

Crystalline Silicon Thin-Film Solar Cells on ZrSiO₄ Ceramic Substrates

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ABSTRACT

Crystalline Si thin-film solar cells on low-cost substrates are promising candidates to reduce costs for photovoltaics. Zirconium silicate (ZrSiO₄) ceramics can meet the physical requirements on the substrate material as well as cost goals. For this investigation different types of ZrSiO₄ based ceramics have been prepared. Their suitability was tested by preparing Si films upon these ceramics and applying a solar cell process. Crystal quality of the Si films was mainly affected by the condition of the barrier layers. First solar cells achieved efficiencies up to 8.3%.

1. Introduction

At Fraunhofer ISE crystalline Si thin-film solar cells are produced following the high temperature route. High Si deposition rates in the CVD process at around 1100°C and the option to improve film quality by melting and recrystallization are the advantages of this approach [1]. From this it follows that the substrate material has to be stable up to the melting point of Si at 1415°C. Further it has to match the thermal expansion coefficient of Si and must be chemically stable. Last but not least the material has to be compatible with the cost goals of 25–50 €/m² [2]. ZrSiO₄ ceramics meet these demands. Its low thermal expansion coefficient which matches well the one of Si [3] makes this material of particular interest.

2. Experimental

Three different kinds of ceramic substrates were prepared for this investigation: Type A was made of fine grained ZrSiO₄ powder ($d_{50} = 0.8 \mu\text{m}$) and a methylphenyl silicone binder. After uniaxial pressing the samples were sintered at 1550°C. Type B was made from the same powder with the addition of 5% metallurgical Si resulting in a closed SiO₂ coating of the surfaces after sintering. This finish could be beneficial for the subsequent depositions. With regard to an industrial fabrication a third type (type C) was prepared using a less fine-grained powder ($d_{50} = 2.5 \mu\text{m}$) and a PVC/glycerin binder. Up to now these samples were also prepared by uniaxial pressing, but this system in principle is compatible with an industrial relevant tape casting process. The open

porosity of type A and type B samples was below 1% while that of type C was in the 20% range.

All samples were coated with a barrier layer system of 1 μm SiO₂, 200 μm SiN_x and 1 μm SiO₂ by PECVD. Then a 5 μm to 15 μm thick highly boron doped ($5 \times 10^{18} \text{cm}^{-3}$) Si film was deposited by atmospheric pressure CVD at 950°C. To prevent balling-up of the liquid Si during the subsequent zone-melting-recrystallization (ZMR) process, the film was capped by an additional 2 μm SiO₂ layer. After ZMR the capping layer was removed and the Si film was epitaxially thickened by CVD. Approximately 30 μm Si with a doping level of $3 \times 10^{16} \text{cm}^{-3}$ were deposited at 1150°C.

Solar cells were fabricated from selected samples. The process included a surface texture for enhanced light trapping, hydrogen passivation and a double layer anti-reflection coating.

3. Results and Discussion

3.1 Film Growth and Properties

Crystal quality of the Si films is mainly determined by the recrystallization process used to transform the microcrystalline Si film into a multicrystalline structure. Therefore the form of the melt zone and the solid-liquid interface were analyzed *in-situ* with a CCD camera integrated in our ZMR system [4]. The crystallographic properties were closely related to the morphology of the solid-liquid interface. A faceted, cellular solid-liquid interface (Fig. 1 left) led to large grains up to several millimeters in width and several centimeters in length with low defect density. Typically these grains are (100)-oriented and allow an easy-to-apply surface texture

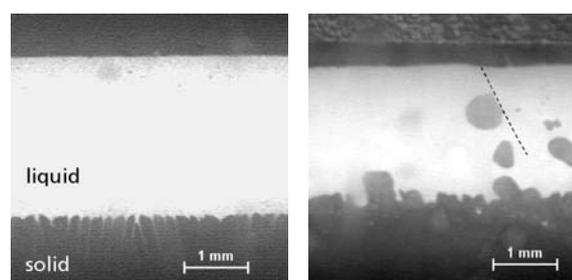


Fig. 1 Molten zone during ZMR. Left: faceted, cellular solid-liquid interface. Right: flaking-off of the Si film induced by cracks (dashed line).

