CHEMICAL VAPOUR DEPOSITION OF SILICON ON CERAMIC SUBSTRATES FOR CRYSTALLINE SILICON THIN-FILM SOLAR CELLS

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ABSTRACT: Cystalline silicon thin-film solar cells (CSiTF) based on the deposition of thin silicon films on foreign substrates represent a promising concept to realise cost effective and still very efficient solar cells. Within the high-temperature approach the choice of deposition technique plays a crucial role. CVD at atmospheric pressure offers the possibility for fast deposition at comparatively small technical expenditure. The application of this process is feasible in industrial production. This paper reports the preparation of silicon thin-film structures on SiAlON and $ZrSiO_4$ ceramic substrates for CSiTF. The silicon layers were grown in an atmospheric pressure CVD reactor constructed at Fraunhofer ISE. The depositions were carried out with trichlorosilane (TCS) as precursor gas and diborane diluted in hydrogen as dopant gas. The morphology of the silicon layer surface and the interface between substrate and silicon layer were investigated by SEM and Nomarski-interference microscopy. A zone-melting recrystallisation (ZMR) step was applied to the silicon seeding layers to enlarge the grain size. In-situ observations and microscopical analysis showed that the layer system on the ceramic samples is unstable and therefore has to be modified to be applicable for solar cells.

Keywords: Deposition - 1: Si-Films - 2: Ceramic Substrate - 3:

1. INTRODUCTION

The concept of crystalline silicon thin-film solar cells combines the advantages of a reduction in silicon solar cell material and therefore in cost and the availability of a well developed silicon semiconductor technology. The high-temperature route allows for fast silicon deposition rates at high temperatures as well as for recrystallisation steps to enlarge the grain size of microcrystalline silicon seeding layers. Efficiencies of 16.45 % [1] have already been demonstrated, showing the potential for this approach. However to make the CSiTF competitive to conventional silicon solar cells stringent cost requirements have to be met. Thermal CVD at atmospheric pressure and high temperature seems to be the most attractive technique for growing silicon layers as it combines several advantages: high deposition rates can be reached, the layers grown are of excellent quality, the processes can be run with high chemical yield, the technical expenditure is comparatively small and the technique is feasible in industrial production.

In this work the deposition of silicon layers by CVD on SiAlON and $ZrSiO_4$ ceramics was investigated. Both ceramics are possible candidates as substrates for CSiTF as they fulfil the physical demands set on the substrate material (for example: thermal expansion coefficient is matched to silicon and the material is thermally stable). Two silicon deposition steps were applied to realise the cell structure: first a thin silicon layer was deposited at low temperatures onto the substrate. This seeding layer was subsequently recrystallised by zone-melting recrystallisation. Secondly the recrystallised layer was epitaxially thickened. The silicon layers were characterised by means of Nomarski-microscopy and SEM. Special emphasis was put on the characteristics of the epitaxial layer as it comprises the active layer of the solar cell. The results gained by ZMR gave further informfation on the silicon seeding layer properties in combination with the substrate material.

2. EXPERIMENTAL

2.1 Sample Structure

The following sample structure was realised: the substrates were encapsulated by a dielectric plasma-enhanced CVD (PECVD) intermediate layer-system of 1μm SiO_2, 0.1μm SiN_x and 1μm SiO_2 (ONO-layer) and a thin microcrystalline silicon-film was deposited. This silicon layer is highly doped and will therefore serve as back surface field (BSF). The silicon film was covered by a SiO_2 capping layer and subsequently recrystallised by ZMR. After the removal of the capping layer and a cleaning of the sample, the base of the solar cell was epitaxially grown. Figure 1 shows a schematic drawing of the sample structure.

For the mc-silicon reference wafer a 2μm thick SiO_2 intermediate layer was applied instead of the ONO-layer system.

epitaxial silicon layer (base)	20-30 μm
recrystallised silicon layer (BSF)	5-10 μm
intermediate layer	2 μm
ceramic substrate	~500 μm

Figure 1: Structure of the prepared samples.

2.2 Silicon deposition by CVD

All silicon layers were deposited by atmospheric pressure CVD in a horizontal, optically heated reactor. Cells with epitaxial layers grown in this system reached efficiencies of up to 17.6% [2] which proves the excellent purity and crystallographic quality of the deposited silicon layers.

A detailed description of the reactor setup can be found in [3]. The deposition process runs as follows: first the

reactor tube, in which the samples are located is purged with hydrogen. In the subsequent phase the sample temperature is ramped up in hydrogen atmosphere to the deposition temperature with a rate of 150 K/min. For the deposition of silicon a mixture of trichlorosilane $SiHCl_3$ (TCS) and hydrogen is used as precursor gas. Boron doping is achieved adding diborane diluted in hydrogen (2500 ppm) to the precursor. In the last phase, the samples are cooled down again under hydrogen.

