Exploring the Engineering of Copper Grains to Electroplate Bamboo-Like Structures and Foster Cu (111) Oriented Films in Pursuit of Enhanced Device Reliability

Abdelhamid El-Sawy, Ph.D.

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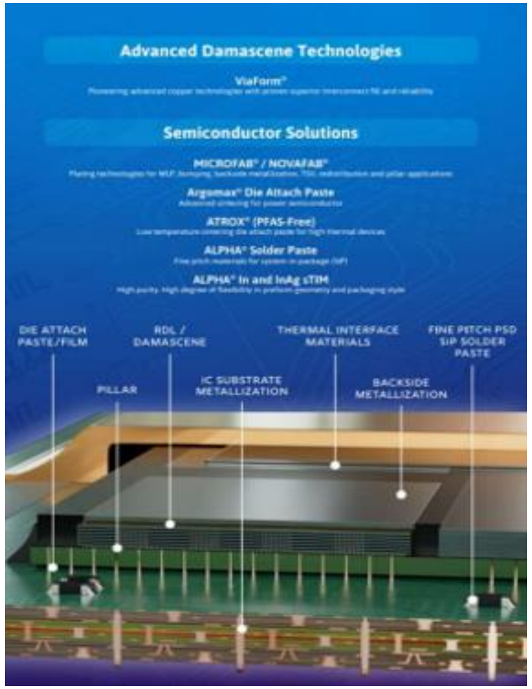
MacDermid Alpha celebrating the 29th Anniversary of the Copper Revolution (Cu atomic #)

AI created image

- This year marks the special 29th anniversary of the Copper Revolution in semiconductor electroplating which is equals to the Atomic number of copper.
- Initiated by IBM in 1995, the Copper Revolution aimed to replace aluminum in semiconductor manufacturing processes.
- MacDermid Alpha has been a key player since the revolution's inception, providing innovative chemical additives and solutions.
- Our dedication to R&D has led to the development of cutting-edge materials, enhancing the performance and reliability of copper interconnects.
- As a leading supplier, we continue to deliver high-quality products and exceptional customer service.
- Let's celebrate 29 years of progress and collaboration in semiconductor manufacturing!



➢ Outline

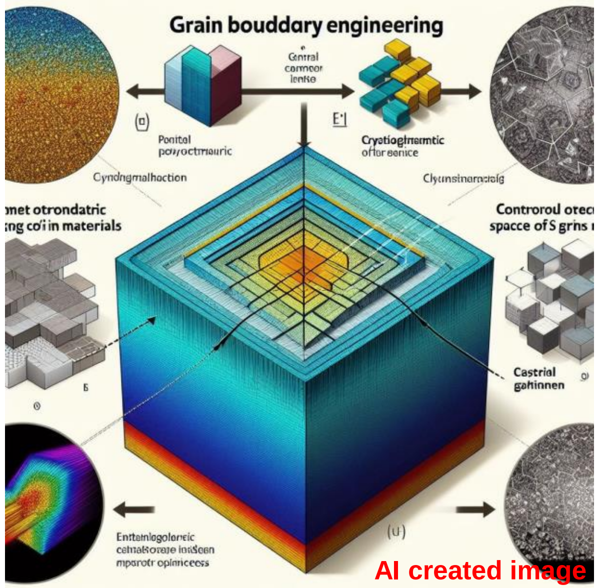
- ➢ **Grain Engineering**
- ➢ **Crystal structures terminology**
- ➢ **Electromigration paths**
- ➢ **Developing Bamboo-Cu Film – One component system**
- ➢ **Bamboo-Cu Film - Three components system**
- ➢ **Tunability and Grain Engineering**
- ➢ **Enhancement of Cu (111) texture**
- ➢ **Control the Grain Size**
- ➢ **Grain Growth – Ex-situ SEM/FIB**
- ➢ **SIMS analysis**
- ➢ **Coefficient of linear thermal expansion (CTE)**
- ➢ **Future: Optimizing Copper Formulations for Semiconductor Reliability with Machine Learning**

Grain Engineering

Bamboo/Near Bamboo process

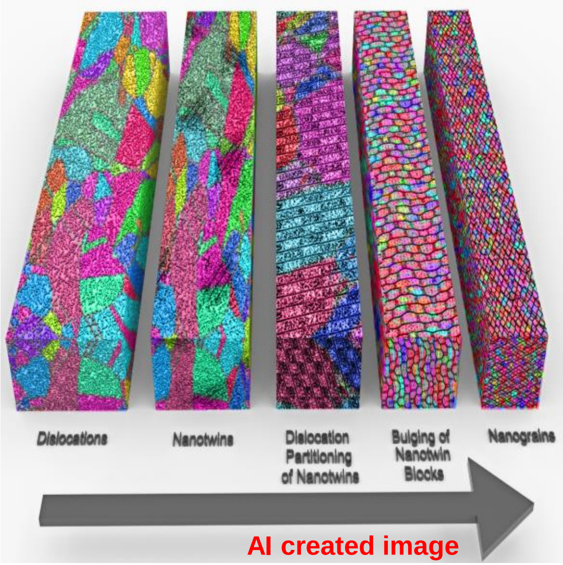
Grain Engineering

- **Grain Engineering is the process to control the arrangement of atoms at the grain boundaries.**
- **Grain Engineering can be used to tune the size, orientation, and texture of grains in microelectronics devices.**
- **By engineering grain boundaries, it is possible to enhance material properties such as mechanical strength, electrical conductivity, and electromigration.**

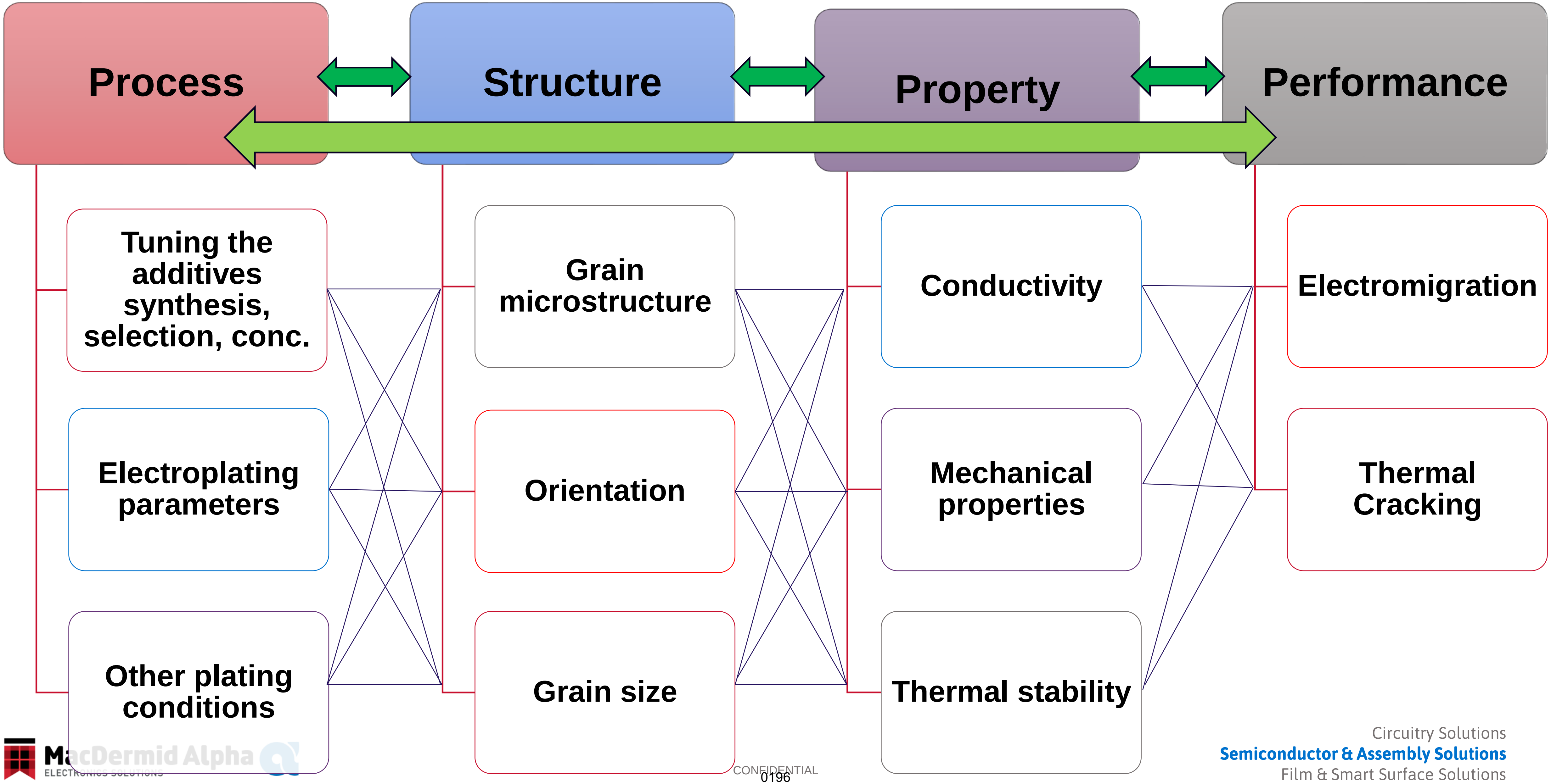


✓ Why Grain Engineering?

