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Understanding and Predicting Metallic Whisker Growth as a Function of Electrodeposited Morphology

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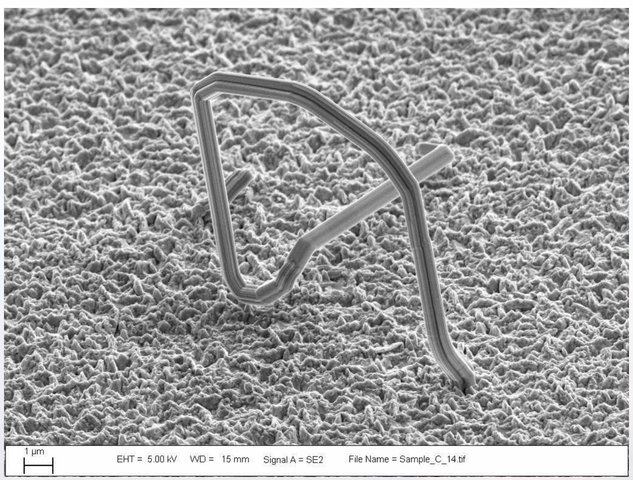
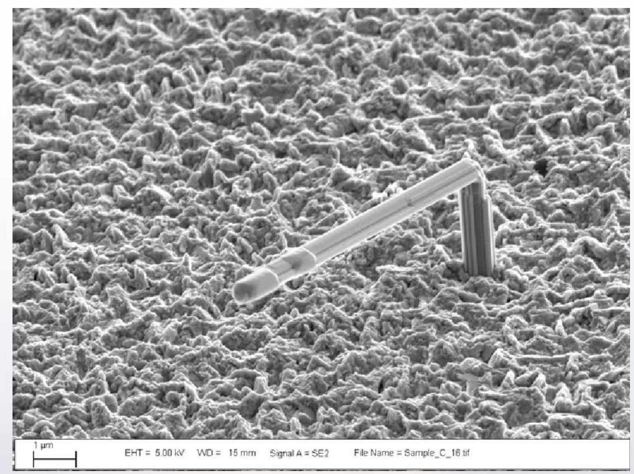
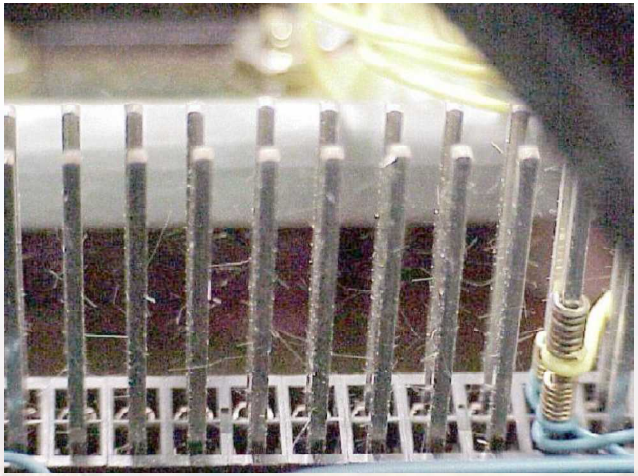




Outline

- Introduction
- Metallic Whiskers
- Experimental details of Electrodeposition
- Electroplating conditions that promote whisker growth
- Electroplating conditions that help retard whisker growth
- Electroplating conditions that help suppress whisker growth
- Conclusion



GE Power Management, *Technical Service Bulletin: Tin Whiskers in MOD10 Relays*, March 27, 2000. (http://www.geindustrial.com/pm/support/dls/dlssb01.

Introduction: *Sn whiskering has become a major concern for the 21st century*

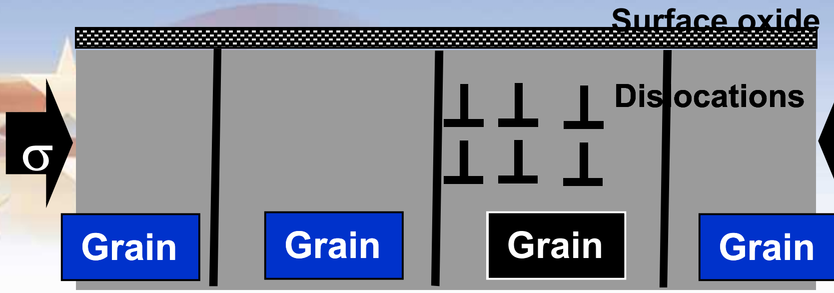
- **History of Solders**
  - Gold-based hard solders: Egypt (3600 BC), Ur (3400 BC), Greece (2600 BC)… (20 AD) Latolita Indians of South America.
  - Soft-solders **Pb-Sn**: King Tut's tomb, Egypt (2000 BC), pluming in Rome (350 BC)
  - Greece (250 BC), solders for water pumps, air pumps
  - 1800's Oxy-gas torch electric soldering (Industrial Revolution)
  - 1946 Major failure of Bell Telephone's equipment
  - *1980's Fundamental study of solder metallurgy (Silicon age)*
- **Role of Lead in Sn solders**
  - Pb lowers the melting temperature for Sn alloys
  - Increasing Pb, decreases electrical and thermal conductivity
  - Pb lowers surface tension
  - *Big impact on mechanical properties (optimum 63Sn37Pb eutectic)*
- **Driving force for Lead-free solders (April 1993 Lead Exposure Red. Act)**
  - Pb listed as one of top 17 chemicals that impose greatest threat to human health
  - Disorders of nerves and reproductive system
  - Delayed neurological and physical development
  - Reduced production of hemoglobin
- **Worldwide users**
  - Total consumption has only *dropped slightly* since 1990's
  - Electronic industry accounts for ~0.4%
  - Storage batteries accounts for ~91%

