SAND2014-3511C

41st ICMCTF - 2014

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

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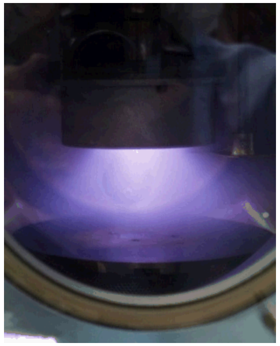

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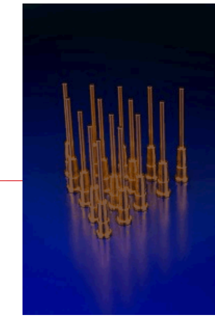
Technical Application

Electronic connectors, switches and relays

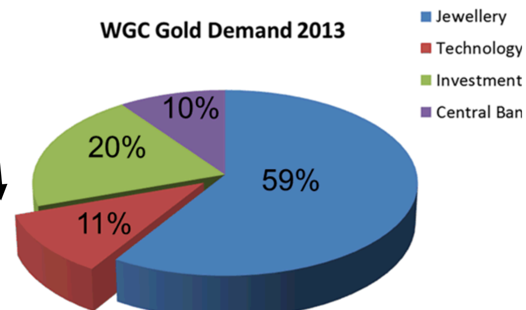
Electronics Applications:
Chemically Inert and low electrical resistance



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)

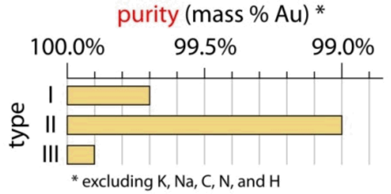
- Pure gold is soft and has unacceptable amount of friction and wear
- Gold is typically hardened by alloying with small amounts of Ni or Co (referred to as hard gold) to achieve the desired balance between friction, wear and ECR
- Current practice is to apply hard gold by electrodeposition
- Nickel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

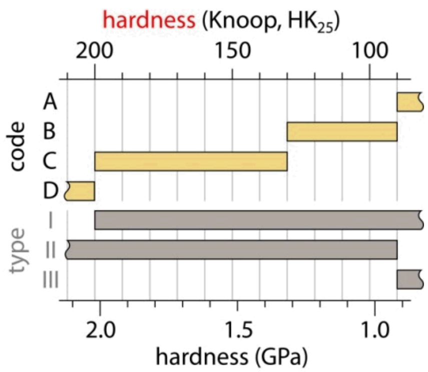
Hard Gold

ASTM Types

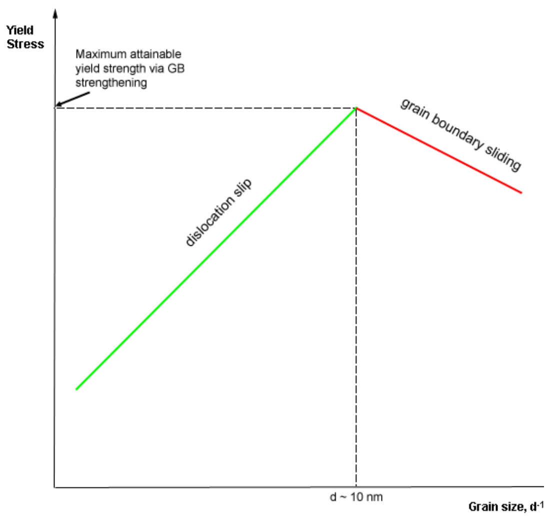
From ASTM B488-11 / MIL-DTL-45204D:

(mass % Au)	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

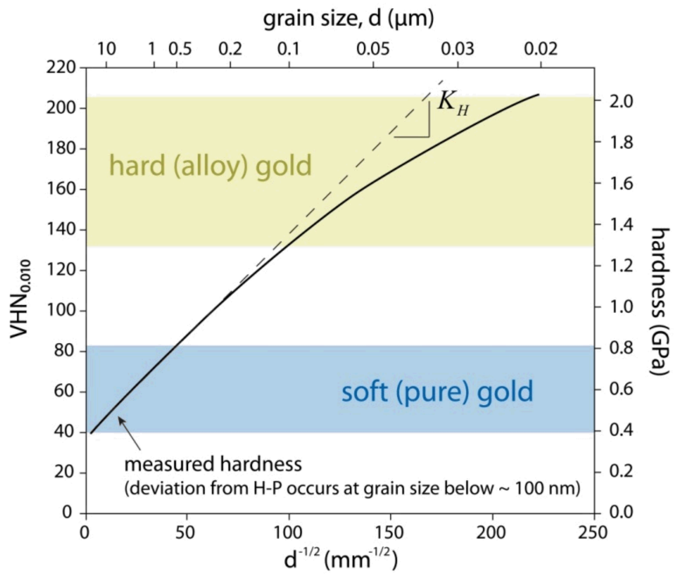




Hall-Petch Strengthening Limit



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



Hall-Petch relationship:

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

H - hardness

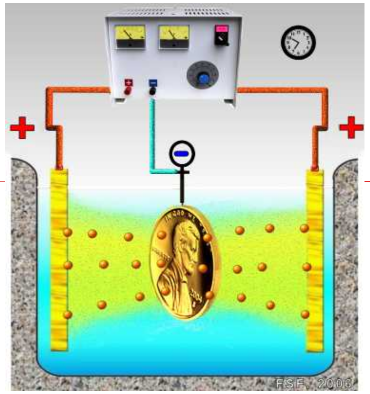
d - avg. grain diameter

Strengthening via grain refinement

Theoretical maximum strength at ~ 10nm

Electrochemical Deposition

Problems: Toxic plating baths & surface oxidation



Electroplating:

Hard Gold is typically plated from cyanide solution $KAu(CN)_2$

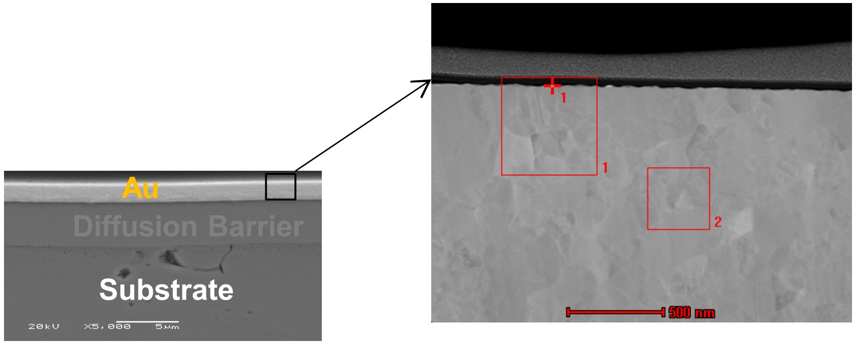
Bath modifiers of As, Pb, Cd or Tl

Small amounts hardening agent such as Ni or Co

Nickel barrier layer applied first

Diffusion and Surface Oxidation:

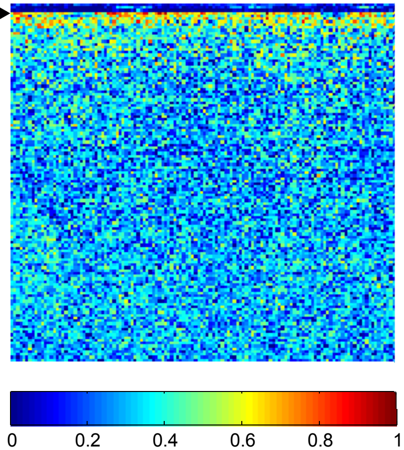
Diffusion and segregation of Ni or Co hardeners to the surface over time, ECR degradation

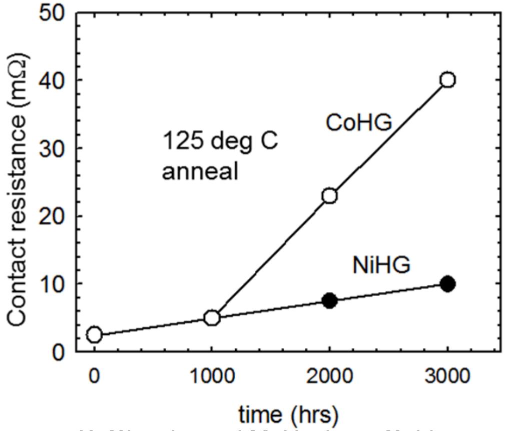


Cross-sectional TEM and Spectral Imaging

Surface NiO layer

Relative Ni concentration After 35+ years





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

PVD Hard Gold Synthesis

Routes to Mitigate Diffusion

- *Not limited to electrochemically compatible materials*
- *Shut-down diffusion by co-deposition of thermodynamically stable ceramic material*
- *Deposition of barrier under-layer would eliminate diffusion of substrate material*
- *Semiconducting ceramic chosen to minimize potential impact on electrical resistance*

These layers applied via Physical Vapor Deposition (PVD)

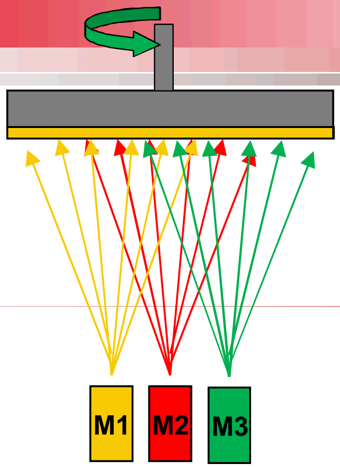
- *Au-ZnO co-deposition by PVD (e-beam evaporation or sputtering)*
- *PVD is environmentally friendly*

