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Long term stability analysis of copper front side metallization for silicon solar cells

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Abstract

In this work the development and evaluation of a copper solar cell front side metallization based on a screen printed silver seed layer, a plated nickel diffusion barrier, a plated copper conductive layer and a plated silver capping is presented. Due to a slight adjustment of the standard screen printing process, and subsequent plating of Ni, Cu and Ag, silver consumption was reduced to < 16 mg per cell front side on standard BSF 15.6 cm x 15.6 cm mono crystalline wafers, produced only with inline capable techniques. Contact adhesion forces of 1.5 N/mm and, efficiencies of 18.4 % were achieved. For the long term stability analysis on cell and module level, cells with different nickel diffusion barrier masses (10-40 mg/cell) were treated on hotplates at 200, 225 and 250°C while detecting degradation due to copper diffusion by measuring the pFF. Sufficient cell life times are predicted for 10 mg Ni by the resulting Arrhenius plot. After 750 h damp heat test of one cell modules no visible degradation was determined. This means that accelerated degradation on hotplates show the degradation due to copper diffusion more strongly than 750 hours damp heat test. In an additional SEM analysis the plated nickel diffusion barrier showed a closed layer on the fingers and an incomplete layer on the busbars, indicating busbars as possible weak points for copper diffusion due to inhomogeneous Ni plating

1. Motivation

To substitute the expensive silver with cheaper copper for the front side metallization of silicon solar cells a stack of nickel and copper can be plated on top of a screen printed fine line silver seed layer [1]. This concept offers the advantage that it can be realized by retrofitting existing production lines just with additional plating tools and an adjustment of the well-known screen printing process. The implementation of this contact architecture has to face

several challenges: the realization of a low silver consumption to maximise the cost benefit, good IV-results, sufficient contact adhesion to enable module integration and long term stability against degradation due to copper diffusion. Results of these issues with a focus on the long term stability are presented and evaluated in this work.

2. Cell production

Standard 15.6 cm x 15.6 cm textured (random pyramids) p-type Cz silicon wafers with PECVD silicon nitride anti reflection coating, a 90 Ω phosphorous emitter and screen printed Al/AlAg rear side metallization were used and screen printed with a fine line Ag seed-layer at the front surface. The used screen for front contact definition featured 400 mesh and a wire diameter of 18 µm. The emulsion opening for the contact fingers was 25 µm. The screen was calendred and covered with a functional coating to allow a better paste release. A commercial Ag fine line paste was used. The cells were co-fired at varied set peak temperatures in an industrial inline furnace. For the fine screen printed Ag seed-layer an average paste consumption of 22 mg wet paste was achieved. Thermo gravimetric measurements show a solid content of 38.5 %$_w$ for that fine line paste, which translates into a silver consumption of ~8.4 mg silver, not considering that an unknown part of the solid is glass frit (usually ~5%). These results have been obtained with standard 3 busbar (1.5 mm width) front side grid geometry, without busbar segmentation etc. Figure 1 shows the weighted paste consumption for the used fine line Ag-paste (green box) compared to a standard Ag front side paste (red box) printed with the same screen on the same substrate.
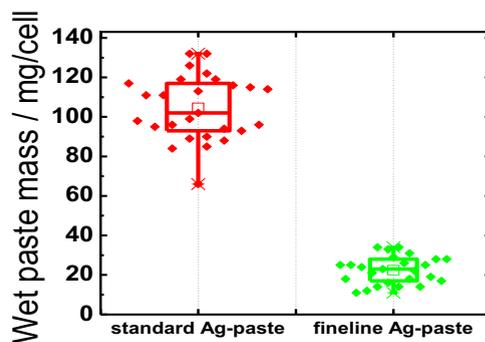

Fig. 1. Weighted wet paste consumption for the used fine line Ag-paste compared to a standard Ag-paste both pastes were printed with the same fine line screen on the same substrate