Metallic Whiskers: *if electrodeposition is the method of application, then it is important to understand the effects of the deposition parameters*

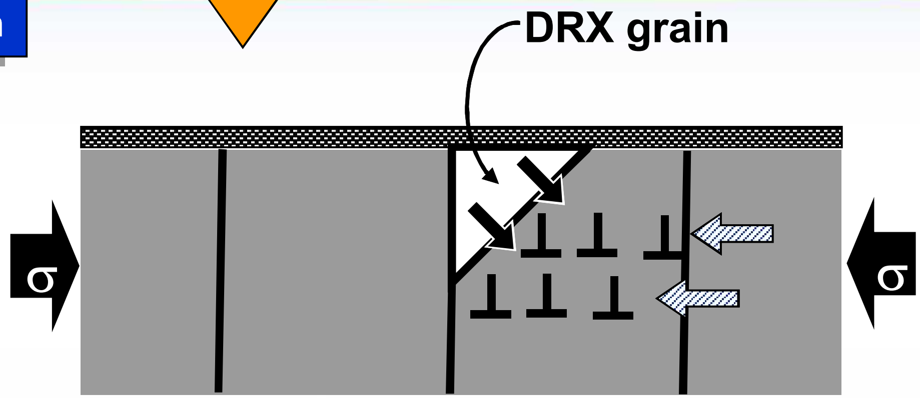
- **What are metallic whiskers?**
  - Whiskers are single crystals
  - Whiskers can change growth direction but remain a single crystal
  - If whiskers are single crystals
  - Then: Angle between singles must be related to angles between crystallographic planes or directions
- **Common metals known to whisker**
  - Sn, Zn, Ag, and Au.
- **What is the driving mechanism (proposed)**
  - P.T. Vianco and J.A. Rejent: **Dynamic Recrystallization (DRX) as the Mechanism for Sn Whisker**

Investigation of Dynamic Recrystallization (DRX) as the Mechanism for Sn Whisker Development – Part I: Model Development

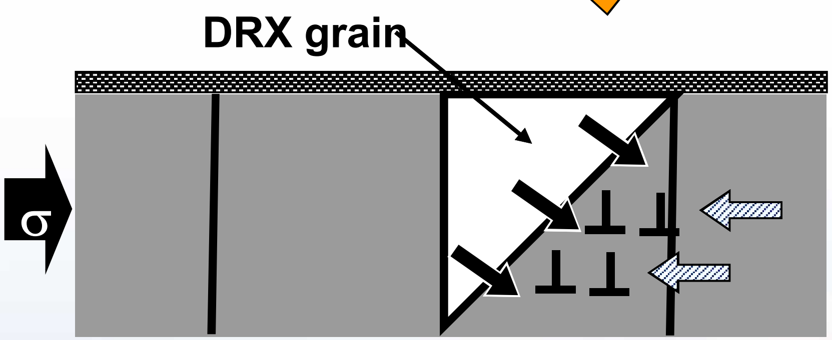
P.T. Vianco and J.A. Rejent



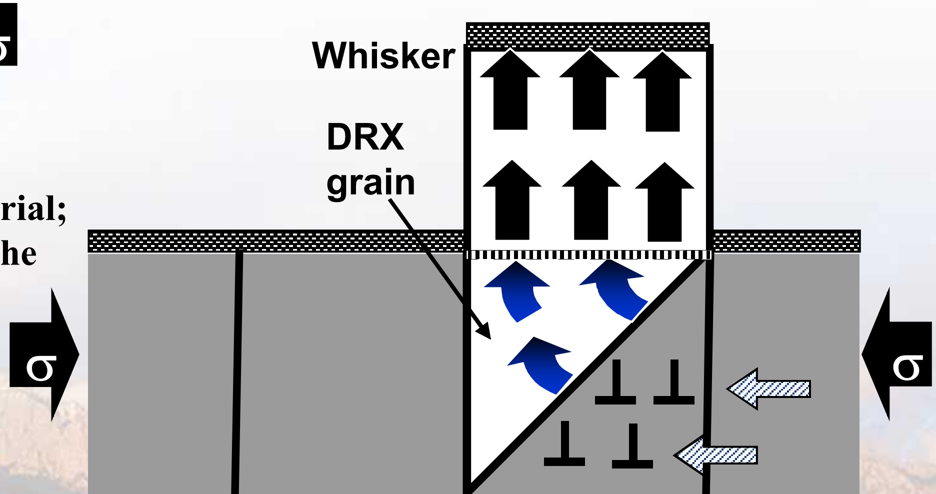
(a) Dislocations are created by the applied stress and pile up at the grain boundary.



