The 21st Interfinish World Congress & Seminar

Synthesis and Performance Research of Copper Plating Additives used for PCB Microvia Filling

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Contents

#01 Background——Key Problem and Technology Roadmap

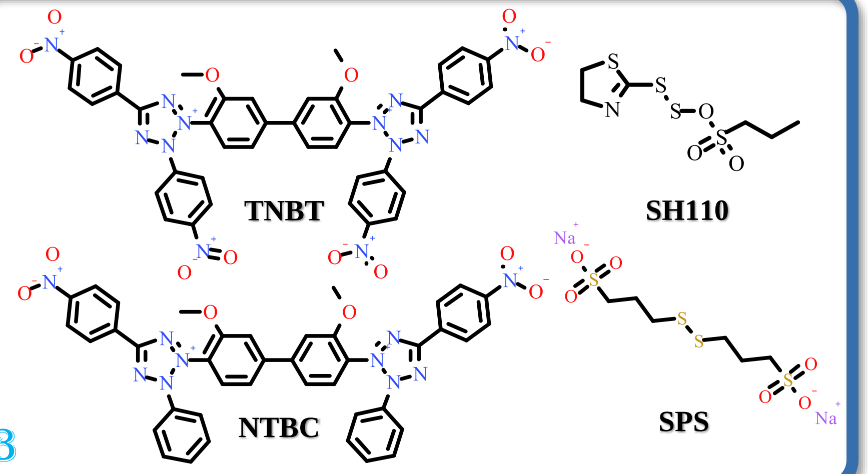
The key of microvia filling by copper electroplating

Few types of functional additives

Functional Additives

Unclear structure-activity relationship and filling mechanisms

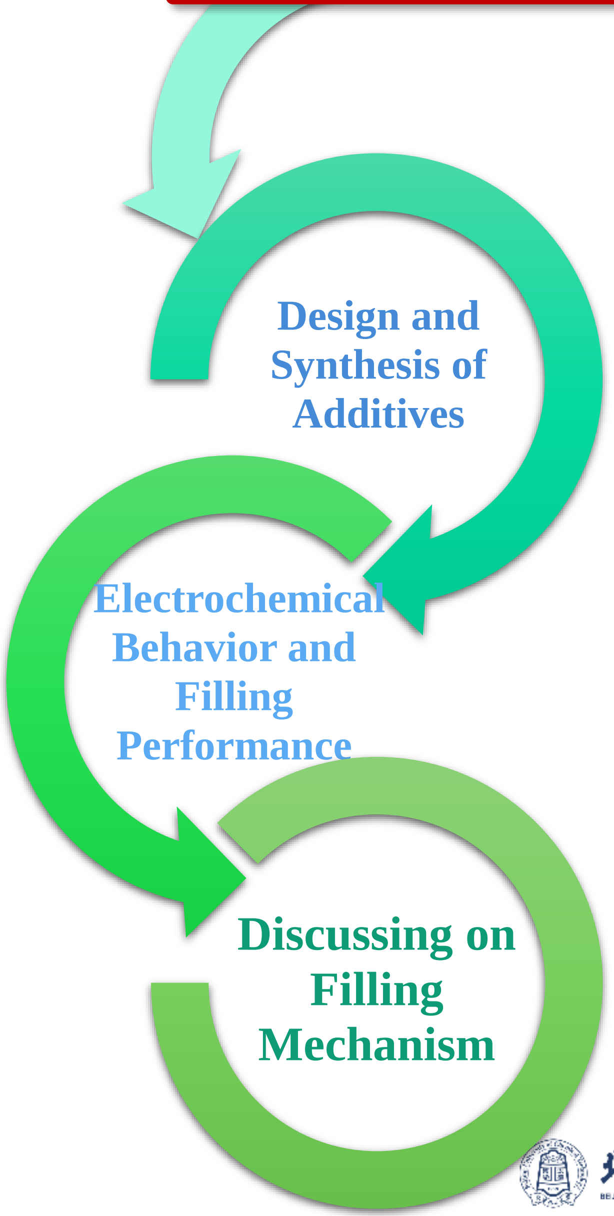
- Curvature Enhanced Adsorption Theory (CEAC)
- Convection-Dependent Adsorption Theory (CDA)
- Transient Diffusion and Surface Adsorption Theory (TDSA)



Currently, only a few levelers (e.g., TNBT, NTBC, SH110) are reported to be used in through-hole filling

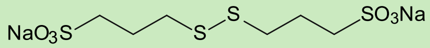
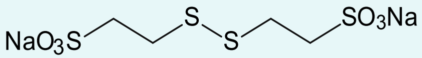
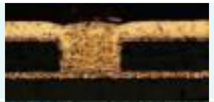
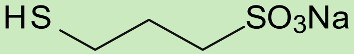
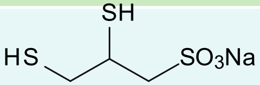
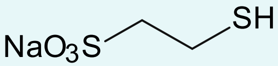
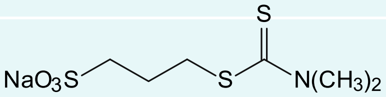
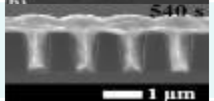
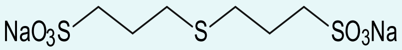
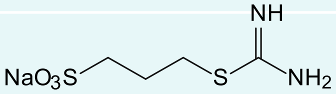
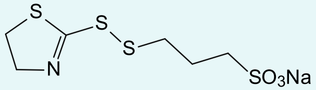
Only a few accelerators (e.g., SPS, MPS, DMPS) are utilized in microvia filling

Technical Roadmap



Contents

#02 Electrochemical behavior and filling performance of the accelerators — Literature review

Classification	Name	Molecular Structure	Microvia Filling Performance	References
Chain structure（containing -HS、-S、-S-S-、-SO_3Na）	SPS			Microvia Filling over Self-Assembly Disulfide Molecule on Au and Cu Seed Layers
	SES			Effects of Accelerator Alkyl Chain Length on the Microvia Filling Performance in Copper Superconformal Electroplating
	MPS			The Role of SPS, MPSA, and Chloride in Additive Systems for Copper Electrodeposition
	DMPS			Function of Sulfhydryl (–HS) Group During Microvia Filling by Copper Plating
	MES			Effects of Accelerator Alkyl Chain Length on the Microvia Filling Performance in Copper Superconformal Electroplating
	DPS			Superconformal Cu Electrodeposition Using DPS: A Substitutive Accelerator for Bis (3-sulfopropyl) Disulfide
	TBPS			Use of 3, 3-thiobis (1-propanesulfonate) to accelerate microvia filling by copper electroplating
	UPS			Effect of 3-S-isothiuronium propyl sulfonate on bottom-up filling in copper electroplating
Heterocycle structure	SH110			Special electrochemical behavior of sodium thiazolinyl-dithiopropane sulphonate during microvia filling

- **Types and quantities of the accelerators are relatively limited;**
- **Try to design some accelerator molecules with new structure and they can be easily synthesized and purified**

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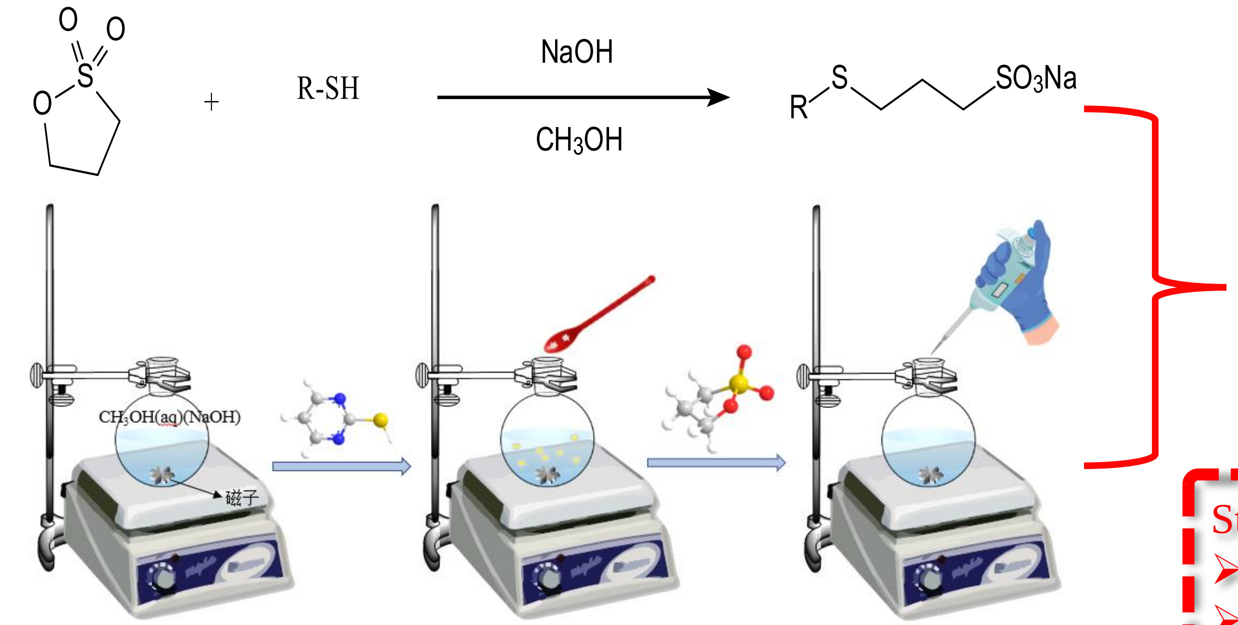
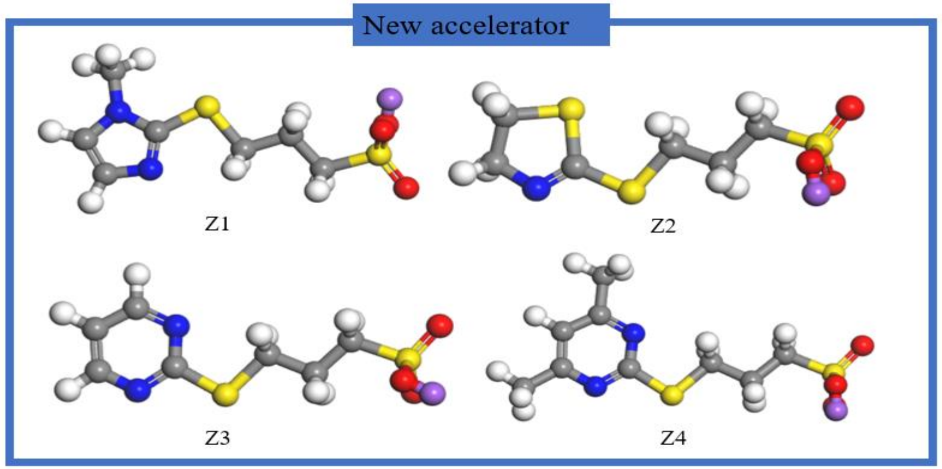
The design and synthesis of accelerator molecules





Structural characteristics of the novel accelerator molecules:

- Adsorptive functional group: nitrogen-containing heterocycle;
- Accelerating functional group: $-SO_3Na$.

