

Fire-Through Ag Contact Formation for Crystalline Si Solar Cells Using Single-Step Inkjet Printing

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Inkjet-printed Ag metallization is a promising method of forming front-side contacts on Si solar cells due to its non-contact printing nature and fine grid resolution. However, conventional Ag inks are unable to punch through the SiN_x anti-reflection coating (ARC) layer on emitter Si surfaces. In this study, a novel formulation of Ag ink is examined for the formation of fire-through contacts on a SiN_x -coated Si substrate using the single-step printing of Ag ink, followed by rapid thermal annealing at 800 °C. In order to formulate Ag inks with fire-through contact formation capabilities, a liquid etching agent was first formulated by dissolving metal nitrates in an organic solvent and then mixing the resulting solution with a commercial Ag nanoparticle ink at various volume ratios. During the firing process, the dissolved metal nitrates decomposed into metal oxides and acted in a similar manner to the glass frit contained in Ag pastes for screen-printed Ag metallization. The newly formulated ink with a 1 wt% loading ratio of metal oxides to Ag formed finely distributed Ag crystallites on the Si substrate after firing at 800 °C for 1 min.

Keywords: Fire-Through Contact, Inkjet Printing, Additives, Si Solar Cell.

1. INTRODUCTION

Inkjet printing is a promising alternative to screen printing for the fabrication of conductive lines on thin and fragile substrates due to its non-contact printing nature and printability of fine resolution patterns. It also offers simple processing without wasting materials. For these reasons, the inkjet printing technique has drawn increasing attention in the photovoltaic industry in an attempt to improve the performance and production yield of solar cells.¹ In order for the inkjet printing method to be cost-effective for the front-side Ag metallization of Si solar cells, Ag inks should be able to etch through the SiN_x ARC layer during the firing process. However, conventional Ag inks require prolonged annealing treatments (>5 min) at high temperatures above 850 °C to penetrate through the ARC layer and form an ohmic contact to the emitter Si.² In order to form ohmic contacts at temperatures below 850 °C using conventional Ag inks, the ARC layer should first be etched out, either lithographically or by printing an etching agent prior to the Ag inkjet printing.³ Since multiple processing is not cost effective, it is desirable to develop an Ag ink that is able

to punch through the ARC layer and form ohmic contacts on the emitter Si.

In order to achieve fire-through contacts on the emitter Si through the single-step printing of Ag inks and firing at temperatures below 850 °C, an etching agent, such as the glass frit contained in Ag pastes for screen printing, should be added to the Ag inks. There are two possible ways of incorporating glass frit into Ag inks: by either dispersion or dissolution. However, the former is limited by size effects such as flocculation,⁴ while the latter suffers from the problem of limited solubility of the metal oxides in the organic solvent of Ag inks.

In this paper, a novel method of formulating Ag inks that are capable of forming fire-through contacts for SiN_x -coated Si substrates using single-step printing is described. A liquid etching additive was first formulated by dissolving metal nitrates, which could decompose into metal oxides and form a molten glass during the firing process, in an organic solvent. The liquid additive was then mixed with an Ag nanoparticle ink. With variations in the relative ratio of the additive mixed with the Ag ink, the formation of Ag crystallites at the fire-through contact interface was examined after rapid thermal firing at 800 °C.

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2. EXPERIMENTAL PROCEDURE

2.1. Formulation of Ag Inks

The liquid additive, which enables the Ag ink to etch through the ARC layer during firing, was prepared by dissolving lead nitrate ($\text{Pb}(\text{NO}_3)_2$, Aldrich) and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Samchun Pure Chemical Co.) in 2 ml of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, Kanto Chemical Co.) at room temperature. The ratio of $\text{Pb}(\text{NO}_3)_2$ to $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was such that the weight ratio of PbO to ZnO was 90:10 (wt%) after the thermal decomposition of $\text{Pb}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.^{5,6} $\text{Pb}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were chosen because they are readily soluble in ethylene glycol at room temperature, and PbO and ZnO are common components of the glass frit contained in Ag pastes.

