Recrystallized Silicon Thin-Film Solar Cells on Zircon Ceramics

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Abstract — This work describes the processing of recrystallized silicon thin-film solar cells and its typical defects. Zircon (ZrSiO₄) ceramic substrates of technical grade with potential production costs of < 20 €/m² were used. Those substrates were encapsulated in crystalline silicon carbide, deposited by atmospheric pressure chemical vapor deposition (APCVD). The active silicon layers were also formed using APCVD. Zone-melting recrystallization (ZMR) was used to enlarge Si grains. Si films crystallized on SiC show characteristic $\Sigma 3$ twin grain boundaries parallel to the growth direction. The Si crystals achieve widths up to several mm and lengths of several cm. Solar cells made from such material achieved open circuit voltages up to 566 mV on zircon and up to 600 mV on equally processed mc-Si.

Index Terms - zone-melting recrystallization, crystalline silicon thin-film solar cells, low-cost ceramics

I. INTRODUCTION

Recrystallized silicon thin-film solar cells are capable of combining the advantages of crystalline silicon material with the advantages of conventional thin-film module concepts. This includes the long term stability of c-Si, the well understood electrical properties and advanced processing techniques, known from wafer processing, which can be applied. Furthermore this concept uses much less high purity silicon, compared to wafers, and the active area can be structured to form integrated interconnected modules [1]. This helps to decrease costs and maintain comparably high conversion efficiencies. On reference material, like oxidized Si wafers, cell efficiencies >16 % have been reported [2, 3].

For industrialization, this concept needs a substrate capable of meeting the demanding requirements on thermal- and chemical stability as well as overall cost. One candidate is sintered zircon (ZrSiO₄) ceramic. Plates of this material can potentially be produced in large areas at costs well below 20 €/m². Such a material is porous and contaminated with more than 400 ppm of iron and many more transition metals. Therefore a stable diffusion barrier is mandatory. Crystalline silicon carbide (SiC) is used in this work to form the intermediate layer, which prevents diffusion of transition metals and dopants and closes open porosity.

Depositing a silicon film directly on a SiC intermediate layer, results in poor electrical properties of the silicon, caused by small grain sizes. Forming a high-quality silicon absorber layer on such encapsulated, low-cost ceramics can be realized using zone-melting recrystallization (ZMR). After epitaxial thickening, such films can be used to make solar cells similarly to c-Si wafers.

II. SAMPLE PREPARATION

The used zircon ceramic substrates were lasered to sizes of 50 x 50 mm² and cleaned using acetone and 2-propanol to remove possible organic residues. A surface cleaning for transition metals was not applied, as the bulk contamination is comparably high anyway. 0.01 Ωcm p-type, mc-Si substrates were used as reference samples.

All samples were encapsulated with 10 µm of crystalline silicon carbide, deposited at 1100°C and 1 atm from methyltrichlorosilane (CH₃SiCl₃) and hydrogen [4]. Some samples were additionally coated with 1 µm of SiO₂ on one side to increase the reflectivity at the back and improve optical confinement.

![sequence of formation of recrystallized silicon thin-films](image)

Fig. 1. Sequence of formation of recrystallized silicon thin-films suitable for solar cell processing.

This is followed by the deposition of 5 µm high purity, highly doped poly-Si deposited from trichlorosilane (HSiCl₃). For ZMR, a SiO₂ capping layer is applied on top of the Si film to protect the liquid silicon from potential contaminations in the gas phase of the ZMR tool and to prevent the formation of silicon droplets [5]. This SiO₂ capping is removed afterwards using hydrofluoric acid, and the recrystallized Si film is chemically polished. The recrystallized seed layer is epitaxially thickened to 15 – 25 µm forming the absorbing silicon layer. The detailed process sequence is depicted in Fig. 1.
All the depositions, except the SiO₂ films, are done at atmospheric pressure, which allows for in-line processing and large throughputs needed for industrialization [6].

III. RESULTS AND DISCUSSION

A. Orientation and Appearance of Recrystallized Si Films

The appearance of recrystallized Si films differs depending on the used IL. When crystallizing Si on top of a SiC IL, the grains mostly grow in <110> direction. Depending on growth conditions (scan speed, temperature, film thickness, etc.) grain width can range from several 100 µm up to several cm. The length of the grains can span the whole substrate. The grains tend to form large amounts of ∑3 twin grain boundaries parallel to the growth direction. This crystallization behavior seems to be unique to SiC intermediate layers, since on SiO₂ intermediate layers, faceted growth in <100> direction is most pronounced and twinning is less common [7]. A picture of a recrystallized and epitaxially thickened Si film on a zircon substrate is depicted in Fig. 2.