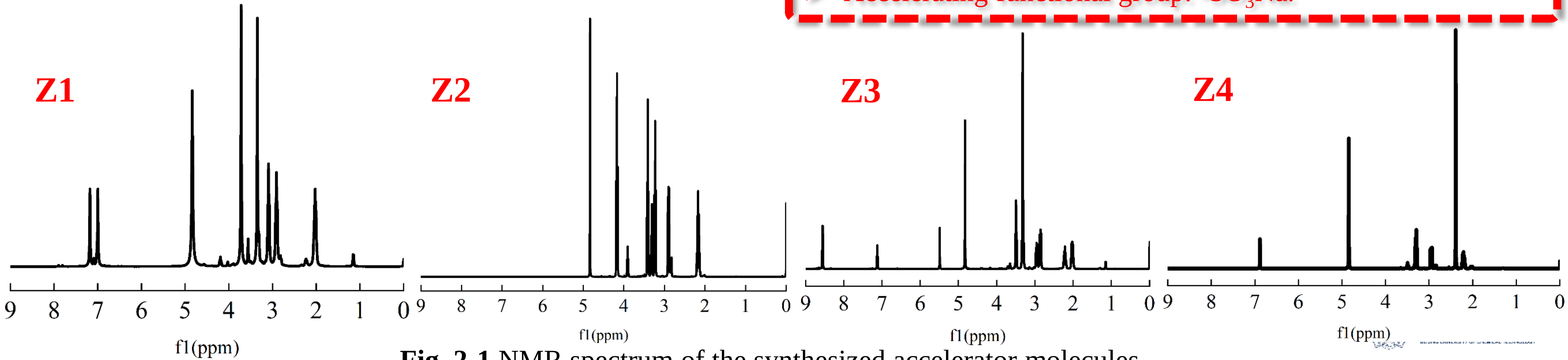


Fig. 2-1 NMR spectrum of the synthesized accelerator molecules

#02 Electrochemical behavior and via-filling performance of the accelerator — Electrochemical testing

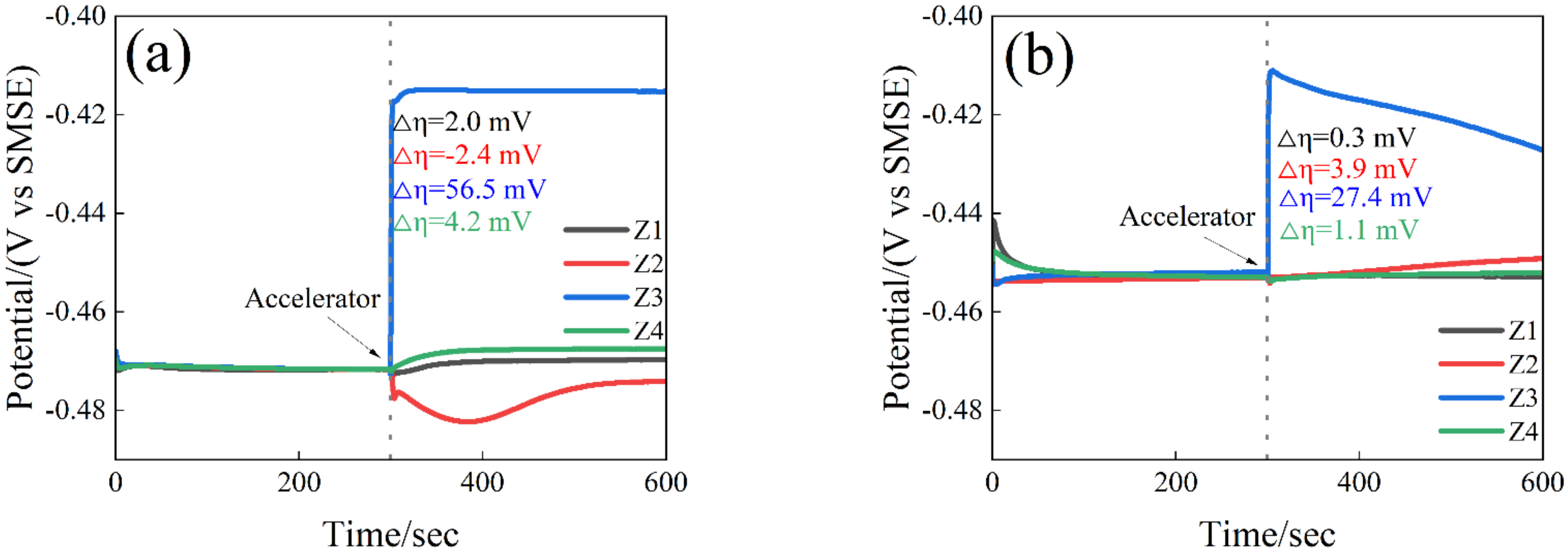
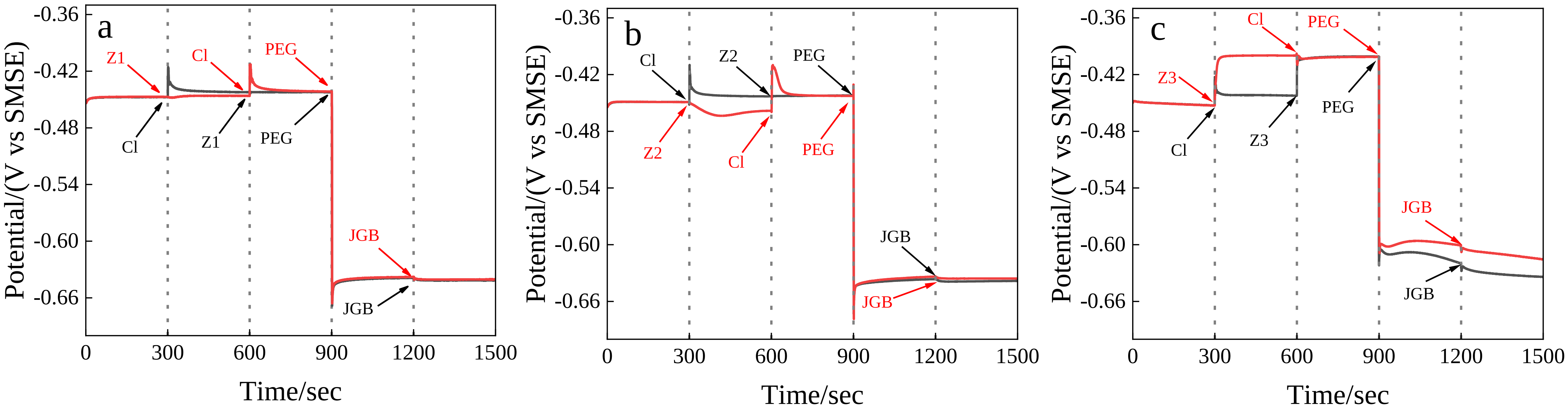


Fig. 2-2 E-t curves obtained in different plating solution: (a) without chloride ions (0 mg/L Cl^-); (b) with chloride ions (50 mg/L Cl^-)
(The base plating solution containing 220 g/L $CuSO_4 \cdot 5H_2O$ and 54 g/L H_2SO_4)

- In the absence of chloride ions, **Z1, Z3, and Z4 exhibit depolarization effect** on copper deposition except for Z2. Among them, **Z3 shows the strongest depolarization effect**.
- In the presence of chloride ions, **Z1, Z2, Z3, and Z4 all exhibit depolarization effect** on copper deposition, among which **Z3 still shows the strongest depolarization effect**.



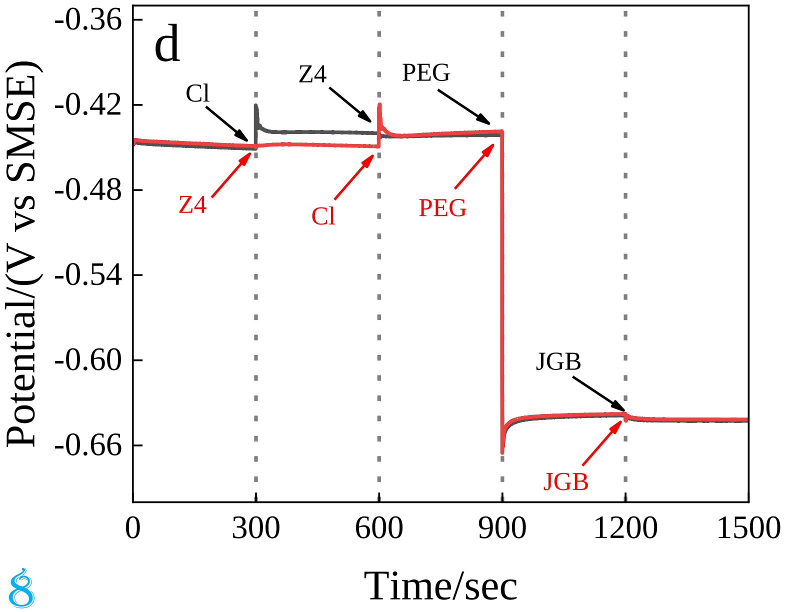


Fig. 2-3 E-t curves measured with different additive addition sequences (a) Z1; (b) Z2; (c) Z3; (d) Z4; (The base plating solution contains 220 g/L $CuSO_4 \cdot 5H_2O$ and 54 g/L H_2SO_4)

- ➢ **Competitive adsorption between the accelerators and chloride ions**;
- ➢ Adsorption strength of Z1 and Z2 are weaker than that of chloride ions;
- ➢ **Negative synergistic effect between Z3, Z4, and chloride ions**;
- ➢ **Z3** and chloride ions exhibit the **strongest depolarization effect**.

#02 Electrochemical behavior and via-filling performance of the accelerator —Molecular dynamic simulation

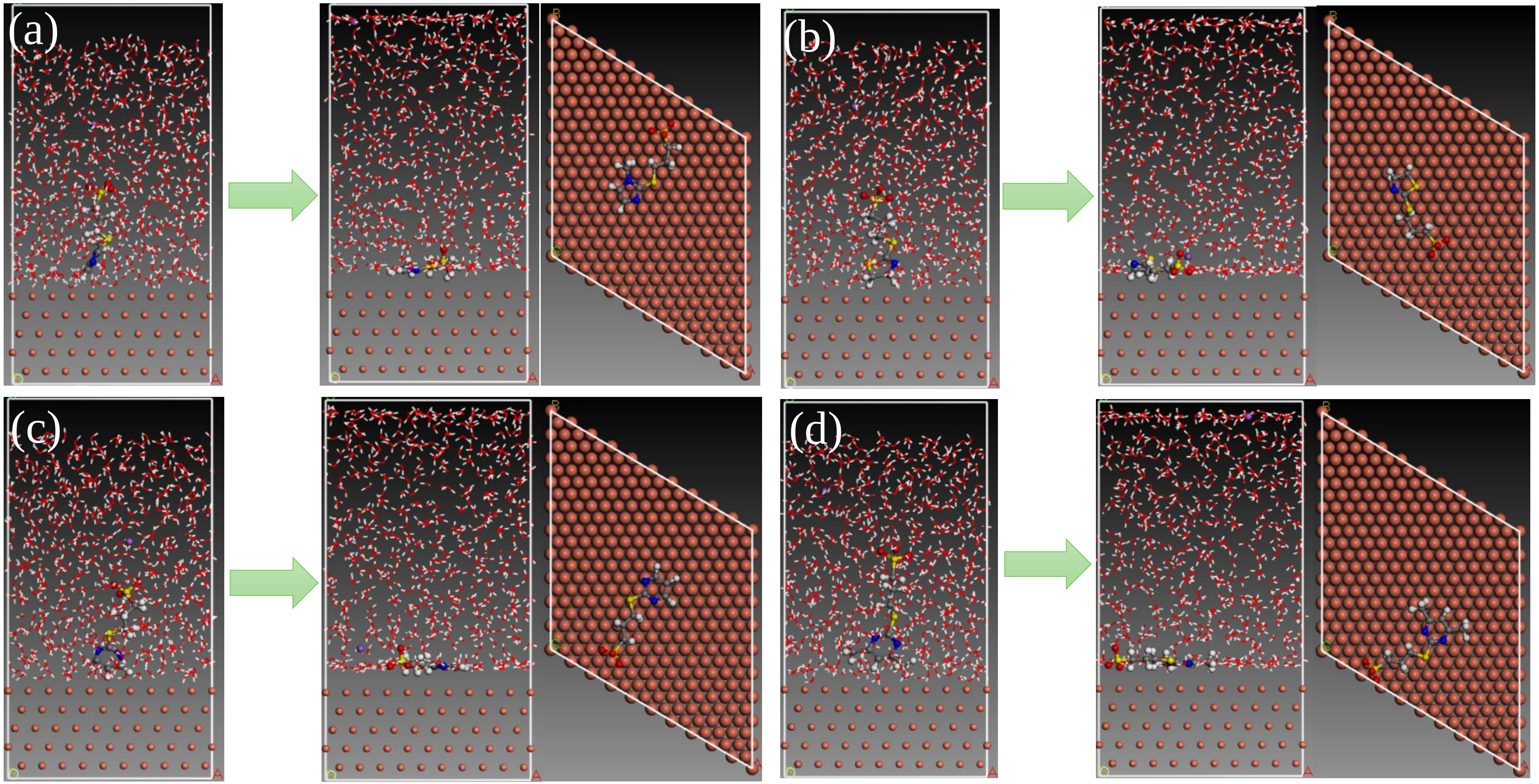
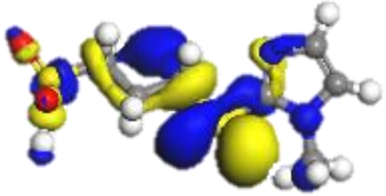
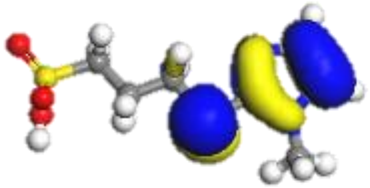
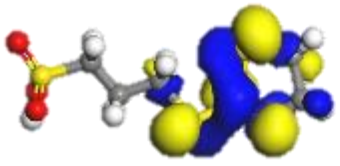
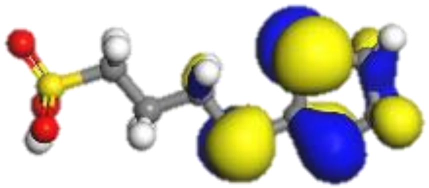
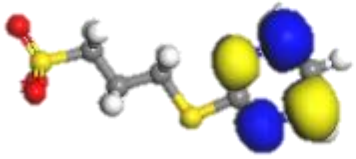
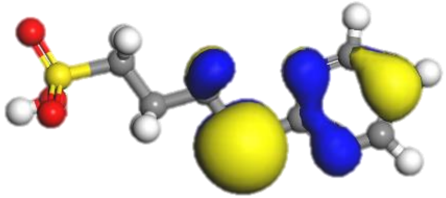
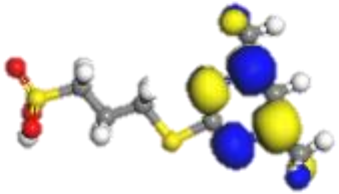
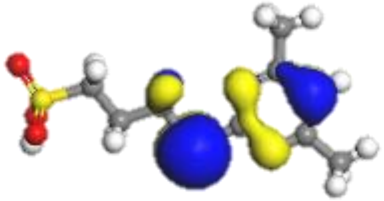


