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Advances with Resist-Free Copper Plating Approaches for the Metallization of Silicon Heterojunction Solar Cells

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Abstract. The metallization of silicon heterojunction (SHJ) solar cells by selective Cu electroplating without any resist-mask is in development. A thin multi-functional PVD Cu-Al stack is deposited to mask the ITO and to promote homogeneous current distribution for simultaneous bifacial plating. This investigation reviews different approaches to perform the Al-patterning – by printing of a metallic ink, laser metal transfer or selective metal etching – to produce a metal-seed susceptible to plate selectively against the self-passivated Al surface. This *NOBLE* – native oxide barrier layer for selective electroplated, metallization allows reaching a first promising efficiency of 20.0% on a full area SHJ solar cell with low contact resistivity to ITO. This simultaneous bifacial metallization features several advantages: low temperature processing, high metal conductivity of plated copper, no organic masking and low material costs (almost Ag-free).

INTRODUCTION

The main manufacturing cost for both sides contacted crystalline silicon heterojunction (SHJ) solar cells is due to metallization. The passivation by amorphous silicon (a-Si) layers would be damaged by high temperature processing required for the standard (more economic) silver paste metallization. A lot of effort is currently dedicated to developing silver pastes sufficiently conductive at low temperature processing (up to 200°C) and to reduce cost of such contacting pastes. In the meantime, the heterojunction technology (HJT) offers a promising path to reduce the levelized cost of electricity (LCOE) with such low-temperature processing [1].

As alternative metallization technology, electroplating of highly conductive copper contacts is intrinsically a low-temperature process [2]. Furthermore, this metallization already proved its potential in silicon heterojunction device application with an outstanding efficiency above 25% on a large area bifacial Cu-contacted SHJ solar cell [3]. Another advantage of this technology is the freedom to metallize the SHJ cell with or without busbar as both are economically almost equivalent in case of copper metallization. However, other challenges have to be faced regarding electroplating on TCOs. Metal adhesion, masking of TCOs and homogeneous plating-current distribution have to be addressed. Some metallization routes (with a dielectric layer as mask) deposit a metal-seed onto the TCOs in the grid-positions and use the full area rear side metallization to distribute the plating current [4,5]. However, these processes are not suitable for simultaneous bifacial plating since the TCO and seed layer conductivity are too low to promote homogeneous current distribution on both sides of the cells [6]. Regarding manufacturing, simultaneous bifacial electrodeposition would be desirable to reduce processing costs and for yield gains of bifacial modules. The printed circuit board processing route for electroplating is less restricted regarding process cost and uses photolithography for masking the plating process, which results in optimal metallization properties. Such a process has also already been adapted for large scale SHJ solar cells and has allowed reaching efficiencies above 24% [7–9]. A thin metal seed-layer is physical vapor deposited (PVD) following the TCOs deposition without any vacuum breaking. This thin layer adheres well on TCOs and simultaneously promotes current distribution during bifacial plating of the contacts [10]. A sacrificial organic resist is then deposited on > 95% of the surface to mask the non-grid positions. Our novel "*NOBLE*" – native oxide barrier layer for selective electroplating, metallization is a resist-free alternative taking advantage of a thin PVD aluminum layer that acts as current distribution layer and simultaneously as mask using its self-passivation [11]. This approach reduces the plating process complexity and processing cost, making this route attractive for industrial implementation in photovoltaics. Several patterning techniques of the aluminum layer might be used [11–15] and our investigations review the progress on the Al-patterning allowing selective plating on a metal-seed.

APPROACH

One key for our novel simultaneous bifacial *NOBLE* – native oxide barrier layer for selective electroplated metallization process is to pattern the self-passivated Al-top layer. This might be realized by depositing a metal-seed onto the Al or by removing the Al – both only on grid-positions (< 5% of the cell area). In the present work, different patterning techniques are investigated and tested on the same batch of commercial SHJ solar cell precursors covered by ITO as depicted in the process flow in FIGURE 1. A reference is realized with the standard screen-printing of Ag-paste on ITO. For the other samples, a thin stack of Cu/Al is first deposited by PVD on ITO. Five different Al-patterning possibilities (all following the currently best known method) are then followed to produce a metal-seed susceptible to selective Cu electroplating of the contacts [14]. After plating, the thin PVD metal stack is etched-back in the non-grid positions to finalize the SHJ solar cells which are then measured by a sun-simulator under 1-sun illumination.

