Opto-electronic properties of rough LP-CVD ZnO:B for use as TCO in thin-film silicon solar cells

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Abstract

Polycrystalline Boron-doped ZnO films deposited by low pressure chemical vapor deposition technique are developed for their use as transparent contacts for thin-film silicon solar cells. The size of the columnar grains that constitute the ZnO films is related to their light scattering capability, which has a direct influence on the current generation in thin-film silicon solar cells. Furthermore, if the doping level of the ZnO films is kept below 1×10^{20} cm^{-3}, the electron mobility can be drastically enhanced by growing large grains, and the free carrier absorption is reduced. All these considerations have been taken in account to develop ZnO films finely optimized for the fabrication of microcrystalline thin-film silicon solar cells. These TCO allow the achievement of solar cell conversion efficiencies close to 10%.
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Keywords: LP-CVD Zinc Oxide; Thin-film silicon solar cells; Grain size; Light scattering; Electron mobility

1. Introduction

Boron-doped Zinc Oxide (ZnO) deposited by Low Pressure Chemical Vapor Deposition (LP-CVD) has proven to be a good candidate as TCO for thin-film silicon solar cells. This is not only because of its high transparency over the visible and near-infrared (NIR) range, and of its electrical resistivity that can be lowered down to 1×10^{-3} Ω cm, but also because of its capability to scatter efficiently the light that enters into the solar cell. This scattering effect enhances the path of the light inside the solar cell, and therefore increases its probability to be absorbed by the cell, leading, thus, to an increase of the photo-generated current. This property is especially important in the case of amorphous and microcrystalline silicon (a-Si:H and μc-Si:H) thin-film solar cells, because of the relatively low values of their absorption coefficient [1,2].

The LP-CVD technology allows one to easily vary deposition parameters over a wide range of values and to obtain ZnO layers having various values of surface roughness, sheet resistance and optical transparency [3]. However, this high flexibility of deposition conditions means that the ZnO layer design

(in particular variation of thickness and doping level) becomes a time-consuming task, if one wants to optimize these layers for a-Si:H or μc-Si:H solar cells. A comprehensive analysis of the deposition of ZnO films by LP-CVD process has been carried out in our institute, with the goal of using these films as TCO for in-house developed thin-film silicon solar cells [4]. In particular, the size of the grains that constitute the ZnO films has been found to have a direct influence on both the light scattering capability and the electrical conductivity of the ZnO films. This dependency is presented in this paper, and the parameters for deposition of optimized ZnO films intended to be used as rough TCO in thin-film silicon solar cells are described.

2. Experimental

ZnO films were deposited by LP-CVD process on glass substrates. Diethylzinc (DEZ) and water (H$_2$O) vapours were used as precursors, and directly evaporated in the system. DEZ and H$_2$O flows were set to 13.5 sccm and 16.5 sccm, respectively. Diborane (B$_2$H$_6$) was used as doping gas, diluted at 1% in Argon. The total pressure was kept at 0.5 mbar ($\sim$0.37 Torr), and the substrate was heated to a temperature of 155 °C.

Doping series of ZnO have been deposited, by varying the gas phase doping ratio (B$_2$H$_6$/DEZ) from 0 (naturally doped

