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Rough ZnO layers by LP-CVD process and their effect in improving performances of amorphous and microcrystalline silicon solar cells

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Abstract

Doped ZnO layers deposited by low-pressure chemical vapour deposition technique have been studied for their use as transparent contact layers for thin-film silicon solar cells.

Surface roughness of these ZnO layers is related to their light-scattering capability; this is shown to be of prime importance to enhance the current generation in thin-film silicon solar cells. Surface roughness has been tuned over a large range of values, by varying thickness and/or doping concentration of the ZnO layers.

A method is proposed to optimize the light-scattering capacity of ZnO layers, and the incorporation of these layers as front transparent conductive oxides for p–i–n thin-film microcrystalline silicon solar cells is studied.

Keywords: TCO; LP-CVD; Zinc oxide; Thin-film silicon solar cells; Light-scattering capacity

1. Introduction

Transparent conductive oxides (TCOs) are an essential part of thin-film solar cells, both cost-wise and performance-wise. Amongst these TCOs, doped zinc oxide (ZnO) is a very promising candidate for future thin-film solar cell technology, especially because of its low cost and because of the wide availability of its constituent raw materials.

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Doped thin-film ZnO layers deposited by the low pressure chemical vapour deposition (LP-CVD) technique are not only transparent and electrically conductive, but possess also a pronounced light-scattering capacity. The light-scattering capacity increases the path of the light within the solar cell, and, hence, enhances also its probability to be absorbed in the cell. This aspect is especially important in the case of amorphous and microcrystalline silicon (a-Si:H and μc-Si:H) thin-film solar cells, because of their relatively low optical absorption coefficient in the red and near infra-red (NIR) spectral range. Moreover, thicker a-Si:H ($>0.4\,\mu$m) and μc-Si:H ($>3\,\mu$m) intrinsic (i)-layers cannot be used within the corresponding solar cells, because (a) the light-induced degradation effect (Staebler–Wronski effect) in a-Si:H p–i–n solar cells becomes more pronounced as the thickness of the a-Si:H i-layer is increased and because (b) the deposition times needed for thicker silicon layers become so long that cell manufacturing becomes economically prohibitive (especially in the case of μc-Si:H solar cells). The light-scattering property is linked to the surface roughness of the TCO layer used in the cell. Indeed, a rough surface allows one to scatter efficiently the light that enters into the solar cells through the TCO layer.

In the present study, ZnO layers have been deposited by LP-CVD, in a pressure range inferior to 1 Torr, well below the usual process-pressure range applied for deposition of ZnO layers [1,2]. Under our deposition conditions, a ZnO with surface roughness well suited for light-scattering in thin film solar cells has been obtained [3]. Our goal has thereby been to incorporate such layers as front TCO layers in microcrystalline/amorphous or ‘micromorph’ tandem [4] thin-film silicon solar cells [5–7].

This paper is a study of the impact of thickness and doping variation of the LP-CVD ZnO layers on their surface roughness and therefore on their light-scattering capacity. Moreover, the variation in the performance of p–i–n μc-Si:H solar cells, when the light-scattering capacity of the front ZnO layer is varied, has also been studied.

2. Experimental

ZnO layers have been deposited by LP-CVD. Diethyl zinc (DEZ) and water (H_2O) vapours have been used as precursors, and directly evaporated in the system. In this case, the vapours were not diluted in a carrier gas. DEZ and H_2O flows have been set to 13.5 and 16.5 sccm, respectively. Diborane (B_2H_6) has been used as doping gas, 2% diluted in helium. The flow rate of B_2H_6 has been varied from 0 to 18 sccm, in order to enhance the doping ratio, i.e., the B_2H_6/DEZ ratio. The total pressure was kept at 0.5 mbar (~0.37 Torr), and the substrate was heated during the ZnO deposition at a temperature of 155 °C. The thickness of the ZnO samples has been varied from 400 to 3 μm. p–i–n μc-Si:H solar cells have been deposited on ZnO front electrode by the in-house very-high-frequency plasma-enhanced-chemical vapour deposition technique (VHF PE-CVD) [8,9].