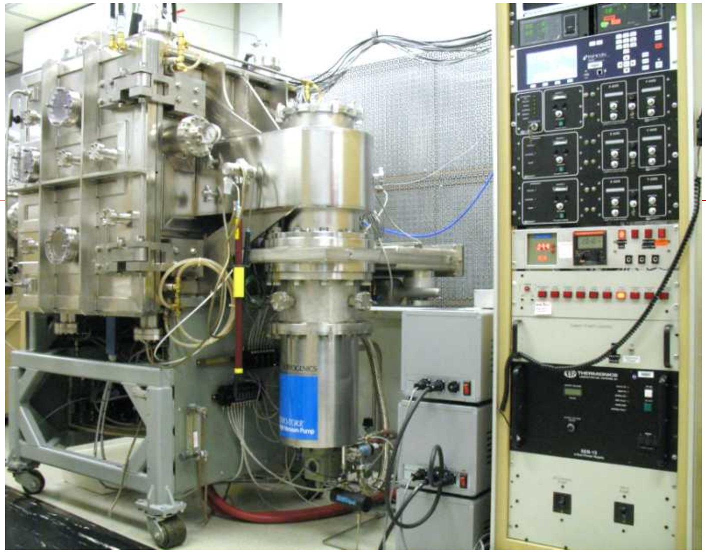
Co-Deposition

Available PVD Options

Evaporation:

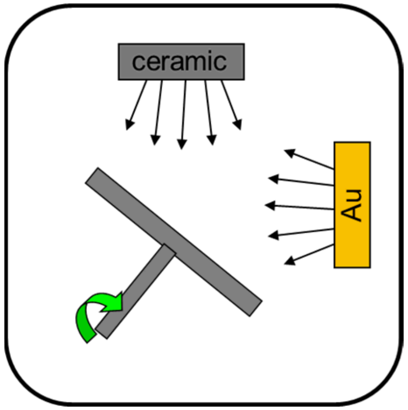
- Triad e-beam evaporation of ternary alloy thin films
- Shutter in front of substrate for consistent composition, graded or layered films
- Independent QCM control of material deposition rate
- Compositional control to < 0.1%

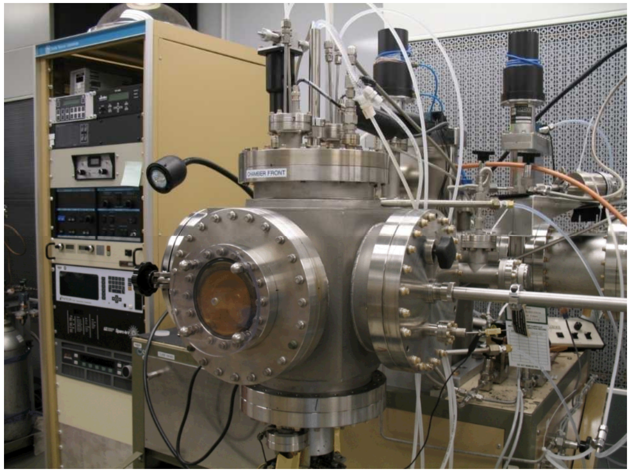




Sputtering:

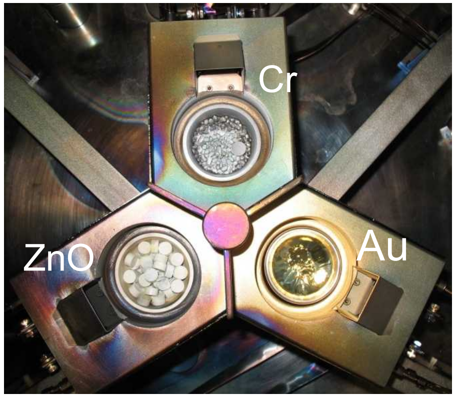
- Co-deposition of elements, alloys and compounds
- Composition control to ~1-2%, limited by minimum power required for plasma ignition
- Composite targets expensive and limits experimental compositional range

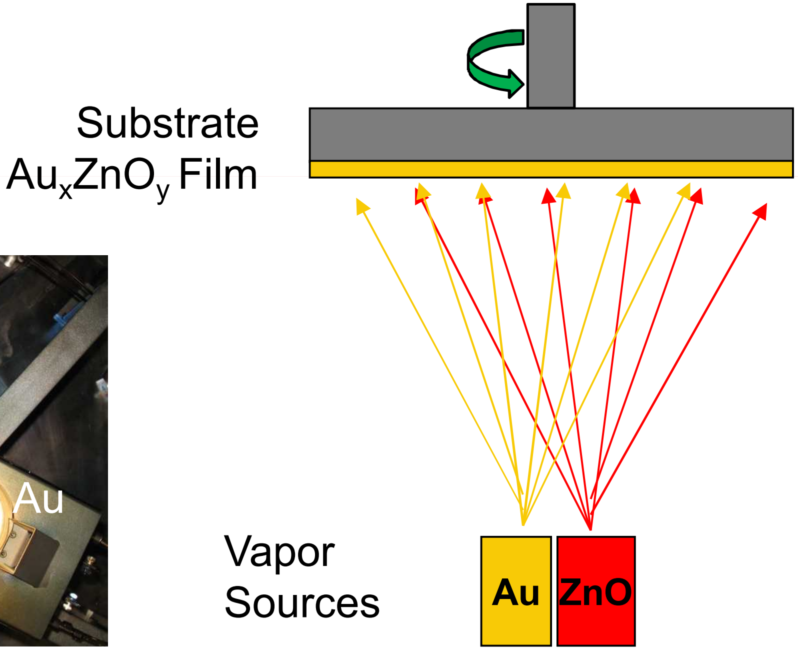




Triad E-Beam Deposition

E-beam approach chosen for compositional control

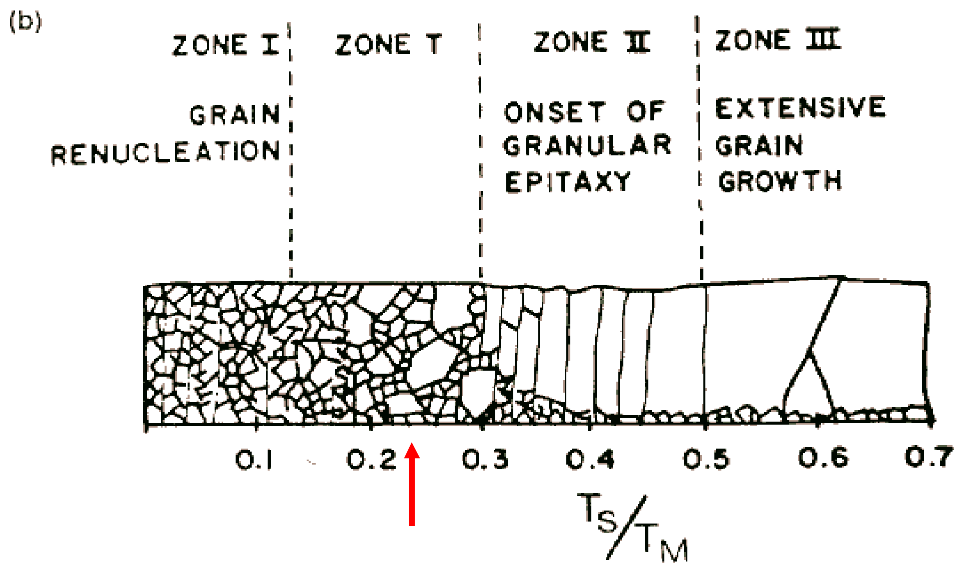




- Triad electron gun for E-beam evaporation
- Co-deposition of Au-ZnO composite thin films
- Third pocket used for adhesion or barrier layer material
- Shutter in front of substrate for consistent composition
- Substrate rotation for improved uniformity
- Line of sight shields on QCMs eliminate cross-talk

