INTRODUCTION

Contact metallisation is an important process that significantly affects the efficiency of Si solar cells. The contact quality between the electrode metal and Si contributes to the series resistance in solar cells. Therefore, the contact material should have high electrical conductivity, thermal stability at high temperature and good adhesion to Si wafer. Additionally, a peak firing process, which includes sintering at temperatures of 700–900°C, is necessary for high-quality contact with the Si wafer. Sintering is performed using a conveyor belt furnace in air; therefore, the contact material should have high oxidation resistance.

Ag is considered as an optimal material for the front- and rear-side metallisation of Si solar cells owing to its low electrical resistivity of 1.59 × 10⁻⁶ Ω cm³ and...
excellent oxidation resistance at temperatures above 700°C. However, the high cost of Ag limits its competitiveness in the Si solar cell industry, necessitating alternative materials. Cu has attracted significant attention as an excellent alternative to Ag owing its high electrical conductivity and low cost. The electrical resistivity of Cu is 5% higher than that of Ag; however, Cu can be easily oxidised at high temperatures, because of which Cu sintering has mainly been conducted at low temperatures of <200°C. This low-temperature sintering provides insufficient thermal energy to transform Cu particles into a bulk conductive film. The Yoshida group attempted the atmospheric sintering of Cu–P alloy paste at a temperature of 600°C. The deoxidisation of Cu2O derived from Cu–P alloy particles afforded a crystalline Cu network. The authors demonstrated the first practical application of the Cu–P alloy electrode by application to Si solar cells. However, the Cu–P alloy electrode exhibited an electrical resistivity of 2.54 × 10−5 Ω cm, which was insufficient to replace the Ag electrode in solar cells.

High temperatures of >700°C are essential for the formation of a Cu conductive film with low electrical resistivity (close to that of Ag). The Cu film formed via atmospheric sintering would be commercially attractive. Herein, Cu paste that is applicable to a conventional firing process employing high temperatures of up to 800°C in air is described. A paste mixture containing Cu–Ag core-shell and B powder was prepared, and atmospheric sintering on a Si wafer printed with Cu paste was conducted. As a result, Cu oxidation could be prevented by B at high temperatures, and a high-quality Cu conductive film with very low electrical resistivity could be formed. To optimise the formation and electrical resistivity of the Cu film, the sintering temperature and B composition ratio of the paste were varied. The characteristics of the Cu film were determined using scanning electron microscopy (SEM) and X-ray diffraction (XRD). In addition, the oxidation resistance mechanism of B was investigated via depth-profiling X-ray photoelectron spectroscopy (XPS) analysis of the Cu conductive film. Ultimately, the commercialisation prospect of the Cu electrodes was tested by applying these to solar cells.

2 | METHODS

2.1 | Sample preparation

The filler particles of the paste were synthesised using the following materials: Cu–Ag core-shell particles (Joinm) with diameters of 3 µm and Ag shell ratios of 9 wt.%, CuP (Pometon, 5 µm), Cu–Mg (Pometon, 3 µm) and Cu (HKK solution, 99.8%) for the metal particles and boron (Unitech), CaB (ESC Ceramics) and Ag powders (JC corp., D50 3.5–4.5 µm) for oxidation-resistant additives. To fabricate the paste, the fillers were mixed with an organic binder at a ratio of 87:13 (wt.%). The binder was synthesised by mixing 300 and 22 cP viscosity ethyl cellulose (Sigma-Aldrich) with 1-dodecyl (Samchun, 98%) and butyl carbitol (Sigma-Aldrich, 99%). Subsequently, the 200 g paste was mixed using a Thinky mixer (K-corp.) at 1000 rpm for 3 min and dispersed using a 3-roll mill (INTEC and TX-3102ST). The pastes were screen-printed on a 360-mesh patterned film onto a Si wafer using printing equipment (Linesystem, LSP-1515TS) and dried at 150°C for 5 min in a drying oven. Sintering was performed at various temperatures (500–800°C) using an electric furnace (Daesung, SJMF4); the samples were placed in the furnace chamber for several seconds and then quickly removed. To fabricate Cu-based front electrodes of the solar cells, various kinds of commercial glass frits (Bass corp.) with base compositions of PbO–B2O3–SiO2, Bi2O3–B2O3–SiO2 and Bi2O3–B2O3–SiO2–ZnO were examined via mixing in the Cu–Ag core-shell paste. The pastes were screen-printed through a 360-mesh screen film patterned by four busbars with 40 µm opening fingers on a 200-µm-thick p-type single-crystalline Si wafer (Shinsung solar, 156.75 × 156.75 mm). Subsequently, the samples were dried in an oven furnace and sintered at a peak temperature of 800°C for 3 s using a conveyor belt furnace (Hengli Eletek Co., HSK6305-0711).

