Application of Te-Based Glass in Silicon Solar Cells

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Abstract $(90-x)\text{TeO}_2-x\text{ZnO}-10\text{Bi}_2\text{O}_3$ ($x = 15, 17.5, 20$ and 22.5 , in mol%) and $70\text{TeO}_2-20\text{ZnO}-(10-y)\text{Bi}_2\text{O}_3-y\text{Na}_2\text{O}$ ($y = 1, 3, 5, 7$, and 10 , in mol%) glasses, and the corresponding Ag paste were prepared in order to prove that the Te-based glass frit could be applied to Ag pastes to fabricate Ag electrode. The relationship between structure and properties of the glasses was analyzed. The effects of glass frit on the microstructure, adhesion force, and resistivity of the Ag electrode were studied. The microstructure of Ag electrodes and the phase analysis of interface between Ag electrodes and the Si wafer were investigated using SEM and XRD. Finally, the $70\text{TeO}_2-20\text{ZnO}-5\text{Bi}_2\text{O}_3-5\text{Na}_2\text{O}$ glass showed better performance in the paste. What is more, Ag crystallites could be found on the Si wafer. These results suggested that the Te-based glass frit could react with SiN_x anti-reflecting coating and Si to serve as a medium for forming Ag crystallites.

KEY WORDS: Solar cells; Ag electrode; Silver paste; Tellurite glass; Ag crystallites

1 Introduction

In the preparation of single-crystalline or polycrystalline Si solar cells, Ag electrode is formed on the front side with a SiN_x anti-reflecting coating (ARC) for stable ohmic contact. The Ag electrode is commonly fabricated by screen-printing using silver paste which consists of Ag powder, glass frit, and organic vehicle [1–3]. Although as an inorganic binder, glass frit only holds 2%–5% in mass, it plays a crucial role in the front-side metallization contact

formation and achieving current paths between Ag electrode and Si wafer. Through etching the SiN_x coating and allowing the formation of Ag crystallites grown into the silicon emitter during the firing process, glass frit not only determines the adhesion strength of Ag electrode to Si wafer, but also determines the final resistance of the electrode [4, 5]. In general, a dense population of fine Ag crystallites at the Ag–Si interface is desirable for improving the quality of the ohmic contacts with the Si emitters [6, 7]. Therefore, it is necessary to choose the appropriate glass system and gain more insight into the mechanism for Ag crystallite formation.

At present, the industrial glass frit for front-side silver paste is almost Pb-based glass which has excellent electrical and mechanical properties. Schubert et al. [8] proposed a growth model of Ag crystallites in the PbO-containing Ag paste, which has been the basic understanding of the Ag electrode formation mechanism. However, since lead exposure and pollution are detrimental to human health and environment, it is necessary to take more emphases on the research and application of

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the lead-free silver paste. In previous studies, the use of Bi-based glass frit in Ag paste has been reported [9, 10]. Kim *et al.* [11] reported that Bi_2O_3 can participate in the reactions with SiN_x coating or Si wafer, which serves as a seed for the Ag dissolved in the glass to crystallization. Che *et al.* [12] prepared the Bi–Si–B–Al–Zn–O glass frit with glass transition temperature of 385 °C by traditional melting rout. The wetting behavior and etching effect of glass frit on SiN_x ARC and silicon were efficient. While the thermal and mechanical properties of Bi-based glass frit are still needed to be optimized. The tellurite glass has been widely used for optical applications [13]. It has a stable performance and a low glass transition temperature which would be a potential material for Ag paste [14]. For example, Vitreous domain phase diagram for the TeO_2 – Bi_2O_3 – ZnO system has been given by Massera *et al.* and the glasses were used in optical applications [15]. However, Te-based glass frit as an inorganic binder for Ag electrodes in Si solar cells has not been studied so far. And there has been no experiment conducted to investigate how Te-based glass frit affects contact formation between Ag and Si.

In this paper, $(90-x)\text{TeO}_2$ – $x\text{ZnO}$ – $10\text{Bi}_2\text{O}_3$ glasses were prepared according to the vitreous domain phase diagram and the Na_2O was added to decrease the glass transition temperature. Finally, the 70TeO_2 – 20ZnO – $(10-y)\text{Bi}_2\text{O}_3$ – $y\text{Na}_2\text{O}$ glasses were used in Ag pastes. The relationship between structure and properties of the glass was analyzed. The effect of glass frit on the microstructure, adhesion force, and resistivity of the Ag electrode was investigated. And the phases of crystallites formed on the Si wafer were studied. Overall, the aim of these experiments is to verify that the as-prepared eco-friendly Te-based glass system could be applied to Ag pastes.

