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Achievements and challenges in two-step metallization processes for crystalline silicon solar cells

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ABSTRACT

One-step screen-printing processes are still the most widely-used technique for the front-side metallization of crystalline silicon solar cells in the PV industry. This is because of the knowledge, stability and speed of the process, and despite some big disadvantages exhibited by the resulting contacts (relatively low conductivity and aspect ratio). Therefore, the metal contacts of high-efficiency laboratory cells are usually produced via advanced two-step metallization processes, which allow the application of optimized contact structures. In a first step, a narrow metal layer is applied to form the contact to the silicon wafer. Several different techniques have been developed for this first stage. In the second step, the seed layer is reinforced electrochemically with a dense layer of a metal of high conductivity, usually by light-induced plating. The transfer of such techniques into industrial scale has been pursued intensively, and may enter solar cell production lines in the near future. However, the process can still be improved based on a better process understanding, in order to benefit from the full potential of the technology.

Introduction

Industrially manufactured crystalline silicon solar cells still offer a lot of potential for economical and technical optimization. A standard solar cell which is produced on a monocrystalline wafer in a state-of-the-art production line will result in an efficiency of 17-18%, whereas laboratory cells will yield values greater than 20% on comparable material. However, the process used for the latter is usually much more complicated, expensive and in many cases not suited for the industrial scale. The transfer of laboratory cell technology into production lines with industrially viable processes is therefore desirable.

Many of the differences between such cells are due to their front-side structure. The laboratory cell collects the incident light much more effectively than the industrial cell. This is achieved by superior texture, low doping and a well passivated emitter, but even more importantly by a reduced amount of metallized area. This approach is very straightforward; the more light actually reaches the silicon surface, the better the efficiency will be, relatively independent of the substrate quality or other cell features. Typically, the very fine structures needed for these features will be produced by photolithography (Fig. 1).

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Industrial silicon solar cells are almost exclusively metallized by screen-printing and firing of metal pastes in current practice. The process is robust, well known and requires only two overall steps. The share of metallized area on these cells will typically be 7-10% of the total cell area (about 3-4% for a lab cell). Due to the limitations of the technique, a further noteworthy reduction of this value will be very difficult to achieve. As the used pastes contain organic compounds and a glass frit system to enable the contact formation of the silicon substrate during the firing step, the metal lines are porous and feature a relatively low conductivity. To lower the electrical losses caused by the series resistance of the metallization to an acceptable level, these contacts must consequently have a large cross-section. This demand becomes more pronounced with increasing cell areas (meaning longer distances between the busbars). As the aspect ratio of the contacts is limited
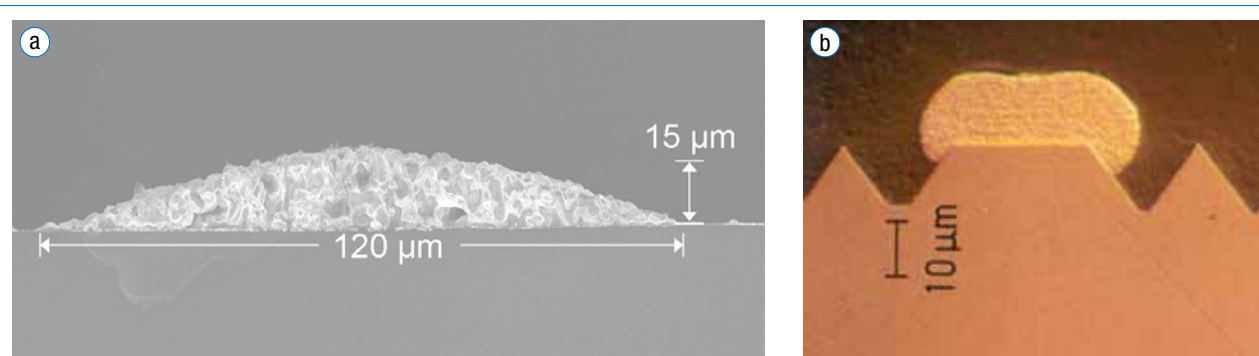

Figure 1. Cross-section of standard screen-printed solar cell contact, typical for industrial production (left) and lab-type solar cell front side, structured photolithographically (right).

due to the printing techniques and the rheological properties of the metal pastes, this is at the expense of increased shading.

Novel metallization techniques are needed, for which the well-known laboratory processes can be used as guidelines. The latter usually comprise two steps: a very fine seed layer is first evaporated onto the wafer (which is usually structured photolithographically), and then reinforced electrochemically with a dense and highly conductive metal layer in a second step, mostly by light-induced plating. The conductivity and aspect ratio of these contacts are much higher. Optically, the shading is reduced even below the geometrical shading of the contacts, as the roundly shaped and bright contact reflects light onto the cell surface directly or via the encapsulation glass [1]. Furthermore, as the seed layer can be optimized separate from the conductive layer, the contact resistance may also be reduced. The reduced area of silicon-metal interface leads to less recombination in the emitter. Also, the use of copper instead of silver as the conducting material, together with a diffusion-preventing seed layer (e.g. nickel) has the potential to drastically reduce the metallization costs [2].

A transfer of this technology into industrial scale requires seeding technologies independent of photolithography. Several suitable techniques have been developed and transferred into industrial scale in the past few years [3, 4], such as fine-line screen-printing [5], metal aerosol-printing [6], metal inkjet-printing [7], and recently thick-film stencil-printing [8], which are all based on the direct printing of metal pastes or inks onto the cell and the contact formation in a firing step. Other techniques, like electroless nickel plating [9] or high-rate inline evaporation processes of different metals [10] make contact in a thermal step at moderate temperature and need an additional step for the structuring of the cell. This can be performed by laser ablation [11] (for electroless plating) or inkjet-masking [9], for example. With the exception of screen- and stencil-printing, all mentioned seeding techniques are contactless, which simplifies wafer handling and may increase yields, especially for ever thinner wafers entering the production lines. Together with the development of devices for industrial-scale plating of solar cells [12] for the second step, the process is ready to enter industrial production lines.

