



Effects of silver nanoparticles on the firing behavior of silver paste on crystalline silicon solar cells



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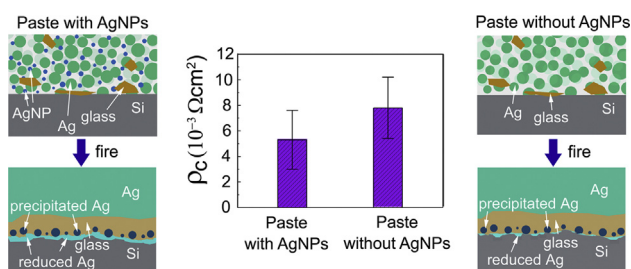
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HIGHLIGHTS

- Ag nanoparticles promote the firing of silver paste on c-Si solar cells.
- A continuous layer of Ag precipitates at the interface between glass frit and Si.
- Ag nanoparticles reduced the contact resistance of silver paste on c-Si solar cells.
- Firing mechanism of Ag nanoparticle-aided silver paste is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

We synthesized silver nanoparticles (AgNPs) with a diameter ranging from 300 to 800 nm by chemical reduction, added them into commercial silver paste used for the front-contact metallization of crystalline Si (c-Si) solar cells, and investigated the effects of AgNPs on the firing behavior of the silver paste on c-Si solar cells by differential scanning calorimetry, electron scanning microscopy, and contact resistance measurement. It was observed that surface sintering of AgNPs occurred at a lower temperature compared with that of micrometer-sized Ag particles in commercial silver paste. With the assistance of AgNPs, more Ag⁺ ions were dissolved in fluidized glass frit during the firing process of the paste, and a continuous layer of Ag was reduced and deposited between glass frit and Si substrate. The Ag layer enhanced electrical conduction and decreased the specific contact resistivity of the paste on c-Si solar cells. Thus, a firing mechanism of AgNP-aided silver paste was proposed. The experimental data demonstrate that AgNPs can be used to improve the properties of the fired paste on c-Si solar cells and AgNP-aided silver paste is a promising material used for the front-contact grids on c-Si solar cells.

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1. Introduction

Solar cell is one of the most important representatives for renewable energy and has recently surged tremendous research interests [1–4]. Crystalline silicon (c-Si) solar cells are the most

widely used photovoltaic (PV) cells and cover ~90% market share of the world total PV cell production [5]. Front-contact silver paste is a key material in high-efficiency c-Si solar cells because it is the essential channel conducting photocurrent. Additionally, silver paste has become one of the major components in the cost of solar cell production due to the rapid reduction of the price of silicon. Therefore, extensive research has been carried out to improve the performance of silver paste [6–11].

Traditional silver paste for front-contact metallization of c-Si solar cells contains Ag particles, glass frit powder, binders, and organics [6,7]. Silver particles are the major component of the paste

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and represent 70–90 wt.%, since silver has an excellent electrical conductivity [6,8,9]. Cho et al. and Ren et al. have studied the effects of forming gas and N_2/O_2 on front silver contact for c-Si solar cells, respectively [10,11]. Development and optimization of silver paste for high-ohmic emitters have also been carried out [12–14]. The formation mechanism of Ag contact during the firing process of silver paste has been studied [15,16]. Besides Ag powder, glass frit powder also plays an important role in the formation of electrical contact during the firing process of silver paste. Glass frit not only enables Ag particles to nucleate and move to the surface of silicon emitter, but also etches through the SiN_x layer during firing [5,15–18].

Recently, Ag nanoparticles (AgNPs) have attracted intense research interest and been used to aid the formation of silver contact because AgNPs have a lower sintering temperature than the bulk counterpart because of the size effect [19–28]. Cho et al. synthesized AgNP-aided silver front contact paste and achieved an increase of 0.7% for the efficiency of c-Si solar cells [22]. Park et al. have adopted AgNPs to increase the sheet resistivity of Pb-free silver paste [24]. However, the firing mechanism of AgNP-aided silver paste has not been studied systematically.

In this work, we prepared AgNP-aided silver paste, studied the sintering behavior of AgNPs in the paste, and investigated the effects of AgNPs on the interfacial reaction and specific contact resistivity between silver paste and c-Si solar cells. Based on the experimental data, a firing mechanism of AgNP-aided silver paste was proposed.

2. Experimental

AgNPs were synthesized according to our previously reported procedure [19]. Silver nitrate (Sinopharm Chemical Reagent Co., 99+%), ascorbic acid (Acros Organics, 99.7%), sodium polyacrylate (mol. wt. 8000, 45 wt.% solution in water, Sigma–Aldrich Chemical Co.), and triple distilled water (TDW) were used as silver precursor, reducing agent, surfactant, and solvent, respectively. In a typical experiment 1.25 g sodium polyacrylate, 1.2 g silver nitrate, and 1.02 g ascorbic acid were added to 150 g TDW sequentially, and the mixture was stirred using a magnetic stirrer at 20 °C for 30 min. The as-synthesized nanoparticles were centrifuged at 10,000 r.p.m. for 10 min and then washed six times with TDW before use. The diameters of AgNPs range from 300 to 800 nm, as shown in Fig. 1a. From the magnified image in Fig. 1b, it was observed that the AgNPs with a size of several hundreds of nanometers were formed actually due to the agglomeration of smaller AgNPs whose grain size was ~20 nm.

