Physical Properties of Spray Pyrolysed CdS Thin Films

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Abstract

Cadmium sulphide (CdS) thin films were prepared by chemical spray-pyrolysis technique. Cleaned glass substrates were used. The substrate temperature was varied in the range 200 – 400 °C and seems to be one of the more important parameters affecting the physical properties of the semiconductor. The films were characterized by X-ray diffraction (XRD). XRD patterns indicated the presence of single-phase hexagonal CdS. The resistivity of the as-deposited films was found to vary in the range $10^3 – 10^5 \, \Omega \cdot \text{cm}$, depending on the substrate temperature. Direct band gap values of 2.39–2.42 eV were obtained from optical absorption measurements.

Key Words: CdS thin films; Spray pyrolysis; Structural characteristics; Electrical and optical properties.

1. Introduction

CdS thin films are regarded as one of the most promising materials for heterojunction thin film solar cells. Wide band CdS ($E_g = 2.4 \, \text{eV}$) has been used as the window material together with several semiconductors such as CdTe [1], Cu$_2$S [2], InP [3] and CuInSe$_2$[4] with 14–16% efficiency [5]. However due to the high cost of such a material, studies were developed towards polycrystalline compound semiconductors and particularly thin polycrystalline films. The deposition of CdS films has been explored by different techniques: thermal evaporation [6, 7], chemical bath deposition (CBD) [8], molecular beam epitaxy (MBE) [9], and spray pyrolysis [10]. Spray pyrolysis though is expensive, requires the use of sophisticated materials and overall, is not very impressive, now gives good quality semiconductors which allows fabrication of solar cells with satisfactory efficiency.

The aim of this work is to produce CdS thin films by spray pyrolysis technique and to investigate their structural, electrical and optical properties.

2. Experimental Details

The spray pyrolysis technique is a simple technology in which an ionic solution—containing the constituent elements of a compound in the form of soluble salts—is sprayed onto over heated substrates using a stream of clean, dry air. The apparatus we used for our sprayed process is diagrammed in Figure 1, and has been described in references [11, 12]. The CdS thin films were prepared by spraying an aqueous solution of...
cadmium chloride (CdCl₂) and thiourea [(NH₂)₂CS] on glass substrate kept at 200, 300 and 400 °C. The atomization of the chemical solution into a spray of fine droplets is effected by the spray nozzle, with the help of compressed air as carrier gas. The spray rate was about 15 cm³/min through the nozzle ensures a uniform film thickness. The substrates are glass substrates 2.5 cm x 1.5 cm x 0.1 cm, and are placed in a fitted socket at the surface of a substrate heater when sprayed. The heater is a cylindrical stainless steel block furnace electrically controlled to an accuracy of ± 2 °C. The substrate temperature was varied, while the other spray parameters were kept constant. The film thickness was measured by a mechanical stylus method (via a Sloan Dektak, model 11A) with an experimental error of ± 3%.

Figure 1. Schematic diagram of the spraying apparatus.

The X-ray diffraction (XRD) patterns of the films were recorded with a JEOL 60 PA X-ray diffractometer operating with a 0.15418 nm monochromatized Cu kα radiation at 40 kV and 30 mA with Ni filter. The electrical resistivity of the prepared films was measured by the Van der Pauw four-probe method [13] with the required correction tables [14]. The potential difference, V, and current, I, were determined using a conventional d.c. technique and a Keithly 616 digital electrometer.

Transmission, T, and reflection, R, spectra of the prepared samples were measured by normal incidence of light, using a double beam UV-3101 PC Scanning Shimadzu spectrophotometer, in the wavelength range 400–1000 nm, using a blank substrate as the reference position. The absorption coefficient α of all investigated samples was deduced.

3. Results and Discussion

3.1. Structural characteristics

Diffractograms of films produced at different substrate temperatures (200, 300 and 400 °C) are shown in Figure 2. XRD analysis showed that the films have highly oriented crystallites with the classical hexagonal structure (wurtzite type) with a preferential orientation along the c-axis ((002) direction) perpendicular to...
Figure 2. X-ray diffractograms of sprayed CdS films with different substrate temperatures, 200, 300 and 400 °C. (t = 500 nm, spray rate = 15 cm³/min).

Figure 3. Effect of substrate temperature on: A) FWHM and B) grain size of CdS films. (t = 500 nm, spray rate = 15 cm³/min).
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the substrate plane. The degree of preferred orientation increased with the substrate temperature. Thus, raising the substrate temperature did not lead to the formation of other phases. In fact, the film prepared at the highest temperature, 400 °C, has a better crystalline quality, as indicated from its XRD spectra. The relative change of the full width at half maximum (FWHM) is shown in Figure 3a. Above 300 °C, a well-crystallized film was obtained. Phase identification revealed that only hexagonal CdS is formed. However, Battisha et al. [10], Laukaitis et al. [15], Mathew et al. [16] and Ashour et al. [17, 18], using spray pyrolysis and different techniques, obtained a single phase of hexagonal phase of CdS thin films. Thus, the preparation conditions of this technique affect the resulting of microstructural characteristics, such as crystallinity.

