



## Effect of basicity of glass frits on electrical properties of Si solar cells

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### ABSTRACT

The purpose of this study is to understand the effects of the basicity parameter of glass frits added to the front contact of three-busbar Si solar cells on the removal of the anti-reflective coating (ARC) and the electrical characteristics of the cell. We investigated PbO-TeO<sub>2</sub>-SiO<sub>2</sub> glass systems by adding oxides to improve the etching of the interface between the Ag electrode and the Si wafer. The thermal properties and viscous flows of the frits were characterized using differential thermal analysis and a hot-stage microscope. The microstructure of the glass layer at the interface of the Ag electrode and Si wafer was observed using scanning electron microscopy and transmission electron microscopy. The results showed that the electrical properties were dependent on the morphology of the interfacial structure. The addition of oxides to the glass system produced more recrystallites on the n<sup>+</sup> emitter with a greater penetration depth in the Si wafer, thereby increasing the efficiency of the solar cell. The reactivity of the glass affected the removal of the ARC and the electrical properties of the Si solar cells were influenced by the charge transport facilitated by the Ag crystallites.

### 1. Introduction

Ag paste has been used in Cu<sub>2</sub>O solar cells and perovskite solar cells [1,2], and is commonly used to form contacts with the n<sup>+</sup> emitter in the front electrodes of Si solar cells. The addition of glass frits to Ag paste has important effects on the etching of the silicon nitride anti-reflective coating (ARC) layers as insulators and, thereby, on the Ag crystallite formation in the glass layer to accomplish electrical contact between the Ag electrode and the Si wafer [3–5]. The current conduction paths from the Si wafer to the Ag electrode are classified into different micro-contact types, depending on the manner of contact formation: (1) direct connections between the Ag electrode and Si [6,7], (2) current transport via Ag crystallites grown on the n<sup>+</sup> emitter [8], and (3) tunneling via hopping through metal granules (nano-metal colloids) precipitated in the glass layer [9,10]. Direct connections between the bulk Ag and Ag crystallites are considered the main path of current transport in such cells.

In order to achieve good Ohmic contact with the Si cell, a thin glass layer between the Ag electrode and Si wafer and uniform Ag recrystallization over the Si emitter surface are required. Previous studies regarding the influence of the front-contact microstructure in Si solar cells have focused on the effects of sheet resistances [11] and firing atmospheres during sintering. Li *et al.* [12] reported an evolution of Ag crystallite and Ag colloids in glass by microstructural comparisons with varied firing conditions to explain the current transport mechanisms.

Kim *et al.* [13] also proposed electron injection into the B emitter during the firing process to increase the Ag crystallite formation and decrease the contact resistance. The size of the glass frits is an important parameter affecting solar cell performance, as nanosized glass frits prevent residual glass from accumulating at the Ag/Si interface [14]. The density and distribution of Ag recrystallites and the thickness of the glass layer vary as a function of the viscous flows of the frits during fast firing [15,16].

The chemical composition of the glass frits affects the electrical performance during the etching of Si<sub>3</sub>N<sub>4</sub>, with or without an ARC layer. Watanabe *et al.* [17] reported that the basicity of the glass frit affected the removal of the ARC coating. Ag paste containing tellurite glass with a high basicity produces a low binding energy for reaction with Si<sub>3</sub>N<sub>4</sub>, resulting in a low-contact-resistance interface between the Ag electrode and Si wafer. Several studies have described the relationship between P doping and microstructural changes in solar cells [18,19]. It has been suggested that the doping profiles can increase recombination by inducing crystallite formations that deeply penetrate the Si, thereby improving device performance. However, no fundamental studies have investigated the relationship between the thermal and chemical properties of glass frits, the interface between the Ag electrodes and the Si wafer, and Si solar cell performance.