After firing, a nickel diffusion barrier was plated on the cells with varied Ni masses between 10 and 40 mg/cell using a Watts-type nickel electrolyte. Subsequently an 8-9 µm thick copper conductive layer and a 0.5 µm thick silver capping layer were deposited. The cells were plated on inline plating tools from RENA, where just the cell front side is in contact with the electrolyte using the light induced plating (LIP) technique [2]. For the silver capping, a silver mass of 7 mg per cell was deposited ending up in a total silver consumption of 15.4 mg per cell for the front side metallization. The backside metallization was not changed in this work; cells with a standard screen printed aluminium metallization with silver pads for soldering were used. The pads consume 18 mg silver per cell. Table 1 shows the silver consumption for cells with standard screen printed front side and cells with fine line printed front side plus Ni-Cu-Ag plating.

Figure 2a shows a microscope cross section picture of a typical front side contact finger, fabricated with the described seed & plate metallization process. A thin and narrow screen printed Ag-seed-layer (1) with a width of 30 µm for the grid fingers is the base for the subsequent plating of nickel (2), copper (3), and silver (3) ending up with a total contact finger width of 61 µm. Figure 1b shows a cross-section SEM-picture of such a grid finger with measured layer thicknesses.

Table 1. Used silver amount for fine line printed cells with Ni-Cu-Ag plating and for standard screen printed cells

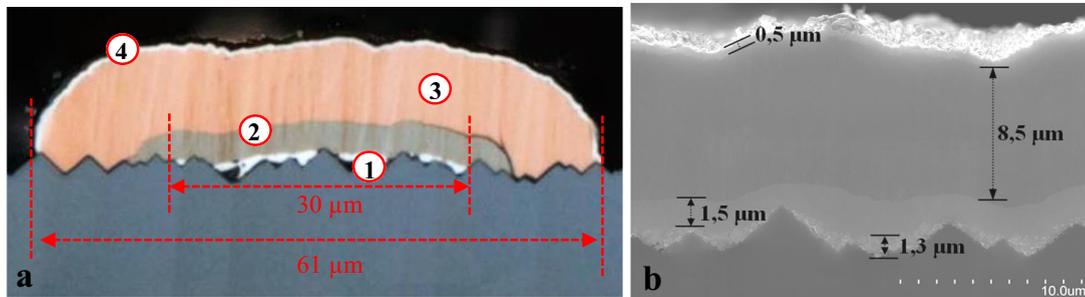|	Average of used Ag-paste amount (mg/cell)	Solid content Ag-paste (%)	Plated Ag-mass (mg/cell)	Total Ag consumption front side (mg/cell)	Total Ag consumption backside (mg/cell)	Total Ag consumption cell (mg/cell)
Fine line print + Ni-Cu-Ag plating	22	38,5	7	15,36	18	**33,4**
Standard screen printed Ag front side	110	97,9	-	107,69	18	**125,7**

Fig. 2. Microscope cross section picture of a contact finger based on a 30 µm wide screen-printed Ag-seed-layer (1) and a total finger width after Ni (2)-Cu (3)-Ag (4)-plating of 61 µm (a). SEM cross-section picture of the front-side metallization stack with measured layer thicknesses (b)

Table 2 shows the efficiencies at a set peak temperature of 930°C. Maximum efficiencies of 18.4 % were obtained on standard BSF cells. After metallization process and IV-measurement the cells where soldered at a soldering station were soldering conditions can be set precisely and reproducible. A standard 1.5 mm wide ribbon (PbSnAg) and a standard flux were used. To measure the quantitative contact adhesion of the front side contacts, the ribbons were peeled off using an automated peel force tester (90° angle). Maximum peel-force values of 1.5 N/mm were reached due to deeper understanding of the interaction between screen-printed contacts and electrolyte solutions [3,4].

Table 2. IV-results at a set-peak firing temperature of 930°C

	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	pFF (%)	η (%)
average / best cell	632.9 / 633.6	37.1 / 37.1	77.5 / 78.6	82,9/83	18.2 / 18.4

3. Long term stability analysis

For the long term stability analysis cells with nickel masses of 10, 20, 30 and 40 mg/cell were plated to verify the impact of the nickel diffusion barrier mass to the long term stability of the cells.

3.1. Hotplate degradation – long term stability on cell level

Cells with varied nickel mass and reference cells without nickel diffusion barrier and without copper were tempered on hotplates at 200°C, 225°C and 250°C for ~1000h. Temperatures >300°C would lead to even lower

degradation times but at such temperatures also the cells without copper show significant degradation. During temperature treatment the pseudo fill factors were measured using Suns Voc to detect the degradation due to copper diffusion into the junction [5]. Figure 4 shows the pseudo fill factor relative to the initial pFF before temperature treatment over time. With higher Ni amount the degradation of the cells slows down.
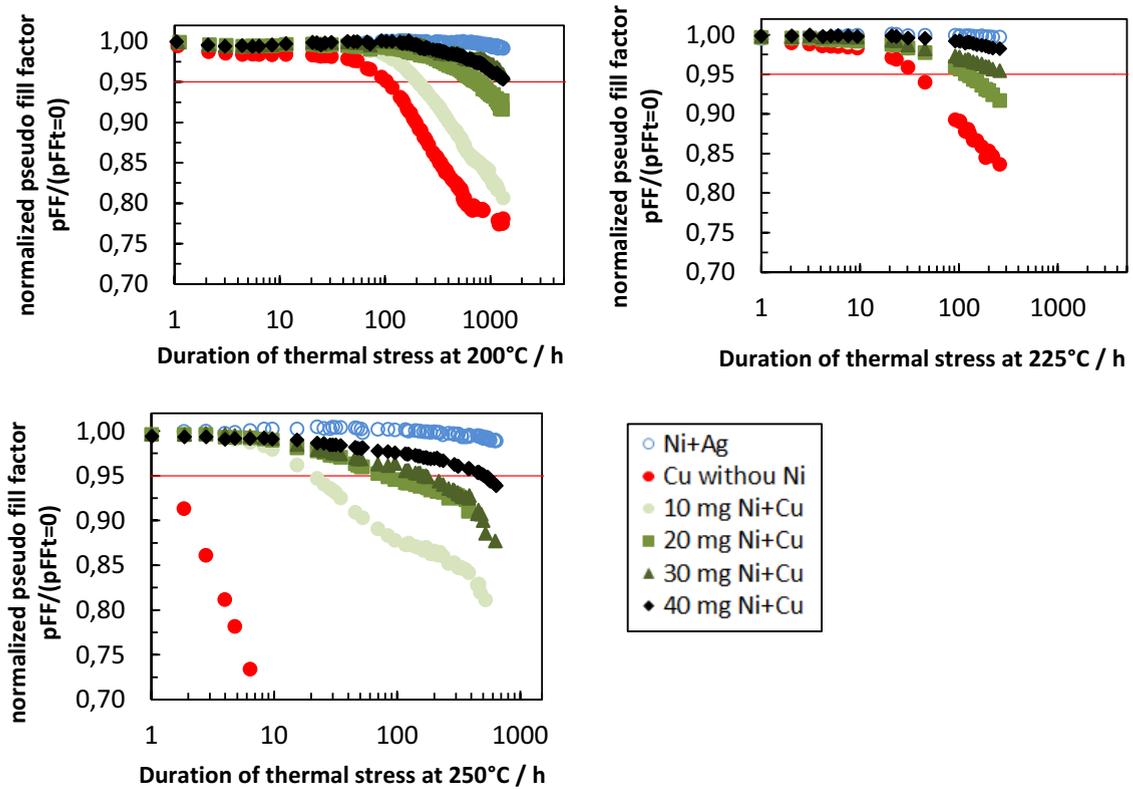

Fig. 3. Pseudo fill factor relative to the initial pFF over time during thermal cell treatment on hotplates at 200, 225 and 250°C

For all three temperatures the pFF of cells with 40 mg nickel degrades slower than for cells with 10 or 20 mg nickel indicating slower copper diffusion into the junction. Cells without any diffusion barrier degrade at 250°C within less than one hour under 95% of the initial pFF. On the other hand, it is worthy to note that a cell without any diffusion barrier layer sustained a thermal budget of 100 hours at 200 °C without more than 5% pFF loss. Whether this is a true effect or due to a particularity in the measured cell needs to be investigated with more statistics.

