SUCCESSFUL IMPLEMENTATION OF THE MICROWAVE INDUCED REMOTE HYDROGEN PLASMA PASSIVATION IN A STANDARD MULTICRYSTALLINE SILICON SOLAR CELL PRODUCTION LINE

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ABSTRACT: A major part of the costs of crystalline silicon solar cell modules is caused by the silicon wafer. In order to reduce this cost factor one can use multicrystalline instead of CZ silicon material. A problem of multicrystalline silicon (mc-Si) is a lower minority carrier lifetime and a larger variation in the electrical parameters of the material which results in a broader distribution of the obtained efficiencies. Hydrogen passivation can be a key technology to increase the electrical parameters of low quality regions for example at the corners of an ingot in order to reduce the width of the efficiency distribution in an industrial cell process. In this study we could successfully implement the microwave induced remote hydrogen plasma (MIRHP) passivation technique in the standard mc-Si solar cell production line at Eurosolare. Due to the MIRHP process the increase in the cell efficiency (cell area: 100 cm²) made out of EUROSIIL material taken from the border of the ingot and Sumitomo Sitix EMC material is nearly 10% relative. For the further demonstration of the industrial importance of this passivation technique first results of the application of the MIRHP process in the industrial like pilot line at Solarex are given.

Keywords: Vienna Conference - 1: Multi-Crystalline - 2: Passivation - 3: TiO₂

1. INTRODUCTION

The cost of the Si wafer contributes to about 46% of the total PV module costs [1] which can be reduced by the use of multicrystalline silicon (mc-Si) instead of monocrystalline Si. The higher recombination activity of mc-Si due to higher defect densities and higher impurity concentrations [2, 3] makes defect passivation techniques such as hydrogen passivation a key issue for high efficiencies on mc-Si solar cells. This fact is even more valid for the next generation Si material such as ribbon or crystalline thin film silicon. Currently, two very promising candidates for mc-Si hydrogen bulk passivation with industrial importance are under development:

- the covering of the cell front side by a hydrogen rich silicon nitride antireflection coating (SiN ARC) deposited by plasma enhanced chemical vapor deposition (PECVD) followed by driving the hydrogen during the contact firing step into the cell or
- the direct incorporation of atomic hydrogen during a microwave induced remote hydrogen plasma (MIRHP) process in combination with the deposition of a standard AR coating as capping layer against the out-diffusion of hydrogen during contact firing.

Two alternative PECVD processes are available the remote [4] and the direct [5] PECVD where only the last one has proven until now the capability of producing highly efficient mc-Si cells. The major advantage of the PECVD process is the combination of the deposition of an AR coating and a bulk passivating agent. The major obstacle in the dissemination of the PECVD SiN process in PV industry is the limited throughput of the commercially available batch-type PECVD reactors combined with the not yet solved automation of the loading and unloading of the systems resulting in not negligible deposition cost.

Currently different different manufacturer of PECVD systems are busy to overcome those limitations. As an possible alternative to the PECVD SiN process we investigated the MIRHP technique applied before the deposition of an ARC and the contact firing. In the following the MIRHP process will be shortly described and its implementation in an industrial environment discussed.

2. THE MIRHP PROCESS

The MIRHP passivation technique used in this study is well described in literature [6-8]. Because of the spatial separation of the generation of H-atoms from the place of its in-diffusion in silicon the MIRHP process does not seriously damage the surface of the cell like most of the other H-passivation techniques such as direct hydrogen plasma passivation [7] and hydrogen ion implantation [9]. The MIRHP has the following attractive features:

- compatibility with standard industrial process sequences using a conventional TiO₂ ARC as shown in this paper,
- almost complete bulk passivation within passivation times of 30 min [10],
- simple 1 Torr vacuum technology with short loading and heating times,
- MIRHP passivation conditions can be directly adjusted to the mc-Si material in use,
- possible full automatic wafer handling,
- simple construction of the MIRHP system and
- MIRHP inline systems thinkable.

3. EUROSOolare

3.1 Cell process

The multicrystalline silicon solar cell production line at Eurosolare consists of the emitter diffusion, the deposition of a titanium dioxide antireflection coating (TiO₂ ARC)
done by atmospheric pressure chemical vapor deposition (APCVD) followed by the printing of the front and back contacts and the firing through the TiO$_2$ (see Fig. 2). Also shown in Fig. 2 is the additional MIRHP process which has to be carried out after the high temperature step of the emitter diffusion and before the coating of the front surface with an ARC. In this passivation concept the ARC has to act as a barrier against the out-diffusion of hydrogen during the contact cofiring step. The function of the annealing process after the deposition of the ARC is explained in the following section. In this first optimization study a long passivation time of 2 h was used, however we have shown that for most mc-Si materials the cell performance improves mainly within the first 30 min [10].

