Influence of the thickness on optical properties of sprayed ZnO hole-blocking layers dedicated to inverted organic solar cells

A. Bedia\textsuperscript{a,b,c}\*, F.Z. Bedia\textsuperscript{a,b,c}, M. Aillerie\textsuperscript{a,b}, N. Maloufi\textsuperscript{d}, B. Benyoucef\textsuperscript{c}

\textsuperscript{a}Université de Lorraine, LMOPS-EA 4423, 57070 Metz, France.
\textsuperscript{b}Supelec, LMOPS, 57070 Metz, France.
\textsuperscript{c}Abou-BakrBelkaid University, URMER,13000 Tlemcen Algeria.
\textsuperscript{d}Université de Lorraine, LEM3-UMR CNRS 7239, 57000 Metz, France.

Abstract

The sprayed pyrolysis technique was carried out to prepare ZnO thin films with different thickness dedicated to the optimization of the growth process of the multi-layers constituting inverted polymer solar cells in the aim to achieved better efficiency in photovoltaic energy conversion. The optical constants and dispersion energy parameters of the zinc oxide thin films were determined using optical characterization method. The transmittance measurements showed that all samples have high transparencies in the visible range, as generally used by solar cells. The band gap is slightly increased from 3.28 to 3.30 eV with the film thickness varying from 446 to 645nm. The oscillator energy $E_0$ and the dispersion energy $E_d$ were deducted. The real and imaginary parts of dielectric constant for ZnO thin films were also determined.

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Keywords: ZnO Thin film, Chemical spray pyrolysis, Thickness effect, Optical properties, Organic solar cell;

1. Introduction

ZnO is an II-VI compound semiconductor with a direct wide bandgap of 3.37 eV and a large exciton binding energy of 60 meV [1]. Films of ZnO based have been widely investigated for their potential in optoelectronic

\* Corresponding Asma Bedia

E-mail address: aphy_bedia@yahoo.fr.
applications as wide-band gap optoelectronic devices such as light emitting diodes, laser diodes and electroluminescent devices, chemical sensors and detectors [1, 2]. By else, due to the electrical and optical properties, ZnO films are promising for the realization of bulk-heterojunction solar cells. These polymer solar cells are a promising source of low-cost renewable energy because of their great potential for large-area, light-weight, flexible, and low-cost devices for solar-energy conversion applications. Conventionally, a polymer solar cell is based on a multi-layer structure composed by a polymer donor and a fullerene acceptor bulk-heterojunction (BHJ) composite layer, sandwiched between a transparent indium tin oxide (ITO) that serves as the front high-work-function anode and a low-work-function metal that serves as the back negative electrode metal cathode. To circumvent the electrode oxidation in ambient air, an inverted structure is proposed in which a hole-blocking layer, is inserted between the ITO and the active layer for selective electron collection so that only electrons can reach the ITO, and the back electrode must become the hole-coll ecting positive electrode. Some research teams have shown that inversion of the device can be accomplished by using zinc oxide (ZnO) as the hole-blocking layer [3- 5]. This fact thereby further increases the interest of ZnO layer, which is subject to numerous investigations concerning both the deposition process that the characterization of its post growth physical properties. Many techniques were used to deposit ZnO films on glass substrates, including sol–gel processes [6], sputtering [7], hydrothermal method [8] and spray pyrolysis method [9]. The optical constants such as the refractive index, the absorption index and the dielectric constant can be analyzed by the transmittance spectrum [10]. The refractive index dispersion in semiconductors can be determined using a single oscillator model [11]. Wemple and DiDomenico [12] used a single oscillator description of the frequency-dependent dielectric constant to define a dispersion energy parameter $E_d$ which is related to the charge distribution within each unit cell and chemical bonding.

The adjustable parameters used in this model are thus very useful to describe the influence of the crystal structure and the iconicity, on the refractive index behavior and more generally on the optical properties of the material.

The aim of our work is to realize low-cost and high-efficiency ZnO layers that could be integrated as hole-blocking layers in inverted organic solar cells. In the present paper, we investigate the effect of thickness film on optical properties of ZnO thin films deposited by the spray pyrolysis method.

