Growth impedance of pure CdS films

L I Soliman, H H Afify & I K Battisha

Solid State Physics Department, National Research Centre, Dokki, Cairo, Egypt

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The effect of Al, Fe and Cu incorporated CdS pure thin films prepared by spray pyrolysis process has been given. It was found that the increase of the element concentration leads to a significant change in pure CdS physical properties. The films have a polycrystalline hexagonal structure as shown from their X-ray diffraction pattern (XRD). The crystallinity of pure CdS film is reasonably decreased by the addition of Al, Fe and Cu. The grain size of the pure CdS films decrease by incorporation of Fe, Al and Cu as revealed by atomic force microscopy (AFM). The roughness of all samples was calculated. The optical constants of the prepared samples were determined. The calculated energy band gap of pure CdS films decreases by increasing Cu contents, while it does not get effected by Al contents.

Keywords: CdS films, Growth impedance, Polycrystalline hexagonal structure, Spray pyrolysis process, Optical constants

1 Introduction

Thin films of pure and doped CdS had been extensively studied\(^\text{15}\). It is found that, the physical properties depend on the preparation technique. The effect of addition of different elements on pure CdS thin films is yet to be studied\(^\text{6-11}\). In this work the morphological, structure and optical properties of polycrystalline CdS films were investigated as a function of Al, Cu and Fe concentrations. This study aims to clarify at to what extent the incorporated element affects the properties of the pure CdS films. The structure and the optical properties of the prepared samples have been examined to explain the range of the expected effect.

2 Experimental Details

The pure CdS thin films and CdS films incorporated with Al or Fe or Cu were prepared by spray pyrolysis technique at constant substrate temperature of 500°C and deposition time of 30 min. using a home made spray system\(^\text{11}\). The spray solution was a mixture of an aqueous solution of 0.1M of CdCl\(_2\) and thiourea with ratio 1: 1. To find out the effect of incorporated elements, 0.1M of an aqueous solution of AlCl\(_3\) or CuCl\(_2\) or FeCl\(_3\) is added to the mother solution with different volumes. It is observed that the most probable percentage of CdCl\(_2\) added to the mother solution of CdCl\(_2\) and thiourea is 10% to have a clear one. The samples were prepared with the following spray parameters, substrate temperature 500°C, deposition time 30 min, air flow rate 7 l/min and solution flow rate 1 ml/min.

The characterization of the prepared samples by AFM, XRD and double beam spectroscopy has been performed in National Renewable Energy Laboratory (NREL) USA. The AFM analysis was performed using a park scientific Auto probe LS instrument in contact mode using silicon cantilevers. The Auto probe LS uses a cantilever with an attached tip as the analytical probe\(^\text{10}\). The root mean square roughness \(R_m\) data for the investigated samples are determined from the AFM measurements. The X-ray diffraction (XRD) patterns of the prepared samples were recorded with Scintag model X1 diffractometer. X-ray tube (Cu target) was operated\(^\text{12}\) at 40 kV and 25 mA and the diffraction patterns were recorded automatically with a scanning speed of 2 degrees/min. Wide angle 20 scans from 4 to 90 degree were used to identify the phases present in the sample while diffraction scans at 1/8 degree per minute performed for individual peaks to determine the relative crystallite size of the prepared films. To calculate the crystallite size the Scherrer formula was used; \(G = \lambda/D \cos\theta\) where \(G\) is the crystallite size, \(\lambda\) is the...
wavelength of the X-rays (1.5418), $D$ is the width of the peak at half maximum and $\theta$ is the angle of incidence of X-ray beam$^{13}$.

Transmittance and reflectance spectra were done by Cary 2300 spectrophotometer in wavelength range (0.2-2.5 μm). The refractive index $n$, absorption and extinction coefficients ($\alpha$ and $K$) for all investigated samples have been calculated. The film thickness was calculated from the envelope of the transmittance spectra, which have maximal and minima extreme due to interference; also it was measured by using the tally-step instrument with an experimental error ± 3.5%, in the National Institute of Standard.