Zone Model for Evaporated Films

RT Au Transitional Zone

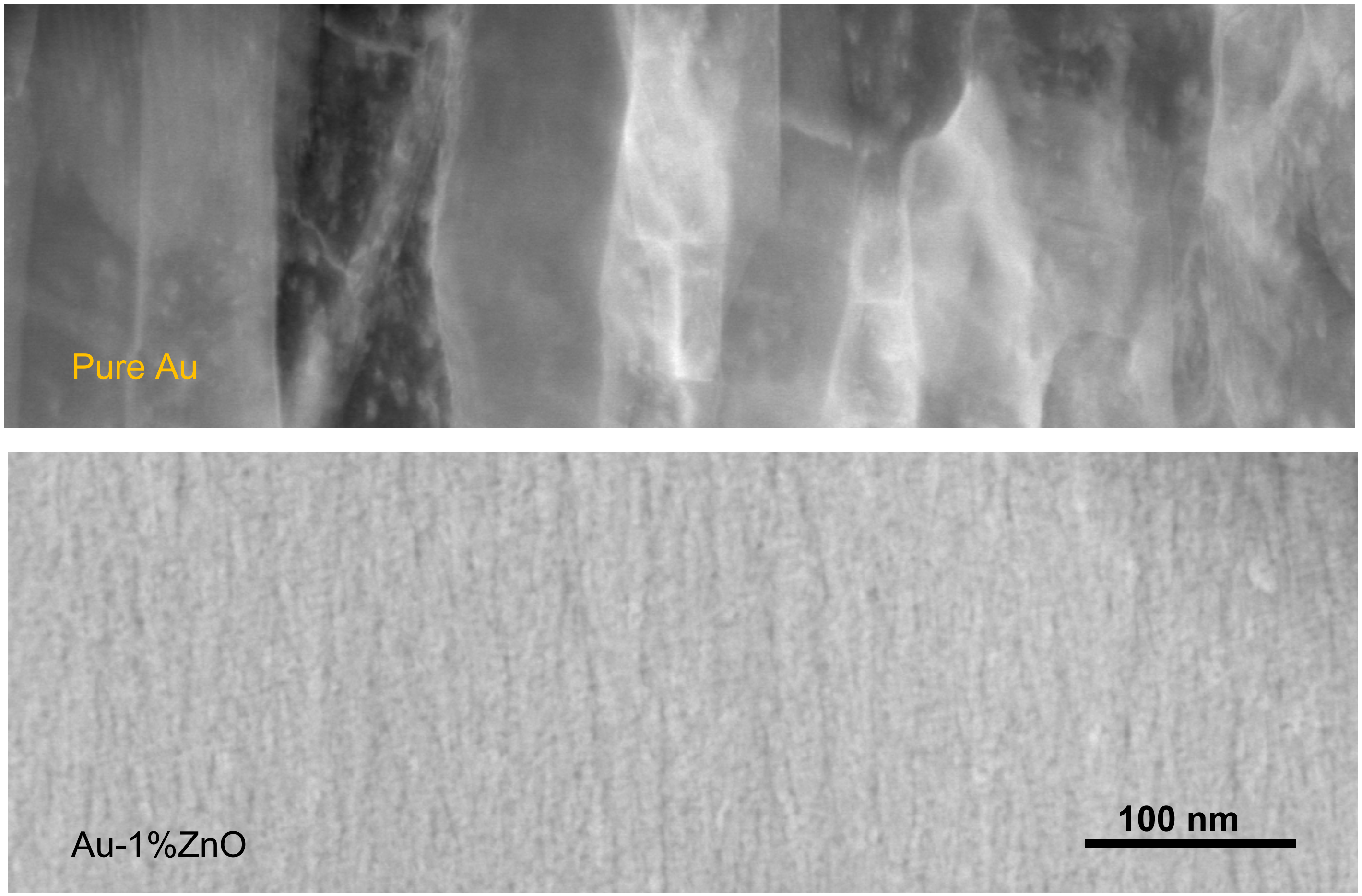


Fraction of T_m	Au Temp (ºC)	Au Temp (K)	ZnO Temp (ºC)	ZnO Temp (K)
T_m	1064	1337	2248	2521
0.5 T_m	396	669	988	1261
0.4 T_m	262	535	735	1008
0.3 T_m	128	401	483	756
0.22 T_m	25	298	281	554

Hentzell, JVST-A 1984

Cross-Sectional TEM

(TEM Specimens prepared by FIB)

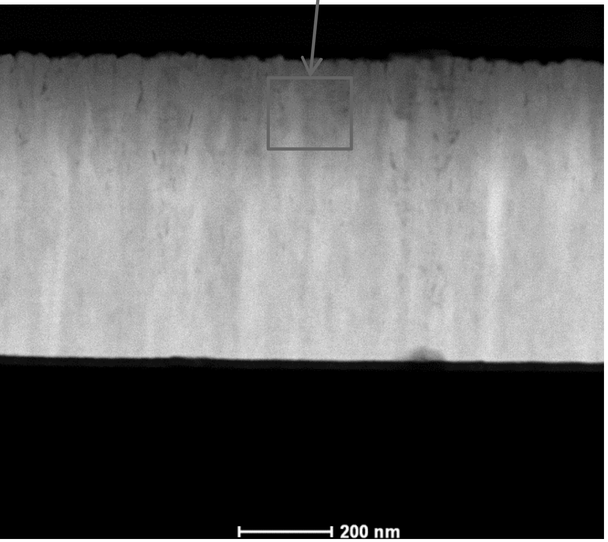


Columnar grain structure is clearly observed with a significant reduction in grain size for Au + ZnO (1 vol%) thin film

