Presented at the 33rd European PV Solar Energy Conference and Exhibition, 25-29 September 2017, Amsterdam, The Netherlands

EASY PLATING – STUDY ON CONTACT INTERFACE PROPERTIES OF PARASITIC PLATING-FREE NI/CU SOLAR CELLS

Benjamin Grübel, Andreas Büchler, Sven Kluska, Jonas Bartsch, Gisela Cimiotti, Andreas A. Brand Markus Glatthaar
Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstr. 2, 79110 Freiburg, Germany
Phone: +49 (0) 761/45 88-5019
Benjamin.gruebel@ise.fraunhofer.de

ABSTRACT: The Easy Plating process sequence is an elegant way to produce Al-BSF or PERC solar cells with laser-structured Ni/Cu-plated contacts. By eliminating the HF-treatment before metal deposition one can avoid parasitic plating at defects of the anti-reflection coating by utilizing native oxide growth to passivate these defects. Recent work demonstrated a significant improvement in terms of metal recombination, optical shading and aesthetical appearance compared to the standard plating approach. However, the Easy Plating sequence is sensitive to laser-induced and native oxide formation at the Si/Ni interface in the laser defined local contact openings.
This work investigates the influence of interface oxides between the Si/Ni layer and the beneficial impact of the thermal anneal for the contact resistance. Therefore, the contact resistance is studied by transmission line measurement (TLM) and SEM is applied for visualization of silicides. Our findings are important for advanced process optimization and an advanced understanding of the processes at the interface.
Keywords: c-Si solar cell, Metallization, Annealing

1 INTRODUCTION

Metal plating of a stack of Ni/Cu/Ag is an industrially feasible alternative to the state-of-the-art Ag screen printing for the front side metallization of silicon solar cells [1, 2]. The substitution of silver by copper leads to material cost reduction. Nickel, as primary layer of the contact, acts as seed layer and diffusion barrier. Furthermore, a low contact resistivity even to lightly doped emitters is feasible. A thin silver capping (< 1 µm) prevents the corrosion of the copper layer.

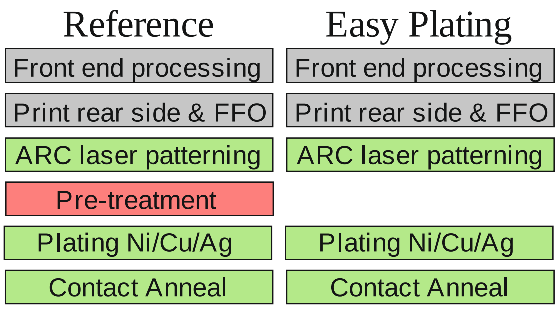

Figure 1: Comparison of the process steps of the *Reference* and *Easy Plating* process for Al-BSF solar cells

At the Fraunhofer ISE the state-of-the-art plating process sequence (*Reference*) is applied as shown in Figure 1 left column [3]: After local removal of the passivation layer (antireflective coating ARC) by laser ablation, oxide layer on bare silicon surfaces are removed by a wet-chemical pre-treatment (e.g. HF) followed by an immediate deposition/plating of metal layers. The silicide formation due to a thermal anneal, can improve the contact system and lead to a reduction of the contact resistance [2]. Unintended metal deposition in non-patterned areas of the ARC is commonly named parasitic plating (PP) or ghost plating. PP is promoted by ARC defects and harms the aesthetics and cell performances by shading and surface recombination [4]. Native oxide can electrically insulate these defects and can prevent the unintended metal deposition. Unfortunately, the HF pre-treatment removes the passivation of ARC defects and provokes an increase of parasitic plating. The *Easy Plating* process sequence, shown in the right column of Figure 1, makes the pre-treatment obsolete, in order to use the native oxides as electrical insulation on the ARC defects. Though, the oxide layers in the laser ablated area are not removed. This requires minimizing process induced oxide formation. While laser-induced oxidation can be minimized by the right choice of laser parameters [5], the delay time between laser ablation and metal deposition is crucial for the native oxide growth [6, 7]. Therefore, within the experiment we tried to reveal the dependency of the native oxide growth from the delay time between laser ablation and plating. The following thermal anneal is assumed to promote the formation of nickel-silicide to improve the contact resistance. While authors stated that the silicide formation was required to reduce the contact resistance [8], no clarified results have shown the direct correlation for contacts plated without oxide removal. In the following we will analyze the impact of a contact anneal process on the contact resistivity of contacts plated with the *Reference* and *Easy Plating* sequence. Furthermore, we will show if the silicide formation occurs at the Si/Ni interface and if it decreases the contact resistance. Throughout the paper, the process sequence without the HF-pre-treatment is called "*Easy Plating*", while "*Reference*" refers to the process sequence including a wet chemical treatment before plating.

