Deposition monitoring of rare earths doped silicon rich oxide films by grazing incidence X-ray fluorescence and reflectivity analysis

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MOTIVATION
The efficiency of thin film solar cells can be improved with the addition of a photon down-conversion top layer. In this down converter layer, incident photons with energy larger than twice the band gap energy will give rise to two photons with lower energy, and then a solar cell efficiency of around 40% can be achieved. In this work, Pr co-doped silicon rich oxide (SRO) thin films were investigated for their suitability as a down-converter layer.

GIXRF analysis
A KETEK Silicon Drift Detector (SDD) has been placed inside the cabin of a Panalytical X’Pert X-ray Diffractometer. The detector was positioned to look in the middle of the sample aligned in the centre of rotation of the theta-theta goniometer at an angle χ=22° and an angle φ=0° fixed in the laboratory and sample frames. Acquisition of the data was performed on two different computers. The acquisition were manually started at the same time. The acquisition was performed in continuous mode. Hence the angle of measurement for the two detectors was set as the mid motor position if the interval of acquisition and differed for the two techniques (XRR and XRF).

Excitation spectrum
The Panalytical X’Pert X-ray Diffractometer was equipped with a Cu tube operated at 40 kV and 40 mA. No monochromator in the primary beam side was present. The primary excitation spectrum was calculated according to: Horst Ebel, X-ray Tube Spectra, X-Ray Spectrom. 28, 255-266 (1999).

Analysis of samples D048 and D050 where no Pr6O11 chips were on the target showed that Se contamination probably comes from the chamber from previous deposition. In fact also Pr and Yb could be clearly detected. Analysis of Samples A1182 and A1183 showed no Se contamination confirming that it was coming from previous work in chamber C1. A small As contamination could be seen. The distribution of Pr in these samples was much more peaked at low angles showing that the Pr accumulated in a region much closer to the surface then samples deposited in chamber C1.

DISCUSSION and CONCLUSION
The reflectivity spectrum does not show any fringes. After long investigations this could be attributed to a misalignment of the instrument and a high background in the reflectivity. This strange behaviour of the reflectivity to a primary beam not well collimated changed according to the height adjustment of the sample. The problem did not affect as much the gixrf spectra in the higher angle range. Qualitatively the scan on D007 shows that the Pr is confined in the top layer whereas teh contaminations Ca, Ti, Fe give a signal at a higher angle indicating that they are accumulated in a deeper region, and were probably present on the substrate surface before deposition. The Selenium signal also shows a presence in the top layer but its shape is different from the Pr signal since the Pr L fluorescence is mainly excited by the Cu Kα line whereas the Se K fluorescence is excited by the high energy part of the Bremsstrahlung spectrum.

Analysis of samples D022 and D023 showed that the increase in the power caused a higher mass deposition of the Pr but also of the contamination.

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**Samples**
Sample were fabricated by reactive magnetron co-sputtering in two different chambers (C1 and C2) to check the deposition and check for possible contamination due to previous uses of the chambers. A pure silica target SiO2 topped with Pr6O11 pellets was sputtered.

Hence some samples were annealed at different temperatures for 1 hour under nitrogen gas flow. Such treatment improves the phase separation between Si and SiO2 and allows recovering of the defects.

Experimental parameters are shown in the tables below.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>SiO2</th>
<th>Target type</th>
<th>Pr6O11 chips</th>
<th>Yb2O3 chips</th>
<th>Type</th>
<th>Substrate</th>
<th>Temp (°C)</th>
<th>Power (W)</th>
<th>Deposited condition</th>
<th>Power (W)</th>
<th>ER (%)</th>
<th>SRSO/SiO2 layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1182</td>
<td>SiO2</td>
<td>Pr6O11</td>
<td>0</td>
<td>0</td>
<td>silicon</td>
<td>no</td>
<td>25</td>
<td>0</td>
<td>44%</td>
<td>60</td>
<td>Mono SiO2</td>
<td></td>
</tr>
<tr>
<td>A1183</td>
<td>SiO2</td>
<td>Pr6O11</td>
<td>0</td>
<td>0</td>
<td>Silicon</td>
<td>no</td>
<td>25</td>
<td>20</td>
<td>60</td>
<td>60</td>
<td>Mono SRSO</td>
<td></td>
</tr>
<tr>
<td>A1195</td>
<td>SiO2</td>
<td>Pr6O11</td>
<td>0</td>
<td>0</td>
<td>silicon</td>
<td>no</td>
<td>400</td>
<td>20</td>
<td>44%</td>
<td>60</td>
<td>Xe22 SRSO 2mm SiO2 4nm</td>
<td></td>
</tr>
<tr>
<td>A1199</td>
<td>SiO2</td>
<td>Pr6O11</td>
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<td>0</td>
<td>silicon</td>
<td>no</td>
<td>400</td>
<td>20</td>
<td>44%</td>
<td>60</td>
<td>Xe25 SRSO 1mm SiO2 4nm</td>
<td></td>
</tr>
</tbody>
</table>

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