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Annealing Behavior of Electroplated Nano-grained Copper

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Background

Why nanograined copper

- The Cu-to-Cu bonding process (both direct and hybrid) - interconnection in advanced packaging. Unified goal - lowering the overall thermal budget

- Nano-twinned copper - proven **lower thermal budget due to the orientation <111>**, ensures the highest lattice diffusivity. Complicated industrial process.

- Nano grained electrodeposited copper - polycrystalline material, but with a **high concentration of fast diffusion paths (lattice and grain boundaries) also a higher creep rate** in the deposit layer likely accounts for its lower temperature bonding properties.

Aim

To show the capabilities of the IntraCu® SC-4 set of additives, with the newly designed Leveler at different electrolysis conditions, that could satisfy the current **requirements for Cu-to-Cu bonding**, with consideration of critical parameters including:

✓ grain size of deposit (as plated)	(less than 200 nm)
✓ impurities	(≤200 ppm)
✓ the time of self-annealing (Q-time)	(4 weeks at room temperature)
✓ geometry of structured mask (size of vias)	(3-10 µm)
✓ grain size of the seed layer	(NT to 200 nm)
✓ No changing the grain size at 150 ºC	
✓ At least 5 time increasing the size of grains after thermal annealing ≤ 200 ºC	

Background. Effect of additives

One of the classical presentation of the role of the additives, from the 90th

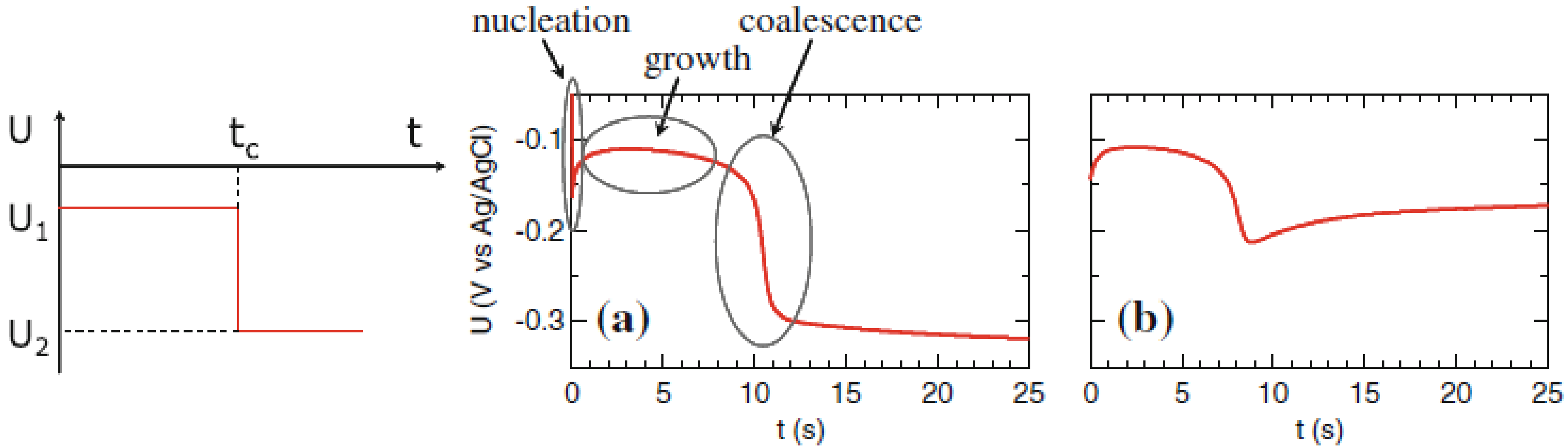
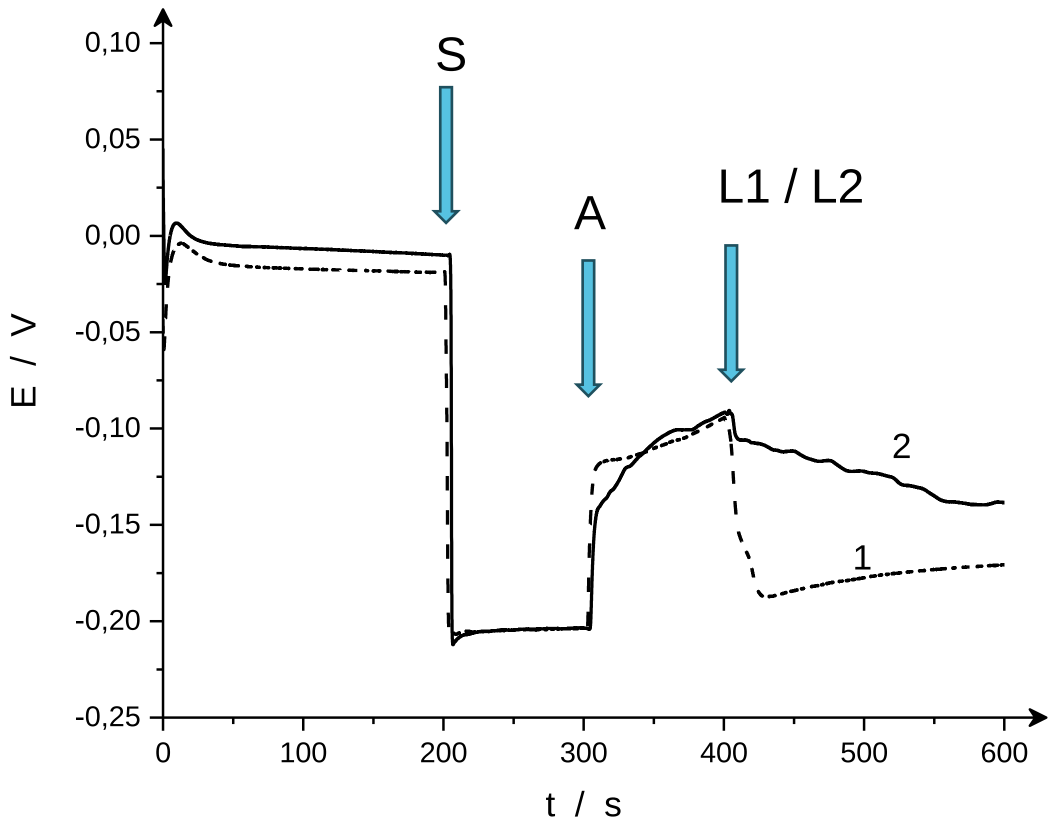


