Effects of multi- Deposition on the structural and optical properties of CdS nanocrystalline thin film prepared by CBD technique

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Abstract

Cadmium sulfide (CdS) nanocrystalline thin films have been prepared by chemical bath deposition (CBD) technique on commercial glass substrates at 70ºC temperature. Cadmium chloride ($CdCl_2$) as a source of cadmium (Cd), thiourea ($CS(NH_2)_2$) as a source of sulfur and ammonia solution (NH_4OH) were added to maintain the pH value of the solution at 10. The characterization of thin films was carried out through the structural and optical properties by X-ray diffraction (XRD) and UV-VIS spectroscopy. A UV-VIS optical spectroscopy study was carried out to determine the band gap of the nanocrystalline CdS thin film and it showed a blue shift with respect to the bulk value (from 3.9 - 2.4eV). In present work effects of thickness on the structural and optical properties of CdS nanocrystalline thin films were discussed.

Key words

Nanocrystalline thin films, optical properties, chemical bath deposition.

Article info

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تأثير عدد مرات الترسيب على الخصائص التركيبية والبصرية لغشاء كبريتيد الكادميوم (CdS) النانوي المحضر بتقنية ترسيب الحوض الكيميائي

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الخلاصة

تم تحضير غشاء كبريتيد الكادميوم ذو التركيب النانوي بتقنية ترسيب الحوض الكيميائي على أرضيات زجاجية وعند درجة حرارة 70 سيليزية ، وباستخدام كلوريد الكادميوم كمصدر لايونات الكادميوم والثايوريا كمصدر لايونات الكبريت وتم إضافة هيدروكسيد الامونيا للحصول على قيمة للأس الهيدروجيني (PH=10). خصائص الغشاء تم دراستها من خلال دراسة الخصائص التركيبية والبصرية باستخدام جهاز حيود الأشعة السينية وجهاز دراسة الطيف البصري للمنطقة الطيفية المرئية وفوق البنفسجية حيث تم تحديد قيمة فجوة الطاقة البصرية للغشاء النانوي ووجد إنها تقل في قيمتها لتصل قيمة فجوة الطاقة البصرية للحالة المحسوسة (3.9-2.4) إلكترون فولت. في هذا البحث تم دراسة تأثير السمك على الخصائص التركيبية والبصرية لغشاء كبريتيد الكادميوم النانوي.

Introduction

The II-VI binary semiconducting compounds, belonging to the cadmium chalcogenide family (CdS, CdSe, CdTe) are considered very important due to their potential use in photoconductive devices and solar cells [1,2,3]. Thickness is one of the most important parameter to be characterized, since it plays an important role in the film properties unlike a bulk material. Microelectronic applications generally require the maintenance of precise and reproducible film metrology (i.e., thickness as well as lateral dimensions) [4]. Thin film CdS has an energy band gap 2.42 eV at room temperature [5,6]. One of the most important properties of this semiconductor material to be considered for this application is its energy band gap (E_g). The value of E_g defines the fundamental light absorption edge and thus the range of the visible light spectrum which can be used to be converted in electricity by a solar cell [7]. The deposition of CdS film has been explored by various techniques, such as thermal evaporation, sputtering, molecular beam epitaxy, spray pyrolysis, chemical bath deposition (CBD) [8]. Chemical bath deposition process is a relatively simple method and has attracted a lot of attention on account of the low cost and the possibility of forming films having large areas. CdS thin films of good quality, adherence and reproducible properties have been grown by the CBD technique. The CdS thin films prepared by this technique are found to be either in the metastable cubic phase or a mixture of cubic and hexagonal phases [9]. Regardless on the deposition technique, the post deposited films characterization and deposition processes optimization is still an open subject. A large number of studies are carried in order to produce CdS thin films with good optoelectronic properties suitable for photovoltaic applications. For this purpose several properties are required for the CdS thin films: (i) relatively high transparency and not too thick to avoid absorption in the buffer layer and favors the absorption in the CIS layer (ii), not too thin to avoid the short circuiting (iii) relatively large conductivity to reduce the electrical solar cells losses and higher photoconductivity to not alter the solar cell spectral response [10]. The main goal of this work is to study the effects of film thickness on the structural and optical properties of CdS thin films.

