This is a pre-peer review version of the paper submitted to the journal Progress in Photovoltaics. It has been selected by the Executive Committee of the EU PVSEC 2019 for submission to Progress in Photovoltaics.

SELECTIVE SEED LAYER PATTERNING OF PVD-METAL STACKS BY ELECTROCHEMICAL SCREEN PRINTING FOR SOLAR CELL APPLICATIONS

K. Gensowski[1]*, M. Kamp[1], R. Efinger[1], G. Mikolasch[1], J. Eckert[1], S. Bechmann[2], R. Weber[2] and J. Bartsch[1]
[1] Fraunhofer Institute for Solar Energy Systems ISE
Heidenhofstr. 2, 79110 Freiburg, Germany
[2] Koenen GmbH, Otto-Hahn-Straße 24, 85521 Ottobrunn-Riemerling, Germany

ABSTRACT: A proof of principle for electrochemical screen printing (ESP) as a patterning process for thin metal stacks that can be employed e.g. in interdigitated back contact (IBC) or silicon heterojunction solar cells (SHJ) is demonstrated. By using the ESP process, a 125x125 mm² interdigitated back contact grid was successfully patterned into a 100 nm PVD aluminum layer. Optimizations of the ESP process were performed to improve the patterning resolution. Rectangular trenches with a mean width of 36 µm ± 5 µm could be demonstrated on a 100 nm thick aluminum layer. Up to now, ESP can be applied to physical vapor deposited (PVD) aluminum, copper, or stacks of both materials. Finally, metal stacks of aluminum and copper were structured, which allows a more homogeneous current distribution for the ESP process and additionally for the subsequent copper electroplating because of the second metal layer underneath the layer to be structured. The successful transfer from wafer substrate to polymer foils increases the application options of ESP technology enormously, where the topography of the surface to be structured, affects the printing results.
Keywords: silicon, interdigitated back-contact (IBC) solar cell, screen printing, electrochemical etching, water-based printing paste, Al/Cu-stack, plating, flexible circuit board

1. INTRODUCTION

To increase the market share of highly-efficient interdigitated back contact (IBC) solar cells, the production costs have to be reduced. A heterojunction back contact solar cell fabricated by Kaneka achieves a record efficiency of 26.7% [1]. Nevertheless, this cell type is still only produced for a niche market due to high processing costs. NREL published several possibilities to reduce the main cost factors of such cells [2]. Until now, one main cost factor is the cell metallization. The present state of the art is screen printing of metallic pastes or plating into a temporarily applied resist mask. Here, either the material costs are high, or there are several process steps that are partly complicated.

In this work an alternative metallization process route for IBC solar cells is presented, the so called electrochemical screen printing (ESP). This approach combines commercial screen printing and electrochemical etching in one single process step. The ESP is a maskless patterning technology, which allows a local removal of thin (< 200 nm) physical vapor deposited (PVD) metal layer. It can be adjusted and controlled not only by printing parameters but also by electrical settings. It is a simple, precisely controllable and fast structuring process. Non-hazardous water-based pastes are required for ESP. The printing speed is comparable to the well-known screen printing of silver pastes. A commercial screen printer with minor adaptions and an adjusted screen can be used for ESP. The process integration is therefore simple.

In the present work, the aluminum patterning is further developed to reduce the widths of removal lines to identify the current process possibilities in that respect. Also, process transfer to larger areas of up to 125x125 mm² is demonstrated. By using the ESP process, the proof-of-principle of the selective removal of a copper layer from Al/Cu stacks deposited on Si or polymer foils is presented for the first time. This opens many possibilities for follow-up processes, such as electroplating. Further on a barrier layer, like TiN, TiW, has to be added to the Al/Cu stack to prevent an inter-diffusion of copper and aluminum to guarantee cell functionality. The barrier layer will be patterned by ESP or etching [3].

2. APPROACH, THEORY AND EXPERIMENTAL DETAILS

2.1. Electrochemical Screen Printing (ESP)

Electrochemical Screen Printing (ESP) combines screen printing with electrochemical etching as known from Electrochemical Machining (ECM) technology to create a pattern in a full-faced thin PVD metal layer in one single process step. ECM technology enables high metal removal rates [4]. Thin metal layers (< 200 nm) can be structured by utilizing the ESP process. Fig. 1 depicts the principle of ESP which is described in detail in [5, 6]. The metal mesh of the screen acts as the cathode. The PVD metal layer on the substrate, e.g., solar cell or foil, is set on anodic potential and the contact is realized via the screen. The needed electrically conductive, water-based non-hazardous pastes, which are under constant development by Fraunhofer ISE, are described in [7]. The rheological properties of these water-based pastes can be adjusted by the particle content.

