Morphological and Optical properties of ZnO thin films prepared by spray pyrolysis on glass substrates at various temperatures for integration in solar cell.

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Abstract

ZnO thin films are widely used as antireflection layer in solar cells and can be grown by various techniques implemented at various temperatures. In this contribution, we present the morphological and optical properties of ZnO thin films prepared by spray pyrolysis on glass substrates at various growth temperatures from 350 to 550 °C. The surface morphology of the films, analysed by scanning electron microscopy SEM, is modified with substrate temperature. Optical characterizations of ZnO films as a function of temperature were carried out by transmittance and photoluminescence (PL) measurements. Main optical properties are as follow: All the films are highly transparent in the visible region of the electromagnetic spectrum. The average transmission in the visible range (400–800 nm) was greater than 80%. The band gap of ZnO films increases with increasing substrate temperatures attributed to the increase of the grain size of the sample. PL spectrum of ZnO films can be divided into the UV emission and the visible broadband emission attributed to the near band edge emission (NBE) and to the deep level emissions (DLE), respectively. The biggest ratio of UV emission on visible emission of the PL intensity is observed for the ZnO thin film deposited at 550 °C by the spray pyrolysis technique. Therefore, we suggest that this original result indicate the most suitable growing conditions for obtaining high quality sprayed ZnO thin films with higher luminescence performances.

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Keywords: Spray pyrolysis, ZnO thin films, Optical properties, Photoluminescence, Temperature effect, Antireflection layer, Solar cells.
1. Introduction

An antireflection (AR) layer is a type of coating applied to the surface of a material to reduce light reflection and to increase light transmission. The AR layers can be used in solar cells, planar displays, glasses, prisms, videos, and camera monitors. Zinc oxide (ZnO) becomes attractive as a dielectric AR layer material because of its good transparency, appropriate refractive index, and ability to form textured coating via anisotropic growth [1].

The application of ZnO in photovoltaics is not limited to act as electron transport material (ETM) in dye sensitized solar cells (DSC) and hybrid solar cells (HSC) [2]. It can also be applied as antireflection coating in inorganic solar cells [3,4] or as optical spacer in polymer solar cells (tandem, hybrid and inverted organic solar cells) [5–8]. The components ZnO are not toxic unlike indium tin oxide, which is one of the most currently used transparent conducting film (TCO). The direct wide band gap of ZnO, $E_g = 3.37$ eV, makes it transparent for a large wavelength range in the solar spectrum. Other advantages of the use of ZnO as layers in photovoltaic cells concern its high chemical and physical stability, thermal stability in hydrogen plasma atmosphere, large exciton binding energy of 60 meV, high electrical conductivity and finally, its low cost price.

ZnO thin films have been prepared using several deposition techniques such as pulsed laser deposition [9], magnetron sputtering [10], spray pyrolysis [11], and sol–gel [12]. Compared to others techniques, spray pyrolysis is simple, non-vacuum and inexpensive method. Moreover, it is useful for producing large scale films. The quality and physical properties of films prepared using the spray pyrolysis technique depend on different deposition and post-deposition conditions such as the nature and concentration of precursor, substrate temperature, spray rate, nozzle to substrate distance, pressure of carrier gas, and annealing. In these parameters, substrate temperature usually plays a crucial role in growth of ZnO films. It has been revealed that these conditions have a significant effect on properties of ZnO based TCO films.

In the present work, we have studied the effect of substrate temperature on morphological, optical, and photoluminescence (PL) properties of sprayed ZnO films. In order to improve properties of ZnO films, the effect of substrate temperature was also investigated.

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2. Experimental

2.1. Thin film preparation

For the growing on glass substrates of ZnO thin films by the spray pyrolysis technique, we have used as original elements a solution of zinc acetate dehydrated ($\text{Zn(CH}_3\text{COO)}_22\text{H}_2\text{O}$) with 0.08 molar concentrations diluted in methanol ($\text{CH}_3\text{OH}$). The glass substrates were emerged in ultrasonic baths in different solution such as ethanol, acetone for 20 to 30 minutes and finally washed by distilled water, in order to clean them. The distance between the substrate and the spray gun nozzle was fixed at 27 cm for a solution flow rate held constant at 5 ml / 2 min during 2 hours. Compressed nitrogen at a pressure of 2 bars is used to atomize the solution. While depositing ZnO thin films,
the substrates of the three films were heated at deposition temperatures 350, 450, 550 °C, respectively. All the films are clear and well adherent on their substrates. The so obtained films present a thickness of about 400 nm which is estimated from transmittance data using Swanepoel’s envelop method [13, 14]. Following the phase of growth, the three films are morphological and optical characterized and experimental results and analyses are presented in the following.

