RELIABLE CONTACT FORMATION FOR INDUSTRIAL SOLAR CELLS BY LASER ABLATION AND NI/CU PLATING

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ABSTRACT: Replacing Ag paste contacts in silicon solar cells by plated Ni/Cu contacts seems a logical next step in the evolution of industrial Si solar cell manufacturing. Ag paste contacts cause a significant share of the solar cell cost today and limit the efficiency of advanced Si solar cells. However, replacing a proven technology by another requires reliability of this technology. Cost and efficiency advantages alone are a high motivation for adopting a new metallization technology in mass production. Reliability of the contacts is a must.
In this contribution we show that laser ablation followed by light induced plating of Ni and Cu and plating of a thin capping layer results in good and reliable contacts on industrial solar cell precursors. After plating of the complete metal stack a thermal annealing step is used to increase mechanical adhesion and to reduce resistive losses of the plated contacts (contact resistance and grid resistance). Excellent solar cell efficiencies can be combined with reliable contacts. Adhesion data and data after 60 cell module testing (as part of IEC61215) are reported next to the most influencing factors.
Keywords: see enclosed list of keywords

1 INTRODUCTION

Cu plated Si solar cells have been used since decades and are still used in industrial solar cell production [1-7]. BP solar modules have been in the field for more than the warranty time of PV modules without issues related to Cu contacts [2]. Nevertheless, it is required to have a close look when moving in mass production to a new metal contact formation process and alternative materials.

The processing sequence that we suggest to apply when forming Cu based plated contacts is probably the simplest and most cost-effective sequence that has been proposed for industrial production so far. This sequence is depicted in Figure 1. The only further simplification - to leave the annealing step away - is not deemed to lead to reliable contacts with low contact resistance and good mechanical adhesion.

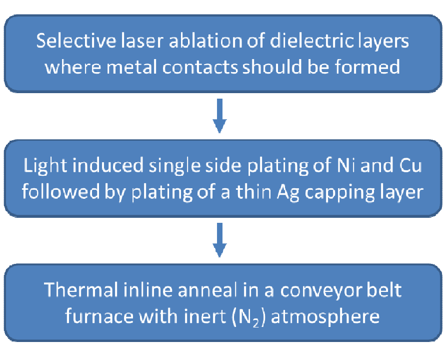


Figure 1: Applied simple process flow to form plated contacts with Ni as barrier and interface layer and Cu as main conducting material.

Both, impact of laser ablation and plating will be discussed. Results from solar cell and module fabrication will be reported. Modules underwent selected test criteria of IEC61215 (LID, thermal cycling and damp heat) to assess if there would be metal related reliability issues. The results of these experiments will be discussed.

Immersing and plating only one side of the solar cell is beneficial as electrolyte wetting of typical solar cell rear contacts may lead to degradation of solar cells and modules. Furthermore, it might lead to contamination of the electrolyte from dissolving paste contacts.

It will be shown that mechanical adhesion of the plated front contacts is comparable to screen printed solar cells applying Ag pastes. In the past there have been reports on poor mechanical contact adhesion for plated contact formation that kept those solar cells from being integrated into modules by conventional stringing methods such as soldering.

In our development and assessment no road block could be identified that would prevent introduction of the suggested metal contact formation technology into mass production.

2 RELIABLE CONTACT FORMATION

2.1 Influence of laser ablation on plated contact formation.

Early experiments have identified that the formation of Ni/Ag contacts (see paper 2013) lead to different requirements with respect to laser ablation processes. While it was possible to form well adherent metal contacts by light induced plating of Ni and Ag layers to selectively laser ablated areas using UV-ns laser pulses when annealing the plated metal stack after plating at moderate temperatures the laser ablation process had to be modified for a plating process using Cu as main conducting material. The result seems surprising on a first view because the interface layer to Si after plating is in both cases Ni.

It is believed that the interaction of Ni with Si is influenced by the surface morphology after laser processing, by the permeability of the plated stack to the atmosphere and temperature during the plating step as well as the interaction of individual metal layers during this annealing step.