The effect of substrate temperature on the grain size (GS) of the obtained phase was also investigated. If the broadening is due only to the effect of crystallite size, grain size can be simply determined from the (002) diffraction line using the Scherrer formula [19]:

\[ GS = K\lambda /\beta \cos \theta, \]  

(1)

where \(\beta\) is the full width at half maximum (FWHM) of the peak corrected for instrumental broadening: \(\lambda\) is the wavelength of the X-rays, and \(K\) is the Scherrer constant, which generally depends on the crystallite shape. Considering that the Scherrer constant \(K\) is equal to unity according to the widespread practice, and that the effect of residual macrostrain is negligible, it is the relative rather than the absolute size data that will be considered. The grain size calculated by Scherrer’s formula from the XRD data is less than 40 nm. The small grain size, which is due to the evaporation of individual fine droplets during the sprayed process, is undesirable for most semiconductor applications because of the barrier effects of grain boundary on the mobility in planar direction [20]. The grain size was found to increase with increasing substrate temperature (see Figure 3b), which is the same behaviour reported in literature for both spray-pyrolysed [10] and vacuum-evaporated [17, 18] CdS thin films. These grain size are smaller than those obtained by Mahmoud et al. [7]. Thus, increasing the substrate temperature decreases the density of nucleation centres and, under these circumstances, a smaller number of centres start to grow, resulting in large grains.

### 3.2. Electrical properties

The resistivity was measured at room temperature for all the films. The variations in resistivity and thickness of the films deposited at 300 °C as a function of spray rate are shown in Figures 4a and 4b. The film thickness increases with increasing spray rate. This increase may be attributed to the structural characteristics of films. The resistivity decreases with the increase in film thickness. This is due to an improvement of the crystallinity and grain size [16] of the CdS with less stacking faults [5].

Figures 5a and 5b show the variations in resistivity and thickness with substrate temperature, \(T_S\), at a fixed spray rate of 15 cm\(^3\)/min. The decrease in film thickness is attributed to a decrease in the deposition rate of initial constituent with increasing substrate temperature [16, 19, 20].

All films exhibited semiconducting behaviours with the resistivity range of \(10^3 – 10^5\) Ω·cm. The resistivity of the films was found to decrease as the substrate temperature increases. This decrease may be attributed to the growth of the grain size and the improvement in film stoichiometry as indicated by the XRD pattern in Figure 2. This is in accordance with Mathew et al. [16] who suggested that higher substrate temperatures lead to larger grain size and a smooth surface. The order of resistivity in the present work is in the range of \(10^3 – 10^5\) Ω·cm, which is suitable for solar cells. These results of resistivity are quite similar to those obtained by Su and Choy [5], Duchemin et al. [21] and Ashour et al. [6], on sprayed and vacuum evaporated films by a modified source.
Figure 4. Effect of spray rate on: A) resistivity and B) film thickness of CdS films. (spray rate = 15 cm³/min).

Figure 5. Effect of substrate temperature on: A) resistivity and B) film thickness of CdS films. (spray rate = 15 cm³/min).
3.3. Optical properties

The optical properties of the spray pyrolysed CdS films are similar to those produced by using other methods. In Figure 6, the variation of optical transmission as a function of wavelength for the films prepared at different substrate temperatures. The films fabricated at low temperatures have a low transmission, and those prepared at higher temperatures have a higher transmission. It can be observed that in general, an increase in substrate temperature improved the transmission. This improvement can be attributed to either the decrease in thickness or the improvement in perfection and stoichiometry of the films [11].

![Figure 6](image)

**Figure 6.** Transmittance vs. wavelength for CdS films sprayed at various substrate temperatures. (t = 500 nm, spray rate = 15 cm³/min).

The semiconductor band gap $E_g$ was determined by analysing the optical data with the expression for the optical absorbance $\alpha$ and the photon energy $\hbar \nu$ [11] using the relation

$$\alpha = k(\hbar \nu - E_g)^{n/2} / \hbar \nu$$  \hspace{1cm} (2)

where $k$ is a constant, and $n$ is a constant which is equal to one for a direct-gap material, and four for an indirect-gap material. As shown in Figure 7, the plot of $(\alpha \hbar \nu)^2$ versus $\hbar \nu$ was analysed using the above equation. Extrapolation of the linear portion of the plot to the energy axis yielded the direct band gap value, 2.39–2.42 eV, which is in agreement with the reported value by others [5, 6, 22].

![Figure 7](image)

**Figure 7.** Variation of $(\alpha \hbar \nu)^2$ with photon energy for films sprayed at various substrate temperatures. (t = 500 nm, spray rate = 15 cm³/min).
4. Conclusion

CdS films were fabricated by a spray pyrolysis technique using a solution of cadmium chloride and thiourea. The films were deposited onto glass substrates at the selected temperatures of 200, 300 and 400 °C. Substrate temperatures during deposition were found to have influenced the phase and preferred orientation of the films. The film prepared at the lowest temperature was found to have the least quality crystallinity and, as the temperature increased; so did the quality of the crystallinity. It was also noticed that film thickness decreased with increased substrate temperature. Films produced at the highest temperature were found to have a lower resistivity to those produced at the lower temperatures. The films have good optical quality properties larger grain size and are well-suited for solar cell applications. The electrical resistivity was found to be in the range $10^3 - 10^5 \Omega \cdot \text{cm}$, varying with substrate temperature. The films exhibited a direct transition in the range 2.39–2.42 eV. These results suggest that the method of spray pyrolysis for the deposition of CdS thin films should be further investigated for application towards the fabrication of solar cells.

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