Effect of Pb-Te-Si-O glasses on Ag thick-film contact in crystalline silicon solar cells

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Abstract. In the paper, the influences of Pb-Te-Si-O (PTSO) glasses on Ag thick-film contact in crystalline silicon solar cells were investigated. Thermal properties of PTSO glasses and the dissolution process of Ag were studied. The formation of a new low-softening-temperature glassy-phase, induced by the crystallization of PTSO-1 glass, accelerated the dissolution of Ag at lower temperature. When silver paste was sintered, high-viscosity PTS-1 glass could flow to the surface of the cell and etch SiNx ARC layer at relative high temperature and the time for etching through SiNx ARC layer was shorter. Viscosity-temperature properties of PTSO glass has played a great role in the microstructures of contact finger and Ag/Si interface and have a great effect on the quality of Ag/Si contact and electrical properties of cells by affecting the sintering process of Ag, the etching behavior of interfacial glass with SiNx and Si, and the size and size distribution of Ag crystallites grown into the Si emitter at the position of inverted-pyramid etching pits.

Keywords: Pb-Te-Si-O glass; Ag paste; thick-film contact; solar cells.

1. Introduction

The front side metallization is usually achieved by screen printing and rapid thermal processing[1,2] and as a key process step in the fabrication of crystalline Si solar cells, it has a great effect on the optical and electrical properties of the cells. The solar cell front side is commonly metallized by silver (Ag) front side metallization pastes consisting of Ag powders, low-melting glass frit and an organic vehicle. In the metallization procedure, the glass frit melts could wet and dissolve the Ag powders at elevated temperature and generate a liquid glassy-phase, which would facilitate the sintering of Ag powders[3-8]. Additionally, the Ag-containing glass-phase would flow downward to the surface of the solar cell, etch through the anti-reflection layer, and thereby expose the emitter surface and establish electrical contact between the silicon and the silver contact[3,7-9].

Two models are helpful to interpret the Ag/Si interface conduction mechanism. The first model is based on the fact that Ag crystallites directly grow on the silicon emitter surface[10]. According to this model, the Ag crystallites have created a possible current transport paths from Si emitter to Ag finger[5,9]
by direct connection to Ag fingers and a multi-step tunneling process through the modified glass layer. Another model is based on the tunneling conduction mechanism, which has been established on the discovery of nano-Ag colloids (Ag precipitates) in the thin glass layer between Ag finger and Si emitter[11,12]. It is suggested that photoelectrons are extracted from Si emitter through a thin interfacial glass decorated with nano-Ag colloids.

The objective of this work is to achieve better understanding of the role of PTSO glasses in the metallization of crystalline silicon solar cells. To be specific, the influences of PTSO glasses on the sintering process of Ag, the etching behavior of interfacial glass with SiNx and Si, dissolution-precipitation process of Ag during the firing cycle, and their effects on the quality of silver screen-printed contact are studied.

2. Experimental procedures

2.1. Glass frits preparation and characterization

The compositions of Pb–Te–Si–O glasses are shown in Table 1. The glasses were prepared using the conventional melt-quenching method. Reagents grade oxides were mixed in appropriate proportions and melted in a platinum crucible at 1100°C for 30 min in an electric furnace. The melts were poured onto a copper plate. Subsequently, the obtained bulk glasses were milled into fine powders with D50 of 1-2 μm prior to further use. To verify the amorphous state of as-prepared samples, X-ray diffraction (XRD) analysis was carried out on as-prepared glass frits with a powder diffractometer (Bruker D8 advanced) using CuKα radiation (λ = 0.154 nm). The crystallization temperature (Tc) and peak liquefaction temperature (Tl) were determined by differential scanning calorimetry with a Netzsch STA-449 apparatus at a heating rate of 10 K/min.

The melt rheology of glasses was studied by controlled strain oscillatory measurements. The glasses were fabricated into disks (12mm diam.) for parallel-plate rheological experiments. Temperature sweep tests were applied to the glass disks using a controlled stress/rate rheometer (Anton Paar Physica MCR 302) equipped with a CTD-1000 temperature control unit and a disposable parallel-plate (12mm in diameter) system. The complex dynamic shear viscosity (η*) was measured as a function of temperature at a heating rate of 5 K/min, a frequency of 1 Hz and an amplitude of 0.1 %.

