Interplay between Roughness and Haze of CVD Grown ZnO:B Layers for a-Si:H/μc-Si:H Solar Cells

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Abstract: A broad use of ZnO:B TCO (transparent conductive oxide) layers as a front contact material for amorphous (a-Si:H) and tandem (a-Si:H/μc-Si:H) silicon thin film solar cells is achieved due to an excellent combination of good optical transparency, electrical conductivity and rough surface structure. The latter provides a light trapping effect within the underlying absorber, which is characterized by the optical haze value, i.e. a ratio between diffuse and total transmittances. The synthesis of such kind of surfaces requires the precise optimization of deposition processes, which in turn may significantly affect the further formation of silicon absorber layers and, as a result, influence the solar cells performance. Following the industrial fabrication, one has to consider both the physical properties of deposited TCO layers (resistivity, optical transparency and haze) and their processing parameters (a deposition rate, adjustable for the enterprise production tact time, and an optimum material consumption for the lowest synthesis and reactor’s cleaning costs). In the present study, the growth of ZnO:B layers by CVD (chemical vapour deposition) is discussed. The film properties and their production process characteristics were optimized in order to keep the balance between the optimum parameters of TCO layers, the best chemical conversion efficiency and the fastest deposition rate at various gas flows, pressure and temperatures. The highest attention was paid to obtain ZnO:B films with controllable optical haze, which was varied between 2 and 50% (at 600 nm wavelength) by changing the layer thickness and CVD process regimes. It was found that the crystallinity of subsequently deposited a-Si:H/μc-Si:H structures correlates with the optical haze and surface roughness of ZnO:B substrate layers, which leads to the significant effect on the light trapping and band-gap values of silicon films.

Key words: TCO, thin film solar cells, optical haze, light trapping, deposition rate, material consumption.

1. Introduction

The high optical transparency and good electrical conductivity of ZnO films have greatly expanded their practical application as transparent conductive electrodes in various types of photovoltaic devices [1]. It is also well known that the rough surface at the interface between the top conductive layer and light absorber stimulates the light trapping, what is particularly important for a-Si and μc-Si thin film solar cells since it compensates a low light absorption coefficient of silicon [2]. The main advantage of using ZnO films for the design of such kind of structures is a possibility to obtain any necessary texture at the interface. This goal can be achieved either by post deposition etching, when the initial smooth surface produced by standard sputtering technique is modified after its fabrication by RF sputtering [3, 4], or by direct adjustment of the growth mechanism following the CVD (chemical vapour deposition) process, where the rough surface with a high diffuse transmittance can be obtained in a controllable way [4-6]. Therefore, in order to synthesize ZnO layers suitable for further application in high efficiency and low cost, Si thin film solar cells, the optimization of their CVD production parameters by tuning the optical haze, i.e. the ratio between the direct and diffusive transmittances, have to be considered [7].

In addition, the obtained rough TCO (transparent conductive oxide) surface may play a well-defined role in the growth of upper a-Si and μc-Si films. It can influence the ratio between formed amorphous and crystalline silicon phases, which is efficiently

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Distinguished by means of Raman measurements [8, 9]. The previous study [10] has shown a significant dependence of Si crystallinity on the haze values (varied by changing their thickness) of applied ZnO precursors layers. Nevertheless, the investigation of the above mentioned effects, in particular, the role of the interface surface structure and the dependence of optical haze on CVD process conditions (temperature, pressure and gas flows) is remaining a significantly important task. It is also crucial from the practical point of view to take into account the industrial production output, where other aspects, such as the controllable deposition rate and optimum material consumption, have to be followed in order to minimize the fabrication and device maintaining costs [11].

