



Executive Summary

- Mobile devices are a leading driver to growth in the IC market, specifically WLP and FC
 - WLP expected to grow ~20% CAGR
- Enthone focused on leveraging core IP in Cu electrodeposition to various applications and packaging schemes
 - Enthone has ~70% of Cu electroplating market share
- Copper plating (bump,pillar,RDL,via fill) focus of current business and New Product Development
- Copper plating market is becoming fragmented due to various packaging schemes and requirements for Cu.
 - Customization of chemistries and collaboration with tool vendor becoming a requirement
- New Product Development considers coplanarity, bump shape, Kirkendall voids, and plating rate as essential attributes
- High purity films with resistance to Kirkendall voiding desirable for specific applications

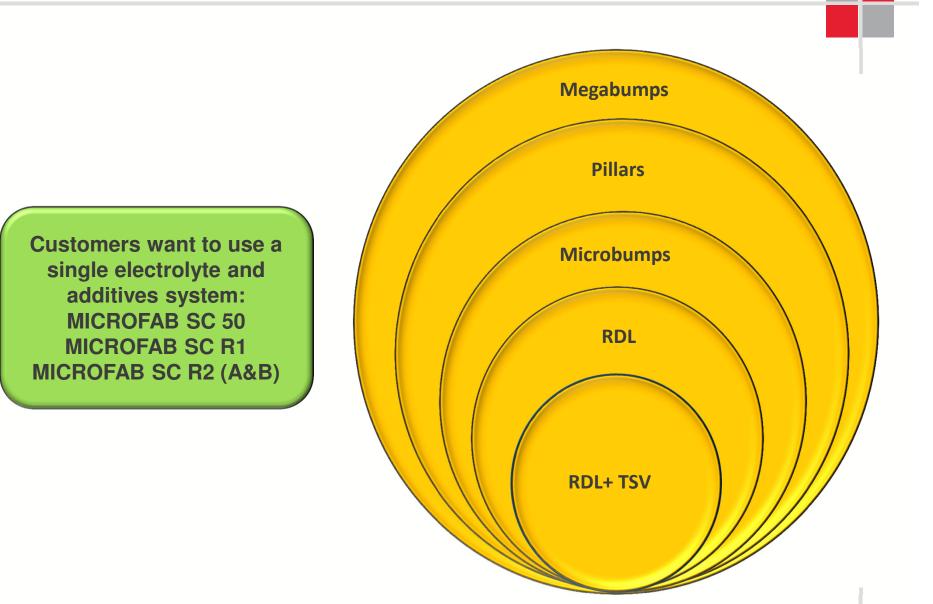


Summary

- Having a <u>copper rich</u> electrolyte while imperative for some processes (megabumps, pillars, TSV), may be detrimental to others (microbumps, rdl).
- Playing a critical role in nucleation, wetting properties, the relative strength of the <u>inhibitor component</u> plays a crucial role in establishing the bump shape. This may be important for RDL applications
- The <u>leveler component</u> is the corner stone of the process constantly jockeying for position with the activator component, and at times with the inhibitor as well.
 - The requirements will be application specific



Complexity of WLP





Technology Platform	Dimensions	Desired Plating Rate (μm/min)					
Megabumps	200x200	6.0+					
Pillars	40×50	3.5					
Microbumps	20x30	3.0					
RDL + Via Fill	Various Line Widths	1.0- 2.0					
RDL + TSV + Pillar	Various Line Widths and Aspect Ratios	TBD					
Market is driving a a wide range of feature sizes Customers want optimal performance for each							



Attributes	ibutes Electrochemistry Primary Control Factor		Secondary Control Factor
Bump Height Uniformity	High Tafel slope (Wa)	Leveler	[H ⁺], current density, temp, [Cl]
Flat Bump Shape	Minimal difference in polarization between high and low agitation (ΔE)	Leveler and "suppressor"	[Cu], [Cl], agitation
Kirkendall Void-free	Non steady state Chronopotentiometry	Leveler	Accelerator

There are many hardware and chemical "knobs" that have a direct impact to the end result