| Frit ID | PbO | TeO₂ | SiO₂ | Al₂O₃ | B₂O₃ | ZnO | MgO | Li₂O | Sum |
|--------|-----|------|------|-------|------|-----|-----|------|-----|
| PTSO-1 | 48  | 27.5 | 10   | 2.5   | -    | 7   | 3   | 2    | 100 |
| PTSO-2 | 48  | 25   | 16   | 2.5   | 2    | 6   | 0.5 | -    | 100 |

2.2. General paste preparation, printing and sintering

The silver powder is commercially available from Hunan National Silver Materials Co. Ltd. (Changsha, China). The surface of silver powder was encapsulated by oleic acid. The morphology of the powder is nearly spherical as determined by scanning electron microscopy (SEM). The specific surface area of silver powder is between 0.3 and 0.6 m2/g as determined by its BET value. The organic medium consists of ethyl cellulose resins, thixotropic and dispersing additives dispersed in Texanol.

The procedures for the preparation of PTSO glasses containing silver pastes include the following steps. First, the appropriate amounts of solvent, ethyl cellulose resins, thixotropic and dispersing additives were well mixed and aged at room temperature for 24 h. Silver powder was mixed with the above-mentioned organic medium and glass frits in an automatic Rev-Rot Gravity Mixer (SINO Science & technology, China) for 4 min. The ratio of Ag powder/PTSO glass frit/organic medium was 86.2/4.8/9.0 (wt. %). After mixing, the paste was repeatedly passed through a 3-roll mill at progressively decreasing gaps from 100 to 20 μm. The degree of dispersion was measured by fineness of grind (FOG). The FOG values were between 6/4 and 12/6 for our pastes.

The prepared pastes were screen-printed on multi-crystalline wafers with area of 156 × 156 mm², thickness of 200 μm, and sheet resistivity of 80 Ω/□. The screen-printed pattern was three-busbar “H”
grid patterns with 85 gridlines. An automatic screen printer was used. Back side Ag paste PV506 (DuPont) and aluminum paste RX8212E (Retech) were screen-printed onto the backside of wafers. Ag pastes screen-printed on wafers were fired in a rapid heating furnace at a belt speed of 225 inch/min using a setting peak furnace temperature of 900 °C.

2.3. Analytical methods for cells and Ag contact
The conversion efficiency of the cells fabricated was measured by commercial IV tester (Baccini, ITA). Open-circuit voltage (Voc), short-circuit current (Isc), fill factor (FF), series resistance (Rs), and efficiency (Eff) were calculated from the cell’s I-V curve. Microstructural characterization of the Ag contact and Si emitter interface was performed using high resolution scanning electron microscopy. To observe Ag crystallites at the interface, the samples were firstly soaked in HNO3 solution to dissolve away the bulk Ag, followed by buffered-HF etching that selectively removed residual interfacial glass.

3. Results and discussion

3.1. Pb-Te-Si-O glasses properties
As listed in Table 1, PTSO-1 glass shows little difference with PTOS-2 in the content of PbO, TeO2 and Al2O3, but has a higher content of Li2O and MgO. Fig. 1 shows the DSC curves of PTSO glasses at a heating rate of 20 K/min. It can be seen that due to the difference in glass composition, the thermal behavior of PTSO-1 glass shows great difference with PTOS-2. Especially, PTSO-1 glass appears higher tendency of crystallization than PTOS-2. Li+ and Mg2+ are extra-network ions of high field strength, and thereby also have the effect of attracting broken bonds when providing free oxygen to break up the network. Therefore, Li+ and Mg2+ in PTOS-1 glass can accumulate the glass network because of their high field strength, forming a large network structure and consequently cause high tendency of crystallization.

![Fig 1. DSC curves for Pb–Te–Si–O glasses](image1)

![Fig 2. The complex dynamic shear viscosity |\eta*(\omega)| of Pb–Te–Si–O glasses as a function of temperature](image2)

Fig. 1 depicts the complex dynamic shear viscosity, |\eta*(\omega)|, as a function of temperature. It is found that |\eta*(\omega)| of both PTSO glasses obviously decreases with the increase of temperature and |\eta*(\omega)| of PTSO-1 is much higher than that of PTOS-2 in the whole temperature range of measurement. In addition, different from PTOS-2 glass, PTSO-1 glass appears a viscosity increasing and stabilization process due to the crystallization of glass, and shows high-viscosity solid-liquid two phase state from the onset crystallization temperature (Tc,onset) of about 550 oC to high temperature of 830 oC.
3.2. The dissolution process of Ag in molten glasses