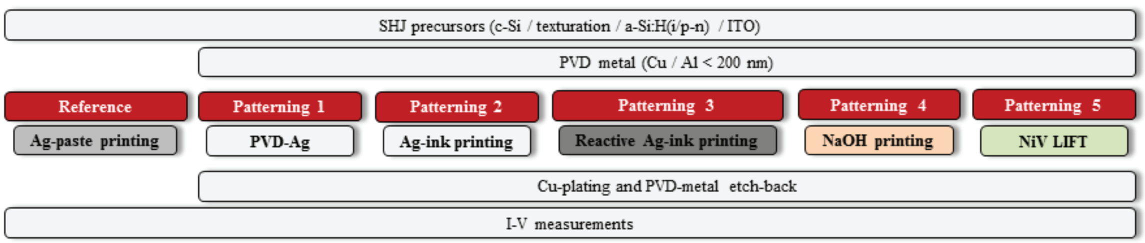

FIGURE 1. Approaches followed in this investigation to metallize SHJ solar cells by screen-printing on ITO as reference or after deposition of a thin PVD Cu / Al stack on ITO, plating of Cu-contacts on a metal-seed patterning the Al layer by (1) PVD-Ag deposition on Al (shadow mask applied to deposit by PVD only in grid positions), (2-3) inkjet-printing of respectively a commercial Ag-ink and a self-made reactive particles-free Ag-ink onto Al, (4) printing of a self-made low-concentrated NaOH ink etching Al and (5) laser induced forward transfer (*LIFT* [5]) of a NiV-seed onto Al.

RESULTS AND DISCUSSIONS

Al Patterning – Reviewing of the Metal-Seeds Structure

After the deposition of the thin PVD metal-layers with Al on top, the grid-positions are patterned. As illustrated in FIGURE 1, several approaches were followed to produce a metal-seed susceptible to selective Cu-plating. Patterning the grid positions on the Al determines the contact characteristics and is then primordial before copper plating. Indeed, the metal-seed properties show a huge influence on the fingers properties: continuity, width, morphology, adhesion, contact resistivity after selective Cu-plating and etch-back processing. The metal-seed surface on the textured SHJ precursor before and after Al patterning were characterized by scanning electron microscopy as observed in FIGURE 2. The amorphous Al surface – after PVD deposition on the random pyramids, presents a porous round nanostructure typical [6] for such thin coating as depicted in FIGURE 2 (a). In FIGURE 2 (b), the Ag-seed deposited by PVD through a shadow mask (patterning 1 – FIGURE 1) is similarly shaped, maybe less porous due to the thicker layer (≈ 500 nm). The surface after selective etching of the Al layer (patterning 4 – FIGURE 1) exposes a denser Cu (PVD) surface with a seeding-nanostructure (FIGURE 2 (c)). However, both patterning results are quite homogeneous.

On the contrary, inkjet-printing or laser induced forward transfer of particles or coating lead to more discontinuous of the metal-seeds. After curing, the round Ag nanoparticles inkjet-printed in patterning 2 (FIGURE 1) are predominantly found in the valleys of the pyramid texture and the Al layer on the pyramid summits remains mostly free as observed in FIGURE 2 (d). This phenomenon is further increased by inkjet-printing of the reactive silver ink (patterning 3 – FIGURE 1) were only a few nanoparticles or clusters act as metal-seed (FIGURE 2 (e)). The NiV-seed (patterning 5 – FIGURE 1) presents also discontinuities but not really impacted by the textured surface (FIGURE 2 (f)). This metal-seed is composed of nanoparticles and wider clusters. It has to be pointed out that all results shown here represent the currently best known method in our labs. It is very likely that a focused development will lead to improvements for each of the patterning schemes.

The metal-seed used to pattern the Al layer can be sorted in two groups – patterning 1, 4 permeable but continuous (PVD-metal) and 2, 3, 5 denser but less homogeneous (particles). Besides the optimal PVD-Ag seed (patterning 1) – not industrial relevant, two distinct high throughput technologies are investigated: inkjet-printing or laser processing.

