Novel Ceramic Additives for Screen-Printable Silicon Solar Cell Metallization

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The interfacial structure between front-side silver electrodes and *n*-type silicon emitters plays a very crucial role for the electrical and mechanical properties of silicon solar cells. Studies show that the residual glass layers at the Ag/Si interfaces will significantly increase the contact resistance, and this subsequently leads to a decrease in the overall efficiency of the silicon solar cells. In this work, silver-coated nano-sized non-glass frits using an electroless plating method were employed to improve the interfacial conductivity. Transfer length method was applied to evaluate the electrical performance of the samples made with different ceramic additives. For samples made with nano-sized silver-coated ceramic additives, the improvement of conductivity was found to be about 22% compared to additives with the same compositions with no surface treatment. The results indicate that the silver layer on the surface of ceramic additives provides a conducting channel within the residual insulating layer and therefore reduces overall electrical resistance.

Key words: Nanoparticles, solar cells, electroless silver plating, TLM, interfacial structure, silver pastes

INTRODUCTION

Although there are other techniques such as photolithography and light-induced electroplating, which provide high quality silver electrodes, screen printing is still the most common technique used to form the front-side silver electrodes on silicon photovoltaic cells due to its cost- and time-effectiveness.^{1–4} Silver pastes used in screen printing primarily consist of three constituents including metal silver powders, micro-sized glass frits, and organic carriers. The purpose of adding glass frits is to etch through the Si₃N₄ anti-reflection coating (ARC) layer above the *n*-type silicon layers and then silver and *n*-type silicon layers can form electrical conductive channels. Glass frits can also assist with formation of stable mechanical contacts between silver electrodes and silicon layers. Formulation of glass frits must be precisely controlled in order to provide sufficient mechanical adhesion of silver

electrodes on silicon layers, while minimizing the internal stress that arises during the firing process and operation. High stress levels that have arisen from cells can lead to cracks and eventually fractures of the entire solar panel, and this issue is increasingly important while the solar photovoltaic (PV) industry is aggressively pushing the use of thin solar cells for cost reduction.^{5,6}

After firing steps at above 700°C, organic carriers are burned out and the residual glass constituents will form an electrically insulating layer at the interface between silver electrodes and the *n*-type silicon emitters, which results in high contact resistance at the Ag/Si interfaces and subsequently lowers the overall efficiency of the silicon photovoltaic cells. It is evident that the composition of the glass frits, as well as the process conditions, should be well controlled to achieve a thin, discontinuous residual glass layer.^{1–4} Nano-sized non-glass frits have been proven to effectively reduce the thickness of the discontinuous residual glass layer due to their excellent etching ability, and specific contact

resistivity between Ag/Si interfaces of the samples made with nano-sized ceramic additives is only about 40% of that of the samples made with micron-sized ones.³ Ceramic additives of smaller sizes possess larger surface areas, and therefore can achieve faster etching rates to remove the ARC layer with less material, which also reduces the firing duration and prevents the residual glass from experiencing accumulation at the Ag/Si interfaces. The silver electrodes remain porous after the firing process and thus provide an escape route for nitrogen produced from the firing process. If the nitrogen cannot escape from the interface, it will either form a bubble, or react with the residual ceramic components and form the glass layer, and either result will introduce extra resistance to the Ag/Si interfaces. Therefore, the use of nano-sized ceramic additives is beneficial in terms of electrical conductivity, which enhances the overall efficiency of the solar photovoltaic, and process duration, which reduces the cost and increases the production rate.

In this work, in order to further reduce the contact resistance at the Ag/Si interfaces, nano-sized ceramic additives with silver coating by the electroless plating method were employed to form the silver paste. Silver coating on the ceramic additives can prevent them from making direct contact with each other during and after the firing step. Even if a phase separation between the silver coating and ceramic substrates happens during the firing step, these two materials remain close to each other if the firing duration is very short. The electroless plating technique has attracted much attention in the semiconductor industries due to its low processing temperature, low overall cost, high coverage, and uniform coating.^{7–9} Moreover, electroless plating can deposit metals onto substrates with complex shapes and the process does not require a vacuum system. Coating coverage and thickness can be easily controlled by changing the processing parameters, such as activation time, plating duration, and pH value. Electroless silver plating has been well developed and applied to the deposition of metallic silver onto various substrates, such as micron-sized spheres and rods, nanoparticles, and glass substrate for microcontact.^{7–9} Different formulae were employed to investigate the effect of silver plating on the etching rate and the resultant specific contact resistivity. To avoid the complex interaction between different ceramic components at high firing temperatures, only Bi₂O₃, Al₂O₃, fused SiO₂, and ZnO were used in this work, and the firing conditions including firing temperature and duration were the same as in our previous study.³ In order to maintain the function of ceramic additives, parameters of electroless plating were controlled to obtain a partial coverage of silver coating on the ceramic substrates. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) were used to identify the silver deposition on the ceramic additives. Scanning electron microscopy

(SEM) was applied to investigate the Ag/Si interfaces, and the results were compared with the electrical performance acquired by the transfer length method (TLM).