A commercial Ag ink (DGP-45HTG, ANP Co.), which contained 32.21 wt% of Ag nanoparticles with an average diameter of 40 nm in triethylene glycol monoethyl ether (TGME), was used as the Ag source. Different Ag ink mixtures were formulated by mixing the additive solution with the commercial Ag ink at various volume ratios, so that the weight ratio of (PbO + ZnO) to Ag during firing varied from 5:95 to 1:99. All Ag ink mixtures were stable without separation or sedimentation during storage at room temperature for months.

2.2. Inkjet Printing, Firing, and Characterization

The formulated Ag ink mixtures were printed in line patterns onto polished *n*-type Si wafers with an 80 nm thick SiN_x ARC layer using an electro-hydrodynamic inkjet printer. The printing was performed at room temperature with a nozzle diameter of 0.83 mm, forming lines with a width of 1 mm. After oven drying at 150 °C for 5 min, the printed samples were fired in a rapid thermal annealing (RTA) furnace under air ambient. For the firing process, the temperature was increased to 800 °C at a rate of 30 °C/s. After firing at 800 °C for various times of up to 60 s, the samples were cooled in the RTA furnace chamber.

The fired samples were metallographically polished to reveal the cross-sectional microstructure of the contacts. The reaction zones were examined using field emission scanning electron microscopy (FESEM) in conjunction with energy-dispersive X-ray spectrometry (EDX). The microstructural observations were made in the backscattered electron imaging mode and the compositional analyses were performed using the EDX operated at 15 keV.

3. RESULTS AND DISCUSSION

Before examining the fire-through reactions of the Ag ink mixtures, the reactions of the commercial Ag ink and the etching additive with the SiN_x -coated Si wafers were examined first. Figures 1(a and b) show the cross-sectional

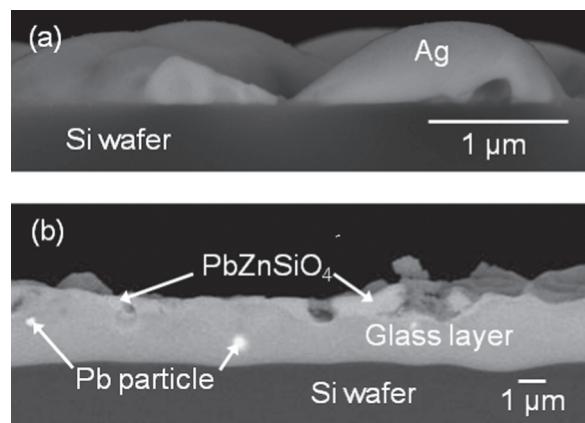


Fig. 1. Cross-sectional SEM images after the Ag nanoparticle ink and etching additive were separately inkjet-printed on the SiN_x -coated Si wafer and then fired at 800 °C for 60 s: (a) Ag nanoparticle ink and (b) etching additive.

SEM micrographs in the cases of the commercial Ag ink and the etching additive, respectively, after firing at 800 °C for 60 s. The flat interface without features between the sintered bulk Ag and the substrate, as shown in Figure 1(a), implies that there was no fire-through reaction between the commercial Ag ink and the SiN_x -coated Si. However, when only the etching additive was printed and fired, the interface between the residue of the etching additive and the substrate became widely corrugated, as shown in Figure 1(b), indicating that the additive etched through the SiN_x ARC and reacted with the Si wafer during the firing process. The EDX revealed that the additive residue contained a significant amount of Si, even though the etching additive did not initially contain Si. It is also noted in Figure 1(b) that pure Pb particles and a Zn-rich phase, as confirmed through the EDX, are present in the oxide residue.

In order to verify the phase state of the etching additive during the rapid thermal firing process, X-ray diffraction (XRD) measurements were performed for the residues obtained after firing the etching additives at 800 °C for 60 s and the results are shown in Figure 2. When the etching additive was fired on an alumina plate, the additive residue consisted of PbO (JCPDS 05-0570) and ZnO (JCPDS 36-1451), which resulted from the decomposition of the initially dissolved nitrates. Glass phases were not formed. However, when the etching additive was fired on the SiN_x -coated Si substrate, as shown in Figure 1(b), the residue was a mixture of glass and crystalline phases. The crystallite peaks were identified as PbZnSiO_4 (JCPDS 20-0607) and Pb (JCPDS 04-0686), which is in accordance with the observation in Figure 1(b). Therefore, it is clear that the nitrates initially dissolved in the etching additive subsequently decomposed into oxides and then reacted with SiN_x and Si to form a molten glass phase during the firing process. The Pb particles present in the glass matrix

