21ST INTERNATIONAL CONFERENCE & EXHIBITION ON
DEVICE PACKAGING
SHERATON GRAND AT WILD HORSE PASS · PHOENIX, AZ
MARCH 3-6, 2025 · WWW.DEVICEPACKAGING.ORG

Advanced Electrochemical Plating Processes of Nano-Twinned Copper for Hybrid Bonding

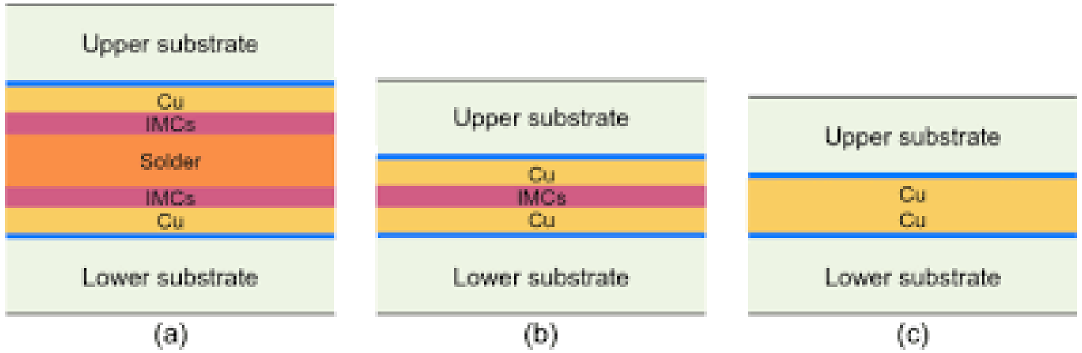
Jianwen Han
Principal Research Scientist, R&D
MacDermid Alpha Electronics Solutions

March 05, 2025

MacDermid Alpha
ELECTRONICS SOLUTIONS

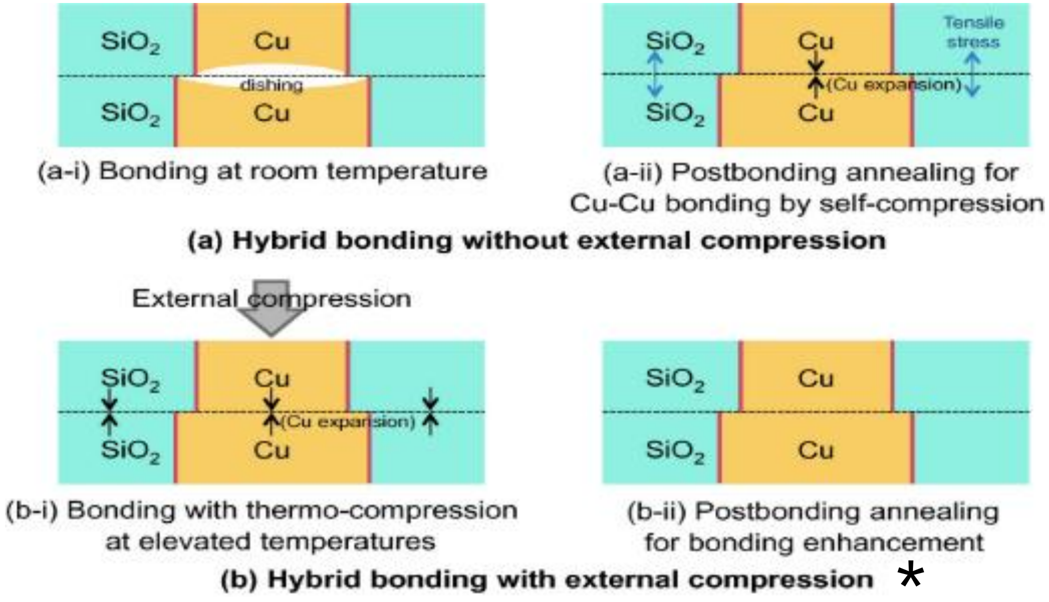
Hybrid bonding technology

- Finer features and pitch - higher I/O -2.5D/3D stacking
- Bonding :
  - Solder → solderless → direct Cu-Cu/hybrid bonding
    - Advanced packages < 10 µm Pitch



Schematic diagram of the bonded structures using method of (a) soldering, (b) SLID/SSID bonding and (c) Cu–Cu bonding *

- Hybrid bonding processes



(a-i) Bonding at room temperature

(a-ii) Postbonding annealing for Cu-Cu bonding by self-compression

(a) Hybrid bonding without external compression

(b-i) Bonding with thermo-compression at elevated temperatures

(b-ii) Postbonding annealing for bonding enhancement

(b) Hybrid bonding with external compression

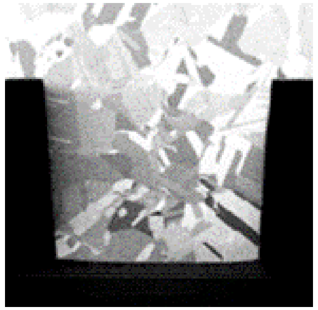
- Key to sensitive memory applications (HBM) that require a reduction in thermal budget & stress for 3D stacking

Hybrid bonding has emerged as a promising technology for microelectronic device assembly, enabling the integration of different materials with superior electrical and thermal performance

*3D Microelectron IC Packaging: From Architectures to Applications, second edition, Springer

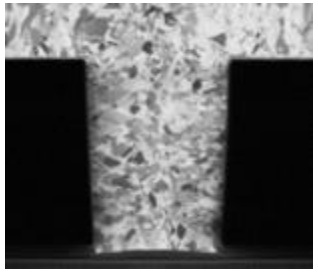
Hybrid bonding technology - thermal budget reduction paths

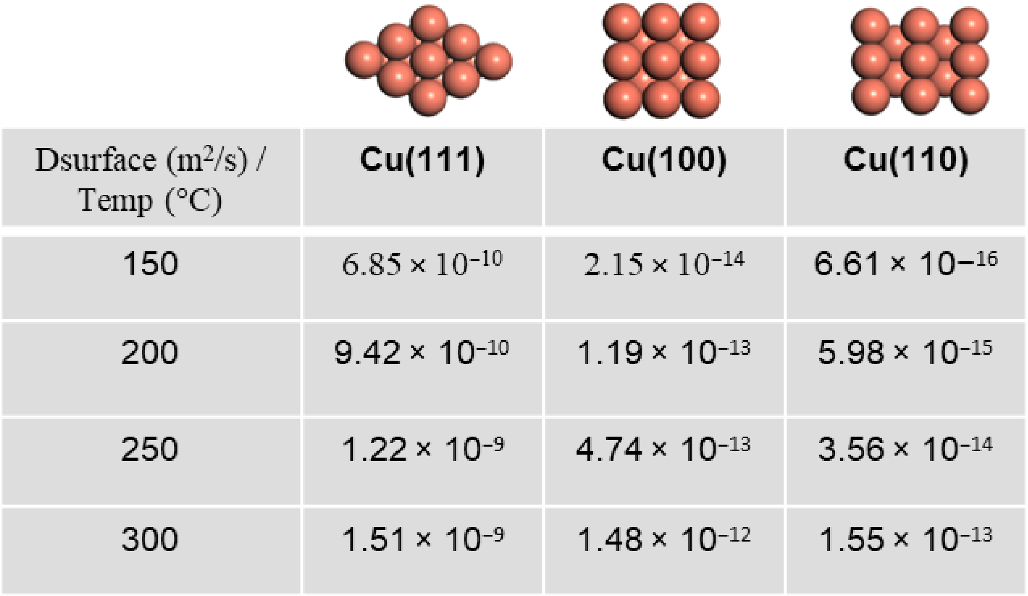
- Polycrystalline Cu: High temp thermal compression / high temp annealing



- Two paths of Cu grain engineering to reduce thermal budget
  - **Nano-twinned Cu**
    - **Cu (111) dominated**

  - **Fine grain Cu**





Dsurface (m^2/s) / Temp (°C)	Cu(111)	Cu(100)	Cu(110)
150	6.85×10^{-10}	2.15×10^{-14}	6.61×10^{-16}
200	9.42×10^{-10}	1.19×10^{-13}	5.98×10^{-15}
250	1.22×10^{-9}	4.74×10^{-13}	3.56×10^{-14}
300	1.51×10^{-9}	1.48×10^{-12}	1.55×10^{-13}

Calculated Cu surface diffusivity on (111), (100), and (110) planes at various temperatures, ranging from 150 °C to 300 °C *

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

Why Nano-twinned Copper?