Fig. 7.13 U-t response in the presence of suppressor (**a**) and all the additives (**b**). Insert on the left shows idealized step-function response with parameter definition

After initial charging nucleation peak=> island-growth plateau. Potential becomes more negative. The steep – direction of polarization => inflection point; the potential levels off again

E-t transient curves

Galvanostatic deposition at 2 A/dm² onto rotation disc electrode (Pt)



S (suppressor) – polarizes process. Ensures fine grains of the deposit. Full adsorption;

A (accelerator) – depolarization of the process, partial deactivation of the suppressor;

L1 – conventional leveler. Strong secondary inhibitor;

L2 – unconventional, mild designed Leveler. Smaller polarization. Easier via filling. Stabilizes size of grains;

Injected additives: dashed curve 1 – S, A and L1

solid curve 2 – S, A and L2

Experimental

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Set up for deposition

Bath Composition		Content	Unit
VMS	Cu	28	g/L
	H_2SO_4	175	g/L
	Cl	50	ppm
Additive	A	4	ml/L
	S	10	ml/L
	L2	5, 20	ml/L

Parameter		Unit
Current density	0.75, 1 and 2	A/dm^2 (ASD)
Bath temperature	25	℃
Substrate	Coupons 5x5 cm2	Blanket wafer; 3 µm vias, 10 µm vias with NT seed layer
Anode	CuP	
Rotation	200	rpm

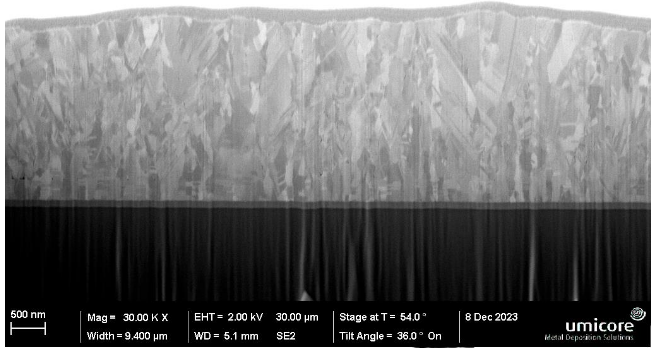
Effect of current density onto grain size

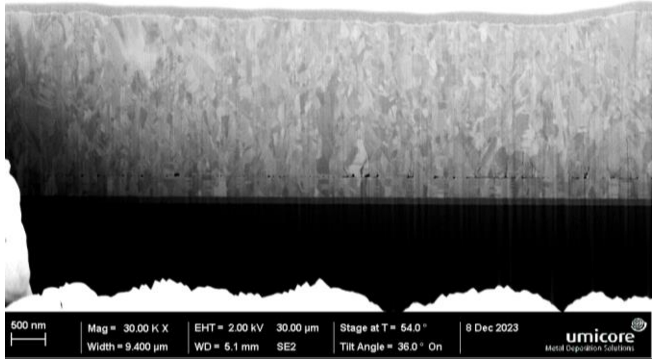
Blanket wafer, 20 ml/ L2

0.75 A/dm^2

2 A/dm^2

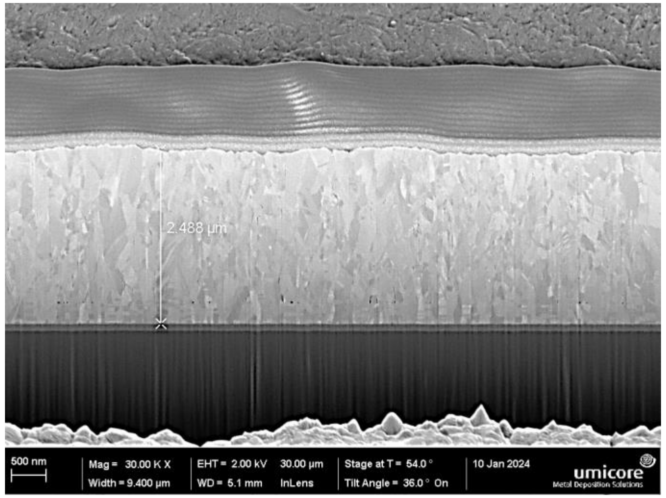
As plated

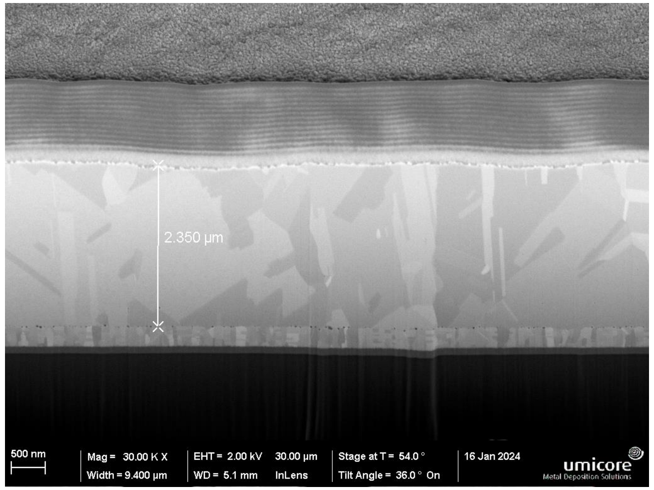




As plated layers at both current densities shows fine grained crystalls.

