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Characterization of CdS/ZnS and CdS/CoS Multilayer Thin Films Synthesized by Chemical Bath Deposition

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Abstract: In this work multilayer films of CdS/ZnS and CdS/CoS were prepared using the chemical bath deposition technique. The influence of substrate materials on structural, morphological, compositional and optical properties of the films was investigated. The powder X-ray diffraction (XRD) pattern of CdS/ZnS thin film showed nearly similar structure to that of the cubic ZnS structure. The XRD pattern of CdS/CoS thin films confirmed the co-existence of hexagonal and orthorhombic CdS phases. A cubic CdS structure is observed for CdS/glass thin film. The scanning electron microscopy (SEM) micrograph of CdS/glass film revealed spherical grains of size 125 nm covering the substrate uniformly without voids and cracks. The as large grain size as 800 nm with distinct grain boundaries was observed for CdS/ZnS multilayer film with some voids on the surface. The SEM micrograph of CdS/CoS thin film showed spherical surface grains of size 450 nm on flat and compact background. The energy dispersive X-ray spectra of single and multilayer CdS films confirmed the presence of Cd and S. The optical analysis of the CdS/glass, CdS/ZnS and CdS/CoS thin films confirmed band gaps of 2.5, 2.3 and 2.27 eV respectively.
Keywords: heterostructure, Crystal structure, Cadmium sulfide, Cobalt sulfide, Zinc sulfide, Chemical bath,

1 Introduction

Cadmium sulfide (CdS) is an important II-VI group semiconductor material owing to its optical properties, photoconductivity, high electron affinity and stability [1]. It exhibits n-type conductivity because of native defects such as sulfur vacancies and interstitial cadmium [2]. CdS is widely used in optical detectors, optoelectronic devices and as a window material in various heterojunction solar cells [3]. CdS thin films can be prepared by different techniques such as closed space sublimation [4], RF magnetron sputtering [5], chemical bath deposition (CBD) [1, 3], vacuum evaporation [6], and spray pyrolysis [2]. CBD of CdS is a common practice since 1960s [7]. The CBD has many benefits like low cost for equipment and operation, simplicity in operation, low deposition temperature, low energy consumption, and large area deposition in a single procedure [8, 9]. The nature of chemical bath deposited thin film depends on the preparation parameters such as nature of precursors [10-12], the deposition temperature [13, 14], pH [15-17], duration [18-20] and the substrate type [21-23]. Any solid material that does not dissolve in the chemical bath can be used as a substrate. However, type of substrate has substantial impact on the structural, optical, morphological and other properties of a film [24]. Glass is commonly used substrate for the deposition of CdS films by CBD technique. Other materials like polycarbonate, polyethylene terephthalate, Si wafer and indium–tin–oxide were also used as a substrate to deposit CdS. The substrate surface treatment either by heat or by chemicals also modifies the film properties [3, 25-28]. A semiconductor multilayers film, heterojunction, is formed when a semiconductor substrate is used to deposit another semiconductor of dissimilar bandgap and lattice constants. Semiconductor multilayer thin films are the basics of heterostructure devices that exploits the interface properties of these structures. Such structures inject nonequilibrium charge carriers, control the type of conductivity and other fundamental parameters: band gaps, effective mass of the charge carriers and the mobilities, refractive indices, the electron energy spectrum etc. inside the semiconductor crystals and devices [29]. The operation of semiconductor lasers, light-emitting diodes, photodetectors, highest-performance optical sources and detectors, and high-speed and high-frequency digital and analog devices exploit the heterostructure of semiconductors [30, 31].

In this work, we report on the structural, optical and

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morphological properties of chemical bath deposited CdS thin films and its heterojunctions with ZnS and CoS. The heterojunction of the CdS with ZnS and several types of their mixtures can be used as an n-type buffer layer to form thin film heterojunction solar cells [32, 33], quantum wells [34], light emitting devices [35] etc. Similarly, heterostructure of CdS and various phases of cobalt sulfide, like Co9S8 and Co4S3, are currently used for improving photocatalytic hydrogen production [36-38]. There are very few reports on chemical bath deposited heterojunctions of the CdS with ZnS [9, 32]. However, to the best of our knowledge there are no reports on chemical bath deposited heterostructure of CdS with CoS.

