Impact of Si Surface Topography on the Glass Layer Resulting from Screen Printed Ag-Paste Solar Cell Contacts

Enrique Cabrera¹, Sara Olibet¹, Dominik Rudolph¹, Joachim Glatz-Reichenbach¹, Radovan Kopecek¹, Daniel Reinke², Anne Götz², and Gunnar Schubert²

¹International Solar Energy Research Center-ISC-Konstanz, Rudolf Diesel-Str.15, 78467 Konstanz, Germany
²Sunways AG, Macairestrasse 3-5, 78467 Konstanz, Germany

Abstract — For the current transport mechanism between the n⁺ Si emitter and the screen printed silver contact, there is strong experimental evidence that the largest current contribution flows through Ag crystallites directly connected with the silver finger, which are preferably concentrated in some tips of the Si pyramid surface. For this purpose, we focused on the origin of these Ag crystallites and we analyzed the contact formation on different surface topographies such as pyramid height and rounding degree variations, and flat smooth surfaces, with and without phosphorus doped emitter and not only on mono- but also on multicrystalline Si material with its dislocations, grain boundaries and impurities. Combining contact resistance measurements with SEM investigations, we discovered that smaller pyramids are more capable of creating better contact than rounded pyramids, even though in our case they cover only a few percent of the area on the Si surfaces. This can be explained with the wetting behavior of the glass, which leads to some pyramid tips being glass-free and thus in direct contact with the Ag-bulk, as long as the pyramid heights exceed the thickness of the glass layer. In the case of surfaces which are smoothly polished or with strongly rounded pyramidal surfaces, a continuous glass-layer separates the Ag crystallites from the Ag-finger preventing good contact. Moreover, without a P doped emitter it is possible not only to create Ag crystallites underneath the glass, but also Ag crystallites in direct contact with the silver finger.

Index Terms — Contacts, photovoltaic cells, silicon, silver, surface texture.

I. INTRODUCTION

Achieving low contact resistances for reaching high fill factors is essential for good Si solar cell performance. Within screen printed front side thick film metallization, the growth of Ag crystallites in the n⁺ Si emitter is believed to be a necessary condition in the achievement of low contact resistivity. The most widely accepted model to explain the Ag crystallite creation during the firing process attributes it to a redox reaction between the PbO of the glass frit and Si [1]. Recent investigations report that this formation results from a direct reaction between Ag⁺ and O²⁻ ions in the molten glass and the Si wafer without the aid of liquid Pb or Bi, and is highly dependent on the oxygen in the firing ambience [2]. The current from the n⁺ Si emitters to the silver finger can take place by predominately four possible paths: (i) via direct connection between Ag crystallites and silver finger [3], which are preferably located in some tips of the Si pyramid surfaces [4], (ii) through Ag crystallites separated by a thin glass layer [1], (iii) through Ag crystallites separated by a glass layer via multi tunneling effects due to metal precipitates in the glass [1] and (iv) via tunneling effects due to nano Ag colloids in the glass [5].

It is observed that textured surfaces are easier to contact by screen-printed silver pastes than flat surfaces [4]. This is supposedly due to: (i) the larger contact surface between the textured Si and Ag-paste, (ii) the presence of Ag-crystallites at the tips and edges of the pyramids and (iii) the higher Si oxidation etching for <111> than <100> Si [6]. However, the coverage of the glass layer on the Si surface should be also a major factor.

II. EXPERIMENTAL

Fig. 1. LSM top views of Si surfaces: (a) flat, (b) ultra small, (c) very small, (d) small, (e) standard and (f) large pyramidal texture.

Standard p-type silicon solar cells were prepared with an emitter sheet resistance of 65 Ω/sq on flat and textured front surfaces. On monocrystalline Si material, after an initial acidic polishing step, different random pyramidal surfaces were created with variations in the time in the alkaline KOH/IPA process, see Fig. 1. The resulting surfaces were evaluated by laser scanning microscopy (LSM) in order to estimate the distribution and height of the Si pyramids [7]. The resulting pyramid heights are in the range of 0.005 µm to 4.6 µm. To achieve the variation in rounding of the pyramids, an acidic
polishing step with varying duration was applied to our standard textured surface. To avoid the influence of the emitter doping concentration, a standard solar cell process without P diffusion was performed. Multicrystalline Si wafers from the same position of the ingot were polished or isotextured, both in an acidic etching solution. In addition, a honeycomb texture was applied to quasi mono- and mc-Si material. Best firing conditions for each group were identified by electroluminescence (EL) in combination with IV measurements. Contact resistance measurements were carried out by the transmission line method (TLM) and then compared with scanning electron microscopy (SEM) to characterize the contact formation on the different surface topographies. To remove the metal and glass layer of the screen printed silver contact, an etching sequence of aqua regia and hydrofluoric acid was applied such as described in [8].

