

Discussion on Metallization Schemes with Less Silver and No Silver

苏州晶银新材料科技有限公司 Suzhou iSilver Materials Co., Ltd.



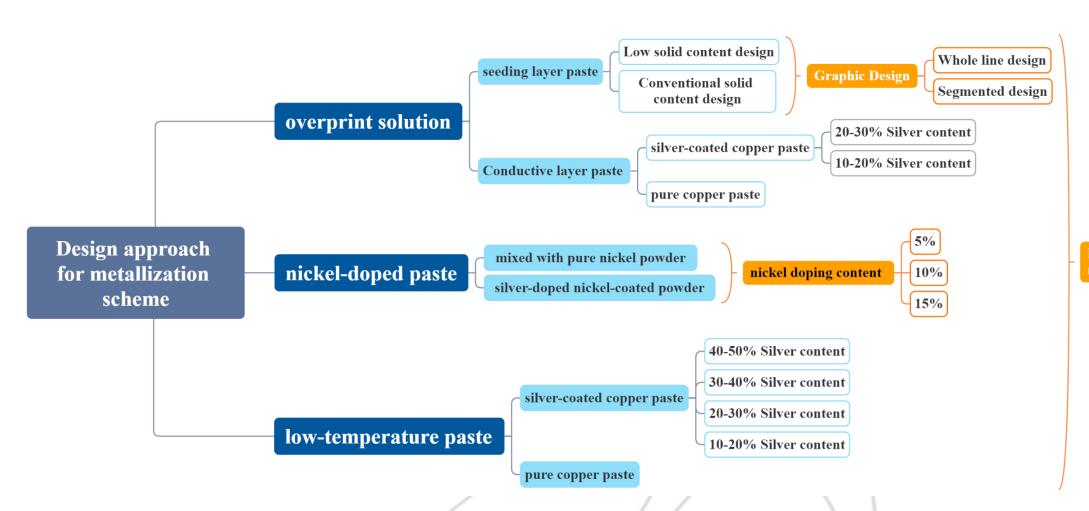


Part

Design ideas for metallization schemes







Ensure efficiency and reliability, reduce costs

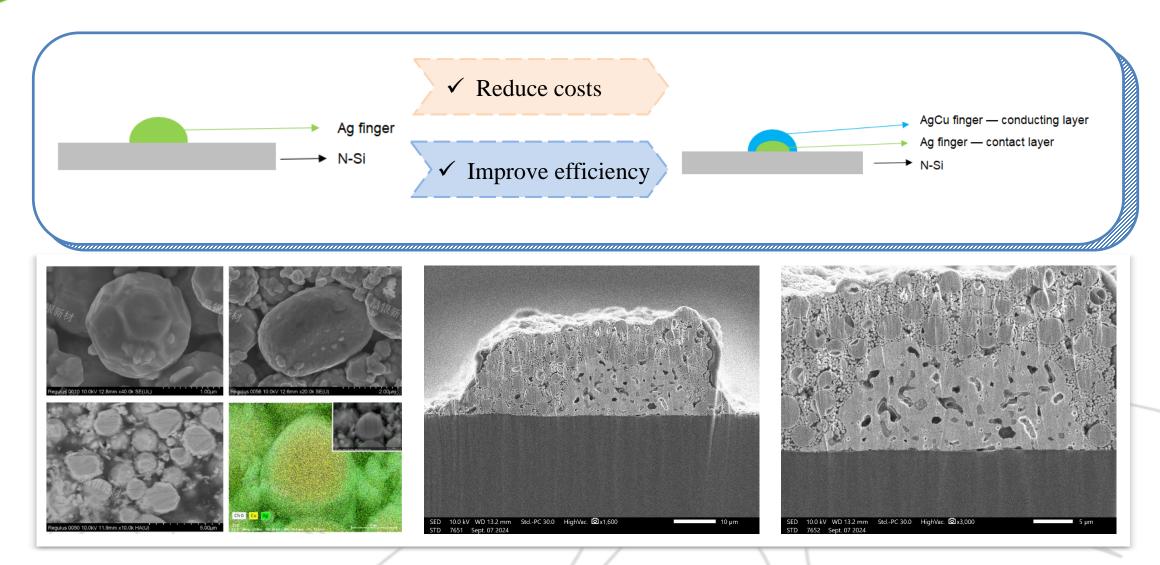


Part 2

The design ideas of overprint cost reduction

Cost reduction design scheme for Ag-Cu paste





Ag-Cu paste overprinting technology is used to reduce silver consumption

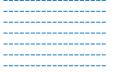
Seed layer — Conductive layer



• Thin silver at the bottom Seed layer

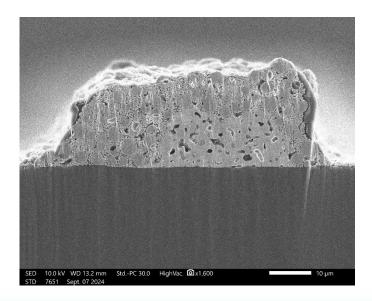
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line segment



◆ The bottom silver can use conventional low solid content Topcon back fine paste. On this basis, the fluidity and ink penetration ability of the paste can be adjusted according to the requirements of the screen and solid content.

- AgCu Conductive layer
- ◆ The conductive layer uses 10-30% AgCu paste.
- ◆ The silver layer thickness is approximately 40-80nm.