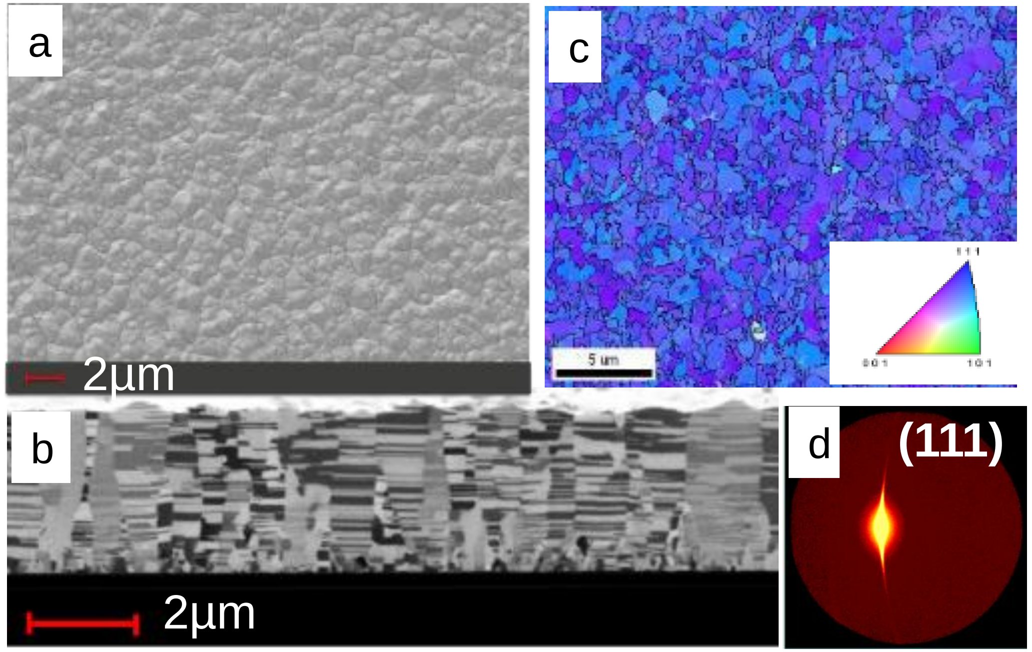
- Nano-twinned Cu demonstrates both superior mechanical, thermal and electrical properties
  - Cu (111) dominated texture: higher atomic diffusivity
  - Highly efficient energy transfer and durable connections
  - Low temperature Cu-Cu direct-bonding / hybrid-bonding
  - RDL anti-cracking
  - Electromigration resistance

  - Other Cu processes with (111) preferred texture

- Evaluation of nt-Cu performance
  - Amount of nt-Cu - percentage
  - Orientation of the nt-Cu growth
    - Vertical vs. Horizontal
  - Transition layer
    - Between Cu seed and nt-Cu initial position
  - Grain Size
    - Correlation with surface roughness

ECP nt-Cu Process

- Strongly textured nt-Cu with (111) preferred orientation
- Rapid transition from substrate to nt-Cu formation – thin transition layer
- Robust process with respect to hydrodynamics, current density, and stability
- Stable additives within process matrix
- Thermal stability, low impurity and low resistivity

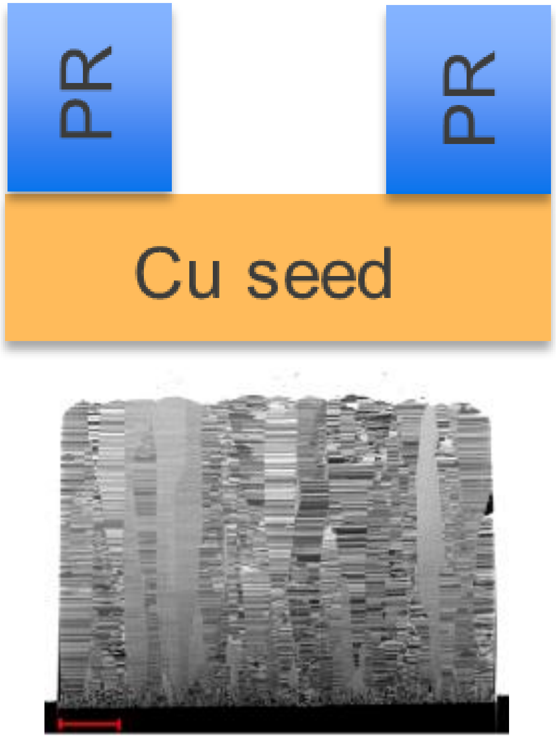


(a) Surface image, (b) FIB cross-section image,
(c) Plan-view EBSD image, (d) 2D XRD diffraction frame

Parameters	Range
Copper Concentration	25 -50 g/L
Sulfuric Acid Concentration	0 – 180 g/L
Chloride	30 – 90 ppm
nt-Cu suppressor	25 – 150 ml/L
Additional additive(s)	Wide process window
Temperature	15 – 35 °C
Cathode Current Density	1 – 12 ASD
Agitation	low to high
Anode material	Inert / Cu-Anode

Nano-twinned Cu on Features

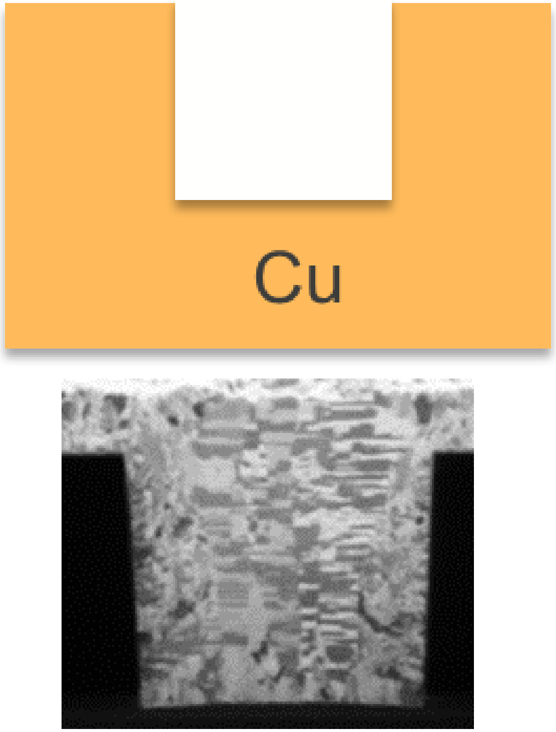
- Typical Features for NT-Cu ECP Process
  - ➢ Bottom-Cu-Seeded Features
  - ➢ Complete-Cu-Seeded Features



- Pillar (50 µm x 40 µm)

A: Bottom-Cu-Seeded Features

- Conformal ECP



- Via (5 µm x 5 µm)