As it is known, the CVD process can be efficiently described by two extreme cases: the surface reaction limitation (controlled by decrease of temperature and/or pressure) or the mass transport (gas flow) limitation [12, 13]. The key characterization parameter in both cases is a deposition rate. It proportionally increases with the temperature or pressure increase in the reaction limited regime, whereas saturates to the maximum value in the mass transport limited conditions, which is mainly defined by the construction of the used chemical reactors [13]. Therefore, one of the most important CVD characteristics for the industrial application becomes a conversion efficiency of applied chemical reaction, which can be calculated as a ratio between grown and supplied materials. In the case of CVD growth of ZnO by decomposition of DEZ (di-ethyl zinc: Zn(C₂H₅)₂) in water:

\[
\text{Zn(C₂H₅)₂} + \text{H₂O} \rightarrow \text{ZnO} + \text{C₂H₆}
\]

the conversion efficiency of corresponding chemical reaction (η) can be simply found as a ratio between the molar quantity of formed ZnO ([ZnO]) and supplied DEZ ([DEZ]) as Eq. (2):

\[
\eta = \frac{[\text{ZnO}]}{[\text{DEZ}]} = \frac{\nu_{\text{Dep}}}{\frac{\rho \text{ZnO} V_m}{M(\text{ZnO}) V_{\text{DEZ}}}}
\]

where \(\nu_{\text{Dep}}\) is a ZnO deposition rate; \(s\) is a surface area of deposited layer; \(\rho\text{ZnO}\) and \(M(\text{ZnO})\) are density and molar mass of ZnO, respectively; \(V_m\) is a gas molar volume at applied process conditions and \(V_{\text{DEZ}}\) is a DEZ supply flow.

At the optimum selection of CVD regimes, one can obtain the highest conversion efficiency of chemical reaction Eq. (1), which minimizes the consumption of DEZ and, therefore, reduces the reactor contamination outside of its deposition area, i.e. decreases cleaning costs. Thus, the fully optimized process has to combine the best physical properties of deposited layers (lowest resistivity, highest optical transmittance and haze) with the most effective growth conditions (the highest DEZ conversion efficiency at the required deposition rate). This paper provides a continuous study on the importance of CVD process optimizations for a large-scale industrial growth of high quality ZnO:B films and their effect on subsequently formed a-Si and μc-Si light absorber layers.

2. Experimental Details

The ZnO:B layers were synthesized by an LPCVD (low pressure (0.5-1.5 mbar) chemical vapour deposition) process within 174-215 °C temperature range on TCO-1200 production set-up [14] (Oerlikon Solar, 130 × 110 cm² glass substrate processing area) at 2.4-8.0 nm/s deposition rates. The H₂O/DEZ vapours mixture in 1.5-2.1 volume proportion ratio was used as a gas precursor (see Eq. (1)), while B₂H₆/hydrogen flow was applied for boron doping. The schematic image of used LPCVD reactor is presented in Fig. 1a. Its working performance can be efficiently described by the characteristic curves representing the correlation between DEZ conversion efficiency and ZnO deposition rates. Then the linear dependences with slopes, inversely proportional to supplied DEZ flows, are observed, which is in a good agreement with Eq. (2). Thus, the upper curve of Fig. 1b shows the highest possible conversion efficiency
for the applied construction of CVD reactor (see Fig. 1a).

The highest attention was also paid to the optical characterizations of deposited ZnO:B layers, where the direct and diffuse transmittance/reflection spectra were measured by Lambda 950 Perkin Elmer spectrometer in the integration sphere configuration (see Fig. 2a) under the subsequent estimation of optical haze as a ratio between diffuse and direct transmittances. The characteristic haze value was selected around 600 nm and it was always followed for the further analysis. The total absorption value for the TCO layers was estimated from methylene iodide (CH$_2$I$_2$) index matched spectra [14] as an average within 400-800 nm (visual range) and 400-1,100 nm (visual and infrared ranges), respectively (see Fig. 2a). The thickness effect on the optical haze [10] can be estimated and corrected with corresponding relative normalized curve (see Fig. 2b). It represents the proportion between the normalized differences of haze and thickness comparing to values obtained from the reference sample (i.e. 1,550 nm thick film with 15% haze). As one can see, these changes stay almost linear in the middle region with a proportion coefficient close to three (Fig. 2b). Therefore, for example, the ~60% increase in haze (from 15 to 25%) requires ~20% thickness increase (from 1,550 to 1,900 nm).