Applications	Critical Plating Attribute	Bump shape
RDL	Coplanarity	Flat to domed on flat substrate
Microbumps	Coplanarity	Flat on passivation substrates, but domed on flat substrates
Cu Pillars	Coplanarity at high speed (≥3.5 μm/min)	Flat on passivation substrates, but domed on flat substrates
Mega Bumps	Coplanarity, <u>Very high</u> <u>Throughput (</u> >6 μm/min)	Flat to dished, to slightly domed on flat substrates



Bump Dimension and Mass Transport



x µm

Т



	<>			
photoresist		mu x	Convection zone, agitation effective depth up to opening size	Applicable current density is much higher due to sufficient mass transfer from agitation
phot			Diffusion zone, solution velocity is zero, and all mass transport rely on diffusion	Applicable current density is limited by diffusion. Too high current density result in very domed shape or nodule in extreme case

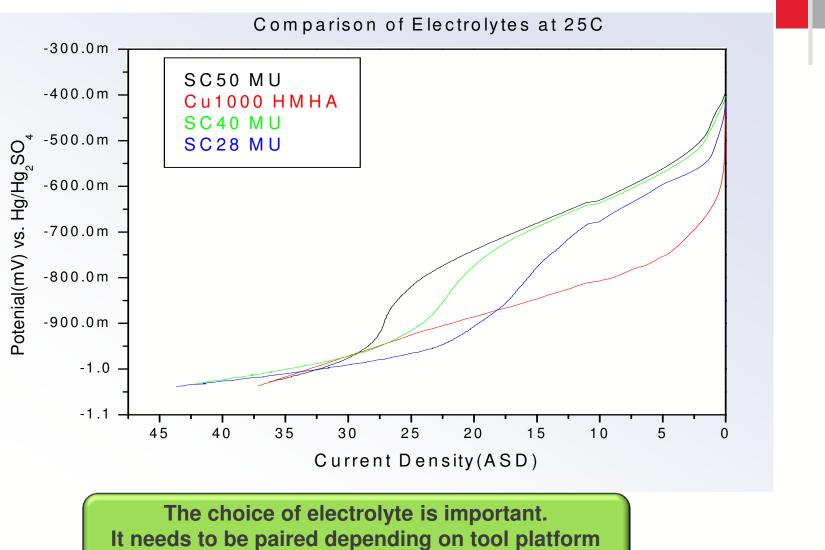
Plating solution, flow velocity by color



$$i_{limiting} = \frac{nFD}{\delta}C$$



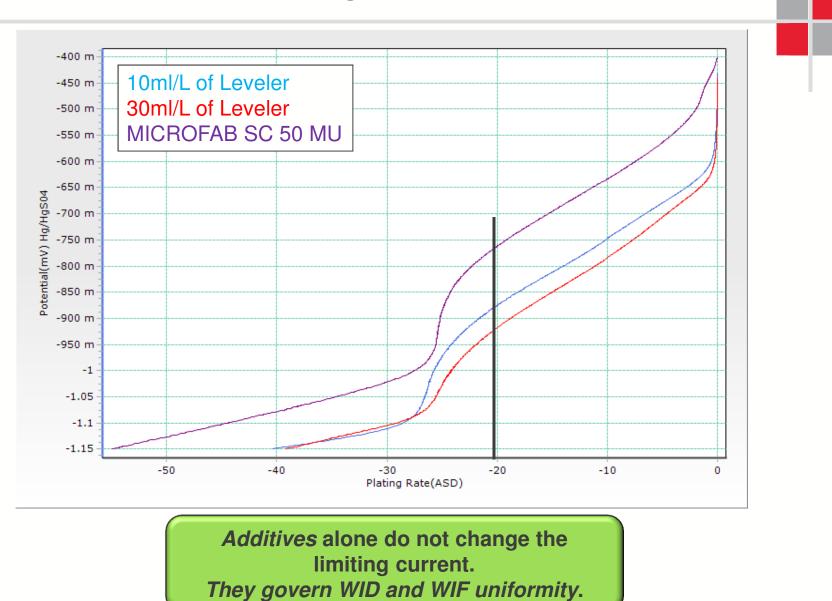
Electrolytes Effects on Limiting Current Density



and applications, i.e. TSV, RDL, Pillars, etc...



