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Energy Procedia 21 (2012) 2 – 13

Energy Procedia

3rd Workshop on Metallization for Crystalline Silicon Solar Cells,

25 – 26 October 2011, Charleroi, Belgium

Summary of the Third Workshop on Metallization for Crystalline Silicon Solar Cells

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Abstract

The Third Workshop on Metallization for Crystalline Silicon Solar Cells was held in Charleroi, Belgium on 25 and 26 October 2011. This paper reports on the different contributions and discussions that took place. Great progress has recently been achieved in paste development, which yet again has stretched the lifetime of screen-printed metallization technology. Nevertheless, a transition towards Cu plating-based metallization is anticipated, and solutions to the different challenges were presented and discussed.

Keywords: Metallization; silicon solar cells

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doi:10.1016/j.egypro.2012.05.002

1. Introduction

Metallization has always been a critical step in solar cell manufacturing, but has recently further increased in importance. First, the drive towards higher solar cell efficiency has put more demanding requirements on the performance of the metallization schemes. Secondly, the strong long-term increase of the price of silver in combination with the falling wafer costs has led to a situation where metallization blatantly dominates wafer-to-cell conversion costs. As a result, the industry has set out an aggressive roadmap concerning metallization, targeting strongly reduced silver consumption and higher performance [1]. In order to discuss and exchange on these crucial issues and strategies to tackle them, a workshop was organized entitled 'Workshop on Metallization for Crystalline Silicon Solar Cells'. It was the third of its kind in a series that started in 2008. It was held in Charleroi, Belgium, on 25 and 26 October 2011, gathering about 200 metallization experts from all over the world. This article provides a general summary of the workshop. Detailed information can be found in the other papers in these proceedings, as well as in the slides posted on www.metallizationworkshop.eu.

2. Fundamentals of printed contact formation

In several talks, the fundamentals of contact formation of silver thick film pastes were discussed.

2.1. Ag crystals or percolated Ag colloids : the controversy

The present general understanding of contact formation is that Ag crystallites (as depicted in Fig.1) nucleate and grow during the final fast annealing step of a solar cell process while a glass layer is simultaneously formed of on top of those. Current transport is considered to be determined by those crystals [2]. Most contributors showed experimental evidence consistent with this model, and based the interpretation and discussions of their results on that mechanism. However, another model, already proposed in previous years [3,4], was presented at this workshop again. It de-emphasizes the importance of Ag crystallites, and sees lateral current transport happening through percolation within the glass layer, enabled by the presence of colloidal Ag within the glass [5]. Review of the evidence and discussions among experts did not lead to a conclusion in this debate. Nevertheless, it did bring up new elements that will help resolve the question in the future, such as the suggestion that several mechanisms may be at play simultaneously with possibly varying relative contributions in different pastes, and the recommendation to carry out temperature-dependent studies to obtain better insights in the transport mechanisms at play.

2.2. Improved understanding of Ag crystals formation and current transport

Enhanced understanding of the nucleation of silver crystal on n- or p-doped silicon was presented. Nucleation centers can be identified as crystal defects e.g. due to high P doping [6] or in recrystallized Al-doped silicon [7,8]. Investigations on etched back Al – doped silicon showed that beside crystal defects there might be other factors influencing the silver crystal growth [7,8]. On B-doped surfaces standard silver pastes do not form sufficient silver crystals for achieving low contact resistances. Adding Al to the paste can increase the number of crystals and thus decrease the contact resistance. However contributions from Fraunhofer ISE gave indications that other approaches are possible and effective. Development of silver inks for aerosol jet printing led to silver inks that form good contact resistivities (down to values below 4 $mOhmcm^2$) in combination with a subsequent plating step, on both lowly doped B-emitters (surface concentration of $2x10^{19}cm^{-3}$) [9] and lowly doped P-emitters (surface concentration as low as 8 $x10^{18}cm^{-3}$!) [10,11]. These contributions and several others hinted that there are non-disclosed possibilities to modify the paste/ink chemistry so that silver crystals grow into silicon without or with less silicon-related nucleation centers. This is a big step forward towards the development of pastes that are able contact lowly doped emitters.