This study investigated the effects of adding oxides to the PbO-TeO<sub>2</sub>-SiO<sub>2</sub> glass system on the contact formation between Ag and Si, the corresponding contact resistance efficiency, and the performance of the

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Si solar cell. Glass frits with high basicity were designed to increase reactivity with  $\text{SiN}_x$ ; hence, this study focused on the effects of the microstructures and phases of the precipitates formed in the Si wafer on the cell performance. The vibration of recrystallites formed on and penetrating the  $n^+$  emitter was quantitatively measured, and the relationship between current conduction via the crystallites and the electrical properties of the solar cell was investigated. Our results showed that Ag crystallites formed on the emitter increased the number of current paths between the Ag electrodes and Si wafer.

## 2. Materials and methods

### 2.1. Fabrication and characterization of glass frits

The  $\text{PbO-TeO}_2\text{-SiO}_2\text{-Bi}_2\text{O}_3\text{-Li}_2\text{O-RO}$  system ( $R = \text{Na, Zn, or B}$ ) with various glass compositions was considered.  $\text{PbO}$  (99.9%; Sigma-Aldrich),  $\text{TeO}_2$  (99%, Sigma-Aldrich),  $\text{SiO}_2$  (99.5%; Sigma-Aldrich),  $\text{Bi}_2\text{O}_3$  (99.9%, Sigma-Aldrich),  $\text{Li}_2\text{CO}_3$  (99.0%; Sigma-Aldrich),  $\text{Na}_2\text{CO}_3$  (99.5%; Sigma-Aldrich),  $\text{ZnO}$  (99.9%; Sigma-Aldrich), and  $\text{H}_3\text{BO}_3$  (99.97%, Sigma-Aldrich) powders were weighed, mixed in the desired proportions using a mixer (Turbula T2 F, Glenmills Inc., Switzerland) for 30 min, and melted at 900 °C for 20 min in an  $\text{Al}_2\text{O}_3$  crucible. After the molten glass was quenched on a ribbon roller, the glass cullet was crushed to a powder with an agate mortar and pestle by hand and then ball-milled using a planetary mill (Pulverisette-7, Fritsch, Germany) for 10 min. The mean  $D_{50}$  particle size of the glass frits was 4–5  $\mu\text{m}$ . The amorphous state of the glass frits was characterized using X-ray diffraction (XRD; DMAX-2500, Rigaku, Japan) at 40 kV and 100 mA in the  $2\theta$  range between 5° and 80° at a scan speed of 1°/min with Cu K $\alpha$  radiation.

The glass transition temperature ( $T_g$ ) was determined using thermogravimetric differential thermal analysis (TG-DTA; STA409PC2, Netzsch, Germany) at a heating rate of 10 °C/min in air from 30 °C to 600 °C. The sintering behavior of the glass frits was analyzed using hot-stage microscopy (HSM; Misura, Expert System Solution Inc., Italy). The composition and thermal properties (Glass-transition temperature  $T_g$ , softening temperature  $T_s$ ) of the glass frits are summarized in Table 1. The design tool adopted in the current work was the basicity parameter of the oxide glasses, which permitted the prediction of the basicity of the resulting glass using the formula [17,20]:

$$\beta = \sum n_i \beta_i \quad (1)$$

where  $\beta$  is the basicity of the resultant glass, and  $n_i$  and  $\beta_i$  are the cation fraction and basicity parameter of the glass component  $i$  in the multi-component glass, respectively.

### 2.2. Cell fabrication and characterization

The Ag pastes were prepared by mixing 90 wt% Ag powder (Daejoo Co. Ltd., Korea), 8 wt% of an organic medium, and 2 wt% of each glass frit (glass matrix, 1L4N, 1L4Z, 1L4B) using a three-roll mill for 20 min. The organic medium consisted of ethyl cellulose, Texanol ( $\text{C}_{12}\text{H}_{24}\text{O}_3$ ), and DE acetate ( $\text{C}_8\text{H}_{16}\text{O}_4$ ). Crystalline Si solar cells were fabricated using the different Ag pastes (PTS, 4N, 4Z, 4B) with  $p$ -type

**Table 1**

The composition and thermal properties ( $T_g$ ,  $T_s$ ) of the glass frits.