Research Status of silver-coated Copper powder

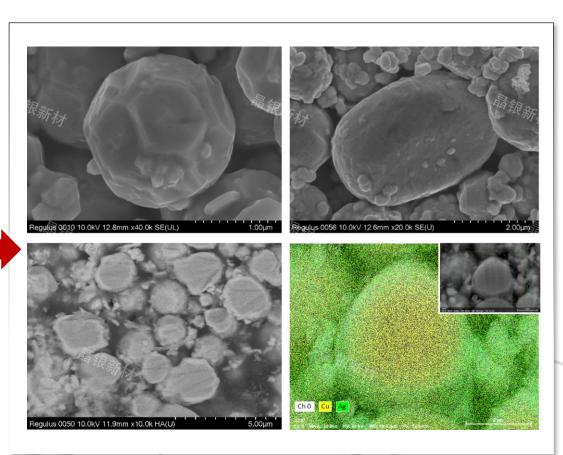


Current research status of preparation processes

- The main component of the plating solution is silver nitrate solution. The electronegativity of copper is higher than that of silver, and it can undergo displacement reactions. Free silver ions undergo displacement reduction reactions on the surface of copper powder, forming a silver coating.
- Modern processes often employ complexing agents to complex free silver ions, increase the complexation constant of silver ions, and ensure the stability of the plating solution during the metal coating process.

Silver-coated copper powder process

• The current electroless plating process can already ensure the uniformity, stability and integrity of the coating.



施玉雷. 银包铜粉的制备、表征及性能研究[D].东南大学

Key technology of low silver copper paste



Surface modification of silver coated copper powder

Modification purpose

- Increase the bond strength of paste
- Improve paste compatibility
- Improve the stability of powder and paste
- Inhibition of ion migration
- Improve powder dispersion
- Improve interface contact
- Improving paste resistivity

Stability

Reliability

Printability

Conductivity

improvemen¹

Modification method

mechanical treatment

Ball milling, sand blasting, etc

• Surface Modification

Treatment

Surfactant

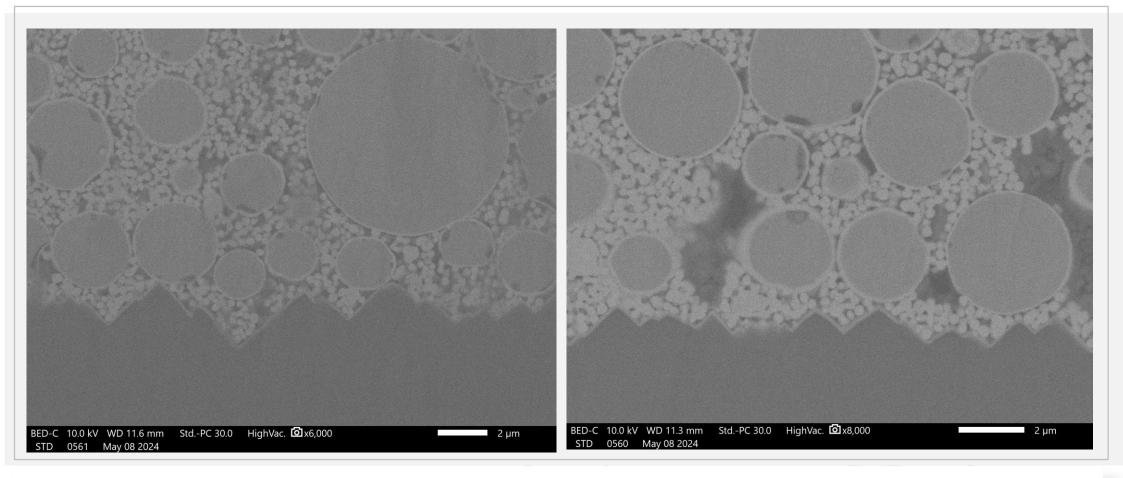
Antioxidant

Coupling agent

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島银新材 ISILVER MATERIALS

The characteristics of silver-coated copper powder



- The overall silver coating of the silver-coated copper powder is uniform, with a silver layer thickness of approximately 60-80nm, and there are no issues of uneven coating or exposure.
- > All 20% Ag-Cu low-temperature pastes have passed the standard IEC reliability tests.



Ag-Cu fine finger paste

	TAC609-T	TAC809-T	TAC899-T	TAC909-T (R&D product)
Silver content (%)	30-32	22-26	15-20	10-15
Bulk resistivity $(\mu\Omega.cm)$	5.0-7.0	6.0-7.0	7.0-9.0	8.0-10.0
Printing speed (mm/s)	≥450	≥450	≥450	≥450

Low-silver silver-containing copper-coated paste, maintaining low bulk resistance and high printing speed;

The high-temperature seed layer on the back and the silver-coated copper finger with 20% silver content or less significantly reduce the metallization cost.

The 30% and 20% silver-containing copper pastes have both passed the standard IEC reliability tests.





	Wet weight (mg)	Eff (%)	Uoc (mV)	Isc (A)	FF (%)	Rs (Ω)
BL	28	_	_	_	_	_
BN-08 (Single-print seed layer)	15	-0.18	1.1	-0.003	-0.68	-3
BN08+TAC589 (Seed layer + silver-coated copper)	15+35	-0.06	1.9	-0.007	-0.33	1

- ➤ The initial test shows that the efficiency of the overprint scheme is 0.06% lower.
- At the current wet weight, the silver-coated copper paste with 20% or less silver content has a cost advantage of about 1 fen /w in metallization cost.
- The contact performance of the seed layer and the wet weight of the silver coated copper paste can be further optimized.





