Effect of indium tin oxide substrate roughness on the morphology, structural and optical properties of CdS thin films

R. Castro-Rodríguez a,⁎, A.I. Oliva a, Victor Sosa a, F. Caballero-Briones b, J.L. Peña a,b

a Applied Physics Department, CINVESTAV-IPN Mérida, C.P. 97310, Mérida, Yucatán, Mexico
b CICATA-IPN, Legaria 694 Col. Irrigación, C.P. 11500, Mexico, D.F. Mexico

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Abstract

Indium tin oxide (ITO) coatings of glass substrates were etched with hydrochloric acid in order to obtain different root-mean-square roughness \( R_{\text{ITO}} \) on its surface. The effect of \( R_{\text{ITO}} \) on the morphology, structural and optical properties of CdS films deposited was investigated. Polycrystalline cadmium sulfide thin films were deposited on ITO/glass substrates by chemical-bath deposition (CBD) at 358 K, and studied by atomic force microscopy (AFM). Roughness of CdS films \( R_{\text{CdS}} \) showed a nearly linear increase with \( R_{\text{ITO}} \). The thickness of CdS films was investigated by Auger Electron Spectroscopy (AES) and showed an increment with \( R_{\text{CdS}} \). X-ray diffraction results showed that CdS films have a cubic zincblende structure with a (111) preferred orientation. The measured residual strain of the CdS films showed an initial increase with \( R_{\text{ITO}} \) reaching a maximum point at 15 ± 2 nm, and after that exhibited a decreasing dependence. The optical band gap \( E_\text{o} \) of the CdS films obtained from transmittance measurements did not depend on \( R_{\text{ITO}} \).

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1. Introduction

The study of the physical properties of CdS films is a subject of current interest. Having a wide fundamental band gap, they have been used in a large variety of applications such as electronic and opto-electronic devices [1]. Polycrystalline CdS thin films are generally used in CdTe solar cells, as a window material for transmitting the light absorbed by CdTe and also as the n-type material for p–n junction of the solar cells [2–4]. Requirements of the CdS films are that they should be conductive (~ 10¹⁶ carrier/cm³), thin to allow high transmission (50–100 nm), and uniform to avoid short circuit effects. Techniques of deposit include molecular beam epitaxy (MBE) [5–10], metal organic vapor phase epitaxy (MOVPE) and metal organic chemical vapor deposition (MOCVD) [11,12], close spaced sublimation (CSS) [13], chemical bath deposition (CBD) [14–22], electrodeposition and successive ionic layer adsorption and reaction (SILAR) [23,24], screen printing [25], and physical vapor deposition (PVD) [26]. Currently, CdS thin films grown by CBD technique are...
commonly used for the fabrication of highly efficient CdTe solar cells by the simple method and low cost.

Physical properties of polycrystalline CdS thin films have not been thoroughly correlated with the roughness of the substrate. The literature on this subject is scarce and limited to some prominent papers. In a heteroepitaxial system, as in CdS on conductor oxide, the role of diffusion, local structural and chemical environments, might change with time during the growth process. The substrate influences the characteristics of the evolution of the growth. In a previous work [27], we deposited CdS thin films by CBD on different substrates such as glass, silicon and indium tin oxide (ITO) in order to understand the initial growth steps and the role of substrates. We concluded that ITO was the best of the three substrates studied because the CdS roughness remained constant from the first stage of growth. As far as we know, the effect of the roughness of ITO substrate on the physical properties of CdS deposited on them has not been investigated yet. In this study, the effect of roughness of ITO/glass substrates on the morphology, structural and optical properties of the polycrystalline CdS films prepared by CBD was investigated.

2. Experimental details

CdS thin films were prepared by the CBD technique on ITO/glass substrates. Details of the deposition process are widely described in Ref. [27]. Briefly, the chemical bath was formed by an aqueous solution of CdCl₂, KOH, NH₄NO₃, and CS[NH₂]₂ (thiourea). The solution was maintained at 358 K and continuously stirred to assure a homogeneous distribution of the chemical reagents. The substrates used were ITO (In₂O₃–SnO₂) coated boro-silicated (Valley) with transmittance of 85%, and the sheet resistance lower than 5 Ω cm⁻² as reported by the supplier. The ITO coatings were etched with hydrochloric acid with different etching times (from 0 to 120 s) in order to obtain different roughnesses. Before CdS deposition, the etched substrates were immersed simultaneously into the chemical bath by means of a holder to support them. The film deposition started when thiourea was added. The holder was retired from the bath after a 40-min deposition time. The resulting films were yellow pale and presented high adherence and bright surfaces.