Out of this data the cell lifetime at standard conditions can be calculated assuming an Arrhenius dependency. Figure 5 shows the Arrhenius plot for the investigated set of cells. For every experimental point one cell was degraded at elevated temperatures. For 10 mg nickel sufficient lifetime is predicted (r^2 =0.99). For the other configurations the r^2 factor was between 0.54 and 0.82, so linear regression is not reliable. Generally more statistics is needed for a reliable lifetime estimation and comparison.

Also, one weakness of the method is that changes in degradation speed play a bigger role than absolute differences at a given temperature. Even though the cells with the high plated mass show the longest resilience against effects caused by copper diffusion, the quick degradation of less plated cells at high temperatures increases the slope of the linear extrapolation so much that these curves predict an even higher stability. Again, it is likely that more statistics will reduce this effect.
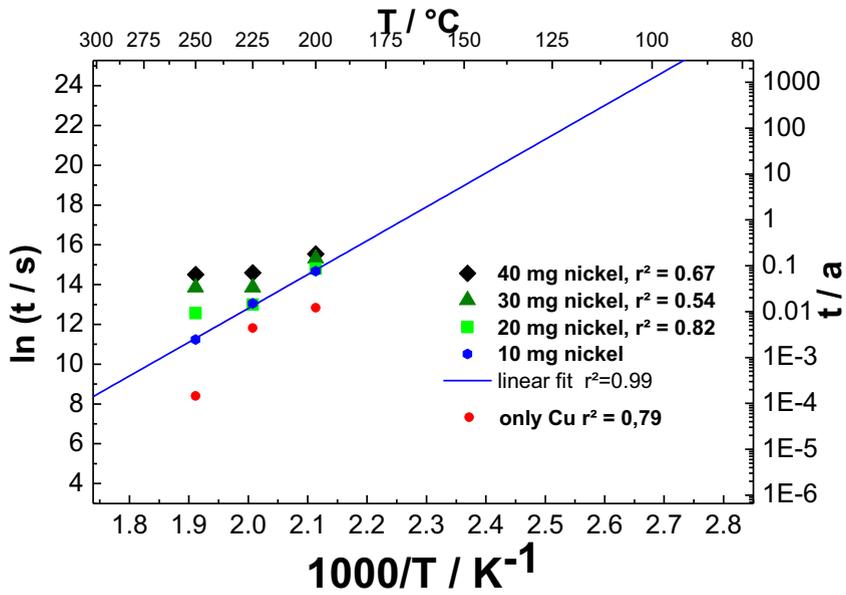
Fig. 4. Arrhenius plot of the degradation data, temperature time pairs leading to a loss in pFF of 5% rel