2.2. Morphological and Optical characterizations of ZnO thin films

The surface morphology of the films was observed by scanning electron microscopy at room temperature. The optical properties were measured by UV-Visible spectrophotometer at room temperature. The room temperature photoluminescence (PL) emission spectrum of the films was recorded using a LS-55 spectrophotometer (Perkin-Elmer). The source of excitation was a Xenon lamp with the excitation wavelength of 325 nm.

3. Result and discussion

3.1. Effects of substrate temperature on the morphologic properties of ZnO thin films

The dependence of the crystallinity and the size of the crystallites of the ZnO thin films with the process temperature during growth were revealed by SEM micrographs. Fig. 1(a), (b) and (c) shows the SEM morphologies of ZnO films deposited at 350, 450 and 550°C, respectively.

Fig. 1. (a, b and c) Scanning electron micrographs of ZnO thin films grown on substrate with different temperatures of 350, 450 and 550°C.
The microstructure of the films consists of many spherical grains uniformly distributed throughout the surface. Nevertheless, we can observe in these three photos, slight changes in microstructure that we can attribute to the role of the temperature during the growth process of the films. Indeed, the surface morphology of the ZnO film deposited at low substrate temperature (350°C) shows a high density of small grains. With the substrate temperature increasing up to 550°C, the crystalline quality of the film is improved and the grain size obviously becomes largest. This behavior confirms the similar observation already done by Zhu et al. [9] in ZnO thin films grown on glass substrates with growth temperature from room temperature (RT) to 500 °C by the pulsed laser deposition (PLD) method and by Zehidi et al. [15] in ZnO thin films prepared by spray pyrolysis technique at substrate temperatures of 200 and 450 °C.

3.2. Effects of substrate temperature on the UV-VIS transmittance spectra of ZnO thin films

The transmittance of antireflection layers is a critical factor for solar cell applications. Thus, we have characterized the transmittance of the ZnO thin films grown at different substrate temperatures in the range of 350–800 nm. The transmittance spectra are reported in Fig. 2. We observe for all samples a large absorption in the UV region and a high transparency in the visible region; the absorption edge being around 375 nm for all the films. In the visible range, all the films present a high average transmittance greater than 80%. The spectra of all the films also point out an absence of contrasted fringes generally linked to a diffusion phenomenon [16]. We explain this result by the fact that all the films have a structure composed by grains having only small size, as previously shown by SEM characterizations. The optical transmittance of the three films increases in the visible region with the increase of their substrate temperatures during the growth process. We associate this behavior to an improvement of the layer quality with the temperature during growth, as already observed in ref [15] who showed the same trend of their ZnO thin films deposited at a temperature varying from 200 to 500 °C. Thereby, even if the transmittance achieves high level, it is limited by a constant surface reflectance, found in our films less than 10% in the visible region. The low absorbance and low reflectance results confirm that the so-produced ZnO thin films could be used as antireflection layer in solar cells working mainly in the visible region, as silicon solar cells or in a large spectrum as GaN based concentration solar cells.

![Fig. 2. Transmittance vs. wavelength of ZnO thin films grown on substrate with different temperatures.](image-url)
3.3. Effects of substrate temperature on the optical band gap and the Urbach energy of ZnO thin films

The optical absorption coefficient $\alpha$ is estimated using its relation with the transmittance $T$ as [17]

$$\alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right)$$

with $d$ the thickness. The optical absorption coefficients $\alpha$, as a function of wavelengths of the three ZnO films deposited at various substrate temperatures are shown in Fig. 3. As can be seen from Fig. 3, all the films are of good quality as all samples present a sharp absorption edge. In the insert of Fig.3, we can see that this absorption edge located near to 375 nm shifts to shorter wavelengths for sample grown at higher temperature.

The UV absorption edge is directly linked to the optical band gap. Indeed, the band gap can be estimated from the absorption edge by applying the Tauc relationship. In this model, the variation of the absorption coefficient $\alpha$ in the strong absorption range is linked to the band gap $E_g$ of the material by the following expression [18]:

$$(\alpha h\nu) = A(h\nu - E_g)^n$$

$E_g$ is the band gap energy and $A$ is an energy-independent constant. The index $n$ is characteristic of the nature of the optical absorption process and is theoretically equal to 1/2 and 3/2 for allowed and forbidden direct transitions, respectively, and to 2 and 3 for allowed and forbidden indirect transitions, respectively. Because the transition in ZnO is direct, $n$ is set equal to 1/2.

![Fig. 3. Optical absorption coefficient of ZnO thin films grown on substrate with different temperatures. Insert shows the zoom of optical absorption coefficient spectra at low wavelength](image)

The band gap energy values $E_g$ are calculated by extrapolation of the linear part of $(\alpha h\nu)^2$ versus $h\nu$ plot, and results for our films are shown in Fig. 4. The shift of the absorption edge to shorter wavelengths indicates that the optical band gap increases with the substrate temperature of the growing process.
The calculated band gap energy of ZnO films deposited at 350 – 550 °C varies from 3.28 eV to 3.30 eV, which correspond to a slight change in the band gap energy with substrate temperature. Nevertheless, this observation confirms that the optical band gap increases with the substrate temperature during the growth, which as previously presented, has a direct influence on the morphological properties of the films. Dutta et al. have reported in [19] an increase of the band gaps of their ZnO films with an increase of the grain size attributed to the lower band bending at the grain boundaries. In a similar study, X. Zhang et al. [20] have reported the enlargement of the band gap in ZnO films with the increase of the grain sizes with the substrate temperature during growth. Therefore, the UV shift of band gaps of our ZnO films deposited by spray pyrolysis can be attributed to the decrease of the band bending effect at the grain boundaries, owing to the larger grain sizes, as observed in SEM in films prepared with substrate at higher temperature.

The absorption coefficient of film shows a tail corresponding to the so-called Urbach tail, for sub-band gap photon energy. It is closely related to the disorder in the film crystalline lattice and is expressed as [21]

\[
\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_U} \right)
\]

With \(\alpha_0\) a constant, \(E_U\) the Urbach energy is directly involved in the slope of the exponential edge. The above equation describes the optical transition between occupied states in the valence band tail to unoccupied states of the conduction band edge. Fig. 5 shows the evolution of the Urbach energy of the ZnO thin films. The value of \(E_U\) was obtained from the inverse of the slope of \(\ln(\alpha)\) versus \(h\nu\).

The Urbach energy values of the films at 350, 450 and 550 °C are 52, 47 and 44 meV, respectively. Urbach energy of the ZnO thin films decreases with the increase of the temperature during the process. Zhanget al. studying ZnO:Fe films synthesized via magnetron sputtering [20] link the decrease of the Urbach energy with an improvement of the quality of the film. In agreement with them, we attribute the decrease of the Urbach energy of our films with the increase of the substrate temperature during growth to an improvement of the optical quality of the films when higher temperature is used during the growth process.
Finally, we report in Fig. 6 the band gaps and Urbach energy of ZnO thin films as a function of the substrate temperature during the growth process.

We can see in Fig. 6 that corresponding to an increase of the substrate temperature during the growth, the band gap of ZnO thin films increases and inversely changes with the corresponding Urbach energy. Thus, as deduced from the above analysis, the increases of \( E_g \) with the increasing of the substrate temperature from 350 to 550 °C, indicates an improvement of the quality of the film. We attribute this phenomenon to the decreasing of the structural defects that can be achieved at higher grown temperature. To confirm this previous conclusion, we have performed characterisation of photoluminescence properties of the films.
3.4. Effects of substrate temperature on the photoluminescence properties of ZnO thin films

The photoluminescence (PL) spectra of samples grown at different substrate temperatures (350, 450 and 550 °C) are shown in Fig. 7. The Gaussian fitting was carefully made to find the various emission peaks contained in these PL spectra.