<table>
<thead>
<tr>
<th>Cell processing sequence at Eurosolare</th>
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<tbody>
<tr>
<td>1. NaOH saw damage etching</td>
</tr>
<tr>
<td>2. emitter diffusion</td>
</tr>
<tr>
<td>3. P-glass etching</td>
</tr>
<tr>
<td>4. optional: MIRHP process (2h, 350°C)</td>
</tr>
<tr>
<td>5. TiO$_2$ ARC with APCVD</td>
</tr>
<tr>
<td>6. Annealing of the TiO$_2$ ARC (30 min, 280°C or 350°C)</td>
</tr>
<tr>
<td>7. Printing of front (Ag) and back (Ag/Al) contact</td>
</tr>
<tr>
<td>8. Cofiring</td>
</tr>
<tr>
<td>9. Cell characterization</td>
</tr>
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</table>

Fig. 2: Processing sequences of the screen-printed silicon solar cells at Eurosolare. The additional processing steps which are necessary to implement the MIRHP process are written in bold letters.

3.2 Results

It was found that an annealing step of the TiO$_2$ ARC prior to the contact printing and cofiring was beneficial to further improve the cell performance due to the MIRHP process. During this annealing step the TiO$_2$ layer became thinner and more dense which could be seen as a change of the color from light-blue to dark blue. The more dense TiO$_2$ layer acts as a barrier against the diffusion of hydrogen out of the cell during the contact cofiring. Fig. 3 shows the short circuit current density $J_{SC}$ and the open circuit voltage $V_{OC}$ of cells based on EUROSIL C50 mc-Si base material with an annealing step (at 280°C or 350°C) of the TiO$_2$ layer prior to the H-passivation compared to non-passivated reference cells. The cells with the annealing step done at 350°C give better $J_{SC}$ and $V_{OC}$ values because the more dense TiO$_2$ blocks the out-diffusion of hydrogen more effectively during the cofiring of the contacts. As seen in Fig. 3 the use of a higher annealing temperature might further improve the cell performance. With the higher annealing temperature the annealing time can be reduced which is important to keep the throughput high. Table I and II show the mean values of the illuminated IV parameters of H-passivated and unpassivated screen-printed cells made on different mc-Si base materials.

Table I: Using EUROSIL P48 base material (taken from the border of the ingot) with different effective bulk lifetimes a clear improvement of the mean illuminated IV parameters (average values of 10 cells) after a MIRHP process was obtained.

<table>
<thead>
<tr>
<th>mc-Si material</th>
<th>$\rho_{baso}$ [\Omega cm]</th>
<th>$t_{eff, baso}$ [\mu s]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>$V_{OC}$ [mV]</th>
<th>FF [%]</th>
<th>$\eta$ [%]</th>
<th>$\Delta \eta_{abs}$ (\Delta$\eta_{oc}$)[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eurosil P48</td>
<td>1-1.5</td>
<td>ca. 2.5</td>
<td>26.2±0.2</td>
<td>571±1</td>
<td>71.3±1.7</td>
<td>10.1±0.2</td>
<td>+0.5 (+5)</td>
</tr>
<tr>
<td>MIRHP</td>
<td>no</td>
<td>yes</td>
<td>585±2</td>
<td>585±2</td>
<td>72.5±1.7</td>
<td>10.6±0.2</td>
<td>+0.9 (+9)</td>
</tr>
</tbody>
</table>

Table II: Using EUROSIL C50 (taken from the border of the ingot) and EMC base material a clear improvement of the mean illuminated IV parameters (average values of 4 cells) after a MIRHP process was obtained.

<table>
<thead>
<tr>
<th>mc-Si material</th>
<th>$\rho_{baso}$ [\Omega cm]</th>
<th>$t_{eff, baso}$ [\mu s]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>$V_{OC}$ [mV]</th>
<th>FF [%]</th>
<th>$\eta$ [%]</th>
<th>$\Delta \eta_{abs}$ (\Delta$\eta_{oc}$)[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eurosil C50</td>
<td>0.5</td>
<td>2.5</td>
<td>25.4±0.1</td>
<td>591±1</td>
<td>71.8±1.6</td>
<td>10.4±0.2</td>
<td>+0.8 (+8)</td>
</tr>
<tr>
<td>EMC</td>
<td>1</td>
<td>1.5-2.5</td>
<td>26.5±1</td>
<td>578±2</td>
<td>72.9±0.1</td>
<td>11.2±0.4</td>
<td>0.6 (+2)</td>
</tr>
</tbody>
</table>

Fig. 3: Influence of the MIRHP-passivation on the illuminated IV parameters averaged over 6 screen-printed solar cells (area 100cm$^2$). Prior to the MIRHP-passivation an annealing step of the TiO$_2$ layer at 280°C or 350°C was carried out.

