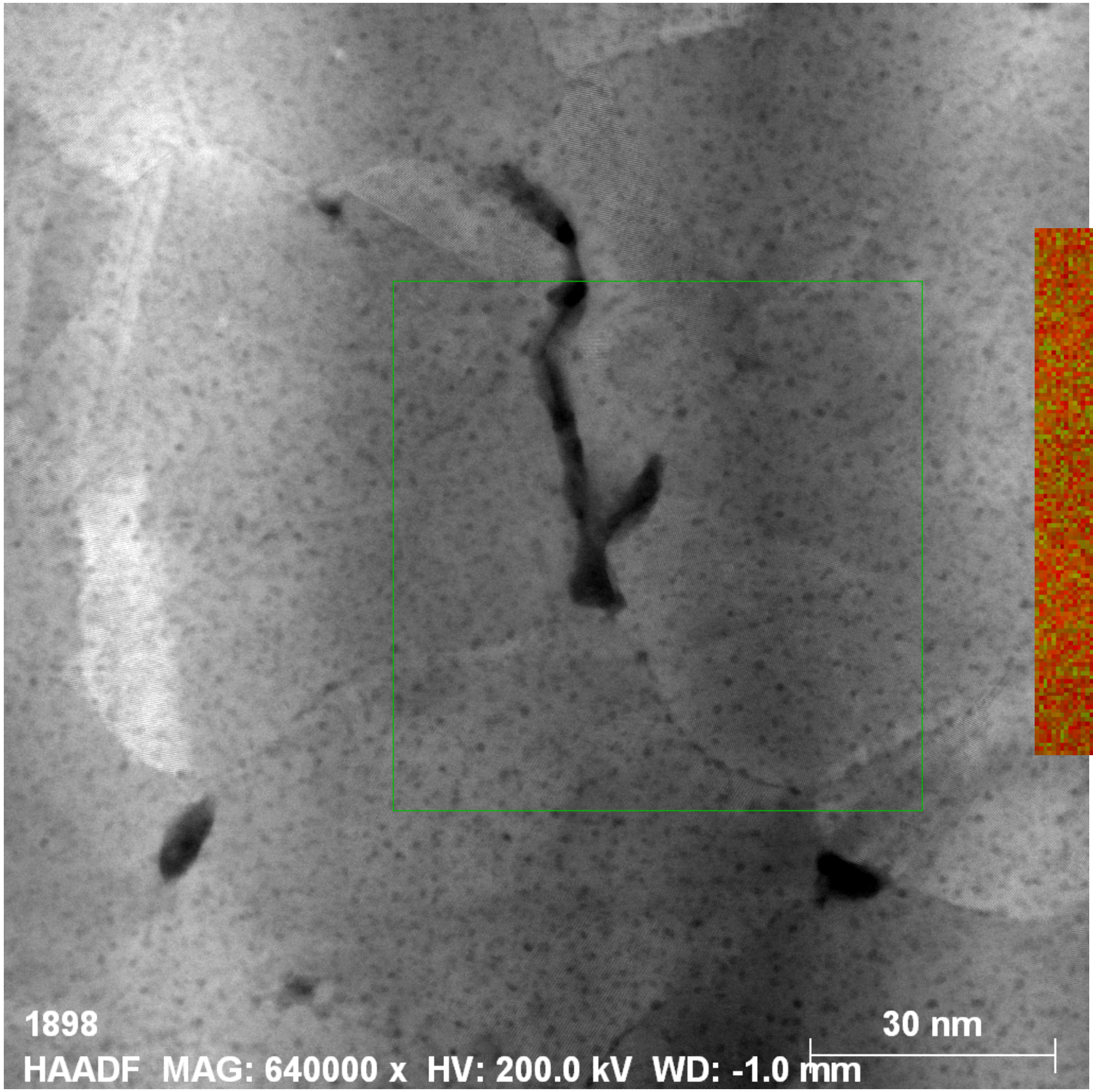
EDS Map

ZnO predominately at grain boundaries

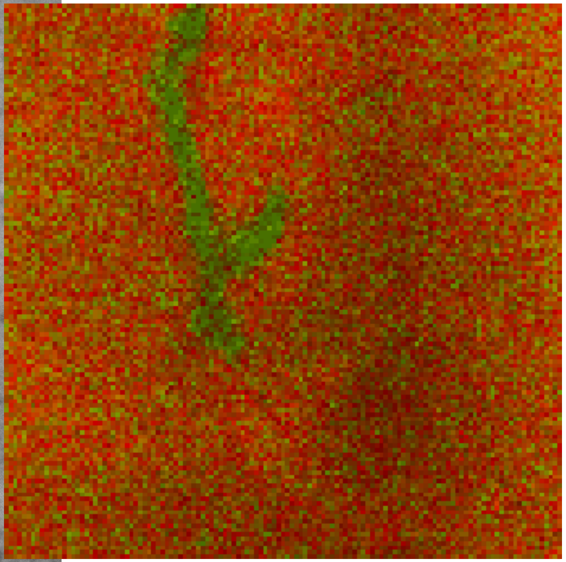


AC-TEM

Au + 10% ZnO



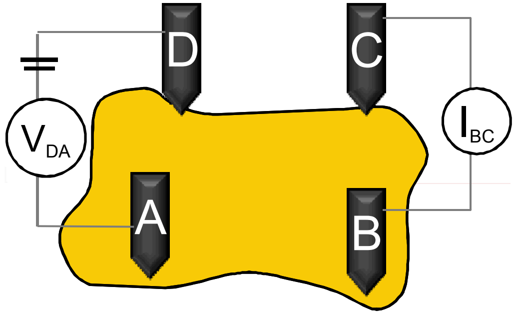
Zn/Au ratio

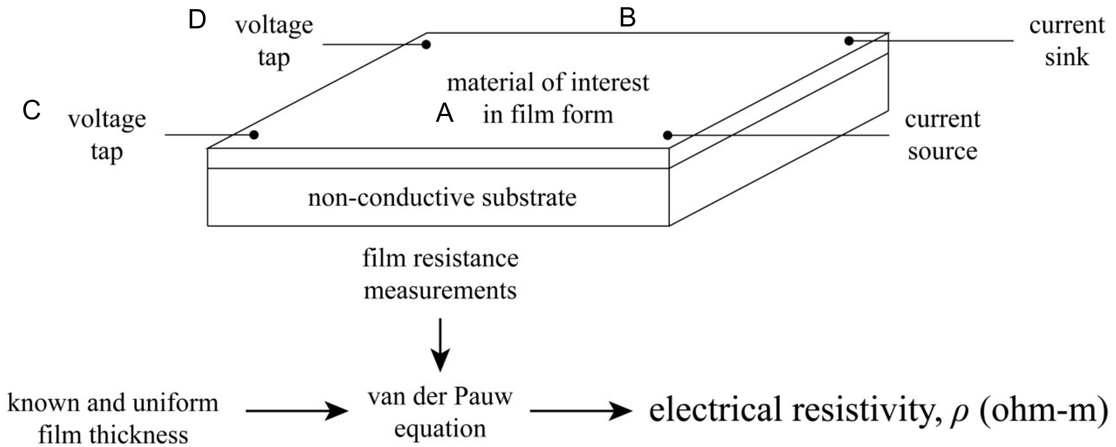


65.5nm field of view

Measurement of Film Resistivity, R_s

Van der Pauw Method





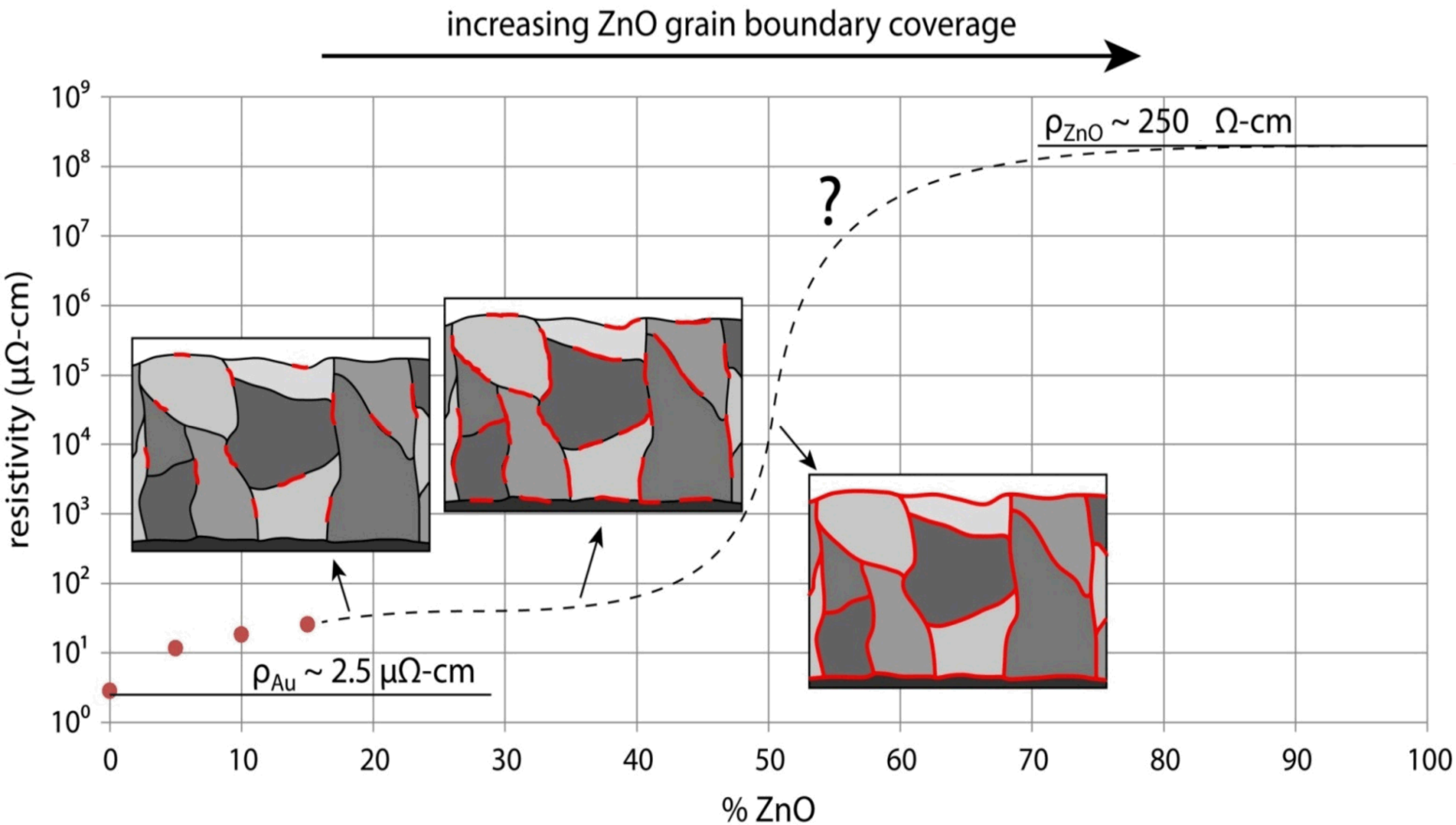
$$exp\left(-\frac{\pi}{R_s}\cdot\frac{V_{CD}}{I_{AB}}\right) + exp\left(-\frac{\pi}{R_s}\cdot\frac{V_{DA}}{I_{BC}}\right) = 1$$

$$\rho = R_s \cdot t$$

Bulk material resistivity is sheet resistance (calculated from measured values) times film thickness. Film thickness confirmed by TEM and QCM