Experimental details

Microscope glass slides with the size of (1×25×75 mm) were used as substrates. Before deposition, the substrates were degreased with chromic acid solution, washed with de-ionized water and finally dried in air. Aqueous solutions of 20 ml each of 0.1 M solutions of $CdCl_2$ (cadmium chloride) as a source of cadmium, $CS(NH_2)_2$ (thiourea) as a source of sulfur were used. First, 20 ml of $CdCl_2$ solution placed in a 60 ml beaker and NH_4OH was added drop by drop in $CdCl_2$ solution under vigorous stirring to maintain the pH value of the solution at 10 and a colorless solution was obtained. After stirring for several minutes, the solution became clear and homogenous. Then under continuous stirring, 20ml thiourea solution was introduced. The beaker contain mixture solution was placed in chemical bath whose temperature were kept at 70±2 ^{o}C during the growth. Once this temperature was reached, the glass slide was immersed in the solution. The reaction solution was no stirred during the deposition process. Deposition time was 60 minute, during which the solution color changed to yellow and finally to orange and precipitation occurs. After deposition, the sample were removed from the bath and washed in distilled water and finally dried in air. Thinner film, prepared by mono-deposition, were not thick enough (less than 100 nm) for solar cells applications. Films of different thickness were obtained by repeating the deposition procedure several times. The CdS films obtained were homogeneous as testing by optical microscope, hard, and had very good adhesion to the glass substrate. The complexing agent to form a cadmium complex, which slowly released Cd^{2+} ions for subsequent reaction with S^{2-} ions, was ammonia. Ammonia chloride of 0.1M was used as the buffer solution. The variation reactions involved and their equilibrium constants at room temperature are as follows [11].

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \; K_1 = 1.8 \times 10^{-5}$ (1)

The source of Cd^{2+}:

$CdCl_2 \leftrightarrow Cd^{2+} + Cl_2^{2-}$ (2)

$Cd^{2+} + 2OH^- \Leftrightarrow Cd(OH)_2 \; K_2 = 1.88 \times 10^{14}$ (3)

Cd^{2+} and NH3 form a complex species of cadmium $(Cd(NH3)4)^{2+}$ (to slowly release Cd^{2+}):

$Cd^{2+} + 4NH_3 \Leftrightarrow Cd(NH_3)_4^{2+} \; K_3 = 3.6 \times 10^6$ (4)

$(NH_2)_2CS + 2OH^- \Leftrightarrow S^{2-} + 2H_2O + C(NH)_2$ (5)

$Cd^{2+} + S^{2-} \Leftrightarrow CdS \quad K_4 = 7.1 \times 10^{28}$ (6)

In the presence of sufficient NH_3, the Cd salt exists predominantly in the form of $Cd(NH_3)_4^{2+}$. The room temperature equilibrium constant of reaction 5 is very small. When the concentration product of Cd^{2+} and S^{2-} in solution exceeds the solubility product of CdS, 1.4×10^{-29} at 25ºC, CdS precipitates.

Characterization techniques

The films were structurally characterized by X-ray diffraction (XRD) using a SHMADZU X-ray diffractometer in the range 0° to 60°. Optical properties of Cadmium sulfide films were measured at room temperature with UV-VIS spectrophotometer in the range of wavelengths 300-1100 nm.