2 Experimental Section

2.1 Synthesis of the Thin Films

In the deposition of CdS/ZnS and CdS/CoS multilayers, the ZnS and CoS layers were first prepared on soda lime glass substrates. Before the deposition of the ZnS and CoS, the soda lime glass slides were immersed in nitric acid for 12 h and in ethanol for 30 min, consecutively. Then the substrates were cleaned by distilled water ultrasonically and dried under ambient conditions. Analytical grade cadmium acetate (BDH), Zinc acetate (CARLO ERBA), cobalt acetate (Loba Chemie), thioacetamide (Titan), and Na_2EDTA (Fine Chemicals) were used as starting reagents. The CoS substrate was prepared on the cleaned soda lime glass substrate from a solution of 1 M (10 ml) cobalt acetate, 0.2 M (9 ml) Na_2EDTA, 1 M (10 ml) thioacetamide and 61 ml distilled water at pH of 6 for 90 min. Similarly, the ZnS substrate was prepared on soda lime glass substrate from a solution containing 0.1 M (15 ml) zinc acetate, 0.2 M (2 ml) Na_2EDTA, 1M (7 ml) thioacetamide and 36 ml distilled water at pH of 2.5 for 100 min. After their corresponding deposition period, the ZnS and the CoS thin films were taken out of the chemical baths, washed with distilled water thoroughly and dried in ambient conditions before used for the preparation of the CdS films. The CdS thin films were deposited on soda lime glass (CdS/glass), ZnS coated soda lime glass (CdS/ZnS) and CoS coated soda lime glass (CdS/CoS) substrates from a solution of 0.1 M (15 ml) cadmium acetate, 0.2 M (2 ml) Na_2EDTA, 1 M (7 ml) thioacetamide and 36 ml distilled water at pH of 2.5 for 100 min. The bath temperature of all the depositions carried out in the present work was adjusted to 80 °C. The optical, morphological, compositional and structural properties of the single and multilayer films were characterized by UV-Vis spectrometer, scanning electron microscope (SEM), energy dispersive X-ray analyzer (EDX) and X-ray diffractometer respectively.

2.2 Characterization of the Thin Films

Structural characterization of the films was carried by Bruker D8 X-ray diffractometer (XRD) with CuKα (λ= 1.5406 Å) radiation working at 40 mA and 40 kV at a scan rate of 0.03°/s. The XRD patterns were analyzed by matching the observed peaks with the standard JCPDS files. The surface morphology and composition of single and multilayer thin films were studied by ZEISS sigma field effect scanning electron microscopy (FE-SEM) attached with ZEISS Analysis Station energy dispersive X-ray (EDX) devices. The optical properties of the thin films were determined from the absorption spectrum using Shimadzu UV-3600 plus UV-Vis Spectrophotometer within the wavelength range of 300 nm-1000 nm for ZnS, CdS and CdS/ZnS, 500- 2000 nm for CoS and 300 – 2000 nm for CdS/CoS films.

3 Results and Discussion

3.1 Structural Studies

The XRD patterns of different substrates and the CdS thin films deposited on these substrates are shown in Figure 1. As it can be observed from this figure, the CdS thin film deposited on soda lime glass substrate has a single peak at 2θ = 26.69° which is indexed to (111) plane of cubic structure (JCPDS # 00-010-0454). The XRD pattern of ZnS thin film deposited on glass substrate has two very weak peaks at 2θ =28.63° and 47.97° which were indexed to (111) and (220) planes of cubic phase (JCPDS # 00-005-0566). The CdS/ZnS multilayer has similar diffraction pattern to that of ZnS thin films deposited on the glass substrate. This implies that new CdS phase has not been grown on the ZnS structure. Three peaks were observed at 2θ = 20. 29, 22.32 and 29.95° on XRD pattern of CoS thin film deposited on soda lime glass substrate. Comparison of this pattern with the PDF files indicates that the CoS film consists of the mixtures of phases.

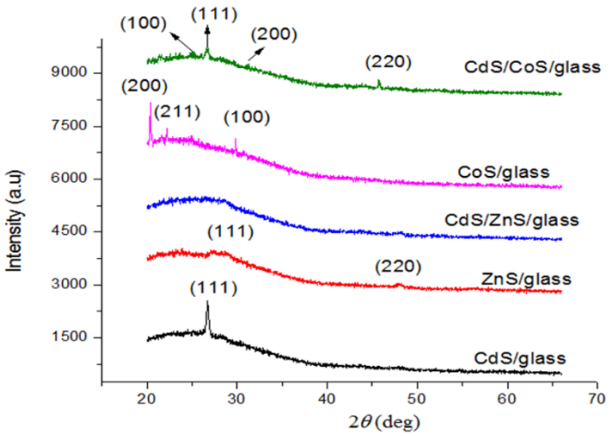

Fig.1: XRD patterns of CdS, CoS and ZnS thin films deposited on glass and CdS thin films deposited on CoS and ZnS coated glass substrates.