- ❑ **As feature sizes shrink through pitch scaling, the grain orientations and grain boundaries have a profound effect on film properties like stress, adhesion, and electromigration.**
- ❑ **By grain engineering, we can manage these effects.**



Grain Engineering protocol (Process-Structure-Property-Performance framework)



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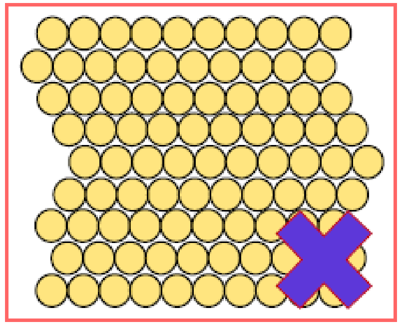
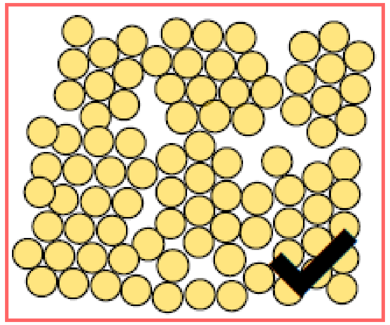
Crystal Lattice Structures Terminology

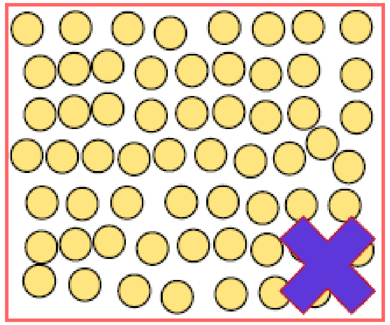
Crystal lattice and lattice defects define characteristics boundaries



Single crystalline



Polycrystalline



Amorphous solid

No crystal lattice or grain boundaries

The most common

Grains density

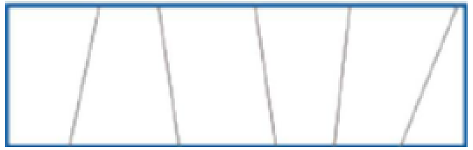
Low density

High density

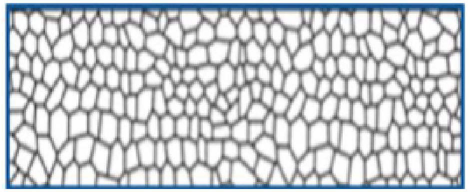
Near-bamboo

Featuring both crystal lattice and grain boundaries

Bamboo



Crystall lattice dominates



Grain boundaries dominate

e.g., Fine-grains or ultrafine grains

It could be nt-copper, or other polycrystalline copper

*Guillermo Mokry et al, High Ampacity Carbon Nanotube Materials Nanomaterials 2019, 9(3), 383;

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Lienig, J., & Thiele, M. (2018). Fundamentals of electromigration-aware integrated circuit design. Springer International Publishing.

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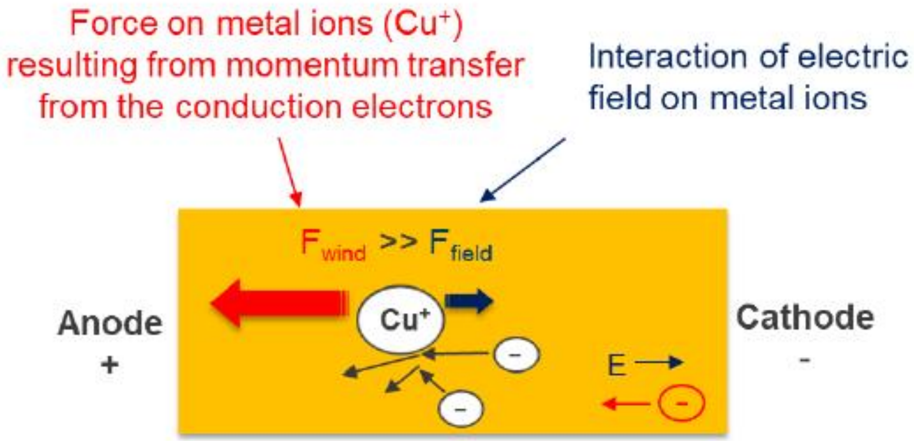
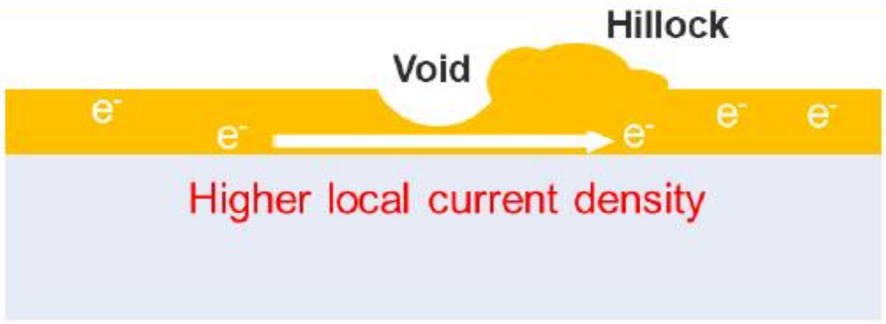
Electromigration in RDL-WLP

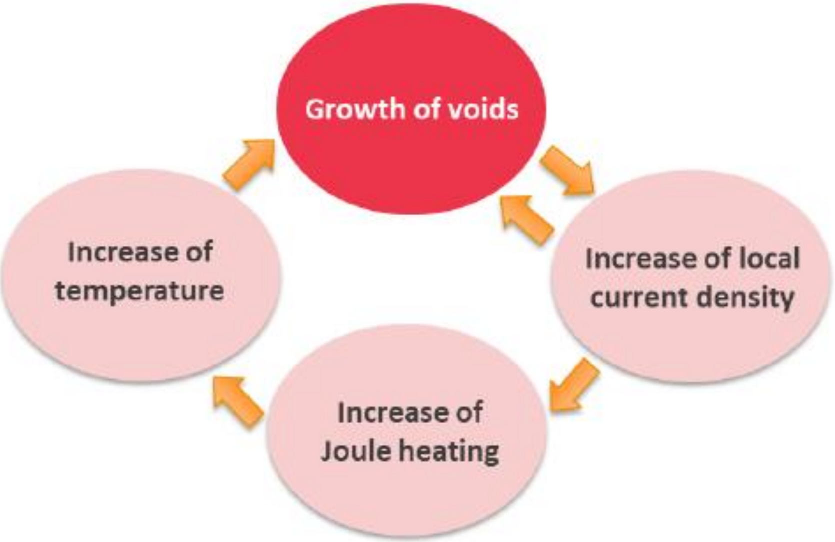


* C.-M. Liu et al, Low-temperature direct copper-to-copper bonding enabled by creep on (111) surfaces of nano-twinned Cu. Sci. Rep. 5, 9734 (2015).