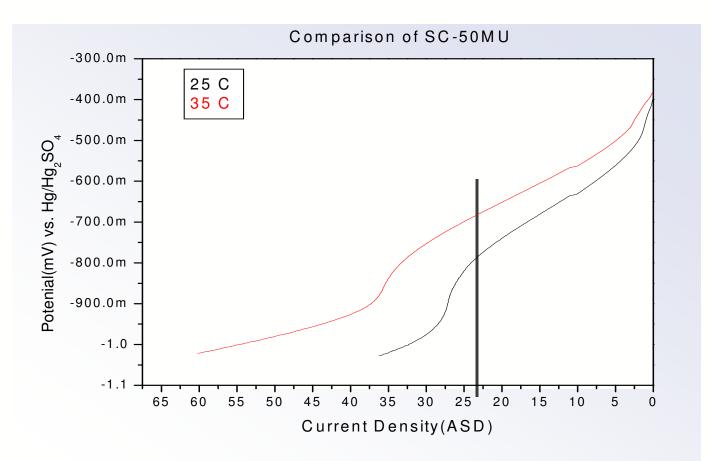
Additives Effects on Limiting Current: Leveler



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Limiting Current MICROFAB SC 50 MU at 25 and 35 °C



Increasing temperature increases the limiting current density. While 20 ASD is within the limiting current the, reaction will primarily be diffusion controlled.



Summary I

- Increasing copper ion concentration increases the limiting current of the electrolyte:
 - Good for TSV and Pillar
 - Detrimental for RDL
- Decreasing the concentration or lower agitation will also affect the limiting current adversely:
 - The lower the agitation the less mass transfer
 - The lower the copper concentration the lower the limiting current, which would favor RDL and yielding the best uniformity
- Increasing temperature increases the limiting current:
 - Favorable for pillar
- The closer the deposition rate is to the limiting current, the less additives(kinetic control) influence the copper transport (diffusion controlled).



The role of the <u>suppressor</u> component:

DOES ONE FIT ALL?



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Effect of Additives on Nucleation Density								
Suppressor (R1S)	Accelerator	Nuclei/cm ²	SEM					
0	0	1.37E+08	Mar BH3331A WINNESS BUY LINE COLONG					
0	20 ml/L	2.61E+08						
20 mL/L	0	6.28E+08	BURNED WERE WERE CONTRACTOR					
20 mL/L	20 ml/L	5.34E+08						
MacDermid Enthor	he	Ą	Platform Specialty Products Company.					

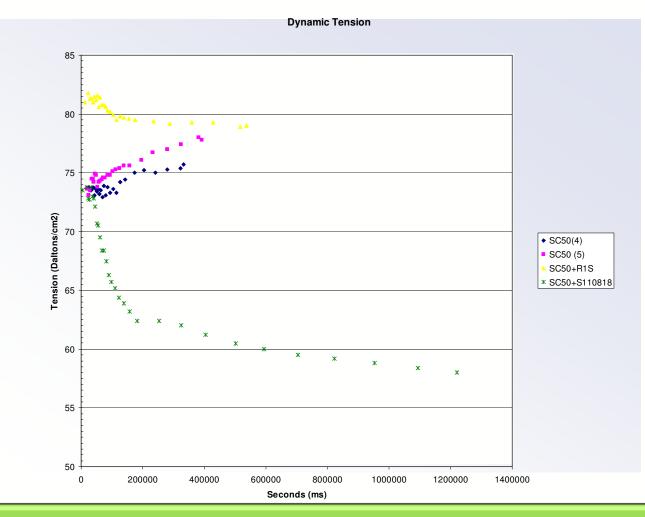
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Suppressor Role: More Important than Just Wetting

Effect Suppressor Concentration on Nucleation Density							
Accelerator	Nuclei/cm ²	SEM					
0	1.37E+08	MURINA STATE OF LOCAL SPECIAL					
0	6.28E+08						
0	1.76E+09						
0	1.10E+09						
0	1.41E+09						
	Accelerator 0 0 0	Accelerator Nuclei/cm² 0 1.37E+08 0 6.28E+08 0 1.76E+09 0 1.10E+09 0 1.41E+09					



Suppressor Type vs. Dynamic Surface Tension



The suppressor (S110818) delivers lower surface tension than that used in MICROFAB SC R1. This is critical for high aspect ratio substrates and fine lines RDL applications.



