

ADVANCES IN PV METALLISATION TECHNOLOGY

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ABSTRACT: Thick film metallisations for solar cells enable low loss current collection and in the case of Al also provide an electric field at the cell's back surface. This paper describes development of new generations of thick film silver and aluminium compositions. The compositions were designed to achieve maximum efficiency over a wide range of processing conditions. Results of systematic firing process variation will be presented that were used to identify best candidate metallisation compositions for future solar cell applications. Performance criteria used were peak efficiency, fill factor, firing process window, wafer bowing, and soldered adhesion. Both n type and p type compositions interact with the cell surface. The nature and degree of the interaction determine the metallisation performance in addition to the fired film properties

Keywords: c-Si, electrical contact, metallisation, soldered adhesion

1 INTRODUCTION:

Thick film metal compositions have been used for over 20 years to make economical, high performance electrical contact to photovoltaic devices. In the case of crystalline silicon solar cells, new generations of thick film metallisations have been developed to enable new silicon cell technology.

1.1 Front Contact through SiNx

Front side silver contact materials and cofiring processing have been developed to enable economical production of high efficiency cells.^[1]

The electrical contact is made after the glass bond phase additive etches the silicon nitride ARC (SiNx) and interacts with silver and silicon to form a very thin layer of electrically conductive glass at the Ag-Si interface^{[2][3][4]} and/or a direct Ag to Si contact. The silver sinters concurrently with the interfacial reactions. It achieves a fairly high conductivity (around one half that of pure, dense silver).

1.2 Back Contact

Aluminium has been used to achieve enhanced cell performance via back surface field formation. Recently, improved aluminium has been developed to enable Al-Si alloying with much reduced stress in and bowing of thin Si wafers.^[5]

1.3 Contact to Shallow Emitter

Work has been reported on contacting shallow homogeneous emitters (70 to 100 Ω/\square) or selective emitters (variable thickness). The resulting cells have higher blue response.^[6]

1.4 Pb and Cd Free Metallisations

More recently attention has turned to removing heavy metals (Pb, Cd) from thick film solar metallisation. This paper describes development of a Pb, Cd free system of thick film metal compositions that contacts both n and p type sides of the Si solar cell.

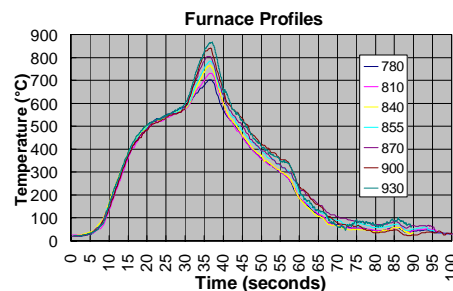
2 EXPERIMENTAL:

Experimental silver, aluminium, and silver-aluminium pastes were designed and evaluated on multicrystalline Si solar cells with emitter R of 45 Ω/\square and 75-85 nm SiNx ARC. Key electrical and mechanical properties were measured. Electrical measurements were done using an I-V tester (ST-1000 or EETS cell tester 200 Xe). Mechanical

measurements were done using a tensile tester (MKS), and the bow was measured using a travelling micrometer.

Electrical test samples were made on 125 mm and 157 mm cells. The front silver was printed using a standard "H" pattern with two busbars and 44 fingers on the 125 mm cells. The screen mesh was 325/in. Screen wire was 1.1 mil diameter stainless steel. The mesh was biased 45 degrees to the frame. Gridline pattern opening was 110 μm . Gridline width of around 130 μm was achieved for all pastes. The back was completely covered with aluminium (PV333). Both front and back metallisations were cofired in an IR furnace RTC at high belt speed 125 ipm and varying temperature settings. Work on aluminium reported in section 3.2 was fired using a Centrotherm 4 zone IR furnace running at a belt speed of 2750 mm/min. A range of firing temperatures were achieved as shown in Figure 1 (RTC work). Five cells were prepared per firing condition. The profiles of were obtained using a thin Type K thermocouple (0.5 mm diameter wire).

Figure 1 Temperature Profiles for all firing conditions



Adhesion was measured by pulling solder coated copper ribbon at 90 degrees from reinforced cells (to prevent cell breakage during pull test). The ribbon was attached to silver by applying a no clean flux to both metal and ribbon (Loctite MF200) and reflowing the Sn-Ag (96.5-3.5) solder with temperature controlled solder iron controlled to 365 – 385°C.