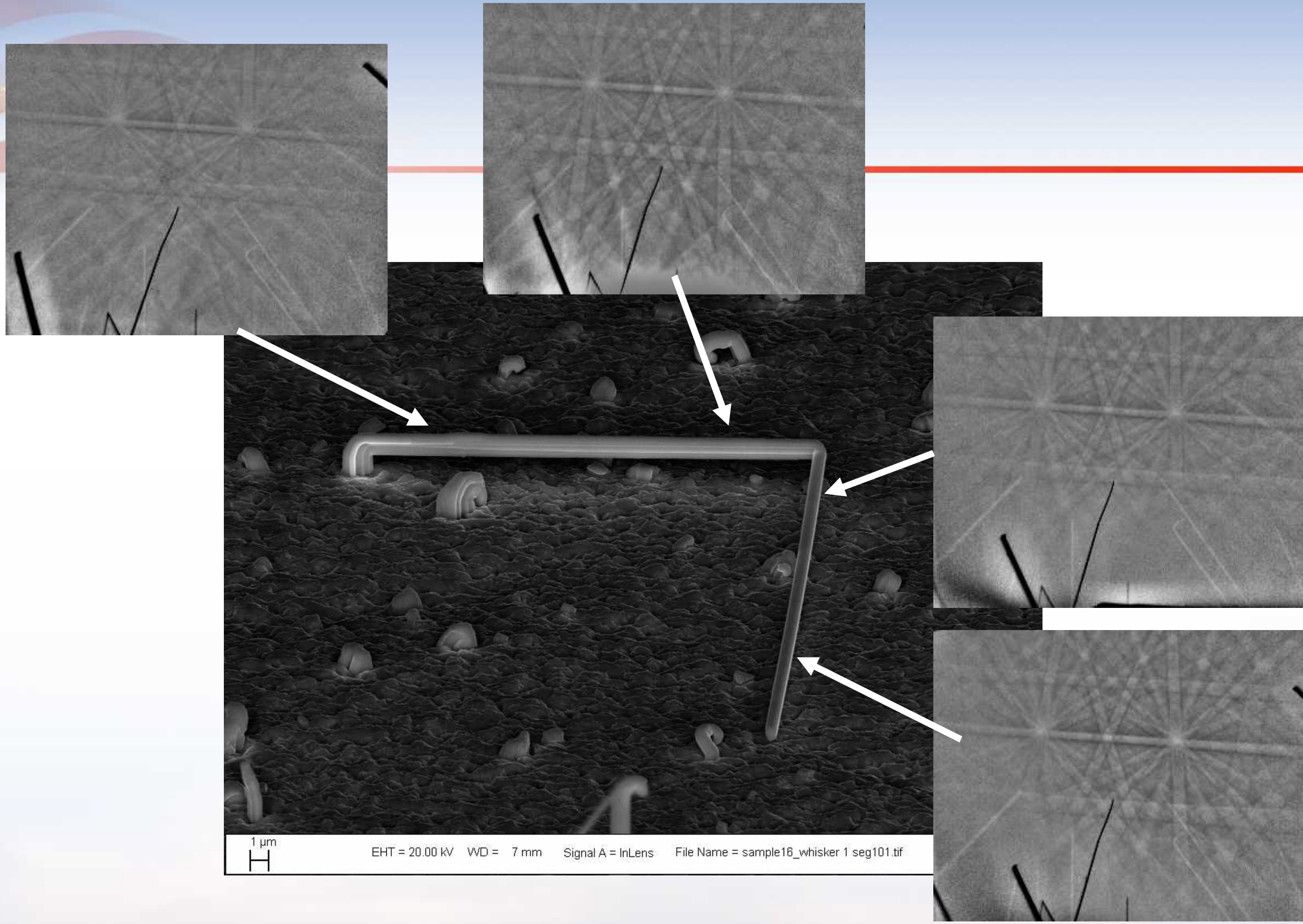
(b) DRX begins at the boundary, creating a new grain that begins the growth stage.



(c) New grain boundary grow into the deformed material; the release of strain energy as the driving force for the DRX grain growth.