According to the Ag crystal hypothesis, current transport into and from those crystals are of critical importance. Theoretical investigations and ab-initio simulations showed that the contact geometry of the pyramids grown into the silicon affects the charge distribution and the Schottky Barrier Height (SBH) [12]. Additionally, phosphorus doping changes the charge rearrangement and the SBH in dependence on the interface orientation leading to lower SBHs on <110> interfaces compared to <111> interfaces. The current transport from silver crystals into bulk silver of the printed contacts was shown to be affected by the surface topography of random-pyramid textured monocrystalline silicon [6]. Rounding of the pyramids leads to higher contact resistances presumably due to a lower probability of direct Ag-Si contacts as most of the crystals might be covered by the glass layer. On flat surfaces the probability of direct contacts is reduced and the contact resistance increases [6]. Subsequent treatment of the screenprinted fingers was shown to improve the contact, for instance a short Ag light-induced plating step [13]. The mechanism for this is not totally clear but seems to be related to better current transport from Ag crystals to bulk Ag at the periphery of the fingers [14].

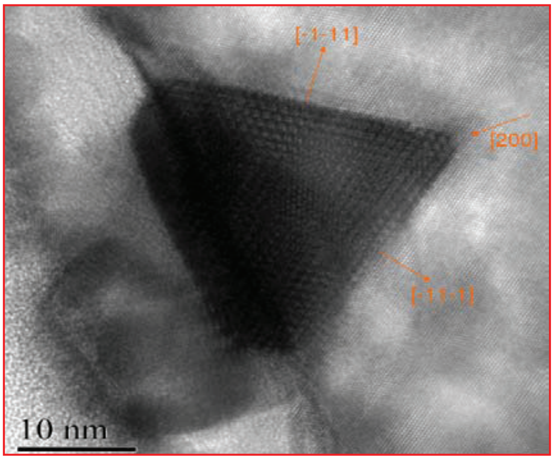

Fig. 1. Transmission Electron Microscope picture of a silver crystallite (dark) grown into silicon (Reproduced with permission from K. Butler, presentation at the 3rd Metallization Workshop, Charleroi, 2011[12])

3. The paste manufacturers did it again!

The improved understanding of the contact formation process gained in the metallization community over the last two years has clearly enabled paste manufacturers to strongly improve their Ag paste products. Some Ag pastes were shown to be able contact P-doped emitters with high sheet resistance and/or with reduced dead layer and surface concentration. Cell results were presented showing very low specific contact resistance and excellent fill factors, and this on emitters with up to 100 Ohm/sq and surface concentrations close to 1×10^{20} cm^{-3} [6, 13].

Apart from the ability to create Ag crystals on more lowly doped emitters, the new pastes often show several additional advantages such as enhanced SiNx removal properties, the ability to achieve ultra-thin

(10nm) interfacial glass layers, a wider firing temperature window, and a higher density, and hence better conductivity, of the screen-printed material [5].

The progress in Ag paste development is remarkable in many respects. First, the impact of this progress on the industry is enormous, enabling substantial further efficiency increases and in some cases challenging more costly approaches of contacting high performance emitters (e.g. selective emitter approaches). Secondly, this has been achieved in a context where substantial progress seemed improbable considering the great progress already achieved in previous years [15]. Finally, this second wave of improved products has hit the market very soon after the first one, turning it into a fast moving target for all emerging metallization technologies.

The topic of removing Pb from Ag paste formulations seemed to be a lower priority at the workshop than improving performance or reducing Ag consumption, yet paste manufacturers do press on with developments to reach Pb-free products [16]. In spite of the problem of high Ag prices and its large impact on wafer-to-cell processing costs, alternatives to Ag in screen-printing paste did not come across as an intensively researched topic. One article was presented on a Cu particles-based paste for low-temperature metallization [17, 18].

4. Progress in printing technology

Progress in application technology was also discussed in detail at the workshop. The important issues reviewed were approaches towards improved efficiencies through printing of fine lines with high aspect ratio, reduced silver usage and industrial application.

While the current industrial finger width is around 90 μm, the goal of the industry is moving towards 50 μm in 5 years, as shown in graphs of the ITRPV committee [1]. To enable fine line print, various options were presented for the print mask: ultra-fine wire mesh screens, V-screen, polyester fabric, calendared mesh, and various stencils. To enhance on the aspect ratio different print approaches were discussed: print on print, dual print and double print [19,20,21,22].