2 Experimental

The glass frit was prepared by traditional melting route at 800–850 °C for 20 min in an alumina crucible, the reagent grade TeO_2 , ZnO , Bi_2O_3 , and Na_2O were employed as raw materials. The glass transition temperature (T_g) and crystallization temperature (T_c) were determined using a differential scanning calorimeter (DSC, NETZSCH, STA449F3) at the heating rate of 10 °C min^{-1} . The glass softening temperature (T_f) and thermal expansion coefficient (α) were measured by a thermo-analyzer (TMA, SETARAM, TMA-16/18). The chemical durability of the glasses was evaluated by dissolution rate (DR) in distilled water at 90 °C for 24 h. The crystal structures of the prepared glass frit was investigated by XRD with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The infrared spectra were recorded with an FTIR spectrometer (Nicolet NEXU

S670). The Raman spectra were obtained with a Raman spectrometer (Labram HR, $\lambda = 514 \text{ nm}$).

The Ag paste consisted of 67 wt% Ag power, 3 wt% glass frit, and 30 wt% organic vehicle. The organic vehicle consisted of ethylcellulose, terpinol, and few additives. The formulated paste was screen-printed through a nylon mesh on Si substrates with SiN_x coating. After oven drying at 190 °C for 10 min, the printed paste was fired in a tube furnace at 800 °C for 10 min to obtain the Ag electrode. The surface and cross-sectional microstructures of the electrode were investigated by SEM (Philips, XL30). The adhesion force and resistivity of electrode were measured by peel force tester and resistivity tester of four-point probe technique. When the Ag bulk and glass layers were removed selectively using HNO_3 and HF solutions, the phases of crystallites formed on the Si wafer were examined using XRD. Tables 1 and 2 present the physico-chemical properties of the $(90-x)\text{TeO}_2$ – $x\text{ZnO}$ – $10\text{Bi}_2\text{O}_3$ and 70TeO_2 – 20ZnO – $(10-y)\text{Bi}_2\text{O}_3$ – $y\text{Na}_2\text{O}$ glass and the adhesion force and resistivity of the corresponding Ag electrodes, respectively.

3 Results and Discussion

3.1 Structures and Properties of $(90-x)\text{TeO}_2$ – $x\text{ZnO}$ – $10\text{Bi}_2\text{O}_3$ Glasses

The infrared spectra of the $(90-x)\text{TeO}_2$ – $x\text{ZnO}$ – $10\text{Bi}_2\text{O}_3$ glasses are given in Fig. 1, where x is 15, 17.5, 20 and 22.5 mol%. The broad band at 655 cm^{-1} belongs to the stretching vibration of axial Te–O bonds (Te-O_{ax}) in the TeO_4 tbp [16]. The band at 740 – 757 cm^{-1} could be ascribed to the stretching vibration of equatorial Te–O bonds (Te-O_{eq}) in the TeO_3 tp, which moves to higher frequency a little when ZnO content in the glass is from 15 to 22.5 wt% [13]. It indicates that some TeO_4 tbp structure units are transformed into TeO_3 tp, which weakens the network structure of tellurite glass. Thus, the changes of properties shown in the Table 1 can be explained reasonably. As the ZnO content in the glass increases, the chemical durability and glass softening temperature decrease, while the thermal expansion coefficient increases, which is attributed to the weakening of the network structure.

Figure 2 shows DTA curves of the $(90-x)\text{TeO}_2$ – $x\text{ZnO}$ – $10\text{Bi}_2\text{O}_3$ glasses. When x is 15, 17.5, and 22.5, the corresponding glasses have two crystallization peaks. However, when $x = 20$, there is only one crystallization peak. The data of crystallization temperature can be seen in Table 1. The thermal stability is represented by temperature difference ($\Delta T = T_{c1} - T_g$). The greater the temperature difference, the better the thermal stability is. Since ΔT appears

Table 1 Physicochemical properties of the $(90 - x)\text{TeO}_2\text{-}x\text{ZnO-}10\text{Bi}_2\text{O}_3$ glass