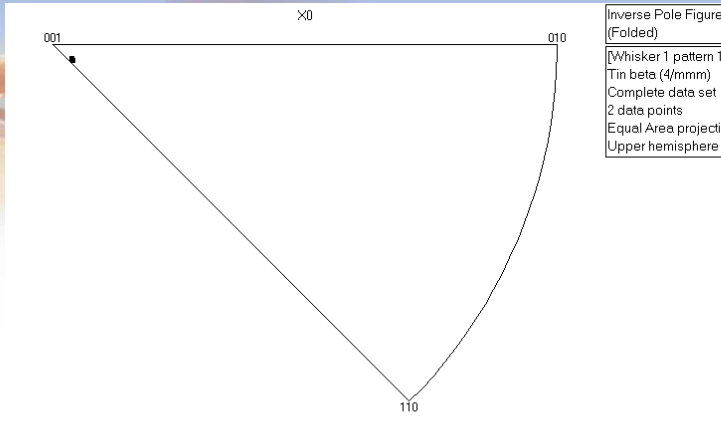


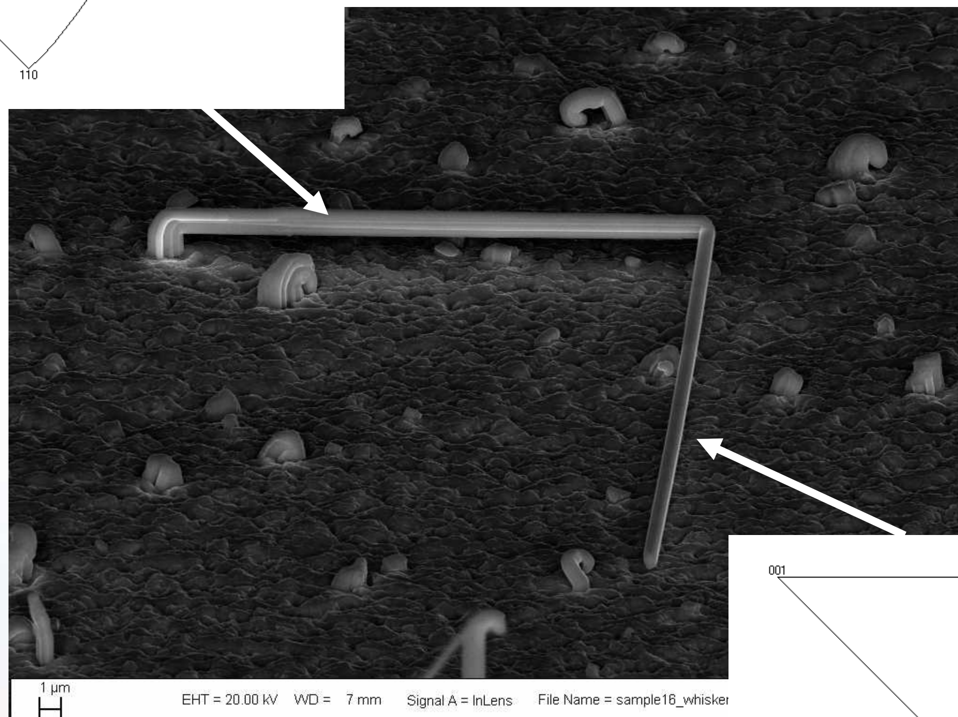
(d) Once the new grain's size is commensurate with other grains, there is a constraint on further growth *into the material*.

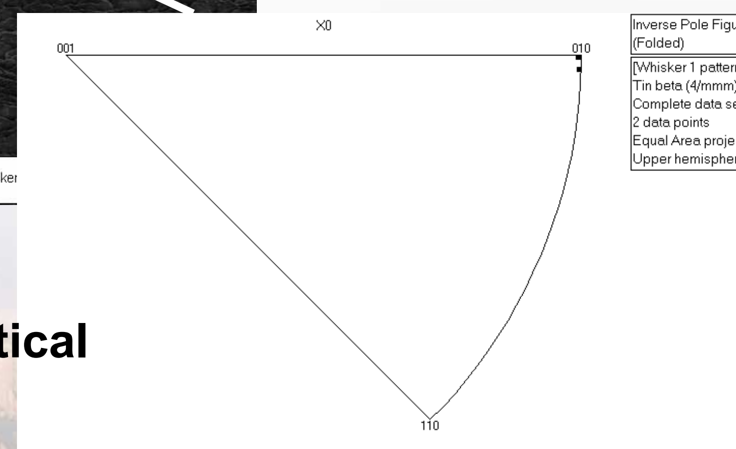


Whisker on sample 16 – Single crystal

Growth axis for horizontal segment is [001]







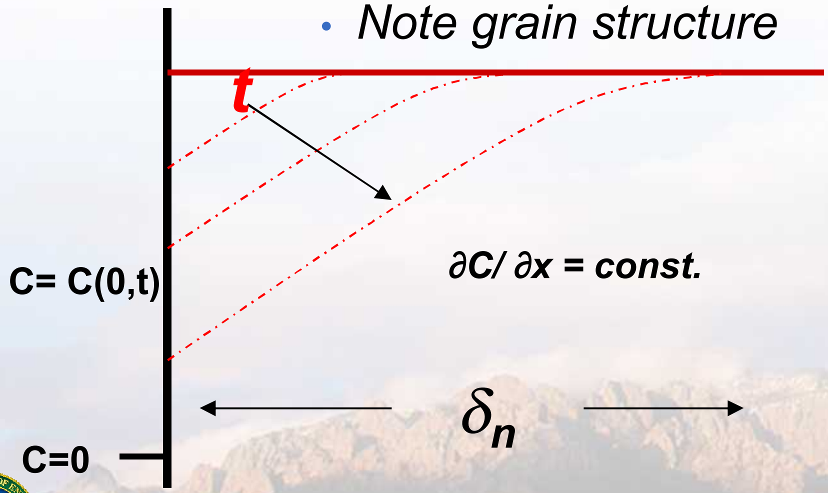
Growth axis for vertical segment is [010]