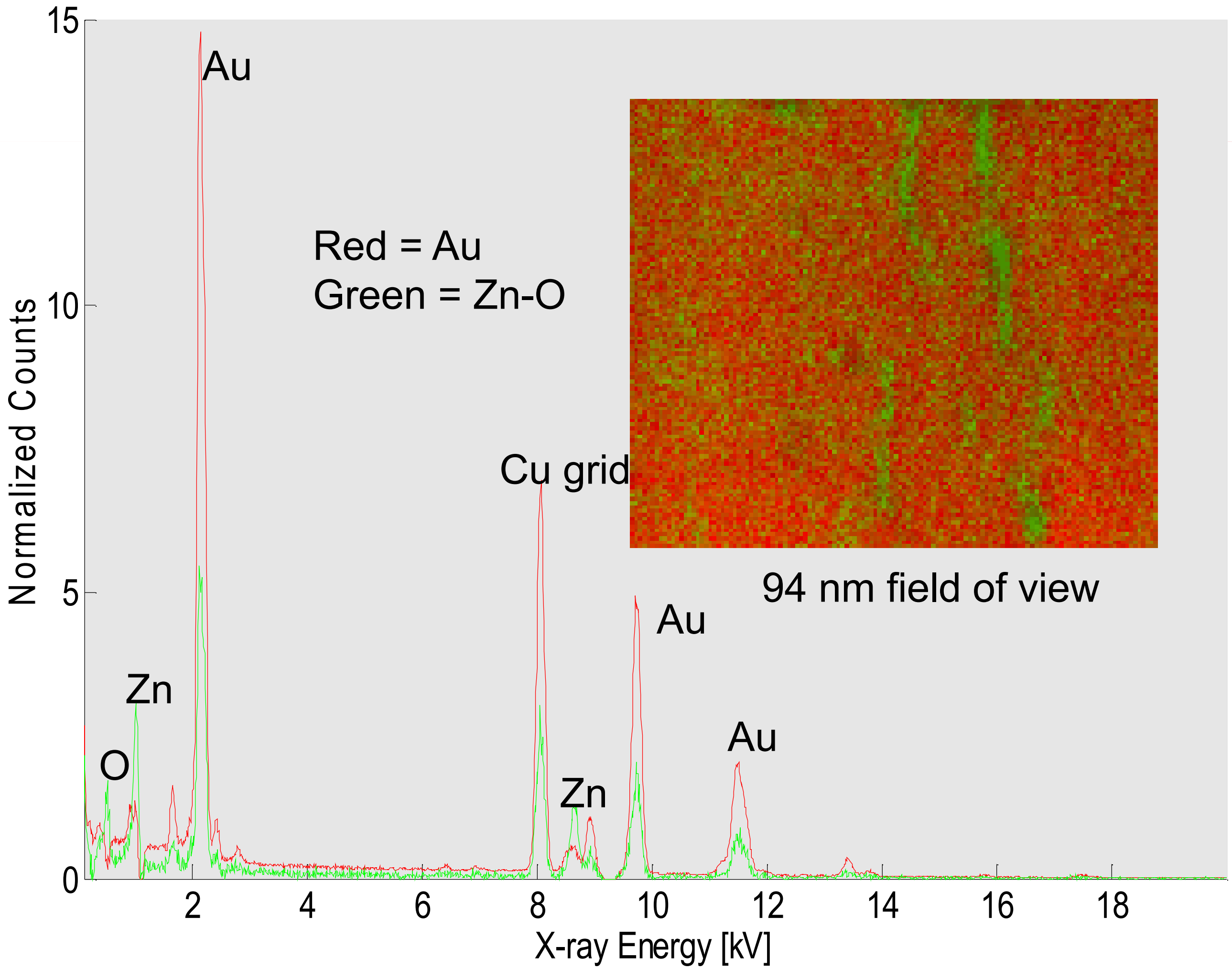
STEM Spectral Analysis

X-Sect Au-ZnO film

Region of spectral analysis

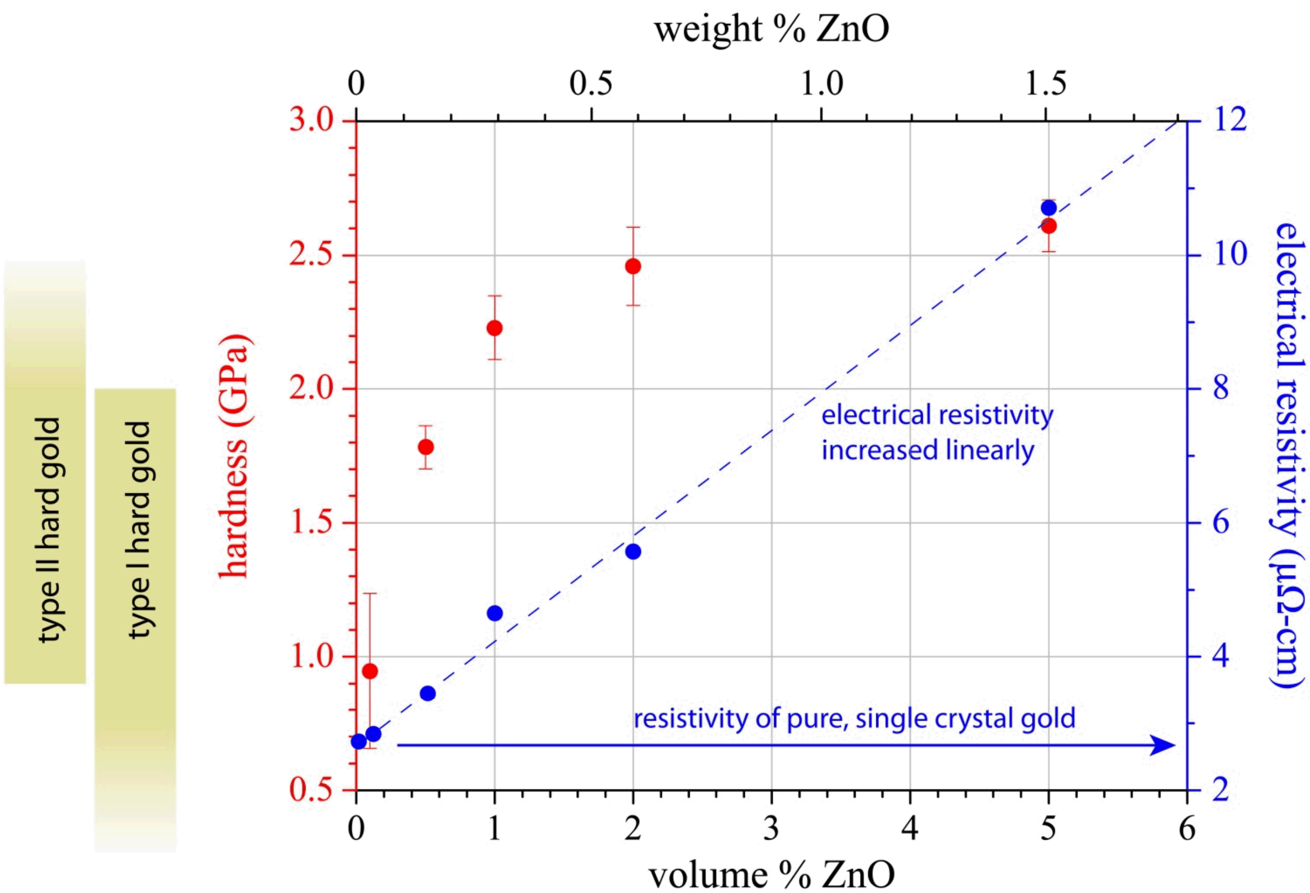


STEM cross-section of Au+ZnO (5 vol%)



Hardness and Electrical Resistivity

Comparison to hard gold specification

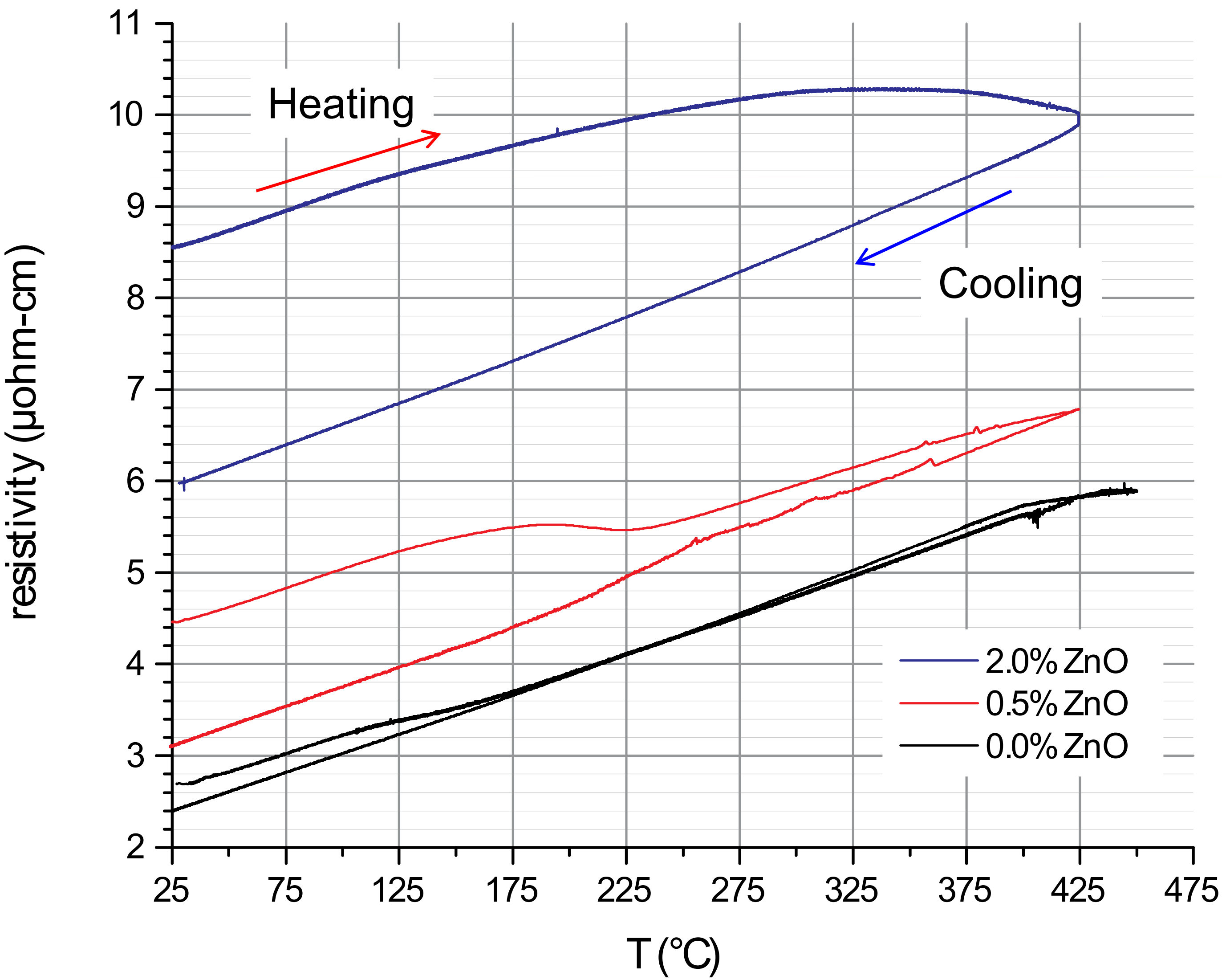


for reference:
0.7 vol % Ni is ~ 0.3 wt % (type I, best ECR performance)
2.2 vol % Ni is ~ 1 wt % (type II, max allowed)

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

Temperature Dependent Resistivity

TCR Stability (0, 0.5, 2.0 vol% ZnO)



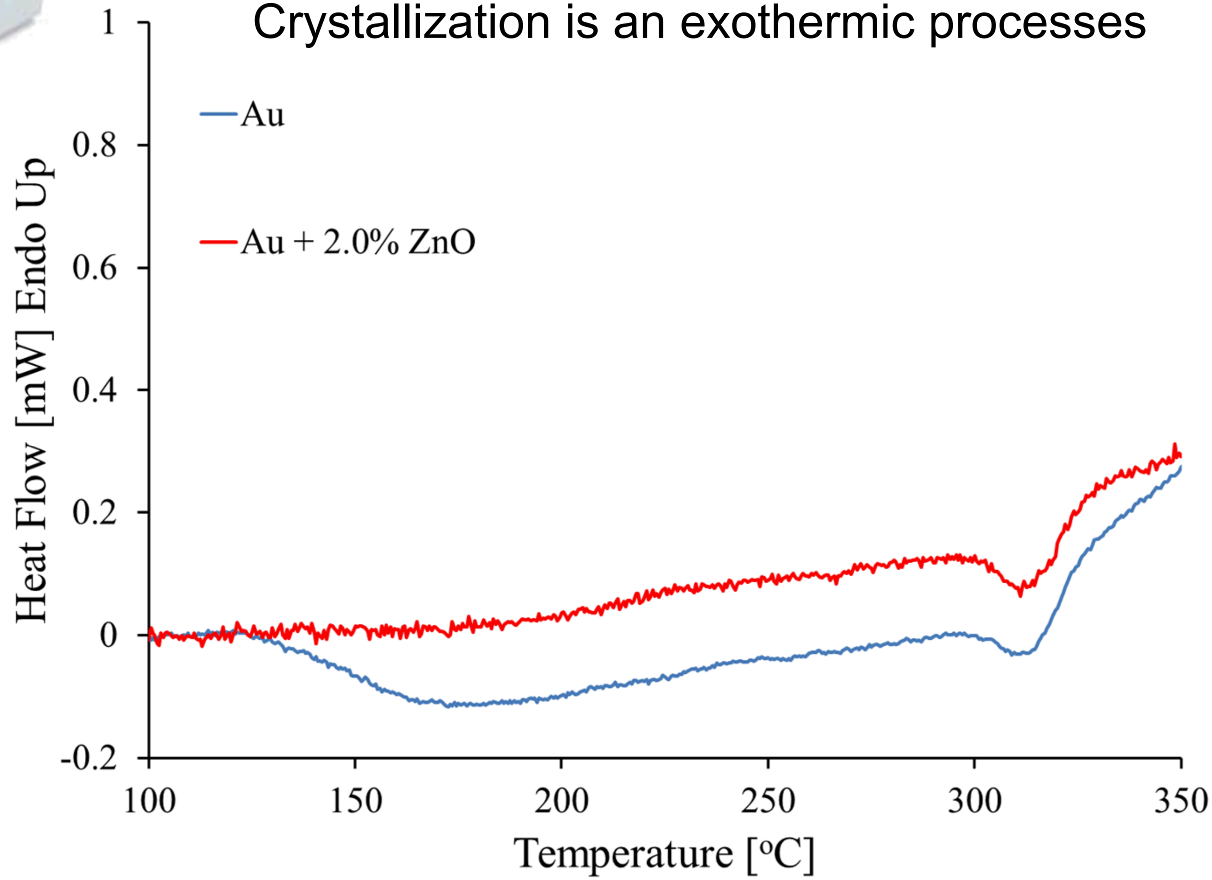
TCR
$\alpha = (1/R)\Delta R/\Delta T$ (/°C)