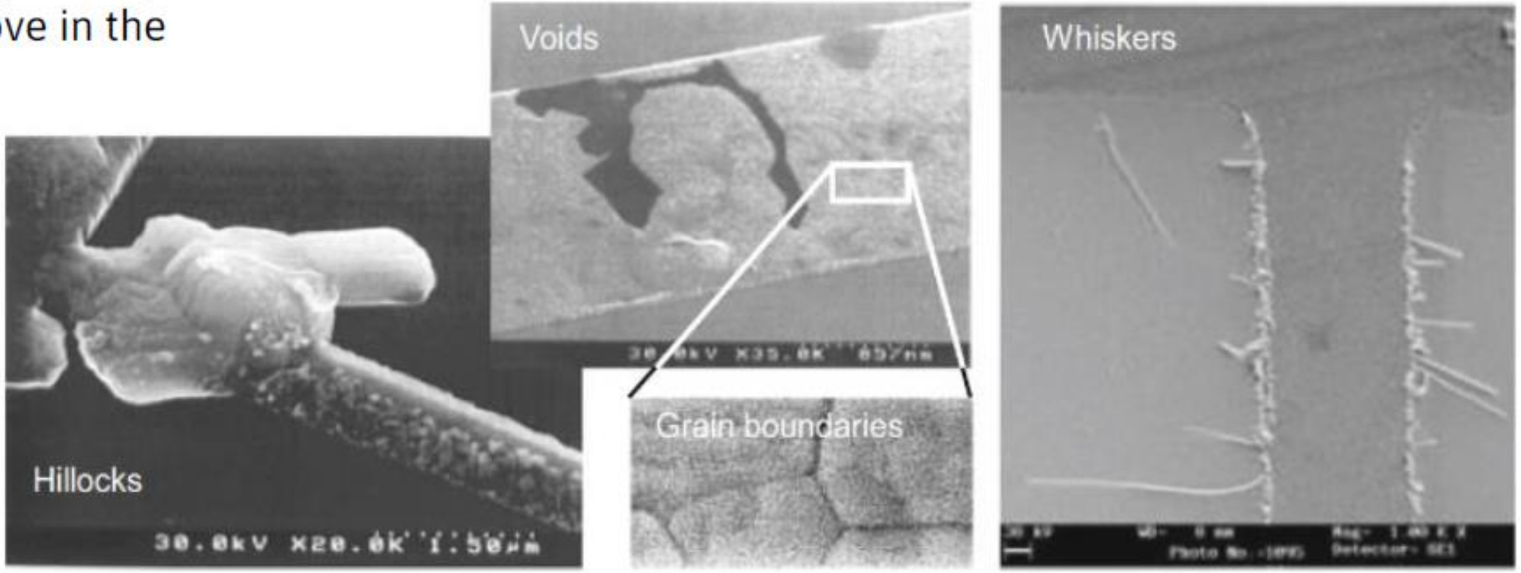


Failure mechanisms caused by electromigration

Electromigration is the result of the dominant force, that is, the momentum transfer from the electrons that move in the applied electric field E



Positive feedback loop



* Jens Lienig, SLIP '05: Proceedings of the 2005 international workshop on System level interconnect prediction April 2005,Pages 81–88

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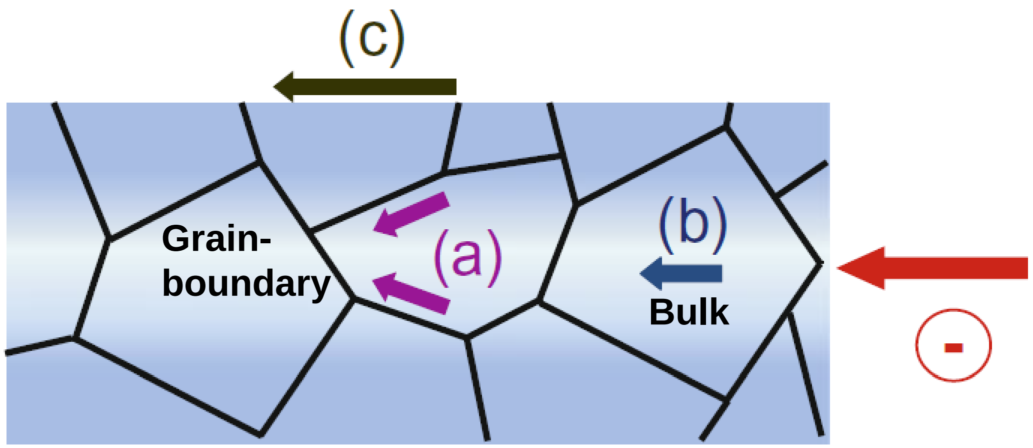
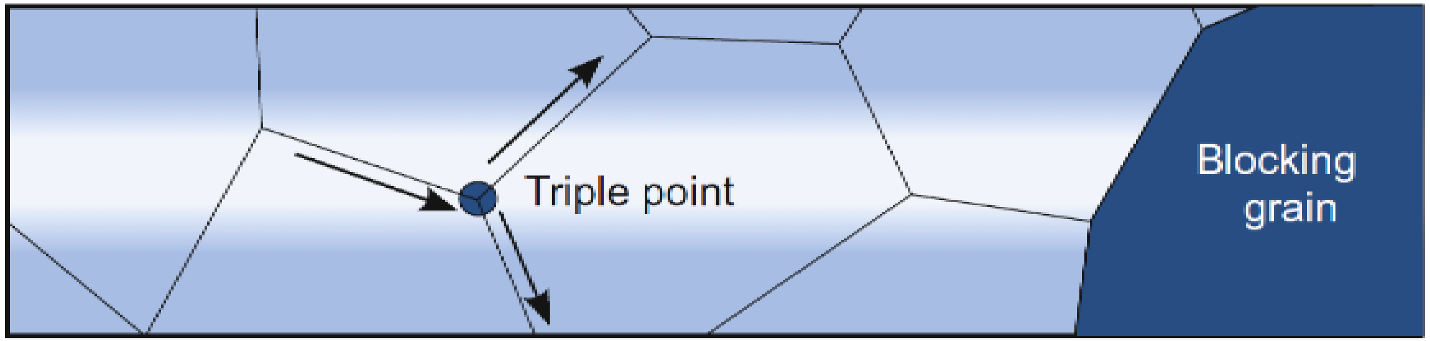
Electromigration paths



Diffusion process	Activation energy in eV	
	Aluminum	Copper
Bulk diffusion	1.2	2.3
Grain-boundary diffusion	0.7	1.2
Surface diffusion	0.8	0.8

Passive layer coated copper surface is required. Then the grain-boundary diffusion will be lowest activation energy and dominate path for EM.

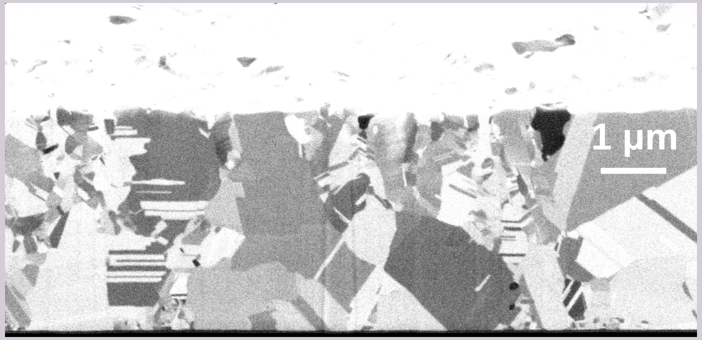
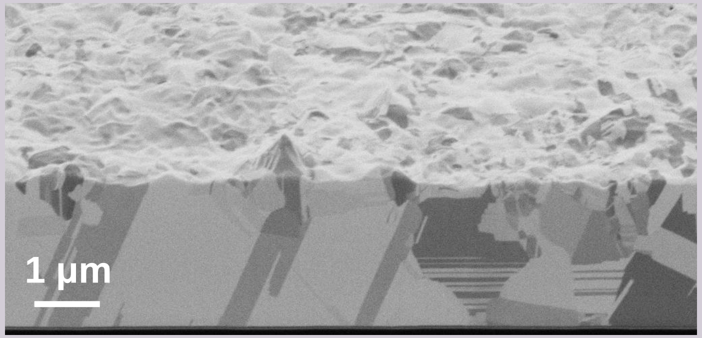
Various diffusion processes within the lattice of an interconnect: a) grain-boundary diffusion, b) bulk diffusion, and c) surface diffusion



Large grains (bamboo or near bamboo) aligned in the direction of current flux are required to act as blocking grain to inhibit the diffusion flux

Thiele, M. and Lienig, J., 2018. Fundamentals of Electromigration-Aware Integrated Circuit Design. Springer International Publishing.

