Optimization of Self-Doping Ag Paste Firing to Achieve High Fill Factors on Screen-Printed Silicon Solar Cells with a 100 Ω /sq. Emitter

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ABSTRACT

Self-aligned selective-emitter cells have been fabricated using a self-doping paste by co-firing the front and back contacts. Good ohmic contacts with ~0.774 fill factor were obtained on 100 Ω /sq. emitters after alloying the self-doping Ag grid by a 900°C spike firing in a belt Screen-printed selective emitter Fz Si cells gave an efficiency of 16.4%. Selective-emitter cells with effective front-surface passivation produced almost 0.4% higher absolute efficiency than the conventional 45 Ω /sq. homogeneous-emitter cell co-fired at 850°C. IQE data showed a 23% higher spectral response at 400 µm wavelength for the passivated selective-emitter cell over the conventional 40-45 Ω /sq. emitter cell. This is due to lower front-surface recombination velocity and reduced heavy doping effects. Long-wavelength response of the selective-emitter cell was also slightly superior due to the improved back-surface field. As a result, the selectiveemitter cell shows a much higher J_{sc} and V_{oc} than a cofired conventional-emitter cell. Rapid firing of the selfdoping paste was found to be more effective than the slow firing process.

INTRODUCTION

Good front-contact formation is critical for achieving highefficiency screen-printed solar cells. Photolithography and buried-contact techniques for contact metallization are time-consuming and expensive compared to screenprinting, which is a simple, rapid and cost effective technique. Currently, high throughput of the screenprinted devices is obtained at the expense of fill factor (FF) and cell performance. In order to achieve highefficiency (>16%) screen-printed multicrystalline silicon (mc-Si) solar cells, short circuit current (Jsc) and open circuit voltage (Voc) need to be improved. Screen-printed cells in production are fabricated on a 40-45 Ω /sq. emitter, resulting in poor surface passivation and blue response. In addition, FFs are around 0.75 due to high series resistance. A lightly-doped emitter with good surface passivation can enhance the blue response of the cell, while heavy doping underneath the grid can improve the FF. To realize the improved blue response due to light doping of the selective emitter, a high-quality

surface passivation scheme must be implemented concurrently.

The use of high sheet resistance in conjunction with screen-printed metallization produces poor ohmic contacts. A self-doping paste could provide good ohmic contacts to the cells when alloyed. Previous work has shown that a reasonably good contact resistance can be attained using the PV168 self-doping paste (SDP) [1,2,3]. The dopant is introduced into Si from the metalorganic paste by an alloying reaction at a temperature (~900°C) higher than the Ag-Si eutectic temperature of 835°C. In this paper, firing a fritted self-doping paste (Dupont PV168) through PECVD silicon nitride (SiNx) single layer antireflection (SLAR) coating is optimized to simultaneously achieve good series resistance, blue response, and back-surface field (BSF). Also, the effectiveness of the self-doping paste is compared to two conventional Ag pastes, paste A and paste B, widely used for front grid contacts on 45 Ω /sq.

EXPERIMENTAL

Five types of n^+ -p solar cells were fabricated on 0.6 Ω cm 300-um thick (100) float-zone (FZ) Si wafers (Table 1). The first one is a conventional screen-printed cell with 45 Ω /sq. homogeneous emitter, the next two are 100 Ω /sq. homogeneous emitter with two commercially available conventional pastes (paste A and paste B) fired through the SiN_x SLAR coating. The remaining two cells (Table 1) are selective-emitter cells with 100 Ω /sq. diffusion between the Ag gridlines formed by the Dupont self-doping Ag paste (PV168). One of the selectiveemitter cells has thin oxide passivation underneath the SiN_x SLAR coating. The emitters were formed in a conventional POCl₃ furnace at 881°C and 858°C to obtain 40-45 Ω /sq. and 100 Ω /sq. emitters, respectively. For SiO₂/SiN stack passivation, 100 Å-thick-oxide first was grown in a conventional furnace after the emitter formation. Prior to screen-printing of Al on the back, a PECVD SiN_x SLAR coating with a refractive index of ~1.98 and a thickness of 860 Å was deposited on the front. The front contact grid was screen-printed on top of the SiNx SLAR coating, and front and back metal contacts were co-fired using temperature profiles established to produce good ohmic contacts. To form the

