

Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 33 (2013) 64 – 69

Energy
Procedia

PV Asia Pacific Conference 2012

Optimisation of Screen-Printed Metallisation for Industrial High-Efficiency Silicon Wafer Solar Cells

Vinodh Shanmugam^{a,b,*}, Jessen Cunnusamy^a, Ankit Khanna^a, Matthew Benjamin Boreland^a, Thomas Mueller^a

^aSolar Energy Research Institute of Singapore, National University of Singapore, 7 Engineering Drive 1, Block E3A, Singapore 117574, Singapore

^bDepartment of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Block EA, Singapore 117576, Singapore

Abstract

In the photovoltaic industry, screen printing accounts for majority of the metallisation processes for silicon wafer solar cells. Contact formation by co-firing of front and rear screen printed metal pastes for mainstream *p*-type standard solar cells is a well-established process. It is of utmost importance to use front and rear metallisation pastes that are co-firing compatible. In this paper, we describe a methodology for front and rear paste selection and process optimisation. We explore the usage of HF dip (20 seconds) on finished cells to differentiate between over-fired and under-fired contacts. Two commercially available front Ag pastes (paste 'A' & paste 'B') with fine line printing capability were tested along with two commercially available rear Al pastes (paste 'C' & paste 'D'). Firing optimisation was conducted to achieve a one-Sun fill factor of 80.7 % and a series resistance at maximum power point (MPP) of 0.4 Ωcm^2 at the optimised firing profile. The Al paste 'C', which resulted in a better and more uniform back surface field at the optimised profile, was selected to study the effect of post-metallisation HF etching. By choosing the correct combination of metal pastes, at the optimised firing profile, efficiencies of 18.5% were realised for standard screen-printed 156 mm \times 156 mm *p*-type pseudo-square monocrystalline solar cells.

© 2013 The Authors. Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Selection and peer-review under responsibility of Solar Energy Research Institute of Singapore (SERIS) – National University of Singapore (NUS). The PV Asia Pacific Conference 2012 was jointly organised by SERIS and the Asian Photovoltaic Industry Association (APVIA)

Keywords: Screen printing; co-firing; metallisation pastes; over fired; under fired; HF dip; high efficiency; standard cells

* Corresponding author. Tel.: +65 6516 5255; fax: +65 6775 1943

E-mail address: vinodh.shan@nus.edu.sg

1. Introduction

Currently, screen printed contact metallisation is the most widely used contacting technique for mainstream *p*-type silicon wafer solar cells. In particular silver (Ag) paste is used for the front contact, aluminium (Al) paste for the rear contact and Ag paste for the rear bus bars. Due to rapid developments in the paste industry, new and advanced versions of front and rear metallisation pastes are constantly released into the market, which requires frequent re-optimisation of the metallisation process. It is of utmost importance to use front and rear metallisation pastes that are co-firing compatible. Ideally, the Ag paste for the front contact should feature fine line printing capabilities, low metal line resistance, low contact resistance to the silicon and good mechanical adhesion. The Al paste for the rear contact should result in a thick and uniform back surface field (BSF) [1]. The front contact grid design needs to be carefully optimised based on the emitter sheet resistance and the characteristics of the front Ag paste. Closely spaced, wide fingers will reduce the series resistance losses but conversely increase the shading losses. Hence optimisation of the front contact grid requires a trade-off between the electrical and optical losses due to the front metal grids. Optimisation of the firing temperature profile is also required to minimise the specific contact resistivity between the Ag paste and the emitter. Note the firing profile also affects the uniformity and thickness of the rear Al-BSF. Hence optimisation of the firing profile requires a complex balance between front contact resistance and BSF quality, which impacts the fill factor (*FF*) and the open-circuit voltage (V_{oc}) of the solar cell.

2. Cell fabrication

In this work, large-area 239 cm² *p*-type pseudosquare monocrystalline wafers with 1-3 Ωcm bulk resistivity were used. The wafers were alkaline textured in KOH/IPA solution, followed by tube diffusion (Tempress) using POCl₃ as the P source to produce a 70 Ω/□ homogeneous phosphorus doped emitter. After PSG (phosphosilicate glass) removal in dilute HF, a silicon nitride film was deposited by plasma-enhanced chemical vapour deposition (PECVD, SiNA-XS, Roth & Rau) on the front surface. The cells were then metallised by screen printing using Al paste on the rear and Ag paste on the front (PV1200, DEK). This was followed by a co-firing step (Ultraflex, Despatch) and all the cells were edge isolated using a laser (Solas, IDI Systems) after co-firing.