The further process adjustment was performed using the optimum DEZ conversion efficiency curve (see corresponding DEZ supply flow lines in Fig. 1b), whereas its complementary dependences of deposition rate on the temperature and pressure are presented in Fig. 3a and Fig. 3b, respectively. The fine tuning procedure was subsequently done following the corresponding variation of TCO optical haze values as it is shown in Fig. 4, where the experimental data of the same CVD processes as in Fig. 3 are summarized with respect to DEZ supply rates, temperatures (Fig. 4a) and pressures (Fig. 4b). The optimum process
Fig. 2 The typical optical spectrum of deposited ZnO:B layers (a) and the dependence of relative normalized changes of their optical haze at 600 nm on the corresponding film thickness varying (b). The zero point corresponds to 1,550 nm thick reference layer with 15% haze.
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Fig. 3  ZnO:B layers deposition rates as a function of substrate temperatures (a) and process chamber pressure (b). The considered DEZ flows are selected from lines in Fig. 2b.

Fig. 4  The dependence of optical haze of ZnO:B layers on their deposition temperatures (a) and pressures (b). Corresponding dependences are presented with the same notations as in Fig. 3, while keeping the thickness of all measured layers constant (1,550 ± 50 nm).
regimes were then selected combining dependences in Fig. 1b, Figs. 3a-3b, and Figs. 4a-4b under additional adjustments of optical haze by ZnO layer thickness (Fig. 2b).

The obtained ZnO:B films with different haze level (varied between 1 and 50%) were used as substrates for silicon layers deposition. They were grown by a PECVD using KAI-1200 production set up [15] (Oerlikon Solar, 130 × 110 cm² processing area) at 40 MHz plasma excitation modes in SiH₄/H₂ gas mixture (2.5 mbar gas discharge pressure with 1,500/3,200 W power levels for depositions of a-Si:H and μc-Si:H, respectively).

The optical properties, primary transmittance and reflection, of silicon layers were also measured by Lambda 950 Perkin Elmer spectrometer (similarly as it is shown in Fig. 2a) with a subsequent derivation of absorption spectra and cut-off frequency in order to estimate the band-gap value. The main part of structural studies was performed using AFM (atomic force microscopy) techniques, where the RMS (root mean square) surface roughness of ZnO and corresponding ZnO/a-Si:H/μc-Si:H films were measured and compared to each other and to TCO optical haze. In addition, the obtained a-Si:H/μc-Si:H structures were investigated by Raman spectroscopy using 514 nm excitation light, followed by further estimation of their Raman crystallinity factor by means of standard fitting procedure [8, 9].

3. Results and Discussion

The AFM images obtained from initial ZnO:B and final ZnO:B/a-Si/μc-Si:H structures are presented in Fig. 5. The surface morphology of formed silicon films in all cases significantly depends on the texture of underlying TCO layers. A linear approximation can efficiently fit the corresponding dependence, where the ZnO surface roughness is smoothed by a factor of 1.6 from grown Si grains (see 0.625 proportion coefficient in Fig. 6a). One can also notice the essential evolution of TCO surface morphology for the higher optical haze. It starts with the small grain structure (~25 nm rough) for ~2% haze (see Fig. 5a) similarly to reported in Ref. [16] with a subsequent change to the pyramidal shape (Fig. 5b) being typical for LPCVD growth [6], which preserves up to 51% haze with a corresponding RMS increase up to ~90 nm (see Fig. 5b). The morphology of upper Si layers consists of spherical grains and their height, i.e. RMS values, increases proportionally to the magnitude of underlying ZnO pyramids (see Figs. 5 and 6b). The obtained results are in a good agreement with the data reported in Refs. [8, 9], where the microcrystalline silicon phase with a cone-shaped structure was growing perpendicular to the substrate plane.

The observed dependence between the ZnO:B film roughness and its optical haze value is not linear. It slowly increases at small roughness values (< 50 nm) reaching a ~10% haze level followed by a fast rise between 50 and 80 nm (10 and 40% haze respectively) and, eventually, stabilization with saturation around 100% would be expected (see gray line in Fig. 6a). The observed dependence can be efficiently approximated by a CDF (cumulative distribution function) versus the ZnO roughness (x), with a central value (μ) close to 89 nm and a standard deviation (σ) around 39 nm:

\[
\text{Haze}(x) = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x - \mu}{\sigma \sqrt{2}} \right) \right]
\]

Eq. (3) is closely related to the physical description of the optical haze as an integration of all diffuse transmitted beams scattered on the rough ZnO surface (see Fig. 6c).

