4th International Conference on Silicon Photovoltaics, SiliconPV 2014

21.8 % efficient n-type solar cells with industrially feasible plated metallization

Jonas Bartsch*, Mathias Kamp, Dominik Hartleb, Carolin Wittich, Andrew Mondon, Bernd Steinhauser, Frank Feldmann, Armin Richter, Jan Benick, Markus Glatthaar, Martin Hermle, Stefan W. Glunz

Fraunhofer ISE, Heidenhofstr. 2, 79110 Freiburg, Germany

Abstract

Using plated contacts, many of the challenges of metallizing high-efficiency n-type solar cells can be overcome. Very low resistivity contacts on boron emitters are hard to achieve by standard screen printing, and voltage reductions of up to 30 mV with currently available printing paste generations have been reported. In contrast, fully plated contacts have many similarities with evaporated contacts, which so far allow the highest efficiencies shown. Using plated contacts, excellent efficiencies of up to 21.74% are demonstrated in this work, contacting boron emitters with surface doping concentrations as low as 6x10^{18} cm^{-3} without significant series resistance losses. Open circuit voltages close to 680 mV show that the detrimental effect as observed for screen printed contacts can be avoided. High adhesive forces > 2 N/mm have been achieved for the contacts by the controlled formation of nickel silicide. Simultaneously, very low series resistance was realized (FF of 81.2%). Plating experiments with 156x156 mm² n-type solar cells in industrial inline tools yielded satisfactory deposition homogeneity over the cell area for contact fingers and busbars (+/- 2 μm deviation), depending on the used ablation method. Fingers were found to systematically plate twice as much as busbars.

© 2014 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

Keywords: Plating; metallization; n-type; PassDop

* Corresponding author. Tel.: +49 761 4588-5737; fax: +49 761 4588-9250.
E-mail address: jonas.bartsch@ise.fraunhofer.de
1. Introduction

Crystalline silicon solar cells made from n-type base material have demonstrated a very high efficiency potential for a multitude of different solar cell concepts [1-6]. Industrial interest in n-type cells is rising, as control of boron diffusion processes on large scale is improving [7] and implantation tools as alternative are coming up [8,9]. Deposition of aluminum oxide by fast inline ALD or CVD offers an industrially viable route for excellent boron emitter passivation. However, many of the needed processes differ significantly from fabrication techniques established for p-type solar cells. Especially the development of industrially feasible metallization processes that allow the exploitation of the full potential of n-type solar cells is a key challenge. Recent reports indicate that present printing paste generations are not fully optimized for boron emitters so far [10]. The cell V\textsubscript{OC} potential is currently reduced by the metallization [11,12], probably due to local spiking of aluminum needed in the paste to improve contact resistance [13]. Additionally, reported contact resistances are still relatively high in the range of several m\Omega cm\textsuperscript{2} [14,15]. All of these factors are problematic especially for advanced solar cell concepts that offer highest efficiencies and thus need very low contact fractions to allow for high V\textsubscript{OC} while avoiding series resistance losses.

On phosphorous emitters, using plated nickel as contacting material has been shown to allow comparable performance to evaporated Ti/Pd/Ag high efficiency lab type contacts even for low surface doping concentration [16]. Nickel is reinforced by plated copper and tin to form a silver- and lead-free, highly conductive, industrially feasible contact system.

In principle, this contact system is quite similar to the high efficiency lab approach. In both cases, the full area on the front side, where the passivation layer is removed, is available for electrical contact. For screen printed contacts most of the area is covered by a contact inhibiting glass layer, and contact formation occurs only locally (silver crystallites for phosphorous emitter, complemented with aluminum crystals in pasted for boron emitter contact). Approaching smaller contact widths or even local contact points for highest efficiency, using all unpassivated area for highly conductive contact formation becomes even more important. Additionally, for such contacts, low barrier heights (table I) are useful, which can be achieved by the formation of silicides. For typical high-efficiency emitters with a surface doping of ~10\textsuperscript{19} cm\textsuperscript{-3}, lowering the barrier height by 0.2 eV lowers the contact resistivity by about two orders of magnitude [17]. Both evaporated and plated contacts achieve contact formation at relatively low temperatures (250-500°C), which is compatible with low-temperature passivation approaches (e.g., a-SiC based PassDop [2]). In contrast to evaporation, costly masking steps can be avoided with a plated metallization scheme. After local laser removal of the anti-reflection coating in a grid pattern, plating works self-aligned on silicon. Also, material costs are reduced by replacing silver with copper.