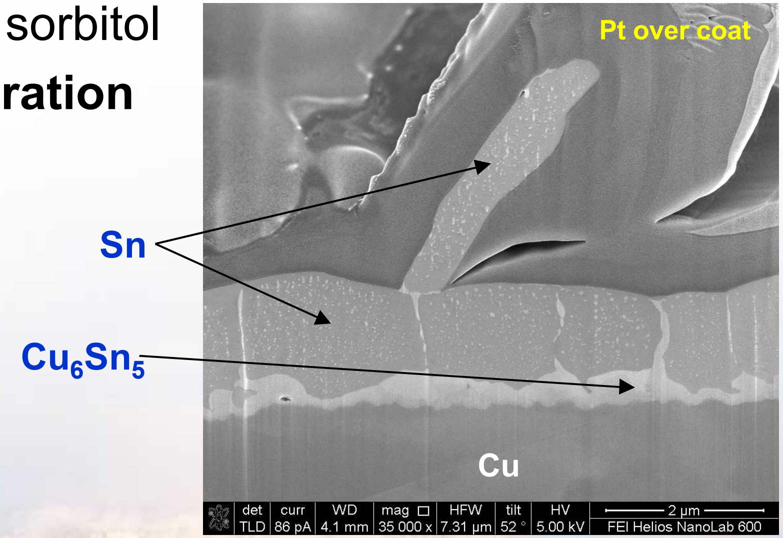
Experimental details of Electrodeposition

- **Chemistry: acid vs. alkaline systems**
  - Both are subject to hydrolysis causing problems with co-deposition
  - Alkaline systems provide greater throwing power (better uniformity)
  - Deposits from alkaline systems occur at very neg. potentials evolving hydrogen which helps leveling
- **Sodium vs. Potassium alkaline based systems**
  - Two systems: Na stannate/NaOH or K stannate/KOH
  - Cathode efficiency: increase w/temp. lower for Na (50% @ 75ºC); K better (75% @90ºC)
  - Solubility of potassium stannate is greater (K-based increases with temp., Na-based decrease w/temp.)
  - Conductivity: since K+ has greater mobility, plating solutions are more conductive
  - Cathode (main) reduction pH>13 $[Sn(OH)_6]^{2-} + 4e^- $ » $ Sn + 6OH^-$

Electroplating conditions that promote whisker growth: *Controlled Current (Galvanostatic mode)*

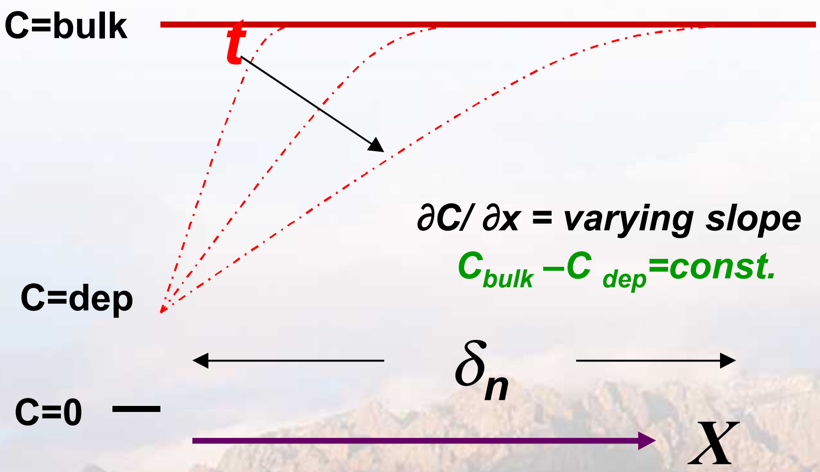
- **Electrochemical driving conditions** (OCP~-450 mV, N2 purge, Pt counter, Cu working)
  - -0.5 to -30 mA/cm^2
  - RDE (5 mm) @ 1000 rpm
  - 10 to 30 minutes
  - RT to 70ºC
  - Some deposits with 3.6 mM sorbitol
- **Possible mechanism of generation**
  - *Note grain structure*