EXPERIMENTAL

All four nano-sized ceramic components used in this work are commercially available from Alfa Aesar. Table I summarizes the composition of the different silver paste formulae used in this work. The following procedure was used for the preparation of silver pastes: first, the appropriate amounts of solvent and polymer medium were well mixed and aged at 40°C for 24 h. Silver powder, with an average size of 2 μm , was mixed with the above-discussed organic medium and ceramic additives in a Thinky (Thinky USA) mixer for 4 min, followed by a de-airing for 10 s. In order to ensure better mixing and to avoid agglomeration, the solid phase was added into the organic medium incrementally.

AgNO₃ (99.95%) was obtained from Salt Lake Metals. Ethylenediamine and 3,5-diiodotyrosine were obtained from Sigma-Aldrich. Rochelle salt (potassium sodium tartrate) was obtained from Mallinckrodt Chemicals. Hydrochloric acid (36%) and nitric acid was obtained from J.T. Baker. Stannous chloride dehydrate (SnCl₂·2H₂O) was obtained from Alfa Aesar. All of these chemicals were used as received. The following procedure was used to form the electroless plating solution. First, the silver ion solution (denoted as solution A) and reducing agent solution (denoted as solution B) were prepared separately. Solution A is an aqueous solution composed of AgNO₃ and ethylenediamine. Solution B is composed of Rochelle salt and 3,5-diiodotyrosine in another aqueous solution. The two solutions were well mixed to form the electroless plating solution right before the silver plating step. The activation solution is composed of stannous chloride dehydrate and hydrochloric acid.

The procedure is as follows: first, the ceramic additives were poured into the activation solution to form the seed layer on the particle surface. Once the activation duration finished, the colloid was washed by isopropyl alcohol (IPA) twice and then centrifuged at 3000 rpm for 15 min. Once the supernatant was removed, water was added to form an aqueous solution for the next step. Solution A and B, as described above, were then mixed and the solution with ceramic additives was poured into this mixture for silver plating. During the plating, the pH value was controlled to be between 10.0 and 10.9 by diluted nitric acid. After the plating ended, the same washing and centrifuging were performed twice. After removing the supernatant, IPA was added to form a solution. This solution was then placed in an oven at 85°C to remove the solvent. Table II summarizes the experimental parameters in the electroless plating step. The resultant powder was used to form the silver pastes described above.

The pastes were then screen-printed on 3 cm × 1 cm and 200- μ m-thick *n*-type (100) Cz Si wafers with an 80-nm-thick SiN_x ARC layer on the top. For each silver paste used, six samples were made for measurement. TLM measurement was used to determine the specific contact resistivity under dark conditions. The pattern for TLM measurements is shown in Fig. 1a. Figure 1b is the illustration showing the plotted TLM results for determining the specific contact resistivity of Ag electrodes. The specific contact resistivity (ρ_c) is obtained from extrapolating this linear plot of total resistance (R_T) versus the pattern grid spacing (d).¹⁰

$$\rho_c = R_c L_t W, \quad (1)$$

where R_c is the contact resistance, L_t is the transfer length, and W is the grid length.

The screen-printed wafers were then dried at 180°C for 15 min and then fired and sintered at 880°C. The sintered wafers were tested by Agilent 4156A to get the total resistance and the results were plotted according the TLM illustration shown above to determine the specific contact resistivity for these samples. Firing conditions and TLM results for different samples are summarized in Table III.

A transmission electron microscope (FEI/Philips CM-20 conventional TEM) and x-ray diffraction (Rigaku SmartLab x-ray Diffractometer) were used to identify the silver coating on ceramic additives. A scanning electron microscope (Philips XL-30 FEG

SEM) was used to investigate the microstructure at Ag/Si interfaces.

RESULTS AND DISCUSSION

Figure 2 shows TEM images of SiO₂ nanoparticles before and after electroless silver plating with a plating time of 10 min. In Fig. 2b there are small dots on the surface of SiO₂ substrates. Figure 3 shows the comparison between pure SiO₂ and SiO₂ powder after 30 min of electroless silver plating. The plating time is prolonged to enhance the signal of silver plating. From the XRD patterns, SiO₂ after plating shows signals of metallic silver. The peaks of AgCl indicate that there are residual chloride ions after the activation step. With TEM images and XRD patterns, silver coating on the surface of ceramic additives is confirmed.