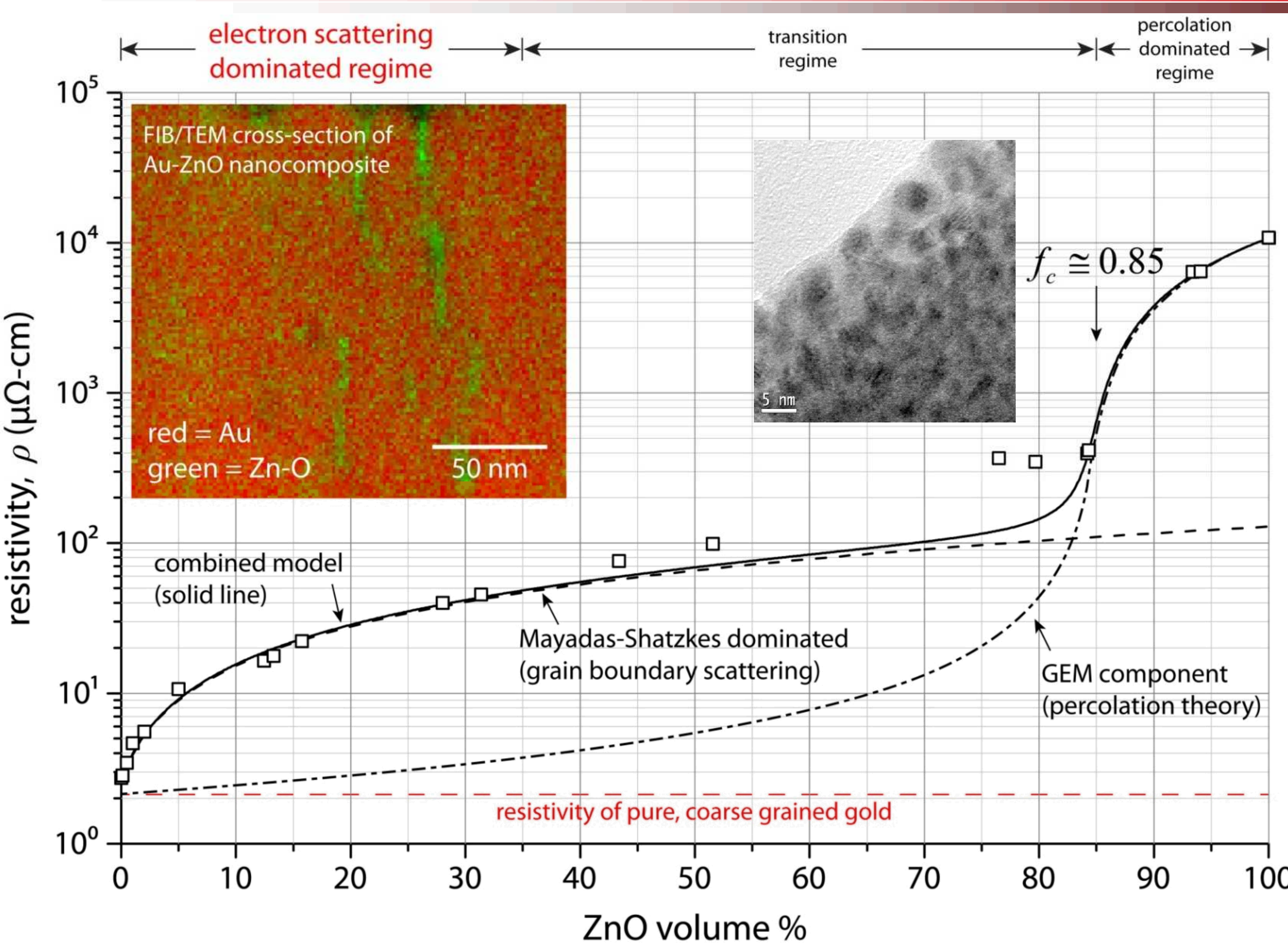
Evolution of Grain Structure

with increasing ZnO content



Electrical Resistivity Modeling

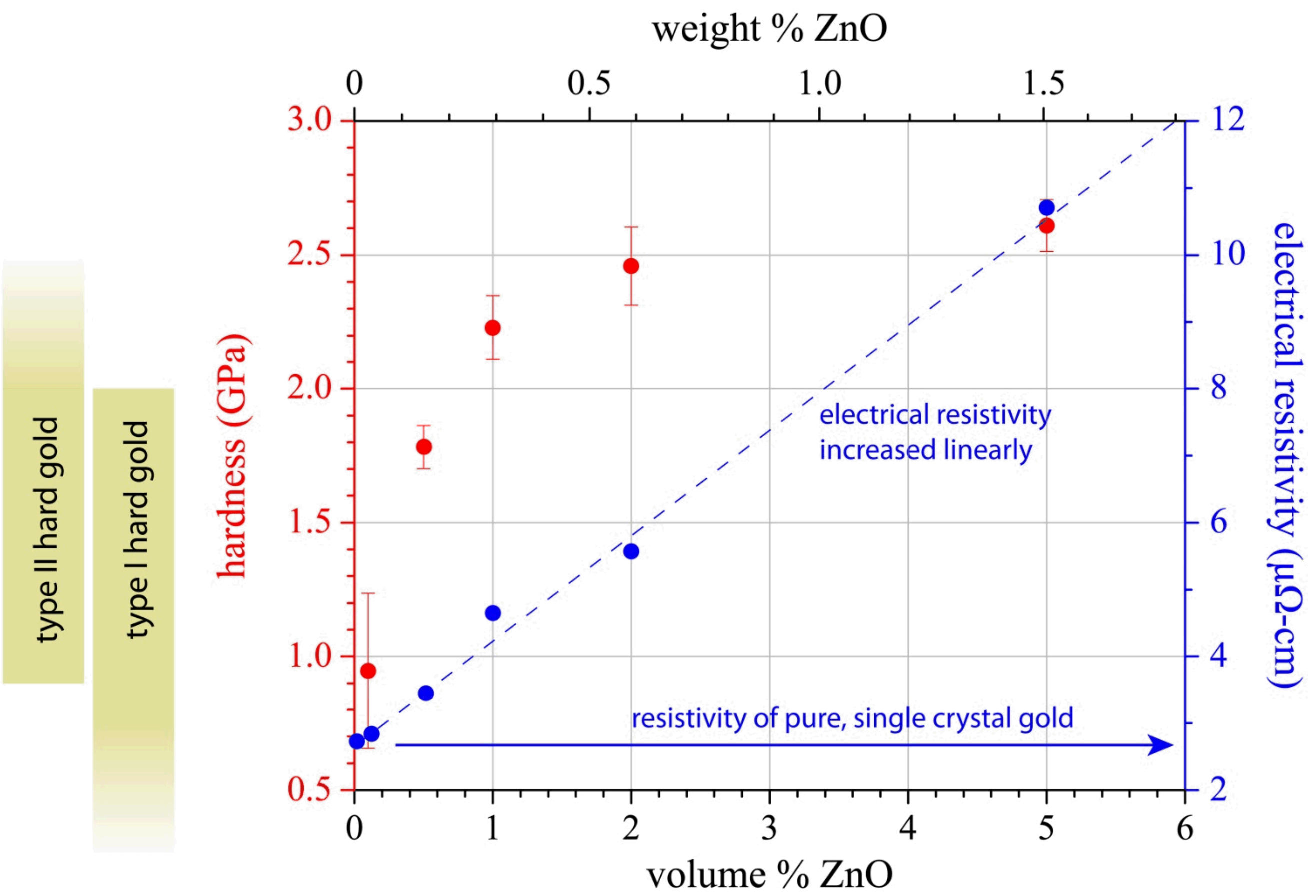
Resistivity explained by grain size



N. Argibay, R.S. Goeke, J. R. Michael, M.T. Dugger, and S.V. Prasad, “Electrical Resistivity of Au-ZnO Nanocomposite Films”, Journal of Applied Physics **113** (2013), 143712.

Hardness and Electrical Resistivity

Comparison to hard gold specification

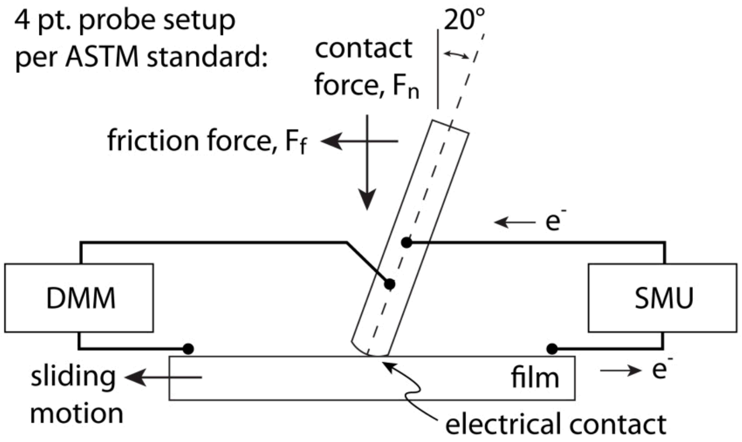


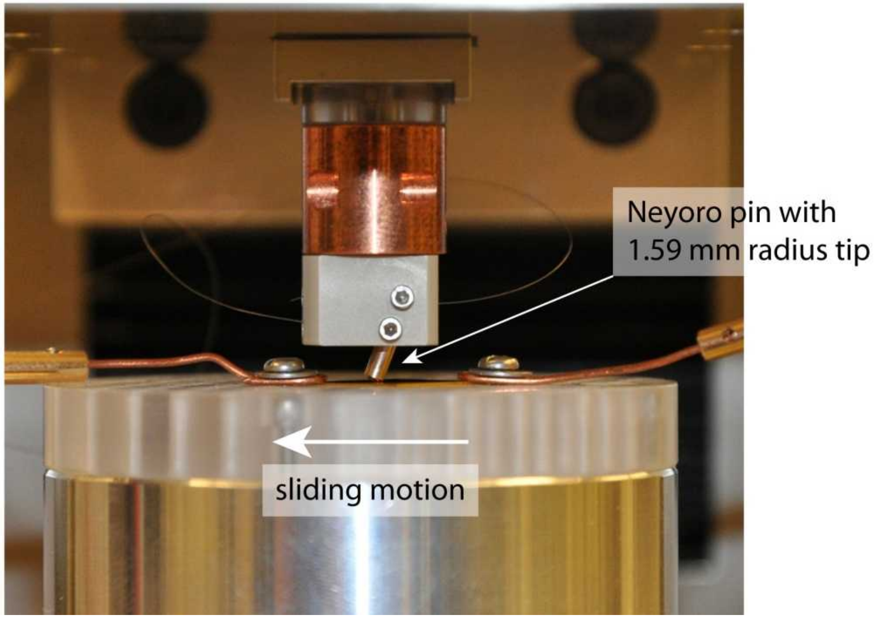
for reference:
0.7 vol % Ni is ~ 0.3 wt % (type I, best ECR performance)
2.2 vol % Ni is ~ 1 wt % (type II, max allowed)

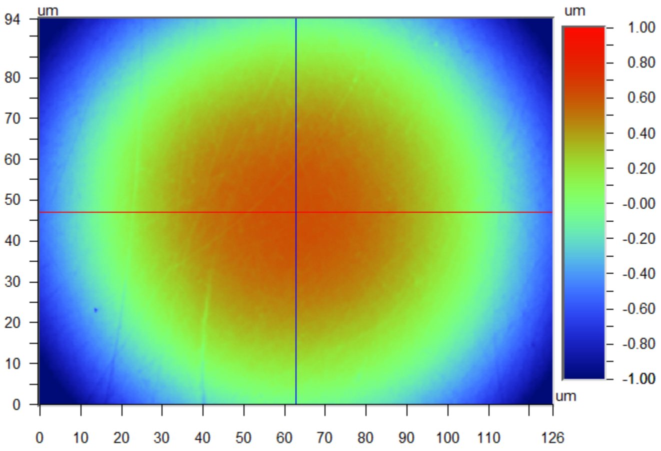
Electrical resistivity measured via van der Pauw method -- square Si wafers pieces coated with composite, no adhesion layers