Sample	T_g (°C)	T_{c1} (°C)	T_{c2} (°C)	ΔT (°C)	T_f (°C)	α ($10^{-6}/^\circ\text{C}$)	DR ($\text{g cm}^{-2} \text{ min}^{-1}$)
$x = 15$	371	448	566	77	654	9	4.0621×10^{-8}
$x = 17.5$	377	470	570	97	615	11	4.1458×10^{-8}
$x = 20$	384	561	N/A	177	610	12	4.2592×10^{-8}
$x = 22.5$	368	476	578	103	593	15	4.3605×10^{-8}

Table 2 Physicochemical properties of the $70\text{TeO}_2\text{-}20\text{ZnO-}(10 - y)\text{Bi}_2\text{O}_3\text{-}y\text{Na}_2\text{O}$ glasses and the adhesion force and resistivity of the corresponding Ag electrodes

Sample	T_g (°C)	T_{c1} (°C)	ΔT (°C)	T_f (°C)	α ($10^{-6}/^\circ\text{C}$)	DR ($\text{g cm}^{-2} \text{ min}^{-1}$)	Ag electrode code	Adhesion force (N)	Resistivity ($\mu\Omega \text{ cm}$)
$y = 1$	375	475	100	573	13	1.3678×10^{-7}	ZN1	2.1	2.6021
$y = 3$	366	465	99	540	15	2.4239×10^{-7}	ZN2	2.7	2.5378
$y = 5$	354	457	103	500	16	4.5617×10^{-7}	ZN3	3.3	2.4752
$y = 7$	330	428	98	485	21	1.0648×10^{-6}	ZN4	4.7	2.4124
$y = 10$	310	411	101	450	24	2.0216×10^{-6}	ZN5	6.0	2.3569

Fig. 1 Infrared spectra of $(90-x)\text{TeO}_2\text{-}x\text{ZnO-}10\text{Bi}_2\text{O}_3$ glasses

maximum value at $x = 20$, it shows that the thermal stability of $70\text{TeO}_2\text{-}20\text{ZnO-}10\text{Bi}_2\text{O}_3$ glass is the best one among the as-prepared glasses.

The SEM micrographs corresponding to surface of the Ag electrodes and cross section between Ag and Si wafer using $70\text{TeO}_2\text{-}20\text{ZnO-}10\text{Bi}_2\text{O}_3$ glass in the paste are displayed in Fig. 3. From Fig. 3a, it is seen that the Ag grains gathered together, which resulted in poor evolution in the Si wafer. What is more, the pore distribution was not uniform. In addition, clear interstices existed between the Ag electrodes and Si wafer in Fig. 3b, which indicates that the adhesion of Ag electrodes is very weak. The measured adhesion force is 1.2 N. It is suggested that the glass softening temperature (610°C) is too high to etching the

Fig. 2 DTA thermograms of the investigated glasses in the $(90-x)\text{TeO}_2\text{-}x\text{ZnO-}10\text{Bi}_2\text{O}_3$ (heating rate is 10°C/min)

SiN_x coating and participating in the reaction to form a thin glass layer. Therefore, it is necessary to optimize the $70\text{TeO}_2\text{-}20\text{ZnO-}10\text{Bi}_2\text{O}_3$ glass to obtain a good comprehensive performance.

3.2 Effect of Na_2O Content on the Structures and Properties of $70\text{TeO}_2\text{-}20\text{ZnO-}(10-y)\text{Bi}_2\text{O}_3\text{-}y\text{Na}_2\text{O}$ Glasses

The Na_2O with different contents (1, 3, 5, 7, and 10 mol%) was added to the $70\text{TeO}_2\text{-}20\text{ZnO-}(10-y)\text{Bi}_2\text{O}_3\text{-}y\text{Na}_2\text{O}$ glasses. The IR spectra of the glasses are given in Fig. 4. The band at 665 cm^{-1} and $755\text{--}773 \text{ cm}^{-1}$ are attributed to

Fig. 3 SEM images of the surface of the Ag electrode **a**, cross section between Ag electrode and Si wafer **b**, corresponding to the paste using 70TeO₂–20ZnO–10Bi₂O₃ glass

Fig. 4 Infrared spectra of the 70TeO₂–20ZnO–(10–y)Bi₂O₃–yNa₂O glasses

Fig. 5 Raman spectra of the 70TeO₂–20ZnO–(10–y)Bi₂O₃–yNa₂O glasses

TeO₄ tpb and TeO₃ tp, respectively. It can be seen that the intensity of bands at 665 cm⁻¹ decreases and the position of bands at 755–773 cm⁻¹ shifts to lower frequencies with the increasing of Na₂O content, which indicates that both of the TeO₄ tpb and TeO₃ tp structure units are decreasing.

