



# Effect of sub-micrometer sized silver particle on the performance of the front Ag paste for c-Si solar cells

Libin Mo<sup>a,\*</sup>, Yuyang Zhang<sup>a</sup>, Lei Zhao<sup>a,b</sup>, Chunlan Zhou<sup>a,b</sup>, Wenjing Wang<sup>a,b</sup>

<sup>a</sup> Key Laboratory of Solar Thermal Energy and Photovoltaic System, Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100190, China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China



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## ABSTRACT

Front side Ag pastes with different sub-micrometer silver particle contents for c-Si solar cells were prepared. The corresponding screen-printing performance, sintering behavior and electrical properties were investigated systematically. The results show that the Ag particle incorporation could improve the surface morphology and the densification of the Ag grids to achieve low resistivity. However, too much addition of the Ag particles may have a negative influence on the printing performance of Ag paste and result in a reduced aspect ratio of the Ag grids. Therefore, the content of Ag particles should be compromised for the solar cell to realize high conversion efficiency.

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## 1. Introduction

The front side electrode grid on crystalline silicon (c-Si) solar cells strongly influences the optical and electrical properties of the solar cells [1,2]. It acts as a contact with the Si and transports the photogenerated current [3]. Screen-printing technique is widely used for the grid fabrication, due to its simplicity, cost effectiveness and high throughput [4,5]. In general, series resistance ( $R_s$ ) will be low if the cross-sectional area of the front-side Ag grid is large, while the shading loss of solar cells will be reduced if the width of the front-side Ag grid is small [6]. Therefore, tall and narrow screen-printed Ag grid is required in order to simultaneously gain a low series resistance and a high short-circuit current. Thus, to realize such kind of Ag grid, Ag paste with good screen-printing property and conduction property after sintering is eagerly desired.

The Ag paste for screen-printing metallization usually consists of three components: glass frit, organic vehicle, and silver powder. Glass frit plays a role as binder phase to bind the Ag grid and the Si substrate. It is used to promote the sintering performance of Ag powders during firing process and etch the  $\text{SiN}_x\text{:H}$  layer [7]. The main role of organic vehicle is to make the Ag paste have a specific rheological behavior to meet requirements of the screen-printing

process [8]. In the screen-printing process, the Ag paste is forced through a screen mesh towards the substrate by applying some pressure with a squeegee and forms the pattern of the front side Ag grid for the solar cells [9]. So the Ag paste usually has a high viscosity in order to avoid spreading on or through the screen during pre- and post-printing steps and exhibits a shear-thinning behavior to allow the paste through the mesh apertures under the squeegee passage [10]. Hoeng et al. [11] found that cellulose nanofibers act as a thickener and stabilizer for the silver nanowires suspension which influence the rheology and the screen-printed property of the Ag paste. Silver powder serves as the conductive filler in the Ag paste, which is the most important factor to determine the conductivity of the silver grid directly [12]. Hilali et al. [13] reported that the size and the shape of Ag particles influenced the structure of the contact interface, quality of Ohmic contacts, and the solar cell performance, such as the open-circuit voltage ( $V_{oc}$ ) and the fill factor (FF). The flaky Ag powder can form dense contact surface and good interface structure with plenty of large Ag crystallites [14]. Furthermore, due to the size effect, Ag nanoparticles have higher conductivity and lower sintering temperature than its bulk counterpart. Therefore, Ag nanoparticles have attracted intensive research interests [15–18]. However, small Ag nanoparticles can penetrate across the Si emitter easily and induce detrimental current leakage [19,20]. Besides, Ag paste gradually becomes one of very costly components for c-Si solar cells with the decrease in the price of silicon wafers. Ag nanoparticles are even more expensive

\* Corresponding author.

E-mail address: [molibin@mail.iee.ac.cn](mailto:molibin@mail.iee.ac.cn) (L. Mo).

than the ordinary several micronized Ag powders. In this case, the size and content of Ag particles in the paste is worthy of careful study and optimization. Especially, the effect of incorporation of sub-micrometer sized Ag particles with both performance and cost merit into the silver paste is still lacking and worth systematical investigation. In this study, silver pastes with sub-micrometer sized Ag particles of different contents were prepared and utilized to fabricate the front side electrode grid on c-Si solar cell by screen printing. Via exploiting the screen-printing performance, sintering behavior and electrical properties of the final grid and solar cell, the effect of the Ag particle incorporation was revealed clearly.

## 2. Experimental

### 2.1. Preparation of the silver pastes

Silver powder was mixed with organic vehicle and glass frit by three roller grinding machine (LX200-EC) to prepare 3 pastes (A1, A2, A3) according to the recipes shown in Table 1. The solid content (silver powder and glass frit) of all the 3 pastes is 88 wt%. The content of organic vehicle and glass frit is 12% and 2%, respectively, which has been optimized for this study. The incorporation content of the Ag particles for A1, A2 and A3 is 0 wt%, 5 wt% and 10 wt%, respectively. Then they were printed on the multicrystalline silicon wafers (156 mm × 156 mm) by screen printing to make 3 series of c-Si solar cells labeled as SC1, SC2 and SC3, respectively. Each series contains at least tens of samples. The average performance was utilized to make comparison analysis.

