UNDERSTANDING AND DEVELOPMENT OF AG PASTES FOR SILICON SOLAR CELLS WITH HIGH SHEET-RESISTANCE EMITTERS

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ABSTRACT: The effect of different properties of the inorganic constituents of the Ag paste used for the front metal grid is investigated for high sheet-resistance emitters. Our results show that both glass frit chemistry and Ag particle size are important for achieving good quality ohmic contacts to high sheet-resistance emitters. The melting characteristics of the glass frit determine the firing scheme suitable for low contact resistance and high fill factors (FFs). In addition, small to regular Ag particles were found to help achieve a higher open-circuit voltage (V_{oc}) and maintaining a low contact resistance. P self-doping from the paste was not necessary for good contacts to high sheet-resistance emitters for the rapid firing schemes in this paper. High FFs (>0.78) were achieved on untextured FZ Si cells using rapid firing in a lamp-heated belt-furnace with efficiencies of up to 17.4% on a 100 Ω/sq emitter. This corresponds to an efficiency improvement of ~0.3% absolute over the 45 Ω/sq emitter cells.
Keywords: Ag thick-film contact, silicon solar cell, high sheet-resistance emitters.

1. INTRODUCTION

The optimization of the inorganic constituents of the Ag paste can help achieve good-quality thick-film ohmic contacts [1]. This is particularly important when dealing with high sheet-resistance emitters. As reported in [2] there are two possible routes to achieve good-quality ohmic contacts on lightly doped emitters. First is through self-doping techniques [3,4] and the second is via optimization of the Ag paste and firing. Since the diffusivity of Ag [5] is faster than that of P [6], the self-doping technique involves the risk of junction shunting or introducing an excessive amount of Ag into the emitter region. This could degrade the open-circuit voltage. We reported elsewhere on high-quality screen-printed contacts on 100 Ω/sq emitters using PV168 Ag paste from Dupont [7,8]. However, this paste only worked for higher than conventional firing temperatures (>810°C instead of 750°C). In this paper an attempt is made to study the effect of glass frit and Ag particles on the electrical characteristics of the cell. In particular, the effects of glass frit chemistry and Ag particle size and morphology have been investigated to help in the development of Ag paste for high sheet-resistance emitters using normal firing conditions.

2. EXPERIMENT

In this study, screen-printed n^+-p-p^+ solar cells (4 cm^2) are fabricated on single-crystal Si using different Ag pastes and firing conditions on a ~100 Ω/sq emitter. P-type, 0.6 Ω-cm, 300-μm thick (100) float-zone (FZ) substrates were used for all the experiments to amplify the effect of high sheet-resistance emitter on cell performance. Untextured FZ silicon wafers were first chemically cleaned followed by $POCl_3$ diffusion to form an n^+-emitter. After the phosphorus-glass removal and another clean, PECVD SiN_x AR coating was deposited on the emitter. Next, an Al paste was screen-printed on the backside and dried at 200°C. The Ag grid was then screen-printed on top of the SiN_x film and then the Ag and Al contacts were co-fired (single firing step) in a lamp-heated three-zone belt-line furnace. Nine 4 cm^2 cells on each 4 in. diameter wafer were fabricated and isolated using a dicing saw and annealed in forming gas at 400°C for ~15 minutes. Cells were fired either at a conventional temperature of ~750°C or at a temperature of ~840°C (over-fired) for different pastes to study the effect of firing temperature. TLM test patterns were screen-printed simultaneously with the Ag grid for specific contact-resistance (ρ_c) measurements [9]. Nine different pastes (Table 1) were formulated and studied. These pastes have different glass frit chemistry that controls the glass transition temperature (T_g) and aggressiveness (etching of the SiN_x layer) which are independent. The pastes also contain different particle morphology and size. Pastes 33-462 and 33-456 have self-doping properties (contain P) whereas pastes 33-452, 33-455 and 33-460 have no P in the paste. Table I describes the key differences in the Ag pastes investigated.