2.2 | Characterisation

The thickness of the Cu-based films was measured using a digital thickness gauge (Protec, MG-500C). The electrical resistivity of the films was characterised using the four-point probe method (Mitsubishi Chemical, Loresta-EP MCP-T7000). The Cu-based film samples for cross-sectional views were prepared via mechanical cutting and polishing using sandpaper and 0.3-µm alumina suspension. The morphologies were observed by optical microscopy and scanning electron microscopy (SEM, JEOL and JSM-7500F). X-ray diffraction (XRD, Bruker, D8 Advance) using Cu Kα radiation was performed to confirm the crystal structure of the sintered Cu-based films. The chemical analysis was conducted using X-ray photoelectron spectroscopy (XPS) (Thermo Electron K-Alpha), and the obtained XPS depth profiles were analysed using the Thermo Advantage program. The J–V characteristics of the solar cells were probed using a DC voltage current source monitor (ADC, 6244) under simulated illumination (AM1.5G) using a class AAA solar simulator (McScience, K3000).
3 | RESULTS AND DISCUSSION

Studies to develop a Cu paste applicable to high-temperature sintering were initiated. In the beginning, various types of Cu metal particles such as Cu, Cu–Ag core-shell, Cu–P alloy and Cu–Mg alloy were selected as conductive fillers for the paste, and CaB$_6$, B and Ag particles were selected as oxidation-resistant additives. Subsequently, Cu pastes were prepared by mixing various combinations of the above materials. After adjusting the ratios of the filler materials and sintering temperatures, the Cu paste film obtained by mixing Cu–Ag core-shell particles with B exhibited the best electrical conductivity (Table S1). Among the metal particles, Cu with Ag shell particles showed a better oxidation resistance effect at high temperatures than the pure Cu particles, and enhanced electrical conductivity was observed for the Cu–Ag film with an Ag shell content up to 9%. However, additional Ag shell content did not contribute to further improvement in the electrical conductivity. Figure 1 shows the Cu–Ag film after atmospheric sintering of the Cu–Ag core-shell paste with and without B at 700°C for 10 s. As shown, the paste film containing B powder has a light brown colour, whereas the film without B has a dark grey colour, which indicates that the film has undergone severe oxidation. The electrical resistivity is $7.11 \times 10^{-6}$ Ω cm for the film with B and $5.12 \times 10^3$ Ω cm for the film without B, which clearly suggests that B can prevent Cu oxidation during high-temperature sintering.

Next, the sintering conditions were modified and controlled to optimise the electrical conductivity of the Cu–Ag film with B. The sintering was performed at 500–800°C by varying the holding times, and the colour and electrical resistivity of the film were subsequently observed (Figure S1). The highly electrically conductive Cu–Ag film required a suitable sintering temperature of >600°C and a holding time within 10 s. An extension of the sintering time at the temperature caused Cu oxidation. At 600°C, the electrical resistivity of the Cu–Ag film sintered for >10 s increased again, implying that Cu oxidation commenced at this temperature (no considerable change in resistivity was observed at 500°C), and thus indicating that the long sintering time promoted oxidation. The colour of the film also changed according to the sintering conditions. Typical copper-coloured films were obtained at temperatures of >700°C, and Cu–Ag films with the lowest electrical resistivity were obtained at temperatures of 700 and 800°C with sintering times of 10 and 5 s respectively. However, excessive sintering at these temperatures afforded reddish films that eventually turned blue, leading to Cu–Ag films with extremely high electrical resistivity. In addition, the sintering time required to obtain Cu–Ag films with high electrical conductivity was decreased, indicating that Cu oxidation was also accelerated according to the sintering temperature.