2.1. Front metal grid optimisation

Two commercially available front Ag pastes with fine line printing capabilities were used for the front contacts in this experiment. The simulation tool *GridSim* [2] was used for determining the optimal number of fingers required, taking into account electrical losses in the emitter, the bus bars, the fingers and the contact resistance as well as optical losses due to shading by the front metal grid. The Transfer Length Method (TLM) [3] with a circular pattern was used to determine the specific contact resistivity of the Ag paste to a 70 Ω/□ phosphorus diffused emitter. The TLM samples were printed on 'print-ready' wafers (textured, 70 Ω/□-diffused emitter and silicon nitride coated) using the two Ag pastes and fired over a range of peak firing temperatures. The peak firing temperatures were recorded using a *Datapaq* data logger with a K-type thermocouple soldered onto a metal plate. Fig. 1 shows the specific contact resistivity value measured for Paste 'A' and Paste 'B' with respect to different peak firing temperatures on a 70 Ω/□ tube diffused phosphorus emitter. The optimum peak firing temperature was defined as the temperature at which the lowest specific contact resistivity was achieved. Paste 'B' has a wider firing window and a lower specific contact resistivity value of 2.1 mΩ cm² when compared to Paste 'A', which has a higher contact resistivity of 4.0 mΩ cm².

The metal line sheet resistance of the front Ag pastes were determined by printing test lines of varying widths ranging from 70 μm to 270 μm . To minimise measurement error due to the conductance of the underlying silicon, the test lines were printed on a non-diffused wafer with high bulk resistivity to ensure that no contact is formed between the screen printed metal and the silicon wafer. The conductance was plotted against the line width to determine the line sheet resistivity of the Ag paste and was found to be 1.6 $\text{m}\Omega/\square$ for Paste 'A' and 1.4 $\text{m}\Omega/\square$ for Paste 'B'. Based on the results of the *GridSim* simulations, a 70 μm finger width grid design with 79 fingers and 3 bus bars was chosen for the 70 Ω/\square n^+ emitter cells.

2.2. Rear Al paste selection

Two commercially available Al pastes (Paste 'C' and Paste 'D') were printed on the rear of the silicon wafers and fired at the optimal firing temperature profile determined from Fig. 1. The samples were cleaved and "stain etched" in a mixture of 1:3:6 (HF:HNO₃:CH₃COOH) to reveal the BSF formed after firing by cross-sectional SEM (see Fig. 3 and Fig. 4). These SEM images clearly show that paste 'C' resulted with a deeper and more uniform BSF when compared to paste 'D'.

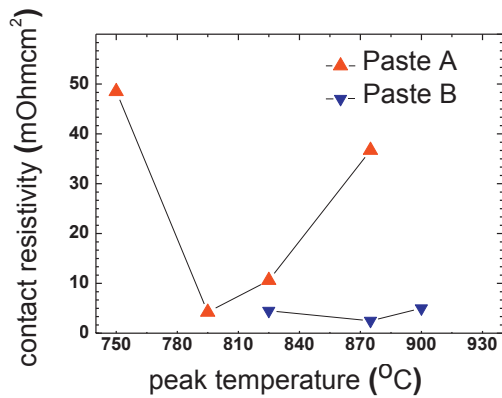


Fig. 1. Specific contact resistivity of Paste 'A' and Paste 'B' to a 70 Ω/\square tube diffused phosphorus emitter as a function of the peak firing temperatures. Paste A requires an optimum firing temperature of 795°C and Paste B requires 875°C. The lines serve as guide for the eye.

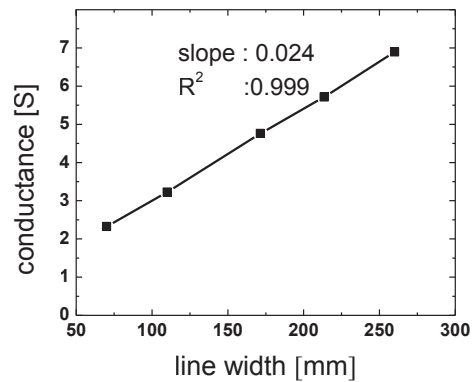


Fig. 2. Plot of conductance as a function of the printed metal line width for Paste 'A'.