	Wet weight (mg)	Eff (%)	Uoc (mV)	Isc (A)	FF (%)	Rs (Ω)
BL	39.5	_	_	_	_	_
BN07 (Single-print seed layer	20.4	-0.044	-0.2	0.0006	-0.171	0.00011
TAC809 (25%)	59.6	0.018	0.8	0.0046	-0.058	0.00002

- The overprint scheme is 0.018% more efficient.
- The silver content of the silver-coated copper paste with 25% silver content and the seed layer is 2-3 mg lower than that of pure silver.
- The contact performance of the seed layer and the wet weight of the silver coated copper paste can be further optimized.





	Wet weight (mg)	Eff (%)	Uoc (mV)	Isc (A)	FF (%)	Rs (Ω)
BL	44.4	_	_	_	_	_
BN07 (stencil printing: Opening 11.5µm, total thickness 24µm Single-print seed layer)	21.5					
TAC809 (25%)	48	-0.001	0.9	0.0052	-0.139	0.00006

- ➤ The efficiency of the overprint scheme is 0.001% low.
- The silver content of the silver-coated copper paste with 25% silver content and the seed layer is 7-8 mg lower than that of pure silver.

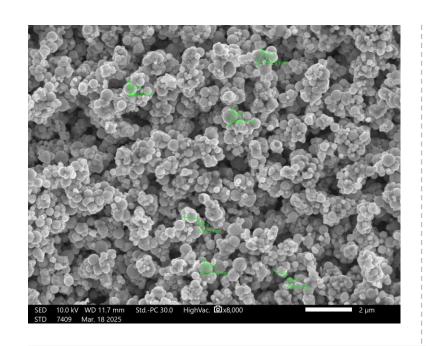


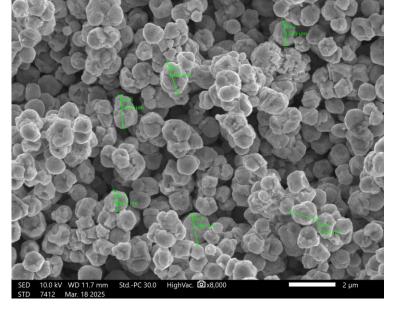


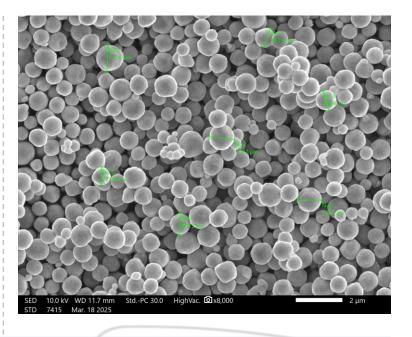
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Nickel-doped (silver-coated nickel) cost reduction design scheme







