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Screen Printable Silver Paste For Silicon Solar Cells With High Sheet Resistance Emitters

Yi Yang^a, Shahram Seyedmohammadi^a, Umesh Kumar^a,
Dave Gnizak^b, Ed Graddy^a, Aziz Shaikh^a

^aFerro Corporation, ECGM Division, 1395 Aspen Way, Vista, CA 92127, USA

^bFerro Corporation, ECGM Division, 7500 E Pleasant Valley Rd, Independence, OH 44131, USA

Abstract

In silicon solar cells, forming good ohmic contact between the emitter and the metal with minimum contact resistance is critical to achieve peak electrical performance [1]. In commercial solar cells, screen printable silver paste is commonly used to form contact. Factors related to paste chemistry, process conditions and the solar cell wafers influence the contact quality. In this paper, the effect of paste chemistry and emitter sheet resistance on contact quality is described. Several paste chemistries were tested for contact resistance with Transmission Line Model (TLM) measurements on wafers with sheet resistance between 45-100 Ω/\square . The series resistance of the solar cells was recorded over 50°C firing window. The paste chemistry was further refined to form low resistance contacts on solar cells with emitter sheet resistance on 100 Ω/\square .

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1. Introduction

In commercial silicon solar cells, screen printable silver paste with silver particles and glass particles is commonly used to form contacts to the emitter. Based on experimental observations, several researchers proposed the contact formation mechanism [2-5] as follows. During the rapid thermal processing step, glass etches the passivation layer and exposes silicon. Silver precipitates on silicon, epitaxially. The shape, size and density of the silver islands vary as a function of firing conditions and the crystallographic orientation of silicon. One of the important parameters influencing ohmic contact formation is the sheet resistance of the emitter layer. In this paper, we investigated the effect of emitter sheet resistance on contact properties. We identified optimum paste recipes and the firing conditions to form good contacts to the wafers with sheet resistances between 45 and 90 Ω/\square . The paste chemistry was further

Corresponding author. Tel.: +0-1-760-305-1000; fax: +0-1-760-305-1100.
E-mail address: yangy@ferro.com.

modified to improve the contact quality on wafers with sheet resistance of $100 \Omega/\square$. Contact formation was also evaluated through microstructural observations.

2. Experimental procedure

Commercial silicon solar cells with SiNx coating and emitter sheet resistance of 45 to $100 \Omega/\square$ were selected for the investigation. The role of sheet resistance on contact formation and electrical performance was investigated with a series of silver pastes. Silver particles with appropriate particle size distribution, glasses from Pb-B-Silicate family, and other additives constituted the inorganic part of the paste chemistry [6]. Paste A and B were formulated with glass frits having similar chemistry. Paste C was formulated with higher Tg (glass transition temperature) glass. In paste D, an inorganic additive was introduced. In paste B, slightly coarser silver particles were used. Samples for electrical and microstructural characterization were processed in a 6-zone Infrared Despatch furnace. The set points for six zones were 400-400-500-700-800-peak temperature (870 to 960 °C) and the belt speed was 200 ipm. The difference between set point of last zone and actual peak temperature was about 110 °C measured using a SunKIC profiler [7]. In this paper, the mentioned peak firing temperature is the set point peak temperature.

For contact resistance (R_c) measurement, TLM pattern with 20 mm x 1 mm wide lines with varying line spacing was utilized [6]. The test procedure elaborated in Ref. [4] was used to record the relative value of contact resistance. On each TLM sample wafer, the R_c is averaged on nine sets of isolated patterns. TLM results were used to select paste recipes for further investigation. The electrical properties of the solar cells with appropriate front and back side pastes were characterized with a NPC solar cell I-V tester equipped with a bent-design solar simulator. The series resistance (R_s) was recorded as a function of firing conditions. The role of firing condition on the electrical properties was further investigated with Sinton WCT-100 photoconductance tool (Suns-Voc). The leakage current J_{02} specifically was utilized to monitor the impact of front contact paste on device p-n junction. In addition, internal quantum efficiency (IQE) spectra were collected by an Oriel IQE200. The result was used to study combined impact of emitter sheet resistance along with R_c on spectral response of the solar cell. The procedure elaborated in Ref. [3] was used to observe the silver precipitates on silicon through the use of an Amray 3300FE field emission Scanning Electron Microscope (SEM).