Stencil printing received a lot of attention [22,19,20,21]. Currently there are several stencil types available and being tested, i.e. single layer, two layer, hybrid (i.e. metal with emulsion) and in stainless steel and nickel. The single layer approach in a dual-print mode (printing busbars and fingers sequentially) as presented at the 2nd Metallization Workshop [23] seems to be most favorable with regards to uniformity, linewidth and process simplicity [22,19].

Evidence was shown that it is possible to move towards 50 μm wide lines and below while keeping a sufficiently high aspect ratio [19]. This is possible using a screen with ultra-fine mesh with fine wires and with stencils, the latter being favored because of uniformity and good height in single print.

Though these results are remarkable, a more directly implementable way of increasing aspect ratio while reducing linewidth and paste consumption might be applying double printing (or 'print-on-print') with fairly conventional screen printing equipment [24,25,26]. Interesting data were shown from pilot production that uses double printing, confirming the potential for efficiency increase compared to single print but highlighting the need for screens with sufficient lifetime to provide an economic advantage [20,21].

Screenprinting process development is also anticipating the needs of emerging solar cell technologies, in particular those of Metallization Wrap Through (MWT) technology. Special attention was given for the deposition of paste in the holes or vias, regarding the partial or full filling of the holes and the electrical implications after firing. Influence of paste characteristics and tool specs, such as vacuum pulling and pattern alignment were discussed [27].

5. Hybrid approach

Interesting results were also shown for the 'seed and plate' approach. This is a hybrid technique where a very narrow line is first printed by a fine line printing method, fired through silicon nitride, and then thickened by plating. This approach was proposed a while ago [28] but has not yet found acceptance in the industry. Although failed adoption of the hybrid approach in the industry was commented on during the workshop, evidence of promising industrial application was also given [29]. The process was optimized in large testing campaigns on lab-scale using various printing techniques for the seed layer such as fine-line screenprinting, inkjet printing and aerosol printing. The optimized process was then implemented in pilot production (see Fig. 2). A stable process resulting in average line width of 65 µm and a best cell of 18.8% efficiency was reached for several thousands of cells.

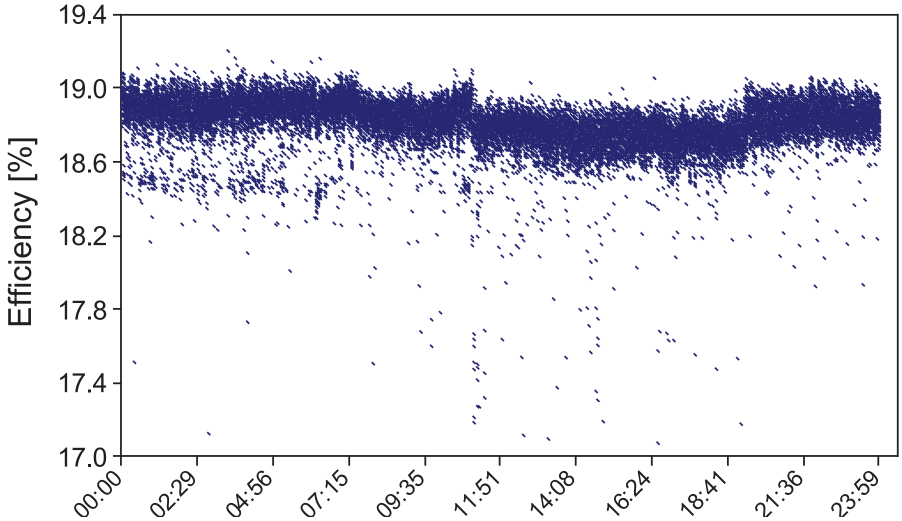

Fig. 2. Efficiency results of 1 day pilot line production using fine-line screenprinting and Ag plating (Reproduced with permission from A. Mette, presentation at the 3rd Metallization Workshop, Charleroi, 2011 [29])

No other presentation showed results on the hybrid approach, apart from the promising results at Fraunhofer on aerosol printed seeds on high performance emitters in laboratory cells, as already mentioned [9,10,11].

