DEVELOPMENT OF A LOW TEMPERATURE SILVER PASTE FOR HIGH EFFICIENCY SCREEN-PRINTED SOLAR CELLS

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ABSTRACT: The screen-printing technology provides a low cost high-throughput approach to good contacts for silicon solar cells. However, currently screen-printed contacts are formed at the expense of slight performance and fill factor loss. The front grid contact is particularly important and requires low contact resistance, high shunt resistance, and low junction recombination for high fill factor. Often contacts are fired in the moderate to high temperature range (750-800^{o}C) to achieve low series resistance. However, high temperature firing can lead to junction shunting and recombination, which degrades fill factor. Moreover shallow or higher sheet resistance emitters (50-100 Ω/sq) are desirable for high performance, which makes devices even more vulnerable to high temperature firing. Therefore, in this study, we modify the paste composition by adding some dopants and additives to lower the peak firing temperature for good ohmic contacts. This also reduces the wafer bowing and enhances SiN-induced defect hydrogenation in multicrystalline silicon substrates. The results show that increasing the additives concentration lowered the optimum firing temperature from 780 to 720^{o}C. In addition, the ideality factor is reduced significantly at the lower firing temperature. Thus additives used in this study were able to lower the peak firing temperature and increase the fill factor without hurting the series resistance. Fill factor of 0.774 on textured CZ was obtained at ~720^{o}C peak firing temperature for paste G (SOL9807). These pastes were formulated at Heraeus. Heraeus paste formulation differs in the nature and the amount of additives in the pastes.

Keywords: screen-printed cells, low temperature Ag paste, Heraeus

1. INTRODUCTION

The efficiency of a solar cell is defined as the product of the open circuit voltage, short circuit current density and the fill factor, which is a measure of squareness of the current-voltage curve. The open circuit voltage and short circuit current density depend on minority carrier diffusion length in the substrate and the surface recombination velocities. The fill factor is partly dictated by the front grid contact resistance, which is the resistance associated with metal/semiconductor barrier at the metal/semiconductor interface [1]. The silver paste and the firing cycle determine the contact resistance. The firing cycle depends on the quantity, nature and transition temperature of glass frit, silver particle size and type, and the modifiers. It is particularly important to select a silver paste and firing cycle that will produce low contact resistance, high shunt resistance, and low junction recombination for high fill factor. Often contacts are fired in the moderate to high temperature range (750-800^{o}C) to achieve low series resistance. However, high temperature firing can lead to junction shunting and recombination. Moreover, shallow or higher sheet resistance emitters (50-100 Ω/sq) are desirable for high performance, which makes devices even more vulnerable to high temperature firing.

Therefore in this study, an attempt is made to modify the paste composition by adding some dopants and additives to lower the peak firing temperature for good ohmic contacts. This could also help in reducing the wafer bowing for thin wafers and enhance SiN-induced defect hydrogenation in multi-crystalline silicon substrates. The silver pastes were formulated at Heraeus and evaluated at Georgia Tech through fabrication, characterization and analysis of large area (100 – 225 cm^2) silicon solar cells on CZ, FZ, HEM and EFG. The silver powder, glass type, and the level of additives and dopants were varied. Seven silver pastes were investigated with two silver powder type, three glass types and three levels of additives and dopants.

2. PASTE FORMULATIONS

In general, the thick film conducting paste for solar cells and printed circuit boards (PCB) constitutes three components including (a) metal powder, which provide the conductive phase, (b) glasses (lead containing) or oxides which promote sintering of the metal powder during contact firing and enable binding of the metal contact to the substrate; and (c) organic phases, which disperse the metal and binder components to impart the desired rheological characteristics to the paste [2, 3]. It is not uncommon to add some elemental metals such as Ge, Bi, Pb, Li, Cd, In, Zn etc, as modifiers to the paste. The quantity and type of modifier is proprietary to the paste manufacturer. Also, there is addition of phosphorus dopant to improve contact resistance between silver finger and silicon. In table 1, the level of the modifier and dopants in each paste is indicated as low, medium or high. The Ag powder type is specified as Flake I or II and the glass transition temperature is referred to low, medium or high in Table I.

