EFFECT OF LI DOPING ON THE STRUCTURAL AND SOME OPTICAL STUDIES OF CdS THIN FILMS FABRICATED BY SOL–GEL TECHNIQUE

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ABSTRACT

This research deals with the study of the structural and some optical properties of as-deposited CdS and CdS:Li thin films, grown on ultrasonically cleaned glass substrates at 300K by sol-gel spin-coating technique with the spin speed and spin time of 1000 rpm and 10 seconds, annealed to annealing temperatures 623K during 150min in digital furnace. XRD analysis revels that the films crystallize in polycrystalline hexagonal structure. The average crystallite size of CdS:0, 0.05, 0.1, and 0.15 mol% Li thin films calculated from the most intense peaks are equal to 8.666nm, 9.341nm, 9.933nm, and 11.112nm, respectively. The optical transmittance values of CdS film reaches to 91.8% inter VIS(longer than 500 Å) and NIR regions, then decrease to 89.3% for 0.15 mol% Li, which is important for its applications as window layers in solar cells. The values of optical energy gap of CdS and Li doping by 0.05, 0.1, and 0.15 mol% were equal to 3.08 eV, and 2.97, 2.93, 2.89 eV respectively. Dielectric constant and loos had been investigated in this work.

KEYWORDS*: CdS: Li Thin Films, Sol-Gel Spin Coting, Structural, Optical Energy Gap*

INTRODUCTION

Cadmium Sulphide (CdS) is one of the important II – VI group semiconductor, belonging to the cadmium chalcogenide family continues as a subject of intense research due to its potential applications in solar cells especially as a window material because of its a very suitable band gap 2.42 eV and stability [1]. A number of film deposition methods such as thermal evaporation in vacuum deposition (TEVD), sputtering technique, chemical vapor deposition (CVD), pulse laser deposition (PLD), thermal pyrolysis deposition (TPD),and sol-gel spin-coating technique, have been used for preparing II-VI compound. Among these, spin-coating technique is one of the important used methods, which is extensively studied as a matrix material method to produce nanocomposites because it gives a higher specific surface area, superior homogeneity and purity, better microstructural control of metallic particles, narrow pore size and uniform particle distribution [2]. In this article we report about the preparation of nanocrystalline CdS thin films and also discuss about the effect of volume percentage of Li doping on structural, and some optical properties of the prepared CdS thin films.

MATERIALS AND METHODS

Thin film of cadmium sulphite (CdS) were deposited on glass substrate by using sol– gel technique. Two different path compositions were used. The first one a prepared from pure CdS two solutions the first one was achieved by mixing 0.6 ml polyethylene glycol (PEG 400, Merck), 0.5 ml acetic acid(CH_3COOH) and 8.9 ml of ethanol (CH_3CH_2OH), then stirred one hour, and the second was prepared by mixing 0.2 M Cadmium nitrate ($Cd(NO_3)_2$) and 0.1 M thiourea ($CS[NH_2]_2$) was dissolved in 100 ml ethanol and stirred for one hour. Solutions 1 and 2 were mixed together and stirred

again for 4 hours to obtain the final sol-gel. The second path achieved by adding exact volumes of 0.1M of Lithium chloride (LiCl) (which is prepared by dissolving of 0.61 g of this salt in 100 ml ethanol) to prepare different mole ratio of Li as a dopant on CdS to deposited on ultrasonically cleaned glass substrates at room temperature (300K) by sol-gel spin-coating technique. The solution was dropped onto glass substrates at spin speed of 1000 rpm for 10 seconds, dried on hot plate at 120 ^{0}C for 1 hour and then annealed to annealing temperatures 623K during 150min in digital furnace.

BASIC RELATIONS

The relationship between diffraction angle and the distance between parallel atomic planes (d) is given by the Bragg's law [3].

$$2d\sin\theta = n\lambda \tag{1}$$

Where θ is the Bragg angle, n is an integer and λ is the wavelength of the incident X-ray beam.

The crystallite size (D) of the films is estimated by the Debye-Scherrer formula [3].

$$D = 0.91\,\lambda\,/\,\beta\cos\theta \tag{2}$$

Where λ is the X –ray wavelength (CuKα = 1.5405 Å), β is measured in radian as full width at half maximum (FWHM) of the diffraction peak.