Results and discussion

1. Structural characteristics of the films

CdS thin films, which were deposited on glass, can have either a hexagonal or a cubic structure or, a mixture of them, depending on the preparation conditions [12]. The hexagonal structure is the stable phase of CdS at room temperature. All the films prepared by this method are smooth, uniform and adherent to substrate surface. Fig. 1 shows the X-ray diffraction patterns of the three CdS thin films deposited on glass substrate. For one deposition, XRD observation show that a small but broad peak appears at an angle $2\theta = 26.779º$. which correspond to (111) cubic planes. When we repeating the deposition procedure for the resulting film in the first stage, it is clear from the figure 1(b and c) of XRD, that the peak intensity in the diffraction patterns increases as the film thickness increase, this indicating an the degree of crystallinity of the film increases. The prominent peaks for both films (b,c) appear at $2\theta = 26.7$ º, 44.2 º, 52.3º belong to (111), (220), and (311) cubic CdS, respectively. It can be seen from Table 1that the increases thickness of the CdS film causes an increase of grain size. The effects of annealing on the structure of CdS thin film for 1 hr. at 400 °C are shown in Figure 2. Heat treatment helps the atoms to rearrange themselves and eliminate defect density in the film resulting in good crystallinity. Also the diffraction peak of annealing film becomes sharper due to the coarsening of grains. From (111) peaks of the XRD patterns it is possible to evaluate the average grain size of the samples by using the Well-known Deby-scherrer formula [13,14]:

$D_{hkl} = k \lambda / \beta \cos\theta$

where k =0.94, λ is the wavelength of X-ray, β is the full width at half the peak maximum in radians and θ is Bragg's angle.

Table 1: The varying of grain size with different thicknesses.

Slide No.	Vol. of ($CdCl_2$) (ml)	Vol. of $CS(NH_2)_2$ (ml)	Temperature (^oC)	PH	E_g (ev)	Thickness (nm)	Grain Size (nm)
1	20	20	70±2	10	3.9	145.68	5
2	20	20	70±2	10	3.55	218.53	11
3	20	20	70±2	10	2.4	255.16	14

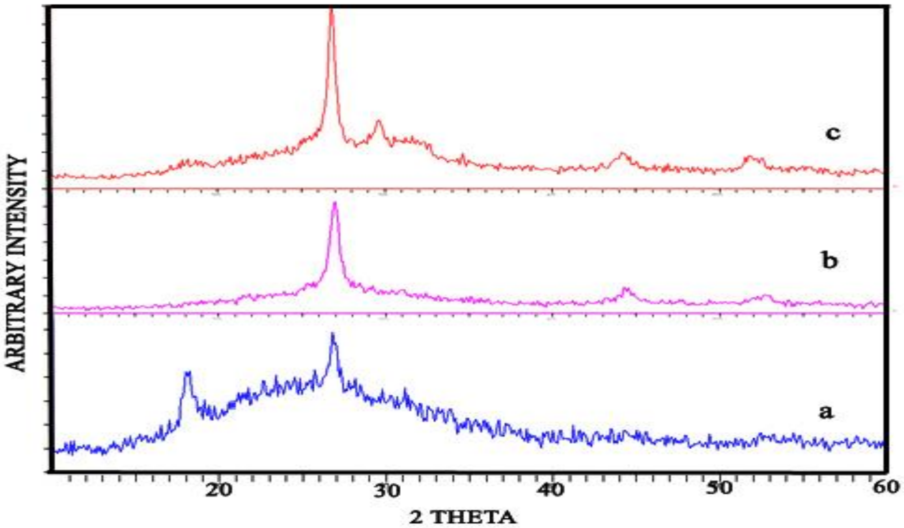

Fig. 1: X-ray diffraction patterns of the three CdS thin films deposited on glass substrate. (a) one deposition (b) double deposition (c) triple deposition.