The peaks at 2θ =20.29 ° and 29.95° are diffractions from the hexagonal CoS (Pdf# 01-1279) and cubic Co9S8 (Pdf# 75-2023) respectively and the one at 2θ =22.32° is due to either the hexagonal CoS (Pdf# 01-1279) or the cubic Co9S8 (Pdf# 190364) [39]. The CdS thin film deposited on CoS substrate has grown in both hexagonal and orthorhombic CdS structures which is manifested by four very weak peaks. The peaks at 2θ =24.9° and 26.67 respectively represent (100) and (002) planes of the hexagonal CdS structure (JCPDS # 01-07-2553) and the peaks at 2θ = 31.2 and 45.6°consecutively represent (110) and (021) planes of orthorhombic CdS structure (JCPDS # 00-043-0985). The structural analysis confirms that the substrate has significant impact on the crystal structure of CdS thin films. Comparable results showing the effect of substrates on the properties of the CdS thin films were reported by [21-24, 40].

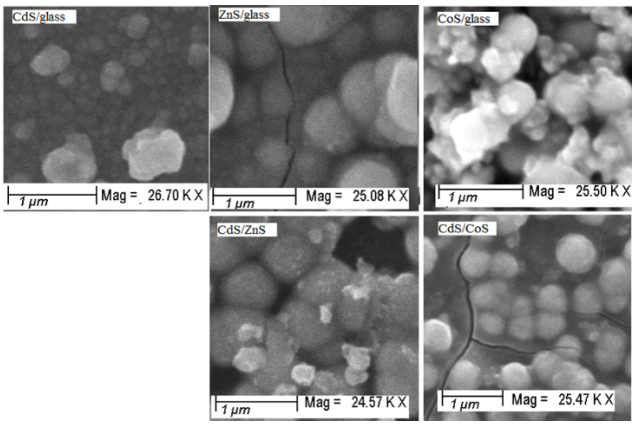

Fig.2: SEM micrographs of CdS thin films and the substrates used to deposit the films.

3.2 Surface Morphology and Composition Analysis

The surface morphology of the CdS/glass, ZnS/glass, CoS/glass, CdS/ZnS and CdS/CoS thin films are represented in Figure 2. The CdS thin film deposited on glass substrate has a uniformly covered surface morphology formed by spherical shaped grains of average size 125 nm. The grains completely covered the substrate without pinholes and cracks. Except few larger grains on the most top surface, the film has uniform grain size distribution. The surface morphology of ZnS thin films revealed larger spherical grains of average size of 710 nm. Some of the grains coalesce forming large grains and others have distinct grain boundaries. No pinholes were observed except few cracks. The surface morphology of CdS/ZnS multilayer is similar to that of ZnS thin films grown on the glass substrate, however, the average grain size increased to 800 nm and few voids appeared. This result strengthens the XRD result showing that no distinct CdS phase is formed on ZnS layer, rather than diffusion of Cd and S in to the ZnS structure. The SEM micrograph of the CoS thin films deposited on the glass substrate shows non-compact spherical and irregular shaped grains with a number of voids. The SEM micrographs of CdS/CoS signifies spherical surface grains of average size 450 nm on flat and compact background grains. No voids were observed on CdS/CoS layer; however, cracks were appeared. Similar variation on the surface morphology of CdS thin films deposited on different substrates was reported by O'Brien and co-works [28].

The EDX spectra of the CdS thin films deposited on different substrates are shown in Figure 3. As confirmed by EDX investigation, the ratio of Cd:S, Zn:S and Co:S in the CdS/glass, ZnS/glass and CoS/glass thin films are 49: 51, 50:50 and 39:61 respectively. In CdS/ZnS, the element ratio of Cd:Zn:S is 19:26:55, which shows a slight dominance of S in the film. The dominance of Zn over Cd could be resulted from very thin layer of CdS over the ZnS. However, for CdS/CoS films S has significant dominance over the metal ions with Cd:Co:S percentage composition of 17: 16: 67 which is resulted from the CoS layer as we reported in our previous work [39].

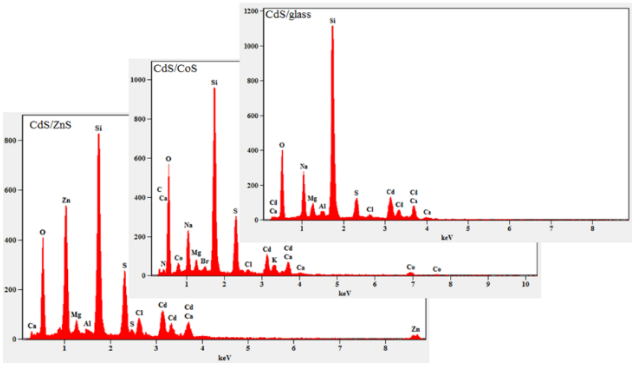

Fig. 3: EDX spectrum of CdS/galss, CdS/CoS and CdS/ZnS thin films.

