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Process – Structure – Properties Relationship of Electrodeposited Au Thin Films used in Thermoelectric Power Generation Device

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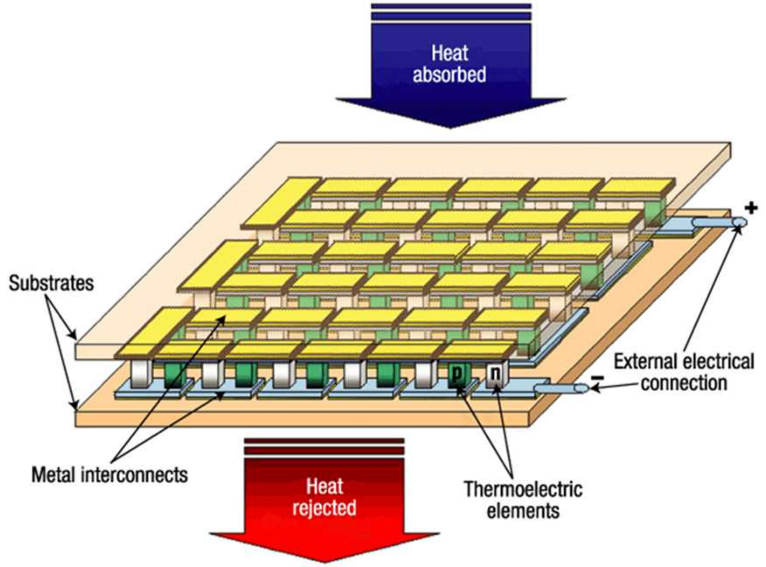
Purpose & Approach

- ❑ Develop an in-house S&T knowledge base for thermal mitigation and thermoelectric contact electrodeposition of the next generation high performance TE power source device.

- ❑ Understand how grain structure affects growth properties and performance of Au electrodeposits.

- ❑ Optimize <u>emissivity</u> and <u>electrical conductivity</u> through the formation of <u>twins</u> in Au films using pulsed electrodeposition.

Typical Thermoelectric Device



Nature Materials 2, 528 - 531 (2003)

Outline

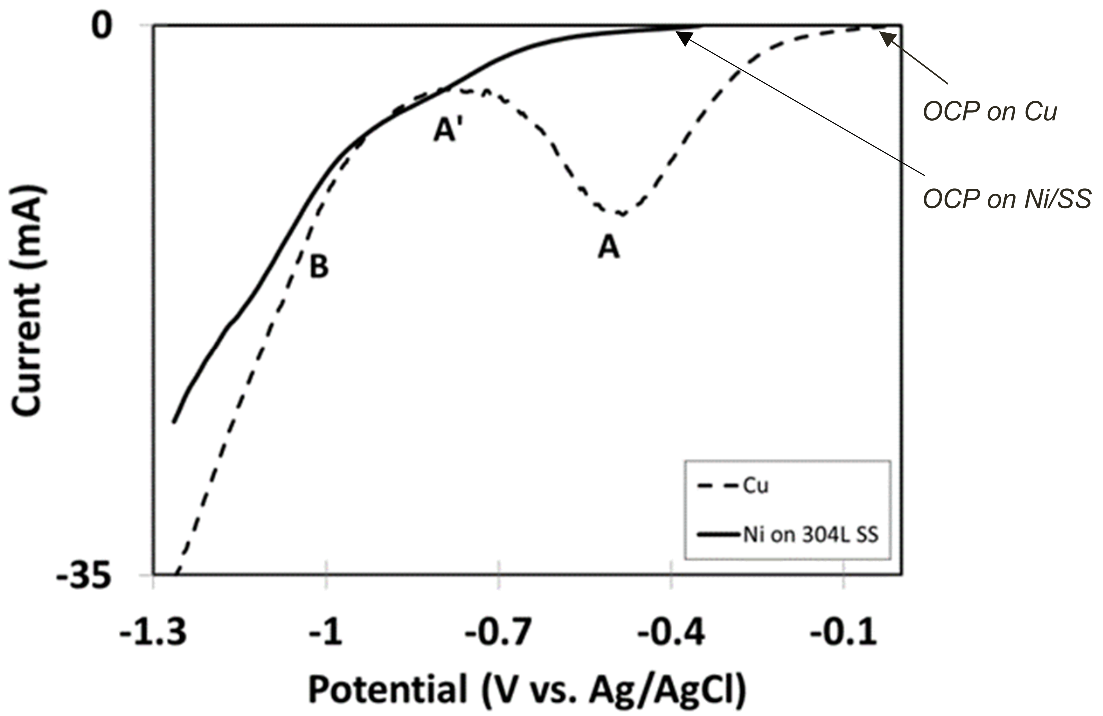
- Electrochemical analysis of Au electrodeposition
- Effects of applied potential on the microstructure, crystal structure and emissivity in DC electrodeposition
- Compare microstructure, properties and performance in DC and pulsed electrodeposition modes

Electrochemical Analysis of Au Electrodeposition

Bath Content and Conditions

- 0.03M of $KAu(CN)_2$
- Dequest 2000LC (containing amino trimethylene phosphonic acid)
- pH 4.6
- Temperature 120°F
- Agitation 150 rpm

