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FABRICATION OF HIGH EFFICIENCY MICROCRYSTALLINE AND MICROMORPH THIN FILM SOLAR CELLS ON LPCVD ZnO COATED GLASS SUBSTRATES

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ABSTRACT: The fabrication of high efficiency (9-10%) microcrystalline silicon (μc-Si:H) p-i-n solar cells on glass has been so far reported mostly for cells deposited on sputtered and etched zinc oxide (ZnO). In this paper, we describe the preparation of μc-Si:H devices with efficiencies close to 10%, using glass coated with ZnO deposited by low pressure chemical vapor deposition (LPCVD). These results are achieved both by improving the transparency of the TCO in the infrared part of the spectrum and by changing the surface morphology.

The LPCVD front and back contacts are first optimized for p-i-n microcrystalline silicon solar cells by decreasing the free carrier absorption (FCA) of the layers and by increasing the surface roughness of the front contact. These modifications result in an increase of the current density but also in a reduction of the fill-factor (FF) and of the open-circuit voltage (V_{oc}). To avoid these reductions, a surface plasma treatment of the ZnO is introduced. It modifies the surface morphology by turning the typical V-shaped valleys of the LPCVD ZnO into U-shaped valleys and by erasing from the surface small-sized pyramids and asperities. As a result, for fixed deposition parameters, the p-i-n μc-Si:H silicon solar cell efficiency increases from 3.3% to 9.2%. This increase is caused by the disparition of microcracks and damaged areas which appear otherwise at the bottom of the V-shaped valleys. Further optimization of the modified ZnO front contact and of the cell process lead to an efficiency of 9.9%. Finally, we report the fabrication of micromorph cells with 11.8% initial efficiency on the modified ZnO.

Keywords: Thin film silicon, microcrystalline Si, PECVD, ZnO.

1 INTRODUCTION

LPCVD zinc oxide is used successfully at the laboratory level in amorphous (a-Si:H) and micromorph tandem solar cells as a front transparent conductive oxide (TCO). a-Si:H solar cells have reached independently confirmed stable efficiency (η) of 9.47% and micromorph tandem stable efficiencies of 10.8% [1]. The first result represents one of the highest stable efficiencies ever reported for a-Si:H solar cells. LPCVD ZnO deposition is now been upscaled at 1.4m^2 by Oerlikon Solar, with a-Si:H single junction modules showing up to 8.6% aperture area initial efficiency [2].

This successful use of LPCVD ZnO could not be extended so far to μc-Si:H single junction solar cells. The best p-i-n cells on LPCVD ZnO only attained efficiencies slightly over 8%, whereas, on sputtered and etched ZnO, several groups managed to produce cells achieving efficiencies over 9% [3-5].

The present contribution addresses the issue of fabricating single junction μc-Si:H solar cells with efficiencies higher than 9% on LPCVD ZnO. To reach this goal, the front TCO used previously at IMT for a-Si:H and micromorph solar cells is modified for use within single junction μc-Si:H solar cells. The modifications are threefold:

- Reduction of the free carrier absorption (FCA)
- Increase of the light-trapping capability for long wavelengths (700-1000nm)
- Adaptation of the morphology to the growth of μc-Si:H material

The first two modifications to the standard front TCO optimized for a-Si:H solar cells are motivated by the broader absorption spectrum of μc-Si:H. These are easy to implement technologically: (a) by lowering the doping concentration of the LPCVD ZnO film, to reduce the FCA; (b) by increasing the film thickness to increase the surface roughness and thereby improve the light trapping at long wavelengths. As both modifications affect the sheet resistance of the TCO layer in opposing ways, it is possible to keep the latter below 10Ω/□ [6].