The corresponding Raman spectra of 70TeO₂–20ZnO–(10–y)Bi₂O₃–yNa₂O glasses are given in Fig. 5 when x is 1, 5, and 10 mol%. Three major Raman absorption bands are observed. The band at 401–437 cm⁻¹ is due to the stretching of the Te–O–Te or O–Te–O bonds [17]. The band at 657–674 cm⁻¹ belongs to the stretching vibration of Te–O_{ax} in the TeO₄ tpb, while the band at 744–759 cm⁻¹ can be ascribed to the stretching vibration of Te–O in the TeO₃ tp [18–20]. The positions of those bands both shift to lower frequencies with the increase of Na₂O content. These results are consistent with the analysis of infrared spectra. Therefore, it is suggested that the Na₂O

is the network modifying oxide and the glass network would be increasingly depolymerized as the Na₂O content increases.

The properties of 70TeO₂–20ZnO–(10–y)Bi₂O₃–yNa₂O glasses are given in Table 2. Figure 6 shows the dependence of the values of glass transition temperature, softening temperature, and thermal expansion coefficient on the content of Na₂O in the 70TeO₂–20ZnO–(10–y)Bi₂O₃–yNa₂O glass. It is seen that the glass transition temperature and softening temperature decrease with increasing Na₂O content, whereas the values of thermal expansion coefficient increases. These results are in good agreement with the weakening of structural network, which are observed by IR spectra and Raman spectra. The chemical durability of the studied glasses is shown in Fig. 7. The DR increases exponentially with the amount of Na₂O doping, which means Na₂O doping can greatly decrease the chemical

Fig. 6 Variation of the glass transition temperature, softening temperature, and thermal expansion coefficient with the Na₂O content of 70TeO₂–20ZnO–(10–y)Bi₂O₃–yNa₂O glasses

Fig. 7 Variation of the dissolution rate with the Na₂O content of 70TeO₂–20ZnO–(10–y)Bi₂O₃–yNa₂O glasses

durability of the as-prepared glasses. This could be mainly attributed to the continuous ion exchange between the network modifying Na⁺ in the glass and H⁺ in the water. Only when the amount of Na₂O is 5 mol%, the values of softening temperature, thermal expansion coefficient, and dissolution rate remain relatively low. It is supposed that the 70TeO₂–20ZnO–5Bi₂O₃–5Na₂O glass could be applied in the Ag paste with the highest potential.

3.3 Effect of Glasses on the Microstructures and Properties of Ag Electrodes

In order to verify the performance of 70TeO₂–20ZnO–5Bi₂O₃–5Na₂O glass, the ZN1, ZN3, and ZN5 Ag electrodes were prepared and compared. The SEM images corresponding to surface of the ZN1, ZN5, and ZN3 Ag

electrodes and cross section between Ag and Si wafer are displayed in Fig. 8.

Ag grains gathered together in the ZN1 electrode (Fig. 8a), which resulted in poor evolution and some big pores on the Si wafer. What is more, the connection between the Ag electrodes and Si wafer is just interlocking in ZN1 (Fig. 8b), which indicates the adhesion of Ag electrodes is very weak. Both of these could be attributed to the higher *T_f* (573 °C) of glass in the ZN1 electrode.

It can be seen from Fig. 8c that the surface of the Ag electrodes has a hazy effect and the Ag grains gathered together, which probably related to the lower *T_f* (450 °C) of glass. The holes and pits were appeared in the cross section between Ag electrode and Si wafer (Fig. 8d), which indicates that the glass has etched and even damaged the Si wafer. As expected, the corresponding electrode brings about better adhesion. However, the damage of Si wafer which would decrease the efficiency of Si solar cell is not expected.

The SEM image in Fig. 8e of ZN3 shows that the wettability of glass for the Ag powder is excellent since the distribution of Ag grains is uniform and a horizontal growth of Ag grains can be seen. From Fig. 8f, it can be seen that there were no interstices in the interface between Ag electrode and Si wafer and the interface was continuous and smooth. In ZN3, the Ag crystallites of 5-nm average grain size coated by the glass layer of about 10 nm thickness have generated in the interface (Fig. 8g), which was essential to stable ohmic contact.