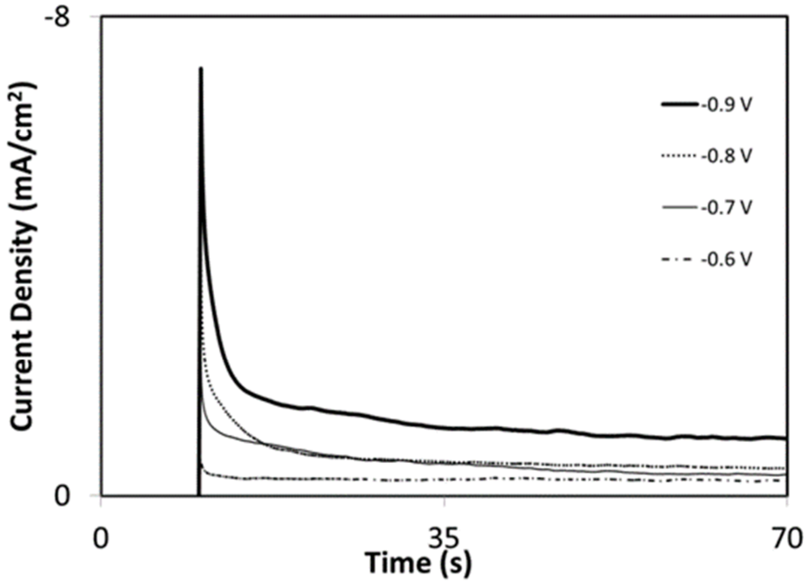
Linear Sweep Voltammetric I – E Curves at a scan rate of 50 mV/s



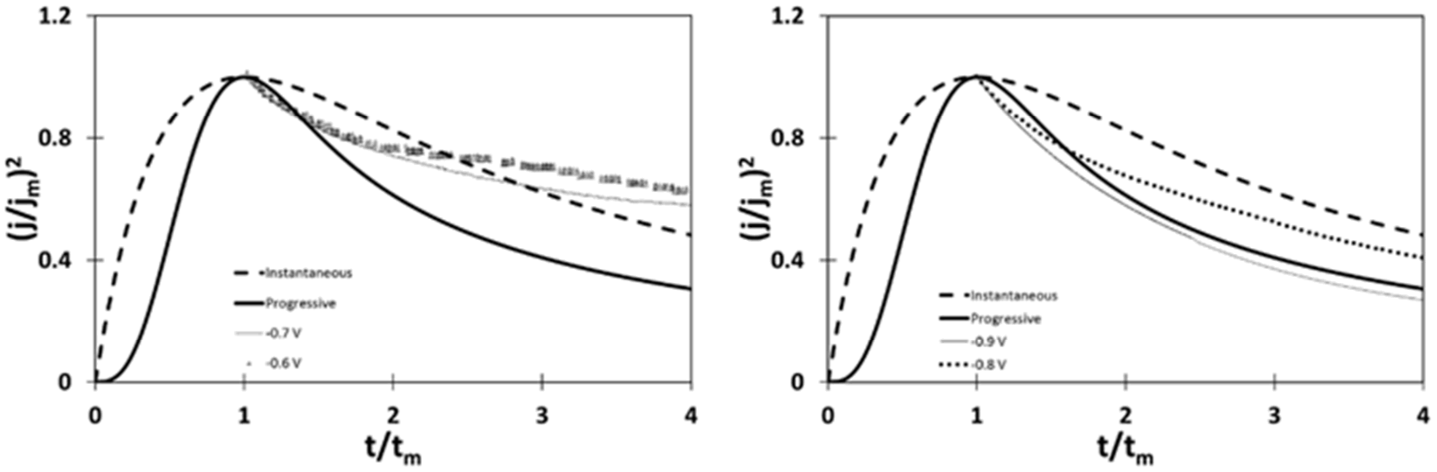
- Presence of two main Au reduction regions
- Cu more reactive than the Ni coated stainless steel

Electrochemical Analysis of Au Electrodeposition

Current Transients of Au Electrodeposition at Different Overpotentials on Ni/SS



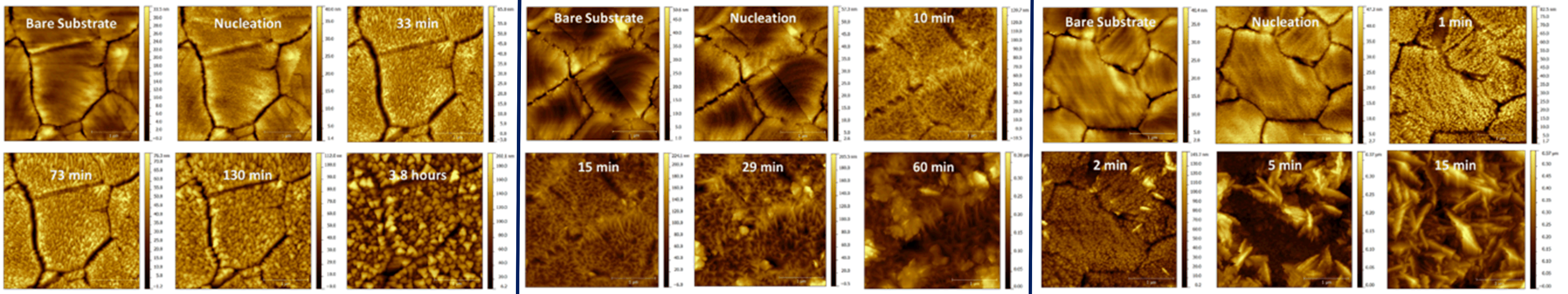
Non-dimensional Plots $(j/j_m)^2$ vs (t/t_m) of the Experimental Potentiostatic Current Transients and Theoretical Curves of Au Electrodeposition



- ❑ Instantaneous nucleation at -0.6 V and -0.7 V
- ❑ Progressive nucleation at large overpotentials

Electrochemical Analysis of Au Electrodeposition – In-situ AFM (contact mode)

