Novel Low-Temperature-Sintering Type Cu-Alloy Pastes for Silicon Solar Cells

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Abstract

This paper describes a novel Cu paste for low temperature sintering, which is required to fabricate electrodes on transparent conductive films in heterojunction solar cells. For this, glass-fritless Cu-alloy pastes containing a low melting point alloy (LMPA) were prepared. The pastes were evaluated in terms of printability, contact resistance, line resistance, adhesive property, diffusion of Cu in Si, and oxidation resistance. It was concluded that the pastes could be applicable to silicon solar cells requiring low temperature processes.

Keywords: Heterojunction, Screen printing, Contact, Interfaces, Copper paste

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1. Introduction

Glass-frit plays an important role during Ag/Si metal-semiconductor contact formation. However, the process requires high temperature melting, typically above 600 °C, which often causes problems. These problems include warping wafers, shunting of the p-n junction regions, and the need for high-cost facilities. Although Ag is expensive, Ag paste is often used as a conductive paste for solar cell electrodes because of its intrinsic low conductivity. On the other hand, Cu used for paste printing [1]–[3] or plating [4]–[7] is much less expensive than Ag and still has a relatively high conductivity, and therefore, it is one of the candidates to replace Ag. Moreover, Cu easily oxidizes in air compared to Ag, which makes it difficult to decrease the resistance and requires an elaborate reductive atmosphere (typically, 3%H₂ + N₂). As a result, we developed glass-fritless Cu-alloy pastes containing a low melting point alloy (LMPA), which allows low temperature sintering (< 200 °C) without any reductive conditions. These pastes are also applicable to metal solar cell electrodes that require low temperature processes such as heterojunction solar cells (< 250 °C). Furthermore, we present the design concept of the new Cu-alloy. As shown in Fig. 1, in conventional curing type metal pastes, electrical contact formations between adjacent metal particles rely on the shrinkage of the binder polymers. Therefore, these contacts are of the physical type. On the other hand, the Cu-alloy paste is composed of copper particles and LMPA particles. After the LMPA particles melt, metal contact is formed with the copper particles, which prevents Cu particle oxidation.

![Fig.1 Schematic diagram of the difference between Cu-alloy paste and conventional resin paste.](image-url)
2. Experimental

Novel Cu-alloy pastes were prepared by blending Cu particles with diameter of several micrometers and homogeneously mixed alloys as a low melting point solder. An SEM image of a mixed alloy clearly shows the homogeneity of the alloy particles compared to the alloy prepared by a conventional atomizing method (see Fig. 2). Note that after resolidification, the alloy forms an equiaxed crystal while the conventional method yields random crystals.

The pastes were screen printed on the Indium Tin Oxide (ITO) glass or textured Si substrates followed by sintering at < 200 °C.

They were also evaluated in terms of printability, contact resistance, line resistance, adhesive property, diffusion of Cu in Si, and oxidation resistance.

3. Results and Discussion

3.1. Melting behavior:

Figure 3 shows the differential scanning calorimetry (DSC) data of the new Cu-alloy paste. The melting point of the LMPA was estimated at 143 °C. Below the melting point, the printed paste pattern was not conductive. On the other hand, beyond the melting point, the LMPA particles were rapidly melted and the printed paste patterns became conductive. As shown in Fig. 3, the DSC peak of melting LMPA is very sharp. This is because the LMPA particles have nano-level uniformity as shown in Fig. 3.
3.2. Printability.

In the screen printing technique, printability of conductive paste is an important factor. Therefore, we have checked the printability of the Cu-alloy paste on a textured Si wafer by using a screen printing machine. The printed patterns of the Cu-alloy paste have very flat surfaces and sharp edges as shown on the right in Fig. 4. This indicates that the Cu-alloy paste has excellent self-leveling and resolution. On the other hand, the printed patterns of the conventional Ag paste with glass-frit have obvious rough surfaces because of screen-mesh marks.

These results indicate that the new paste has a good printability for screen printing, which can lead to the production of fine and high-aspect electrode patterns.
3.3. Line resistivity and contact resistivity:

The resistivity of a screen-printed pattern was determined by the four-point probe method (Resistivity meter: Loresta GP Model MCP-T600 - Mitsubishi Chemical Analytech Co., Ltd.). As shown in Table 1 and Fig. 5, using the Cu-alloy paste, the resistivity of the printed pattern that sintered at 150 °C for 10 min was c.a. 3.10–5 Ω cm. This is one of the lowest values among the typical commercially available Cu pastes, except for nano-particle pastes.