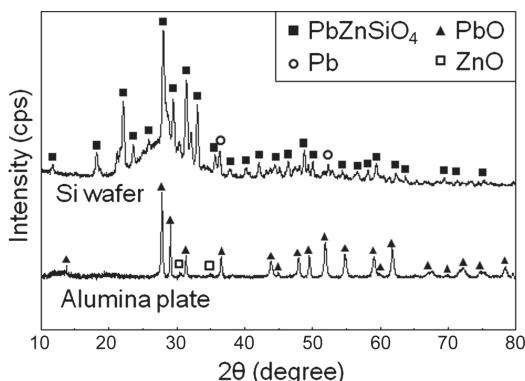


Fig. 2. XRD patterns of the additive residues obtained after firing the etching additive on the SiN_x -coated Si wafer and an alumina plate at 800 °C for 60 s.

most likely originate from a redox reaction between the PbO in the molten glass and the Si substrate.^{7,8}

Figure 3 shows the cross-sectional microstructures of the products obtained when the mixtures of the commercial Ag ink and the etching additive at various volume ratios were fired on the SiN_x -coated Si substrates at 800 °C for 60 s. It is interesting to note that the overall microstructures were similar to those typically observed in screen-printed Ag contacts, irrespective of the ratio of ($\text{PbO} + \text{ZnO}$) to Ag in the range from 5:95 to 1:99.^{9,10} This indicates that the additive plays a similar role to the glass frit contained in Ag paste during firing. A glass layer was present between the sintered bulk Ag and the Si substrate, which was revealed by the EDX to be composed of lead-silicate with a trace amount of Zn. As an indication of the fire-through of the SiN_x ARC, inverted pyramidal crystallites embedded onto the Si substrate were observed along with the particles distributed within the glass layer. The EDX revealed that both the crystallites and particles were composed of pure Ag. As expected, the thickness of the glass layer decreased with decreasing the amount of additive in the Ag ink mixture. Since a thinner glass layer between the Ag crystallites and the bulk Ag is more desirable for achieving good quality ohmic contacts,¹¹ it is particularly interesting that the addition of an amount of the additive resulting in as little as 1 wt% of $\text{PbO} + \text{ZnO}$ in the conventional Ag ink was sufficient to form fire-through Ag contacts to the Si substrate.

From the observations in Figures 1(b) and 3, it is clear that molten glass was readily formed during the rapid thermal firing process. Even when the Ag ink mixtures were spike-fired at a peak temperature of 800 °C, fine Ag crystallites were formed on the Si substrate. Based on the mechanism of the screen-printed contact formation,⁷ the presence of molten glass during firing is essential for the formation of Ag crystallites because it acts as a transport medium allowing the Ag to precipitate onto the emitter Si surface. The eutectic temperature of the PbO-ZnO system is ~850 °C, which is above the firing