B: Complete-Cu-Seeded Features

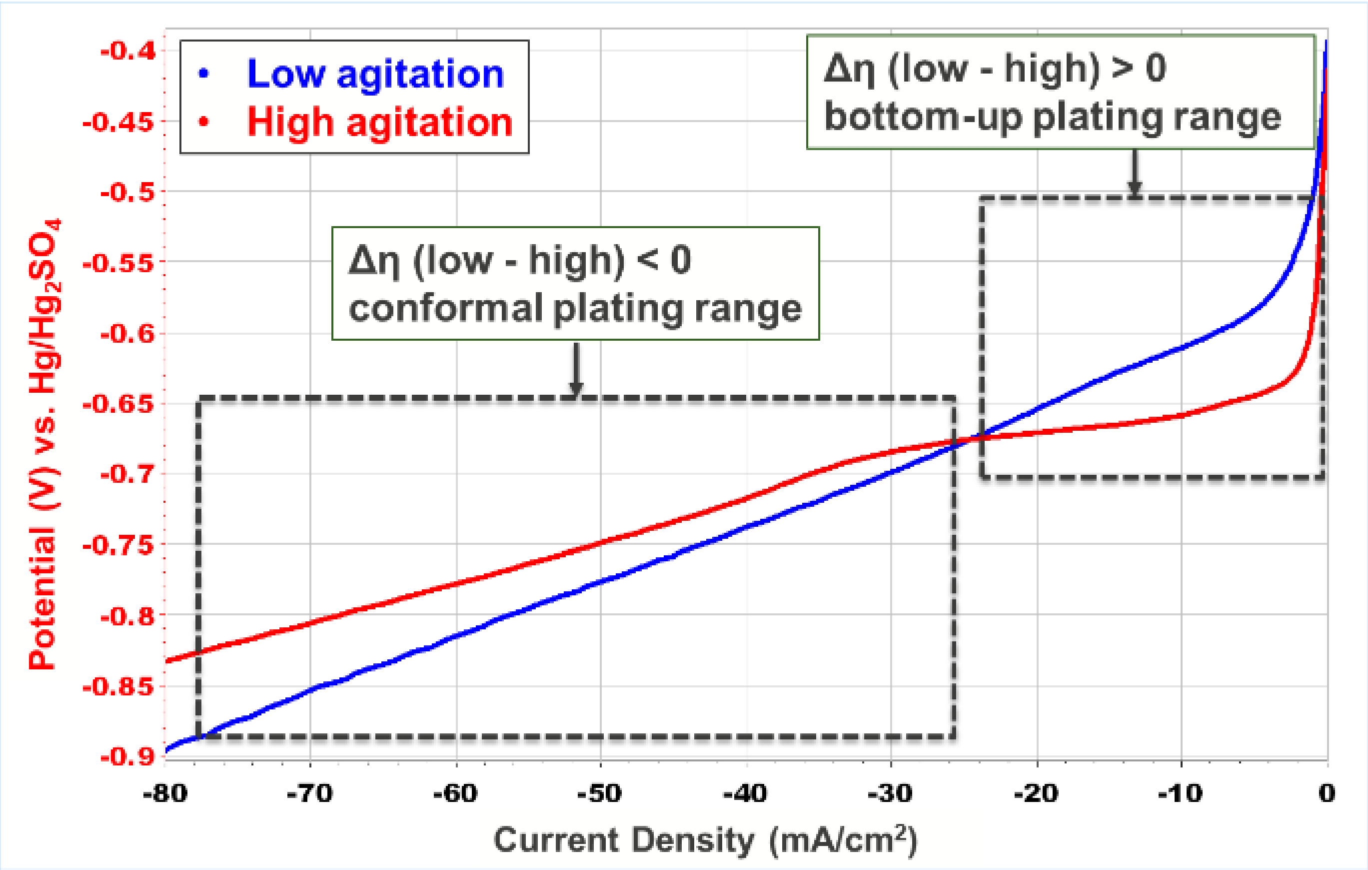
- Bottom-up ECP

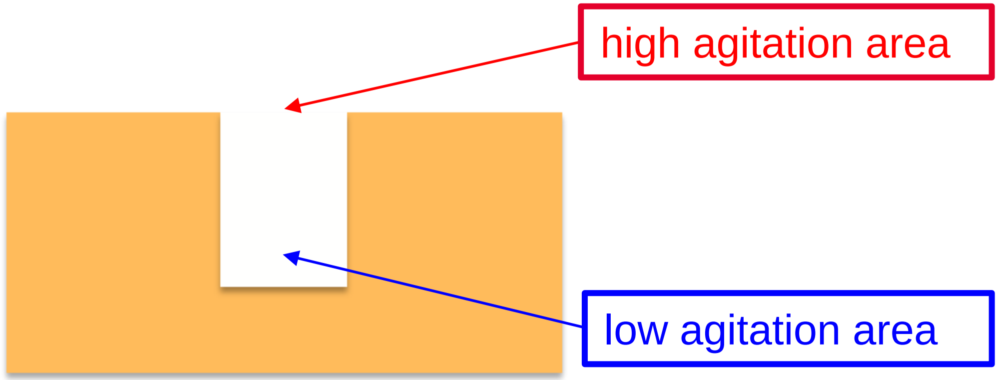
Complete-Cu-Seeded Features

1. Vertical growth nt-Cu
   - Lines
   - Vias
2. Horizontal growth nt-Cu
   - Vias

Additives/ Bath Screening for Bottom-up Fill

- CDA (Convection Dependent Adsorption) - Linear Sweep Voltammetry (LSV) at different agitation



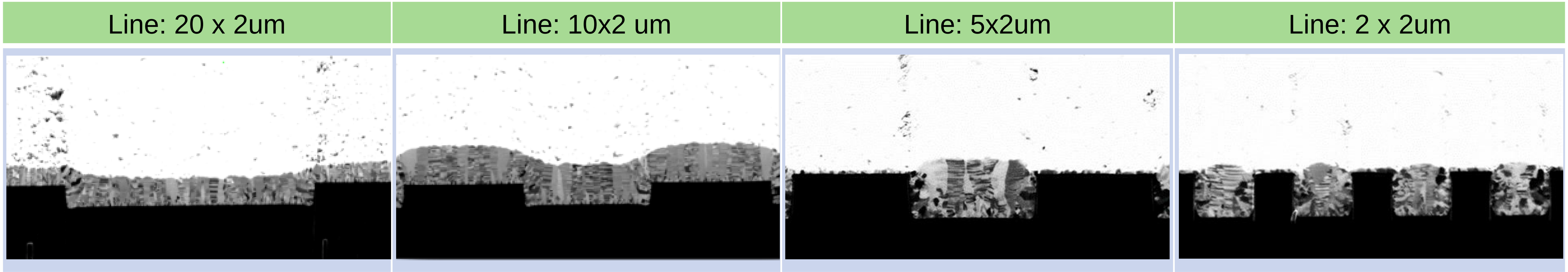


Conformal Plating vs. bottom-up fill

- Conformal Plating:
  - The electrolyte at lower agitation is more polarized than (or similar as) that at higher agitation
- Bottom-up fill
  - The electrolyte at higher agitation is more polarized than that at lower agitation
- CDA behavior is mainly controlled by additives and current density rather than by the electrolyte

Vertical Growth NT-Cu in Lines

- Vertical growth nt-Cu orientation process – Bottom-up Fill
  - Lines: CD = 20, 10, 5, 2um, depth = 2um
  - Two or Three-additive process


