Influence of tellurite glass on reaction between Si₃N₄ anti-reflection coating film and Ag paste for electrodes in Si solar cells

Shizuharu WATANABE,† Takayuki KODERA* and Takashi OGHARA*

Graduate School of Engineering, Advanced Interdisciplinary Science and Technology, University of Fukui, 3–9–1 Bunkyo, Fukui 910–8507, Japan
Graduate School of Engineering, Materials Science and Engineering, University of Fukui, 3–9–1 Bunkyo, Fukui 910–8507, Japan

The reactivity of tellurite glass with Si₃N₄ was investigated using X-ray diffraction (XRD) analysis and was discussed in terms of basicity parameter, B, and the O1s binding energy, as a measure of the basicity of tellurite glasses. Through XRD analysis, it was revealed that tellurite glasses with a high basicity react significantly with Si₃N₄ to produce SiO₂. Observation of an Ag electrode containing glass and the microstructure of a Si wafer by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) revealed that Ag paste containing highly reactive tellurite glass can effectively decompose the anti-reflection coating (ARC) composed of Si₃N₄. When glass with a high reactivity decomposed the ARC and the calcined Ag electrode contacts with the Si wafer, Ag/Te alloy particles were observed to precipitate from the tellurite glass phase at the interface between the Si wafer and Ag electrode. SEM and STEM observations also revealed that these Ag/Te alloy particles form a conductive path between the silicon wafer and Ag electrode.

Key-words : Ag electrode, Ag paste, Ag–Te alloy, Si solar cell, Anti-reflection coating, Contact resistance

1. Introduction

Silver electrodes are formed by firing a Ag paste that contains Ag powder in combination with glass frit and vehicle. In order to inhibit the reflection of light, an uneven surface is fabricated on the light-receiving surface through the formation of an anti-reflection coating (ARC) composed of insulative Si₃N₄. The glass frit added to the Ag paste is intended to remove the ARC, and when melted during sintering, flows over the Si-wafer surface to react with the ARC. A conduction path between the Ag electrode and Si-wafer surface is formed when the Ag is converted to Ag⁺ and dissolved in the glass, with these Ag ions then being reduced to form Ag precipitates on the Si-wafer surface. However, as it is not clear how the physicochemical characteristics of the glass affect the removal of the ARC, it was assumed in this work that the basicity of the glass influences the removal of the ARC. The relation between the basicity of the glass and the reactivity of Si₃N₄ was therefore investigated along with the microstructure at the interface and specific contact resistivity between Ag electrodes and a Si-wafer.

2. Experimental procedure

2.1 Preparation of tellurite glass

Tellurite glass was chosen for use as the frit in Ag paste because it has a low viscosity and exhibits good wettablility for a Si-wafer surface with an ARC. Ternary Pb–Te–Bi, Ba–Te–Zn, and Pb–Te–Si glass frits were used as raw materials. The Pb–Te–Bi and Ba–Te–Zn glass frits were of commercial grade (Okamoto Glass Co., Ltd.), while the Pb–Te–Si glass frit was prepared from a mix of Pb₃O₄, TeO₂ and SiO₂ that was heated for 1 h in an alumina crucible at 1000°C until fully melted, and then quenched and subjected to ball milling. The average particle size of the tellurite glass obtained was approximately 2.0 μm regardless of the glass composition. The experimental data were not influenced by the alumina crucible, because the contamination by Al₂O₃ was very low (0.005 mol %).

2.2 Reactivity of tellurite glass with Si₃N₄

The reactivity of tellurite glass with Si₃N₄ during the heating was evaluated from the change in the XRD patterns of Si₃N₄. At first, Si₃N₄ powder (Kojundo Chemical Laboratory, 99.9%, average particle size of 0.5 μm) was calcined for 6 h at 800°C to observe for any change in the crystal structure. Next, PbO powder (Kishida Chemical 99%) and Si₃N₄ powder were mixed at the molar ratio of 100:10 and then calcined for 6 h at 800°C to investigate for any change in crystal structure due to the reaction of Si₃N₄ and oxide. Finally, the tellurite glass and Si₃N₄ powder were mixed at the volume ratio of 100:10 and then calcined for 300 s at 800°C. The X-ray diffraction (XRD) pattern of the Si₃N₄ before and after the calcination was measured using a Shimadzu XRD-6100 with CuKα radiation, and the diffraction peaks of (101) and (110) were used to estimate the reactivity of the tellurite glass with Si₃N₄. This was determined by dividing the area under the diffraction peak for each of the mixed powders before calcination by that after calcination. The reactivity is indicated by a reactivity index in this paper, with a reactivity index of 1 indicating that the tellurite glass and Si₃N₄ powders do not react. The reactivity index increases as the reactivity of the tellurite glass and Si₃N₄ increases.
The resistance between neighboring electrodes, $R$, in Fig. 1(b) was measured using an ohmmeter (HIOKI, AC mHiTESTER 3560) to determine the current transfer length, $L_n$, and sheet resistance of the emitter, $R_{sh}$. The resistance between neighboring electrodes, $R$, was measured using the transfer length model (TLM)\(^7\) to determine the current transfer length, $L_n$, and sheet resistance of the emitter, $R_{sh}$.