6. Cu plating

With the strong downward pressure on cell prices and the increasing share of Ag cost in the total solar cell cost, the case for switching to a completely new metallization process that is not based on Ag is compelling. The ITRPV roadmap reflects this urge and sees a fast substitution of Ag by an alternative occurring in the coming years, with an almost complete phase-out by 2020 [1]. An appealing approach is to create the bulk of the conductive material by copper plating, as bulk copper is about a hundred times cheaper than Ag but has a similarly high conductivity. In order to create a good contact with doped silicon and to provide a diffusion barrier to prevent Cu atoms from diffusing into Si, a Ni layer is usually formed at the interface with Si prior to Cu plating and allowed to react to form a highly conductive Ni silicide. Another approach is to print and fire a fine line of Ag-paste and palte Ni and Cu on top of this seed layer. Although Ni/Cu plating metallization is much more complex to implement than screenprinting Ag metallization, it holds the promise of high performance at lower cost.

At the workshop, good progress was presented in the various aspects of the process. The potential of the Ni/Cu metallization scheme was confirmed with very high efficiency (up to 21.4 %) laboratory cells demonstrated, equivalent to the reference cells using the traditional laboratory Ti/Pd/Ag metallization scheme [30]. On large-area cells, excellent results were also obtained with a process involving laser ablation of the silicon nitride and PVD Ni deposition, as well as a dielectric passivated rear surface. A peak efficiency of 19.6 % was reached [31,32].

From the presentations, it was clear that there is still a lot of issues to solve before a robust industrial process is available that can be successfully implemented in manufacturing. However, each potential roadblock has been identified and progress was shown towards solving them.

One challenge is the deposition of uniform Ni layers in a cost-effective way. The proposed processes include electroless Ni plating [33,34], preferably in a high pH solution, and Light-Induced Plating [30]. A possible method to control the thickness of the Ni-silicide layer is to use porous silicon to precisely define the depth of silicidation [35]. Another challenge is to avoid background (or ghost) plating – i.e. the phenomenon of undesired plating on tiny spots between fingers, which has a strong negative visual impact. It was shown that impurities, particles and cracks were the cause of background plating, which could be solved by proper cleaning prior to diffusion and low-stress handling of the wafers [36,37] Enhanced process complexity compared to Ag screen-printing is also viewed as an issue. Different ways of simplifying the metallization process sequence were proposed. An attractive approach is to combine nitride ablation with a Ni seed layer formation in a single step using a laser process and a Ni electrolyte (Laser Chemical Metal Deposition). Encouraging results were obtained using a continuous wave laser [37,38]. Long term reliability is another challenge for Cu metallization, as Cu is known to diffuse easily and affects performance when it reaches Si. The key here is the use of effective barrier layers [39]. The SiN_x antireflection coating was suggested to be the weak point in present schemes that involve thickening of the contacts by electroplating [31]. Front coatings or layer stacks might be introduced in the future that provide better barrier properties and possibly even reduced recombination under the contacts [40, 41]. Finally, indications were shown that the problem of poor adhesion, often reported as the major hurdle on the path toward Cu plating metallization, could be mastered by proper process tuning. Soldered tab adhesion larger than 1 N/mm were reported for cells involving laser ablation, Ni silicide, and Cu plating [31,32]. It was moreover suggested that plated metallization might present an advantage when the switch to Pb-free solder occurs, as plated contacts offer better solder wettability than screen printed Ag metallization [42].

In order to gain insight into the industry's view on the roadblocks towards Cu metallization, a panel discussion was organized with the provocative title of „Is the future of solar cell metallization copper plating?" The panel consisted of metallization experts from equipment and material manufacturers. The panel participants discussed the pros and cons of the metallization sequences involving Cu plating. During the discussion participants emphasized that a major parameter to evaluate the different technologies options is reliability. Several panelists questioned if it is possible to get sufficient mechanical adhesion or long-term stability for the copper-based contacts at the moment. It was emphasized that to achieve sufficient reliability a high quality of the seed, whether it is printed or plated, is of major importance. The width of the seed compared to a fully printed contact is usually a factor of 2 to 5 smaller. Thus, the specific electrical and mechanical properties have to be better to reach similar overall performance. For process sequences where a silver seed is first printed and then thickened by plating, the interaction between the seed and the plated contacts is essential since the electrolyte can react with the printed seed. Since mechanical adhesion is a crucial parameter at the interface between cell and module technology, a closer cooperation between the cell and module R&D communities would be desirable. The mechanical adhesion problem was viewed by the panel as more critical than the issue of copper diffusion into silicon, where it was felt that the industry will be able to tap into past experience from microelectronics and past attempts at manufacturing solar cells with NiCu contacts.

