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CHARACTERIZATION OF CdS THIN FILMS SYNTHESIZED BY CHEMICAL BATH DEPOSITION USING GLYCINE AS COMPLEXING AGENT

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In this report, using the chemical bath deposition, we have employed glycine as an alternative complexing agent for the synthesis of CdS thin films. The films were deposited on glass substrates at 80 °C. The product was characterized with X-ray diffraction, atomic force microscope, optical absorption and X-ray photoelectron spectroscopy (XPS). Homogeneous CdS thin films with hexagonal crystalline structure and energy band gap of 2.53 eV were obtained after deposition process. The high purity of the sample was corroborated by the XPS measurements.

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1. Introduction

The chemical bath deposition (CBD) is a simple, low temperature, large area compatible and low cost process for the synthesis of several types of semiconductor thin films. High quality semiconductor films can be achieved by CBD by adjusting the pH [1], temperature [2] and reagent concentrations [3] of the reaction solution. It has been used for the deposition of CdS semiconductor thin films since the 60s decade [4,5]. There are many reported methods for the deposition of CdS thin films, such as electrodeposition, CBD, molecular beam epitaxy (MBE), metal organic vapor phase epitaxy (MOVPE), metal organic chemical vapor deposition (MOCVD), close spaced sublimation (CSS), successive ionic layer adsorption and reaction (SILAR), screen printing (SP) and physical vapor deposition (PVD) [6]. The application of CdS films as window layers in high efficiency CdS-CdTe and CdS-Cu(In,Ga)Se_2 solar cells has increased considerably the interest on this semiconductor material in the recent years [7]. CdS films deposited by CBD (CBD-CdS) are currently being employed in both types of these solar cells because their excellent properties for this specific application. In the nanometric scale, Hullavarad [8] review their applications as nanoscale devices in diverse technology areas from electronics to target drug delivery.

The formation of a uniform and adherent film on appropriated substrates by means of the CBD process requires the control of the solid phase precipitation from the precursor ions in the aqueous solution. This issue is addressed by employing a complexing agent which forms complex ions by reacting with the free metal ions in the solution and gradually releases them under suitable conditions.

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In previous works, for the CBD of CdS films, the ammonium was generally the complexing agent, in this case, the stirring was always employed. Soundeswaran [9] used ammonium sulphate as a complexing agent along with ammonium for precise control over the pH of the solution; Feitosa [10] reported the development of a new route to obtain cadmium sulphide (CdS) thin films by using ethylene-diamine-tetra-acetic acid (EDTA) ligand on the CBD chemical method and Zhang [6] studied CdS films by CBD without stirring using weak and strong complexing agents (EDTA) and Moloto [11] used Tetramethylthiuram disulphide cadmium complex for the synthesis of CdS nanoparticles. In 2008 Philippe [12] used glycine as complexing agent for the electrochemical deposition of a Fe−Ni−Cr all on stainless steel and copper substrates, and it was resulted ideal for the Cr. However, ammonia has several drawbacks such as volatility, toxicity and harmfulness for the environment. Alternative complexing agents to ammonia have been the subject of research in the last few years [13,14,15,16]. It has been shown that ethylene-diamine (ED), ethylene-diamine-tetra-acetic acid (EDTA), sodium citrate, among others, yield to good quality CBD-CdS films. Glycine is the smallest of the 20 amino acids commonly found in proteins. It has been used as complexing agent for the electrochemical deposition of Fe, Ni and Cr thin films on stainless steel and copper substrates [10]. In this paper, we have used glycine as the complexing agent in the synthesis of CdS thin films by means of the CBD technique. We report the properties of the CdS thin films obtained by this alternative CBD process.

2. Experimental

The CdS films were deposited on glass slide substrates in a 100 ml beaker containing the reaction solution prepared by the subsequent addition of 31 ml of deionized water, 4 ml of 0.1M cadmium nitrate tetrahydrated ($Cd(NO_3)_2 \cdot 4H_20$), 5 ml of 0.5 M glycine (NH_2CH_2COOH), 2 ml of pH 11 buffer, 5 ml of 1M thiourea [$(NH_2)_2CS$] and deionized water to complete 60 ml. The mixture was initially stirred to homogenize and then its temperature was set at 80°C in a thermal water bath. The substrates were immersed in the solution at this temperature and removed after 18 min when the reaction finished, according to its appearance. There was not stirring during the deposition process. The deposited CdS films were yellowish, homogeneous, specularly reflecting with very good adhesion to the substrate. The thickness of the films was about 60 nm as determined from depth profiles performed with Veeco Dektak 8 profilometer. The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) measurements with a Rigaku Ultima III diffractometer. The absorption spectra of the films were measured in a Perkin Elmer Lambda 19 spectrophotometer in the 350–800 nm wavelength range. The morphology and roughness of the surface films were investigated by atomic force microscopy (AFM) using a JSPM-4210 scanning probe microscope (JEOL Ltd).