Storage 4 weeks





After 4 weeks storage, grain size of crystalls is fine of the sample deposited at **0.75 A/dm^2**

At lower current densities the leveler is not easily desorbed from the deposited surface and, therefore, prolongs the activity of its inhibiting effect.

Crystal orientation

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Blanket wafer, 20 ml/l L2

Sample	Intensity of Diffraction Peak (a.u.)		
	(111)	(200)	(220)
Plated at 2 A/dm^2	100.0	12.9	8.0
Plated at 0.75 A/dm^2	100.0	5.6	14.7
The Powder Diffraction File of Copper (PDF)	100.0	46.0	20.0

The samples are with <111> preferred orientation

Effect of concentration of L2

Blanket wafer, 0.75 A/dm²

As plated

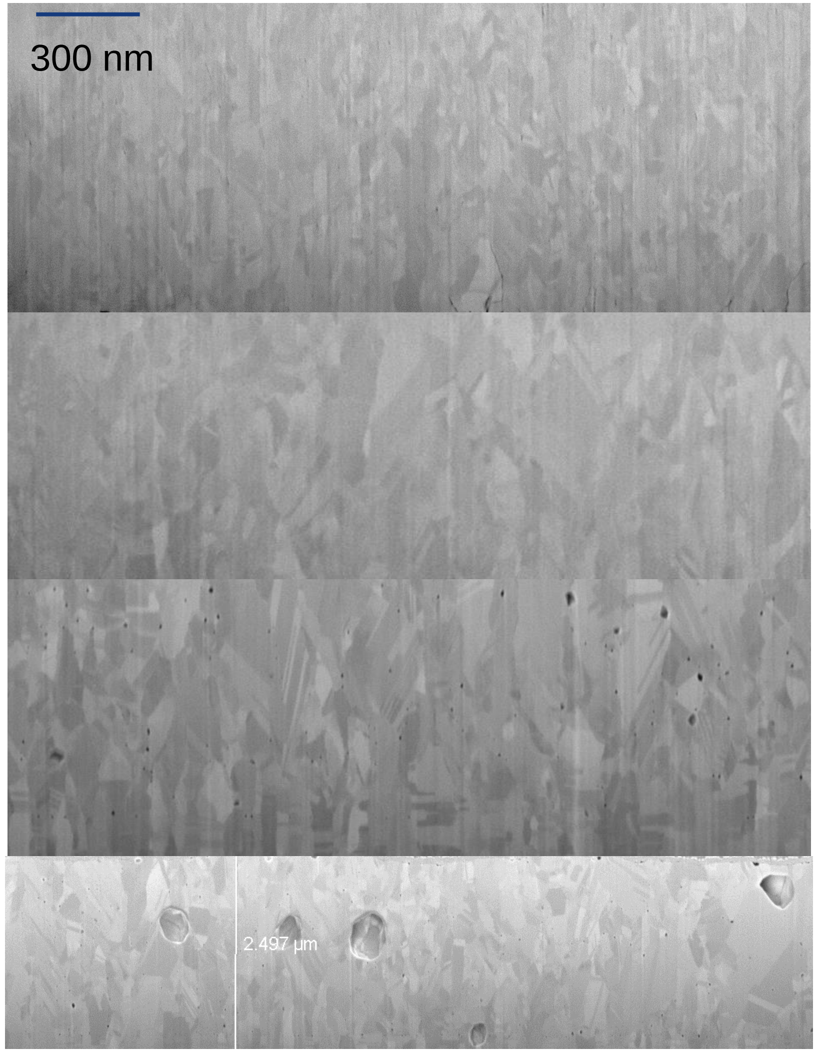
After 4 weeks storage

150 ºC, 2 h

200 ºC, 2 h

5 ml/l

20 ml/l



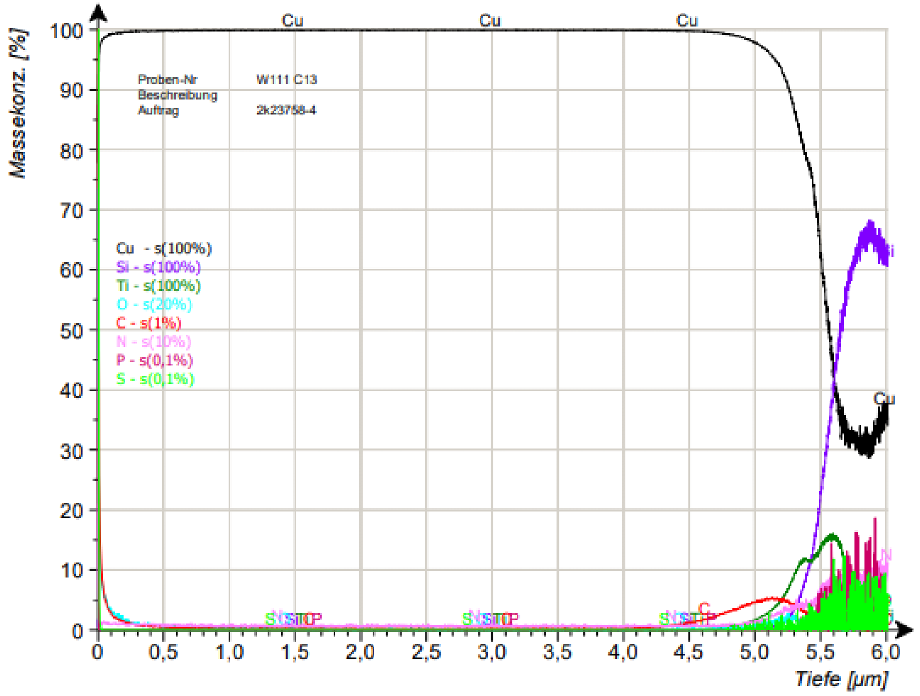
Glow discharge optical emission spectrometry – GDOES