Figure 2 shows the cross-sectional SEM and optical images of the Cu–Ag core-shell films with B sintered at different temperatures. As shown in Figure 2A, the film sintered at 500°C is filled with unmelted Cu–Ag core-shell particles due to insufficient thermal energy, which is responsible for the low electrical conductivity of the Cu–Ag film. The Cu–Ag core-shell particles begin to melt and neck each other from 600°C, and a complete bulk film is formed at temperatures above 700°C. The results suggest that sintering at >700°C is required to convert Cu particles into a bulk film with the lowest electrical resistance. However, sintering at >800°C leads to severe Cu oxidation on the film surface. Moreover, some part of the film was found to swell due to the excessive sintering, resulting in non-uniform thickness. The results are also consistent with the XRD patterns of the sintered Cu–Ag films. As shown in Figure 2B, the XRD patterns confirm that the Cu–Ag particles retain their pristine crystalline structures without any Cu oxidation at 500°C. The formation...
of Cu oxide species was confirmed at temperatures above 600°C, indicating that Cu oxidation commenced at 600°C. Furthermore, peaks for highly crystalline Cu corresponding to the (111) and (200) planes were observed for the Cu–Ag film sintered at 700°C. This suggested that boron effectively inhibited the oxidation of Cu at high temperatures. The sharp increase in the Cu$_2$O peaks at 800°C was also consistent with the severe surface oxidation of the Cu–Ag film.

The oxidation resistance effect of B was further investigated by adjusting the B ratio in the Cu–Ag core-shell paste. Figure 3 shows the electrical resistivity of the 3 µm Cu–Ag particle film with different B ratios upon sintering at 800°C for 5 s. As previously discussed, the B-free Cu–Ag film undergoes severe oxidation, and the electrical resistivity is very high (Figure 3). However, the electrical resistivity of the Cu–Ag film decreases rapidly with an increase in the B content; the lowest electrical resistivity
of $5.31 \times 10^{-6}$ $\Omega$ cm is obtained at a B content of 5 wt.%. However, the electrical resistivity of the Cu–Ag film with a more than 5 wt.% ratio of B increased, which is presumed to be a result of an excessive addition of B with high electrical resistance. However, the particle size effect of the Cu–Ag core-shell is not observed. It is comprehensively determined that a Cu film with very low electrical resistance can be obtained by controlling the sintering conditions and B content. However, the experimental methods used to date are not so specific, and it is expected that further optimisation of the Cu film with an even lower electrical resistivity can be achieved if an advanced fabrication method is employed.

X-ray photoelectron spectroscopy (XPS) analysis of the sintered Cu–Ag film was performed to elucidate the oxidation resistance mechanism of B. Figure 4 shows the O 1s and B 1s core-level XPS profiles (by depth) of the Cu–Ag film. O 1s peaks are observed at binding energies of 532.0 and 530.3 eV, corresponding to B$_2$O$_3$ and Cu$_2$O respectively. The peak intensity of B$_2$O$_3$ decreases sharply and that of Cu$_2$O peak increases, with increasing depth inside the film. This is consistent with the rapid decrease in the peak at 192.3 eV for B$_2$O$_3$ in the B 1s spectrum. The result indicates that the surface layer of the Cu–Ag film mainly comprises B$_2$O$_3$, which is converted into Cu$_2$O deeper inside the film. Therefore, it can be assumed that the evenly distributed B in the paste diffuses out to the surface of the film during high-temperature sintering. Subsequently, the B-rich surface layer is oxidised to B$_2$O$_3$ and speculated to act as a passivation layer to prevent the inter-diffusion of external oxygen into the Cu–Ag film during sintering.

This can also be confirmed by the Cu 2p and Ag 3d regions of the XPS data as shown in Figure 5. First, for the B-free Cu–Ag film (Figure 5A), the Cu 2p$_{3/2}$ core-level spectra of the top layer show a major peak at 934.4 eV and a broad, small peak between 940.3 and 946.2 eV, which are characteristic of CuO. Furthermore, the major peak shifts to 933.2 eV inside the film, implying that CuO gradually converts into Cu$_2$O. This indicates the severe oxidation of the Cu–Ag film without B, and the diffusion of oxygen from the surface into the bulk of the film through a gradual decrease in the oxygen ratio towards the inside of the film. For the B-containing Cu–Ag film (Figure 5B), the main peak of the Cu 2p spectra is consistently positioned at 932.5 eV for the entire film depth, which corresponds to Cu$_2$O or Cu (these species have similar binding energies). Notably, the main peak increases with increasing depth inside the film, which implies that pure Cu species are predominant in the layers. This is in contrast to the result obtained for the Cu–Ag film without B, and indicates that the surface B$_2$O$_3$ layer effectively acts as a barrier to the inter-diffusion of oxygen.