3 Results and Discussion

3.1 Microstructure properties

To investigate the surface morphology of the investigated samples and to obtain quantitative information about the surface roughness and AFM measurements are performed. As deposited CdS films (prepared at 500 °C and constant deposition time 30 min) were exhibited a very fine grain structure with some amorphous characteristic and tendency to preferred orientation. The three-dimensional surface morphology image of pure CdS thin films is shown in Fig. 1. It is clear that, the film showed a continuous grain structure this result is in agreement with Moutinho et al.$^{14}$.

The microstructure of CdS films incorporated with different Al concentrations (2%, 4%, 6% and 16%) were measured. The AFM image of CdS films incorporated with 6% Al is shown in Fig. 2(a) as a representative example of the doping material contents. It is observed that, the samples incorporated with 6 and 16% Al showed a change in the microstructure with more rounded grains. Also, these images show that, the grain size decreases with increasing the Al concentration. The three dimension surface morphology of CdS films incorporated with 8% Al is represented in Fig. 2(b). It is found that the film showed a continuous grain structure.

The AFM images of CdS films incorporated with different Cu concentrations (10%, 8%, 4% and 2%) were measured. Fig. 3(a) showed the AFM image of CdS films incorporated with 10% Cu as a representative example of the doping material contents. In these images we observed that, the grains are formed by a nanograins structures. The existence of this nanograin structure is very important as the transport properties of these films are usually limited by recombination of the minority carriers at grain boundaries. It is found from these images that the grain size decreases with increasing Cu concentration. The three-dimensional surface morphology of CdS thin film incorporated with 6% Cu is represented in Fig. 3(b). This image showed a continuous structure.

The AFM image of CdS film incorporated with 10% and 2% iron were measured. Fig. 4 represented the AFM image of CdS films incorporated with 2% Fe as a representative example. From these images it is clear that, the grains are formed by nanograin

Fig. 1 — AFM three-dimensional surface morphology image of pure CdS thin films

Fig. 2 — AFM image of CdS incorporated with 6% Al (a) and (b) represents the AFM three-dimensional surface morphology of sample (8%).

is clear that, the grains are formed by nanograin
structure. Also, the three-dimensional surface morphology image of CdS films incorporated with 6% Fe showed a continuous structure as shown in Fig. 4(b). It is found that the grain size decreases by increasing the doping concentrations for all samples. Table 1 summarized the roughness of pure and incorporated CdS films with different concentration of Al, Cu and Fe.

From the study of all pure and doped films we can conclude that the pure CdS films were uniform and had well defined grains. The doped films with different Al, Cu and Fe content did not change the morphology of the films but promoted the appearance of small grains distributed mainly at the grain boundaries. This clearly represented in the case of the CdS films doped with 10% Cu as shown in Fig. 3(a).

3.2 XRD analysis

The X-ray diffraction patterns of pure and incorporated CdS thin films with Al, Cu and Fe (10 %) are shown in Fig. 5. The characteristic peaks (101), (110) and (112) for pure CdS are clearly appeared. The addition of foreign elements (Al, Cu and Fe) did not change the peaks position but enhance the appearance of other CdS peaks (002) and (100) as well as a change in peak intensity and FWHM. Also no characteristic peaks corresponding to each incorporated element or its sulphides or oxides are detected in the XRD patterns. The crystallinity of pure CdS film is highly distorted by the addition of Al or Fe or Cu. The peaks height goes to its lower values as the concentration of the added elements increases especially in case of aluminum. In contrast the peak broadening increases as the concentration of the incorporated elements increases. These two peaks features reflect the decrease in crystallinity and crystallite size. This result was confirmed by AFM results presented in Table 1.
The X-ray diffraction pattern of CdS thin films incorporated with 2%, 4%, 8%, and 10% and 16% Al element as a representative example of the incorporated materials is represented in Fig. 6. These patterns show the significant decrease in the principal peak (101) intensity with increasing the Al contents. Generally the degree of crystallinity for CdS samples incorporated with Al decreases gradually by increasing the Al concentration, this could be attributed to the adsorption of the incorporated atom on the surface of the growing CdS microcrystal and impeding growth along or perpendicular to the substrate. The Al incorporated element may impede the growth of nuclei of CdS crystallites which cause the formation of small crystallites. The observed induced change in the peaks height as well as the broadening could be attributed to the change in the scattering factor corresponding to Al incorporated element and als to the decrease in the crystallite size.