The data pertaining to adhesion force and resistivity are given in Table 2. From the table, it is seen that the adhesion force enhances as the glass softening temperature decreases. These results are consistent with the analysis of SEM micrographs of Ag electrodes. Therefore, it is suggested that glass with appropriate glass softening temperature could wet the Ag powder and improve the adhesion effect between the Ag electrode and Si wafer by etching the SiN_x ARC to form a thin glass layer.

From the above, the 70TeO₂–20ZnO–5Bi₂O₃–5Na₂O glass is found to be ideal for the present Ag paste formulation.

3.4 Analysis of Interface Between Ag Electrode and Si Wafer

Figures 9a and b show the XRD patterns of surface after selectively removing ZN3 Ag electrode using HNO₃/HF solution. Specifically, the wafer samples were immersed in 100 mL HNO₃/HF solution for 10 min, which contains 2 mL HF (40 wt%), 6 mL HNO₃ (68 wt%), and 92 mL deionized water. Figure 9c shows the XRD pattern of Si surface after removing Ag electrode without glass frit. XRD was used to detect the Ag crystallites formed on the Si wafer.

Fig. 8 SEM images of the Zn1, Zn3, and Zn5 Ag electrodes: **a** Zn1 surface; **b** Zn1 cross section; **c** Zn5 surface; **d** Zn5 cross section; **e** Zn3 surface; **f** Zn3 cross section; **g** Zn3 interface

Fig. 9 XRD patterns obtained from the surface Zn3 Ag electrode **a**, Si surface after removing Zn3 Ag electrodes using HNO_3/HF **b**, Si surface after removing Ag electrodes without glass frit **c**

There are only diffraction peaks of Ag crystals in Fig. 9a. But the Si is found in both the Fig. 9b and c. However, the diffraction peaks of Ag crystals were found in the Si surface corresponding to the Zn3 Ag electrode in sharp contrast to that of Ag electrode without glass frit. It proves that $70\text{TeO}_2\text{--}20\text{ZnO--}5\text{Bi}_2\text{O}_3\text{--}5\text{Na}_2\text{O}$ glass frit plays a very important role in the process of forming Ag crystallites.

4 Conclusions

By traditional melting route, homogeneous glasses can be prepared in the series $(90-x)\text{TeO}_2\text{--}x\text{ZnO--}10\text{Bi}_2\text{O}_3$ ($x = 15, 17.5, 20$ and 22.5 mol%) and $70\text{TeO}_2\text{--}20\text{ZnO--}$

$(10-y)\text{Bi}_2\text{O}_3\text{--}y\text{Na}_2\text{O}$ ($y = 1, 3, 5, 7$, and 10 mol%). The infrared spectra and Raman spectra indicate that the based network of Te-based glasses is mainly formed by TeO_4 and TeO_3 units. When $x = 20$ mol%, the thermal stability of $70\text{TeO}_2\text{--}20\text{ZnO--}10\text{Bi}_2\text{O}_3$ glass is best ($\Delta T = 177^\circ\text{C}$). However, it cannot benefit Ag electrode to integrate with Si wafer and offers good adhesion due to its high glass softening temperature. The Na_2O with different contents was added to the $70\text{TeO}_2\text{--}20\text{ZnO--}(10-y)\text{Bi}_2\text{O}_3\text{--}y\text{Na}_2\text{O}$ glasses. Na_2O acts as the network modifying oxide and the glass network would be increasingly depolymerized as its content increases. For the $70\text{TeO}_2\text{--}20\text{ZnO--}5\text{Bi}_2\text{O}_3\text{--}5\text{Na}_2\text{O}$ glass, the values of softening temperature, thermal expansion coefficient, and dissolution rate remain relatively low, which meets the requirements of Ag paste.

The $70\text{TeO}_2\text{--}20\text{ZnO--}5\text{Bi}_2\text{O}_3\text{--}5\text{Na}_2\text{O}$ glass could wet the Ag powder to form a uniform electrode and improve the adhesion effect between the Ag electrode and Si wafer. What is more, the Te-based glass could serve as a medium for forming Ag crystallites by etching and react with SiN_x ARC, and Si. Therefore, the Te-based glass could be a promising substitute for Pb-based glass frit for preparing environmental friendly front-side Ag paste for crystalline silicon solar cells in the future.

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