Line: 20 x 2um

Line: 10x2 um

Line: 5x2um

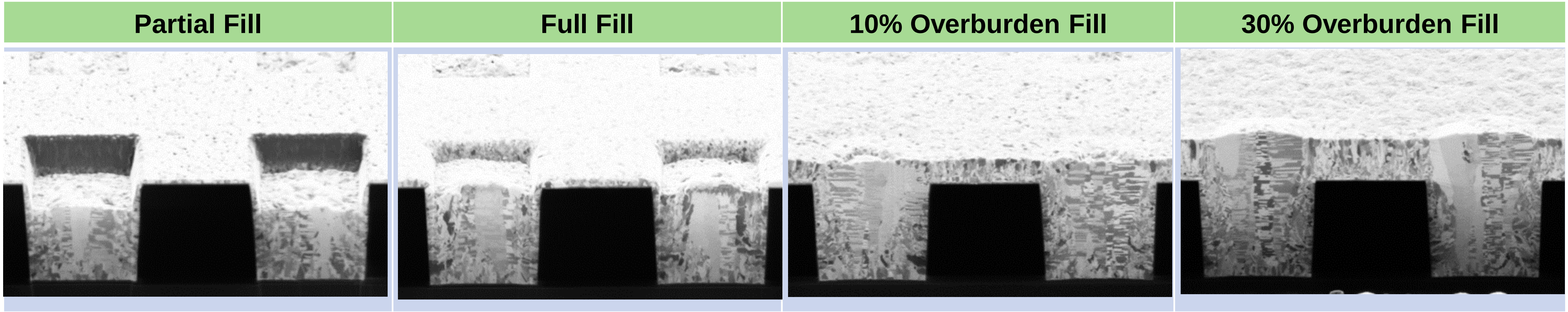
Line: 2 x 2um

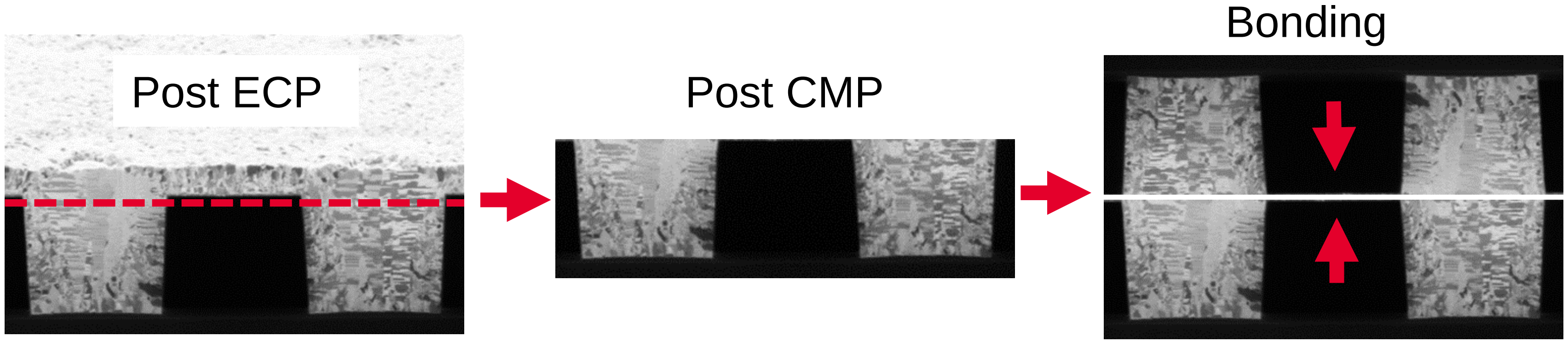
Increasing Aspect Ratio

- With the feature opening decreasing (A/R increasing) the bottom-up fill of ECP nt-Cu becomes more challenging, and the percentage of nt-Cu inside the features decreases.

Vertical Growth NT-Cu in Vias

- Vertical growth nt-Cu orientation process – Bottom-up Fill
  - Via: CD = 5um, depth = 5um
  - Three-additive process