2 EXPERIMENTAL

All the results shown in this paper are generated using industrially fabricated Cz Al-BSF solar cell precursors. The precursor front-side features a random pyramid texture passivated by a silicon nitride (SiN_x) layer optimized for silver screen printing. The experiment was carried out as shown in Figure 2.

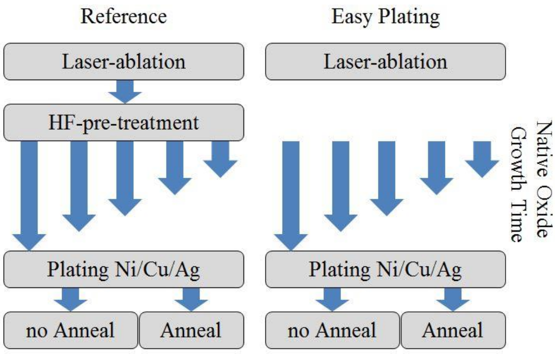

Figure 2: Process scheme of the experiment. Each process sequence features a variation of native oxide growth time before plating in which native oxides are grown at the contact interface

The laser patterning/ablation of the passivation layer was performed using a picosecond-pulsed UV laser system (Coherent Lumera Super Rapid, laser pulse duration < 15 ps, 355 nm). The laser pulse energy was set to result in contact openings with a diameter of 20 µm. After laser-ablation half of the cells follow the *Reference* sequence being transferred in the inline wet chemical pre-treatment (1%-HF, 30 s). This step is followed by a controlled oxide growth on the laser-ablated contact openings varying the delay time (from now on native oxide growth time) between HF-pre-treatment and metal deposition in the range of 20 s – 1440 min. The native oxide growth time variation of cells for the *Easy Plating* sequence starts directly after laser-ablation. In both cases the samples are stored at room temperature under ambient atmosphere. Using light induced plating (LIP), the metal contact consisting of Ni (~1 µm), Cu (~10 µm) and Ag (~ 0.5 µm) was deposited in inline plating tools of the company Rena. To analyze the effect of the thermal treatment certain cells were annealed in an inline furnace under forming gas atmosphere (250°C, 5 min). Each process group featured TLM test structures that were manufactured identically other than the pre-treatment. The characterization of the contact resistance was conducted by using the transmission line measurement. Microstructure analyzes were performed in a Zeiss Auriga SEM.

3 RESULTS AND DISCUSSION

3.1 Oxide influence

To analyze the influence of oxide layers between silicon and nickel the native oxide growth time before metal deposition is varied. Figure 3 shows independently of the process sequence (*Reference* / *Easy Plating*) increasing contact resistivity for increasing native oxide growth time. Assuming native oxide growth rates on n^+-Si [7] the according native oxide thickness after 1440 min is estimated to be about 8 nm. The results of Fig. 3 illustrate the native oxide-induced contact resistance increase. Moreover, an increased contact resistivity between both process sequences is visible as a result of oxide layers grown while laser-ablation, as the only difference is the HF-pre-treatment.

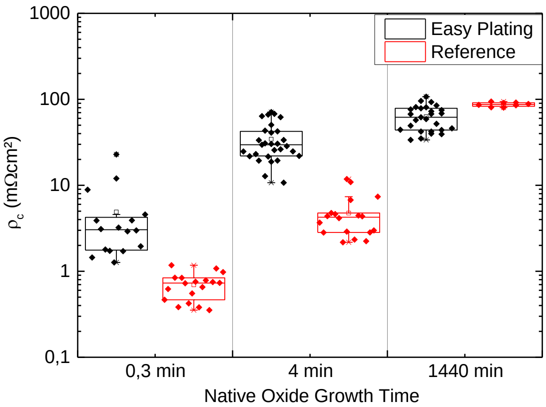

Figure 3: Results of contact resistivity for different native oxide growth times between laser-ablation respectively HF-pre-treatment and metal deposition for the *Easy Plating* (black) and *Reference* (red) process sequence.

As the backside metallization and the plated front-side metal grid are identical on all wafers the contact resistivity is the only influencing factor on the solar cell series resistance. Therefore, Figure 4 displays the interface configuration between silicon and nickel depending on the process and the native oxide growth time. As the surface of the precursor is textured, the input of the laser-pulses is not homogenous respecting to the height of the pyramid. Therefore, the growth rate of the laser-induced oxide might differ over the surface. For a minimal native oxide growth time of 0.3 min no oxide layers are located on the interface for the *Reference* process. With an increase of the native oxide growth time between HF-pre-treatment and plating native oxides occur on the interface. For the *Easy Plating* process sequence, since no HF-pre-treatment is executed, laser-induced oxide layers cover the interface. While the native oxide growth time between laser-ablation and plating increases additional native oxide layers grow on the interface. Higher thickness of oxide layers in the *Easy Plating* process compared to the *Reference* process reveals the higher contact resistivity displayed in Figure 3. After 1440 min the contact resistivity of the *Easy Plating* and the *Reference* process reaches approximately the same value. Thus, the oxide layers for both processes seem to feature equivalent electrical properties regarding the contact resistivity.

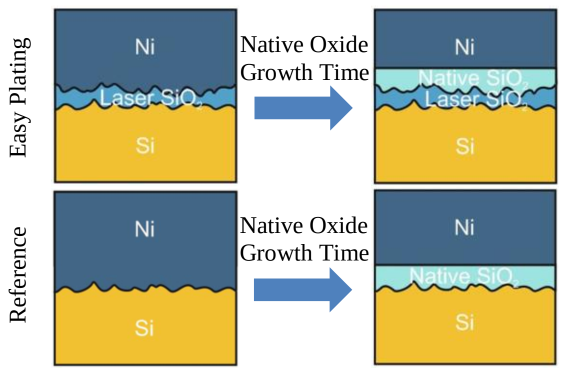

Figure 4: Schematic representation of the interface layers for the *Easy Plating* (up) and *Reference* (down) process and native oxide growth time between laser ablation respectively HF-pre-treatment (left) and plating (right).

To ensure minimized losses of the contact resistivity and a high efficiency a native oxide growth time between laser ablation, HF-pre-treatment and the metal deposition as short as possible is recommended. Furthermore, the reduction of laser-induced oxides has the potential to minimize the increased contact resistivity of the *Easy Plating* against *Reference* process and can make HF-pre-treatment of the *Reference* process obsolete.

3.2 Influence of thermal treatment

Silicides are known from literature to decrease the contact resistivity at a Si-Ni interface. Interface oxides layers can prevent the Ni diffusion into Si and hinder the formation of silicides [9].

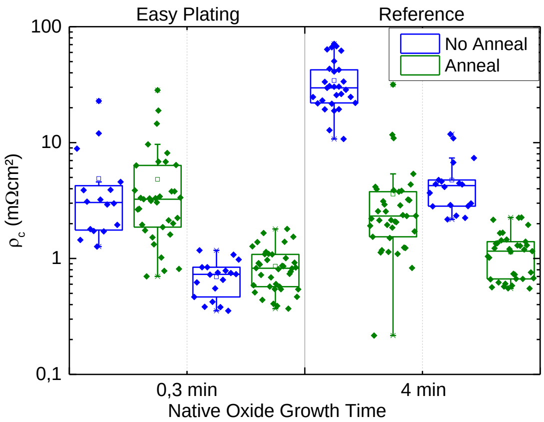

Figure 5: Results of contact resistivity at two different native oxide growth times between laser-ablation and HF-pre-treatment and laser-ablation and metal deposition for *Easy Plating* (left side) and *Reference* (right side), respectively. Process groups with and without anneal are colorized green and blue, respectively.