Fig 3. TG curves of the mixtures of Ag powder and PTSO glass frits with the ratio of 50/50 (wt. %) under air atmosphere

To investigate the dissolution process of Ag in PTSO glasses, the mixtures of Ag powder and PTSO glass frits with the ratio of 50/50 (wt. %) under air atmosphere were analyzed using TG measurement. TG curves of both PTSO glasses recorded at 20 °C/min were presented in Fig. 3. According to the TG curves of the mixtures, the mass loss of both samples from 200 to 400 °C is attributed to the burning-out of organic compounds coated on silver powder. Subsequently, the mixtures underwent a mass increment with increasing temperature. The mass increment during heating is correlated to Ag dissolution in glass melts as Ag2O according to equation (1)[4,13].

\[
4\text{Ag(bulk)} + O_2^{\text{glass}} \rightarrow 2\text{Ag}_2\text{O(in glass)}
\] (1)

In addition, in comparison with the mixture of Ag powder and PTSO-2 glass, a distinct rapid mass increment occurring at about 500°C was found in the mixture of Ag powder and PTSO-1 glass which was most likely attributed to the formation of a new liquid low-melting point glassy-phase induced by the crystallization of glass and its higher reaction rate with Ag powder. However, when the crystalline phase crystallized from PTSO-1 began fusing into glass-phase at high temperature, the saturated solubility of Ag gradually decreased with the increase of temperature and the Ag dissolved was re-precipitated. Therefore, the mixture of Ag powder and PTSO-1 glass underwent a mass decrement at high temperature.

At the same condition, the saturated solubility of Ag in PTOS glass is solely correlated with the composition of glass and can hardly be reached during the rapid thermal processing. In addition, during thermal processing, the densification of Ag powder and the flow behavior of liquid glass-phase downward to the interface of Ag/Si will cause the Ag/glass contact to decrease and retard the subsequent dissolution process of Ag. Therefore, in compared with high saturated solubility of Ag in glass, the distinct rapid dissolution behavior of Ag at relative low temperature is more beneficial to raise the amount of Ag dissolved in interfacial glass layer due to the rapid decrease of Ag/glass contact caused by Ag sintering densification at high temperature as well as the separation of Ag from the flowing glass during heating procedure.

3.3. Characterization of Ag thick-film contact

The measured IV-parameters of cells fabricated at peak temperature of 790 °C using with PTSO glass containing Ag pastes are shown in Table 2. The result indicates that the Voc, Isc, Rs, Rsh, FF, and η of the cell fabricated using Ag paste with PTSO-2 glass is worse than the cell with PTSO-1 glass. To
understand the major reason responsible for the resulting electrical properties of the cells, microstructures of Ag contact and Si emitter interface must be revealed.

Table 2. IV-parameters of cells metallized by Pb–Te–Si–O glass containing paste

| FritID | Uoc (V) | Isc (A) | Rs (Ω) | Rsh (Ω) | FF (%) | η (%) |
|--------|---------|---------|--------|---------|--------|-------|
| PTSO-1 | 0.629   | 8.653   | 0.0028 | 90.2    | 79.05  | 17.68 |
| PTSO-2 | 0.606   | 5.401   | 0.0158 | 134.8   | 64.98  | 14.45 |

Fig. 4(a) and 4(b) show microstructures of contact fingers fabricated using PTSO-1 and PTSO-2 containing pastes, respectively. Contact fingers fabricated using PTSO-1 containing paste were densified after firing with some pores in Ag matrix. However, there is almost no pore existing in Ag fingers fabricated using PTSO-2 containing paste and the fingers are only composed by Ag matrix and trapped glass phase. It is acknowledged that low-viscosity PTSO-2 glass is expected to have a greater role in facilitating the sintering of Ag powder in compared with PTSO-1, so the densification rate of Ag finger fabricated using PTSO-2 containing paste is much higher. The rapid densification of Ag finger caused the continuous pore channels between Ag powders closed earlier and thereby the gas near the interface of Ag/Si could hardly be eliminated through the continuous pore channels. For this reason, there is a quasi-continuous interfacial glass layer together with less pores existing at Ag/Si interface of the cell metallized using PTSO-1 containing paste and the interfacial glass layer of the cell metallized using PTSO-2 containing paste was discontinuous with many pores at Ag/Si interface. The pores at Ag/Si interface hindered the direct contact of Ag/Si and caused the increase of contact resistance and series resistance of the cell.