The laser ablation step shows similarities and differences when comparing laser ablated regions after ns and ps laser ablation of PECVD SiNx:H layers on alkaline textured Cz-Si solar cell front sides with $POCl_3$ diffused emitters. The ns laser ablated regions shown in Figure 2 c) and d) differ from the ps laser ablated regions in Figure 2 a) and b) but are similar in the sense that in both cases melting of Si underneath the SiN_x:H layers is required to detach and ablate those SiN_x:H layers. Even for short wavelengths it is impossible to absorb most of the laser power within the 70-80 nm thin SiN_x:H layers. These are /(fortunately for the solar cell) not absorbing enough and would only evaporate at a sublimation temperature of 1900° C. Therefore each laser ablation process will first have to melt Si underneath the SiN_x:H coating before this layer can be detached and ablated. As a result of the textured surface and the monochromatic laser light interference effects happen and lead locally to higher temperatures. Thus areas where SiN_x:H is ablated are neighbouring to areas where SiN_x:H is still locally attached to Si surfaces that had been partially molten during the laser pulse.

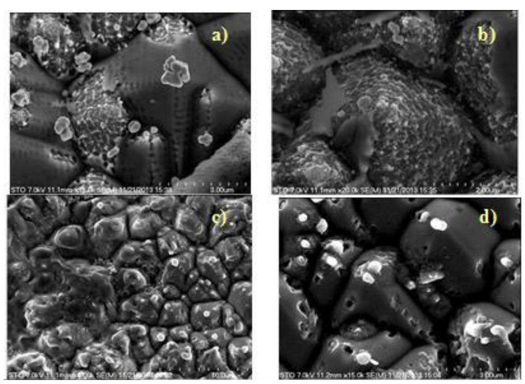


Figure 2: SEM top view on laser ablated SiN_x:H coated areas on alkaline textured surfaces. Top: a) and b) show for ps laser ablation relatively rough surfaces where SiN_x:H has been completely ablated while in neighbouring areas SiN_x:H layers seem to be only partially detached and show in particular on pyramid ridges interference patterns from local melting underneath these layers. Bottom: REM pictures for ns laser ablation. c) shows that in the laser spot (left side of the picture) pyramids have been molten down and the surface is now much smoother. On the right there are individual ball-shaped Si areas on top of the pyramid tips and ridges. The adjacent damage zone d) shows that interference effects lead also here to local melting of Si underneath the SiN_x:H layer. Some ball shaped Si structures are visible on top of pyramid tips and ridges.

In both cases, ns- and ps- pulse duration range, the melting and recrystallization processes are extremely fast. Within this very short duration a perfect epitaxial regrowth of c-Si is not possible and crystal defects in the zone that had been molten during laser ablation are unavoidable. However, with shorter pulse durations it is better possible to minimize the affected zone in the Si solar cell surface. This makes it also easier to limit the ablation diameter in order to result in narrow ablation lines. In parallel to the melting of surface near emitter regions under the dielectric SiNx:H coating there happens a re-distribution of dopant atoms. Typically the originally molten and then regrown Si areas have afterwards a plateau in the doping atom concentration. The steep decrease of dopant concentration in function of distance to the surface that is typical for diffused emitter regions, gets levelled to an average dopant concentration in the region that has been molten and regrown.

It should be noted that the starting dopant depth profile has influence on the ablation result in two important aspects. The absorption of laser light depends to some extent on this dopant concentration. Maybe even more important is that electrically inactive dopant atoms get now re-distributed in the molten zone. As result the net electrically active doping might increase in the laser ablated areas. It is even possible that larger areas than before laser ablation contain now electrically inactive dopant atoms that were before limited to the very surface region. In this context it is good keep the influence of the pulse duration in mind. Together with the wavelength that is defining the absorption probability for monochromatic laser light as function of the penetration depth into the Si the pulse duration together with the minimum fluence needed for ablation influence the depth of the molten zone during ablation.

