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Pb-free glass frits prepared by spray pyrolysis as inorganic binders of Al electrodes in Si solar cells

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ABSTRACT

Pb-free glass frits prepared by spray pyrolysis for Al electrodes were of fine size, spherical morphology and dense structure. Their mean size and geometric standard deviation when prepared at 1,200 °C were 1.0 μm and 1.4, respectively. Their glass transition temperature (T_g) was 374 °C. An Al electrode formed from Al paste with glass frits had a dense structure and good adhesion to the Si substrate. It had a well-developed back-surface field layer of 17.5 μm thickness. Al electrodes formed from Al paste without glass frits had sheet resistances between 21 and 32 mΩ sq^{-1} as the firing temperature changed from 600 to 900 °C. This compared with values from electrodes formed with frits that decreased from 20 to 7 mΩ sq^{-1} over the same range of firing temperatures.

1. Introduction

Thick Al films are widely used as backside contacts in single-crystalline or polycrystalline Si solar cells. Al electrodes are commonly formed by firing a screen-printed layer using Al paste containing Al powder, glass frits, and a resin binder [1–5]. Al electrodes formed by firing at high temperature serve as electrical contacts. Al is also used to create a back-surface field (BSF), which reduces back-surface recombination and enhances efficiency [3]. The use of thinner wafers is sought to reduce solar cells' costs. With decreasing wafer thickness, cells bow because of sintering stress due to the aluminum.

The powders and frits composing the Al paste affect the formation of the BSF layer and a cell's bowing. Al powders for use in electrodes are usually prepared by gas atomization. Inorganic binders are usually irregular and rough Pb-based glass frits prepared by conventional melting [5–7]. Therefore, the effects of fine, spherical glass frits on the formation of Al electrodes are not well studied. There is also an environmental incentive to exclude lead from solar cells.

The characteristics of glass frits prepared by spray pyrolysis have been reported [8–11]. Spray pyrolysis involves one glass particle forming from one droplet through drying, decomposition, melting and quenching. Glass frits prepared in this way are spherical, of fine size and homogeneous composition because of microscale reactions inside the micron-sized droplets. They therefore are suitable as inorganic binders for Ag electrodes.

In this study Pb-free glass frits, for use as inorganic binder in Al electrode backside contacts in single-crystalline or polycrystalline Si solar cells, were prepared by spray pyrolysis and their properties investigated.

2. Experimental procedure

Bi_2O_3–B_2O_3–SiO_2 glass frits with small amounts of Na_2O and Li_2O were directly prepared by spray pyrolysis. Spray pyrolysis consisted of six ultrasonic spray generators operated at 1.7 MHz, a 1000 mm-long tubular alumina reactor of 50 mm ID, and a bag filter. The preparation temperature of the glass frits varied from 1000 to 1300 °C. The carrier gas flow rate was fixed at 20 L min^{-1}. Spray solutions were obtained by adding Na_2NO_3 (99%, Junsei, Japan), H_3BO_3 (99.5%, Kanto), tetraethyl orthosilicate (TEOS, Aldrich, 98%), $Bi(NO_3)_3\cdot 5H_2O$ (Junsei, 98%), and $LiNO_3$ (Aldrich, 98%) to distilled water containing an appropriate amount of nitric acid. The overall concentration of the metal in solution was fixed at 0.5 M.

The Al powders and glass frits were mixed with an organic vehicle of ethyl cellulose, α-terpineol, and butyl carbitol acetate (BCA). Commercial Al powders of 8.3 μm mean diameter prepared by gas atomization were used. Al paste was screen-printed on to a single-crystalline Si wafer. The printed Si wafer was dried at 120 °C for 30 min and fired at temperatures of 600–900 °C for 10 min at a heating rate of 7 °C.