3.3 Optical Properties

The plot of product of absorbance and photon energy squared $(Ahv)^2$ versus photon energy (hv) of the single and multilayer films are shown in Figure 4 (a) and (b). The plot for ZnS/glass thin film revealed two transition edges (Figure4 (a)). The transition at low energy photon could be due to defect states in the crystal structure of the film, however, the transition at photon energy of 2.6 eV is due a fundamental transition. For CdS/ZnS multilayer thin film, the two transition edges in the ZnS thin film changed to a single broad transition edge. The result implies that the defect states in ZnS thin films were significantly minimized by depositing CdS on ZnS layer. The ZnS/glass and CdS/ZnS layers have higher absorbance of visible and near infrared light than the CdS/glass layer. This could be resulted from the higher thickness and defect states of the former layers. Similarly, the CoS/glass and CdS/CoS layers have higher absorbance than CdS/glass layer in the same region

of light. However, the reverse is true in the infrared region.

The energy band gaps of the thin films were obtained using Stern relationship (Eqn. 1) at the near-fundamental absorption edge [41].

$$A = \frac{[k(h\nu - E_g)]^{\frac{n}{2}}}{h\nu} \qquad (1)$$

where A is absorbance, k is a constant, h is the Planck's constant, ν is the frequency of the radiation, and n is 1 for the direct transition which is true for almost all compound semiconductors and 4 for the indirect transition. In the case of direct transition$(Ah\nu)^2$ and the photon energy $(h\nu)$ (Eqn.1) has linear relation in the region next to the onset of fundamental absorption [42].

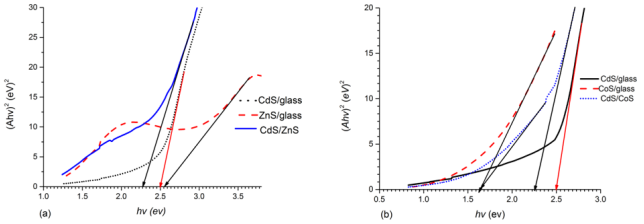

Fig. 4: Optical band gap of different substrates and the CdS thin films deposited on these substrates.

The band gap energy (E_g) was obtained by extrapolating the linear portion of the $(Ah\nu)^2$ vs $(h\nu)$ curve towards $h\nu$ axis . The band gaps of the CdS/glass, ZnS/glass, CdS/ZnS and CoS/glass thin films are equal to 2.5, 2.6, 2.3 and 1.6 eV respectively (Figure 4). The CdS/CoS multilayer has two band gaps of 1.6 and 2.27 eV corresponding to CoS and CdS phases, respectively. The presence of a single bandgap in CdS/ZnS confirms the homogenization of ZnS and CdS layers instead of forming their own phases. The decrease in band gap when CdS deposited on ZnS and CoS could be due to strain and increase in the grain size as shown in SEM micrograph of CdS/ZnS and CdS/CoS films (Figure 2) [43, 44]. In the case of CdS/CoS, the band gap decrease can also be resulted from the substitution of some of the Cd ions specially at the interface region by relatively larger atomic radius Co ions [45].

4 Conclusions

The CdS thin films were synthesized on different substrates by solution growth technique from a solution of cadmium acetate, thioacetamide and Na_2EDTA in acidic condition. The XRD investigation confirmed that the type of substrate has significant influence on the growth and crystal structure of the CdS thin films. The CdS thin film deposited on soda lime glass substrate was grown in cubic structure and the one grown on ZnS substrate forms a homogenized phase with cubic ZnS structure. The XRD pattern of CdS/CoS multilayer shows a mixture of hexagonal and orthorhombic CdS structures. The single and multilayered CdS thin films deposited on different substrates possessed different morphology in terms of shape and size of grains, voids and cracks. A stochiometric CdS thin film was deposited on a glass substrate, however, films deposited on ZnS and CoS substrate are dominated by sulfur. The optical bandgaps of the CdS films on ZnS and CoS substrates decreased as compared to that of deposited on a glass substrate. The structural, morphological and optical results confirmed that CdS thin film deposited on ZnS substrate forms homogenized phase with cubic ZnS structure and that deposited on CoS substrate forms a mixture of hexagonal and orthorhombic CdS phases. The present investigations showed that substrate has significant influence on structural, morphological, compositional and optical properties of the CdS thin films.

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