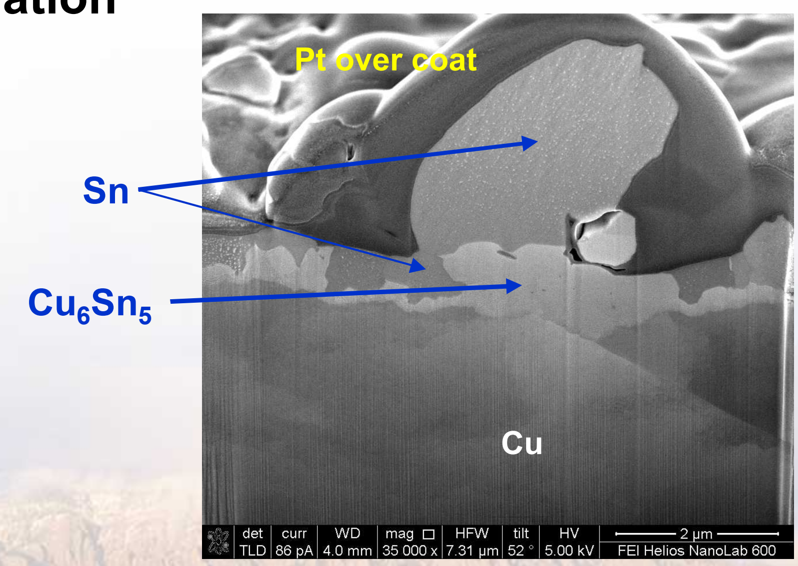




Electroplating conditions that promote whisker growth: *Controlled Potential (Potentiostatic mode)*

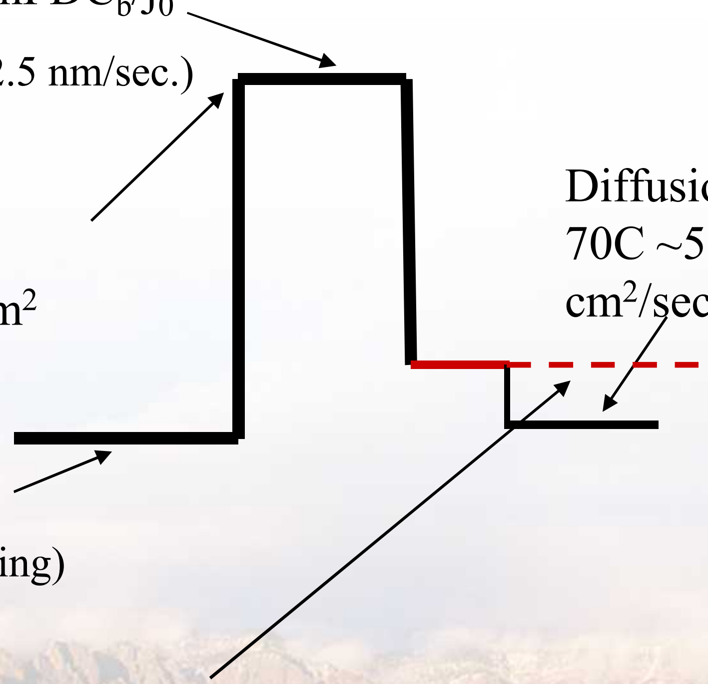
- **Electrochemical driving conditions**
  - -1900 to 2400 mV vs. ref [Hg:HgO 0.1 M NaOH, 926 mV vs. NHE]
  - RDE (5 mm) @ 1000 rpm
  - 10 to 30 minutes
  - RT to 70ºC
  - Some deposits using 3.6 mM sorbitol (provide brightening/leveling)
- **Possible mechanism of generation**
  - *Note grain structure*





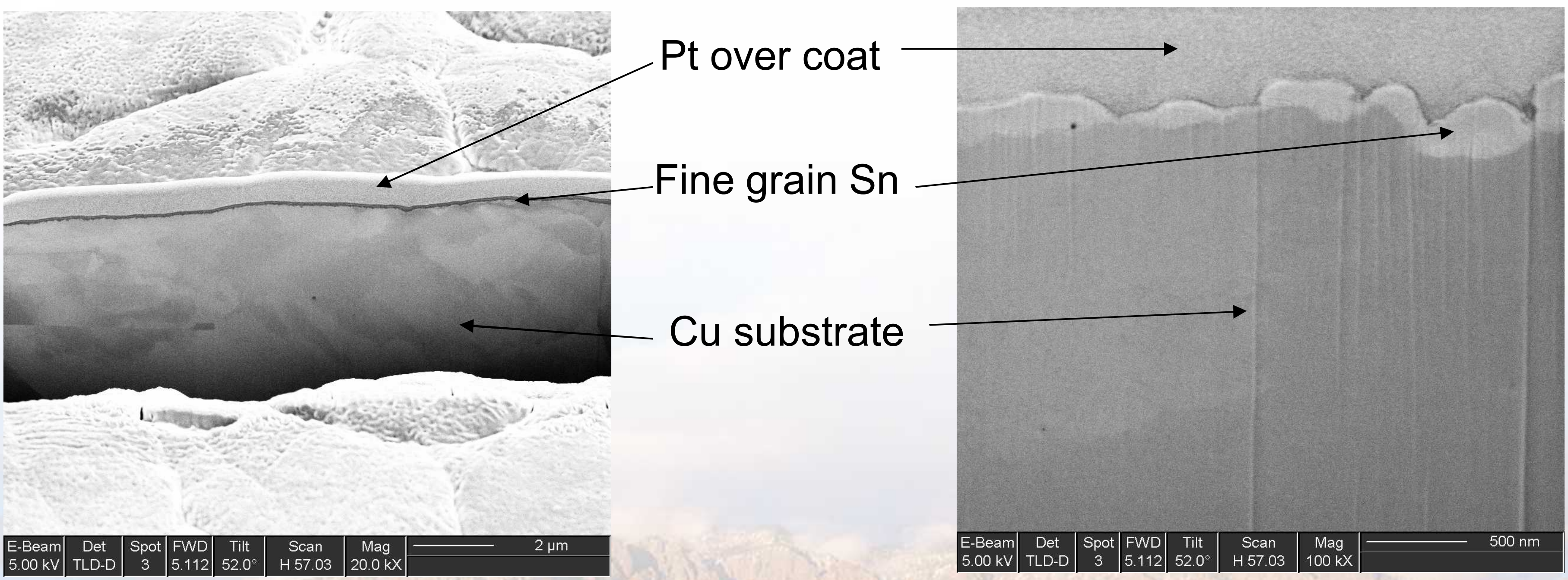
Experimental details for pulse Electrodeposition