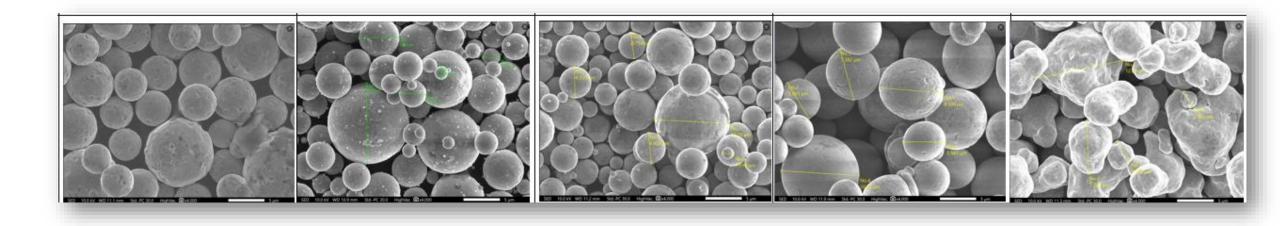


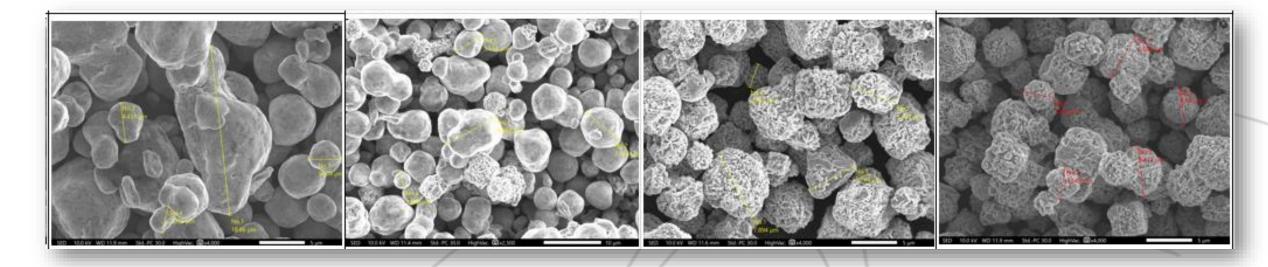
Silver-coated nickel powder A

Silver-coated nickel powder B

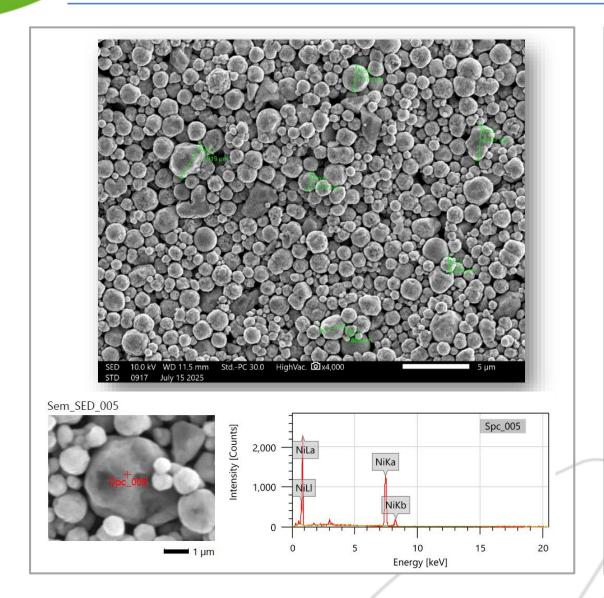
Nickel powder

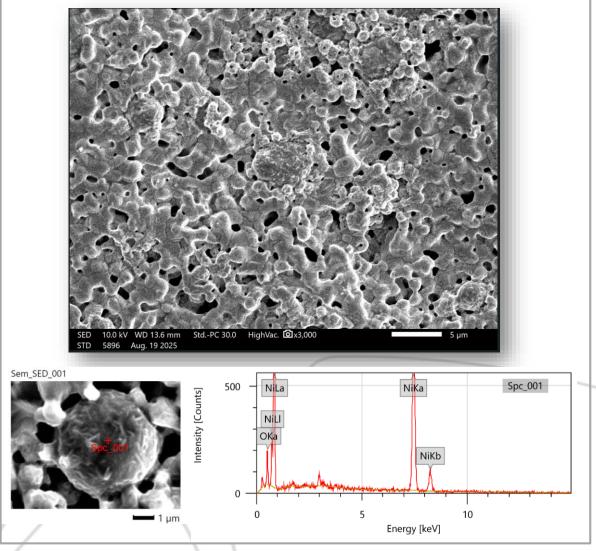




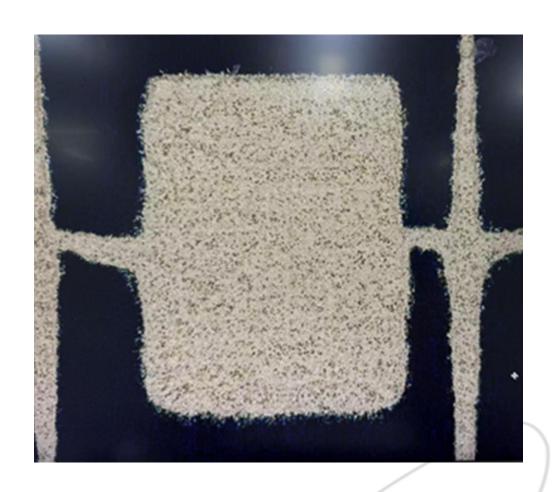


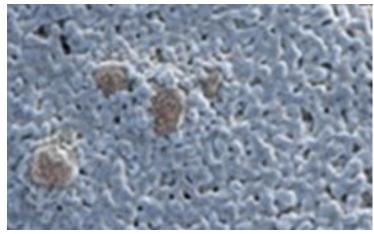


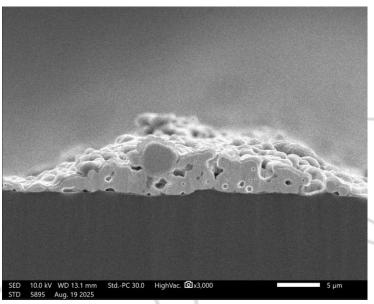




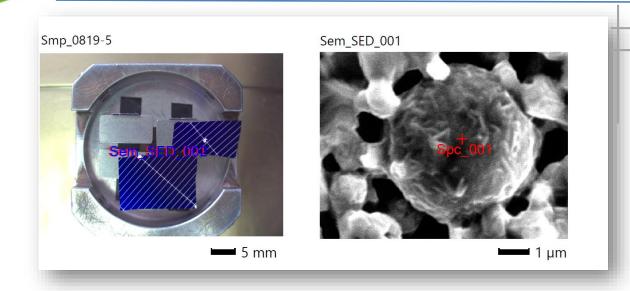


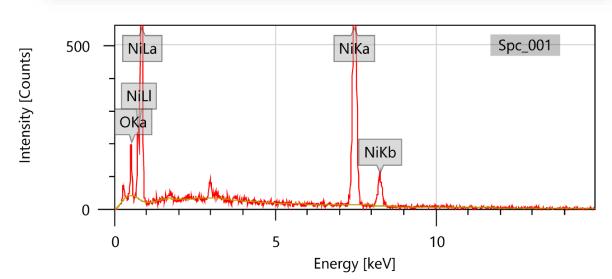












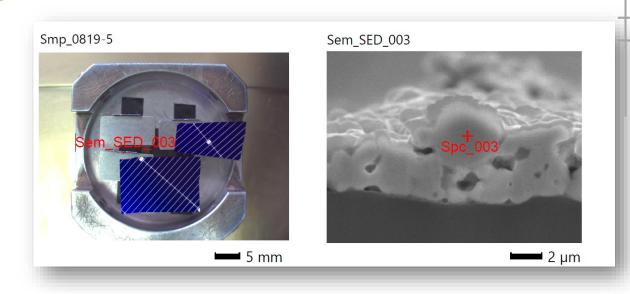
Signal SED Landing Voltage 20.0 kV WD 13.7 mm Magnification x16,000 Vacuum Mode HighVacuum

Items	Value
measurement conditions	
Acceleration voltage	20.00 kV
Probe current	-
Magnification	x 16000
Process time	T4
Measurement detector	First
Live time	10.00 seconds
Real time	10.91 seconds
Dead time	8.00 %
Count rate	4161.00 CPS
<u> </u>	