Potential of plated contacts regarding conductivity

As mentioned, the conductivity of screen-printed contacts is limited because of their porosity. Electrochemically deposited layers have the potential to reach the conductivity of the bulk material that is plated. This is achieved if the deposit is dense, homogenous and shaped in such a way that all of the material contributes to the conduction. In practice, the conductivity of bulk silver is difficult to achieve.

The properties of the metal layer depend much on the chemical basis of the process. In an experiment, we compared several electrolytes for silver deposition regarding the conductivity of the plated contacts. For comparison, we used an electrolyte which has been long been used industrially and is consequently very well optimized. This cyanide-based (CN) electrolyte is also used for contacts of high-efficiency cells, where conductivity values close to bulk silver could be achieved. However, alternatives are necessary to the PV industry as the CN electrolyte is very toxic. The two other electrolytes were commercially available solutions on a different chemical basis. After measuring the contacts "as plated", a tempering step was carried out to check for any positive influence on the contact properties (e.g. by micro-sintering of grain boundaries).

As can be seen in Fig. 2, the first tested electrolyte (NCN1) gave only moderate conductivities and required a tempering step to achieve a value comparable to a very good screen-printed contact. This additional step would make the process less attractive. Using a different commercial electrolyte (NCN2) led to far better results, even before the thermal treatment. Conductivities close to the high-efficiency reference could be achieved in an industrial inline machine. The differences can be
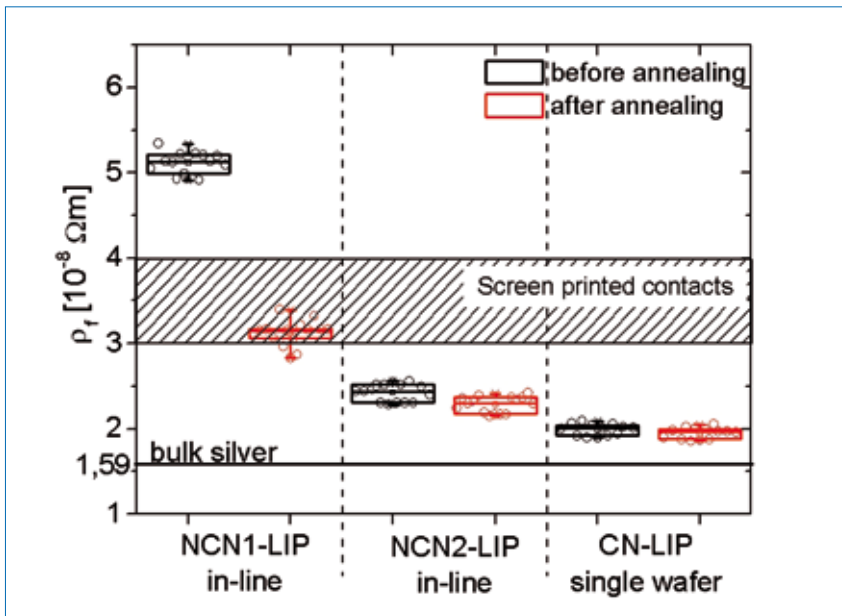
Figure 2. Conductivity of solar cell contacts plated with different electrolytes.
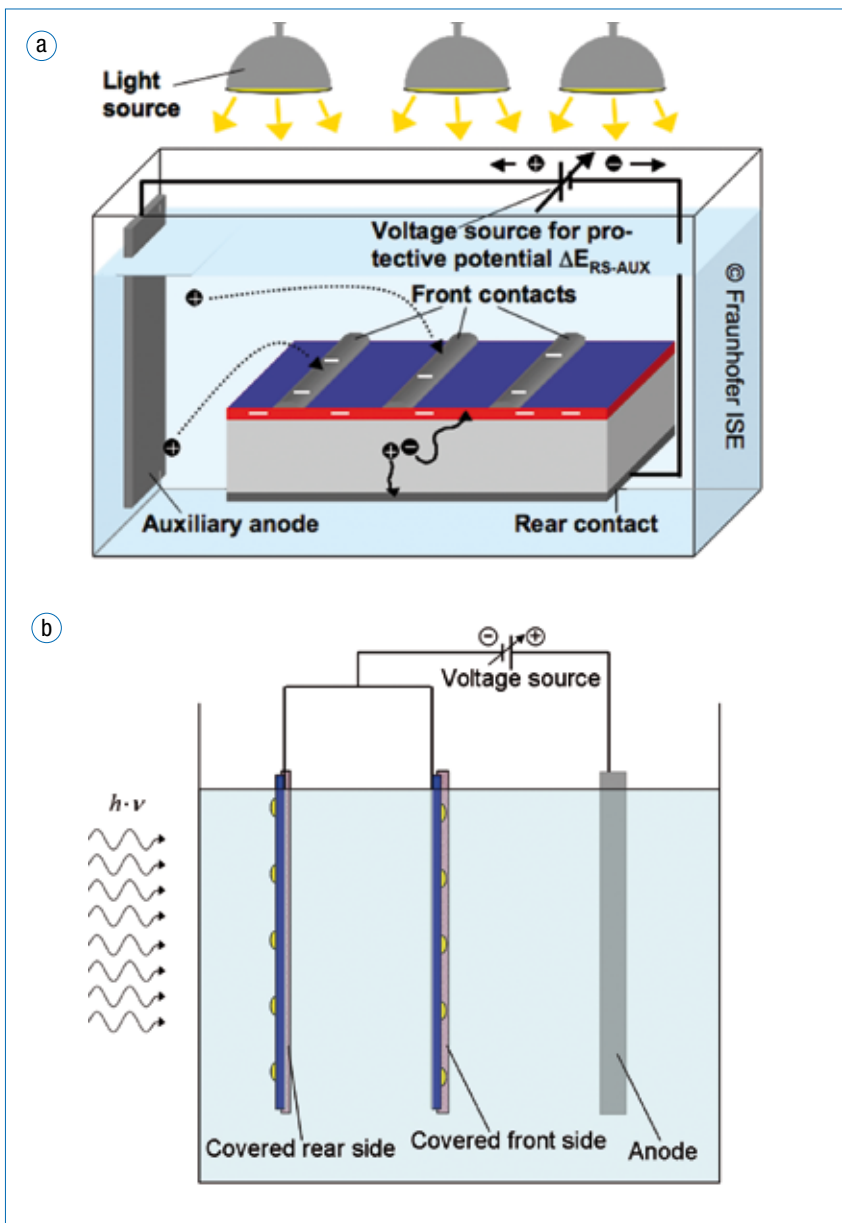

Figure 3. Usual setup for light-induced plating (top) and setup for the separated consideration of rear-side and front-side processes (bottom).

explained by the different microscopic contact structures [13].

Seeding technologies and plating behaviour

Most investigations on the plating process so far have been carried out on screen-printed or fine-line screen-printed seed layers [14, 15]. It has been shown that significant efficiency gains can be achieved compared to one-step screen printed contacts, even despite the fact that the initial contacts still feature most of the same unwanted properties. The full benefit of the two-step process will only be obtained using narrow advanced seed layers, which make the contact to the silicon, while the conduction is realized by the dense plated metal layer.

The conditions needed to achieve metal layers of high quality for plating processes depend on the properties of the used substrate, and are very different for various materials and seeding technologies. For plating, the current density (current per metal surface area) and the local field density play key roles.

The current density can be estimated with the metal area and the current. However, the current over the front side is not accessible by direct measurement. We developed an experimental setup to measure it indirectly, via weight gain [16]. This setup enables a separate consideration of the rear and the front side of the solar cell (Fig. 3, bottom). The difference in current density for such contacts has been calculated to be of a factor of approx. 1.1 for early stages of the deposition and up to 1.9 in the maximal case, compared to current densities on screen-printed seed layers [17].

Fig. 4 shows silver disc electrodes that have been plated at different current densities in the electrolyte also used for silver deposition onto solar cells. The plating conditions have been controlled galvanostatically. The effect of the increasing current density on the deposition quality is clearly visible.

The local field density is difficult to quantify, but qualitatively, the different seed layers show important differences. Thick-film seed layers like screen-printing are relatively wide and shaped like a segment of a circle, with a relatively smooth, porous surface. The texture of the silicon substrate is levelled out by the seed layer. In contrast, very thin seed layers (e.g. aerosol-printed metal lines) keep the surface features of the silicon substrate. This is expected to lead to locally increased field densities, especially at sharp edges, which will result in higher local deposition rate and possibly disordered growth.

Experimental results

To experimentally validate these expectations, we made a series of experiments on two different seed layers. Test cells (5 x 5cm²) were created on
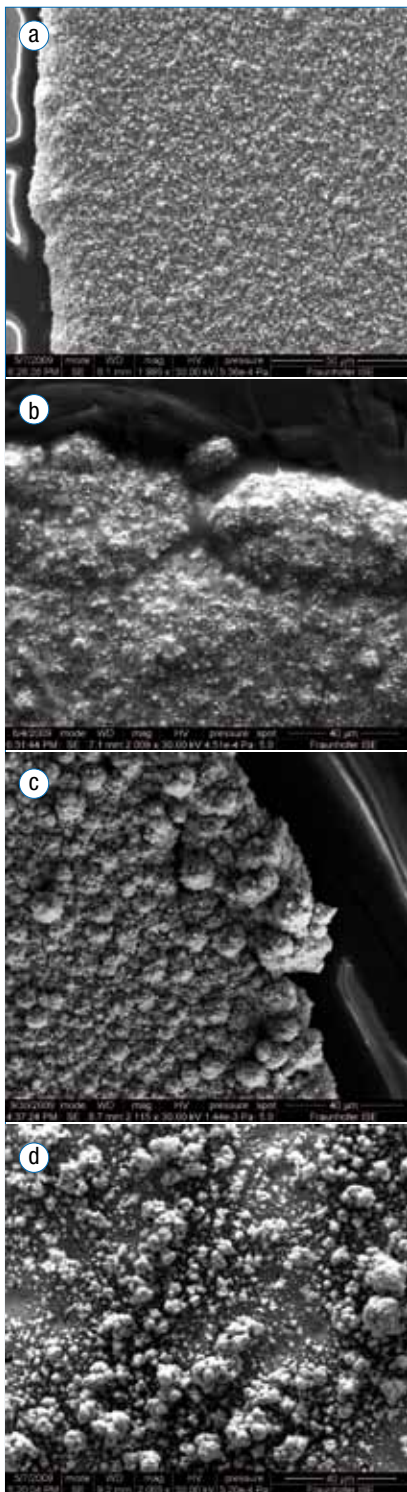
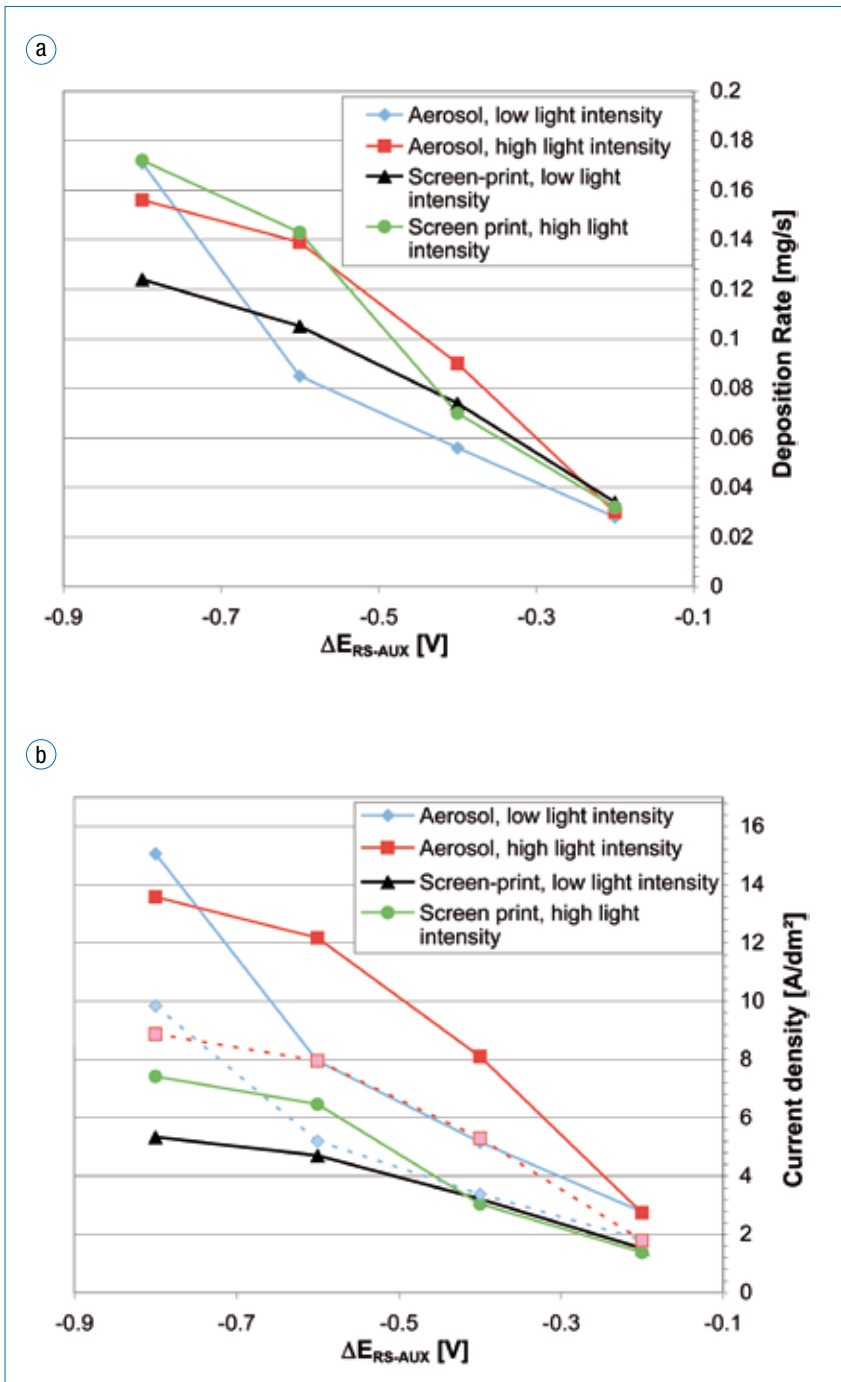Figure 4. Silver disc plated at current densites of 0.6, 2, 4 and 6A/dm² (from top to bottom).

Figure 5. Deposition rates (top) and current densities (bottom) for different plating conditions (light intensity, ΔE_{RS-AUX}).

monocrystalline precursors (55Ω/sq sheet resistance, random pyramid texture, SiN$_X$-ARC, full rear-side Al-BSF) with screen-printed and aerosol-printed seed layers (20 fingers, two busbars of 1mm at the edges). These were plated at different conditions of rear-side potential (ΔE_{RS-AUX}) and light intensity. As can be seen in Fig. 5 (left), the deposition rate increases as light intensity and absolute ΔE_{RS-AUX} are increased, independent of the seed layer. Calculating the geometrical area of

the initial contacts based on a microscopic evaluation, this leads to higher calculated current densities for the aerosol-printed seed layers (Fig. 5, right).

"However, screen-printed seed layers proved to be less sensitive to higher deposition rates, as can be seen at ΔE_{RS-AUX} = -0.6V."

The resulting contacts were comprehensively characterized with respect to their optical and electrical

properties. The contact fingers of our sample cells were separated with a dicing saw. Thus, the resistance from busbar to busbar for single fingers could be measured with the four-point probe method. The cross-sectional area of the contacts was evaluated with a confocal microscope, where profiles of the contacts were averaged over a length of 560µm at several different spots of each cell (Fig. 6). With length, resistance and cross-sectional area, we could calculate the conductivity of the contacts.

The measured values show the electrical properties of the plated metal layer improving with decreasing plating speed (Fig. 7). However, screen-printed
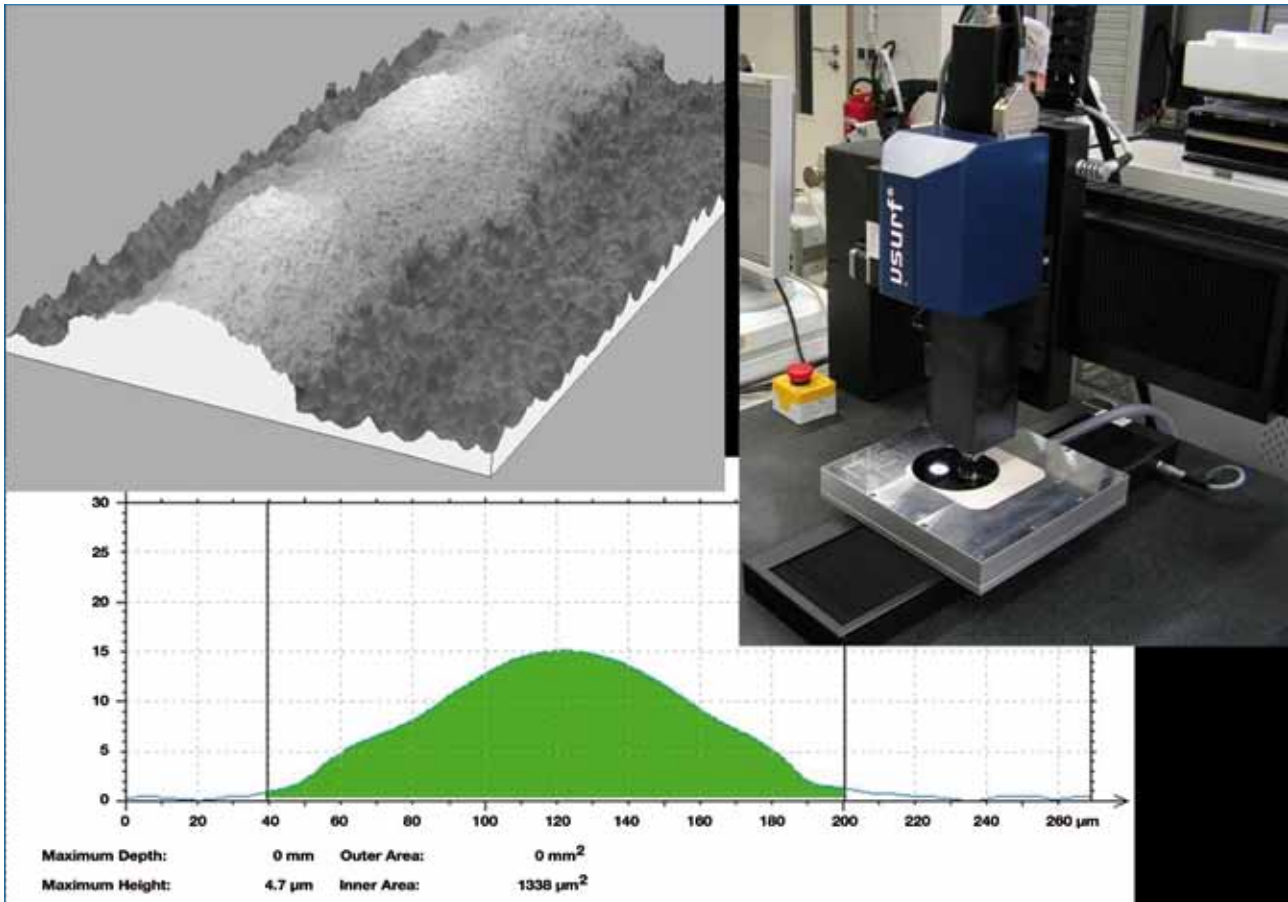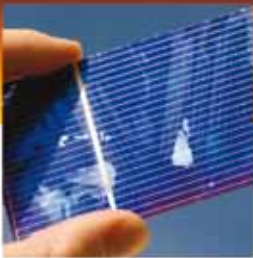
Figure 6. Contact property evaluation with the confocal microscope.