3.2. Damp heat test – long term stability on module level

To test the long term stability of the cells on module level one cell modules (200 x 200 mm) were laminated using standard EVA, a white back sheet and a standard solar glass. These modules were put in a climate chamber executing a damp heat test at 85°C and 85% air moisture. Electroluminescence pictures were taken before, after 500 h and after 750 h. The electroluminescence pictures in figure 5 do not show a visible degradation due to copper migration into the junction of the cells after 750h. It is worthy to note that this is again also true for the module where no nickel barrier layer was plated between printed seed layer and copper conducting layer for cell metallization.
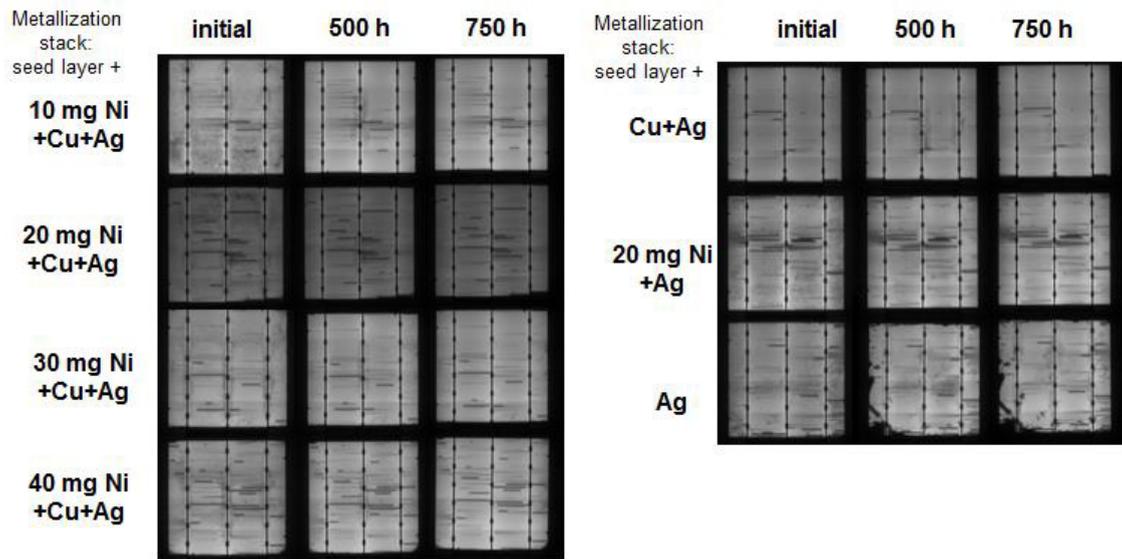
Fig. 5. Electroluminescence images of the one cell modules before, after 500h and 750h damp heat test (85°C, 85% r.h.)