Partial Fill
Full Fill
10% Overburden Fill
30% Overburden Fill

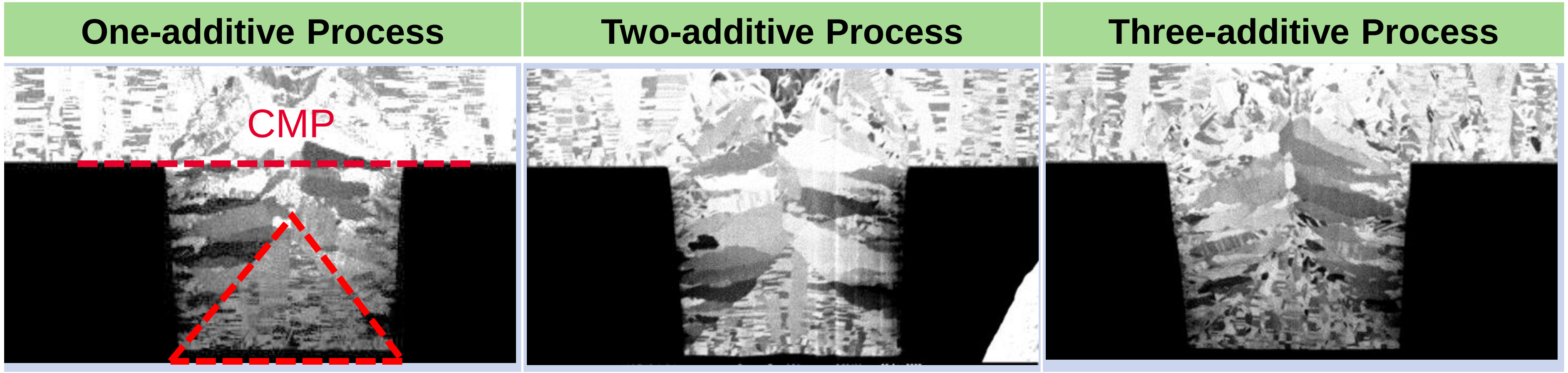


Nt-Cu orientation matches - Vertical

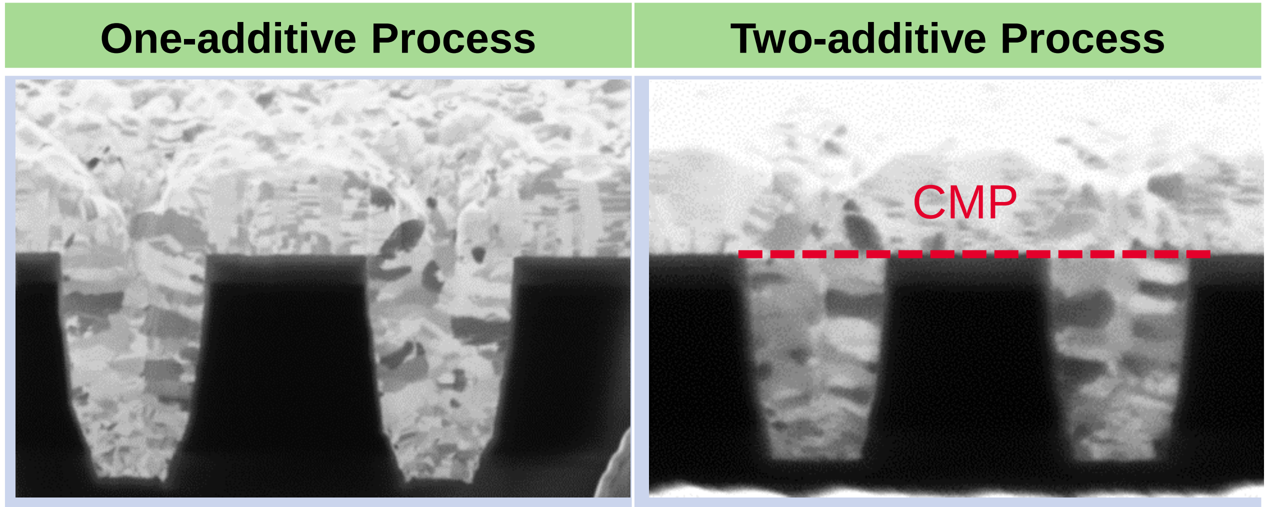
FIB image of nt-Cu hybrid bonding

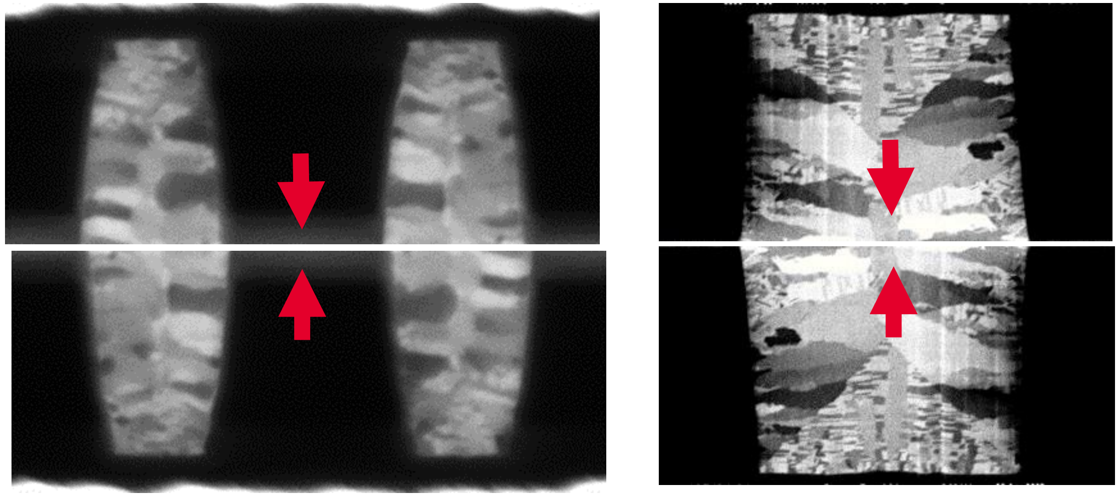
Horizontal Growth NT-Cu on Vias

- Via – CD = 5um, depth = 5um – Mix of Conformal Fill & Bottom-up Fill


One-additive Process
Two-additive Process
Three-additive Process

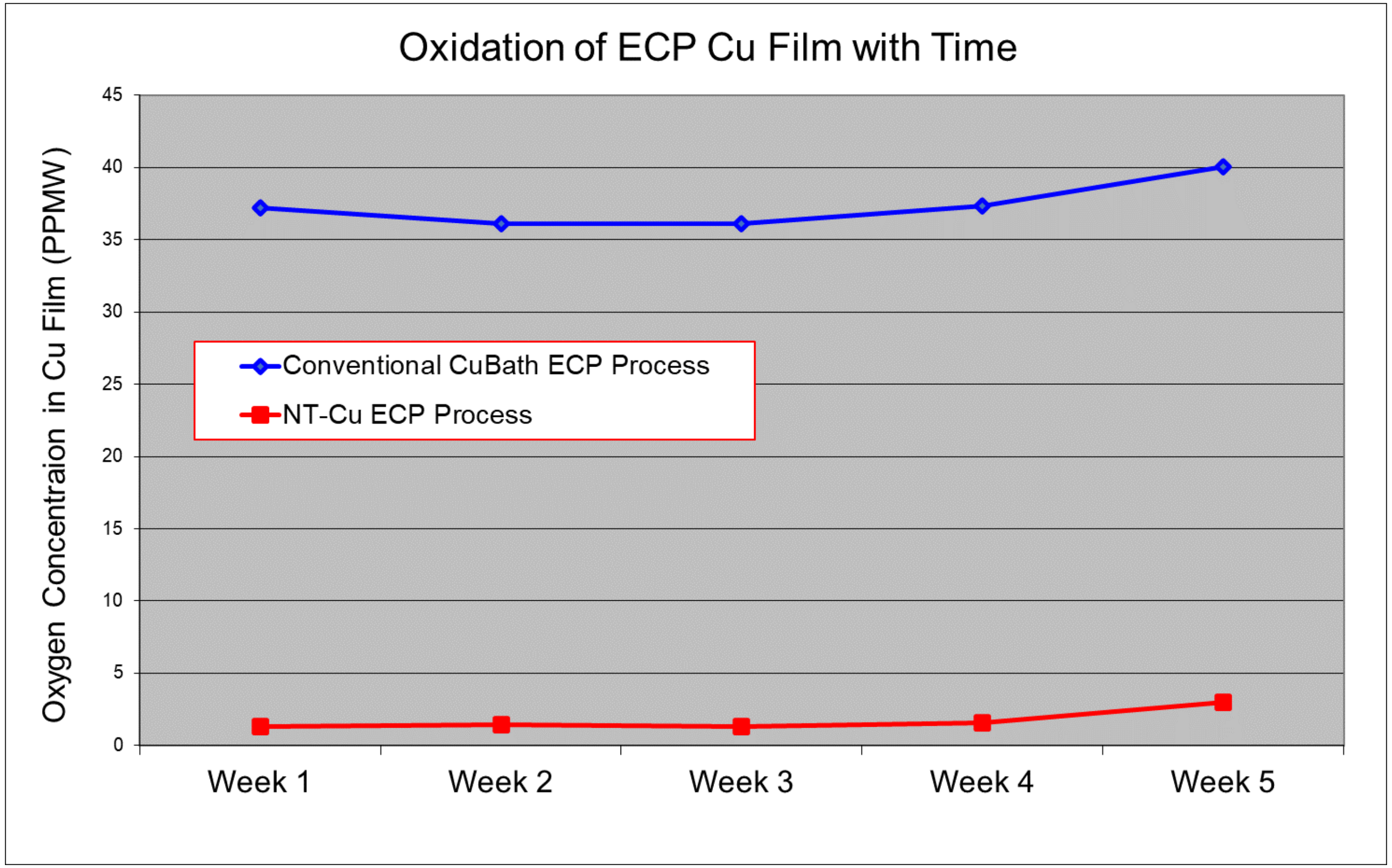
- Via – CD = 1.6um, depth = 2um


One-additive Process
Two-additive Process


CMP & Bonding
Nt-Cu orientation matches - Horizontal