Blanket wafer, 5 µm thickness of deposit

Sample No	ASD	L2, ml/l	C, ppm 1 µm in depth (2 spots)
1	0.75	5	40(30)
2	2	5	50 (50)
3	0.75	20	190(40)
4	2	20	100 (20)

Total impurities do not exceed 200 ppm

GDOES results, 20 ml/l, 2 ASD

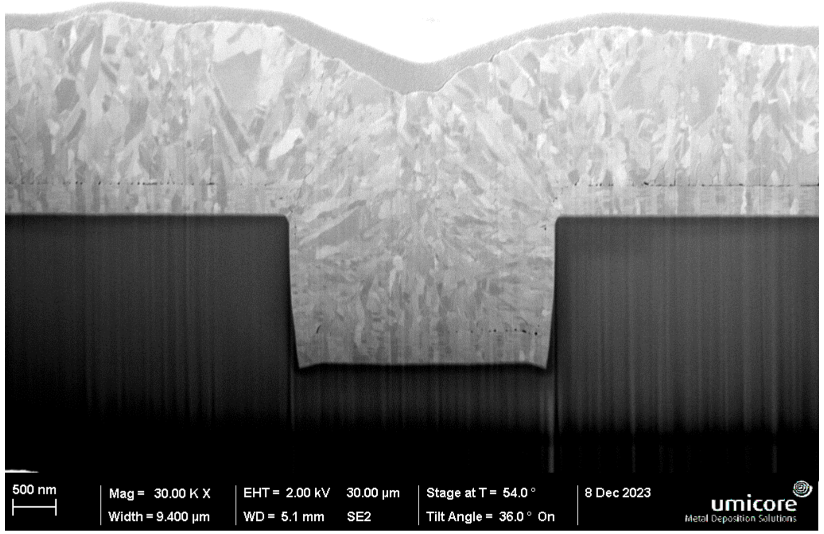


Effect of current density

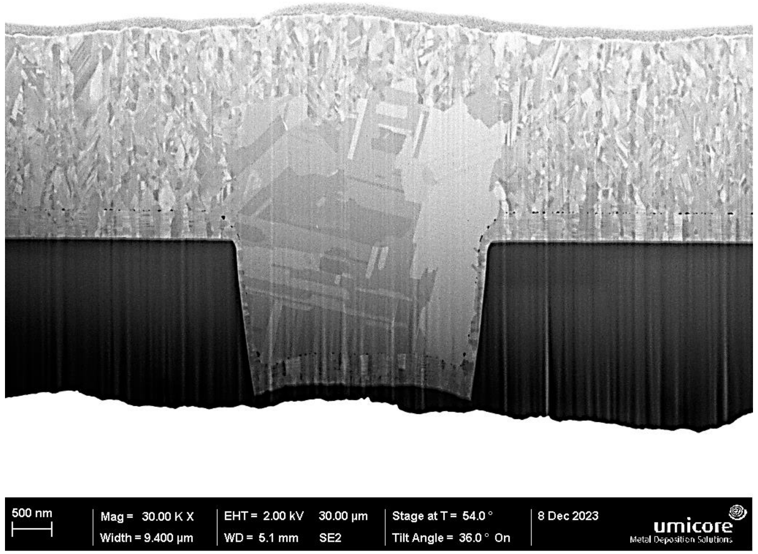
3 µm vias, 20 ml/l L2

As plated

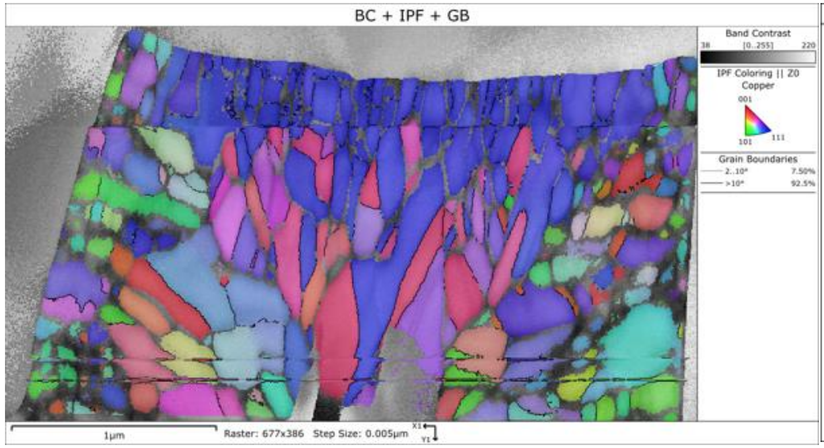
0.75 A/dm^2

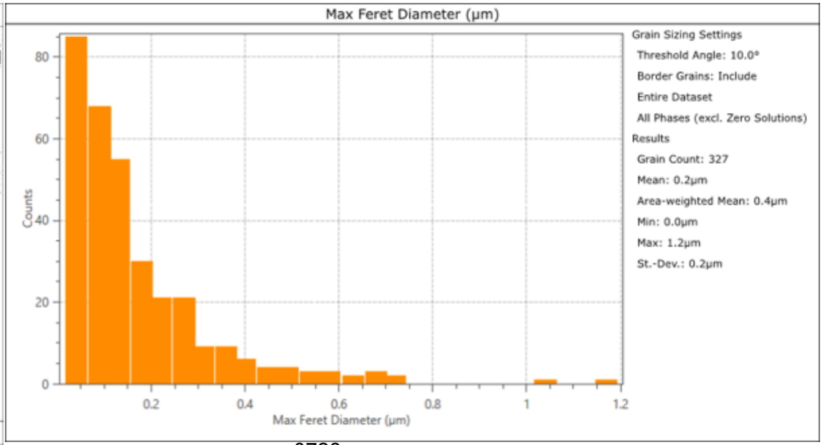


2 A/dm^2



EBSD





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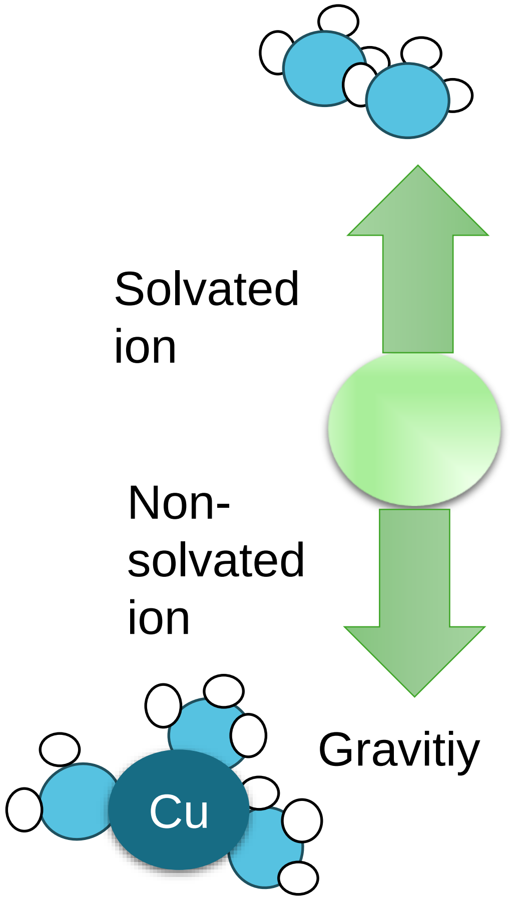
Phenomenology: Fine grains in vias

Microconvection in the vias

Phenomenology: In the vicinity of the Nernst diffusion layer (NDL) (0.01-0.001 mm) there is a phenomenon of a micro-convection .

Appears due to the flow of the solvated ions - after the reduction, the solvated ion becomes lighter and goes up. The new, non-solvated ion is heavier and flows down.

The driving force => is the Archimedean force in vias. This same force made the motion in vias at higher current densities much more active and does not allow the inhibitors to be adsorbed => no time to stabilize fine grains