Figure 5 shows the results of TLM measurements for the *Easy Plating* (left side) and the *Reference* (right side) for a native oxide growth time of 0.3 min and 4 min. In addition, each process results are divided into two groups differentiating before (blue) and after (green) anneal. For the *Easy Plating* process at minimum native oxide growth time of 0.3 min, no appreciable difference of the contact resistivity before and after anneal can be noticed. Also for the *Reference* no noticeable difference can be observed for the contact resistivity before and after anneal for a native oxide growth time of 0.3 min. After a native oxide growth time of 4 min the anneal was capable of reducing the contact resistivity for the *Easy Plating* and the *Reference* group. The *Easy Plating* process sequence is improved at the same level as the contact resistivity after a native oxide growth time of 0.3 min. Equivalent results are obtained for the *Reference* process sequence. Therefore, the anneal process can compensate the negative impact induced by the native oxide layers on the contact interface. Laser-induced oxide layers on the contrary cannot be influenced by the anneal process as shown by the comparison of *Easy Plating* and *Reference* group at a native oxide growth time of 0.3 min. Thus, the structural properties of laser-induced oxides are expected to differ from native oxides.

By SEM investigations the influence of the anneal on contact resistivity can be compared to growth of nickel silicides. According to the SEM images in Fig. 6 the *Reference* process sequence with anneal and a native oxide growth time of 0.3 min reveals the existence of a structure of local areas with increased brightness on the surface assumed to be a local distribution silicides compared to the same process without anneal.

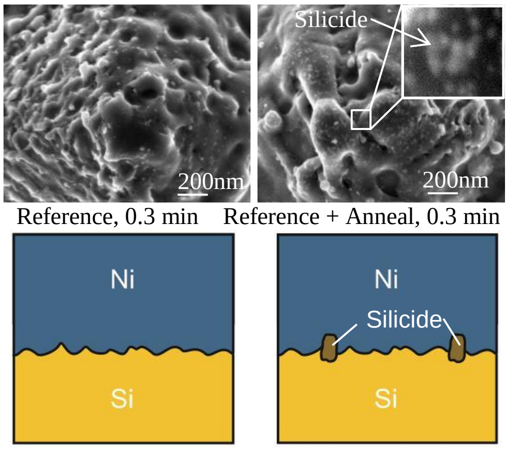

Figure 6: Top View SEM images and of laser ablated surface after metal removal for *Reference* process with a native oxide growth time of 0.3 min without (up left) and with anneal (up right) and the corresponding schematic layer structure before anneal (down left) and after anneal with local silicides (down right)

The diffuse pattern on the surface was characterized by EDX-measurements in the SEM. Figure 7 shows the results of an analysis of two points. Point 1 is located on diffuse structure on the surface while Point 2 is placed on a bare part of the surface. For both points the EDX measurement shows mainly a response at 1.74 eV which stands for silicon. Just a small peak can be noticed for Point 2 at 0.85 eV related to Nickel. At Point 1 the silicon signal reveals to be a bit lower while a Peak rises at the Nickel position. Although a silicide formation occurred for the *Reference* process sequence, no improvement of contact resistivity is observed (Fig. 7).