The crystal structures of the prepared glass frits were investigated by X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation (λ = 1.5418 Å). Their thermal properties were investigated using a thermoanalyzer (TG-DSC, Netzsch, STA409C) between 40 and 900 °C (10 °C/min). The morphological characteristics of the glass frits and the fired Al electrodes were investigated by scanning elec-

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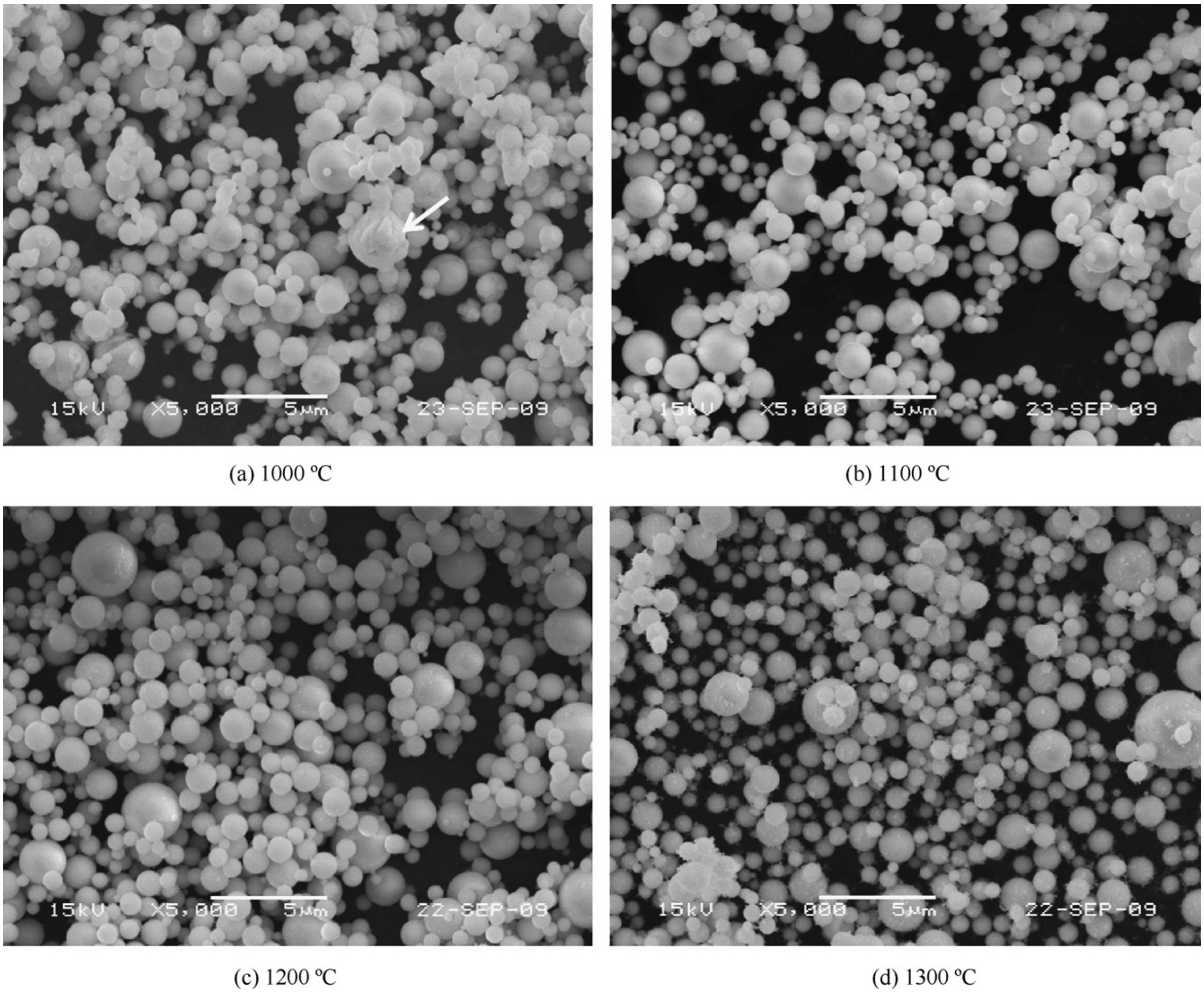

Fig. 1. SEM images of Pb-free glass frits prepared by spray pyrolysis at various temperatures.

tron microscopy (SEM, JEOL, JSM-6060). Sheet resistances of the Al electrodes were measured by a four-point probe (CMT-SR 1000N, Advanced Instrument Technology).