As shown in the figure, PL spectra of all samples contain a narrow and sharp emission peak in the UV region and a broad band in the visible range. In agreement with Qui et al. in Ref. [22], the UV emission can be attributed to the near band edge emission (NBE) and originate from the recombination of free excitons. Regarding the visible emission of ZnO thin films, it is generally attributed to defects forming deep energy levels in the band gap [23]. With the increase of the temperature of substrates, the UV emission intensity of the PL spectra of ZnO thin films increased monotonously whereas the intensity of the visible emission band decreases.

This phenomenon is link to the decrease of the defects concentration in sample grown on substrate at higher temperature. The appearance of sharp and strong UV emission and very weak deep-level emission in the PL spectra indicates that the ZnO thin film deposited at 550°C have good crystalline structure, adding to its excellent optical properties already presented above.

We report in Fig. 8 the position of the UV peak and its variation in the different films as function of the substrate temperature during growth. We observe a continuous shift down to shorter wavelength of the UV peak with the substrate temperature. It correlates with the increase of the grain size of the films already observed by SEM characterizations when the substrate temperature growth increases (see paragraph 3.1.). We have also reported in Fig. 8, the ratio of the PL emission intensities in UV and in visible (I_{UV}/I_{VIS}). This ratio increases with the increase of the substrate temperature. In Ref. [24], Cui et al. shown that biggest is the PL emission intensities ratio, highest is the quality of the ZnO thin films. Finally, this result confirms that less defects are generated and, thus the quality of the films increases when deposition temperature of sprayed ZnO thin films increases up to 550 °C.
We note also that, the observation of the curves presented in Figs 6 and 8, represented from experimental results obtained by two different experimental techniques, i.e. transmittance and photoluminescence measurements as function of temperature, the gap energy and the position of the UV peak (UV peak energy), on the one hand and the Urbach energy and the ratio $I_{UV}/I_{Vis}$, on the other hand, have the same behaviours, respectively. In fact, the position of the UV peak describes the gap energy calculated from the transmission measurements (extrapolating the linear part of $(\alpha h\nu)^2$ vs. $h\nu$) and that can be calculated from the position of the UV peak (E$_g$ = $1240 / \lambda$ (nm)) from photoluminescence measurements. Similarly, the Urbach energy and intensity ratio $I_{UV}/I_{Vis}$ also have the same behaviour because these values are both directly link to the defects in the crystal layer: At a low value of Urbach energy and high intensity ratio $I_{UV}/I_{Vis}$ directly correspond a high crystalline quality. Thus, by two optical experimental methods allowing the determination of functional parameters of the film, we confirm that the density of defects in ZnO thin films, synthetized by spray pyrolysis technique, is reduced thus inducing an improvement of the crystallinity in films prepared on a substrate at higher temperature.

4. Conclusion

In this contribution, we have analyzed the influence of the substrate temperature during the growth process on morphological and optical properties of sprayed ZnO an antireflection layers dedicated to inverted solar cells. ZnO thin films were fabricated, using the spray pyrolysis method, on glass substrates at different temperatures deposition varying from 350 to 550°C. SEM analysis revealed that the surface morphology of the so-obtained films is uniform and evolves with the substrate temperature during the growth. Mainly, the grain size increases and the surface of the films become rougher with the increase of the substrate temperature to 550 °C. The optical properties were discussed from the effect of substrate temperature. All ZnO films show a high average transmittance above 80% in the visible range of the optical spectrum. The optical band gap value of the films increases when substrate temperature increases, attributed to the decrease of the disorder in the material. For all samples, the photoluminescence emission spectra shows a narrow and sharp peak around 383nm, assigned to the exciton recombination, and a broad band emission in the visible range, attributed to defects forming deep energy levels in the band gap. The intensity of the UV peaks of ZnO thin film increased whereas the visible emission decreased with the increase of the substrate temperature in the growth process. This phenomenon corroborates the highest quality of the ZnO thin film achieve when the film is prepared at an optimized temperature equal to 550 °C. These results
show that the produced ZnO thin films could be used as an antireflection layer in solar cells and that the properties can be improved by choosing a high growth temperature.

References