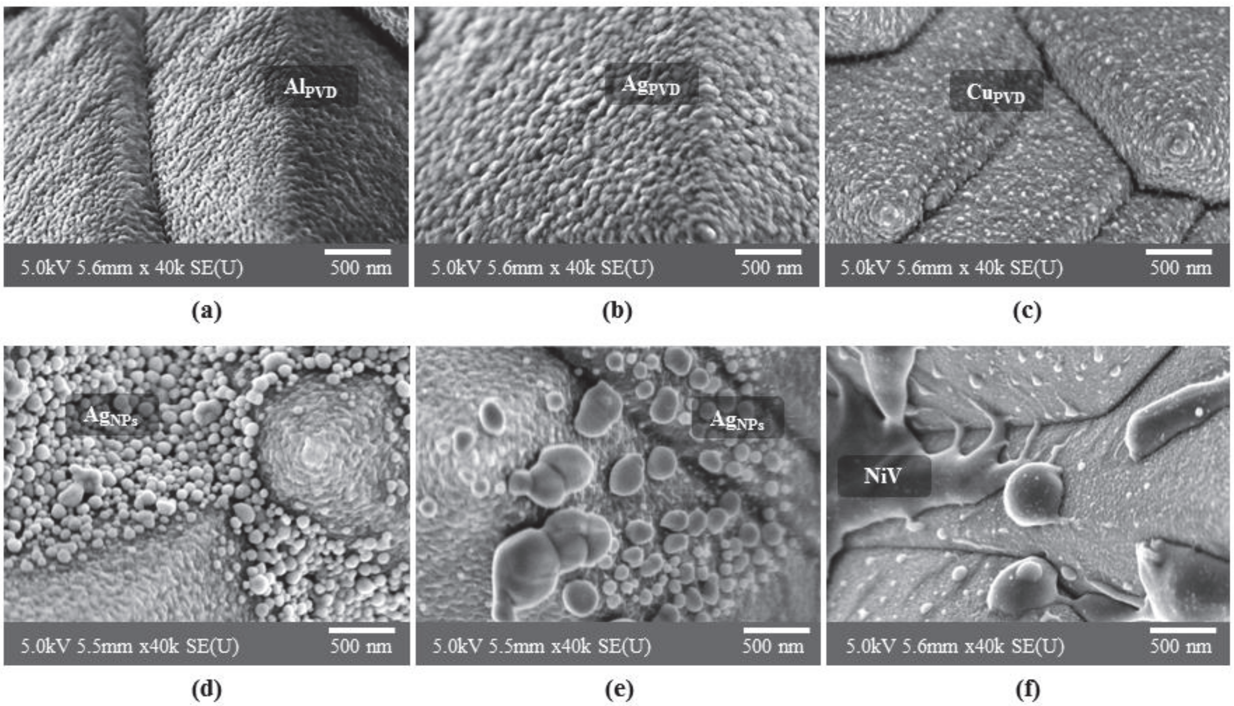

FIGURE 2. SEM pictures (in top view) of the SHJ solar cell surface and nanostructures on textured surface covered by ITO / Cu / Al (a) and after patterning of the Al with (b) PVD-Ag layer, (c) selective etching of the Al, (d) printing of Ag-paste, (e) printing of reactive silver ink and (f) *LIFT* of NiV-seed.

Selective Copper Plating

The native oxide covering the multi-functional Al layer allows performing selective Cu plating onto the metal-seed. The current for electroplating is homogeneously distributed within the PVD metal stack (Cu / Al). For a good plating selectivity – only onto the metal-seed designed, the contact resistivity (ρ_c) between the electron transporting PVD layers and the metal-seed should be low enough to avoid Cu^{2+} reduction on Al by tunneling current through the native oxide as competing process.

The PVD Ag-seed deposited on the Al – Al_2O_3 allows performing homogeneous and selective Cu-plating as already described in an earlier study [14]. However, the wide fingers and the use of a shadow mask during PVD do not make this patterning 1 (FIGURE 1) relevant for industrial use. Even if the pyramid tips remain uncovered by Ag nanoparticles, the metal-seed area from inkjet printing of a nanoparticle ink (patterning 2 – FIGURE 1) is sufficient to avoid interruption along the fingers. However, the contact resistivity Al – Al_2O_3 / Ag-nanoparticles seems to exceed a critical value in some areas, leading to inhibition of Cu-plating in these positions. Increasing the plating current density does not fully overcome this inhibition and leads to loss of selectivity since the electrons might take alternative paths for copper ion reduction, leading to deposition on the Al_2O_3 in non-grid positions. Adaptation of the ink to yield homogeneous and low contact resistivity over the entire grid is expected to fix this currently observed issue. The alkaline reactive Ag-ink (patterning 3 – FIGURE 1) may also overcome this issue since a

ρ_c of 1 mΩ·cm² was measured for the full metal stack [14]. Nevertheless, more finger interruptions still occur after plating since the area covered by Ag is not sufficient after printing, probably due to the bad wetting of the droplet on the Al surface and the low Ag^+ concentration of the ink. Removing the Al – Al_2O_3 layer to plate on the PVD Cu-seed (patterning 4 – FIGURE 1) overcomes the mentioned ρ_c issues since the copper does not self-passivate and almost reaches the characteristics of the patterning 1 (FIGURE 1) by much less process complexity. After printing optimization (to avoid the remaining finger interruptions) this route is expected to quickly reach the full potential of the SHJ solar cells. As the hurdles seem lowest in this case, this route is one of the currently most intensively studied ones. However, the NiV-seed deposited on Al – Al_2O_3 by laser processing (patterning 5 – FIGURE 1) also presents a good Cu-plating selectivity. The *LIFT* technology typically yields in continuous fingers and already enabled high efficiency on monofacial SHJ solar cells by firing the NiV-seed through a dense 15 nm Al_2O_3 layer, which was deposited by atomic layer deposition [5].