The deposition of the silicon seeding layers were carried out at a temperature of 950 °C. The comparatively low temperature was chosen in order to prevent the intermediate oxide-layers from evaporating during the heating up of the samples. The Cl/H ratio was set to 0.16. With these parameters deposition rates of 1.0μm/min were reached. The thickness of the seeding layers was set to 8 to 10 μm at a doping level of $7x10^{18}cm^{-3}$.

Prior to the deposition of the epitaxial layers the samples were chemically treated by hydrofluoric acid plus a CP133 etch. For the growth of the epi-layers a pre-bake step was applied, i.e. the samples were heated up under hydrogen to 1200 °C to remove native oxide from the surface. For the actual deposition the temperature was set to 1170 °C. With a Cl/H ratio of 0.43 average deposition rates of 10 μm/min could be reached. Epitaxial layers of 30 μm thickness and approximately 0.3 Ωcm resistivity corresponding to a doping concentration of $6x10^{16}cm^{-3}$ were deposited on the substrates.

Doping levels were determined by spreading resistance measurements on reference samples.

3. RESULTS AND DISCUSSION

3.1 Seeding layers

In general the mean surface roughness of the as-deposited silicon seeding layers on all three substrate types was found to be in the range of 0.5 to 1μm. Minor whisker growth was observed on some of the ceramic-based samples.

SEM characterisation on cross sections revealed a severely damaged intermediate layer for the samples on SiAlON and $ZrSiO_4$ substrates. The ONO layers were not dense any more but showed many cracks. Figure 2 shows a typical SEM image of a sample cross section with SiAlON substrate. There are two possible reasons for the appearance of these cracks. First, the cracks could be due to thermal stress between the substrate and the intermediate layer which built up during the heating or cooling phase in the silicon deposition process. Second, some kind of chemical reaction could take place between the substrate components and the intermediate layer. This again could happen during the silicon CVD process where the sample temperature reaches 950 °C.

In contrast the deposition of silicon on mc-silicon reference samples resulted in seeding layers without crystallographic defects and with an undamaged intermediate layer. This result confirms the assumption that the problems encountered for the ceramic-type samples are not due to the silicon deposition process but can be referred to the physical or chemical characteristics of the ceramic substrates or to the combination of the substrate material with the intermediate layer system. In case of the SiAlON samples further experiments were carried out with a single

3μm thick SiO_2 layer as intermediate layer. However, similar results were achieved with this structure.
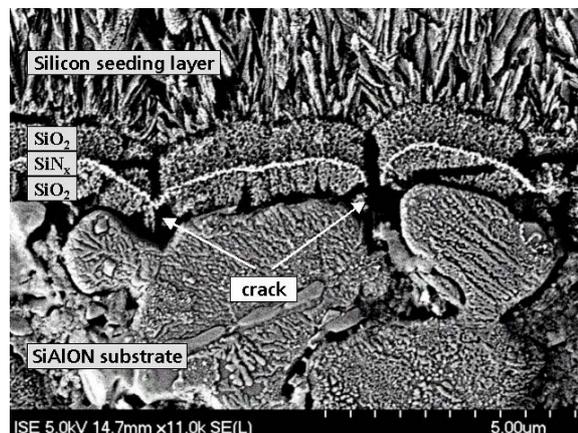

Figure 2: Cross section SEM image of a sample on SiAlON substrate.

3.2 ZMR

More information about the seeding layers and also about the layer system as a whole was obtained by means of *in-situ* observations during ZMR.

Figure 3, top, shows a typical shape of a molten zone for the reference structure on a mc-silicon substrate. The light areas correspond to molten silicon whereas the dark areas represent the solid silicon. The width of the molten zone is homogeneous and the solidification front shows a cellular morphology indicating an oriented crystal growth. The ZMR process runs without problems and the recrystallised layers showed large grains of good crystal quality and a <100> preferential orientation.
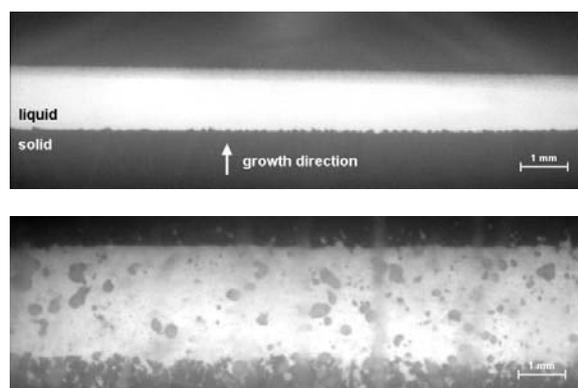

Figure 3: Molten zone during ZMR. Top: cellular solid-liquid interface on mc-silicon substrate. Bottom: balling-up and flaking off of the silicon-film on $ZrSiO_4$ substrate.