![Fig. 2. Picture of ZMR-Si film after epitaxial thickening on SiC encapsulated zircon substrate.](image)

The existence of ∑3 twin grain boundaries could be verified using electron backscatter diffraction (EBSD) [8, 9] on a cross-section perpendicular to the scan direction. When treated with a defect sensitive etching solution, like Secco etch, the twin grain boundaries become visible, as well as line defects (visible as etch pits) as depicted in Fig. 3. Twin grain boundaries are considered less active recombination sites, but they can be decorated with impurities.

Typical values for etch pit densities (EPD) of recrystallized Si films on SiC coated mc-Si wafers are ranging from 7x10³ 1/cm² to 3x10⁶ 1/cm². The etch pit densities were measured by defect counting of preferentially etched layers.

On the SiC encapsulated zircon samples etch pit densities are about one order of magnitude higher. Furthermore, the cross-sections show areas with increased defect densities exceeding etch pit densities of 10⁴ 1/cm², grown out of sub-grain boundaries or random grain boundaries during epitaxial thickening (Fig. 3, bottom). The small grain sizes and high etch pit density indicates that the recrystallization on the ceramic still has potential for improvements. Adjustments to the temperature profiles during ZMR are needed to compensate the reduced lateral heat transport in the ceramic. The used ZMR process in this work was optimized for thermally conductive substrates like silicon. Therefore the supercooling was not ideal on the isolating ceramic. With optimizing the thermal profiles, we are confident to achieve crystal qualities comparable to films crystallized on mc-Si substrates as the growth regime is only determined by the intermediate layer material.

![Fig. 3. Cross-section of a recrystallized Si film on SiC encapsulated mc-Si wafer (top) and on SiC encapsulated zircon (bottom) after Secco etch. ∑3 twin-grain boundaries (T) and defect multiplying sub-grain- and random grain boundaries (D) are marked.](image)

B. Electrical Characterization and Solar Cells

Regions with increased etch pit density have reduced minority carrier lifetimes, as shown by photoluminescence (PL) mapping in Fig. 4. The photoluminescence measurements were made on a cross-section perpendicular to the growth direction, similar to the one shown in Fig. 3. The measured sample was a zircon ceramic with SiC intermediate layer and an epitaxially grown Si layer with increased thickness of 45 µm for characterization. In the 5 µm thin recrystallized seed layer (below the dotted line in Fig. 4) only a small area of reduced PL intensity is caused by the sub-grain boundary (1).

![Fig. 4. Uncalibrated photoluminescence mapping of defect propagation in a cross-section of epitaxially grown Si (2), caused by a sub-grain boundary in the recrystallized seed layer (1).](image)
The slight tilt (< 2°) of the two grains neighboring the sub-grain boundary causes a region of line defects and defect planes (region (2) in Fig. 4) to grow during Si epitaxy. Similar effects are already known from ZMR experiments on SiO2 ILs [10], but typically sub-grain boundaries are less frequent on SiC intermediate layers.

Solar cells on zircon substrates were produced to evaluate the electrical properties of the recrystallized Si. In the first batch, zircon ceramic substrates were coated only with SiC; for the second batch first light trapping structures have been implemented. We therefore added 1 µm of SiO2 between the poly-Si and the SiC encapsulation. As a reference, a third batch with sole SiC encapsulation on 0.01 Ωcm p-type mc-Si wafers was produced. Due to the isolating character of the zircon, all solar cells had to be contacted from the front. The active cell area was limited to 1 cm², using mesa-etch technique which was also providing the edge isolation. The recrystallized seed layer was doped with 1x10¹⁸ at/cm³ boron for the zircon ceramic samples and with 1x10¹⁹ at/cm³ on mc-Si, forming the back surface field (BSF). The absorber layer was doped with 3x10¹⁶ at/cm³, the thickness was ~18 µm. We applied an emitter with ~100 Ω/□ resistivity diffused from POCl₃.

A double layer anti-reflective coating was applied to the untextured front side of batch A and the mc-Si references. Batch B, with additional SiO2 IL, had a textured front side realized by plasma etching. To limit bulk recombination, a remote plasma hydrogen passivation (RPHP) was applied. An overview of the solar cell results is shown in Table I.

On mc-Si substrates with SiC IL open circuit voltage (VOC) of up to 600 mV could be achieved. This is in the range of the best VOC of 614 mV achieved at ISE via ZMR on mc-Si with SiO2 IL [11] and proves the potential of Si films crystallized on SiC IL. We are confident, that there is no general shortcoming of Si films crystallized on SiC compared to SiO₂ IL. The Si layer quality can be improved further by fine-tuning the ZMR process.

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On zircon ceramic substrates the reduced VOC of 566 mV is compared to the solar cells on mc-Si substrates, indicate the lower material quality. Nevertheless, as far as we know these are the highest reported VOC and FF of recrystallized Si thin-film solar cells on real cost efficient ceramics.