2.3 Microstructure of interface between Ag electrode consisting of tellurite glass and Si wafer

To observe the microstructure of the interface between the Ag electrode and Si wafer, a Ag electrode consisting of tellurite glass was fabricated on the surface of a Si wafer coated with the ARC. For this, a powder mixture with a Ag (PV-3, Ames Goldsmith, average particle size of 1.5 $\mu$m)–to-tellurite glass ratio of 100.0:3.2 vol% was first mixed with a vehicle prepared by dissolving ethyl cellulose in texanol, and then dispersed using a triple-roll mill to produce a uniform Ag paste. This paste was screen printed onto a Si wafer to produce the pattern shown in Fig. 1(a), dried in an oven for 600 s at 150°C, and then calcined at a peak temperature of 770°C in a tunnel furnace. The sheet resistance of the textured Si wafer was 80 $\Omega$/square without the ARC. The microstructure and composition of a cross section of the calcined Ag electrode containing tellurite glass were investigated using field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6340F) and scanning transmission electron microscopy with an energy dispersive X-ray analyzer (STEM/EDS JEM-3000F). The spatial resolution was $\sim$5 nm with an accelerating voltage of 300.0 keV.

2.4 Measurement of specific contact resistivity

The specific contact resistivity, $\rho_c$, of the calcined Ag electrodes containing tellurite glass (as described in subsection 2.3) was measured using the transfer length model (TLM)\(^7\)-\(^9\) shown in Fig. 1(a) and 1(b). Here, the value of $\rho_c$ ($\Omega$cm\(^2\)) was calculated using the following equation:

$$\rho_c = R_{sh}L_n^2$$  \hspace{1cm} (1)

The resistance between neighboring electrodes, $R$, in Fig. 1(b) was measured using an ohmmeter (HIOKI, AC mHiTESTER 3560) to determine the current transfer length, $L_n$, and sheet resistance of the emitter, $R_{sh}$.

2.5 Basicity of tellurite glass

It is known that the ARC is removed when glass in a Ag paste reacts with ARC during firing.\(^1\) The reactivity of the glass is related to its basicity. A number of methods for determining basicity have been proposed. For instance, it has been reported by Duffy et al. that the basicity of a glass matrix can be determined by measuring the chemical shift of an absorption peak in the ultraviolet range of an ion probe doped in the glass.\(^10\)

Alternatively, the basicity of a glass can be characterized by its electron-donating ability, as oxide ions (which have an electron-dense outer shell) have a high basicity. That is, the basicity can be determined by measuring the O1s binding energy, because the electrostatic force of core electrons is influenced by the state of the outer shell electrons.\(^11\),\(^12\) The O1s binding energy of the tellurite glass powder was therefore investigated using an X-ray photoelectron spectrometer (XPS, JEOLEPS-9010MC) with Mg-K$\alpha$ radiation (1253.6 eV). The accelerating voltage and probe current were 12.0 kV and 25.0 mA, respectively. The XPS was calibrated using the Si2p3/2 binding energy (103.5 eV) of SiO$_2$ powder (Kishida Chemical, 99% purity). The O1s binding energy in the glass was corrected by referencing the measured C1s binding energy for the hydrocarbon impurities (284.6 eV).

An alternative method to determine the basicity was to use calculations, with Duffy and Ingram proposing that optical basicity, $A_0$, can be calculated from the Pauling electronegativity using:\(^13\)

$$\chi_i = 1.36(\chi_i - 0.26)$$  \hspace{1cm} (2)

$$A_0(\chi) = \sum Z_i r_i / 2\gamma_i$$  \hspace{1cm} (3)

where $Z_i$ is the oxidation number of the cation $i$, and $r_i$ is the ionic radius with respect to the total number of oxides. Note that $\gamma_i$ is the basicity moderating parameter and is empirically given by using the Pauling electronegativity, $\chi_i$.