α=0.004
agrees with literature

Differential Scanning Calorimeter

DSC

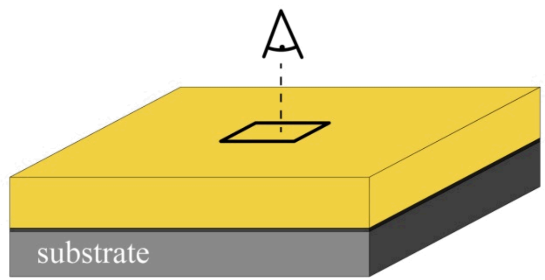
DSC-8500 (PerkinElmer)
of 20°C/min in N_2 (40°C to 450°C)
2 um thick Au-ZnO films removed from substrate
samples ~ 10mg
Crystallization is an exothermic processes



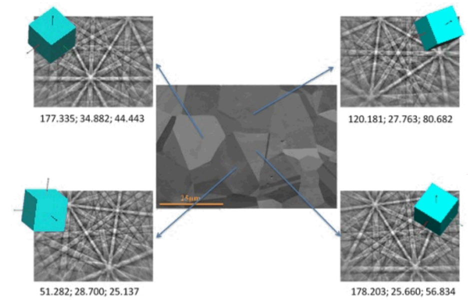
EBSD

Grain size and texture impact

surface normal EBSD maps

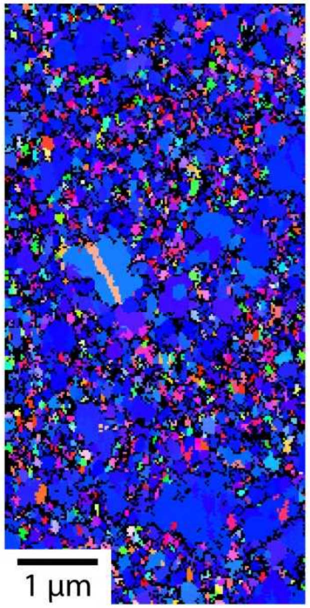


Oxford Instruments - http://www.ebsd.com

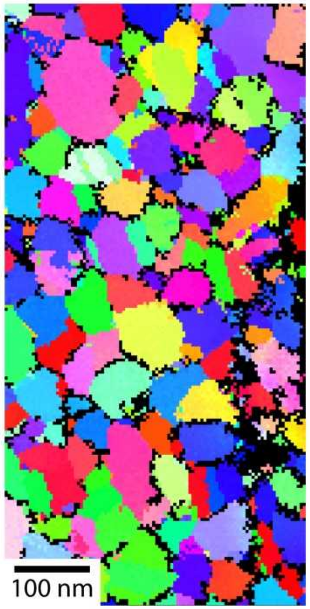


large avg. grain size (> 250 nm)
preferential <111> surface texture
bimodal distribution
hardness ~ 900 MPa

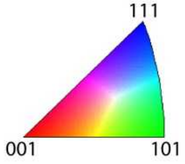
pure Au film:



2.0 vol. % ZnO film



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



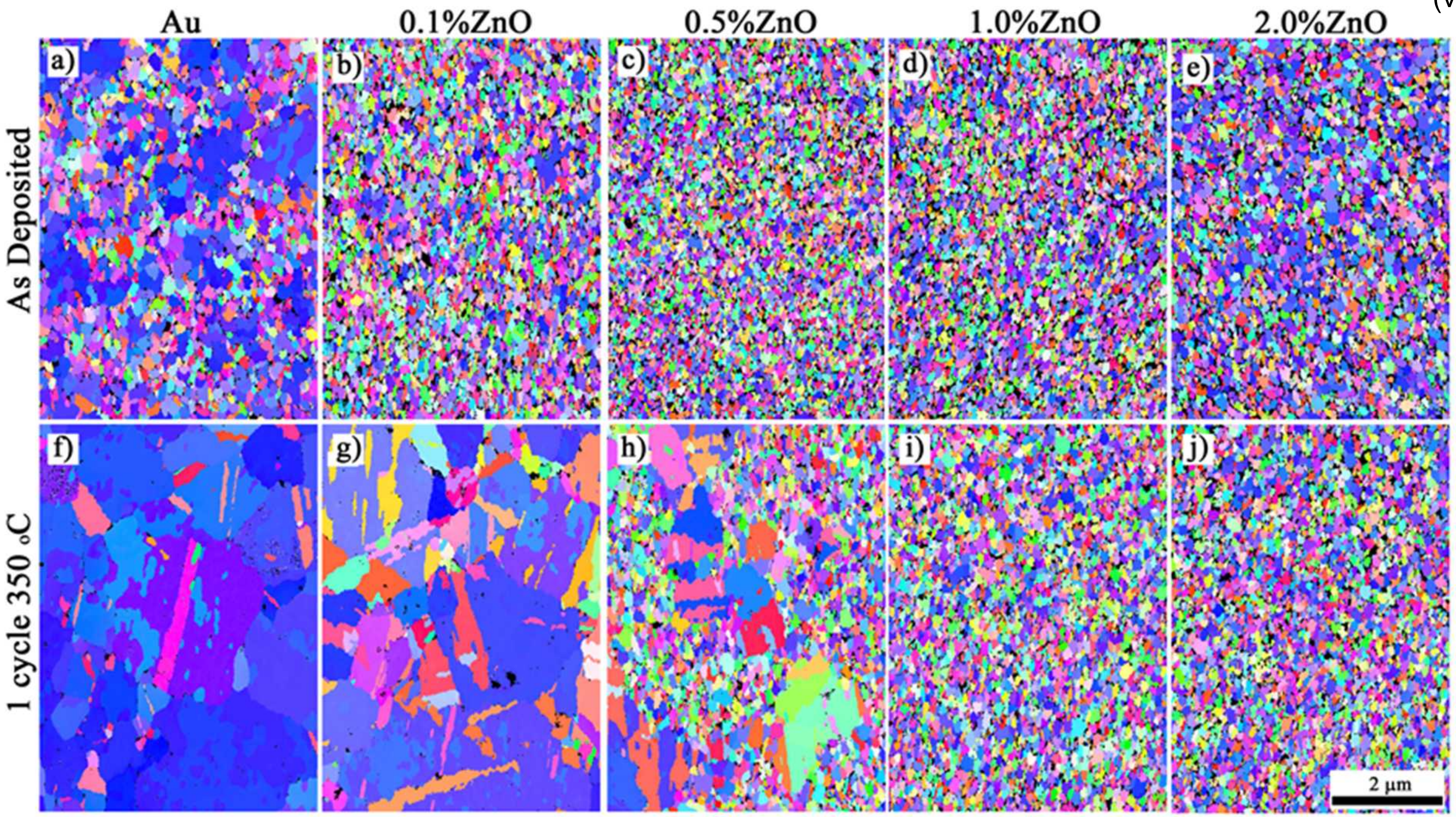
* note the difference in scale bars *

Thermal Stability

EBSD

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

(vol %)