Barrier heights of nickel and palladium and especially their silicides indicate that both metals are ideal for contacting boron emitters. This is especially emphasized by a comparison with the barrier height of titanium silicide, which is so far the material used for contact formation in high-efficiency devices. Besides barrier height, redistribution of dopants in the emitter during silicidation (“snowplowing effect”, accumulation of dopant at silicide / silicon interface) may add to achieve low contact resistance [18,19]. An increased boron concentration at the interface of silicon and nickel silicide grown into boron doped silicon has been shown [20].

<table>
<thead>
<tr>
<th>Material</th>
<th>$\phi_{B,n}$ (eV)</th>
<th>$\phi_{B,p}$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSi\textsubscript{2}</td>
<td>0.60</td>
<td>0.51</td>
<td>[21]</td>
</tr>
<tr>
<td>Ni</td>
<td>0.67</td>
<td>0.51</td>
<td>[22]</td>
</tr>
<tr>
<td>NiSi</td>
<td>0.67</td>
<td>0.39</td>
<td>[18, 23]</td>
</tr>
<tr>
<td>Pd</td>
<td>0.78</td>
<td>0.61</td>
<td>[17, 24]</td>
</tr>
<tr>
<td>Pd\textsubscript{2}Si</td>
<td>0.70</td>
<td>0.18</td>
<td>[17]</td>
</tr>
</tbody>
</table>

The history of plated contacts in solar application teaches that process complexity (problem of BP solar Saturn cell, [25]) and adhesion (problem of SunTech Pluto cell [26]) are two key aspects to bear in mind when attempting...
the development of an industrially relevant metallization. The presence of silicides can solve often-discussed adhesion challenges with plated metallization, offering more than 2 N/mm adhesive force after standard soldering at 90° peel angle [27]. A newly developed well-controlled thermal contact formation process enables shallow silicide formation which helps to avoid shunting of the p-n junction and simplifies the process sequence. An optimized ARC deposition techniques helps to avoid parasitic metal deposition to the ARC.

Process control for plating on n-type solar cells is even simpler than on p-type base silicon solar cells, where light-induced plating (LIP) is used. The fully metallized rear side can be contacted and current can be driven through the cell in forward bias (“forward bias plating”, FBP). In contrast to LIP, this approach does not require irradiation of the cell. As the solar cell rear side is on a more cathodic potential than the front side, single sided processing is required to keep the back side dry. In the present work, technological aspects of this process are discussed and a demonstration of its capabilities is given on small scale solar cells.

2. Experimental

Different solar cell samples were created in the context of this work. All solar cells feature a random pyramid front surface texture, a front boron emitter (for emitter details see results section) and a front surface passivation consisting of atomic layer deposited (ALD) Al₂O₃ and SiNx. Rear side architecture was varied.

High efficiency solar cells were produced from 4” and 5” n-type FZ silicon wafers. On 4” wafers, seven small solar cells (2x2 cm²) per wafer were defined by oxide masked boron emitter diffusion. 5” wafers were laser-cut into 125x125 mm² format, where 16 solar cells (2x2 cm²) were created by masked emitter implantation and thermal annealing. Different rear side architectures were realized, ranging from a diffused BSF to PassDop [2] passivated rear sides. Front contact definition was done by photolithographical masking and local anti-reflection coating (ARC) removal by wet chemical etching for PassDop cells, or by ns laser ablation for diffused BSF cells. For reference samples, TiPdAg seed layers were selectively evaporated into these photolithographically structured openings using a lift-off process. Rear side metallization was done by e-gun evaporation of aluminum.