Effect of concentration of L2

Vias 3µm. 0.75 A/dm²

5 ml/l

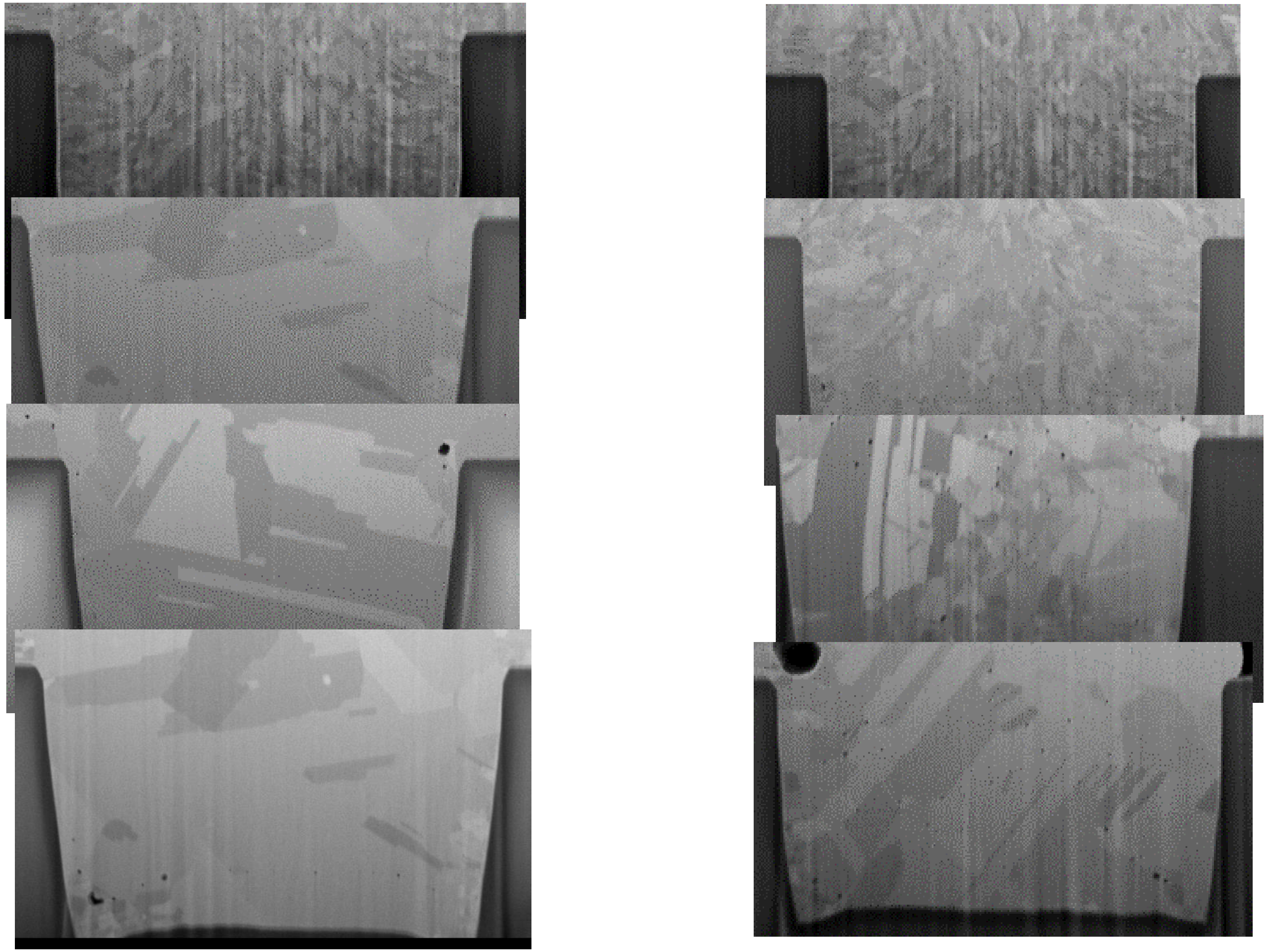
20 ml/l

As plated

After 4 weeks storage

150 ºC, 2 hours

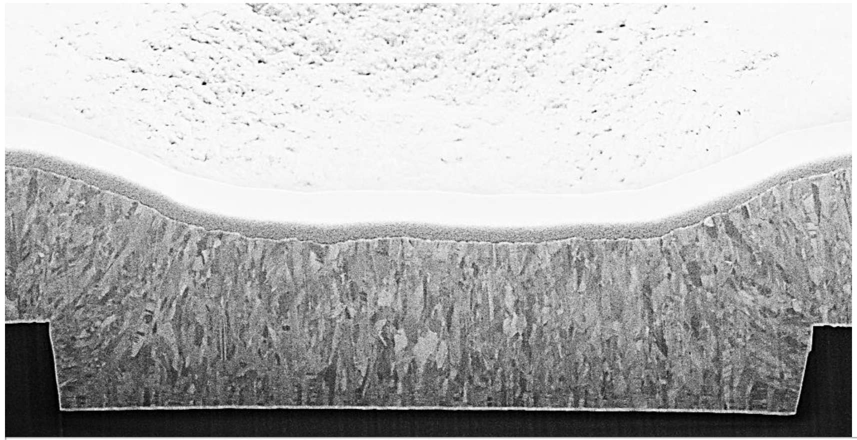
200 ºC, 2 hours

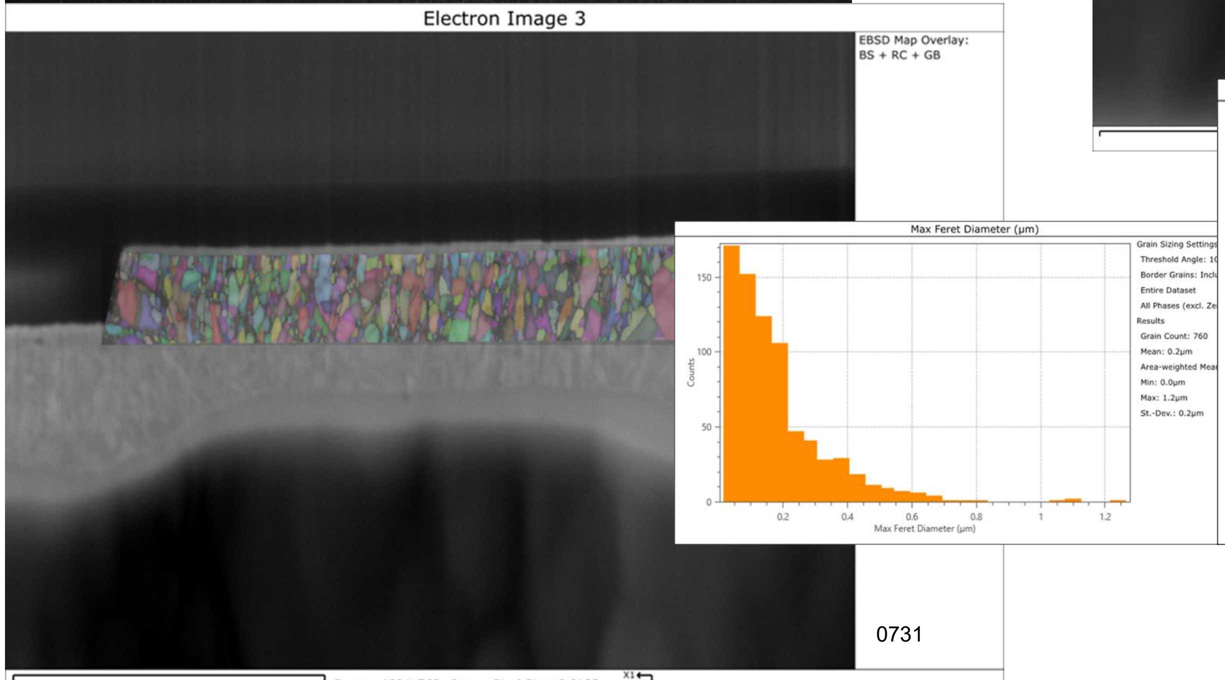


Effect of seed layer

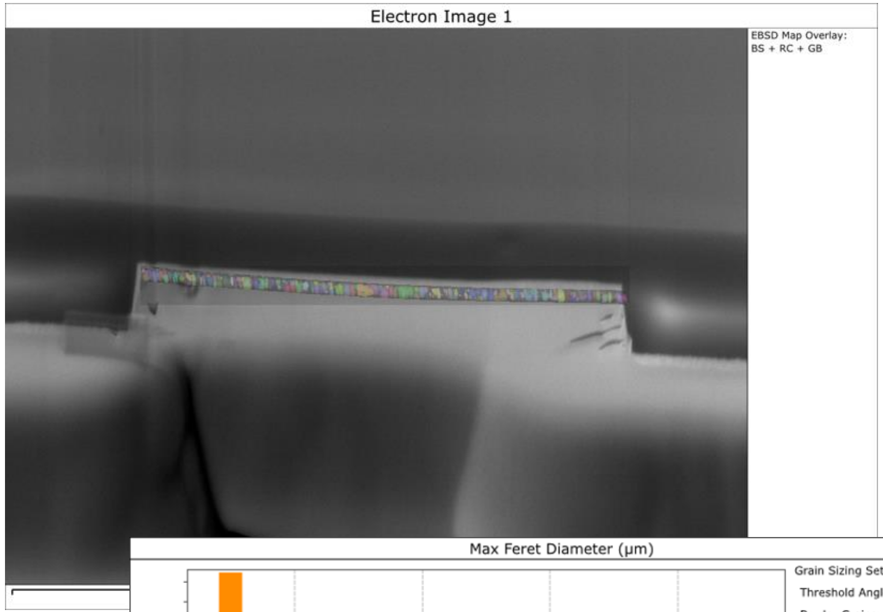
Vias 10 µm; 2 A/dm² 20 ml/l L 2

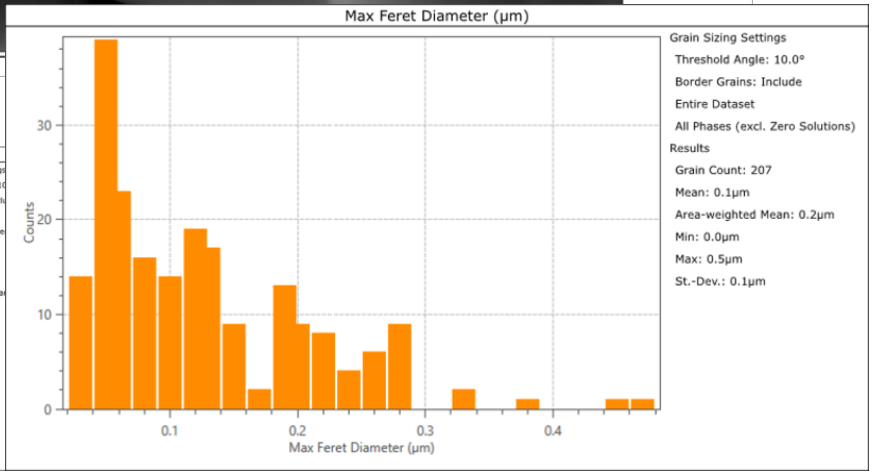
As plated





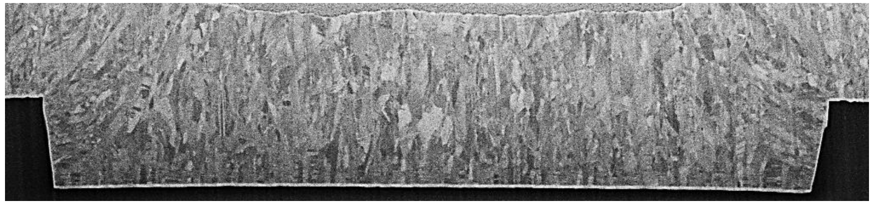
Nanotwinned substrate



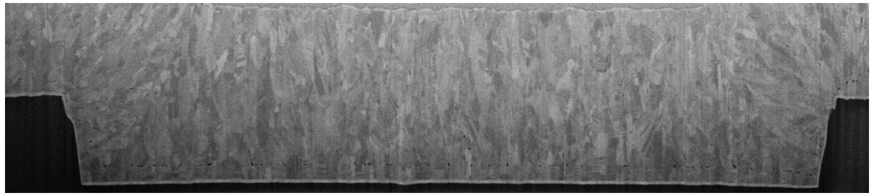


Vias 10 µm, 2 A/dm^2 20 ml/l L2

As plated

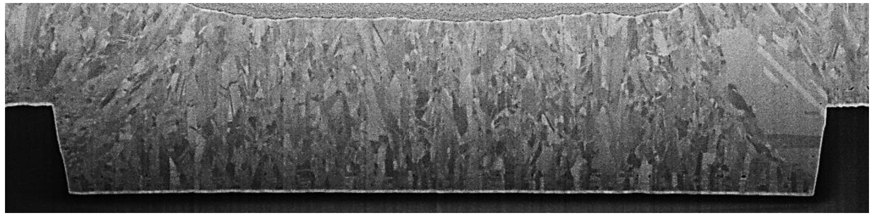


After 4 weeks storage