selective-emitter cells, a self-doping Ag paste (Dupont PV168) was screen-printed on top of the SiN_x SLAR coating and alloyed in the belt furnace. The front and back contacts of the conventional-emitter cells were cofired at a set point of ~850°C in the belt furnace. To assess the recombination current in the emitters (J_{oe}), n^+ -i- n^+ samples were prepared with 45 Ω /sq. and 100 Ω /sq. n^+ layers with SiN_x, and SiO₂/ SiN_x surface passivation.

RESULTS AND DISCUSSION

In order to investigate the quality of the selectiveemitter cells, the electrical and optical properties of the cells were measured. The self-doping metal paste was fired at high temperature in order to achieve an alloying reaction with Si and introduce the phosphorus dopant from the self-doping paste into Si. Joe measurements were performed using a photoconductance-decay (PCD) technique [4]. A Joe of 337 fA/cm2 was obtained for the conventional 45 Ω /sq. homogeneous-emitter cell. The J_{oe} values for the selective-emitter cell were 125 fA/cm² and 185 fA/cm² with and without oxide passivation, respectively. However, these measurements do not take into account the leakage current due to the metal contact grid. Table 1 shows that the FFs obtained for the selective-emitter cells (SE-100 and SEO-100) without and with oxide passivation, are only slightly less than that of the conventional 45 Ω /sq. screen-printed cell (C-45). Fill factors for cells made on the 100 Ω /sq. emitter without the self-doping paste were less than 0.7 (CA-100 and CB-100).

In order to further understand the quality of the metal contacts on the selective-emitter cells, Suns-Voc measurements [5] were performed to obtain a pseudo-FF without the influence of series resistance. Suns-Voc measurements revealed that the pseudo-FFs are around 0.818 and 0.815 for the selective-emitter cells SE-100 and SEO-100, respectively, and 0.816 for the conventional-emitter cell (C-45). Moreover, the ideality factor for the selective-emitter cells is around 0.98 while that for the conventional paste cell is 1.04. Cell results in Table 1 shows that the conventional cell (C-45) has a FF of 0.785 which is 0.012 higher than the selective-emitter cell (SE-100). This difference in the FF is attributed to series resistance only since the Suns-Voc measurements show that the pseudo-FFs of the conventional and selective-emitter cell are almost equal and ideality factors are close to 1. Furthermore, the front-contact grid used for the selective-emitter cells is not optimized for a 100 Ω /sq. emitter. The grid used is the same for all the fabricated cells and it is optimized for a 45 Ω /sq. emitter with a gridline spacing of 0.22 cm. Hence, increasing the sheet resistance from 45 Ω /sq. to 100 Ω /sq. will decrease This is validated by [6] where the series resistance loss due to sheet resistance and gridline spacing is given by

$$R_{ds} = \frac{\mathbf{r}_s b^2}{12} \tag{1}$$

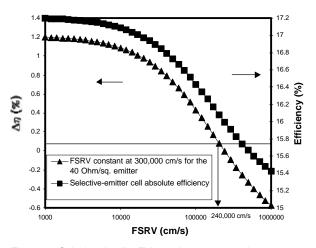


Figure 1: Calculated cell efficiency improvement due to a 110 Ω /sq. selective emitter over a 40 Ω /sq. conventional homogeneous emitter as a function of FSRV. The FSRV of the conventional-emitter cell was fixed at 300,000 cm/s.