After carrying out these modifications it is, however, no more possible to obtain high values of open-circuit voltage (V_{oc}) and fill-factor (FF). The reason invoked in ref. [7] is the high roughness and inappropriate surface morphology of the front TCO layer. The third modification to our standard TCO is thus an adaptation of the surface morphology, which favors a proper growth of μc-Si:H. This last task is challenging as the optimal morphology for the growth of μc-Si:H cells is not yet known. We present here a novel surface plasma treatment that renders the surface morphology of LPCVD ZnO fully adapted to subsequent growth of μc-Si:H solar cells. The time used for the surface treatment , is varied from 0 to 140’; the efficiency of the μc-Si:H solar cells subsequently grown on these substrates, increase from 3.3 to 9.2% after 40’ of surface treatment. This surprising effect is described here in detail. Further optimization of the solar cell deposition parameters lead to the realisation of μc-Si solar cells with conversion efficiencies as high as 9.9%. Finally, we show that high efficiency micromorph devices can also be prepared on this modified TCO. So far, however, the gain compared to a TCO without surface treatement, cannot not be clearly evidenced. Also the possibility to reduce the process time for cost effectivness needs to be investigated

2 EXPERIMENTAL

ZnO is deposited by LPCVD, from a vapor-gas mixture of water, diethyl-zinc and diborane, on a glass substrates (Schott AF45). The sheet resistance of the resulting front TCO layers is below 10Ω/□.

μc-Si:H solar cells are deposited by very-high frequency (VHF) plasma enhanced chemical vapor deposition (PECVD) on the front TCO, from a gas phase mixture of silane and hydrogen. The thickness of the μc-Si:H intrinsic layer is approximately 1.8μm, unless otherwise stated. The back contact consists of ZnO deposited by LPCVD covered by a white dielectric reflector. The micromorph devices incorporate a ZnO intermediate reflector prepared by sputtering. The fully patterned cells have an area of approximately $20mm^2$.

The short-circuit current density is calculated from the measurement of the external quantum efficiency (EQE) curve, by integrating, over the wavelength range from 350 to 1000nm, the product of EQE times the incoming spectral density of photon flux of the solar spectrum.

The current density-voltage (IV) curves are measured under a WACOM solar simulator in standard test conditions (25°C, AM1.5g spectrum) and calibrated with the short-circuit current-densities obtained from the EQE measurements.

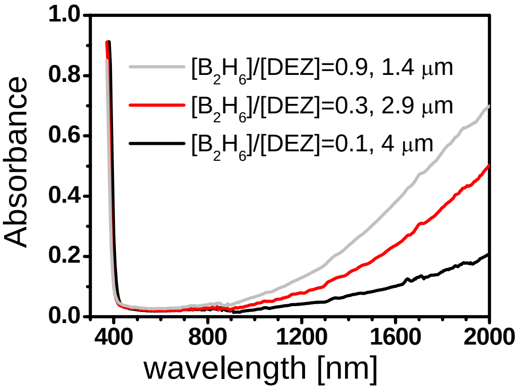

Figure 1: absorbance curves of ZnO layers with similar sheet resistance of 10 Ohm/sq, prepared with different gas doping concentration. The ratio of doping gas and the layer thicknesses are given in the graph.

3 RESULTS

3.1 Reduction of FCA in ZnO

The figure 1 shows the absorbance curves for ZnO layers with similar sheet resistance of 10 Ohm/sq, prepared with different doping gas concentration. To avoid light trapping effects, the absorbance is measured with an index matching liquid. The layer with a lower doping has an absorbance a factor 5 to 10 lower compared to the standard highly doped ZnO, in the range of 1000 to 1200 nm. The reduction of FCA is attributed to an increase of the carrier mobility inside the ZnO grain [8], which is limited by ionized impurity scattering for strongly doped samples.

3.2 Changes in surface morphology

The scanning electron microscopy (SEM) images of Fig.2 illustrate the three different surface morphologies obtained: a) standard LPCVD ZnO optimized for a-Si:H cells, b) new LPCVD ZnO optimized for μc-Si:H before surface treatment and c) same as b), after surface treatment of 80'.

The surface features of the new front ZnO layer, optimized for μc-Si:H solar cells, are typically two times larger than those of the ZnO layer optimized for a-Si:H cells. At the same time, the root-mean square roughness (σ_{RMS}) also increases from approximately 60nm to 200nm. Both of these facts improve the light scattering for longer wavelengths, i.e. for the range between 700nm and 1000nm, for which μc-Si:H has a low absorption coefficient. The absorption length (defined as the inverse of the absorption coefficient) is approximately 2μm and 100μm at these 2 wavelengths, respectively.