Thickness (d) has been measured using a profilometer, and sheet resistance (R_{sq}) has been measured by the four-probe method. Resistivity values have been deduced from both d and R_{sq} measurements. Optical transmission, both total and diffuse (TT and TD, respectively), have been measured using a spectrometer with an integrating sphere, in the visible and NIR wavelength range. The haze factor has been defined as the TD/TT ratio measured at 600 nm. This factor quantifies the light-scattering capacity of the ZnO layers.

X-ray diffraction (XRD) measurements and transmission electron microscopy (TEM) cross-sections have been performed to characterize the crystallographic orientation and the microstructure of the ZnO layers. Finally, surface topography images have been taken by scanning electron microscopy (SEM) to analyse the surface morphology of the ZnO samples. The grain boundaries observable at the scanned surface have been detected with the help of the ‘AnalySIS’ software, and the mean projected area of these grains has been deduced.

3. Results and discussion

3.1. *LP-CVD ZnO layers*

The doped LP-CVD ZnO layers developed at our institute have a high transparency over the visible and NIR ranges, and their resistivity can be lowered down to $1 \times 10^{-3}\,\Omega\,\mathrm{cm}$. The XRD pattern and the TEM micrograph of a cross-section of a 2 μm-thick doped LP-CVD ZnO layer shown in Fig. 1 indicate that these layers are constituted of large grains having a columnar shape and a pronounced orientation perpendicular to the crystallographic planes $(1\,1\,\bar{2}\,0)$. The extremities of these grains appear at the ZnO surface as pyramids, as can be observed in Figs. 2(b) and 3(b). These pyramidal grains yield an as-grown surface texture that efficiently scatters the light that enters into the solar cell.

3.2. *Thickness variation of the ZnO layers*

Increasing the thickness of doped LP-CVD ZnO layers from 400 nm to ~2.5 μm allows one to reduce the sheet resistance (R_{sq}) from ~70 to ~5 Ω_{sq}. This latter value is low enough to consider the ZnO layer as good electrical contact for solar cells.

The TT and TD of LP-CVD ZnO layers are represented in Fig. 2(a), in function of the thickness (d) of these layers, which are doped with a B_2H_6/DEZ ratio of 0.6.

TT stays over 85% in the range 350–1000 nm for $d < 1.5$ μm. As there is about 15% of the light that is reflected at the various interfaces air/ZnO/glass/air, this means that for $d < 1.5$ μm, the absorption of the ZnO layers is too low to be measured by the spectrometer. TT is reduced to slightly less than 80% for $d = 3$ μm, a value of TT that is still high for such very thick layer. Furthermore, TD is strongly enhanced when d is increased from

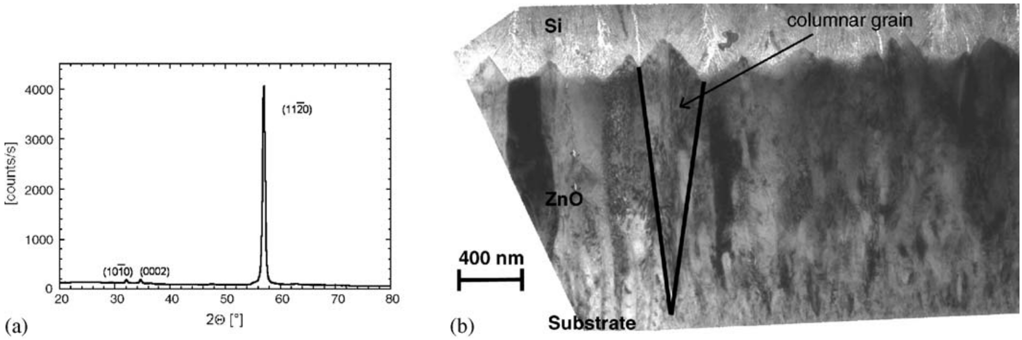

Fig. 1. (a) XRD pattern of a 2 μm-thick doped LP-CVD ZnO layer. (b) TEM micrograph of a cross-section of this layer. These figures indicate that ZnO layers deposited by the LP-CVD process are constituted of large grains having a columnar shape and a pronounced orientation perpendicular to the crystallographic planes $(1\,1\,\bar{2}\,0)$.