A high contour sharpness with a uniform width along the line length defines a successful printing result. Additionally, the patterned trenches have to be free of any metallic residuals to achieve electrical contact separation in the full-area PVD-metal layer. The printing result is affected by the following variables:

- Printing paste properties
- Applied current and current distribution
- Screen characteristics
- Layout design – percentage of area to be patterned

A significant advantage of the ESP is the precise process control by current/voltage profile and by printing speed during this process, which allows the etching depth to be precisely adjusted. This approach can be used for several applications in the photovoltaics sector, such as IBC solar cells and SHJ solar cells [8]. If the substrate is a polymer foil, applications for organic solar cells and flexible electronics are imaginable.

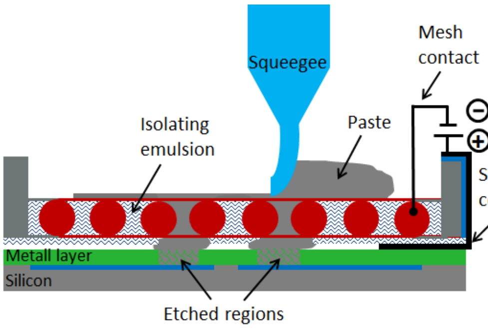


Figure 1: Schematic depiction of the Electrochemical Screen Printing process during the ongoing structuring of a thin metal layer [6].

For the ESP experiments, a commercial ASYS EKRA screen printing machine X5 STS with a Teflon table is used. A set-up for realizing the electrical part of this approach was adapted. The standard printing speed is 100 mm/s. The chosen process current and the process voltage depend on the pattern and open area fraction to be printed. For all ESP processes in this paper, the same electrically conductive, water-based printing paste is applied. The printing paste has no particles. The company KOENEN GmbH developed and manufactured the required specialized screens.

2.2. IBC solar cells as application

IBC solar cells are currently industrially manufactured predominantly by SunPower [9], while several more companies are in lab- or low-volume production [10, 11]. Copper plating into a resist mask applied onto a PVD seed layer or screen printing of silver paste are the used metallization approaches. ESP as an alternative metallization processing route for IBC is illustrated in Fig. 2. Such a process starts with a full-faced PVD metal stack of aluminum and copper on the rear side of the cell, similar to highly efficient IBC solar cell configurations shown in literature [12]. With the ESP process, the copper part of the stack can be patterned in the desired IBC design, so that the trenches are free of any residuals (Fig. 2b). The aluminum layer ensures a homogenous current distribution during the electrochemical printing process and the subsequent plating.

Immediately after the ESP process, the printing paste is removed with water. In case that the paste has dried on the sample, the paste is removed with water in an ultrasonic cleaner. This ensures the complete removal of the printing paste.

In the next processing step, the patterned layers act as a seed layer for plating to increase the layer thickness (Fig. 2c). The uncovered aluminum areas in the trenches are passivated by its native aluminum oxide and will not be plated if a suitable plating process is applied [8]. A commercial copper-sulfate based electrolyte from OMGroup is used. The plating parameters also depend on the geometry of the patterned structures and the desired copper thickness.

The remaining aluminum in the grooves has to be removed by using sodium hydroxide solution as last step to achieve the required electrical contact separation between the n-type and p-type doped areas (Fig. 2d). Depending on the cell design, copper and aluminum will inter-diffuse at temperatures reached in module operation, so it is certain that an additional diffusion barrier will be required. This layer would either be removed in the ESP process or would need to be insusceptible to plating similar to the aluminum.

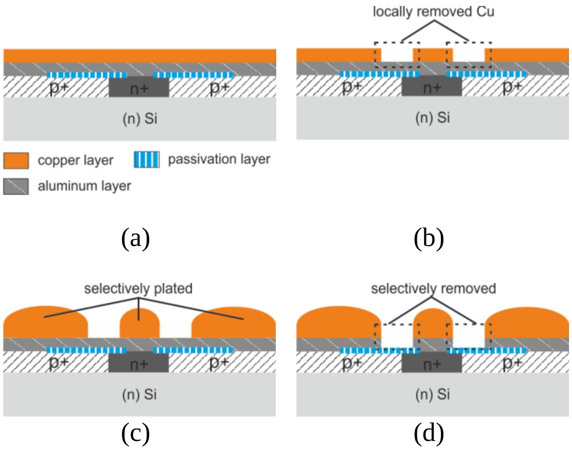


Figure 2: Schematic depiction of metallization process sequence for IBC solar cell. (a) IBC solar cell with PVD metal stack, Cu layer is on top. (b) Local patterning of metal stack by using Electrochemical Screen Printing (ESP). Cu is selectively etched compared to Al layer. (c) Plating of non-patterned Cu areas to thicken the Cu seed layer. (d) Removing Al areas in ESP-structured trenches to achieve electrical contact separation between n-type and p-type doped regions.