3. Results and discussion

The morphologies and crystal structures of the Bi_2O_3–B_2O_3–SiO_2 glass frits that contained small amounts of Na_2O and Li_2O are shown in Figs. 1 and 2. The glass frits were spherical and non-aggregated irrespective of preparation temperature. Some of the glass frits prepared at 1000 °C had rough surfaces, indicated by the arrow in Fig. 1(a). Complete melting of the powders did not occur in the hot wall reactor maintained at 1000 °C. Therefore, the glass frits prepared at 1000 °C were found to have crystalline phases by XRD analysis (Fig. 2). However, glass frits prepared at 1100 and 1200 °C had smooth surfaces and narrow size distributions. Each amorphous glass particle was prepared from one droplet by complete melting and quenching at 1100 and 1200 °C. The frits prepared at 1300 °C, however, had a bimodal size distribution of submicron and nanometer sizes. The high temperature of the hot wall reactor caused the evaporation of some of the glass. Nucleation and growth of the evaporated vapors formed nanometer-sized glass powders. The mean size and geometric standard deviation of the glass frits prepared at 1200 °C were 1.0 μm and 1.4, respectively.

Fig. 3 shows the results of dot mapping of the glass frits prepared at 1200 °C. The glass components were well distributed inside the frits. Spray pyrolysis produced homogeneous frits because of microscale reactions inside each micron-sized droplet. Therefore,

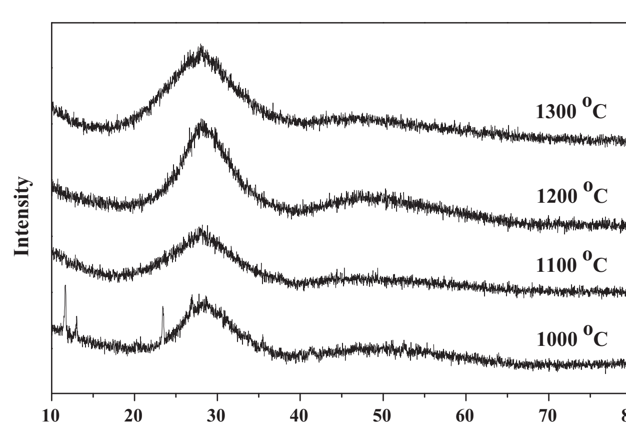

Fig. 2. XRD patterns of Pb-free glass frits prepared by spray pyrolysis at various temperatures.