The dislocation density (δ) and strain (ϵ) of CdS nanostructures were determined by the following relations, respectively [4].

$$\delta = 1\,/\,D^2 \tag{3'}$$

and $\epsilon = \beta\cos\theta\,/\,4$ $\tag{4}$

In addition, the lattice parameters a and c of unit cell are calculated by following relation [3]:

$$d_{hkl}^2 = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \tag{5}$$

The equation for the energy gap is given by[5] :

$$\alpha h\upsilon = B\,(h\,\upsilon - E_g^{\,opt.})^{\,r} \tag{6}$$

Where $E_g^{\,opt.}$ is the optical energy gap, B is the constant depended on type of material, r is the exponential constant, its value depended on type of transition, r =2 for the allowed direct transition, and r =3/2 for the forbidden direct transition.

The transmittance part of incident light T is depending on α through the following equation [6].

$$T = \exp(-2.303\,A) \tag{7}$$

Where A is the absorption. Thus the absorption coefficient α corresponding to any wavelength λ can be calculated by applying the relation [5]:

$$\alpha = 2.303\,A/t \tag{8}$$

Where t is the thickness.

RESULTS AND DISCCUSSIONS

X-Ray Diffraction XRD

The X-ray patterns with the monochromatic Cu Kα line (λ=1.5405 Å) of spin coated pure CdS and Li (0.05, 0.1, and 0.15 mol%) doped CdS thin films of thicknesses consistently around 80 nm, grown on ultrasonically cleaned glass substrates at 300K with the spin speed and spin time of 1000 rpm and 10 seconds, annealed to annealing temperatures 623K during 150min are presented in Figure (1). The peaks of the XRD were observed between 20° and 70° at room temperature. The spectrum of CdS and CdS:0.05% Li thin films exhibited peaks at (24.650, 26.502, 28.246, 36.815, 43.217) and (24.724, 26.488,28.273, 43.789, 47.804) in 2θ corresponding to the (100),(002), (101), (102),(110) planes, and (100),(002),(101), (110),(103) planes, respectively (JCPDS card No: 06-0314),with a preferential orientation of (002) plane. For CdS:0.1, 0.15mol%Li thin films exhibited peaks at (25.072, 26.530,28.342,44.180,47.791) and (24.703, 26.463,28.102, 43.788, 48.706) in 2θ corresponding to the [(100), (002), (101), (110), (103)] and [(100), (002), (101), (110), (103)] with a preferential orientation of (100) plane. Changes that have occurred in the intensity of the main peaks are scribed to the rotation of some crystalline grains during the preparation processes. The same phenomena have been observed for Zn doped CdS thin films reported by [7].

The pattern indicate that all the samples are polycrystalline hexagonal structure. Apart from these peaks, no diffraction peaks of metallic, impurity phase like CdO or Li_2O are detected in all the CdS pattern with Li doping which imply that Li atoms are solved successfully in the CdS host structure. Generally, it can be notice from such Figure that the diffraction peaks shifted towards higher 2θ values with lithium additions, which is confirms that the doped Li substitutes Cd in Li doped CdS samples. This may be due to the smaller ionic radii of Li^{+1} (0.76 Å) [8] when compared with that of Cd^{+2} (0.97 Å) [9]. Calculated lattice parameters of CdS thin film, $a = 2.d_{100}/\sqrt{3}$ and $c = 2.d_{200}$, obtained from the position of the peaks (100) and (002) [10].The lattice parameters a = 4.167Å and c = 6.726 Å are slightly greater than bulk CdS lattice parameters a=4.136 Å, and c= 6.713Å (JCPDS card No: 06-0314). This indicates that the films are under tensile strain along the (002) plane parallel to the substrate surface [11].The lattice parameters of CdS:0.05, 0.1 and 0.15mol%Li thin films, a=4.157,4.101, 4.161 Å,and c=6.730, 6.719, 6.736 Å, respectively. The average crystallite size of CdS and CdS:Li of various compositions 0.05, 0.1, and 0.15 mol% thin films calculated from the most intense peaks are equal to 8.666, 9.341nm, 9.933nm,and 11.112nm respectively. Crystallinity is found to improve with increase in doping concentration. The change in the values of dislocation density(δ), and strain (ε) of CdS nanostructures follow the change that has accompanied the crystallite size, which listed in Table(1). It has been found that when the strain increases the crystallite size decrease, because of the delayed crystal growth which is due to the pressures that can increase the lattice energy and reduce the driving force to growth [12].

