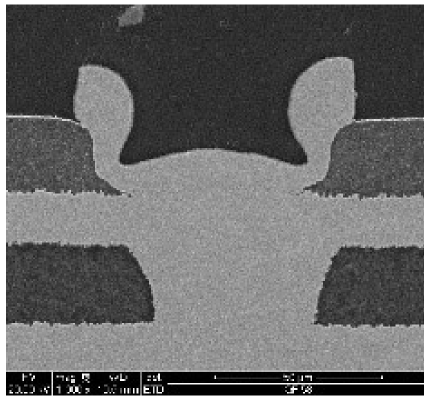
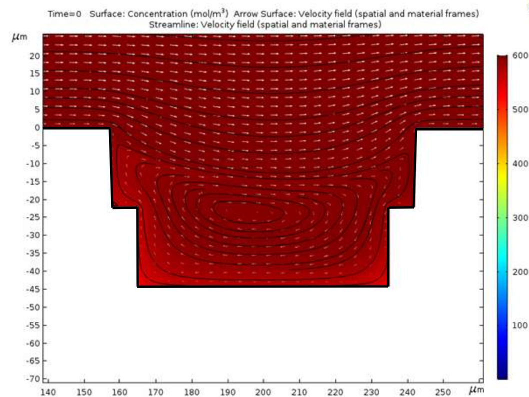
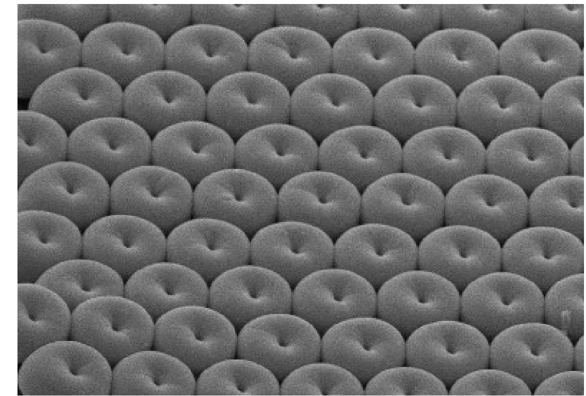
Electrochemical Calculations and Microstructural Analysis in Copper Electroplating to Fill Patterns at Various Feature Scales







Hyo-Jong Lee

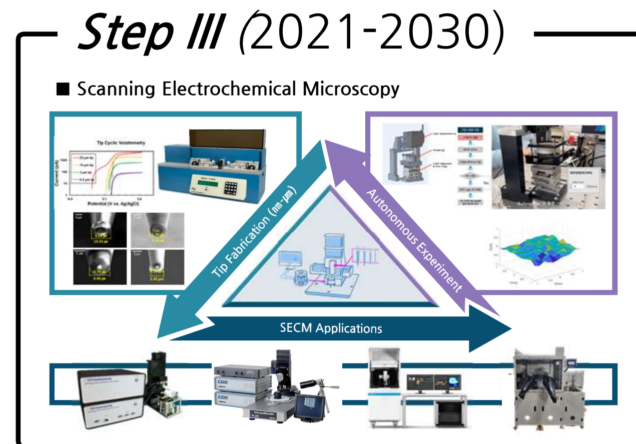
Materials Science and Engineering, Dong-A University

2024. 3. 25

Intro

Step III (2021-2030)

■ Scanning Electrochemical Microscopy



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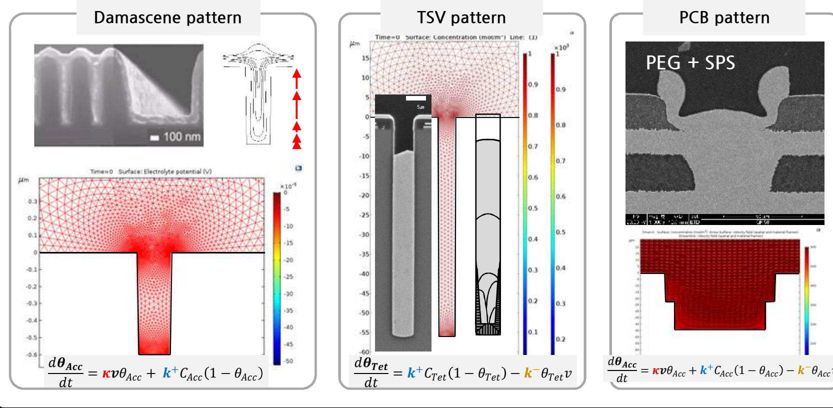
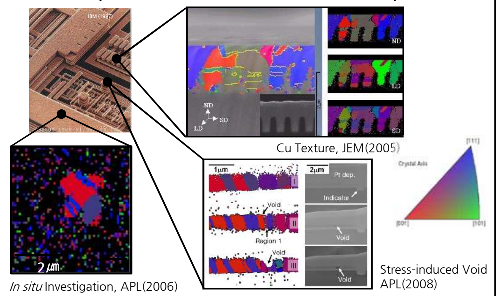
Step II (2011-2020)

■ Estimation of k⁺/k⁻ Models for Organic Additives



Step I (2000-2010)

■ EBSD (Electron Backscattered Diffraction)



Crystallography → Electroplating → Electrochemistry

Contents

I. Texture Evolution in Multi-scale Patterns

- ① Submicron / ② Micron / ③ Millimeter scale patterns

II. In situ Investigation of Growth Anisotropy

- Anisotropic 〈111〉 grain growth, Twin formation

III. Texture Phenomenon

- Stress-induced voiding : T.J. and equi-biaxial modulus

Contents

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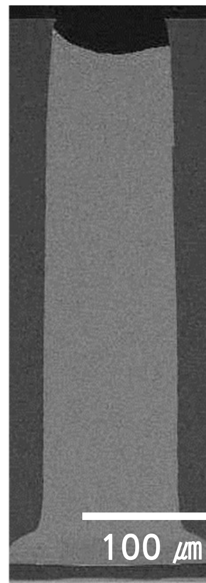
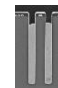
Pattern Size in Electrical Wiring - 경박단소, 輕薄短小

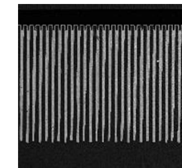
NIST
National Institute of Standards and Technology

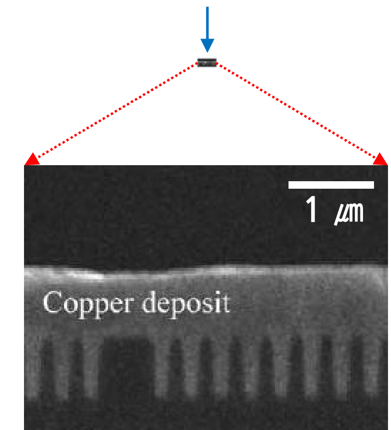
- Millimeter scale - 6G Antenna
- Micron scale - TSV (Through-Silicon Via)
- Nano/Submicron scale - X-ray 3 EHz, Copper Interconnection

6G Antenna	TSV	X-ray 3 EHz	Cu Interconnection
Human hair	Blood cell	Spider web	Virus
Millimeter scale	Micron scale	Submicron scale	Nano scale









Courtesy of Dr. Moffat and Dr. Josell (NIST)

Three Kinds of Copper Patterns

/. Texture Evolution in Multi-scale Patterns

- Submicron/Micron/Millimeter scale patterns

① Nano/Submicron Scale Electroplating - **Cu Damascene Pattern**

② Micron Scale Electroplating - **Cu TSV and Ni TSV**

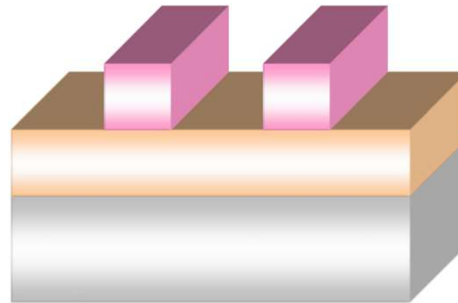
③ Sub-millimeter Scale Electroplating - **PCB Pattern**

I. Nano/Submicron Scale Electroplating

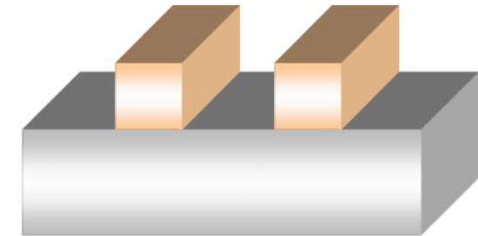
■ **Comparison between** Al Dry Etching and Cu Damascene Electroplating Processes

Al Dry Etching Processes

Al Deposition

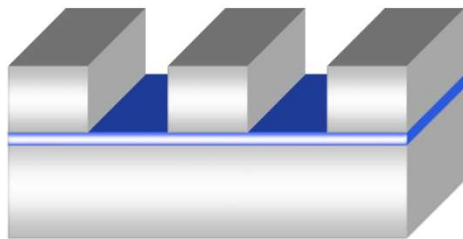


PR Lithography

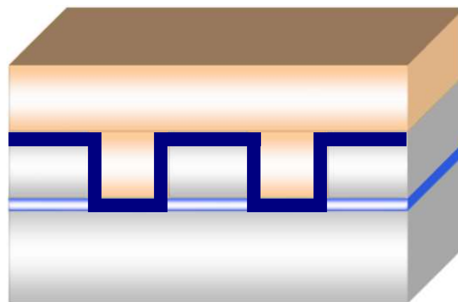


Metal Patterning

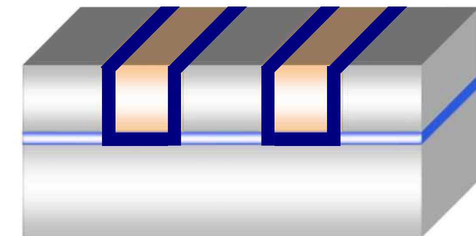
Cu Damascene Electroplating Process



Oxide Patterning



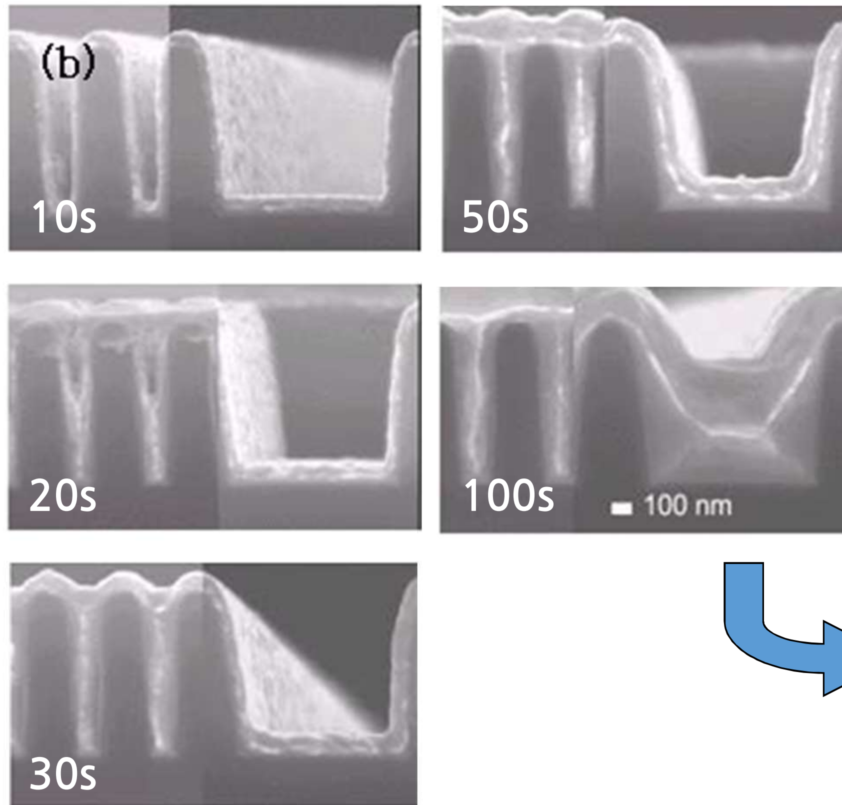
BM & Seed, EP

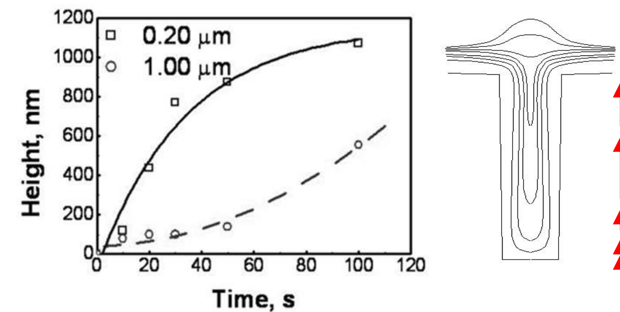


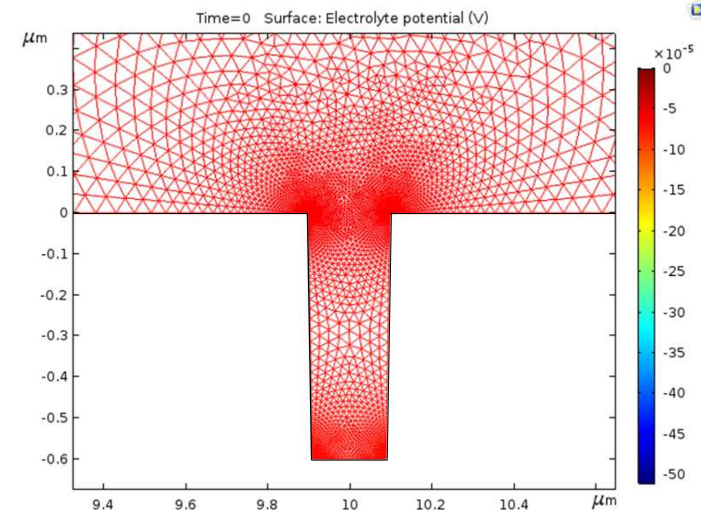
CMP

I. Nano/Submicron Scale Electroplating

■ Nano/Submicron Scale - Calculation of Damascene Cu filling





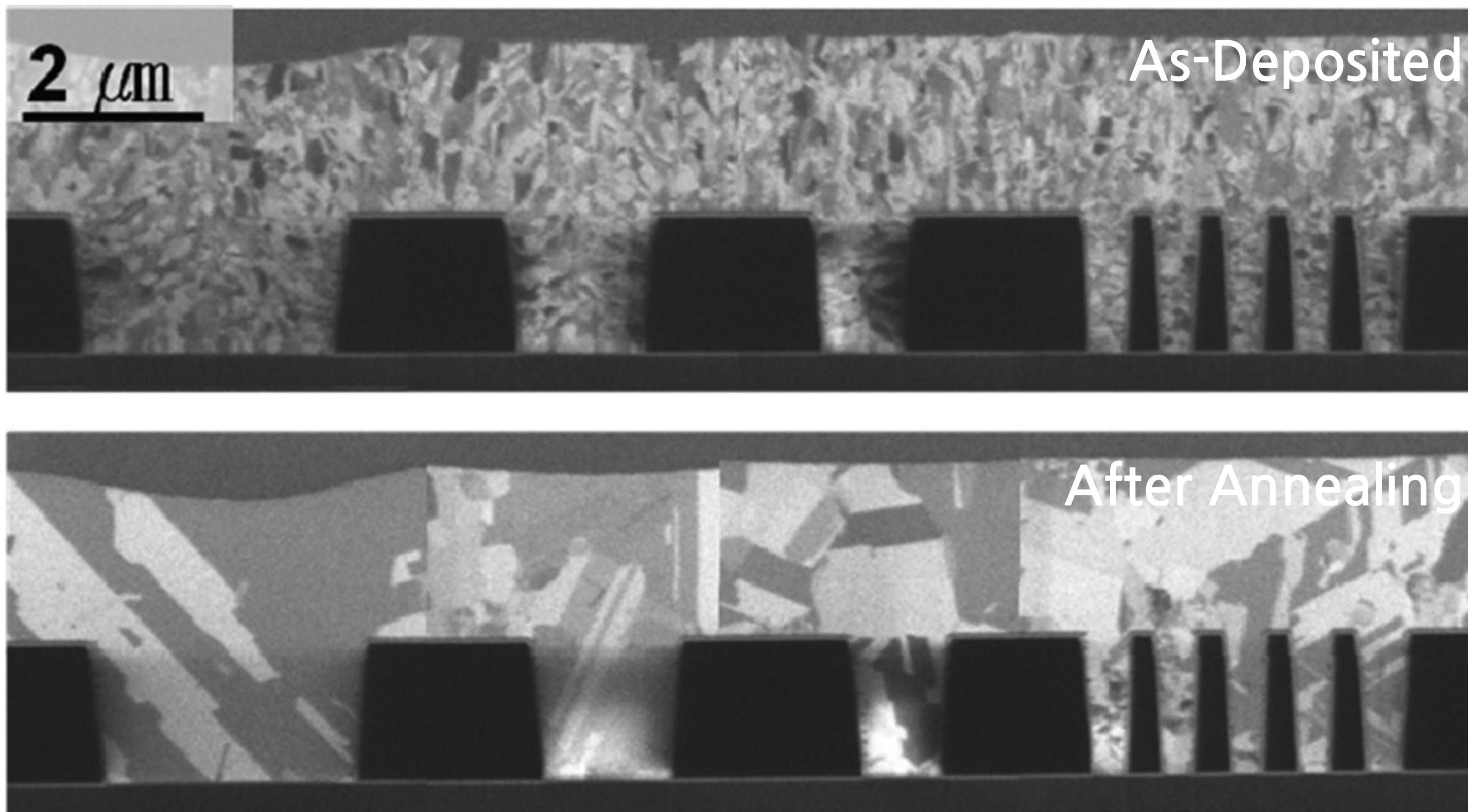


Time=0

$$\frac{d\boldsymbol{\theta}_{Acc}}{dt} = \boldsymbol{\kappa v}\theta_{Acc} + \boldsymbol{k}^{+}C_{Acc}(1-\theta_{Acc})$$

I. Nano/Submicron Scale Electroplating

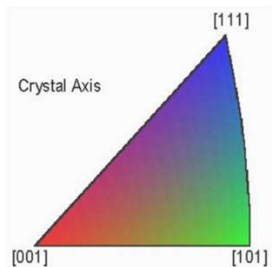
■ Metal Interconnection Technology for Packaging and Integration

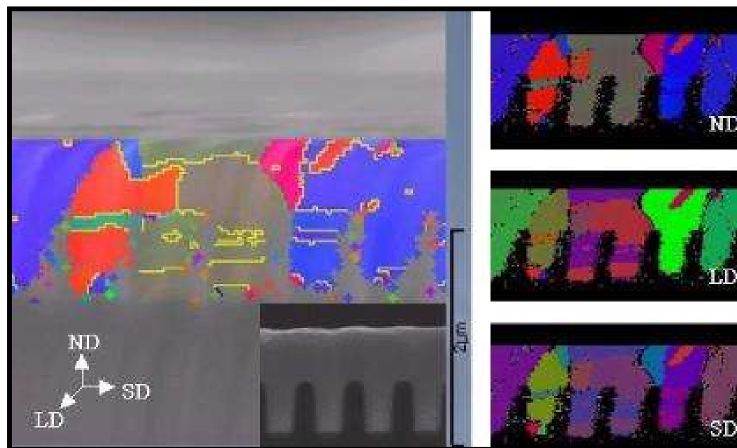


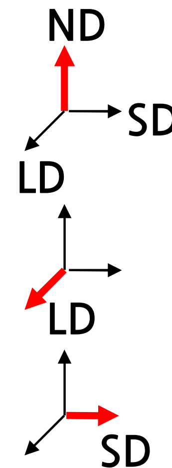
Ref : Lee *et al*, JECS 2011

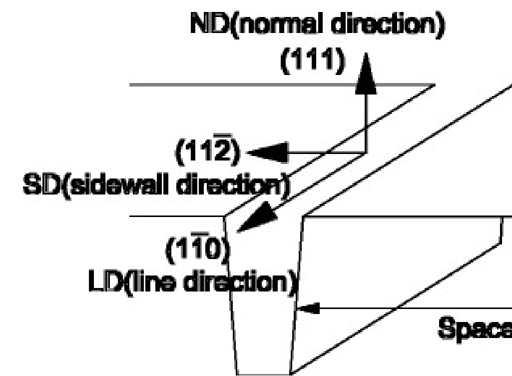
I. Nano/Submicron Scale Electroplating

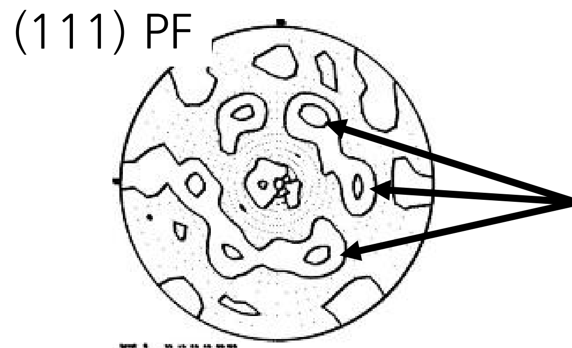
■ Preferred Orientation in ULSI Cu Interconnection











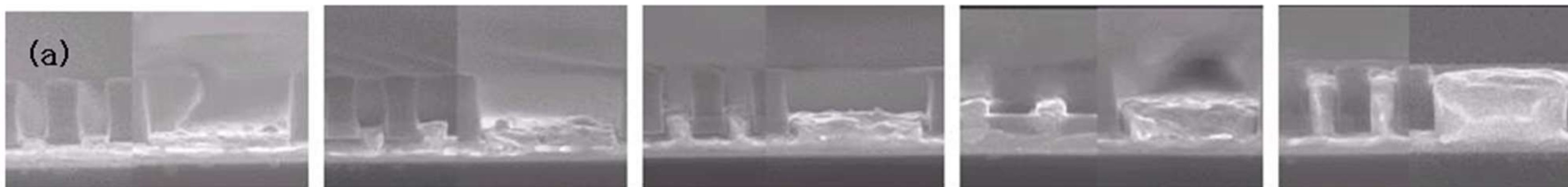
(111) Poles

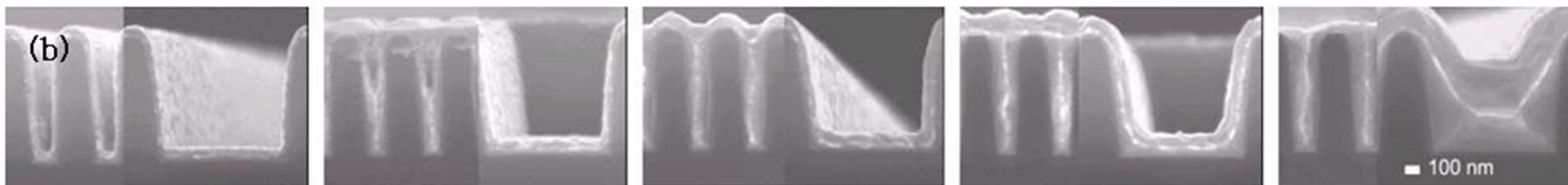
➔ {111}〈110〉

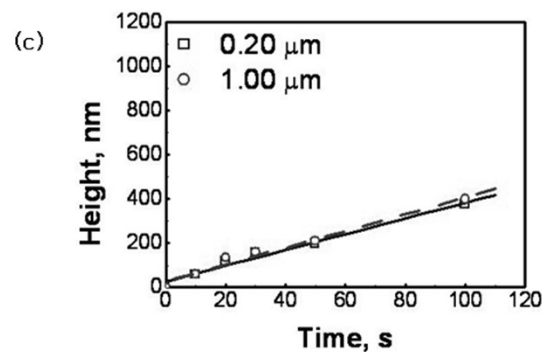
ND LD (Lee *et al*, JEM2005)

