Investigation of structural properties of CdS thin films grown by chemical bath deposition technique

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Abstract

Using chemical path technique, thin films of CdS have been prepared with two different thicknesses on a glass substrate. An attempt to relating structure properties of cadmium sulphide (CdS) thin film with variation of thickness was reported. X-ray diffraction (XRD) was used to characterize the samples. One peak of (111) orientation is appeared in X-ray chart indicating the cubic phase of the films .The lattice parameter, grain size, average internal stress, microstrain and dislocation density are calculated and correlated with changing the thickness of the films. .

Introduction

The films formed by wide gap II-VI semiconductors are of considerable interest, as their emissions cover the technologically attractive blue and green spectral region. In particular, thin CdS films deserve attention because their expected gap emission lies very close to the highest sensitivity of the human eye.**[1]** CdS is a technologically useful material, as many devices based on CdS, including sensors have come up in the recent years. The thin film cadmium sulphide solar cell has for several years been considered to be a promising alternative to the more widely used silicon devices.**[2]** A survey of the literature shows that different techniques of deposition have been developed to obtain device grade CdS thin films, and among which electrodeposition, rf sputtering, spray pyrolysis, screen printing and thermal evaporation are worth mentioning.**[3]** In several deposit techniques that have been using to prepare CdS films in various morphologies and structures, chemical bath deposition (CBD) is one of most promising and has proved advantageous for photovoltaic applications, because it is most ease to do efficiently, cost effective and its suitability for large area high quality thin films. In this work, I tried to investigate the action of changing the thickness of the films on structure properties of CdS films.

Experimental details

The deposition process of CdS thin films were done on commercial glass slides with 1mm thick and $2.5 * 7.5\ cm^2$ size. Before the deposition they were cleaned by detergent solution then washed by deionised water and finally they were cleaned by using ethanol solution. Every two samples should be put with their back sides facing each other so as to insure that the growth of the film well be done on one side of each glass substrates. The deposition arrangement consisted of a water bath on a hot plate. I used a 250 ml borosilicate glass flat bottom baker for the process. The aqueous solutions of the reaction were 0.1 M cadmium chloride, $CdCl_2$, 1 M thiourea, $CS(NH_2)_2$, 0.7 M ammonium chloride, NH_4Cl, and 2 M ammonium hydroxide, NH_4OH. 50 ml of NH_4Cl and 50 ml of NH_4OH were dispensed into the baker and 50 ml of $CdCl_2$ was added in drops to prevent $Cd(OH)_2$ formation in the solution. Substrates were placed vertically into the baker and heated in the water bath to 85 °C. 50 ml solution $CS(NH_2)_2$ was slowly dropped into the preheated solution in the baker. The deposition process time was 120 minute. Samples deposited for one time were 200 nm thick while samples deposited for two times were 300 nm thick.

Results and discussion

XRD was used to characterize the structural properties of CdS thin films. These thin films which were obtained by Chemical bath deposition (CBD) possess cubic structure. It is confirmed by comparing the peak positions (2θ) of the XRD patterns of the films with the standard X-ray powder diffraction data file (card no. 42-1411). Figure (1) represents the XRD patterns of CdS thin film with two thickness 200nm and 300 nm. All films show the most preferred plane [111] reflection . No other peak beside these is observed which establishes the single phase cubic structure of the films. This result corresponding to a result which was obtained by Abdullah who used (CBD) method to prepared CdS thin films. **[4]**

