FUNDAMENTAL STUDIES ON THE FRONT CONTACT FORMATION RESULTING IN A 21% EFFICIENCY SILICON SOLAR CELL WITH PRINTED REAR AND FRONT CONTACTS

M. Hörteis, J. Benick, J. Nekarda, A. Richter, R. Preu, S. W. Glunz
Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, D-79110 Freiburg, Germany
Phone: +49-761-4588-5493; Fax: +49-761-4588-9250;
email: matthias.hoerteis@ise.fraunhofer.de

ABSTRACT

The contact formation on high efficiency solar cells using a high temperature process is the subject of this research. The chemical reactions between ink components and solar cell during the contact firing process are studied in detail by thermal gravimetric - differential thermo analysis. The mechanism behind the etching process and the opening of the dielectric layer are explained and the impact of the glass frit is investigated. Based on these studies, a seed layer ink was developed, optimized and tested on silicon solar cells. The developed ink was applied on high efficiency solar cells with printed front and rear contacts. At the rear side, we used a firing stable passivation layer consisting of Al2O3 and SiNx, which additionally resists the reactive compounds of the screen printed Al-paste. After applying laser fired contacts at the rear and light induced silver plating at the front, cell efficiencies of $\eta = 21\%$ and fill factors of 81% could be measured.

INTRODUCTION

For industrial fabrication of silicon solar cells, the dominant metallization process is still based on printing technologies. Independent of the technique in use, screen printing, ink jet printing, extrusion or jet printing, the main challenge is to achieve finer metal lines with high lateral conductivity and excellent contact properties. This can be achieved by fine line printed and successively light induced plated contacts [1,2]. All printing technologies have one thing in common: it is always a metal ink/paste that is deposited, and the contact is formed during a high temperature step. The contact materials are fired through the anti-reflection coating and a contact between emitter and front side grid is formed. The high temperatures are necessary to open the ARC and to support the reaction between contact ink and the silicon. Thus, the firing step is the most crucial part for the contact formation and thus for the ink development. In addition to investigation by the authors at the cell level [3,4] we have studied the chemical reactions occurring during the firing process between the ink components and the solar cell on a more fundamental level. The reactions are investigated by differential-thermo gravimetric analysis, bringing ink ingredients like lead oxide, bismuth oxide, glass frit, and silver in reaction with silicon and silicon nitride. The results were used to develop a seed layer ink which, first of all, allows the formation of a low ohmic contact on a lowly doped emitter in order to reduce the recombination losses and to increase the blue response and thus the efficiency potential of a solar cell. Additionally, the shading needs to be reduced by optimizing the front side grid, especially by using fine line printed contacts in combination with plating. The seed ink, developed at Fraunhofer ISE – which is called SISC (seed layer ink for the metallization of solar cells) - was already tested on emitters with a sheet resistivity up to $R_{sh} = 130\, \Omega/\text{sq.}$ [5] and successfully applied on a high efficiency solar cell where cell results up to $\eta = 20.3\%$ were achieved [2]. In this paper we present the fundamental investigations upon which the ink development is based. Additionally, we combined our optimized front side, emitter and metal grid, with different rear side passivation layers and metallization techniques on high-efficiency solar cells. The rear side dielectric in this cell concept needs to meet two demands. The passivation should resist high temperatures; the solar cell is exposed during the firing step and the passivation layer should not be attacked by the screen printed Al-paste. It could be demonstrated that a stack system of ALD-Al2O3 and SiN, is not influenced by a firing step and keeps its passivation quality. Similar results have been found elsewhere [6]. It was also proven that a layer of 70 nm SiN can be used to protect the passivation layer from Al-paste during contact firing [7]. In this solar cell concept we combined a thin ALD-Al2O3 passivation layer with a stable SiN, protection layer.

EXPERIMENTAL

Thermo-gravimetric differential thermal analysis (TG-DTA), see Fig. 1, was used to study the reaction mechanism behind the front-contact formation in a firing step. The TG-DTA uses the temperature difference between the sample and a reference during a controlled-temperature program. A DTA sample holder consists of two ceramic cups, each connected to a thermocouple (TC1, TC2). The sample holder is placed in a furnace on a sensitive balance. During the controlled-temperature program, the measured temperature of the reference, usually an empty cup, and the sample can be different, which is dependent on the chemical reactions or phase changes of the studied samples. It can distinguish between exothermic reactions, where additional reaction heat is produced (such as due to condensation energy), and endothermic reactions, where reaction heat is “consumed” (such as during melting). The
difference in the thermal voltage, as measured by the thermocouples, is plotted as a function of time, which reflects the time-dependence temperature. In addition the mass signal is monitored. In all of the TG-DTA diagrams a strong offset in the DTA signal is visible every time the temperature program changes. Due to the different masses of the reference and the sample and due to the fact that they are spatially separated, the two possess different temperatures. This, however, can be neglected, as it is related to the measurement unit. In our experiments we used a TG-DTA from Netzsch STA 409C, an alumina sample holder, and type-S thermocouples. After one temperature cycle, the resulting products were analyzed using SEM-images and EDX-analysis.

