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Effect of Pb–Te–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–O (PTO) glasses with different Pb/Te ratios on silver screen-printed contact formation in crystalline silicon solar cells were investigated. Thermal properties of PTO glasses such as crystallization behavior, liquidus temperature and viscosity–temperature features are determined by Pb/Te ratio. Glass etching reaction, Ag dissolution–precipitation process and all key processes of Ag thick-film contact to crystalline silicon solar cells, are closely related to glass chemistry and Pb/Te ratio of PTO glasses. The dissolution process of Ag in PTO glasses with different Pb/Te ratio was studied. XPS measurement shows that Ag^+ is the dominant form of silver dissolved in PTO glass melts. TG and XRD results reveal that the formation of a new B-rich liquid glassy-phase, induced by the crystallization of glass, accelerates the dissolution of Ag at lower temperature. Glass with higher Pb/Te ratio has a weaker glass etching reaction ability and is expected to have a high high-temperature viscosity, resulting in higher Ag-precipitate density in the glassy-phase. The observed microstructures, I–V electrical performance and contact resistance maps lead to a better understanding of the relationship between glass properties and contact resistance.

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1. Introduction

Crystalline silicon wafers with planar p–n junctions are extensively used in solar cell industry. In order to minimize optical losses in solar cells, the front side of the wafers is chemically textured and coated by a thin SiN_x:H anti-reflection (AR) layer which has a thickness of 70–80 nm. The front side metallization of solar cells, which strongly influences the overall optical and electrical properties, is usually achieved by screen printing and rapid thermal processing [1]. The applied silver (Ag) contact paste consists of Ag powder, low-melting glass frit and an organic vehicle. Low-melting glass frit must be able to etch through the SiN_x:H layer without damaging the emitter layer, thereby exposing the emitter surface and establishing electrical contact between the silicon and the silver contact [2,3]. In the metallization procedure, the glass frit melts could wet and dissolve the Ag powder at elevated temperature to generate a liquid glassy-phase, which would facilitate the sintering of Ag powder [2,4,5]. The flow behavior of the glassy-phase, to a degree, is associated with the capillary attraction force caused by the tiny spacing between Ag particles, and it also depends on the wetting ability of the glassy-phase itself to the anti-reflection layer [5]. In particular, while the silver

dissolved in the liquid phase during metallization, the silicon would undergo an oxidization–reduction reaction in the meantime, which results in the formation of numerous Ag precipitates in the Ag/Si interface layer [3,6]. Therefore, the glass frit and the generated liquid glassy-phase determine the electrical conductivity between Ag fingers and Si wafer, in consequence having a crucial influence on the cell efficiency.

Two different models have been proposed 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 [7]. So it is suggested that the Ag crystallites, including those directly connected to Ag fingers and a multi-step tunneling process through the modified glass layer, have created a possible current transport paths from Si emitter to Ag finger [3–5]. Another model, the tunneling conduction mechanism, has been established on the discovery of nano-Ag colloids (Ag precipitates) in the thin glass layer between Ag finger and Si emitter [8,9]. According to this model, photoelectrons are extracted from Si emitter through a thin interfacial glass which is decorated with nano-Ag colloids; and the thickness of the glass layer is critical to the tunneling mechanism.

It has also been found that Ag precipitates in glassy-phase tend to coarsen into larger crystallites with smaller total interfacial area which is dependent on the firing and atmospheric conditions. Ag precipitates and crystallites are always coexisting at the Ag/Si interface of optimally fired cells [8–10]. But the abnormal growth

of Ag crystallites, together with re-dissolution of Ag precipitates, is undesirable for Ag/Si ohmic contact due to less-conductive interfacial glass layer and the degradation of the narrow Si emitter by shunt defects. Particularly, the ratio of Ag precipitates to Ag crystallites in the cell, the most important feature of Ag/Si contact interface, is highly dependent on the interfacial glassy-phase and firing conditions. However, the role of the glassy-phase and its detailed influence on the dissolution–precipitation process of silver during the firing cycle is not fully understood so far.

Pb–Te–O (PTO) glasses, commonly used as the Low-melting glass frits in Ag contact paste in the industry, have been found to be helpful to obtain high fill factor (FF) and low contact resistance [11]. The objective of this work is to achieve better understanding of the role of PTO glasses in the metallization of crystalline silicon solar cells. To be specific, the influences of PTO glasses on the dissolution–precipitation process of the silver during the firing cycle, and its effects on the formation of silver screen-printed contact are studied.