Table I: Description of the different pastes investigated in this study.

Paste	Ag Powder Size	Ag Powder Morphology	Glass frit
33-460	blend	spherical	low T_g, less aggressive (GF1)
33-452	blend	spherical	low T_g, more aggressive(GF2)
33-462(A)	ultra-fine	spherical	medium T_g, more aggressive (GF3)
33-462(B)	fine	spherical	medium T_g, more aggressive (GF3)
33-462(C)	small	spherical	medium T_g, more aggressive (GF3)
33-462(D)	regular	spherical	medium T_g, more aggressive (GF3)
33-462(E)	large	spherical	medium T_g, more aggressive (GF3)
33-456	large	flake	medium T_g, ,more aggressive (GF3)
33-455	blend	spherical	high T_g, less aggressive (GF4)

3. RESULTS AND DISCUSSION

3.1 Effect of Ag Particle Size on Screen-Printed Ohmic Contacts and Cell Performance

Five different Ag particle sizes, ranging from ultra-fine to large (Table 1), were investigated for the same frit chemistry and firing condition (840°C/120 ipm). Figure 1 shows that the specific contact resistance decreases for larger Ag particle size. Figure 1 also indicates that larger Ag particles show a decrease in R_s; however, the lowest n factor is achieved for the small to medium size Ag particles (pastes C and D). The same trend was observed

for 750°C as well as 840°C firing at 120 ipm belt speed. An R_s close to 0.5 Ω-cm^2 and an n factor close to unity are desirable for high FFs. The combined impact of the change in R_s and n factor, because of the Ag particle size, on V_{oc} and FF of the cells is shown in Fig. 2. The V_{oc} was highest for the ultra-fine particle size and lowest for the largest particle size, however, the FF showed an optimum (>0.78) around the small to medium particle size (paste C) because of the trade-off between the R_s and n factor. Both the R_s and n factor decrease initially with the increase in the particle size but for the larger particle size the n factor starts to increase, while R_s shows a slow decrease (Fig. 1).

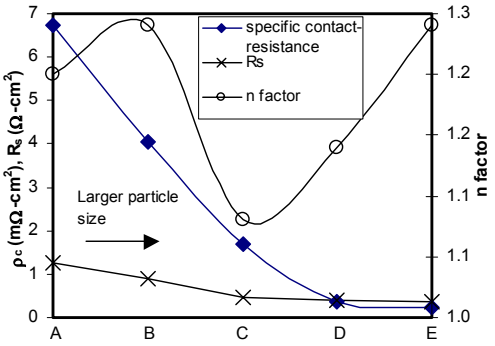

Figure 1: Effect of Ag particle size on specific contact-resistance, series resistance, and n factor.

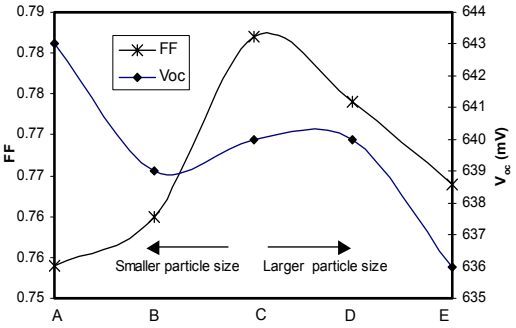

Figure 2: Effect of Ag particle size on V_{oc} and FF.