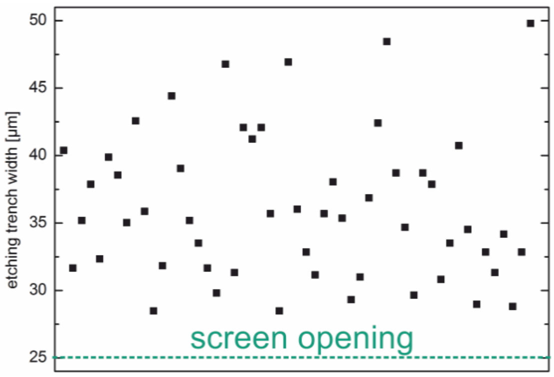
3. RESULTS AND DISCUSSION

3.1. ESP on aluminum layers on Si substrate

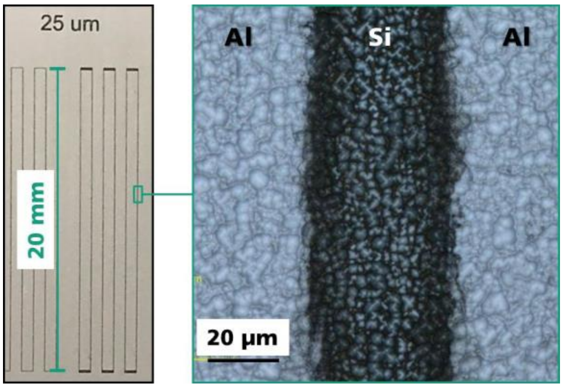
The proof-of-principle of ESP on aluminum layers and a follow-up treatment of zincate activation and plating were published by Kamp et. al. [6]. In this work, the ESP process on 100 nm PVD layers was tested regarding its limits in resolution of line width. Quite narrow lines with an average width of 36 µm ± 5 µm were obtained by using 25 µm screen openings (Fig. 3). The total length of the rectangular trench is 42 mm (Fig. 3b). Fig. 3a shows the measured widths of the trench in different positions (53 positions measured in total). The values scatter by more than 20 µm. Due to the small structure size, the current distribution should be almost homogeneous, which provides no explanation for the variance of the measured values. Our hypothesis is that the textured silicon surface can lead to an increased paste spreading and a more inhomogeneous printing result. If the paste is on the pyramid tip, the paste spreading can be enhanced compared to if the printing paste is located between two pyramids. The paste spreading might also be increased by the process current, which causes the electrowetting [13, 14]. Depending on the paste properties e.g. yield strength and viscosity, the electrowetting can be reflected in the electrical and optical aspect ratio. The aspect ratio of a printing paste without process current is higher compared to the aspect ratios of the printing paste with process current. Consequently, the contact angle between substrate and paste increases. So far, the effect of electrowetting was estimated in a few isolated experiments in our lab. These indicate that it is relevant for the patterned line width.

The result presented here gives a first impression of the resolution capabilities of ESP with the currently used materials. Advances in screen printing technology, paste properties, etc. are expected to allow even higher resolution, i.e., lower line width. However, depending on the application, requirements regarding line width are quite relaxed. For IBC solar cells, the subsequent plating step will close the trench to some extent, which advocates the use of not too narrow trenches to avoid short circuiting.

The electrical contact separation of the depicted structures in Fig. 3b was demonstrated, although few aluminum residuals are visible in the trenches. The smaller the screen openings and the corresponding mesh size, the faster single screen meshes become permanently clogged. The drying of the paste in the screen meshes is accelerated by the electrochemical counter reaction at the cathode (hydrogen formation). Several strategies to overcome this issue are already under investigation.