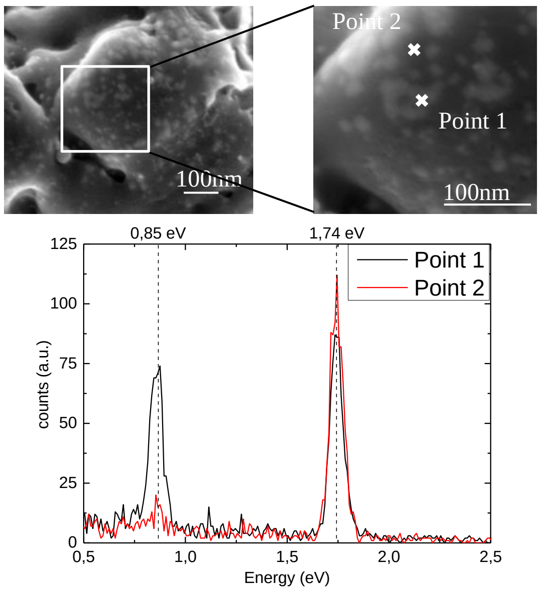

Figure 7: Top View SEM images of laser ablated surface after metal removal for *Reference* process with a native oxide growth time of 0.3 min (up). EDX measurement of two points in an area with and without silicide (down)

For a waiting time of 4 min the SEM images in Figure 8 displays the absence of silicides after the anneal for the *Easy Plating* and the *Reference* process. Therefore, laser-induced and native oxide layers prevent the formation of silicides. However the anneal process sequence manages to reduce the contact resistivity without the occurrence of silicides (Fig. 5). Presumably, as shown in the schematically drawn cross-sections of Fig. 8, local conductive channels are formed due to the anneal that allow the reduction of the contact resistance.

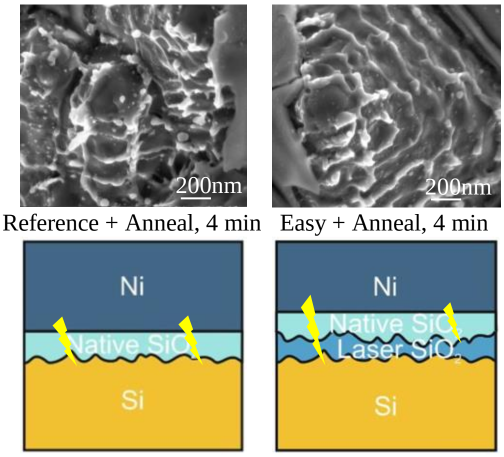

Figure 8: Top View SEM images of laser ablated surface after metal removal for *Reference* (up left) and *Easy Plating* (up right) process with a native oxide growth time of 4 min and the correspondent schematic layer structure (down) with local conductive channels

Thus, for the only process group that showed formation of nickel-silicides (HF-pre-treatment / 0.3 min native oxide growth time) there was no visible improvement of the contact resistivity by the anneal. But the process groups that showed an improvement by the anneal did not show formation of nickel silicides.

To ensure low contact resistivity and high efficiency, oxide layers have a crucial influence. The data suggest that the influence of native oxides on the contact resistivity can be compensated by an anneal for native oxide growth times of at least 4 min. Laser-induced oxides seem to lead to a firm increase of the contact resistivity. This seems in contrast to the theoretical model that predicts an improvement of the contact resistivity by the formation of silicides.

3.3 Optimization of Easy Plating

During the course of this study we applied subtle changes to the processing parameters for both processes (*Easy Plating* and *Reference*) and found that in principle even more favourable values for the contact resistivity could be achievable. As illustrated in Fig. 9 resistivity values under 1 mΩcm² could be achieved with the *Reference* process for the 0.3 min native oxide growth time case. It is remarkable that a very low resistivity value (under 1 mΩcm²) could also be recorded after *Easy Plating* with an anneal which might be indicative of a very favourable amount of laser induced oxide in this specific case. Therefore, the structure of the laser-induced oxides might affect the effect of an anneal. It is however noteworthy for this case that the contact resistivity before anneal was unusually high (above 10 mΩcm²). This observation certainly warrants future studies.