3. DEVICE FABRICATION

The pastes were tested on all types of promising silicon materials for PV, including textured CZ, textured FZ, planar HEM mc-Si and EFG ribbon. The wafers were cleaned in 1:1:2 H_2SO_4:H_2O_2:H_2O for 5 minutes, followed by a 3-min rinse in de-ionized (DI) water. This was followed by a clean in 1:1:2 HCl:H_2O_2:H_2O for 5 minutes and a 3-min rinse in DI water. Next the wafers were etched in 15:5:2 HNO_3:CH_3COOH:HCl for 5 minutes followed by a 5-min rinse in DI water. A final dip in 10% HF for 2 minutes was performed, followed by a 30 second rinse in DI water. After the cleaning, the emitters were formed in conventional tube furnace using $POCl_3$ at a set temperature of 877°C, which resulted in a 40-45 Ω/square emitter. After the phosphorus glass removal and DI water rinse, a single layer low frequency PECVD SiN anti-reflection coating was deposited on the front at 400°C. Next, the Al back contact was printed and dried at 200°C. This was followed by front Ag grid printing (for the solar cell samples) and dried at 200°C. Next, the samples were co-fired in the IR belt furnace after a controlled profile to ascertain the peak firing temperature, which ranged from 720-770°C. This was followed by I-V characterization and analysis to optimize the firing cycle for each paste based on the additive and dopant level.

Table I: The characteristics of the Ag front grid pastes

Paste	Ag powder type	Glass Transition Temperature	Additives & Dopants
A	Flake I	Medium	0
B	Flake I	Medium	Low
C	Flake I	Medium	High
D	Flake II	Medium	High
E	Flake I	Low	High
F	Flake I	Medium	Medium
G	Flake I	High	High

4. RESULTS AND DISCUSSION

4.1 Cell characterization

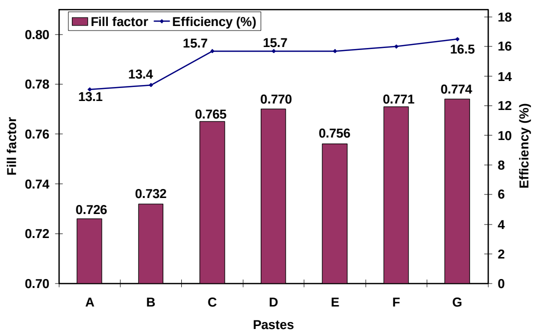

Figure 1: Fill factor and efficiency as functions of the evaluated silver paste on CZ silicon wafers.

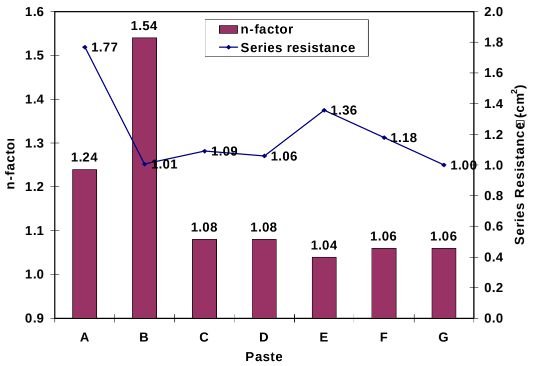

Figure 2: Series resistance and n-factor as functions of the evaluated silver paste on CZ silicon wafers.

Figure 1 shows the effect of paste composition on fill factor and efficiency of 149-cm^2 textured CZ silicon wafers. The initial peak firing temperature was chosen based on the commercial paste and optimized for the Heraeus formulated paste. Paste A, which consists of flake Ag powder type I, medium transition temperature glass and no oxide and dopant additives, produced fill factor of only 0.726 at 760°C peak firing temperature. Figure 2 shows this paste gave a moderately high n-factor and highest series resistance. The high n-factor indicates high junction recombination, which may be caused by impurities or Ag crystallite getting close to the p-n junction, and the high series resistance could be due to thick glass layer at the silicon/Ag grid interface (Figure 3). Thus, some modification of this paste was necessary to obtain better performance.

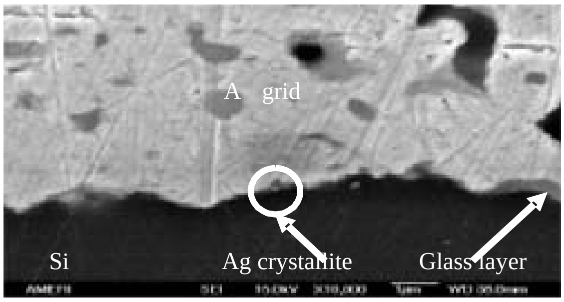

Figure 3: SEM micrograph showing the cross section of the Ag grid using paste A fired at 760°C peak firing temperature.