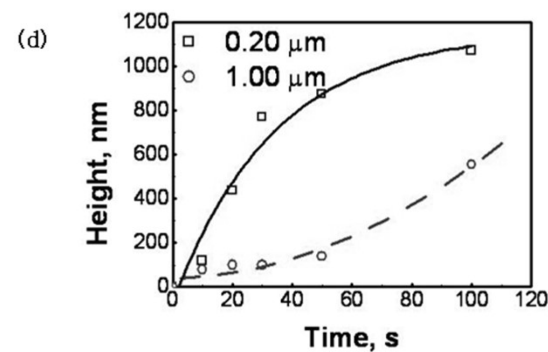
I. Nano/Submicron Scale Electroplating

■ One Direction Growth Pattern vs. Three Direction Growth Pattern









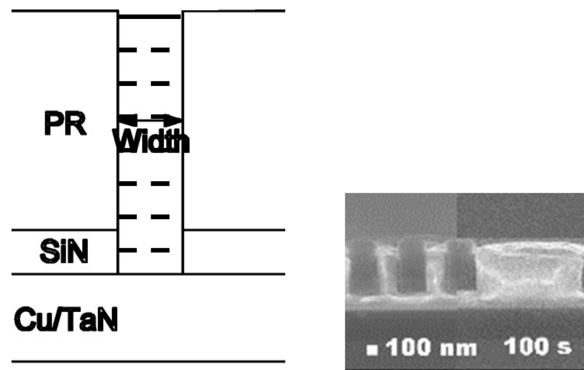
One Dir. EP → Same speed plating

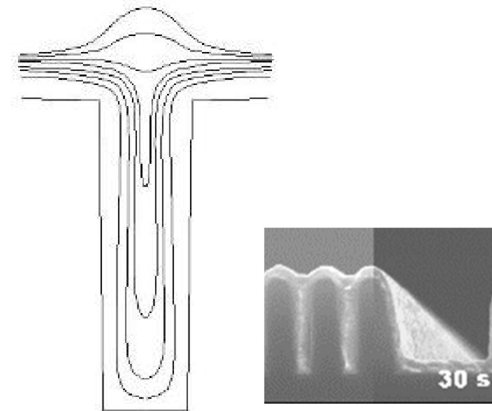
3 Dir. EP → Superfilling

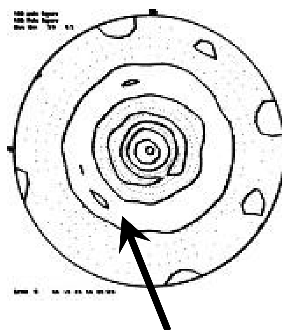
Lee et al., ESL(2005)

I. Nano/Submicron Scale Electroplating

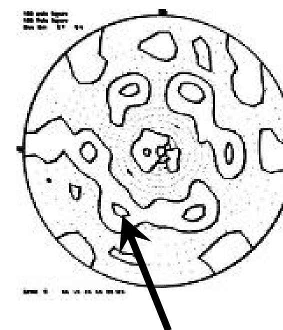
■ Annealed Texture Between 1D and 3D Patterns





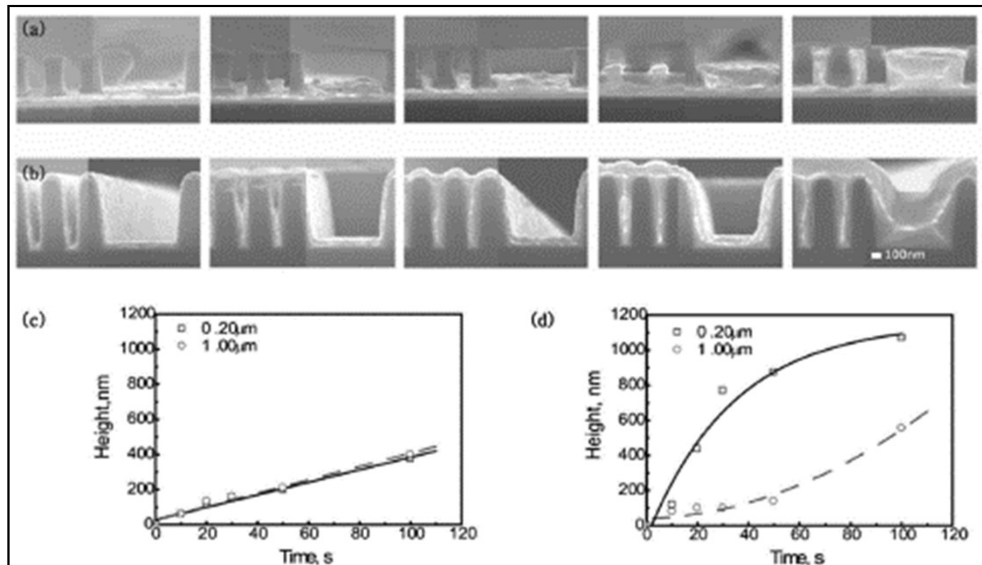


1D growth → {111} fiber

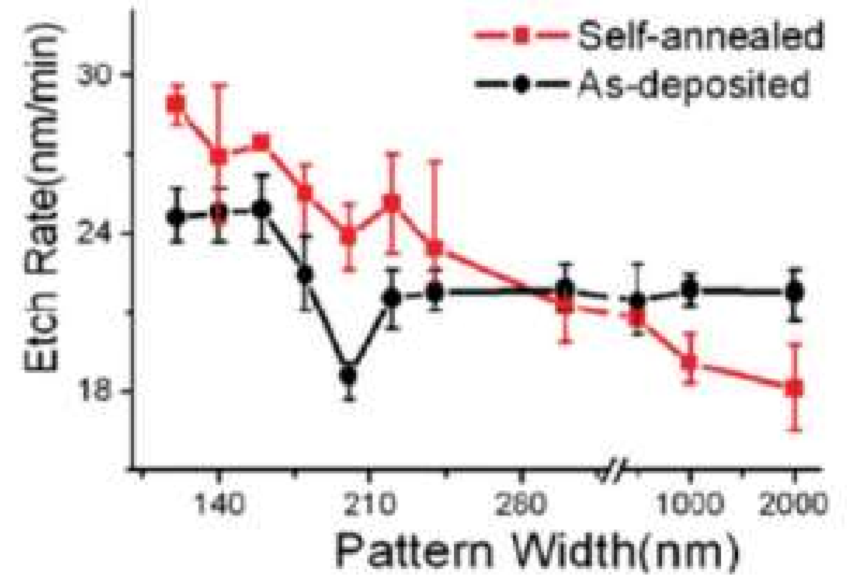


3D growth → {111}⟨110⟩

Electroplating and Etching of Cu



ESL (2006)



JECS (2011)

Texture Evolution in Patterns

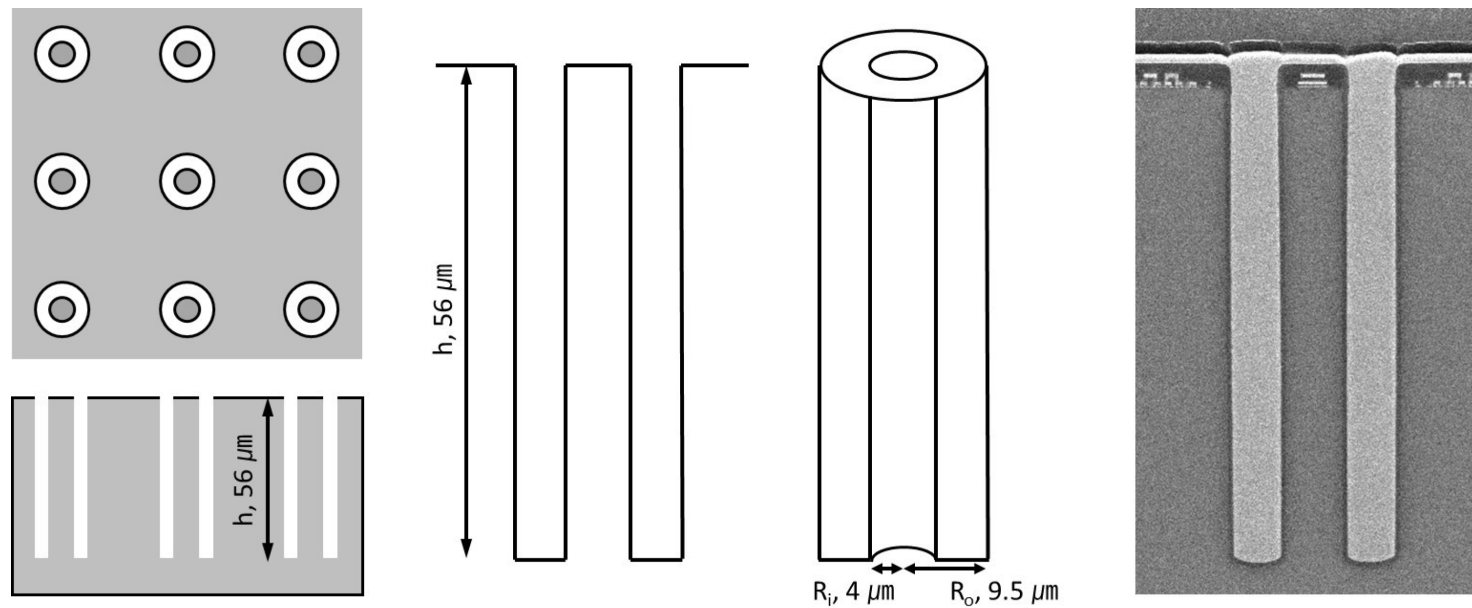
- Submicron/Micron/Millimeter scale patterns

① Nano/Submicron Scale Electroplating - **Cu Damascene Pattern**

② Micron Scale Electroplating - **Cu TSV and Ni TSV**

③ Sub-millimeter Scale Electroplating - **PCB Pattern**

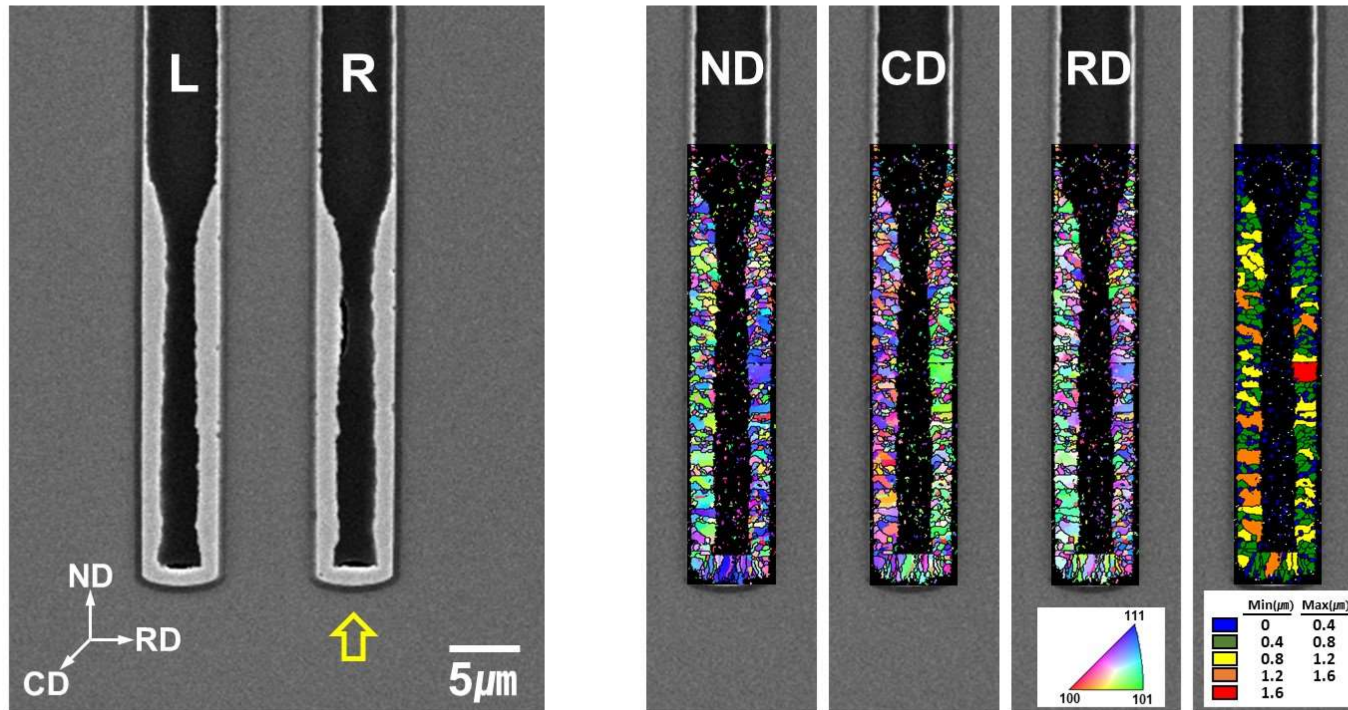
Schematic diagrams of annular TSVs



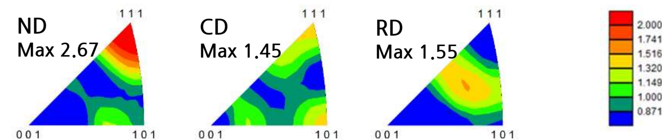
Solution: 1 mol/L $CuSO_4$, 0.5 mol/L H_2SO_4, 1 mmol/L NaCl, 6~25 μmol/L Tetronic 701

Courtesy of Dr. Moffat and Dr. Josell (NIST)

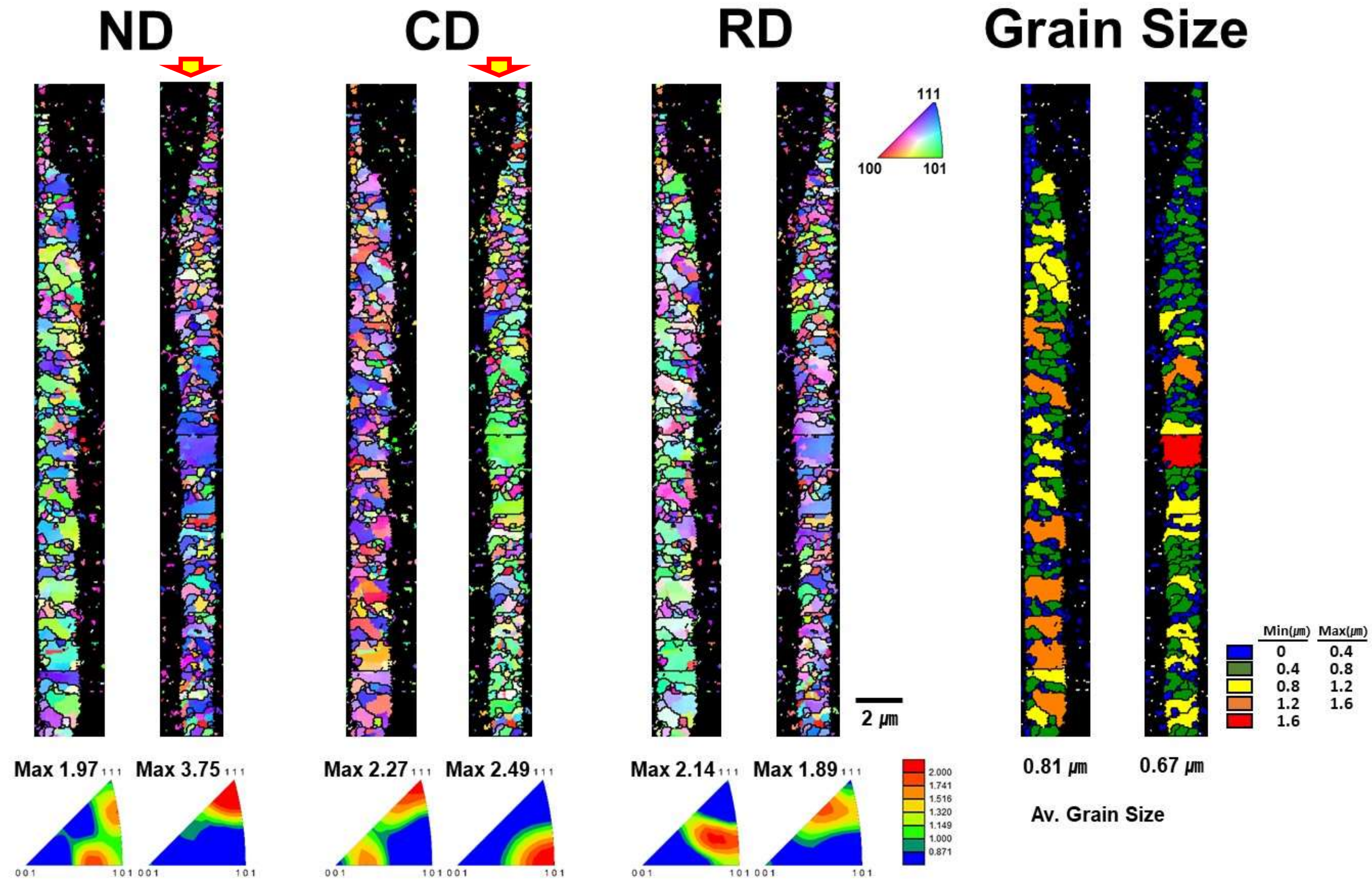
Cu TSVs in 6 μmol/L TET at -0.64 V_{SSE} for 4 min



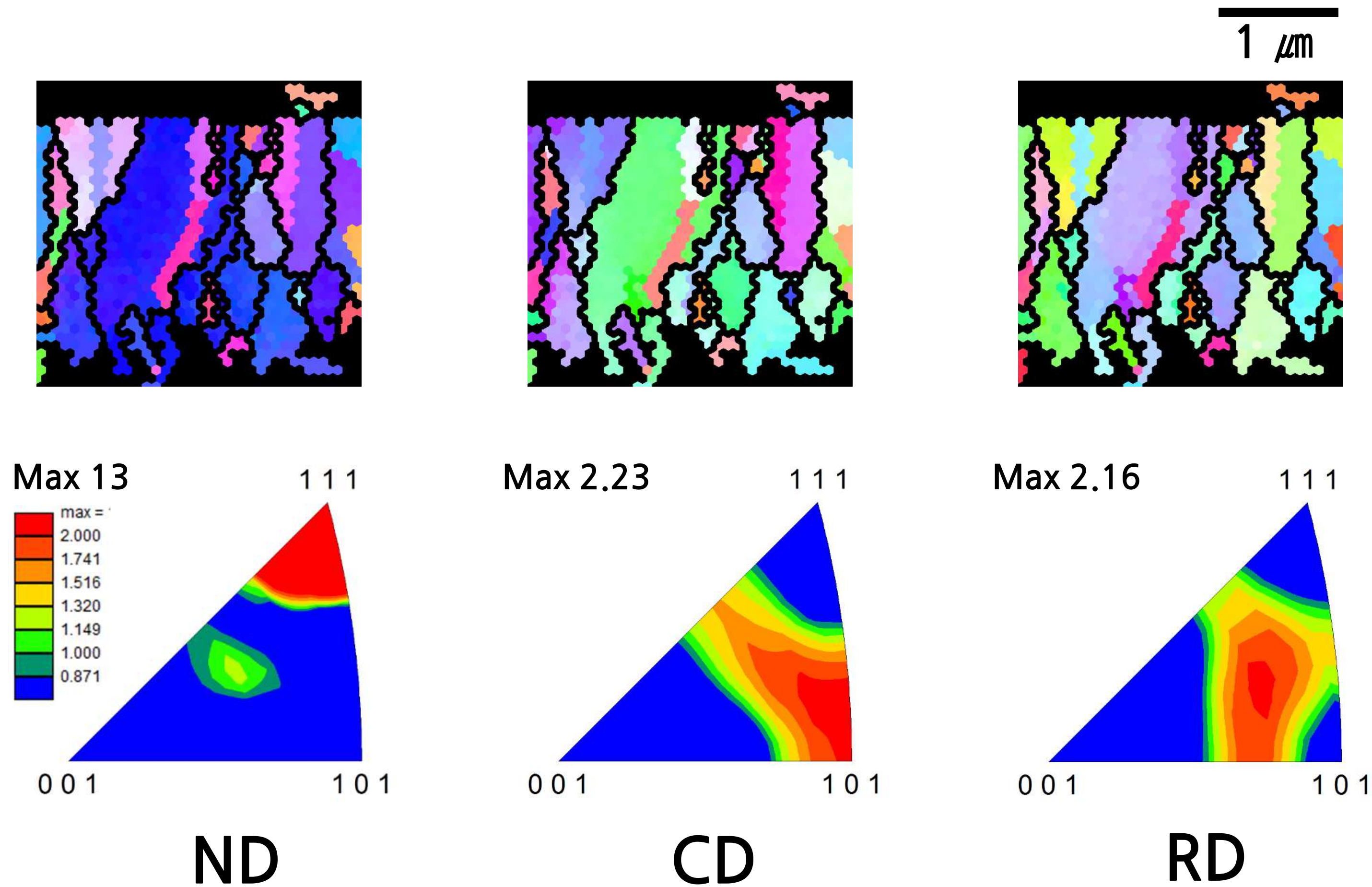
ND: normal direction
CD: circumferential direction
RD: radial direction



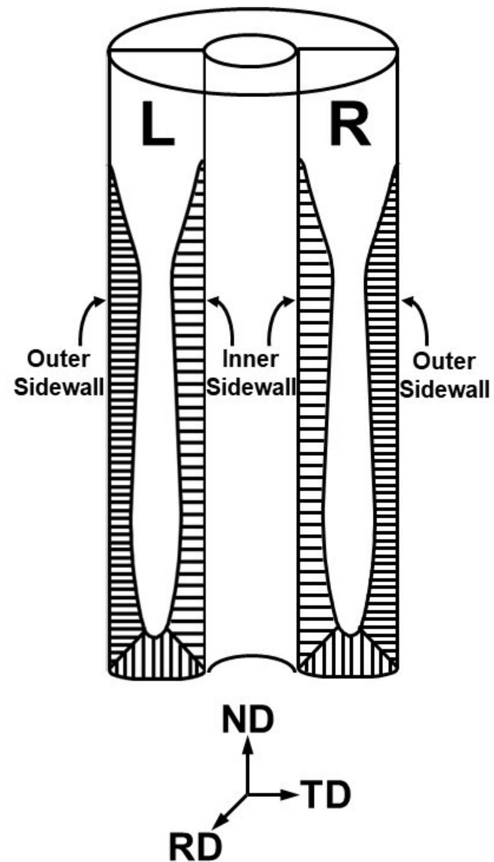
Left-Inner and Right-Outer Sidewalls for Annular TSV