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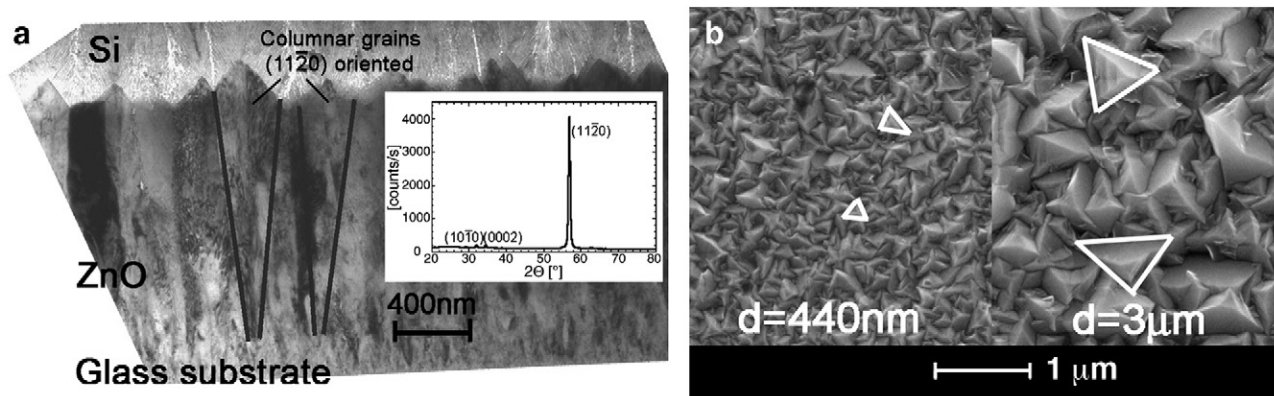*E-mail address:* sylvie.fay@unine.ch (S. Faÿ).

Fig. 1. (a) TEM micrograph of a cross-section of a 2 μm-thick LP-CVD ZnO:B layer constituted of columnar grains. The associated XRD pattern shows the strong preferential crystallographic orientation of this kind of layers. (b) SEM micrographs of the surface of two LP-CVD ZnO layers with different thicknesses (440 nm and 3 μm). The surface is constituted of pyramidal grains, which are the extremities of the columnar grains shown in a. The width of the columnar grains and the height of the pyramidal grains are increased while the thickness of the ZnO films is increased.

thereafter be called undoped ZnO) to 2 (highly doped ZnO). By this way, the carrier concentration of the ZnO films has been varied from 3×10^{19} cm^{-3} to 2.2×10^{20} cm^{-3}. Thickness series of ZnO have also been deposited, in order to vary the grain size of the ZnO films from ~ 100 nm to ~ 600 nm.

Optical transmission of the resulting films, both total and diffuse (TT and TD, respectively), were measured using a spectrometer with an integrating sphere, in the visible and NIR wavelength ranges. The wavelength-dependent haze factor is defined as the TD/TT ratio. This factor quantifies the light scattering capability in air of the ZnO films. The resistivity ρ, the Hall carrier concentration N, and the Hall mobility μ were deduced from Hall measurements using a Van der Pauw configuration at room temperature. Transmission Electron Microscopy (TEM) micrographs were performed to characterize the microstructure of the ZnO layers. Finally, surface topography

images were taken by Scanning Electron Microscopy (SEM). The borders of the grains observable at the scanned surface were detected with the help of the "AnalySIS" software, and the grain size δ of the ZnO films has been deduced from these measurements.

3. Results and discussion

3.1. Influence of the grain size on the light scattering capability of LP-CVD ZnO films

The TEM micrograph of a cross-section of a 2 μm-thick LP-CVD ZnO layer shown in Fig. 1a indicates that these layers have a polycrystalline structure. They are constituted of large grains having a columnar shape. The corresponding XRD graph for this LP-CVD ZnO:B film, which is also shown in Fig. 1a, reveals a strong preferentially-oriented growth perpendicular to the (11$\bar{2}$0) crystallographic planes [5]. The extremities of these
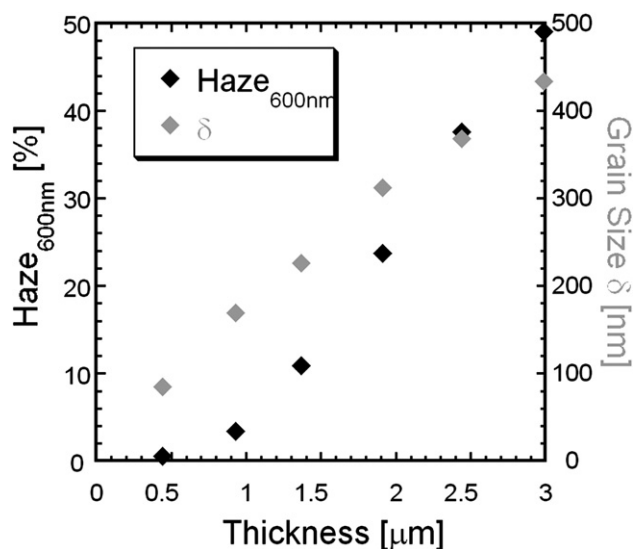

