Structural and optical properties of ZnO thin films prepared by laser ablation using target of ZnO powder mixture with glue

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Abstract. ZnO thin films were deposited on ITO/glass substrates by pulsed laser deposition (PLD) using two different kinds of targets. One of the targets was made of pure ZnO powder and the other one consisted of a mixture of ZnO powder with cyanoacrylate glue. The structural and morphological properties of the films obtained using both targets were compared, in order to determine which one produces samples with properties more suitable for their use as buffer and antireflective layer in CdTe-based solar cells, also different heterostructures were deposited to study the optical properties of the obtained thin films and their utility in the applications mentioned before. The films deposited with the mixture powder target were polycrystalline with preferential orientations in the planes (100) and (101) with a high transmittance in the range of 70–90% in the 540–850 nm wavelength region and showed a high resistivity of $\sim 1.30 \times 10^2 \Omega \text{ cm}^{-1}$, such properties are considered to be appropriate for thin films that are wanted to be used as a buffer and antireflective layer in CdTe solar cells.

Keywords. ZnO thin film; pulsed laser deposition; cyanoacrylate; mixed target; ZnO buffer layer.

1. Introduction

Zinc oxide (ZnO) is an important member of the II–VI group of semiconductors, which is considered as a promising material in the field of blue and ultraviolet (UV) optical devices such as light-emitting and laser diodes due to its wide energy gap of 3.37 eV at room temperature [1]. Its electrical, optical and mechanical properties are considered excellent for many other applications, which make it a widely investigated material in many fields [2,3]. In order to obtain ZnO thin films, there are various deposition methods such as thermal evaporation, magnetron sputtering, molecular beam epitaxy, pulsed laser deposition (PLD) and metal organic chemical vapour deposition [4–8]. The PLD method is widely employed to obtain ZnO thin films; this is because it presents the advantages of allowing to deposit at a relatively low substrate temperature, deposition in controlled reactive gas pressure and high deposition rates. All these properties taken together enable sufficient control of film composition and film properties [7]. One of the recent applications of the PLD technique is its using with hybrid and organic targets [9]. Organic and hybrid materials suffer the disadvantage of decomposition during ablation due to the high energy that is liberated during the deposition process, to solve this issue there are new laser techniques being developed, to name a few: matrix-assisted pulsed laser evaporation, resonant infra-red PLD, and other techniques where sometimes freezing the target is required

[10,11]. However, it is still possible to employ conventional PLD with hybrid and organic targets [12].

Cyanoacrylates (CAs) are a group of very strong organic glues employed in many industrial applications, such as sealants, coatings and adhesives for gluing a variety of substrates [13]. In this work, we compared the structural and optical properties of the ZnO thin films deposited on ITO/glass substrates by the PLD technique using a target made up of ZnO powder mixture with CA glue to those of thin films obtained from a traditional target made of pure ZnO powder. We found that the thin films grown with the CA glue target had superior properties that made them more suitable to be used in CdTe solar cells as a buffer and antireflective layer than the thin films from a traditional target.

2. Experimental

ZnO thin films were deposited on ITO/glass substrates using a Nd:YAG-laser operating in the Q-switch mode with $\lambda = 1064 \text{ nm}$ and 10 ns full-width at half-maximum at a repetition rate of 5 Hz. The pulse energy was of $\sim 300 \text{ mJ}$ per pulse and the laser beam diameter was reduced to $\sim 1.3 \text{ mm}$ by means of a spherical quartz lens. The energy density of the beam on the target surface was $\sim 2 \text{ J cm}^{-2}$. During laser irradiation, the target was rotated at 30 rpm. The laser was focused through a 50 cm focal length lens onto a rotating