Another question brought up by the audience is the complexity and costs for waste treatment of plating processes. However, the panel thought that this is no major issue since other industries have been using copper and nickel plating for decades and thus a transfer of know-how is easily possible.

7. Rear contact

Although front metallization was the topic that received most attention at the workshop, there were several contributions on rear side metallization. Here the focus was on rear metallization of emerging solar cell concepts, such as industrially applicable PERC cells (Passivated Emitter and Rear Cells), where the rear surface is covered by a passivating dielectric layer and local contacts at the rear are created through the passivating layer.

There are two main approaches to create the vias between Si and Al. The first one is to remove the dielectric locally, usually by laser ablation, prior to the Al deposition and firing, while the second is to apply a Laser Firing Contact process (LFC), where the laser pulses are used to simultaneously ablate through the dielectric and form the alloyed contact. Apart from these two techniques, some approaches make use of Al pastes that can etch through the dielectric layer during firing. Such fire-through Al paste have been developed by paste manufacturers [43]. Whatever the technique used for via formation, the metallization community has come to realize that the type of pastes used in rear contact schemes of PERC-type cells has an important impact on cell performance, and that pastes and passivation stacks need to be matched and optimized together. This was evidenced in a specific study for LFC contacts [44].

An important topic in PERC metallization is the understanding and control of the alloying process between Al and Si at the local contacts. As described in the 1st Metallization Workshop for the first time, the process consumes Si below the contact points and needs to be controlled [45]. Over the last two years, experts in the field have developed a more fundamental understanding of the phenomena at play, which by now has enabled device makers to control them for optimal performance. The amount of Al involved in the alloying process in relation the surface area of the exposed Si plays a critical role in the contact depth and the local BSF thickness, with larger Al mass resulting in deeper contacts and thinner BSF [46,47,48,49]. A simple model was proposed that appears to predict the trends quite well [47]. The observation that the cavity created by the alloying process is sometimes not filled by Al-Si eutectic was studied in detail. This occurrence was shown to be determined by the diffusivity of Si in Al (which may be different for different Al materials used) and the amount of Al available for the alloying process [50].

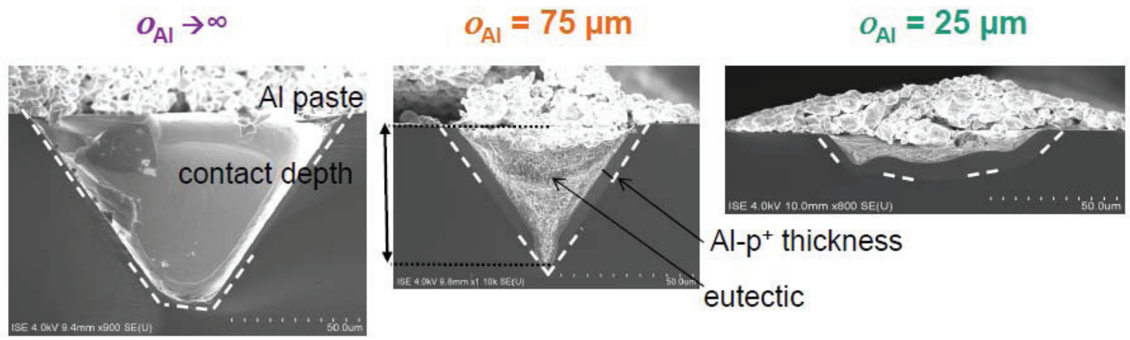

Fig. 3. Cross section SEM pictures of locally alloyed contacts. O_{Al} refers to the distance between the edge of the opening through the dielectric and the edge of the printed Al pad, and is a measure for the amount of Al available for alloying (Reproduced with permission from K. Ruehle, presentation at the 3rd Metallization Workshop, Charleroi, 2011 [46])

Although screenprinted Al, which is the incumbent material and relatively cheap, is regarded as the main contender for the rear metallization of PERC cells, an alternative method of Al deposition, namely in-line Al evaporation has been available for a few years and is being further developed. A study presented at the workshop showed that thermal management is critical as the wafers can reach high temperatures during the evaporation process, up to 300 ºC for thin wafers and an Al layer of 2 µm thickness [51]. The bow induced by thermal stress can however be kept below 1 mm. Soldering interconnection ribbon onto such evaporated electrode is a challenge that can be tackled through the deposition of thin solderable layers such as Ni:V and Ag. Soldering tabs on such layers using lead free solder was shown to provide adequate adhesion and durability, provided the encapsulation material is compatible [52,53].