Glass frits	Composition (mol%)								$T_g$ (°C)	$T_s$ (°C)
	PbO	TeO <sub>2</sub>	SiO <sub>2</sub>	Bi <sub>2</sub> O <sub>3</sub>	Li <sub>2</sub> O	Na <sub>2</sub> O	ZnO	B <sub>2</sub> O <sub>3</sub>		
glass matrix	52	30	15	4	–	–	–	–	245	553
1L4N	48	29	14	4	1	4	–	–	232	482
1L4Z	48	29	14	4	1	–	4	–	275	454
1L4B	48	29	14	4	1	–	–	4	244	407

$T_g$ : Glass-transition temperature,  $T_s$ , Softening temperature of glass.

**Table 2**

Basicity and I–V parameters of each cell with Ag pastes with different glass frit compositions.

Cell	Glass frit	Basicity	$V_{oc}$ (mV)	$I_{sc}$ (A)	FF (%)	$\eta$ (%)	$R_s$ (m $\Omega$ )
PTS	Glass matrix	0.72	638	8.97	63.83	15.28	14.21
4N	1L4N	0.78	639	8.97	74.58	17.89	7.99
4Z	1L4Z	0.72	629	7.17	18.22	3.45	110.41
4B	1L4B	0.69	635	9.03	49.67	11.92	21.56

monocrystalline commercial Si wafers (15.6 cm  $\times$  15.6 cm) with the sheet resistance of 95  $\Omega$ /sq. as emitters. The front Ag electrode and back Al electrode were screen-printed using the corresponding metallic pastes and then co-fired in a belt furnace at a peak firing temperature of 800 °C.

The electrical performance of the solar cells, as characterized by the open-circuit voltage ( $V_{oc}$ ), short-circuit current ( $I_{sc}$ ), fill factor ( $FF$ ), and efficiency ( $\eta$ ), were measured using a solar simulator (Oriol Sol3A, Newport Corp., USA), and is summarized in Table 2. A map of the contact resistance of the front side of the solar cell was determined using a Correscan instrument (SCRA 10 9001, SunLab, Netherlands). The cross-sections of the solar cells were characterized using high-resolution scanning electron microscopy (HR-SEM, SU 8010, Hitachi, Japan). The average thickness of the glass layer was determined by using five cross-sectional SEM images. For transmission electron microscopy (TEM) examinations, cross-sectional samples of the interfaces between the Ag electrodes and Si wafers were prepared by dual-beam focused ion beam milling (Nova 600, FEI's NanoLab, USA).

The phases of the recrystallites formed on the  $n^+$  emitter were examined using an energy dispersive X-ray spectroscopy (EDS) system integrated with the TEM (Talos F200X, FEI, USA). To observe the Ag crystallites on the  $n^+$  emitter of the Si solar cells and the shape of the pits, the Si wafers were cut to a size of 7 mm  $\times$  7 mm. These samples were firstly dipped into a 5% HF buffer solution for 2 min to remove the Ag electrodes and glass layer, followed by immersion in a 68%  $\text{HNO}_3$  solution for 3 min to selectively remove Ag crystallites grown inside the Si wafer. The surface microstructure below the glass layer between the Ag electrode and Si wafer was examined using SEM (S-4300, Hitachi, Japan). In order to analyze the number of Ag recrystallites and crystallite imprints (pits) quantitatively, we chose four images of each sample at different analysis positions. The average crystallite size, total crystallite area ( $A_{cryst}$ ), imprint area ( $A_{pit}$ ), and their distribution over each imaged area (the dimensions of each sample area were 10.65  $\mu\text{m}$   $\times$  7.25  $\mu\text{m}$ ) was calculated using image analysis software (Image-Pro Plus, Version 6.0, Media Cybernetics Inc., USA) and the selected SEM micrographs.

## 3. Results and discussion

The efficiency of the Si solar cells is proportional to the basicity parameter of the different glass frits used in the Ag pastes, and sample 4N shows the highest efficiency (Fig. 1a). This result verifies that the hypothesis of reacting with the  $\text{SiN}_x$  to increase the basicity parameter was valid. However, no significant correlation is observed between the

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