Next, paste B was formulated by maintaining the Ag and glass types with low amounts of additives and dopants added to the pastes A. The paste was tested on textured CZ wafer and a best fill factor of 0.732 was obtained at a peak firing temperature of 755°C. Although the series resistance was low (Figure 2), the n-factor was very high indicating shunting of the p-n junction. This suggested the need to fire at a lower temperature to avoid shunting of the p-n junction. However, firing at lower temperature resulted in much higher series resistance with good n-factor. Figure 4, shows the SEM micrograph of the Ag grid using paste B fired at 745°C. It is not clear from the SEM micrograph whether a thick glass is responsible for the high series resistance or there is not enough crystallite formation underneath the glass layer.

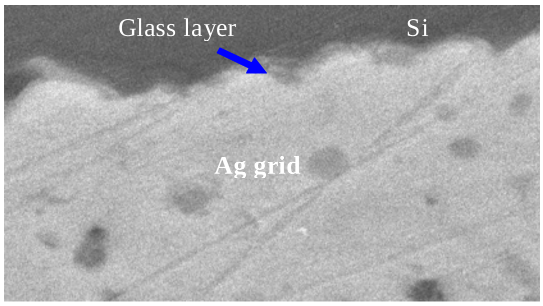

Figure 4: SEM micrograph showing the cross section of the Ag grid using paste B fired at 745°C peak firing temperature.

Since the addition of some additives and dopants resulted in junction shunting when fired at high temperature and high series resistance was observed when fired at 15°C lower temperature, a third paste (paste C) was formulated with high contents of additives and dopants. The paste was printed and fired at a much lower temperature, 720-745°C. This resulted in average fill factor of 0.756 for >10 cells. The series resistance and n-factor were very good as shown in Figure 2. Given this near ideal n-factor, the paste was applied on textured FZ, HEM multi-crystalline and EFG. Excellent fill factor (>0.770) were obtained as shown in Figure 5. Figure 6 shows the SEM cross section of the Ag front grid using paste C fired at 720-745°C. Since the series resistance is low, it can be inferred that the glass at the interface between silicon and the Ag front grid is thin, enhancing the current collection probability relative to the previous two pastes. However, paste C gave good fill factor over a very narrow peak firing temperature range. Therefore more work was conducted to widen the firing temperature range. This led to paste D formulation with modified Ag powder – flake type II with the same glass transition temperature, additives and dopants. However, this modification led to the comparable fill factor and the peak firing temperature range.

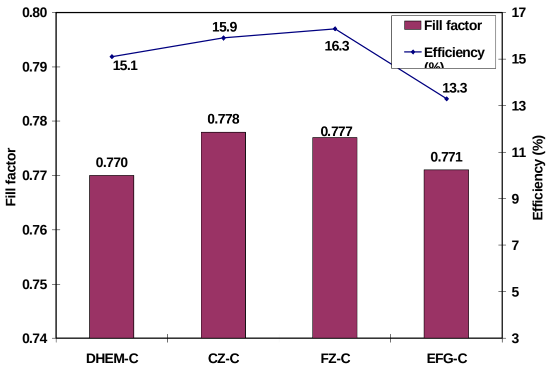

Figure 5: Comparison of paste C performance on ribbon (EFG), cast multi-crystalline (HEM), Cz and Fz silicon fired at the same peak temperature.

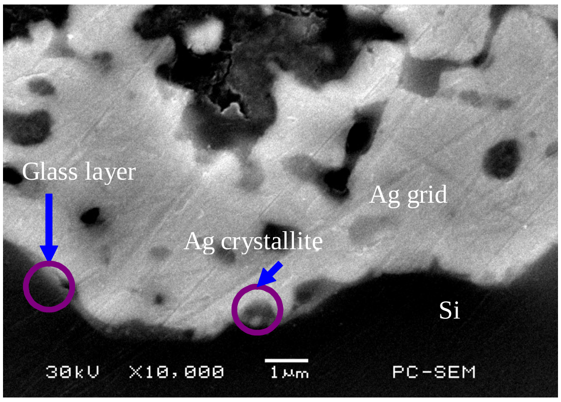

Figure 6: SEM micrograph showing the cross section of the Ag grid using paste C fired at 720-745°C peak firing temperature.