8. Survey

A questionnaire was distributed to all participants at the end of the workshop to probe the participants' satisfaction with the workshop, but also to survey the metallization experts' view on the developments in the industry over the coming years. 142 out of the 200 participants provided their answers, ensuring a representative sample of the metallization experts community. A summary of the survey results has been posted on the Metallization Workshop website and provides interesting insights. For instance, the metallization community anticipates the introduction of plating in the industry as substitution for screenprinting. Yet, the decline of screenprinting is foreseen to be gradual, with still 81 % of production lines using screenprinting in 2014, 68 % in 2016, and 49 % in 2021. Interestingly, this anticipated decline is somewhat slower than forecast in the surveys at previous metallization workshops, which reflects the recent success in stretching the performance of screenprinted metallization. To the question 'What in your opinion will be the percentage share of the metals used for front grid in solar cell production?', answers were given consistent with the question on the metallization technique, with a steady decrease of silver consumption and increasing use of copper. It should be noted however that the substitution of Ag by Cu is not going to take place as fast as anticipated by the ITRPV roadmap [1], which foresees that Ag will be practically eliminated from production by 2020. Instead, the survey predicts that about 50 % of cells will still use Ag for the front grid as the next decade begins.

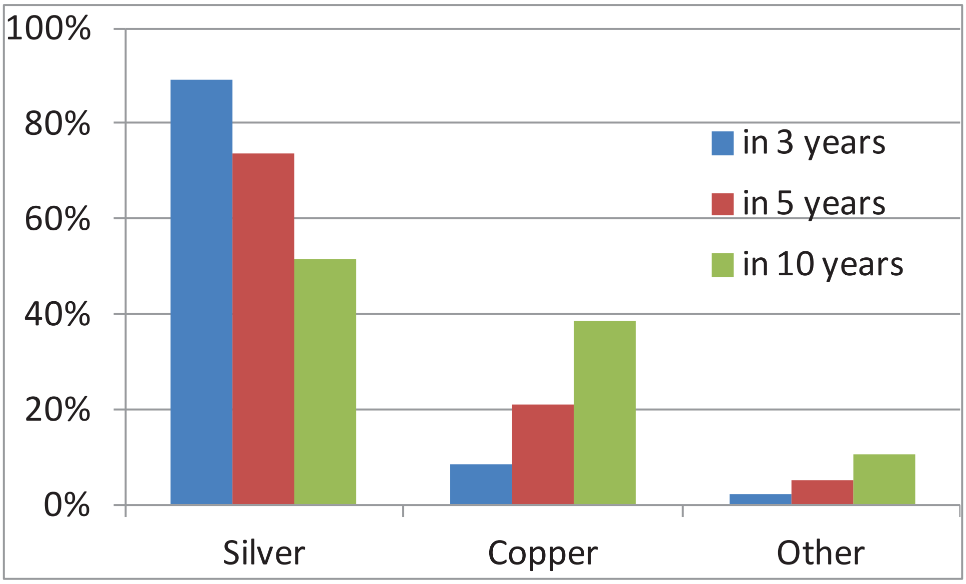

Fig. 4. Answers to the question 'What in your opinion will be the percentage share of the metals used for front grid in solar cell production?' asked in the survey

9. Conclusion

The 3rd Workshop on Metallization for Crystalline Silicon solar cells provided an effective forum for scientific exchange and discussion on the topic of metallization for crystalline silicon solar cells. Recent progress was highlighted and reviewed. There has been great progress in front side Ag pastes, with commercial pastes now providing excellent contact for emitters with surface concentration close to 10^{20} cm^{-3}, effectively stretching the applicability of screenprinting technology, and development materials showing potential to contact emitters with surface passivation below 10^{19} cm^{-3}. Application technology has also improved, leading to high performance metallization with reduced Ag consumption and enabling emerging solar cell concepts. The switch to plated Cu metallization is seen as an inexorable but slow transition, and the roadblocks are being tackled one by one, long term reliability being the major potential stumbling block.

Acknowledgements

We thank all presenters and participants to the 3rd Metallization Workshop for their contributions. We are also grateful to the sponsors for making this workshop again possible. Finally, we would like to thank all members of the Scientific Committee for their involvement in ensuring a high scientific quality of the Workshop.

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