Fig. 2-4 The initial and final states of the four molecules before and after molecular dynamic simulation: (a) Z1; (b) Z2; (c) Z3; (d) Z4

#02 Electrochemical behavior and via-filling performance of the accelerator — Quantitative calculation

Table 2-1 The Quantitative calculation results of the four levelers

Additives	LUMO	HOMO	E_{HOMO}(eV)	E_{LUMO}(eV)	ΔE (eV)
Z1			-0.184249	-0.033688	0.150561
Z2			-0.203882	-0.05135	0.152532
Z3			-0.210856	-0.089145	0.121711
Z4			-0.205085	-0.079183	0.125902

- **$\Delta E = E_{LUMO} - E_{HOMO}$,** A smaller ΔE value indicates a stronger adsorption strength of the molecule on the metal surface.
- **Adsorption strength: Z3＞Z4＞Z1＞Z2**

#02 Electrochemical behavior and via-filling performance of the accelerator — Pre-adsorption and desorption experiments

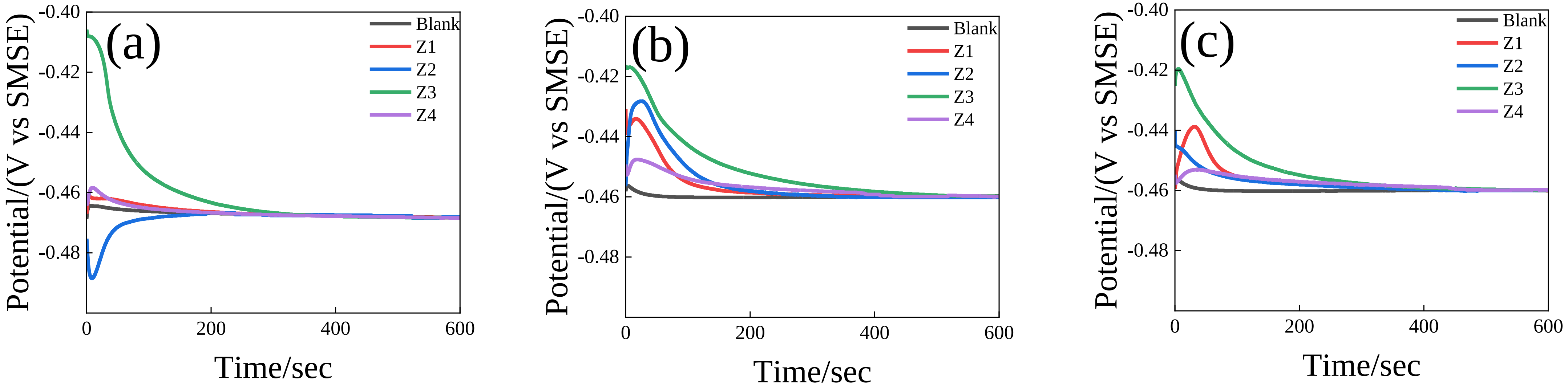


Fig. 2-5 Pre-adsorption and desorption experiments: (a) both testing solution and pre-adsorption solution containing no Cl^-; (b) only testing solution containing Cl^-; (c) both testing solution and pre-adsorption solution containing Cl^-

Table 2-2 The desorption time of the levelers in different solutions

Leveler desorption time	Z1	Z2	Z3	Z4
(a)	210 s	181 s	348 s	249 s
(b)	423 s	339 s	470 s	430 s
(c)	486 s	430 s	537 s	493 s

- **Adsorption strength of the accelerator can be enhanced by Cl^-**

Base plating solution： 220 g/L $CuSO_4 \cdot 5H_2O$、54 g/L H_2SO_4、50 mg/L Cl^-

Additive： **X mg/L Z1 or Z2**、100 mg/L PEG8000

Plating conditions： 0.5 L/min、1.5 A/dm^2、90 min

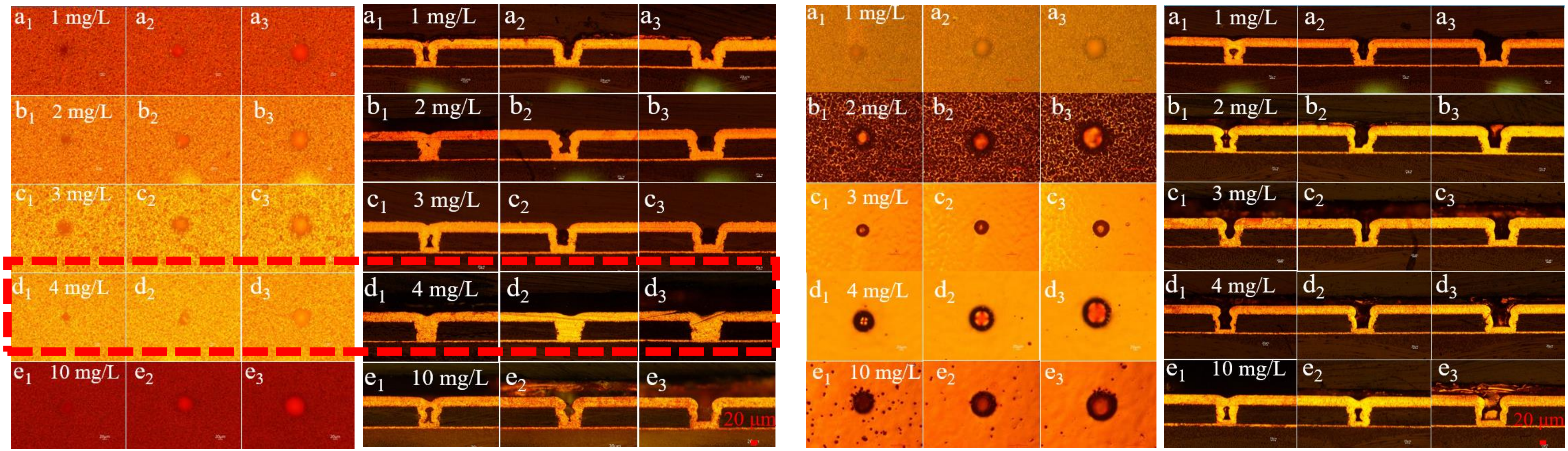


Fig. 2-6 Surface morphology and filling performance of the microvia obtained in the plating solution containing different concentration of accelerator Z1 (Left) or Z2 (Right)

Base plating solution: 220 g/L $CuSO_4 \cdot 5H_2O$、54 g/L H_2SO_4、50 mg/L Cl^-

Additive： **X mg/L Z3 or Z4**、100 mg/L PEG8000

Plating conditions: 0.5 L/min、1.5 A/dm^2、90 min

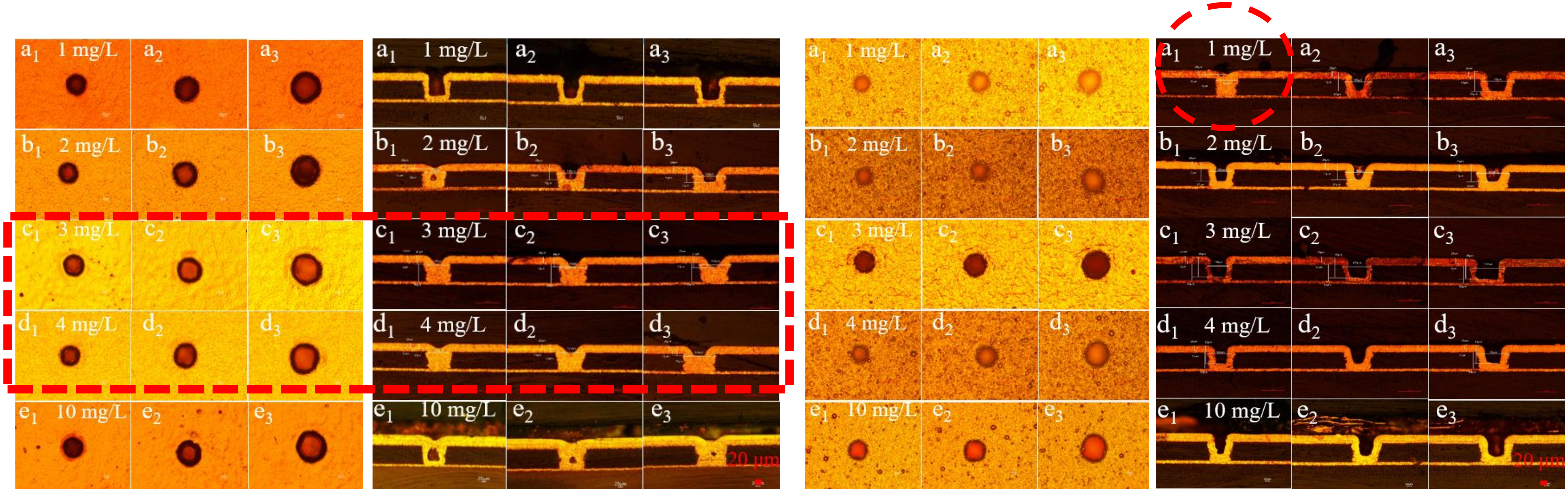


Fig. 2-7 Surface morphology and filling performance of the microvia obtained in the plating solution containing different concentration of accelerator Z3 (Left) or Z4 (Right)

➢ Microvia filling performance regulated by suppressor of PEG8000

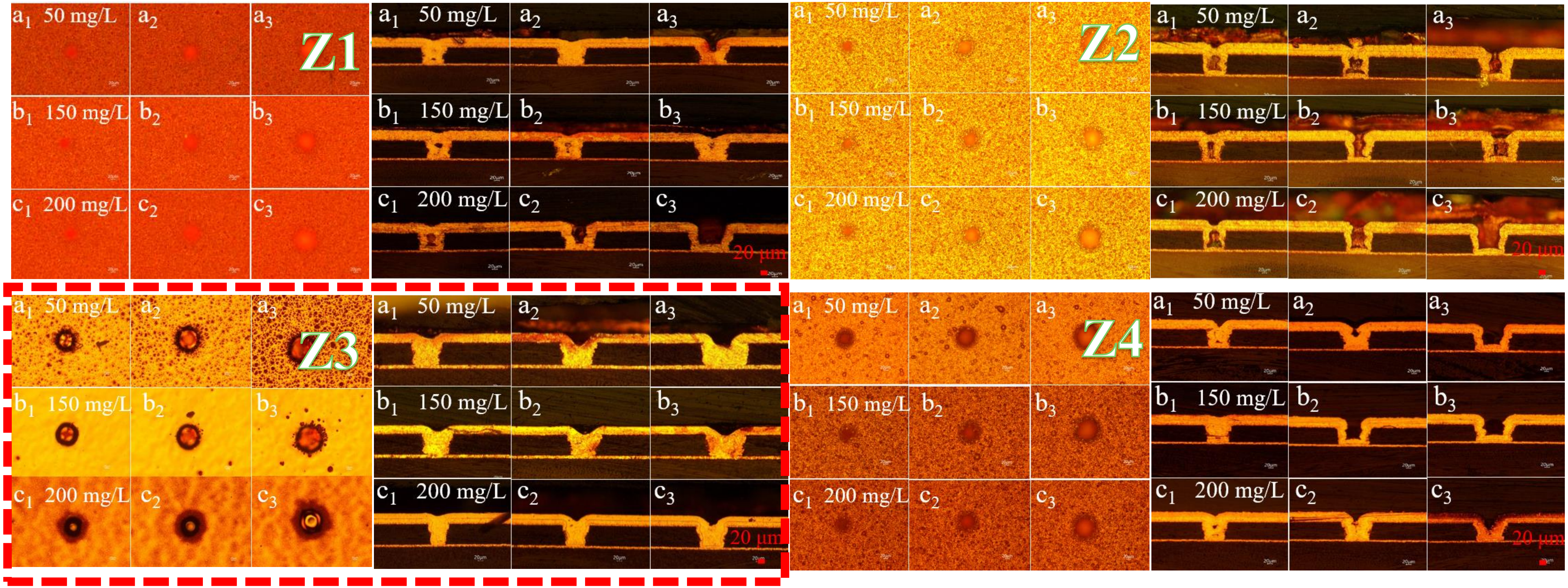


Fig. 2-8 Surface morphology and filling performance of the microvia obtained in the plating solution containing different concentration of PEG8000