AFM images of every sample of the ITO and CdS surfaces were taken ex situ at atmospheric pressure and room temperature on four different sites. We used an AFM Auto-Probe CP from Park Scientific Instruments in the constant force mode with a high-resolution scanner (1 μm × 1 μm). Images were analyzed with the Proscan software, calculating the average root-mean-square roughness value of ITO ($R_{\text{ITo}}$) and CdS ($R_{\text{CdS}}$). For a comparison, AFM images were taken with the same tip-cantilever, the same force value, and the same gain in the feedback loop. This way, and given that AFM images represent the convolution of the tip with the surface sample, different images obtained under similar conditions can be compared among them.

Compositional depth profiles were performed by the AES technique with an ESCA/SAM Perkin Elmer PHI 560 equipped with a double pass cylindrical mirror analyzer, with a base pressure of $\sim 2 \times 10^{-9}$ Torr. AES signals were obtained in the differential mode using a 3 keV, 0.2 μA electron beam incident at 45° to the surface normal. AES profiles were obtained with an Ar⁺ beam with energy of 4 keV and current density of 0.36 μA cm⁻², yielding a sputtering rate of about 10 nm/min. The calibration of the sensitivity factor of Auger data was made using stoichiometric samples of CdS and ITO substrate.

X-ray diffraction (XRD) measurements in the grazing incidence geometry with 0.5° of beam inclination, were done under CuKα radiation at 40 kV with 35 mA and aperture diaphragm of 0.2°, using a D5000 Siemens X-ray diffractometer with monochromatic radiation ($\lambda = 1.5418$ Å). The films were carefully mounted so no misalignment was present. The scanning step of the goniometer was 0.01° with a counting time of 10 s. The scattered radiation passed through an arrangement of horizontal slits to the detector. Data where collected sequentially at angles (2θ) between 20° and 60°.

Optical transmission measurements were performed with a Jobin-Yvon/Spex H20-VIS spectrophotometer using a 250 W tungsten halogen lamp. The incidence photon flux was normal to the film surface. The investigated wavelength ranged from
300 to 700 nm. The signal was received and processed with a Data Scan-2 controller coupled to a computer. Optical analysis was realized after eliminating one of the CdS films deposited on both faces of the substrate.

3. Results and discussion

Fig. 1 shows $1 \times 1 \mu m^2$ size typical AFM images obtained for ITO and CdS films. Fig. 1a represents the surface of ITO without etching. Fig. 1b corresponds to CdS film deposited on it. In this case, CdS surface roughness is slightly minor than ITO surface roughness. Only some holes were filled with CdS, but the surface does not show major changes. Fig. 1c represents the ITO surface after 120 s of etching time. It can be seen that roughness of ITO increased by the acid attack. After CdS was deposited on it (Fig. 1d), a similar topography was observed but with minor peak-to-peak heights. Then, based on the AFM topographic images, we conclude that CdS films deposited on ITO only presented a slight decrement on the surface roughness. As can be seen in Fig. 1, the CdS films display uniform surface features with cluster structures, hills with various heights, and lateral extensions. The average grain size measured was $\sim 200 \pm 20$ nm for films with $R_{ITO}$ between 10 to 23 nm. However, for films with higher $R_{ITO}$ (30 to 42 nm) the average grain size was calculated to be about 400 ± 20 nm.

$R_{CdS}$ as a function of $R_{ITO}$ is shown in Fig. 2. Roughness values represent here the mean value of the four AFM images taken from different regions of

Fig. 1. AFM images of CdS films prepared by chemical bath deposition on different ITO substrates: (a) $R_{ITO} = 10$ nm, (b) $R_{ITO} = 42$ nm.
each sample (ITO and CdS). $R_{\text{CdS}}$ shows a nearly linear increment with $R_{\text{ITO}}$. The result is in agreement with our observations reported in a previous work [27], where we concluded that $R_{\text{CdS}}$ remained almost constant and with the same value of $R_{\text{ITO}}$ from the first growth stages.

CdS thickness was estimated by means of Auger depth profiling. Typical results are shown in Fig. 3, corresponding to the samples whose AFM images were shown in Fig. 1, i.e., sample without etching and with 120 s of etching. Cd and S elements were monitored until ITO components appeared. The crossing between these two signals was taken as the film thickness. ITO thickness was 240 nm as measured by this technique, and CdS film grown on ITO was 32 nm thick in Fig. 3a. In Fig. 3b, it can be seen that a wider CdS/ITO interface appears, and CdS thickness seems to be higher. A plot of $R_{\text{CdS}}$ vs. CdS thickness ($t_{\text{CdS}}$) is shown in Fig. 4. It is interesting to note that the surface roughness of CdS increases with the film thickness $t_{\text{CdS}}$, and this dependence can be approximated by a power-law behavior $R_{\text{CdS}} \propto t_{\text{CdS}}^\beta$, as shown in Fig. 4. From this plot, an exponent $\beta = 3.4 \pm 0.6$ was obtained. The functional form of the interfacial roughness in terms of the layer thickness is of basic physical interest.
Important progress has been made in a dynamic scaling approach, and application of this method to the study of epitaxial growth of thin films has been reasonably successful [28–32]. If the film thickness is assumed to be directly proportional to the time of growth, this result also suggests a possible roughness scaling in the growth dynamics [32]. These dependence between CdS thickness and the $R_{\text{CdS}}$ can be explained due to the larger area presented for deposition because of the higher roughness.

