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Effects of different annealing atmospheres on the properties of cadmium sulfide thin films

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ABSTRACT

Cadmium sulfide (CdS) thin films were prepared on glass substrates by using chemical bath deposition (CBD) technique. The effects of different annealing atmospheres (air and sulfur) on the structural, morphological and optical properties of CdS thin films were studied at three different pH values. Compactness and smoothness of the films (especially for pH 10.5 and 11) enhanced after sulfur annealing. pH value of the precursor solution remarkably affected the roughness, uniformity and particle sizes of the films. Based on the analysis of X-ray diffraction (XRD) patterns of the films, micro-strain and dislocation density values of the sulfur-annealed films (pH 10.5 and 11) were found to be lower than those of air-annealed films. Air-annealed films (pH 10.5, 11 and 11.5) exhibited higher transmittance than sulfur-annealed films in the wavelength region of 550–800 nm. Optical band gap values of the films were found between 2.31 eV and 2.36 eV.

1. Introduction

CdS is an n-type compound semiconductor of II-VI group and has a direct optical band gap of 2.42 eV (bulk CdS) at room temperature [1]. CdS thin film is used in various areas such as solar cells, optical detectors, opto-electronic devices and is the most commonly used n-type semiconductor for thin film p-type cadmium telluride, p-type copper indium diselenide hetero-junction solar cells due to its compatibility with the p-type absorption layers [2–4].

CdS thin films have been deposited by various deposition methods such as spray pyrolysis [5], vacuum evaporation [6], electrodeposition [7], thermal evaporation [8], radio frequency sputtering [9], chemical vapor deposition [10], successive ionic layer adsorption and reaction [11], CBD [12], etc. Among these methods, CBD is the most common and widely used deposition technique due to its simplicity [13].

CBD process uses a controlled chemical reaction to achieve thin film deposition by precipitation. In this technique, thin films are deposited on substrates immersed in dilute solutions containing metal and chalcogenide ion sources. Generally, fabricating of CdS thin films can be achieved by CBD in an alkaline aqueous solution consisting of thiourea, cadmium salts and ammonia. Ammonia is mainly used in the CBD method as a complexing agent. CdS thin films can be deposited with either of two different structural phases such as a meta-stable cubic phase and a stable hexagonal phase [12,13].

Up to now, the effects of annealing under different atmospheres have been studied. Kong et al. [14] studied the effects of $CdCl_2$-assisted annealing under different atmosphere (vacuum, Ar and air) on the structural, morphological and optical properties of CdS nano-films. They found that the treatment in air with $CdCl_2$ coating layer increased the crystallinity and the mean grain size of CdS film. In a comparative study, Wan et al. [15] prepared CdS thin films via CBD method and annealed them in air with or without $CdCl_2$ coating. They investigated the effect of two types of heat treatment on the structural and optical properties and surface composition of CdS films. They reported that large CdS grains with good crystalline quality formed through re-crystallization during the $CdCl_2$ heat treatment. However, there is no study which compares the effects of air and sulfur atmospheres in the literature.

In the present work, a comparative study was carried out to investigate the effects of different annealing atmospheres (air and sulfur) on the structural, morphological and optical properties of CdS thin films fabricated through the CBD technique.

2. Experimental procedure

2.1. Deposition of CdS thin films

CdS thin films were fabricated on glass substrates using the CBD technique. All the chemicals used for the deposition were an

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analytical grade and purchased from Sigma–Aldrich. All solutions were prepared in double distilled water and films were deposited on 75 mm × 25 mm × 1 mm commercial glass substrates. Before the deposition, the substrates were ultrasonically cleaned in a dilute sulfuric acid solution (H_2SO_4/H_2O, 1:5, v/v) to remove native oxide layer and then in acetone and double distilled water for 5 min and finally dried in air. In order to obtain 0.2 M $CdCl_2$ and 0.2 M $(NH_2)_2CS$ solutions, 3.67 g of cadmium chloride and 1.52 g of thiourea were weighed and solved in 100 ml of double distilled water, respectively. Then the solutions were stirred in a magnetic stirrer at room temperature for 2 h in order to obtain transparent and well-dissolved solutions. Then the solutions were poured into a beaker. pH value of the solution was adjusted by using aqueous ammonia and measured by Hanna pH 211/213 pH meter. Previously cleaned glass substrates were vertically dipped into the solution and the solution heated and kept at about 85 °C. During the deposition process the solution was stirred to get homogeneous medium. After deposition, the substrates were taken out and washed ultrasonically with double distilled water to remove the loosely adhered CdS particles on the film and finally dried in air. The deposited CdS thin films were found to be uniform and well adherent to the substrates.

In order to study the effects of different annealing treatments, the as-deposited CdS thin films were annealed in two different atmospheres including sulfur and air at 300 °C for 60 min. A schematic description of the annealing set up is given in [16]. Due to the high vapor pressure of sulfur at the annealing temperature, certain amount of elemental sulfur in an alumina crucible was put into the quartz tube to compensate for any possible sulfur loss during the sulfur-annealing process. Before the annealing, the tube furnace was evacuated to pressure of 5×10^{-4} mbar. The heating rate was 5 °C/min. After the annealing process, the samples were allowed to cool naturally to room temperature.