3. Results and discussion

Figure 1 shows the XRD pattern of a typical CdS thin film obtained by using glycine as complexing agent in the CBD process. This pattern displays an intense peak at about 26.7° and weaker diffraction signals at about 28.6, 48.3 and 52.3°, which can be assigned to the reflections by (002), (101), (103) and (112) planes of the CdS hexagonal crystalline phase.

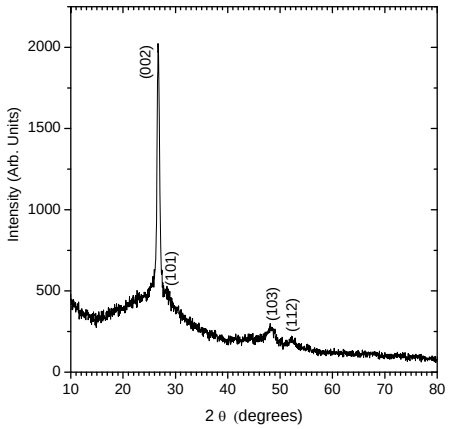

Fig.1. XRD pattern of a CdS thin film, verifying its hexagonal crystalline.

The relative large intensity of the (002) diffraction peak clearly evidences the preferred crystalline orientation of the CdS crystallites along the [002] direction. The lattice constant, *c*, calculated from this pattern is 6.677 Å, which is shorter than 6.713 Å, the lattice constant of bulk CdS. The percentage of variation of the value of *c* for the CdS films, related to that of the bulk, is -0.54 %. Because the (002) crystalline orientation of the CdS film, the [002] direction is perpendicular to the substrate. Since *c* is measured along the *c*-axis in the [002] direction, the shrinkage of this lattice constant can be related with tensile stress along the film-substrate interface, as has been observed in other chemically deposited CdS films [17]. In Fig. 2 are shown a) two-dimensional and b) three-dimensional AFM images of the CdS film surface.

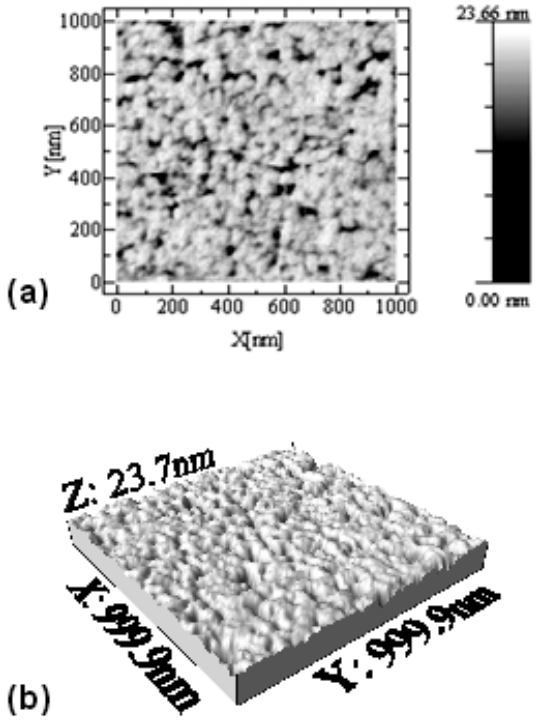

Fig. 2. a) Top view AFM image of a representative area of the CdS thin film, showing its nanometric grains sizes and b) Perspective view of AFM image of the same representative area of the CdS thin film, showing its nanometric grains sizes

The smooth surface of the films exhibits a well-defined granular structure with nanometric-sized grains. The rms average roughness of the film measured in the displayed area is 2.3 nm

[18]. Due the low roughness of this thin films the optical transmission increase in the visible region.

The figure 3 shows the optical properties of CdS thin films, measured using UV/Vis/NIR spectrometer, has can be seen, the film presents a low absorbance in the region from 450 to 900 nm, i.e. high transmission. This is important in the thin solar cells, CdS is normally used has the windows materials this is required to have high transmission in the visible range, so that much more visible light penetrate into the active region. After 18 min of deposition the films has reached enough thickness, and the reaction finished. The figure shows the result obtained for the optical absorption property (absorbance) versus the wavelength, for deposited CdS thin film. The Figure 3 leads permits to conclude that CdS thin films have an average transmittance of slightly major than 80 % within the optical region.