where r_s is the sheet resistance in Ω /sq. and b is the gridline spacing in cm. For all the cells b is 0.22 cm, thus the contribution to the series resistance from the diffused sheet is 0.181 Ω -cm² for 45 Ω /sq. and 0.403 Ω -cm² for 100 Ω /sq. emitter. Since the difference in series resistance from 45 Ω /sq. to 100 Ω /sq. is 0.222 Ω -cm² and each 1 Ω -cm² in series resistance causes a decrease of 0.041 in FF (assuming that the shunt resistance is high enough) [6], the total loss in FF due to the increase in emitter sheet resistance is 0.0091. Subtracting 0.0091 from 0.785 (FF for C-45) gives a FF of ~0.776 which is close to the measured FFs of 0.773 and 0.768 in Table 1 obtained for the two selectiveemitter cells (SE-100 and SEO-100). Therefore, the loss in FF is not due to contact resistance and can be restored by optimizing the grid design.

In order to exploit the full potential of a selective-emitter cell, the front-surface recombination velocity (FSRV) must be reduced. Model calculations in Figure 1 show that for an FSRV greater than 240,000 cm/s, the selective-emitter cell under-performs the conventional screen-printed cell since a transparent emitter with a high FSRV decreases $V_{\rm oc}$ and $J_{\rm sc}$. This crossover point ($\emph{Dh}{=}0$, SRV=240,000 cm/s) is a function of the FSRV assumed for the conventional emitter (40-45 $\Omega/{\rm sq.}$). PC1D calculations were performed to assess the efficiency improvement due to the selective emitter over the conventional emitter. Since PC1D is a one-dimensional model, the selective emitter was modeled as a 110 $\Omega/{\rm sq.}$ homogeneous emitter with a constant FSRV.

Table 1: I-V data for conventional cells and selective-emitter cells using the self-doping paste.

Cell Name	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF	Eff(%)	n	$R_s (\Omega - cm^2)$	$R_{sh} (\Omega - cm^2)$
C-45	626	32.6	0.785	16.0	1.09	0.64	188,040
CA-100	612	32.1	0.704	13.9	1.09	2.41	1,707
CB-100	291	32.7	0.479	4.6	2.02	1.11	3,071
SE-100	623	33.4	0.773	16.1	1.04	0.94	2,378
SEO-100	635	33.6	0.768	16.4	1.09	1.06	23,165

Table 1 also shows a current enhancement of ~0.8 mA/cm² due to the selective emitter with SiN_x passivation only (SE-100), and 1.0 mA/cm² due to the selective emitter with the oxide and SiN_x passivation (SEO-100). In addition, we observed an enhancement in $V_{\rm oc}$ of 9 mV for the selective-emitter cell with oxide passivation. The corresponding absolute efficiency enhancement over the conventional cell (C-45) is 0.4% and 0.1% for the selective-emitter cells with and without oxide passivation, respectively. Thus, without good oxide passivation, the selective emitter does not provide much benefit.

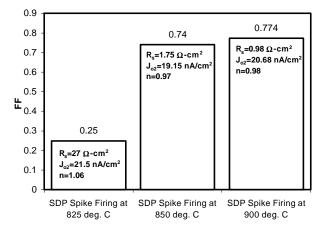


Figure 2: Effect of paste and firing temperature on the fill factor of screen-printed solar cells on a 100 Ω /sq. emitter.

The firing temperature and cycle is critical for the cell performance because it affects FF, series resistance, and leakage current. Figure 2 shows fill factor and contact parameters for spike firing at different temperatures. Spike firing of the SDP at a temperature lower than the Si-Ag eutectic (835°C) gave the lowest FF of 0.25 along with the highest series resistance. The FF improved to 0.74 at 850°C, which is close to the Ag-Si eutectic temperature. Finally, 900°C gave the best FF of 0.774. The $J_{\rm o2}$ values were similar for all cases.