In order to observe Ag grains in contact fingers after firing, the samples prepared for characterizing the microstructure of contact fingers were treated using Potassium dichromate solution. Top-view and cross-sectional SEM images of treated Ag fingers fabricated using PTSO-1 and PTSO-2 containing paste were illustrated in Fig. 5(a) and 5(b), respectively. It can be observed that Ag grains in contact fingers fabricated using PTSO-2 containing paste is much larger than that in contact fingers fabricated using PTSO-1 containing paste. It is because the diffusion rate of Ag in low-viscosity PTSO-2 glass is
relative higher in compared with high-viscosity PTSO-1 glass and hence Ag grains in contact fingers fabricated using PTSO-2 containing paste coarsened quickly during firing via Ostwald ripening mechanism. Additionally, after treatment, the glass phase trapped in Ag matrix was etched off completely and exposing many isolated pores in contact finger. The pores in contact fingers fabricated using PTSO-2 containing paste are less but larger due to the rapid densification of Ag finger together with the combination of trapped glass phase which can hardly transported to the interface of Ag/Si through isolated pore channels.

Fig 5. Top-view and cross-sectional SEM image of treated Ag finger fabricated using with PTSO-1 (a) containing paste and PTSO-2 (b) containing paste.

Fig 6. SEM images of Ag crystallites: the cell metallized by PTSO-1 (a) containing paste and the cell metallized by PTSO-2 (b) containing paste.

The aforementioned HNO3/HF etching technique was used to expose the surface of the emitter. Numerous SEM top-view images have shown that Ag crystallites were grown all over Ag/Si interface.
(Fig. 6(a) and 6(b)), indicating a complete etching of SiNx:H antireflective (ARC) layer (~70 nm thick) though the redox reaction (2) [4]. However, Ag crystallites attached to the silicon surface of the cells were found to be different in cells metallized by paste with different PTSO glasses. In contrast with PTSO-1, the cells metallized by PTSO-1 containing paste show more and larger Ag crystallites grown at the surface of the emitter. It is acknowledged that nucleation and epitaxial regrowth of Ag crystallites is at the position of etching pits from the dissolved Ag atoms [5, 10]. So this result verified the excessive silicon etching with noticeable emitter damage to same degree and is in accord with abnormally low Voc and Rsh parameters as shown in Table 2. It is because after the etching of the SiNx:H antireflective layer, the silver and oxygen ions in the fluidized glass modified by reaction product SiO2 from the reaction (2) will diffuse toward the glass/Si interface and etch the Si wafer via the reaction (3). The reaction rate is highly dependent on the ion diffusion velocities in interfacial glass. Therefore, PTSO-2 with higher high-temperature viscosity and ion diffusion velocities, has the enhanced glass etching reaction ability at the glass/Si interface. The enhanced etching of the Si wafer caused the formation of many larger-sized pits on the Si surface during the firing process, which in turn resulted in the formation of many larger-sized Ag crystallites at the glass/Si interface during the subsequent cooling process.

\[
2\text{Ag}_2\text{O} \text{(in glass)} + \text{SiN}_x \rightarrow 4\text{Ag} + \text{SiO}_2 \text{(in glass)} + \frac{2}{3}N_2 \tag{2}
\]

\[
\text{Ag}_2\text{O} \text{(in glass)} + \text{Si} \rightarrow \text{Ag} + \text{SiO}_2 \text{(in glass)} \tag{3}
\]

In conclusion, the microstructure of contact fingers and the interface of Ag/Si is highly related with PTSO glass properties. PTSO glass has a great effect on the sintering process of Ag powder, the transportation of glass phase to Ag/Si interface and the etching reaction with ARC layer and Si emitter, and thereby influences the quality of Ag/Si contact and electrical properties of cells.

4. Conclusion
The formation of a new low-softening-temperature glassy-phase, induced by the crystallization of glass, can accelerate the dissolution of Ag at lower temperature. When silver paste is sintered, high-viscosity glass flow to the surface of the cell and etch SiNx ARC layer at relative high temperature and the time for etching through SiNx ARC layer is shorter. Viscosity-temperature properties of PTSO glass play a great role in the microstructures of contact finger and Ag/Si interface and have a great effect on the quality of Ag/Si contact and electrical properties of cells by affecting the sintering process of Ag, the etching behavior of interfacial glass with SiNx and Si and the size and size distribution of Ag crystallites grown into the Si emitter at the position of inverted-pyramid etching pits.

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