The samples of CdS thin films will be hereafter denoted as A1 (CdS thin film fabricated with pH 10.5 and annealed in air atmosphere), A2 (CdS thin film fabricated with pH 11 and annealed in air atmosphere), A3 (CdS thin film fabricated with pH 11.5 and annealed in air atmosphere), S1 (CdS thin film fabricated with pH 10.5 and annealed in sulfur atmosphere), S2 (CdS thin film fabricated with pH 11 and annealed in sulfur atmosphere), S3 (CdS thin film fabricated with pH 11.5 and annealed in sulfur atmosphere). The detailed list is given in Table 1.

2.2. Characterization of the CdS thin films

The crystal structure of the samples was analyzed via a Bruker AXS D8 Advance Model X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å, with Si (NBS, 640B) internal standard) in the range $2\theta = 2–80°$ with a scan speed of 3°/min and a step increment of 0.02° at room temperature. Surface morphology of each film was observed by using a JEOL JSM-500LM scanning electron microscope (SEM). Optical absorption spectra in the UV–vis spectral range (190–1100 nm) of the films were determined by using a UV–visible spectrophotometer (Thermo Scientific Genesys 10S).

Table 1
Preparation and annealing conditions of the deposited films.

Name	pH value of the precursor solution	Annealing atmosphere
A1	10.5	Air-annealing
A2	11.0	
A3	11.5	
S1	10.5	Sulfur-annealing
S2	11.0	
S3	11.5	

3. Results and discussion

3.1. Morphological properties

Fig. 1 shows the surface morphology of the samples prepared under different pH conditions and annealing atmospheres. As seen from Fig. 1, the films are continuous and fairly uniform without any crack. However some residual particles are seen on the surface of the film. The samples series in the left column (A1–A3) were produced at the pH value of 10.5, 11 and 11.5, respectively and heat treated in air at 300 °C for 60 min in a tube furnace. As can be seen from Fig. 1 that pH value of the precursor solution remarkably affects the surface morphology, roughness, uniformity and grain sizes of the films. The images in the right column (S1–S3) belong to the samples which were annealed in sulfur atmosphere at 300 °C for 60 min. From the images, it can be seen that the compactness and smoothness of the films (especially for S2 and S3) enhance after sulfur annealing. Moreover, the residual particles on the surface decreases after annealing in sulfur atmosphere, especially in samples S2 and S3. For comparison, SEM image of as-deposited CdS film was also given (Fig. 1g). As it is proven by Fig. 1g that chemically grown CdS films have usually morphological disorders and poor crystallinity without heat treatment (as shown in Fig. 2).

3.2. X-ray analysis

XRD analyses were employed to investigate the crystal structures of the films. Fig. 2 shows the obtained XRD patterns of the CdS samples annealed in different atmospheres. The pattern of the as-deposited CdS film was also given for comparison. It is clear that as-deposited CdS film has poorer crystal structure than those of air- and sulfur-annealed films. It has been reported that CdS film can grow with cubic (zinc blende) or hexagonal (wurtzite) structure depending on deposition conditions [17]. As can be seen from the figure that only one clear peak can be observed at the diffraction angle of 26.58° on the patterns. By using the Joint Committee on Powder Diffraction Standards (JCPDS) data [18] and comparing with the published results, observed diffraction patterns matched very well with cubic CdS 00-010-0454 (space group $F\text{-}43m$, $a = b = c = 0.5818$ nm). The peak observed at 26.58° of Bragg angle indicates the (1 1 1) reflection of cubic structure. Another peak which is seen in all air annealed films (marked with #) was observed at 17.50° and indexed to (0 0 1) plane of hexagonal $Cd(OH)_2$ (JCPDS Card No.: 31-0228). The reason of absence of this peak in the patterns of sulfur-annealed films can be related to high vapor pressure of sulfur penetrating into the lattice and substituting with OH^- groups.

Average crystallite size of a thin film sample can be estimated by using the related XRD pattern. We have estimated the sizes of crystallites of CdS films from the peak width at the half maximum (β), using the Debye–Scherrer equation [19]:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the wavelength of X-ray radiation and θ is the Bragg angle of the (0 0 2) peak. The values are given in Table 2. It can be seen that average crystallite sizes of the sulfur annealed samples S2 (pH 11) and S3 (pH 11.5) are higher than those of air annealed samples A2 and A3. In contrast, an adverse effect was seen in the samples A1–S1 (pH 10.5).

Each peak acquired in an X-ray diffractometer is broadened due to instrumental and physical factors (lattice strains and crystallite size) [20]. The micro-strain (ε) and dislocation density (ρ) for an orientation can be estimated using the formula given below [21]: