Structural and optical analysis of CdS thin films grown by magnetron sputtering technique

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Abstract. Structural and optical characterizations were performed on CdS polycrystalline thin films grown by magnetron sputtering method. The thicknesses of the films were estimated to be 200-550 nm by scanning electron microscopy (SEM) measurements. X-ray diffraction (XRD) data show that CdS films are in the stable hexagonal crystalline structure. Using Debye-Scherrer's formula, the average grain size for the samples was found to be 40 ~ 45 nm. X-ray photoelectron spectroscopic (XPS) experiments indicate that the CdS samples are Cd rich in the surface region and S rich in the bulk region of the film. Photoluminescence (PL) bands, including green emission band, yellow emission band, orange emission band, and red emission band, were observed at room temperature and analyzed for the CdS films. The energy gap of the samples was also estimated and discussed from the room temperature optical transmittance spectra.

1. Introduction

Cadmium Sulphide (CdS) material has attracted much attention due to its applications in optical-electro devices, such as solar cells and light emitting diodes \cite{1, 2}. Owing to the wide band gap of about 2.4 ~ 2.5 eV, CdS polycrystalline thin films are widely used as the window material in heterojunction solar cells \cite{1}. CdS can crystallize in hexagonal (h) wurtzite and cubic (c) zinc blende structures, in which the hexagonal structure is more stable than the cubic structure. Since sulphur is a volatile element, CdS is prone to generate lattice defects during fabrication procedures. For CdS, interstitial Cd atoms and S vacancies act as donors, and Cd vacancies and interstitial S atoms behave like acceptors. These native defects introduce trapping states into the energy gap, which can significantly influence the optical-electric properties of CdS material.

CdS polycrystalline films have been grown by a variety of film deposition techniques such as thermal evaporation \cite{3}, sputtering \cite{4}, pulsed laser deposition \cite{5}, and chemical bath deposition (CBD) \cite{6}. Meanwhile, various structural and optical characterizations have been done to CdS films, as widely reported in literatures. However, since the crystal structure and optical-electric properties of CdS films are sensitive to the specific methods and conditions employed during fabrication, investigations on structural and optical properties of CdS films are still underway to enrich the

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knowledge in this area [6, 7]. For instance, although photoluminescence (PL) measurements have been extensively used to obtain the information of band-edge transitions and defect-associated transitions in CdS films, the unambiguous origins of some PL emission peaks are still unclear. In this work, CdS thin films were prepared by magnetron sputtering method. Room temperature (RT) structural and optical properties of the CdS films were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopic (XPS), PL spectra, and optical transmittance spectra.

2. Experimental
The studied CdS thin films were grown by magnetron sputtering method with the deposition temperature of about 300°C. After the deposition procedure, CdS films were annealed in the Ar + S2 mixture of gases flow for two hours at about 500°C. Substrates used in this work include glass slices coated with F-doped transparent conductive tin oxide (FTO) layer and quartz slices. The film thickness was controlled by varying the sputtering time and measured by SEM. The crystalline structure of CdS samples was analyzed through the XRD measurement by using the Cu Kα radiation with the wavelength of about 0.154 nm. The XPS experiments were performed at RT with a Perkin-Elmer PHI 550 spectrometer to investigate the elemental composition in the samples. The PL spectra at RT were recorded in the range of 1.4 – 2.75 eV by using a He-Cd laser with the wavelength of 325 nm (3.82 eV) as the excited light source. The RT optical transmittance measurements were carried out with a double beam ultraviolet-infrared spectrophotometer (PerkinElmer Lambda 950) in the photon energy range from 1.5 eV to 3.1 eV.

3. Results and discussion
A series of four CdS thin films with different thicknesses and substrates were studied in this work, as listed in Table 1. The typical surface micrograph obtained by SEM for CdS sample C was given in figure 1(a). By SEM measurements, the thicknesses of the four films were estimated to be 200-550 nm. Meanwhile, columnar shape growth in the CdS films is visible from the cross section view, as shown in figure 1 (b). From XRD measurements, it is found that CdS films grown on the same substrate possess the same XRD pattern. Therefore, only the XRD results for samples A and C were presented in figure 2. The XRD spectra of the substrates are also presented in figure 2 for comparison. Diffraction peaks with the Bragg angle 2θ = 26.7° were due to the (002) reflections in the hexagonal phase for the CdS films. CdS films grown on quartz substrates exhibit only the {002} reflection peaks, indicating a single preferential orientation and better crystal quality in these samples. As for CdS films grown on FTO substrates, apart from {002} reflection peaks, (101), (102), and (103) reflection peaks of the hexagonal phase were also observed in the XRD patterns, as designated in figure 2. The average grain size of the CdS was estimated by using Debye-Scherrer’s formula [5], 

\[ D = \frac{0.9\lambda}{\beta\cos\theta} \]

in which \( D \) is the average grain size, \( \lambda \) is the X-ray wavelength, and \( \beta \) is the full-width at half-maxima (FWHM) in radians and \( \theta \) is the diffraction angle. The grain size for all the CdS samples was found to be 40 ~ 50 nm, as given in Table 1. Since all the CdS films were prepared by employing nearly the same growth procedure as described previously, XPS measurements were performed only on CdS sample B to obtain the information of the elemental composition. XPS results reveal the CdS sample are Cd rich with the molar ratio of S: Cd = 0.73:1 in the surface region. Whereas, the molar ratio of S: Cd is 1.16:1 at the depths of about 20 nm after a etching procedure, indicating the fact of S rich in the bulk of the film.