Four-Point Probe ECR Setup

Measured with hemi-spherically tipped Au-Cu alloy rider



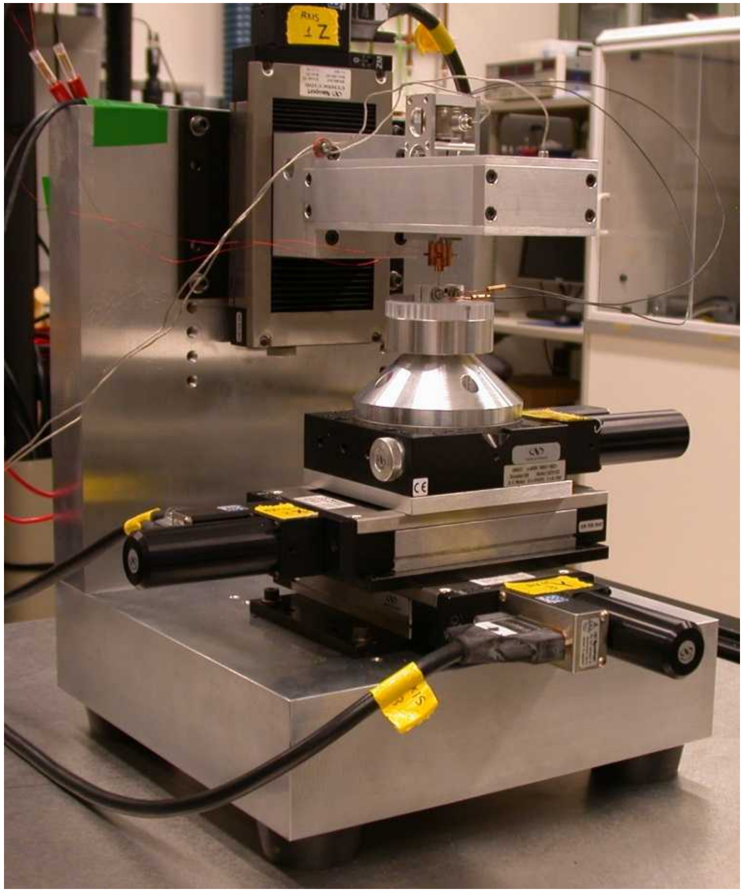




Hemi-Spherically tipped rider

ECR-Friction Tribometer

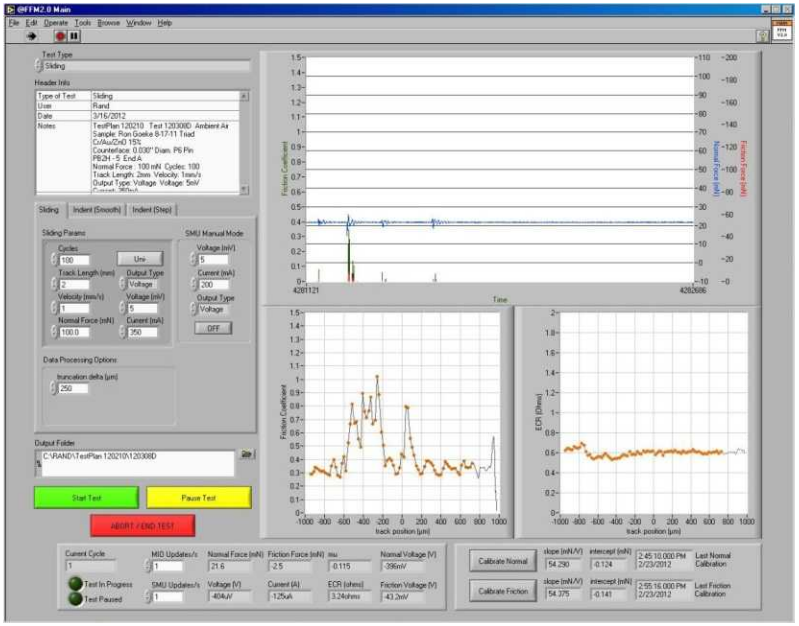
Simultaneous friction force and contact resistance



Up to 2000 mA
1 mN to 1.5 N

Test Conditions

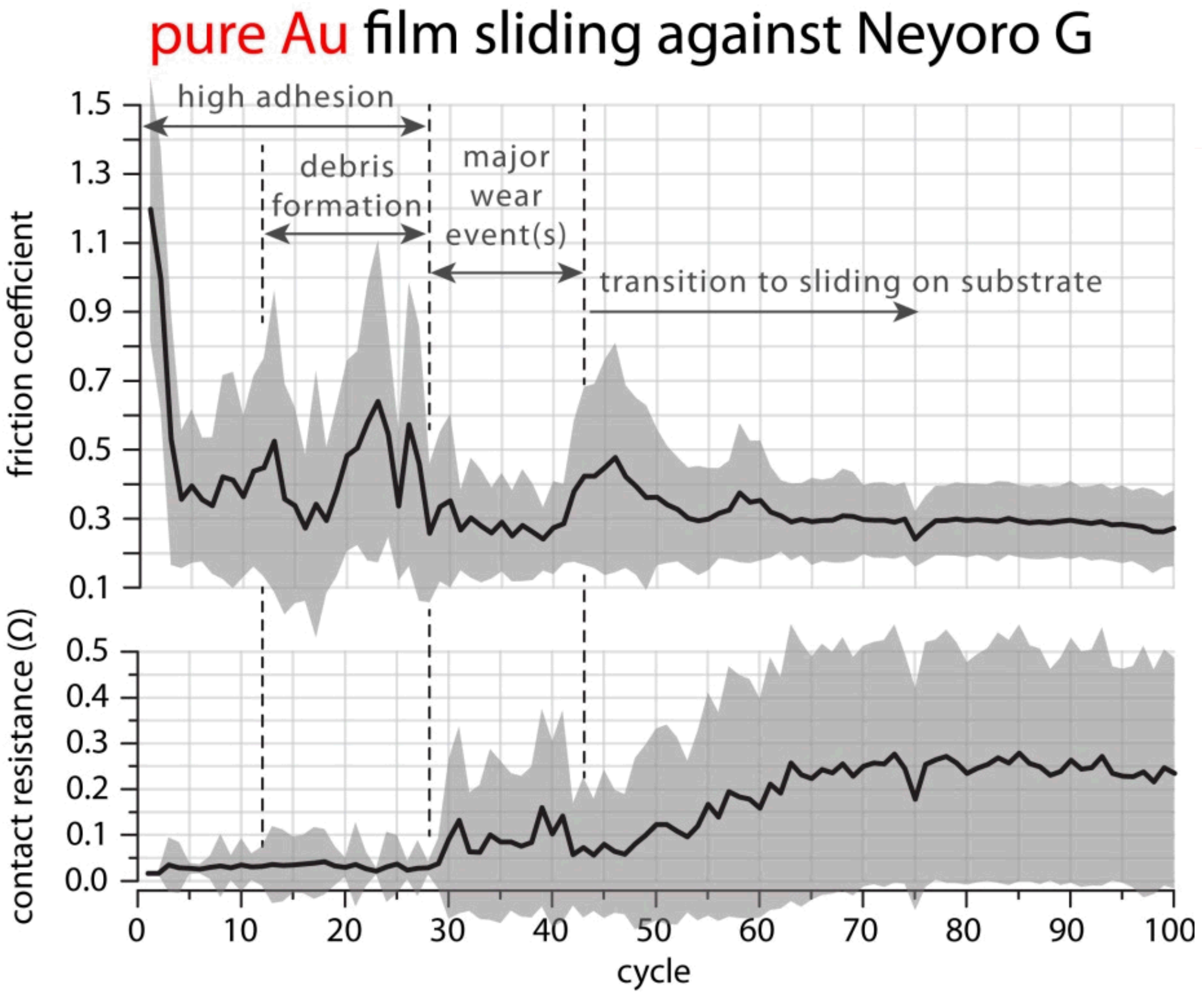
- Neyoro G (Au-Cu), $\frac{1}{16}$ in. radius hemispherical tip rider
- F_n = 100 mN (≈290 MPa contact stress)
- 100 Cycles @ v = 1 mm/s
- 1 – 2 mV bias to achieve approximately 100 mA
- Lab air environment at room temperature