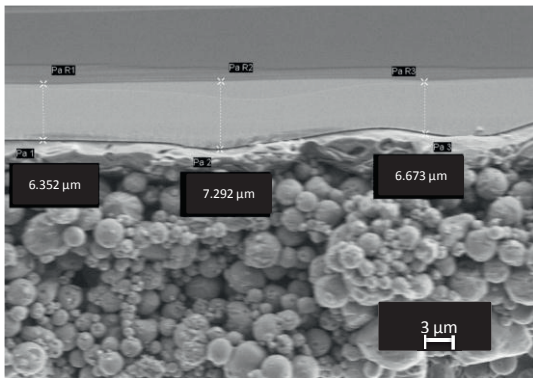


Fig. 3. Paste 'C' with thick and uniform BSF of 6-7 μm thickness.

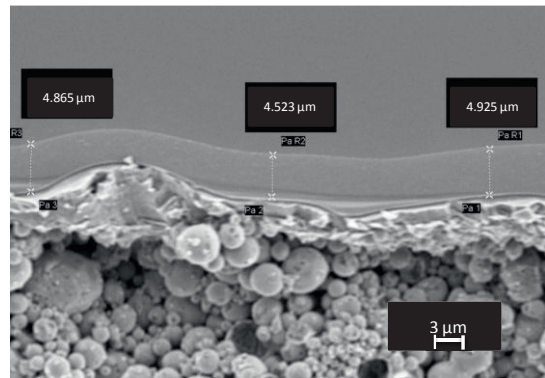


Fig. 4. Paste 'D' with thick and uniform BSF of 4-5 μm thickness.

2.3. Co-firing process optimisation

Solar cells were metallised with the optimised grid pattern on the front (using Ag Paste ‘B’) and using a full-area print on the rear (using Al paste ‘C’) and were fired at optimised profile. A *FF* of 80.7% was obtained with a series resistance of $0.4 \Omega\text{cm}^2$. By choosing the metal pastes that are co-firing compatible and optimising the process, efficiencies of 18.5% were achieved for standard screen-printed $156 \text{ mm} \times 156 \text{ mm}$ *p*-type pseudo square monocrystalline solar cells.

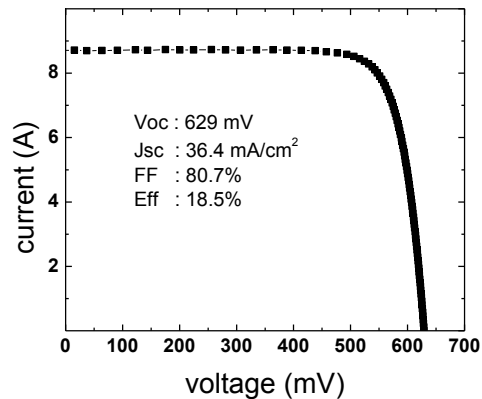


Fig. 5. One-Sun *I-V* curve of the best solar cell obtained in this study.

2.4. Impact of the HF dip on screen printed front contacts

Screen printed front contact formation and current transport mechanisms are not yet fully understood. The major reason is the non-uniformity of the structure and composition of the metal-silicon interface in the case of screen printed fingers [4]. The screen printed contact comprises a complex interfacial region consisting of a resistive glassy layer, silver crystallites, colloids and pinholes. High series resistance is often a problem with screen printed contacts on solar cells. Mainly due to melted glass frits that flows preferentially towards Ag-Si interface during firing. This creates an interfacial glass layer between the Ag contact and the silicon which increases the series resistance of the solar cell. From the different parameters, the melting characteristics of the glass frits, presented in the Ag paste, have a significant influence on the contact resistivity and therefore on the *FF* of finished cells [5]. In this paper we explored the possibility of using a quick HF dip (20 seconds) on finished cells to differentiate between over fired and under fired contacts.

The cells were metallised using Ag paste ‘A’ (as it has a very narrow firing window when compared to paste ‘B’) and fired at different peak firing temperatures above and below optimum temperature, determined from the TLM experiments. At temperatures below and above the optimum conditions, the cells were series resistance limited. Hilali *et al.* [4] reported an increase in interfacial glass layer thickness with increasing peak firing temperatures. This interfacial glass layer is highly resistive (in the order of 10^9 ohm-cm), and with its thickening, the series resistance of the over-fired solar cell increases. In the case of under fired cells, the high series resistance is attributed to insufficient crystallite formation [6] (even though the interfacial glass layer is thin) due to lower peak firing temperatures. After a quick dip in HF it was found that over and under fired cells showed an improvement in *FF*, whereas cells fired at the optimum peak temperature were unaffected. Moreover, the improvement in the *FF* for the over-fired cells

was significantly larger when compared to the under-fired cells. The delineated effect of the HF etch provides the possibility to differentiate between under-, optimum and over-firing. The reduction in the series resistance for the over-fired cells after HF dip is attributed to the thinning down of the glass layer at the edges of the grid lines [7, 8]. This does not have much impact on the under-fired cells, as there are not sufficient Ag crystallites formed to promote conduction after HF treatment.