- **Deployment parameters for pulse deposition dynamics**
  - Kinetic vs. Diffusion limits



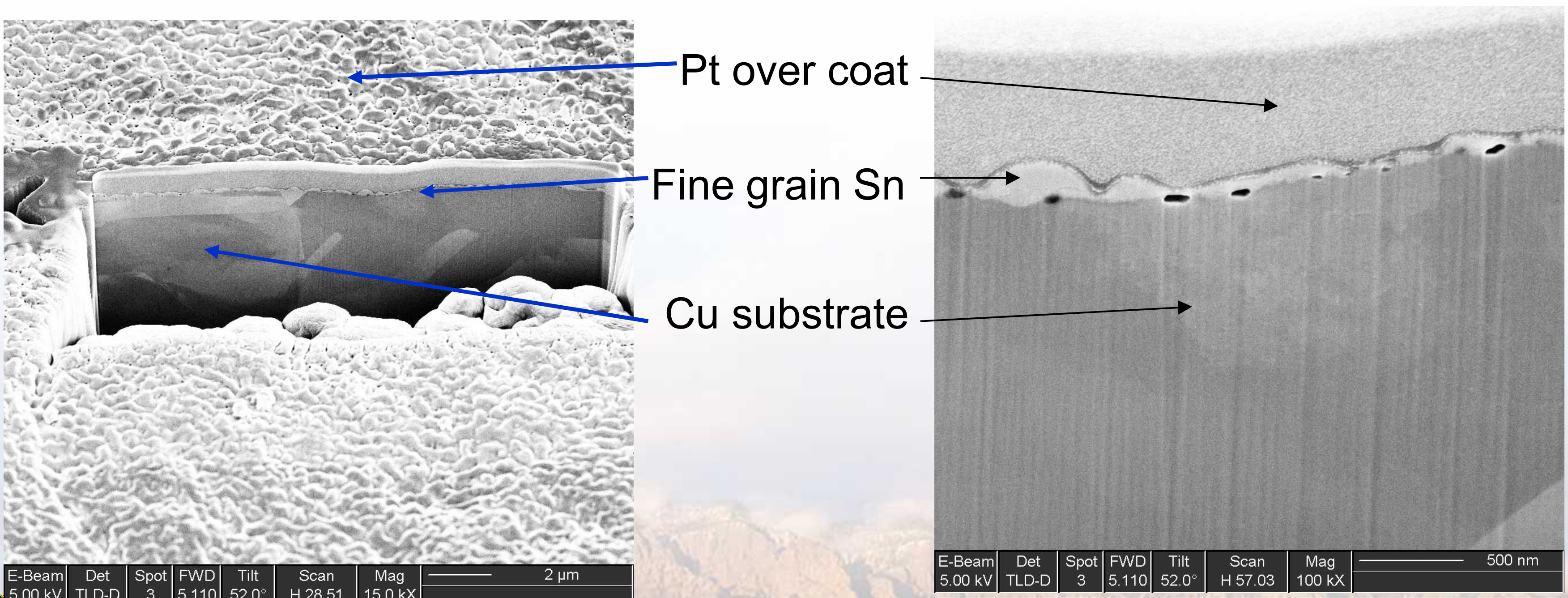
Electroplating conditions that retard whisker growth (Galvanostatic mode)

- **Pulse plating additive free systems**
  - 70ºC, no additives, -2mA for 100 msec, 0 mA for 250 msec.
  - Total cycles 400, very thin deposit (conditions for high residual surface stress)



Electroplating conditions that retard whisker growth (Potentiostatic mode)