### 2.2. Characterization

#### 2.2.1. Measurements of the Ag pastes

The morphology of Ag particles was observed by using scanning electron microscopy (SEM) (CARL ZEISS, SIGMA). The size distribution of Ag particles was calculated by image software (Image J). The viscosity was measured by viscometer (Brookfield DV2T) and the thixotropic behavior of Ag pastes was tested by rheometer (Anton Paar MCR302).

#### 2.2.2. Measurements of the Ag grids

The 3D morphologies of Ag grids were observed by 3D measuring Laser microscopy (Olympus OLS4000). The morphology of the surface and cross-sectional microstructure of the Ag grids were observed by using scanning electron microscopy (SEM) (CARL ZEISS, SIGMA). The size distribution of porosity in the Ag grids was calculated by image software (Image J). In order to observe the surfaces of the recrystallized Ag granules, the c-Si solar cells were processed by using hydrofluoric acid (HF) corrosion. The glass frit at the interface between the Ag grids and the Si emitter surface could be removed by such corrosion [21,22]. Then the Ag grids above the glass frit was peeled off by adhesive tape. Subsequently, the exposed interfaces were observed by SEM (CARL ZEISS, SIGMA).

#### 2.2.3. Measurements of the solar cells

The electrical performance of the solar cells was measured by AM1.5 sunlight simulator (Berger). The specific contact resistance

measurements were carried out by applying the transmission line (TLM) method at room temperature [23,24].

## 3. Results and discussion

### 3.1. The parameters of silver powders

Fig. 1 shows two kinds of Ag powder with difference sizes for preparing the Ag pastes. The size of the silver particles (Fig. 1(a)) concentrates mainly between 200 nm and 400 nm, and the shape is anomalous sphere. Fig. 1(b) shows the silver powders whose average particle size is about 1 μm, and the shape of the particles is spheroid. Therefore, the silver particles have bigger surface area than the spheroid silver particles with the same weight.

### 3.2. The influence of silver particles on the printing properties of the Ag pastes

Although the rheological behavior of Ag paste is mainly determined by organic vehicle, the shape and the size of Ag particles also affect the paste rheology and subsequently alter the densification behavior of the screen-printed grids [25]. Fig. 2 shows the rheological properties of the Ag pastes with different Ag nanoparticle contents. Fig. 2(a) shows the viscosity of the Ag pastes from low shear rate to high shear rate. Clearly, all the Ag pastes show the shear thinning behavior, indicating that such pastes belong to typical pseudoplastic fluids. Compared with the sample without silver particles, the viscosities of the Ag pastes with silver particles are higher at the low shear rate and lower at the high shear rate. With increasing the content of Ag particles, the viscosity of Ag pastes and a steep slope of the plot of viscosity vs. shear rate also increased. Particles with a higher surface area have higher viscosities while particles with lower surface have lower viscosities. Fig. 2(b) shows the thixotropy testing results of the Ag pastes, which are utilized to simulate the screen printing process. The table inserted in Fig. 2 (b) presents several characteristic ratios between the viscosities of the Ag pastes at some specific shear rates. A is the original viscosity of the Ag pastes. B is the paste viscosity when a large shearing stress is applied. C is the viscosity when the applied shearing stress is just taken off, and D is the final viscosity after recovery. The value of B/A reflects the shear thinning property of the Ag pastes. When the Ag pastes were printed through a screen mesh, the viscosity should rapidly decrease in a short period of time while the squeegee passes and applies a stress on the pastes. After the squeegee pass and the screen leave the substrate, the viscosity should rapidly increase so as to prevent from spreading and caving of the grids [4,26]. The value of C/A reflects the ability of the obtained grids to resist spreading. And the value of D/A reflects the shape preservation ability of the grids. The result shows that the thixotropic property of the Ag paste with the submicrometer-sized Ag particle addition is better than that of the Ag paste without the particles, including the abilities of shear thinning, spreading prevention and caving of grid and preserving shape of grids. In a word, adding submicrometer-sized Ag particles into the Ag paste has a beneficial effect on the rheological behavior of the Ag pastes for screen printing.

**Table 1**  
Experimental recipes of the front side Ag pastes.

| No. | organic vehicle/wt% | glass frit/wt% | silver powder/wt% | sub-micrometer sized silver particles/wt% |
|-----|---------------------|----------------|-------------------|---|
| A1  | 12                  | 2              | 86                | 0   |
| A2  | 12                  | 2              | 81                | 5   |
| A3  | 12                  | 2              | 76                | 10  |

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