3. Results and discussions

Contact resistance is a major component of series resistance. TLM technique was used to evaluate R_c between the Ag and Si as the first step screening of front silver pastes for different types of emitters. In Table 1, relative values of R_c between four paste chemistries and four different wafers with emitter sheet resistance from 45 to $100 \Omega/\square$ at two peak firing temperatures are listed. Low contact resistance values were recorded with paste C and D on the wafers with sheet resistance up to $90 \Omega/\square$. To understand the effect of firing temperature, contact resistance of paste C and D on emitters of $100 \Omega/\square$ were measured after firing at 940°C and 960°C, respectively. The contact resistance with paste C increased to $45 \text{ m}\Omega\text{-cm}^2$ after firing at 940°C, whereas the value with paste D decreased to $30 \text{ m}\Omega\text{-cm}^2$ after 960°C.

Table 1. Relative values of contact resistance measured by TLM on different sheet resistance wafers

Type	Wafer Info		Peak T (°C)	Rc (mΩ-cm ²)			
	Source	Sheet Rho (Ω/□)		Paste A	Paste B	Paste C	Paste D
Multi	I	65	880	19	11	32	16
			910	6	2	3	3
	II	90	880	23	32	79	
			910	6	17	2	2
Mono	III	45	880	8	3	4	11
			910	5	2	2	5
	II	100	880	199	333	77	
			910	64	91	21	65

In Figure 1, the series resistance (R_s) of the solar cells with paste C as a function of processing temperature is presented. Low R_s values were recorded over a wide firing window between 870 to 920°C for both 70 and 90 Ω/□ emitters. As high R_s value was observed on 90 Ω/□ emitter at high peak firing temperature of 940°C, the diode quality was tested with leakage current measurements. As seen in Table 2, very low leakage current indicates good diode quality. In Figure 2, SEM images of etched fingers are presented. Comparable Ag island densities and shapes from both 70 and 90 Ω/□ emitters indicate a similar contact formation mechanism, independent of emitter sheet resistance. Larger Ag islands at higher peak temperature indicate an over-fired condition.

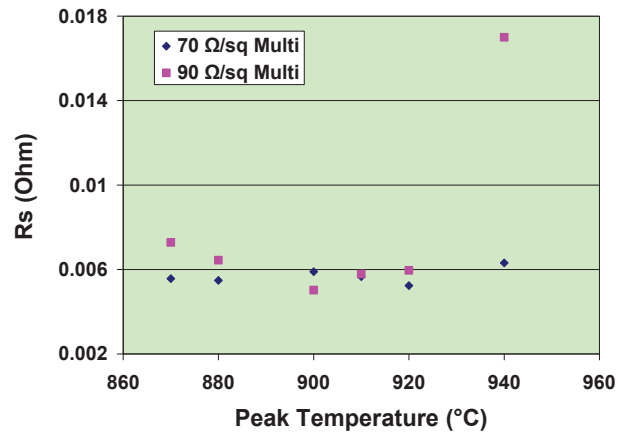
Fig. 1. R_s of multi-crystalline wafers with paste C processed as a function of peak firing temperature.

Table 2. Diode quality of 90 Ω/\square wafers with paste C (Suns-Voc)

Peak T ($^{\circ}\text{C}$)	J01 (A/cm^2)	J02 (A/cm^2)
870	1.03E-12	2.45E-08
880	8.03E-13	3.16E-08
910	1.16E-12	4.21E-08
940	1.12E-12	2.03E-08