Display name	Standard data	Quantification method	Result Type
Spc_001	Standardless	ZAF	Metal

Element	Line	Mass%	Atom%
0	K	5.29±0.18	17.00±0.58
Ni	K	94.71±1.19	83.00±1.04
Total		100.00	100.00
Spc_001			Fitting ratio 0.0531





Signal SED
Landing Voltage 20.0 kV
WD 13.2 mm
Magnification x8,000
Vacuum Mode HighVacuum

Items	Value
1001110	Value
measurement conditions	
Acceleration voltage	20.00 kV
Probe current	-
Magnification	x 8000
Process time	T4
Measurement detector	First
Live time	10.00 seconds
Real time	10.98 seconds
Dead time	9.00 %
Count rate	4787.00 CPS
-	

400 NiLa	Nika Spc_003
300 NILI	
200	NiKb
100 — OKa	
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0	5 10
	Energy [keV]

Intensity [Counts]

Display name	Standard data	Quantification method	Result Type
Spc_003	Standardless	ZAF	Metal

Element	Line	Mass%	Atom%
0	K	0.42±0.07	1.52±0.25
Ni	K	99.58±1.18	98.48±1.17
Total		100.00	100.00
Spc_003			Fitting ratio 0.0386

Test data from Customer



	Wet weight (mg)	Eff (%)	Uoc (mV)	Isc (A)	FF (%)	Rs (mΩ)	Rsh (Ω)	Irev2
BL			—		—	_		
10%Ni	1.2	-0.004	0.1	0.006	-0.05	1	-22	-0.02

	Wet weight (mg)	Eff (%)	Uoc (mV)	Isc (A)	FF (%)	Rs (mΩ)	Rsh (Ω)	Irev2
BL				_	_	_		_
12%Ni	4.0	-0.02	-0.3	-0.024	0.10	0	-88	-0.001

Test data from Customer



	Wet weight (mg)	Eff (%)	Uoc (mV)	Isc (A)	FF (%)	Rs (mΩ)	Rsh (Ω)	Irev2
BL	_	_	_	_	_	_	_	
15%Ni	4.0	-0.011	0.5	0.005	-0.12	0.0001	67	0.001

	Wet weight (mg)	Eff (%)	Uoc (mV)	Isc (A)	FF (%)	Rs (mΩ)	$\operatorname{Rsh} \\ (\Omega)$	Irev2
BL			_	_				
15%Ni A	-0.4	-0.012	-0.1	0.014	-0.10	0.0001	122	-0.005
15%Ni B	-1.8	-0.004	0.2	0.007	-0.08	0.00000	164	0.016





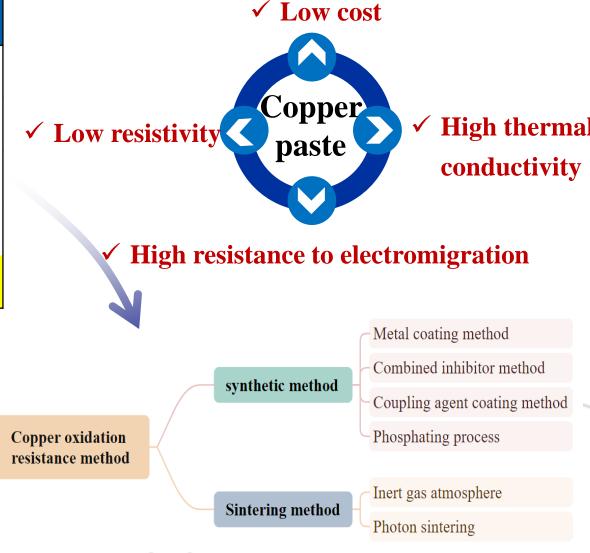
Part 3

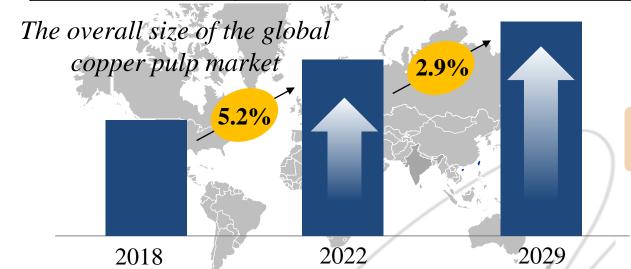
Pure copper paste solution

Pure copper paste



	silver	copper	
World reserves	530000 tons	880 million tons	
Price	8000yuan/Kg	80yuan/Kg	
Chemical property	stabilize	Easily oxidized	
Conductivity	63.01×10 ⁶ S/cm	59.6×10 ⁶ S/cm	
Volume resistivity	1.59 μΩ.cm	1.75 μΩ.cm	





Challenges in the development of pure copper metallization



Antioxidant issue

- The sintering performance of copper oxide is poor,
 which affects the sintering compactness.
- Poor conductivity, seriously affecting battery efficiency and reliability.
- Prone to brittle fracture, leading to functional failure

silicon substrate etching

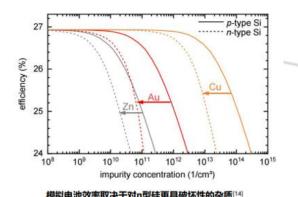
The diffusion of copper into silicon materials can form composite active precipitates, reducing the lifetime of minority carriers in solar cells and decreasing the open-circuit voltage.