seed layers proved to be less sensitive to higher deposition rates, as can be seen at $\Delta E_{RS-AUX} = -0.6V$. The conductivity is already improved for these conditions, and not far below the best values which have been realized. This can be explained by the lower current density and the relatively smooth surface. For aerosol-printed seed layers, the conductivity is far lower at the same conditions. It starts to increase at $\Delta E_{RS-AUX} = -0.4V$ and reaches the highest values (three times higher than a standard screen printed contact) only for $\Delta E_{RS-AUX} = -0.2V$.
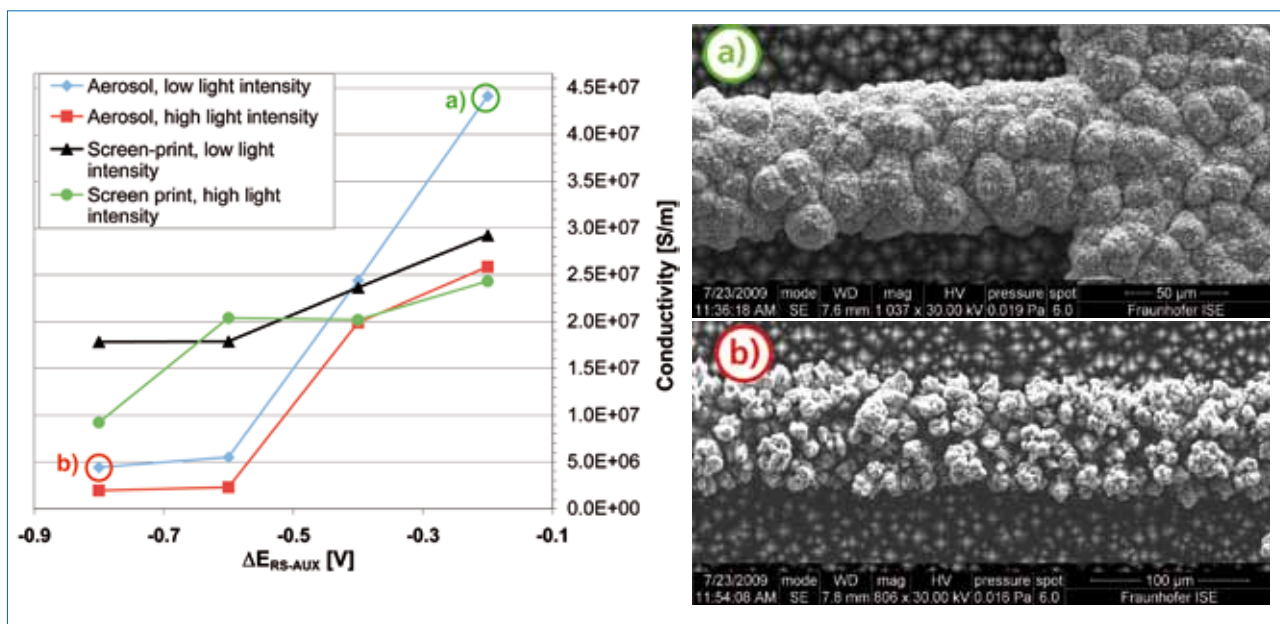