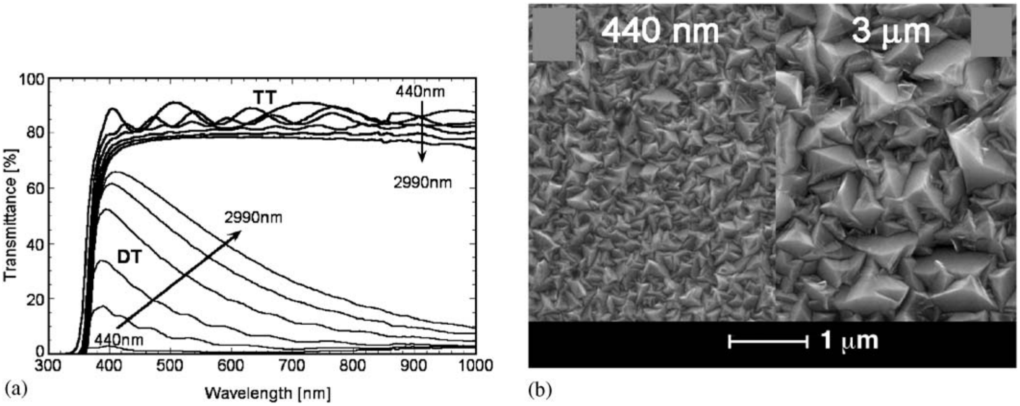

Fig. 2. (a) TT and TD of LP-CVD ZnO layers in function of the thickness (*d*) of these layers, which are doped with a B_2H_6/DEZ ratio of 0.6. TT is slightly reduced, whereas TD is strongly enhanced when *d* is increased from 440 nm to ~3 μm. (b) SEM micrographs of the surface of thin (440 nm) and thick (3 μm) LP-CVD ZnO layers. The size of the pyramidal grains of the ZnO surface increases with the thickness of the ZnO layers.

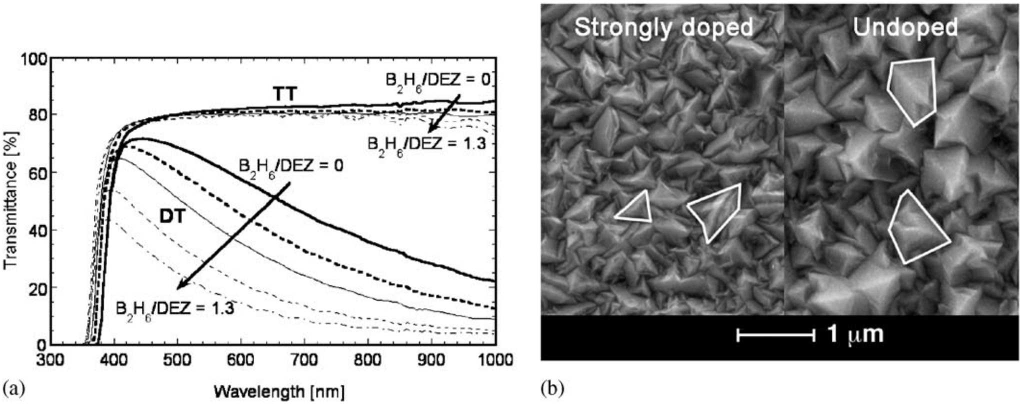

Fig. 3. (a) TT and TD of 2.4 μm-thick LP-CVD ZnO layers in function of the B_2H_6/DEZ ratio used to dope these layers. The drop of TT in the NIR wavelength range is due to the free-carrier absorption, which increases when the doping ratio and therefore, the free-carrier concentration, is increased. TD is reduced when the doping ratio is increased. (b) SEM micrographs of the surface of a strongly doped and an undoped LP-CVD ZnO layers. The size of the pyramidal grains of the ZnO surface is reduced when the doping ratio is increased.

