Preparation and sintering of tellurium-doped silver powder for electrodes in silicon solar cells

Shizuharu WATANABE, Takayuki KODERA* and Takashi OGIHARA*,†

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

Silver electrodes were prepared on the silicon wafer surface using the wetness of an alloy liquid phase produced in the sintering process of the silver powder. Tellurium, which forms a low-melting-point alloy with silver, was doped to the silver powder, and the physical and chemical properties of the synthesized tellurium-doped silver powder were investigated. When silver and tellurium powders were mixed to produce a low-melting-point eutectic crystalline mixture with a silver-to-tellurium ratio of 33.0:67.0 (mol %), a rapid mutual diffusion occurred by heating, following which fusion occurred at the eutectic temperature. When tellurium-doped silver paste prepared with a silver-to-tellurium ratio of 98.5:1.5 (mol %) was printed onto a silicon wafer with texture formed on the surface and then sintered, wetting due to a phase which have been a liquid phase during the sintering process was confirmed at the interface between the silver electrodes and wafer. Silicon was dispersed in silver and tellurium in this phase, and physical contacts of a phase composed of silver, tellurium, and silicon were confirmed between the silver electrodes and wafer.

Key-words: Silicon solar cell, Silver pastes, Ag thick film, Eutectic alloy, Contact resistance

1. Introduction

Silver electrodes formed on the light-receiving surface of a silicon solar cell are fabricated by printing silver paste composed of silver powder, glass frit, and a vehicle for gaining screen printability on a silicon wafer and then sintering the product. An anti-reflection coating (hereafter referred to as “ARC”) composed of insulative silicon nitride is formed on the surface of the silicon wafer, but the ARC needs to be removed in order for the silver electrodes to come into contact with the silicon wafer for conduction. The removal of the ARC is achieved when the glass is softened during sintering and flows over the silicon-wafer surface to react with the ARC. The silver electrodes and the silicon surface have to be in physical contact in order to bring out the electrons generated within silicon to the silver electrodes. The conduction paths are formed when silver is converted to Ag⁺ and is dissolved in the glass to undergo a reduction precipitation on the silicon surface.⁶⁻⁷

Furthermore, processing of an uneven surface referred to as a texture is implemented on the silicon-wafer surface in order to inhibit the reflection of light.⁶ Point contacts exist between the surface of the silicon wafer and the silver powder, as shown in Fig. 1(a), with hardly any silver powder contacts achieved in the recessed areas. When calcination is performed after the silver paste is dried, as shown in Fig. 1(b), gaps occur between the silver electrodes and the silicon-wafer surface because the silver powder shrinks because of sintering. This inhibits the conduction between the silver electrodes and silicon wafer, which results in the problem of increased contact resistance.

We tried to improve the contact structure of silver electrodes

* Corresponding author: T. Ogihara; E-mail: ogihara@matse.u-fukui.ac.jp
† Preface for this article: DOI http://dx.doi.org/10.2109/jcersj2.123.P5-1

Fig. 1. Schematic representation of the cross section of Ag electrode before and after sintering.

©2015 The Ceramic Society of Japan. All rights reserved.

DOI http://dx.doi.org/10.2109/jcersj2.123.345

345
2. Experimental procedure

2.1 Thermal behavior of tellurium powder and tellurium-doped silver powder

Silver powder (PV-3, Ames Goldsmith, average particle size of 1.5 µm) and tellurium powder (Kishida Chemical, 99.9% purity) were used as the starting materials. A powder with a silver-to-tellurium ratio of 33.0:67.0 (mol %), which is a low-melting-point eutectic crystalline mixture of silver and tellurium, was prepared. Thermal behavior of powder mixture was investigated using DTA-TG (Shimadzu, DTG-60) in order to evaluate the reactivity of the silver and tellurium powders. The thermal behavior of tellurium powder was also investigated for comparison. Measurements were taken with a temperature increase rate of 10°C/min in air and N2 atmospheres. Similarly, the thermal behaviors of powder mixtures prepared with silver-to-tellurium ratios of 85.0:15.0 (mol %) with high melting point and 98.5:1.5 (mol %) were investigated using DTA-TG in air at a phase equilibrium condition with a small amount of tellurium doping.