3.2 Effect of Ag Particle Morphology on Screen-Printed Contacts and Cell Performance

Pastes 33-456 and 33-462(E) were formulated with identical glass frit chemistry and particle size (large), but a different Ag particle morphology (flake versus spherical). Table II shows that the flake morphology in paste 33-456 gave higher V_{oc} and FF compared to paste 33-462(E) with large spherical Ag particles. The same firing condition of 840°C and a belt speed of 120 ipm were used for both pastes (Table II). However, this behavior was also observed for the conventional firing condition of 750°C/120 ipm. Thus, the overall efficiency is also higher (17.1% compared to 16.5%). The n factor was found to be lower (1.08) for paste 33-456 compared to an n factor of 1.24 for paste 33-462(E), resulting in ~0.7% higher absolute efficiency (17.2%) compared to 16.5% for paste 33-462 (E), Table II. Dark IV analysis revealed a higher junction leakage current (J_{o2}) of ~35 nA/cm^2 for the large spherical particle size of paste 33-462(E) compared to ~6 nA/cm^2 for the flake particle morphology. However, regular spherical particles in paste 33-462(D) gave cell parameters comparable to the flake morphology (Table II).

Table II: Performance of spherical versus flake morphology.

Paste	Voc (mV)	FF	Eff(%)	n factor	ρ_c (mΩ-cm^2)
33-462 (E)	636	0.761	16.5	1.24	0.24
33-456	642	0.771	17.2	1.08	1.34
33-462(D)	639	0.780	17.3	1.07	0.36

3.3 Effect of Soilds (Ag+frit) Content on Contact Quality and Cell Performance

Pastes 33-455 (HS) and 33-455 (LS) have identical glass frit chemistry and Ag particle shape and size, but a different solids content. We did not observe a significant difference in cell performance resulting from the solids content of paste 33-455. As shown in Table III, the V_{oc}, FF and ρ_c are very similar for both the lower-solid (LS) and higher-solid (HS) content pastes. The firing process used for this study was 750°C and a belt speed of 120 ipm. Untextured FZ cell efficiencies of up to ~17.4% are obtained in both cases (Table III).

Table III: Effect of solid content on cell performance.

Paste	V_{oc} (mV)	FF	Eff(%)	ρ_c (mΩ-cm^2)
33-455 (HS)	644	0.783	17.4	0.91
33-455 (LS)	645	0.778	17.4	0.76

3.4 Effect of Glass frit on Contacts, Firing Process, and Cell Performance

The effect of glass frit in the Ag paste is studied for different firing schemes. First, we study the effect of 830-840°C firing at 80 ipm belt speed on high- (90-95 Ω/sq) and low- (40-45 Ω/sq) sheet-resistance emitters (Fig. 3). On the 90-95 Ω/sq emitter, paste 33-455 with lower Pb content in the glass and a higher T_g (at least 75°C higher than the glass of paste 33-452), gave a FF of less than 0.70 because of high series and contact resistance. Paste 33-455 gave a ρ_c of ~7.5 mΩ-cm^2 on the 90-95 Ω/sq emitter, which is 10 times greater than the specific contact-resistance of 0.72 mΩ-cm^2 on the 40 Ω/sq emitter. This gave a series resistance of 2.6 Ω-cm^2 on the 90-95 Ω/sq emitter relative to an R_s of ~0.643 Ω-cm^2 on the 40 Ω/sq emitter. Pastes 33-452 and 33-462, which have low and medium glass transition temperatures, respectively, gave acceptably low ρ_c (0.35 mΩ-cm^2 for 33-452 and 1 mΩ-cm^2 for 33-462) on the 90-95 Ω/sq emitter.

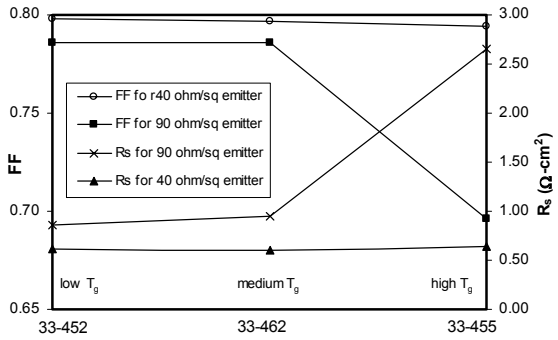

Figure 3: Response of Ag pastes with different glass frit T_g on 90-95 Ω/sq emitters fired at ~840°C/80 ipm.