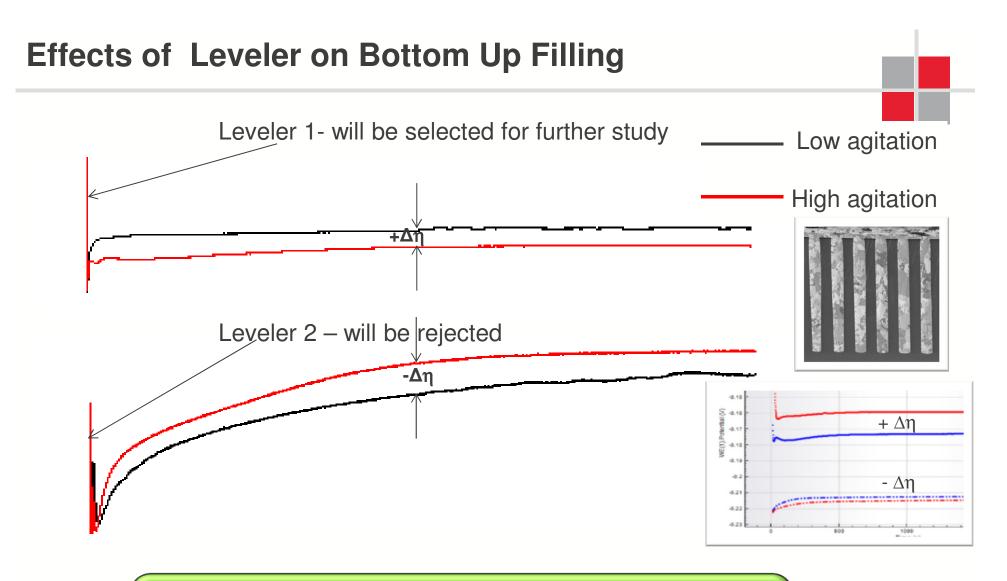
The role of the <u>leveler</u>:

WHAT ARE THE NECESSARY PROPERTIES OF THE LEVELER WHICH WOULD ALLOW IT TO WORK RELATIVELY WELL IN NUMEROUS SPACES: RDL; RDL+ TSV; AND PILLARS?



- The degree of polarization is important to obtain both bottom up fill (TSV), yet not too strong for RDL applications (bi-corn, devil horn, etc...)
- A very polarizing suppressor is adequate for RDL, but could generate poor gap fill (TSV). However, this is a good attribute for Megabumps applications.
- Too strong a leveler will cause conformal fill, undesirable for RDL, but excellent for Pillars, and Megabumps.
- There needs to be a competitive adsorption of both leveler (High Wagner Number, appropriate $+\Delta E$, good mass transport) and suppressor (appropriate suppression strength and functionality) so a certain degree of polarization is maintained to counterbalance the effects of the accelerator.





 Δh value at different agitation conditions can be one of the predictors for gap fill. There is a direct correlation between the degree of separation (polarization/depolarization) and the likely bottom up fill, or a lack thereof.



Wagner Number (Wa) ~ Throwing Power, degree of uniformity of the macroscopic current distribution

 $W_{a} = \frac{\text{activation resistance}}{\text{ohmic resistance}}$ $= \frac{R_{a}}{R_{\Omega}} = \frac{\kappa}{\ell} \left(\frac{\partial \eta_{a}}{\partial i}\right)$ $= \frac{\kappa}{\ell} \frac{\beta}{i}$