2.2 Preparation of tellurium-doped silver powder

A powder mixture with a silver-to-tellurium ratio of 33.0:67.0 (mol %), which is a low melting point eutectic crystal composition, was mixed with a vehicle prepared by dissolving ethyl cellulose with texanol and dispersed using a triple roll mill to prepare a uniform paste. A silicon wafer with a texture and ARC was used as the substrate for solar cell. A sheet resistance of the silicon wafer with a texture was 60 Ω/square without ARC. The prepared paste was evenly applied on the light-receiving surface (N face) of the silicon wafer. The silicon wafer with the prepared paste was dried for 10 min in an oven at 150°C and then heat treated on a hot plate at a temperature range of 300 to 600°C to investigate the effect of the heat-treatment temperature on the crystal phase. The heat treatment was performed in air. The crystal phase of the heat-treated powders was identified by powder X-ray diffraction (XRD, Shimadzu, XRD-6100) using Cu Kα radiation.

2.3 Microstructure on interface between tellurium-doped silver electrodes and silicon wafer

Generally, the resistivity increases when metals form alloys. Since the resistivity increases with larger quantities of alloys, it would be better to produce smaller quantities of alloys when using the tellurium-doped silver paste as electrodes for solar cells. A tellurium-doped silver paste prepared with a silver-to-tellurium ratio of 98.5:1.5 (mol %), with a lower amount of tellurium doping, was screen printed in the pattern shapes shown in Fig. 2(a) on the light-receiving surface of the silicon wafer of solar cells described in subsection 2.2 and then dried in an oven for 10 min at 150°C and calcined at a peak temperature of 785°C in a tunnel furnace. The microstructure and composition of the calcined tellurium-doped silver electrode cross section were investigated using a field emission scanning electron microscopy with energy dispersive X-ray analyzer (FE-SEM/EDS, JEOL, JSM-6340F JED-2200F), and field emission auger electron spectroscopy (FEAES, JEOL, JAMP-9500F). The spatial resolution was approximately 20 nm with the accelerating voltage of 10.0 keV and probe current of 5.09 × 10⁻⁹ A.

2.4 Measurement of specific contact resistivity (ρc)

Measurements of ρc, of the calcined tellurium-doped silver electrodes described in subsection 2.3 were performed using the transfer length model (TLM) shown in Fig. 2. The ρc (Ω·cm²) was calculated using the following equation:

\[ \rho_c = \frac{R_{sh}}{W} L_t^2 \]  

The resistance between the neighboring electrodes (R) in Fig. 2(b) was measured with an ohmmeter (HIOKI, AC mΩ HiTESTER 3560) to determine the current transfer length (Lt) and the sheet resistance of the emitter (Rsh).

3. Results and discussion

3.1 Thermal behavior of tellurium powder and tellurium-doped silver powder

Silver and tellurium had melting points of 962 and 450°C, respectively, but alloys consisting of approximately 67.0 mol % tellurium formed a low-melting-point eutectic crystal alloy with a melting point of 353°C. This suggests that when a silver and tellurium powder mixture is heat treated and an alloy with a low melting point is produced because of a diffusion reaction of silver and tellurium, then it would be conceivable that such a product can melt at a temperature that is lower than the melting points of silver and tellurium.

DTA-TG curve of the Tellurium powder in air is shown in Fig. 3(a), and DTA-TG curves of a powder mixture of silver and tellurium low-melting-point eutectic crystalline composition in air and N2 atmosphere are shown in Fig. 3(b). As shown in Fig. 3(a), an endothermic peak was detected in the vicinity of 462°C, which is the melting point of the tellurium powder, and an increase in weight, which is associated with an exothermic reaction, was detected from 500 to 620°C. It was found that the oxidation of tellurium was gradual until the melting point was reached, but the oxidation became more noticeable beyond the melting point. As shown in Fig. 3(b), the melting temperature shifted to a lower temperature with the powder mixture of low-melting-point eutectic crystalline composition made of silver and tellurium powders in comparison with that of tellurium powder in both air and N2 atmosphere, with an endothermic peak detected at 359°C, which is a silver and tellurium low-melting-point eutectic...
crystalline region. An exothermic peak was detected at approximately 300°C in both air and N2 atmospheres. It was considered that the heat of mixing resulted in an exothermic reaction. Above 400°C, no weight changes, endothermic reactions, or exothermic reactions were detected in the N2 atmosphere. On the other hand, in air, a rapid weight gain was detected at temperatures higher than the melting point in air. It was confirmed that the oxidation of tellurium led to weight gains, which was similar to the results for the tellurium powder.