Table 1: Values of Crystallite Size, Dislocation Density and Strain of CdS and CdS: Li Thin Films

Symbol	Crystallite Size (nm)	Dislocation Density δ($^*10^{14}$) (Line/m^2)	Strain (ε)
CdS	8.666	1.33156	0.243490352
CdS:0.05mol%Li	9.341	1.14607	0.214959747
CdS:0. 1mol%Li	9.933	1.01353	0.21084823
CdS:0.15mol%Li	11.112	0.809	0.198678278
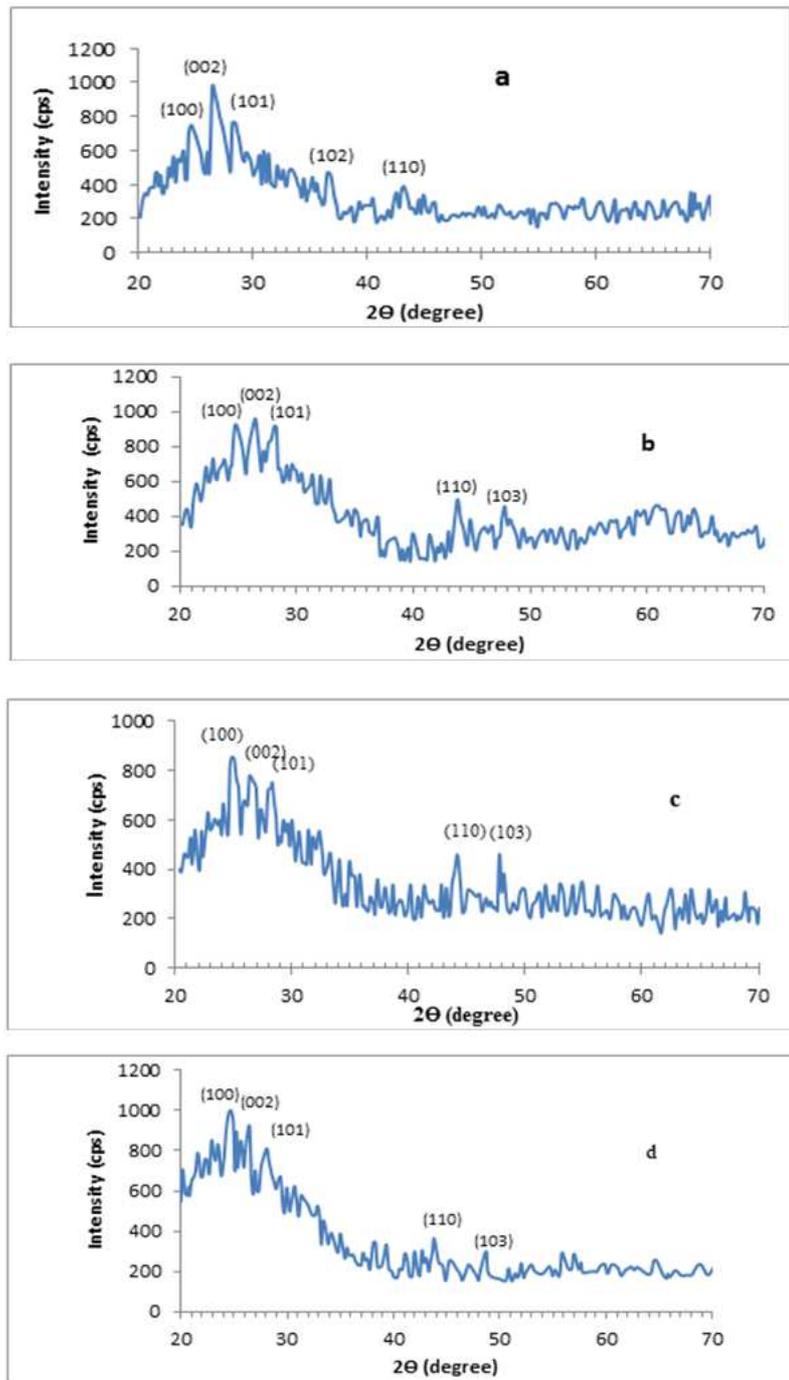
Figure 1: XRD of Deposited CdS: Li for : a- Pure CdS, b- 0.05 mol % Li, c- 0.1 mol % Li, and d- 0.15 mol %