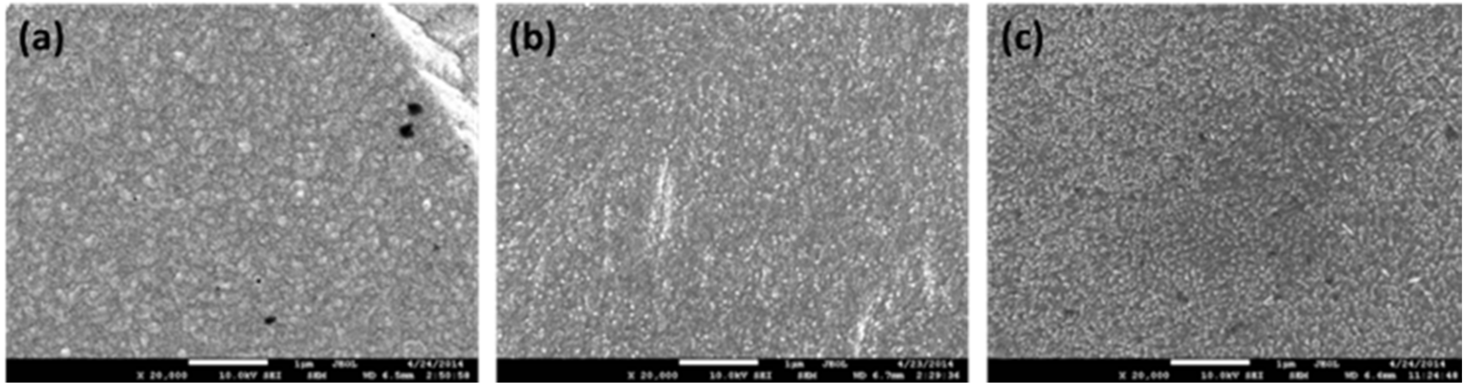
-0.7 V | **-0.9 V** | **-1 V**



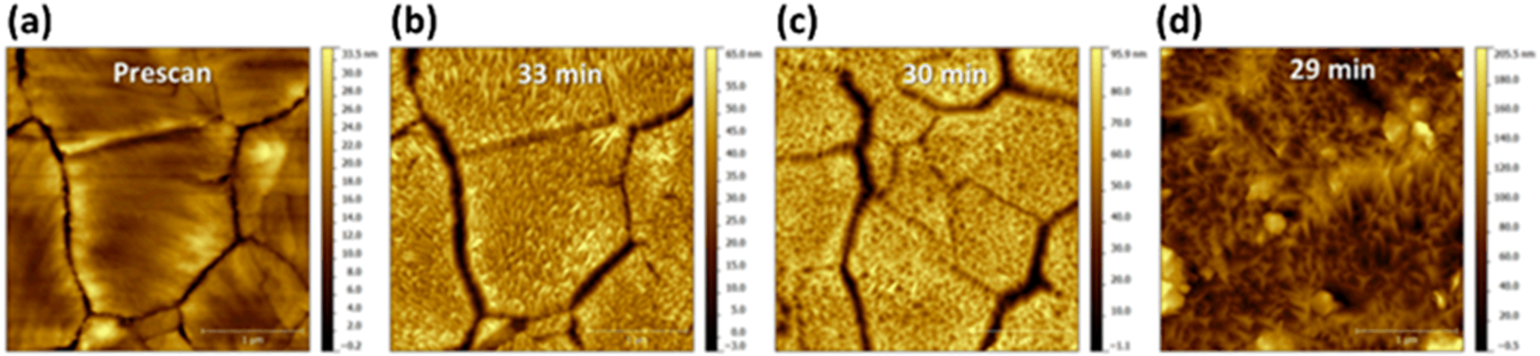
AFM confirmed the evidence of **instantaneous** nucleation at small overpotentials and **progressive** nucleation at large overpotentials in the Au bath

Effects of Applied Potential on the Microstructure

SEM Images of Au Films Electrodeposited on Ni/SS Sheets at (a) -0.7 V, (b) -0.8 V, and (c) -0.9 V



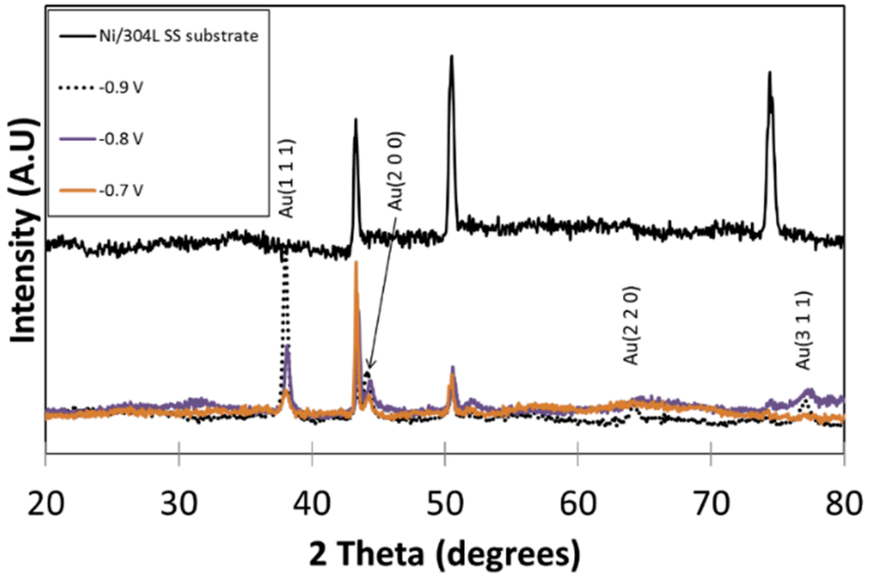
AFM Images of (a) an Evaporated Au on glass slide Substrate and Au Films Electrodeposited at (b) -0.7 V, (c) -0.8 V, and (d) -0.9 V