NT-Cu ECP Process: Oxidation Rate

- ECP NT-Cu Process vs. Conventional CuBath CEP Process

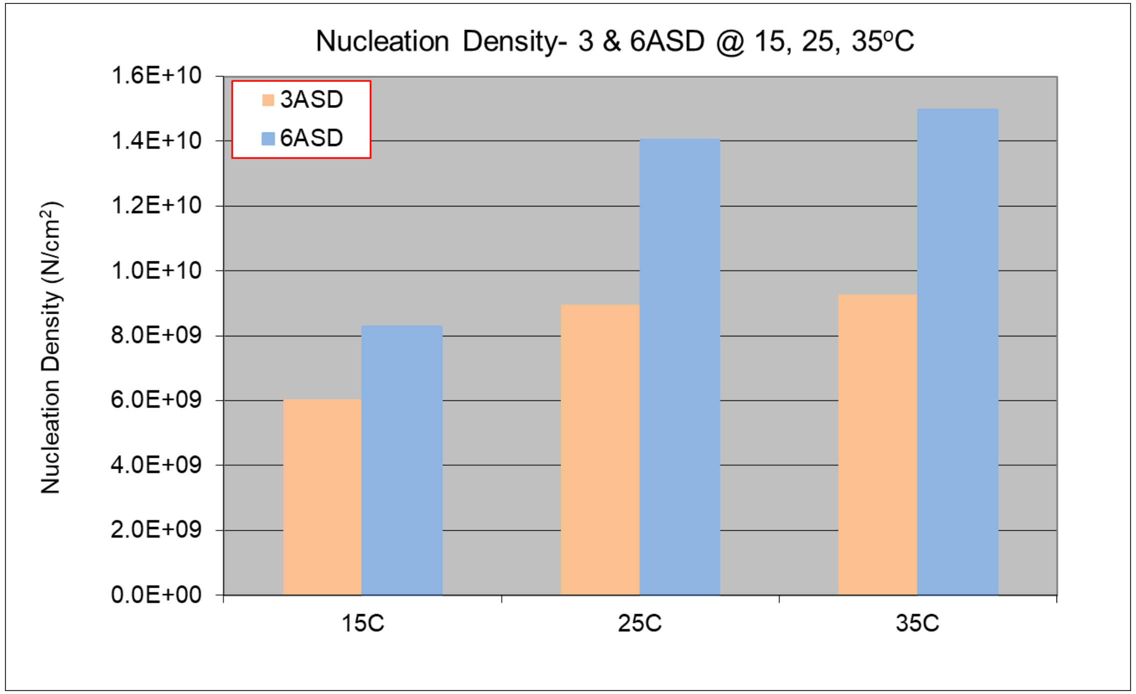


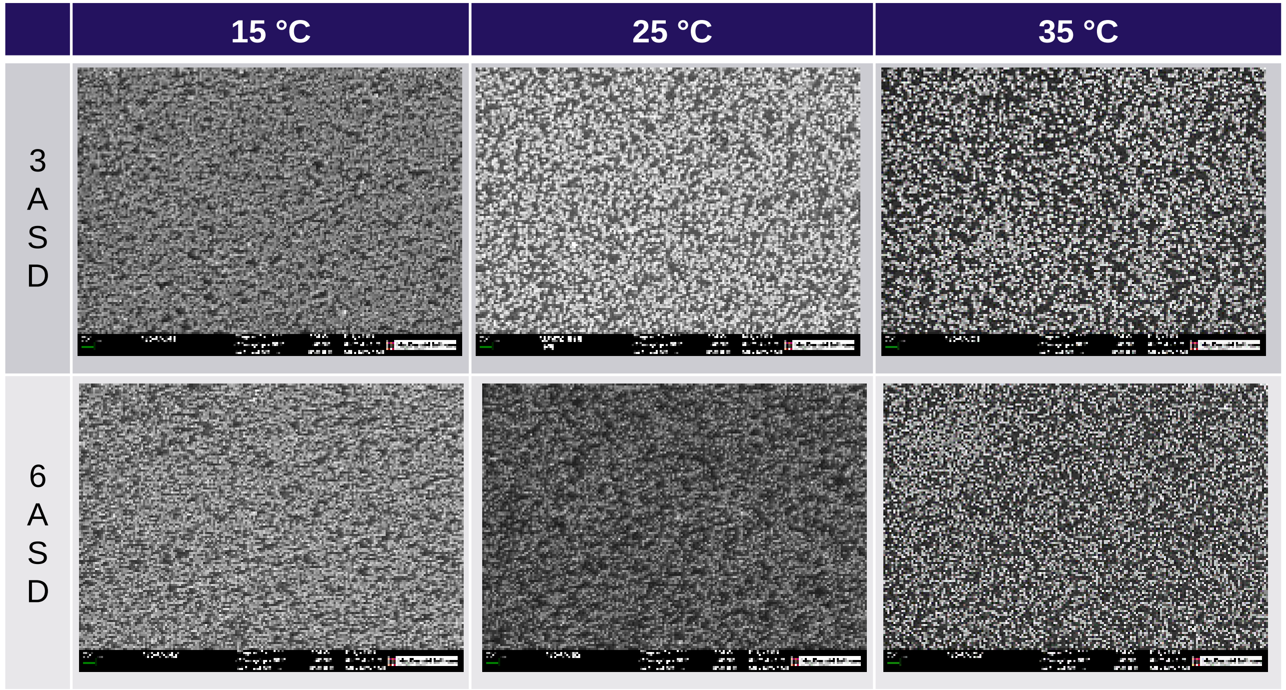
- Oxygen Level:
  - NT-Cu: 1.7 ppmw
  - CuBath: 37.4 ppmw

- Oxidation Rate:
  - NT-Cu: 0.05 ppmw/day
  - CuBath: 0.09 ppmw/day

NT-Cu ECP Process: Nucleation Process

➢ ECP NT-Cu nucleation density at various temperature





- Nucleation density increases with increasing ECP bath temperature and current density
- 6ASD shows higher nucleation density than 3ASD
- Nucleation density is more sensitive from 15°C to 25°C than from 25°C to 35°