In order to achieve the best FF on a 100 Ω/sq . emitter, the belt-firing cycle had to be optimized. Figure 3 shows the absolute cell efficiency after firing the SDP at slow, moderate, and rapid belt speed in the belt furnace. Slow firing at 910°C resulted in a very high J_{o2} value of 510 nA/cm², causing the efficiency to decrease to 10.5%. Moderate belt speed firing gave a decent FF of 0.758 with a somewhat high series resistance of 1.3 Ω -cm². The optimized spike firing condition gave the best cell efficiency of 16.17% with a good FF (0.774) and a reasonable series resistance of 0.9-1 Ω -cm².

In order to support the understanding that the SDP (PV168) works because of selective self-doping or selective emitter formation, a few conventional Ag pastes were used to make cells on the same 100 Ω /sq. emitter. Figure 4 shows contact parameters and the open-circuit voltage of cells using conventional Ag pastes (paste A and paste B), and the Dupont PV168 SDP on the 100 Ω /sq. emitter. The open-circuit voltage is obtained from

the I-V measurements of the finished cells. Paste A gave a FF of 0.70, V_{oc} of 612 mV, and high series resistance of 2.4 $\Omega\text{-cm}^2$. Paste B gave the worst result with a very low V_{oc} of 291 mV and a FF of 0.48. Finally, spike firing of the SDP gave the highest V_{oc} (625 mV) with a FF of 0.774 and series resistance of 1 $\Omega\text{-cm}^2$ on a 100 Ω/sq . emitter.

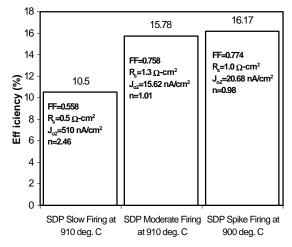


Figure 3: Contact parameters and absolute efficiency of cells fabricated using different firing schemes in the belt furnace on a 100 Ω/sq . emitter.

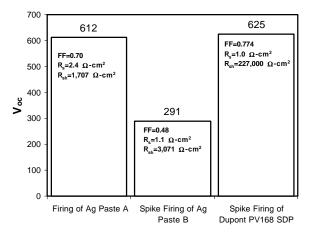


Figure 4: Firing of different pastes on 100 Ω /sq. emitter.

The IQE plots for the three cells (C-45, SE-100, SEO-100) in Figure 5 show that the short-wavelength response is greatly enhanced due to good surface passivation, resulting in Jsc improvement. Selectiveemitter cells with oxide passivation show a higher IQE (87% at 400 nm) compared to the cells without oxide passivation (80% at 400 nm) and much higher than the conventional screen-printed cell which shows the lowest short-wavelength response (63% at 400nm). In order to understand further and explain the performance difference between the selective-emitter and conventional screen-printed cells, calculated IQE data using PC1D were matched to the measured IQE data.

For the conventional screen-printed cell (CE-45), an FSRV of 300,000 cm/s gave a good IQE match in the short-wavelength range. For the selective-emitter cell with SiN_x passivation only (SE-100), a lower FSRV of 200,000 cm/s was obtained, while the selective-emitter cell with oxide and SiNx passivation (SEO-100) gave an FSRV of ~100,000 cm/s. These FSRV values take into account the recombination at the metal grid as well. According to the model calculations shown in Figure 1, an FSRV of 200,000 cm/s for the selective emitter should give 0.08% enhancement in efficiency compared to a 40 Ω /sq. cell which has an absolute cell efficiency of 16.08%. Moreover, the calculated improvement in the cell efficiency for a selective ~110 Ω/sq . emitter cell with an FSRV of 100,000 cm/s is 0.43% (over a 40 Ω /sq. cell) with an absolute cell efficiency of 16.43%. These modeling results are in very good agreement with the actual cell results. The modeled cell efficiency for a 40 Ω /sq. emitter cell is 16.0% while the actual experimental result is 16.02%. The selective-emitter cell with no oxide passivation (SE-100) has an FSRV of ~200,000 cm/s and the experimentally obtained cell efficiency is 16.1% which is 0.1% higher than the conventional 45 Ω /sq. cell. The selective-emitter cell with oxide passivation (SEO-100) has an FSRV of ~100,000 cm/s with an efficiency of 16.4%. Thus, the measured efficiency enhancement of ~0.4% is in excellent agreement with the 0.43% enhancement from the model calculations.