An additional set of samples was created on 156x156 mm² n-type Cz wafers. These were equipped with a 70 Ω/sq diffused boron emitter and a phosphorous BSF applied in a masked diffusion. In this case, grid definition for direct front side plating was done by ns laser processing. For comparison, some cells of this group were equipped with an aerosol printed seed layer [1] and with a screen printed seed layer, to check for effects on the plating result.

Plating processes for 4” and 125x125 mm² wafers were done in manual plating tools at Fraunhofer ISE [28], utilizing cell connectors for single sided plating (figure 1a), or in cup plating tools from RENA (figure 1b). Plating processes for 156x156 mm² wafers were done using semi industrial single track plating tools for single sided plating provided by RENA (figure 1c and 1d) that is suited for LIP and FBP. For nickel plating, a standard Watt’s type electrolyte was used, while copper plating was done in standard sulfuric acid based copper electrolytes. Tin capping was done using a standard methanesulphonic acid based solution.

Contact finger and busbar geometries were evaluated with an Olympus LEXT confocal 3D laser microscope, averaging profiles on different cells over several hundred micrometers to several millimeters at a magnification of 550x.

3. Forward bias plating

Plating on solar cells differs from plating on metallic substrates due to their semiconductive properties. An external current cannot be distributed in the solar cell as it can be in metallic workpieces that are more common in plating. The presence of metallic seed layers can support plating on solar cells, although these are hard to contact especially if very narrow features typical for solar cells are addressed.

On n-type doped regions of solar cells (e.g., phosphorous doped emitters of p-type solar cells), the ability of the cell to generate an electric current under irradiation can be exploited for plating (light-induced plating, LIP [29]). Metal dissolution on the p-type doped area can either be used for metal replenishment [30], or be prevented by contacting metal layer and applying a protective cathodic potential towards an anode. As for standard BSF solar cells the p-type rear side is often fully metallized, this can be achieved simply. Inhomogeneities in metal layer
distribution have been observed for LIP due to inhomogeneous current distribution during plating, especially in the absence of a metallic seed layer that allows easy current transport [28]. LIP is widely known and has been researched intensively [28-30].

Fig. 1. (a) single sided cell connector for FBP on lab scale; (b) cup plating tool for FBP on lab scale; (c) inline plating tool for LIP and FBP; (d) process detail showing single sided FBP in inline tool.

On p-type doped regions, a similar plating technique is possible. If it is possible to contact the n-type doped area of the solar cell (e.g., the fully metallized rear side of a solar cell with a front boron emitter), an external current can be driven from n-type to p-type region easily by applying a forward bias, as this is the forward direction of the junction. We call this method of metal deposition to p-doped semiconductor areas “Forward Bias Plating” (FBP). FBP allows plating of very small metallic features on the p-typed doped areas of solar cells without contacting these. To avoid possibly undesired plating to the n-type area contact, where electrons of suitable potential are provided, it is beneficial to keep these parts of the solar cell out of the electrolyte. This is possible e.g. by single sided processing of cells with front boron emitter. This also allows controlling the speed of metal deposition directly by adjusting the current, which is proportional to metal deposition according to Faraday’s laws. On laboratory scale, such a process can be realized by sealing the respective wafer surface against electrolyte contact with a customized current connector, or by using a fountain plating tool (fig. 1a and b). On an industrial scale, a suitable solution is already commercially available as single sided inline plating tool (fig 1 c and d).
Current distribution and thus plating always depend on the presence of resistances, which in this case concerns the metallic contact on the n-type region, the junction and situation at the n-type doped surface. In the n-type contact, the current may distributed relatively homogeneous over the cell area (e.g., for the discussed cell with front boron emitter). The local properties of the junction as well as the resistive situation at the front surface (dielectric layers hindering current flow, local ablation or even metallic contacts allowing it) are likely to influence the amount of current passing the junction locally.