Data Acquisition

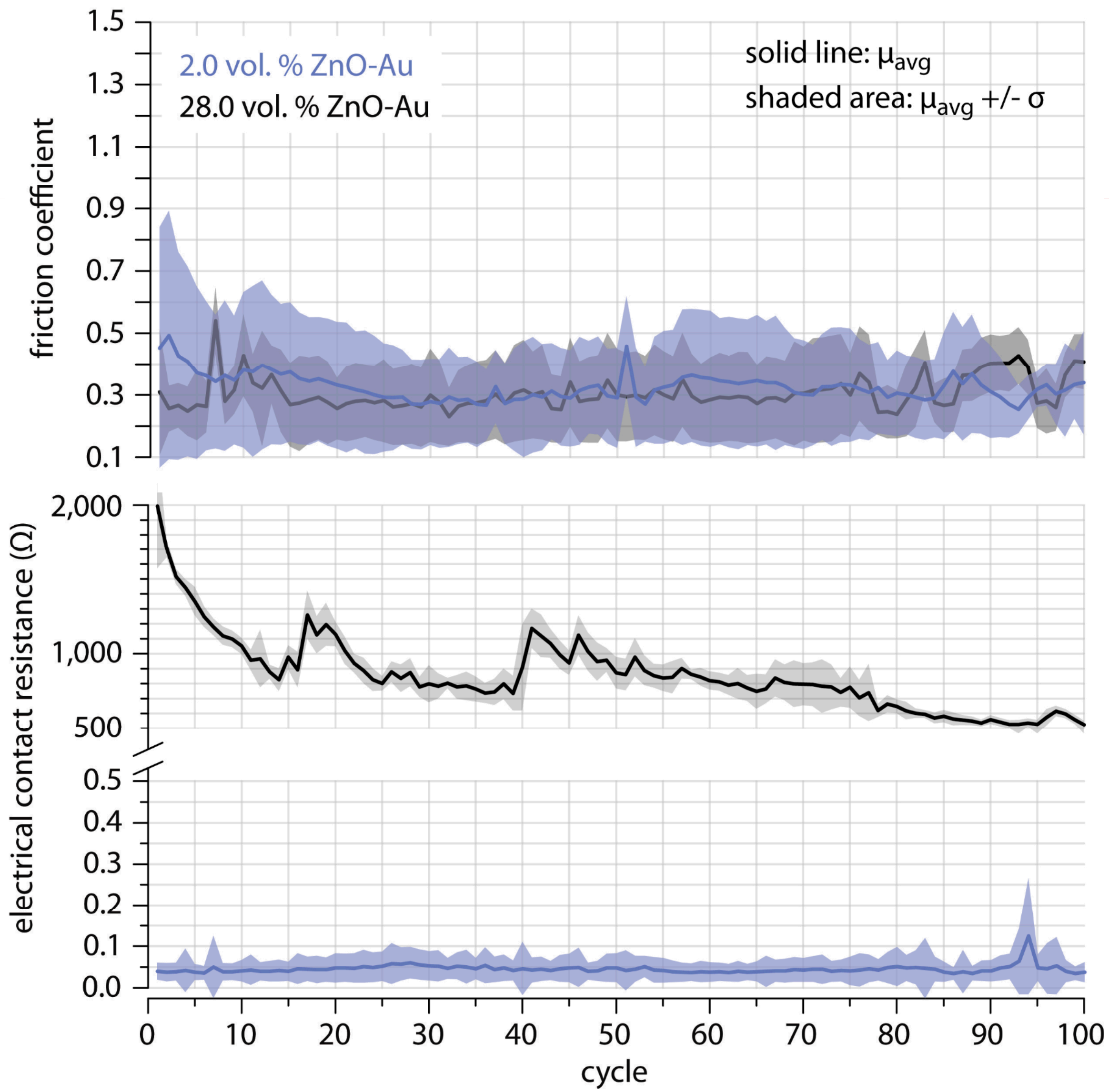
ECR-Friction Behavior

Pure Au



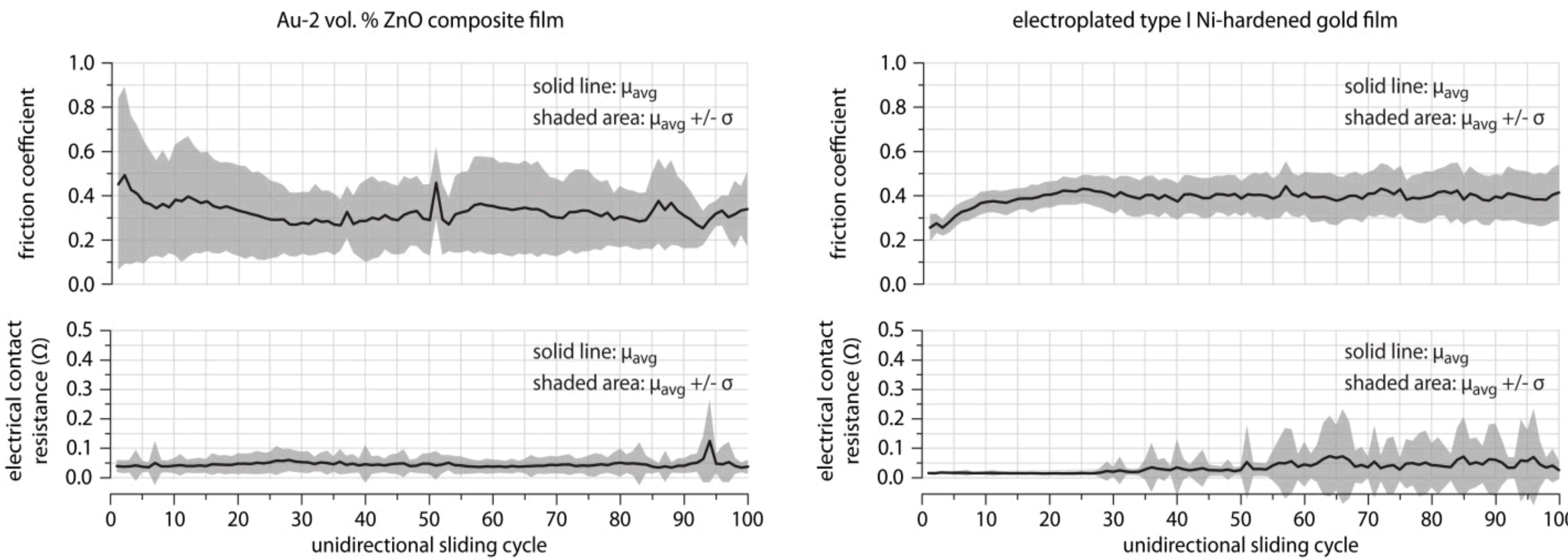
ECR-Friction Behavior

Au-ZnO



ECR-Friction Behavior

Comparison to electroplated hard gold

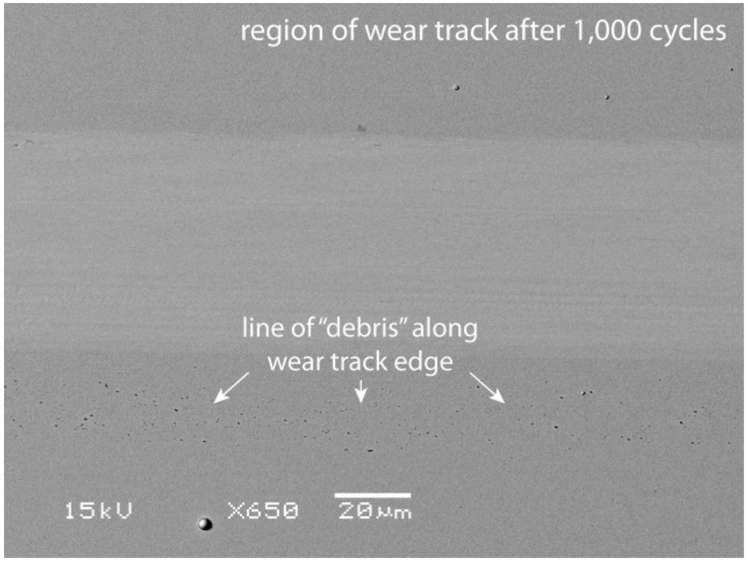


common parameters:

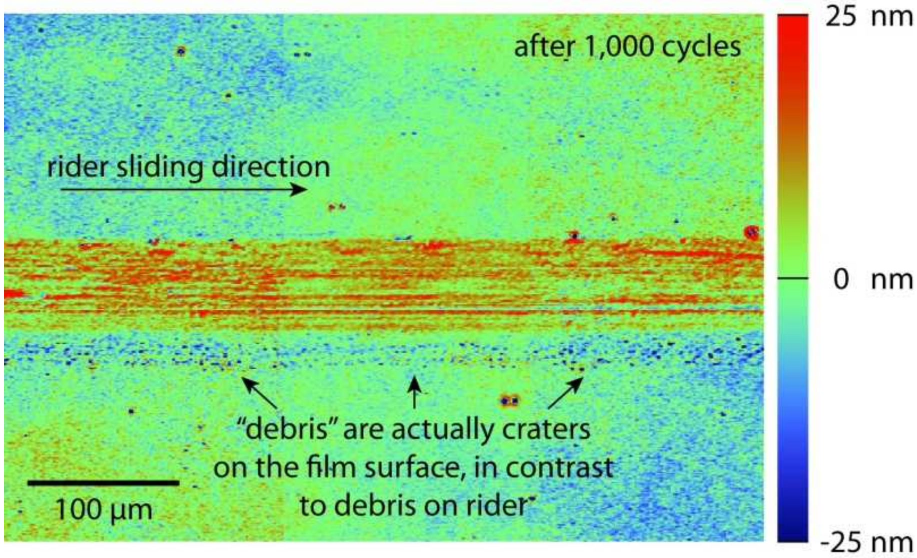
- sliding against a bulk hard gold alloy rider or pin (nominally 72-14-8-5-1 wt. % Au-Cu-Pt-Ag-Zn)
- rider tip radius was 3.175 mm
- contact force was 100 mN
- electrical current was approx.100 mA (voltage driven)
- sliding environment was lab air and room temperature
- substrate material was alloy 52 (nominally 50/50 wt. % Fe/Ni)
- film thicknesses 2 - 5 μm; Ti/Pt bonding layers

Wear Surfaces

Au-2% Nanocomposite ZnO after 1000 cycles of sliding



SEM micrograph of wear scar

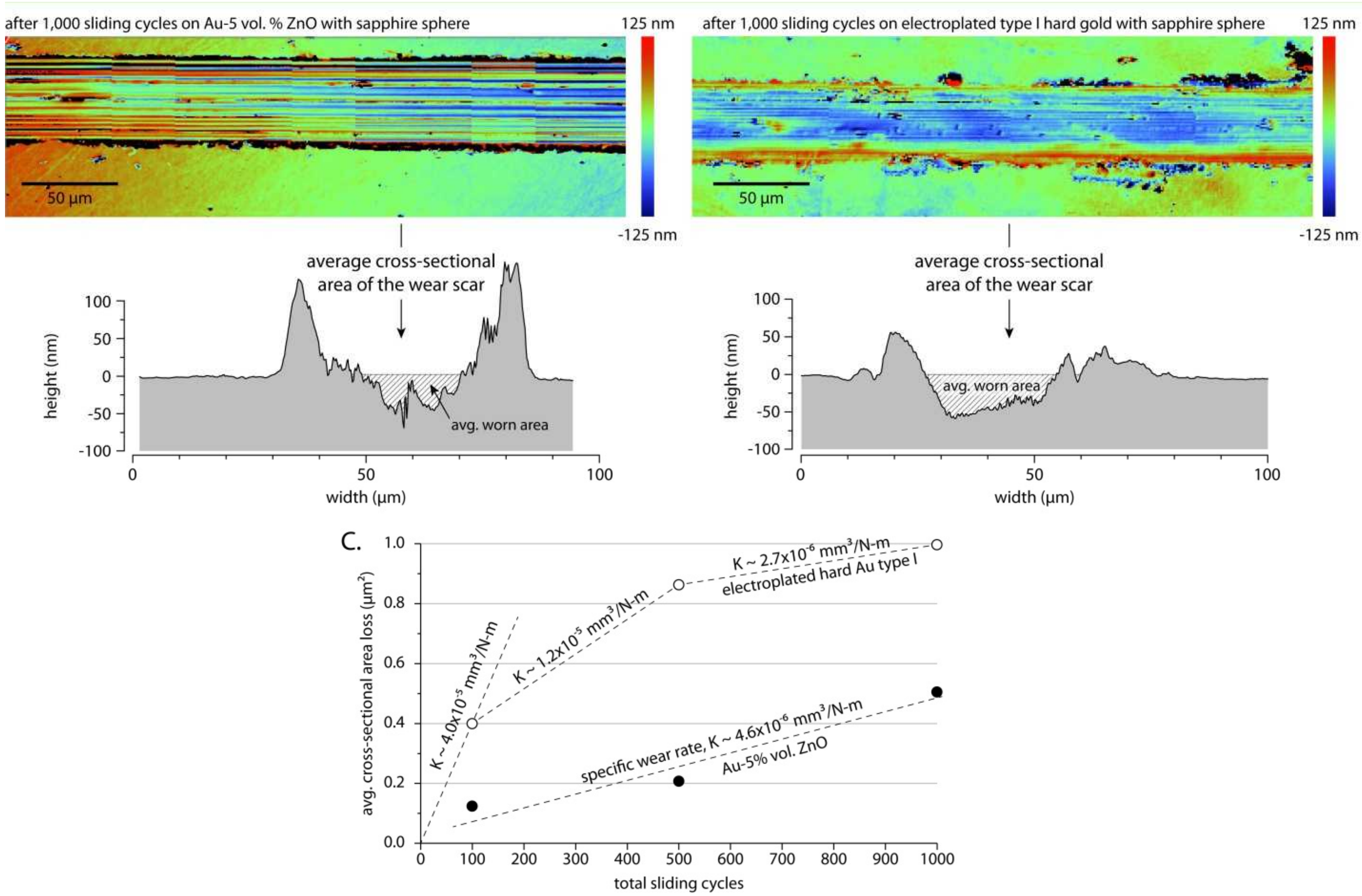


SWLI topography Map

N. Argibay, S. V. Prasad, R. S. Goeke, "Wear Resistant Electrically Conductive Au-ZnO Nanocomposite Coatings Synthesized by E-Beam Evaporation", Wear 302 (2013) 955-962 .