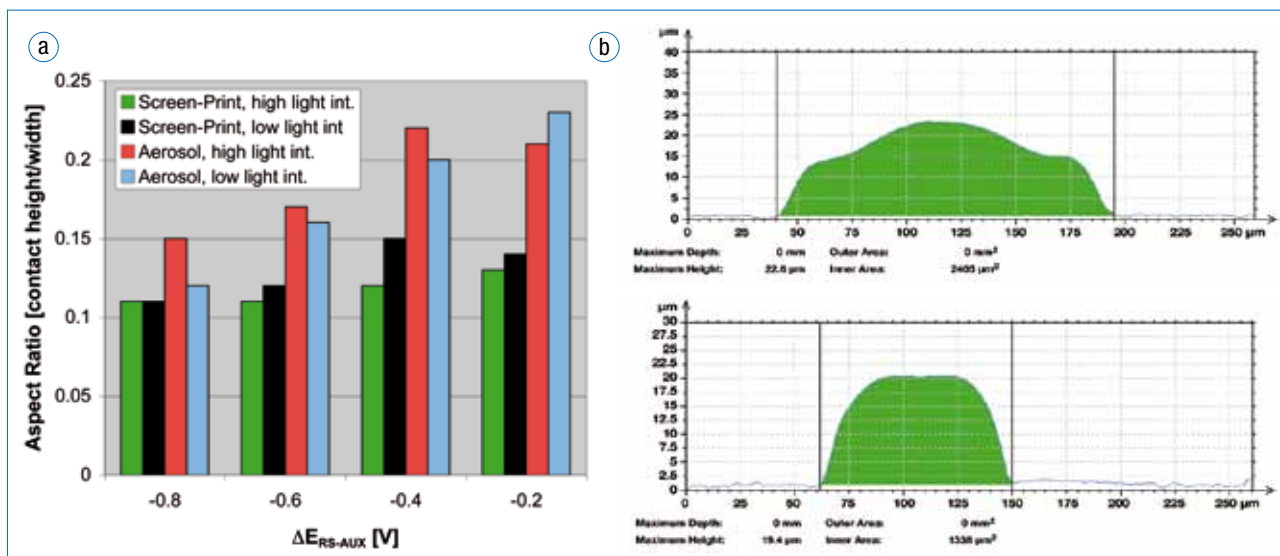**Figure 7. Electrical properties of the resulting contacts (left); SEM images at two extreme deposition rates (right).**

Figure 8. Aspect ratios of the contacts for different plating conditions (left); averaged cross-sections for a screen-printed and plated and an aerosol-printed and plated contact (right).
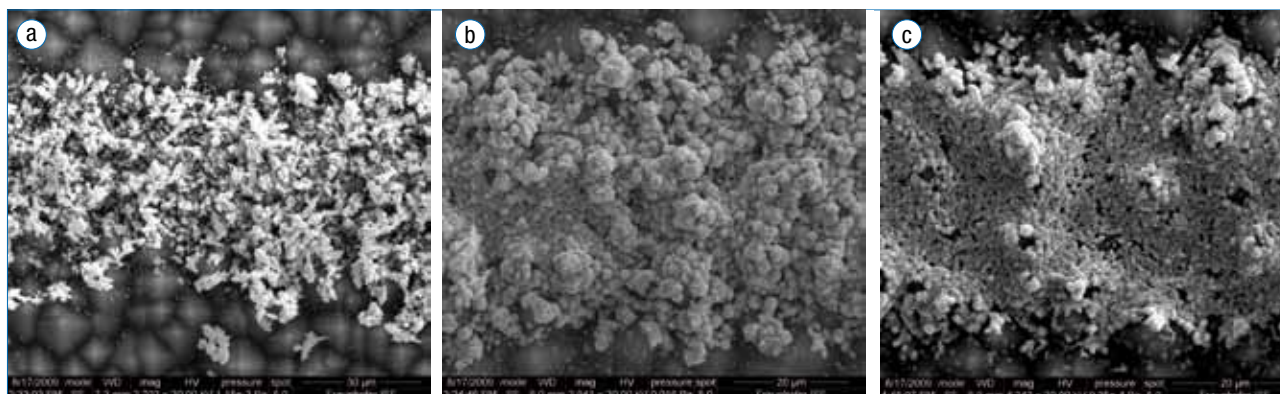

Figure 9. Metal layers after 10 seconds of depostition at -0.8V, -0,6V and -0.4V ΔE_{RS-AUX} (from left to right).

Looking at SEM images of the resulting contacts, this behaviour is understandable. The metal layer grown at higher deposition rate looks porous, silver columns have been created that are not interconnected and thus unsuitable to conduct current laterally. The layer grown at lower deposition rate appears homogenous and dense. In our evaluation of the optical parameters (confirmed by light microscope measurements) we found that these contacts are also superior in terms of aspect ratio and thus shadowing losses. The disordered growth that appears at high deposition rates seems to be less directed, whereas the good contacts grow comparably in height and less in width (Fig. 8).

As process speed is a key factor for industrial applicability, we took a look at process times that are to be expected per wafer for the best plating conditions. As can be seen in Fig. 5, the deposition rate is about 0.03mg/s for these conditions. Experimentally, we found that the optimal mass of silver per wafer (156 x 156mm^2) is around 200mg. Such a wafer is about nine times larger than our test cells, so the deposition rate should be larger in the same order of magnitude. (The optimal mass on our test structures is between 20-25mg, which was also the desired mass in our experiment.) This leads to a deposition of 0.27mg/s per wafer, which means that the process time for one wafer would be about 740 s for 200mg of silver plated. Such a process time is perfectly acceptable for industrial production. A slightly higher deposition rate will still lead to very good contacts, and an inline machine with a fitted size can grant an industrially compatible throughput. Furthermore, advanced plating techniques and an optimized mass transport to the wafer surface may support the deposition quality even at higher deposition rates.

To improve our understanding of the mechanisms that induce the described behaviour, we took a look at the first seconds of the deposition process. Test cells with aerosol printed seed layer were plated for 10 and 60 seconds for all plating conditions. The plating mechanism was evaluated with SEM images (Fig. 9). For the highest deposition rate, a localized deposition was found at the pyramid tips. The silver crystals show a typical dendrite-like appearance and multi-directional growth. This result fits well with the expected high field density at these spots. This behaviour was strong for -0.8V ΔE_{RS-AUX}. For -0.6V, the surface structure was found to be rather rough, but already the valleys show a lot more deposition. However, the pyramid tips still show the beginnings of a columnar growth with a rough surface structure that may be caused by the high current density. The metal layer deposited at -0.4V looks quite homogenous.

> **"Advanced plating techniques and an optimized mass transport to the wafer surface may support the deposition quality even at higher deposition rates."**

We expect a comparable behaviour for differently created seed layers with similar geometrical properties. The effect of high field density should not be as pronounced for multicrystalline wafers with acidic texture.