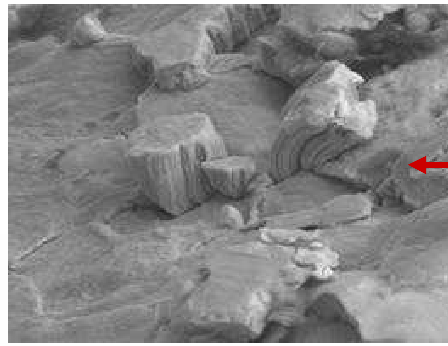
- **Pulse plating additive free systems**
  - 70ºC, no additives, -1800 mV vs. Hg:HgO for 100 msec, -1350 mV for 250 msec.
  - Total cycles 400, very thin deposit (conditions for high residual surface stress)



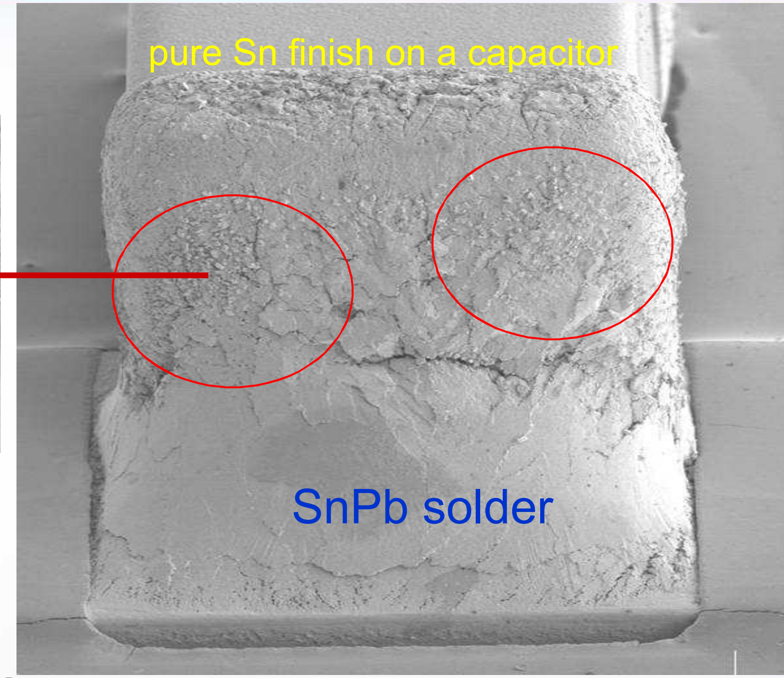
Electroplating conditions that suppress whisker growth

- **Additives (old system) SnPb**

Capacitors soldered with SnPb solder:
750 thermal cycles
No whiskers in "Pb-alloyed" Regions
-remaining pure Sn regions showed short nodules/whiskers



Sn nodules/whiskers



- **New co-deposition alloys/additives,**
  - Tin/Bismuth (52Sn48Bi)
  - Tin/Silver (96.5Sn3.5Ag)
  - SnBiAg, SnInAg
  - SnBiAgCu, SnAgSbBi

Candidates to replace eutectic solders (Tin/Bismuth and Tin/Silver)

  - ppm levels of Bi appears to suppress whiskers

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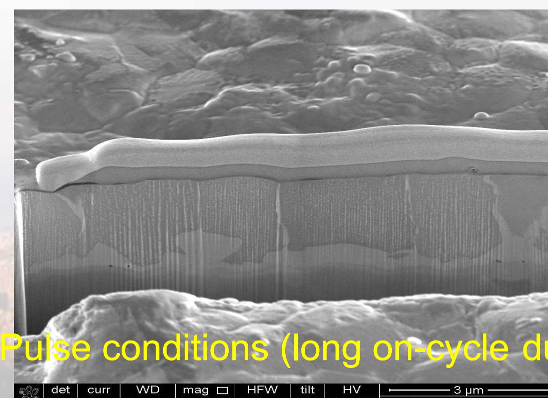
Conclusion

- **History**
  - Long history grown dependent on SnPb properties
- **Binary/Ternary/Quaternary lead-free candidates**
  - Numerous candidates possible, but difficult to replace the performance of SnPb
- **Pure Tin**
  - Necessary to understand ***fundamental*** coating properties
  - DC plating conditions (additive-free) appear to ***promote*** whisker growth (often within days)
  - Pulse plating conditions appear to ***retard*** whisker growth
    - Of over 40 samples pulse-plated a few (very long cycle ca. 25 sec) have grown some whisker after 7 months

DC (galvanostatic conditions)



Pulse conditions (long on-cycle durations)

Acknowledgments

- **SEM:** *Bonnie McKenzie (1822 Materials Characterization)*
- **FIB:** *Michael Rye and Garry Bryant (1822 Materials Characterization)*
- **Plating/electrochemical analysis :** *Natalia Gurule and Laura Montoya (01725 Photonic Microstructure Technol.)*
- **LDRD # 09-130800**

- **Future work**
  - Temperature depend whisker growth
  - Whisker growth dependence on grain-size
  - Whisker growth dependence on residual film stress