440 nm to ~3 μm. This means that the light-scattering capacity of the LP-CVD ZnO layers can be considerably improved by increasing the thickness of these layers.

The SEM micrographs shown in Fig. 2(b) indicate that the size of the pyramidal grains of the ZnO surface increases with the thickness of the ZnO layers. This observation can be correlated with the cross-section of the ZnO layer shown in Fig. 1(b). Indeed, while the columnar grains are growing, they are also gaining in width, and therefore their extremities, which are the pyramids observed on the surface of the layer, are also enlarged. Measurements of rms value of the surface roughness of ZnO layers have shown that the height of the pyramids also increases with the thickness of these layers.

3.3. *Doping variation of the ZnO layers*

Doping the ZnO layers allows one to reduce considerably the resistivity of these layers, in order to use them as electrical contact for solar cells. Indeed, the sheet resistance of a 2.5 μm-thick ZnO layer can be lowered from $\sim 50\,\Omega_{sq}$, for the undoped layer, to $\sim 5\,\Omega_{sq}$, for the layer doped with a B_2H_6/DEZ ratio of 0.6.

The TT and TD of 2.4 μm-thick LP-CVD ZnO layers are represented in Fig. 3(a), in function of the B_2H_6/DEZ ratio used to dope these layers.

The drop of TT in the NIR wavelength range is due to the free-carrier absorption, which increases when the doping ratio, and therefore the free-carrier concentration, is increased [10]. This drop should in principle be as low as possible, because it occurs in a wavelength range for which our ‘micromorph’ solar cells are photovoltaically active (i.e., for photon energies above the energy gap of μc-Si:H, which is 1.12 eV). This highlights the importance of minimizing the amount of dopant needed in the ZnO film.

Furthermore, increasing the doping ratio reduces also the light-scattering capacity of the ZnO layers, as illustrated by the diminution of TD for higher B_2H_6/DEZ ratios.

Finally, the SEM micrographs of the surfaces of an undoped and a strongly doped ZnO layers, represented in Fig. 3(b), show that the size of the pyramidal grains of the ZnO surface is also reduced when the doping ratio is increased.

3.4. *Correlation between grain size and light-scattering capacity of ZnO layers*

In order to quantify the evaluation of the size of the pyramidal grains that are visible at the surface of the ZnO layers, the dimensional parameter has been defined. The mean of the projected area of the pyramids has been evaluated from the SEM micrographs, as illustrated by the white drawings in Fig. 3(b). δ is set equal to the square root of this mean projected area, and is therefore a one-dimensional parameter.

Fig. 4 represents haze factor values in function of the dimensional parameter δ, for about 30 different ZnO samples deposited by LP-CVD with various deposition parameters like various values of thickness, doping concentration, etc. This graph demonstrates the direct dependency of the light-scattering capacity of the ZnO layers on the size of the pyramidal grains located at the surface of these layers: the larger the pyramidal grains, the higher the haze factor and therefore, the higher the light-scattering capacity.

These observations highlight the importance to have an improved ZnO structure, i.e., ZnO layers with large crystals, in order to enhance the light-scattering capacity of these layers.

3.5. *Proposed method for optimizing the light-scattering capacity of ZnO layers while keeping them conductive and transparent enough*

Enhancing the thickness of the ZnO layers allows one to increase δ and therefore, the light-scattering capacity of these layers. Furthermore, thicker ZnO layers are more electrically conductive. The only limit to this increase of the thickness is the absorption of ZnO that can start to become significant. But this limit is quite far, as even thick ZnO layers are highly transparent.