Figure 5 shows that high temperature (900°C) firing of the SDP also improved the long-wavelength response slightly. This is attributed to the deeper and better BSF. IQE matching of the measured and modeled PC1D data in the long-wavelength range gave back-surface recombination velocities (BSRV) of 1000 cm/s and 600-800 cm/s for the conventional and the selective-emitter cells, respectively. Thus, rapid co-firing of the self-doping paste at high temperature improves the short-wavelength response of a passivated 100 Ω/sq , emitter, gives very good FFs, and also improves the BSRV.

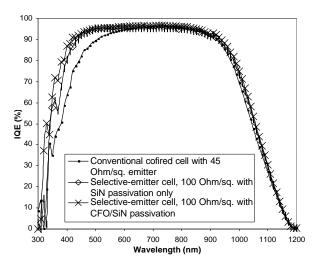


Figure 5: IQE plots for conventional and selective-emitter

CONCLUSION

A screen-printed selective-emitter cell improved J_{sc} and V_{oc} in comparison to a screen-printed homogeneous-emitter cells. A combination of light doping in the emitter and effective surface passivation improved the short-wavelength response. In addition, 900°C rapid co-firing of the self-doping paste with Al on the back formed a more effective Al-BSF, reducing the BSRV and improving the long-wavelength response. IQE analyses showed a reduction in FSRV from 300,000 cm/s to 100,000 cm/s and BSRV from 1000 cm/s to 600 cm/s as a result of the selective emitter formation. The FF on the 100 Ω /sq. selective-emitter cell was 0.774 with a reasonable series resistance of 0.9-1 Ω -cm². On the other hand, conventional pastes and firing schemes on 100 Ω /sq. emitters gave very poor FF and high series resistance, supporting the self-doping and selective emitter formation achieved with the PV168 Dupont paste.

ACKNOWLEDGMENTS

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REFERENCES

- [1] D. L. Meier, H. P. Davis, R. A. Garcia, J. A. Jessup, and A. F. Carroll, "Self-doping contacts to silicon using silver coated with a dopant source," *Proc. of the 28*th *IEEE PVSC*, 2000, pp. 69-74.
- [2] A. Rohatgi, M. Hilali, D. L. Meier, A. Ebong, C. Honsberg, A. F. Carroll, and P. Hacke, "Self-aligned self-doping selective emitter for screen-printed silicon solar cells," *Proc. of the 17th European Solar Energy Conference,* Munich, Germany, 2001, in press.
- [3] D. L. Meier, H. P. Davis, P. Hacke, R. A. Garcia, S. Yamanaka, J. Salami, and J. Jessup, "Self-doing, screen-printed silver contacts applied to IBC and PhosTop Dendritic Web Silicon Solar Cells," *Proc. of the 17th European Solar Energy Conference,* Munich, Germany, 2001, in press.
- [4] D. MacDonald, A. Cuevas, "Trapping of minority carriers in multicrystalline silicon," *Appl. Phys. Lett.*, **vol. 74**, no. 12, 1999, pp. 1710-1712.
- [5] R. A. Sinton, A. Cuevas, "A quasi-steady open-circuit voltage method for solar cell characterization," *Proc. of the 16th European Solar Energy Conference*, **vol. II**, Glasgow, United Kingdom, 2000, pp. 1152-1155.
- [6] A. L. Fahrenbach and R. H. Bube, *Fundamentals of* Solar Cells: Photovoltaic Solar Energy Conversion, Academic Press, 1983, p. 222.