The Ag 3d spectra show that Ag atoms are widely distributed across the entire layer of the Cu–Ag film without B (Figure 5C), whereas an Ag layer is detected on the inside for the film with B (Figure 5D). It is speculated that Ag melts and flows downward owing to a relatively higher specific gravity and lower melting point than Cu. The presence of the B-rich surface layer can also contribute to this phenomenon. As mentioned earlier, for the pastes with B, the Cu–Ag core-shell film has a lower electrical resistivity compared with that of the pure Cu particle film, which is attributed to the oxidation resistance of the Ag shell in addition to the passivation effect of the B$_2$O$_3$ surface layer. However, the oxidation resistance of Cu is significantly affected by the presence of B, suggesting that the B$_2$O$_3$ surface layer shows a more dominant effect than the Ag layer.
An effective method to prevent Cu oxidation during high-temperature sintering was identified. Furthermore, the Cu–Ag core-shell electrode was applied to the front metallisation of Si solar cell. For the metallisation, glass frit is essential to etch the SiNₓ anti-reflection coating on Si wafer. To this end, various commercial PbO-based and Bi₂O₃-based glass frits were explored by mixing optimal amounts into the Cu–Ag core-shell pastes with B. The pastes were screen-printed using the four-busbar pattern on an Al back-surface field crystalline Si wafer, and the co-firing process was conducted employing a typical temperature profile with a peak temperature of 800°C for 3 s using an infrared belt furnace. As a result, it was found that the Cu–Ag core-shell electrode solar cells using Bi₂O₃-based glass frit showed higher photovoltaic efficiencies than those using PbO-based glass frit, as shown in Figure 6. The exact cause of this result has not yet been identified, but crystallised Cu precipitates in the form of small particles were more frequently found in the Bi₂O₃-based glass layer than in the PbO-based glass layer (Figure 6B), and it is presumed that this increases the electrical conductivity of the insulating glass layer. This is also consistent with the improvement in the series resistance component of the Cu electrode solar cell containing Bi₂O₃ glass frit observed in the I–V curve (Figure 6A). Consequently, the Cu–Ag core-shell electrode with the Bi₂O₃–B₂O₃–ZnO–SiO₂ glass frit showed the best performance and a maximum photovoltaic efficiency of 17.55% was obtained (Figure 6D); it was only 2.45% lower than an efficiency of 19.90% for the Ag electrode solar cell fired under the same condition. This is the first report describing such performance for a Cu-based electrode solar cell, which demonstrates the possibility of using Cu electrodes as alternatives to Ag electrodes in the solar cell industry. Further improvement in the efficiencies of Cu-based...
electrode solar cells can be achieved if glass frits and firing technologies suitable for Cu paste are developed.

4 | CONCLUSIONS

A method to prevent Cu oxidation during sintering at high temperatures of up to 800°C is described. For the Cu paste, various types of Cu metal particles and oxidation-resistant additives were examined via sintering. The paste film composed of Cu–Ag core-shell and B showed the best electrical property after sintering. In particular, the oxidation of the Cu–Ag film was substantially suppressed by the addition of B. The film formation at different sintering temperatures was observed, and high-density bulk films with low electrical resistivities were formed at temperatures above 700°C. Furthermore, the lowest resistivity of 5.31 × 10⁻⁶ Ω cm was obtained by controlling the B ratio and particle size of the filler in the paste. XPS data of the Cu–Ag metallic film revealed that B was diffused out to the surface of the film during sintering and formed a B₂O₃ layer, which acted as a passivation layer to prevent the inter-diffusion of external oxygen. Finally, a Cu-based electrode solar cell using the Cu–Ag core-shell paste with B was fabricated, which afforded the maximum photovoltaic efficiency of 17.55%. These results show the potential applicability of Cu-based electrodes in the solar cell industry. In the future, it is believed that a more advanced structured Si cell such as passivated emitter and rear cell (PERC), sintering process and the development of glass frit compatible with copper paste will further increase the performance of solar cells with Cu-based electrode.

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