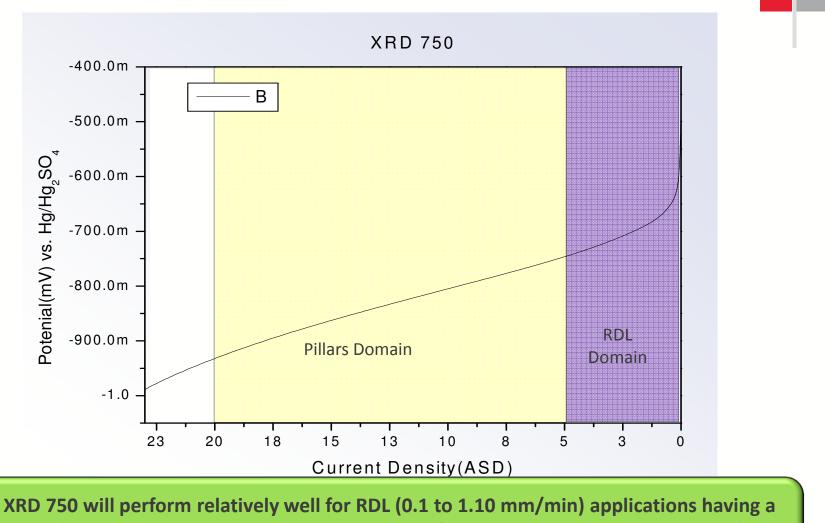
 κ : electrolyte conductivity *l*: distance between anode and cathode β : Tafel slope

Higher Wa number, better uniformity

- higher κ: higher acid conc.
- lower I: closer wafer to anode distance
- higher β: stronger suppression from suppressor or leveler
- lower i : lower throughput



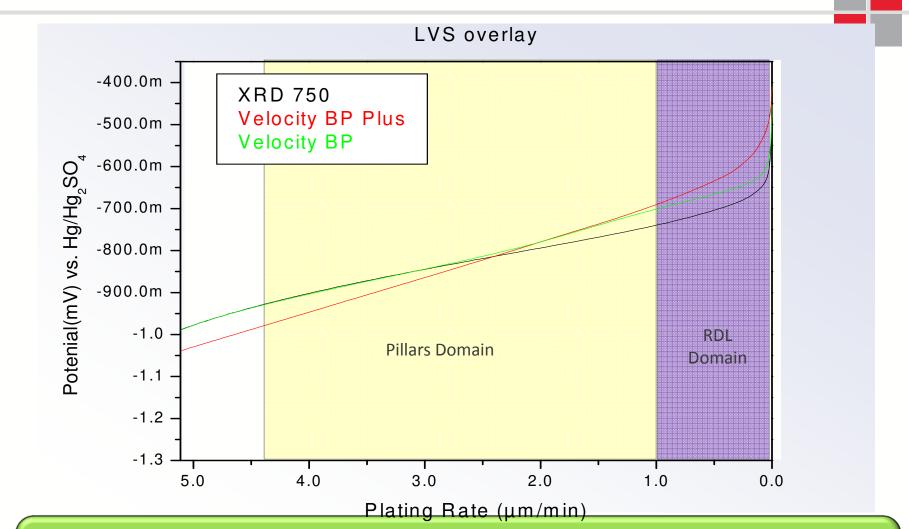
Linear Voltammetry Sweep of a Likely 2-1 Leveler



KRD 750 will perform relatively well for RDL (0.1 to 1.10 mm/min) applications having a Wa of 89. For pillar applications, acceptable performance is expected with a Wa of 50 from 1.1 to 4.4 mm/min.



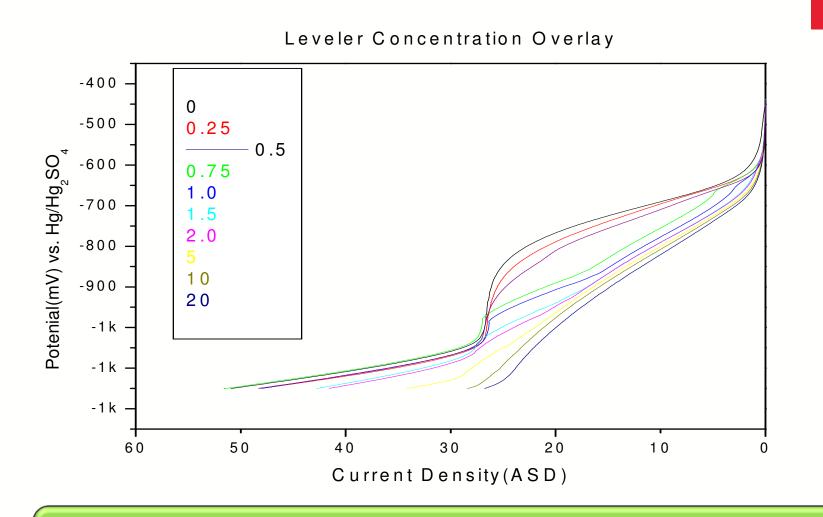
Linear Voltammetry Sweep of Various Levelers