Internal quantum efficiencies (IQE) calculated from spectral response and reflection measurements show a clear increase in the long wavelength region of hydrogen passivated compared to non-passivated solar cells based on EMC material (see Fig. 4). Due to the MIRHP process $J_{SC}$ increases by 1.3 mA cm$^{-2}$, $V_{OC}$ by 7 mV and the absolute cell efficiency by 0.7%. Due to the MIRHP process the minority carrier bulk diffusion length $L_b$ increases from...
115 \mu m to 171 \mu m. I_b was determined by a linear fit of I_{off} to the inverse internal quantum efficiency according to the Basore extended spectral analysis [11]. The improvement of the dark current characteristics of the H-passivated cell compared to the non H-passivated cell is seen in Fig. 5.

Fig. 4: Influence of the MIRHP passivation on the IQE of solar cells based on EMC material. Due to the MIRHP process the minority carrier bulk diffusion length L_b increases from 115 \mu m to 171 \mu m.

![Fig. 4: Influence of the MIRHP passivation on the IQE of solar cells based on EMC material.](image)

Fig. 5: The measurement of the dark current characteristics of the same cells as in Fig. 4 show the reduction of the second diode current and the increase of the shunt resistance for the H-passivated cell which is due to a passivation of the space charge region.

![Fig. 5: The measurement of the dark current characteristics of the same cells as in Fig. 4 show the reduction of the second diode current and the increase of the shunt resistance for the H-passivated cell which is due to a passivation of the space charge region.](image)

Tab. III: Using compensated EUROISIL C50 base material nearly no improvement of the mean illuminated IV parameters (average values over 10 cells) after a MIRHP process was obtained.

<table>
<thead>
<tr>
<th>Cells based on compensated C50 Si material</th>
<th>$\rho_{bulk} [\Omega cm]$</th>
<th>$\eta_{eff}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIRHP no</td>
<td>590.8±2.2</td>
<td>72.4±1.5</td>
</tr>
<tr>
<td>MIRHP yes</td>
<td>592.4±0.9</td>
<td>10.7±0.2</td>
</tr>
<tr>
<td>$\Delta \rho_{bulk}$ (MIRHP) [%]</td>
<td>+0.3 (+3)</td>
<td></td>
</tr>
</tbody>
</table>

4. SOLAREX

4.1 Cell process

In contrast to the production line at Eurosolare the TiO₂ at Solarex is deposited after the firing of the contacts [12] (see Fig. 6).

![Cell processing sequence at Solarex](image)

Fig. 6: Processing sequences of the screen-printed silicon solar cells at Solarex as applied in this study. Written in bold letters is the additional MIRHP processing step.

4.2 Results

In order to find the optimum MIRHP passivation time uncoated solar cells of the processing sequence shown in Fig. 6 were passivated by the MIRHP process. For this investigation cast mc-Si base material from Solarex was used. From measurements of the dark current characteristics (see Fig. 7) it is obvious that a clear improvement in cell performance is obtained for MIRHP process times up to 90 min. However during the following 90 min a degradation in cell performance occurs which is seen in the increase of the dark current density and the decreases in $J_{SC}$ and $V_{OC}$. During the first 90 min $J_{SC}$ increases by 0.6 mACm⁻² and $V_{OC}$ by 10 mV.
The influence of the MIRHP process on the dark current characteristics of two mc-Si cells one with (cell B) and one without (cell A) TiO$_2$-ARC are shown in Fig. 8. The dark current density, $J_{sc}$ and $V_{oc}$ of cell A improve due to the MIRHP process, whereas only a small change is seen on the TiO$_2$ coated cell B which shows that the diffusion of hydrogen is impeded by the TiO$_2$ layer.

**Fig. 7**: Influence of the MIRHP process time on the dark current characteristics of one mc-Si cell based on Solarex material. A clear improvement is seen for process times up to 90 min. However during the following 90 min a degradation in cell performance occurs.

**Fig. 8**: Influence of the MIRHP process on the dark current characteristics of two mc-Si cells one with (cell B) and one without (cell A) TiO$_2$-ARC. $J_{sc}$ and $V_{oc}$ of cell A improve due to the MIRHP process whereas only a small change is seen on the TiO$_2$ coated cell B which shows that the diffusion of hydrogen is impeded by the TiO$_2$ layer.

**CONCLUSIONS**

The successful implementation of the MIRHP process in a solar cell production line at Eurosolare could be demonstrated. Due to the MIRHP process the cell efficiency increases of nearly 10% relative for Eurosol material taken from the border of the ingot and for EMC material. Our results suggest that the MIRHP process together with a conventional TiO$_2$ ARC is an alternative to the PECVD process for the bulk passivation. Further work will be done to develop an industrial prototype MIRHP system. We expect that with the MIRHP technique the industrial bench mark of 3 s per wafer can be reached.

**ACKNOWLEDGEMENTS**

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