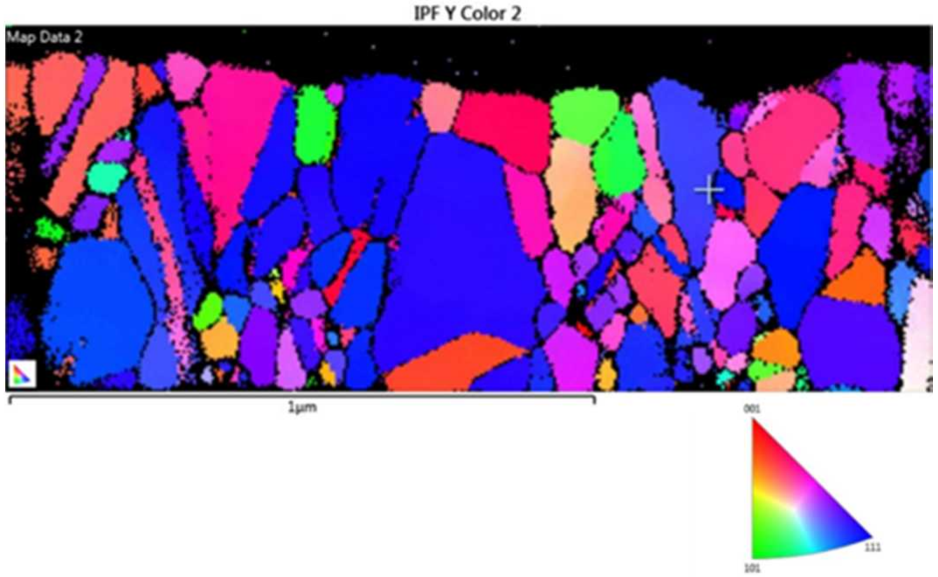
- ❑ Evidence of microstructural changes as a function of potential in both SEM and AFM
- ❑ Increase in surface roughness with increasing overpotentials visible in the AFM images

Effects of Applied Potential on the Crystal Structure

XRD Patterns of Au Films on Ni/SS at -0.7 V, -0.8 V and -0.9 V

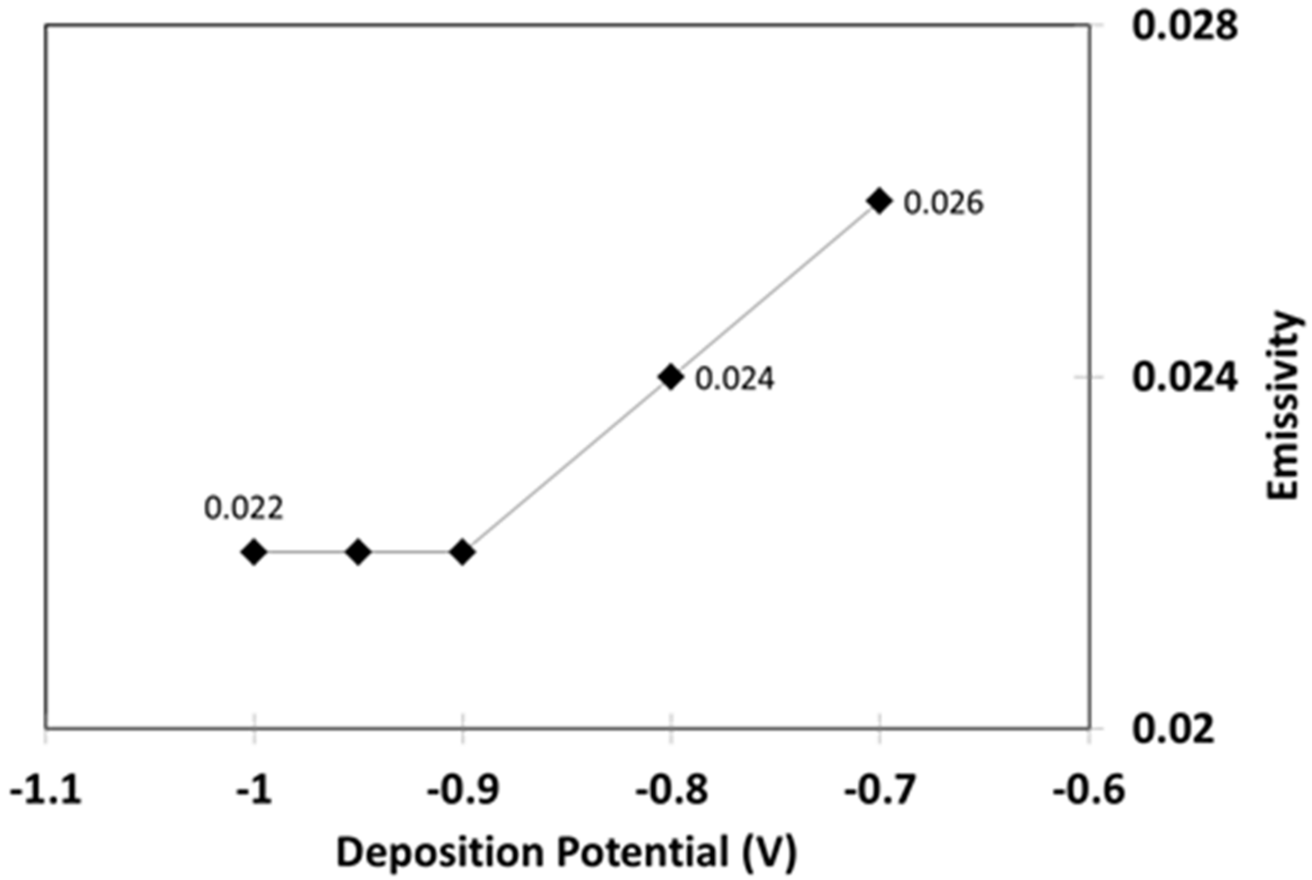


EBSD of Au Film Electrodeposited Ni/Si Wafer Substrate at -0.9 V. Inset: The orientation color key