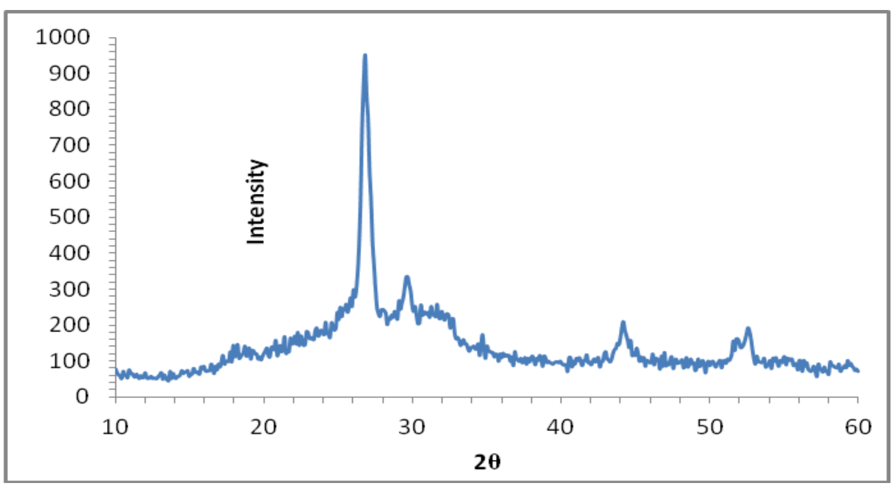

Fig. 2: X-ray diffraction pattern of annealed film obtain after three deposition at 400 ºC.

2. Optical properties of CdS thin films

Transmission spectra of films were recorded as a function of wavelength. In semiconductors, the relation connecting the absorption coefficient α, the incident photon energy (hν) and optical band gap E_g takes the form [15]:

$$(\alpha h\nu) = k(h\nu - E_g)^m$$

where k is a constant related to the effective masses associated with the bands and m=1/2 for allowed direct-gap material. To determine whether the CdS films deposited using CBD technique have direct or indirect band gap, The band gap of the films was determined by plotting a graph between $(\alpha h\nu)^2$ and (hν). The band gap energy (E_g) was estimated by a linear interpolation of each curve to energy axis [16]. Fig. 3 shows the variation optical energy gaps of the films as a function of the deposition number.

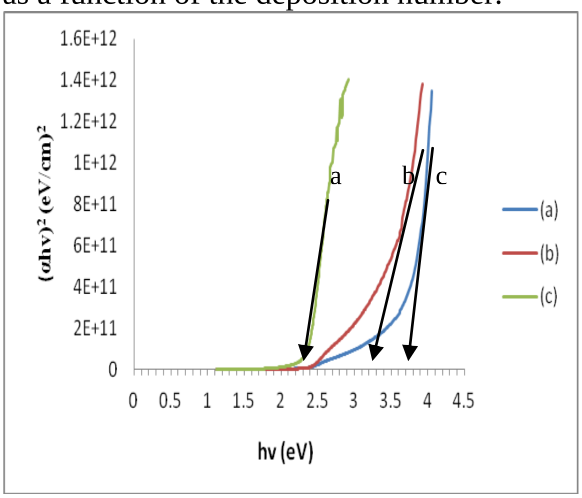

Fig. 3: Optical energy gaps of the films; (a) one deposition (b) double deposition and (c) triple deposition.

CdS thin films grown here have the energy gap in the range of 2.4 to 3.9 eV. The calculated optical band gap values of one and two deposition are somewhat larger than the typical value of the bulk CdS (2.4 eV), may be due to the quantum size effect as expected from the nanocrystalline nature of the CdS thin films. The increment in band gap is approximately inversely proportional to the square of the crystal size based on the effective mass approximation. The film with three dip have the higher thickness in comparison with one and two dips which produced lower optical energy gap.

Fig. 4 shows the optical transmittance spectrum for wavelengths of 300–1100 nm for CdS nanocrystalline thin film deposited with different thickness as a result of multi-dip.