SEM images (Fig. 4(b)-(d)) of the Ag-Si interface show an increase in the number and size of Ag crystallites with the lower T_g glass frit (GF2). These Ag crystallites aid in current transport from Si to the Ag grid [1]. All the samples shown in the SEM images (Fig. 4)

were fired at the same condition (840°C/80 ipm). The lower T_g glass frit dissolves more Ag during the firing process, and therefore, larger and more frequent Ag precipitates grow epitaxially in the Si upon cooling. The sizes of the Ag crystallites are ~800 nm in width for the lower T_g glass frit in paste 33-452 and are smallest (~150 nm in width) in the higher T_g glass frit in paste 33-455. However, when paste 33-455 is fired at the same condition (840°C/80 ipm) on a 40 Ω/sq emitter the Ag crystallites at the Ag-Si interface grow in size (up to 600 nm in width), thus, the Ag area coverage at the Ag-Si interface is increased (Fig. 4(a)). This helped in producing high FFs (0.79) and low R_s (~0.6 mΩ-cm^2). Thus, higher P doping in the Si emitter may aid the growth of the Ag crystallites. An increase in the width and number of Ag crystallites at the interface can improve the probability of the encounter of thin glass regions where tunneling can take place. The results in Fig. 4 (b)-(d) also agree with our specific contact-resistance values which are lowest for paste 33-452 (ρ_c=0.35 mΩ-cm^2) with larger and more frequent Ag crystallites at the Ag-Si interface (Fig. 4(d)) compared to paste 33-462 (ρ_c=1.01 mΩ-cm^2) (Fig. 4(c)).

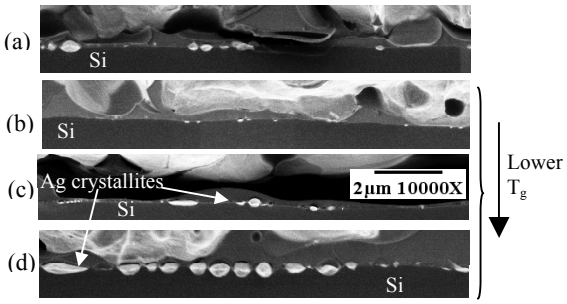

Figure 4: SEM images of (a) paste 33-455 fired on a 40 Ω/sq emitter, and pastes (b) 33-455, (c) 33-462 and (d) 33-452 fired on a 90-95 Ω/sq emitter.

Next, we studied the effect of conventional (750°C) firing compared to 840°C firing using a faster belt speed of 120 ipm. Figure 5 shows that high FFs were achieved on 100 Ω/sq emitters using several different Ag pastes from Ferro Corporation. Unlike our finding for PV168 Ag paste [7,8], a high firing temperature of ~835°C is not necessary to achieve a good ohmic contact to the 100 Ω/sq emitter. Figure 5 shows that Ferro pastes 33-462 (C-E) as well as paste 33-456, which have the same glass frit type (GF3) gave similarly high FFs (>0.775) at 750°C as well as 840°C firing. Glass frit types (GF1 and GF2) gave significantly lower FFs for the 750°C firing compared to the 840°C firing. Thus, the glass frit chemistry is important in producing good ohmic contacts at the desired firing temperatures. Paste 33-460, which has a low T_g glass and is less aggressive, gave poor FFs (0.686) at lower temperature firing. However, for the 840°C firing paste 33-462 gave excellent FFs of 0.789. Paste 33-452 which has a lower T_g compared to pastes 33-462 and 33-455, gave a lower FF of 0.710 at 750°C firing temperature, which increased to ~0.777 at 840°C firing. This increase in FF was reflected in a decrease in ρ_c from 9.07 mΩ-cm^2 (for 750°C firing) to 1.09 mΩ-cm^2 (for the 840°C firing). Although it is possible, the lower FF for paste 33-452 fired at 750°C is not expected to be as a result of incomplete SiN_x etching because the glass frit in 33-452 is similarly more aggressive as that of paste 33-462 which gave high FFs (>0.77) for the 750°C firing. Paste 33-455, which has a higher T_g and is less aggressive, also showed a slight improvement in FF from 0.773 to 0.783. Thus, from figures 3 and 5 the combined effect of glass T_g (low, medium, high), firing temperature (750°C versus 840°C), and the belt speed (80 versus 120 ipm) on the performance (FF) of high sheet-resistance emitters can be summarized as follows:

1) Low and medium T_g glasses gave high FFs at 840°C at both faster (120 ipm) and slower (80 ipm) belt speeds.
2) High T_g (less fluid) glass gave high FFs only at faster belt speed for both 750°C and 840°C temperatures.
3) At conventional firing conditions (750°C/ 120 ipm) medium and high T_g glasses give good FFs.

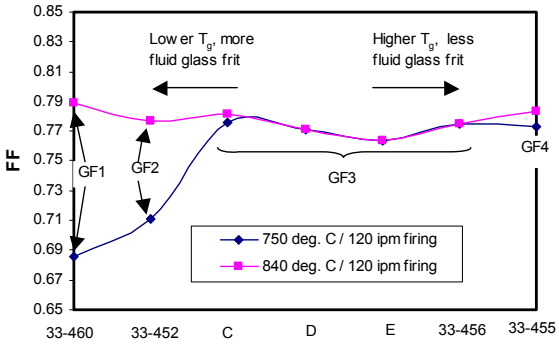

Figure 5: Effect of glass frit chemistry and firing temperature on the FF of solar cells.

In [1], metal precipitates in the glass were only observed for over-fired samples. It is possible that for the low T_g glass frits (GF1 and GF2), metal precipitates are not present in the glass layer for lower firing temperatures (~750°C, 120 ipm) and current transport would take place via tunneling through ultrathin glass regions from the Ag crystallites to the bulk Ag. In this case FGA would not be expected to play an important role rather the thickness of the glass layer would become more important for better current transport. More work is needed to understand this phenomenon.

The combination of glass frit T_g and the firing process plays an important role in achieving good contact to high sheet-resistance emitters because it can dictate the thickness as well as the conductivity of the glass layer involving Ag precipitates and multi-step tunneling [10]. Thinner glass layers have been shown to give lower contact resistance [11]. Faster firing is expected to give thinner glass regions.

3.5 Effect of P Self-Doping from the Ag Paste

Cells fabricated on 100 Ω/sq emitters show that self-doping P contained in the paste does not seem to influence the contact quality for the 840°C 120 ipm firing (Table IV). Results in Table IV show that low ρ_c (≤1 mΩ-cm^2) and high FFs (>0.77) were achieved for pastes

Table IV: Effect of P self-doping on ρ_c and FF.

Paste	P Self-Doping Property	ρ_c (mΩ-cm^2)	Best FF
33-462	self-doping	1..01	0.782
33-456	self-doping	1.34	0.776
33-455	no self-doping	0.82	0.783
33-452	no self-doping	1.09	0.777
33-460	no self-doping	0.30	0.789

with and without P self-doping. Moreover, for lower firing temperature (~750°C, 120 ipm), where P doping is not expected to take place because of the low solubility of P in Si high FFs (~ 0.78) were achieved. Paste 33-455, which has no P self-doping gave a FF of 0.783. P SIMS profiles after our rapid firing of P self-doping Ag gave a sheet resistance of ~1000 Ω/sq on an undiffused Si wafer, which represents a much lower doping relative to the emitter doping.