Developing Bamboo-Cu Film – One component system

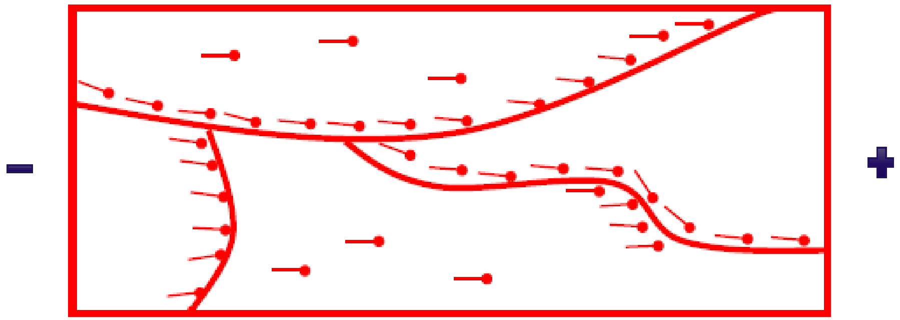
WF-1	WF-2
	
Near-Bamboo (NB-Cu)	Bamboo (B-Cu)

Bamboo grains can be defined as microstructure grains in which boundaries of the grains tend to be aligned vertically with direction of film growth through the thickness.

- We developed low density grains with large size grain **Near-bamboo and Bamboo** across the deposited film

Why Bamboo Grains?

- **Small grains** provides additional paths for material transport due to the formation of grain boundaries running parallel to the current flow and triple points.



$$\frac{\text{Average grain size}}{\text{Line width}} > 1,$$

Coarse-grained or Bamboo

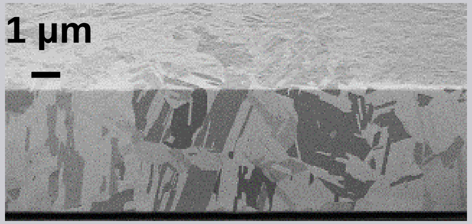
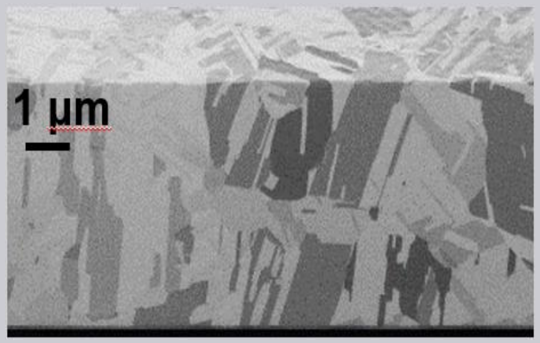
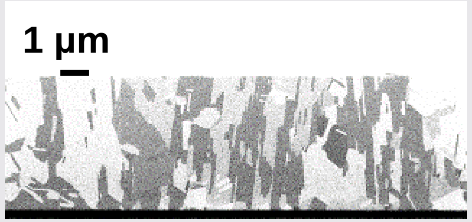
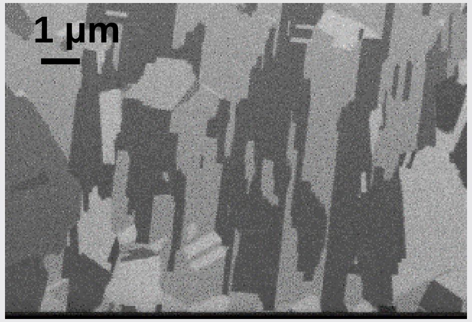
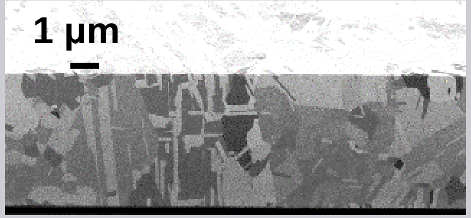
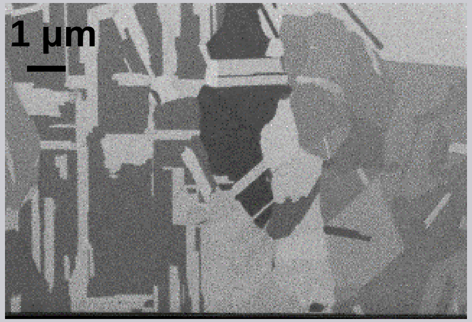
- **Bamboo grains** with low density grains boundaries will have blocking grains to block the mass transport

The lower number of triple points is the better EM reliability

E. Arzt, W.D. Nix, A model for the effect of line width and mechanical strength on electromigration failure of interconnects with 'near-bamboo' grain structures. J. Mater. Res. 6(4), 731–736 (1991).

Lienig, J., & Thiele, M. (2018). Fundamentals of electromigration-aware integrated circuit design. Springer International Publishing.

Near-Bamboo three components - Blanket (Cu-PVD)

A/S/L (mL)	Low Mag	High Mag
1/6/4		
4/6/4		
4/8/4		

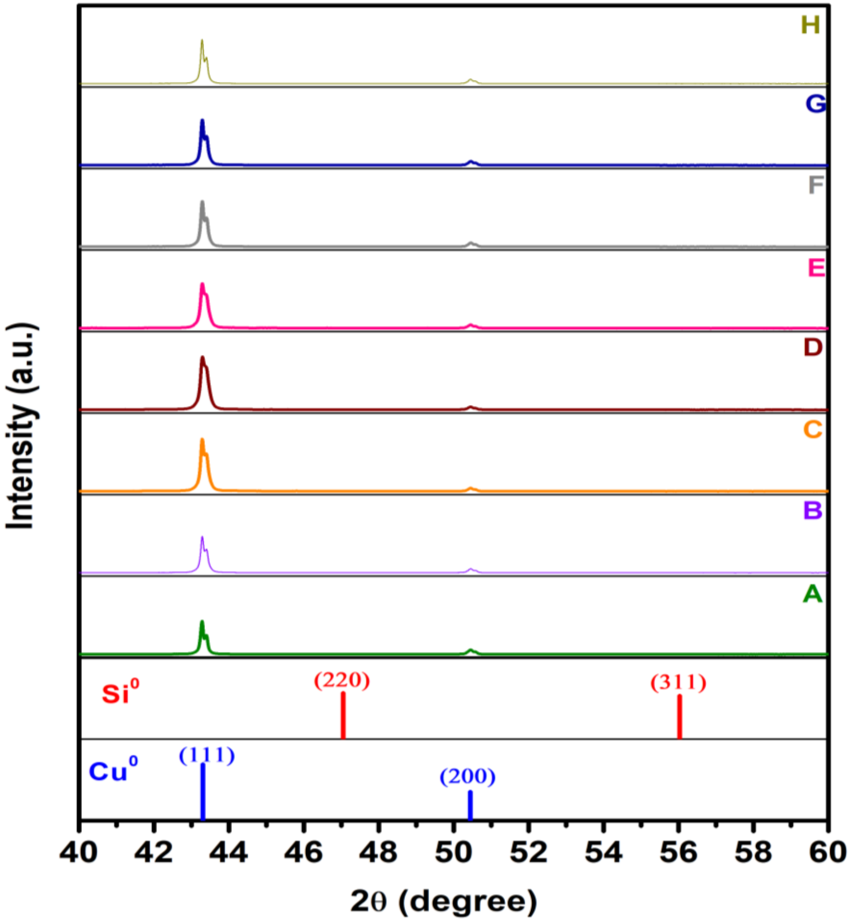
- Through the optimization of the additives concentration, applied current density, and other plating conditions (temp. agitation:
  - ✓ Control the grain size (small-large)
  - ✓ Tune the grain orientation

Enrichment of Cu (111) texture

Additives, Waveform

Enhancement of Cu (111) texture: Additives Concentration

XRD

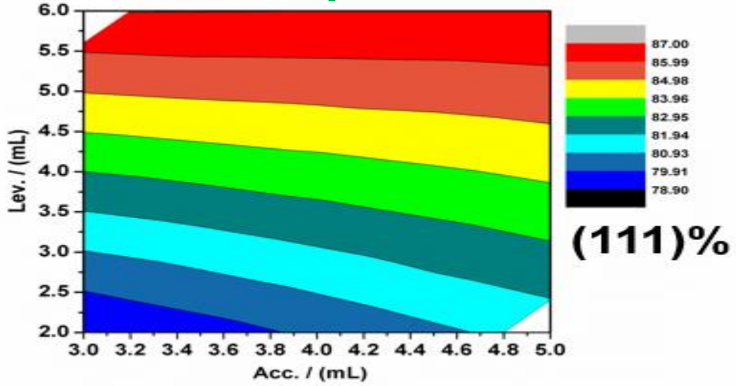


Why??