As-received commercial silver paste that contains Pb-based glass frit (Xian Nate Materials Co.) was used in this study. AgNPs were mixed with the silver paste homogeneously by ultrasonic dispersion. Silver pastes with and without AgNPs were screen-printed on p-type polycrystalline silicon solar cells with 80 nm thick SiN_x anti-reflection coating layer provided by Beijing Jiechen Shine Technology Development Co., Ltd. The printed pastes were baked in a convection oven at 150 °C for 10 min, and then fired in a muffle furnace at 300, 400, 650, or 800 °C for 10 min. The samples were taken out from the furnace and cooled down to room temperature after firing.

Thermophysical analysis was carried out by differential scanning calorimetry (DSC, STA 449 F3, NETZSCH) in air with a heating rate of 5 °C/min. The morphology at the interface between fired silver pastes and solar cells was observed with field-emission scanning electron microscopy (SEM, MERLIN VP Compact, ZEISS). The specific contact resistivity ρ_c was determined by transfer length method (TLM) measurement [10,29,30]. The electrical measurement was carried out on a four-probe station with a data logger

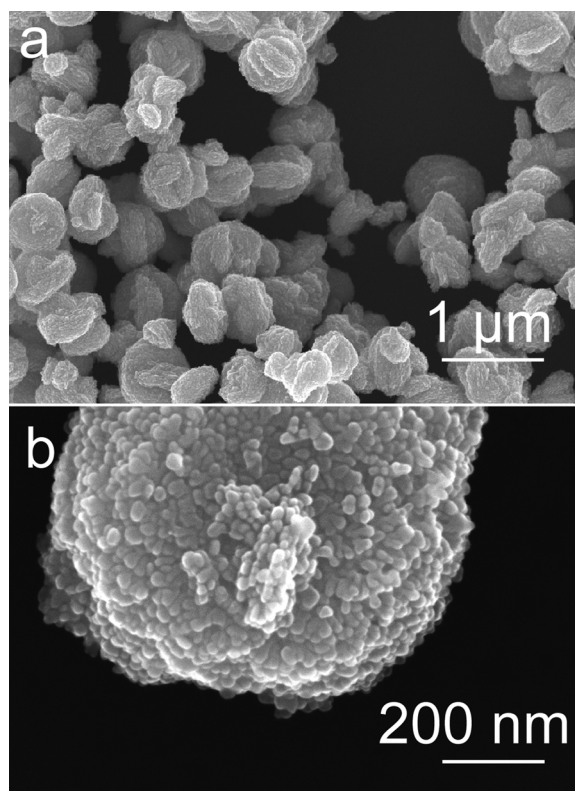


Fig. 1. (a) SEM image of synthesized AgNPs, and (b) magnified image of a silver nanoparticle.

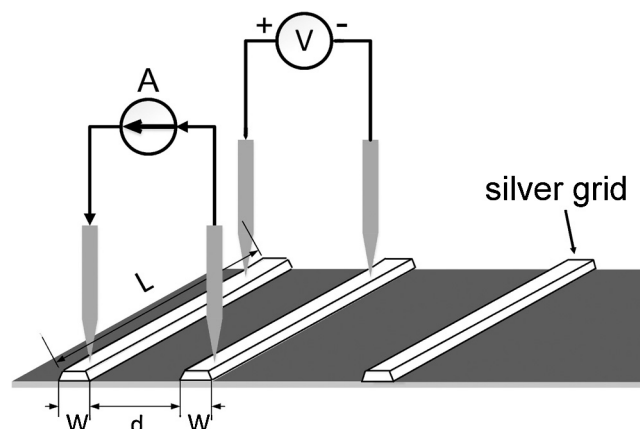


Fig. 2. Schematic of TLM method for contact resistivity measurement.

switch unit (34970A Date Acquisition, Agilent) and DC current source (6221, Keithley). The schematic of the ρ_c testing was displayed in Fig. 2. The width (W), length (L), and thickness of silver grid lines were 500, 9000, and 60 μm , respectively. The spacings (d) between the grid lines were 400, 800, 1200, 1600, and 2000 μm [10]. ρ_c was obtained by the following equation

$$\rho_c = \frac{A^2}{4B}L, \quad (1)$$

where A and B were the intercept and slope of the resistance-spacing curve, respectively [29,30].

3. Results and discussion

To investigate the sintering properties of AgNPs and silver paste, thermophysical analysis was carried out first. Fig. 3 summarizes the

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