➢ Z3: Good filling performance by using 50 mg/L ~ 200mg/L PEG8000

- Microvia filling performance regulated by leveler of JGB

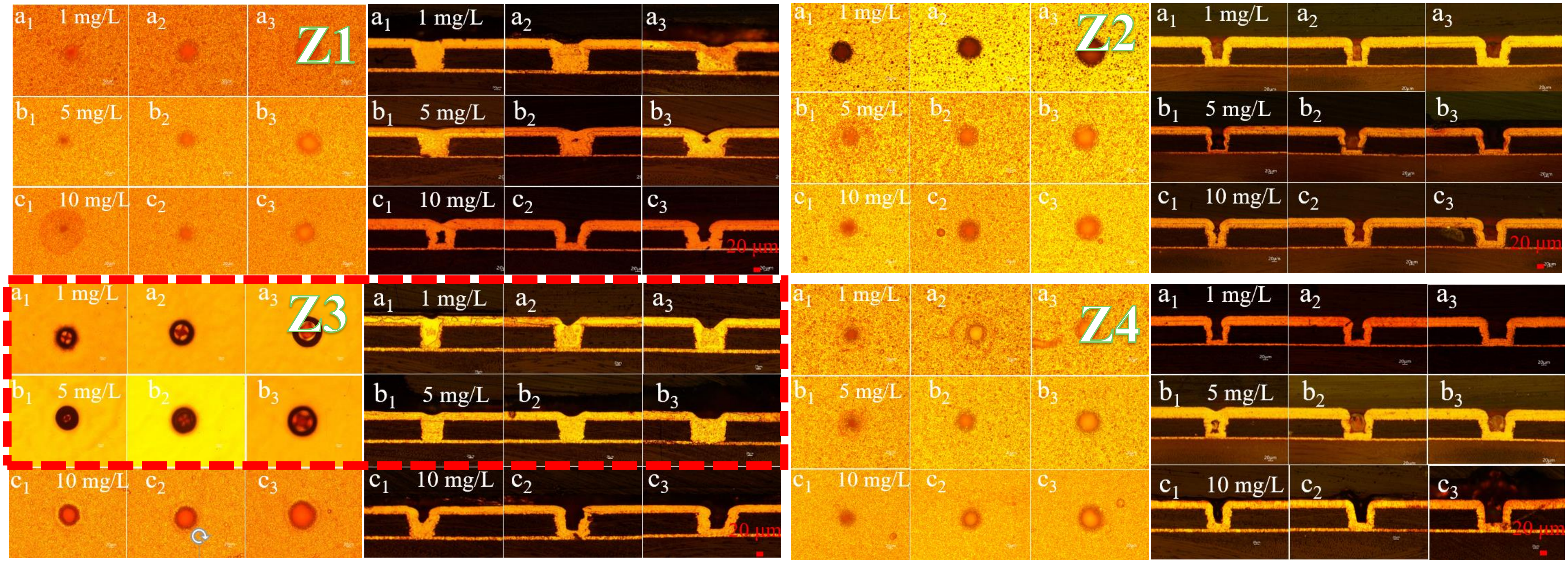


Fig. 2-9 Surface morphology and filling performance of the microvia obtained in the plating solution containing different concentration of JGB

- **Z3: Good filling performance by using 1 mg/L ~ 5mg/L JGB**

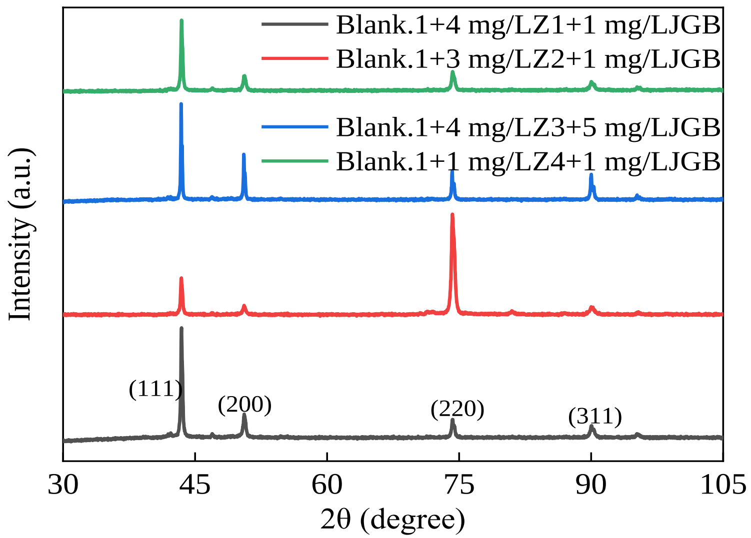
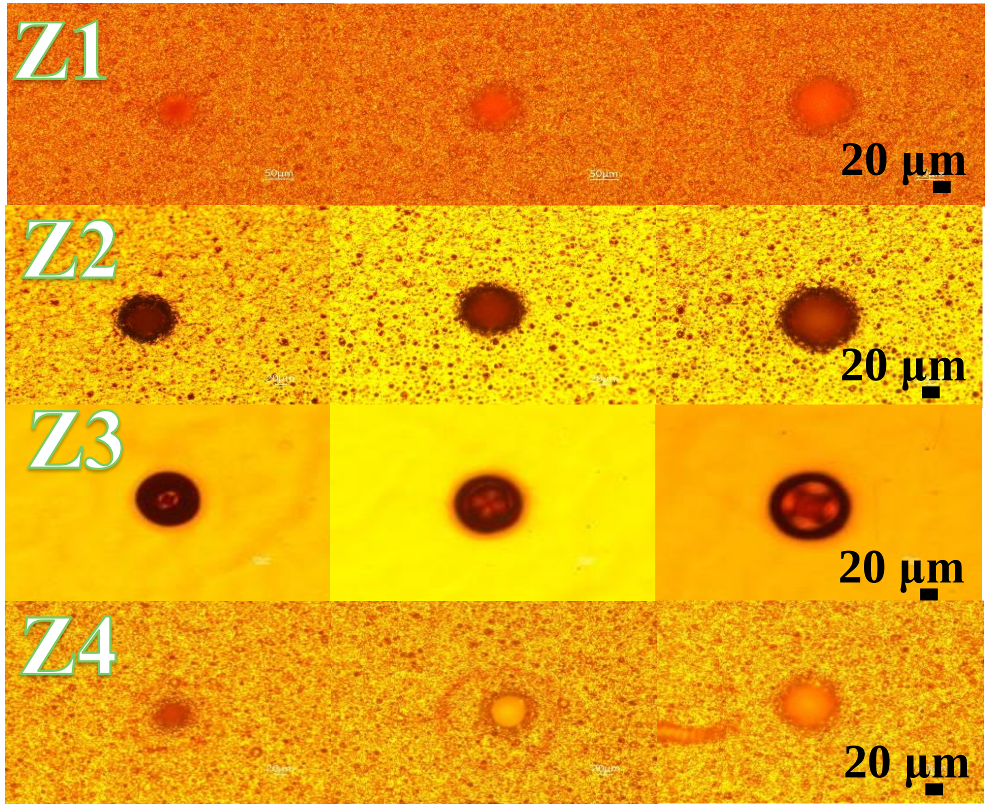


Fig. 2-10 X-ray diffraction spectrum of the copper layer obtained in different plating solution

Table 2-3 Grain size effected by the accelerator

Plating solution with different accelerators	Average grain size (nm)
Z1	33
Z2	38
Z3	30
Z4	31



- The copper layer obtained with Z2 is dominated by (220) crystal orientation, while the other copper layer are **all dominated by (111)** crystal orientation;
- The deposited copper layer by using **Z3** as the accelerator has the **smallest grain size and the smoothest surface**.

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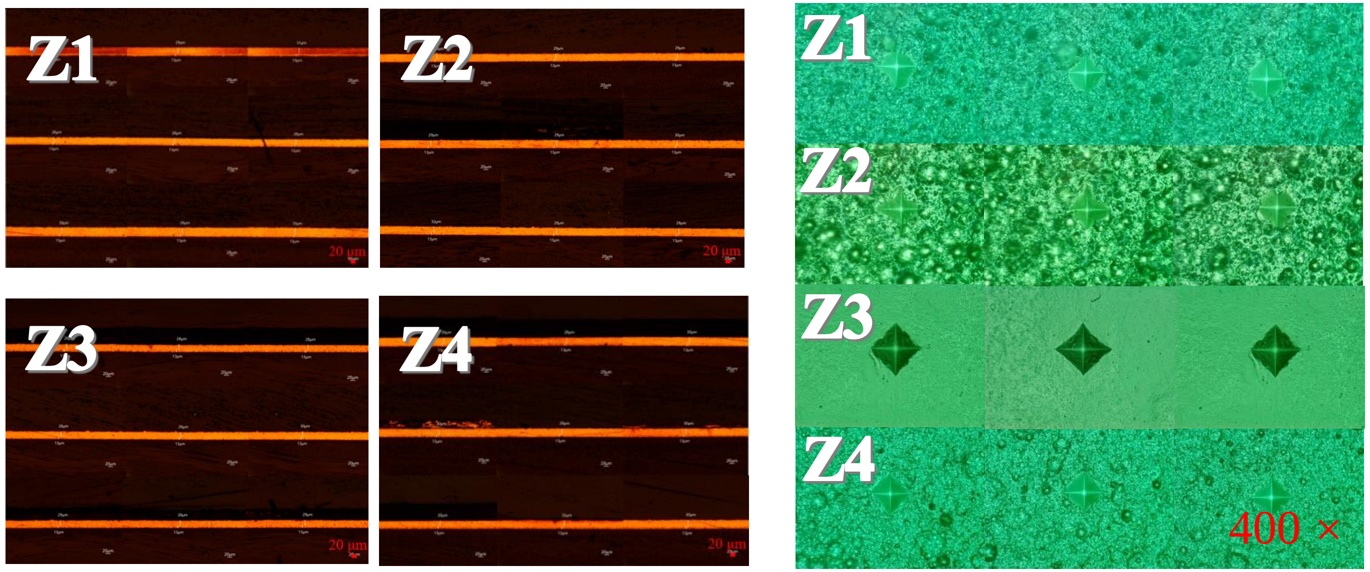

Fig. 2-11 Testing results of the uniformity and hardness of the deposited copper

Table 2-4 Hardness of the deposited copper layer

加速剂分子种类	平均硬度/HV	平均镀铜层厚度/μm
Z1	144.8	30
Z2	117.5	32
Z3	**185.5**	**28**
Z4	163.7	29

Table 2-5 Tensile strength and elongation of the deposited copper layer

	Z1	Z2	Z3	Z4
拉伸强度(MPa)	523.4	417.5	662.8	550.6
	509.8	408.8	658.5	557.2
	522.2	403.9	653.6	549.6
延伸率(%)	6.4	5.1	4.7	5.6
	6.6	5.3	4.9	5.8
	6.5	5.4	4.8	5.9
平均拉伸强度(MPa)	**518.5**	**410.1**	**658.3**	**552.5**
平均延伸率(%)	6.5	5.3	4.8	5.8

- Thickness range of the deposited copper layer < 2μm
- Hardness: Z3>Z4>Z1>Z2
- Tensile strength: Z3>Z4>Z1>Z2

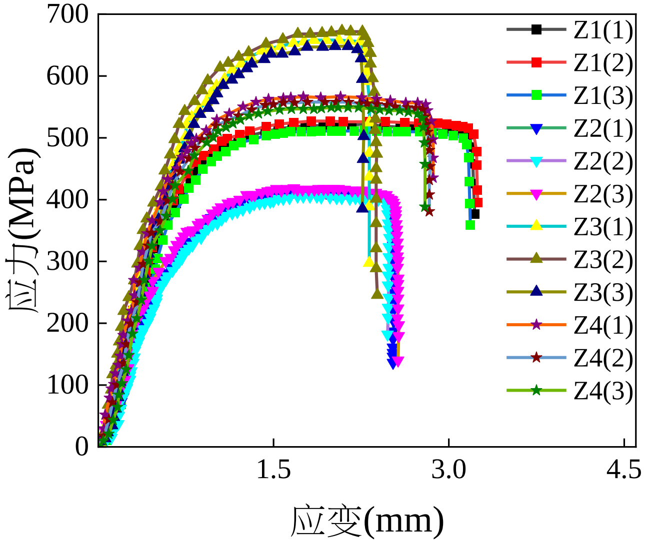

Fig. 2-12 Testing results of the ductility of the deposited copper

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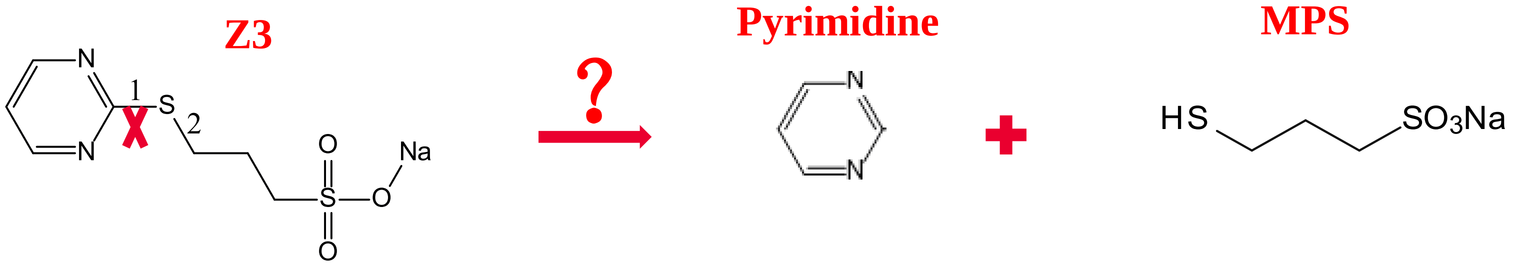