The seed layer ink, which was developed based on the TG-DTA results, was applied on high efficiency solar cells. The used cell structure is shown in Fig. 2. We used 0.5 Ωcm p-doped FZ-base material. The front side has a shallow emitter with a sheet resistance of $R_{\text{SH}} = 110$ Ω/sq, on a randomly textured surface, which was passivated with a PECVD-nitride layer. The front side grid was jet printed with a seed layer of width $w_c = 25$ µm, fired in an RTP-furnace, and plated with light induced silver, resulting in a total finger width of $w_f = 45$ µm. The optimum finger distance was calculated using the simulation tool Gridsim to $d = 1.3$ mm.

At the rear side two different stack systems were investigated and compared to a standard screen printed Al-BSF:

- a) A passivation layer of 10 nm atomic layer deposited (ALD) $\text{Al}_2\text{O}_3$ covered with a layer of 90nm PECVD $\text{SiN}_x$, metalized by screen printed (SP) aluminum which is co-fired with the printed front side and contacted by laser fired contacts (LFC).
- b) A passivation layer of 10 nm atomic layer deposited (ALD) $\text{Al}_2\text{O}_3$ covered with a layer of 90nm PECVD $\text{SiO}_2$, metalized by thermal high rate deposition of aluminum [8] followed by LFC-contacts.

**FUNDAMENTAL REACTIONS**

Before an ink can be designed, the basic reactions of the ink components and the solar cell need to be understood. Pastes or inks used to contact silicon solar cells mainly contain a contact metal and a glass frit. The metal is responsible for the electrical contact and the lateral conductivity, and the glass frit is used to open the ARC and to promote the contact formation. The most important component of the glass frit is a metal oxide which is able to react with silicon at firing temperatures up to approximately $T = 850^\circ$C. Commonly used oxides are lead oxide, or in case of a lead-free ink, bismuth oxide.

**Basic Reactions between ink components and Silicon**

Initially, the reaction between PbO/Bi$_2$O$_3$ and silicon was studied in order to explain why the reactive component is lead oxide or bismuth oxide and why it is typically incorporated into a glass matrix. Further on, the influence of silver on the reaction was studied and the origin of silver crystallites at the contact interface is explained. More details are presented elsewhere [9].

The reactive component in a contact metal paste is the glass frit, in particular the lead oxide or bismuth oxide, incorporated in a glass. The idea to transfer the reactive oxides into a glass frit, instead of using the oxide directly, has several advantages. On the one hand, the glass melts at a lower temperature than the pure oxide, wetting the entire contact area homogenously, and the reactive oxide is brought in close contact with the silicon, whereas on the other hand the redox reaction given in Eq.1 occurs in a broad range of temperatures, making the contact formation during a fast firing step more controllable. In Fig. 3 the DTA measurement between lead oxide and
silicon and Bi₂O₃ and Si shows significant peaks at 650°C and 720°C. Bismuth oxide reacts at a slightly higher temperature and releases more energy during the reaction. These results are quite consistent with values found in the literature, where the Gibbs free energy change at 1000K for the studied reaction is given as \( \Delta G_{PbO} = -59.2 \) kcal/mol and \( \Delta G_{Bi_2O_3} = -191.9 \) kcal/mol [10]. Both reactions between silicon and the oxides are abrupt exothermal reactions, which are not easy to control during a fast firing of a solar cell. That is one of the reasons why the oxide is incorporated into a glass frit. The redox reaction is moderated and the process window for contact firing is increased.

The glass frit, or more correctly its reactive components like lead oxide, is reduced to elemental lead and at the same time silicon is oxidized. The oxidized silicon is solved and added to glass, which is present as an insulating layer at the contact interface. The same reaction (Eq.2) occurs when Si₅Nₓ is used as an antireflection or passivation layer. With other words, a glass frit (lead oxide) is necessary to promote the contact formation, but too much of it is detrimental to the electrical contact.

\[
2PbO + Si \rightarrow SiO_2 + 2Pb \tag{1}
\]
\[
12PbO + 2Si₅Nₓ \rightarrow 6SiO_2 + 12Pb + 4N_2 \tag{2}
\]