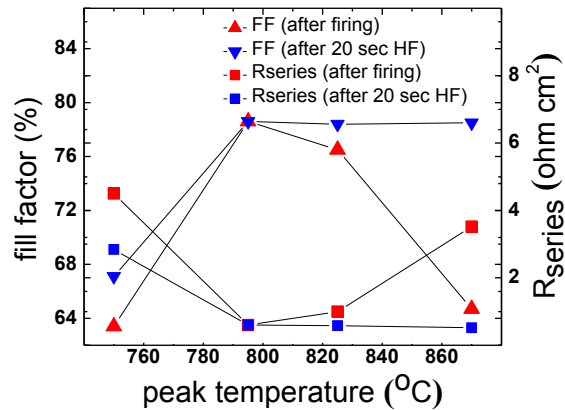


Fig. 6. Impact of HF dip on over-fired and under-fired cells.

3. Conclusion

In this work we have presented a comprehensive methodology, involving TLM measurements, line resistance measurements and BSF thickness determination for the selection of co-firing metal pastes. A technique of using HF dip to differentiate between the under fired and over fired cells and determine the optimum firing condition was explored as well. HF dip on over fired cells can increase the FF from 64% to 78% mainly due to the reduction in series resistance of the cell from $3.5 \Omega\text{cm}^2$ to $0.7 \Omega\text{cm}^2$. This is attributed to the thinning of the glass layer at the edges of the grid lines. For cells fired at the optimised condition the series resistance is low and this is due to the large number of Ag crystallites and a very thin glass layer. For under fired cells the HF treatment does not result in an as significant improvement in FF since the cells are series resistance limited due to the lack of Ag crystallites.

Acknowledgements

The authors thank their colleagues from the Silicon Photovoltaics Cluster at the Solar Energy Research Institute of Singapore (SERIS) for their assistance in sample processing and measurements. SERIS is sponsored by the National University of Singapore (NUS) and Singapore's National Research Foundation (NRF) through the Singapore Economic Development Board (EDB).

References

- [1] Kaminskia A, Vandellea B, Favea A, Boyeaux JP, Le Quan Namb, Monnab R, Sartib D, Laugiera A. Aluminum BSF in silicon solar cells. *Solar Energy Materials and Solar Cells* 2002;72:373-9.
- [2] Mette A. New concepts for front side metallization of industrial silicon solar cells, PhD thesis, University of Freiburg, Germany, 2007.
- [3] Schroder DK, Meier DL. Solar cell contact resistance – a review. *IEEE Transactions on Electron Devices* 1984; 31:637-47.

- [4] Hilali MM, Rohatgi A. Review and understanding of screen printed contacts. *Proc. 14th Workshop on Crystalline Silicon Solar Cells and Modules*, Colorado; 2004, pp. 109-116.
- [5] Lin CH, Hsu SP, Hsu WC. Silicon solar cells: structural properties of Ag-contacts/Si-substrate, solar cells - silicon wafer-based technologies, L.A. Kosyachenko (Ed.), Intech,2011.
- [6] Grupp G, Huljic DM, Preu R, Willeke G, Luther J. Peak firing temperature dependence of the microstructure of Ag thick-film contacts on silicon solar cells-a detailed AFM study study of the interface. *Proc. 20th European Photovoltaic Solar Energy Conf.*, Barcelona, Spain; 2005, pp. 1379-1382.
- [7] Ebong A, Kim DS, Rohatgi A, Zhang W. Understanding the mechanism of light induced plating of silver on screen-printed contacts for high sheet resistance emitters with low surface phosphorus concentration. *Proc. 33rd IEEE Photovoltaic Specialists Conf.*, San Diego; 2008, pp. 1-5.
- [8] Ebong A, Kim DS, Yelundar V, Upadhyaya V, Upadhyaya AD, Tate K, Rohatgi A. Understanding the role of forming gas anneal on the screen printed crystalline silicon solar cell front grid. *Proc. 21st European Photovoltaic Solar Energy Conf.*, Dresden, Germany; 2006, pp. 1519-1522