The surface of the LP-CVD ZnO layers used as front contact is constituted of pyramids of different sizes, irregularly packed on the surface (see Fig. 2a° and 2b). These pyramids have flat sides and sharp edges. Between large pyramids, smaller pyramids can be observed as well as asperities.

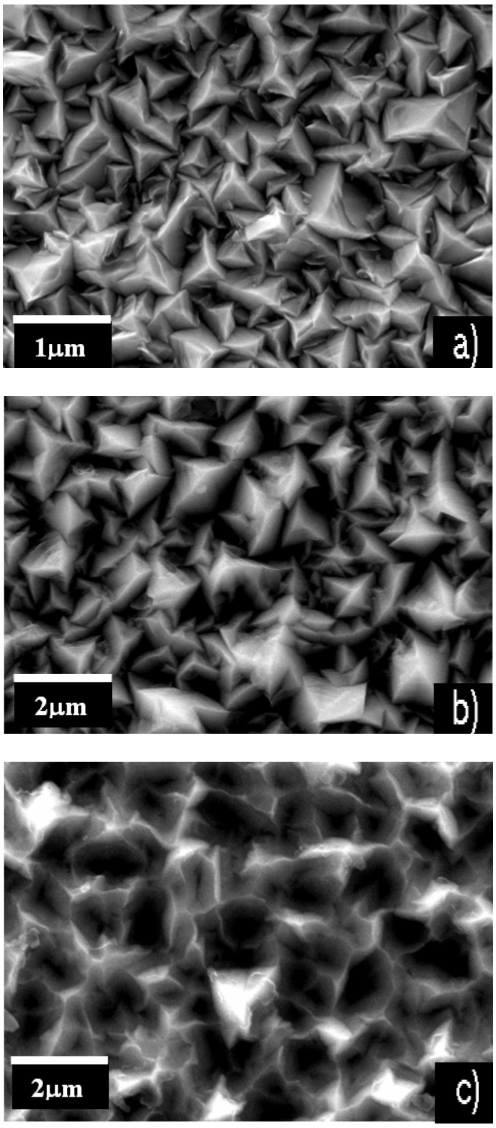

Figure 2: Fig. 1. SEM micrographs of the different surface morphologies of: a) standard front LPCVD ZnO optimized for amorphous cells, b) and c) new LPCVD ZnO optimized for μc-Si:H cells, before and after 80' of surface treatment, respectively.

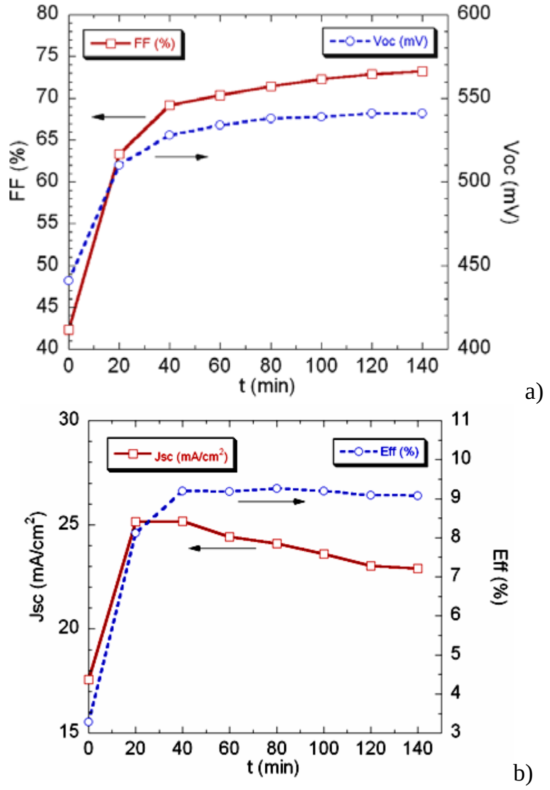

Figure 3: Evolution of the electrical characteristics of the solar cells as a function of the duration of the surface treatment (0 minute stands for no surface treatment): a) V_{oc} and FF, b) I_{sc} and efficiency η.