target at an angle of incidence of 45° . The targets were prepared from solid disks of 5 mm thick and 15 mm diameter. The mixed target (hybrid target) was made up of ZnO powder (99.999% Cerac) nanoparticles with a size less than 100 nm mixed with commercial Loctite 495 CA Super Glue, mainly composed by ethyl 2-cyanoacrylate (ECA). The mixture of ECA and ZnO powder (mixed target) was made with nominal ratio of 70:30 wt% (ZnO being the compound present in a greater proportion) and dried for 72 h at room temperature. The target made of pure ZnO was prepared from ZnO powder, which was subjected to a pressure of 10 tons for 5 min and after that was placed in a furnace at 600°C for 2 h; this process is called sintering (sintered target). The films were deposited at a substrate temperature of $T_s = 300^\circ\text{C}$ in a vacuum of $\sim 1.3 \times 10^{-7}$ Pa. The film deposition is achieved with 3×10^3 laser shots. The target–substrate distance was 40 mm. The ITO/glass substrates were cleaned in an ultrasonic bath for 10 min with acetone and finally with methanol. Before deposition, the substrate was maintained at T_s for 30 min and after deposition, the film was cooled to room temperature at a rate of 5°C min^{-1} . The structural properties were determined by measurements in the grazing incidence geometry using a D5000 Siemens X-ray Diffractometer with $\text{CuK}\alpha$ filtered monochromatic radiation ($\lambda = 0.15418$ nm) at 40 kV with 35 mA and aperture diaphragm of 0.2 mm. The diffractograms were registered in the step scan mode with a beam incidence angle of 1° and recorded in $2\theta = 0.02^\circ$ steps with a step time of 10 s in a 2θ range of $25\text{--}70^\circ$. The superficial morphology of the thin films was analysed by atomic force microscopy (AFM) using a Park Scientific Instruments auto probe in the topography contact mode, with Si tips. The thicknesses of the films were measured by a surface Profilometer Dektak-Veeco. Optical transmittance measurements in the range of 350–850 nm were performed with an Agilent 8453 UV–visible Spectroscopy System, and the optical band gap was calculated taking into account only direct transitions.

3. Results and discussions

The measurements for the thin film thicknesses (h) were ~ 101 nm for the sample grown from the mixed target and ~ 111 nm for the sample grown from the sintered target. Figure 1a and b shows the X-ray diffraction (XRD) patterns of ZnO thin films for mixed and sintered targets, respectively. The observed diffraction peaks are (100), (002), (101), (102), (110), (103) and (112) for both films, and are consistent with the wurtzite ZnO phase [14]. Figure 1a shows a preferential orientation in the planes (100) and (101) parallel to substrate, while figure 1b shows a preferential orientation in the (002) plane. All peaks in figure 1a are shifted to the right with respect to the 2θ position of the ZnO powder standard pattern, as indicated by the dashed vertical lines, which are evidence of negative (compressive) strain [15], the inset in figure 1a shows the mentioned shifting for the most intense peak corresponding

Figure 1. XRD profiles of ZnO films grown from (a) mixed and (b) sintered targets. Inset shows XRD (101) and (002) peaks of ZnO for a and b, respectively.

to the (101) plane ($2\theta = 36.25^\circ$). In figure 1b all peaks are shifted to the left, which are evidence of positive (tensile) strain [15], the inset in figure 1b shows the mentioned shifting for the most intense peak corresponding to the (002) plane ($2\theta = 34.43^\circ$). The negative strain value of the sample grown from the sintered target indicates shrinkage in the volume of the unit cell, while the positive strain value for the samples grown from the mixed target shows an expansion in the volume of their unit cell, as it is observed from the shift of peaks in the inset up-right of both figure 1a and b.

The crystallite size (t) and strain (ε) depend on the 2θ peak position, which enables us to determine the effect of peak broadening using the Williamson–Hall method [16]. In order to distinguish the effect of crystallite-size-induced broadening and strain-induced broadening of the FWHM on the XRD profile, the Williamson–Hall plot was performed using the following equation:

$$\beta \cos \theta = \frac{m\lambda}{t} + 2\varepsilon \sin \theta, \quad (1)$$

where β is FWHM in radians, λ the X-ray wavelength ($\text{CuK}_\alpha = 0.154186 \text{ nm}$), θ the Bragg diffraction angle and m a correction factor which is considered as 1. By plotting $\beta \cos \theta$ vs. $\sin \theta$, we obtained a linear fit for the XRD data, which allowed us to calculate the values of t and ε as $\sim 40 \text{ nm}$ ($\pm 1 \text{ nm}$) and 2.13×10^{-1} , respectively, for the sample grown from the mixed target, while the specimen grown from the sintered target had t and ε values of $\sim 9.6 \text{ nm}$ ($\pm 1 \text{ nm}$) and -2.03×10^{-2} , respectively. The negative strain value of the sample grown from the sintered indicates shrinkage in the volume of the unit cell, while the positive strain value for the samples grown from the mixed target shows an expansion in the volume of their unit cell, as it was described before from the shifting in the XRD peaks. To exemplify the behaviour of FWHM value for both types of specimens, we compared the FWHM value for the (002) peak plane, being 5.1×10^{-3} and 1.0×10^{-2} rad for the mixed and sintered targets, respectively, this indicates that the samples grown from a mixed target had greater crystallinity. To calculate the lattice parameters and their error propagation, we employed the standard lattice geometry equations [17,18]. We estimated the c lattice parameters, and they were found to be 0.52 nm ($\pm 0.03 \text{ nm}$) for both the mixed and sintered targets, which agree very well with the pattern value $c_0 = 0.5207 \text{ nm}$. To calculate the lattice parameter a , we employed the Nelson–Riley–Sinclair–Taylor function [19], we found the lattice a parameters to be 0.33 ($\pm 0.06 \text{ nm}$) and 0.32 nm ($\pm 0.06 \text{ nm}$) for the mixed and sintered targets, respectively, which also agree with the pattern value $a_0 = 0.32495 \text{ nm}$ for the ZnO.