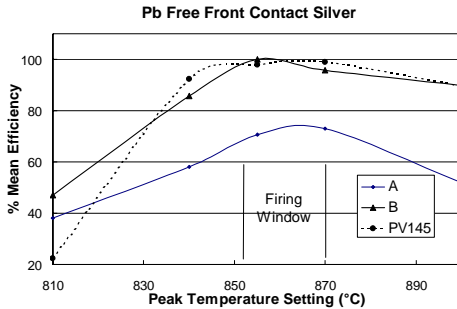
Aluminium was evaluated for its effect on wafer bowing by printing and firing candidate pastes at a specified print weight of about 8 mg/cm² and by varying firing temperature conditions.

3 RESULTS AND DISCUSSION

3.1 Pb Free Front Contact Ag

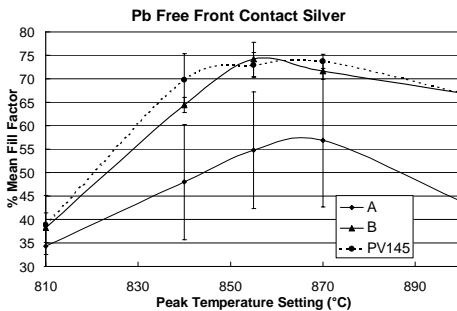
Figure 2 shows the mean efficiency of three silver pastes fired over a range of peak temperature. DuPont PV145 front contact silver represents state of the art paste containing Pb.

Figure 2 Mean efficiency of n-type contact pastes fired over a range of temperatures



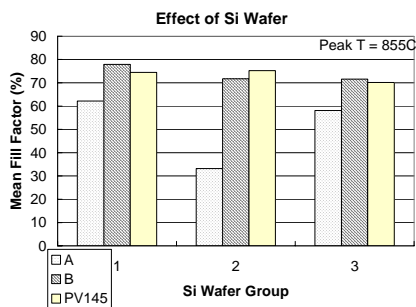
Experimental Pb free pastes A and B contain glass free of both Pb and Cd that is designed to penetrate SiNx and

Figure 3 Mean FF of n-type contact pastes fired over a range of temperatures



contact the Si emitter without need for post-firing processing such as annealing or etching or forming gas treatment.

Figure 4 Mean FF of Front Contact Ag vs Si Wafer Group



A firing window of around 20°C is indicated by the fairly flat peak performance curve for paste B. Mean fill factor

(FF) for the same cells is shown in Figure 3. The similarity of Figure 2 and Figure 3 indicates the efficiency variation is primarily a result of metallisation contact quality. Pb free paste B is shown to be equivalent to PV145 in this lab study as seen by overlapping error bars. Pb free paste A was more sensitive to firing and other process variables as indicated by its much larger error bars.

Best cell properties are shown in Table 1. Increased thickness of Paste B can potentially increase FF beyond 78.1%.

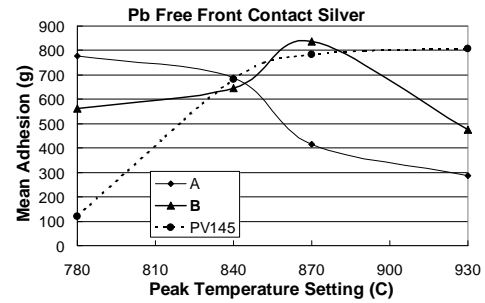
Table 1 Best cell properties

Paste	Eff Rel (%)	FF (%)	Voc (V)	Jsc (%)	Rs (mΩ)	Firing Set T (C)	LW (μm)	Th (μm)
B	100	78.1	0.605	99	5	855	131	9.9
PV145	100	77.5	0.604	100	7	840	128	13.1
A	88	69.6	0.599	98	13	870	129	13.8

SRc of B and PV145 < 0.6 mΩ-cm²
 Measurement temperature = 25C
 Incident flux = 1000 mW / cm²

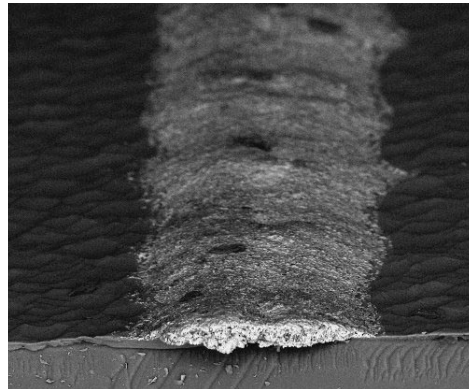
High quality electrical contact is very sensitive to cell (Si quality, emitter diffusion, and ARC) and metal (printing

Figure 5 Mean Soldered Adhesion



and firing) processing. Figure 2 through to Figure 4 show paste B and the industry proven PV145 capable of achieving excellent electrical contact to a full distribution of