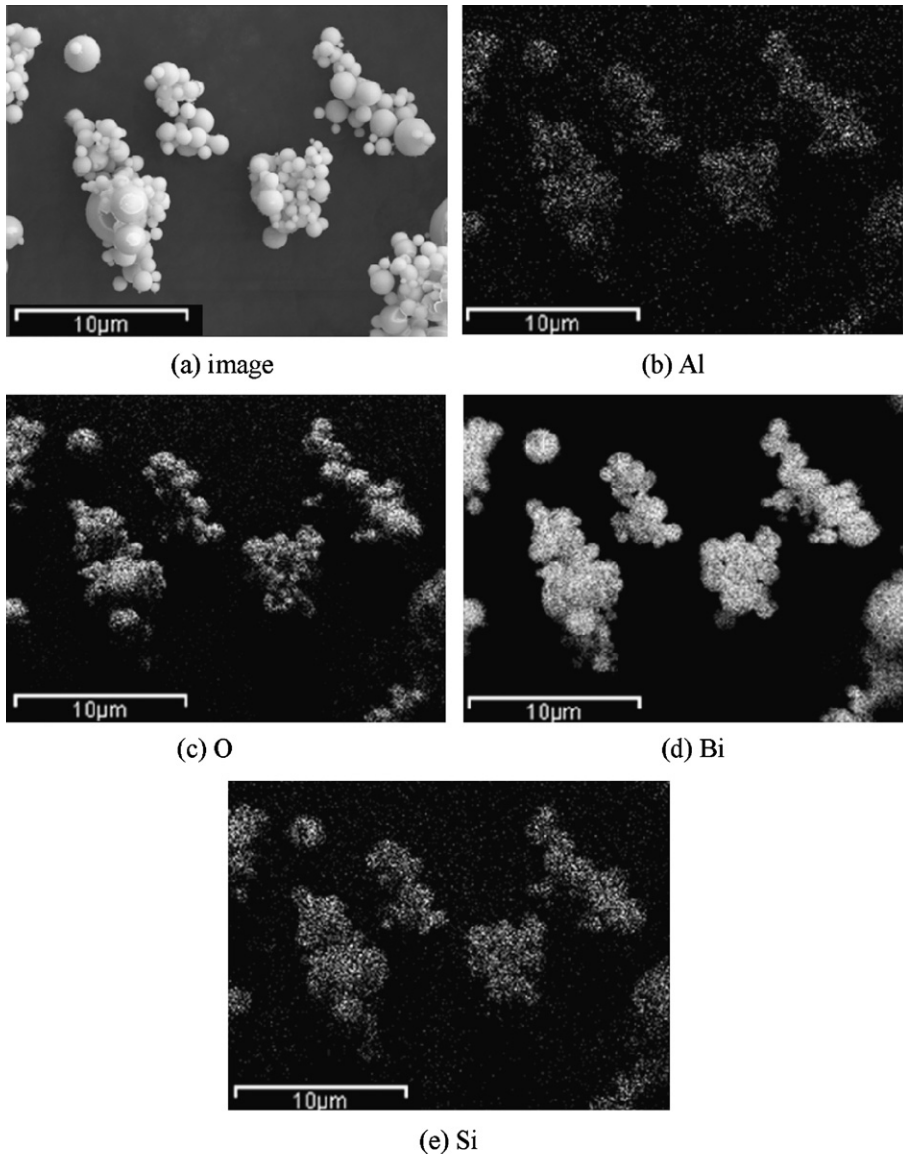

Fig. 3. Results of dot mapping of Pb-free glass frits prepared by spray pyrolysis.

amorphous frits with dense structures were directly prepared by spray pyrolysis even at powder residence times inside the hot wall reactor as short as 0.7 s.

Fig. 4 shows TG/DSC curves of the frits prepared at 1200 °C. Slight weight loss was observed on the TG curve at 40–800 °C. The frits' glass transition temperature (T_g) was 374 °C.

The frits prepared at 1200 °C were used as an inorganic binder for Al electrodes. Fig. 5 shows SEM images of the surfaces of the Al electrodes fired at various temperatures. Spherical Al powders were maintained at firing temperatures between 600 and 800 °C. The roughness of the Al powders forming the electrode increased with increasing firing temperature through the oxidation of the powders, as they were fired in air. The powders' spherical shape was destroyed by oxidation when the firing temperature reached 900 °C. Aluminum has a low melting temperature of 660 °C. However, the Al powders used in this study has oxide coating layer by oxidation of powders in air atmosphere. Therefore, melting of the Al powders did not occur in the firing process. Spherical shape of the Al powders is maintained at firing temperatures below 800 °C. The high oxidation degree of the powders at a firing temperature of 900 °C destroyed the spherical shape of the Al powders. Fig. 6

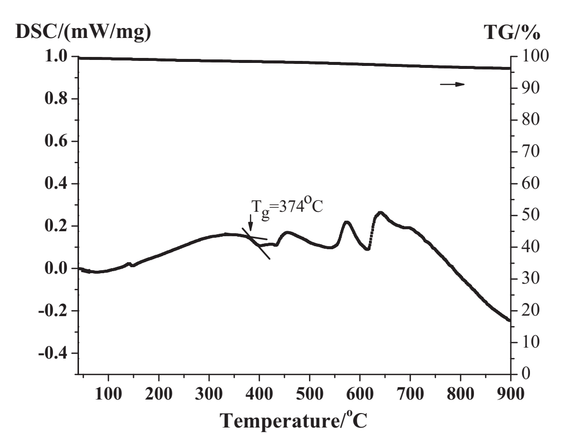

Fig. 4. TG/DSC curves of Pb-free glass frits prepared by spray pyrolysis.