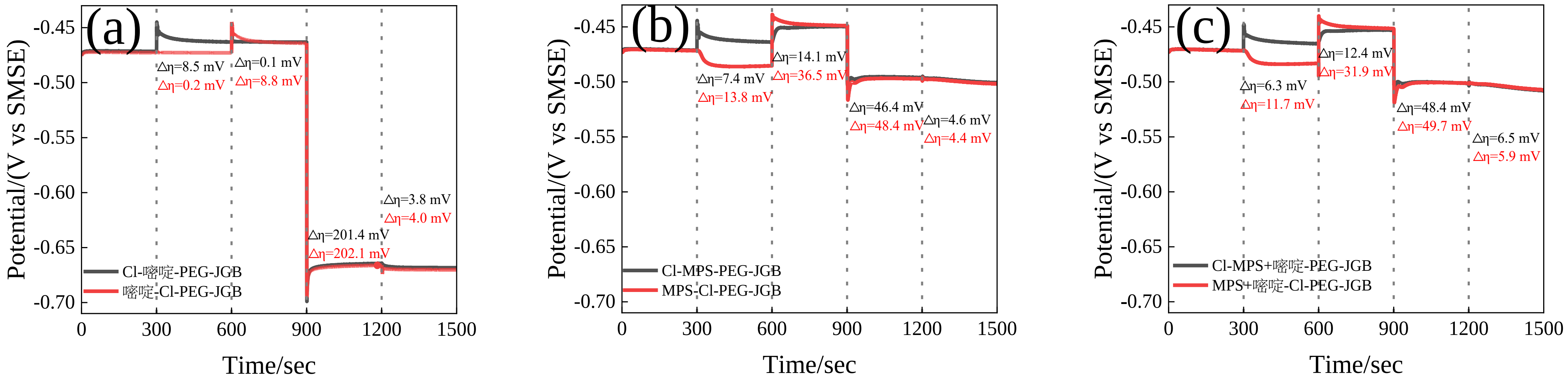


Fig. 2-13 E-t curves obtained in the plating solution with different additive addition sequences

- **Pyrimidine has almost no effect on the copper deposition;**
- **MPS and Cl^- can synergistically accelerate the copper deposition process;**
- Z3 is not a simple mixture of MPS and pyrimidine;
- Z3 is a completely **new accelerator with a new molecule structure.**

Contents

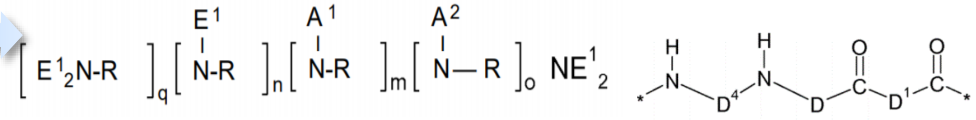
Table 3-1 Patent research summary of copper electroplating levelers

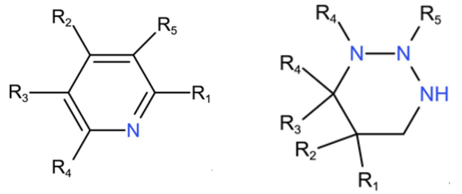
Domestic Patent Number	Global Patent Number	Year of Publication
1. MacDermid Enthone		
CN1918327B		2004
CN101855714	US7670950B2	2008
CN101715495B	US7887693B2	2008
CN102362013A	US8388824B2	2009
2. Atotech		
CN1908240B	US7374652B2	2006
CN103703167B	EP2537962A1	2012
CN105683421B	EP2865787A1	2014
CN107922611A	EP3135709B1	2016
CN107923060B	EP3344800B1	2016
CN109790638A	EP3497267B1	2017
3. Rohm and Haas		
CN102492133A	US8012334B2	2008
CN102276796B	US8268157B2	2011
CN102304218A	US8262895B2	2011
CN102534702B	US9365943B2	2011
CN102953097B	US8747643B2	2012
CN103103584B	US8454815B2	2012
CN103451691B	JP5952093B2	2013
CN105705491A	WO2015074190A1	2013
CN104726902B	US9403762B2	2014
CN104694981B	US9783903B2	2015
CN105418891B	US9439294B2	2015
4. Okuno Chemical		
CN100595343C	JP4973829B2	2005
CN102021616B	JP5637671B2	2010
CN107079591B	US10294574B2	2015
CN109952390A	US20190390356A1	2017
5. BASF		
CN102257035B	EP2199315B1	2009
CN102639639B	US9598540B2	2010
CN102803389B	EP2547731B1	2011
CN102939339B	US9683302B2	2011
CN103547631B	US9631292B2	2012
TW1527937B		2016
6. JCU		
CN111235555A	JP5385625B2	2009
CN102906078B	WO2011135716A1	2010
CN111108235A	WO2020044432A1	2018

Summarize

Novel Leveler Classifications from Manufacturers:

1. Linear/Cyclic Amino Compounds and Their Derivatives
2. Polymerization Products of N-heterocycles and Epoxy Compounds
3. Polymerization Products of Halides and N-heterocycles

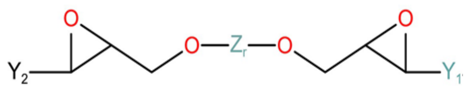


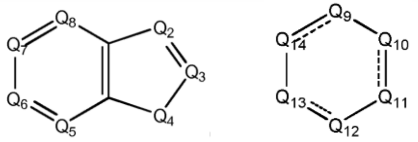


Inspiring

Table 3-2 Screening classification of levelers

No.	Category	Quantity	Description
1	FL Series	2	Conventional Levelers
2	ZL Series	5	Novel Levelers from Patents
3	BL Series	11	Commercial Reagents
4	**SL Series**	**30**	**Self-designed and Synthesized Levelers**





#03 Electrochemical behavior and filling performance of the levelers (through-hole)

— Electrochemical behavior of SL-0021

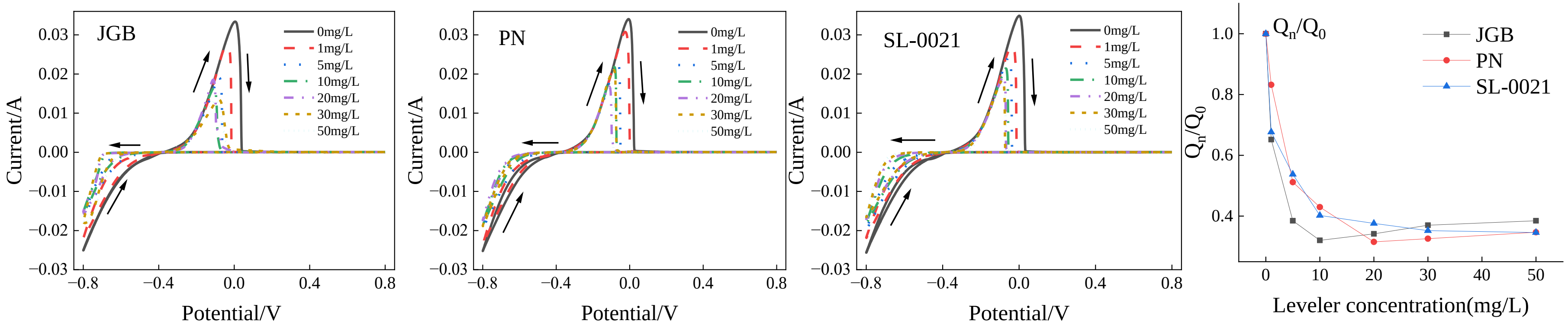
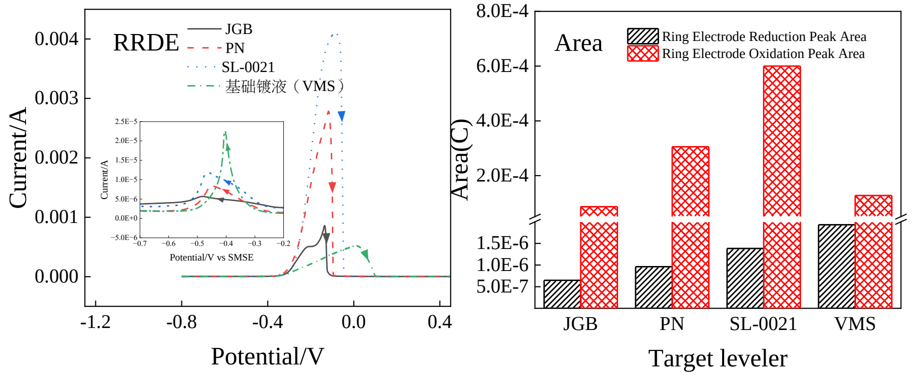


Fig. 3-1 Cyclic voltammograms obtained in the plating solution with different levelers

1. Inhibition strength: JGB > PN、SL-0021；
2. RRDE testing results demonstrated that levelers effectively inhibit copper deposition process by suppressing RDS；
3. EIS results revealed that L64-Cl^--SL-0021 inhibition layer showed relatively weak inhibition strength and was more susceptible to destroyed at low potentials.



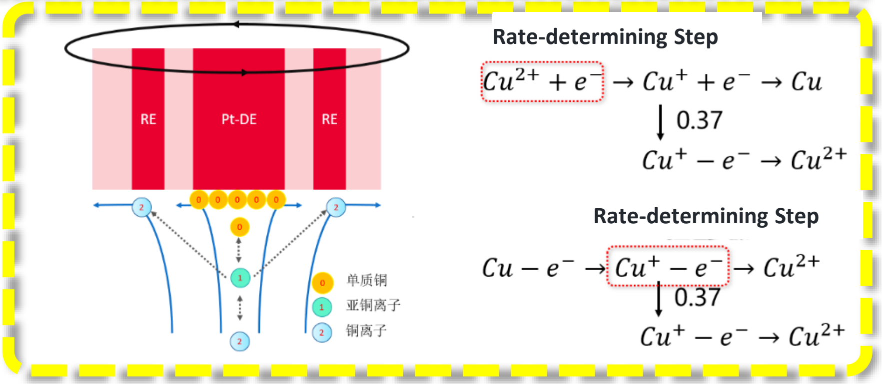
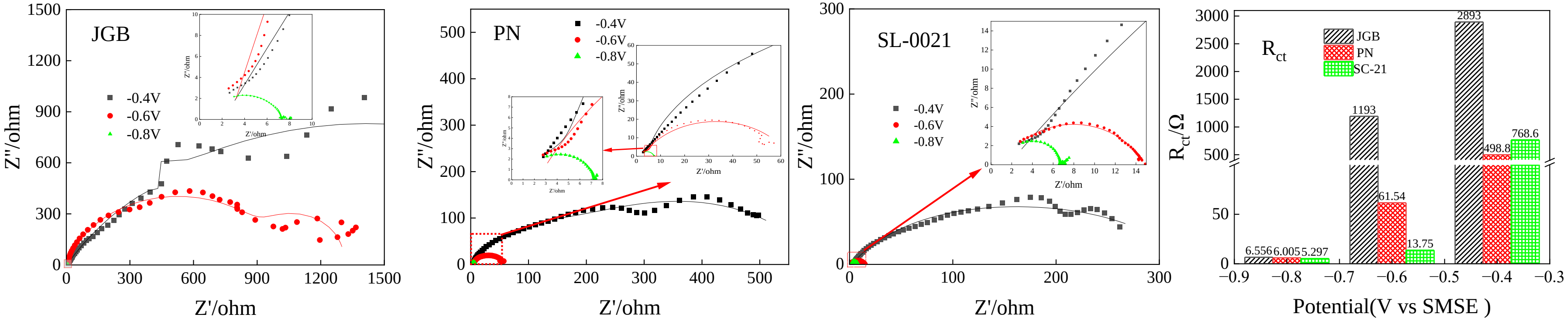