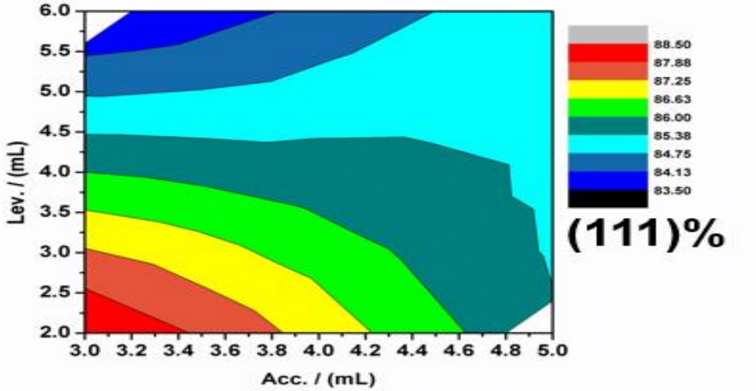
1- Increasing the (111) orientation % Enhance the conductivity, EM, mechanical properties.

2- It could affect the CMP process

Low Sup. Conc.



High Sup. Conc.

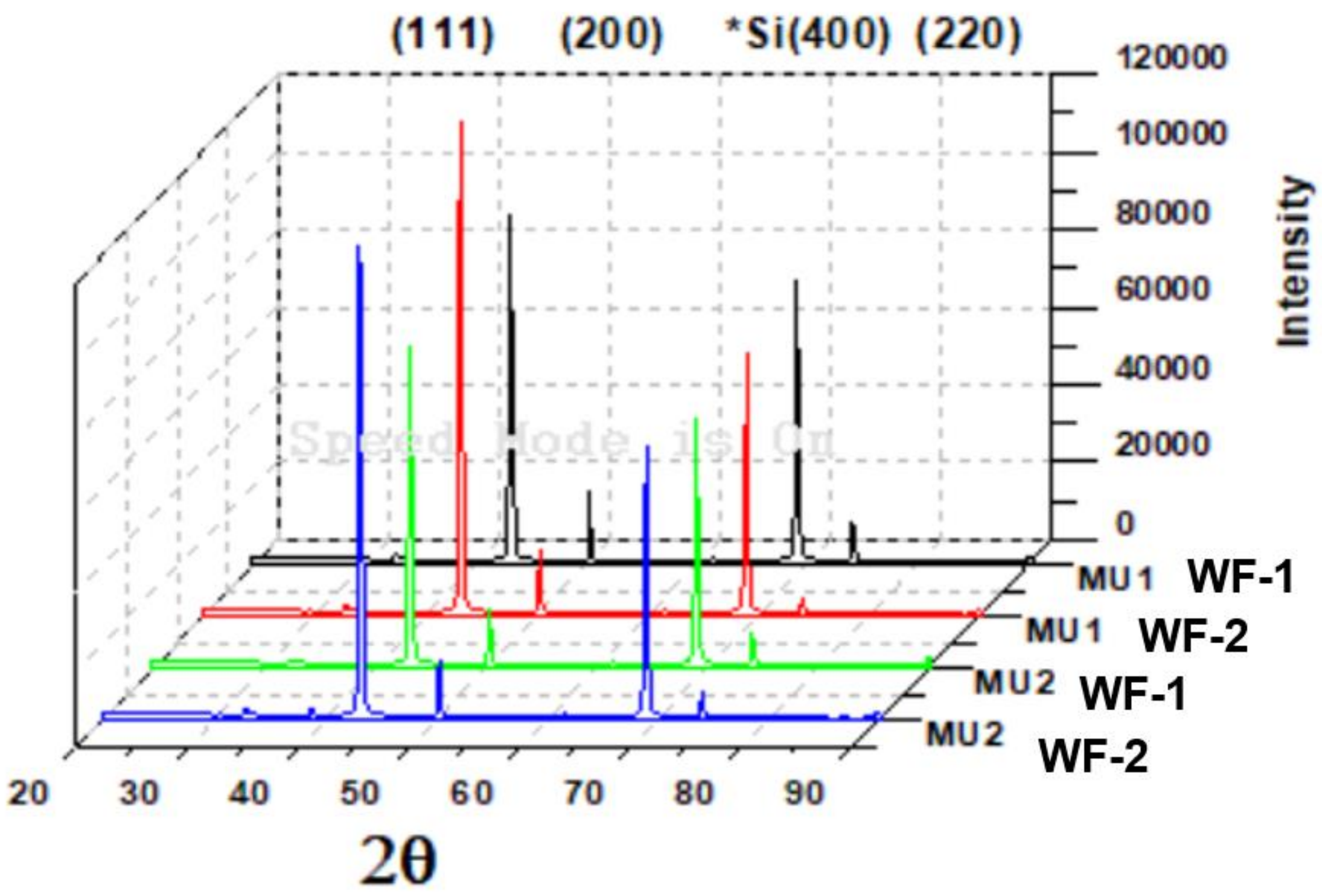


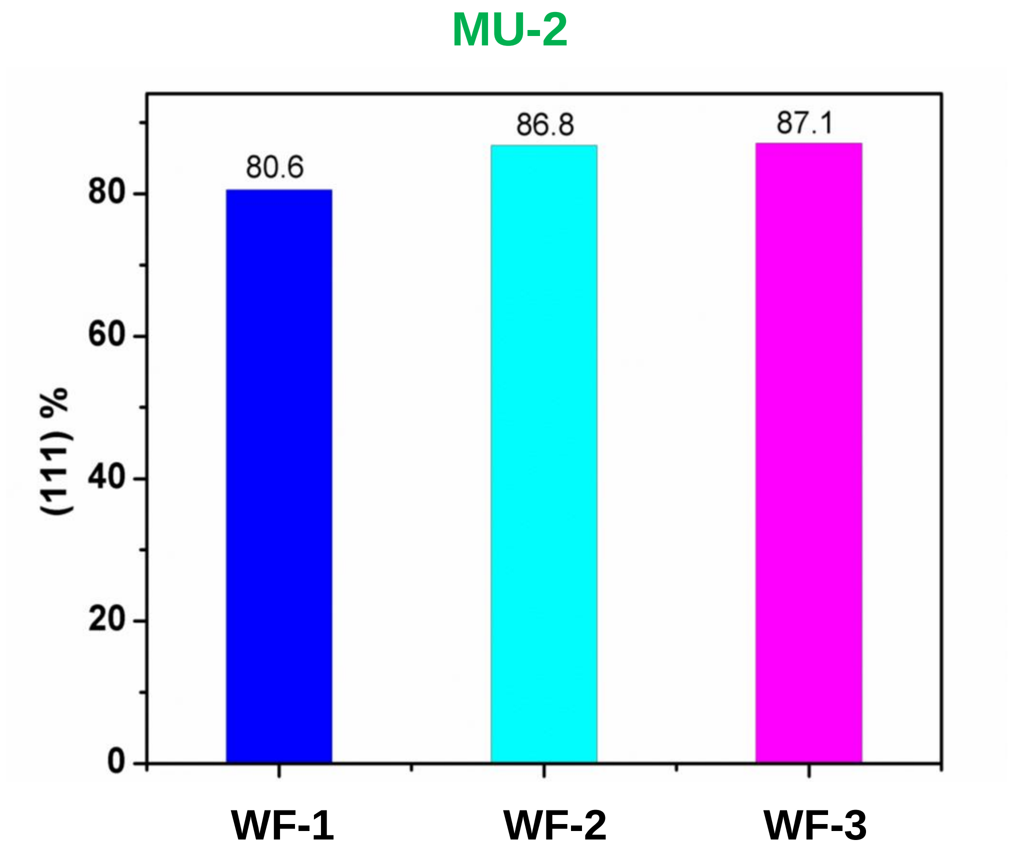
		A: 3/4/2	B: 5/4/2	C: 5/4/6	D: 3/8/2	E: 5/8/2	F: 5/8/6	G: 3/4/6	H: 3/8/6
Copper (111)	Peak Position (2θ)	43.29	43.29	43.28	43.28	43.28	43.3	43.3	43.29
	Relative percentage (%)	78.9	81.3	87.0	88.5	85.5	85.1	87.0	83.5