(a)

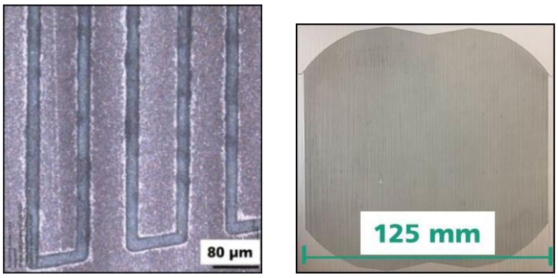


(b)

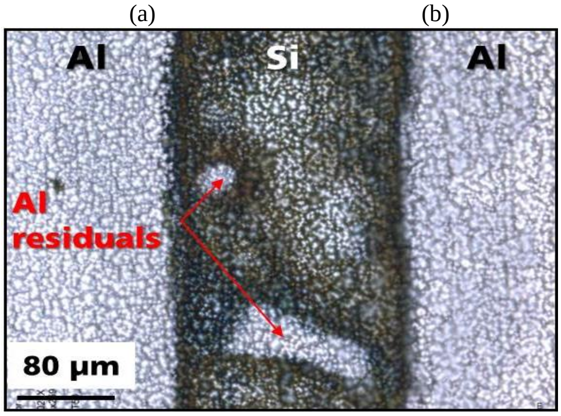
FIGURE 3: ESP patterned structures of 42 mm perimeter each on 100 nm aluminum on Si substrate (screen openings of 25 µm). (a) Width measurements of one etched trenches. (b) Narrow etched trenches of an average width of 36 µm ± 5 µm in 100 nm Al layer, electrically separated. Confocal-microscope image of an etched line (right).

Furthermore, the work aimed to transfer the ESP process to larger areas of up to 125x125 mm² areas. Based on the results in [6] and in Fig. 3, the ESP process was transferred successfully to 125x125 mm² areas (Fig. 4) with the restriction that no electrical contact separation was achieved over a structure length of 28.48 m. The reached line width is 115 µm ± 11 µm for a screen opening of 100 µm. The screen printing and electrochemical etching step lasted 1.2 sec to pattern the entire cell. These samples can be activated and plated with copper, as described in [6].

The confocal-microscope image in Fig. 4c shows aluminum residuals in the patterned trench. These residuals in the electrochemically etched structure can cause short circuiting between the two polarities. Possible causes are inhomogeneous current distribution and blocked screen meshes. While patterning single metal layers with the ESP process, the inhomogeneous current distribution is one big challenge. The confocal-microscope image in Fig. 4c shows aluminum residuals which are separated from the rest of the aluminum layer. It is not possible to remove this metal residual by using ESP process, as no current can reach this metal portion. The amount of metal residuals in the patterned trenches can be controlled to a certain degree by the used squeegee pressure and process parameters. A chemical post-treatment is beneficial to remove metal residuals in these trenches.



(a) (b)



(c)

Figure 4: ESP result on 100 nm aluminum layer of 125x125 mm² IBC grid design on Si substrate (screen openings of 100 µm). (a) Image section of edge zone of the IBC grid design. (b) Photo of the whole patterned IBC grid design. (c) A patterned trench with aluminum residuals in the etched zone. The line width is 111 µm.

3.2. ESP process on Al/Cu metal stack with IBC design

The ESP process was transferred to metal stacks with a similar process that was used under 3.1 to pattern single layers of the stack. Patterning a stack offers several advantages compared to a single metal layer in terms of IBC solar cell application, i.e., metal stacks lead to a more homogenous current distribution as more conductive material is available. This is especially true if one metal is etched preferentially as compared to the underlying one.

The thin Cu layer of the Al/Cu stack acts as a seed layer for the Cu plating. So, plating is also possible without activation by using Al/Cu stacks. The process sequence of the metallization process for IBC solar cells on Al/Cu stack is depicted in Fig. 2.

Long patterning trenches of more than 28 m on Si substrate

In addition to working on an aluminum layer, the 125x125 mm² IBC grid shown in Fig. 5 has been manufactured according to the metallization process route depicted in Fig. 2. The layer thickness of PVD aluminum was 100 nm, the layer thickness of PVD copper was 50 nm. These layers were deposited on Si substrates. The sample was fully electrochemically etched in 1.2 sec. The length of the trench of this IBC grid design was 28.48 m. Copper was completely removed selectively in the trenches, while aluminum was mostly unaffected by ESP (Fig. 5a).