Low temperature sintering problem

- High specific surface area and abundant uncoordinated atoms make it extremely prone to oxidation reactions.
- The smaller the particle size, the easier it is for copper powder to agglomerate
- The bonding force between copper and silicon interface is weak, and the contact resistance is high.

Long-term stability issues



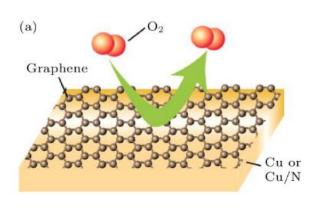
Antioxidant method for copper powder



Surface coating treatment

Metal/non-metal inorganic coating

- Silver/Nickel/Tin-coated Copper
- Carbon/Graphene-coated Copper



organic polymer coating

- Corrosion inhibitor
- coupling agent
- reducing agent

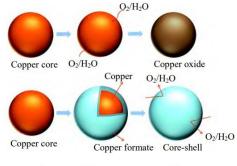


图 8 铜-甲酸铜核-壳颗粒示意图

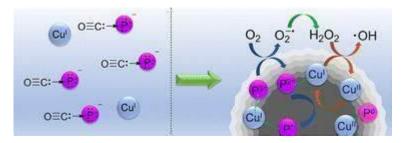
Principle: A stable, high-density, and low-porosity film is formed on the surface of micro-nano copper powder through coating treatment, preventing direct contact between surface copper atoms and air. This slows down the movement of oxygen atoms, preventing the effective formation of surface oxides

Surface conversion treatment

Surface phosphating treatment

A chemical treatment method for metal surfaces, where the metal surface comes into contact with an acidic solution containing phosphate, undergoing a chemical reaction to form a stable, insoluble inorganic compound film layer on the metal surface.

$$3Cu^{2+} + 2PO_4^{3-} \rightarrow Cu_3(PO_4)_2$$
.



Surface passivation treatment

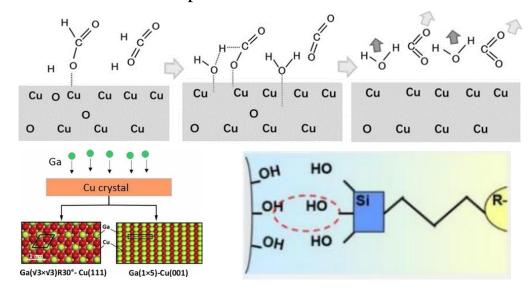
Using passivating agents or antioxidants to render the surface inactive, thereby providing protection and preventing oxidation.

Antioxidant method for copper powder



surface functional group modification

- Long-chain functional groups increase oxygen diffusion pathways.
- Form coordination bonds or chemical bonds with copper surface to reduce the electronic activity of copper
- Hydrophobic polymers reduce surface hydrophilicity and reduce water molecule adsorption



surface crystal reconstruction

Crystal plane	Atomic coordination number	Oxygen dissociation energy	Compactness of oxide layer	Antioxidant activity
(111)	9	High	Close-packed atoms	Excellent
(100)	8	Medium	Medium loose	Average
(110)	7	Low	Open and loose	Poor
(10	00)	(110)		(111)

Principle: By utilizing the energy and crystallinity differences of different crystal faces formed by copper atoms, the higher crystallinity results in a highly ordered and tightly packed arrangement of copper atoms with low defects, making it difficult for oxygen atoms to erode, thereby significantly reducing the rate of oxidation.

Copper metallization antioxidant idea



Restore and remove oxides

- Removal of oxide from copper particle surface by short-chain carboxylic acid.
- In-situ treatment of copper powder using reducing conditions (powder surface, slurry components, sintering environment, etc.) can effectively remove the surface oxide layer

Copper formate and 1-Dodecanethiol Cu NPs paste Pressure-assisted bonding process Sintered structure Cu NP Cu NPs structure Cu NPs structure HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + e' + CO₂ + H' + H HCOOH(g) + HCOO (ads) + OH(ads) + HCOOH (ads) + CO₂ + H' + E' + CO₂ + H' + H HCOOH(g) + HCOOH (ads) + HCOO

Low melting point alloy oxidation resistance

- After melting, the low-melting alloy forms metal contact with copper particles enhancing conductivity, and infiltrates the surface of copper particles to prevent oxidation.
 - Conventional Resin Paste
 Thermosetting polymer
 & solvent

 Curing

 Conductive metal particles
 Shrinkage, Physical contact

 Binder is an insulator

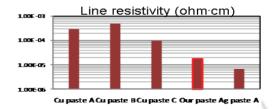
 Curing

 Conductive metal particles

 LMPA is metal

 Surface Cu-alloy layer is formed

 Binder is metal



low temperature short time sintering

- Isolating from air to prevent oxidation.
 - Organic system and low melting point alloy help rapid solidification at low temperature.
- Copper particles melt when heated, forming a conductive path.