Fig. 2. Values of Haze factor measured at 600 nm and grain size δ of the pyramidal grains that constitute the LP-CVD ZnO surface, as a function of the thickness d of LP-CVD ZnO films. The thicker the films, the larger the pyramidal grains, the higher the haze factor and therefore, the higher the light scattering capability of the ZnO films.
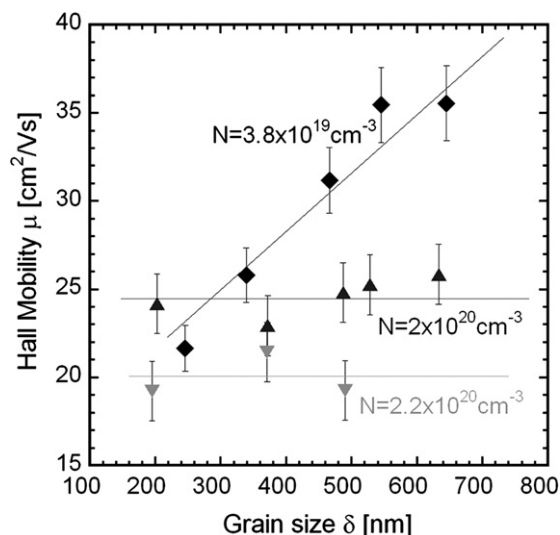

Fig. 3. Hall mobility as a function of the size δ of the pyramidal grains which constitute the LP-CVD ZnO surface, for ZnO films with carrier concentration (N) of 3.8×10^{19} cm^{-3}, 2×10^{20} cm^{-3} and 2.2×10^{20} cm^{-3}.
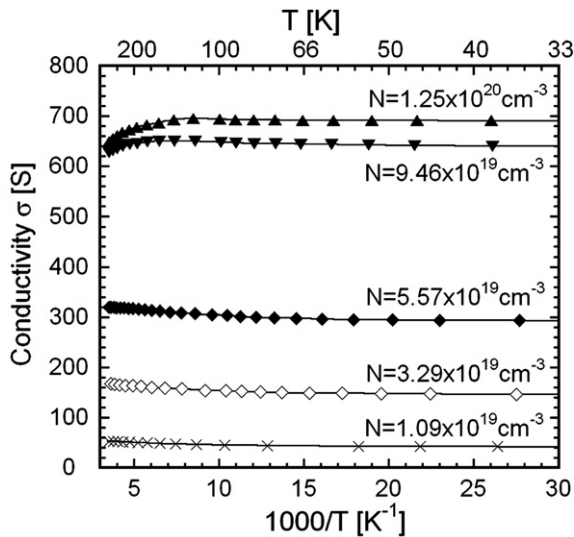
Fig. 4. Conductivity σ as a function of 1000/T for LP-CVD ZnO films with different carrier concentrations.

columnar grains appear at the ZnO surface as pyramids, as can be observed in Fig. 1b. It is precisely such a pyramidal structure that gives to the ZnO layers an as-grown surface texture that efficiently scatters the light that enters into the solar cell [6].

The grain size of the ZnO films has been evaluated from the SEM micrographs, by detecting the borders of the grains observable at the scanned surface, as illustrated by the white drawings in Fig. 1b. The mean projected area of the grains was deduced, and the square root of this value was taken as dimensional parameter δ for the grain size.