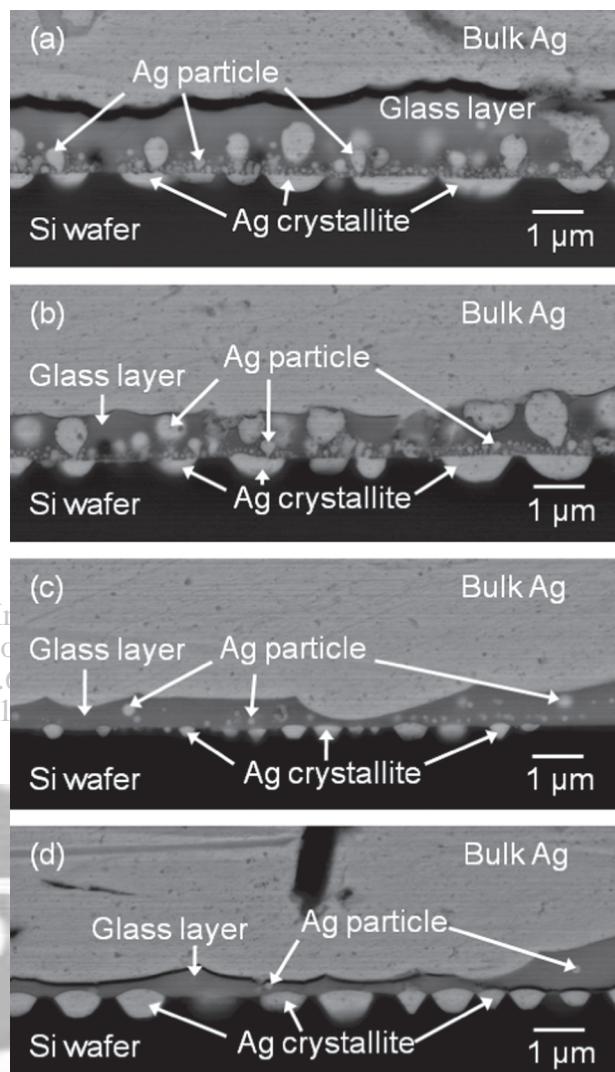


Fig. 3. Cross-sectional SEM images after the mixtures of the Ag nanoparticle ink and etching additive were inkjet-printed on the SiN_x -coated Si wafers and then fired at 800 °C for 60 s. The mixtures were formulated so that the weight ratios of $\text{PbO} + \text{ZnO}$ to Ag nanoparticles would be (a) 5:95, (b) 4:96, (c) 2:98, and (d) 1:99.

temperature, whereas the PbO-SiO_2 system has a eutectic temperature of approximately 700 °C.¹² The decomposition temperatures of $\text{Pb}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in the etching additive are known to be 455 °C and 145 °C, respectively.^{5,6} Therefore, during the rapid thermal firing after oven drying at 150 °C, $\text{Pb}(\text{NO}_3)_2$ is expected to decompose into PbO , NO_x and O_2 , and the decomposed PbO should react sequentially with SiN_x and Si to form a molten PbO-SiO_2 phase under the $\text{NO}_x + \text{O}_2$ atmosphere. The formation of the molten PbO-SiO_2 phase is in accordance with the observations in Figure 3.

Once the molten glass is formed, the glass wets the Si substrate and is expected to act in a similar manner to the lead-boro-silicate glass in the formation of screen-printed Ag contacts.^{7,9,10} In the absence of Ag, a part of

the PbO in the molten glass can react with the Si to form a liquid Pb phase via a redox reaction, as observed in Figures 1(b) and 2. However, when Ag is in contact with the molten glass, the redox reaction between the PbO in the glass and the Si is suppressed. Instead, Ag dissolves as Ag^+ ions into the molten glass under an oxidizing ambient and these Ag^+ ions react with the Si wafer to create inverted pyramidal pits on the Si surface.⁷ The Ag atoms reduced by the reaction with the Si substrate can precipitate as Ag particles in the molten glass during firing or as Ag crystallites in the inverted pyramidal pits during the subsequent cooling process, consequently resulting in the microstructure shown in Figure 3.

4. CONCLUSIONS

A novel method of formulating Ag inks was examined for the inkjet-printed front-side Ag metallization of Si solar cells using single-step printing followed by rapid thermal firing at 800 °C. In order for the Ag ink to be able to punch through the SiN_x ARC layer and form an electrical contact to the Si, a liquid etching additive was formulated by dissolving $\text{Pb}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in ethylene glycol and the additive was mixed with the conventional Ag nanoparticle ink. During the firing process, the dissolved nitrates decomposed into PbO and ZnO, and the decomposed PbO readily reacted with SiN_x and Si to form a molten PbO– SiO_2 glass. This molten glass acted in a similar manner to the lead-boro-silicate glass in the formation of screen-printed Ag contacts. The present results demonstrate that a contact microstructure similar to that of screen-printed contacts, exhibiting finely distributed Ag crystallites with a thin glass layer in between the bulk Ag and emitter Si, could be achieved through

single-step inkjet printing, followed by rapid thermal firing at a peak temperature below the Ag–Si eutectic temperature of 835 °C.

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