Enrichment of the Cu (111) texture by modulating the additives concentration

- ✓ At Low Sup. Increasing the Acc and Lev. concentrations increasing the preferential orientation of (111)
- ✓ At High Sup. Increasing the Acc and Lev. concentrations decreasing the preferential orientation of (111)

Effects of waveform on the Cu (111) texture





Enrichment of the Cu (111) texture by increasing the current density

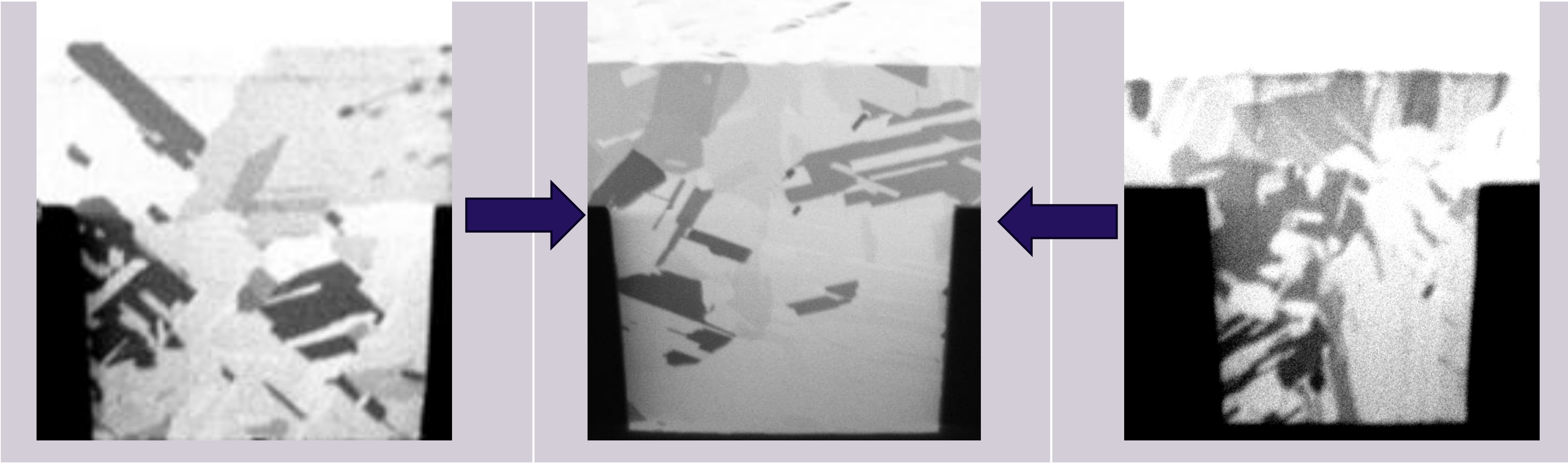
Grain Size

Additives concentration, waveform

Waveform (one-bath)

Electrolyte + A/S/L (4/6/4) at 300 rpm, 25 ˚C

WF-1	Combined WF	WF-2



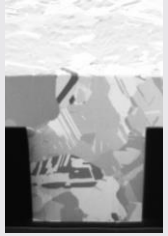
✓ **Combining waveforms leads to the formation of larger grain size.**

Additives concentration

(A/S/L) 3/4/2 | **5/4/2** | **5/4/6**

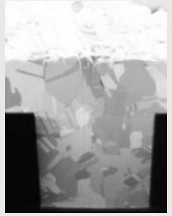
Average Grain Size

337 nm



325 nm

299 nm



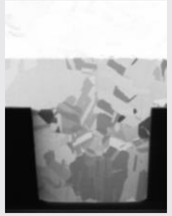
(A/S/L) 3/8/2 | **5/8/2** | **5/8/6**

Average Grain Size

289 nm

295 nm

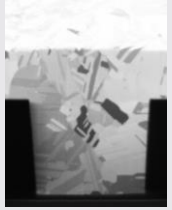
315 nm



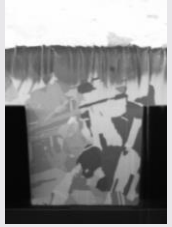
(A/S/L) 3/4/6 | **3/8/6** | **4/6/4**

Average Grain Size

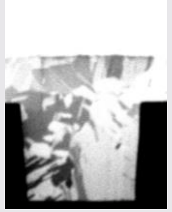
317 nm



345 nm



490 nm



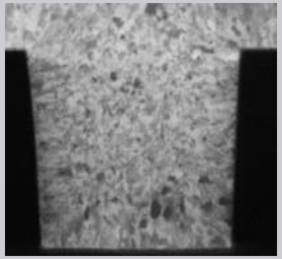
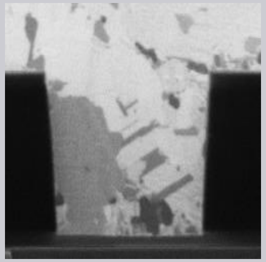
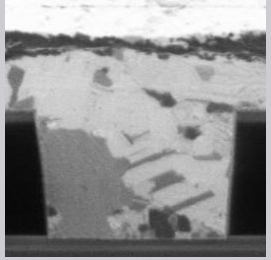
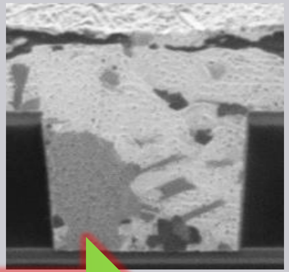
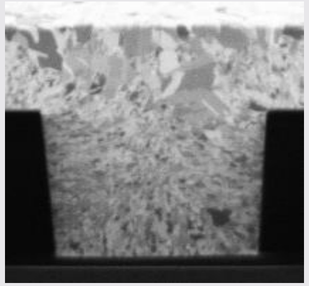
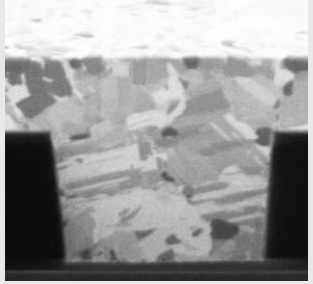
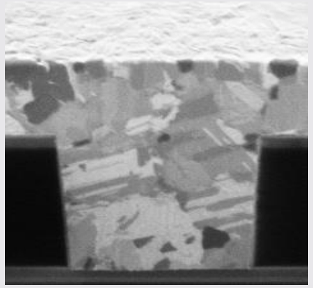
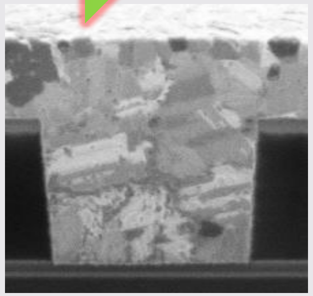
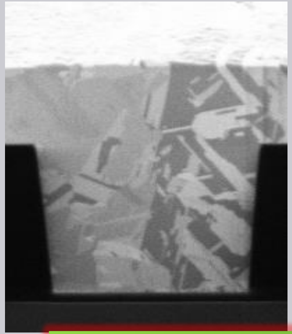
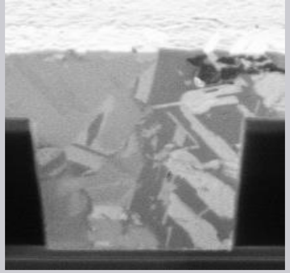
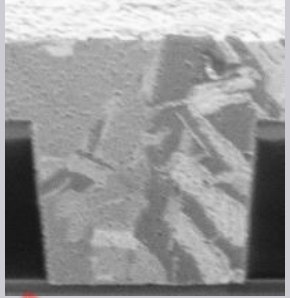
- ✓ **Additives concentration effect on copper grain size, adjustable from 300 to 500 nm.**

Grain growth

Heat-annealing

Heat-annealing- *Ex-situ* FIB study

Electrolyte + A/S/L (4/6/4) at 300 rpm, 25 ˚C

	As-plated	125 °C	150 °C	200 °C
WF-1				
WF-2				
WF-3				

Tremendous grain growth upon annealing @ 125 °C

Small grain growth up to 200 °C

- ✓ For WF-1, and 2 there was substantial grain growth upon annealing at 125 ºC.
- ✓ For WF-3 there was small grain growth up to 200 ºC.