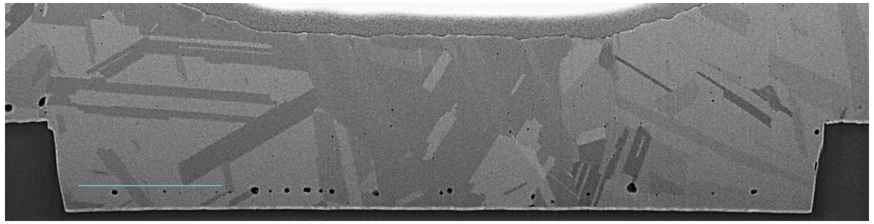
There is no changing of the grain size

150 ºC, 2h



There is no changing of the grain size

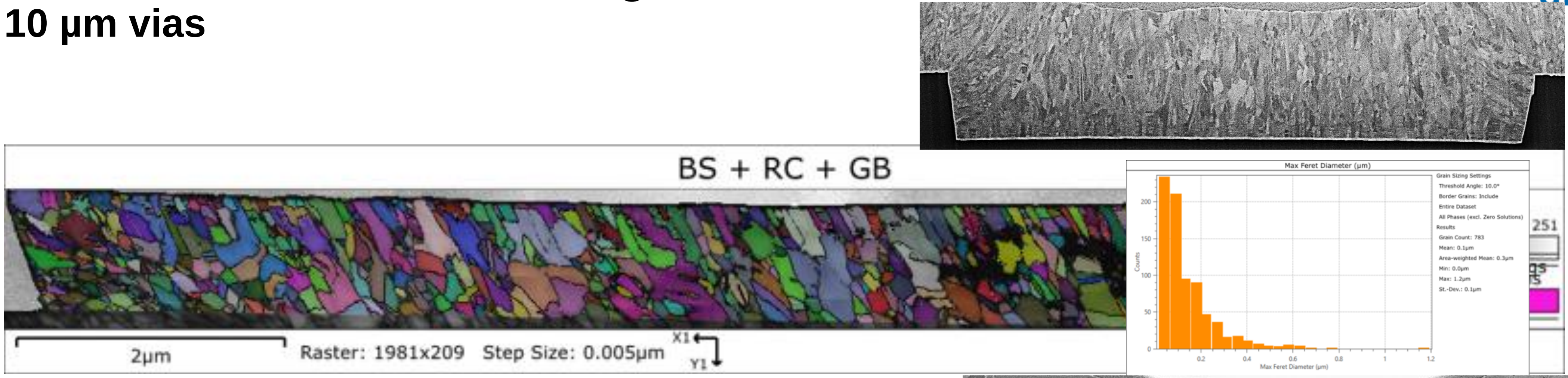
200 ºC, 2h

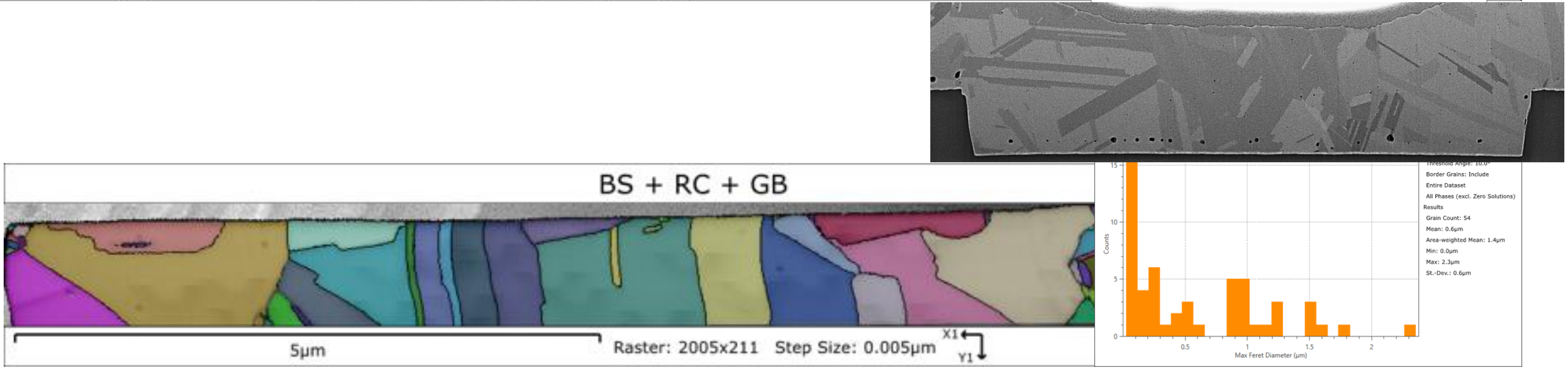


Grain size increase more than 7 times

EBSD. Effect of annealing

10 µm vias





NT seed layer – fine grains at higher CD

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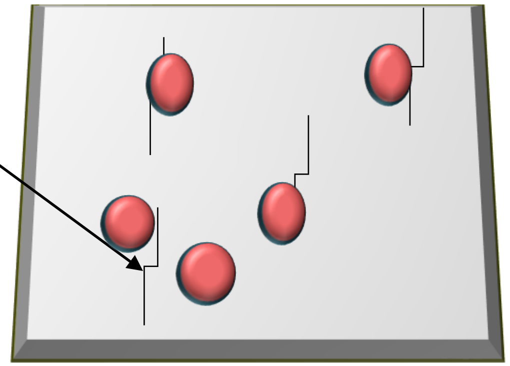
Schematical view of process of nucleiation and growth

Based on the Terrace Step Kink Model (TSK): the energy of an atom’s position on a crystal surface is determined