Fig. 3-2 RRDE testing results



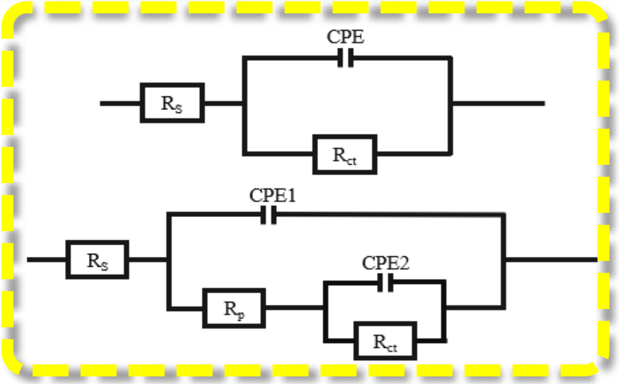


Fig. 3-3 Nyquist plots of copper plating solution with different levelers

— Filling performance of SL-0021

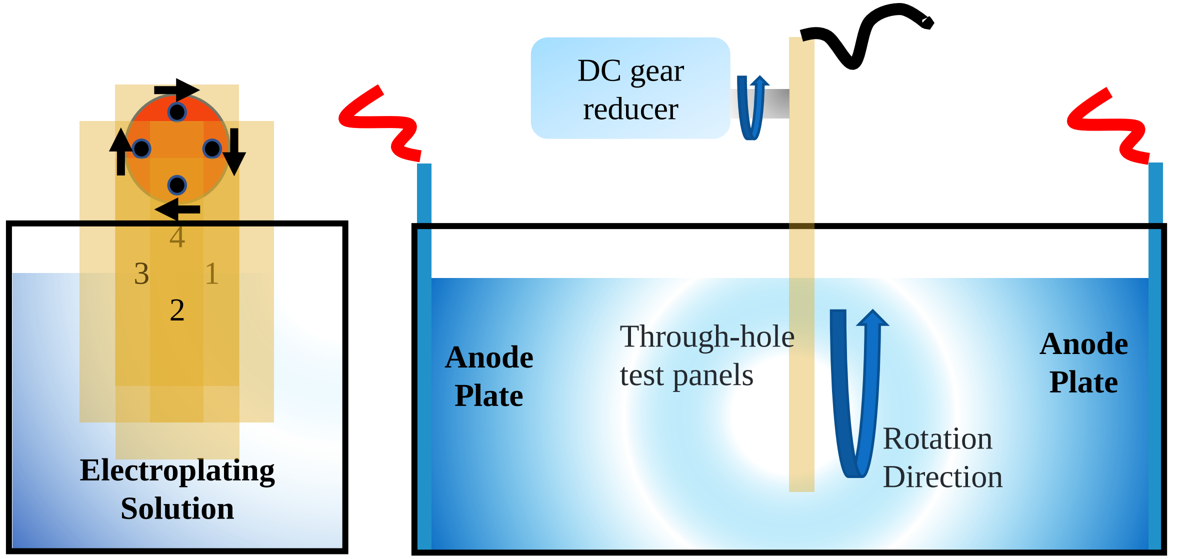


Fig. 3-4 Schematic diagram of the Haring cell electroplating experimental setup

Table 3-2 Composition of the electroplating solution

	JGB	PN	SL-0021
$CuSO_4\cdot5H_2O$(g/L)	250	250	250
H_2SO_4(g/L)	50	50	50
Cl^-(mg/L)	60	60	60
SPS(mg/L)	6	6	6
L64(mg/L)	100	100	100
Leveler(mg/L)	5~50	5~50	5~50
Cathode Rotation Speed (r/min)	15	15	15

Step current：0.25 A/dm²(210 min)→3.0 A/dm²(30 min)

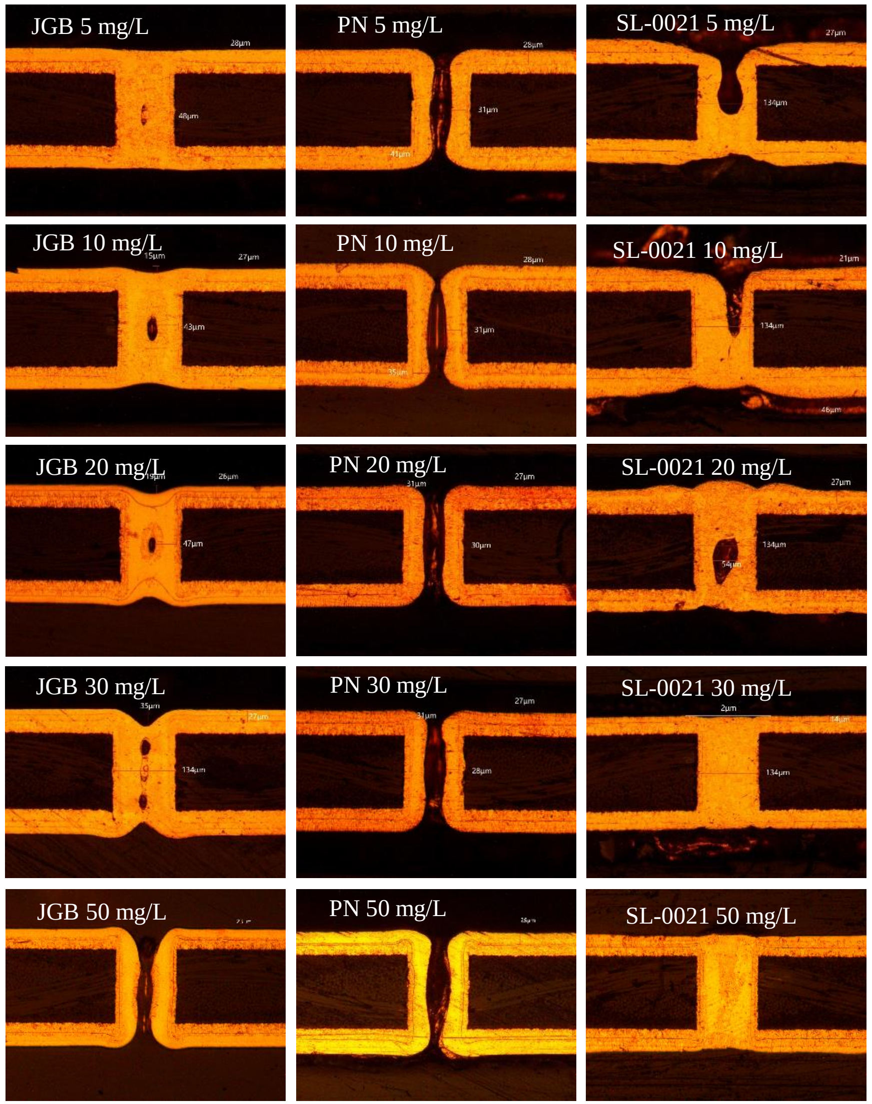


Fig. 3-5 Cross-sectional images of the through-holes after electroplating

#03 Electrochemical behavior and filling performance of the levelers (through hole)

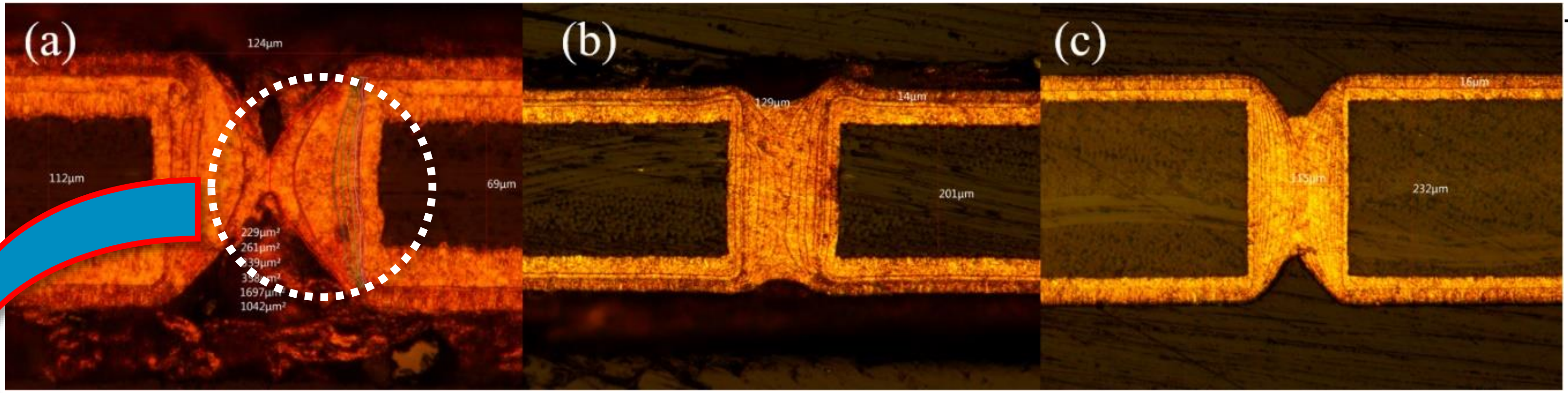


Fig. 3-6 Metallographic cross-sectional images showing the development trends of through-hole filling at different aspect ratios (a) 1.2:1 (b) 2:1 (c)2.4:1

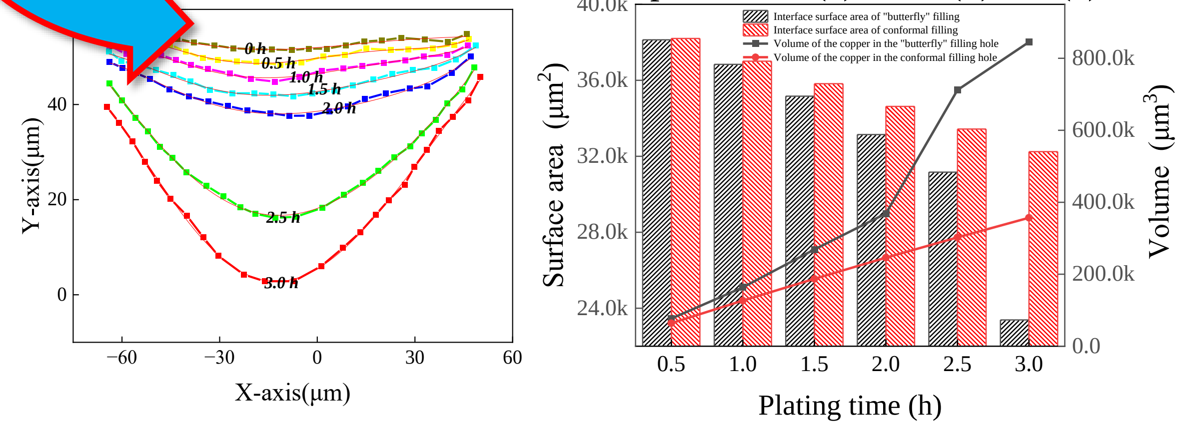


Fig. 3-7 Volume and surface area of the copper deposition layer (a) Fitted curve (b) Changes in the volume and surface area

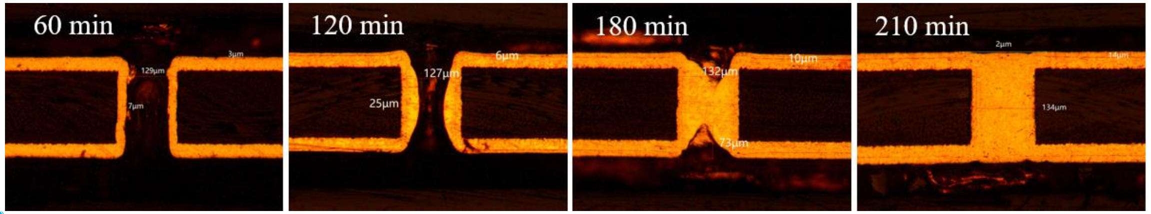


Fig. 3-8 Progressive development process of copper plating filling in through-holes