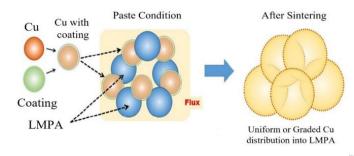
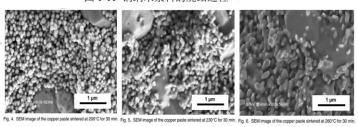


图 1-11 铜纳米浆料的烧结过程[56]



Research and development direction of pure copper metallization - organic system



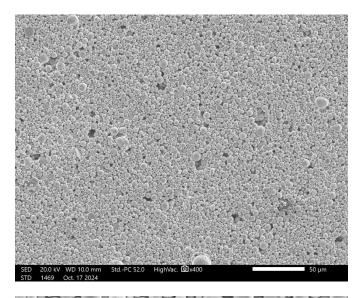
Bonding effect: maintain close contact of copper particles Low temperature curing characteristics: lower Tg, low temperature crosslinking Dispersibility: Help copper powder disperse evenly resin Interface compatibility: Forming coordination bonds with hydroxyl groups or oxide layers on the copper surface to enhance interfacial bonding principal system Chemical reduction: It has reducibility and can reduce the oxide layer on the copper surface Curing agent: low temperature curing, reducing property, and reaction with resin groups to promote cross-linking structure **Solvent:** low boiling point, reactive, reducing solvent Organic system Reducing agent: Reacts with the surface oxide layer of copper powder to reduce copper to its elemental form **Antioxidant:** A dense protective film is coated on the surface of copper powder to slow down the oxidation rate additive agent **Coupling agent:** Promotes the close combination of organic materials and inorganic materials **Dispersant:** Prevents copper particles from aggregating

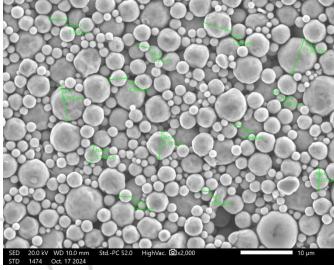
Leveling agent, defoaming agent, thickening agent

Pure copper paste product



	HCT145 series (Pure copper paste)
Copper content (%)	86-90
Volume resistivity (Ω ·cm)	$8-12\times10^{-6}$
Match screen printing (μm)	≥16
Printing speed (mm/s)	≥400
Curing temperature (°C)	≥240
Curing time (s)	10-30







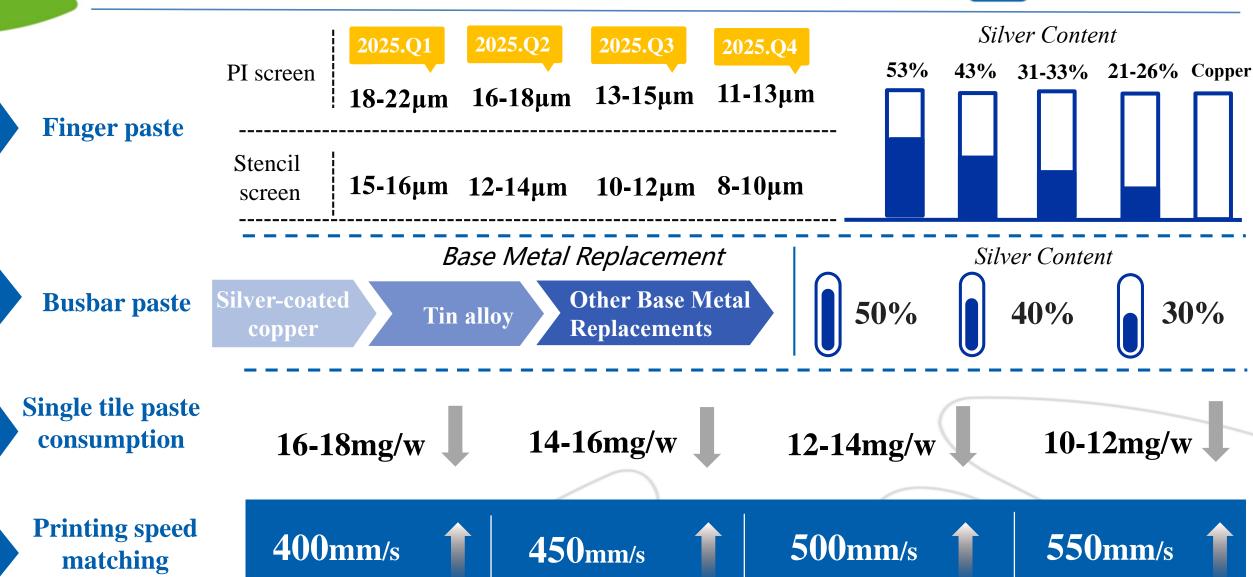


Part 4

Cost Reduction Scheme for Low-Temperature Paste

The roadmap for HJT paste







Low-silver content silver-coated copper finger paste

	HAC589-T	НАС609-Т	HAC809-T	НАС899-Т	НАС909-Т	HAC939-T (R&D product)
Silver content (%)	40-45	30-35	25-27	21-23	15-20	10-15
Volume resistivity (μΩ.cm)	5.0-7.0	5.0-7.0	6.0-7.0	7.0-9.0	7.0-9.0	8.0-10.0
Printing speed (mm/s)	≥450	≥450	≥450	≥450	≥450	≥450

The silver-coated copper paste with low silver content still maintains low volume resistance and high printing speed, and its efficiency is basically equal with pure silver paste;

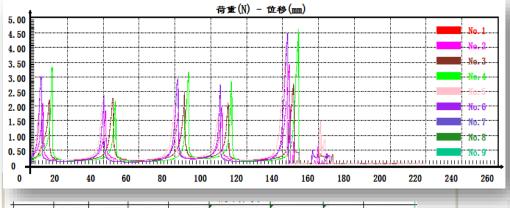
The combination of 10 - 20% silver - containing low wet-weight fine finger on the back and 20 - 30% silver - containing fine finger on the front significantly reduces metallization costs;

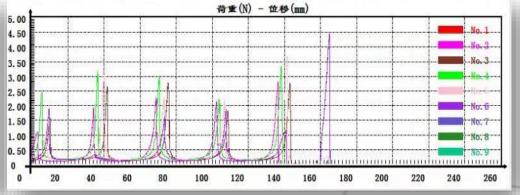
HAC809-T, HAC899-T, HAC909-T, HAC939-T have all passed the standard IEC reliability test.

