Abstract
We discuss two electrochemical plating approaches for nanotwinned copper (ECP nt-Cu) – Gen 1 and Gen 2. These two approaches allow control over columnar width and transition layer thickness on Cu substrates, enabling the filling of nanotwinned Cu for bonding applications. Both approaches produce stable nt-Cu structures with minimal transition layers when electroplated on (111) Cu substrate. However, grain size, transition layer thickness on polycrystalline substrates, and feature-filling behavior differ. The researchers suggest that the choice between Gen 1 and Gen 2 depends on the feature size, aspect ratio, and applications. In addition, further exploration into other additives improves bottom-up filling capabilities, enabling more versatility for applications. Both approaches enable the filling of nanotwinned Cu inside bottom-seeded and complete-seeded features, with 100% nanotwin growth parallel to the substrate for bottom-seeded features. However, nanotwin growth percentage and direction depend on feature size and aspect ratio for complete-seeded features. Gen 2 tends to have less sidewall growth due to its smaller grain size and is more compatible with other additives, making it promising for high aspect ratio small features.

Keywords
Nanotwinned Cu, hybrid bonding, WLP

I. Introduction
Heterogeneous integration of wafer-level packaging enables more I/O counts on smaller footprints with shrinking feature sizes and pitch sizes [1]. The interconnect technology evolved from C4 bump, C2 bump, and micropillar with SnAg cap into the most advanced Cu-Cu direct bonding or hybrid bonding without solder cap for high density 2.5 D and 3 D packaging [2]. Sony utilized this Cu-Cu bonding for its image sensor applications, and AMD partners with TSMC, using hybrid bonding for its 3D V-Cache device [3,4]. However, current bonding technology requires elevated bonding temperature above 300 °C. This temperature is too high and unsuitable for sensitive memory applications like HBM. Nanotwinned Cu (nt-Cu) can offer lower temperatures for the Cu-Cu direct bonding because its (111) plane-dominated texture has higher atomic diffusivity and leads to a lower thermal budget [5-8]. It also possesses excellent mechanical properties and better electromigration resistance, crucial for device reliability [9,10].

This paper reports two nt-Cu electrochemical plating chemicals: Gen 1 and Gen 2. Both nt-Cu generations produce stable nt-Cu structures with minimal transition layers when electroplated on (111) Cu substrate. However, the difference lies in their grain size, transition layer thickness on polycrystalline substrates, and feature-filling capability. We will elucidate the similarities and differences between these two nt-Cu generations and their applications for various features of WLP, especially potentially for smaller via with a high aspect ratio.

II. Material and methods
A. Plating chemical and apparatus
The basic makeup solution consists of copper sulfate, sulfuric acid, and hydrochloric acid for chloride ions. The plating bath includes makeup solutions and single or multiple
proprietary organic additives. We utilize VSP Biologic
Potentiostat to perform coupon-level testing with a mini-cell
and water jacket. A water bath controls the plating
temperature at 25 °C. The anode is an insoluble Titanium
anode.

B. Microstructure and mechanical characterization

We observed the electroplated nanotwin microstructure
using a dual beam focus ion beam (FIB, Zeiss, Aurira). We
characterized the film's texture using X-ray diffraction
(XRD, Bruker AXS, D8 discovered with VANTEC-500 area
detector). Further, we characterized the texture and the grain
size using electron backscattered diffraction (EBSD, EDAX). We performed the tensile test with the Instron 5567
at a strain rate of 0.2 inches per minute with a gauge length
of 2 inches per IPC-TM-650 standard and measured the
internal stress with 1194 Cu alloy test strips per ASTM
Standard B975. We also utilized nanoindentation to measure
the film strength and hardness per ASTM Standard E2546
(iNano, KLA). SIMS determines the impurity of plated nt-
Cu.