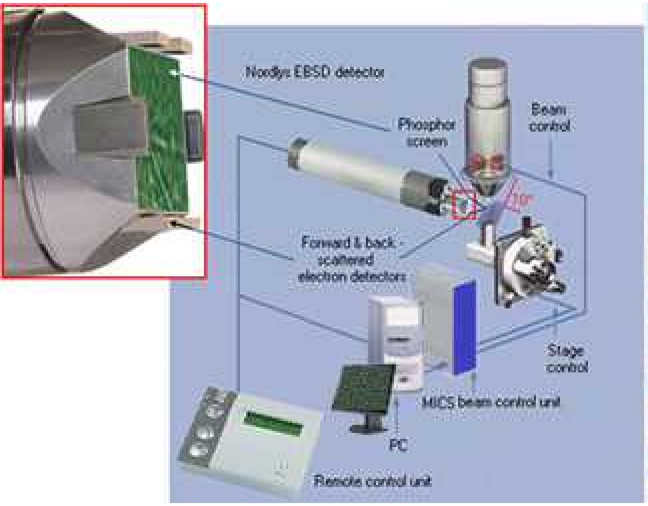
Wear Scar

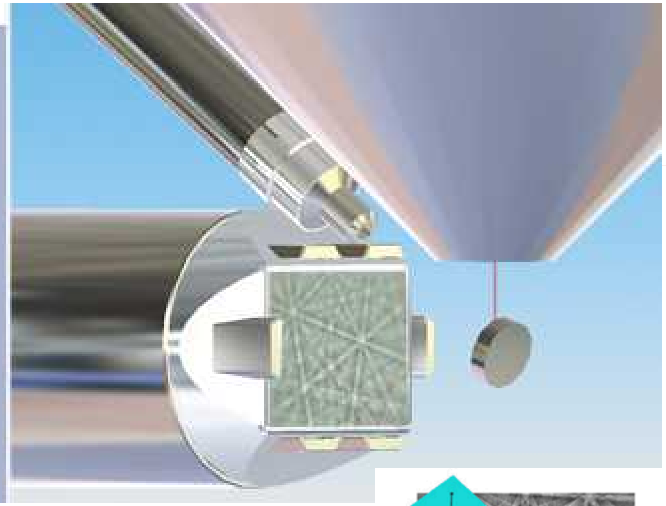
Material loss

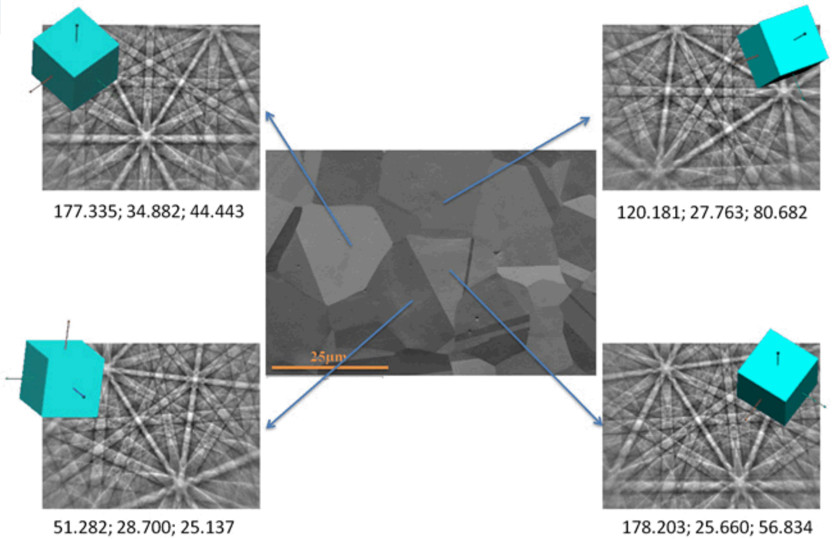


Electron BackScatter Diffraction

EBSD - Kikuchi patterns



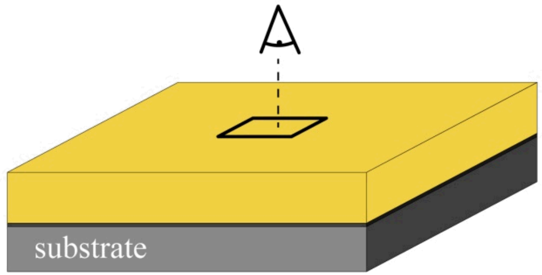




EBSD

Grain size and texture impact

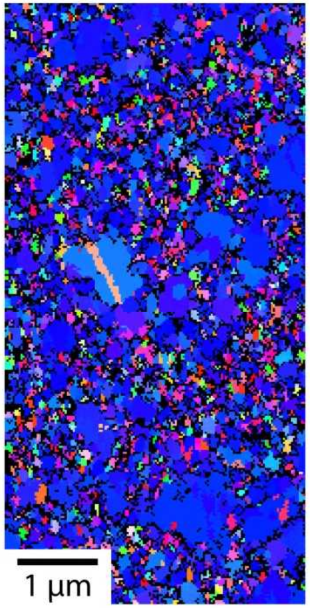
surface normal EBSD maps

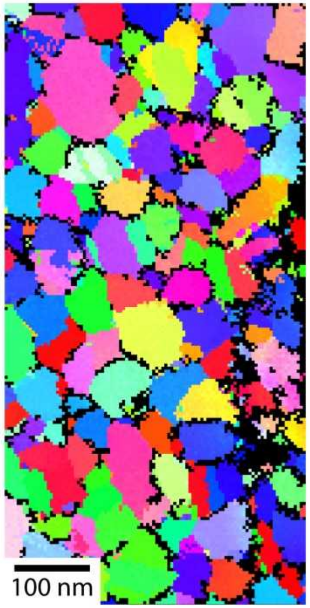


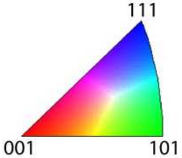
pure Au film:

2.0 vol. % ZnO film

large avg. grain size (> 250 nm)
preferential <111> surface texture
bimodal distribution
hardness ~ 900 MPa





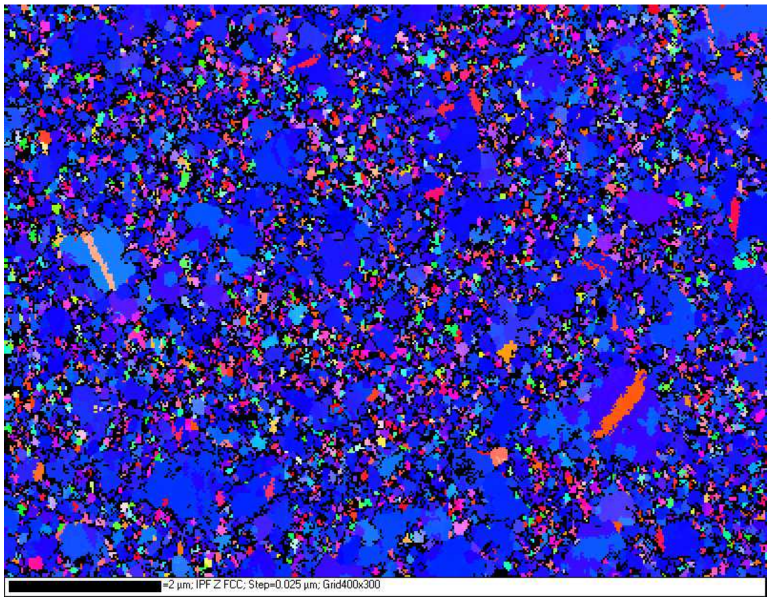


equiaxed & non-textured
avg. grain size ~ 50 nm
hardness ~ 2.5 GPa

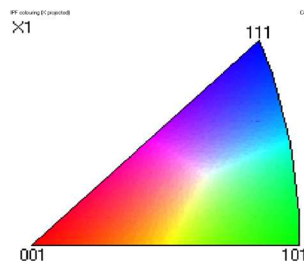
* note the difference in scale bars *

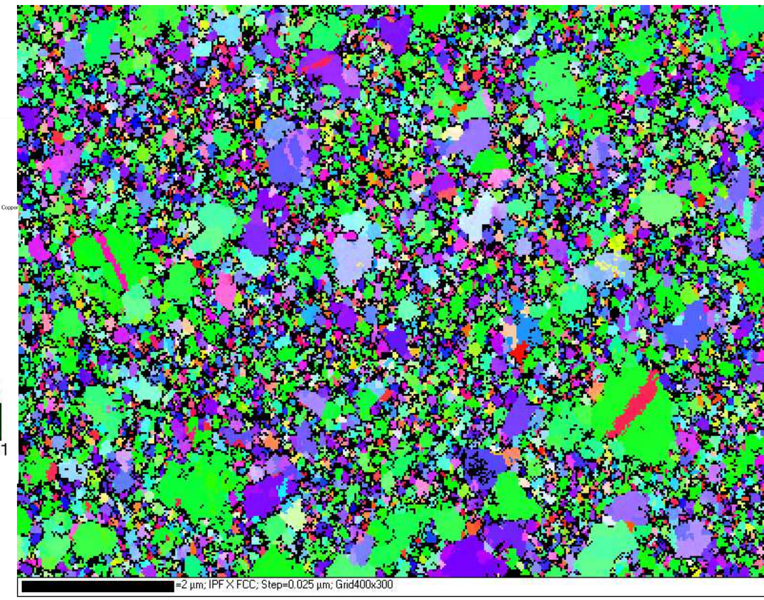
EBSD on pure e-beam deposited Au

showing (111) texture



Surface normal direction

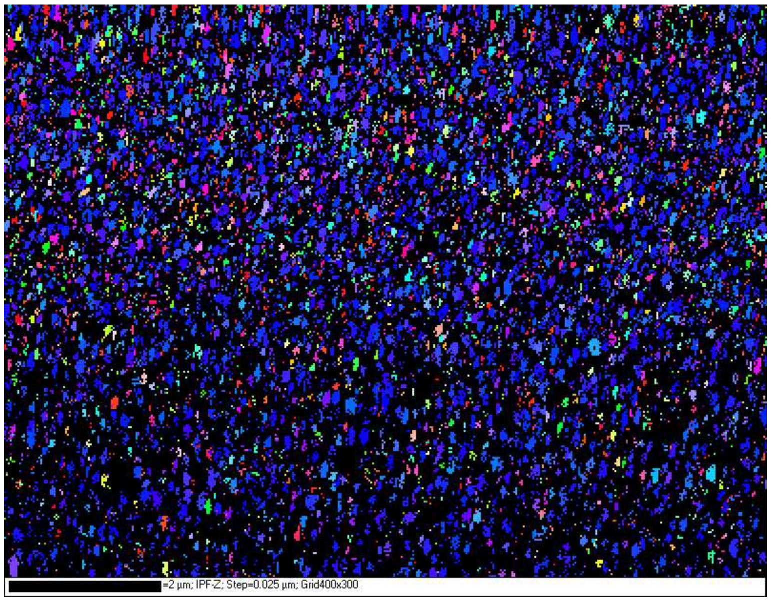




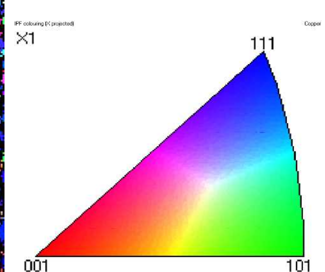
In-plane x direction (horizontal)