Comparing the SEM pictures of Figure 2 b) for ps-ablated areas with that in the SEM pictures c) for ns-ablated areas it is visible that in the centre of the laser pulse (Gauss type intensity profiles) the ns laser ablated areas have molten down the random pyramid surface completely (left part of picture c). In picture b) it is clearly visible that the ps laser ablation affected only the top part of the pyramid texture and the Si surface is significantly roughened in the areas where SiNx:H has been detached by the ablation process. In both cases the pulse intensity has been minimised to just still ablate continuous lines on which can be plated. We expect positive influence of this roughened surface on mechanical contact adhesion on reducing the contact resistance and on the interaction of Ni and Si during the thermal annealing step in an inert atmosphere with low oxygen concentration.

For a simple Ni/Cu based plating sequence as depicted in Figure 1 we compared contact formation for UV ns- and ps- laser ablation. Most striking are the results with respect to mechanical adhesion of those contacts as shown in Figure 3. Varying plating conditions for Ni and Cu plating in a wide range it was not possible to achieve acceptable adhesion results for ns-ablated solar cells. Also variation of thermal annealing conditions within a range that is acceptable for electrical performance of the plated solar cells did not improve adhesion of the contacts for ns- ablation.

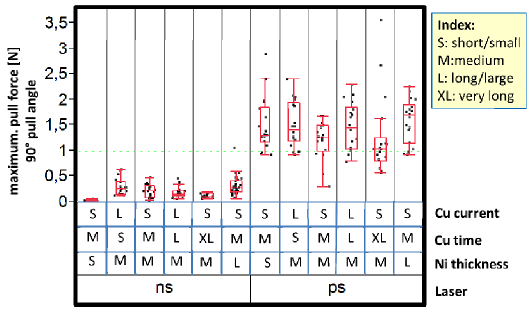


Figure 3: Comparison of ns- and ps- laser ablation for plated contact formation (LIP-Ni/Cu + immersion Ag capping) as outlined in Figure 1.

In general it can be stated, that laser ablation is an essential processing step in the processing sequence for industrial high throughput contact formation of Cu based contacts as indicated in Figure 1. Ultra-short laser pulses and short wavelength in laser ablation help to limit the laser impact to a very surface near region and to leave a roughened Si interface area for plating. Pulse shaping (homogeneous local laser intensity distribution over the ablated areas) might be a beneficial option to improve the process window for ablation. Heating of the solar cell during laser ablation to temperatures >500° C might be an option too to limit the absorption of laser light to the very surface near region of the Si wafer even when longer wavelengths of the laser light are used. The absorption of Si to visible or IR light changes drastically with temperature. For very high repetition rates an increase in local wafer temperature during ablation might be also achieved by sufficient area overlap between subsequent ultrafast pulses as the time between subsequent pulses can be reduced to the ns-range. Finally, it might be interesting to consider having the laser area in an inert atmosphere preventing oxidation of the topmost molten Si areas that are exposed during ablation to the atmosphere. Much deeper considerations and analysis with respect to laser ablation for plated contact formation is reported in a parallel paper during this conference [8].

2.2 Reliability aspects related to plating

It is the intention of this contribution to show that the chosen process for forming plated contacts with Cu as main conducting material has no negative impact on the reliability of solar cells and modules. Potential concerns are i) missing or non-reliable mechanical contact adhesion properties of the formed metal stack to Si, ii) potential diffusion of Cu into Si, iii) potentially required differences for module interconnection, iv) impact on rear contacts by the plating process.

Most efforts of RENA in developing an adequate plating process for front contact formation in industrial mass production focused on conventional interconnection methods by soldering pre-soldered Cu interconnectors to the busbars of the plated solar cells. This process requires good mechanical adhesion of the contacts that result in sufficiently high pull strength forces when testing the adhesion of the soldered interconnection ribbons to the busbars. This adhesion is essential when handling strings into solar modules. Furthermore, forces implied by different thermal expansion properties of the contacts compared to Si, the module encapsulant materials and glass should not detach the metal contacts during thermal cycles of the module in the field.