Figure 2a and b shows typical 3D-dimension $1 \times 1 \mu\text{m}^2$ images of the ZnO films grown from mixed and sintered targets, respectively. The roughness of the films shows a root mean square (RMS) of 6.50 and 17.8 for the mixed and sintered targets, respectively. The samples grown from the mixed target show uniform grain size and shape, and marked improvement in packing density, thickness uniformity and film surface roughness, as the RMS is three times smaller. The uniform grain size and shape observed in ZnO films from mixed target indicate that these films are morphologically superior in comparison with the ZnO films from the sintered target, and this affects the electrical conversion of solar cells CdS/CdTe. Tsuji *et al* [20] have demonstrated that the conversion efficiency of CdS/CdTe solar cells strongly depends on a small roughness of the film's surfaces; a reduction of surface roughness tends to increase the conversion efficiency of these solar cells. The ZnO made from the mixed target leads to a reduced surface roughness of 6.50 nm when compared to the sintered target, which was 17.8 nm; we think that the conversion efficiency of solar cell can be increased with ZnO made from the mixed target.

A practical solar cell as CdS/CdTe has losses, which reduce its efficiency. The quantification of these losses can identify promising pathways for further cell improvements. One of the most important losses in these solar cells is the short-circuit photocurrent density J_{sc} . The J_{sc} losses are due to glass reflection, TCO, ZnO buffer layer and CdS film absorptions and

Figure 2. Three-dimensional AFM images of ZnO films grown from (a) mixed and (b) sintered targets.

other factors. The J_{sc} in a glass/ITO/ZnO/CdS structure could be calculated and estimated by integrating the transmittance spectrum $T(\lambda)$ of this structure multiplied by the AM 1.5 solar photon current density $J_{solar}(\lambda)$. The J_{sc} in mA cm^{-2} defined as the fraction of photons transmitted across of a glass/ITO/ZnO/CdS structure that can be used to generate an electron–hole ($e-h$) pair can be defined as [21]

$$J_{sc} = \int_{\lambda_{min}}^{\lambda_{max}} T(\lambda) J_{solar}(\lambda) d\lambda, \quad (2)$$

where $T(\lambda)$ is the transmittance spectrum of the glass/ITO/ZnO/CdS structure, $\lambda_{min} = \lambda_{ITO}$, $\lambda_{max} = \lambda_{CdTe}$, and $J_{solar}(\lambda)$ is defined as

$$J_{solar}(\lambda) = e P_{solar}(\lambda) \frac{\lambda}{hc} \quad (3)$$

$P_{solar}(\lambda)$ is the AM 1.5 solar spectrum in $\text{J cm}^{-2} \text{ nm}^{-1}$, λ is the wavelength in nanometres (nm), e the electron electrical charge ($1.60 \times 10^{-19} \text{ C}$) and $e/hc = 8.08 \times 10^{-4} \text{ C J}^{-1} \text{ nm}^{-1}$ [21]. In order to determine J_{sc} in a glass/ITO/ZnO/CdS structure, three different heterostructures were prepared to make a comparison; one structure without a ZnO film, and two others with ZnO grown from the mixed and sintered targets, respectively. CdS thin films with thickness of $\sim 120 \text{ nm}$ were deposited using the standard close-spaced sublimation

Figure 3. Transmittances of several heterostructures, including those using ZnO layer grown from mixed and sintered targets, glass/ITO/ZnO_{mixed}/CdS and glass/ITO/ZnO_{sintered}/CdS, respectively.

technique [22]. From an ideal CdTe cell with band gap of 1.5 eV and $T(\lambda)$ of 100%, equations (2) and (3) yield a photocurrent of 30.5 mA cm^{-2} which is the maximum photocurrent available for a CdTe-based cell under the standard global spectrum normalized of 100 mW cm^{-2} . Then, the J_{sc} losses can be evaluated by subtracting J_{sc} from 30.5 mA cm^{-2} value. Figure 3 shows the $T(\lambda)$ spectrum for the glass substrate, glass/ITO, glass/ITO/CdS and glass/ITO/ZnO/CdS with a ZnO thin film grown from the mixed and sintered targets, respectively. From the $T(\lambda)$ spectrum of the glass and the $T(\lambda)$ spectrum of the glass/ITO/ZnO/CdS structure as can be seen in figure 3, and using equations (2) and (3) we found that the values of J_{sc} were 18.57 , 19.1 and 19.03 mA cm^{-2} to the structures made without ZnO and with ZnO grown from the mixed and sintered targets, respectively. The heterostructure prepared with the mixed ZnO target shows a transmittance of 70–90% in the range of 540–850 nm region, having a maximum value of 90% maximum at 778 nm; the heterostructure prepared with the sintered ZnO target shows a transmittance of 70–85% in the range of 540–850 nm region, having a maximum value of 85% at 696 nm, having an abrupt decrease of 74% which started after the wavelength of 696 nm. These differences indicate that the structures prepared from the mixed target showed higher transmittance values than those of the films from the sintered target.