The contact resistivity between the metal paste and the ITO electrode was determined by the transfer length measurement (TLM) method (electrode pad size is 0.2 cm × 0.2 cm). The sheet resistance of the ITO electrode was c.a. 10 Ω/□. As a result, contact resistivity of the Cu-alloy paste/ITO electrode was lower than that of commercially available resin type Ag paste for heterojunction type solar cells (see Table 1 and Fig. 5). Furthermore, the measured work function of the new paste was about 4.8 eV. Therefore, this paste showed excellent electrical contact on the ITO electrode. This fact indicates that the new paste is suitable for a solar cell with heterostructure.

Table 1. Electrical and adhesive properties of various conductive pastes on the ITO electrode.

<table>
<thead>
<tr>
<th>Product type &amp; Paste Maker</th>
<th>Contact resistivity (Ω cm²)</th>
<th>Resistivity (Ω cm)</th>
<th>Tape peeling test*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu paste A ACP-051 : Asahi Chemical Research Laboratory Co., Ltd</td>
<td>2.30E-03</td>
<td>3E-04</td>
<td>10/10</td>
</tr>
<tr>
<td>Cu paste B ACP-080 : Asahi Chemical Research Laboratory Co., Ltd</td>
<td>1.20E-03</td>
<td>5E-04</td>
<td>10/10</td>
</tr>
<tr>
<td>Cu paste C NF2000 : Tatsuta Electric Wire &amp; Cable Co., Ltd</td>
<td>3.60E-04</td>
<td>1E-04</td>
<td>10/10</td>
</tr>
<tr>
<td>Our paste Our developed Cu-alloy paste</td>
<td>5.30E-04</td>
<td>3E-05</td>
<td>10/10</td>
</tr>
<tr>
<td>Ag resin paste A For hetero junction type</td>
<td>8.90E-04</td>
<td>7E-06</td>
<td>0/10</td>
</tr>
</tbody>
</table>

* The number of remaining patches / the number of all patches

Fig.5 Comparison of electrical properties of various conductive pastes on the ITO electrode.
3.3.1. Interpretation of electrical contact condition:

We usually employ the transfer length measurement (TLM) method for evaluating the contact resistivity of metal paste on substrates. As shown in Fig. 6, in the case of an ideal contact, the relation between the interelectrode distance and resistance is linear. In general, in many cases, non-linear relations are observed. An electrical contact that forms at the interface between a resin type paste and a textured surface tends to be non-ideal because binder polymer in the paste works as a thin insulator at the interface. Such insulator layers work as tunneling barriers. Therefore, the contact resistance \( R_c \) depends on the applied electric field. In the experiments, the resistance tester applies a constant voltage between electrodes. Thus, applied electric fields increase with decreasing interelectrode distance while the contact resistance is gradually decreasing.

![Fig. 6 Schematic diagram of interpretation of non-linear TLM result.](image)

As shown in Fig. 7, an apparently non-linear relation was observed when using the resin type Ag paste. On the other hand, a linear relation was obtained when using the Cu-alloy paste. This is because the textured Si surface was covered with a melted LMPA layer and the LMPA layer formed metal contact with the textured Si surface such that the contact condition was almost ideal.
As shown in Fig. 8, when pressure was applied during the cure process of the resin type Ag paste, the relation between the interelectrode distance and the interelectrode resistance became approximately linear. This is because the insulator layer at the interface became thinner because of the pressure application during the cure process.
3.4. Adhesive property

The adhesive strength between a printed pattern and a wafer was estimated by the typical tape-peeling test. The samples for these tests were prepared as shown in Fig. 9. An adhesive tape was pasted onto the part and then the tape was peeled off. As seen on the left side in Fig. 9, the Cu-alloy paste has excellent adhesive strength to the ITO electrode. On the other hand, the Ag paste for the heterojunction solar cell was easily peeled off from the ITO surface. This is because the Ag paste has very low binder polymer content to reduce the line resistivity. Thus, this paste has very low adhesive strength.

Fig. 9 Schematic diagram of tape peeling test and a picture of tape peeling test result.

4. Conclusions

We have developed a novel Cu-alloy paste having low resistivity, low contact resistance, and low sintering temperature. For this Cu-alloy paste, the LMPA is able to form excellent electrical contact at the paste/ITO interface. Various estimation results indicated that the Cu-alloy paste could be used for solar cells that require low-temperature processes.

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References