Evaluation on an industrial scale

To evaluate the capability of this two-step front-side metallization on an industrial scale, solar cells were produced in our inline plating machine in the PV-TEC pilot line (Fig. 10). In a first experiment, we evaluated the optimal mass of silver to be deposited onto an aerosol-printed seed layer. We used multicrystalline solar cells and successively increased the plated silver mass in multiple deposition steps. After each step, the
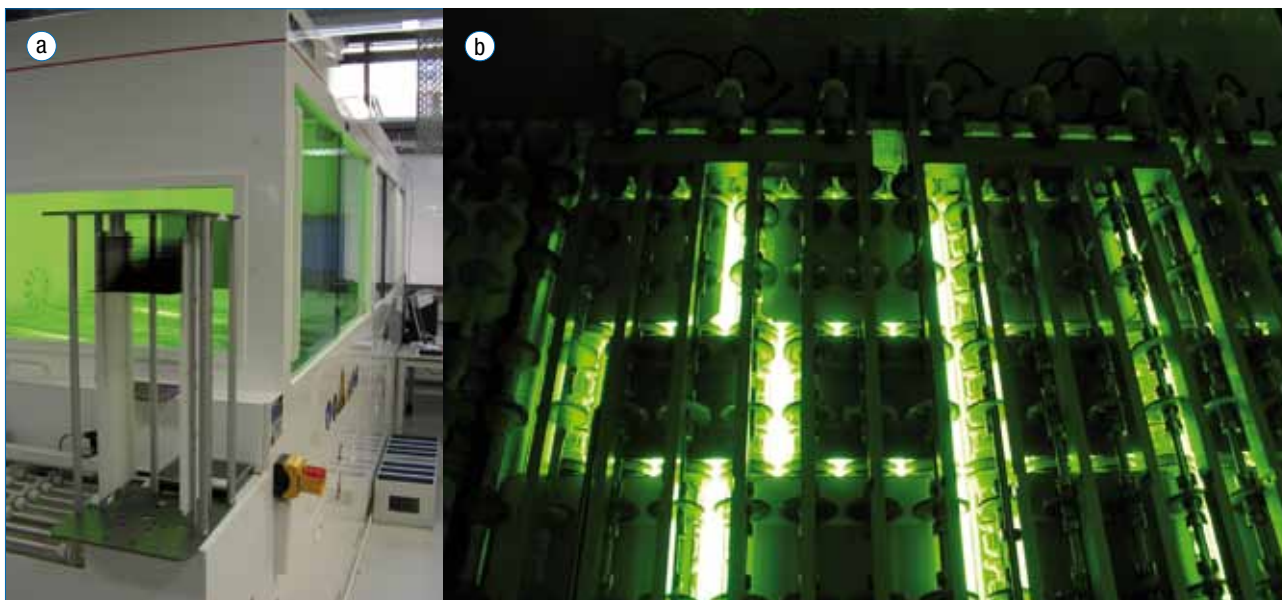
Figure 10. Inline plating machine in PV-TEC at Fraunhofer ISE (left), cells during the plating process (right).
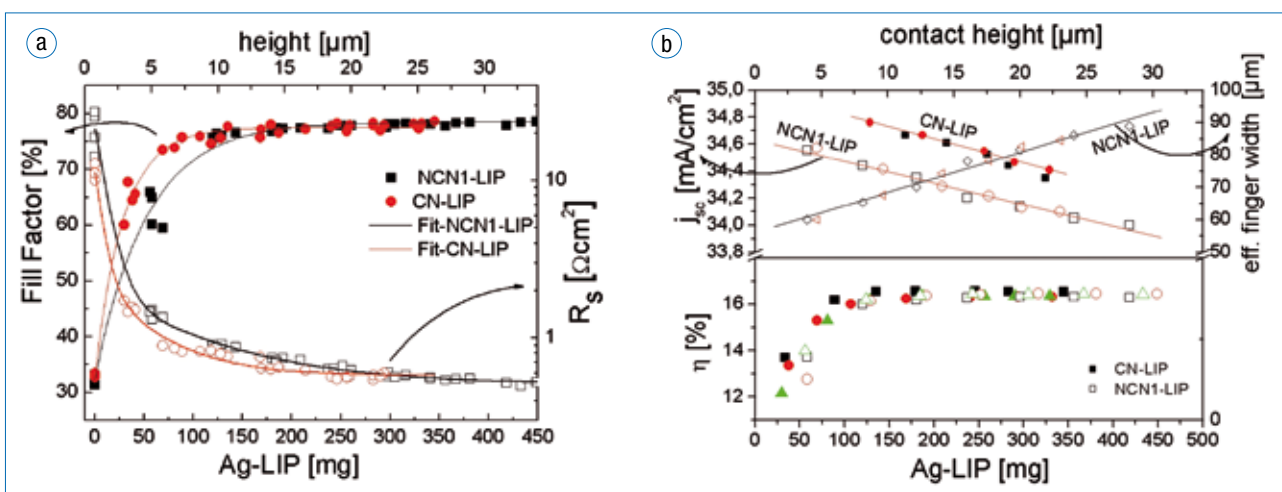

Figure 11. Fill factor, series resistance, current, effective finger width and efficiency as a function of the plated silver mass for two electrolytes (CN and NCN1).

electrical parameters were measured. To compare the inline contacts to high-efficiency contacts, we plated one group of cells in a manual setup comprising the cyanidic (CN) electrolyte as a reference.

As can be seen in Fig. 11 (left), the cells plated with the CN electrolyte need less deposition to reach very good values for series resistance and fill factor. The

quality of the deposited layer is higher; nevertheless, the group of cells processed in the inline machine eventually reaches almost the same level. The CN-reference group shows only two minor advantages: the slightly lower consumption of silver, and the narrower effective finger width (Fig. 11, right). The second effect is due to the better reflective properties of the

silver layer from a cyanidic bath, which will enable more direct and indirect reflection of light to the active cell area. Despite all of this, the value for the industrial process is still better than for a screen-printed finger. Naturally, the current shows an inversely proportional behaviour that has the highest impact on module scale.