III. RESULTS AND DISCUSSION

A. Si pyramid height- and tip-rounding-variation

Table I provides an overview of the surface characterization and the contact performances for each pyramidal topology, including the initial polished surface. The surfaces area ratio (Sdr) is a useful parameter characterizing the topographic roughness. This factor expresses the increment of the interfacial surface area relative to the area of the projected perfectly polished surface. Thus, Sdr increases from flat to large pyramid distribution. In addition, the number of pyramids higher than 0.005, 0.2, 0.3 and 2.7 μm per area were calculated. These heights were chosen according with the glass layer thickness measurements by SEM ranging in average from 0.1 to 0.6 μm. The pyramid height was defined as the distance between the tip and the highest adjacent pyramid valley.

<table>
<thead>
<tr>
<th>Pyramid distribution</th>
<th>ρc [mΩcm²]</th>
<th>FF [%]</th>
<th>Sdr [%]</th>
<th>Number of Pyramids in (100μm)² higher than:</th>
<th>0.005 μm</th>
<th>0.2 μm</th>
<th>0.6 μm</th>
<th>2.7 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>flat</td>
<td>150</td>
<td>60</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ultra small</td>
<td>30</td>
<td>76</td>
<td>1.2</td>
<td>239</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>very small</td>
<td>1.5</td>
<td>80</td>
<td>4.4</td>
<td>571</td>
<td>206</td>
<td>34</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>small</td>
<td>1.7</td>
<td>79.9</td>
<td>17</td>
<td>239</td>
<td>226</td>
<td>137</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>standard (std)</td>
<td>1.2</td>
<td>79.9</td>
<td>72</td>
<td>222</td>
<td>215</td>
<td>153</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>large</td>
<td>1.2</td>
<td>79.8</td>
<td>81</td>
<td>192</td>
<td>188</td>
<td>129</td>
<td>18</td>
<td>0</td>
</tr>
</tbody>
</table>

For the flat surface the contact resistivity (ρc) is 150 mΩcm² resulting in a fill factor (FF) of only 60%. Note that our flat surfaces created by acidic inline polishing result in very smooth surfaces with Sdr of 0.5%. In comparison, saw damage etching by NaOH creates a flat surface with 1-3 μm deep step structure achieving a better contact and thus a lower contact resistivity and higher fill factor [8]. For ultra small pyramids with only 9 tips in (100 μm)² higher than 0.2 μm the values of ρc and FF already improve. For very small pyramids with 34 tips per (100 μm)² higher than 0.6 μm, ρc decreases by around two orders of magnitude in comparison with flat and FF improves to 80%. For very small to large pyramids similar values of ρc and FF were achieved, around 1.4 mΩcm² and 79.9% respectively. Note that only for standard and large pyramids the random pyramids cover the entire Si surface, see Fig.1(e)-(f).

For standard pyramids, ρc is 1.2 mΩcm² and FF is 79.9% achieving a solar cell efficiency of 17.9%. From standard to std. strongly rounded pyramids, ρc increases to 14 mΩcm² and FF decreases to 74.4 %. Note that Sdr decreases from 72% to 10%, which correlates with our LSM observations indicating that as the rounding was increased, the height and the 54.7° angle of the pyramids were reduced but the same pyramid base maintained. Moreover, the number of pyramids was decreased because the pyramids adjacent to each other were etched away.