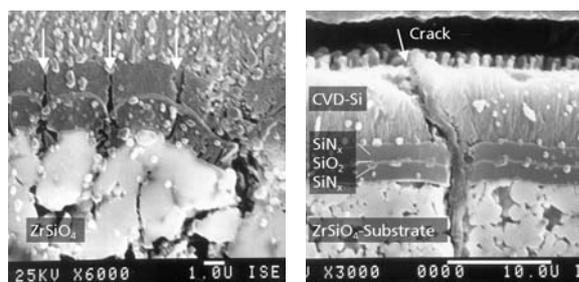


Fig. 2 Cross section SEM image of a type A (left) and a type B sample (right).

by anisotropic etching. However at many samples the Si film was flaking off during ZMR (Fig. 1 right). The analysis of cross sections revealed that cracks in the substrate or in the barrier layer were responsible for this behavior (Fig. 2). With samples of type A and type C microscopic perforations of the barrier layers were found whereas with samples of type B macroscopic cracks were penetrating the Si film as well as the barrier layers and the substrate. The first phenomenon could be caused by the quite high surface roughness of the substrates. The cracks in the type B substrates could be due to the transformation of SiO_2 – resulting from the oxidation of the free Si in the substrate – into cristobalite.

Impurity concentrations in the Si films were measured by glow discharge mass spectroscopy (GDMS). In Fig. 3 the transition between the Si layers and the substrate is noticeable by an increase of the Zr signal. The concentrations of harmful transition metals in the Si layers are below or close to the detection limit. This is especially true for the metals Ti, Fe and also for Al. According to the supplier of the ZrSiO_4 these elements are present in the powder in significant concentrations. In conclusion the barrier layer system fulfills its purpose or the impurities are tightly bound in the substrate's matrix.

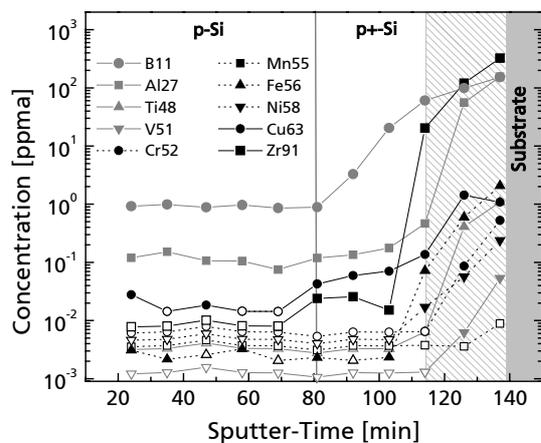


Fig. 3 Impurity profile in the Si film measured by GDMS. Open symbols represent the detection limit.

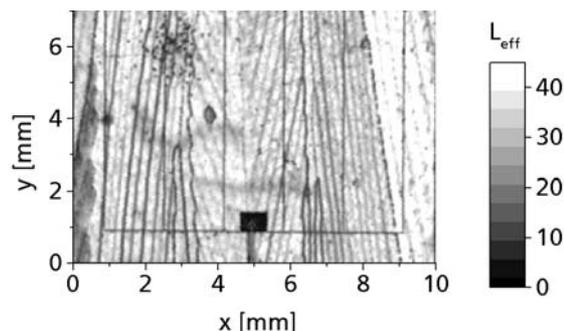


Fig. 4 Diffusion length topography measured by SR-LBIC.

3.2 Solar Cell Results and Electrical Analysis

Solar cells were prepared from some of the Si films. The best cell achieved an efficiency of 8.3%, with $V_{oc} = 536$ mV, $I_{sc} = 26.7$ mA/cm² and FF = 58.1% for an area of 0.67 cm². Remarkable is the high short circuit current which can be attributed to two effects. First the effective diffusion length (Fig. 4) is quite high with a distribution maximum around 37 μm . Second an increasing response for wavelengths above 800 nm can be seen in quantum efficiency measurements. This effect is due to light trapping realized by a combination of surface texture and internal reflexivity at the intermediate SiO_2 layer. Currently cell performance is limited by the poor fill factor. With an improvement of this parameter cell efficiencies above 10% are not unrealistic for this cell type.

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