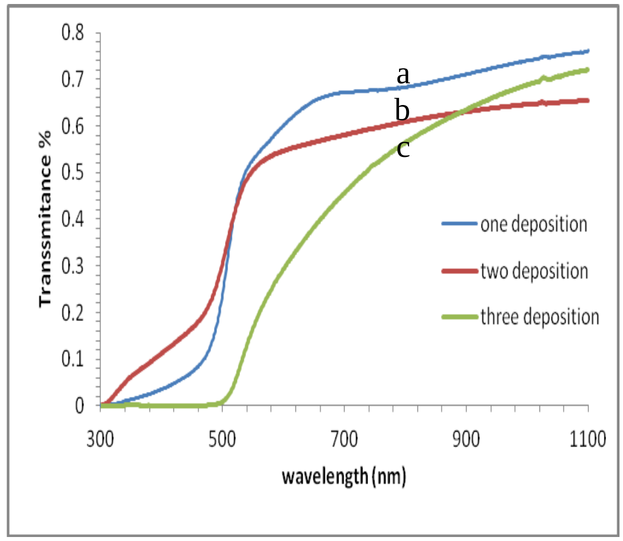

Fig. 4: Transmittance of the films for ; (a) one deposition (b) double deposition and (c) after triple deposition.

Optical transmission spectra of the thin films are observed to be decreases with continuous dip film due to the increase in film thickness. The spectra show an average transmission of above 60 % was obtained in the middle of visible range. Also optical transmission curves are observed to be shifted towards the longer wavelengths with increasing deposition time. These characteristics make the film a good layer for solar cell application. Fig. 5 shows the varying of refractive index with respect to wavelength for the as prepared films. The refractive index found to increase by increasing the number of deposition . This may be due to the change in nanocrystallite size of CdS films.

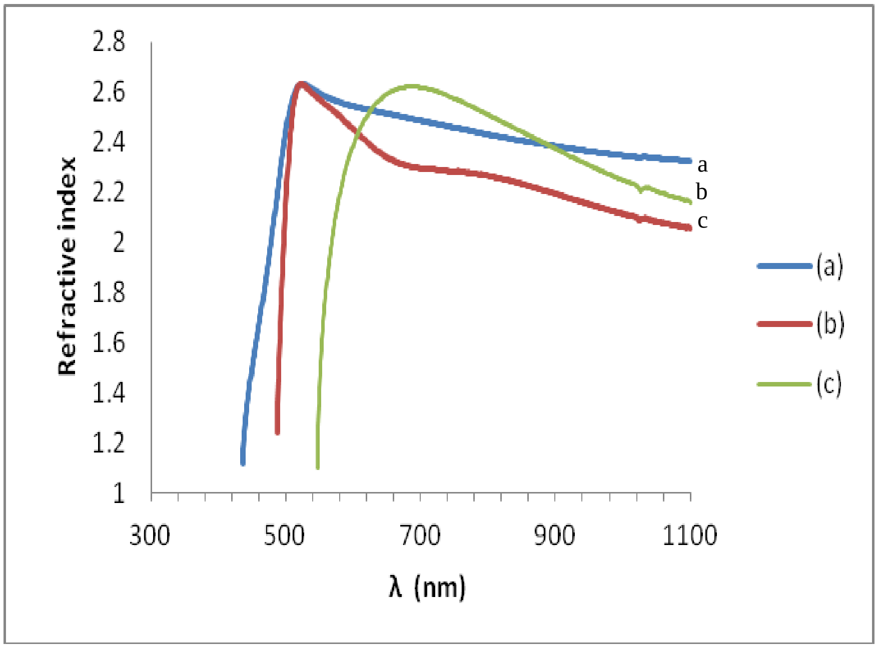

Fig.5: Refractive index of the films for ; (a) one deposition (b) double deposition and (c) after triple deposition.

Conclusions

The chemical bath deposition method was successfully used to deposit CdS nanocrystalline thin films. These deposition films are smooth, uniform and adherent to substrate surface. The prepared films were found to be nano-crystalline. Film thickness can be increase by repeating the deposition procedure several times. When the thickness of the films increase the grain size increase. Also annealing temperature is increase the average size of the particles. The film with multiple depositions can use in making solar cells.

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