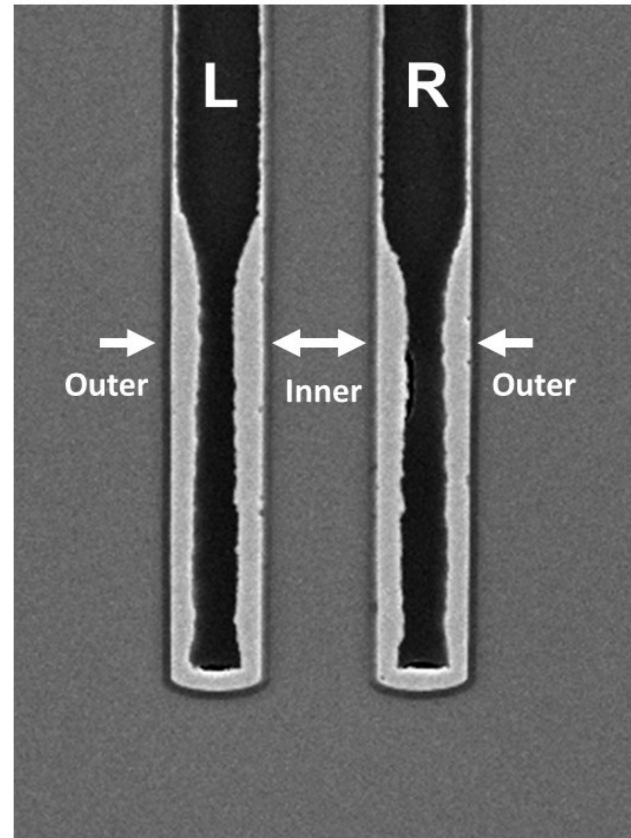


EBSD of Bottom Region for Annular TSV

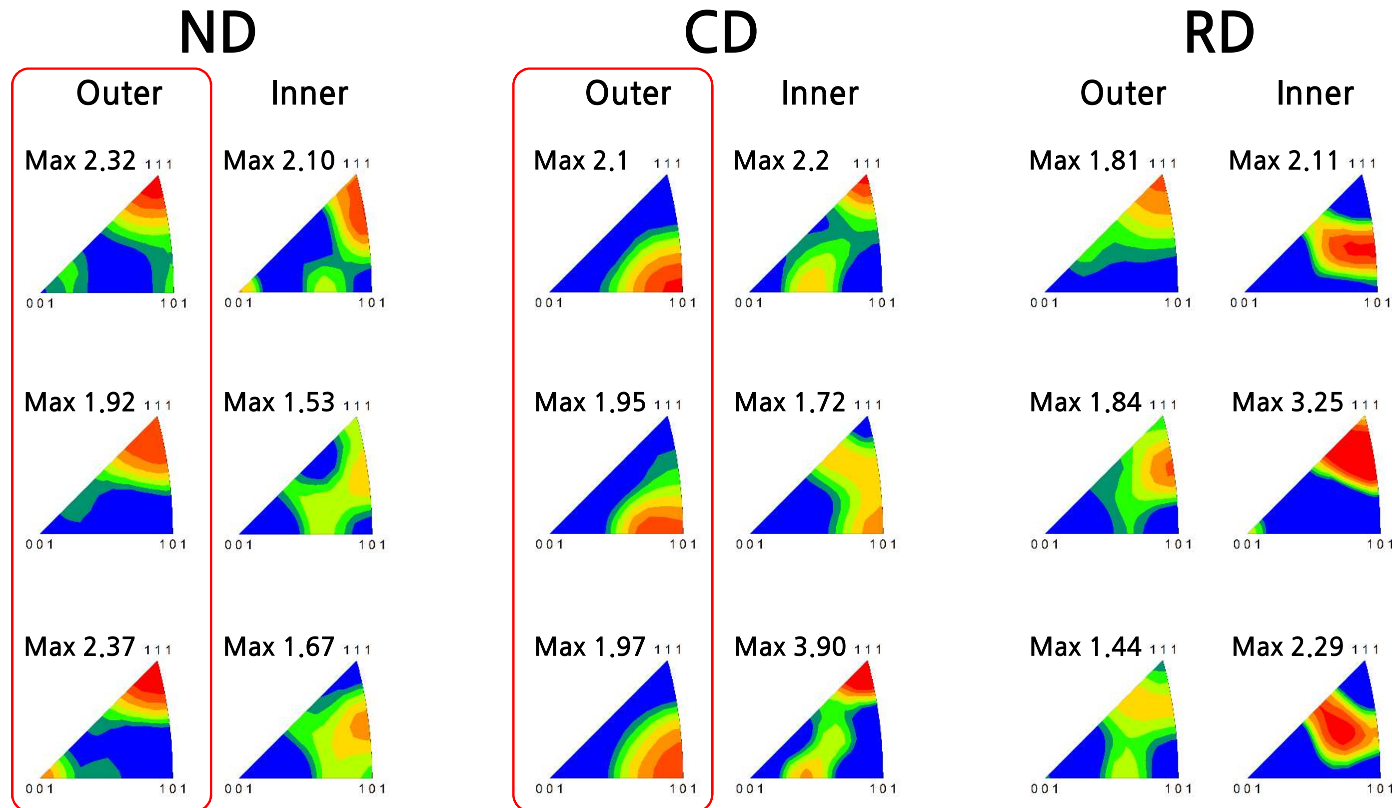


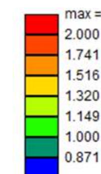
Grain Size Difference of Inner and Outer Sidewalls

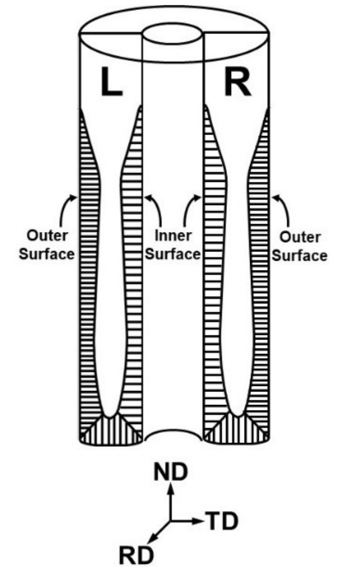




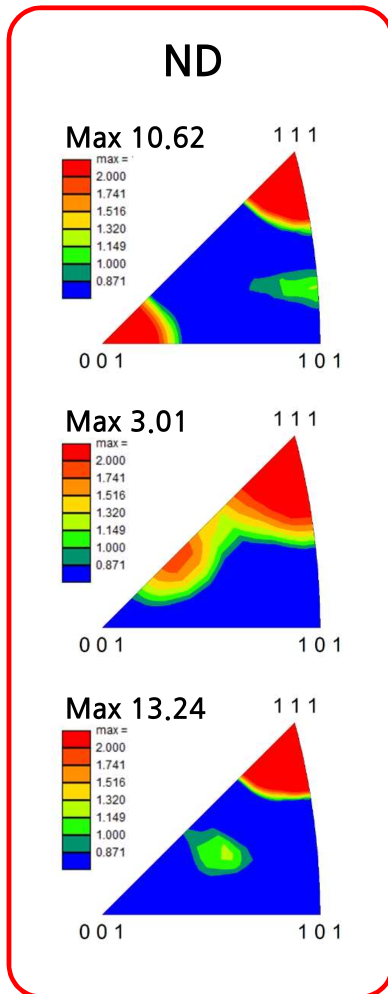
IPF Images for Inner and Outer Sidewalls

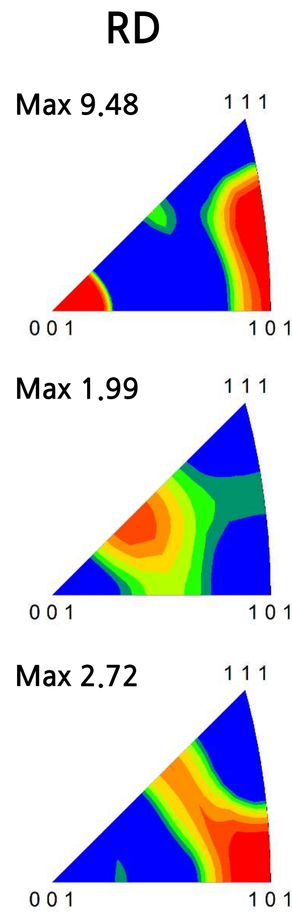


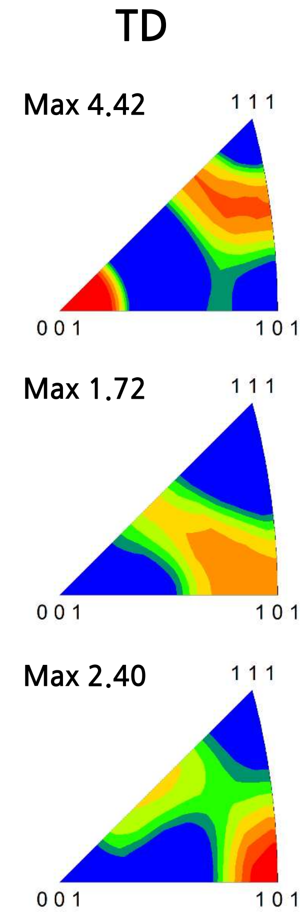




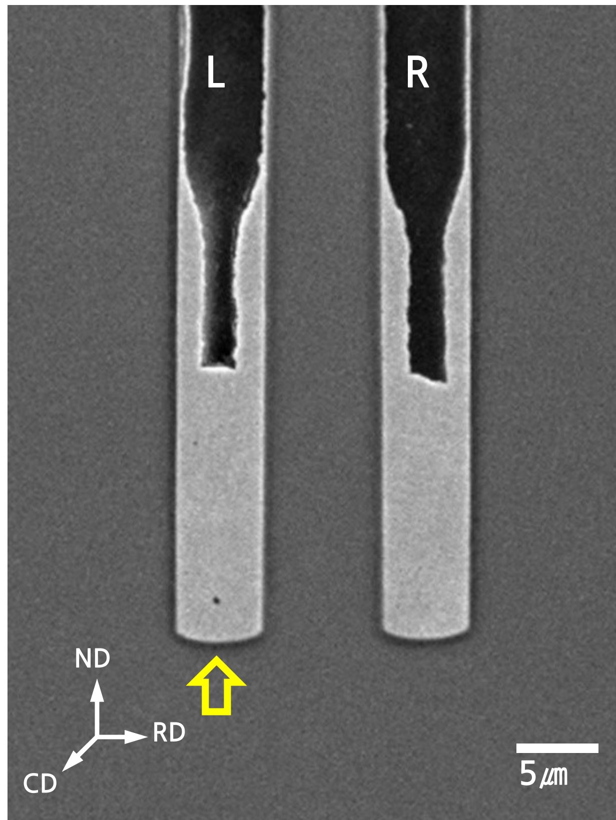
IPF Images for Bottom Region

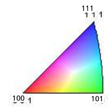


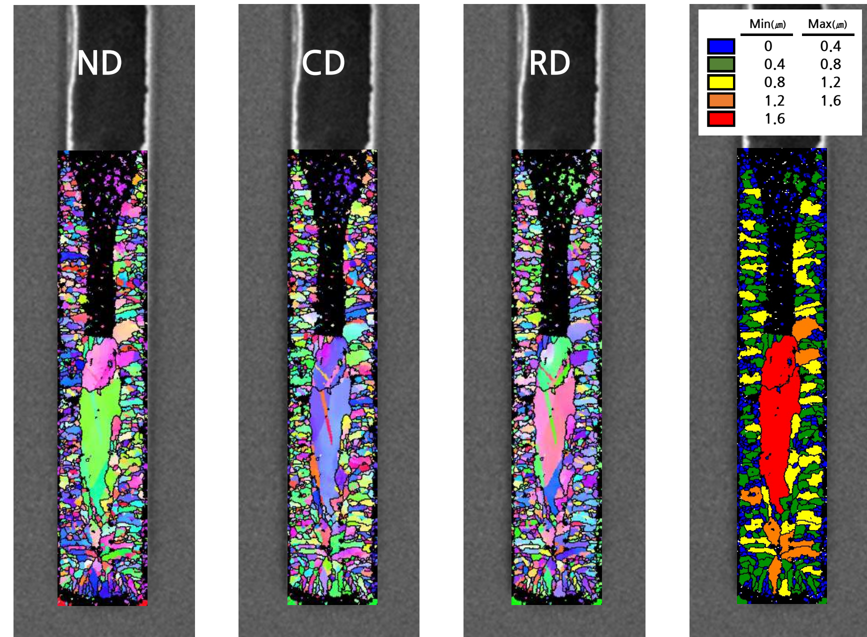


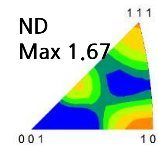


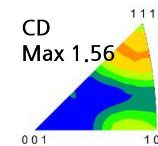
Cu TSVs in 6 μmol/L TET at -0.64 V_{SSE} for 8 min

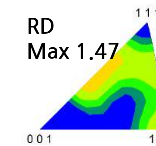


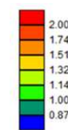








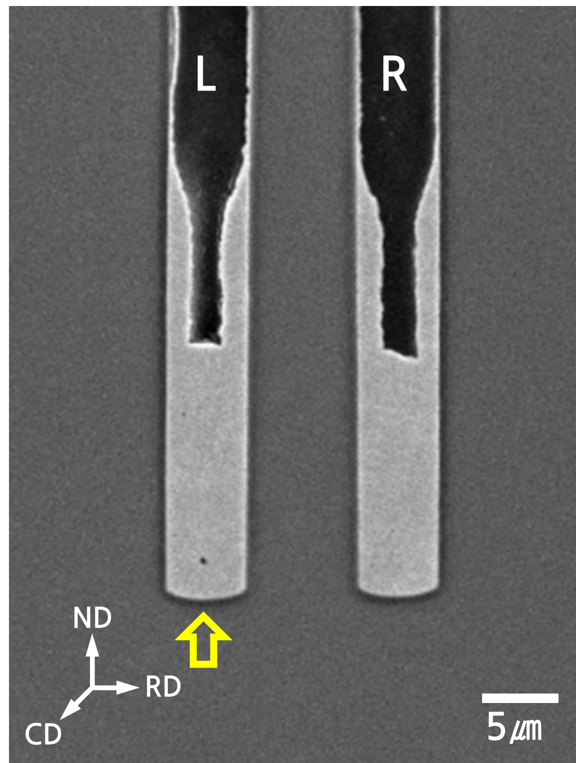


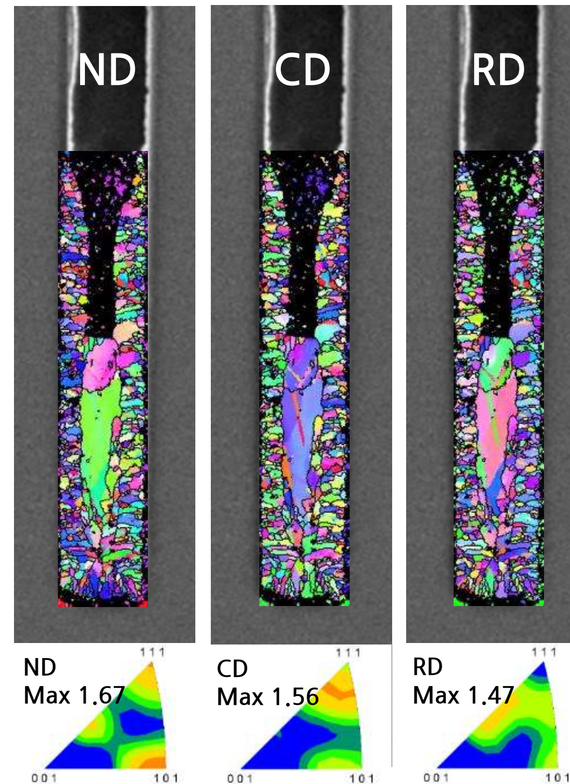


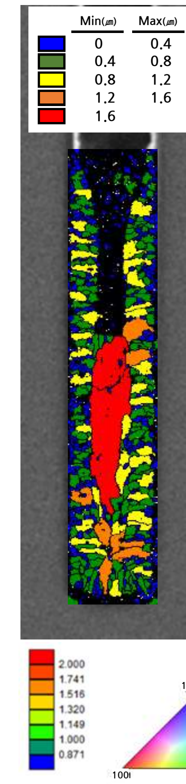
II. Micron Scale Electroplating

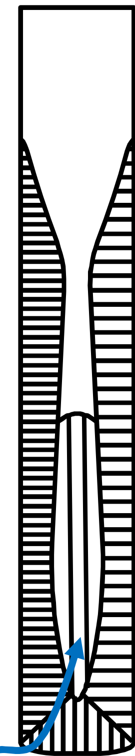
■ High Chloride annular Cu TSV

Cu TSV in 6 μmol/L TET at -0.64 V_{SSE} for 8 min



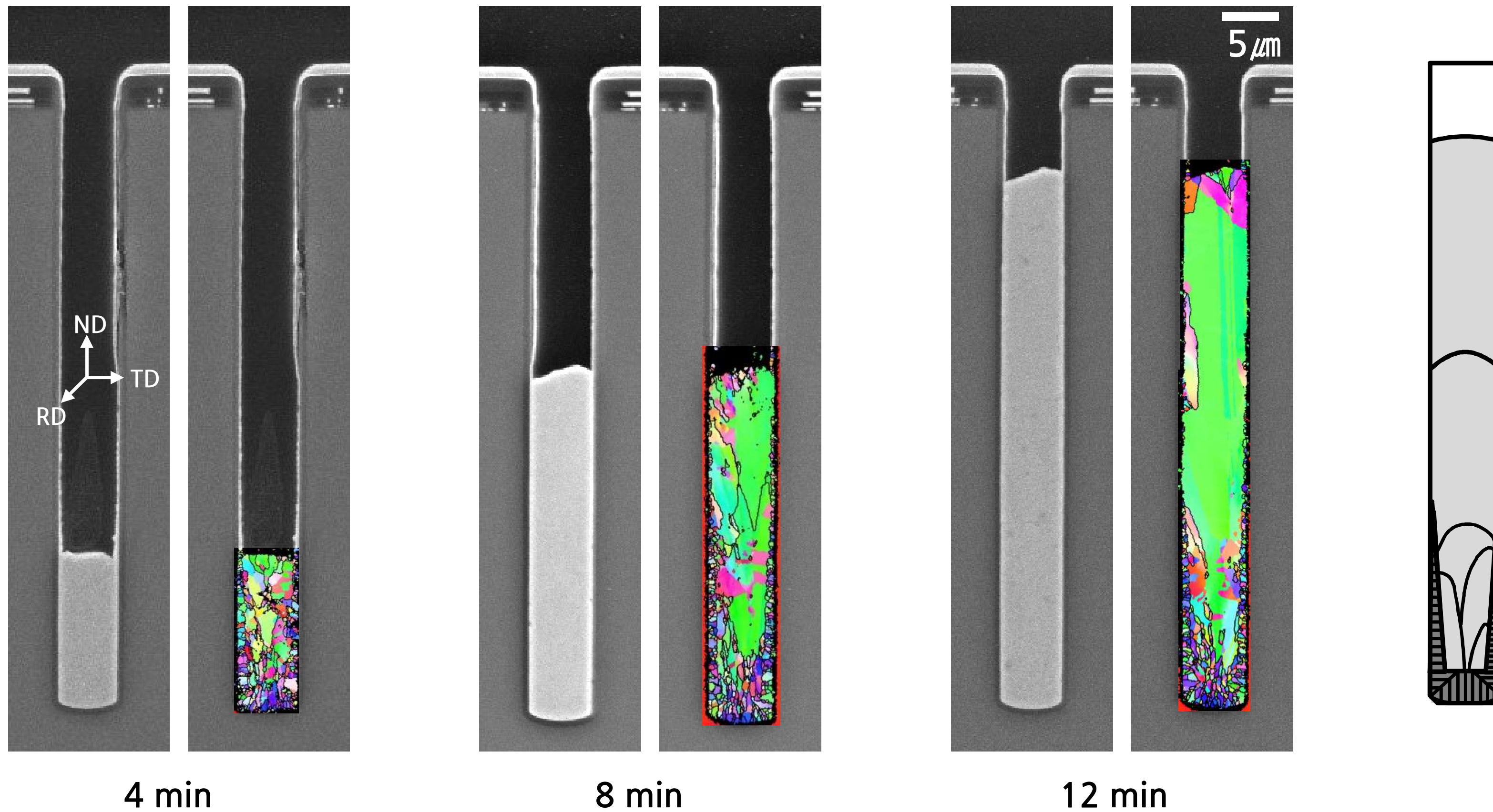






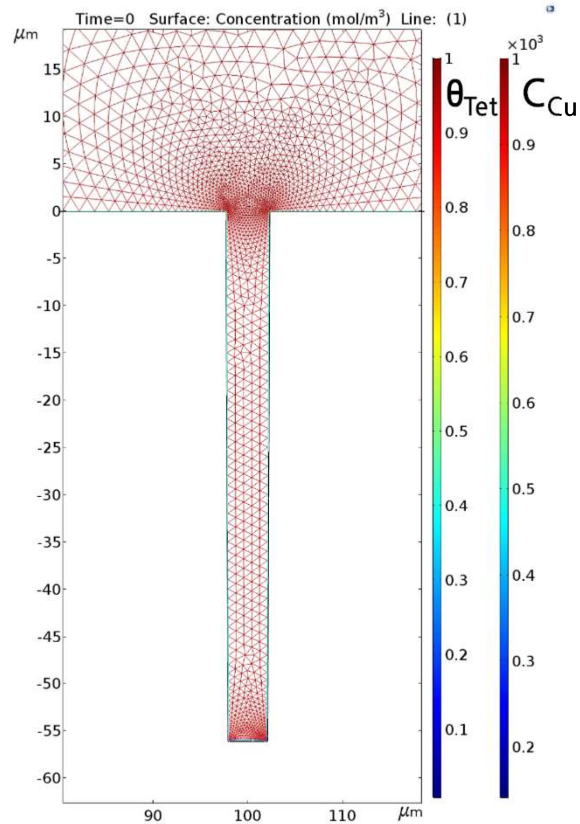
(110) Orientation

Cu TSVs in 12 μmol/L TET at -0.64 V_{SSE}



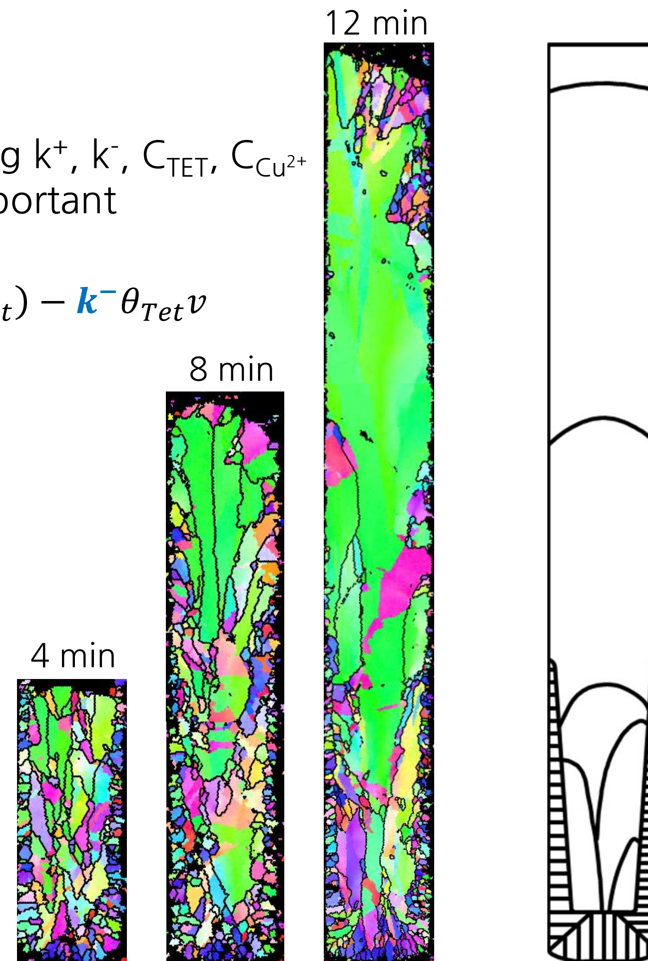
Calculation for TSV Filling

Cu TSV in 12 μmol/L TET at -0.64 V_{SSE}



Calculation considering k^+, k^-, C_{TET}, $C_{Cu^{2+}}$
➔ TET coverage is important

$$\frac{d\boldsymbol{\theta_{Tet}}}{dt} = \boldsymbol{k^+} C_{Tet}(1-\theta_{Tet}) - \boldsymbol{k^-}\theta_{Tet} v$$