III. Results and Discussion

A. Gen 1 nanotwinned Cu

We formulated Gen1 nt-Cu with a single additive in an acidic
makeup solution with expansive operating windows,
including concentration, agitation, and current density [11,
12]. Fig. 1 shows one example of 4 µm thick nt-Cu film
plated on blanket PVD Cu with a direct current of 6 ASD and
agitation of 300 rpm at room temperature of 25 °C. The
single additive concentration is 4 ml / L. The SEM surface
image shows 100% nt-Cu coverage on the surface. The grain
size is distributed uniformly across the surface. FIB cross-
section further confirms that 100% nt-Cu grain throughout
the coating depth with barely any transition layer between
the Cu seed layer and the nt-Cu structure. One of the
attributes of nt-Cu for the low-temperature Cu hybrid
bonding application is the high diffusivity rate of Cu (111),
enabling a low thermal budget during the bonding process
[5-7]. Both XRD and EBSD indicate that Gen 1 nt-Cu with
Cu (111) lattice plane paralleled to the Cu seed. We also
demonstrate that the Gen 1 nt-Cu structure is very stable even
after 400 °C annealing for 2 hours. Fig 2 shows the FIB
cross-section images of nt-Cu annealing at 200, 300, and
even 400 °C for 2 hours. The nt-Cu structure upholds under
all these annealing conditions. Literature shows that nt-Cu
performs better in electromigration [7], and this stable nt-Cu
structure in a wide range of temperatures benefits the
device's electromigration resistance. In addition to the stable
structure, the coating impurity is low. Organic inclusion is
only ten ppm, including C, O, Cl, S, and N. The low impurity
is associated with low resistivity and, in some cases,
resistance to electromigration; therefore, it is exceptionally
critical to device reliability. Using Four Point Probe, we
measured the resistivity of 5 µm thick nt-Cu film. The
current density is 3 ASD and 6 ASD, and the annealing
conditions are at 100, 200, 300, and 400 °C for 30 minutes
under forming gas. Fig 3 shows all measured resistivity is in
the range of 17 to 18 n·Ω·m, which is close to the standard
bulk Cu of 17.2 n·Ω·m.

Fig. 1 (a) Surface image, (b) FIB cross-section image,
(c) Plan-view EBSD image, (d) 2D XRD diffraction
frame with preferred (111) orientation
B. Comparison of Gen 1 and Gen 2 nanotwinned Cu

In the last section, we introduced our Gen 1 nt-cu, which enables the formation of 100% nt-Cu with a columnar structure and less than 100 nm thick transition layer on the commercial PVD Cu seed on Si wafer. This Gen 1 nt-Cu can fill different WLP bottom-seeded features, such as pad, pillar, and RDL line. By incorporating a secondary additive, Gen 1 nt-cu can even fill the via with tapered recess, resulting in a high percentage of nt-Cu parallel to the bottom seed of a flat surface [12]. However, for features with the completed seed, such as the damascene structure, there is an intense competition between the sidewall direction growth and bottom-up direction growth, as shown schematically in Fig 4. Therefore, the conformal plating alone process cannot meet the requirement for a high percentage of nt-Cu growing from the bottom when the feature diameter is smaller than 2-3 µm and the aspect ratio is more significant than 1. Fig 5 shows Gen 1 nt-Cu filling performance on the trench with a width of 20 µm down to 2 µm and an aspect ratio from 0.1 to 1. For the broader feature with a low aspect ratio, a high percentage of nt grows from the bottom. However, for smaller features (less than 2-3 µm) with a high aspect ratio (more than 1), the percentage of nt-Cu decreased significantly to 25%. It becomes even more challenging for vias with surrounding sidewalls. There is a need to develop an additive system to promote bottom-up nt-Cu growth while inhibiting sidewall growth to meet the demand for shrinking
feature size and pitch size. However, in many cases, adding secondary and third additives into the nt-Cu suppressor-only bath will disrupt the nt-Cu formation, and, in some cases, it will inhibit the bath's nt-Cu formation capability. Therefore, we develop the Gen 2 suppressor.

Despite differences in the additives' nature, there are similarities between Gen 1 and Gen 2. For example, both Gen 1 and Gen 2 have a minimal transition layer when electroplated on (111) dominated Cu substrate and produce very stable (111) dominated nt-Cu structures that are maintained even after 300 °C annealing for 4 hours. The main differences lie in the grain size (nt-Cu Column width), transition layer thickness plated on polycrystalline substrates, the resistance to nt-Cu disruption with additional accelerator or combination of accelerator and leveler, and associated feature-filling behaviors.