- Strongly textured and polycrystalline structures
- Improved crystallinity at increasing overpotentials
- Confirmation of the <111> textured microstructure in the growth direction
- Presence of irregular size grains in the film

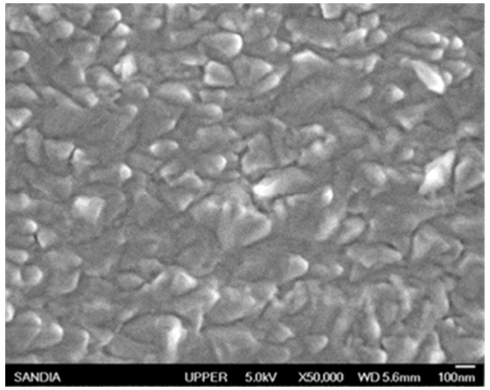
Effect of Applied Potential on Au Emissivity



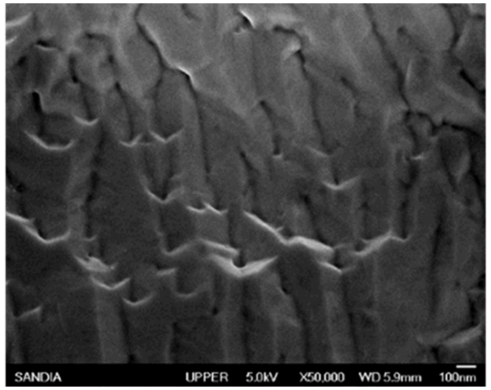
Emissivity decreased with more negative overpotentials attesting to improved microstructure and crystal structure at those potentials.

Surface Structure Comparison of Direct and Pulsed Au Films Electrodeposited on Ni/SS (-0.9 V) – SEM

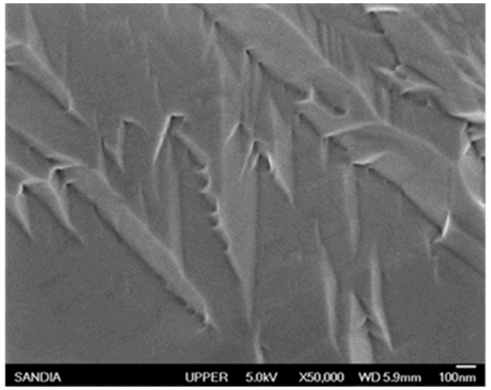
DC



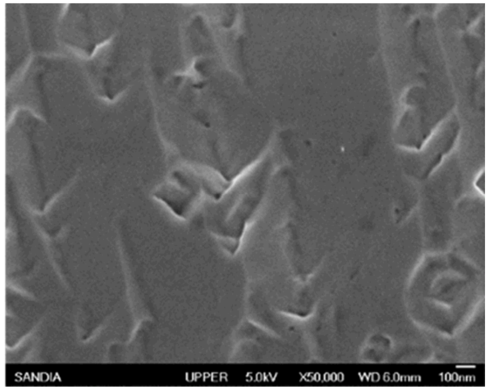
PC – 1ms t_{on}



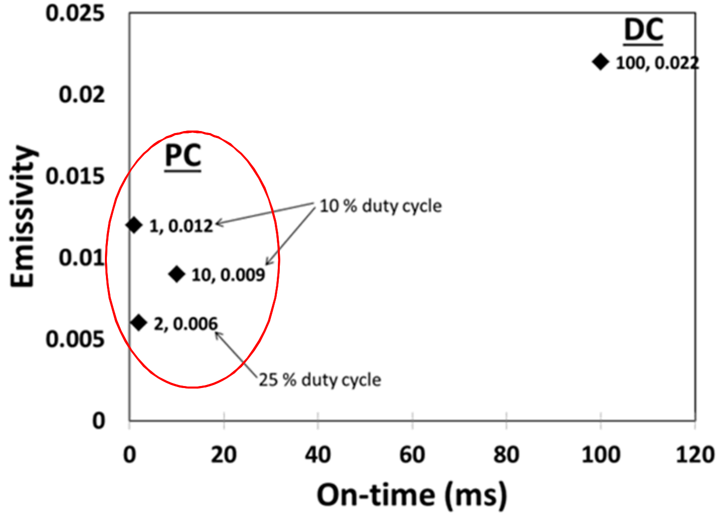
PC – 10ms t_{on}



PC – 100ms t_{on}



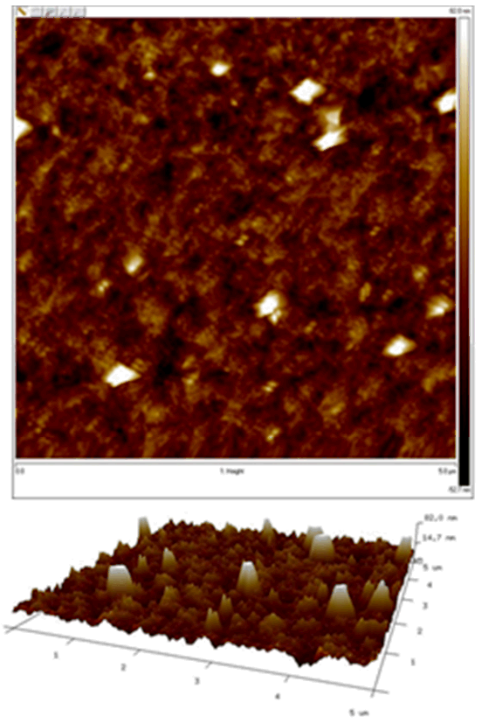
Emissivity



- ❑ Surface smoothing in pulsed films
- ❑ Improvement in emissivity in pulsed films
- ❑ Smooth surface structure known to improve emissivity