An other way to enhance δ, and therefore the light-scattering capacity of the ZnO layers, is to reduce the doping ratio. This will also reduce the absorption of these layers,

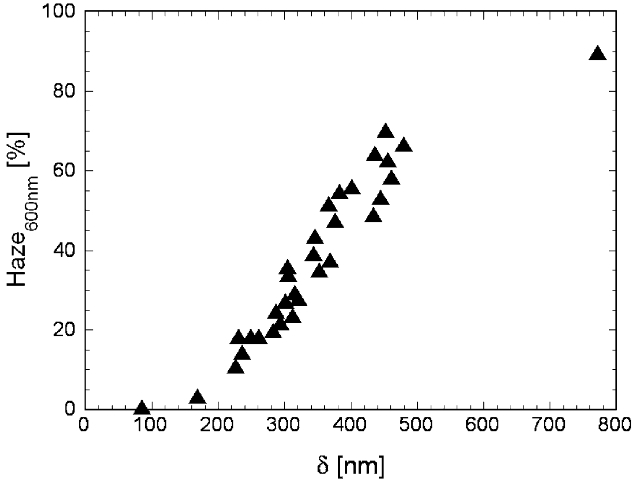

Fig. 4. Haze factor values in function of the one-dimensional parameter δ (defined as the square root of the mean of the projected area of the pyramids, which has been evaluated from the SEM micrographs), for about 30 different ZnO samples deposited by LP-CVD with various deposition parameters. The larger the pyramidal grains, the higher the haze factor and therefore, the higher the light-scattering capacity.

particularly in the NIR range. However, R_{sq} will in this case increase when the doping ratio is reduced. The highest R_{sq} value still acceptable depends on the solar cell contacting configuration, and this is the major limitation of reducing the doping ratio in order to enhance the light-scattering capacity of ZnO layers.

In conclusion, we can estimate that an efficient way to enhance at maximum the light-scattering capacity of ZnO layers while still keeping high transparency and conductivity values for these layers is, first, to enhance their thickness until their absorption begins to be significant, and then, to reduce the doping ratio until reaching the maximum value of R_{sq} that can still be accepted for our particular solar module.

3.6. Performances of p–i–n μc-Si:H solar cells deposited on rough LP-CVD ZnO front contacts

This study has been conducted in order to observe the impact of the light-scattering capacity of the front TCO layer on the absorption of a p–i–n μc-Si:H solar cell in the long-wavelength range (the thickness of the i-layer is generally high enough to absorb the short wavelengths but not the long wavelengths).

The same p–i–n μc-Si:H solar cell has been deposited on four front ZnO substrates, having various thicknesses and therefore, various light-scattering capacities. In order to observe only the contribution of the light-scattering produced by the front ZnO layer, no back reflector has been deposited on this solar cell. In fact, only a single LP-CVD ZnO layer has been deposited on the rear side in order to contact the cell. The surface of the solar cells has been set at $0.25\,\mathrm{cm}^2$ and defined by plasma etching.

For each kind of substrate, more than 75% of the cells have good electrical characteristics, i.e., open circuit voltage, $V_{oc} > 500\,\mathrm{mV}$ and fill factor, $\mathrm{FF} > 63\%$.

Fig. 5 shows the quantum efficiency (QE) curves of solar cells deposited on these four different substrates. With the use of a thicker ZnO front layer, there is a clear increase of