SIMS analysis for Bamboo chemistry

	PPMW from SIMS					
A/S/L; 4/6/4	**C**	**O**	**S**	**Cl**	**N**	**Total impurity**
Electrolyte @ WF-1	1.84	0.89	0.19	0.22	0.09	3.2
Electrolyte @ WF-2	2.71	1.90	0.41	0.99	0.167	5.6
Electrolyte @ WF-3	2.87	0.94	0.25	0.76	0.184	5.0

✓ **SIMS analysis shows that the total impurities are 3.2, 5.6, 5.0 ppm for wide range of different waveforms**

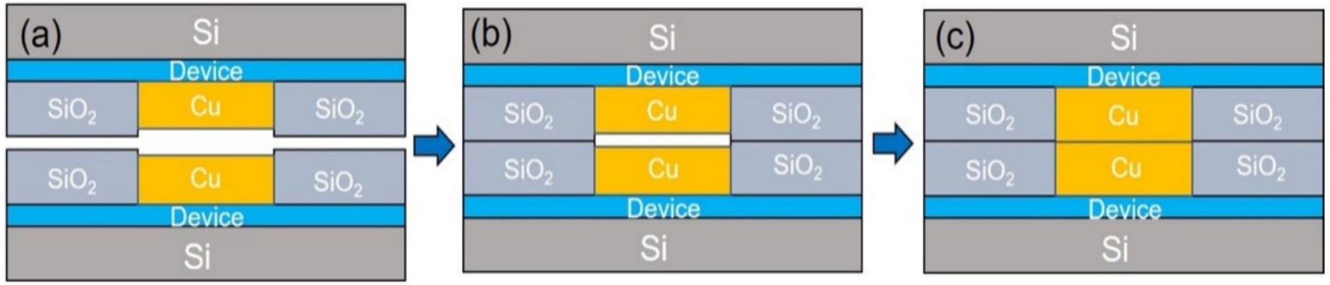
Coefficient of linear thermal expansion (CTE)

Fine grains, Nanotwin, and Bamboo Copper

Coefficient of linear thermal expansion (CTE)

$$CTE = \frac{\Delta L}{L_0 \Delta T}$$

Where ΔL is the change in length, L_0 is the initial length, and ΔT is the change in temperature.



$$\Delta L = \Delta\alpha\, L_0\, \Delta T$$

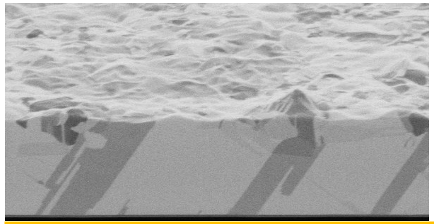
where L_0 is the thickness at room temperature in this study, ΔL is the height difference due to the mismatch between the thermal expansion of Cu and the oxide, Δα is the difference in CTE, and ΔT is temperature difference

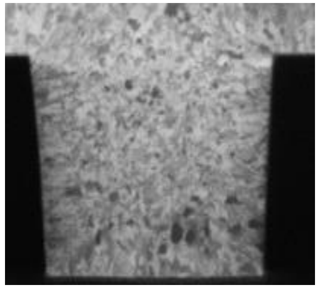
$$\Delta L = \Delta\alpha\, L_0\, \Delta T = (16.6 - 4.4) \times 10^{-6} \times 2000\ \text{nm} \times (200 - 25) = 4.3\ \text{nm}$$

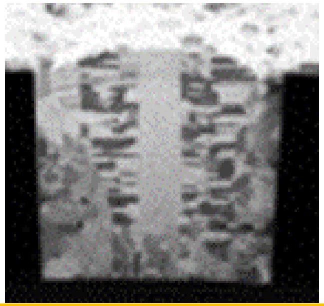
✓ All Cu-processes should not be treated equally

Ong, Jia-Juen, Wei-Lan Chiu, Ou-Hsiang Lee, Chia-Wen Chiang, Hsiang-Hung Chang, Chin-Hung Wang, Kai-Cheng Shie et al. "Low-temperature Cu/SiO2 hybrid bonding with low contact resistance using (111)-oriented Cu surfaces." *Materials* 15, no. 5 (2022): 1888.

CTE comparison for different copper grains (Bamboo, fine grains, Nanotwin)



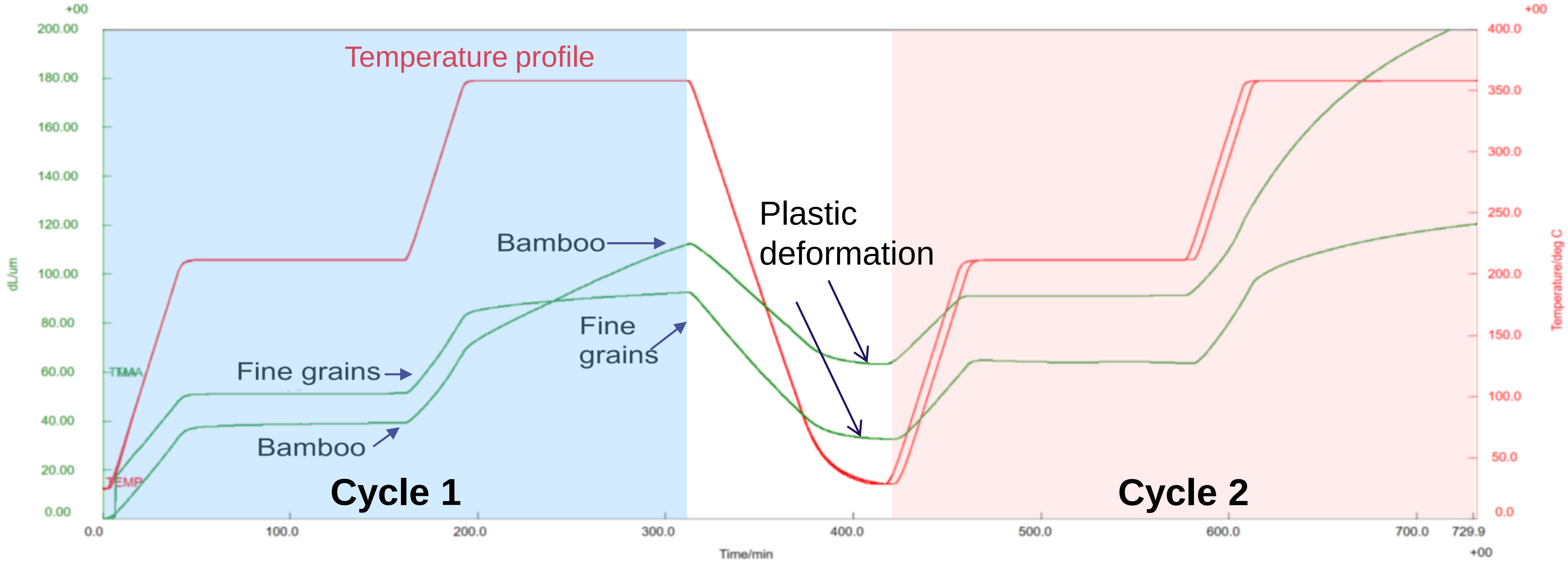




Temp. (°C)	CTE ($\times 10^{-6}$ / °C) Bamboo		Fine grains-WF-1		Fine grains-WF-2		Nanotwin	
	1st Cycle	2nd Cycle	1st Cycle	2nd Cycle	1st Cycle	2nd Cycle	1st Cycle	2nd Cycle
100	16.96	13.46	16.63	15.26	19.26	15.22	16.77	15.83
150	17.88	14.32	17.04	16.30	21.12	16.11	17.14	15.60
200	18.6	14.67	18.01	16.82	23.25	16.30	18.27	15.51
250	19.97	14.80	18.71	16.78	24.04	16.34	18.55	15.56
300	19.75	15.42	19.11	17.67	24.22	16.48	20.20	15.36
350	20.53	17.25	20.05	19.02	25.51	16.97	20.56	14.84