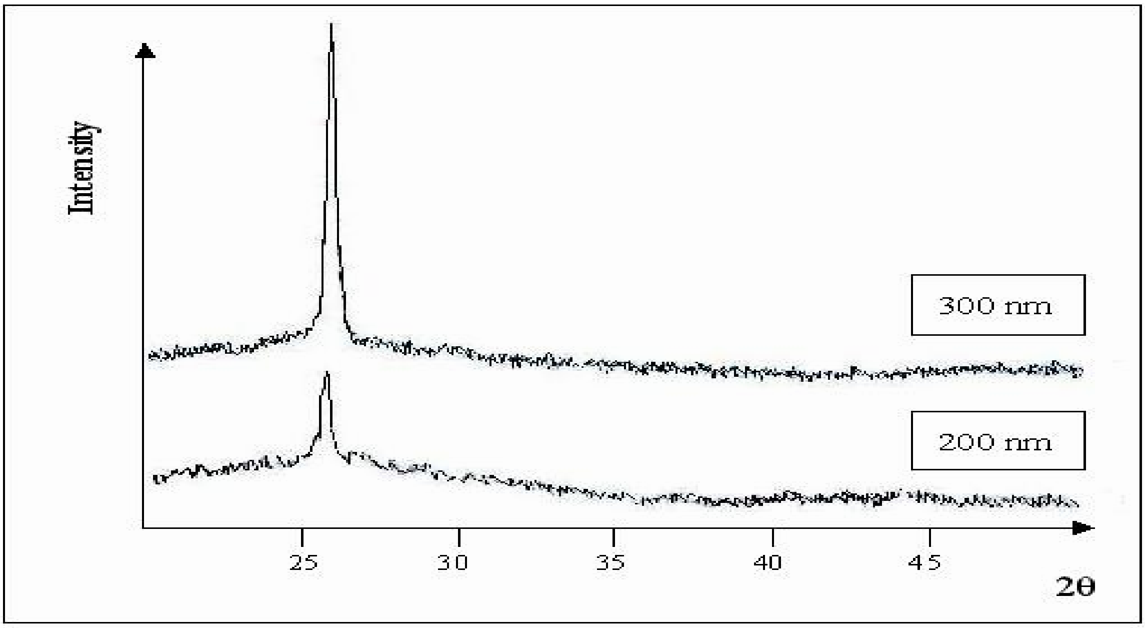

Figure (1) XRD pattern of CdS films.

With increasing thickness, it is seen that the peaks become narrower, the full width at half maximum (FWHM) decreases from 0.4364^0 to 0.335^0 , and these peaks are shifted to higher diffraction angle from 26.74^0 to 26.80^0.The various structural parameters for CdS thin films are calculated using the relevant formulas and are systematically represented in Table 1.The lattice constant `*a*' for the cubic phase structure is determined by the relation**: [5]**

$$\mathbf{a = d^*(h^2+k^2+l^2)^{1/2}}$$

where'd' is the distance between atomic planes, which is calculated by using bragg law, as it is clear in Table 1 'a' decreases for thicker film. The lattice contraction occurs because of higher surface to volume ratio. **[6]** One very important use of XRD when dealing with nanocrystals is to estimate crystal dimensions through the Scherrer relationship: **[7]**

$$\mathbf{t = 0.9\ \lambda / B \cos\theta}$$

where **λ** is the X-ray wavelength (0.154056 nm), **B** is (FWHM) in radians of peaks, and **θ** is the peak position. Actually, to be more precise, what is measured is not necessarily crystal size but coherence length, the length over which the periodicity of the crystal is complete. It's value before and after increases the thickness are (18.7123 and 24.3793 nm) respectively for (111) plane.

Other causes for XRD peaks being broader than expected based on crystal size is the presence of strain in the crystals or other defects, such as dislocations, which destroy the long-range lattice order. The microstrain (ε) developed in the CdS film is calculated from the relation: **[8]**

$$\varepsilon = (B\cos\theta)/4$$

The change in lattice constant ‘as seen above’ for thicker thin film suggests that the film grains are *strained* and that may be owing to the change of nature and concentration of the native imperfections. As shown in Table (1), the microstrain decreases from **(0.001852)** to **(0.00142)** after increasing film's thickness.

There is a close correlation between microstrain decreasing and crystallite size increasing , because both phenomena lead to the phase crystallinity changing.**[9]** Due to the increase in crystallite size with increasing film's thickness, the defects in the lattice is reduced, which in turn, reduces the microstrain.**[10]**

A dislocation is an imperfection in a crystal associated with the misregistry of the lattice in one part of the crystal with that in another part. Dislocation density is defined as the length of dislocation line per unit volume of the crystal. **[11]**

Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections, i.e. thermodynamic considerations are insufficient to account for their existence in the observed densities. In fact, the growth mechanism involving dislocation is a matter of importance. In the present study, the dislocation density (ρ) is estimated from Williamson and Smallman method using the relation **[8]**

$$\rho = 15\,\varepsilon / a\,t$$

for cubic CdS thin films. Dislocation density (ρ) decreases from **2.5×10^{13}** $(\mathrm{cm})^{-2}$ to **1.51×10^{13}** $(\mathrm{cm})^{-2}$ with increasing the thickness of the films.