When applying the tellurium-doped silver powder to the silver electrodes, the amount of alloy liquid phase produced would be sufficient when they come into contact with the silicon wafer because of wetting. Since the resistivity increases with larger amounts of alloys, it is considered that producing smaller quantities of alloys is better. The thermal behaviors of the powder mixtures with silver-to-tellurium ratios of 85.0:15.0 (mol %) and 98.5:1.5 (mol %) were investigated. Figure 4 shows the DTA-TG curves of the powder mixtures with silver-to-tellurium ratios of 85.0:15.0 (mol %), 98.5:1.5 (mol %), and 33.0:67.0 (mol %), which is a eutectic composition. The silver and tellurium phase equilibrium diagram reveals that in the vicinity of the low-melting-point eutectic crystalline composition, there existed a eutectic region of Ag5Te3 and tellurium.12),13) Therefore, Ag5Te3 was formed. When the heat-treatment temperatures were 400 and 430°C, diffraction peaks attributed to tellurium, TeO2, Ag5Te3, and Ag2Te (2θ = 31°) were detected. The oxidation of tellurium led to the production of Ag2Te, which has less amount of Te than Ag5Te3. No diffraction peak of tellurium was detected with heat-treatment temperatures of 500°C and higher, where phases of TeO2, Ag5Te3, and Ag2Te existed. The results from DTA-TG and XRD revealed that a low-melting-point alloy was produced by diffusional reactions of silver and tellurium, when the powder mixtures of silver and tellurium powders were heat treated.

3.2 Effect of difference in heat treatment temperatures on crystal phase of tellurium-doped silver powder

The powder mixture of low-melting-point eutectic crystalline composition of silver and tellurium powders was heat treated at 300, 350, 400, 430, 500, 530, and 600°C. The crystal phase of the heat-treated powder was investigated using XRD in order to examine the reaction process of the powder mixture composed of silver and tellurium. The heat treatment was performed on a hot plate set to the aforementioned temperatures for 3 min in air. Figure 5 shows XRD patterns of the heat-treated powders. Furthermore, XRD patterns of the silver and tellurium powders used as starting materials are also shown. The crystal phases of the tellurium powders were tellurium and TeO2. At heat-treatment temperatures of 300 and 350°C, the crystal phases of the heat-treated powders were tellurium, TeO2, and Ag5Te3 (2θ = 34° to 35° and 41.3° to 41.6°). The silver and tellurium phase equilibrium diagram reveals that in the vicinity of the low-melting-point eutectic crystalline composition, there existed a eutectic region of Ag5Te3 and tellurium.12),13) Therefore, Ag5Te3 was formed. When the heat-treatment temperatures were 400 and 430°C, diffraction peaks attributed to tellurium, TeO2, Ag5Te3, and Ag2Te (2θ = 31°) were detected. The oxidation of tellurium led to the production of Ag2Te, which has less amount of Te than Ag5Te3. No diffraction peak of tellurium was detected with heat-treatment temperatures of 500°C and higher, where phases of TeO2, Ag5Te3, and Ag2Te existed. The results from DTA-TG and XRD revealed that a low-melting-point alloy was produced by diffusion reactions of silver and tellurium, when the powder mixtures of silver and tellurium powders were heat treated.

3.3 Microstructure at interface between tellurium-doped silver electrodes and silicon wafer

Figure 6(a) shows an FE-SEM image of the cross section of a silver electrode consisting of a paste prepared using silver powder. The silver powder was printed and dried on the silicon wafer.
and then heat treated for 3 min at 700°C on a hot plate. FE-SEM image of a tellurium-doped silver electrode prepared using a tellurium-doped silver paste with a silver-to-tellurium ratio of 98.5:1.5 (mol %), which was heat treated under the same conditions, is also shown in Fig. 6(b). The gaps were observed between the silver electrodes and the silicon wafer with the paste made of silver powder shown in Fig. 6(a), particularly in the recessed area with an uneven textured surface where many gaps were observed. When silver paste was printed and dried on a textured silicon wafer, the surface of the silicon wafer and the silver powder had point contacts, and hardly any silver powder had a contact with the wafer in the recessed area. Therefore, it is considered that the gap have occurred between the silver electrodes and the silicon wafer because of the shrinkage due to the sintering of the silver powder, when calcination was performed after the silver paste had dried. On the other hand, only a small number of gaps occurred on the interface between the tellurium-doped silver electrodes and silicon wafer, as shown in Fig. 6(b). Figure 6(b) revealed that the interface between the tellurium-doped silver electrodes and the wafer was in close contact.