On 156x156 mm² n-type solar cells with front boron emitter, studies of the plating homogeneity and metal layer conductivity achieved with FBP have been made. The rear sides of the cells have been metallized with 2 μm of evaporated aluminum that enables a uniform distribution of the plating current on the cell. Stacks of nickel and copper have been plated in industrial inline tools both on aerosol printed seed layers and directly onto silicon exposed by ns laser structuring of the ARC.

It has been found that conductivity of the produced metal layers is similar to the conductivity of the respective bulk metals, which is in accordance with general experience with plating processes. Fig 2 shows an SEM image of a contact finger plated with FBP. Series resistance losses can be minimized while keeping shading low.

![Fig. 2. Morphology of FB-plated Ni-Cu contact.](image)

Regarding the homogeneity of the plated layers, all considered seeding techniques (aerosol printed seed / screen printed seed / direct plating on silicon) show reasonably well homogeneity regarding the contact fingers at different positions on the cell (fig. 3a). Given is the percentage of plated layer thickness at 16 different positions of a 156x156 mm² solar cell with respect to average plated layer thickness. For typical contact fingers of 10 μm height, a deviation of 10 % means 1 μm more or less plated layer absolute, which is perfectly acceptable. No trend of predominant deposition at certain cell positions was found. It should be noted that some sites on isolated cells showed weaker plating than others. This effect was found strongest for direct plated solar cells, where lateral conductance of the p-type area is lowest and additionally, the laser process may exhibit deviations locally. This is attributed to effects of locally increased resistance of single solar cells (e.g., a locally insufficient laser ablation). Similar spots on other cells or neighboring fingers did not follow such trends and none of the runaway values could be confirmed with significance.
An exception is the point of connection between finger and busbar. It was found that the finger thickness decreases significantly towards the busbar within the last few hundred micrometers (fig. 3 b). This point is especially critical regarding series resistance, which makes the observed behavior extremely undesirable. Also, the busbar plate significantly less than the contact fingers. Here, a dependence of the seed layer has been found. Busbars with a plated seed layer (nickel plating on silicon) plate only around 30-40% of the contact finger layer thickness (fig. 3 c), while those with an aerosol printed seed layer plate between 45-60% (fig. 3 d and fig. 4a). Part of the resistive limitations within the p-type area can apparently be overcome by the limited conductivity of the aerosol seed layer. Less plated metal on the busbar is not critical regarding series resistance as the cell connector levels this contribution. However, if copper as conducting layer is used, too little nickel plating may lead to failure of the barrier function against copper diffusion.

An explanation for the observed layer inhomogeneities is the current distribution in the front side. One effect favoring deposition to the contact fingers is the large surrounding area that does not allow metal reduction (ARC regions, infinite resistance). Current that passes the junction in these areas reaches the contact openings through the relatively well conducting emitter. Fig. 4 b shows a model of such a contact area and some geometrical assumptions made. A similar effect has been observed for LIP, where the current is generated over the complete cell area, but not underneath the busbars. For FBP, current can also be transferred underneath the busbars, but as these account only for ~3% of the cell area, the difference is negligible.

It can be seen that this effect alone should result in an approximately 5-fold higher deposition to the contact fingers compared to the busbar, as the ratio of passivated area surrounding the busbars and the fingers is about 1:5 (fig. 4 c, red arrows representing portions of current). This value drops if just the area close to the busbar is
considered, which explains the observed reduced deposition onto contact fingers there. The busbar, on the other hand, allows metal deposition at the full area and thus exhibits lower resistance to current transfer from the junction. As the ratio of plated layers is larger than 1:5, both effects seem to influence deposition. Of course, the growing conductance of the fingers is another factor to be considered.

A third effect are resistances at the front surface, which allows some lateral leveling effects for current density and lead to the observed differences in plated thickness between direct plating and aerosol seed layer.