The TLM results are summarized in Table III and Fig. 4 shows the boxplot of these results. Sample N-1 consists of pure ceramic additives without any silver plating and this sample shows the intermediate specific contact resistivity among all different samples. For sample NE-2 with all four ceramic additives coated, because the silver coating actually blocks the contact between the etching agents (Bi₂O₃ and ZnO) and the Si₃N₄ ARC layer, the etching rate of this paste is lowered and it takes a long time to remove the ARC layer and form the conducting channel at Ag/Si interfaces. Sample NE-1 shows the lowest specific contact resistivity among all three types of samples. Al₂O₃ and SiO₂

Table I. Composition (wt.%) of silver pastes for different samples

Sample code	Ceramic additives					Silver	Organic medium
	Bi ₂ O ₃ (140 nm)**	Al ₂ O ₃ (45 nm)**	SiO ₂ (80 nm)**	ZnO (70 nm)**	Total ceramics		
N-1	1.28	0.23	0.48	3.00	4.99	75.01	20
NE-1	1.28	0.23*	0.48*	3.00	4.99	75.01	20
NE-2	1.28*	0.23*	0.48*	3.00*	4.99	75.01	20

*With electroless silver plating. **Average particle size.

Table II. Composition and process conditions of activation and plating solutions for electroless silver plating

Activation solution		Plating bath	
Compound	Parameter	Compound	Parameter
SnCl ₂ ·2H ₂ O	2.1 × 10 ⁻¹ M	AgNO ₃	3.0 × 10 ⁻³ M
HCl (36%)	3.4 × 10 ⁻¹ M	Ethylenediamine	1.8 × 10 ⁻² M
		Rochelle salt	3.5 × 10 ⁻² M
		3,5-Diiodotyrosine	4.0 × 10 ⁻⁵ M
pH	9.5–10.2	pH	10.0–10.9
Temperature	50°C	Temperature	50°C
Bathing time	45 min	Bathing time	3–30 min

Fig. 1. The schematic graphs of (a) TLM pattern employed in this work. Here $a = 0.25$ cm, and (b) the generic TLM result for determining the specific contact resistivity.

Table III. TLM results for tested samples

Sample code	Total glass and oxide (wt.%)	Firing conditions	Average ρ_c (Ωcm^2)	Average R_c (Ω)
N-1	4.99	20 s/880°C	0.0140	2.19
NE-1	4.99	20 s/880°C	0.0109	1.70
NE-2	4.99	40 s/880°C	0.0221	3.45

Fig. 2. TEM images of SiO_2 nanoparticles used in this work: (a) pure SiO_2 and (b) SiO_2 powder with silver coating and 10-min plating time.

can enhance the adhesion between the Ag electrodes and *n*-type silicon layers, but they are not the major etching agents.³ Therefore, silver coating on the surface of these two additives does not affect the etching rate through the ARC layers.

Figure 5 shows SEM images for three different types of samples. For Fig. 5a and b, the images look very similar but the glass clusters in Fig. 5a are larger. The difference in the size of residual glass

clusters indicates that the silver coating on the surface of the ceramic compositions can ensure the formation of discontinuous residual glass clusters, as well as a discontinuous glass layer at the Ag/Si interfaces. Due to short firing duration, the pores and the large glass clusters near the interface can block the entire conducting route in the local section. Figure 5c shows a denser silver electrode because of the prolonged firing duration, which results in a longer time for the residual glass to accumulate at and cover most of the interface. However, because the silver electrode is denser and

Fig. 3. Comparison of XRD patterns between pure SiO_2 and silver-coated SiO_2 with 30-min plating time.

Fig. 4. Boxplot of TLM results for different tested samples. All tested samples have the same configuration as shown in Fig. 1a.

Fig. 5. SEM images of test samples made with (a) N-1, (b) NE-1, and (c) NE-2.

all ceramic additives are accompanied by silver coating, the resultant specific contact resistivity is not much lower than the other two.

CONCLUSION

Nano-sized ceramic additives incorporated with silver coating by electroless plating was tested and compared with pure ceramic additives in terms of electrical performance. The results indicate that the formula consisting of silver-coated ceramic additives, as long as they are not the major etching agent, shows improved specific contact resistivity. Since low specific contact resistivity of the silver metallization contact is the most desirable property and is strongly affected by the interfacial microstructure and firing conditions, silver pastes with surface-modified ceramic additives are proven to possess a high etching rate of ARC layers, and subsequently form a desirable interfacial microstructure, which results in the preferable low specific contact resistivity. It is evident that with lower specific contact resistivity, the overall efficiency of silicon photovoltaic cells will be higher under otherwise identical conditions. The results of this present study demonstrate the importance of surface modification for chemical reactions, and also

provide a new method for further enhancement in solar cell efficiency.

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