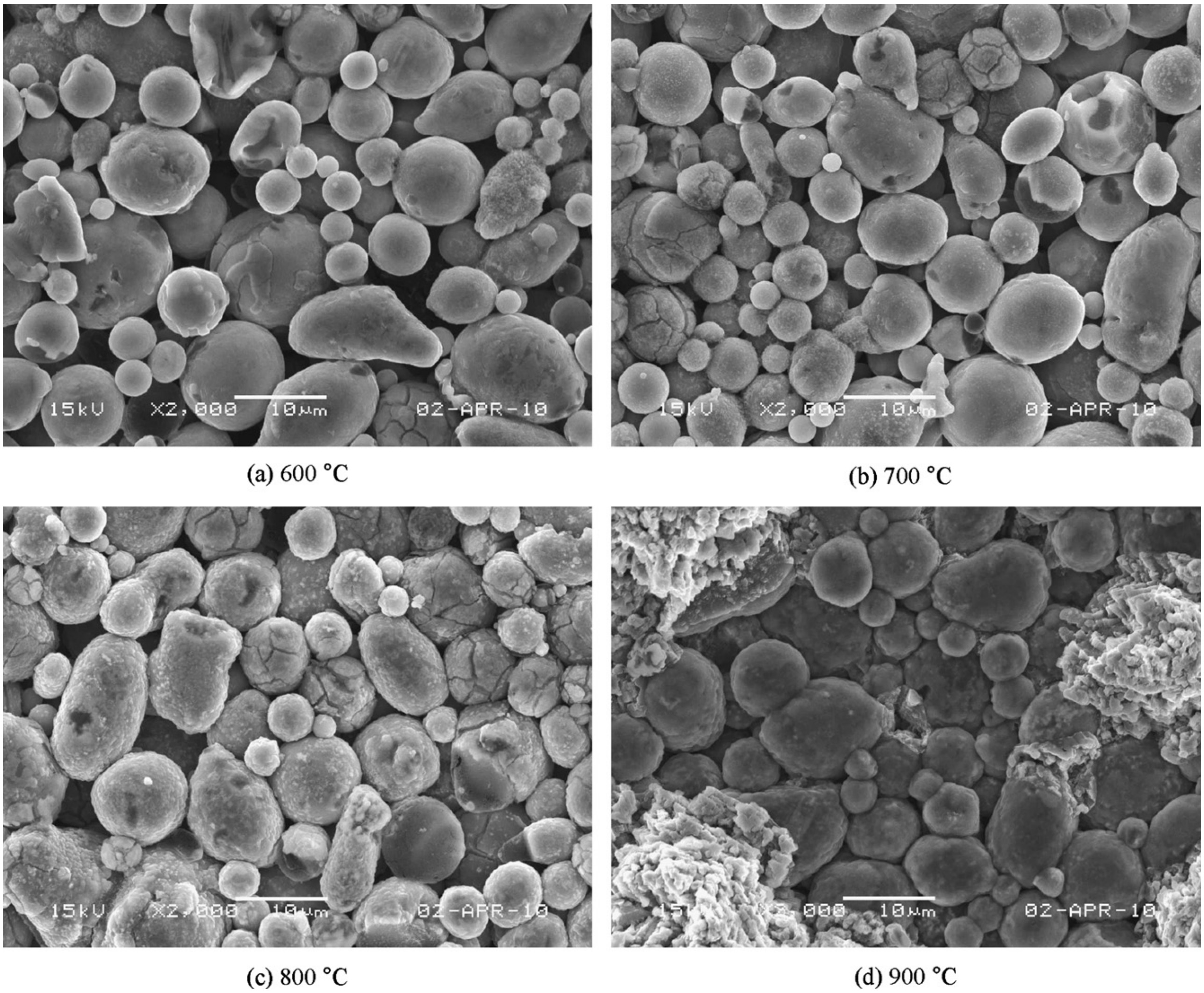

Fig. 5. SEM images of the surfaces of Al electrodes fired at various temperatures.

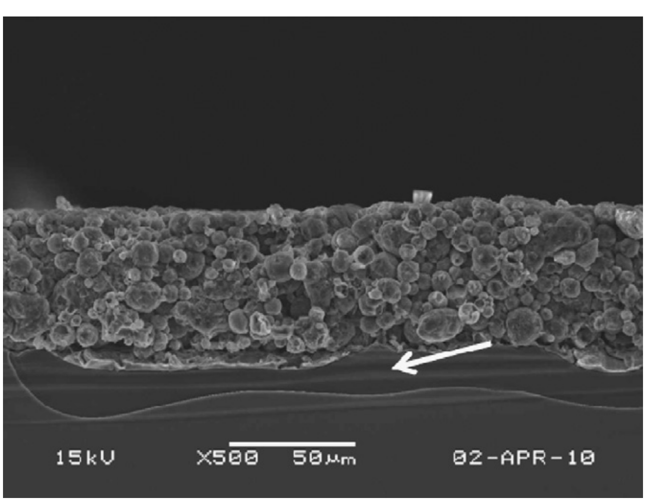

Fig. 6. SEM image of the cross section of the Al electrode containing frits fired at 800 °C.