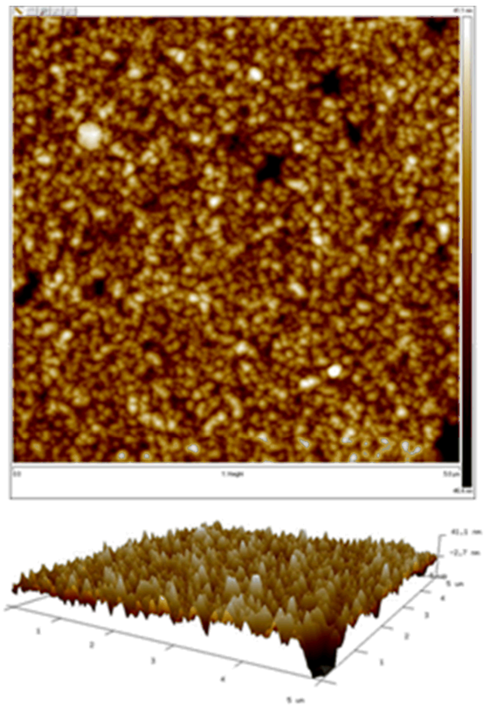
Surface Structure of DC vs PC Au Films Electrodeposited on Au on Glass (-0.9 V) – AFM