3.3. SEM analysis of the nickel diffusion barrier

For the long term stability of the cells a dense diffusion barrier is crucial to avoid copper diffusion into the junction, which means that the Ni plating homogeneity over the whole cell is a key aspect. Figure 6 shows top view SEM images of the nickel diffusion barrier for the different plated Ni masses on one exemplary contact finger and on a busbar for middle positions of the cell. A closed nickel layer can be observed on the fingers for every plated Ni mass, whereas on the busbars the Ni layer shows gaps. For 10 and 20 mg a lot of small gaps and some bigger areas without Ni (marked with dashed circles) were observed. For 30 and 40 mg the open seed layer area on the busbars is much smaller but some spots that might still be offering possible gate ways for copper diffusion were found (marked with dashed arrows). The change in the density of the nickel diffusion barrier explains the different degradation behavior of the cells (section 3.1). It shows that the plated nickel is not homogeneously distributed on the wafer. There is less nickel plating at the busbars probably due to smaller current density during the plating process. This can possibly be improved by optimization of the anode position and form or electrochemical shielding.
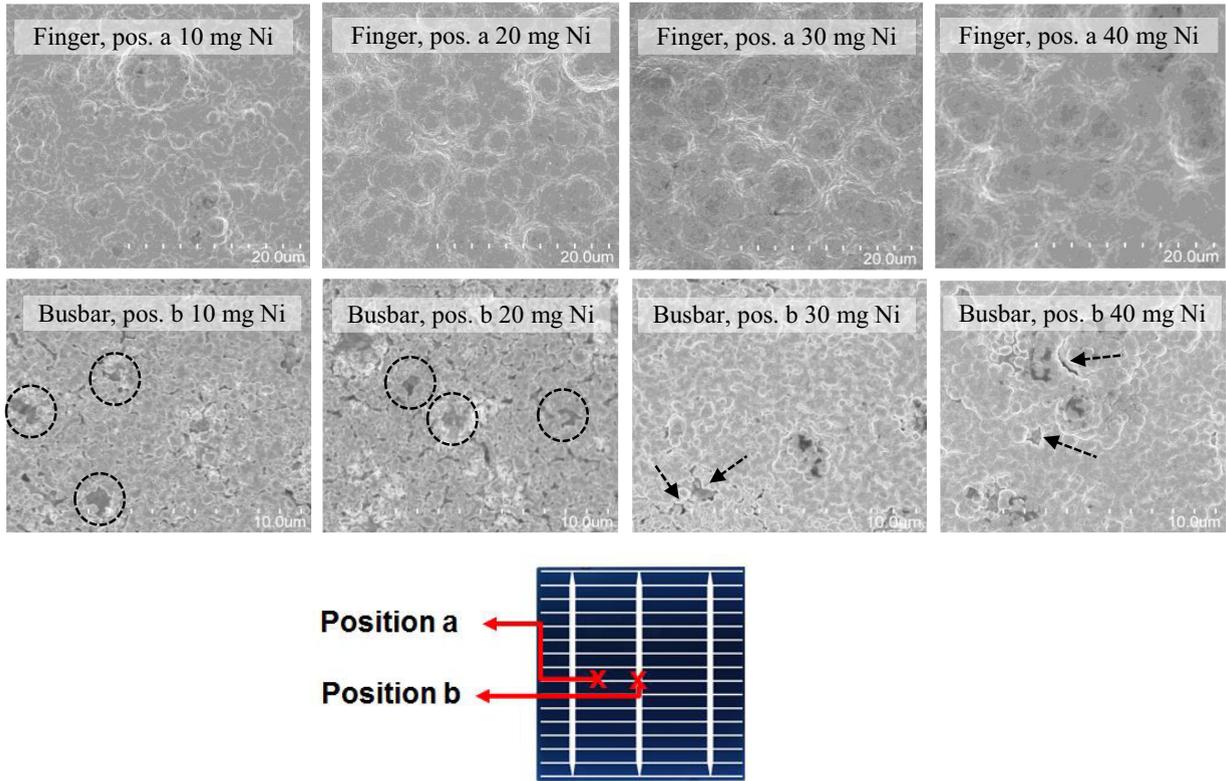
Fig. 6. SEM top view images of the plated nickel diffusion barrier for every plated nickel mass on the fingers (upper line) and on the busbars (lower line) and schematic drawing of the measurement position on the wafer

4. Conclusion

Solar Cells with copper front-side metallization based on a screen printed fine line silver seed-layer with subsequent Ni, Cu and Ag plating were produced using only inline capable techniques. A total silver consumption of < 16 mg for the front side metallization, contact adhesion forces of 1.5 N/mm and efficiencies of 18.4 % on mono crystalline standard BSF cells were achieved. The long term stability analysis on cell level show, that the plated Ni mass, varied between 10 and 40 mg/cell, influences the degradation behavior due to copper diffusion into the junction in the expected fashion. For 40 mg Ni/cell the degradation of the cells at temperatures between 200°C and 250°C, is a lot slower than for 10 mg Ni/cell. Electroluminescence images after 750h damp heat test of one cell modules do not show visible degradation effects. This means that the accelerated degradation on hotplates shows the degradation due to copper diffusion more strongly. It is worthy to note that even the reference module without any diffusion barrier seems so far unaffected. All modules are expected to pass 1x IEC criteria. However, it is uncertain whether a correlation between module degradation and hotplate degradation will be possible, as module materials might fail before reduction of cell performance due to copper diffusion. So far, it remains an open question whether IEC testing or hotplate degradation or another test is best suited to test modules for effects induced by copper migration during their expected lifetime under environmental exposure.

To find the cause of the difference in degradation on a microstructure scale, a SEM analysis of the plated Ni diffusion barrier was made. It shows, that the Ni layer on the fingers is closed, whereas on the busbars an incomplete layer was found independent of the plated Ni mass (between 10 and 40 mg/cell). This reveals that besides the total plated nickel mass/cell the plating homogeneity of the diffusion barrier over the whole cell area is a key issue to avoid copper diffusion.

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