To assess mechanical adhesion RENA applies so far two test procedures. The adhesion of contact fingers is so far only checked by attaching scotch tape to the solar cell surface and pulling it off. If fingers are detaching from the Si solar cell and stick afterwards to the tape, this is a hint that contact adhesion might be not sufficient. A more quantitative second test procedure performs a typical stringing process: Conventional Cu interconnection ribbons (1,5 mm * 0,15 mm with 20 µm Sn62%Pb36%Ag2% coating) are simultaneously soldered in a semi-automatic stringer from SOMONT to six positions of each of the three busbars. We apply interconnection ribbons from different suppliers in this procedure. In a semiautomatic pull tester from XYZtec these interconnection ribbons are pulled off at 90° angle in a precise movement of ribbon (upwards) and solar cell (horizontal to maintain the 90 ° angle). For each of the 18 co-soldered areas the maximum pull force is recorded and afterwards plotted. Figure 4 shows pull force data for a number of solar cells that had been tested when fabricating modules for IEC61215 testing.

In addition to recording the pull force we evaluate the failure mode at each of the soldered areas to see whether adhesion is limited at the metal Si interface, within the metal interfaces of the metal stack, by Si chipping or by Si wafer breakage. In our testing the most dominant failure mechanism is Si wafer breakage at sufficiently high pull force values. The failure mechanism and pull force values are similar to reference solar cells with screen printed contacts that we evaluated in parallel.

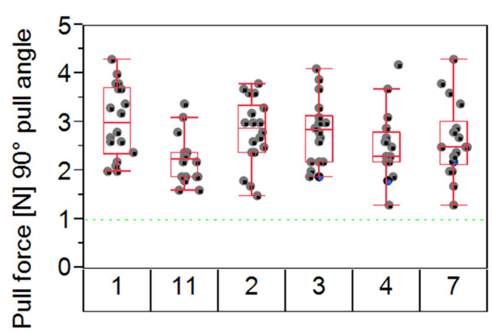


Figure 4: Test data from pull testing. Interconnection ribbons soldered to the busbars are pulled off under a 90° angle to detach from the solar cell that is kept down.

We conclude therefore that the pull forces are not limited by adhesion of the plated metal stack and that the adhesion is sufficient for stringing and module fabrication.

Therefore, we fabricated in a next step solar modules. CZ-Si precursor wafers from an industrial PV manufacturer haven been used to perform laser ablation on a laser platform from our partner Innolas Solutions in

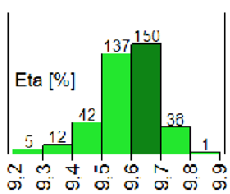
Krailing. The plating sequence applying MacDermid electrolytes and with support of MacDermid experts has been performed in the plating laboratory of RENA in Freiburg where also inline thermal annealing of the contacts in an inert atmosphere took place. The precursors had an alkaline texture, a 65 Ω/sq. emitter (as used for screen printed contacts), a PECVD SiNx:H coating on the wafer front side and a printed Al-BSF with Ag paste busbars on the rear side.

Table I: Average plating results on alkaline textured CZ-Si precursors with 65Ω/sq. emitters, SiNx:H AR coating on the front and Al BSF on the rear side.

400 cells	Jsc [mA/cm²]	Voc [mV]	FF [%]	Eta [%]	pFF [%]
Average	38,1	640,4	80,3	19,6	82,8
Std. Dev.	± 0,2	± 1,2	± 0,2	± 0,1	± 0,2

Good solar cell performance distributions have been achieved applying the inline plating process shown in Figure 1. Even though better performance would be expected when using more advanced emitters (optimised for plating instead of screen printing) or by applying a passivated rear side the average results and narrow distribution shows that the inline plating process is well under control. This is also visualised in the distribution plots for efficiency and fill factor in Figure 5.

Main intention of the module fabrication from those solar cells and the subsequent damp heat and thermal cycling procedures as part of IEC61215 was to unambiguously identify potential influence of the contact formation process on module reliability.