One way to easily increase δ is by increasing the thickness d of the ZnO films, as illustrated by the two SEM micrographs of Fig. 1b, representing surfaces of two ZnO films having two different thicknesses. Indeed, the columnar grains observed in Fig. 1a are widened with the increasing thickness and the small

grains disappear, leading to higher pyramidal shapes at the film surface.

In order to evaluate the influence of the grain size on the light scattering capability of the LP-CVD ZnO films, the haze factor values measured at 600 nm of a thickness series of ZnO films were correlated with δ. The resulting graph shown in Fig. 2 demonstrates the direct dependency of the light scattering capability of the ZnO films on the size of the pyramidal grains located at the surface of these layers: the thicker the ZnO films, the larger the pyramidal grains, the higher the haze factor and therefore the higher the light scattering capability of the LP-CVD ZnO films.

In order to observe directly the influence of an improved light scattering capability of the front TCO in a thin-film silicon solar cell, a thickness series of LP-CVD ZnO films was deposited. An increase of almost 30% of the photo-generated current was observed in the [550 nm–1000 nm] wavelength range, for the same microcrystalline silicon solar cell deposited on the ZnO films with δ varying from ~ 100 nm ($d=840$ nm) to ~ 400 nm ($d=2.5$ μm), respectively [7].

3.2. Influence of the grain size on the electrical properties of LP-CVD ZnO films

In polycrystalline thin films like LP-CVD ZnO, the electron mobility can be limited mainly by two mechanisms: the electron scattering within the grains (e.g. the scattering by the ionized impurities, lattice defects, or phonons) or the electron scattering that occurs at the grain boundaries, due to the potential barrier formed at these locations [8,9]. In the latter case, the electron mobility should increase if the grain size is increased, because of the decrease of the grain boundary density. Fig. 3 shows the Hall mobility μ versus grain size δ for three ZnO thickness series with different carrier concentrations. The mobility of ZnO films with low carrier concentration ($N=3.8\times10^{19}$ cm^{-3}) is dependent on the grain size, and increases from 22 to 35 cm^2
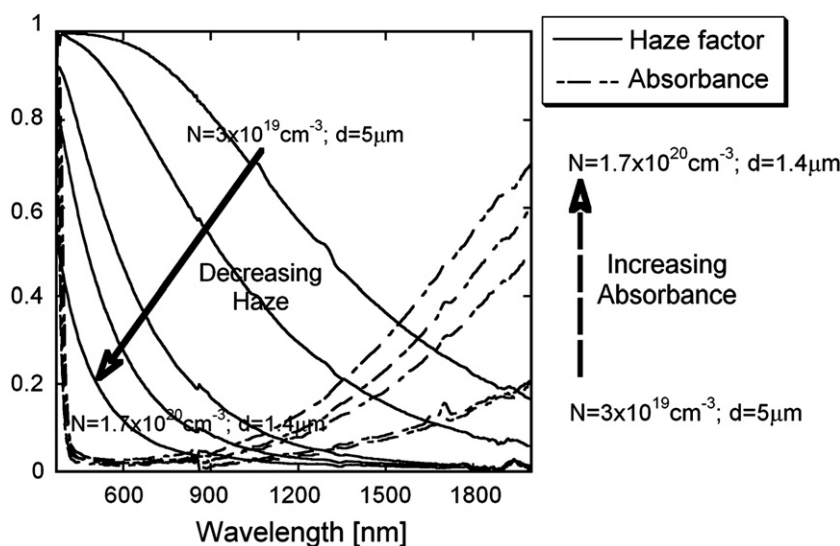

Fig. 5. Haze factor and absorbance spectra of LP-CVD ZnO films with different carrier concentrations and thicknesses, but possessing all a similar sheet resistance close to 10 Ω/□.