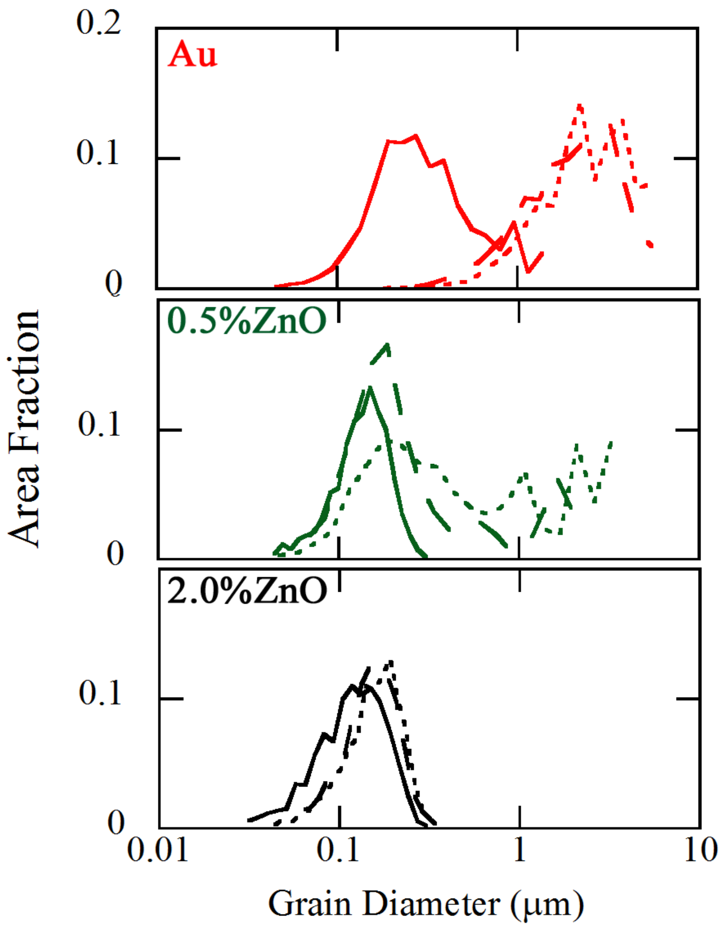


Temperature cycled to 350°C at 10°C/min

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

Thermal Stability

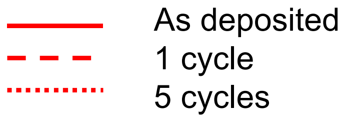
Grain Size Distribution



Large grain growth

Abnormal grain growth, large grain sintering observed only in regions

Addition of ZnO impeded grain sintering



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

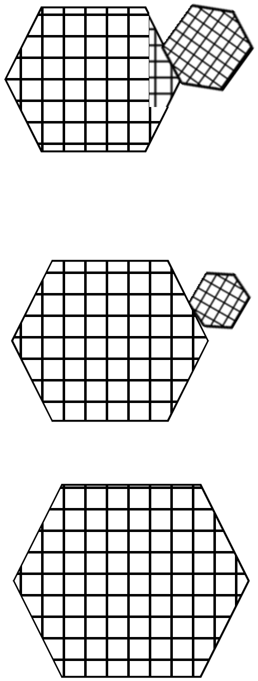
Sintering

Grain Growth Mechanisms

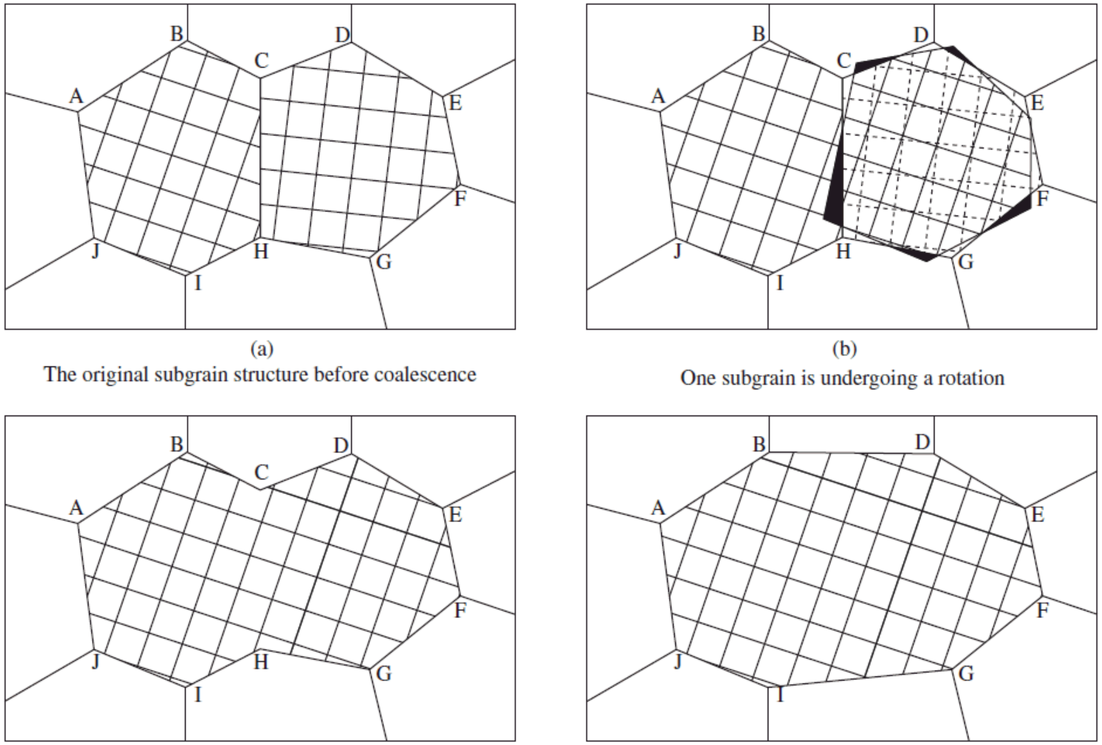
The two common mechanisms for grain growth are:

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

Ripening:



Coalescence:



(a) The original subgrain structure before coalescence

(b) One subgrain is undergoing a rotation

(c) The subgrain structure just after coalescence

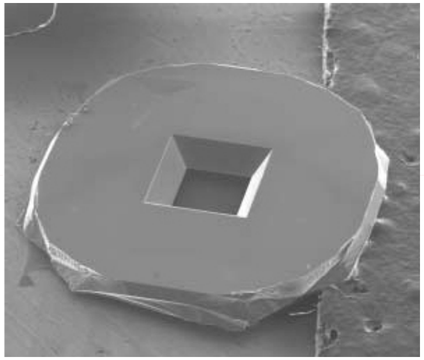
(d) The final subgrain structure after some subboundary migration

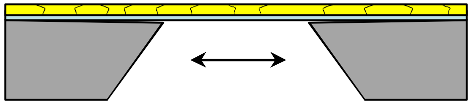
Rios, et.al. Mat. Res. 2005

In Situ Heating

TEM Study

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



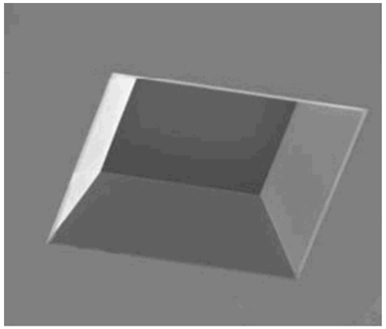


50 nm Au + ZnO

20 nm Si_3N_4

200 μm Si

100 nm window



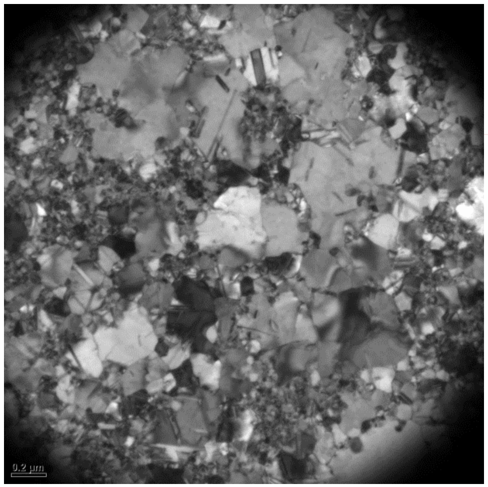
Imaged on Philips CM30 Transmission Electron Microscope in Bright Field