The Raman spectra measured for ZnO films with Si layers grown on their top are presented in Fig. 7. These measurements were done considering the front (irradiation from the silicon surface side) and back (irradiation from the glass/ZnO side) configurations under the subsequent estimation of peaks intensities corresponding to crystalline (510 and 520 cm⁻¹) and amorphous (480 cm⁻¹) silicon phases (see Fig. 7a).
The Raman crystallinity factor ($R_c$) was found as a ratio between integrated intensity of crystalline signals ($I_{520} + I_{510}$) to the total integrated intensity of all Si peaks ($I_{520} + I_{510} + I_{480}$) as described in Refs. [8, 9] as Eq. (4):

$$R_c = \frac{I_{520} + I_{510}}{I_{520} + I_{510} + I_{480}}$$

Although this method has such a disadvantage as a low locality, which is ~20-30 nm in deep from the light excitation surface [17], and may neglect the differences in Raman diffusion cross-section values between c-Si and a-Si:H phases [18], it can provide the sufficient information about the quality of grown silicon layers and variations of their crystallinity [8].

The summarized Raman crystallinity data of measured TCO/silicon structures are presented in Fig. 7b as a function of their RMS roughnesses. It includes the front and back side measurements for a-Si/μc-Si and a reference μc-Si layers. As can be noticed from the plots, the Raman crystallinity factor stays almost constant (its variation interval is 0.59-0.61 r.u.), when the corresponding surface roughness is below 60 nm (which corresponds to ~25% TCO haze level (see Fig. 6a)) and sharply decreases for higher RMS values remarkably observed for all of the studied structures. These variations are significantly smaller in comparison to the data reported for similar experiments [9], where Raman crystallinity factor was decreasing from 50 to 20% following the transitions between flat (low haze) and rough (large haze) surface structures (unfortunately, no exact roughness values were mentioned). The observed difference can be explained by very similar surface texture of our ZnO:B layers (see Fig. 5), which all were grown by identical LPCVD processes, while in Ref. [9] several TCO materials deposited by different methods are compared.

The light trapping properties of ZnO:B/a-Si:H/μc-Si:H structures were studied by optical measurements of their transmittance ($T$) and reflectance ($R$) spectra in 300-2,000 nm range (see Fig. 2a and the following descriptions). The optical absorption spectrum ($A$) has been calculated from the measured values as Eq. (5):

![Fig. 5 AFM profiles of ZnO:B layers (upper line) and a-Si:H/μc-Si:H structures, deposited on their top (bottom line), for 2% (a), 24% (b) and 51% (c) substrate haze level.](image)
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Fig. 6 Dependences of the optical haze and AFM roughness of grown a-Si/μc-Si layers upon the roughness of ZnO:B substrate films (a) together with the schematic image showing the relationship between these two surface roughnesses over the glass substrate (b) and the representation of the diffusive light transmittance on the rough ZnO/Si interface (c).

\[ A(\lambda) = 1 - T(\lambda) - R(\lambda) \]  

(5)

This curve was further applied to estimate the light absorption edge (see Fig. 8a) and corresponding silicon band-gap values as a function of substrate’s optical haze (Fig. 8b). It has been found that the value of a-Si/μc-Si band-gap dramatically decreases (from 1.37 to 1.12 eV) with haze of underlying ZnO layers increasing from 0 to 20% followed by its subsequent stabilization around ~1.1 eV at the higher haze level (see Fig. 8b), which can be efficiently described by exponential decay function. Based on previous data [10] and current studies, where no significant crystallinity change of grown silicon film structures is detected (see Fig. 7b), the observed variations can be linked to the different hydrogen content within grown a-Si:H/μc-Si:H layers [19]. As PECVD process conditions were exactly the same for all processed layers, the observed effect has to be related to the surface reaction at the TCO/Si interface, where hydrogen content can be affected by ZnO during/after its growth [20]. Thus, it can be concluded that the used TCO substrate with low haze and flat surface stimulates an enhanced hydrogenation of grown Si layers,
which leads to the increase of their band-gaps. The maximum value reaches 1.46 eV, which corresponds to the level of reference sample grown on the glass substrate without ZnO coating. The rough ZnO:B surface, which has the higher optical haze, prevents the hydrogen accumulation and, therefore, band-gap values of a-Si/μc-Si layers formed on its top decrease up to 1.1 eV, i.e. close to the level of non-hydrogenated silicon [19]. All of these factors influence the light absorption and light trapping properties.