V^{-1} s^{-1}, while δ is increased from 240 nm to 640 nm. In contrary, μ remains nearly constant for highly doped samples ($N=2\times10^{20}$ cm^{-3} and $N=2.2\times10^{20}$ cm^{-3}). These results mean that the conduction mechanisms within LP-CVD ZnO depend on the doping level of the films. In order to investigate further these transport mechanisms, the temperature dependency of the conductivity σ has been measured. Fig. 4 shows σ as a function of the inverse of the temperature T measured from $T=300$ K down to $T=30$ K, for ZnO films with various doping levels but with a constant grain size. Below 150 K, σ remains almost constant. This can be explained by a temperature independent mechanism such as field assisted tunneling conductivity through grain boundaries [10], whereas the bulk of the grains remains degenerated. From 150 K to room temperature, σ becomes temperature dependent with two different trends, according to the doping level of the films. It increases with T for undoped and lightly doped samples (i.e. N less than 1×10^{20} cm^{-3}). This trend, correlated with the increase of μ with δ in Fig. 3, is characteristic of thermally-activated mechanisms like thermo-ionic field emission occurring at grain boundaries. For highly doped films (i.e. N more than 1×10^{20} cm^{-3}), σ is reduced while T is increased. This trend is characteristic of a metal-like behavior, and suggests the presence of mechanisms such as lattice vibration scattering. These mechanisms are likely to occur within the grains and explain the fact that μ does not depend on the grain boundary density for highly doped ZnO samples (see Fig. 3).

In order to use the ZnO as electrical contact for solar cells, it is necessary to lower the sheet resistance R_{sh} of these films down to 8–10 $\Omega/\square$. This can be achieved by either increasing the electron mobility μ or the free carrier density N. However, increasing N induces an increase of the so-called Free Carrier Absorption (FCA) effect, which appears in the NIR range [11]. If N becomes too high, the FCA effect becomes significant, and therefore the transparency of the LP-CVD ZnO films can be affected within the wavelength range for which the silicon thin-film solar cell are still absorbing light, i.e. up to 1100 nm for μc-Si:H solar cells. Therefore, the efficient way to decrease ρ while keeping the FCA low is increasing μ rather than N. We conclude from Fig. 3 that if we keep a sufficiently low doping level (i.e. $N<1\times10^{20}$ cm^{-3}), μ can be significantly increased by increasing the grain size, which can be done easily by increasing the thickness d. Furthermore, the value that needs to be decreased is the sheet resistance R_{sh}, which is actually reduced by increasing d ($R_{sh}=\rho/d$).

From all the results presented in this paper, we can conclude that the less absorbing LP-CVD ZnO films should be the one with a low doping level. Furthermore, a high thickness allows one to obtain both a high light scattering capability and a sufficiently low R_{sh} value. Fig. 5 shows the absorbance and haze spectra of ZnO films with different doping levels and thicknesses in order to keep their sheet resistance constant to 10 $\Omega/\square$. As predicted, the films with the highest transparency and the highest light scattering capability (i.e. the haze curve) is the one which has the lowest doping level but a thickness of 5 μm. Recently, such optimized ZnO films have been success-fully integrated into μc-Si:H solar cells, and photo-generated currents of up to 24.7 mA/cm^2 have been obtained, leading to conversion efficiencies close to 10% [12].

4. Conclusion

In this paper, we highlighted the direct influence of the grain size and the doping level of polycrystalline LP-CVD ZnO:B films on both light scattering capability and electrical conductivity of these films. These two properties are of prime importance when the ZnO films are used as TCO for thin-film silicon solar cells. We demonstrated that optimized ZnO films possess large grains that can be obtained for thick films (i.e. $d>4$ μm) with a low doping level (i.e. $N\sim6\times10^{19}$ cm^{-3}). This high thickness induces a high light scattering within the solar cells, and keeps both the absorbance and the sheet resistance of the ZnO films low enough to be considered as efficient TCO films. These films are suitable for the fabrication of high efficiency microcrystalline and micromorph solar cells.

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