XRD analysis was used for structural studies. For a small grazing incidence angle ($0.5^\circ$), CdS peaks clearly appear. The main peak can be associated both with (002) direction of the hexagonal phase or (111) direction of the cubic phase. However, the diffractograms agree well with the previous result for the cubic zincblende structure of CdS [33,34]. This result reveals that these films have high preferential direction in (111) plane. The X-ray diffractograms of CdS thin films are shown in Fig. 5(a–e), in decreasing order of their $R_{\text{ITO}}$. The intensity of the (111) peak decrease, meanwhile, the (222) ITO peak shows an undefined behavior with its $R_{\text{ITO}}$. These effects may be due to the interference caused by the CdS distribution through the surface cavities in the ITO substrate. By the other hand, to explain the physical mechanisms responsible for the residual strain ($\varepsilon_{\text{res}}$) relaxation, we calculated the $\varepsilon_{\text{res}}$ defined as

$$\varepsilon_{\text{res}} = \left( a^\parallel - a^o \right) / a^o$$

where $a^o$ and $a^\parallel$ are the unstrained lattice parameter and the parallel to substrate lattice parameter of the film, respectively. Using the lattice parameter value $a_s = 5.818 \ \text{Å}$ for cubic CdS, different values of the $\varepsilon_{\text{res}}$ along the (111) direction have been obtained. Fig. 6 shows the dependence of $\varepsilon_{\text{res}}$ with $R_{\text{ITO}}$. As we can see, $\varepsilon_{\text{res}}$ shows an initial increase reaching a maximum at $15 \pm 2$ nm, and after that shows a decreasing dependence. Starting from this maximum, $\varepsilon_{\text{res}}$ goes as $R_{\text{ITO}}^{-0.25}$. On the other hand, the inset in Fig. 6 shows the $\varepsilon_{\text{res}}$ vs. the CdS thickness, and the decreasing dependence can be approximated by a power-law behavior as $\varepsilon_{\text{res}} = t_{\text{CdS}}^{-0.39}$. This last exponent is near the 0.5 value predicted by the energy balance model for the strain relaxation dependence.
with the layer thickness in heteroepitaxy semiconductors system [35]. Then, the variation of this residual strain relaxation (as shown in Fig. 6), could be explained as follows: when the $R_{\text{ITO}}$ is small (small cavities), the unit cell of the CdS film is elastically distorted along the growth direction. The residual strain relaxation increases reaching a maximum value. After $15 \pm 2$ nm of $R_{\text{ITO}}$ (deep cavities on surface), a critical residual strain is exceeded, then a transmission from the elastically distorted configuration to the plastically relaxed one occurs.

In order to investigate the relation between $R_{\text{ITO}}$ and the optical properties, the absorption coefficient $\alpha$ was determined from optical transmittance measurements. The optical band gap $E_o$ was obtained from the relation for direct transitions,

$$\alpha (h \nu) = C (h \nu - E_o)^{1/2}$$

where $h$ is the Planck constant, $\nu$ is the frequency, and $C$ is a proportionality constant. $E_o$ was found by extrapolating the linear portion of the $\alpha^2$ vs. $h \nu$ curve to zero. Fig. 7 shows that $E_o$ was found to be invariant under variations of $R_{\text{ITO}}$ or $t_{\text{CdS}}$ (see insert). These experimental results suggest that the optical properties of the CdS films will not be affected by $R_{\text{ITO}}$ and film thickness, in the analyzed range. However, it has been reported that the optical absorption coefficient of CdS films deposited on ITO depends on the film thickness [36].

4. Conclusions

CdS thin films were deposited by chemical bath deposition on ITO/glass substrates with different roughness values. Our approach has been basically organized from repetitive morphology, structural and optical measurements of the CdS films. The thickness of CdS films showed an increment with $R_{\text{CdS}}$. $R_{\text{CdS}}$ showed a linear increment with $R_{\text{ITO}}$. From the XRD results, the CdS films showed a cubic zincblende structure with a (111) preferred orientation. The measured residual strain of the CdS films showed an increasing dependence with $R_{\text{ITO}}$ until a maximum value was reached, and after that, it diminished at higher roughness. Finally, we found that the optical band gap of the CdS films was not affected by $R_{\text{ITO}}$.

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