2. Experimental

ZnO thin films were grown at 350°C on glass substrates by spray pyrolysis. A solution of zinc acetate dehydrated with 0.08 molar concentrations diluted in methanol was used as original elements. The glass substrate were emerged in ultrasonic bath 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. Compressed nitrogen is used to atomize the solution. The so obtained films present a thickness of about 446 nm, 596 nm and 645 nm, which is estimated from transmittance data using Swanepoel’s envelop method [13].

Among the functional properties of the ZnO thin films, their optical properties were studied according to the UV-VIS-NIR spectrum recorded at room temperature with Perkin–Elmer Lambda 900 spectrophotometer in the wavelength range 300–1100 nm, taking the glass substrate as reference.

3. Result and discussion

3.1. Determination of the optical band gap and Urbach energy of the films

Transmittance spectra $T(\lambda)$ and reflectance $R(\lambda)$ of the ZnO thin films for different thickness are presented in Fig. 1. These films show a high transparency within the visible range with an average transmittance lying between 68% and 83%. As expected, the transmittance of the films increases when the thickness decreases. It is seen that the transmittance is limited only by the surface reflectance of about 5% in the visible region.
The energy gap of all films is determined from the absorption coefficient ($\alpha$) that can be calculated from the transmittance ($T$) of the ZnO thin films. The absorption coefficient ($\alpha$) of the film were calculated by the expression [10]

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

(1)

Where $d$ and $T$ are the film thickness and transmittance, respectively.

Optical energy gap was determined from the equation (1). The energy gap ($E_g$) was estimated by assuming a direct transition between valence and conduction bands from the expression [14]

$$(\alpha h \nu) = [A(h \nu - E_g)]^{1/2}$$

(2)

Where $A$ is a constant, $h \nu$ is the photon energy and $E_g$ is the optical energy band. Fig. 2 (a) shows plot of $(\alpha h \nu)^2$ versus $h \nu$ where the optical band gap of the film was determined by extrapolating the linear region to $(\alpha h \nu)^2 = 0$. The calculated of optical energy gap of ZnO thin films are summarized in table 1.
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 network, is expressed as [15]

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

(3)

With \( \alpha_0 \) a constant, \( E_U \) the Urbach energy, which characterizes the slope of the exponential edge. The above equation describes the optical transition between occupied states in the valence band tail to unoccupied state of the conduction band edge. Fig. 2 (b) shows Urbach plot of ZnO films. The value of \( E_U \) was obtained from the inverse of the slope of \( \ln(\alpha) \) versus \( (h \nu) \), as regrouped in Table 1. Urbach energy of ZnO films is decreased from 76 meV to 67 meV as thickness film is increased from 446 nm to 645 nm. The decrease of the Urbach energy with an increase of the film thickness is attributed to an improvement of film quality.

<table>
<thead>
<tr>
<th>Thickness of samples (nm)</th>
<th>( E_g ) (eV)</th>
<th>( E_U ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>645</td>
<td>3.30</td>
<td>67</td>
</tr>
<tr>
<td>596</td>
<td>3.29</td>
<td>64</td>
</tr>
<tr>
<td>446</td>
<td>3.28</td>
<td>76</td>
</tr>
</tbody>
</table>

3.2. The dispersion of the refractive index of the films

The refractive index of the semiconductor is a measure of its transparency to incident spectral radiation. The refractive index of the film was determined by solving the Fresnel equation [16]

\[ n = \left( \frac{1 + R}{1 - R} \right) + \sqrt{\frac{4R}{(1 - R)^2 - k^2}} \]  

(4)

Where \( n \) is the refractive index and \( k = \lambda \alpha /4\pi \) is the extinction coefficient. Figs. 3 present the refractive index and extinction coefficient of ZnO thin films dependence on wavelength range 300 nm to 1100 nm. We can observe in Fig. 3, that the refractive index and the extinction coefficient for all samples decrease when the wavelength increase. This phenomenon is attributed to light scattering and to the decrease of absorbance. The refractive index and the extinction coefficient in visible region of all films increase with the increase of the film thickness.