In order to investigate the reason for the drastic contact resistivity changes, a selective etching was applied to remove the silver finger leaving in place the glass layer and the silver within and underneath it. The inhomogeneous glass layer covers the flat Si surface, see Fig 2(a). For very small and standard pyramids it can be observed that some tips are sticking out of the glass layer, containing imprints of etched-away Ag crystallites that were in direct contact with the silver finger, see Fig. 2(b)-(c). Although the std. strongly rounded pyramids are higher than the very small pyramids and contain many Ag crystallites, no Ag crystallites in direct contact were found, see Fig. 3(d). This explains why higher ρc and lower FF were measured for the std. strongly rounded distribution. Thus smaller pyramids are more capable of creating a better contact than strongly rounded pyramids.
As demonstrated above, for good contact formation, the sharpness is more important than the height of the Si pyramid due to the wetting behavior of the glass layer and creation of Ag crystallites in direct contact with the silver finger, which provide the best conductive path in the current transport mechanism [4]. However, it is observed that contact formation strongly depends on the excess phosphorous doping concentration [1], which is known to be higher at sharp tips. When the silver finger was selectively removed on a sample without emitter, see Fig. 3, in the tips of the pyramid imprints of Ag crystallites can be observed, which were in direct contact with the silver finger. This result indicates that without P doping not only Ag crystallites underneath the glass can be created, but also Ag crystallites in direct contact with the silver finger.

C. Multi-crystalline Si surfaces

For the isotextured mc-Si surfaces, we measured contact resistivities of 4.5 mΩcm² and fill factors of 78.8%. For flat mc-Si surfaces $\rho_C$ increases to 108 mΩcm² and FF drops to 70.8%. When selectively etching the silver finger in order to investigate the contact formation, as expected for isotextured mc-Si surfaces with its sharp texture peaks of around 3 µm height, imprints of Ag crystallites which were directly connected with the silver finger can be observed, see Fig. 4(a). After etching all contact components, imprints of Ag crystallites can be observed, which are mainly concentrated on the tips of the isotextured surface, see Fig. 4(b). Although a higher density of imprints of Ag crystallites for mc-polished than isotextured surfaces can be observed, see Fig. 4(c), no Ag crystallites in direct contact can be found. This result confirms that for low contact resistivity, a high density of Ag crystallites is not necessary to achieve a good contact, but the role of the wetting of the glass layer on the Si surfaces is more important for creating Ag crystallites in direct contact with the Ag-finger.

Honeycomb texture was applied to quasi mono- and mc-Si surfaces. On the investigated solar cells, see Fig. 5, the contact resistivity is 2.5 mΩcm² and fill factors of 76.8% are reached. Fig. 5(a) shows a top view of the honeycomb texture, after selective removal of the silver finger. As expected, some imprints of Ag crystallites which were directly connected with the silver finger can be observed as well as Ag crystallites underneath the glass layer, see Fig. 5(b). After etching all contact components, imprints of Ag crystallites can be observed, which are concentrated at the edges of the honeycomb surface, see Fig. 5(c).
IV. CONCLUSION

Several Si surface topographies were analyzed to gain a better understanding of the origin of the Ag crystallites in direct contact with the silver finger. On one hand, we observed that as the Si pyramid heights increased and exceeded the thickness of the glass layer, very similar values of contact resistivity and fill factor were achieved. These results were correlated with the presence of Ag crystallites, which were directly connected with the silver finger. On the other hand, as we increased the rounding degree of the Si pyramid tips, the contact resistivity deteriorated and the fill factor decreased despite the many Ag crystallites we observed underneath the glass layer. Thus pyramids covering only a few percent of the Si surfaces, which are smaller than strongly rounded pyramids, can create a better contact and achieve the same contact performance than a standard Si pyramidal texture. This result can be explained with the wetting behavior of the glass layer, which is highly dependent on the Si surface topography, resulting in glass free pyramid tips and thus creating Ag crystallites in direct contact. Due to these topography dependent surface energy variations, the same results can be reproduced for mc-Si material, where again a
better contact resistivity on isotextured than flat surfaces results, even though the latter contains more Ag crystallites underneath the glass. Also honeycomb textured Si features direct contacts at its elevated texture edges. Our observations indicate that not necessarily a high density of Ag crystallites is synonymous for a good contact, but of highest importance is how many of these Ag crystallites provide a direct connection with the silver finger. But it is known that also P doping is highest at texture tips, creating Si surface defects where Ag crystallites preferentially nucleate. However, on textured surfaces, also without P doping we observed Ag crystallites underneath the glass layer and more importantly, in direct contact with the silver finger, because the glass coverage on Ag crystallites depends on the corresponding surface energies produced by the abrupt surface features.

ACKNOWLEDGEMENT

The research leading to these results has received funding from the Seventh Framework Programme under grant agreement n° 228513.

REFERENCES