NT-Cu ECP Process: Nucleation Process

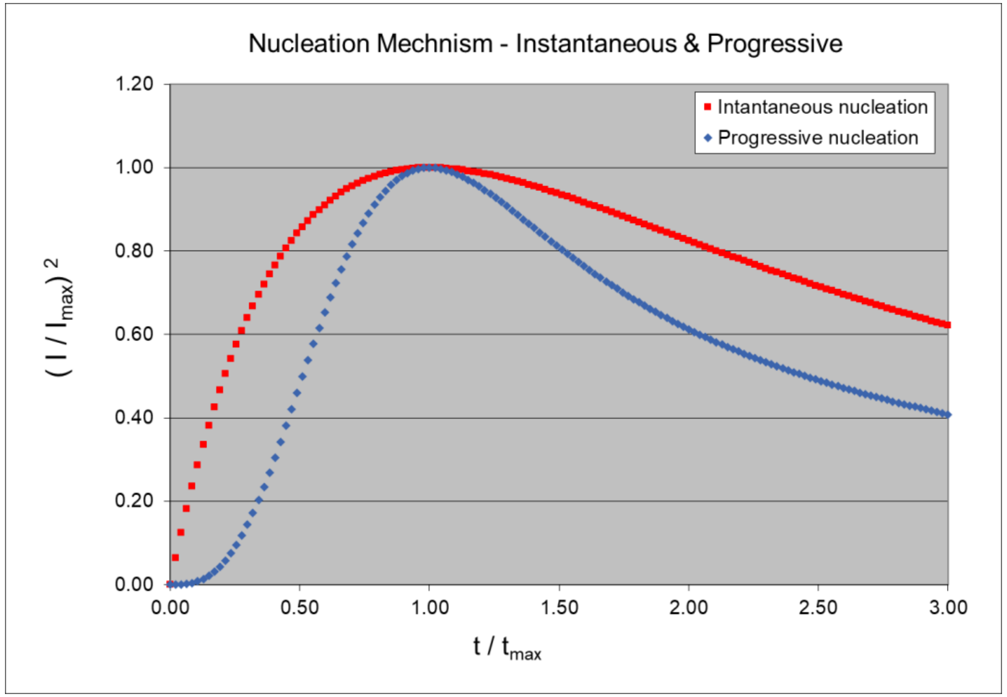
➢ ECP NT-Cu nucleation mechanism *

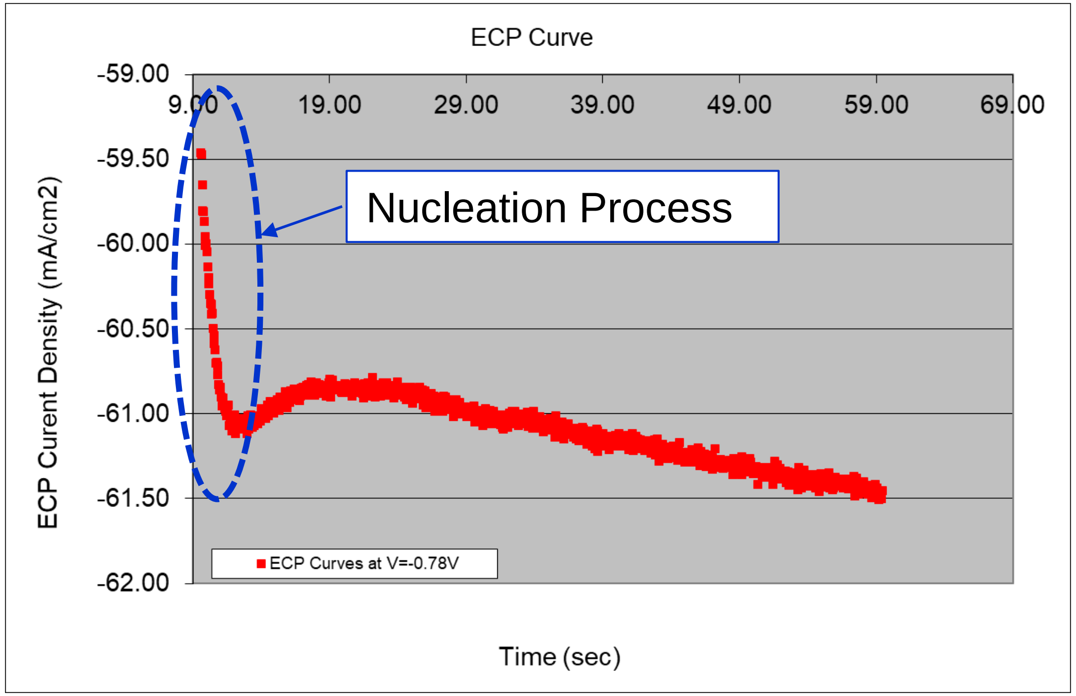
- ***Instantaneous*** vs. ***Progressive nucleation***
  - The nucleation transient followed by growth process can be described by a growth law of dimensionless form*
  - For instantaneous nucleation:

$$\frac{i^2}{i_{\max}^2} = 1.9542\,\frac{t_{\max}}{t}\left[1-\exp\left(-1.2564\,\frac{t}{t_{\max}}\right)\right]^2$$

  - For progressive nucleation:

$$\frac{i^2}{i_{\max}^2} = 1.2254\,\frac{t_{\max}}{t}\left[1-\exp\left(-1.23367\,\frac{t^2}{t_{\max}^2}\right)\right]^2$$

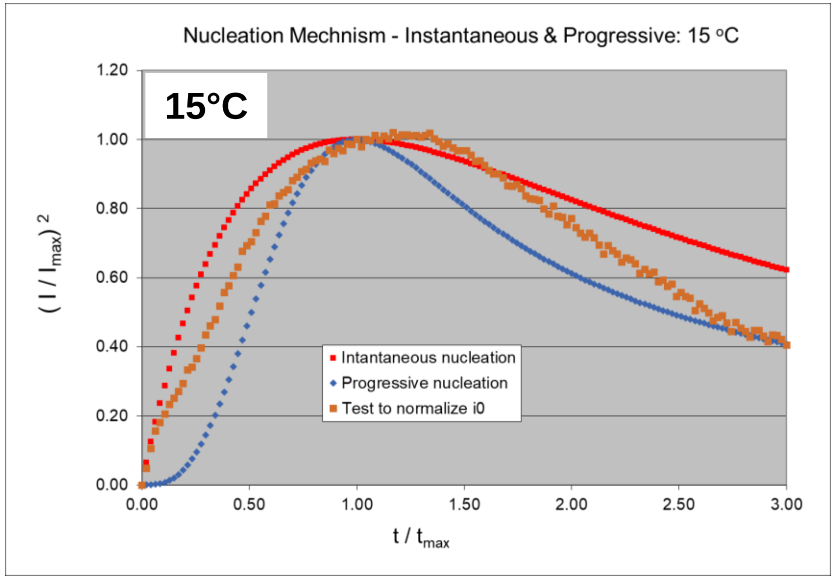


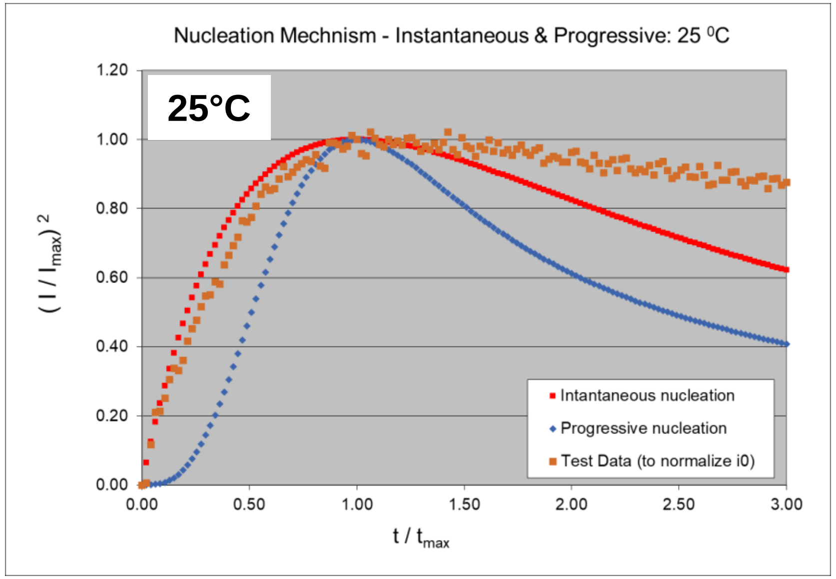


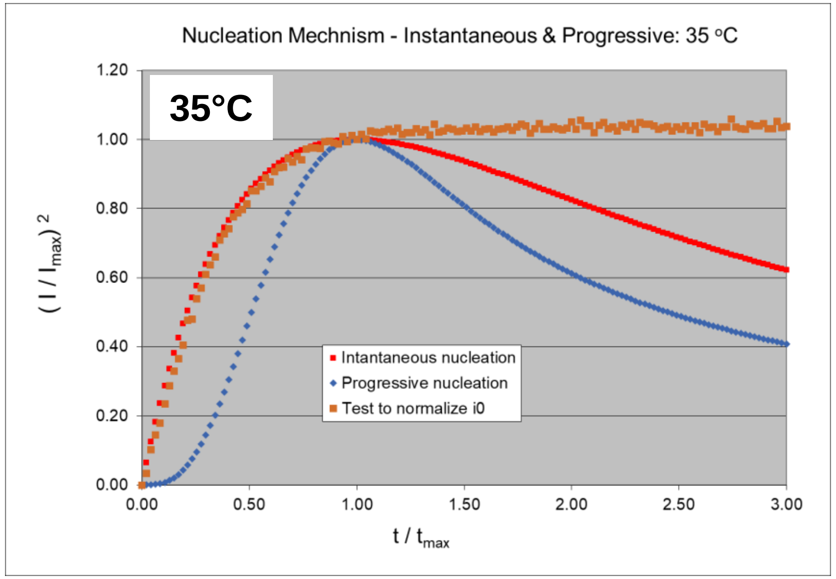
* Benjamin Scharifker, Electrochim. Acta, 28, 879 (1983).

NT-Cu ECP Process: Nucleation Process

- ECP NT-Cu nucleation mechanism







Temperature increases

- With temperature increases, the ECP nucleation process fits more with instantaneous nucleation model
  - At 25^{o}C, routine nt-Cu ECP temperature, the nucleation close enough to instantaneous mechanism

NT-Cu ECP Process: Thermodynamic Study

- Exchange Current Density & Activation Energy
  - NT-Cu ECP Process vs. Conventional CuBath CEP Process

- Butler-Volmer equation:

$$i = i_0 \left[exp\left(\frac{\alpha nF\eta}{RT}\right) - exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right)\right]$$

  - When the overpotential is small enough (linear range), the BV equation can be reformed as:

$$i_0 = \frac{RT}{nFR_{ct}}$$

- By linear potential scan, the exchange current density can be obtained.