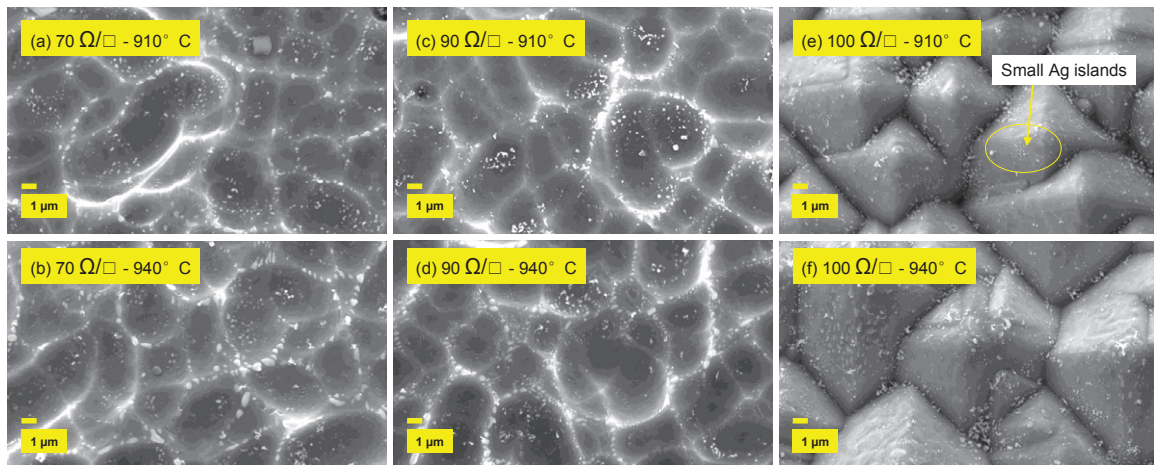


Fig. 2. SEM image of etched fingers of 70 Ω/\square (a, b) and 90 Ω/\square (c, d) multi-crystalline wafers, and 100 Ω/\square (e, f) mono-crystalline wafers with paste C processed at different peak firing temperatures.

R_c of 100 Ω/\square mono wafers with paste C is significantly larger compared to those of wafers with lower sheet resistance (Table 1). R_s of 100 Ω/\square mono-crystalline emitter with paste C at various peak firing temperatures are shown in Fig.3. Compared to R_s with lower sheet resistance emitters (Fig 1), the R_s values with 100 Ω/\square emitter are much higher. These results indicate that cell performance is primarily controlled by the nature of the contact between silicon and silver. Forming a good Ag-Si contact becomes very critical to improve electrical performance with high sheet resistance wafers. SEM images of etched fingers of paste C on 100 Ω/\square emitter (Fig 2e,f) also showed lower Ag island densities and smaller Ag island sizes compared to those on low sheet resistance emitters at low peak firing temperature. At higher firing temperature, though the size of the Ag islands increased, the density still remained low [8].

Paste D was also tested on 100 Ω/\square wafer (Fig. 3). With paste D, low R_s was recorded at a high peak temperature of 950 $^{\circ}\text{C}$ which correlated with the observation that R_c values decreases as peak temperature increases. Through modification of paste chemistry as mentioned earlier, improved contact with high sheet resistance emitter is achieved. However, higher firing temperature and narrowed firing window indicates that forming good contact with high sheet resistance emitter is more difficult. Low leakage current of paste D with 100 Ω/\square emitter at different peak temperatures (Table 3) shows that junction quality is preserved over a wide firing window. This indicates that diffusion of ions from the paste is confined to the emitter area.

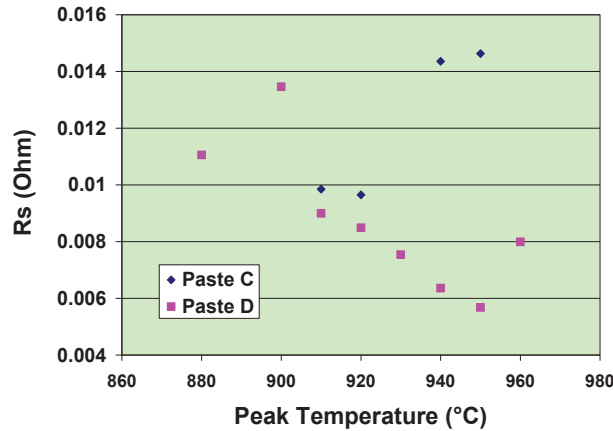


Fig. 3. R_s of $100 \Omega/\square$ mono-crystalline wafers with paste C and D as a function of peak firing temperature.