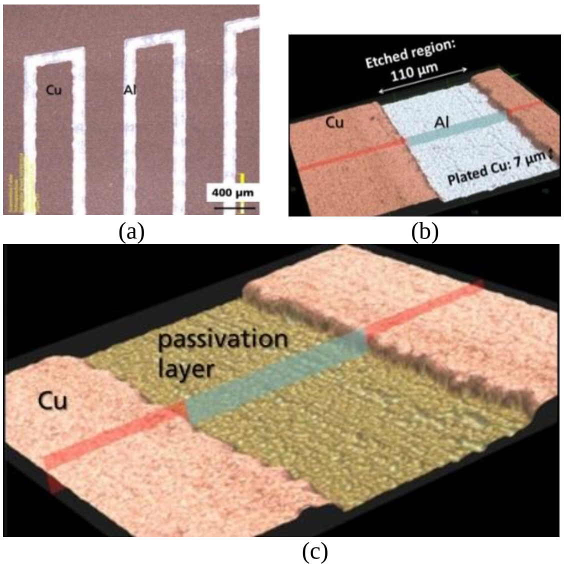


Figure 5: ESP result on metal stack Al(100 nm)/Cu (50 nm) of 125x125 mm² IBC grid design on Si substrate. (a) Confocal-microscope image presents that the ESP process patterned the metal stack selectively and locally (screen opening 100 µm). (b) Confocal-microscope image shows a section of the Cu-plated region, average height of 7 µm. The line width is 110 µm. (c) Confocal-microscope image depicts a structured groove after removing the aluminum layer.

Copper was selectively plated on PVD copper areas after ESP. If copper residuals were present in the structured trenches, those would also be thickened during Cu plating. This could result a short circuit in an IBC solar cell. On the other hand, even if the underlying aluminum layer was partially electrochemically etched by the ESP process, this would neither affect the plating process nor the eventual functionality of the IBC solar cell. The aluminum is removed in the trenches of the ESP process as last step to achieve an electrical contact separation between the n-type and p-type doped areas. The structured grooves contain no copper residuals and are in average 110 µm wide.

The aluminum layer below the patterned copper seed layer allows an excellent current distribution for the plating. The layer thickness was increased homogenously to 7 µm (Fig. 5b). As in theory, the aluminum areas stay free of copper deposition [8]. To reach an electrical contact separation between n-type and p-type doped areas, the full-faced aluminum layer is etched selectively by using highly diluted NaOH. The trenches are free of any metal residuals and the plated copper layer was not etched (Fig. 5c).

After the successful structuring of Al/Cu-stack using ESP, a further metal layer in the Al/Cu-stack will be necessary in the next step. This layer would act as a diffusion barrier to guarantee the long-term functionality of IBC solar cells [15].

Results on polymer foil

As described in section 2, the ESP process is a versatile process concerning its application. In addition to photovoltaics applications, this approach can also be used for flexible printed circuit boards. For this, the ESP process and the following process steps (Fig. 2) were transferred to PET foil material.