Heating in 10C steps from 150C to 350C

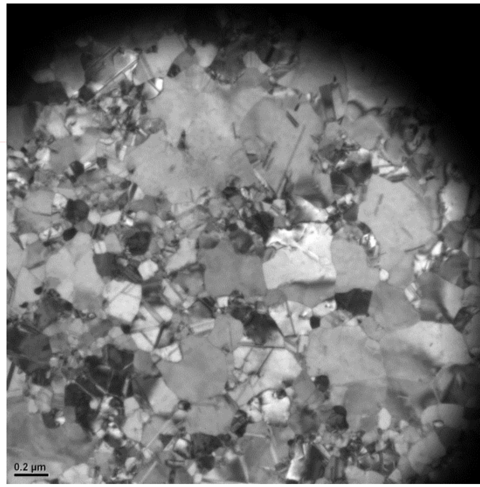
In Situ Heating TEM

Pure Au - 50nm thick

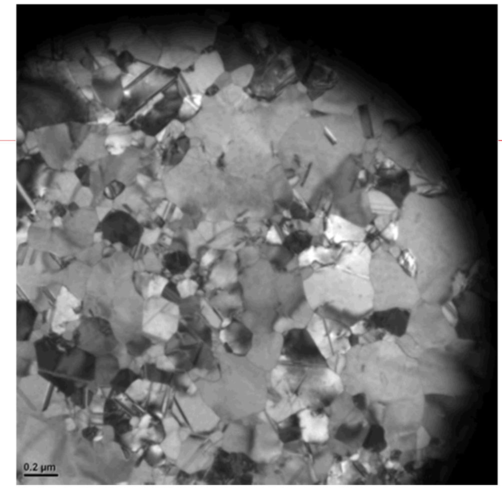
RT



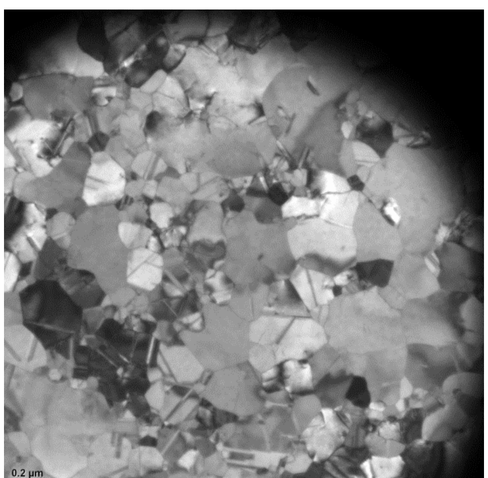
159C



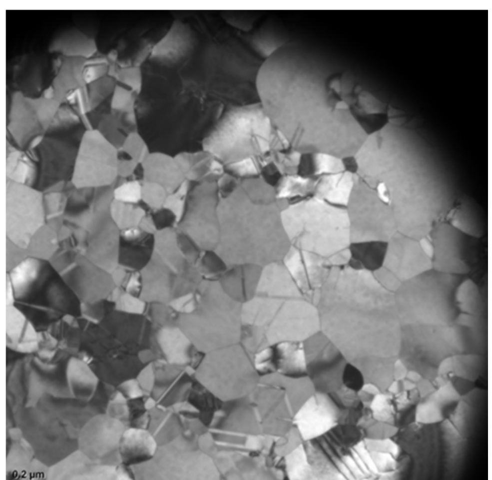
218C



279C



352C



FOV 2.78 µm

As dep. Grain size 50 – 200nm

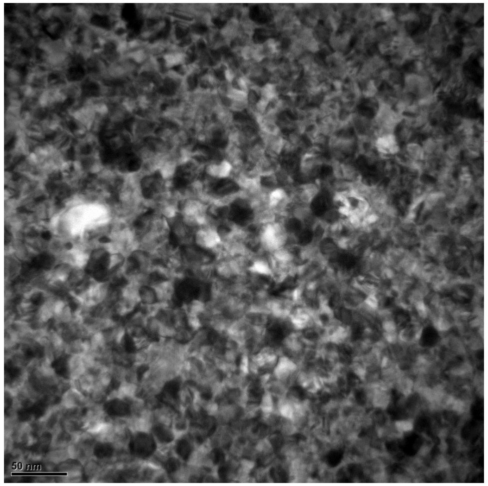
Small grains gone by 159°C

@ 352°C grain size 100 – 400nm

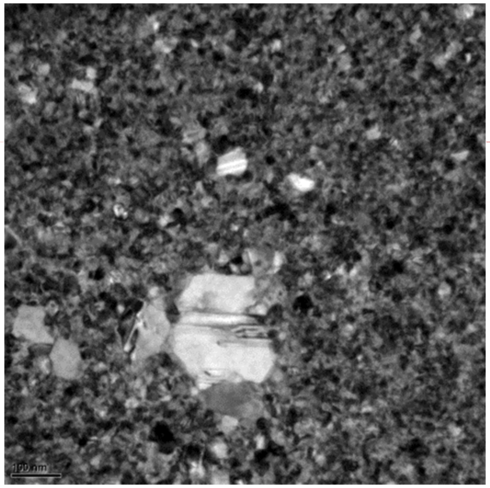
In Situ Heating TEM

Au – 2% ZnO 50nm thick

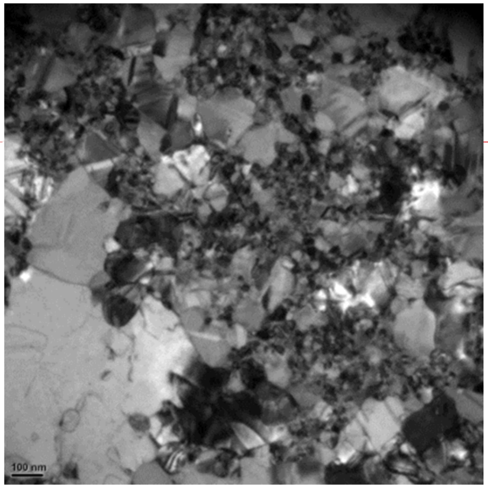
RT



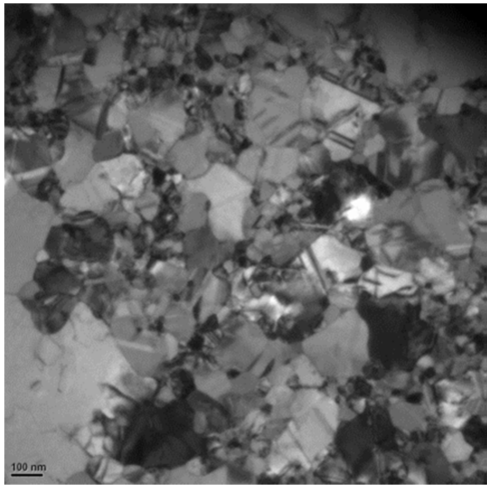
155°C



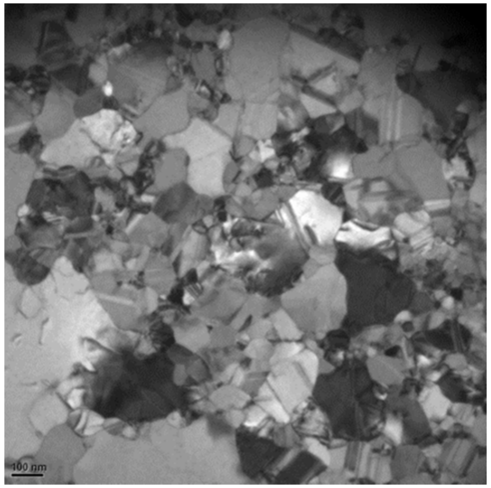
222°C



300°C



347°C



FOV 1.5 μm (1st image 450nm)