![Fig. 3. The variation of (a) refractive index; (b) extinction coefficient of the ZnO thin films with wavelength.](image-url)
The refractive index values for all samples are lower, as compared to theoretical refractive index of ZnO film in the visible region $n = 2$. Besides, the extinction coefficient value is considerably low. This indicates that the ZnO film has the low dielectric losing.

The evolution of the refractive index along the Cauchy distribution [17] was observed in all ZnO thin films following the relation given by

$$n = A + \frac{B}{\lambda^2}$$  \hspace{1cm} (5)

where $A$ and $B$ are the Cauchy’s parameters and $\lambda$ is the wavelength of the light. These parameters are regrouped in Table 2.

<table>
<thead>
<tr>
<th>Thickness of samples (nm)</th>
<th>A</th>
<th>B (µm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>645</td>
<td>1.40</td>
<td>0.058</td>
</tr>
<tr>
<td>596</td>
<td>1.48</td>
<td>0.033</td>
</tr>
<tr>
<td>446</td>
<td>1.26</td>
<td>0.059</td>
</tr>
</tbody>
</table>

In addition to the Cauchy extrapolation described above, which was done to provide reasonable values for refractive index in the spectral range of low absorption, the dispersion energy was also evaluated using the single-oscillator model as described by Wemple and DiDomenico [18]

$$n^2 = 1 + \frac{E_d E_0}{E_0^2 - (h\nu)^2}$$  \hspace{1cm} (6)

where $E_0$ is the energy of the effective dispersion oscillator, which is expected to correspond to the photon-energy

![Fig. 4. Plots of $(n^2-1)^{-1}$ versus $h\nu^2$.](image-url)
position of the ultraviolet band gravity center. $E_d$, called the dispersion energy, is a measure of the average strength of the interband optical transitions. Wemple–DiDomenico model is used to fit the experimental data. $E_0$ and $E_d$ can be both determined from the intercept, $(E_0/E_d)$ and the slope, $(1/E_0E_d)$, seen in Fig.4. Their values are listed in Table 3.

<table>
<thead>
<tr>
<th>Thickness of samples (nm)</th>
<th>$E_0$ (eV)</th>
<th>$E_d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>645</td>
<td>4.74</td>
<td>5.72</td>
</tr>
<tr>
<td>596</td>
<td>5.75</td>
<td>7.64</td>
</tr>
<tr>
<td>446</td>
<td>4.55</td>
<td>4.27</td>
</tr>
</tbody>
</table>

### 3.3. Determination of complex dielectric functions and oscillator energy

The complex dielectric constant $\varepsilon(\omega) = \varepsilon_1(\omega) - i\varepsilon_2(\omega)$ characterizes the optical properties of the solid material. The real, $\varepsilon_1$ and imaginary, $\varepsilon_2$ parts of the dielectric constant for ZnO thin films with different thickness are determined by [19]:

$$\varepsilon_1(\lambda) = n^2(\lambda) - k^2(\lambda)$$
$$\varepsilon_2(\lambda) = 2n(\lambda)k(\lambda)$$

(7)

The variation of $\varepsilon_1$ and $\varepsilon_2$ with the thickness of the films is illustrated in Fig. 5. These figures reveal that the values of the real part are higher than the imaginary one, which confirms the good transparency of these thin films. From the optical data, it is also observed that refractive index $n$, the extinction coefficient $k$, the real $\varepsilon_1$ and imaginary $\varepsilon_2$ parts of the dielectric constant follow the same behavior as a function of the wavelength.

**Fig. 5.** (a) The variation of real parts of dielectric constant; (b) imaginary parts of dielectric constant of the ZnO film with wavelength.

### 4. Conclusion

In this contribution, we have analyzed the influence of the thickness on some optical properties of sprayed ZnO hole-blocking layers dedicated to inverted organic solar cells. ZnO thin films were prepared with different thickness grown on glass substrates by spray pyrolysis technique. The optical properties were discussed from the effect of thickness film. The optical band gap values decreased when thickness film decreased, due to the increase of disorder.
of the material. The refractive index and extinction coefficient values were determinate. The oscillator energy \( E_0 \) and the dispersion energy \( E_d \) were deducted. The real and imaginary parts of dielectric constant for ZnO thin films were also determined.

References