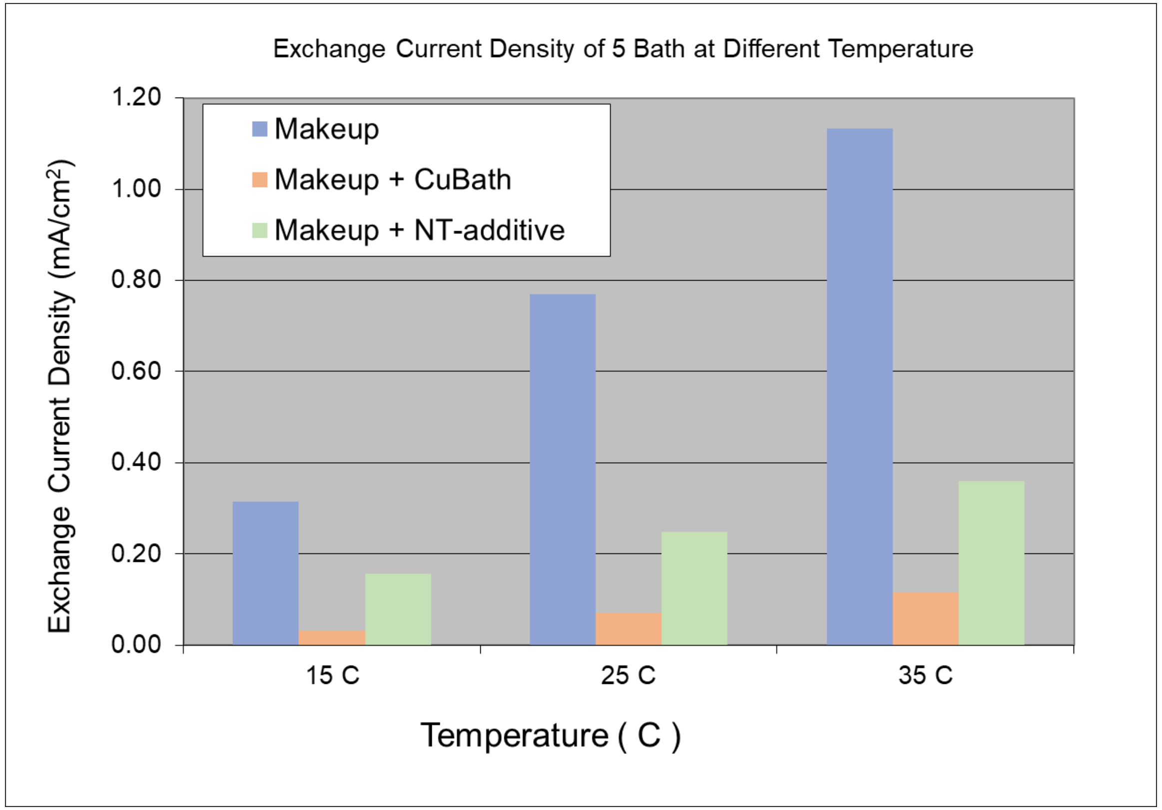
- Arrhenius equation:

$$k = A \cdot exp\left(\frac{-Ea}{RT}\right) \quad \text{or} \quad ln(i_0) = -\frac{E_a}{R} \cdot \frac{1}{T} + constant$$

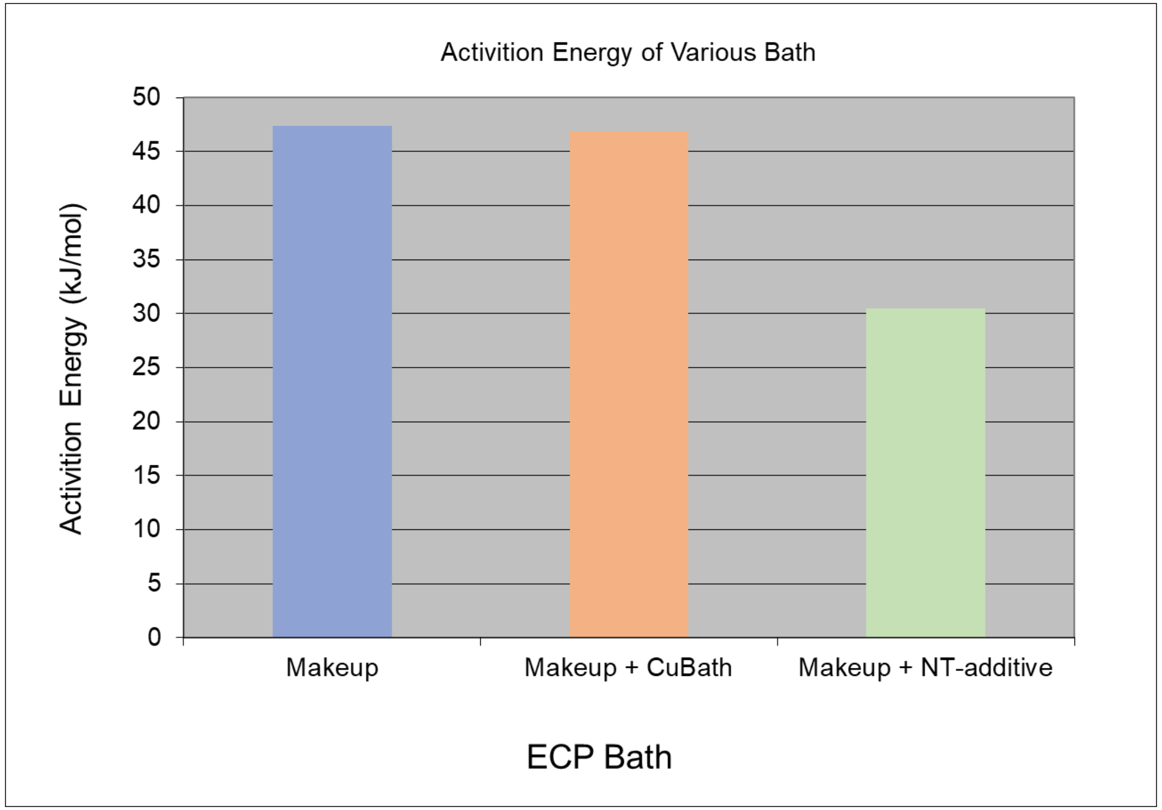
  - By plotting $ln(i_0)$ vs. $1/T$, which is linear relationship, the activation energy (Ea) can be obtained.

NT-Cu ECP Process: Thermodynamic Study

- NT-Cu ECP Process vs. Conventional CuBath CEP Process



Exchange Current Density



Activation Energy

Conclusions

- A new nano-twinned copper (nt-Cu) ECP system has been developed to produce high-density nt-Cu films with a columnar structure and a minimal transition layer.

- Two nt-Cu orientation processes—vertical growth and horizontal growth—have been successfully developed to achieve high-density nt-Cu in fully Cu-seeded features, including lines and vias.

- Vertical growth process: ECP nt-Cu can be generated in lines as small as 2 µm CD and vias as small as 5 µm CD.

- Horizontal growth process: ECP nt-Cu can be generated in vias as small as 1.6 µm CD.

- The ECP nt-Cu process demonstrated higher exchange current density and lower activation energy compared to conventional CuBath ECP Cu.

- While the vertical growth (bottom-up fill) process is still preferred for small features, it remains a challenge and requires further research and optimization.

Acknowledgment

- Thanks to my colleagues
  - Pingping Ye, Stephan Braye, Abdelhamid ElSawy, Adam Letize, Kyle Whitten, Thomas Richardson and Elie Najjar
  - Harshul Khanna, Veronica Hayes and David Doughty for their assistance with SEM/FIB
  - Ashley Kuppersmith and Bud Troche in Marketing team
- Thanks to IMAPS 2025 Arizona conference