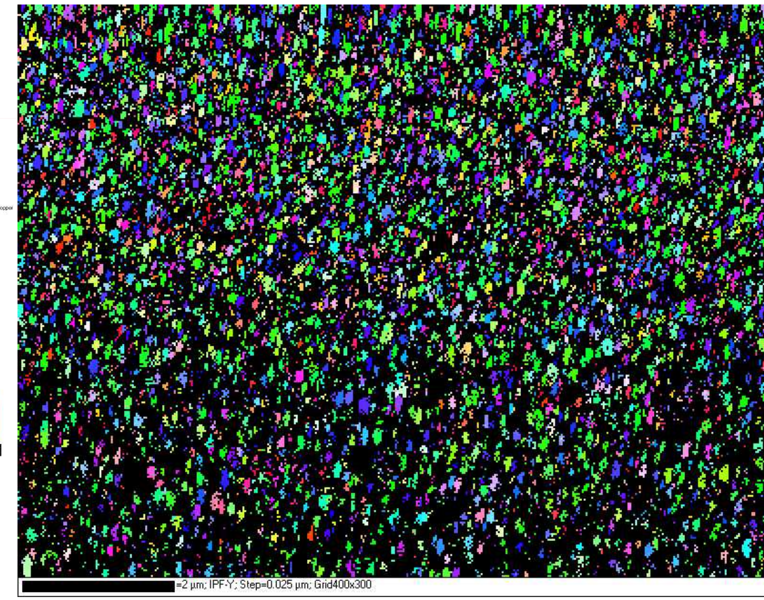
EBSD on e-beam deposited

Au-(1.0 vol.%)ZnO Composite



Surface normal direction





In-plane x direction (horizontal)

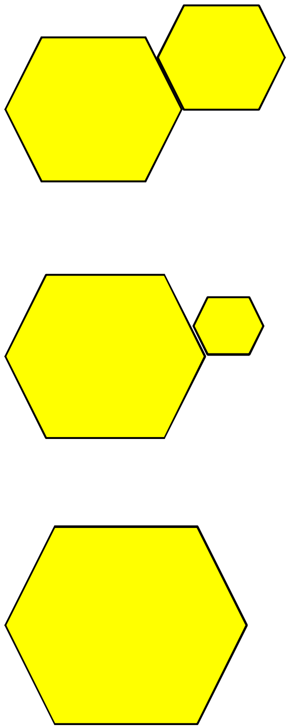
Grain size is significantly reduced but the (111) texture remains

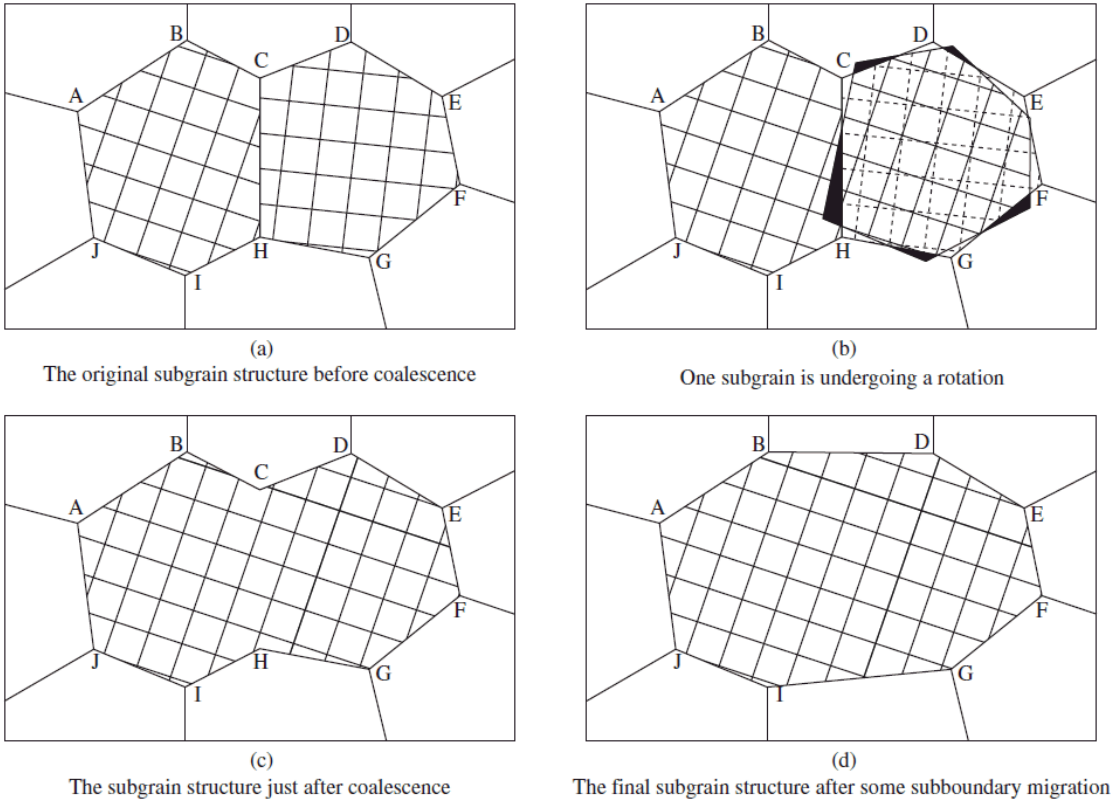
Sintering

Grain Growth Mechanisms

The two common mechanisms for grain growth are:

1. Ostwald Ripening– Diffusion of atoms from smaller grain to larger grain
2. Coalescence – adjacent crystallites join to become one larger grain



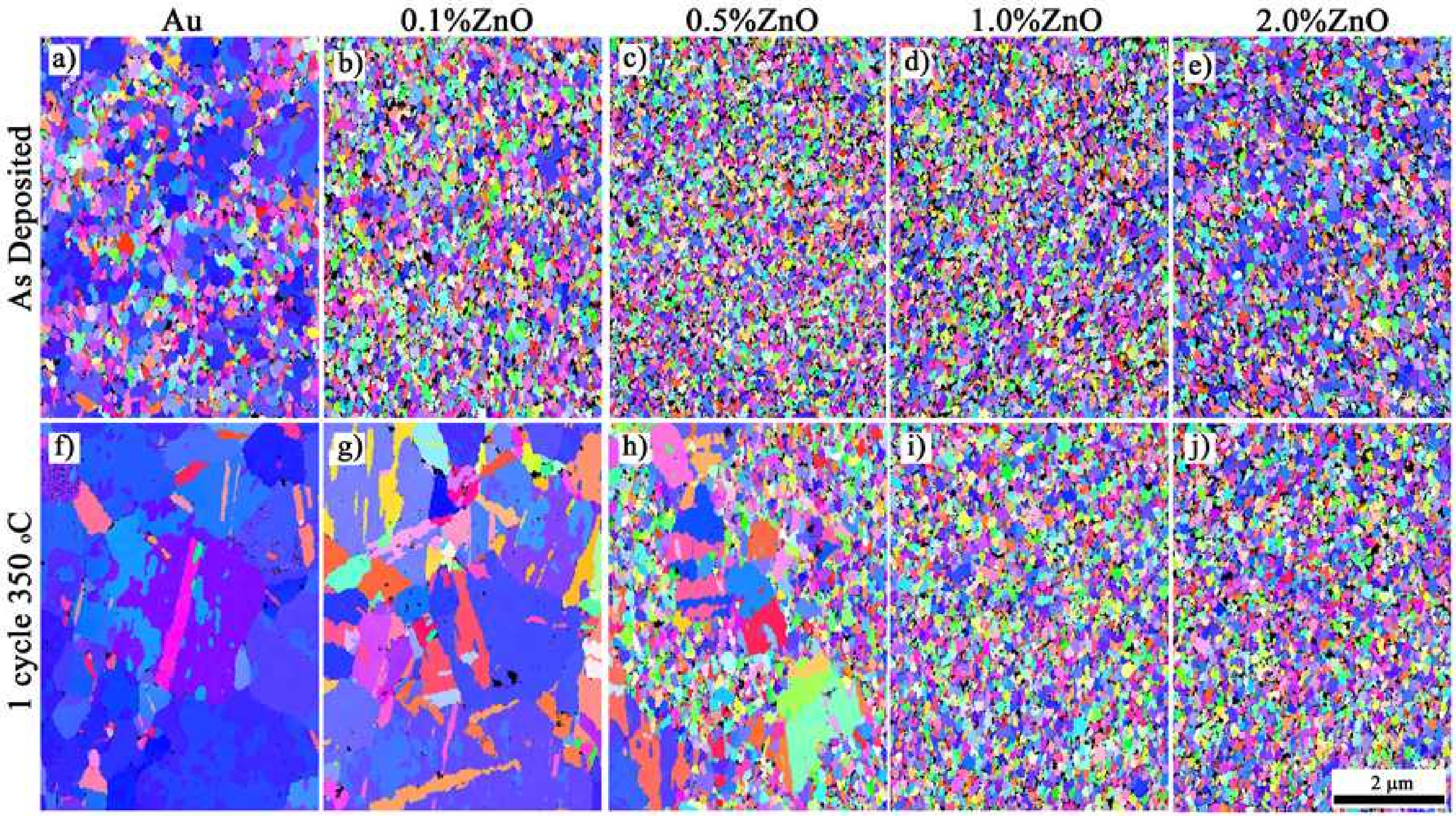


Rios, et.al. Mat. Res. 2005

Thermal Stability

EBSD

Au-ZnO thin films 2 μm thick on Pt/Ti/Si

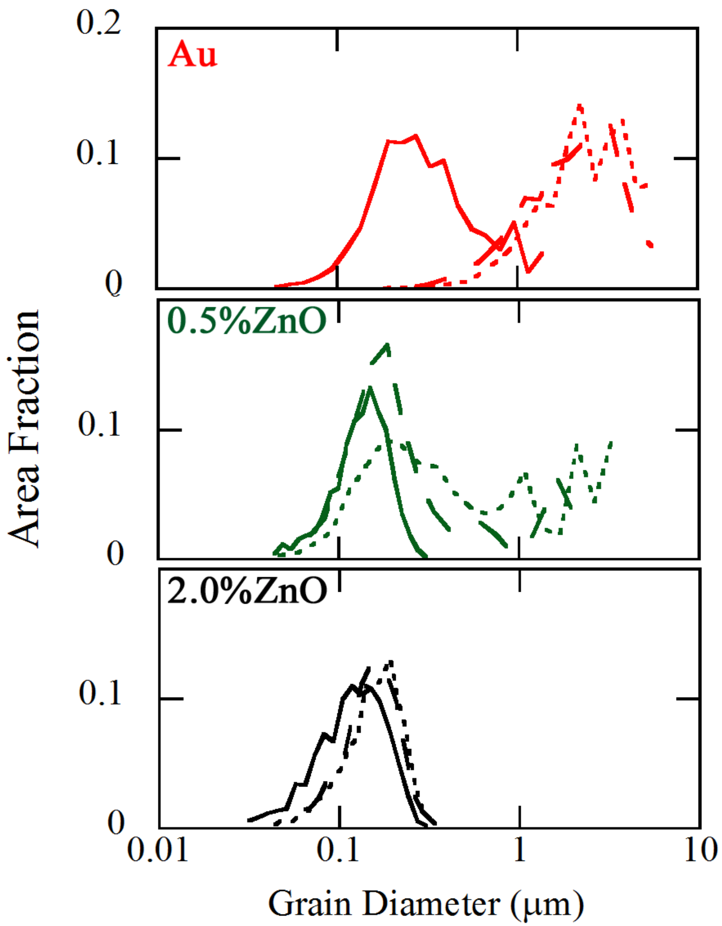


Temperature cycled to 350°C at 10°C/min

Paper in process …. R.L. Schoeppner, D.F. Bahr, R.S. Goeke, N.R. Moody, S.V. Prasad