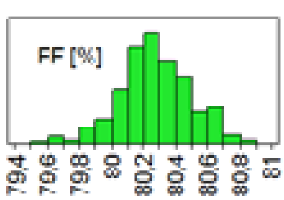


Figure 5: Efficiency and FF distributions of CZ-Si solar cells with plated (LIP-Ni/Cu + immersion Ag) contacts used for module fabrication

Therefore, it was decided to expose the solar cells first to sunlight prior to module fabrication. In that way solar cell measurement and binning was possible another time after light induced degradation. This was thought to be beneficial as no information on the LID behaviour of the delivered CZ-Si precursors was available prior to module fabrication but it is known that different parts of a CZ-Si ingot may show very different response to LID [9]. If wafers with significantly different LID behaviour would end up in the same module prior to LID this might cause significant mismatch of cells in the finished module after exposing this module to the sunlight. It was thought to be smart to exclude such LID effects having nothing to do with the metallisation process. In that way it is unambiguously possible to interpret potential degradation during thermal cycling or damp heat testing. The LID behaviour solar cell level is caused by boron-oxygen complexes and was similar on screen printed reference solar cells and plated solar cells.

Table II: Relative changes in module performance after full IEC61215 test procedure in damp heat (DH) and thermal cycling (TC)

relative change 100% IEC:	Δ I_{sc} [% rel.]	Δ V_{oc} [% rel.]	Δ FF [% rel.]	Δ Eta [% rel.]
M 1; 200 TC	+ 0.5	+ 1.2	- 0.2	**+ 1.6**
M 2; 200 TC	+ 0.5	+ 0.8	- 0.8	**+ 0.4**
M 3; 1000 h DH	+ 0.0	+ 0.7	+ 0.3	**+ 1.1**
M 4; 1000 h DH	+ 0.2	+ 0.7	+ 0.5	**+ 1.4**
200% IEC				
M 1; 400 TC	+ 0.9	+ 1.3	- 1.1	**+ 1.1**
M 2; 400 TC	+ 0.9	+ 0.8	-1.7	**+ 0.0**

Module fabrication and reliability testing of the modules has been performed by Fraunhofer ISE. The results in Table II show no significant degradation effects of the solar modules with plated contacts. Deviations from the original performance prior to damp heat testing and thermal cycling are within the measurement accuracy and should therefore not be interpreted as improvement in the module performance. This is an excellent result. Testing will be continued until failure according to the IEC61215 criteria which allow a 5% relative decrease in module efficiency compared to the original value.

If there would be Cu related degradation of the solar cells and a path for Cu to penetrate into the Si this would show up as significant degradation in all solar module parameters as Cu would easily spread in the bulk of the solar cell at the temperatures used during damp heat and thermal cycling. Recombination losses would increase and the p-n junction would degrade significantly. This is not the case. As consequence it can be concluded that Ni and Ni silicides formed during thermal annealing act as effective barrier to Cu.

The applied approach having a homogeneous emitter results in basically identical conditions for the case that plating would occur at areas that were not laser-opened. Such so called ‘ghost plating’ occurs if dielectric coatings are having pin holes and when wafer handling leaves contamination or scratches in the surfaces. Ni acts also there as diffusion barrier to Cu.

Scratching has to be prevented by all means between Ni and Cu plating. This would be the only mechanism that might result in Cu plating directly on Si and cause severe degradation. As we process Ni and Cu plating in one inline plating sequence such scratching can be excluded by adequate inline wafer transport. We never observed such a degradation in our experiments.

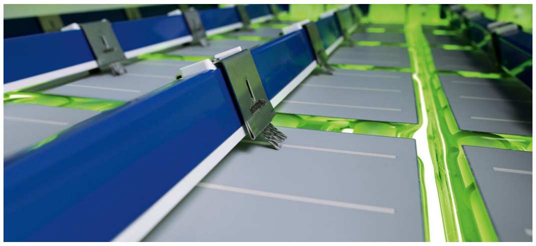


Figure 6: RENA has a patented approach to pass the plating current in a controlled way in reverse direction through the pn junction of p-type solar cells. The solar cell rear sides are kept dry while illuminating the immersed front sides on which the contacts are plated..