Table 3. Diode quality of $100 \Omega/\square$ emitter with paste D (Suns-Voc)

Peak T (°C)	J01 (A/cm ²)	J02 (A/cm ²)
900	9.67E-13	3.00E-08
910	1.05E-12	7.92E-09
920	8.00E-13	2.80E-08
930	8.00E-13	2.50E-08
940	9.89E-13	2.20E-08
950	9.30E-13	6.00E-08
960	8.00E-13	3.50E-08

In addition to paste chemistry, the effect of screen design on R_s was also investigated. As shown in Fig. 4, with optimized screen design, lower R_s can be achieved [9].

One of the advantages of going with higher sheet resistance emitter is to improve cell performance through increasing cell blue response [10]. The IQE measurements of 45 and $100 \Omega/\square$ (Fig. 5) clearly show improved blue response from $100 \Omega/\square$ emitters, even though the R_s of $100 \Omega/\square$ is higher than that of $45 \Omega/\square$ emitter. As seen, in $100 \Omega/\square$ wafers, decreasing the R_s with better paste chemistry further improves IQE of the cell.

4. Conclusions

In this work, the role of paste chemistry on forming very low resistive contacts on wafers with high sheet resistance was discussed. On wafers with emitter sheet resistance of $90 \Omega/\square$, low relative value of contact resistance of $2 \text{ m}\Omega\text{-cm}^2$ was recorded. Low series resistance was recorded over a 50°C firing window. Even at over-fired conditions, the p-n junction did not show any evidence of degradation. On wafers with emitter sheet resistance of $100 \Omega/\square$, the paste chemistry was further modified. Low series

resistance was recorded over a 20°C firing window. Contact quality was improved further with other process variables such as screen design. IQE was boosted up even further with lower Rs.

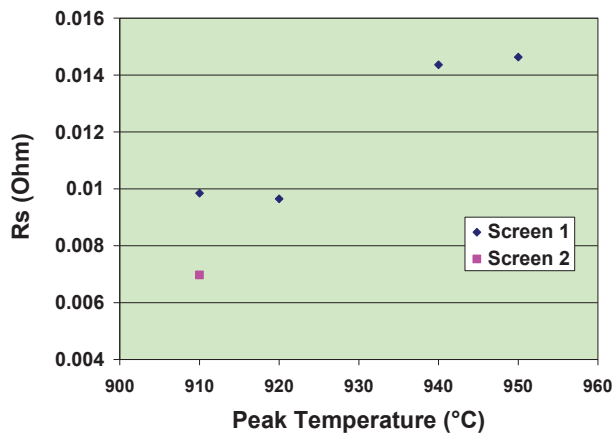


Fig. 4. Rs of 100 Ω/□ mono-crystalline wafers with paste C printed with different screen designs.

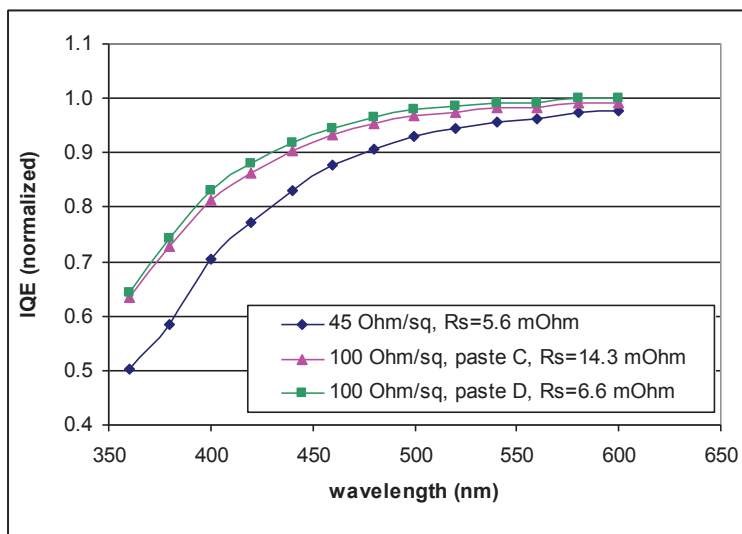


Fig. 5. Comparison of IQE curves of 100 Ω/□ and 45 Ω/□ mono-crystalline wafers with different series resistance.

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