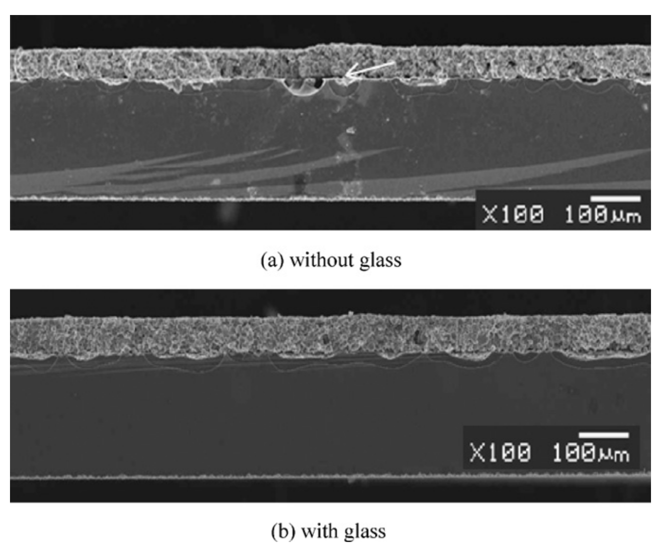

Fig. 7. SEM images of the cross sections of the Al electrodes formed from the Al pastes with and without glass frits at a firing temperature of 800 °C.