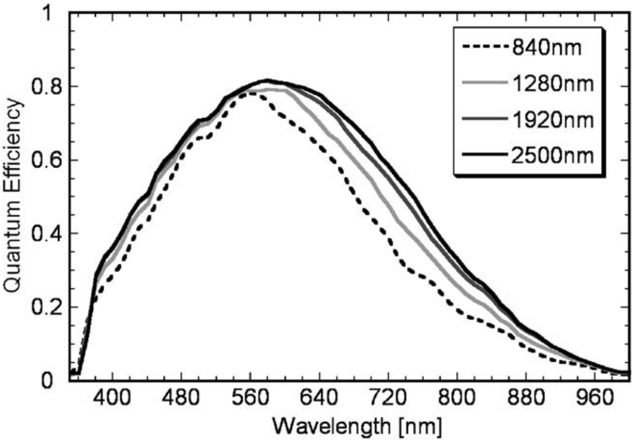

Fig. 5. QE curves of p–i–n μc-Si:H solar cells deposited on four different LP-CVD ZnO front layers, having various thicknesses and therefore, various light-scattering capacities. With the use of a thicker ZnO front layer, there is a clear increase of the QE in the 550–1000 nm range, which results in an increase of the photo-generated current within this range from 10.4 to 13.4 mA/cm^2.

the QE in the 550–1000 nm range, which results in an increase of the photo-generated current within this range from 10.4 to 13.4 mA/cm^2. Within the whole solar spectral range (i.e., [350–1000 nm]), the photo-generated current is increased from 15.2 to 18.8 mA/cm^2. This demonstrates the benefit to have a front ZnO layer with improved light-scattering capacity, which means a ZnO layer constituted of large grains.

Furthermore, the slighter increase of the QE in the blue wavelength range indicates that for the same deposition time, the thickness of the p-layer is lower if this layer is deposited on a rougher substrate. Indeed, the p-layer deposited on the less-rough ZnO substrate is probably too high and therefore, this causes an excessive absorption of short wavelengths within this layer. This aspect highlights the importance of optimizing the deposition time of the silicon layers, individually for each kind of substrate roughness. Moreover, it is not yet clear if the kind of ‘saturation’ observed in Fig. 5 for the increase of the QE in the red range is due to the absorption of the front ZnO, which, however, appears not yet to be significant, even for a thickness of 2.5 μm, or to the silicon layers, which could possess different growth characteristics depending on the extent of the ZnO surface roughness. Indeed, as enhancing the light-scattering capacity of the front ZnO layer to its maximum means enhancing the surface roughness of this layer to its maximum, the deposition of silicon layers on such a very rough ZnO substrate could perhaps also need a further optimization.

4. Conclusions

A direct dependency of the light-scattering capacity of LP-CVD ZnO layers on the size of the pyramidal grains constituting these layers has been observed in this study. Indeed, the larger the grains, the stronger the light-scattering capacity of the ZnO layers.

Furthermore, two ways to widely ‘tune’ the size of these pyramidal grains have been identified: thickness and doping ratio variation yields haze factor values varying from 1% to over 50%. Increasing the thickness of ZnO layers means increasing their light-scattering capacity and decreasing their electrical sheet resistance. Reducing the doping ratio in ZnO layers means also increasing their light-scattering capacity, but in this case, it increases the electrical sheet resistance of the ZnO layers. This large range of possibilities to vary the surface roughness and the optical/electrical properties of ZnO layers allows one to finely match the sheet resistance and transparency needed for a particular solar cell configuration, with a maximum value of light-scattering capacity. This flexibility is a clear advantage of the LP-CVD deposition technique.

A method to enhance to its maximum the light-scattering capacity of ZnO layers while keeping them conductive and transparent enough has been proposed.

Finally, a short study of incorporation of rough ZnO layer as front contact into a p–i–n μc-Si:H solar cell has been presented. This study demonstrated the beneficial effect of the enhanced light-scattering capacity of front LP-CVD ZnO layers on the absorption of thin-film silicon solar cells. However, this study also highlighted the complexity of this kind of incorporation work, which requires not only an optimization of the ZnO layer, but also (interactively) of the solar cell deposited on it.

The property of light scattering is crucial for solar cell technology based on thin-film silicon, and therefore it is important to continue to improve the structure of ZnO layers. In this context, the LP-CVD process seems indeed to be a very suitable process.

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