The losses due to the reflection and absorption in these structures were calculated and had values of 11.93 , 11.40 and 11.47 mA cm^{-2} to structures made without ZnO and from mixed and sintered targets, respectively; these represent a decrease of nearly $\sim 7\%$ on the losses due to reflectance, comparing these results we can conclude that there are more losses in structures without ZnO, and the structure with ZnO grown from the mixed target showed fewer losses than those with ZnO grown from sintered target. This indicates that the films

made from the mixed target had better antireflecting properties than those films made from the sintered target. The absorption coefficient α can be calculated from the equation [23]

$$T = A \exp(-\alpha h), \quad (4)$$

where T is the transmittance of thin film, A a constant and h the film thickness. The constant A is approximated to a value of 1, as the reflectivity is negligible and insignificant near the absorption edge. The band gap of the films is determined by applying the Tauc model [23] in the high absorbance region:

$$\alpha h \nu = D (h \nu - E_g)^n, \quad (5)$$

where $h \nu$ is the photon energy, E_g the optical band gap and D a constant. For a direct transition, $n = 1/2$ or $2/3$ and the former value was found to be more suitable for ZnO thin films as it gives the best linear curve in the band-edge region. A plot of the $(\alpha h \nu)^2$ vs. the energy ($h \nu$) obtained from the transmittance spectra of the heterostructures built using both the ZnO thin films from the sintered and mixed targets is shown in figure 4, to illustrate the absorption profile employed to acquire the band gap. Both absorption profiles clearly display two shoulders, which are evidence of the overlapping of two absorption profiles, which in turn correspond to two different compounds. The highest energy shoulders for both cases correspond to the band gap of the ZnO at $E_{g,\text{ZnO}} = 3.20\text{--}3.30 \text{ eV}$. The intercept for the other shoulder gave a band gap value of $E_{g,\text{CdS}} \cong 2.40 \text{ eV}$, for both profiles, which agrees very well with the standard band gap reported for the CdS of 2.42 eV [24]. All the results mentioned before suggest that the optical properties for the ZnO are highly improved for the mixed target in comparison to the sintered target. Finally, the recommended resistivity for a buffer layer must be $\sim 10^3 \Omega \text{ cm}^{-1}$ with thicknesses of $\sim 110 \text{ nm}$; however, films with electrical resistivity of $\sim 10^2 \Omega \text{ cm}^{-1}$ were obtained in both cases.

Figure 4. Plot of the $(\alpha h \nu)^2$ vs. energy ($h \nu$) calculated from the transmittance spectrum for the glass/ITO/ZnO_{mixed}/CdS and glass/ITO/ZnO_{sintered}/CdS heterostructures.

4. Conclusions

In this study, we used Nd:YAG PLD to obtain ZnO thin films in order to use them as buffer and antireflective layer in glass/ITO/ZnO/CdS structures. Two types of targets were used; the first one was prepared by a mixing method and the second one was obtained by a sintering process. XRD patterns showed that the films grew in the hexagonal wurtzite structure, having nanometric thickness, with crystallite sizes of ~ 40 (± 1 nm) and ~ 10 nm (± 1 nm) for the mixed and sintered targets, respectively. The strain values were 2.13×10^{-1} and -2.03×10^{-2} for the samples grown with the mixed and sintered targets, respectively. AFM images showed that the film surfaces of sintered target are three times rougher than those from the mixed target. Transmittance spectra showed values above 85% in the 540–850 nm of wavelength region, with energy gaps in the range of $E_{\text{gZnO}} = 3.20\text{--}3.30$ eV. Both types of samples were analysed as antireflective layers in glass/ITO/ZnO/CdS structures and it was estimated that the presence of ZnO resulted in a decrease of nearly $\sim 7\%$ on losses due to reflectance, with a photocurrent density of 19.1 and 19.03 mA cm $^{-2}$ for ZnO thin films made from mixed and sintered targets, respectively. The obtained thicknesses were ~ 100 nm for both type of films, while electrical resistivity of $\sim 10^2$ Ω cm $^{-1}$ was obtained in both cases.

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