As dep. Grain size 10 – 20nm

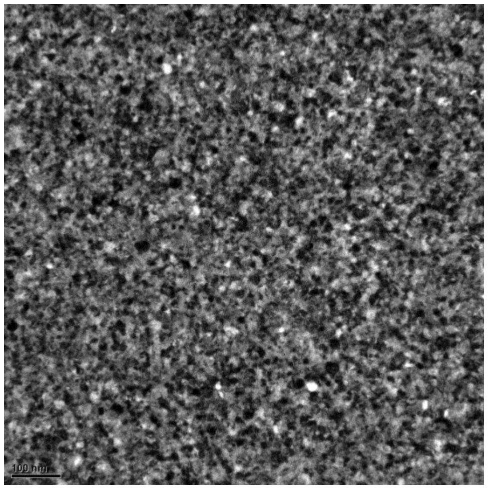
Abnormal grain growth starts @ 155°C

@ 347°C grain size 50 – 200nm

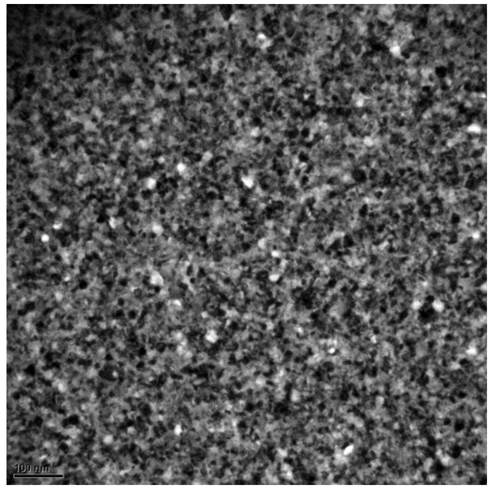
In Situ Heating TEM

Au 5% ZnO - 50nm thick

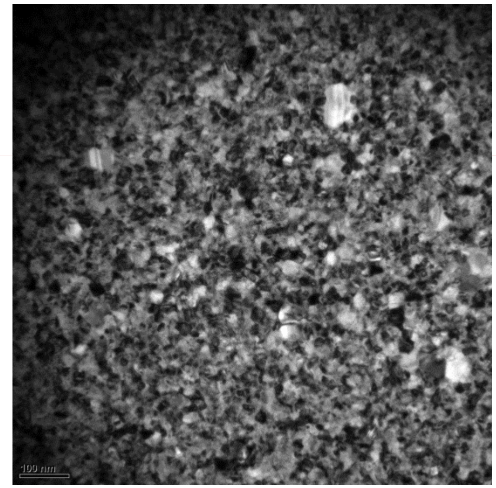
RT



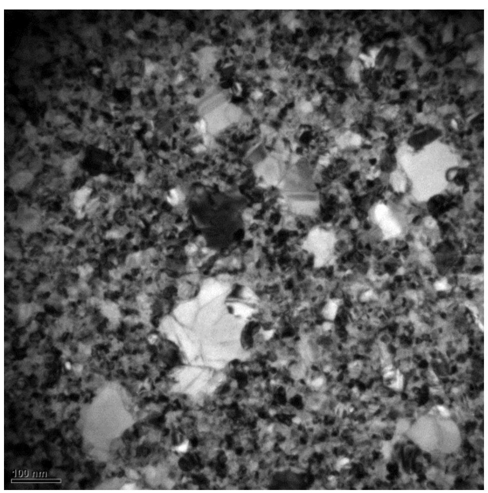
148°C



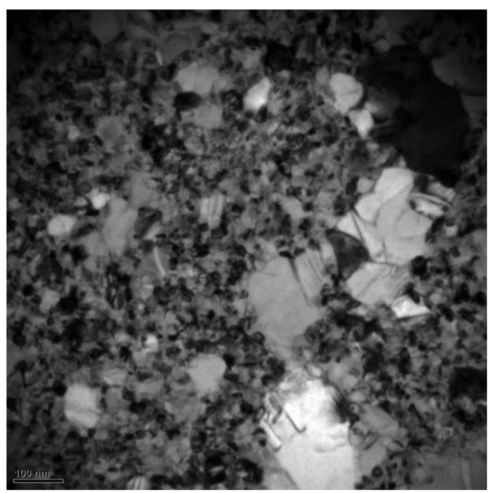
211°C



294°C



349°C



FOV 960nm

As dep. Grain size ~10 nm

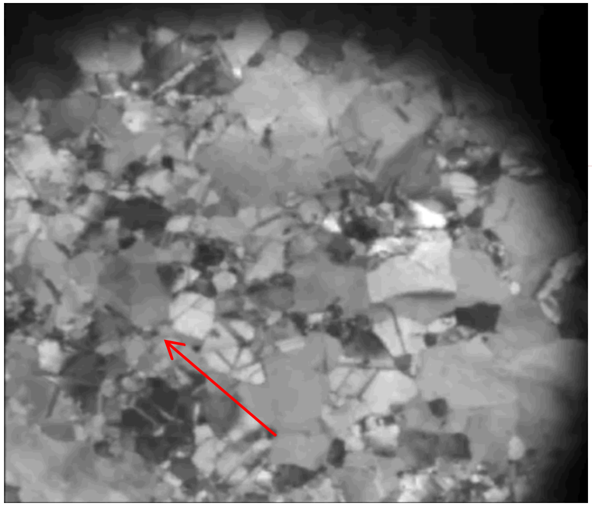
minor grain growth starts @ 211°C

@ 349°C grain size ~10 & 100nm

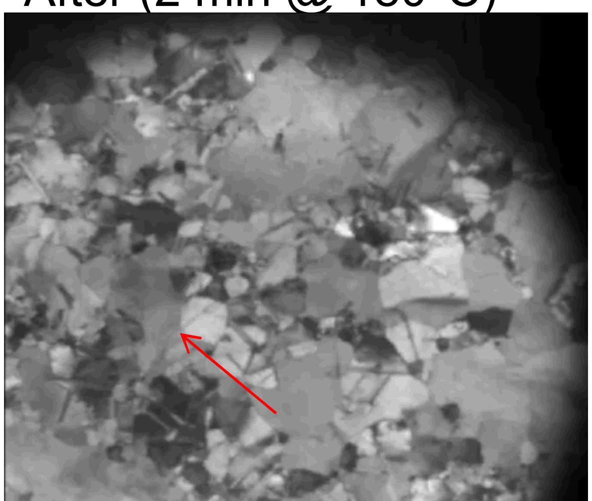
Sintering of Pure Au Film

Sintering movie

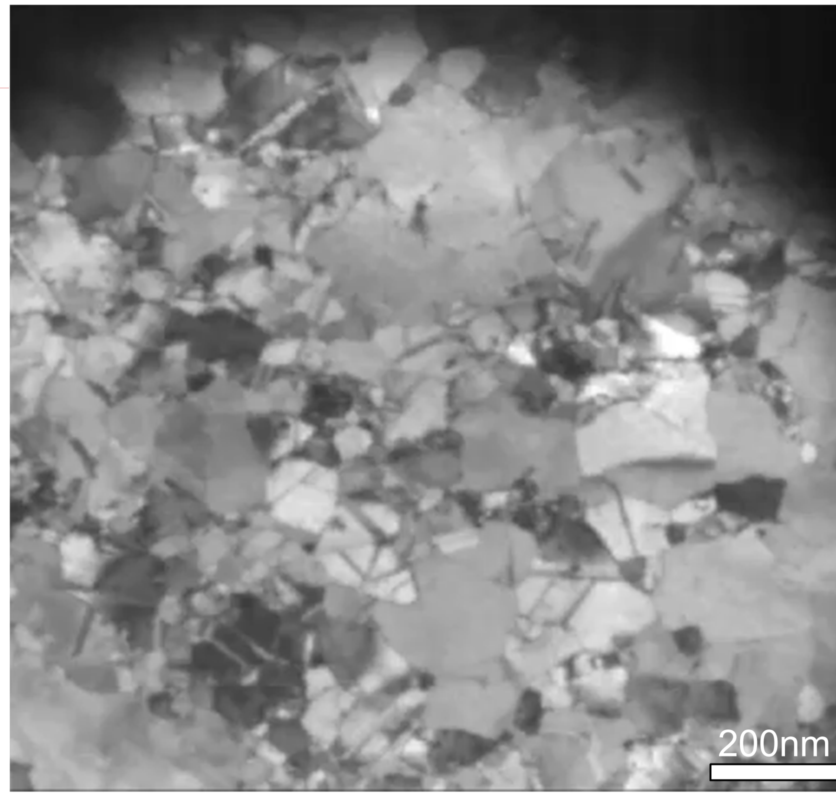
before



After (2 min @ 180°C)



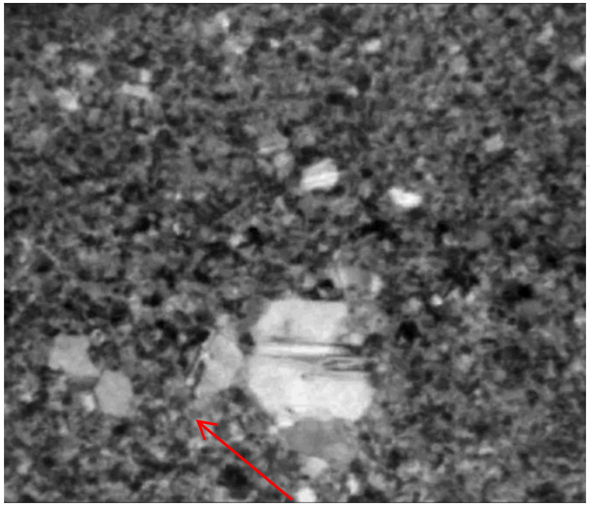
Speed in real time



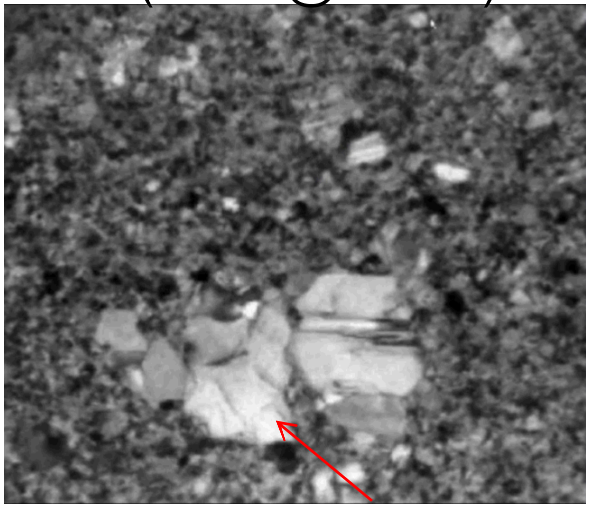
Sintering of Au-2%ZnO

Sintering movie

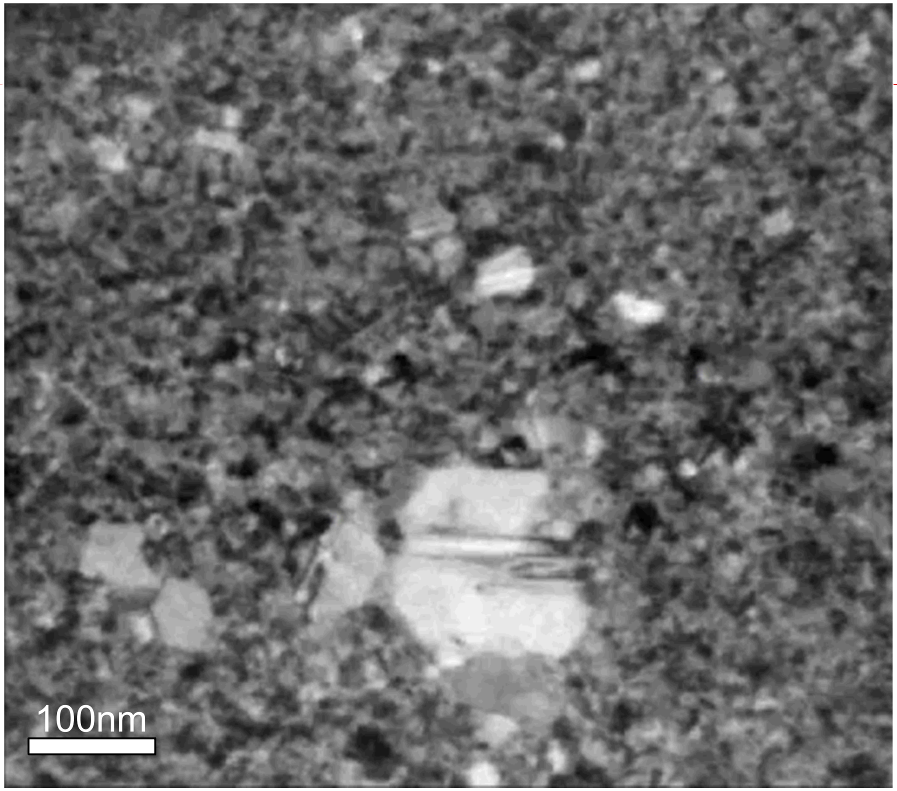
before



After (2 min @ 155°C)



Speed in 16X real time



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 nano-crystalline Au pinned by small amounts of ZnO
- Thermal stability of Au-ZnO(2 vol%) is significantly enhanced over pure gold and shows no surface layer formation which would impact electrical contact resistance.
- PVD processes are environmentally friendly compared with electroplating.

E3-1-9 Thursday 10:40 AM – Nic Argibay

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