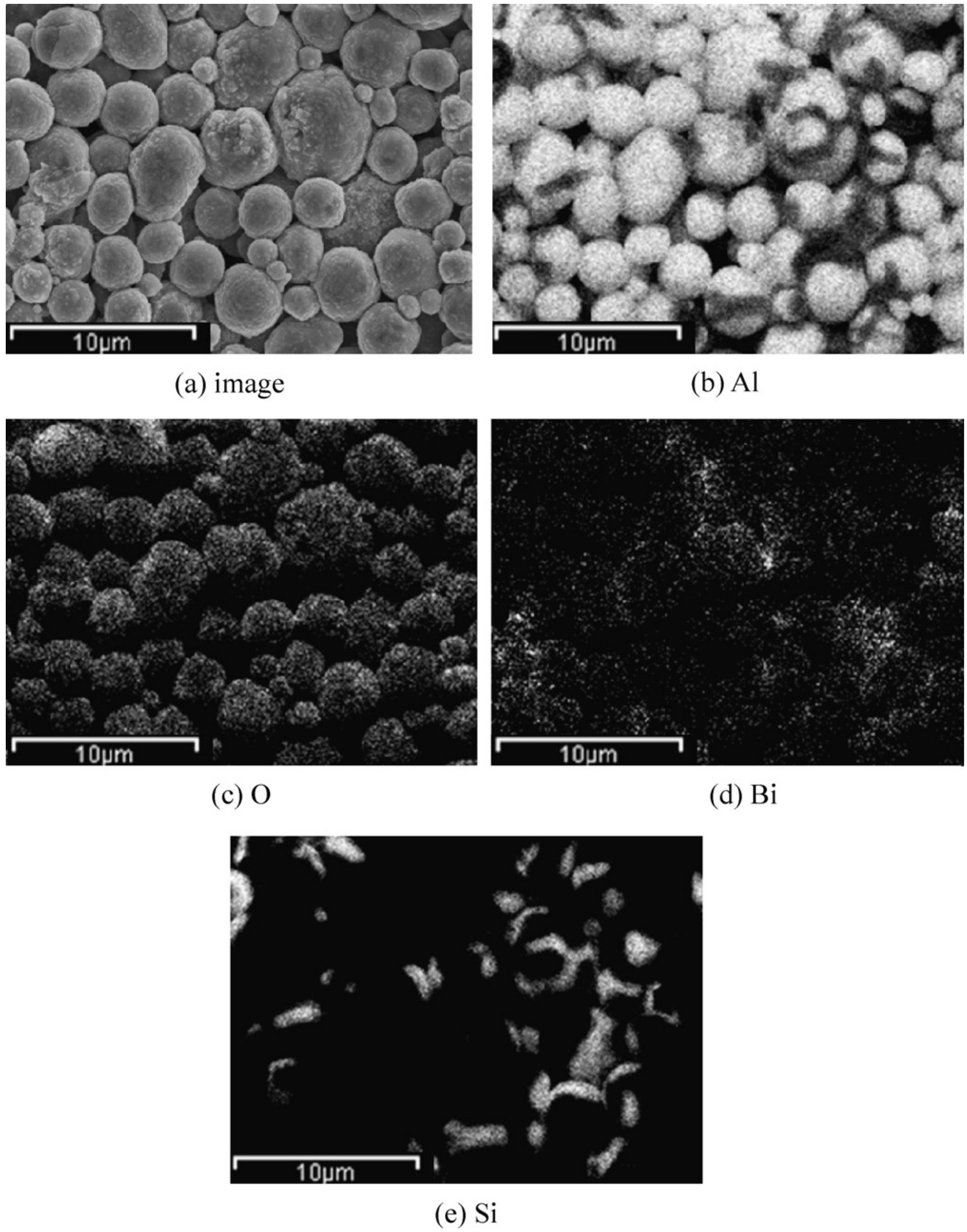

Fig. 8. Results of dot mapping of the surface of the Al electrode fired at 800 °C.

shows an SEM image of the etched cross-section of the Al electrode fired at 800 °C. It was 51.7 μm thick with a dense structure and good adhesion to the Si substrate. It had a well-developed BSF layer of 17.5 μm thickness, shown by the arrow in Fig. 6. Fig. 7 compares the properties of the electrode formed from the Al paste with glass frits with those of the electrode formed from the paste without glass frits. Frits improved the formation of Al–Si alloys by liquid phase sintering. Therefore, the electrode with the frits had a better developed BSF layer than the Al electrode formed without frits. The glass frits improved the adhesion of the electrode to the substrate, with the electrode formed without glass frits having poor adhesion to the Si substrate (arrow in Fig. 7 (a)).

Figs. 8 and 9 show the results of dot mapping of the Al electrodes, in which the glass content was 3 wt% of the Al component. The distributions of Si and Bi inside and on the surface of the Al electrode are observable. Glass was well-distributed between the Al powders through melting and quenching and therefore enhanced contact between the Al powders in the Al films.

The effect of glass frits on the sheet resistances of the Al electrodes is shown in Fig. 10. The sheet resistances of electrodes formed without frits changed from 21 to 32 mΩ sq^{-1} when the firing temperatures changed from 600 to 900 °C. However, those of the electrodes formed with frits decreased from 20 to 7 mΩ sq^{-1} over the same range of firing temperatures. Glass frits improved the contact properties between the Al powders by enhancing the sintering characteristics of the Al electrode formed from the Al powders coated with aluminum oxide. Therefore, the Al electrodes formed from Al paste with glass frit had low sheet resistances.