Table 1. Structural parameters of CdS thin films with 200 and 300 nm thickness.

<table>
<tr><th rowspan="2">Oriantation</th><th colspan="2">2θ[deg.]</th><th colspan="2">Grain Size (nm)</th><th colspan="2">d (nm)</th><th colspan="2">(a) (nm) calculated</th><th rowspan="2">(a) (nm) ASTM</th></tr>
<tr><th>(200nm)</th><th>(300nm)</th><th>(200nm)</th><th>(300nm)</th><th>(200nm)</th><th>(300nm)</th><th>(200nm)</th><th>(300nm)</th></tr>
<tr><td rowspan="4">[111]</td><td>26.7454</td><td>26.8056</td><td>18.7123</td><td>24.3793</td><td>0.33305</td><td>0.3323</td><td>0.5768</td><td>0.57559</td><td>0.5818</td></tr>
<tr><td colspan="3">Microstrain</td><td colspan="3">Dislocation density (cm)⁻²</td><td colspan="3">Stress GPa</td></tr>
<tr><td colspan="2">(200nm)</td><td>(300nm)</td><td>(200nm)</td><td colspan="2">(300nm)</td><td>(200nm)</td><td colspan="2">(300nm)</td></tr>
<tr><td colspan="2">0.001852</td><td>0.001421</td><td>2.5 x</td><td colspan="2">1.51 x 10¹³</td><td>0.0677</td><td colspan="2">0.085</td></tr>
</table>

			10^{13}			

The stress behavior of films is very important in all applications of thin films with respect to durability and hence use. The stress can be either tensile perpendicular to the interface or shearing parallel to the interface.**[12]** The shift of the diffraction peaks ' positions from its normal value - see Figure (1) - is mainly associated with residual stress in the film **[13]**. The total stress is composed of a thermal stress and an intrinsic stress. The thermal stress is due to the difference in the thermal expansion coefficients of the film and substrate material. The intrinsic stress is due to the accumulating effect of the crystallographic flaws that are built in the film during deposition. The average internal stress developed in the films is determined by the relation **[14]**,

$$S = (Y/2\xi)\ (a_0 - a)/a_0$$

Here **Y (42 G pa)** and **ξ (0.38)** are the Young's modulus and Poisson's ratio of CdS film respectively , **a_0 (0.5818 nm)** is the bulk lattice constant of CdS**. [15]** The estimated '*a*' refers to the lattice constant perpendicular to the film plane.

S = 0.0677GPa. for thinner film and **S =0.085GPa.** for thicker one .The average internal stress for all films is found to be tensile in nature. For thin films, the free-surface to volume ratio is high, and the pinning of dislocation by the free surface leads to the high tensile strengths often measured in thin films of materials.**[16]**

Conclusions

XRD peaks show that all films show the most preferred plane [111] reflection. The shift of the diffraction peaks' positions from its normal value is mainly associated with residual stress in the film which was found to be tensile in nature for all films. The XRD peaks are narrower for thicker film due to increase grain sizes and decrease microstrain and dislocation density inside the films.

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دراسة الخواص التركيبية لأغشية كبريتيد الكادميوم الرقيقة المحضرة بطريقة الحمام الكيميائي الحراري

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الخلاصة

باستخدام تقنية الحمام الكيميائي الحراري تم تحضير أغشية كبريتيد الكادميوم الرقيقة على قواعد من الزجاج وبسمكين مختلفين، وباستخدام حيود الأشعة السينية تم دراسة تأثير تغيير السمك على الخواص التركيبية للأغشية. ظهور القمة (١١١) في بطاقة الأشعة السينية دل على التركيب التكعيبي للأغشية. ثابت الشبيكة ،الحجم الحبيبي ، معدل الإجهاد الداخلي ، المطاوعة المجهرية وكثافة الانخلاعات حسبت وربطت بتغيير السمك للأغشية.