The results obtained were used for another experiment, using the superior electrolyte in the inline machine. All cell results can be found in Table 1. We obtained excellent cell results on the same level as the CN reference process.

Outlook

The two-step metallization process with silver as the conducting material has been very well evaluated and understood. It has been integrated into the process chain of Fraunhofer ISE's industrial pilot line in the PV-TEC laboratory. Our research on silver metallization will be extended to different textures, smaller line widths and new seeding systems and plating techniques.

		VOC	JSC	FF	n
		[mV]	[mA/cm²]	[%]	[%]
NCN1-LIP	best cell	**620**	**33.6**	**80.0**	**16.7**
	Ave/15	621	33.6	78.7	16.4
CN-LIP	best cell	**622**	**34.1**	**79.4**	**16.8**
	Ave/15	621	34.3	77.9	16.5
NCN2-LIP	best cell	**621**	**34.2**	**79.4**	**16.8***
	Ave/5	621	34.5	78.7	16.8

* Independently confirmed by ISE CalLab.

Table 1. Cell results for the plating processes using different electrolytes on an industrial scale with multicrystalline solar cells. The CN-LIP group was manually plated as a reference.

However, a main focus in our research will be on new front-side metal stacks that enable the use of copper as the main conducting material. For example, a nickel layer may be grown electrochemically onto an aerosol-printed seed layer to form a diffusion barrier against copper. First solar cell samples with such stack systems prepared in our laboratories already show promising results.

Conclusion

Two-step metallization processes have been shown to have the potential to considerably improve the efficiency of crystalline silicon solar cells. Furthermore, novel metallization techniques may also lower the metallization costs, if less silver can be used or cheaper materials can be applied. The chemical basis must be chosen carefully, and the plating conditions need to be adjusted according to the requirements of different seed layers. However, the process has been shown to be suitable for application in industrial production. To maintain process speeds at higher levels at the same time, advanced plating techniques or setups can be used.

References

[1] Woehl, R. & Hoerteis, M. 2008, "Analysis of the optical properties of screen-printed and aerosol-printed and plated fingers of silicon solar cells", *Advances in Optoelectronics 2008*.

[2] Mason, N.B., Jordan, D. & Summer, J.G. 1991, "A high Efficiency Silicon Solar Cell Production Technology," *Proceedings of the 10th European Solar Energy Conference*, Lisbon, Portugal.

[3] Glunz, S. W. 2008, "Progress in advanced metallization technology at Fraunhofer ISE", *Proceedings of the 33rd IEEE Photovoltaic Specialists Conference*, San Diego, USA.

[4] Posthuma, N.E., John, J., Beaucarne, G. & Van Kerschaver, E. 2009, "Current and Future Metallization Challenges and Solutions for Crystalline Cell Manufacturing", *Photovoltaics International*, 3rd Edition, pp. 67-72.

[5] Hofmann, M., Erath, D., Bitnar, B., Gautero, L., Nekarda, J., Grohe, A., Biro, D., Rentsch, J. & Preu, R. 2008, "Industrial Type CZ Silicon Solar Cells With Screen-printed Fine Line Front Contacts and Passivated Rear Contacted by Laser Firing", *Proceedings of the 23rd European Photovoltaic Solar Energy Conference*, Valencia, Spain.

[6] Hörteis, M., Richter, P. L. & Glunz, S.W. 2008, "Improved Front Side Metallization by Aerosol Jet Printing of Hotmelt Inks", *Proceedings of the 23rd European Photovoltaic Solar Energy Conference*, Valencia, Spain.

[7] "Silberstreif aus der Düse", *Photon Magazine*, Germany.

[8] Hoornstra, J., Heurtault, B. & Carr, A. 2009, "Stencil Print Applications and Progress for Crystalline Silicon Solar Cells", *Proceedings of the 24th European Solar Energy Conference*, Hamburg, Germany.

[9] Alemán, M. & Bay, N. 2008, "Industrially Feasible Front-side Metallization Based on Ink-jet Masking and Nickel Plating", *Proceedings of the 23rd European Photovoltaic Solar Energy Conference*, Valencia, Spain.

[10] Nekarda, J. & Reinwand, D. 2009, "Industrial PVD Metallization for High Efficiency Crystalline Silicon Solar Cells", *Proceedings of the 34th IEEE Photovoltaic Specialists Conference*, Philadelphia, USA.

[11] Grohe, A. & Harmel, C. 2006, "Selective Laser Ablation of Anti-reflection Coatings for Novel Metallization Techniques", *Proceedings of the 4th World Conference on Photovoltaic Energy Conversion*, Waikoloa, Hawaii, USA.

[12] Mette, A. "New Concepts for Front Side Metallization of Industrial Silicon Solar Cells", Ph.D. thesis, Fakultät für Angewandte Wissenschaften, University of Freiburg, Germany.

[13] Hoerteis, M., Bartsch, J., Radtke, V., Filipovic, A. & Glunz, S.W. 2009, "Different Aspects of Seed Layer-printed and Light-induced Plated Front Side Contacts", *Proceedings of the 24th European Photovoltaic Solar Energy Conference*, Hamburg, Germany.

[14] Allardyce, G. & Cahalen, J. 2006, "The Commercial Application of Light Induced Electroplating for Improving The Efficiency of Crystalline Silicon Solar Cells", *Proceedings of the 22nd European Photovoltaic Solar Energy Conference*, Milan, Italy.

[15] Fioramonti, A. 2008, "Cell Efficiency Increase of 0.4% through Light-induced Plating", *Photovoltaics international*, 2nd Edition, pp. 60-63.

[16] Bartsch, J., Radtke, V., Schetter, C. & Glunz, S.W. (under review), "Electrochemical Methods to Analyse the Light-induced Plating process", *Journal of Applied Electrochemistry*.

[17] Bartsch, J., Radtke, V., Savio, C. & Glunz, S.W. 2009, "Progress in understanding the current paths and deposition mechanisms of light-induced plating and implications for the process", *Proceedings of the 24th European Photovoltaic Solar Energy Conference*, Hamburg, Germany.

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