Figure 6 100 μm wide grid line



production cells over a wide range of firing conditions. This performance capability translates into production of high yield of high efficiency cells in large scale manufacturing. In the optimal firing range for electrical efficiency, Paste B has equivalent high adhesion to that of

PV145. Adhesion variations at temperature extremes result from variations in paste bonding and sintering behavior. The solder used in the evaluation was Pb free solder alloy

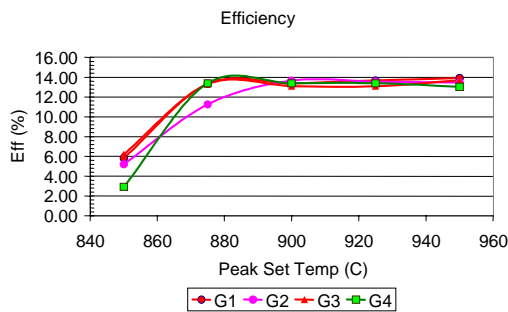
Mean soldered adhesion of the pastes over a wider firing temperature range is shown in Figure 5. Fine line printing capability is shown in Figure 6.

3.2 Back Contact Al

In the fired cells the largest contributor to the lead content is the lead frit often used in the Al paste. Furthermore, since the aluminium back plane dominates the bow behavior, this factor is limiting the move to larger and thinner wafers because of cell handling issues both during cell manufacture and the ribbon interconnection step of module manufacture.

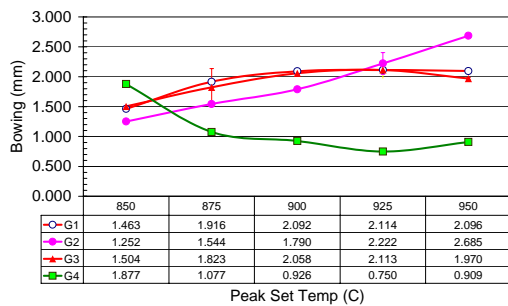
Here, we report data on a Pb containing fritted Al paste (G1) compared to three lead free systems G2, G3 and G4; plus we have Ag and Ag/Al tabbing pastes that have been developed to enable completely Pb free solar cell and module manufacturing. These Al pastes were used on 180 μm thick (5 inch) cells and their electrical performance for firing peak temperatures (furnace set) are shown in Figure 7. Cell manufacturers are interested in the bow

Figure 7 Mean efficiency of pastes G1, G2, G3 and G4 fired over a range of peak furnace set temperature



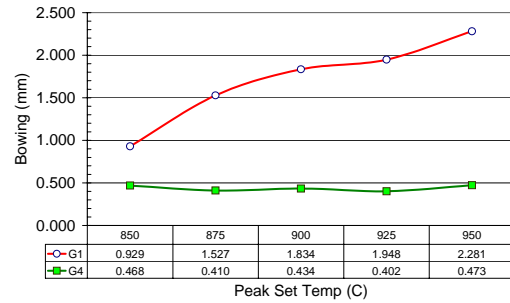
characteristics which are shown in Figure 8, significantly, the system G4 has a bowing tendency that decreases with firing temperature while the electrical properties are maintained.

Figure 8 Bowing of Al paste fired on 180 um cells (5 inch)



To confirm the performance of Al paste G4, we tested it on the larger 6 inch cells with a thickness of around 210 μm and these are shown in Figure 9. The bowing property of G4 on the larger wafers are slightly different to the smaller wafers and is still being understood.

Figure 9 Bowing of Al paste fired on 210 um cells (6 inch)



3.3 Back contact Ag and Ag/Al

Pb free Ag-Al paste has matched electrical performance of PV202 and exceeded its adhesion capability (600g v 400g mean adhesion).

4 CONCLUSIONS:

- A front contact Ag free of both Pb and Cd has been developed with state of the art electrical contact performance. The contact is achieved without need for additional post-fire processing. Very high best case fill factor over 78% indicates excellent potential for even higher performance through further process optimisation.
- The cofiring, high electrical performance window for the Pb free system is around 20°C (785 to 800°C measured peak temperature).
- The Pb free front contact Ag achieved high adhesion with Pb free solder over a very wide firing range of approximately 710°C to 830°C (measured peak temperature).
- Low bow, high BSF Pb and Cd free Al has been developed
- Back tabbing Pb and Cd free Ag and Ag/Al with high adhesion have been developed
- A complete Pb free metal contact system has been developed for use on Si solar cells.

Acknowledgements

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