—Through-hole filling model

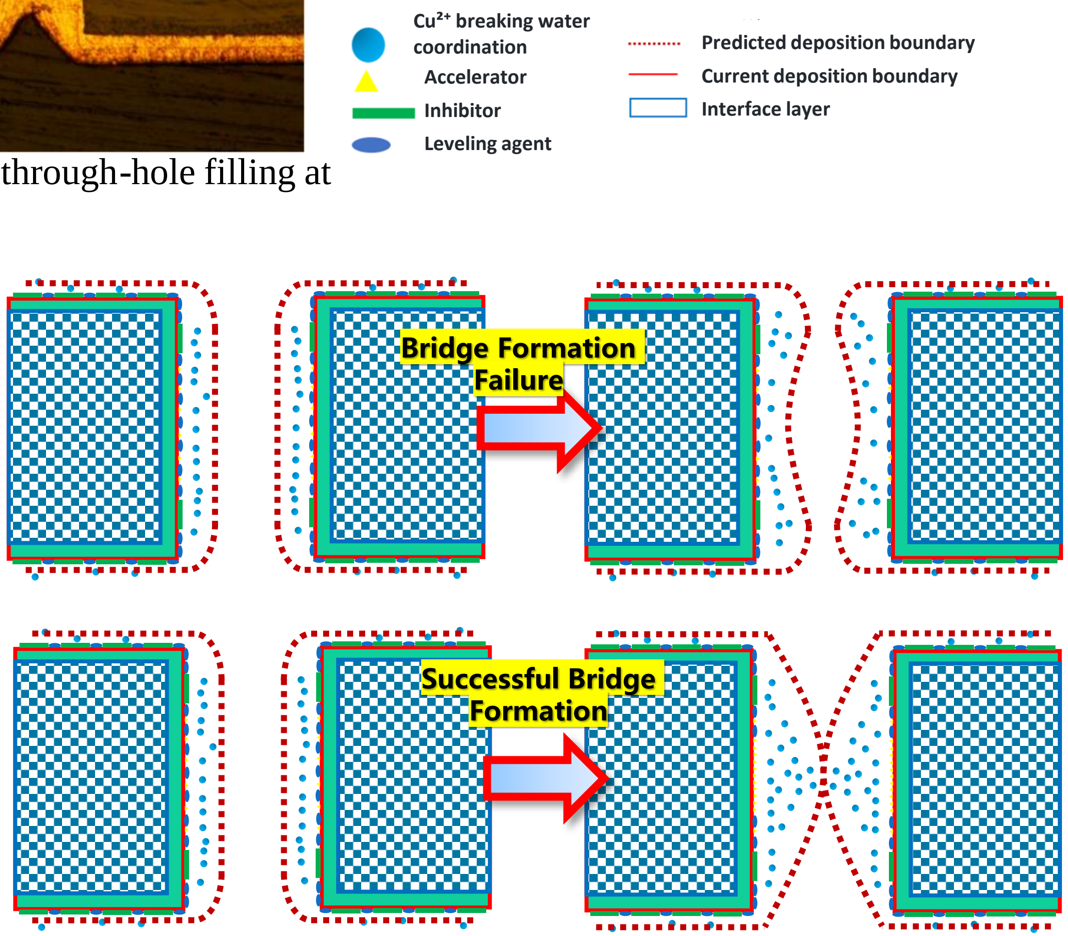


Fig. 3-9 Schematic illustration of the stages in the through-hole filling process

#03 Electrochemical behavior and filling performance of the levelers (blind-hole)

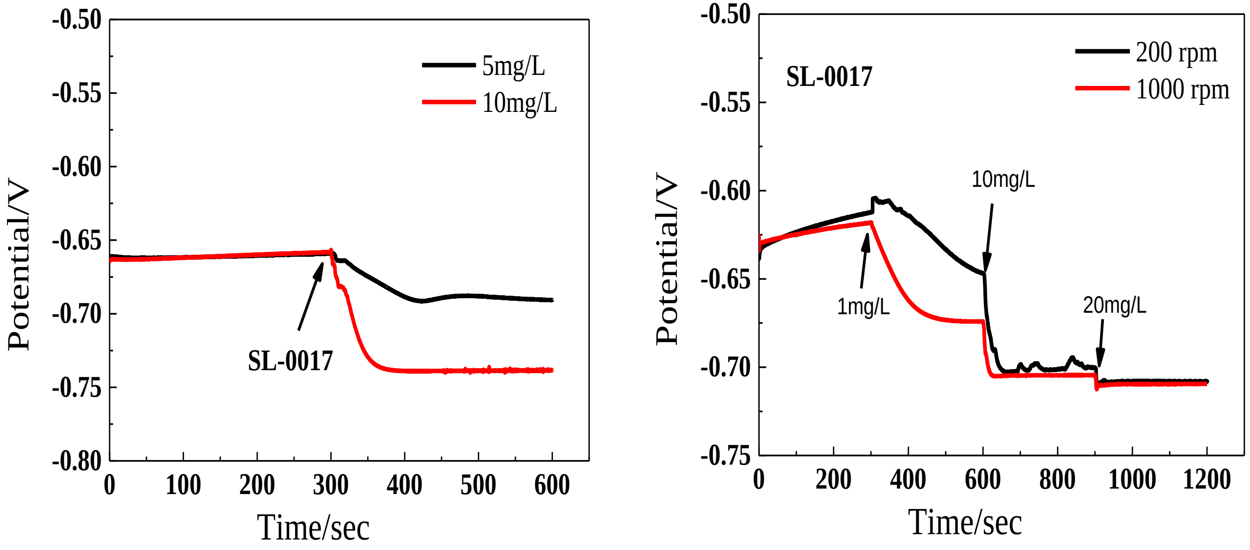


Fig. 3-10 E-t curves obtained in the plating solution with different concentration of SL-0017

Table 3-3 Electrolyte composition for SL-0017 applied to blind via filling

Parameters	Control Conditions
$CuSO_4 \cdot 5H_2O$ (g/L)	220
H_2SO_4 (g/L)	54
Cl^- (mg/L)	50
SPS (mg/L)	1
L64 (mg/L)	100
Leveler (mg/L)	1
Aeration rate (L/min)	2
Plating Current (A/dm^2) / Time (min)	1.5/60

— Filling performance of SL-0017

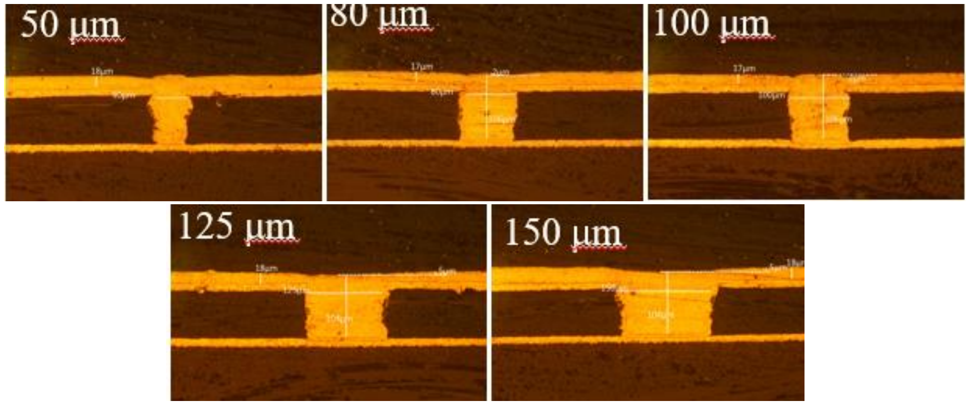


Fig. 3-11 Cross-sectional images of blind via filling with 1mg/L SL-0017

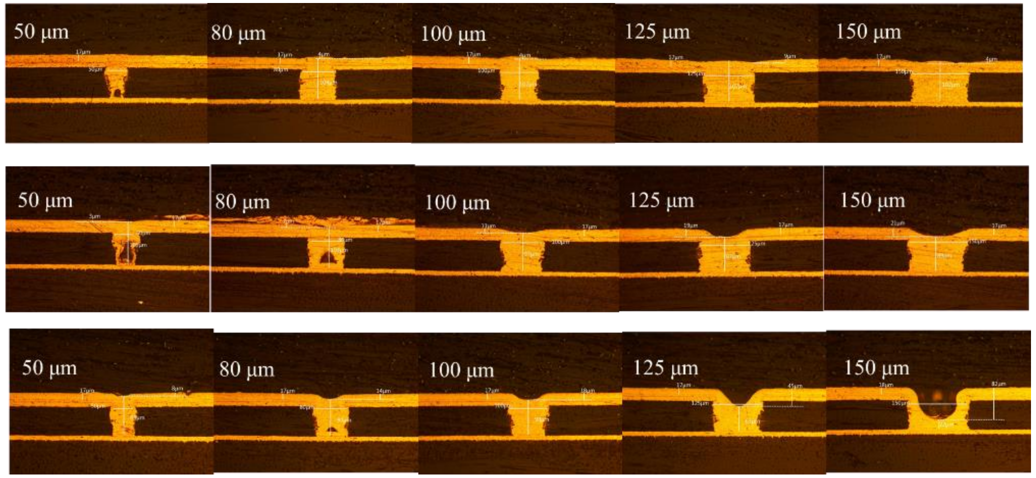


Fig. 3-12 Cross-sectional images of blind via filling with SL-0017 at concentrations of 1mg/L, 10mg/L and 20mg/L (From top to bottom)

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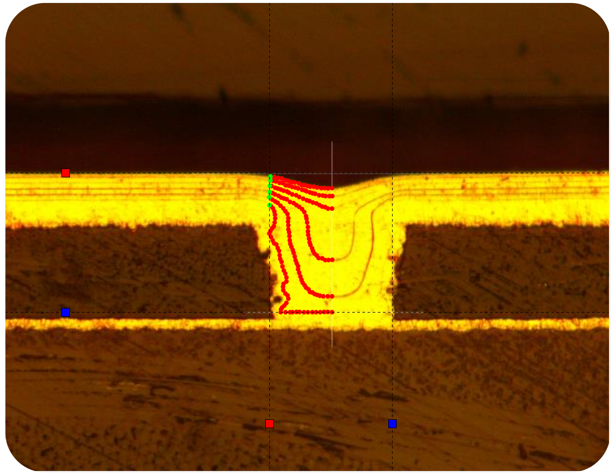
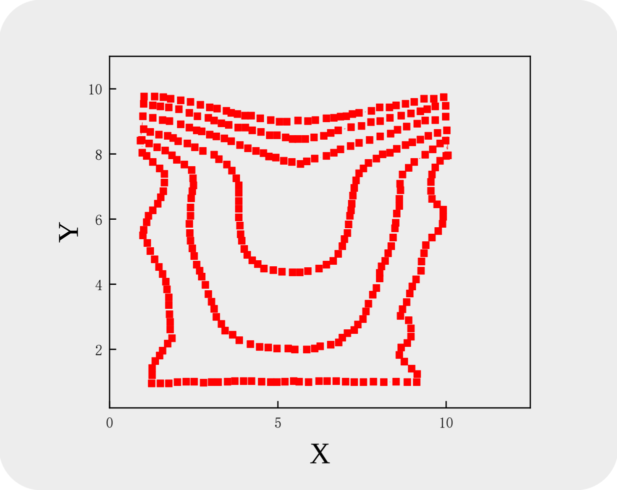
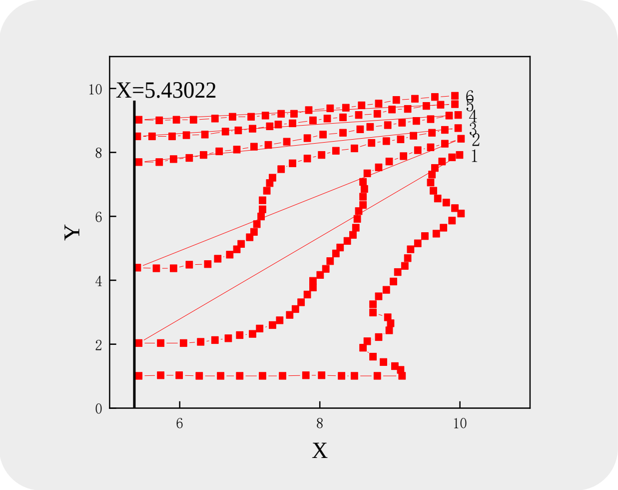
Electrochemical behavior and filling performance of the levelers (blind-hole)

— Filling model

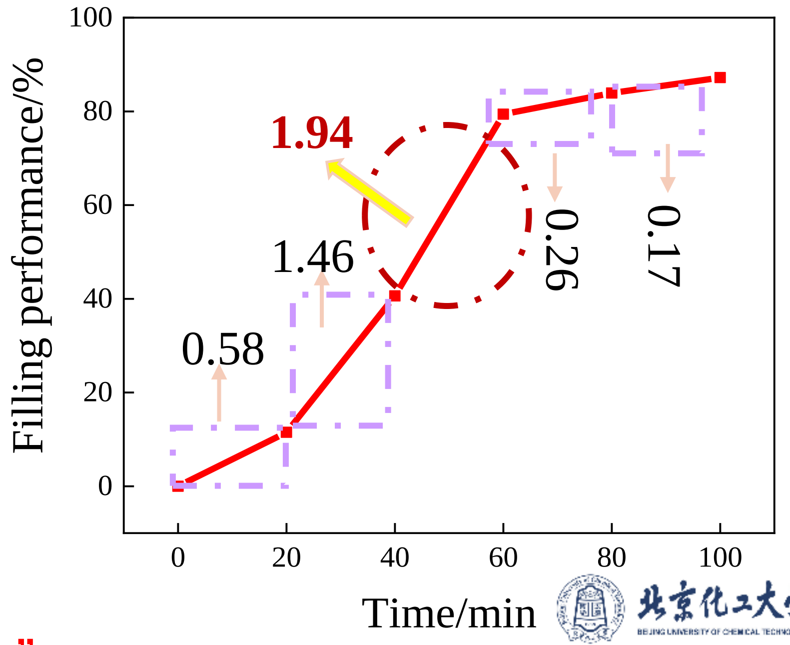
Electroplating process: plating for 20min and then stop plating for 35min, repeat this operation. The total plating time is 100min.