As one can see from the optical absorption of the glass/ZnO:B/a-Si:H/μc-Si:H structures averaged in the range 400-1100 nm (visible and near IR regions) presented in the Fig. 8a, their light trapping properties increase with increasing of the ZnO:B layer’s roughness at the interface area with silicon. This enhancement is very intense at low roughness levels (up to 50 nm, which corresponds to 20% haze), when the corresponding light absorption within the silicon film increases from 53 to 66%, and then slowly saturates toward ~70% for RMS values above 80 nm (see Fig. 9a). Similar measurements of initial ZnO layers with a correction of absorption within the glass substrate were also carried out in order to explore the possible shadowing effect at their higher thicknesses (see Fig. 9b). The TCO optical absorption is then increased from 2 to 5% for the roughness varied from 30 to 70 nm, while subsequently it rises very slowly up to a value of about 5.8% at RMS levels > 85 nm. This
Fig. 8 Absorption spectra of glass/ZnO:B/a-Si:H/μc-Si:H structures (a) and the calculated band-gap values of corresponding silicon absorber layers as a function of optical haze of underlying ZnO:B films (b).
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Fig. 9 The averaged optical absorption and reflection of glass/ZnO:B/a-Si:H/μc-Si:H structures (a) and corresponding ZnO:B front contacts (b) in the visible/IR range (400-1,100 nm) as a function of TCO roughness at its interface with silicon layers.

confirms that the larger light absorption in glass/ZnO:B/a-Si:H/μc-Si:H structures is mostly attributed to light trapping at TCO/silicon interface, but not to the TCO shadowing itself. The observed light trapping effect is becoming close to the optimum at 50-55 nm roughnesses (~20% TCO haze level) and its further increase does not bring any significant improvement (see Fig. 9a). Remarkable, that both measured structures have relatively high optical reflections (~10% for TCO itself and ~15% for TCO/silicon, respectively) coming from the upper glass substrate, which in fact does not depend on the roughness and haze levels.

4. Conclusions

The optimized preparation of ZnO layers for a-Si:H/μc-Si:H thin film solar cells has to combine their optimum physical properties (high electrical conductivity, optical transparency and haze) and low industrial production costs, i.e. the fastest deposition rate together with the best chemical conversion efficiency. Regarding CVD process, the second goal can be efficiently achieved considering its characterization curve, which represents the dependence of Zn utilization during the corresponding chemical reaction on the ZnO deposition rate and allows choosing the optimum precursor (DEZ) supply flow. The further adjustment of growth and physical parameters of ZnO:B layers is made by selecting the most suitable temperature and pressure in order to reach the slight reaction limited condition. Then the highest attention has to be paid to the optical haze of deposited films as it is the most critical characteristic for the manufacturing process control, which makes the main influence on the light trapping effects. Afterwards, the haze level can also be precisely adjusted by means of the layer thickness varying the deposition time.

It is found that the enhancement of ZnO haze level is caused by the increased roughness of its surface (considering RMS parameters from AFM measurements), which can be described by a cumulative distribution function with a central value at ~89 nm (for 50% haze) and a standard deviation around 39 nm. The roughness of upper deposited silicon layers is in a linear proportion to the RMS level of underlying TCO’s, which slightly influences the Raman crystallinity factor of the fabricated a-Si/μc-Si structure. It stays almost constant (~0.6 r.u.) for RMS values below 60 nm with a subsequent decrease up to 0.55 r.u. for higher roughnesses.

The light trapping effect of ZnO:B films (controlled
by measurements of optical absorption of corresponding glass/ZnO:B/a-Si/μc-Si structures in the visible/IR wavelength range) is found to be close to the optimum at 50-55 nm roughness of TCO with its optical haze above 20% (when ~65% of the incident light is absorbed). This is also accompanied by a significant decrease of band-gap values of a-Si:H/μc-Si:H formed at rough hazy interfaces with ZnO, which is exponentially decaying from 1.37 to 1.10 eV for TCO haze increased from 2% up to 40%, respectively. This can be connected with the lowered level of hydrogen gathering within the silicon layers grown by PECVD on rough ZnO:B substrates.

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References