While XRD 750 will perform relatively well for RDL and TSV applications (Wa= 89; 56), the Velocity PLUS additives will outperform it for RDL and pillars (Wa= 109; 78). However, the Velocity PLUS additives do not give good gap fill performance.



Effects of Leveler Concentration on Wa



Clear change in polarization upon increasing the leveler concentration, and increased suppression as well after adding just 0.75 ml/L of leveler



Summary II

- The leveler component plays a critical role in achieving overall uniformity, gap fill, and controlling the bump shape:
 - This is critical for TSV, pillars, and RDL, and megabumps
- For RDL, the choice of suppressor is paramount in providing the necessary nucleation and <u>achieving the proper bump shape</u>, whereas for pillars the role of the suppressor only extend to mere, initial nucleation
- For RDL and microbumps, copper concentration controls the degree of doming:
 - The lower the copper concentration, the lower the degree of doming
- For pillars and megabumps, where throughput is of the essence, and to overcome challenging designs, a higher copper concentration of copper is desired in the electrolyte

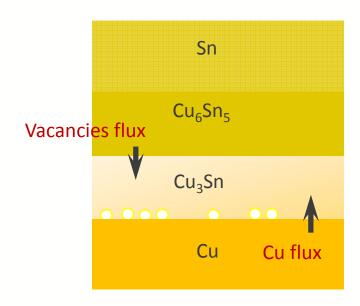


Grain size:

HOW CAN THE GRAIN SIZE BE INFLUENCED WITH THE CHOICE OF ADDITIVES WITHOUT CHANGING THE DEPOSITION RATE? IS THERE A CORRELATION WITH UNDERSTANDING KIRKENDALL VOID FORMATION AND PREVENTION?



Cu diffusion is 3x faster than Sn



Since Kirkendall void is from diffusion

$$\tau = 2\sqrt{D \cdot t}$$
, $D = D_0 e^{-\frac{E}{RT}}$

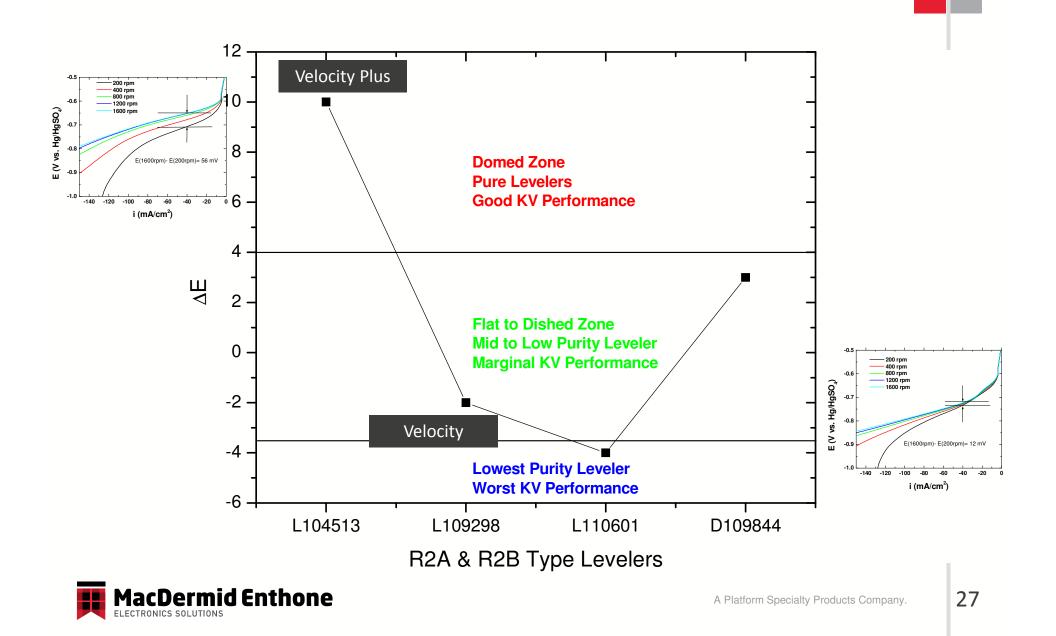
D: diffusivity *t*: time *T*: temperature