Another possibility for degradation of the solar cell would be from the solar cell rear side. In case of RENA plating equipment (see Figure 6) it is possible to keep the rear sides of the solar cells free from electrolytes and pre-treatment chemicals. The plating current is applied between the plating anode that is immersed in the electrolyte baths and the cathode contact that contacts the metallised p-type rear side of the solar cell. This plating current determines how many metal ions will plate from the electrolyte solution to the laser opened Si areas on the solar cell front side. The plating current integrated over the plating time is therefore proportional to the deposited mass. In order to pass a current in reverse direction through the p-n junction of the solar cell it is essential to illuminate the solar cell sufficiently strong. Illumination shifts the I-V curve of the solar cell (blocking diode behaviour in the dark) and allows therefore passing this current in reverse direction.

This approach has the advantage that the solar cell rear side is kept dry. Paste contacts and in particular overlap regions of Al and Ag pastes on the rear side of the solar cell are prone to degrade when exposed to pre-treatment and electrolyte chemicals. Attack of glass components in the paste and penetration of electrolytes in the sponge-like paste contacts may lead to degradation effects. We have seen more than 1% abs. efficiency degradation for solar cells with Ag and Al paste rear contacts that were exposed to the plating chemistry compared to reference wafers on which the wafer rear side was kept dry. Exposure to electrolytes might also cause difficulties with reliable current transfer when exposing the current guiding equipment contacts permanently to the plating solution. Those contacts may cause metal contamination in the electrolytes and changes in plating behaviour over time as they would receive a metal deposit by being exposed to the electrolytes. Corrosion or oxidation of those contacts might occur. This would alter the contact resistance at the interface to the solar cell rear contact over time. Therefore, RENA sees a high motivation to keep the wafer rear side permanently dry during plating.

RENA is open to discuss with potential customers intending to invest in laser ablation and plating technology about sampling experiments in which solar cell precusors of the respective customer are plated at RENA. As outlined in a parallel paper on this conference [10] plating results and in particular efficiency improvement depend on the processing steps prior to plating. Such pre-conditions to success of a sampling campaign are best exchanged in a technical dialogue between the respective interested partner and RENA.

3 OUTLOOK AND CONCLUSION

In the recent months RENA has developed a reliable process for advantageous industrial high throughput contact formation by laser ablation, subsequent plating of Ni, Cu and Ag and a thermal annealing step. The simple processing sequence replaces screen printers, dryers and Ag paste contacts.

This contribution addressed aspects having to do with reliability of this type of contacts. It is shown that selecting adequate laser ablation and plating process parameters good solar cell performance can be combined with well adherent plated contacts that result in reliable modules when applying conventional module fabrication processes. Damp heat and thermal cycling tests have been performed at Fraunhofer ISE and gave no hint to metallisation induced degradation from plated contacts.

The plating technology of RENA inline plating equipment is unique in the sense that the rear sides of the solar cell are kept dry during front side plating. This is deemed to be advantageous for solar cells, modules and the plating equipment in mass production.

RENA and its partners offer already now pilot equipment that should facilitate the technology transfer into mass production and the required qualification at the respective customers. From 2015 on there will be also equipment offered that can run at an inline production throughput of >3000 wafers/hour.

Cost assessment [ref] suggests a significant cost advantage for plated technology compared to screen printed Ag paste contact formation. This cost benefit comes from a significantly reduced consumable cost and the potential to fabricate solar cells with increased performance.

Assessment of plating technology on pilot line and high throughput equipment will allow interested customers to make their own reliability and cost evaluation. In a parallel contribution on this conference we show that the proposed simple processing sequence can be applied as well to mc-Si solar cells and PERC-type solar cells. With an optimised processing sequence efficiencies exceeding 21% on PERC/PERL-type CZ-Si are in reach.

4 ACKNOWLEDGEMENT

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