The surface treatment profoundly changes the morphology, as shown is Fig. 2c. The smaller pyramids or asperities lying between the larger pyramids completely disappear. The surface becomes slightly smoother with a decrease of σ_{RMS} from approximately 200 nm without treatment to 175nm and 150nm after surface treatments of 40’ and 80’ duration, respectively. The sharp edges of the larger pyramids remain visible after the treatment, forming a network of salient and curved lines at the surface of the front TCO. On the other hand, the sides of the pyramids that are initially flat appeared to have been hollowed by the treatment. This is the reason why the V-shaped valleys seen in Fig. 2b turn into U-shaped valleys in Fig. 2c.

In Fig. 3, the evolution of the main electrical characteristics of solar cells deposited in the same conditions is represented as a function of the surface treatment time of the front TCO. Already for treatment times of 20 minutes, all the electrical parameters of the solar cells dramatically improve. Longer treatment times keep improving V_{oc} and FF, however, I_{sc} monotonously decreases. The net result is that for surface treatment times between 60 and 140 minutes η remains almost constant at 9.2%.

The current density for the cell on untreated ZnO layers is low, and is associated with poor carrier collection (the photocurrent at -2V is close to 24 mA/cm^2). Carrier collection immediately improves with 20 minutes of surface treatment. Longer treatment times lead to a reduction of the light trapping and, hence, to lower current, with, however, a good collection of carriers (Fig. 4b).

In Fig. 4a the IV curves of the best cell deposited on front ZnO optimized for µc-Si:H growth with 60’ of surface treatment, is represented. This cell has an efficiency of 9.9% and is obtained after slight re-optimization of the deposition parameters on the new type of substrate. The optimization consists mainly in adjusting the gradient of silane concentration (i.e. the flux of silane divided by the total gas flux) used during the deposition of the intrinsic layer. In Fig. 4b, the EQE of a cell with a thicker 2.5 µm absorber is shown. The minimum difference in the collected photocurrent at 0 and -2V (25.7 and 26.25 mA/cm^2 respectively) illustrates the excellent collection capability of µc-Si:H cells deposited on the new TCO.

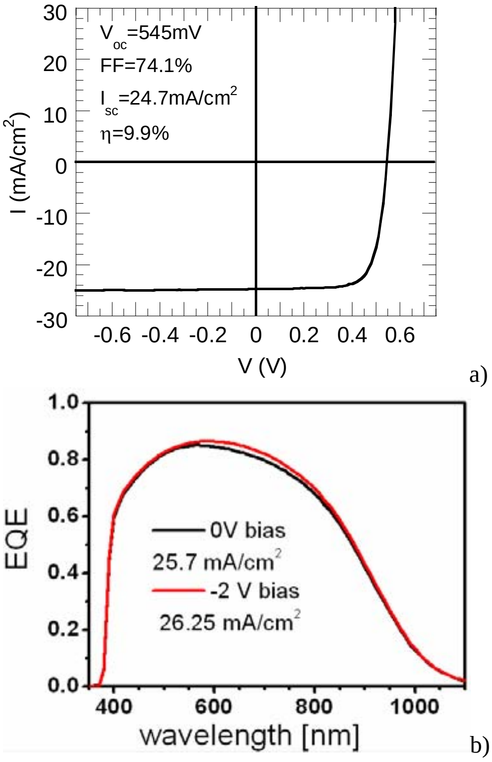

Figure 4: a) I-V curve of an optimized µc-Si:H solar cell on LPCVD ZnO with 60’ of surface treatment. b) EQE of a cell with thicker (2.5 µm) absorber layer at 0 and -2V.

4. DISCUSSION

4.1 Growth of µc-Si:H layers

The new surface morphology of the front ZnO TCO presented here improves dramatically the electrical parameters of the µc-Si:H subsequently grown on it. The two main changes of the surface morphology after the treatment are the following:

- absence of small asperities in-between the large surface objects,
- U-shaped valleys instead of the typical V-shaped valleys of the standard ZnO, as optimized for amorphous cells.

