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Bimodally dispersed silver paste for the metallization of a crystalline silicon solar cell using electrohydrodynamic jet printing

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ABSTRACT

Conventional silver paste for crystalline silicon solar cells exhibits low cell efficiency when deposited by non-contact electrohydrodynamic jet printing because of either high volumetric shrinkage or low packing density when there is no printing pressure applied to the silver paste. Therefore, we develop bimodally dispersed silver paste for electrohydrodynamic jet printing to resolve both volumetric shrinkage and packing density of the conventional silver paste, and its electrical and rheological traits are investigated. The bimodally dispersed silver paste exhibits lower unit-line resistance, which is inversely proportional to the weight ratio of small-to-large silver particles due to the increased packing density, and higher contact resistivity above a certain weight ratio for small-to-large silver particles. This behaviour results from the obstructed melt flow of glass frit by the early coarsened and densified small silver particles at an elevated temperature. The increased weight ratio of the small particles also raises the viscosity of the bimodally dispersed silver paste above the point where electrohydrodynamic jet printing is possible. By employing a binary solvent mixture and metallorganic silver as a viscosity reducing agent, the bimodally dispersed silver paste is tuned for electrohydrodynamic jet printing, and the front-side metallization of a polycrystalline silicon solar cell with the emitter sheet resistance of 60 Ω/sq is constructed. With the abnormally high aspect ratio of silver electrodes at 0.86, a cell efficiency of 16.72% is achieved, which is higher than that of screen-printed cells with the similar emitter sheet resistance by +0.22–0.52%p.

1. Introduction

The global market of crystalline silicon solar cells has demanded higher cell efficiency at a lower manufacturing cost because of the intensive pressure related to the severe manufacturing capacity surplus of crystalline silicon solar cells worldwide [1]. To reduce manufacturing cost, the thickness of crystalline silicon solar cell wafers has been reduced from 370 μm to 180 μm since 1997; the thickness is predicted to be less than 150 μm in the near future [2]. To employ thinner crystalline silicon solar cell wafers, various non-contact printing techniques such as aerosol jet printing [3,4], piezoelectric drop-on-demand (DOD) ink-jet printing [5–7], and dispensing printing [8–10] have been explored to replace the current screen-printing technique.

Aerosol jet printing utilizes a jet stream focused by a sheath gas from the concentric outer nozzle, and silver electrodes could be formed as fine as 14 μm in width [3]. However, the typical thickness of silver electrodes after the firing process does not exceed 2 μm [4], and a sophisticated additional process, *i.e.*, light induced plating, is required to thicken the silver electrodes [11]. One typical problem at occurs as a result of the light induced plating process is that the electroplated silver electrodes are not only thickened but also widened. In particular, the increase in the width is approximately two times the increase in the thickness of the silver electrodes.

Direct front-side metallization of the silver electrodes was demonstrated using piezoelectric DOD ink-jet printing. However, the use of silver nanoparticles, which are capped with a polymeric dispersant, induces high volumetric shrinkage during the firing process because of the high volume ratio of the dispersant to the silver nanoparticles. Consequently, poor contact formation between the silver electrodes and the emitter layer of the crystalline silicon solar cell leads to a low cell efficiency of 12.1% [7].

Dispensing printing has been the most successful non-contact printing technique because it does not require a sophisticated additional process to thicken the silver electrodes. Moreover, the achieved cell efficiency of a polycrystalline silicon solar cell was as

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high as 16.77% [8], which is not only comparable to that of a screen-printed cell but also the highest among directly metallized polycrystalline silicon solar cells produced using non-contact printing techniques. However, the issue of nozzle clogging in dispensing printing would be is a persistent problem because the construction of fine silver electrodes is strongly dependent on the nozzle diameter.

Electrohydrodynamic (EHD) jet printing has recently attracted attention as an alternative to the aforementioned non-contact printing techniques. It has a very unique ability to produce ultra-fine patterns with either an ultra-fine nozzle [12,13] or a large diameter nozzle [14]. Moreover, EHD jet printing can directly print fine conductive lines with an abnormally high aspect ratio [15]. Various sizes of silver particles can be employed unlike piezo-electric DOD ink-jet printing or dispensing printing because EHD jet printing can construct fine conductive lines with a large diameter nozzle. It can also employ moderately viscous silver paste, which is not possible with piezoelectric DOD ink-jet printing.

Despite all of these distinctive features of EHD jet printing, the cell efficiency of a polycrystalline silicon solar cell metallized with EHD jet printing remained as low as 13.7% when commercially available silver paste for screen-printing was used after dilution [15]. In contrast, the cell efficiency of a polycrystalline silicon solar cell metallized with screen-printing was 16.2% with the same silver paste. This discrepancy implies that the simple dilution of silver screen-printing paste is not effective for EHD jet printing in solar cell applications.

Therefore, this study primarily focuses on the development of silver paste for EHD jet printing in the front-side metallization of a crystalline silicon solar cell. With respect to the smooth flow of silver paste through the nozzle, the use of small silver particles is certainly beneficial, but it could also affect the sound contact formation between the silver electrodes and the emitter layer of a crystalline silicon solar cell. To evade the detrimental effects of small silver particles on the contact formation, we consider a bimodal dispersion of small and large silver particles, and the influence of the bimodal dispersion of silver particles on the electrical characteristics such as unit-line resistance and contact resistivity will be investigated. In addition, an effective means for controlling the viscosity of the bimodally dispersed silver paste for EHD jet printing without significantly altering the solid content of the paste will be introduced. Finally, the cell efficiency of a polycrystalline silicon solar cell metallized with EHD jet printing will be presented and compared with that of screen-printed cells.