DC



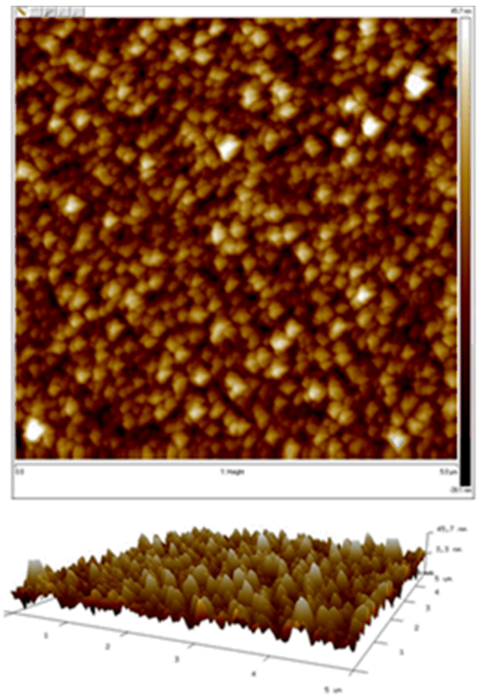
Rq = 15.7 nm
Ra = 10.9 nm

PC – 2ms t_{on}, 25% dc



Rq = 11.5 nm
Ra = 8.72 nm

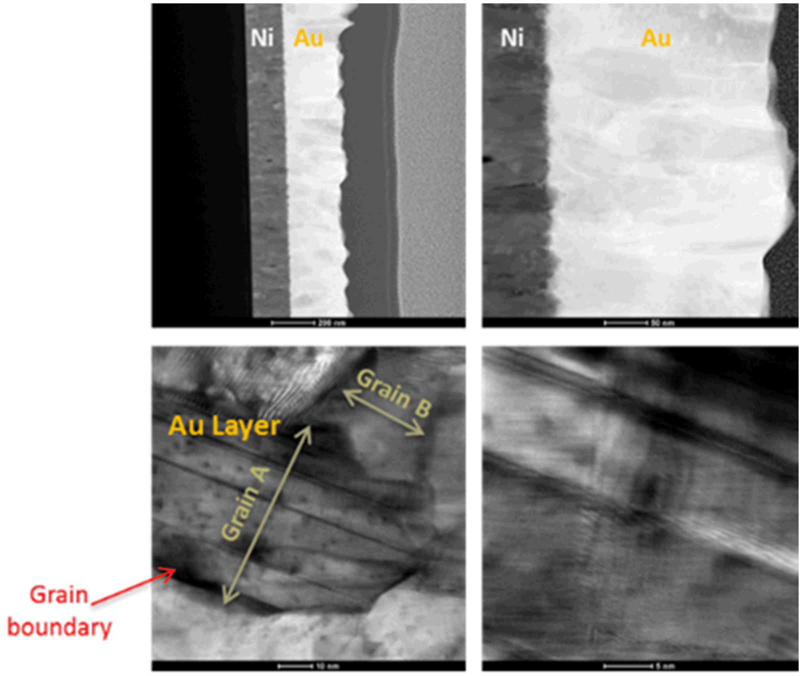
PC – 10ms t_{on}, 10% dc



Rq = 12.2 nm
Ra = 9.61 nm

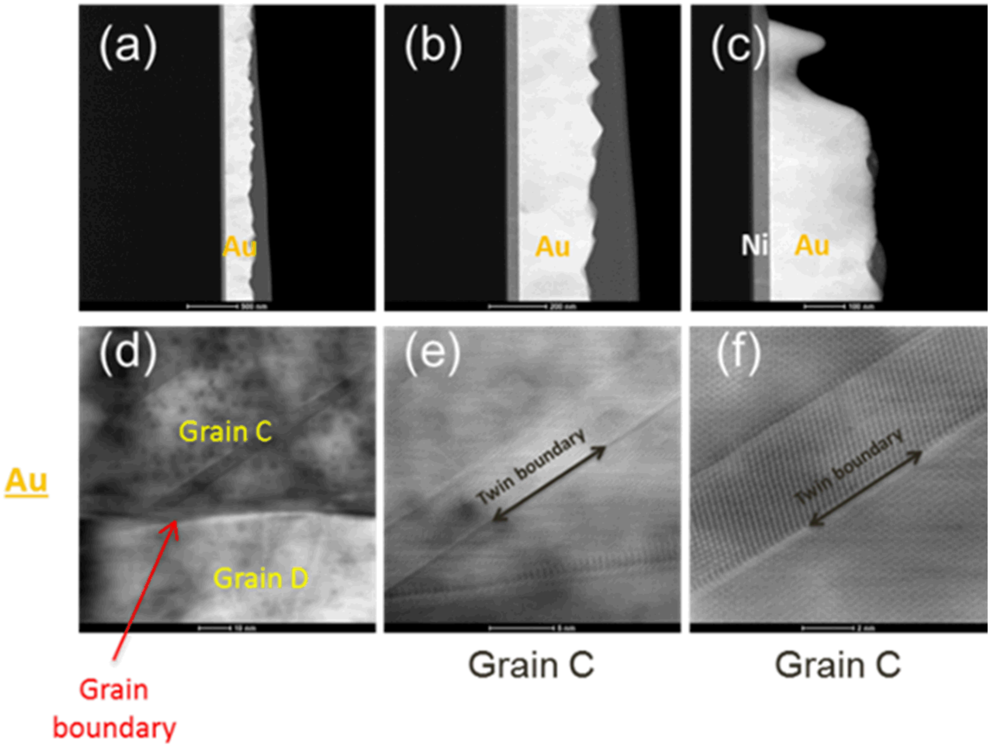
Bulk Microstructure of DC vs PC Au Films – HR-TEM