Plating time/min	Weight of deposited copper/g	Volume of deposited copper/$\times10^{-12}$cm^3	Copper thickness in blind hole/µm	Filling performance/ %
0-20	0.5351	287.3	14	11.5
20-40	0.5368	199.2	38	40.6
40-60	**0.5363**	**84.8**	**56**	**79.4**
60-80	0.5342	36.4	12	83.9
80-100	0.5382	5.8	10	87.2



Define the "Explosive Growth Stage"

#03 Electrochemical behavior and filling performance of the levelers (blind-hole)

— **Filling model**

Improving filling performance by using "Explosive Growth Stage"

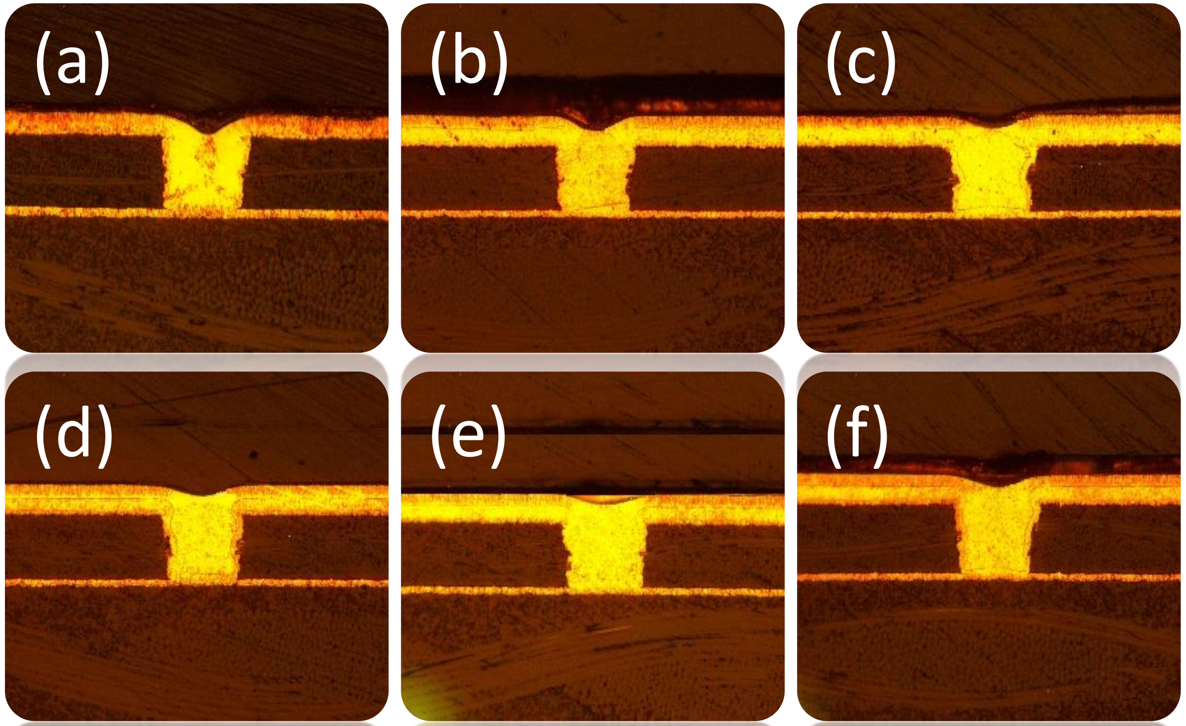


Fig. 3-13 Addition of different concentrations of SPS at the beginning of the explosive growth stage (40min): (a) 0 mg/L; (b) 0.1 mg/L;(c) 0.2 mg/L; (d) 0.3 mg/L; (e) 0.4 mg/L; (f) 0.5 mg/L

Table 3-4 Filling performance effected by the addition of SPS

SPS / (mg/L)	**0**	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**
Filling Performance / %	80.1	84.7	86.1	87.3	**92.0**	87.5

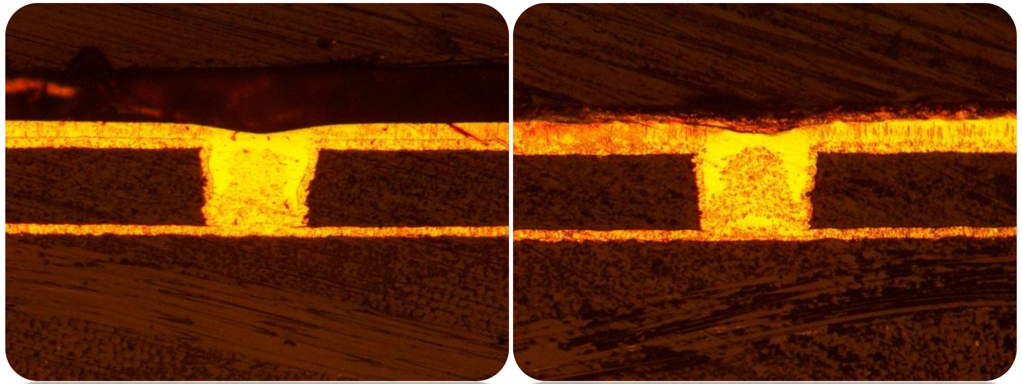


Fig. 3-14 The filling results obtained in the plating solution containing 1.4mg/L SPS

Filling performance increase from 80.1% to 88.5%, but still smaller than 92.0% by using "explosive growth stage"

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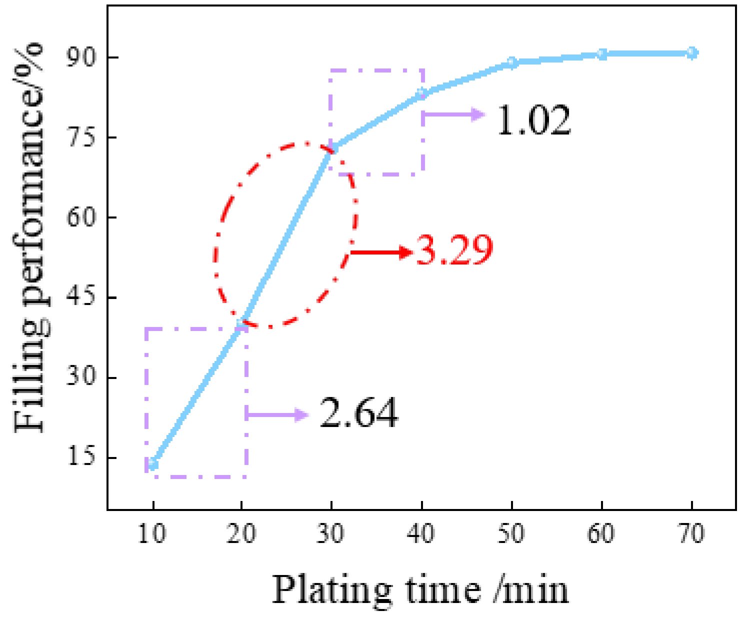
— Filling model

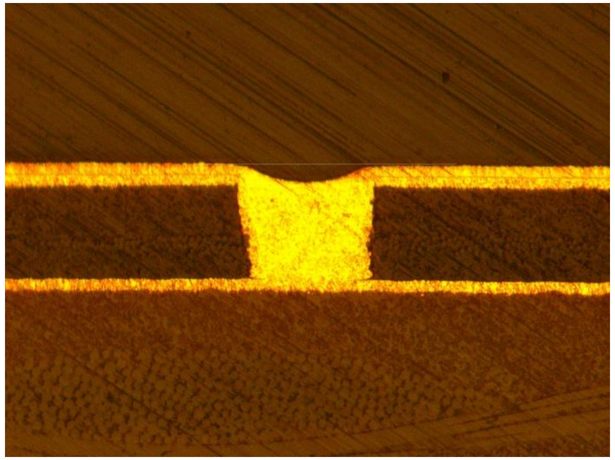
Improving filling performance by using "Explosive Growth Stage"

Plating solution: 220 g/L $CuSO_4 \cdot 5H_2O$, 54 g/L H_2SO_4, 50 mg/L Cl^-, 100 mg/L PEG, 1.5 mg/L SPS, 3 mg/L SH110



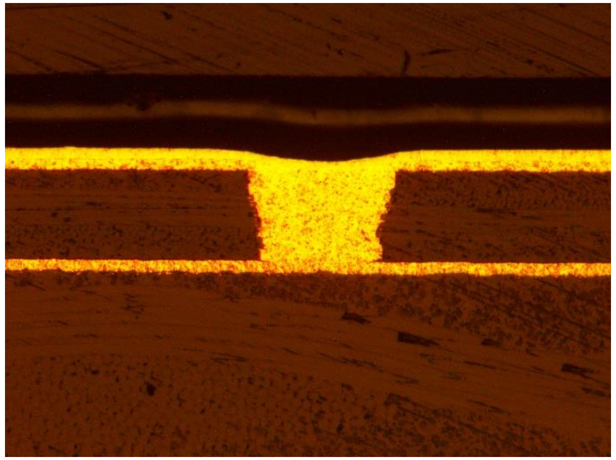
Explosive Growth Stage: 20 – 30 min

Plating for 40min



Filling performance: 83.3%

Plating 30min, adding 1mg/L SPS, plating 10min



Filling performance: 91.2%
The deposited copper layer: 11μm

Filling performance is obviously improved

#03 Electrochemical behavior and filling performance of the levelers (blind-hole)

— Filling model

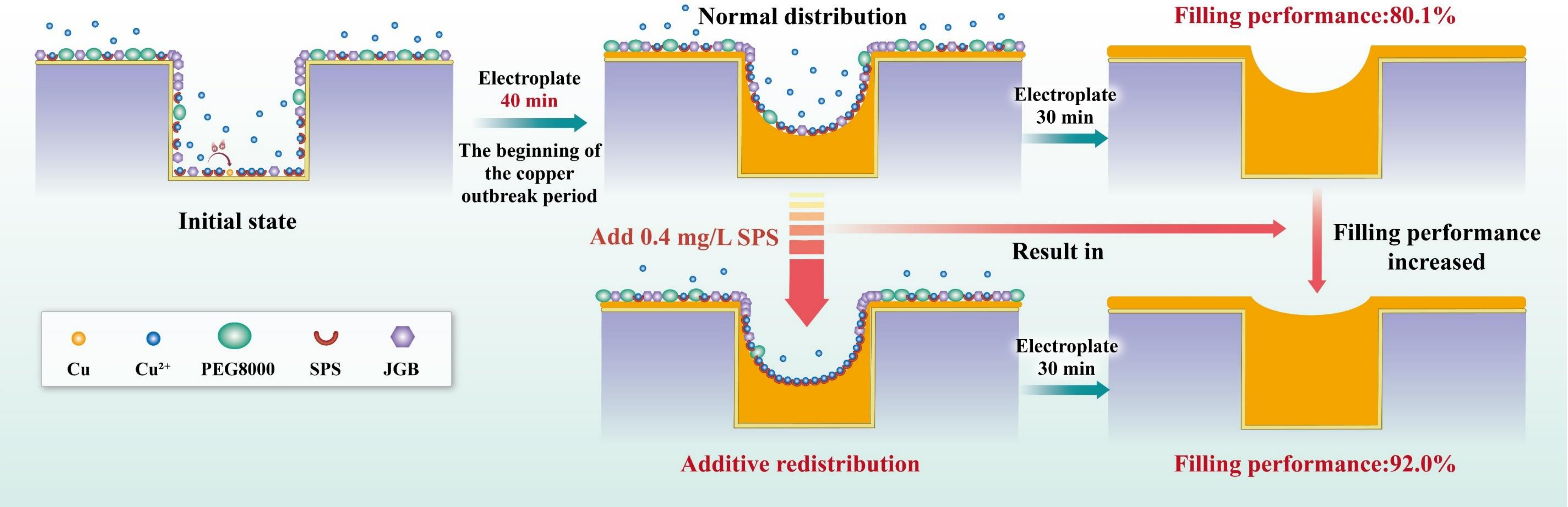


Fig. 3-15 Mechanism diagram of microvia filling by adding SPS at “Explosive Growth Stage”

Contents

#04 Conclusions

- New accelerator molecules have been designed and synthesized, which are composed of -SO_3Na and nitrogen-containing heterocycle. Among them, **Z3 has the strongest depolarization effect** on copper deposition and shows the **best microvia filling performance.**
- **Z3 is not a simple mixture of pyrimidine and MPS,** but a **real accelerator** with the novel molecular structure.
- More than 30 levelers have been successfully synthesized, among them, **SL-0017 and SL-0021** show the best filling performance for blind hole and through hole, respectively.
- During microvia filling process, there is a "**Explosive Growth Stage**" in the microvia. At this stage, the thickness of deposited copper layer in the microvia is increased quickly.
- Microvia filling performance can be greatly improved by adding a certain amount of accelerator at the beginning of the "**Explosive Growth Stage**".

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Thank you for your attention!

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