OPTICAL PROPERTIES

Transmittance (T)

The optical transmittance spectra of spin coated pure CdS and Li (0.05, 0.1, 0.15 mol%) doped CdS thin films of thicknesses consistently around 80 nm, grown on glass substrates at RT with the spin speed and spin time of 1000 rpm and 10 seconds, after annealing temperature at 623K in digital furnace during 150 min, where investigated using UV-Visible

Spectrophotometer in the wavelength range of 300 nm to 1100 nm as shown in Figure (2).

All films exhibit good transmittance that exceeds (87.0 -91.8%) inter VIS region (longer than 500A) and NIR radiation of spectrum for CdS and exceed 83% right before the absorption edge, but it decreases with a high doping concentration of lithium (0.15 mol% Li), to the range (77.4 -89.3%) inter VI region (longer than 500A) and NIR radiation region and exceed 70% right before the absorption edge. These findings are higher than the results of a number of researchers have made a study the compound CdS with nano thickness prepared in a manner similar to the preparation of our study and in other ways too[13, 14,15,16,17]. A red shift (higher wavelength side) in the absorption edge towards lower band gap is noticed in all Li doped CdS thin films. The high optical transmittance is advantageous features of CdS thin films that works as filters, and antireflection coating to improve solar cell efficiency, so it is reduce the energy loss in the incident radiation to its minimum value. The decrease in transmittance of the films with the increase of Li-concentration, may be related to increase the crystallite size, shown from the XRD, where the light (photons) scattering on their rough surfaces.[18,19].
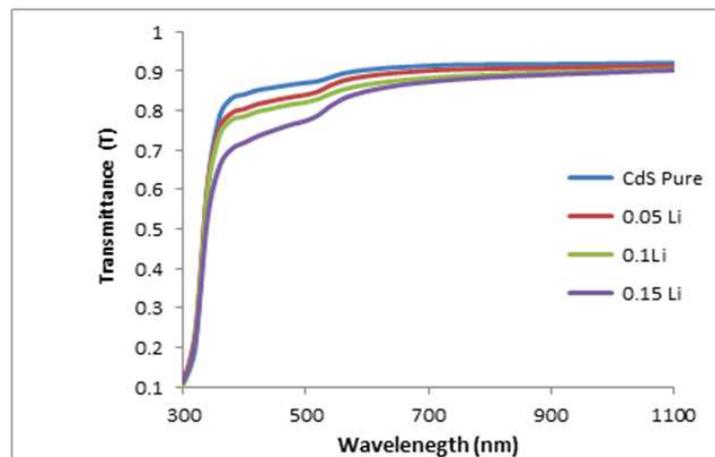
Figure 2: Transmittance as a Function of Wavelength of CdS and CdS: Li

ABSORPTION COEFFICIENT

Figure (3) is a sketch of an absorption coefficient with (hv). It can be seen the absorption coefficient of all samples (pure and doped CdS) are multiply by 10^4 ($\alpha > 10^4$ cm^{-1}), so the optical band gap is direct before and after doping.
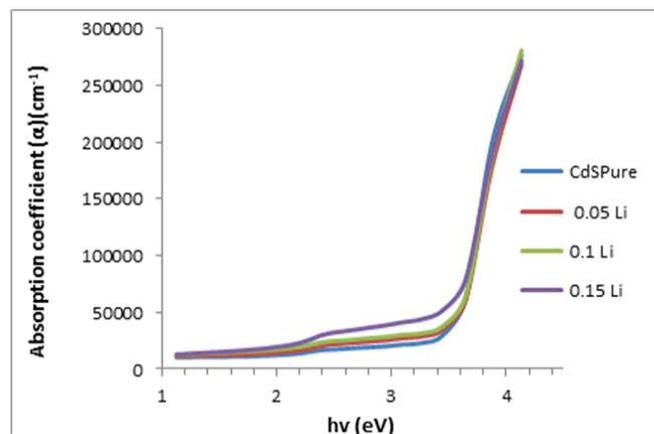
Figure 3: Absorption Coefficient as a Function of Photon Energy of CdS AND CdS:Li