Solar Cells Characteristics

Our novel *NOBLE* metallization with the different Al patterning processes allowed producing first promising SHJ solar cells and the development is still ongoing. The FIGURE 3 reviews the efficiencies achieved on one same batch of SHJ solar cells along the *NOBLE* process development with different metal-seeds to pattern the multi-functional thin Al layer. Even if the ρ_c seems low, the reactive Ag-ink (patterning 3) only allowed to reach an efficiency slightly above 17%. This metallized small area cell was limited by losses at edges (V_{oc} and pFF) and mostly by the fill-factor (FF) due to finger interruptions as discussed above. Removing the Al (patterning 4) in the grid-positions also permits to produce an encouraging small area solar cell with an efficiency up to 18.2%. The first full area plated SHJ cell with NiV-seed (patterning 5) has a limited efficiency of 18.6% due to a non-optimized laser processing impacting the V_{oc} and pFF. However, Rodofili et al. [5] already demonstrated that the *LIFT* process does not need to damage the SHJ cells and the following plating permitted to reach an efficiency up to 22.2% – higher than the screen-printing of Ag-paste (reference) as reported in FIGURE 3. Ongoing investigations should allow to obtain equivalent efficiency with the novel *NOBLE* metallization. In the meantime, the patterning of Al by local etchant printing (patterning 4) after transfer on full area cell was improved and a promising efficiency of 20.0% was already reached for such early development of the process [6].

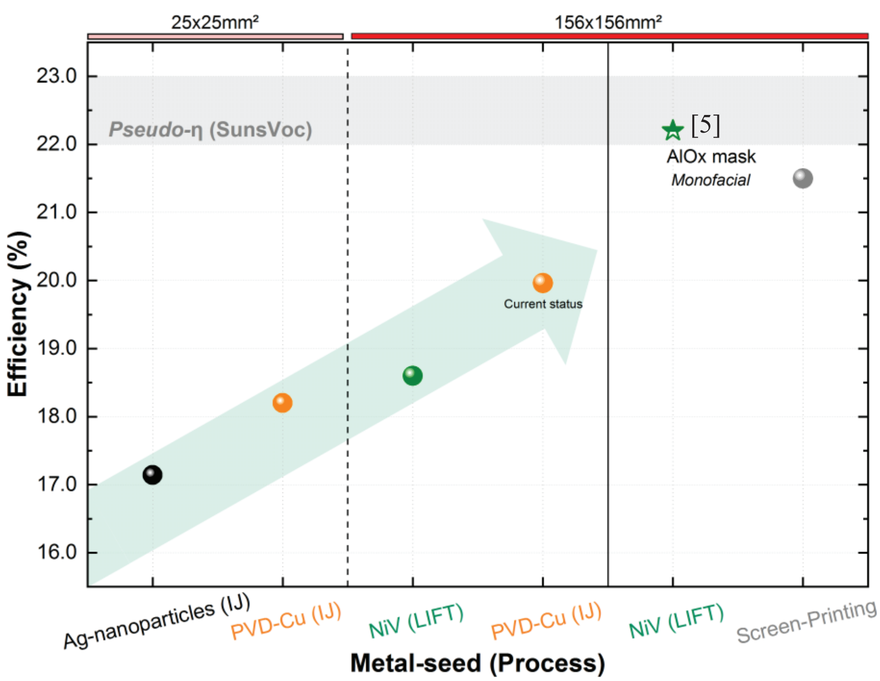

FIGURE 3. History of the *NOBLE* process development with different metal-seed to pattern the Al layer (IJ: Inkjet-Printing and *LIFT*: Laser Induced Forward Transfer) and I-V data on small area SHJ solar cells for the early stage development and on full cell area (156 x 156 mm²) for the current status.

CONLUSION AND OUTLOOK

Our metallization by the novel *NOBLE* approach – i.e. native oxide barrier layer for selective electroplating creates highly conductive copper contacts for solar cells covered by TCO layers without the use of resist mask. The Al surface patterning in the grid-positions may be realized by several technologies as reviewed in this study. Structuring the Al layer by simple inkjet-printing of a low-cost $NaOH_{aq}$ solution or laser-induced-forward-transfer of a NiV-seed currently seem to be the best options. An encouraging efficiency of 20.0% was achieved on a full area SHJ solar cell with the first mentioned technology and both routes are expected to reach the full potential on the heterojunction technology in the near future.

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