Next we investigated type I flake with low glass transition temperature with high amounts of additives and dopants to obtain paste E. The paste E, when tested on textured CZ wafer, resulted in slightly lower fill factor due to somewhat higher series resistance. However, the n-factor was the best. Unfortunately the firing range could not still be enhanced. Paste F was therefore formulated with the same Ag powder type, medium glass transition temperature glass and high contents of additives and dopants. The use of this paste resulted in average fill factor of 0.771, excellent n-factor but slightly higher series resistance. Paste F also showed inferior performance for cells fired at temperatures below and above that which gave fill factor of 0.771. Finally paste G was formulated. Paste G contained flake type I, high transition temperature glass, and high additives and dopants. At the same peak firing temperature as the other six pastes, an average fill factor of 0.774 was obtained with excellent n-factor and series resistance value. Fig. 7 shows the fill factor and efficiency as functions of the peak firing temperature for paste G. It is quite clear that by using a glass with high transition temperature and high additives and dopant contents, a wide peak firing temperature window can be obtained.

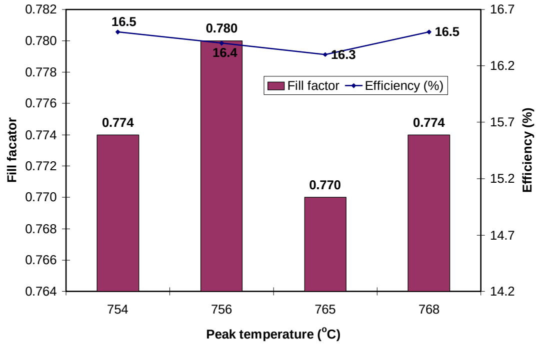

Figure 7: Fill factor and efficiency as functions of peak firing temperature for paste G.

4.2 Paste characterization

4.2.1 Adhesion tests

Figure 8: Picture showing the aftermath of adhesion test for pastes A, without and paste G (SOL9807) with additives and dopants.

To carry on the adhesion test, first an 80x80 m pads were printed, dried and fired. This was followed by copper wire soldering onto the pads using 63/37 solder at

230^{o}C for 5 seconds. Next, the pull test was conducted. Figure 8 shows the picture after the adhesion tests was performed for pastes A (with 0 additives) and G (with high additives and dopants contents). As shown in Figure 8a for paste A, without the additives and dopants, there was no adhesion. However paste G exhibited excellent adhesion with 1.5 lb. This suggests that the modifiers not only enhance the contact formation at low temperature but adhesion to the silicon surface.

5. CONCLUSIONS

The peak firing temperature for any screen-printed solar cell depends on the constituents of the silver paste. Most of the commercial silver pastes used in making screen-printed solar cells are fired at 750-780^{o}C peak temperatures. In this study we have shown that the paste constituents can be engineered to decrease the peak firing temperature by 30-50^{o}C. Without the additives and dopants, paste A, even at high peak firing temperature of 760^{o}C gave very poor contact due to high n-factor and high series resistance. However, a small amount of additives and dopants, paste B, decreased the peak firing temperature to 750^{o}C and improved the fill factor slightly. The reduced peak firing temperature led to somewhat lower series resistance and the fill factor degradation was mainly due to the high n-factor. By increasing the amount of additives and dopants with the same Ag powder type and glass, the peak firing temperature decreased to 720^{o}C and an average fill factor of >76% was obtained. Low series resistance of ~1 Ω-cm^2 and n-factor of ~1 was achieved. Furthermore, this paste fired at the low peak firing temperature gave very good fill factors (>0.77) on FZ, CZ, HEM and EFG silicon wafers.

The use of another Ag powder with the same glass and high level of additives did not change the peak firing temperature (paste D). A Ag powder, flake I, in combination with low glass transition temperature (paste E) and high level of additives gave a fill factor of 0.76. A combination of flake I powder, high additives and dopants and high glass transition temperature (paste G – SOL9807) gave excellent fill factor of 0.774 at low firing temperature. This indicates that higher glass transition temperature, additives and dopants, tend to give higher fill factors. In addition, wider firing window was obtained with paste G. Also, the peel test showed poor adhesion for paste without the addition of additives and dopants; and good adhesion for paste G, which contain some additives. This indicates that, the additives and dopants enhance metal sintering and crystallite formation, which leads to a reduced contact resistance.

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