DC -0.9 V



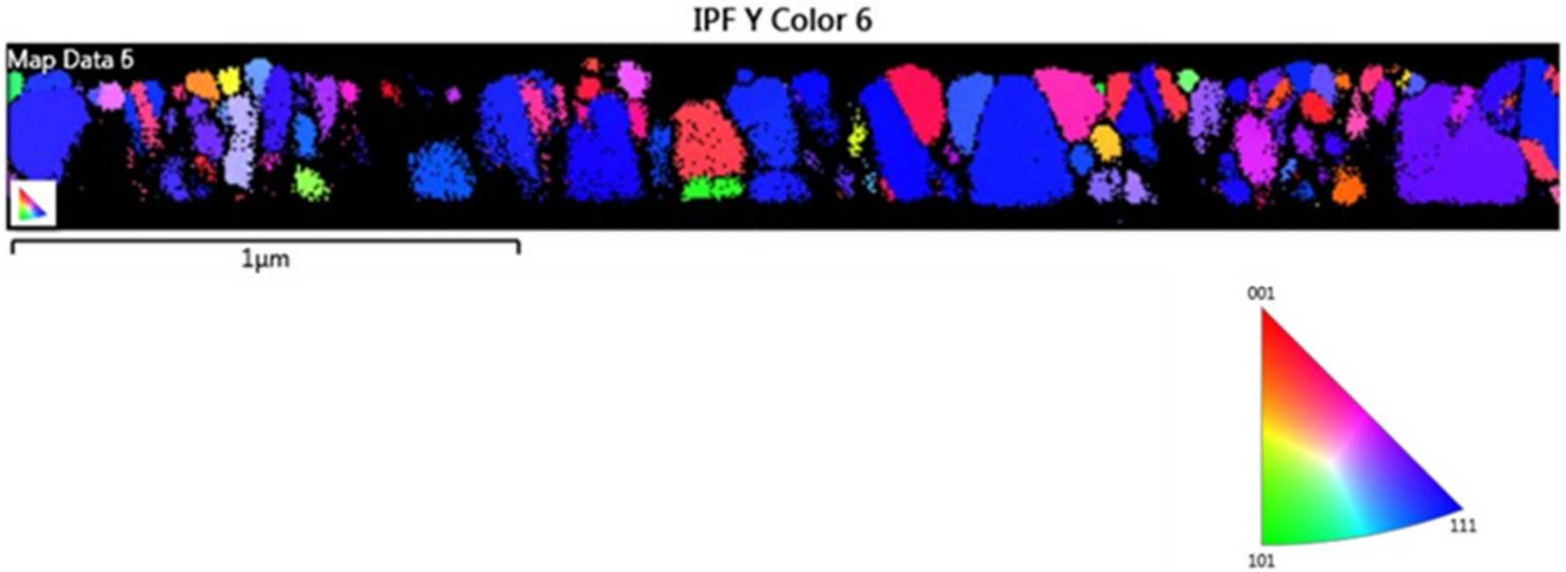
Grain A

PC -0.9 V, 10ms t_{on}, 10% dc



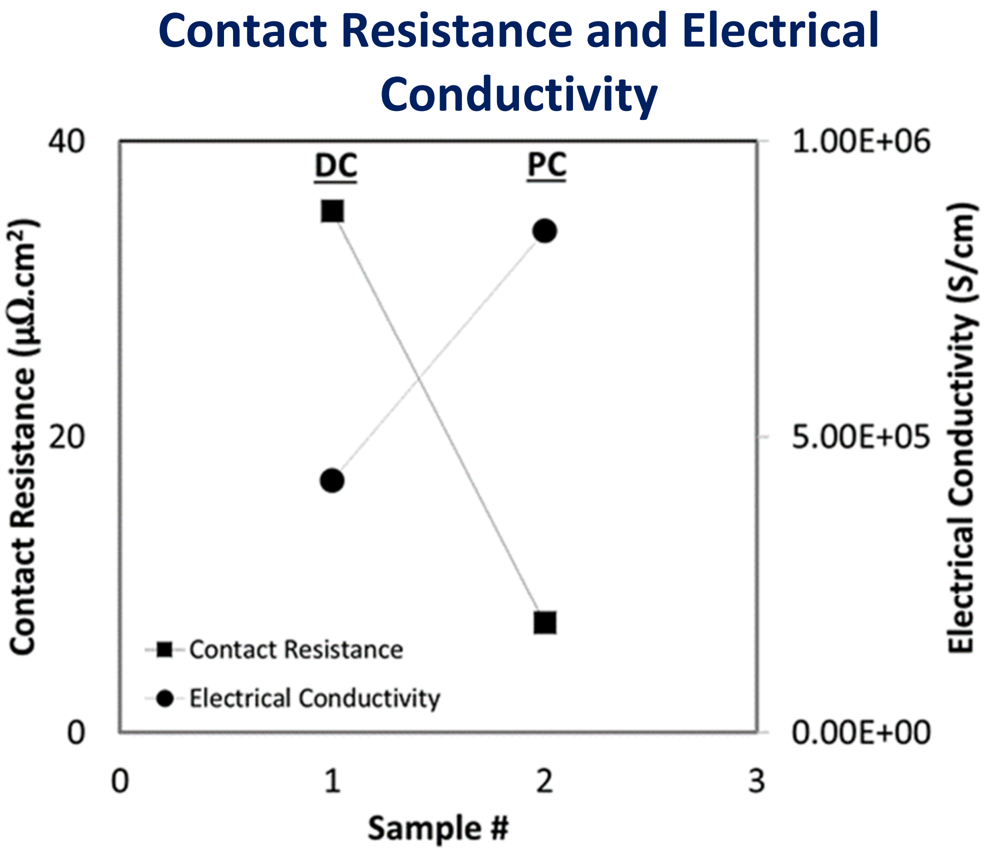
- ❑ Porous free bulk microstructure and clean interface with Ni adhesion layer in both DC and PC films
- ❑ Evidence of highly crystalline atomic structure in the interior of grains and the presence of twins in both DC and PC films
- ❑ Clear indication of more perfectly coherent and atomically sharper nanoscale twins in the PC film
- ❑ Highly crystalline atomic structure is present in interior of the grain in the pulsed film.

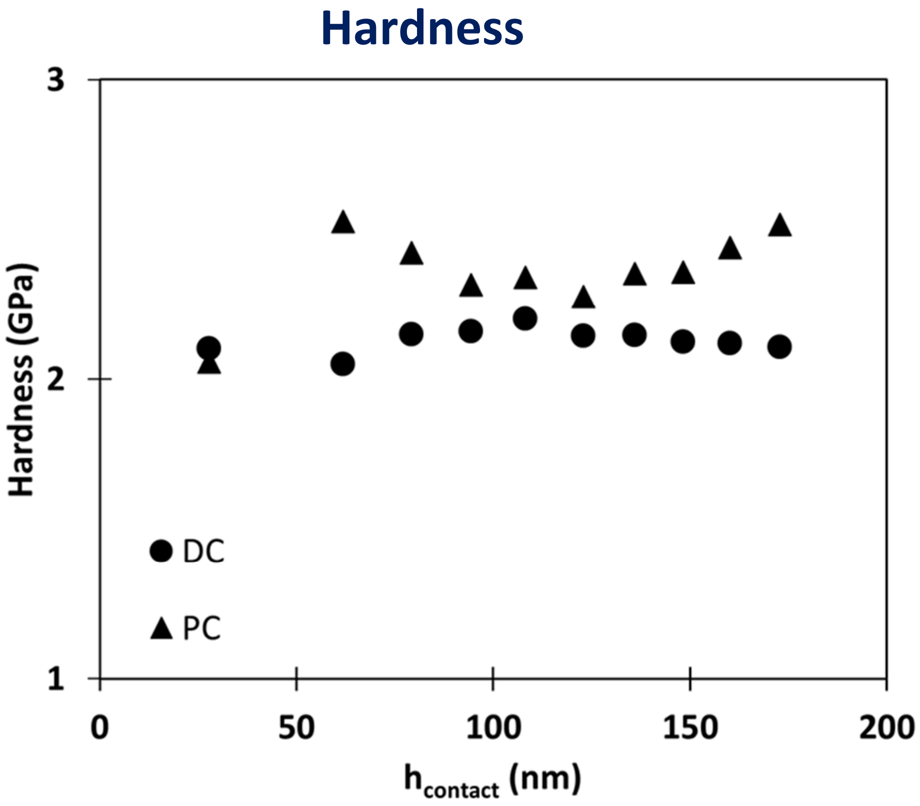
Crystal Structure of the PC Au Film (-0.9 V, 10ms t_{on}, 10% dc) – EBSD



- ❑ Evidence of the existence of a high degree of texture in the deposit
- ❑ Predominance of <111> texture in the pulsed film
- ❑ Presence of irregular shaped, different size and finer sized grains in the bulk microstructure of the film.

Properties of DC vs PC (10 ms t_{on}, 10% duty cycle) Au Films – -0.9 V





Contact resistance, electrical conductivity and hardness improved in the pulsed films

Conclusion

- Both instantaneous and progressive nucleation growth modes can be achieved depending on the overpotential used during Au electrodeposition.
- The use of large overpotentials in DC electrodeposition produced films with improved microstructure and properties.
- Enhanced microstructure, properties and performance were obtained during pulse electrodeposition by successful growth of smooth, porous-free, highly crystalline, strongly textured, low emissivity, reduced contact resistance, high electrically conductive, mechanically strong Au films containing perfectly coherent and atomically sharp nanoscale growth twin boundaries.