OPTICAL ENERGY GAP (E_g^{opt})

The optical energy gap $\mathbf{E_g^{opt}}$ has obtained from intercept of the extrapolated linear part of the curve with the photon energy axis (hυ) at $(\alpha h\upsilon)^n = 0$. The linear nature of the plots at the absorption edge confirmed that all deposited films are a semiconductor with direct band gap. These results showed that E_g^{opt} is depending on doping concentration. The values of direct optical energy gap E_g^{opt} decreases from 3.08eV for the undoped CdS to 2.97, 2.93, 2.89 eV for the doped CdS by 0.05,0.1, 0.15 mol % Li respectively, as shown in Figure (4). This result is in a similar with the findings of worker [20].The higher value of the E_g^{opt} compared with that of the bulk energy gap of 2.42 eV, Indicates the formation of nanoparticles and presence of quantum confinement effects in the prepared films [21]. If the sphere is too small, the movements of the electron and hole are restricted and so they feel confined which raises the energy required to excite the electron into the conduction band [21, 22]. However, the decreases in $\mathbf{E_g^{opt}}$ may be due to the replacement of larger number of substitutional or interstitial cadmium ions by lithium ions to increase the grain size, also due to an increase of the cluster size or grain size.
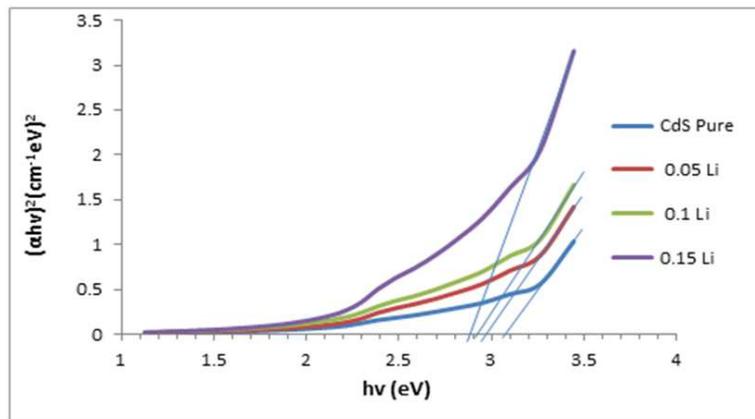
Figure 4: The Energy Gap for the Allowed Direct Transition $(\alpha h\upsilon)^2$

as a Function of Photon Energy of CdS and CdS:Li

REAL AND IMAGINERY PARTS OF DIELECTRIC CONSTANTS (ε_1, ε_2)