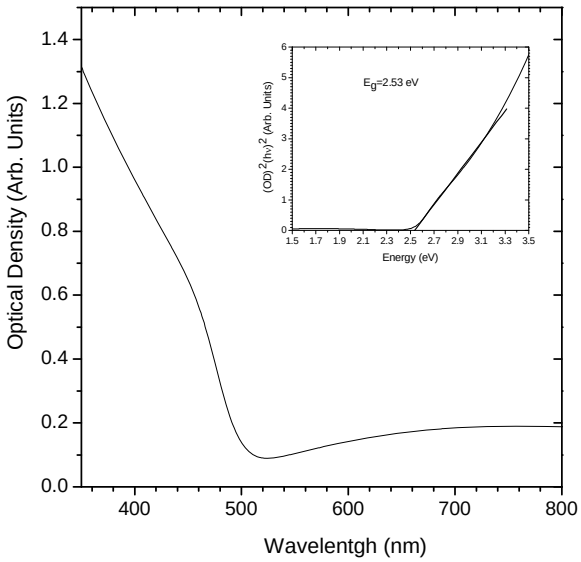

Fig. 3. Optical density, showing low absorption (less than 0.2) between 510 to 800 nm range. Inset: Energy versus $(OD)^2(h\upsilon)^2$, like utility to calculate E_g

In the inset of Figure 3 it is shown $(\alpha\ h\upsilon)^2$ vs $h\upsilon$ plots of typical CdS films deposited by CBD method. Since the absorption coefficient, α, for the allowed direct interband transition in a crystal is proportional to $(h\upsilon)^{-1}(h\upsilon\text{-}E_g)^{1/2}$ for $h\upsilon\ E_g$, where $h\upsilon$ is the photon energy and Eg is the value of the energy gap, we can estimate Eg by plotting $(\alpha\ h\upsilon)^2$ as a function of $(h\upsilon\text{-}E_g)$. The energy bandgap in this case is E_g = 2.53 eV. The CdS thin film can be considered good for use as a visible transmitting thin film since the range of band gap for visible transmitting film is 1.5eV to 3.0eV [19].

XPS chemical analysis was practiced without deep profile, just in order to estimate the very superficial chemical composition of the CdS thin films, as can be observed in a roughly way from the XPS pattern, the identified binding energies peaks show the main presence of Cadmium and Sulphur, but some additional peaks are also present, see the Fig. 4. The extra

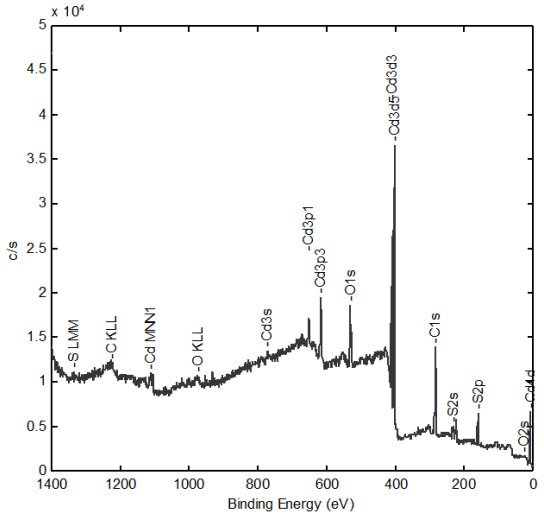

Fig. 4. XPS spectrum of CdS- glycine thin film.

peaks are expected to occur from capping the material. The sample contains oxygen and carbon because the sample is kept in ambient conditions. Which indicates the sample is of high purity. Thickness value measured for CdS films by the using of profilometer was 60 nm, for make this measurement it was necessary to etch the film with a strong acid in order to produce one step until the glass substrate and so measure the thickness.

4. Conclusion

The characterization by grazing incidence X- ray diffraction, XPS, atomic force microscope and optical absorption of our CdS thin films lead us to conclude that the Glycine it is an effective complexing agent for the cadmium ions in the CBD processes. These films shown hexagonal structure with high purity and predominant crystalline orientation, its transmittance is higher than 80 % and the band gap was 2.53 eV. By the above, we hope that this new process can be used to enhance the performance of cadmium sulfide films applied in photovoltaic devices.

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