Low-silver content silver-coated copper busbar paste



	HC539-ZX	HAC539-ZT	HAC589-ZT	HAC609-ZT Series (0BB Ag-Cu busbar paste)
Silver content (%)	92-93	50-60	41-43	30-35
Volume resistivity ($\mu\Omega$.cm)	5.5-6.5	6.5-7.5	7.0-9.0	8.0-9.0
Busbar tensile force(N/mm)	≥2.2	≥2.2	≥2.2	≥1.0





.23 2.27 2.47 2.1 2.76 2.37 .33 2.15 3.15 2.83 4.64 3.22 .89 2.14 2.05 1.61 4.08 2.35 .02 2.36 2.94 2.73 4.47 3.10 .09 1.92 2.29 2.14 2.81 2.05 .55 2.65 2.8 1.82 2.76 2.32 .45 3.17 2.96 2.23 3.34 2.83 .26 3.03 2.27 2.21 3.7 2.49 2.65 4.64 3.22 2.76 2.32 2.45 3.17 2.96 2.23 3.34 2.83 2.213 6A							100		
.33 2.15 3.15 2.83 4.64 3.22 .89 2.14 2.05 1.61 4.08 2.35 .02 2.36 2.94 2.73 4.47 3.10 .09 1.92 2.29 2.14 2.81 2.05 .55 2.65 2.8 1.82 2.76 2.32 .45 3.17 2.96 2.23 3.34 2.83 .26 3.03 2.27 2.21 3.7 2.49 2.655 A6A 正面	2.09	1.85	1.78	2	3.44	2. 23			
.89 2.14 2.05 1.61 4.08 2.35 .02 2.36 2.94 2.73 4.47 3.10 .09 1.92 2.29 2.14 2.81 2.05 .55 2.65 2.8 1.82 2.76 2.32 .45 3.17 2.96 2.23 3.34 2.83 .26 3.03 2.27 2.21 3.7 2.49	2.23	2.27	2.47	2.1	2.76	2. 37			
.02 2.36 2.94 2.73 4.47 3.10 .09 1.92 2.29 2.14 2.81 2.05 .55 2.65 2.8 1.82 2.76 2.32 .45 3.17 2.96 2.23 3.34 2.83 .26 3.03 2.27 2.21 3.7 2.49	3.33	2.15	3.15	2.83	4.64	3. 22	2. 655	合格	正面
.09 1.92 2.29 2.14 2.81 2.05 .55 2.65 2.8 1.82 2.76 2.32 .45 3.17 2.96 2.23 3.34 2.83 .26 3.03 2.27 2.21 3.7 2.49	1.89	2.14	2.05	1.61	4.08	2. 35	1400 104 6400	78-200009	10.000000000000000000000000000000000000
.55 2.65 2.8 1.82 2.76 2.32 .45 3.17 2.96 2.23 3.34 2.83 .26 3.03 2.27 2.21 3.7 2.49	3.02	2.36	2.94	2.73	4.47	3. 10		80)	
.45 3.17 2.96 2.23 3.34 2.83 2.213 合格 背面 .26 3.03 2.27 2.21 3.7 2.49	1.09	1.92	2. 29	2.14	2.81	2.05			
. 26 3. 03 2. 27 2. 21 3. 7 2 . 49	1.55	2.65	2.8	1.82	2.76	2. 32			
	2.45	3.17	2.96	2.23	3.34	2. 83	2. 213	合格	背面
1 9 10 34 1 65 1 97 1 12 1 39	1.26	3.03	2.27	2.21	3.7	2. 49	102000010000000000000000000000000000000	cameagning:	
1.0 0.04 1.00 1.01	1.9	0.34	1.65	1.87	1.12	1. 38		6.00	

The peel force of the front and back sides of the silver coated copper barsbar is not much different from that of pure silver.

Has passed the reliability test.



Part 5

Summary of Schemes and Tests





Product	Base Metal Type	Silver Content	Testing Situation
		30%	Adopting backside overprinting technology, the efficiency can basically be equalized, and the comprehensive wet weight is reduced by about 5mg;
	Silver-plated copper finger ocon Nickel-containing paste	25%	Adopting backside overprinting technology, the efficiency is about 0.05 lower, and the comprehensive silver consumption is reduced by about 8mg;
Topcon		20% and below	Adopting backside overprinting technology, currently in client matching testing;
		80%	Backside paste testing: efficiency is basically equal, wet weight is equal, re-testing is planned subsequently;
		75%	Backside paste testing: efficiency is basically equal, wet weight is equal re-testing is planned subsequently;
		30%	Compared with high-silver-containing paste, efficiency and power are equal, and large quantities are supplied to clients;
	Silver coated copper finger	20-25%	Compared with 30% paste, efficiency and power are equal, reliability has been verified, and mass supply is available;
НЈТ&НВС		10-15%	Efficiency is slightly lower by about 0.05%, reliability has been verified, and small-batch supply is available;
пјі апрс	Silver coated copper	43-58%	Efficiency and module power on SMBB is basically equal, with pure silver, mass production is available;
	busbars	31-35%	Testing is underway on 0BB;
	Alloy main busbar	60-70%	Module power has advantages, but silver content is high;





Thanks!

苏州晶银新材料科技有限公司 Suzhou iSilver Materials Co., Ltd.