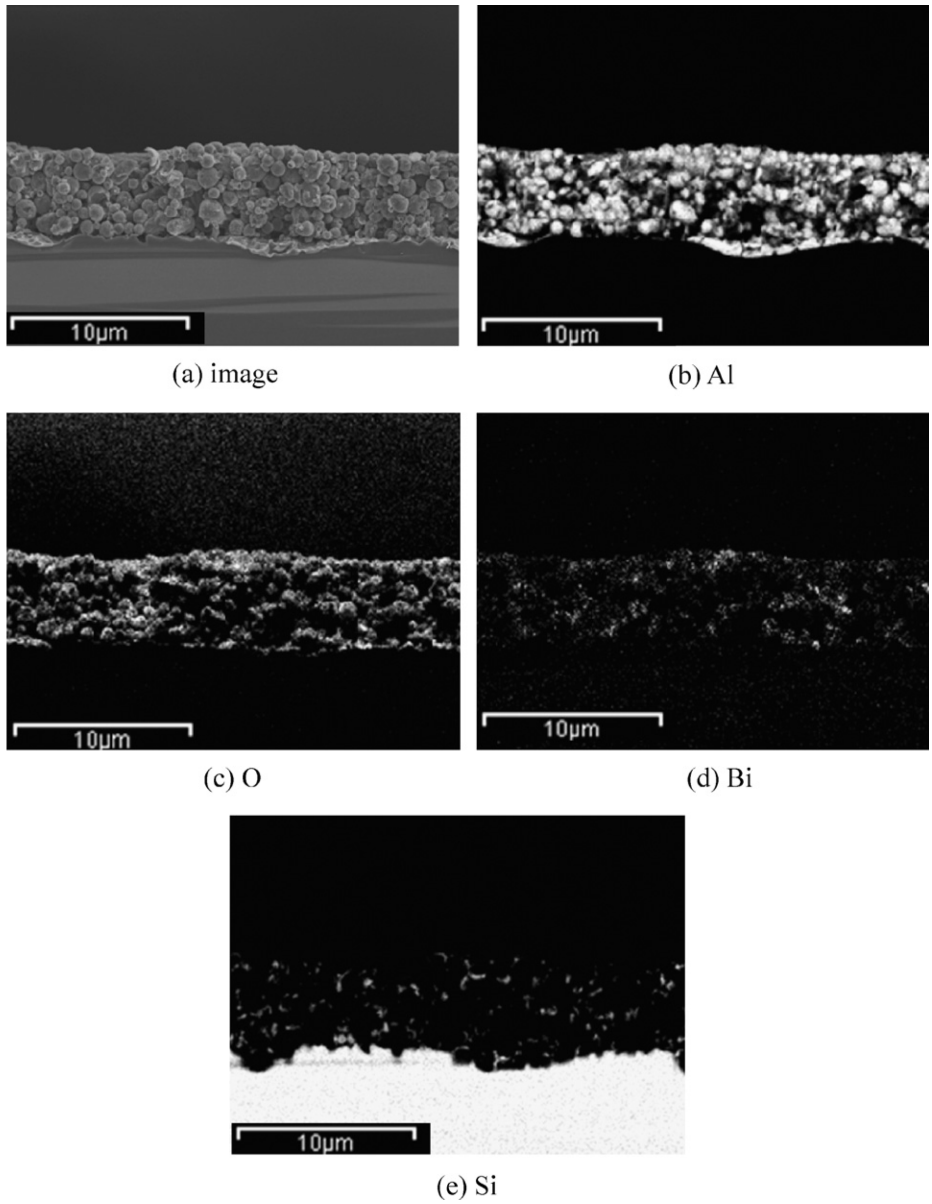

Fig. 9. Results of dot mapping of the cross section of the Al electrodes.

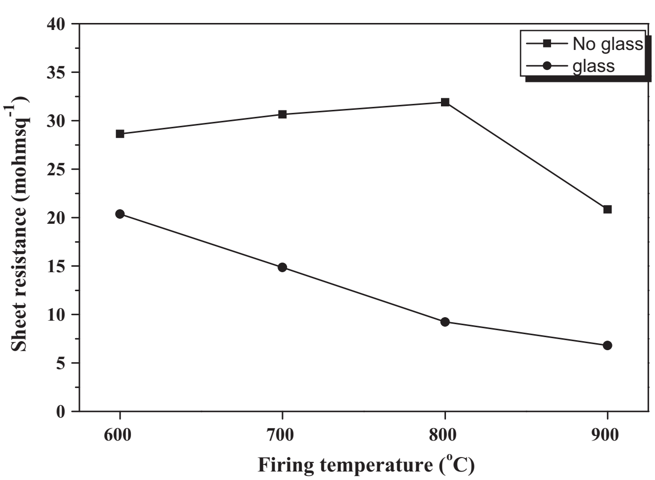

Fig. 10. Sheet resistances of the Al electrodes fired at various temperatures.

4. Conclusions

Pb-free glass frits were prepared by spray pyrolysis and investigated as inorganic binder for Al electrode backside contacts in Si solar cells. They were spherical, of fine size, and homogeneous, with good characteristics as inorganic binder for Al electrodes. An Al electrode formed from Al paste containing such frits had a dense inner structure, good adhesion, and low sheet resistance at firing temperatures between 600 and 900 °C. The frits also improved the formation of BSF layer between the Si wafer and the Al electrode.

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