Morinaga et al. proposed that the basicity is inversely proportional to the Coulomb force between a cation and oxide ion, which is expressed as $B$ in following equation:\(^14\)

$$B_i = \left( \frac{Z_i \times 2}{r_i + 1.40^2} \right)^{-1}$$  \hspace{1cm} (4)

$$B_i = B_i - B_{SiO_2}$$  \hspace{1cm} (5)

$$B = \sum n_i B_i$$  \hspace{1cm} (6)

where, $Z_i$ and $r_i$ are the valency and radius of the cation, respectively, and 2 and 1.40 are the valency and radius of the oxygen ion. $B_i$ is the basicity of the glass component $i$ in a glass system. The values of $B_i$ for SiO$_2$ and CaO are normalized as 0.00 and 1.00, respectively. $n_i$ is the cation fraction of $i$, while $B$ is the basicity parameter for multicomponent glass.

3. Results and discussion

3.1 Reactivity of tellurite glass with Si$_3$N$_4$ and specific contact resistivity of Ag paste containing tellurite glass

To investigate the change in crystal structure, Si$_3$N$_4$ powders were heated at 800°C for 6 h. Figure 2(a) shows the XRD patterns of the Si$_3$N$_4$ powder before and after calcination, from which it was found that no change occurred in the peak area after calcination. The mixture of Si$_3$N$_4$ and PbO powders was heated at 800°C for 6 h to investigate the change in crystal structure due to the reaction of Si$_3$N$_4$ and oxide. The XRD pattern of the powder mixture with a Si$_3$N$_4$-to-PbO ratio of 100:0:10.0 (mol %) before

Fig. 1. Schematic of (a) the TLM test structure and (b) measurement methodology to extract different parameters of planar ohmic contacts. d (cm): Width of contact; l$_1$ (cm): Distance between paths of contacts; W (cm): Contact length; l$_2$ (cm): Current transfer length; R$_{sh}$ ( $\Omega$/square): Sheet resistance of emitter; R ( $\Omega$): Resistance between neighboring electrodes.
and after calcination in Fig. 2(b) shows a clear decrease in the peak area of Si$_3$N$_4$ after calcination. This is due to its conversion to SiO$_2$, with the shift in this peak considered to be due to the formation of oxynitride. Based on Figs. 2(a) and 2(b), it is suggested that the reaction of Si$_3$N$_4$ powder with PbO leads to a decrease in the peak area of Si$_3$N$_4$.

Table 1 shows the composition of the glasses used in this study.

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<th>Glass</th>
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<th>SiO$_2$</th>
<th>BaO</th>
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and after calcination in Fig. 2(b) shows a clear decrease in the peak area of Si$_3$N$_4$ after calcination. This is due to its conversion to SiO$_2$, with the shift in this peak considered to be due to the formation of oxynitride. Based on Figs. 2(a) and 2(b), it is suggested that the reaction of Si$_3$N$_4$ powder with PbO leads to a decrease in the peak area of Si$_3$N$_4$.

Table 1 shows the composition of the glasses used in this study. Figure 3(a) shows the relationship between the basicity parameter $B$ of tellurite glass and its reactivity index, and between (b) the O1s binding energy of tellurite glass and its reactivity index.

Figure 3(b) shows the relationship between the O1s binding energy of the tellurite glasses and their reactivity index. The compositions of the tellurite glasses were the same as those in Fig. 3(a). The O1s binding energy of the Pb–Te–Bi glass ranged from 532.0 to 533.5 eV, that of the Pb–Te–Si glass ranged from 532.6 to 534.4 eV, and that of the Ba–Te–Zn glass ranged from 532.9 to 534.5 eV. As shown in Fig. 3(b), the reactivity index increased as the O1s binding energy decreased. From the results in Figs. 3(a) and 3(b), it was evident that tellurite glass with a high $B$ and low O1s binding energy decomposes Si$_3$N$_4$ with ease. Consequently, it was suggested that the basicity of a glass influences its reactivity with Si$_3$N$_4$.

The $\rho_s$ value was determined using the TLM method. Figure 4 shows the relationship between the reactivity and the $\rho_s$ of the Ag electrodes containing tellurite glass. The $\rho_s$ value was $2.0 \times 10^2$ (\(\Omega\) cm$^2$) when the reactivity index was approximately 2.0, but changed to $3.0 \times 10^{-2}$ (\(\Omega\) cm$^2$) when the reactivity index was approximately 3.0. Thus, the $\rho_s$ was low when the reactivity of the tellurite glass in the Ag electrode was high.