Figure 7 shows FE-SEM image of the magnified view of the interface between the tellurium-doped silver electrodes and the silicon wafer depicted in Fig. 6(b). The layer attributed to an alloy liquid phase was observed in the recessed area of the uneven textured surface of the sintered tellurium-doped silver electrodes and the silicon wafer (area indicated by an arrow shown in the figure). It is considered that the layer attributed to an alloy liquid phase was formed during sintering process of the tellurium-doped silver paste. The layer attributed to an alloy liquid resulted in favorable contacts between the tellurium-doped silver electrodes and the textured surface. The alloy liquid phase segregated only at the interface between the tellurium-doped silver electrode and the silicon wafer. Any alloy liquid phase was not observed in the electrode layer. However, tellurium was detected in the electrode layer in the SEM/EDS analysis. It is considered that the tellurium contained in the alloy liquid phase had diffused into the Ag-rich alloy phase in the electrode layer while producing an alloy phase with a low tellurium concentration and high-melting-point. When the wettability of two kinds of metal was compared, the metal with lower surface tension and the higher reactivity to the silicon nitride had higher wettability to the silicon nitride substrate. The surface tension of the silver and tellurium alloy is lower than that of silver, because the surface tension of tellurium is lower than that of silver. Therefore, it is considered that the alloy liquid phase segregated on the silicon wafer surface with silicon nitride layer by the wettability.

Figure 8 shows the results of analyzing the composition of silver, silicon, and tellurium from the silicon wafer side towards the tellurium-doped silver electrodes, skipping the layer attributed to an alloy liquid phase in Fig. 7. FE-AES was used for the chemical composition analysis. No tellurium was detected at point 1 inside the silicon wafer and point 5 inside the tellurium-
doped silver electrode. 34.0 mol % tellurium, 36.0 mol % silver, and 30.0 mol % silicon were detected at Point 3 in the central area of the layer attributed to an alloy liquid phase. Ag, Te and Si form Ag–Te, Ag–Si, Te–Si and Ag–Te–Si alloys.13) Therefore, it is considered that the silicon had diffused into the alloy liquid phase of silver and tellurium.

3.4 Specific contact resistivity ($\rho_c$)

The tellurium-doped silver paste prepared with a silver-to-tellurium ratio of 98.5:1.5 (mol %), described in Subsection 3.3, was screen printed in pattern shapes, as described in Fig. 2(a), on the light-receiving surface of the silicon wafer of solar cells. It was then dried in an oven for 10 min at 150°C and calcined at a peak temperature of 785°C in a tunnel furnace, after which $\rho_c$ was measured using the TLM method. The measured $\rho_c$ had a high value of 6.96 $\Omega \cdot cm^2$ in comparison with the value of 0.023 $\Omega \cdot cm^2$ of ordinary silver electrodes of silicon solar cells measured in the same manner. The tellurium-doped silver electrodes were securely attached to the silicon wafer, but the resistance was high.

Figure 9 shows FE-SEM image of the cross section of the tellurium-doped silver electrode prepared with a silver-to-tellurium ratio of 98.5:1.5 (mol %), which was calcined at a peak temperature of 785°C in a tunnel furnace. In Fig. 9, in addition to the layer attributed to an alloy liquid phase, a layer indicated by the arrow on the silicon wafer surface was observed. Therefore, the chemical composition at the layer indicated by the arrow (in Fig. 9) and two points inside the silicon wafer were analyzed by using FE-AES [Fig. 10(a)]. Figure 10(b) shows the results of analysis by using FE-AES. Figure 10(b) reveals that nitrogen was detected in the layer on the surface of the silicon wafer and that this layer consisted of the silicon nitride of the ARC. It is considered that the undecomposed ARC that remained as residues was a significant cause for the high resistance.

4. Conclusions

The crystal phases of the tellurium-doped silver powders, the interfacial structure between the tellurium-doped silver electrodes and the silicon wafer, as well as the contact resistance of the tellurium-doped silver electrodes and the silicon wafer were investigated. When the tellurium powder was heat treated in an oxidizing atmosphere, the oxidation gradually increased up to the melting point but was more noticeable beyond the melting point. Therefore, when the tellurium-doped silver powder was heat treated at the temperature below the melting point, a low-melting-point alloy of silver and tellurium was produced by solid-phase diffusion reaction. In addition, it was implied that the alloy liquid phase of silver and tellurium was formed during sintering process. When the tellurium-doped silver powder was made into a paste and then printed onto the silicon wafer of solar cells and was calcined, the alloy liquid phase of silver and tellurium spread wetting in the gaps between the tellurium-doped silver electrodes.
and the silicon wafer surface, which resulted in favorable contacts. However, the ARC existed as an insulation film on the surface of the silicon wafer, was not decomposed and removed. The remained ARC resulted in the high resistance of the tellurium-doped silver electrodes of silicon solar cells. In future, in order to reduce the contact resistance, we consider that it is necessary to find another material that reacts with the ARC and has decomposition and removal effect.

References