- ✓ **FG process has the highest CTE compared to NT and Bamboo @ 200 °C.**
- ✓ **After the first cycle the NT, Bamboo and FG film will behave like a regular Cu.**

Thermal expansion profile for Bamboo and fine grains



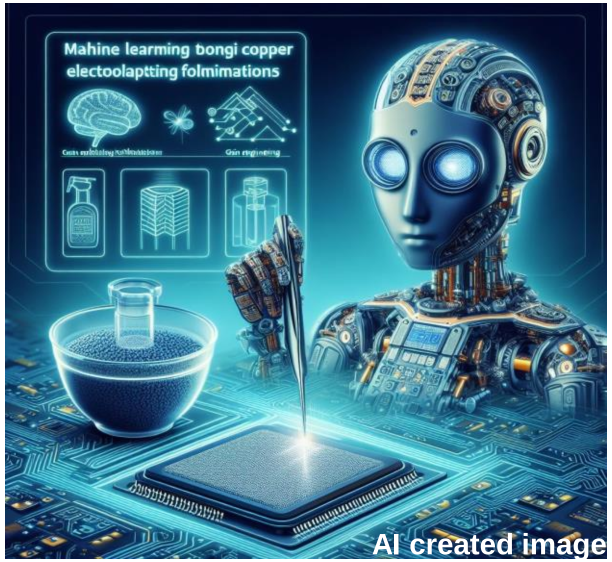
- ✓ At 200°C for 2 h, the both chemistries had a negligible thermal expansion.
- ✓ At 350°C for 2 h, Bamboo grains experienced a larger expansion (39.37 µm compared to 7.60 µm Fine grain).
- ✓ Bamboo grains have more plastic deformation and was 63.30 µm longer than its initial length after the first cycle while Fine grains was 16.43 µm.
- ✓ Both chemistries had a negligible thermal expansion during the second 2h hold at 200°C.
- ✓ The second 2 h at 350°C, the thermal expansion of Bamboo and Fine grains increased by 70.66 and 20.60 µm, respectively.

Conclusion

- Systematically investigated copper grain engineering and growth processes for device enhancement.
- Demonstrated precise control over copper grain properties through electroplating parameter manipulation.
- Emphasized the crucial role of grain engineering in controlling copper film microstructure
- Introduced bamboo suppressors and novel additives for improved bottom-up capabilities in device fabrication.
- Provided valuable insights into grain growth dynamics under heating conditions, crucial for bonding processes.
- Future research may focus on optimizing electroplating processes and exploring novel additives to advance materials engineering and device fabrication.

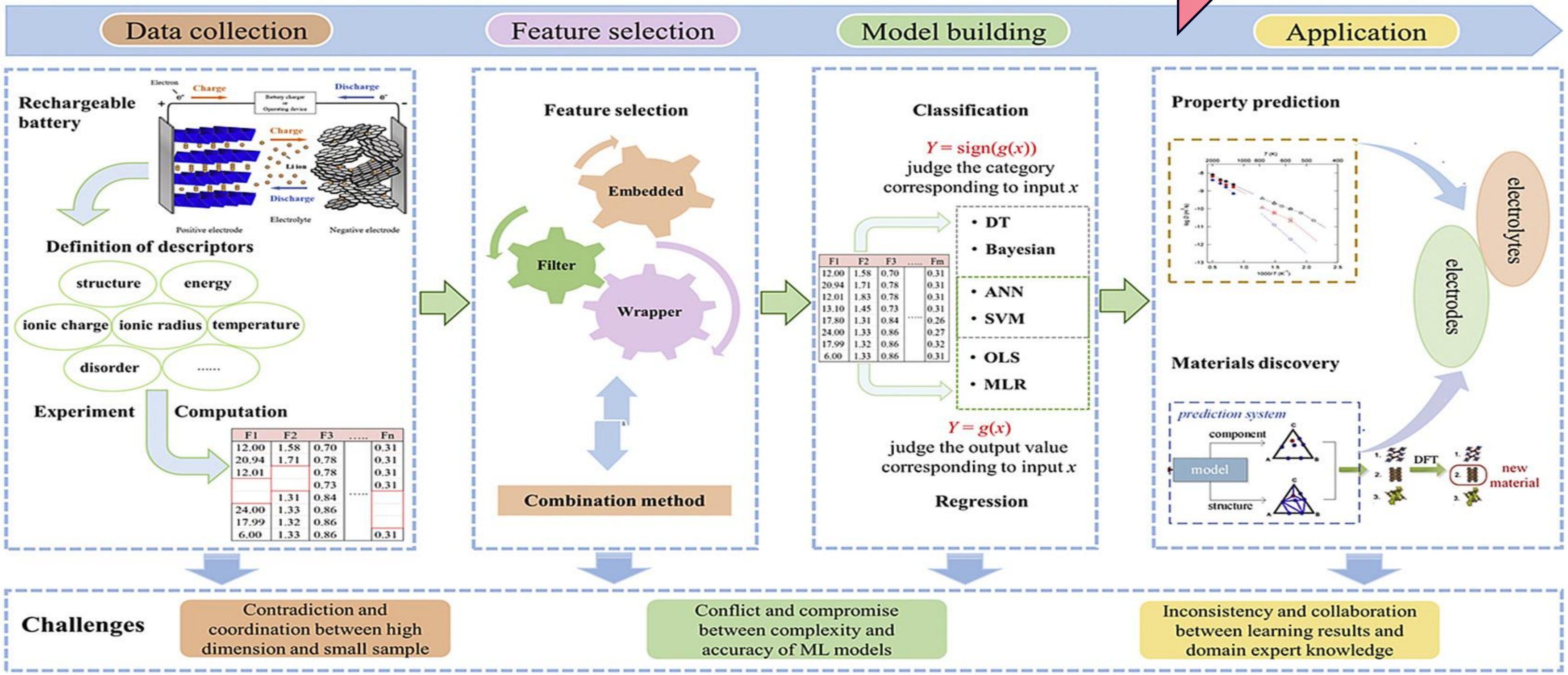
Future: Optimizing Copper Formulations for Semiconductor Reliability with Machine Learning

Collecting Plating Data → Supervised learning → Unsupervised learning → Validate the models → Implement from AI to real plating → Feedback



AI created image

Machine Learning steps for batteries discovery



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Dolores Ross, Ph.D.
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Jianwen Han, Ph.D.
Pingping Ye, Ph.D.
Stephan Braye
Justin Gilbertson
Kyle Whitten, Ph.D. Senior R&D Manger
Adam Letize, Senior Product R&D Manger
Thomas Richardson, Ph.D. Senior R&D Manger
Elie Najjar, Senior Global Director of R&D

Marketing team:

Brain Gokey, Director of IC substrate
Ashley Kuppersmith, Product Manger
Eric Gongora, VP of Wafer Level Packaging

Let's celebrate the 29 years of progress and collaboration in semiconductor manufacturing!

Abdelhamid El-Sawy, PhD

Senior R&D Scientist

Abdelhamid.elsawy@MacDermidAlpha.com

macdermidalpha.com

Abdelhamid El-Sawy, Ph.D.

MacDermid Alpha
ELECTRONICS SOLUTIONS

macdermidalpha.com