The Gen 2 suppressor produces a smaller grain size and narrower columnar structure than Gen 1. Fig 6 FIB/SEM and EBSD images indeed show that. The average grain size measured from EBSD is that the grain size of the Gen 2 suppressor is about 340 nm, while Gen 1 is 500 nm. Different grain sizes change the measured ultimate tensile strength, as shown in Fig. 7. Strips were grown 25 μm thick for pulling. The smaller-grained Gen 2 chemistry demonstrates the ultimate tensile strength of 470 MPa, while Gen 1 demonstrates the ultimate tensile strength of 290 MPa. Per the standard tradeoff between ductility and strength, Gen 2 shows failure at yield for elongation of 2 %, while Gen 1 shows hardening after yield for elongation of 11 %. These results are commensurate with the expectation that smaller grains yield increased strength [13-15]. Nanoindentation measurements supported these results, while Gen 1 and Gen 2 demonstrate Young's modulus of 155 GPa and 165 GPa and hardness of 2.00 GPa and 2.482 GPa, respectively. The improved mechanical properties are attractive for semiconductor devices to decrease warpage during device fabrication.

The second difference between Gen 1 and Gen 2 is the transition layer thickness when plating on a polycrystalline Cu substrate. Fig 8 shows the 4 μm thick Cu film plated on (111) dominated PVD Cu seed or polycrystalline Cu seed. Gen 1 and 2 can produce nt-Cu on (111) dominated Cu seed with a shallow transition layer. EBSD shows more than 99% of (111) plane parallel to the substrate. However, for polycrystalline Cu seed, Gen 2 can produce nt-Cu with a shallow transition layer, and Gen 1 leads to a higher transition layer. EBSD also shows Gen 2 produces nt-Cu with more than 87% of (111) plane parallel to the substrate. For Gen 1, it is about 29%. With increasing plating time, the thick film will produce more nt structure. Therefore, the main difference is the transition layer thickness. This technique provides two approaches for a two-step process for a high aspect ratio, as shown in Fig 9. The first step is the bottom-up process to decrease the aspect ratio to have more nt-Cu grow vertically from the bottom in the second step. However, Cu texture could be (111) dominated or none (111) dominated for this first step of the bottom-up process. In the case of none (111) dominated Cu first step process, if a low transition layer is essential in the second step, Gen 2 will be the preferred choice. In other cases, where the first step is (111) dominated surface or low transition layer for the second step is not critical, Gen 1 and Gen 2 are suitable.
Another difference between these two nt-Cu generations is the resistance to nt-Cu disruption by adding a secondary or third additive into the plating bath. Fig. 10 shows the nt-Cu formation ability by adding a leveler or accelerator and leveler into the plating bath. The electroplated film thickness is 4 µm. For Gen 1 and 2, the additional proprietary leveler and accelerator in the plating bath will produce nt-Cu. There is barely any transition layer for Gen 2. The plating bath can maintain the ability to produce 100% of the fine nt-Cu structure. XRD further confirmed the plated film is nt-Cu with more than 99% of (111) plane parallel to the substrate. This trio additive system provides the possible approach to boost the bottom-up fill for a high aspect ratio and small opening.

### III. Conclusion

We demonstrated two electrochemical nt-Cu plating approaches, Gen 1 and Gen 2, for hybrid-bonding applications. Both Gen 1 and Gen 2 have a minimal transition layer when electroplated on (111) dominated Cu substrate and produce very stable (111) dominated nt-Cu structures even after 300 °C annealing for 4 hours. Gen 1 nt-Cu can fill different WLP features with the bottom and completed seed. However, it is challenging for the completed seed features with a diameter of less than 2 to 3 µm and an aspect ratio larger than 1. One of the methods is a two-step plating process. In the case of none (111) dominated Cu first step process and the requirement of a low transition layer in the second step, Gen 2 will be the preferred choice. In other cases, where the first step is (111) dominated surface or low transition layer for the second step is not critical, Gen 1 and Gen 2 are suitable. The other method is the trio-additives system.

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### References