The variation of the real (ε_r) and imaginary (ε_i) parts of the dielectric constant values versus wavelength in the range (300-1100) nm for pure CdS and doped thin films with various concentration of Li (0.05,0.1, 0.15 mol %) are illustrated in Figures (5) and (6) respectively. The real part of it is associated with the term that, how much it will slow down the speed of light in the material and imaginary part which showed how a dielectric absorb energy from electric field due to dipole motion. The real part is the normal dielectric constant and imaginary part ε_i which showed how a dielectric absorb energy from part represents the absorption associated of radiation by free energy. Generally, it is seen that both ε_r and ε_i increases with increasing Li contents, as well as decreases with increasing wavelength for all films. The figures imply that the values of the real part are higher than that of the imaginary part and follow the almost same pattern.
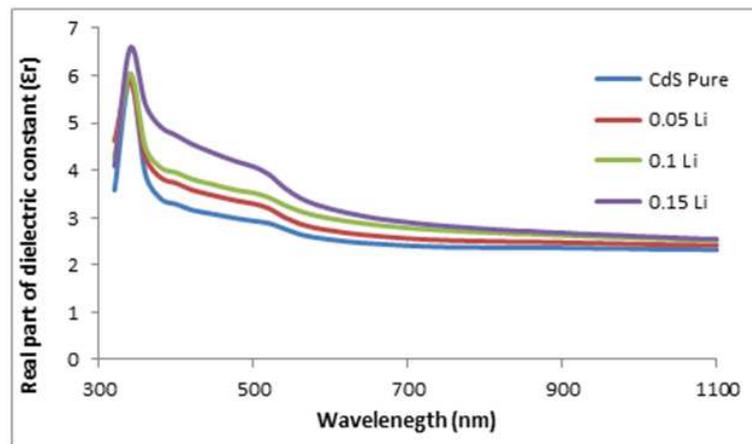
Figure 5: Variation of ε_r as a Function of Wavelength of CdS and CdS:Li
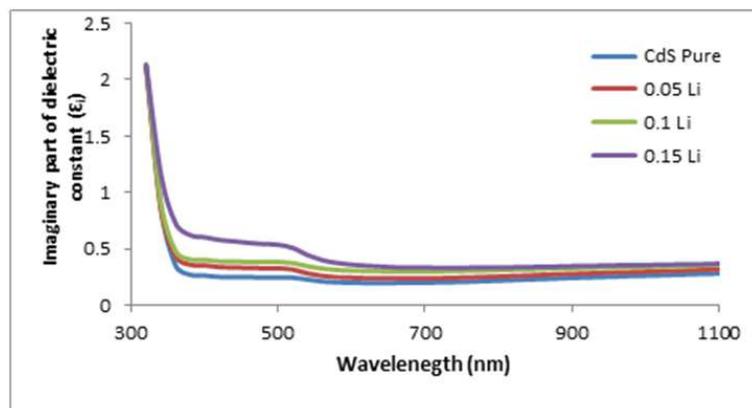
Figure 6: Variation of ε_i as a Function of Wavelength of CdS and CdS:Li

DIELECTRIC lOSS ANGLE

Dielectric loss is a loss of energy that goes into heating a dielectric material in a varying electric field. The variations of dielectric loss with photon energy for pure CdS and CdS:Li thin films, is represented in Figure (7). From the Figure it is observed that dielectric loss decreases with the increase of photon energies.
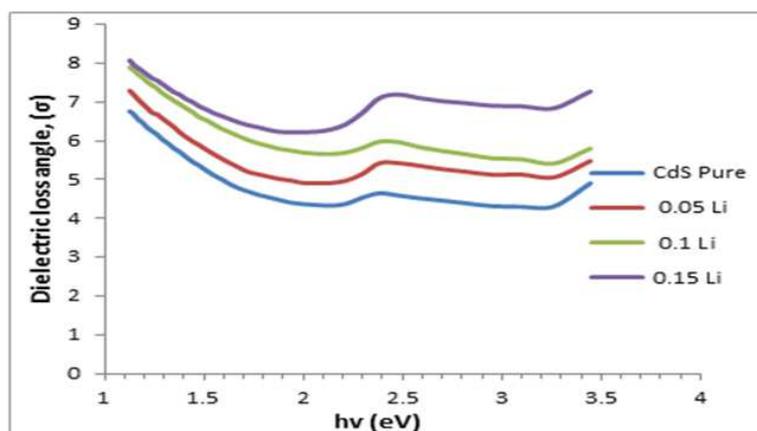
Figure 7: Dielectric Loss Angle as a Function of Photon Energy of CdS and CdS:Li

CONCLUSIONS

CdS thin films have been successfully prepared by the sol-gel spin coating method. XRD studies of CdS and CdS: 0.05,0.1, 0.15 mol % Li films indicated the formation of nanocrystalline with polycrystalline hexagonal phase, and the average crystallite size are equal to 8.666, 9.341nm, 9.933nm,and 11.112nm respectively. The doping with Li did not effect on the nature of crystal structure of CdS. The films have allowed direct transition and the optical energy gap values (2.89–3.08 eV) are greater than the bulk energy gap, which is indicates the formation of nanoparticles and presence of quantum confinement effect in the prepared CdS and CdS:Li films. The optical gap decrease with increasing doping concentration. All films exhibit good transmittance which makes it suitable as a window in solar cell. There is increase in both $\mathcal{E}_r$ and $\mathcal{E}_i$ with increasing Li contents, as well as decreases with increasing wavelength for all films. Dielectric loss decreases with the increase of photon energies.

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