In a further experiment, silver is added and the reaction of the simplest contact ink (silver and lead oxide) with silicon is studied. The DTA signal is identical to the one shown in Fig. 3 apart from the cooling sequence, see Fig. 4. During cooling, two further exothermic peaks are visible, at \( T = 300°C \) and at \( T = 600°C \). Corresponding phases can be found in the Ag-Pb phase diagram. After cooling, the reaction products are analyzed by SEM images and EDX. The products in the crucible are separated into two phases, a silicon-glass phase Fig. 5 (left) and a metal phase shown in Fig. 5 (right). The metal phase consists of an Ag-rich and a Pb-rich phase. It is noticeable that all the silver has been molten even if the temperature was kept below the melting point of silver and below the silver-silicon eutectic. The silver rich phase re-crystallizes in the form of cubic silver crystallites, which are interconnected with the lead-rich Ag-Pb eutectic. The EDX analysis of the reaction products is in good agreement with the expected Ag-Pb phase according to the Ag-Pb phase diagram. For the silver-rich phase, a content of 98.1at% Ag is found and for the Pb-rich eutectic, a composition of Ag·Pb of 3.9:96.1at%.

The silicon-glass phase, see Fig. 5 (left) is characterized by silicon particles embedded in a glass matrix. A layer of small metal precipitates is found in the glass layer, especially in the vicinity of silicon particles; quite large Ag-Pb precipitates are additionally homogenously distributed over the glass phase. Glass close to silicon particles has a low lead content and increased silicon content, whereas glass distant from Si-particles contains a higher lead content. During the redox reaction, silicon is oxidized to silicon dioxide, which is incorporated into the already existing glass layer (increased Si content). At the same time, lead oxide is reduced to lead and an Ag-Pb phase can be formed. The Ag-Pb melt condenses in the form of silver crystallites and as a lead-silver eutectic.
The reaction and therefore the contact formation can be promoted by process parameters like temperature, time, and atmosphere. Under the excess of oxygen the redox reaction is more effective. In addition, the higher the firing temperature and the longer the wafer is kept at peak temperature, the more and the larger Ag-Crystallites can be found, see Fig. 6. However, this does not necessarily mean the higher the crystallite density, the better is the electrical contact. For the shown samples, fired at \( T = 700^\circ\text{C} \) (Fig. 6 left) and \( T = 840^\circ\text{C} \) (Fig. 6 right), we measured a normalized contact resistance of \( R_c \times W = 0.7 \Omega \text{cm} \) (700°C) and \( R_c \times W = 2.0 \Omega \text{cm} \) (840°C). The explanation is the thickness of the glass layer, formed at the contact interface. The larger the Ag-crystallites, the more silicon is oxidized and solved in the glass, which forms an insulating layer.

![Figure 6: SEM images of Ag-crystallites, grown at the contact interface at different firing temperatures: left 700°C and right 840°C.](image)

Therefore, the ink development can not be separated from the firing process. The reactive oxides in the ink allow the formation of contact crystallites; however, their size and density are determined by the firing step. Both the glass content and the contact firing were optimized for the developed ink in a previous study with the goal to form a low ohmic contact on emitters with a high sheet resistivity \([11]\).

**RESULTS ON HIGH EFFICIENCY SOLAR CELLS**

For the solar cells presented in this work, we used a shallow emitter with a sheet resistance of \( R_{side} = 110 \Omega/\text{sq} \), on which the front side grid was adopted according to the contact parameters like contact resistance \( \rho_c = 2-3 \text{m} \Omega \text{cm}^2 \), line conductivity \( \rho_L = 2.0 \times 10^{-8} \Omega \text{m} \), and finger width \( w_f = 45 \mu\text{m} \) (the fired seed layer has a width of \( w_c = 20 \mu\text{m} \)). Using the simulation program Gridsim, we calculated an ideal contact distance of \( l = 1.3 \text{mm} \), resulting in a shaded area fraction of only 3.3%. Fig. 2 shows the used solar cell structure. For the rear side, we compared three different structures, one using a standard Al-BSF and two with a stack system of plasma assisted atomic layer deposited (PA-ALD) Al\(_2\)O\(_3\) and PECVD Si\(_N_x\) / SiO\(_3\). In contrast to previous studies, where we used a thick thermal oxide for the rear passivation \([2,5]\), we combined a thin layer \( d = 10 \text{nm} \) of atomic layer deposited (PA-ALD) Al\(_2\)O\(_3\) with a capping layer \( d = 90 \text{nm} \) of either Si\(_N_x\) or SiO\(_3\), depending on the used rear side metallization, screen printed Al-paste or evaporated Al. For the case where screen printed aluminum is used as a rear metallization, the Al\(_2\)O\(_3\) passivation layer was combined with a PECVD Si\(_N_x\) layer. The thermal stability of a Si\(_N_x\) capping layer on top of a thin thermal oxide and its resistance to screen printed and fired Al-paste was demonstrated by L. Gautero \([7]\). The same silicon nitride was used to protect the Al\(_2\)O\(_3\) passivation layer during the co-firing of front- and rear side contacts. The contact firing was performed in an RTP furnace at a peak temperature of \( T = 820^\circ\text{C} \). During the firing step, no Al-Si eutectic is formed, and also no electrical contact is produced, as the dielectric layer between Si-base and aluminum is present. Therefore the passivation layer was locally penetrated and a contact was formed by laser fired contacts (LFC), which was investigated for screen printed Al-contacts by J. Nekarda \([12]\). The solar cells using SiO\(_3\) as a capping layer on Al\(_2\)O\(_3\) were first fired and then metalized at the rear with a 2 µm thin layer of thermal high rate evaporated aluminum. The use of screen printed Al-paste is not possible, as the Al-paste would react with the silicon oxide and damage the Al\(_2\)O\(_3\)-passivation layer. The actual rear side contacts were again formed by LFC. Theoretically the solar cells where SiO\(_3\) is used as a capping layer are supposed to have an advanced optic. The difference in the ideal current density between a SiO\(_3\) and a Si\(_N_x\) capping layer was calculated using the ray tracing program SUNRAYS \([13]\). For the given cell structure the current density is \( j_{sc,id} = 41.7 \text{mA/cm}^2 \) for SiO\(_3\) and \( j_{sc,id} = 41.3 \text{mA/cm}^2 \) using Si\(_N_x\) as a capping. However, a difference is neither visible in the quantum efficiency nor in the reflectance measurement, see Fig. 7, and the IV-measured current densities are almost the same for the two cell structures, see Table 1. In contrast to the BSF-solar cell, the passivated solar cells have higher quantum efficiencies in the long wavelength region and thus an increased \( j_{sc} \) by almost 3 mA/cm\(^2\). The open circuit voltages are also increased by approximately 15 mV, demonstrating that both stack systems can be used as rear side passivation.