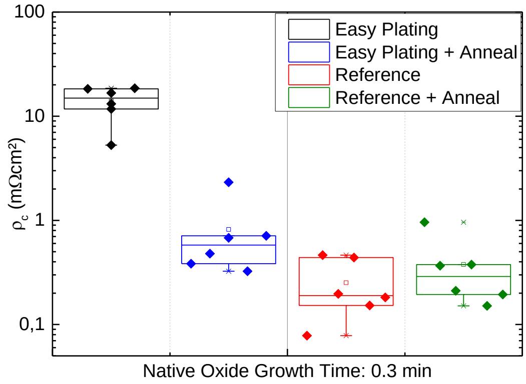

Figure 9: Contact resistivity for Easy Plating and Reference process before (black, red) and after (blue, green) anneal with a minimum native oxide growth time of 0.3 min

5 CONCLUSION

We presented the crucial impact of interfacial oxide layers on the contact resistance that affects the series resistance. As recommended the native oxide growth time between laser-ablation respectively HF-pre-treatment and metal deposition should be kept as short as possible. In the case that the minimum native oxide growth time cannot be applied, a thermal anneal can still compensate the harmful impact of native oxide layers. However, laser-induced oxides layers seem to be the limiting factor for the *Easy Plating* process as they seem to be uninfluenced by that process step. Therefore, the *Easy Plating* process sequence exhibits a slightly higher contact resistance of 3 mΩcm² as the *Reference* process sequence. However further studies seem reasonable as contact resistivities in the range of the *Reference* data were achieved for the *Easy Plating* process. In contrast to the *Reference* process involving parasitic plating, the *Easy Plating* process offers advantages such as a perfect aesthetical appearance, a reduced shaded cell surface and allows to avoid the critical wet chemical pre-treatment step.

6 REFEFERENCES

[1] J. T. Horzel *et al.*, “Industrial Si Solar Cells With Cu-Based Plated Contacts,” *IEEE J. Photovoltaics*, vol. 5, no. 6, pp. 1595–1600, http://ieeexplore.ieee.org/ielx7/5503869/7300475/07279053.pdf?tp=&arnumber=7279053&isnumber=7300475, 2015.

[2] S. Kluska *et al.*, “Electrical and Mechanical Properties of Plated Ni/Cu Contacts for Si Solar Cells,” *5th International Conference on Silicon Photovoltaics, SiliconPV 2015*, vol. 77, pp. 733–743, 2015.

[3] G. Cimiotti, J. Bartsch, A. Kraft, A. Mondon, and M. Glatthaar, “Design Rules for Solar Cells with Plated Metallization,” *Energy Procedia*, vol. 67, pp. 84–92, http://www.sciencedirect.com/science/article/pii/S1876610215005974, 2015.

[4] S. Braun, A. Zuschlag, B. Raabe, and G. Hahn, “The Origin of Background Plating,” *Energy Procedia*, vol. 8, pp. 565–570, http://ac.els-cdn.com/S1876610211016924/1-s2.0-S1876610211016924-main.pdf?_tid=0eb15574-9142-11e7-b172-00000aacb361&acdnat=1504510035_0f487e6b5dd656e4443d4f987bddcf43, 2011.

[5] T. E. Orlowski and D. A. Mantell, “Ultraviolet laser-induced oxidation of silicon: The effect of oxygen photodissociation upon oxide growth kinetics,” *Journal of Applied Physics*, vol. 64, no. 9, pp. 4410–4414, http://aip.scitation.org/doi/pdf/10.1063/1.341263, 1988.

[6] T.-a. Miura, M. Niwano, D. Shoji, and N. Miyamoto, “Kinetics of oxidation on hydrogen-terminated Si(100) and (111) surfaces stored in air,” *J. Appl. Phys.*, vol. 79, no. 8, p. 4373, 1996.

[7] M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and M. Ohwada, “Growth of native oxide on a silicon surface,” *Journal of Applied Physics*, vol. 68, no. 3, pp. 1272–1281, 1990.

[8] D. J. C. a. E. H. Rhoderick, “Silicide formation in Ni-Si Schottky barrier diodes,” *Journal of Physics D: Applied Physics*, vol. 9, no. 6, p. 965, 1976.

[9] A. Büchler *et al.*, “Interface oxides in femtosecond laser structured plated Ni-Cu-Ag contacts for silicon solar cells,” *Solar Energy Materials and Solar Cells*, vol. 166, pp. 197–203, 2017.