Figure 5 shows the XRD patterns of samples in which a mixture of Ba–Te–Zn glass (A) and Si$_3$N$_4$ powders and Pb–Te–Bi glass (B) and Si$_3$N$_4$ powders were heated at 800°C for 300 s. Note that when the Pb–Te–Bi glass (B) had a high basicity and reactivity, the Si$_3$N$_4$ converted to SiO$_2$. It is considered that the nitrogen is released as nitrogen gas, and so it is assumed that the reduction of the specific contact resistivity of Si$_3$N$_4$ is directly related to its decomposition.
3.2 Microstructure of interface between a Ag electrode containing tellurite glass and a Si wafer

The FE-SEM images in Fig. 6 show cross sections of a Si wafer with the ARC in a solar cell and a Ag electrode consisting of Ba–Te–Zn glass (A), which as shown in Fig. 4, has a low reactivity and high $\mu_c$. As seen in Fig. 6(b), an insulating glass layer and ARC were observed between the Ag electrode and Si wafer, which accounts for the fact that the $\mu_c$ was high when the reactivity index was low.

Figure 7 presents an FE-SEM image of the cross section of a Ag electrode containing Pb–Te–Bi glass (B), which as shown in Fig. 4, has a high reactivity and low $\mu_c$. The ARC was not observed between the Ag electrode and Si wafer in this instance, but particles with a size of ~300 nm were observed between the Ag electrode and Si wafer in Fig. 7. Figure 8(a) shows a bright-field (BF)-STEM image of the cross section of a Ag electrode containing Pb–Te–Bi glass (B), while Figs. 8(b)–8(d) show STEM/EDS elemental mapping images of the same region. Note that an ARC was not observed on the Si-wafer surface, with no oxygen detected in the particles deposited at the interface of the Ag electrode and Si wafer by STEM/EDS analysis. It was therefore considered that the deposit was a Ag/Te alloy, because both Ag and Te were detected by STEM/EDS. As the glass with high basicity decomposed Si$_3$N$_4$ to SiO$_2$ as shown in Fig. 5, it was found that the Pb–Te–Bi glass (B) decomposed the ARC because of its high reactivity, thus allowing the tellurite glass to come into direct contact with the Si-wafer surface. It is considered that the Te ions and Ag ions in the tellurite glass were
reduced to metal by the Si wafer,\textsuperscript{9,13,15} leading to alloy particles of Ag and Te precipitating from the glass phase onto the Si-wafer surface. However, nanometer-sized particles observed in the glass phase were not reduced to metal by the Si wafer directly. It has been previously reported that Ag particles first deposit, and then grow, when Ag paste with Pb–Si–B–Al glass is heated in a quartz crucible.\textsuperscript{10,12} As the present results are similar to this, it is believed that Ag dissolves in the glass at elevated temperatures, and then precipitates under cooling conditions due to its decreased solubility; the precipitated Ag particles then grow to a size of 10 nm through Ostwald ripening. As shown in Fig. 7, particles in contact with the Ag electrode were observed in the case of Ag/Te alloy particles deposited on Si wafer, suggesting that electric conduction from the Si wafer to the Ag electrode is caused by a percolation mechanism through the metal particles.

4. Conclusions

The relationship between the basicity of tellurite glass and its reactivity with Si$_3$N$_4$ was investigated by using the basicity parameter, $B$, and the O1s binding energy, as a measure of the basicity of the glass. The reactivity of tellurite glass with Si$_3$N$_4$ was evaluated by calcining a powder mixture with a Si$_3$N$_4$-to-tellurite glass ratio of 100:0:10.0 vol%, with a high $B$ and low O1s binding energy producing a high reactivity with Si$_3$N$_4$. It was therefore considered that the basicity of the glass influenced the removal of the ARC. A Ag paste containing tellurite glass with a low $B$ and high O1s binding energy did not decompose the ARC, with the remaining ARC resulting in a high contact resistance. However, a Ag paste containing tellurite glass with a high $B$ and lower O1s binding energy was capable of decomposing the ARC. Furthermore, Ag/Te alloy particles were precipitated from the glass phase when the ARC was decomposed, which allowed the glass to contact the Si wafer. These Ag/Te alloy particles formed a conductive path between the Si wafer and the electrode, resulting in a low contact resistance interface between the two.

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References