• Time and temperature are two factors in the Kirkendall void formation.

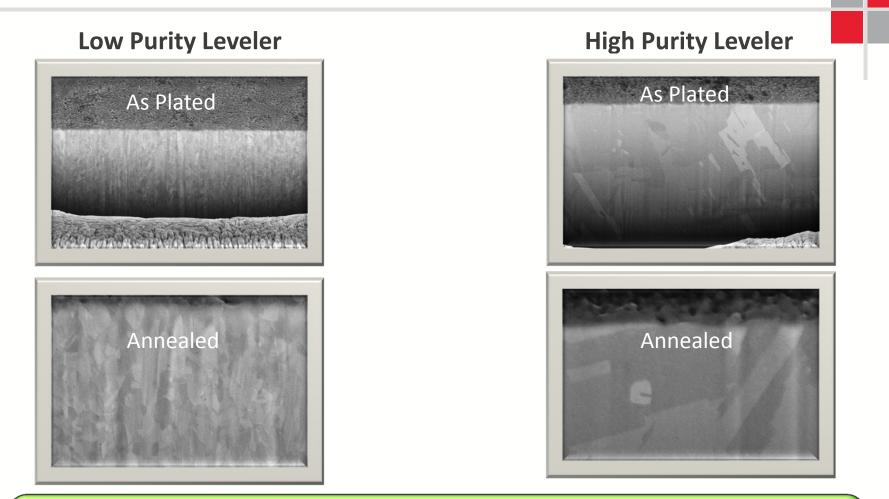
Once vacancies accumulate to super-saturation at the Cu/Cu₃Sn interface, Kirkendall voids nucleate and grow.



Predicting Kirkendall Void Performance



Controlling Grain Size: Leveler Design



The average crystal size can be controlled through leveler design and its subsequent interactions with suppressor and accelerator. As such, the level of impurities in the copper film can be controlled. This will impact eventually KV performance, and perhaps etching rate.



- 1. Film properties of several MicroFab copper plating processes were evaluated after one dielectric bake cycle of 225°, 60 min
- 2. Copper films were plated at 4.54 ASD ($1 \mu m/min$), 15 μm thickness representative of typical RDL plating speeds on Si wafers
- 3. Film properties such as texture, crystallite size, and stress were evaluated by X-ray Diffraction
- 4. Film impurities were measured by SIMS
- 5. Film elongation was measured by Bulge test



POST-ANNEAL: ORIENTATION, STRESS, & CRYSTALLITE SIZE

Index		Post Anneal Orientation					(MPa) Post-Size	Crystallite Size (Å) Post Anneal	Total Impurity (ppm)	Pre- Anneal Bulge	Post- Anneal Bulge Test
	(-111)	(-100)	(-110)	(-311)	(-331)	(-210)				Test	
MICROFAB SC Process A	1%	3%	5%	4%	22%	65%	120	686	157	1 20	4.25
Times random	0.05	0.19	0.31	0.26	1.29	3.89	120	000	157	1.38	4.35
MICROFAB SC Process B	0%	0%	0%	2%	2%	95%	- 33	887	53.4	0.53	1.03
Times random	0	0.01	0.03	0.12	0.12	5.72		007	53.4	0.53	1.05
MICROFAB Process C	3%	3%	4%	6%	19%	64%	109	856	124.5	0.55	1.00
Times random	0.15	0.19	0.26	0.39	1.15	3.85	109				
MICROFAB Process D	1%	1%	3%	15%	13%	66%	106	847	2.6	1.10	5.13
Times random	0.08	0.09	0.2	0.89	0.78	3.96					
Process X	8%	7%	11%	8%	33%	33%	114	14 886	5.5 2.6	2.60	4.87
Times random	0.46	0.44	0.66	0.5	1.95	2	114			2.60	4.87

