Research and development of low temperature pastes for silicon heterojunction solar cells

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Part 1

Company profile
Suzhou isilver Materials was founded in 2011.

A high-tech enterprise engaged in the field of new energy and semiconductor.

Purchased and listed by Suzhou Good-ark (SZ002079) in 2020.

Focus on photovoltaic and semiconductor electronic materials

Core technology system of independent innovation

> 27 acres
Area
> 1000 tons
Plant capacity
> 200 tons
Capacity of LTP
> 160 people
Employee
> 10 million yuan
Per capita output value
Part 2

The direction of low temperature pastes
Three difficulties:

➢ High consumption——1.5-2 times higher than that of the high temperature paste

18-22mg/W on regular production line of heterojunction cells, compared with PERC cells (10-12mg/w)

➢ Low printing speed——Low productivity

• the printing speed of 300-350mm/s on production line, compared with PERC cell (450-500mm/s)

➢ Wider grid —— Heavy use of paste,Low efficiency

• About 35-40μm in width on production line, compared with PERC cell (20-25μm)
R&D roadmap of low temperature paste

Heterojunction low temperature paste

- Construction of conductive system
  - Electrical performance
    - Reduce 20% Line resistance
    - Reduce 10% Contact resistance
  - Parameter selection of silver powder and silver-coated copper powder
    - Selection of silver powder and silver-coated copper powder
    - Powder sintering technology

- Construction of organic system
  - Printing performance
    - Openings 14um Screen opening
    - Speed 300mm/s Printing speed
  - Selection and proportion of curing agent
    - Selection and proportion of additives

- Silver-coated copper replacement technology
  - Cost reduction
    - Silver paste consumption
      - Reduce consumption by 10-30%
    - Silver coated copper powder replaces more than 50%
    - Surface modification technology of silver-coated copper powder
    - Reliability of silver-coated copper powder
    - Matching and optimization of silver-coated copper powder and organic phase

- Study on the reliability of paste
  - PV module reliability
    - Type and amount of resin and solvent
    - Curing process matching
    - Paste stability analysis
    - Particle size distribution of powder
  - Infra-red (IR) from 1000-2000 nm
    - Type and amount of curing agent and auxiliary agent
    - Holographic interferometer

- Construction of powder and paste detection system
  - Process optimization
    - LF-NMR
    - Multi-reflection spectrometer
    - Multiple light scattering instrument
    - Laser particle size analyzer
R&D direction of low temperature paste

- **Develop paste with high conductivity**
  - Select suitable particle size range and thickness ratio of sheet powder and spherical powder to optimize the ratio.
  - Select suitable resin curing system, control shrinkage rate and optimize interface contact.
  - Selecting suitable additives and solvents, optimizing the formulation of carrier, and further increasing the content of conductive powder.

- **Develop ultrafine printing technology**
  - Design metal powder system, improve the ability of ultra-fine printing, reduce wet weight.
  - Select suitable high dispersion organic system to improve powder dispersion, avoid screen blocking, grid break.
  - Optimize the formula, help the paste pass through and back.

- **Develop paste with high welding tension**
  - Reduce the internal stress concentration: Reduce the defects after curing resin, add flexibilizers.
  - Improve weldability: Control solid content and add welding aid.
  - To improve the adhesion of TCO layer: Select appropriate resin, add coupling agent and other additives.

- **Develop low-cost technology**
  - Choose base metal powders instead, such as silver clad copper, silver clad alloy powder.
  - Select suitable surface coating system and develop matching organic system to improve dispersion and conductivity, reduce the loss of efficiency caused by base metal substitution.
  - Develop novel processes, optimize formulations, improve the reliability of base metal replacement technologies.

- **Compactness of paste and interface contact**
- **Printability**
- **Adhesive force and weldability**
- **Production cost of paste**
### Comprehensive properties

#### Third generation paste

<table>
<thead>
<tr>
<th>Category</th>
<th>HC639-ZX</th>
<th>HC649-H</th>
<th>HC689-H</th>
<th>HSC639-Z</th>
<th>HD689-G</th>
<th>HAC639-T</th>
<th>HAC689-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver content (%)</td>
<td>92-93</td>
<td>92-93</td>
<td>92-93</td>
<td>60-70</td>
<td>89-91</td>
<td>43-50</td>
<td>30-40</td>
</tr>
<tr>
<td>Volume resistivity (μΩ.cm)</td>
<td>6.0-7.0</td>
<td>5.0-6.0</td>
<td>5.5-6.5</td>
<td>8.0-9.5</td>
<td>5.0-6.0</td>
<td>7.0-8.5</td>
<td>7.5-9.0</td>
</tr>
<tr>
<td>Viscosity (Pa•s)</td>
<td>250-300</td>
<td>250-300</td>
<td>≥350</td>
<td>≥350</td>
<td>≥350</td>
<td>≥350</td>
<td>≥350</td>
</tr>
<tr>
<td>Printing speed (mm/s)</td>
<td>—</td>
<td>≥21</td>
<td>≥12</td>
<td>—</td>
<td>≥18</td>
<td>≥18</td>
<td>≥16</td>
</tr>
<tr>
<td>Pulling strength (N/mm)</td>
<td>≥2.0</td>
<td>—</td>
<td>—</td>
<td>≥2.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