Solutions to the observed inhomogeneity issues are already known from LIP. Ramped currents can lead to the creation of a more conducting grid that will distribute currents to all parts of the cell area, leading to a more homogeneous plating result. Also, narrower busbars or structured busbars will lower the inhomogeneities as the ratio of accessible current to plating area will be increased in accordance with the above presented current distribution model. As another alternative, shielding can be used within the plating tools to lower field strength in cell areas that are otherwise overplated. The current distribution for LIP and FBP seems to be relatively similar.

The plating rates that have been obtained on these solar cells (~15-20 mg/min) with the industrial inline process show that an industrial throughput of 2400 cells per hour can be well achieved with a plating tool of reasonable length (~7-8 m of plating section for typically needed ~100 mg of metal). Faradaic behavior (limited to electrolyte efficiency) was found over a wide range of plating conditions, facilitating process control.

4. Results on high-efficiency n-type solar cells

The investigations presented in section 3 show the applicability of FBP for industrial size solar cells. To demonstrate the capability and potential of directly plated contacts on n-type solar cells, different cell concepts were complemented with a plated front side metallization. The grid design of those 2x2 cm² solar cells does not feature any large structures, which improves plating homogeneity in accordance with the above presented theory. Table 2 lists the cell results for the different cell concepts and some aspects of boron emitter design and plating process.

![ECV profiles of the used boron emitters. Red curve: shallow 90 Ω/sq emitter; green curve: deep 135 Ω/sq emitter](image)

It can be seen that for cells with a diffused phosphorous BSF, high efficiencies were reached for both a shallow 90 Ω/sq emitter (surface doping concentration of 8x10¹⁹ cm⁻³, red curve in fig. 5) and a deep 135 Ω/sq emitter (surface doping concentration of 6x10¹⁸ cm⁻³, green curve in fig. 5). For these cells, a reference group featuring evaporated contacts was created. It is worthy to note that the best obtained open circuit voltages are very similar for plated and evaporated contact system, irrespective of the emitter type. For the lowly doped emitter, nickel and palladium (the latter deposited by exchange reaction) were tested for contacting. As no difference in fill factor was observed (meaning contact resistance did not limit cell performance), nickel alone seems to be capable of contacting any emitter while using the contact geometry applied for these samples (~20 μm contact openings). For even higher
efficiencies, using an alternative metal may be beneficial to further reduce the contact fraction. Contact resistance measurements are difficult in the orders of magnitude relevant for the presented contact systems. Using standard structures for the determination, very low or even negative values were obtained by TLM measurements and errors of the technique are believed to be too great to give reliable data.

On PassDop PERL cells, an even higher efficiency could be demonstrated. The best measured cell shows an efficiency of 21.74%, with a fill factor of 81.2% and a \( V_{OC} \) of 677 mV. Especially the \( V_{OC} \) potential is remarkable, as it is very close to the calculated maximum of \( \approx 680 \) mV for this cell structure. The value for the \( V_{OC} \) potential is calculated as there is no direct comparison with evaporated contacts for the PassDop cells. A simulated value for \( j_{0,\text{met}} \) for the used emitter profile on random pyramid texture computes to 1600 fA/cm\(^2\). As further contribution from the front side, \( j_{0,\text{pass}} \) has been calculated to be \( \approx 30 \) fA/cm\(^2\). By area weighting these parameters, \( j_{0e} \) calculates to \( \approx 67 \) fA/cm\(^2\). Taking rear recombination into account with a total \( j_{0,\text{base}} \) of 56 fA/cm\(^2\) (area weighed recombination at passivated and metallized areas), a \( V_{OC} \) potential of the structure of about 680 mV is realistic. Due to the ability of the plated metallization to achieve low contact resistance on the very small 20 \( \mu \)m wide wet-chemically etched finger openings, this \( V_{OC} \) potential has been fully exploited. At the same time, excellent adhesion and a high \( FF \) have been obtained. As the plating process itself and thermal contact formation were not optimized for these cell structures, further \( FF \) improvements are likely. It is also worth to mention that the efficiency distribution is already quite good for this first experiment over one wafer and also between different wafers.