Table 1. Substrates, thicknesses, average grain sizes, and values of energy gap for the four CdS thin films.

| CdS Samples | Substrate | Thickness (nm) | Grain size (nm) | \( E_g \) (eV) |
|-------------|-----------|----------------|-----------------|---------------|
|             |           |                |                 |               |

2
As known, PL spectra reveal radiative recombination processes, which are usually related to the variety of the defects, in the material. Therefore, the analysis of PL spectra could be a complicated issue since the types of defects are related to the specific sample preparation procedures. Figure 3 then shows the room temperature PL spectra of the studied CdS thin films as a function of the emission energy. One can see from figure 3 that there are two well resolved emission structures in the PL spectra for each CdS sample: the emission band centered at the photon energy of about 2.37-2.43 eV and the broad band with the photon emission energy approximately ranging from 1.5 to 2.2 eV. As for
the latter band, it is a superposition of several bands, which is evidenced by the peaks and weak shoulders in the PL features.

![Figure 3](image-url)  
**Figure 3.** Experimental photoluminescence spectra and deconvoluted emission bands for CdS films.

We try to decompose the experimental PL spectra into several Gaussian curves for each CdS film, as given in figure 3. Emission bands centered at 2.37-2.43 eV are attributed to the green emission (GE) bands. At RT, GE bands centered at about 2.4 eV or above might origin from band to band transitions and/or recombinations associated with shallow trapping states [8, 9]. Note that a second GE peak located at about 2.3 eV has been observed and attributed to the transitions of donor-acceptor pairs (DAP) in CdS by some authors [3, 9]. The second GE band is also considered as the sign of the presence of cubic to hexagonal phase transition in CdS [10]. The lower GE peak energy of 2.37 eV for CdS sample C could be ascribed to the band tailing effect. Emission bands centered at 2.13-2.17 eV are yellow emission (YE) bands, which are ascribed to the transitions from interstitial Cd to the valence band [3] or Cd related DAP transitions [8, 11].

Emission bands centered at 1.98-2.00 eV in figure 3 are assigned to be orange emission (OE) bands. The well-resolved OE bands were only observed in CdS samples grown by CBD and microwave-assisted hydrolysis methods to our knowledge [6, 7]. OE bands might originated from deep DAP associated radiative recombinations [6] or transitions from S vacancies to the valence band [7]. Emission peaks centered at 1.81-1.86 eV and 1.64-1.70 eV are attributed to red emission (RE) bands in this work [4, 6]. Generally speaking, RE bands are related to the transitions from surface states to the valence band [4]. O. Vigil et al. have argued that the emission peaks centered at 1.83 eV peak might be related to the transitions from S vacancies at the surface to the valence band [12]. Meanwhile, the more than one RE band might be due to the coupling effects with local vibration modes as reported in a recent work [6].

From figure 3, it is seen that the dominate emission band for the CdS films grown on quartz substrates is GE bands. Whereas, the intensities of the YE and OE bands increase relative to the GE bands in the films grown on FTO substrates when compared to those grown on quartz substrates. Combining with the XRD data, it is inferred that CdS films grown on FTO substrates possess a higher structural disorder (lattice defects). The intensity of RE band for CdS sample D increases due to the
less thickness of the film, and therefore, radiative transitions from surface states become more important. Figure 4 shows the optical transmission spectra of CdS films, in which the transmittances have been divided by the ones of substrates. For CdS films grown on the same substrates, the absorption edge shifts towards the higher photon energy when the film thickness decreases. At the photon energy higher than the absorption edge, the transmittances increase in thinner CdS films when compared to the thicker ones which grown on the same substrates, as shown in figure 4, indicating the less absorption to the incident light in these thinner samples [13]. By using the well known Tauc plot of $(αhν)^2$ versus photon energy $hν$, the energy gap of CdS films was determined, as shown in the inset of figure 4. The absorption coefficient $α$ were calculated by the relation $α = \ln(1/T)/d$, where $d$ is the film thickness, and $T$ is the transmission coefficient. The energy gap can then be obtained by extrapolating the linear region of the plot $(αhν)^2$ versus photon energy $hν$ to $α = 0$. The obtained values of the energy gap for CdS films are listed in Table 1. It is found that CdS films grown on FTO substrates have nearly the same value of energy gap, and the energy gap for CdS films grown on quartz substrates shows an increase for the thinner sample. We also found the energy gap determined by transmission spectra is close to the values of GE peak for each CdS film, indicating the GE bands are associated with the radiative recombination near the band edge.

![Figure 4](image-url)  
**Figure 4.** Transmission spectra of CdS thin films. The inset shows the Tauc plot of $(αhν)^2$ versus photon energy $hν$ to determine the energy gap.

4. Conclusions
In the present study, structural and optical properties were investigated on CdS hexagonal polycrystalline films which are grown on the FTO and quartz substrates by magnetron sputtering method. The thicknesses of the films were in the range 200-550 nm and the average grain size was found to be 40 ~ 45 nm. It is also inferred that CdS samples are Cd rich in the surface region and S rich in the bulk of the film from the XPS data. The observation of PL emission bands, including green emission band, yellow emission band, orange emission band, and red emission band, allows one to predict the possible defects in the CdS samples. Meanwhile, the energy gap for the CdS thin films was also estimated and discussed from the room temperature optical transmittance spectra.
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