Published in Journal of Non-Crystalline Solids 299-302, 1219-1223, 2002
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# Influence of substrate on the microstructure of microcrystalline silicon layers and cells

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**Abstract**

Hydrogenated microcrystalline silicon i-layers were deposited with a fixed silane concentration on various substrates and incorporated into n–i–p solar cells. 'Average crystallinity' and detailed microstructure of layers and devices were evaluated by X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. The role of the substrate is thereby shown to be very critical; a change in the substrate can cause a transition from amorphous to microcrystalline growth in micrometer-thick layers. When crystalline growth occurs, the layer microstructure is depth-dependent.

## 1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H, [1,2]) is at present considered to be one of the most promising materials for silicon-based thin-film solar cells [3]. It is at this moment mostly used in 'micromorph' (*micro*crystalline/a*morph*ous) silicon solar cells [4]. Whereas amorphous silicon (a-Si:H) solar cells have already been extensively studied over the past two decades, the design and fabrication of μc-Si:H solar cells are still in the initial stage.

Hydrogenated microcrystalline silicon is, in general, deposited by plasma enhanced chemical vapor deposition (PECVD), from a gas mixture of silane and hydrogen. The microstructure of the resulting μc-Si:H films strongly depends on the silane gas phase concentration ($[SiH_4]/[SiH_4 + H_2]$) used for deposition [5–7]. It has already been reported that the μc-Si:H solar cells with the highest open-circuit voltage are deposited with a silane concentration near to the μc-Si:H/a-Si:H transition [4]. In this region of deposition parameter space, crystallinity and microstructure of the resulting i-layer is strongly substrate-dependent, as reported in [8] for silicon thin films deposited with the layer-by-layer (LBL) technique. The purpose of the present paper is to investigate the influence of the substrate and especially ZnO-based transparent conductive oxide (TCO) layer on the microstructure of the i-layer.

## 2. Experimental

This study is based on the investigation of four samples: two individual i-layers (samples A and B)

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and two entire n–i–p solar cells (samples C and D), deposited by very high frequency glow discharge (VHD-GD) PECVD, on various substrates; all i-layers (individual i-layers and those within the n–i–p cells) were deposited with the same deposition parameters: 250 C, 0.5 mbar, 30 W, 130 MHz and a silane gas phase concentration close to the a-Si:H/μc-Si:H transition. The thickness of all i-layers is between 2.3 and 2.5 μm. The underlying substrate material was in all cases sodium free AF-45 glass substrate. Layer A was deposited directly on glass, layer B on sputtered ZnO, cell C on sputtered ZnO and cell D on ZnO grown by low pressure chemical vapor deposition (LPCVD). The n-μc-Si:H layers of both cells were deposited with the same deposition conditions, i.e. conditions that should result in highly microcrystalline structure. Both i-layers (A and B) were deposited in the same run, as were both n–i–p cells (C and D).

X-ray diffraction (XRD) was used on all the four samples to characterize the 'average' crystallinity (averaged over thickness) and to check whether preferential crystallographic growth (textured growth) did occur. XRD measurements were made on a Philips PW3020 diffractometer using the Bragg–Brentano geometry ($\vartheta$–$2\vartheta$ scans). An accelerating 30 kV voltage and a current of 30 mA were used to produce $CuK_\alpha$ radiation at a wavelength of 1.5418 Å.

Transmission electron microscopy (TEM) observations were performed on all the four samples. Sample A was prepared by scraping the layer from the glass and TEM observations were then made on small fragments directly picked on a carbon-coated grid. The other samples (B, C and D) were prepared as cross-sections for TEM examination with the help of the technique described in [9]. This technique consists of glueing head to tail two pieces of the sample in order to obtain a 'sandwich'. Then, a corner with an angle between 0.6° and 0.8° is made by mechanically polishing the sandwich. The last step of this type of sample preparation is a short ion beam cleaning and polishing procedure.

TEM observations were made on a Philips CM200 microscope operated at 200 kV. They allow one to observe directly the amorphous/crystalline nature of the layer and its possible local variations. Furthermore, crystallite size and orientation can here also easily be observed.

## 3. Results

XRD spectra of layers A and B (an individual i-layer on glass and on sputtered ZnO, respectively) show a dramatic dependence on the substrate (Fig. 1): the i-layer is amorphous when deposited directly on glass substrate and microcrystalline when deposited on sputtered ZnO. Here, under the same deposition conditions and in the same run, the substrate influence is so critical that it induces a full phase transition. TEM observations of layer A, confirming the XRD spectra, showed an amorphous microstructure without any nano/protocrystalline phase. TEM bright-field micrograph of layer B is shown in Fig. 2.

Samples B and C (an individual i-layer on sputtered ZnO and an i-layer, within an n–i–p cell, deposited on sputtered ZnO, respectively) exhibit similar XRD spectra (Fig. 1) with a (2 2 0) pref-

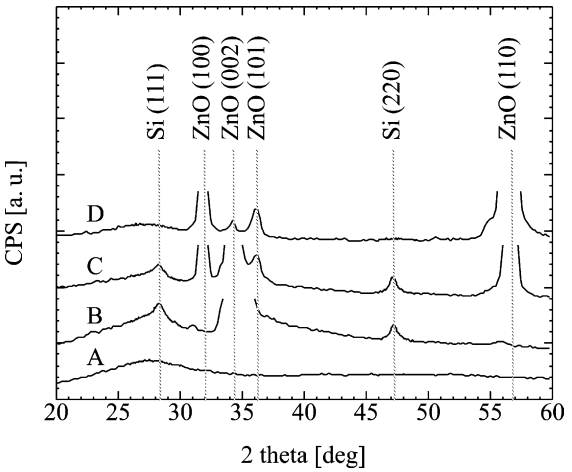


Fig. 1. XRD spectra of (A) i-layer deposited directly on glass, (B) layer deposited on sputtered ZnO, (C) full cell with sputtered ZnO as back TCO and LPCVD ZnO as front TCO, (D) full cell with LPCVD ZnO as TCO (when the integrated peak intensity is larger, the 'average' crystalline fraction is higher). Note that both TCOs do not have the same crystallographic texture and that microcrystalline silicon grows here with a (2 2 0) preferential orientation on sputtered ZnO (spectra B and C).

erential growth. On the other hand, their TEM micrographs differ slightly. In sample B, nucleation of the crystalline phase starts after a few hundreds of nanometers of an amorphous incubation layer, as shown in Fig. 2, while it occurs directly when the i-layer is grown over the n-μc-Si:H layer (sample C, Fig. 3). As already observed in [10], the i-layer grains grow epitaxially over the n-μc-Si:H layer and follow a direction normal to the substrate. In both cases, the microstructure is characterized by conical conglomerates of crystallites having diameters of tens of nanometers. This conical growth is characterized by an average opening angle of 23°, w.r.t. an axis normal to the substrate, in sample B and an average opening angle of 15° in sample C.

Samples C and D (the n–i–p cell on sputtered ZnO and the n–i–p cell on LPCVD ZnO, respectively) differ dramatically: cell C has a considerable crystalline fraction, whereas cell D is mostly amorphous, as seen on the XRD spectrum of the whole cell in Fig. 1. Electrical characteristics measured under AM 1.5 of cell C were an open-circuit voltage of 530 mV, a short-circuit current of 15.5 mA/cm$^2$ and a fill factor of 68%. On the other hand most of the cells deposited on LPCVD ZnO substrate were shunted, however we estimate that their $V_{oc}$ is over 500 mV. From the microstructural point of view, the two different types of ZnO used in these two cells differ in their surface roughness (LPCVD ZnO is rougher than sputtered ZnO), in their crystallographic texture ((1 1 0) preferential growth of LPCVD, in Fig. 1) and in the grain size (sputtered ZnO has smaller grains), as shown in Figs. 3 and 4. We also observed that the n-μc-Si:H layer 'quality' is not as good on LPCVD ZnO as on sputtered ZnO: on the latter, the grains constituting the n-μc-Si:H layer are close-packed crystallites of a diameter approximately equal to the thickness of the n-μc-Si:H layer; the thickness of the n-doped layer is homogeneous and the n–i interface clearly defined. On the other hand, with LPCVD ZnO (sample C), n–i interface is not as well defined and the n-μc-Si:H layer thickness presents fluctuations on the scale of tens of nanometers. The n-μc-Si:H layer grown on the rougher LPCVD ZnO looks, thus, more disordered than the n-μc-Si:H layer grown with the same conditions on sputtered ZnO. Furthermore, we observed in sample C cracks/voids occurring at the bottom of valleys as already reported in [5,6].

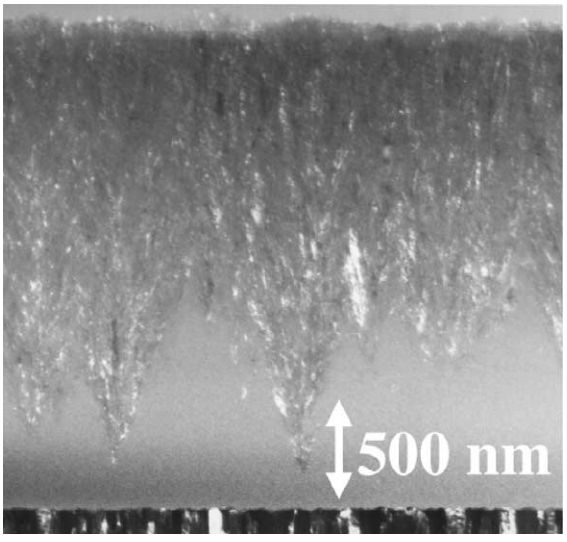


Fig. 2. TEM dark field micrograph of an i-layer deposited on sputtered ZnO (sample B). Crystallites appear bright in this imaging mode; ZnO layer is at the bottom of the picture.

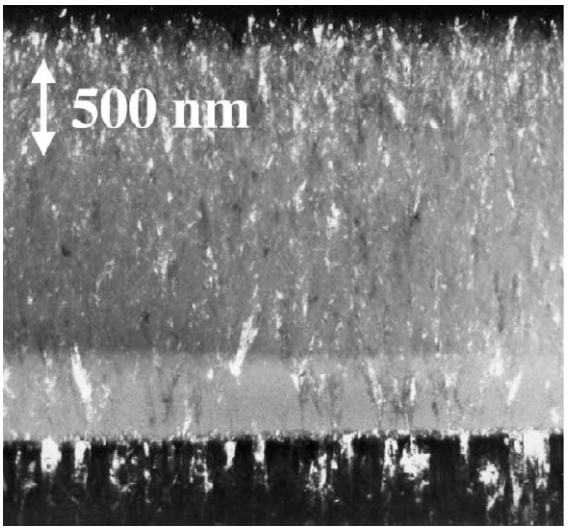


Fig. 3. TEM dark field micrograph of an n–i–p solar cell deposited on sputtered ZnO (sample C). ZnO is at the bottom of the picture, n-μc-Si:H layer appears as a thin dotted layer.

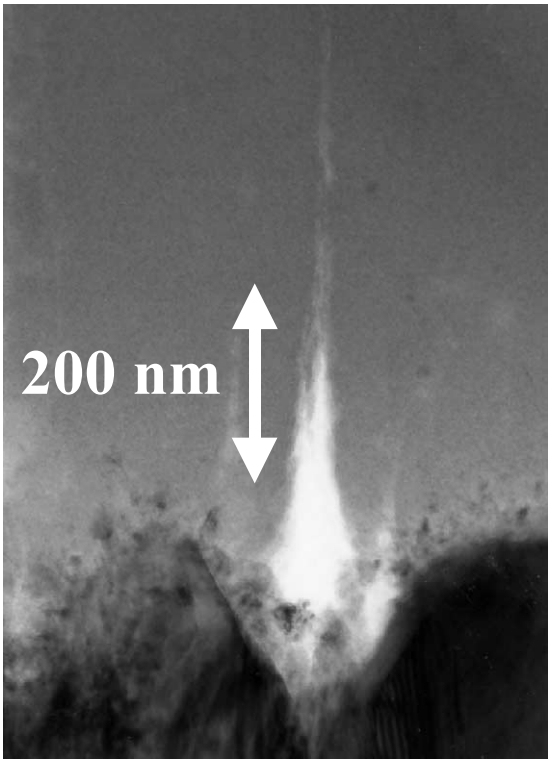


Fig. 4. TEM bright field micrograph of the ZnO–n–i interface of a solar cell deposited on LPCVD ZnO. ZnO pyramids are at the bottom of the picture. Note the disordered grainy contrast of the n-layer. Crack/void at the bottom of ZnO valley appears bright.

## 4. Discussion

We have shown above that the nature of the layer over which intrinsic μc-Si:H layer is deposited is critical for the amorphous/microcrystalline nature of the intrinsic layer itself. This was observed in the case of deposition with silane concentrations close to the amorphous to microcrystalline phase transition. From our TEM micrographs, we can observe a pronounced depth inhomogeneity; this fact must be considered when analyzing mixed-phase amorphous/microcrystalline layers [11]. Such a depth inhomogeneity can, in fact, not be inferred from the XRD spectra alone. The latter are only relevant for the evaluation of the 'average' crystallinity. Furthermore, our TEM observations clearly demonstrate the strong effect of the substrate and the underlying layer on the growth of the i-layer.

Our observations on samples B and C reveal a conical shape of conglomerates, an opening angle of approximately 23° and 15°, respectively, and a crystalline percolation threshold of a few hundreds of nanometers. These data are in agreement with the growth model proposed in [12], where an opening angle of 15° was assumed. Yet little is known about the microscopic mechanism responsible for such a columnar growth in silicon-based material.

As our samples were all deposited with the same silane concentration, the only parameters influencing the phase transition are the nature of the substrate and the nature of the n-μc-Si:H layer (if any). These two parameters influence the thickness of the incubation layer. For sample B (i-layer on sputtered ZnO), the thickness of the amorphous incubation layer is in the range of hundreds of nanometers, while for sample C (n–i–p cell on sputtered ZnO) the role of the incubation layer is played by the n-μc-Si:H layer. In this case, the n-μc-Si:H layer seems to influence the cone opening angle by controlling the incubation layer thickness. The cone opening angle varies from 15° (with a n-μc-Si:H layer) to 23° (without a n-μc-Si:H layer). However, after crossing the crystalline percolation threshold, the microstructure of both samples B and C is similar. Consequently, the influence of the n-μc-Si:H layer vanishes when the thickness increases, resulting for thick enough layers, in the same XRD spectra.

In sample C, the n-μc-Si:H layer deposited on a flat sputtered ZnO, is of higher 'quality' (w.r.t. its microstructure as seen from TEM) than the one deposited on rough LPCVD ZnO (sample D). For sample D, this leads to a thicker amorphous incubation layer. In fact, sample D never reaches the crystalline percolation threshold. The quality of the n-μc-Si:H layer is, thus, of importance for the control of the microcrystalline growth of the i-layer.

We have, thus, showed that in a typical n–i–p solar cell deposited on a ZnO layer, the surface microstructure of ZnO (surface roughness, crystallographic orientation and grain size) is of paramount importance to control the orientation of the grains and the quality of the n-μc-Si:H layer.

Furthermore, the n-μc-Si:H layer affects the amorphous or microcrystalline growth of the i-layer. As the 'quality' of the n-μc-Si:H layer is influenced by the surface microstructure of the underlying TCO layer (here ZnO), the deposition parameters for the n-μc-Si:H layer have to be optimized for each different TCO layer.

## 5. Conclusions

In this paper comparisons between four samples were made with the help of XRD and TEM in order to study the influence of substrate and the underlying layer on the microstructure of μc-Si:H layers and cells:

1. A comparison between a layer directly deposited on glass and a layer on sputtered ZnO revealed that in the latter case one has an amorphous incubation layer of a few hundreds of nanometers which further upwards grows into a microcrystalline phase, whereas the layer directly deposited on glass remains amorphous throughout the whole thickness.
2. A comparison between a layer and a cell on sputtered ZnO shows the importance of the n-μc-Si:H layer for reducing the thickness of the incubation layer. Indeed, in the cell deposited on sputtered ZnO, nucleation occurs at the n-μc-Si:H layer itself, whereas the layer on the same substrate requires first the deposition of an incubation layer that is a few hundred nanometers thick before microcrystalline growth can take place.
3. A comparison between a cell deposited on sputtered ZnO and one deposited on LPVCD ZnO shows the influence of the roughness of the substrate on the microstructure. On one hand, roughness influences the orientation of the grains, i.e. the grains are in general oriented normal to the facets of the substrate; on the other hand roughness affects the quality of n-μc-Si:H layer, the latter being of importance for the nucleation and the crystalline i-layer growth.

These three comparisons lead us to call for extreme prudence when comparing i-layers and entire solar cells deposited on different substrates, because parameters such as the roughness of the substrate (i.e. TCO) and the quality of the initial n-μc-Si:H layer exhibits a considerable influence on the microstructure of the absorbing i-layer.

## Acknowledgements

The authors thank Mrs M. Leboeuf for her help in sample preparation and Dr M. Dadras for his helpful advice. We aknowledge financial support from the Swiss 'Office Fédéral de l'Energie (OFEN)', under contract No. 36487 as well as from the Swiss National Science Foundation under grant FN59413.

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