The internal quantum efficiency (IQE) measurements of these cells also show the reduced absorber qualities of the Si films grown on zircon (batch A, Fig. 5) compared to similar films on mc-Si substrates (Reference, Fig. 5). The IQE drops rapidly at wavelength higher than 500 nm indicating recombination losses in the absorber. The effective diffusion length (L_eff) of the best cell of batch A, calculated from the IQE, was 12 µm. This means that L_eff is significantly lower than the absorber thickness of ~18 µm. On the mc-Si substrate, L_eff was calculated to be 25 µm which exceeds the absorber thickness by about 40 %.

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Table I: Illuminated cell parameters of recrystallized silicon thin-film solar cells on c-SiC IL, (uncalibrated, in-house measurements).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Batch</th>
<th>Intermediate Layer</th>
<th>Anti-reflective coating</th>
<th>Texture</th>
<th>Voc [mV]</th>
<th>J_Sc [mA/cm²]</th>
<th>FF [%]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>mc-Si (20)</td>
<td>Reference</td>
<td>SiC</td>
<td>yes</td>
<td>no</td>
<td>586±7</td>
<td>21.9±0.4</td>
<td>77.1±0.8</td>
<td>9.9±0.3</td>
</tr>
<tr>
<td>mc-Si (best cell)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>600</td>
<td>22.6</td>
<td>78.0</td>
<td>10.6</td>
</tr>
<tr>
<td>Zircon (20)</td>
<td>A</td>
<td>SiC</td>
<td>yes</td>
<td>no</td>
<td>549±8</td>
<td>19.2±0.6</td>
<td>71.4±1.5</td>
<td>7.5±0.3</td>
</tr>
<tr>
<td>Zircon (best cell)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>566</td>
<td>19.3</td>
<td>74.1</td>
<td>8.1</td>
</tr>
<tr>
<td>Zircon (20)</td>
<td>B</td>
<td>SiC/SiO₂</td>
<td>no</td>
<td>yes</td>
<td>534±4</td>
<td>19.8±0.7</td>
<td>68.1±2</td>
<td>7.2±0.2</td>
</tr>
<tr>
<td>Zircon (best cell)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>541</td>
<td>20.6</td>
<td>67.8</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Fig. 5: Quantum efficiencies and reflectance of recrystallized silicon thin-film solar cells on zircon ceramic and mc-Si substrates.

The short circuit current densities (J_Sc) of the processed batches are still limited by the lack of optical confinement. On mc-Si J_Sc values of 22.6 mA/cm² could be achieved which resulted in an overall conversion efficiency of 10.6 %. On zircon batch A, J_Sc was 19.3 mA/cm² which is further reduced due to recombination losses. Therefore, the overall conversion efficiency was 8.1 %.
On zircon batch B with improved optical confinement, the overall performance is lower than on batch A. The $V_{oc}$ and $FF$ were further reduced to 541 mV and 67.8 %. Nevertheless, an improvement in current generation at longer wavelength is evident from the IQE (batch B, Fig. 5) resulting in a $J_{sc}$ of 20.6 mA/cm$^2$ from an absorber thickness of only ~15 µm. These benefits however are still negated by the reduced crystal quality of batch B compared to the mc-Si references.

IV. CONCLUSION

It could be shown that producing silicon thin-film solar cells on cost effective, technical grade ceramic substrates like zircon is possible using SiC as diffusion barrier and intermediate layer. All the depositions, including SiC, poly-Si and Si epitaxy, as well as the recrystallization, were done using technologies capable of, or already scaled to, industrial needs.

The measurements indicate that the typical features in the so formed Si films seem to be unique to films formed on SiC ILs. The most common defects are $\Sigma 3$ twin grain boundaries. However, there are still sub-grain boundaries and clusters of line defects present, which lead to reduced carrier lifetimes.

The Si films crystallized on zircon still exhibit more crystal defects compared to Si films crystallized on reference substrates. A possible explanation is the reduced thermal conductivity of the ceramic, which needs to be compensated by the ZMR process.

Solar cells produced on zircon ceramic substrates reached conversion efficiencies up to 8.1 % with $V_{oc}$ up to 566 mV and $FF$ of 78 %. We are not aware of higher $V_{oc}$ or $FF$ values of recrystallized Si thin-film solar cells on ceramics.

On mc-Si reference substrates the same cell structure achieved a $V_{oc}$ of 600 mV and an efficiency of 10.6 % showing the potential of recrystallized Si films on SiC IL. Still the current generation of these cells is limited, caused by the lack of a front side texture as well as a not fully optimized absorber layer thickness.

First tests of adding light trapping structures to this concept have been performed. We added a SiO$_2$ IL and textured the front of the cell increasing the QE at 1000 nm by over 20 %.

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