Texture Evolution in Patterns

- Submicron/Micron/Millimeter scale patterns

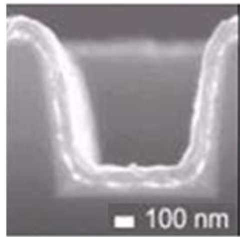
① Nano/Submicron Scale Electroplating - **Cu Damascene Pattern**

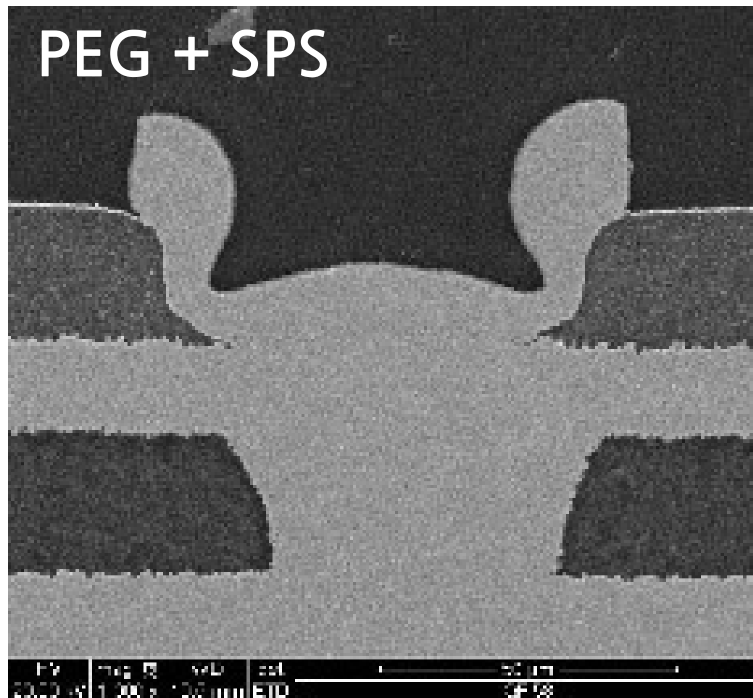
② Micron Scale Electroplating - **Cu TSV and Ni TSV**

③ Sub-millimeter Scale Electroplating - **PCB Pattern**

III. Sub-millimeter Scale Electroplating

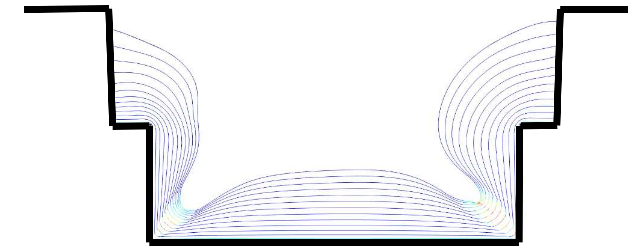
■ Calculation for Filling the Cu Bump Pattern

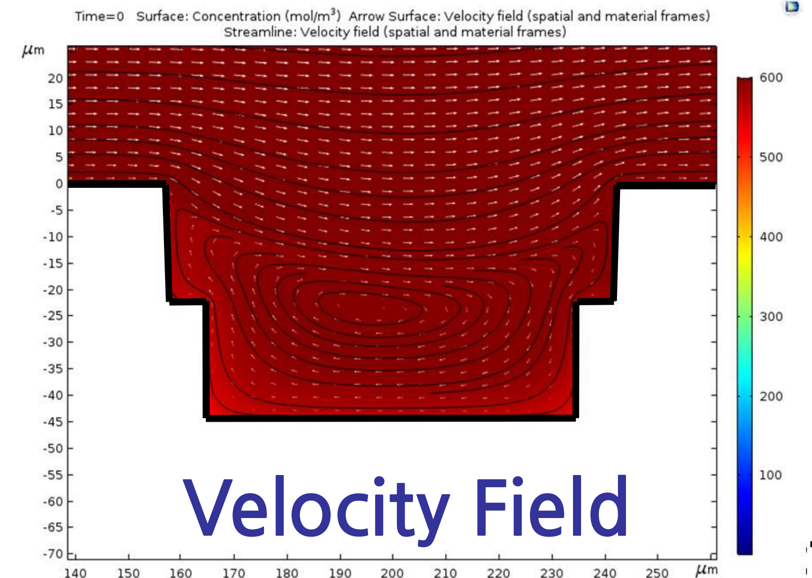




Asymmetric growth and corner plating inhibition are due to the increase and decrease in concentration of Cu ions due to flow

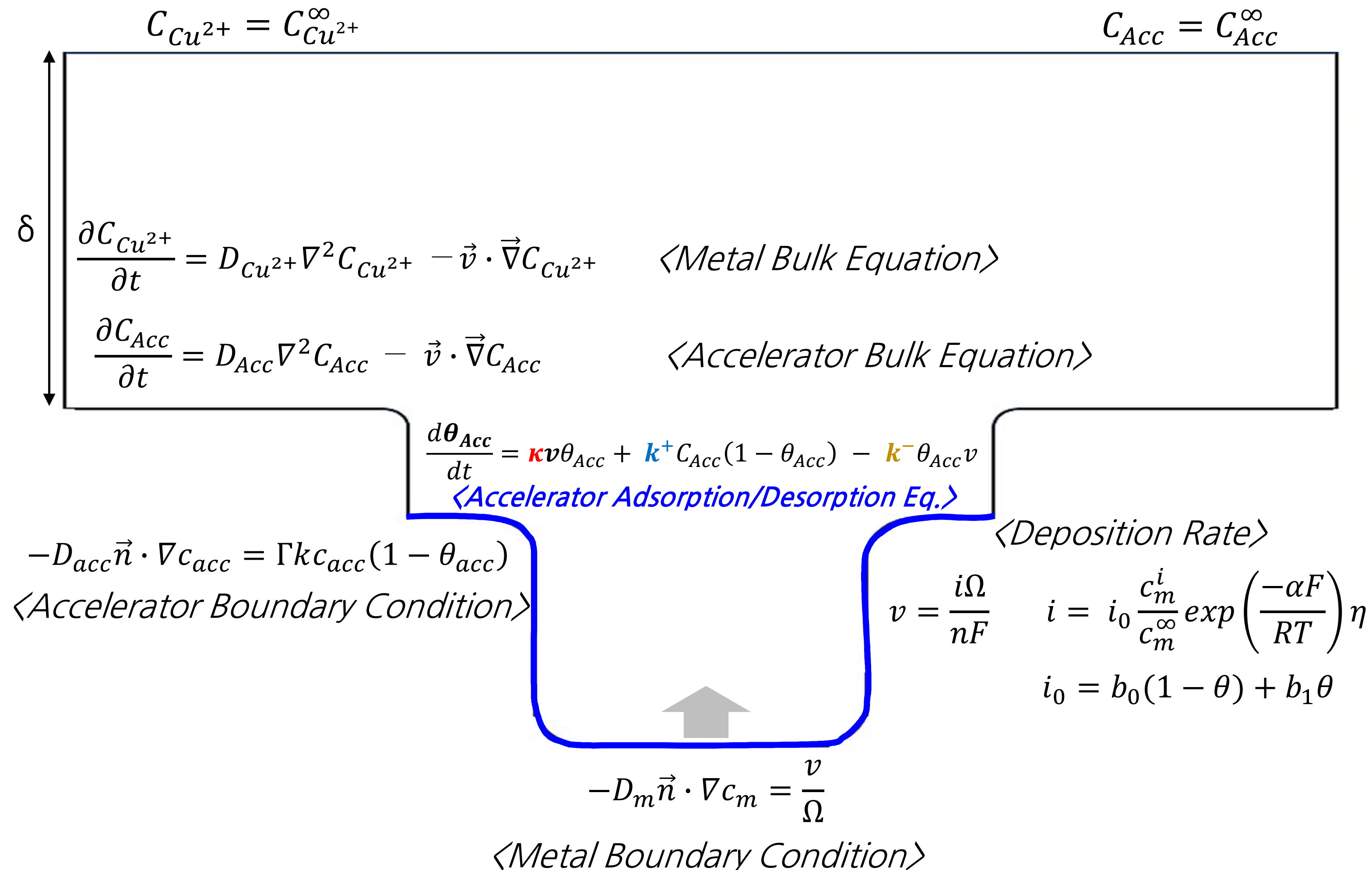
High overvoltage conditions with accelerator (η = -0.35 V)





III. Sub-millimeter Scale Electroplating

■ Schematic of the PCB geometry and the Model Formula



III. Sub-millimeter Scale Electroplating

■ Schematic of the PCB geometry and the Model Formula

Parameter	Name	Units	Value	Reference
Diffusion coefficient, copper	D_{Cu}	m^2/s	2.65×10^{-10}	[1]
Diffusion coefficient, SPS	D_{SPS}	m^2/s	4×10^{-10}	[2]
Bulk concentration, copper	C_{Cu}^{∞}	mol/m^3	280	-
Bulk concentration, SPS	C_{SPS}^{∞}	mol/m^3	0.05	-
Electrolyte conductivity	κ	S/m	15.26	[1]
Boundary layer thickness	δ	m	100×10^{-6}	[2]
Unsuppressed Cu exchange current density	i_0^0	A/m^2	20	[1]
Suppressed Cu exchange current density	i_1^0	A/m^2	0.13	[1]
Saturation SPS coverage	Γ	mol/m^2	6.35×10^{-6}	[2]
Adsorption coefficient of SPS	k^+	$m^3/(s \cdot mol)$	0.0895	[2]
Desorption coefficient of SPS	k^-	1/s	0.00212	[2]
Deposition charge transfer coefficient	α	-	0.5	[1]
Copper ionic charge	n	-	2	[1]
Copper molar volume	Ω	m^3/mol	7.1×10^{-6}	[1]

Einstein-Smoluchowski equation

$$\overline{\Delta^2} = nl^2 = 2Dt\ ,\quad \overline{\Delta} = \sqrt{2Dt}$$

$$\Delta = \sqrt{2 \times 2.65 \times 10^{-10} m^2/s \times 1s}$$

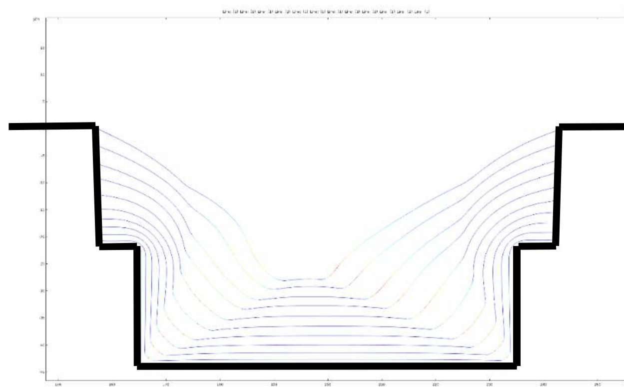
$$= 23\ \mu m$$

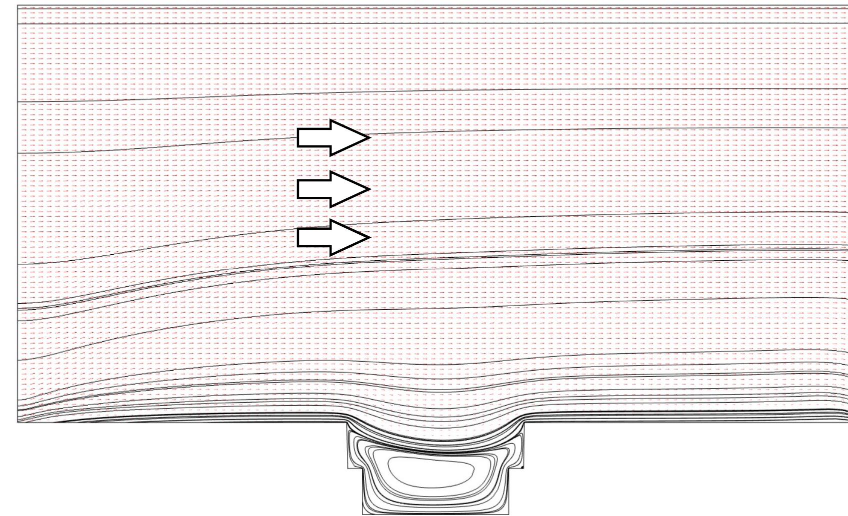
[1] T. M. Braun *et al.*, J. of ECS 166, D3259 (2019)
[2] T. P. Moffat *et al.*, IBM J. of Res. Dev. **49**, 19 (2005)

III. Sub-millimeter Scale Electroplating

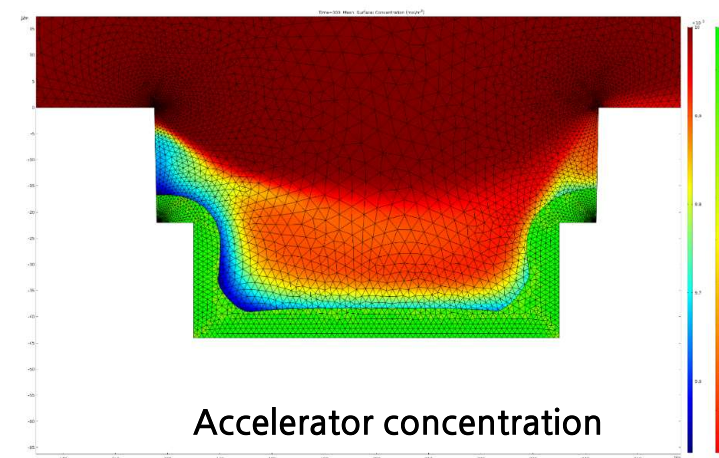
■ Asymmetric Growth

Accumulating accelerators in the corner





The growth rate on the right side is high
➔ The supply of Cu and accelerator is large due to the influence of the flow field (stream line)



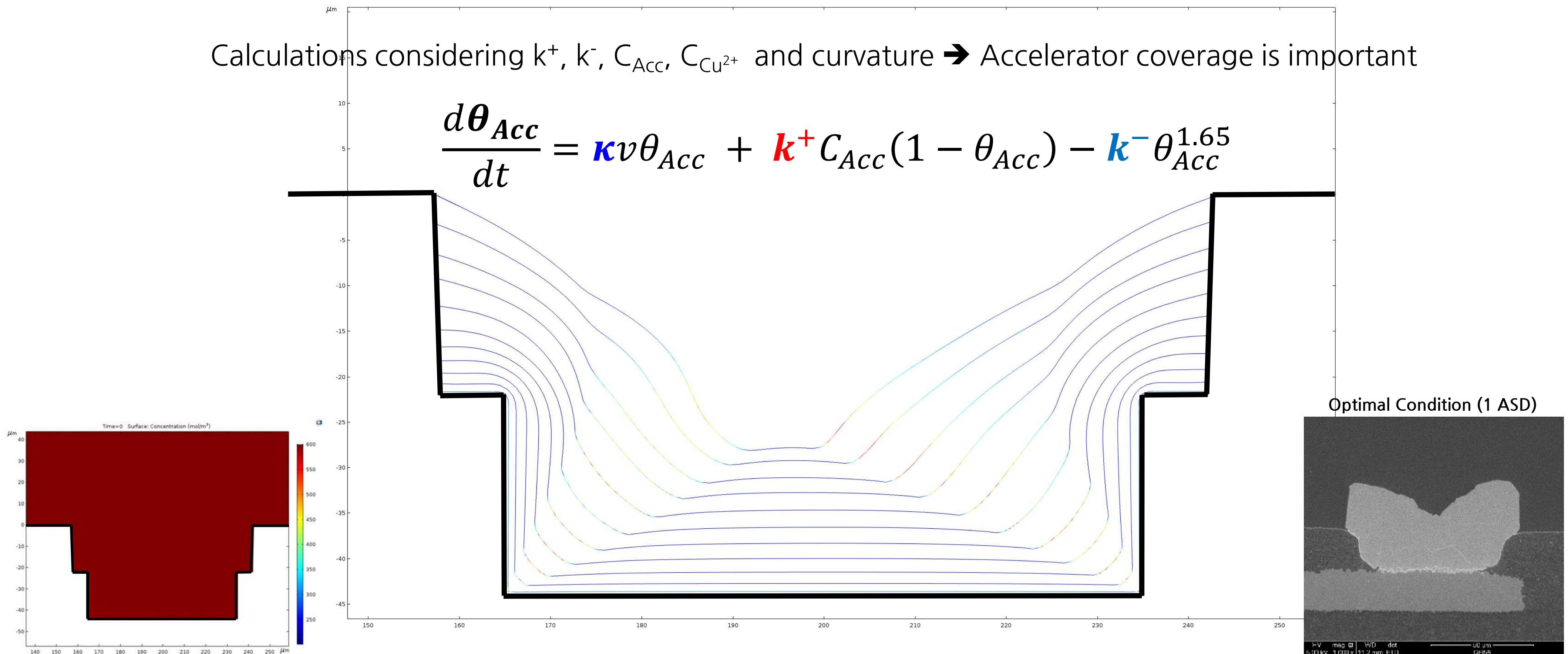
Accelerator concentration

III. Sub-millimeter Scale Electroplating

■ Pattern Filling of PEG+SPS : Asymmetric Growth

Calculations considering k^+, k^-, C_{Acc}, $C_{Cu^{2+}}$ and curvature ➔ Accelerator coverage is important

$$\frac{d\boldsymbol{\theta}_{Acc}}{dt} = \boldsymbol{\kappa} v \theta_{Acc} + \boldsymbol{k}^{+} C_{Acc}(1-\theta_{Acc}) - \boldsymbol{k}^{-} \theta_{Acc}^{1.65}$$

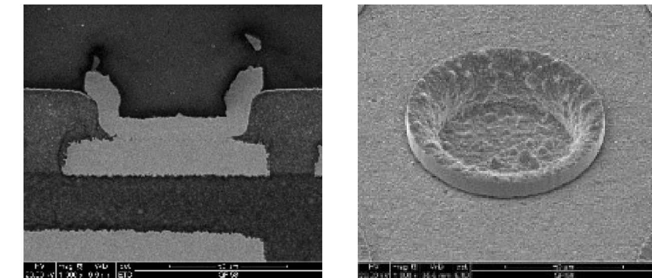


III. Sub-millimeter Scale Electroplating

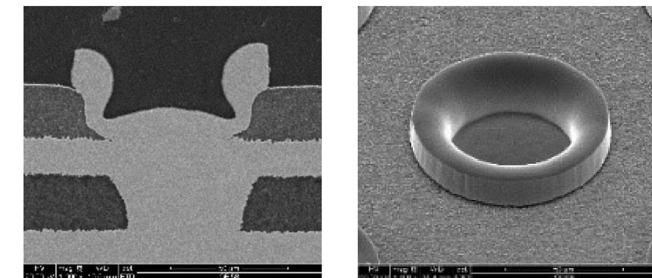
■ Comparison of Pattern Filling for PEG and PEG+SPS

		5 min	10 min	20 min	50 min	100 min
PEG	Top view					
	Tilt view					
	Cross section					
PEG+ SPS	Top view					
	Tilt view					
	Cross section					

PEG only (20 min)



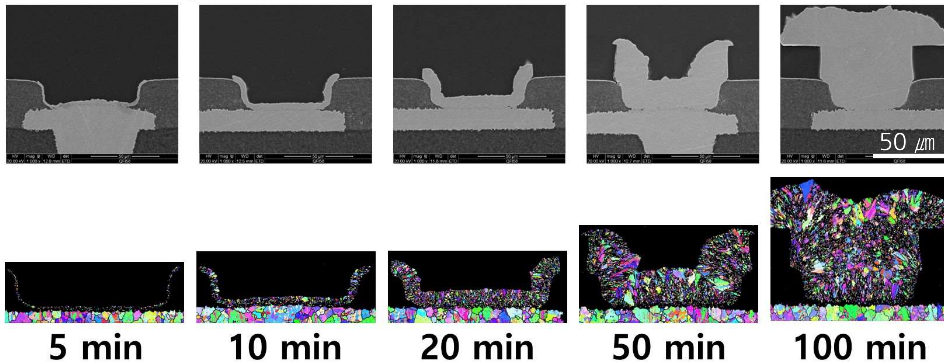
PEG + SPS (20 min)

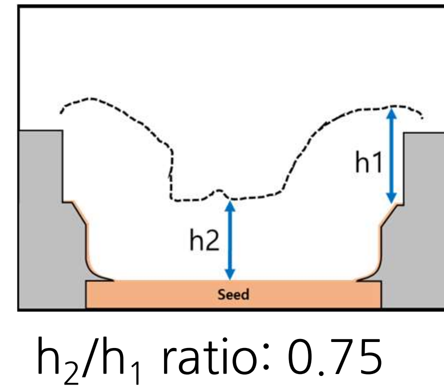


III. Sub-millimeter Scale Electroplating

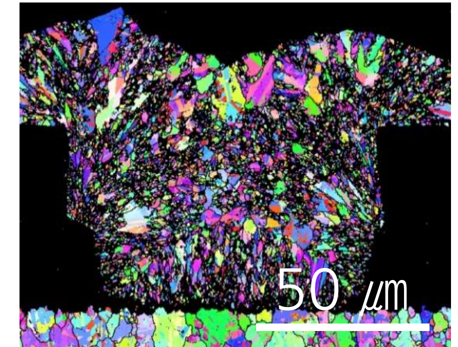
■ Comparison of Pattern Filling for Various Conditions