2. Experimental

The in-house-developed bimodally dispersed silver paste for EHD jet printing was composed of (1) small (HP-0702, D50= 0.13–0.35 μm, Heesung Metal Ltd., Republic of Korea) and large silver particles (HP-0710, D50=0.9–1.4 μm, Heesung Metal Ltd., Republic of Korea), as shown in Fig. 1(a) and (b); (Fig. 2) glass frit (V2172, D50 ≈ 4.52 μm, Ceradyne Inc., USA), as shown in Fig. 1(c); (Fig. 3) a dispersant (Zephrym PD 2246 SF, Croda International Plc., UK); (4) an organic binder (ethyl cellulose, CAS No. 9004-57-3, Order No. 200646 for low molecular weight or order No. 200654 for high molecular weight, Sigma-Aldrich Corp., USA); (5) a carrier vehicle made with butyl carbitol acetate (BCA) (2-(2-butoxyethoxy) ethyl acetate, CAS No. 124-17-4, Samchun Pure Chemical Co., Ltd., Republic of Korea), xylene (*o*-xylene, CAS No. 95-47-6, SK Chemicals Co., Ltd., Republic of Korea) and/or α-terpineol (CAS No. 98-55-5, Kanto Chemical Co., Inc., Japan); and (6) metallorganic silver (CXSV060, Gelest Inc., USA) as an additive to adjust the viscosity of the bimodally dispersed silver paste.

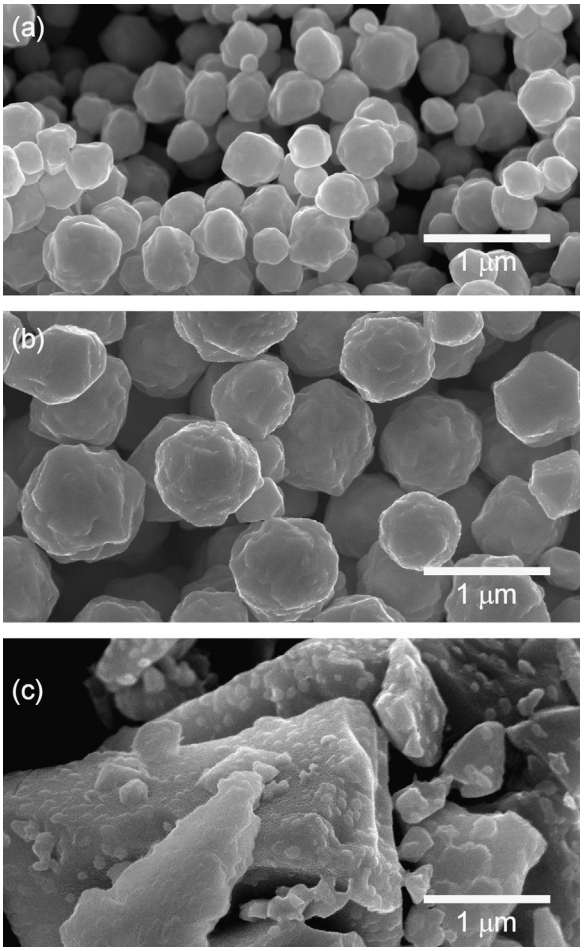

Fig. 1. Microscopic images of the used silver particles and glass frit: (a) small silver particles (HP-0702), (b) large silver particles (HP-0710), and (c) glass frit (V2172).

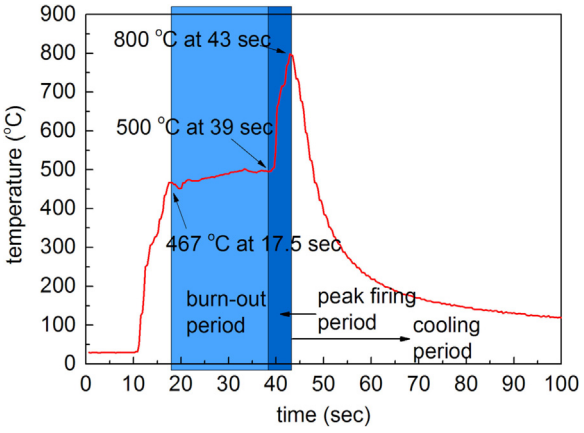

Fig. 2. The exemplary thermal profile used for the high-temperature firing process.

For the formulation of the bimodally dispersed silver paste, the organic binder, dispersant, and metallorganic silver were dissolved in the carrier vehicle, and the mixture was stirred overnight on a hot plate stirrer (DH.WMH03506, DAIHAN Scientific Co., Ltd., Republic of Korea) at the temperature and stirring speed of 70 °C and 700 rpm, respectively. Then, silver particles and as-received glass frit were pre-dispersed into the prepared carrier vehicle using a planetary centrifugal mixer (ARE-310, Thinky Corp., Japan). After removing the air bubbles in a vacuum desiccator (VDC-41U, Jeio Tech Co., Ltd., Republic of Korea) for 1 h, the bimodally dispersed silver paste was processed with a three-roll mill (EXAKT