#### Fourth generation paste

- Dual printing Busbar
- Dual printing Finger
- Dual printing Alloyed Busbar
- Dual printing Finger with low-cost model
- Dual printing Finger with silver-coated copper
- Dual printing Finger with silver-coated copper
Cost reduction roadmap of low temperature paste

Cost reduction of heterojunction paste

- Consumption
  - Further improve the tension, cooperate with the screen plate to reduce the weight by 10%-30%.
  - Busbar high tensile paste
  - Front ultra-fine line size, line width 18-22 μm. It is estimated that the weight can be reduced by another 10-20%. The back low-cost scheme can reduce weight by 20-30%.
  - Finger high performance paste
  - Reduce silver content of paste by 40%
- Base metal introduction
  - Introducing silver coated copper powder to partially replace silver powder
  - Reduce silver content of paste by 60%

The overall weight reduction is expected to be 20%-30%
Comprehensive cost reduced by 50-60%
High conductivity technology of low temperature pastes
## Difference between high and low temperature paste

**Different point:**

<table>
<thead>
<tr>
<th>High temperature front silver paste</th>
<th>Difference</th>
<th>Heterojunction paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>700-800°C</td>
<td>Temperature</td>
<td>170-200°C</td>
</tr>
<tr>
<td>Contact with $p$-$n$ junction, burn through anti - reflection layer</td>
<td>Contact theory</td>
<td>Not in direct contact with $p$-$n$ junction, but contact with TCO</td>
</tr>
<tr>
<td>Spherical silver powder, flake glass powder, organic component</td>
<td>Composition</td>
<td>Flake, spherical silver powder, organic component</td>
</tr>
<tr>
<td>mainly plays a printing role</td>
<td>Organic component</td>
<td>Printing and adhesion</td>
</tr>
</tbody>
</table>

- **Development situation:**
  - Start early, mature
  - Start late, developing
Conductive theory and Ohmic contact of low temperature paste:

- After baking, the solvent in the paste evaporates, the resin is crosslinked and solidified, and there is resin on the surface of the conductive powder, which cannot directly transfer electrons.
- Conduction theory: electron transmission mainly through seepage effect and tunneling effect.

Research content

- Study on ohmic contact mechanism between low temperature paste and TCO layer.
- Optimize conductive phase and organic phase, improve the densification of the paste after curing, enhance the contact, and reduce the bulk resistance and contact resistance through the nano size effect.
Part 4

Ultra-fine printing properties of low temperature paste
The new generation of front pure silver paste

### Series HC649
- **Solid content (%)**: 92-93
- **Screen opening (μm)**: ≥22
- **Printing speed (mm/s)**: 230-280

### Series HC689
- **Solid content (%)**: 92-93
- **Screen opening (μm)**: ≥12
- **Printing speed (mm/s)**: ≥350

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**Second generation front fine grid (in development)**

- 480/11 PI knotless/opening 17μm
- 520/11 PI knotless/opening 12μm
HC series paste matching metal stencil printing:

- **Full-open stencil** is made of stainless steel with high strength, wear resistance and corrosion resistance as the main material.

- **Full-open stencil** adopts advanced laser technology for full open cutting of stainless steel sheet, and adopts special process to treat the steel plate, so that its opening is smoother and flat, and the line type is better.

- At present, the fine grid printing with the width of 22-25μm can be achieved.
Laser transfer equipment uses a special scraper to press the heterojunction low-temperature paste into a special bearing film, and then uses a special laser head and its scanning transfer process, combined with a high-precision CCD system, to accurately transfer the paste from the bearing film to the silicon wafer.

At present, extremely fine grid line printing with width as low as 20μm has been achieved.
Welding tensile properties of low temperature paste
Pull-out failure form of low temperature pastes

- Interface failure between the welding tape and the paste
- Interface failure between paste and TCO layer
- Cohesive failure in paste
- Mixed failure (interface and cohesive failure)

The failure of paste itself is the ideal failure form, that is, 100% cohesive failure, because this failure can obtain the maximum bonding strength when the material is bonded.

Bonding failure occurs at the weakest point and may not always occur at the interface. This indicates that the bonding strength is not only related to the force between the paste, the welding tape and the TCO layer, but also to the intermolecular force of the polymer resin. The chemical structure and aggregation state of polymer molecules will greatly affect the bonding strength.
The internal stress of low temperature paste

Shrinkage stress
- Shrinkage stress caused by volume shrinkage due to volatilization, cooling and chemical reaction during paste curing.