2. Experimental procedures

2.1. Glass frits preparation and characterization

The compositions of Pb–Te–O glasses with variable Pb/Te molar ratio (PTO-1 to PTO-3) are shown in Table 1. The glasses were prepared using the conventional melt-quenching method. Reagents grade oxides were mixed in appropriate proportion and melted in a platinum crucible at 850 °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 D_{50} 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 with a powder diffractometer (Bruker D8 advanced) using CuKα radiation ($\lambda = 0.154$ nm). The densities of the glasses were determined by an Archimedes method using distilled water as the immersion liquid. Glass transition temperature (T_g), the onset temperature of crystallization ($T_{c,onset}$), crystallization peak temperature (T_p), and peak liquefaction temperature (T_l), were determined by using Differential scanning calorimetry measurements 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 (12 mm diam.) for parallel-plate rheological experiments. Temperature sweep tests were carried out on 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 (12 mm in diameter) system. The dynamic viscoelastic properties, dynamic (G') and loss (G'') modulus, and the complex dynamic shear viscosity (η^*) were 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%.

Glasses prepared were analyzed using an ESCALAB250Xi spectrometer (Thermo Scientific, UK), equipped with a monochromatic Al-Kα (1486.68 eV) X-ray source and operating at 2×10^{-9} mbar. For the XPS measurements, fresh surfaces were generated by cleaving the bulk glass sample before the experiments to avoid surface pollution. The bonding energy positions of the O 1s, Pb 4f and Te 3d core electrons were measured and the chemical shifts of XPS peaks were standardized by the C 1s peak at 284.6 eV. The dissolution process of Ag in molten glasses was investigated by thermogravimetry (TG) analysis under air atmosphere. The phase composition of these samples was evaluated by X-ray diffraction (XRD) analysis. The valence of Ag dissolved in PTO-3 glass was investigated by measuring the binding energy of Ag 3d5/2 and Ag MNN Auger.

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 m^2/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 PTO glasses contained silver pastes are shown as follows. 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/PTO-1 glass frit/organic medium was 88/2.5/9.5 (wt%) while the PTO-3 glass content was adjusted to have the same volume with PTO-1 glass according to the densities measured and listed in Table 2. 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 mm^2, 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. The screen for printing the back side Ag electrode was 325 mesh, 28 μm wire and 15 μm emulsion. The screen for printing Al back surface field layer was 325 mesh, 28 μm wire and 20 μm emulsion. The screen for printing the Ag front-side was 400 mesh, 18 μm wire, 15 μm emulsion and 45 μm line width. Ag pastes screen-printed on wafers were fired in a rapid heating furnace at a belt speed of 225 in./min using a setting peak furnace temperature of 900 °C. The actual firing temperature profile is shown in Fig. 1.

2.3. Analytical methods for cells

The conversion efficiency of the cells fabricated was measured by commercial IV tester (Baccini, ITA). Open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), fill factor (FF), series resistance (R_s), and efficiency (E_{ff}) were calculated from the cell's I–V curve. Advanced

Table 1
Compositions of Pb–Te–O system glass (wt%).

FritID	Pb/Te (molar ratio)	PbO	TeO$_2$	B$_2$O$_3$	Li$_2$O	Bi$_2$O$_3$	Sum
PTO-1	1:1.2	49.45	42.43	0.48	0.44	7.20	100
PTO-2	1:1.5	44.51	47.74	0.48	0.44	6.83	100
PTO-3	1:1.8	40.17	51.71	0.48	0.44	7.20	100

Table 2
Thermal properties of as-prepared Pb–Te–O glasses.

FritID	Pb/Te molar ratio	ρ (g/cm^3)	T_g (°C)	$T_{c,onset}$ (°C)	$T_{l,\ peak}$ (°C)	T_{tr} (°C)	$\Delta T = T_{c,onset} - T_g$ (°C)
PTO-1	1:1.2	6.90	236.2	260.4	508.5	511	24.2
PTO-2	1:1.5	6.69	250.0	281.9	524.4	530	31.9
PTO-3	1:1.8	6.52	262.7	302.3	545.3	544	39.6