3.6 High Efficiency Cells on 100 Ω/sq Emitters

Untextured FZ cell efficiencies as high as 17.4% on 100 Ω/sq emitter were achieved. However, sometimes there is a slight scatter or non-uniformity in cells made on the 100 Ω/sq emitter. FFs are generally higher for the 40 Ω/sq-emitter cells because of the lower sheet-resistance loss. When good ohmic contact is achieved on 90-100 Ω/sq emitters, an improvement of ~0.2-0.4% in absolute efficiency is observed over the ~40 Ω/sq emitter. Tables V and VI show the best and average cell efficiencies achieved on 100 and 40 Ω/sq emitters using the Ferro paste 33-462. Figure 6 shows the best spatial distribution for nine 4-cm^2 cells achieved on a 4 in. diameter FZ wafer. This was obtained using the Ferro paste 33-455 and a firing condition of 840°C/120 ipm followed by FGA. These cells had an average FF of 0.779 and an average efficiency of 17.2%.

Table V: 90-100 Ω/sq-emitter cells using paste 33-462.

Cell Name	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	Eff (%)	n factor	R_s (Ω-cm^2)	R_{sh} (Ω-cm^2)
Best Cell	642	34.31	0.786	17.32	1.03	0.948	27725
Average	640	34.34	0.773	17.00	1.12	0.553	233546
Standard Dev.	1	0.16	0.009	0.23	0.03	0.162	599234

Table VI: 40 Ω/sq-emitter cells using paste 33-462.

Cell Name	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	Eff (%)	n factor	R_s (Ω-cm^2)	R_{sh} (Ω-cm^2)
Best Cell	638	33.66	0.797	17.1	1.03	0.592	94677
Average	637	33.50	0.790	16.87	1.05	0.719	50409
Standard Dev.	1	0.13	0.010	0.22	0.02	0.168	79500

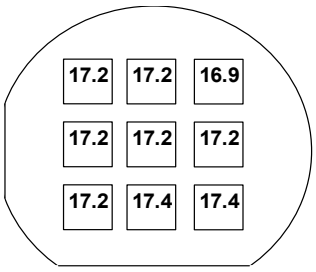

Figure 6: The efficiency distribution of nine 4 cm^2 cells on a 4 in. FZ Si wafer on a 100 Ω/sq emitter using paste 33-455.

4. CONCLUSIONS

This paper shows that good ohmic contacts can be achieved on high sheet-resistance emitters by properly formulating the glass frit chemistry. Glass frit with a medium-high T_g (less fluid) makes better contact to the Si emitter at conventional firing conditions (750°C/120 ipm). Also, glass frit with a low-medium (more fluid) T_g appears to be less sensitive to firing rates. Glass frit primarily determines the optimum firing temperature. However, the Ag particle size is also important in achieving a good ohmic contact and controlling excessive Ag diffusion into the emitter region. Silver particle size in the small to medium range gave the highest FF for the firing conditions used in this study. A Ag flake morphology performed better than the large spherical Ag particles of similar size. Also, we found that the P self-doping from the Ag paste did not play an important role in achieving good contacts for our rapid firing schemes. In fact paste 33-455 with no P self-doping gave a FF of 0.783 on 100 Ω/sq emitter cells. Untextured FZ cell efficiencies as high as 17.4% with FFs >0.78 were achieved on 95-100 Ω/sq emitters. High sheet-resistance emitter cells tend to give 0.2-0.4% higher efficiency over the 40 Ω/sq cells, partly because of higher short-wavelength response or J_{sc}. Generally, slightly higher FFs are achieved on cells made on 40-45 Ω/sq emitters with somewhat less scatter in the cell efficiency compared to the 100 Ω/sq-emitter cells. The introduction of texturing, fine-line printing and further development of paste and process optimization can raise screen-printed FZ cell efficiencies beyond 18.5%.

ACKNOWLEDGEMENTS

The authors would like to thank Kenta Nakayashiki at UCEP (Georgia Institute of Technology) for helping with the emitter diffusion. The authors would also like to thank Bobby To at NREL for performing SEM.

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