![Figure 7: Quantum efficiencies and reflectance measurements for rear side passivated solar cells and a solar cell with an aluminium BSF at the rear.](image)
The IV-results for all tested solar cells, including the values for a solar cell passivated with a thick thermally grown SiO$_2$ at the rear side, are summarized in Table 1. The front side grid for the SiO$_2$ passivated solar cell was not optimized, explaining why it is limited in $J_{sc}$. In general, the IV-values for the rear side passivated solar cells are higher compared to the solar cell using an Al-BSF. Similar values for $V_{oc}$ have been achieved for all passivated solar cells, demonstrating comparable passivation qualities. It also proves that the stack of Al$_2$O$_3$ and SiN$_x$ is stable under co-firing using a screen printed Al paste at the rear side.

<table>
<thead>
<tr>
<th>Rear side</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thick thermal SiO$_2$ + PVD-Al + LFC [14]</td>
<td>658</td>
<td>38.5</td>
<td>81.1</td>
<td>20.6*</td>
</tr>
<tr>
<td>AL-BSF</td>
<td>645</td>
<td>37.5</td>
<td>79.9</td>
<td>19.3*</td>
</tr>
<tr>
<td>ALD Al$_2$O$_3$ + SiN$_x$ + Screen print Al + LFC</td>
<td>656</td>
<td>40.3</td>
<td>80.0</td>
<td>21.2*</td>
</tr>
<tr>
<td>ALD Al$_2$O$_3$ + SiO$_x$ + PVD-Al + LFC</td>
<td>663</td>
<td>40.4</td>
<td>80.4</td>
<td>21.5*</td>
</tr>
</tbody>
</table>

Table 1 IV-parameters for the best solar cells with different rear side structures. The solar cell material is FZ-Silicon and the solar cell size is 4 cm$^2$.

*All results were independently confirmed by CalLab ISE.

CONCLUSION

The fundamental reactions between a silver contact ink and an n-type silicon surface were investigated by thermogravimetric differential-thermal analysis. The reaction mechanism between lead oxide and silicon in the presence of silver were clarified. Lead oxide reacts exothermically with Si at a temperature of 680°C; the contact formation with silicon is actively promoted and silver contact crystallites are formed from a liquid Ag-Pb phase. The measurements together with results on solar cells were used to develop a seed layer ink that was applied to high efficiency solar cells with different rear side structures: ALD Al$_2$O$_3$ + SiN$_x$ + SP-Al, ALD Al$_2$O$_3$ + SiO$_x$ + PVD-Al. Both stack systems are stable under fast firing, and for the case where SiN$_x$ was used as a capping layer, even a screen print Al-paste could be used as rear side metallisation. For a full printed and co-fired solar cell, an efficiency of η=21.2% could be measured.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the contribution of other members of ISE, A. Leimenstoll and S. Seitz for cell preparation in the clean room, N. Kohn for PECVD-deposition, K. Zimmermann for the Al$_2$O$_3$ ALD, D. Schmidt and A. Filipovic for printing and firing of the cells and E. Schäffer and J. Spannagel for electrical solar cell characterization.

REFERENCES