All copper films show tensile stress after one dielectric bake cycle MicroFab SC Process B differentiated in terms of lower tensile stress and strong texture MicroFab Process D differentiated by elongation after first bake cycle and lowest impurities

Random orientation values 16% and above mean that direction has more crystallites oriented in that direction. This would indicate that MICROFAB SC Process B is strongly <210> textured with the majority of the crystallites favoring that orientation, based on a Times random value of 5.72 (The Times random range is from 0 to 6). The other processes are mostly random. In addition,
MICROFAB SC Process B is relatively stress neutral when compared against the other process which have become more tensile upon annealing. For the most part, the crystallite size is not affected much by the purity of the process. The tendency is toward formation of large grains post annealing.



Summary III

- The electrolyte must be carefully chosen to fulfill the requirements of many applications:
 - Electrochemical data have shown its composition is important for controlling deposition rate, and macro-uniformity
- For the accelerator, it is imperative to gauge its operating window so adequate polarization can be achieved and controlled.
 - Its interaction especially with the leveler component is extremely critical
- The suppressor component is most critical to establish proper nucleation necessary for determining bump shape:
 - This nucleation might be important in providing relative adhesion
 - Further, e delicate balance must be established between leveler and suppressor
- Leveler, the corner stone of any process:
 - Its strength and type control parameters such as WID, WIF, gap fill capability, and the propensity for mitigating/controlling Kirkendall voids



Process	[Cu] g/L	Accelerator	Suppressor	Leveler	
Megabumps	50-90	Strong	Strong	Strong	
Pillars	40-50	Strong	Weak-Strong	Strong	
Microbumps	10-30	Strong	Strong	Weak	
RDL	10-20	Strong	Strong	Weak-Strong	
RDL + TSV	40-50	Weak	Weak-Strong	Weak-Strong	



Acknowledgements

<u>R&D</u>

Stephan Braye John Commander Tony Delgobbo Emile Kuo Vivian Lin Tao Chi Liu Vin Paneccasio Wenbo Shao Mike Toner Kyle Whitten

Marketing

Eric Gongora Ken Lai Rich Hurtubise



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Outside Lab X-ray Wizards

WLP Product Summary

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- Proliferation of WLP driven by specific cost, size and performance required by market
- Wafer Level Cu plating requirements continue to be pushed to limits

Feature	Critical Plating Attribute	Diameter/ L/S	/ L/S Height Package Type Cu pillar / RDL on		Application		
Microbump	Coplanrity , KV free	<30um	<20um	2.5D & 3D IC	Wafer	HMC, FPGA	
Cu pillar	Coplanarity with higher throughput	30-60um	30-50um	FC & 2.5D	Wafer	CPU, APU, baseband, DDR4 DRAM	
Cu pillar	Coplanarity with higher throughput	60-80um	50-70um	FC & 2.5D	Wafer	Power Amplifier	
Large bump	Higher Throughput	90-110um	40-60um	FC & 2.5D	Wafer	FPGA	
High Cu Pillar	Coplanarity with higher throughput	110-200um	130-180um PoP Substrate		Substrate	Memory + AP / baseband	
Mega bump	Higher throughput	200um	200um	m 3D fan out Wafer		Memory + AP / baseband	
RDL	Coplanarity, Lines/Space control	1.5um/ 1.5um	<2um	Fan-Out	Wafer	Memory + AP / baseband	
3 in 1	All of the above	Broad range	NA	Several	Wafer	Mobile	

- Close collaboration between OEM, IDM, Foundry, OSAT, Chemistry supplier, Tool OEM required
- Mass Reflow vs. TCB driven by pitch/cost/performance trade-offs