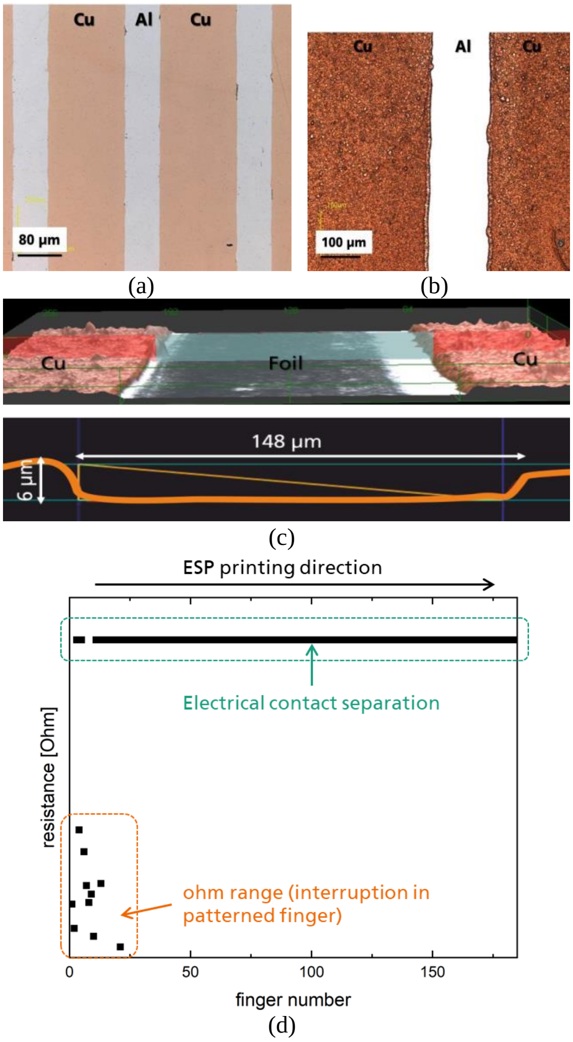


Figure 6: ESP result on metal stack Al(100 nm)/Cu (20 nm) and on single metal layer (100 nm) of 125x125 mm² IBC grid design on PET foil. (a) Confocal-microscope image presents that the ESP process patterned the metal stack selectively and locally (screen openings of 100 µm). (b) Confocal-microscope image shows a section of the Cu-plated region, average height of 6.7 µm ± 0.5 µm. (c) Confocal-microscope image depicts a structured groove after removing the aluminum layer. The line width is 150 µm ± 3 µm. (d) Resistance measurements on 100 nm silver layer. The electrical contact separation was realized over a large part of the

IBC grid. The patterned structure shows a few interruptions at the printing beginning.

A polymer foil was used as a substrate with a PVD aluminum layer of 100 nm and a PVD copper layer of 20 nm on top. The 125x125 mm² IBC grid was fully patterned in 1.2 sec. The ESP result is shown in Fig. 6a, the line width is 150 µm (screen opening 100 µm). The confocal-microscope image shows that the copper was selectively removed from the aluminum in the trenches. The electrochemically etched trenches are free of any Cu residuals. It is simpler to pattern planar surfaces than textures surfaces with the ESP process. This approach was successfully demonstrated on PET foil substrate.

The 20 nm Cu patterned layer acts as seed layer for Cu electroplating. This seed layer was thickened to a homogenous Cu layer with an average height of 6.7 µm ± 0.5 µm (Fig. 6b). The last step of the process sequence was to remove the aluminum from the patterned trenches. Fig. 6c depicts aluminum residue-free trenches with an average line width of 150 µm ± 3 µm. The trenches are now transparent because of the transparent polymer foil substrate. The appearance of the foil does not show any visible change. Because of the neutral used paste and the limited temperature (< 100°C), no impact on the substrate is expected.

The graph in Fig. 6d shows resistance measurements between each line of the 125x125 mm² IBC grid on a 100 nm metal ESP structured silver layer on PET foil that was patterned in another experiment. An electrical contact separation was achieved between most lines (infinite resistance). A few measurements at the beginning of the print show resistances in the ohm range. Contact problems at the beginning of the ESP process would need to be optimized to avoid this behavior. It is assumed that the electrical contact separation achieved on the 100 nm silver layer also applies to the ESP result of the metal stack (Al(100nm)/Cu(20 nm), see above).

4. CONCLUSION

The ESP process was demonstrated on 125x125 mm² 100 nm aluminum layers as well as on Al(100 nm)/Cu(20 nm) stacks on Si wafers and on foils, where single layers could be removed selectively. The printed pattern corresponds to a structure length of 28.48 m. The achieved electrochemical etched trenches on the metal stacks were in average 110 µm wide on Si substrate and 150 µm wide on foil substrate. These trenches were free of any residues in microscope inspection. Still, no full electrical contact separation was achieved on Si substrate, which has to be investigated in more detail. The patterned copper seed layer was thickened in average to a height of 7 µm by copper plating.

Furthermore, it was shown that currently a resolution of 36 µm ± 5 µm on 100 nm aluminum layer could be achieved. The rectangular trench was 42 mm long, electrical contact separation was reached. First steps comprising the key factors to successfully create an IBC cell metallization, such as patterning with the required resolution, selective plating, and selective etch back have thus been demonstrated. These features will be used to create a pattern with all properties of a real IBC pattern in a first step (including a thin diffusion barrier layer between aluminum and copper, full contact separation and greatly increased plating height), and actual IBC solar cells in a second step.

Additionally, this technology has the potential to be used not only in photovoltaics but also in other industrial branches for local structuring of thin metal layers.

5. ACKNOWLEDGMENTS

The authors want to acknowledge the colleagues at the Fraunhofer ISE and the project partners for productive discussion and technical assistance. This work was supported by the German Federal Ministry for Economic Affairs and Energy within the research project "KAluS50" (contract no. 0324009A) and by the European project NEXTBASE (grant agreement no. 727523) under the European Union's Horizon 2020 research and innovation program. The authors are responsible for the content.

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