by its bonding to neighboring atoms and that transitions involve the counting of broken and formed bonds

Rate of nucleation is higher

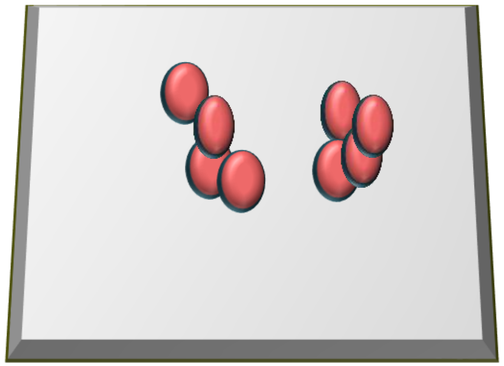
‚Defect‘
(or small grain
of seed layer)



Substrate with defects (dislocations)

Growth of nuclei is higher

‚Defect - free‘
(or big grain of
seed layer)



Dislocations - free substrate

- Energetically **growth mode of nuclei** is favored by using defect-free (without dislocations) substrate. As bigger is a substrate (size of seed layer) as more energetically favorably is growth of the nuclei.

Summary

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IntraCu® SC-4 set of additives, with newly designed unconventional leveler:

- Shows lower inhibiting properties
- Allows to obtain deposits with a grain size of about 200 nm for different substrates and via geometries
- Suppress the self-annealing process for at least 4 weeks
- Has less than 200 ppm impurities
- Ensures stability of the nanosized grains up to 150 ºC
- Allows increase the grains up to 5 times after annealing at 200 ºC

It is shown, that using IntraCu ® SC-4 set of additives, fulfil the current requirements for Cu-to-Cu bonding.

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