Thermal Stability

Grain Size Distribution



Large grain growth

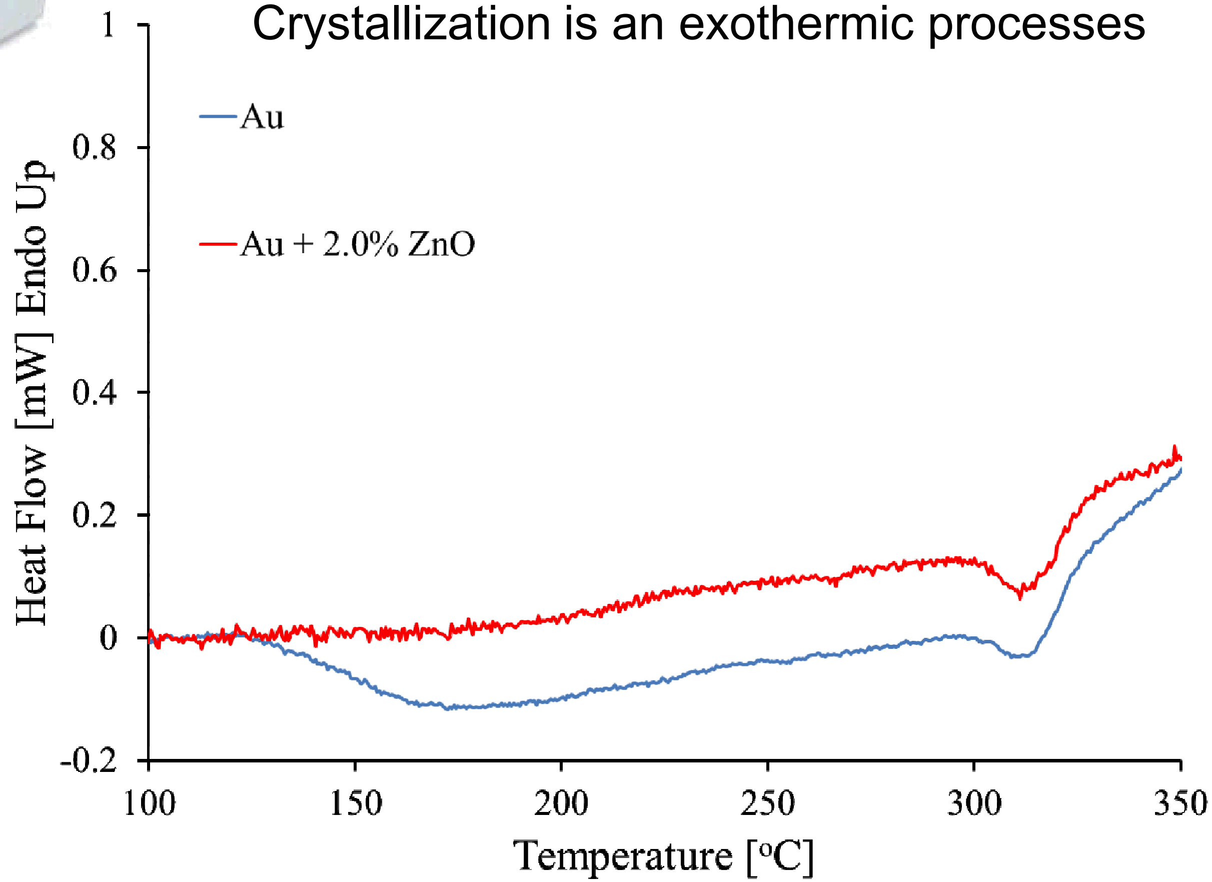
Abnormal grain growth, large grain sintering observed only in regions

Addition of ZnO impeded grain sintering

Differential Scanning Calorimeter

DSC

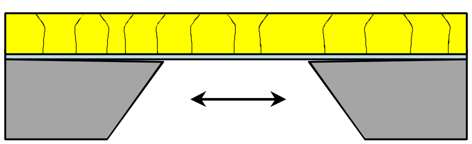
DSC-8500 (PerkinElmer)
of 20°C/min in N_2 (40°C to 450°C)
2 um thick Au-ZnO films removed from substrate
samples ~ 10mg
Crystallization is an exothermic processes



In Situ Heating

TEM Study

Au – ZnO Thin Films Deposited Directly on SPI Si_3N_4 TEM Membranes

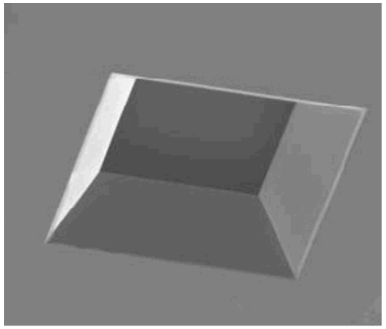


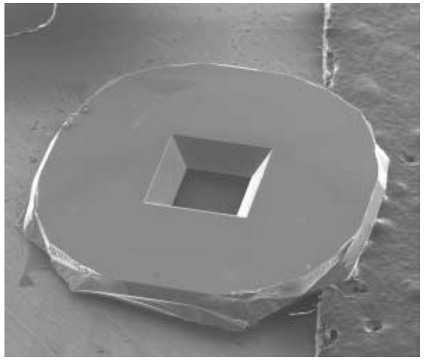
50 nm Au + ZnO

20 nm Si_3N_4

200 μm Si

100 nm window





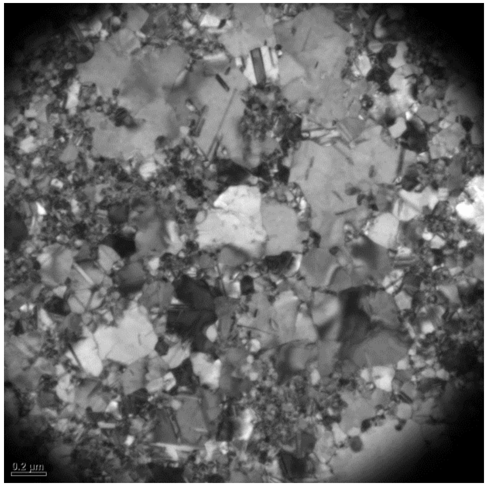
Imaged on Philips CM30 Transmission Electron Microscope in Bright Field