In contrast several problems were encountered for the recrystallisation process on the ceramic-based samples. Figure 3, bottom, shows an in-situ image of the recrystallisation process for a $ZrSiO_4$ based sample. Some typical features can be seen here: the interface of the solidification front is not sharp but diffuse. No oriented crystal growth is observed. The liquid spots in the otherwise solid region indicate a balling-up of the silicon

layer. Apart from these features other irregularities, which are not present on the image in figure 3, were observed. The inhomogeneous width of the molten zone is to be mentioned here. This effect is caused by differences in physical properties of the substrate, for example an inhomogeneous spatial distribution in heat conductivity or thickness. Unoriented crystal growth, dendritic growth and infiltration-like behaviour are other commonly observed features. However the main problem for the recrystallisation process on the SiAlON and $ZrSiO_4$ samples is a balling-up and a subsequent flaking off of the silicon layer. This feature can be ascribed to an instability in the layer system ONO/silicon seeding layer/capping layer. The damaged intermediate layer could be responsible for this instability.

3.3 Epitaxial layers

The crystallographic properties of the layers were also investigated by microscopical analysis. For the epitaxial silicon layers deposited on the recrystallised seeding layers whisker growth was found on the ceramic-based samples (see Figure 4). Whereas the samples on SiAlON suffered from a severe whisker growth spread over large areas of the sample surface, the epitaxial layers on $ZrSiO_4$ based substrates were less affected. An examination of cross sections by SEM revealed epitaxial layers with very high defect densities. In contrast the epitaxial layers of the reference samples were of excellent crystal quality, completely free from whisker growth.
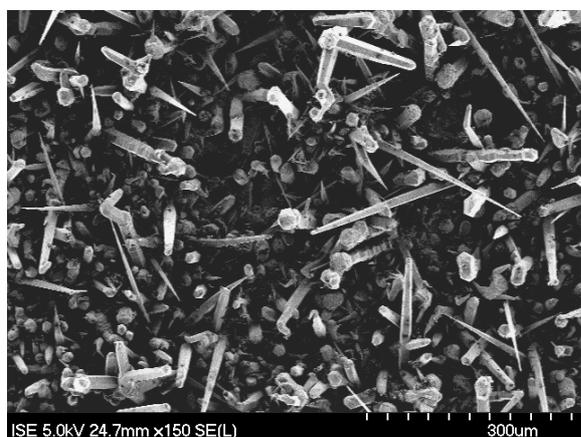

Figure 4: Whisker growth on the surface of a silicon epitaxial layer on SiAlON based sample (SEM).

According to the VLS (vapour-liquid-solid) model [4] the growth of whiskers can be ascribed to the presence of impurity atoms on the sample surface. From this it follows that the surface of the ceramic samples exhibited some kind of impurities which were not removed prior to epitaxy. All samples received the same chemical treatment before the CVD process, including an HF-dip to remove the SiO_2 capping layer and a subsequent CP-133 etch. The presence of impurity atoms on the surface of the ceramic-type samples can be explained by assuming an already contaminated recrystallised silicon seeding layer. Impurity atoms which are present in the seeding layer could either diffuse from the bulk to the surface during the heating-up

in CVD or otherwise they might not even be removed from the sample surface by the cleaning procedures.

During the recrystallisation the samples are exposed to high temperatures up to the melting point of silicon. Impurity atoms which exist in the ceramic substrates might diffuse through the cracks in the intermediate layer and by this way reach the silicon seeding layer.

The presence of whiskers on the surface of epitaxial layers is detrimental for solar cells. The samples on ceramic substrates were all affected by whisker growth and were therefore not further processed to solar cells.

4. SUMMARY

We have deposited silicon seeding layers and epitaxial layers by CVD on SiAlON and $ZrSiO_4$ ceramic substrates. The CVD processes on mc-silicon reference material were found to produce silicon layers well suitable for further ZMR and solar cell application. Characterisation of the layer systems on ceramic substrates revealed several defects which could be traced back to the ceramic material itself or its interaction with the applied intermediate layer respectively.

The results achieved in this paper show that the physical and chemical characteristics of the substrate material play a very crucial role for the presented solar cell structure. At Fraunhofer ISE the same sample structure has been realised before on SiAlON and $ZrSiO_4$ substrates of different composition, resulting in very promising solar cell efficiencies of 8.3 % on $ZrSiO_4$ [5] and 5.5 % on SiAlON [6]. A major concern for future activities will therefore be the development of ceramic material and intermediate layer systems suitable as substrates for crystalline silicon thin-film solar cells.

5. ACKNOWLEDGMENTS

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