### Table 2: Cell results on different types of lab type cells (2x2 cm\(^2\)) with direct plating of Ni and Cu

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Metal by</th>
<th>( V_{OC} ) (mV)</th>
<th>( J_{SC} ) (mA/cm(^2))</th>
<th>( FF ) (%)</th>
<th>( \eta ) (%)</th>
<th>( N_i ) (cm(^{-3}))</th>
<th>( R_{Sh} ) (( \Omega )/sq)</th>
<th>Depth [( \mu )m]</th>
<th>Ablation type</th>
<th>Similar to Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSF BSF Ni-Cu FBP</td>
<td>653</td>
<td>38.4</td>
<td>81.5</td>
<td>20.5</td>
<td>8x10(^{19})</td>
<td>90</td>
<td>0.3</td>
<td>ns laser</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>BSF Ni-Cu FBP</td>
<td>655</td>
<td>38.3</td>
<td>81.8</td>
<td>20.5</td>
<td>6x10(^{18})</td>
<td>135</td>
<td>1.5</td>
<td>ns laser</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BSF Ni-Cu FBP</td>
<td>660</td>
<td>38.5</td>
<td>80.1</td>
<td>20.4</td>
<td>6x10(^{18})</td>
<td>135</td>
<td>1.5</td>
<td>ns laser</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BSF Pd-Ni-Cu Plating</td>
<td>656</td>
<td>38.0</td>
<td>81.2</td>
<td>20.3</td>
<td>6x10(^{18})</td>
<td>135</td>
<td>1.5</td>
<td>ns laser</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BSF TiPdAg</td>
<td>656</td>
<td>38.7</td>
<td>81.8</td>
<td>20.8</td>
<td>8x10(^{19})</td>
<td>90</td>
<td>0.3</td>
<td>etched</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>BSF TiPdAg</td>
<td>662</td>
<td>38.7</td>
<td>81.6</td>
<td>20.9</td>
<td>6x10(^{18})</td>
<td>135</td>
<td>1.5</td>
<td>etched</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PassDop PERL Ni-Cu FBP ( \oplus ) 18 cells</td>
<td>675</td>
<td>39.7</td>
<td>78.5</td>
<td>21.1</td>
<td>1x10(^{19})</td>
<td>110</td>
<td>1.5</td>
<td>etched</td>
<td>[2]</td>
<td></td>
</tr>
<tr>
<td>PassDop PERL best</td>
<td>677</td>
<td>39.6</td>
<td>81.2</td>
<td>21.74*</td>
<td>1x10(^{19})</td>
<td>110</td>
<td>1.5</td>
<td>etched</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*independently confirmed by CalLab PVCells at Fraunhofer ISE

### 5. Conclusion and outlook

A plated metallization has been shown to be a promising alternative to screen printing to contact boron emitters for high-efficiency n-type solar cells. Forward bias plating has been shown to be a technique that allows plating on boron emitters on industrially relevant scale. Challenges of reduced metal deposition to busbars and to the busbar-finger junction need to be addressed to further improve the method. Similar issues have been found for LIP and solution approaches in terms of grid optimization and process optimization will probably be transferrable. Shielding techniques and ramped currents are one possibility to achieve better homogeneity coming from the plating side, an adjusted front grid using structured busbars, alterations in the finger-busbar junction or an adjusted rear design are other possibilities to overcome this matter. However, care needs to be taken to still meet electrical and mechanical requirements to the front grid when realizing such adjustments.

Further work will comprise an optimization of the laser structuring process and FBP evaluation on the TopCon cell structure [3].
Acknowledgements

Authors would like to thank the team of Fraunhofer ISE EtaLab for support with processing and RENA for support with plating tools. Financial support by the German Federal Ministry for economic affairs and energy (Contract Numbers 0325456 and 0325586B) is gratefully acknowledged.

References