3.3 Optical properties

The optical energy band gap $E_g$ is related to the absorption coefficient $\alpha$ in accordance with the equation

$$\alpha \cdot h\nu = A \cdot (h\nu - E_g)^p$$

where $t$ is the film thickness.

The transmittance ($T$) and reflectance ($R$) using the following relation:

$$T = (1-R)^2 \exp (-\alpha t)/[1 - R^2 \exp (-2\alpha t)]$$

Table 1 — Roughness of the pure CdS thin films and incorporated with different Al, Cu and Fe contents

<table>
<thead>
<tr>
<th>Doping samples %</th>
<th>Al</th>
<th>Cu</th>
<th>Fe</th>
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<tr>
<td>0</td>
<td>167</td>
<td>167</td>
<td>167</td>
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<tr>
<td>2</td>
<td>176</td>
<td>58</td>
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<td>64</td>
<td>173</td>
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<tr>
<td>6</td>
<td>62</td>
<td>173</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>42</td>
<td>292</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>356</td>
<td>167</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6 — XRD patterns of (a) pure CdS film and incorporated with different Al concentrations ranging from 2 up to 16% (b-h)

Fig. 7 — Transmittance ($T$) and reflectance ($R$) of pure CdS film and incorporated with different Al contents.
where $A$ is a constant, $h$ the Planck's constant and $P$ is a constant that depends on the type of the electronic transitions. For allowed direct transition $P$ is equal to $1/2$, $3/2$ for forbidden direct transition, $2$ for indirect allowed transition and $3$ for indirect forbidden transitions. It is well known that, CdS is a direct band gap semiconductor; therefore the optical band gap is obtained by plotting $(\alpha h\nu)^2$ as a function of photon energy $(h\nu)$. Typical plots of $(\alpha h\nu)^2$ as a function of $(h\nu)$ for pure and incorporated CdS thin film with different Al concentrations is shown in Fig. 8a. Also Fig. 8b represents the plotting of $(\alpha h\nu)^2$ as a function of $(h\nu)$ for CdS incorporated with different Cu contents. The intercept of the extrapolation to zero absorption with photon energy axis gives the values of the direct energy gap $E_g$. It is clear from these intercepts that the direct energy gap decreases by increasing the Cu doping, while does not affected by Al incorporation, as seen from Fig. 8 (a and b) and Table 1. The decrease of the direct energy gaps by increasing Cu contents is probably due to the reduction of Cu vacancies in these films.

The refractive index $n$ and the extinction coefficient $K$ of pure and incorporated CdS films with different Al concentrations as a representative example of the incorporated materials were determined from the reflection $R$ at normal incidence and the absorption coefficient $\alpha$ measurements using the following equation:

$$\alpha = 4\pi K/\lambda \text{ and } R = [(n-1)^2 + K] / [(n+1)^2 + K]$$

The variation of optical constant $n$ and $K$ with photon energy for pure and incorporated CdS films with different Al concentrations were shown in Fig. 9 (a and b) as a representative example of the incorporated materials. From Fig. 9(a), it is clear that, the $n$ values slightly decrease with increasing the photon energy beyond the absorption edge. The extinction coefficient $K$ increases with increasing the Al contents as shown in Fig 9(b). This behaviour may be due to the change in the crystallite size of these films.

4 Conclusion

CdS thin films were prepared by home made spray pyrolysis system. The AFM analysis revealed the crystallite size of pure and incorporated CdS film with different concentration of Al, Cu and Fe decreases by increasing the doping concentration indicating the formation of nanostructure phase in CdS thin films. The roughness of the investigated samples was determined. Al, Cu and Fe incorporated
CdS thin films have polycrystalline hexagonal structure. The crystallinity of pure CdS film is highly decreased by the addition of incorporated elements, which is clearer with Al incorporation. Also no characteristic peaks corresponding to each incorporated element or its sulphides or oxides are detected in the XRD patterns.

The transmission and reflection were measured at room temperature at the wavelength range from 0.2 up to 2.5 µm. The analysis of the optical absorption spectra revealed the existence of direct transition. The optical energy gap of CdS films decreases by Cu incorporation because of Cu deficiency while, it does not get affected by Al incorporation.

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References