- **PEG only(3 ASD)**

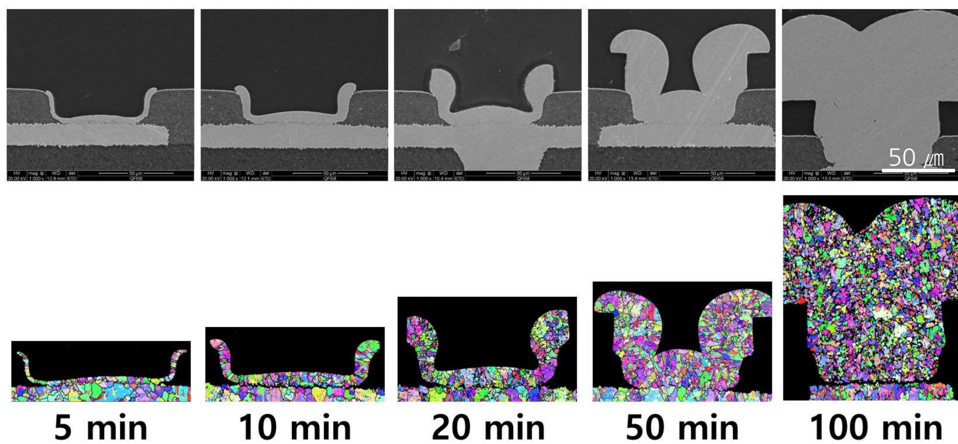


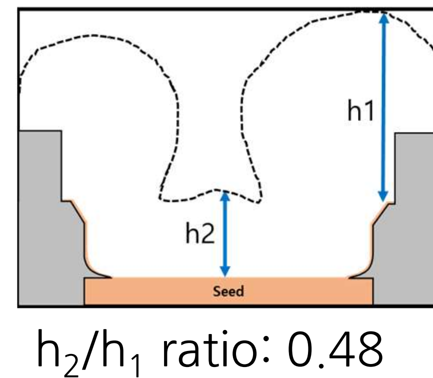


h_2/h_1 ratio: 0.75

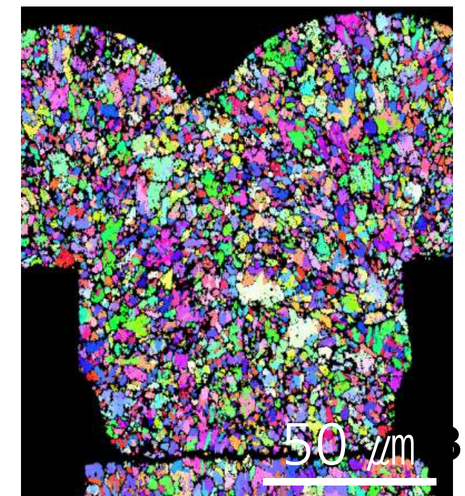


- **PEG+SPS(3 ASD)**





h_2/h_1 ratio: 0.48



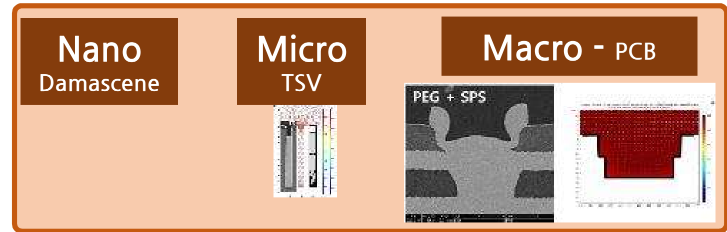
Summary of Multi-scale Electroplating

■ Estimation of k^+/k^- Models for Organic Additives

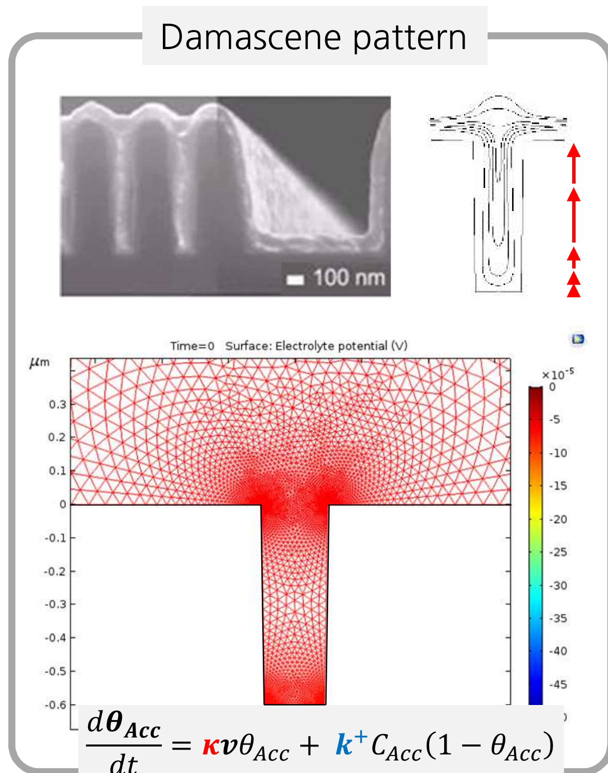
① Damascene pattern(submicron scale - nano)

② TSV pattern(micron scale - micro)

③ PCB pattern(tens/hundreds micron scale - macro)

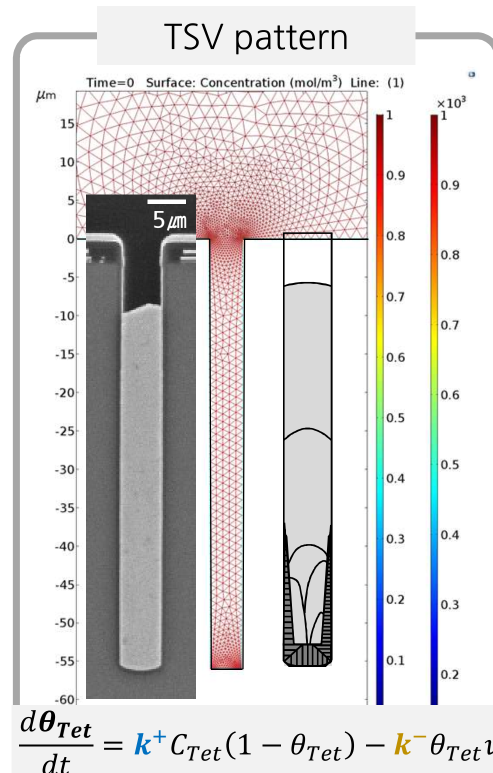


Damascene pattern



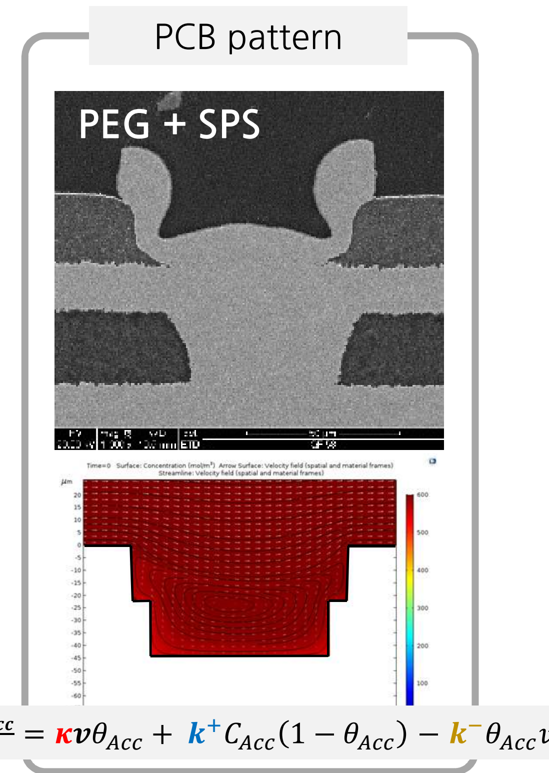
$$\frac{d\theta_{Acc}}{dt} = \kappa v\theta_{Acc} + k^+C_{Acc}(1-\theta_{Acc})$$

TSV pattern



$$\frac{d\theta_{Tet}}{dt} = k^+C_{Tet}(1-\theta_{Tet}) - k^-\theta_{Tet}v$$

PCB pattern



$$\frac{d\theta_{Acc}}{dt} = \kappa v\theta_{Acc} + k^+C_{Acc}(1-\theta_{Acc}) - k^-\theta_{Acc}v$$

Contents

I. Texture Evolution in Multi-scale Patterns

- ① Submicron / ② Micron / ③ Millimeter scale patterns

II. In situ Investigation of Growth Anisotropy

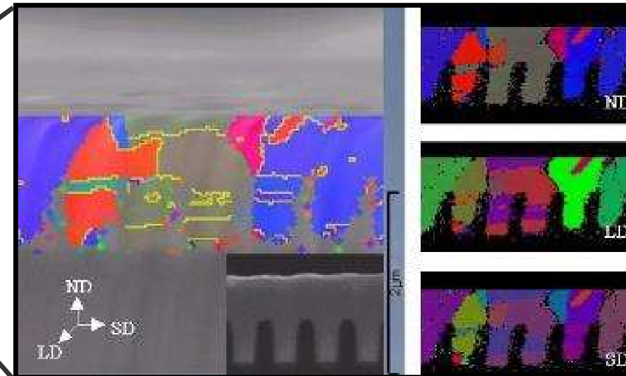
- Anisotropic <111> grain growth, Twin formation

III. Texture Phenomenon

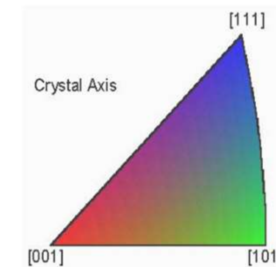
- Stress-induced voiding : T.J. and equi-biaxial modulus

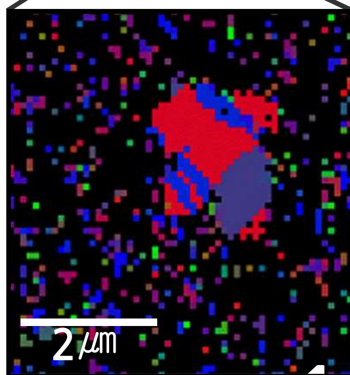
Elastic Anisotropy and Microstructure in Cu

EBSD (Electron Backscattered Diffraction)

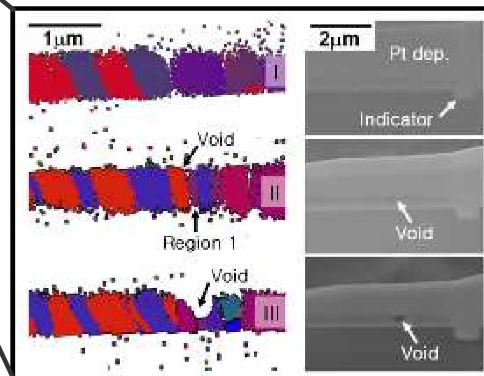


Cu Texture, JEM(2005)



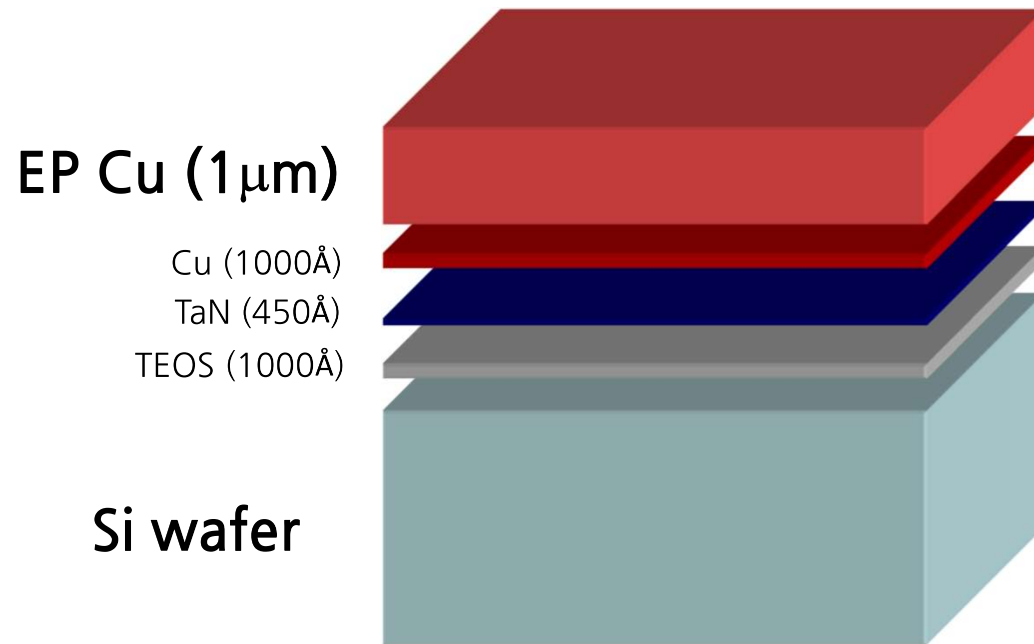


In situ Investigation, APL(2006)

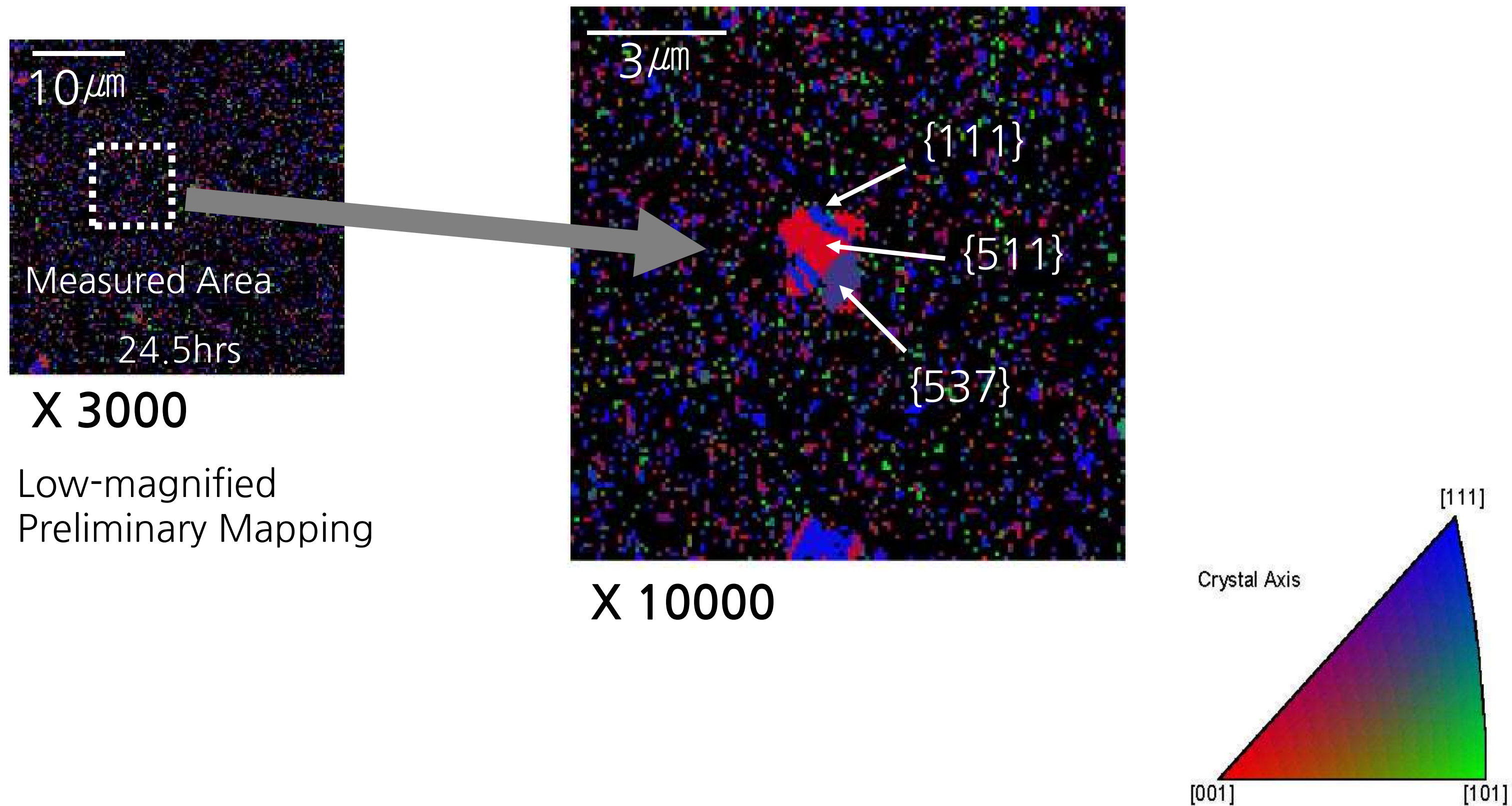


Stress-induced Void
APL(2008)

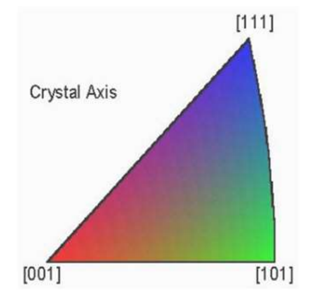
Sample Preparation for Self-annealing



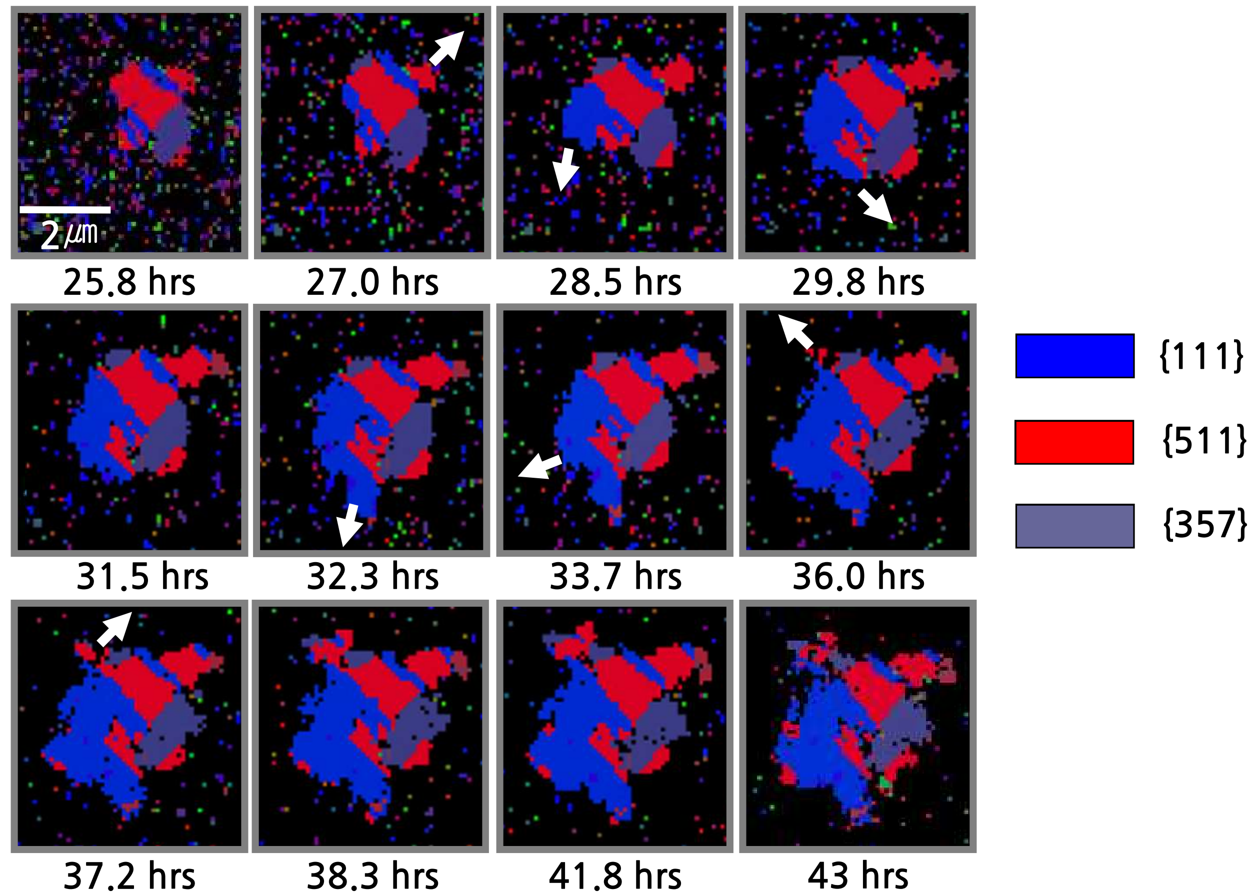
Experimental Procedure - EBSD Analysis



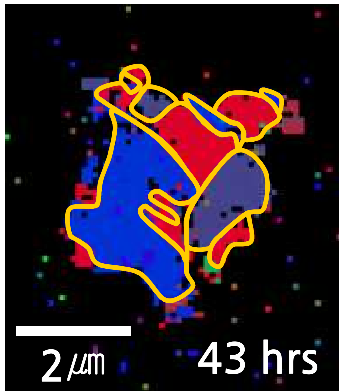
1 μm

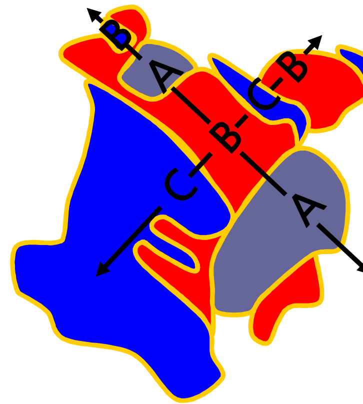


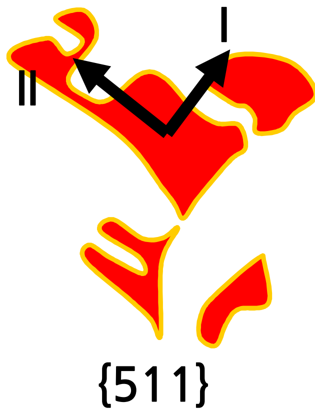
In situ Planar EBSD Measurements



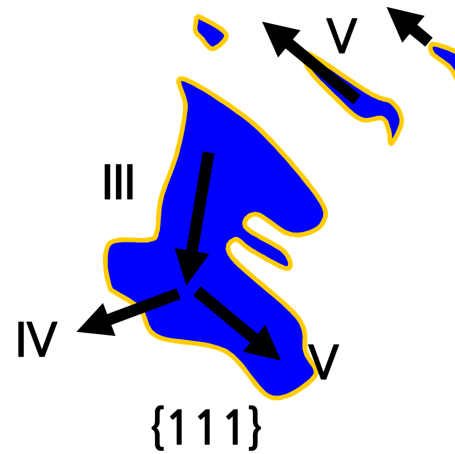
Grouping Growth Directions



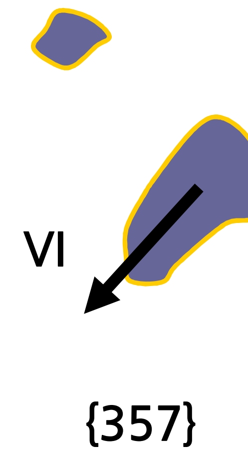




{511}



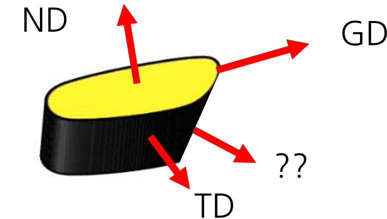
{111}



{357}

Crystalline Analyses for Growing Grains

ND : Plane normal direction
GD : Apparent growth direction
TD : Transverse direction for the growth
TD' : Calculated transverse direction



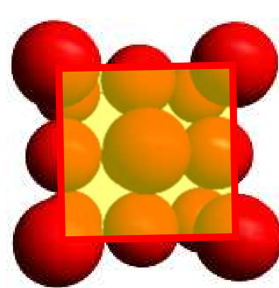
Case	ND	GD	TD	TD'
I	[1 -1 -9]	[1.0 1.0 0.0]	[1.0 -1.0 0.2]	[1.0 -1.3 0.3]
II	[1 -1 -9]	[1.0 -1.0 0.2]	[1.0 1.0 0.0]	[1.0 1.0 0.0]
III	[4 -3 4]	[1.0 0.7 -0.5]	[1.0 -5.0 -4.7]	[1.0 -8.0 -7.0]
IV	[4 -3 4]	[1.0 -0.7 -1.5]	[1.0 1.4 0.0]	[1.0 1.1 -0.1]
V	[4 -3 4]	[1.0 3.4 1.5]	[1.0 0.1 -0.9]	[1.0 0.0 -1.0]
VI	[5 -3 -7]	[1.0 3.0 -0.6]	[1.0 -0.2 0.8]	[1.0 -0.2 0.8]

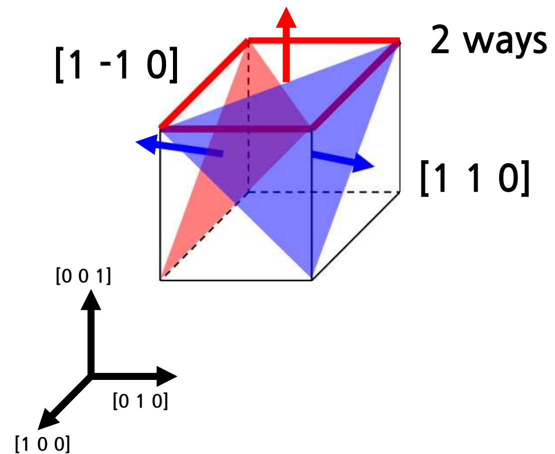
TD ≒ ⟨110⟩

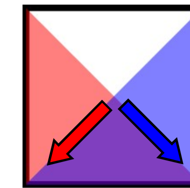
$$TD' = ND \times <111>$$

Crystalline Analyses for {100} and {111} Planes

{100}

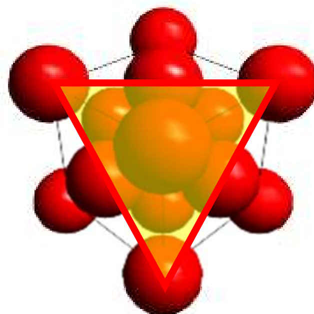


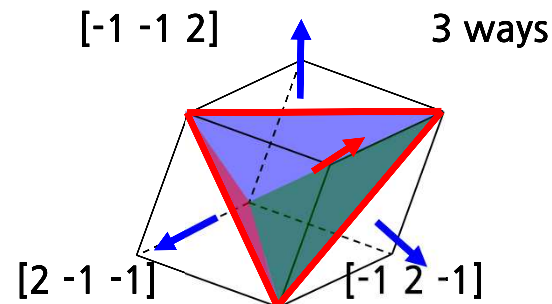


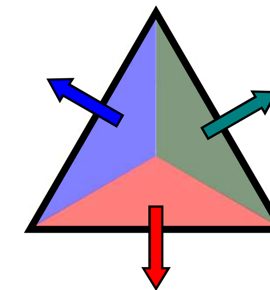


{100}
projection

{111}

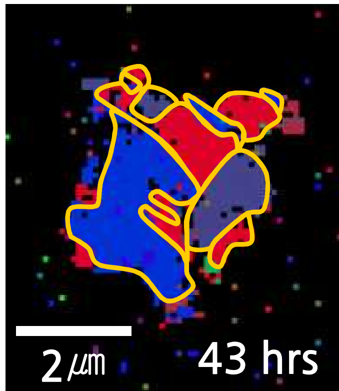


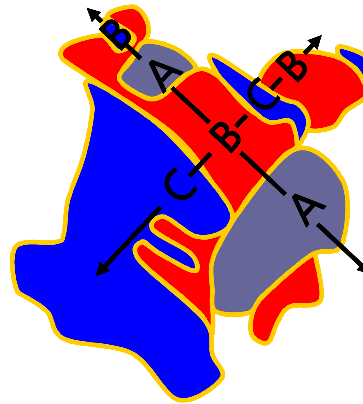


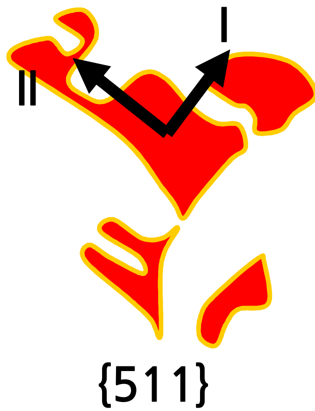


{111}
projection

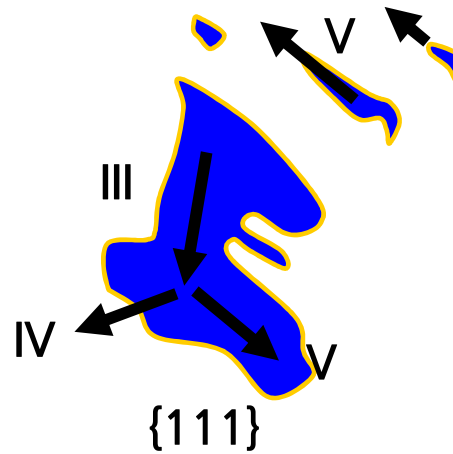
Grouping Growth Directions







{511}



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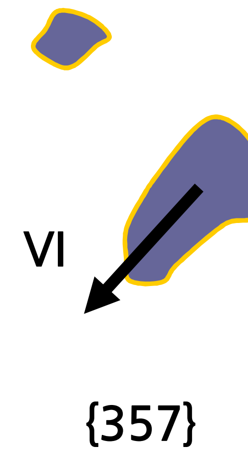
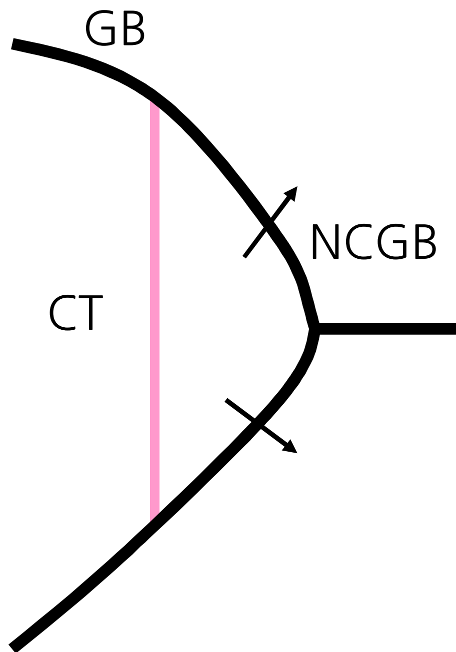


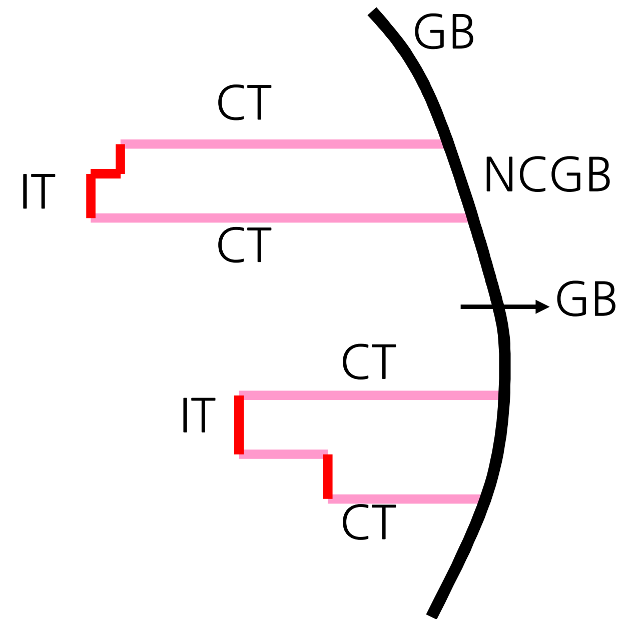
{357}

Models of Twin Formation

Model I



Model II

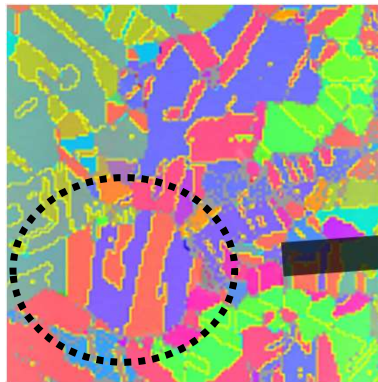


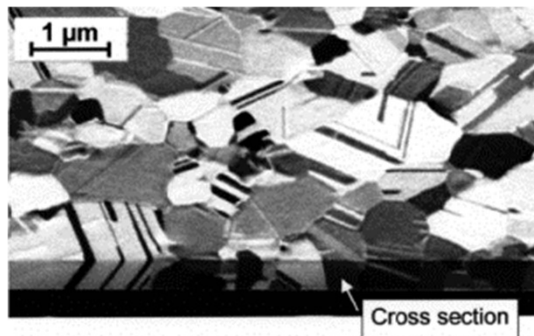
NCGB: newly created grain boundary

P.J. Goodhew, Metal Science (1979)

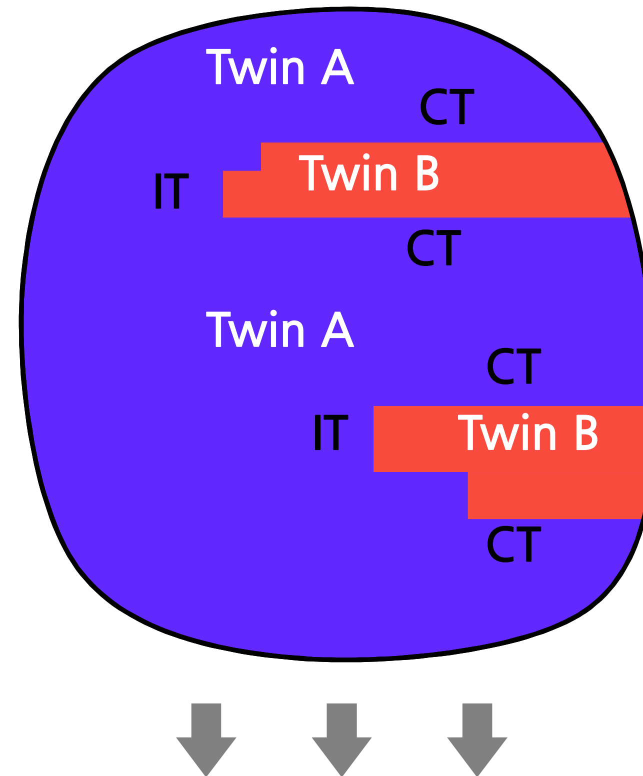
Growth Direction vs. Twin Boundary

After Grain Growth





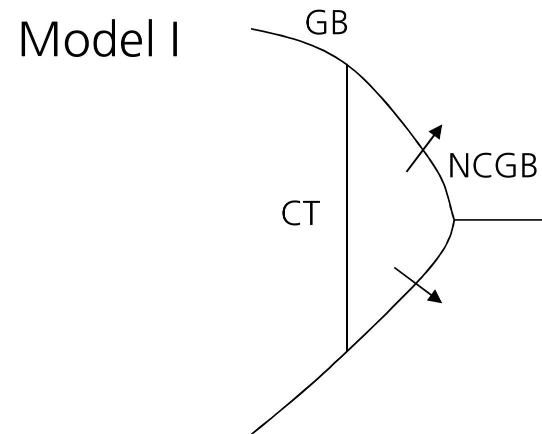
V. Weihnacht *et al.*, TSF **418**, p.136 (2002)



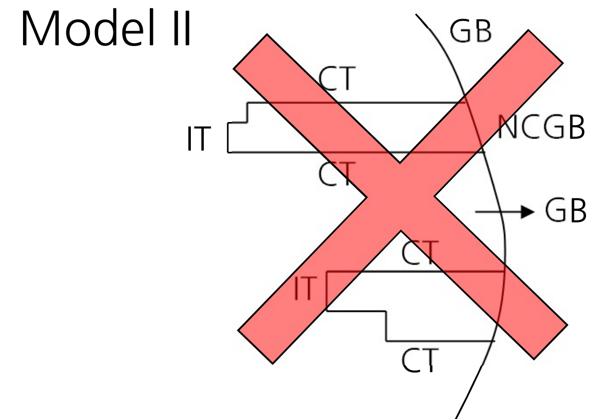
Which is the direction of grain growth?

Twin Formation

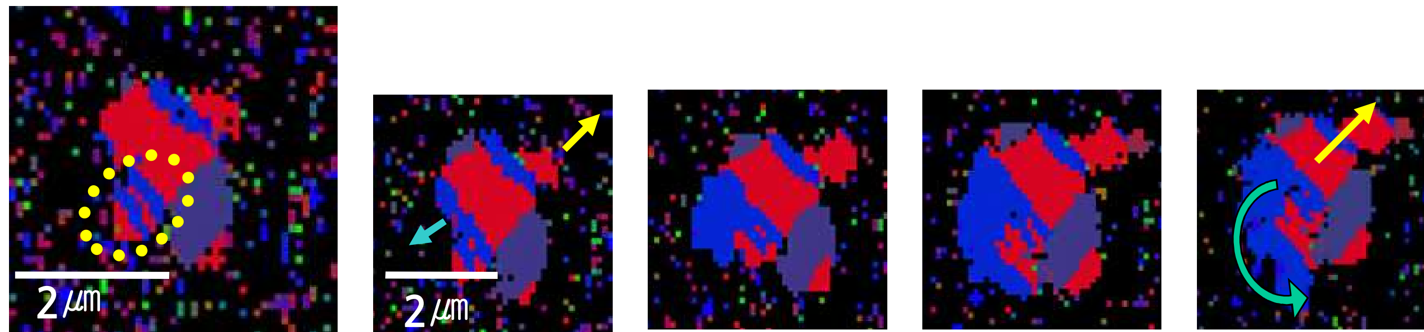
Model I



Model II

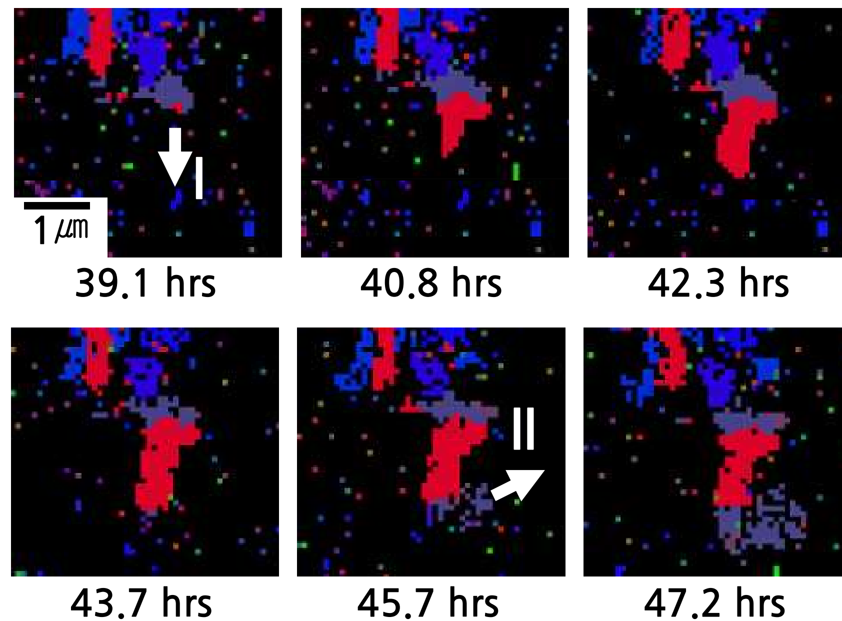


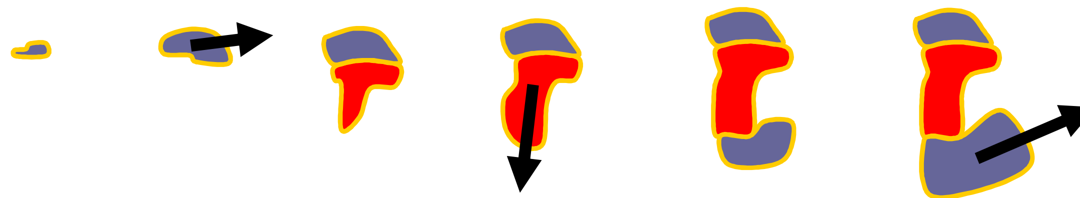
NCGB: newly created grain boundary
P.J. Goodhew, Metal Science (1979)



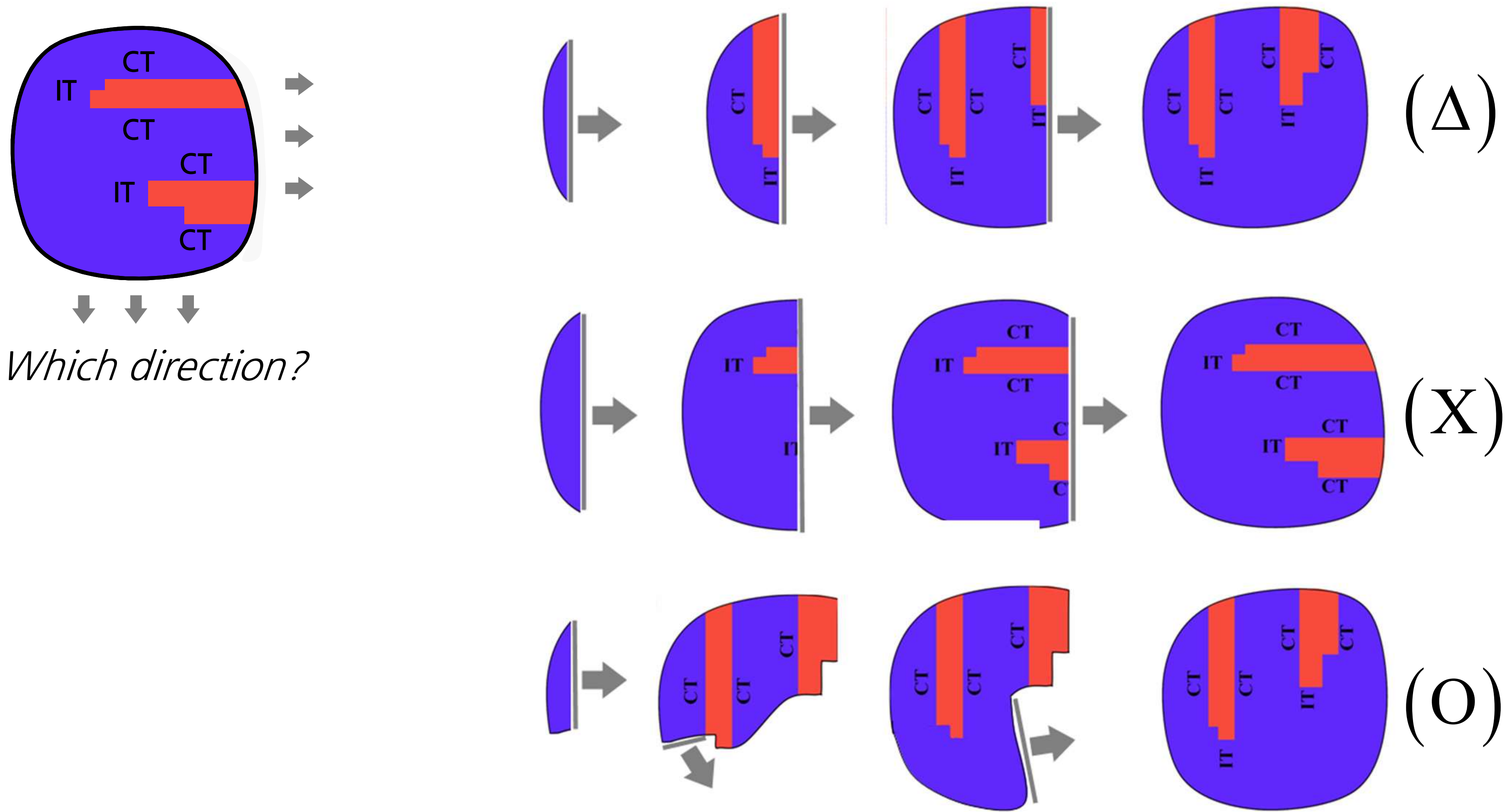
Model I seems to be more favorable for twin formation than Model II !!

In situ Investigation of Grain Growth





Crystalline Analyses for Growing Grains



Contents

I. Texture Evolution in Multi-scale Patterns

- ① Submicron / ② Micron / ③ Millimeter scale patterns

II. In situ Investigation of Growth Anisotropy

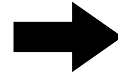
- Anisotropic 〈111〉 grain growth, Twin formation

III. Texture Phenomenon

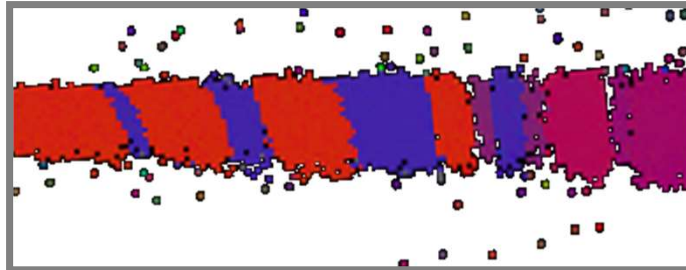
- Stress-induced voiding : T.J. and equi-biaxial modulus

Self-annealing on Cu Thin Film with Additive

Grain size : < 10 nm
Purity > 99.95% Cu



Room temperature annealing or
Self-annealing



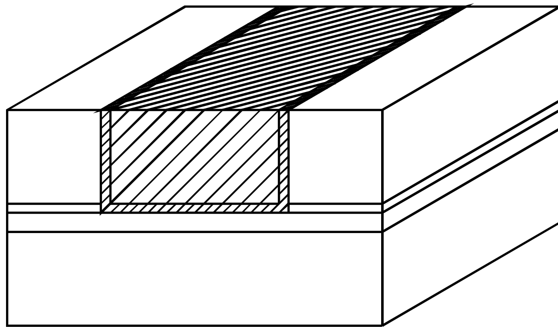
Electroplated Cu (1μm)

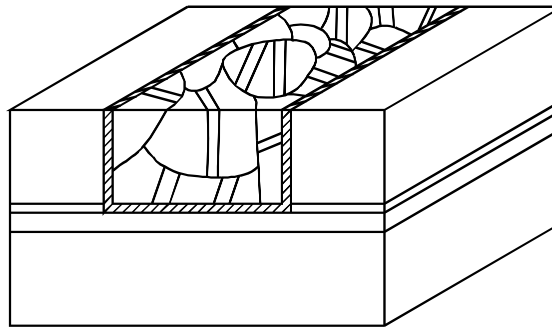
Cross-sectional image by FIB and EBSD

Texture Evolution in Electrodeposits

As-deposited film
(plating condition, substrate)

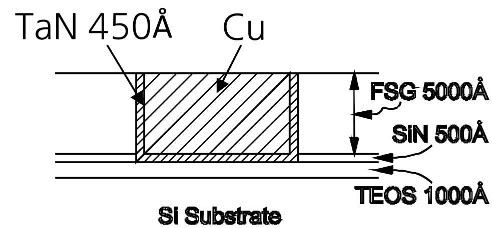
Annealed structure
(stress relaxation, defect<g.b., disl.> reduction)



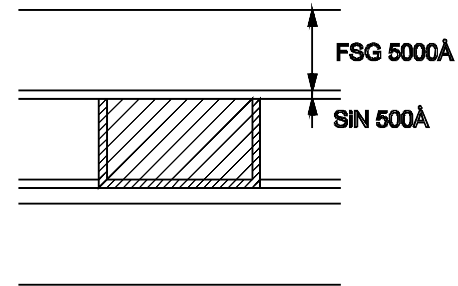


Stress : residual, thermal expansion, geometry
Grain growth **Anisotropy**
Effect of microstructure on **Voiding**

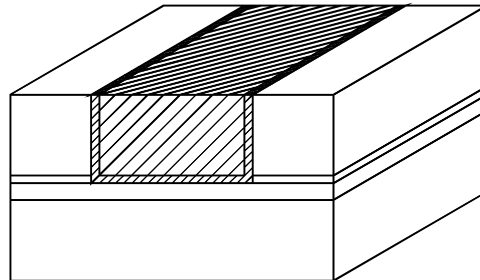
Sample Preparation for SIV



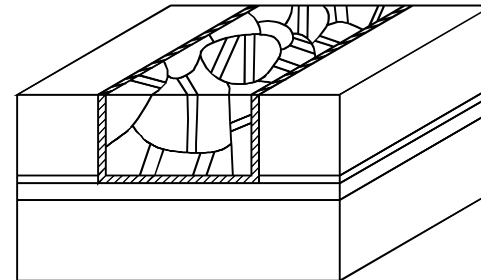
under metal layer after CMP



SiN and FSG capping

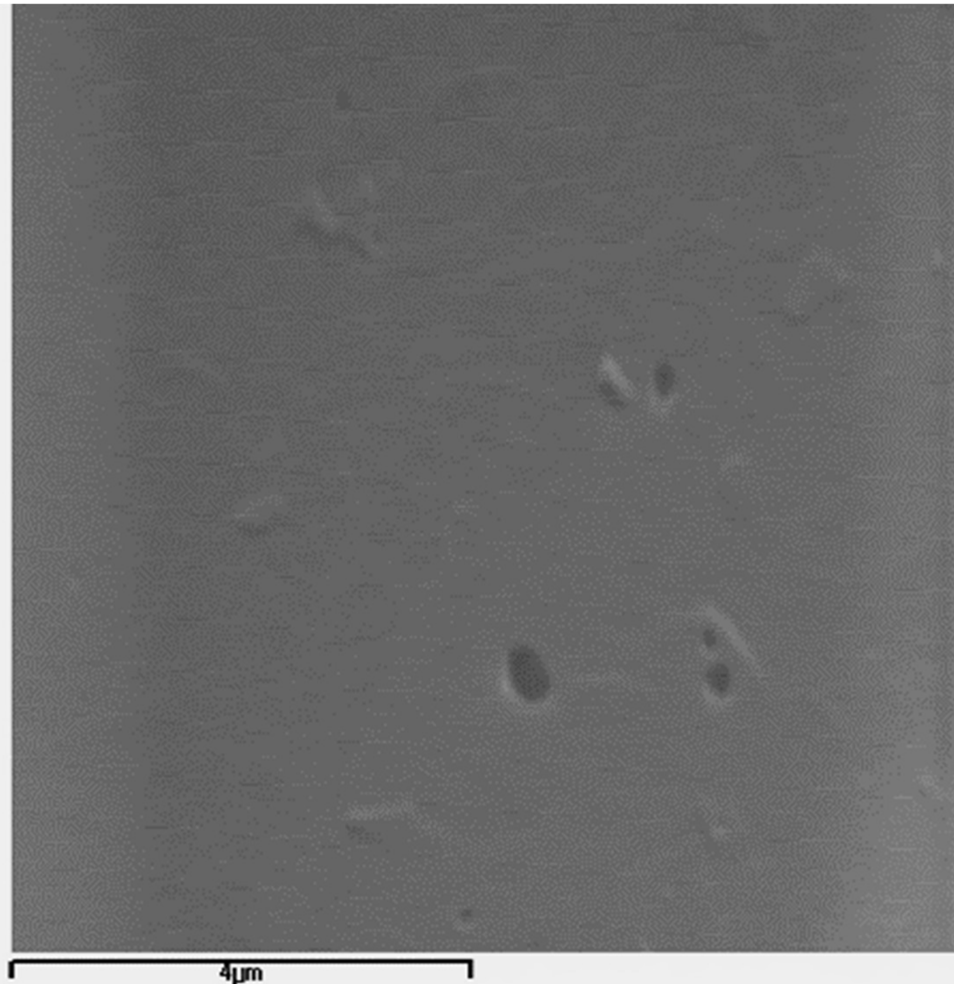


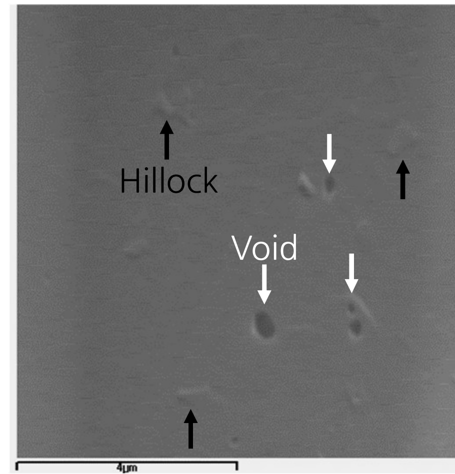
Stripping of the capping layer after oven bake at 200 °C for 500 hrs (HTS test)

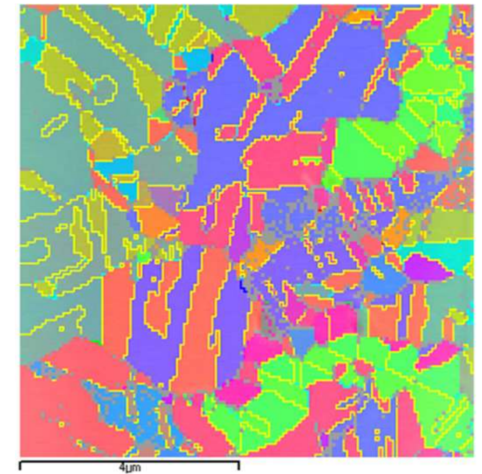


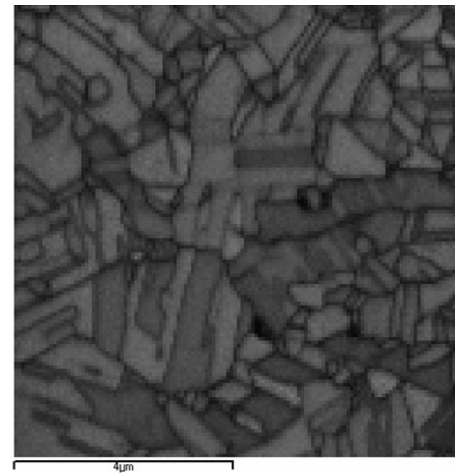
Schematic image of metal line with grain boundaries after EBSD analysis

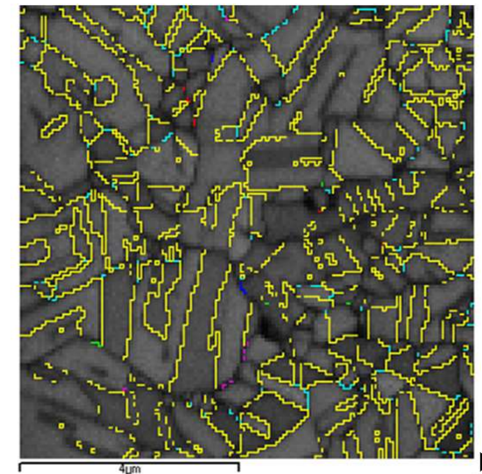
EBSD Measurement for Voids and Hillocks



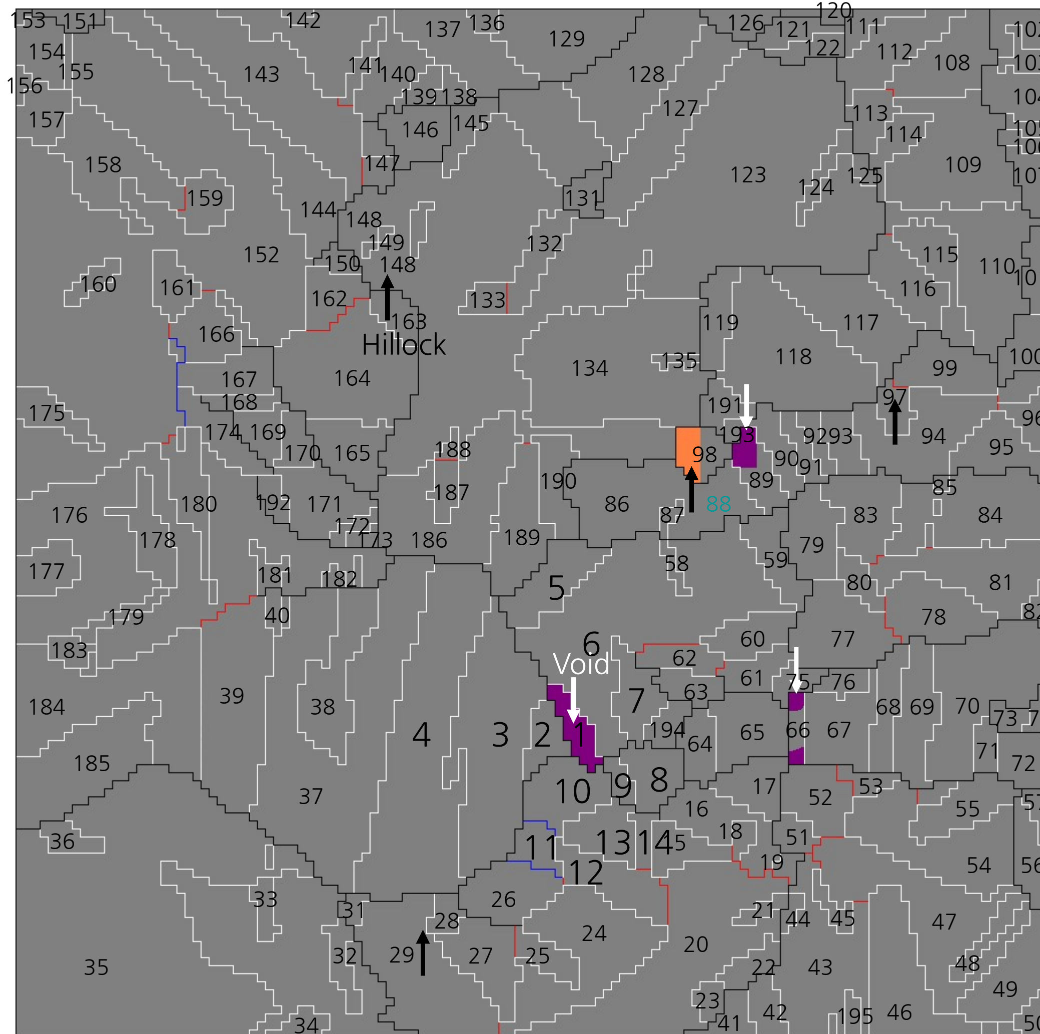




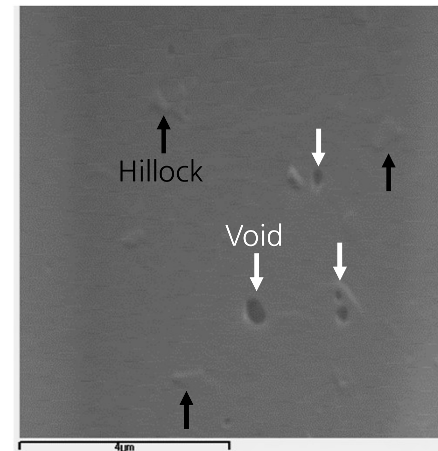




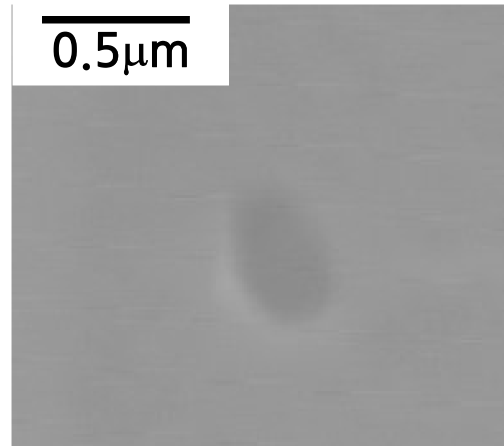
Labeling Grains and Their Orientations

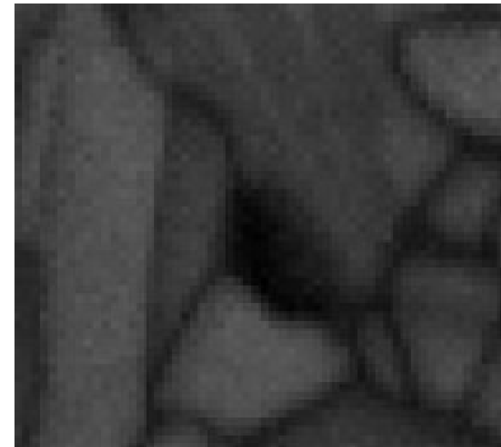


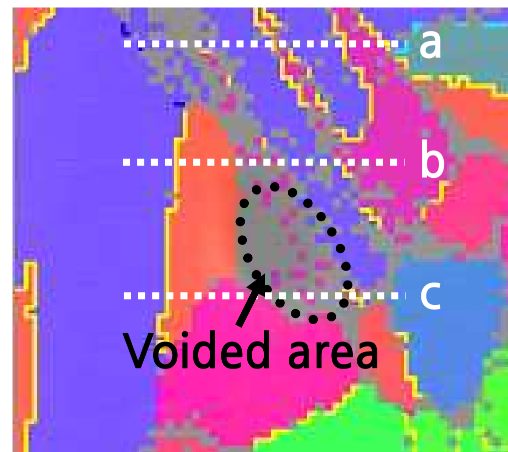
Position	h	k	l	u	v	w
1	-6	4	-13	29	11	-10
2	17	1	-3	3	-12	13
3	7	5	4	-18	26	-1
4	-1	17	-3	12	3	13
5	-1	0	3	24	7	8
6	4	5	7	3	-1	-1
7	3	-9	-4	24	-20	63
8	6	11	-14	1	2	2
9	-2	17	-1	23	3	5
10	7	6	-20	30	5	12
11	3	2	-10	2	-3	0
12	9	0	8	8	2	-9
13	2	16	15	13	4	-6
14	17	1	15	4	7	-5

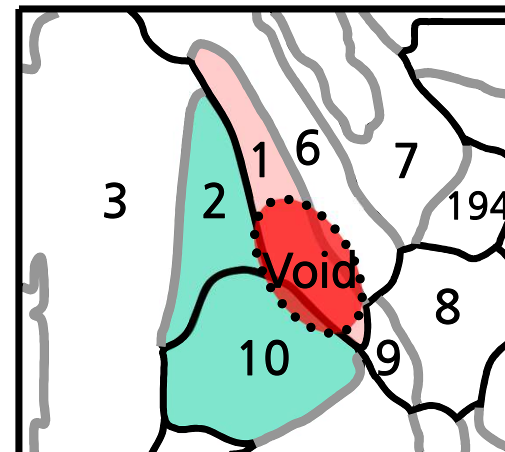


EBSD Measurement on a SIV

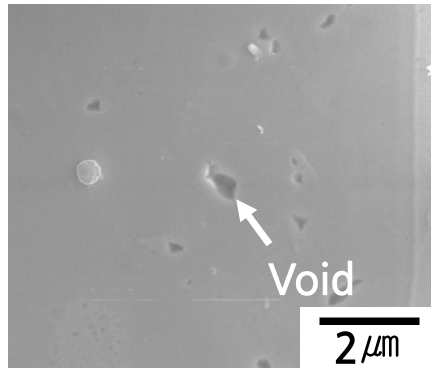




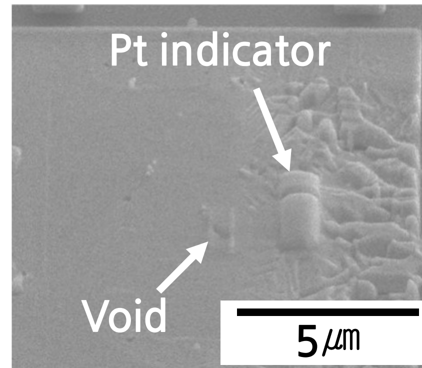




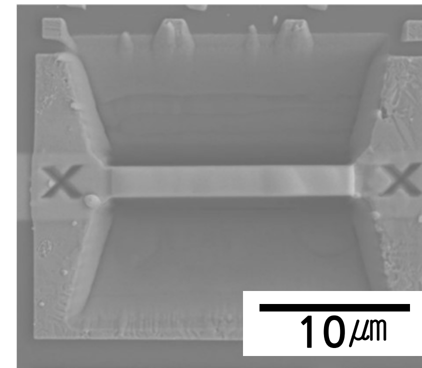
Sample Preparation for cross-sectional EBSD



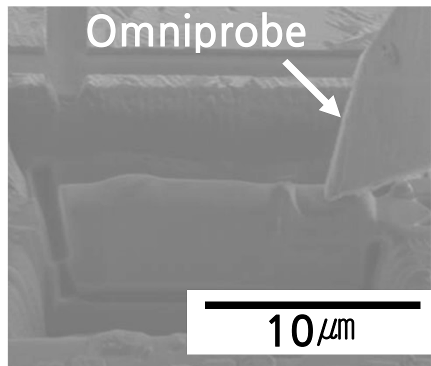
Initial sample



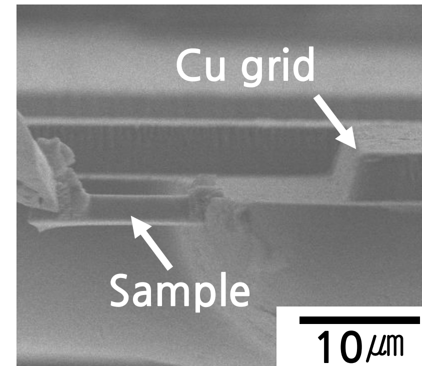
Indicator by Pt dep.



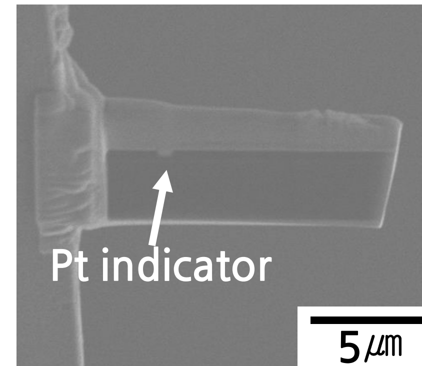
FIB sectioning



U-cutting and sample attachment

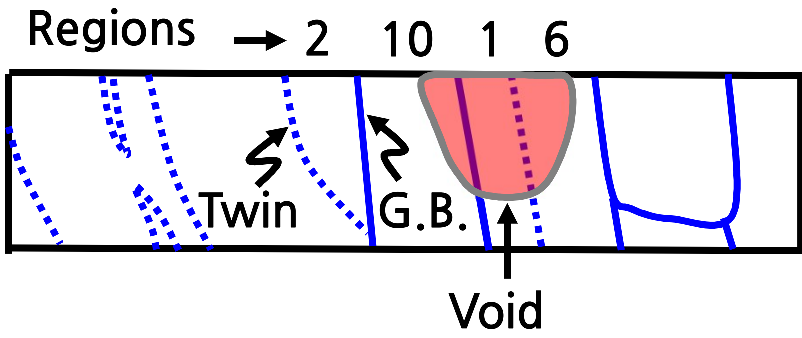


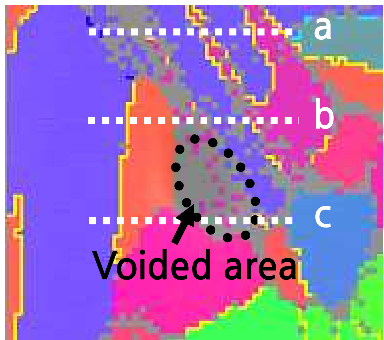
Transferring the sample on Cu grid

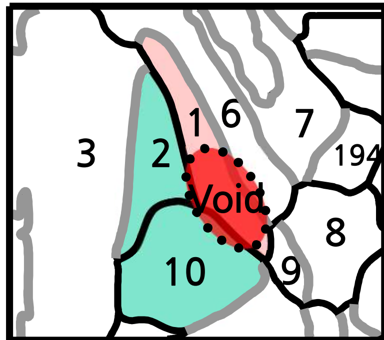


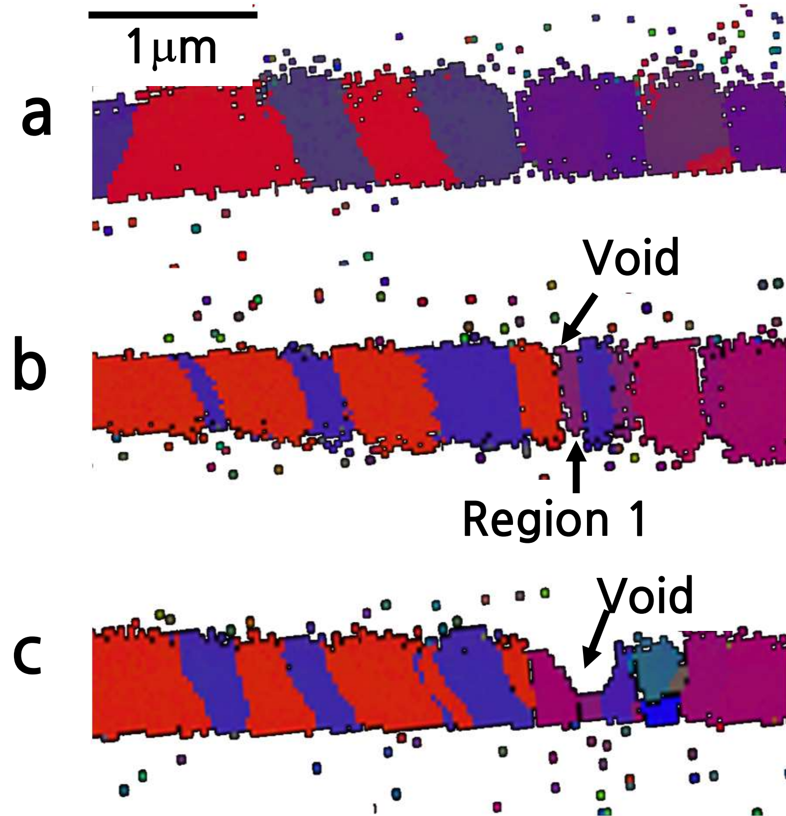
Sample ready for EBSD

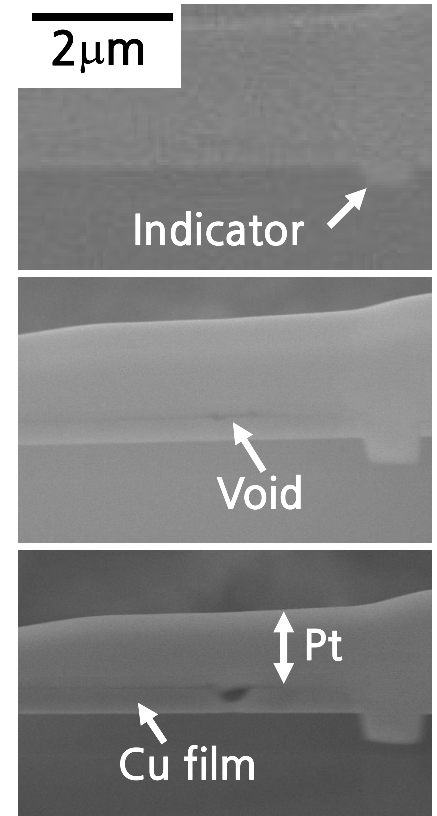
Cross-Sectional EBSD Measurements on a SIV