Internal stress caused by aging
- During the aging process of the paste after curing, the internal stress is easy to occur at the main fine grid joints due to temperature change or water vapor.

Thermal stress
- The CET of the paste is different from that of the TCO layer and the welding strip, so the change of temperature will cause thermal stress.
The internal stress of low temperature paste

01. To copolymerize or increase the molecular weight of the polymer for lower concentration of functional groups in the system.

02. Adding toughening agent to reduce curing shrinkage stress.

03. Add inorganic additives to reduce internal stress.

04. The lower curing temperature is beneficial to reduce the thermal expansion stress, but may have an effect on the resistivity.

05. Adjust the CET of the paste, as close as possible to the TCO layer and welding tape.

06. In the selection of resin, use some better elastic resin to match the system.
## Low silver alloy busbar paste (in development)

<table>
<thead>
<tr>
<th></th>
<th>HC639-ZX</th>
<th>HSC639-Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver content (%)</td>
<td>92-93</td>
<td>70-75</td>
</tr>
<tr>
<td>Volume resistivity (μΩ.cm)</td>
<td>5.5-6.0</td>
<td>8.0-9.5</td>
</tr>
<tr>
<td>Busbar tension (N/mm)</td>
<td>≥2.2</td>
<td>≥2.2</td>
</tr>
</tbody>
</table>

- Preliminary test results: compared with the pure silver busbar paste, the **efficiency is equal**, and the tension of hand welding has no difference.
- Pilot and reliability tests are following.
- In this scheme **without copper** on busbar, the density of alloy powder is relatively low, and the wet weight decreases significantly.
Part 6

Study on low temperature silver coated copper paste
Core material - silver coated copper powder

**Current situation:**

- The main component of the plating solution is composed of silver nitrate solution. The electronegativity of copper is higher than that of silver, and a replacement reaction can occur. Free silver ions undergo a replacement and reduction reaction on the surface of copper powder to form silver coating.

- At present, most processes often use complexing agents to chelate free silver ions, increasing the complexing constant of silver ions and ensuring the stability of the plating solution during the metal coating process.

**Production process:**

At present, electroless plating technology can ensure the uniformity, coating rate and stability of the coating.
**Oxidation resistance:**

- After calcination at different temperatures, the characteristic peak of Cu weakens obviously or even disappears.
- There is no CuO characteristic peak in the silver-coated copper powder calcined at 200 ℃, indicating that the powder is not oxidized or the oxidation degree is very low.
- After calcination at 400 ℃ and 600 ℃, the (−111), (111) and (−202) crystal faces of CuO appear at 2θ of 35.5°, 38.7° and 48.7°, respectively.

**Characteristic:**

*Only can only be used in low temperature paste, high temperature silver layer will melt resulting in exposed copper.*

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*XRD pattern of silver-coated copper powder after calcination at different temperatures*

LIN Jiali ZHANG Ying; CAO Mei; GONG. Effect of calcination temperature on properties of electroless silver-plated copper particles Electroplating & Finishing. 2020(19):1348-1351
Silver coated copper finger paste

<table>
<thead>
<tr>
<th></th>
<th>HAC639-T (Currently import)</th>
<th>HAC689-T (Next import)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silver content (%)</strong></td>
<td>43-50</td>
<td>30-40</td>
</tr>
<tr>
<td><strong>Volume resistivity</strong> (μΩ.cm)</td>
<td>7.0-8.5</td>
<td>7.5-9.0</td>
</tr>
<tr>
<td><strong>Printing speed (mm/s)</strong></td>
<td>≥300</td>
<td>≥300</td>
</tr>
</tbody>
</table>

➢ The 50% silver coated copper fine grid paste has been used in several demonstration power stations with no abnormal power generation.

➢ 50% Ag silver coated copper fine grid paste has been mass produced.

➢ **Back 37% silver containing fine grid paste + Front 50% silver containing finger paste**, the efficiency is the same as that of sterling silver production line, and the metallization cost is greatly reduced.
Silver coated copper paste matching “No busbar" process

Heterojunction silver coated copper paste

Screen parameter matching
- Front screen
  - Knotless 24-30μm
  - 50% silver content
- Back screen
  - Knotless 24-30μm
  - 16mg/w

Paste consumption per watt (No busbar process)
- 16mg/w
  - 14-15mg/w
  - 1.3-14mg/w
  - 1.2mg/w

Printing speed matching
- 250mm/s
- 350mm/s
- 400mm/s

The cost of single wafer metallization is basically the same as that of PERC

Balancing screen opening and number of fingers
Thanks for you attention!

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