Cracks and voids have often been observed in µc-

Si:H solar cells grown on LP-CVD ZnO [9]. These cracks usually arise from the tip of the V-shaped valleys within the intrinsic layer. Investigations by transmission electron microscopy (TEM) on samples similar to the ones presented here with 80’ of treatment show that cracks and voids are no more observed when the valleys have a U-shape, i.e. after the treatment. We hence suppose that the absence or presence of cracks during the subsequent deposition of the μc-Si:H layers is caused by the TCO surface having, depending on its surface morphology, a different shading effect on the impinging silicon precursors. Computer simulations [10] of the growth process including shading effects illustrate qualitatively the situation in Fig. 5: when changing from the substrate morphology from V to U shape, cracks tend to disappear.

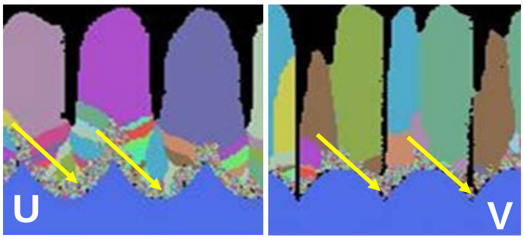

Figure 5: Growth simulation of μc-Si:H solar cell on substrates with different morphology.

4.2 Electrical characteristics and surface treatment time

The surface treatment clearly improves the electrical characteristics of the cells already for durations below 40 minutes. Our TEM investigations indicate that the removal of cracks and voids is responsible for the improved values of FF and V_{oc}. For some intermediate morphology, we expect that cracks are not readily observed, but that structures similar to grain boundaries are formed, which might be difficult to observe by TEM. However, we assume in all cases that these defective areas constitute zones of enhanced recombination for the photogenerated carriers. They are also thought to affect the distribution of the electrical field inside the cell.

Above 40’ of surface treatment, the V_{oc} and FF continue to increase, whereas I_{sc} decreases in the same way. The result is that from 60’ to 140’ of treatment, η remains almost constant at approximately 9.2%. The decrease of I_{sc} is caused by a smoothening of the surface roughness due to the treatment. Noticeably, it is possible to compensate this current loss by starting with a TCO with a higher roughness.

Note that the process chosen to realize the cells considered in Fig. 3, is not “optimized” for the untreated ZnO. By adjusting the thickness of the different layers and by tuning the plasma parameter, it is possible to come to efficiencies close to 8% on untreated ZnO. However, so far, we can achieve higher efficiencies up to 9.9% only on the modified ZnO.

4.3 Micromorph devices

The modified TCO is suitable for the fabrication of micromorph devices. Cells with total current of 26 mA/cm^2 (13.2 for the a-Si:H top) using an intermediate reflector can be fabricated, with initial efficiencies of 11.8% [11]. These cells still have limited V_{oc} of 1315 mV and FF (70%), which is attributed to the presence of the intermediate reflector. Cells prepared on the modified TCO without IR reflector show high V_{oc} of 1.41 V, but without current matching. Better micromorph devices should be realizable in a next future.

It should be noted, however, that the microcrystalline cells is grown on top of the amorphous cell, which modifies the surface morphology of the TCO. The question remains open whether the new TCO morphology is necessary to achieve the highest efficiency micromorph devices.

5 CONCLUSIONS

We have demonstrated that LPCVD ZnO is perfectly suited for the fabrication of high efficiency μc-Si:H single junction solar cells. This is mostly achieved by using a novel plasma treatment. The versatility of the LPCVD technique for the deposition of the TCO help us to tune the front TCO properties to the requirements of μc-Si:H solar cells by lowering the doping concentration and increasing the layer thickness. The best μc-Si:H solar cell obtained so far on this new kind of front TCO reaches FF=74.1%, V_{oc}=545mV and I_{sc}=24.7mA/cm^2, leading to η=9.9%. This efficiency is the highest reported for cells deposited on front ZnO deposited by LPCVD and it compares very well with the best results of other groups on sputtered and etched ZnO.

The reason for this improvement is found in the change of the surface morphology of the front TCO. Apparently, the surface is slightly smoothened by the treatment and small asperities are erased. The typical V-shaped valleys of the LPCVD ZnO are replaced by U-shaped valleys that are better suited for the subsequent growth of μc-Si:H single junction solar cells.

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