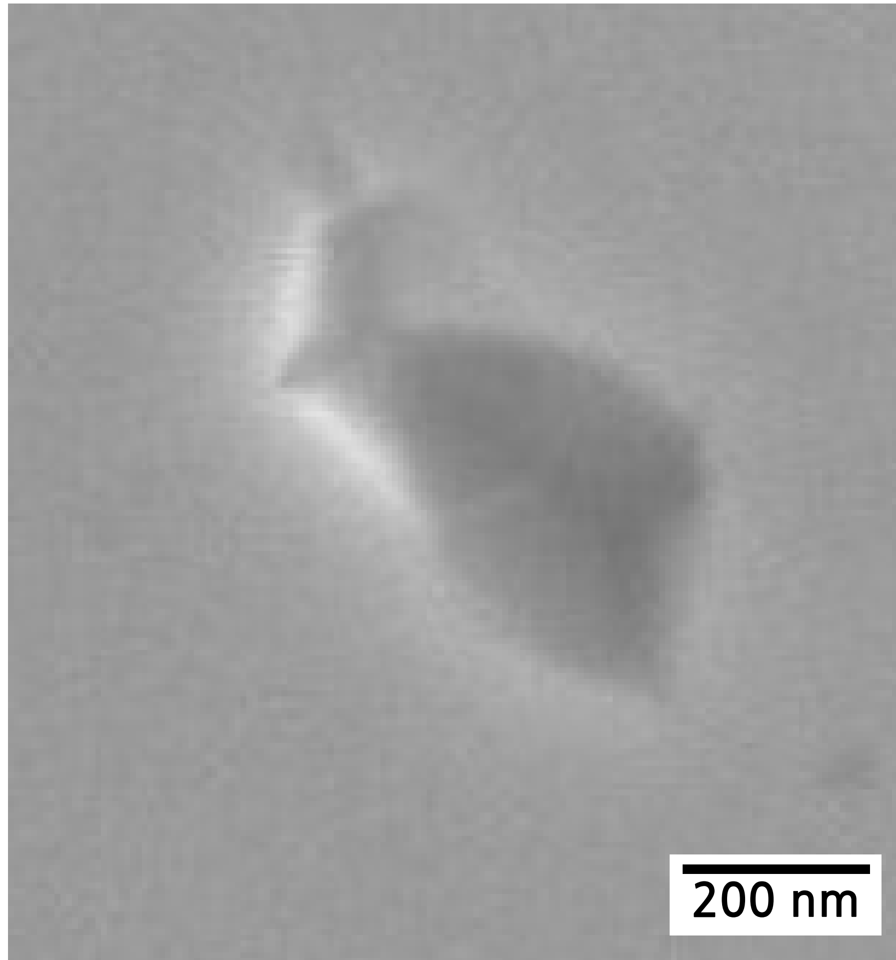


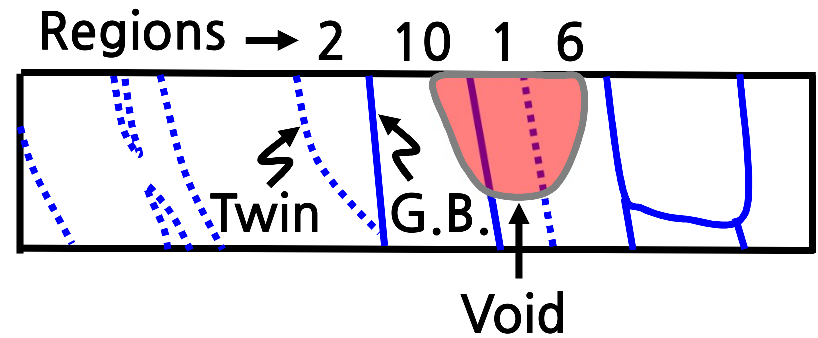


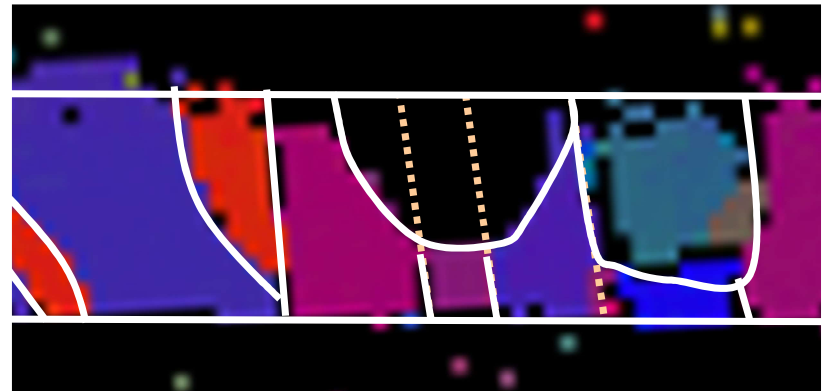




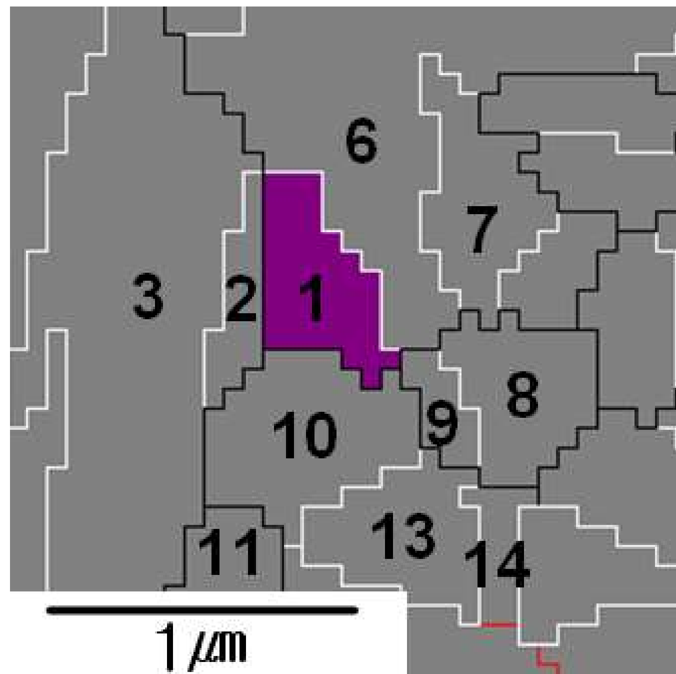
Cross-Sectional EBSD Measurements on a SIV

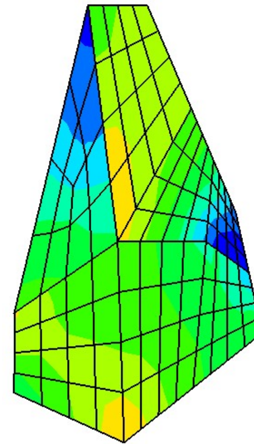


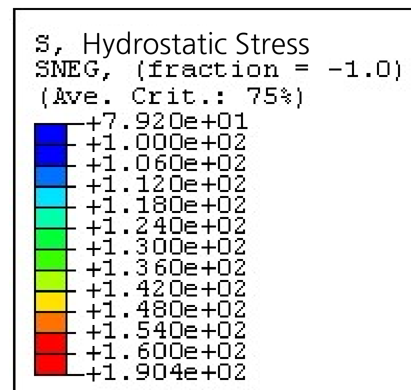


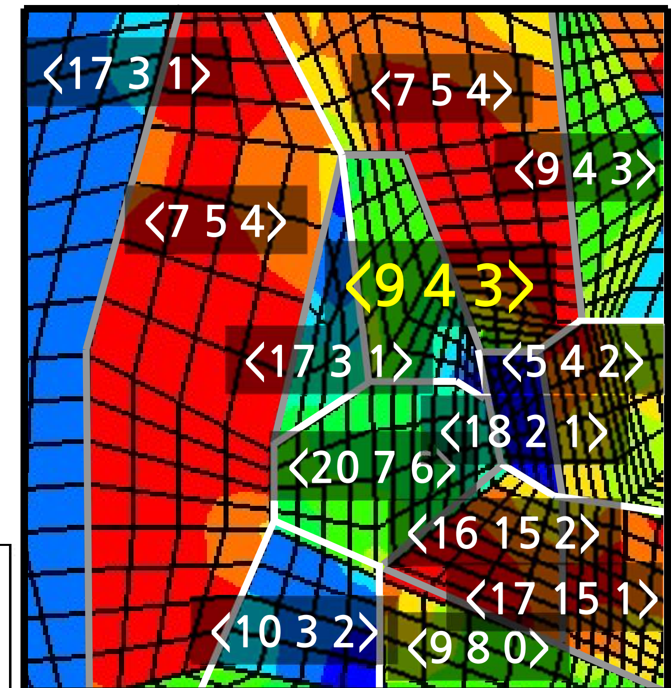


Thermal Stress Calculation Considering Crystal Orientation



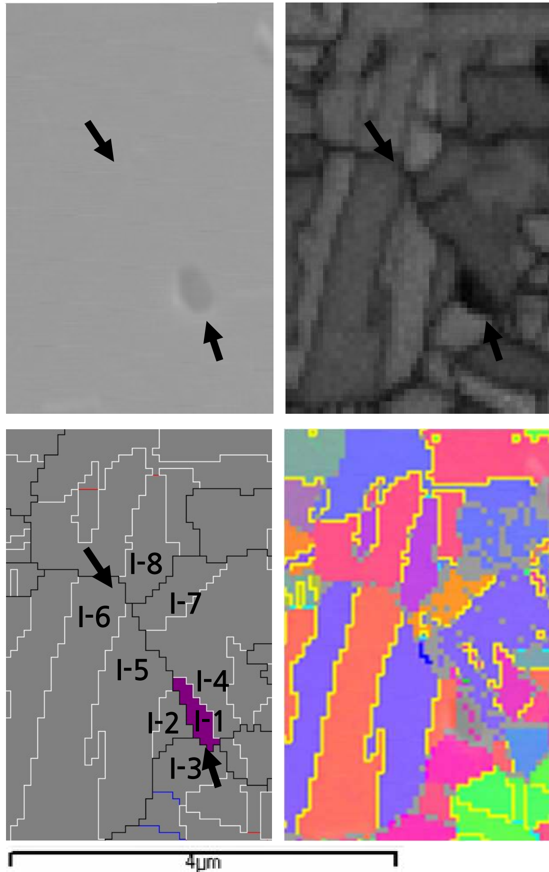




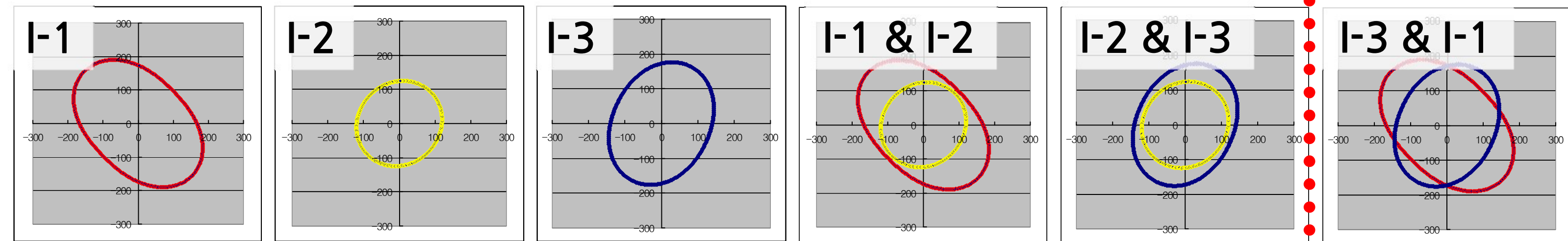


EBSD Measurement near TJs

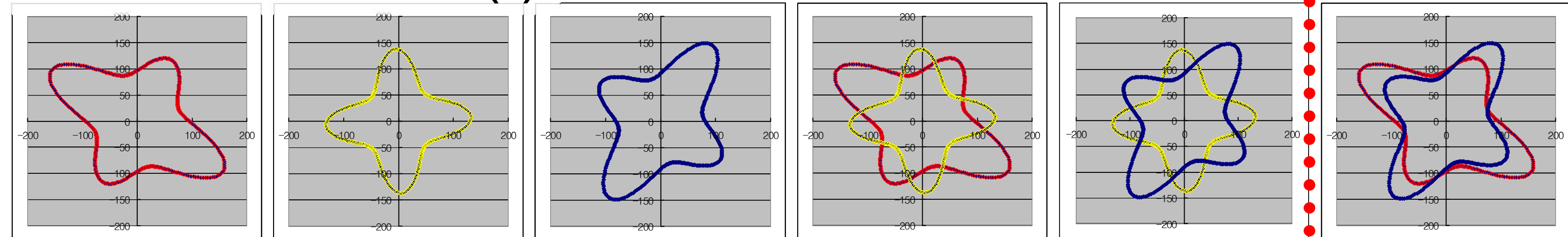
Case I



Equi-bi-axial Elastic Modulus (M_σ)



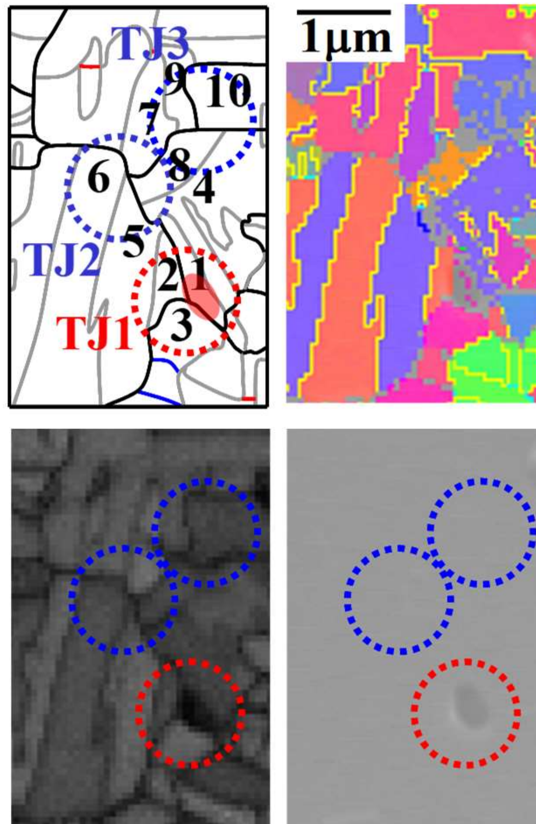
Uniaxial Elastic Modulus (E)



$$M_{av} = \frac{2}{\pi}\int_0^{\pi/2} M_\sigma \, d\theta$$

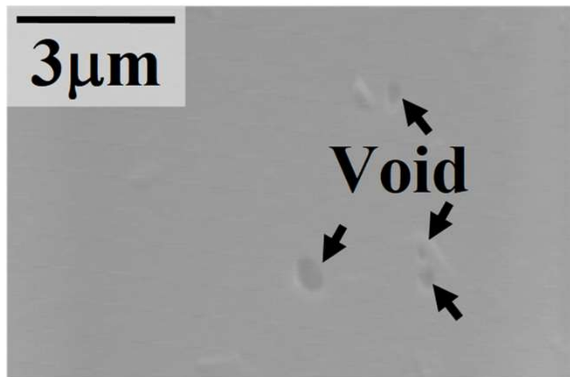
Voiding

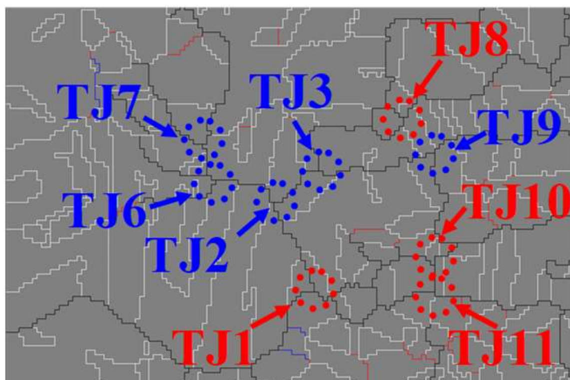
EBSD Measurement near TJs



Region	Index	**Bi-axial Modulus (M_σ)**	**Remark**
1	(9 4 3)	172	Void : TJ1 (1~4)
2	(17 3 1)	122	
3	(20 7 6)	155	
4	(7 5 4)	235	
5	(7 5 4)	235	Unvoid : TJ2 (5~8), TJ3 (8~10)
6	(17 3 1)	122	
7	(13 7 5)	192	
8	(3 1 0)	137	
9	(5 1 1)	130	
10	(7 6 5)	254	

EBSD Measurement near TJs





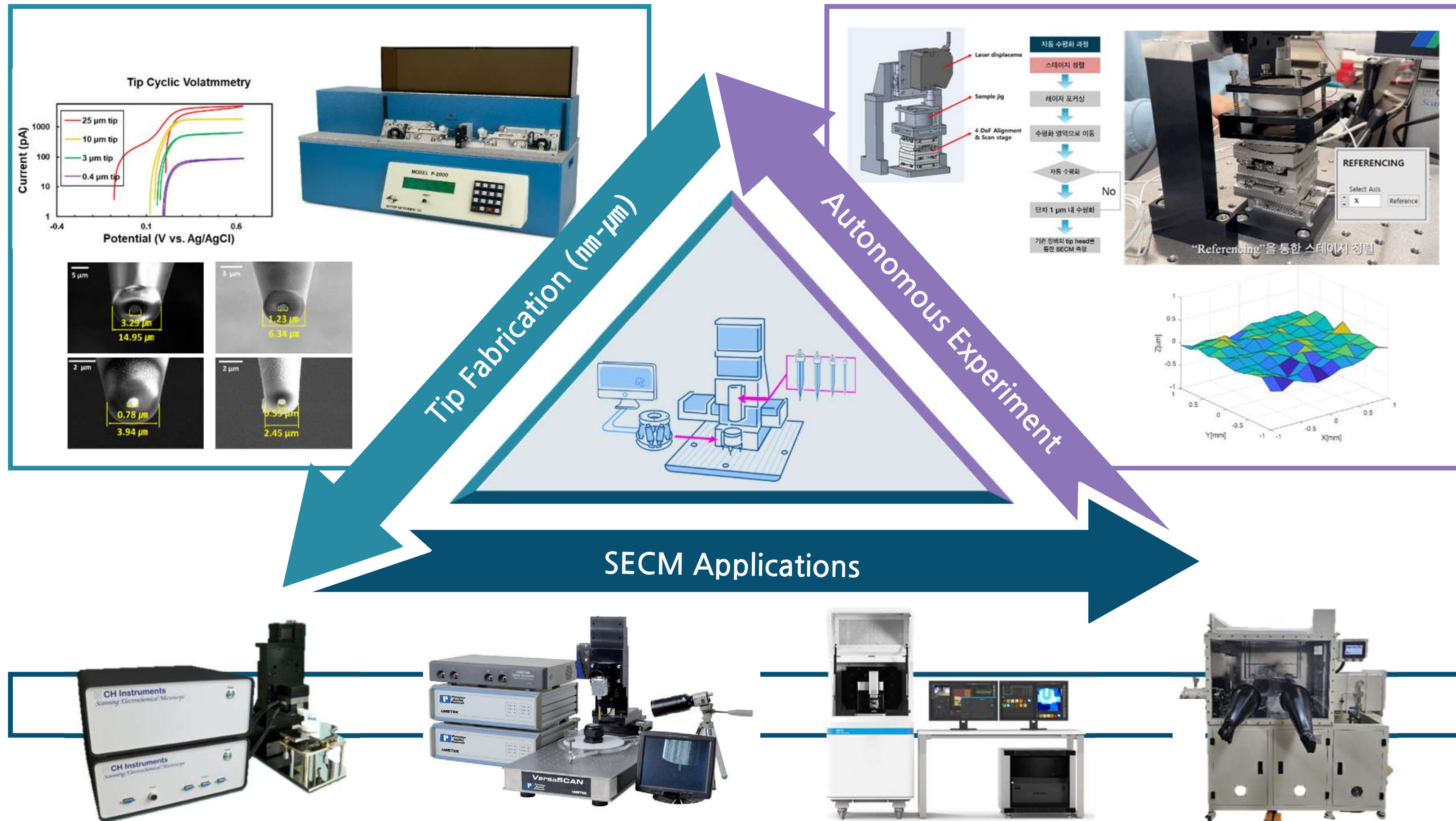
Triple Junction	Bi-axial Moduli	Remark
TJ6	206, 141, 130	Unvoid
TJ7	206, 141, 130	Unvoid
TJ8	168, 165, 143	Void
TJ9	172, 148, 117	Unvoid
TJ10	247, 215, 155	Void
TJ11	234, 228, 215	Void

Summary

- ✓ Through *in situ* investigation, a twin exhibits a tendency to nucleation and anisotropic growth behavior.
- ✓ If the front surface of grain growth is {111}, the anisotropic grain growth and alternatively stacked twins are well explained.
- ✓ Twin boundary is normal to the growth direction.
- ✓ SIV happens at the TJ where two grains with relatively high equibiaxial elastic modulus face each other.

Present Works

■ Scanning Electrochemical Microscopy



Thank You