Heating in 10C steps from 150C to 350C

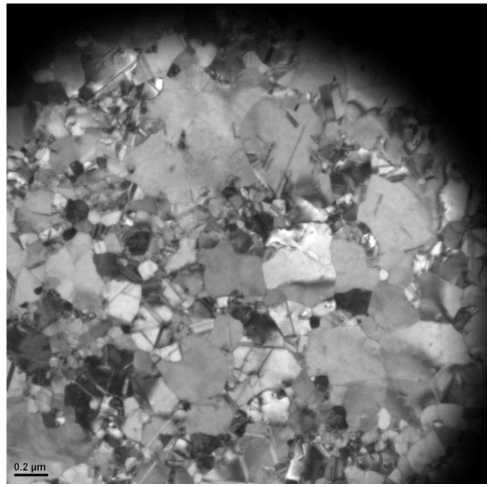
In Situ Heating TEM

Pure Au - 50nm thick

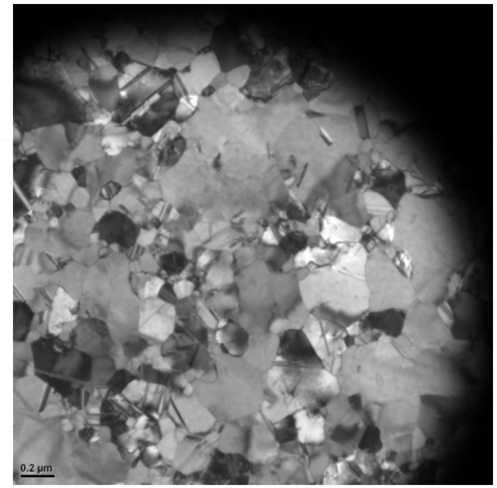
RT



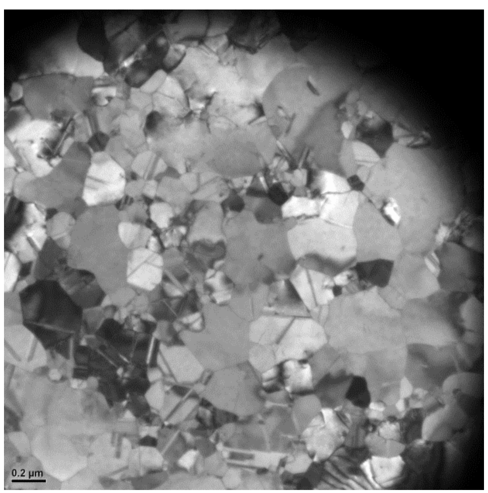
159C



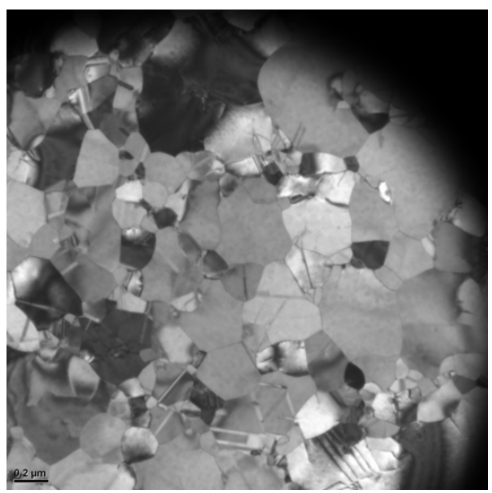
218C



279C



352C



FOV 2.78 µm

As dep. Grain size 50 – 200nm

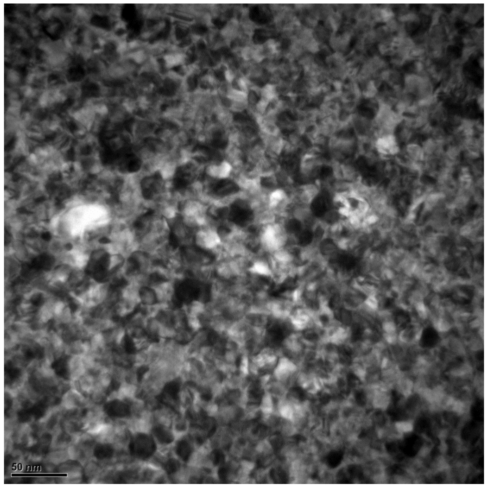
Small grains gone by 159°C

@ 352°C grain size 100 – 400nm

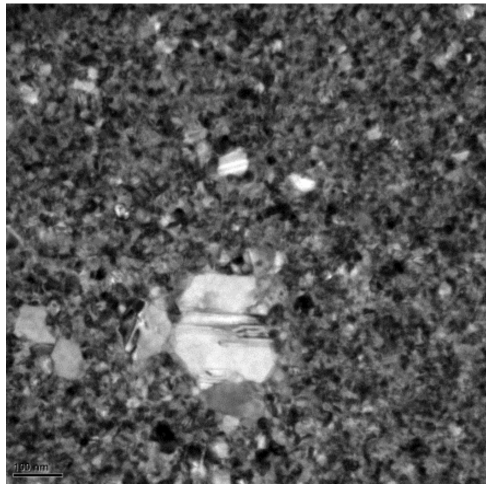
In Situ Heating TEM

Au – 2% ZnO 50nm thick

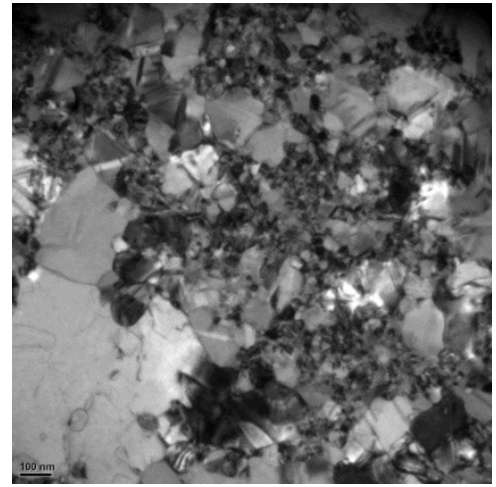
RT



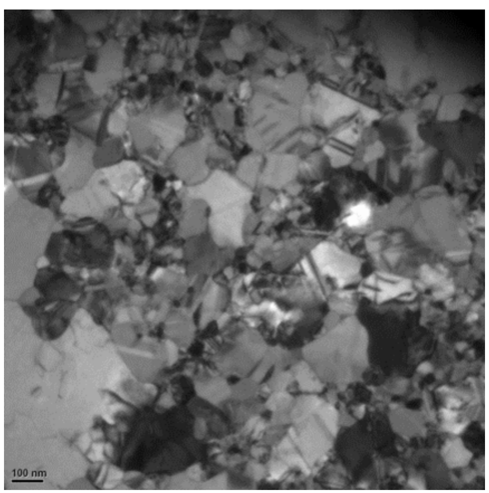
155°C



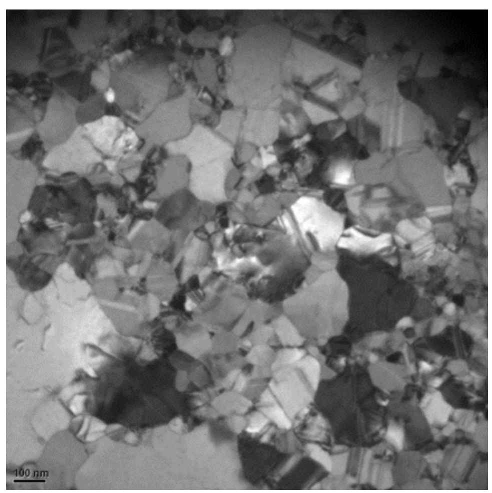
222°C



300°C



347°C



FOV 1.5 μm (1st image 450nm)

As dep. Grain size 10 – 20nm

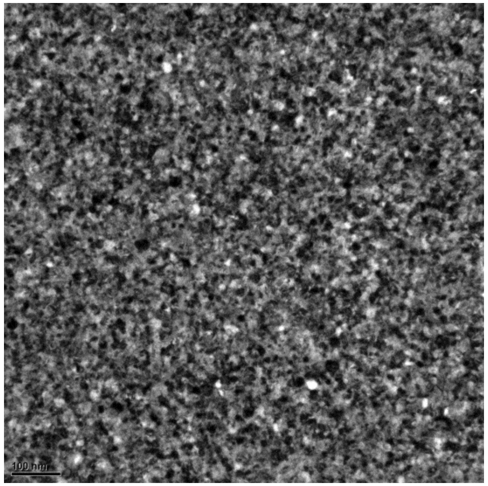
Abnormal grain growth starts @ 155°C

@ 347°C grain size 50 – 200nm

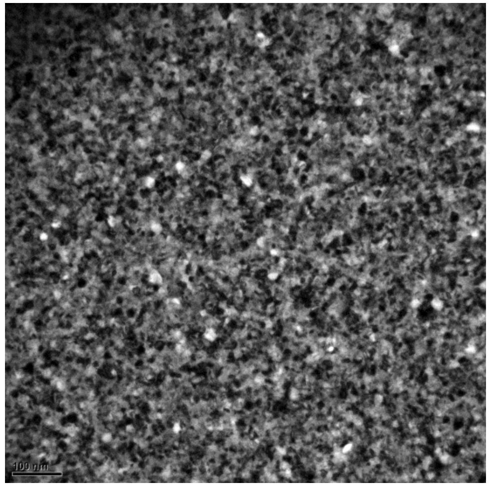
In Situ Heating TEM

Au 5% ZnO - 50nm thick

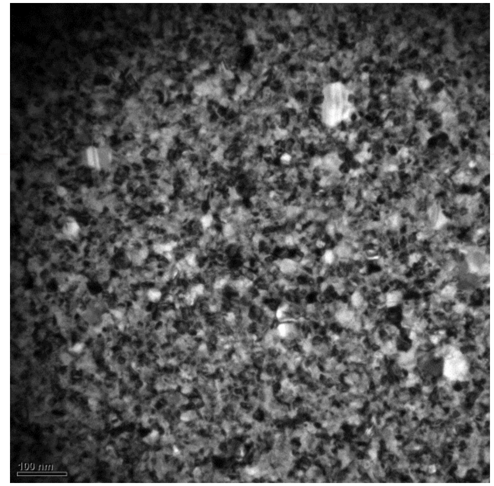
RT



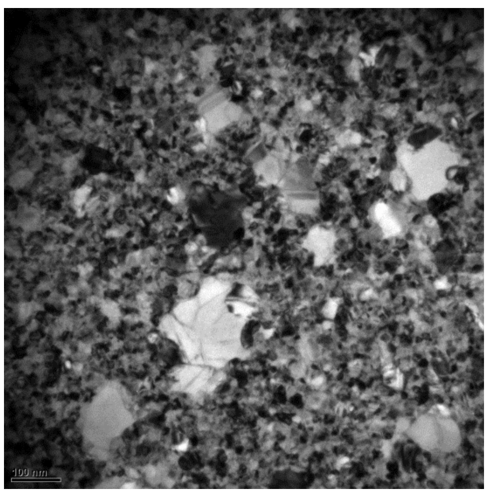
148°C



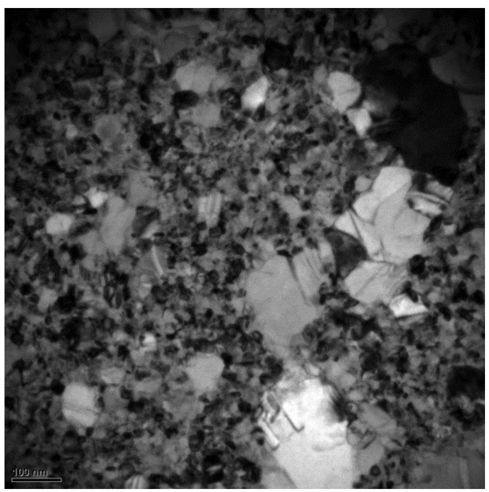
211°C



294°C



349°C



FOV 960nm

As dep. Grain size ~10 nm

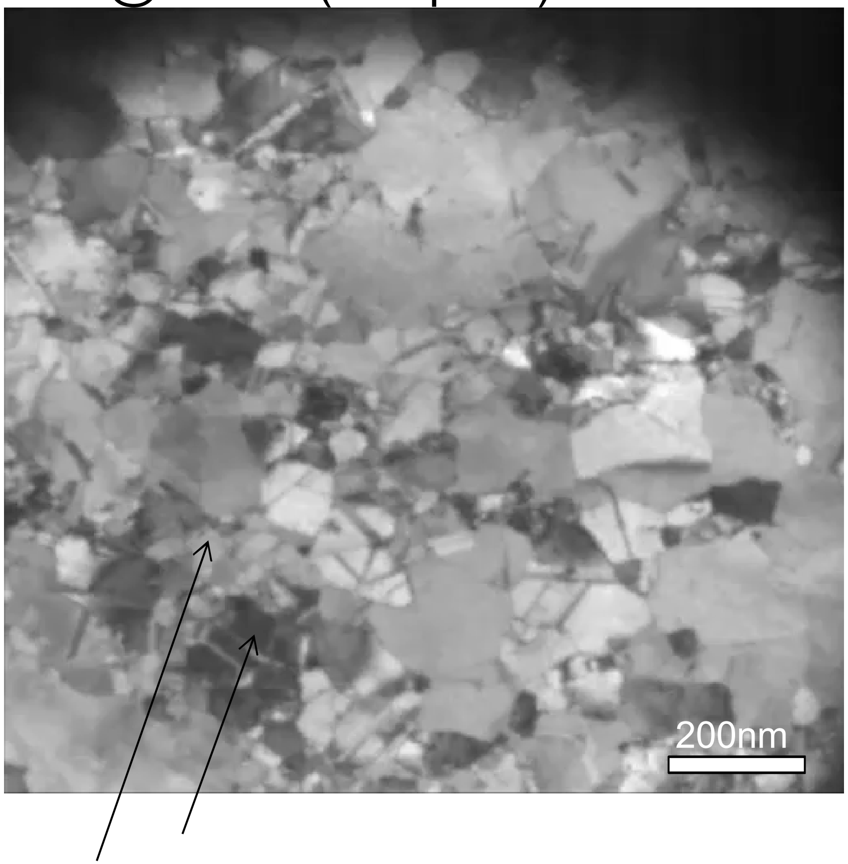
minor grain growth starts @ 211°C

@ 349°C grain size 10 & 100nm

In Situ TEM

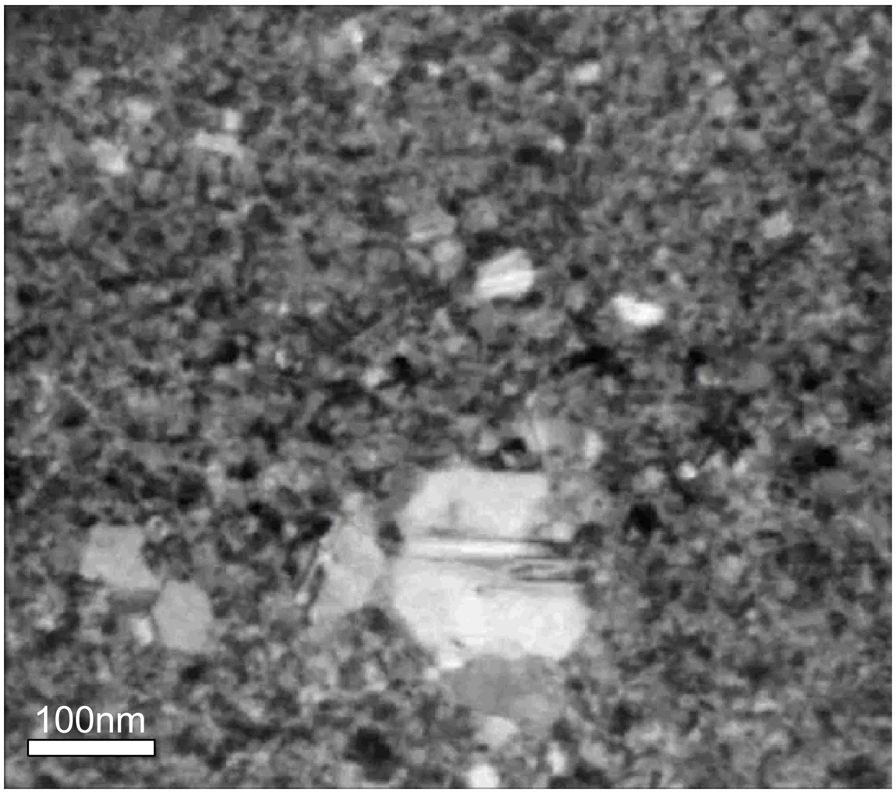
Grain Boundary Motion

Au @ 180°C (1X speed)



Watch these areas

Au – 2% ZnO @ 155°C (16X speed)



Abnormal growth is when a few grains grow much larger than the remaining majority

Conclusions

- A hard gold thin film has been synthesized by co-evaporation comprising nanocrystalline Au pinned by small amounts of ZnO
- Au-ZnO material has potential for electrical contact applications
- Thermal stability of Au-ZnO is significantly enhanced over pure gold and shows no surface layer formation which would impact electrical contact resistance
- PVD process are evironmentally friendly compared with electroplating.

Acknowledgements:
Somuri Prasad for project lead and tribology testing
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Kahlid Hattar, Paul Kotula, Joe Michael for Microscopy

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