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Characterizations of CdS Thin Film Prepared by Chemical Drop Method

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ABSTRACT

A simple technique has been utilized to grow cadmium sulfide (CdS) nano size. The obtained nanoparticles powder was formed as thin films by chemical drop method. The prepared samples were annealed at 200 ^{0}C then illustrated by XRD, UV-VIS spectrum, AFM images and some dielectric properties. The results indicated that high purity of Nano sized CdS was successfully obtained with hexagonal crystalline structure with particles size estimated to be 35nm using x-ray line broadening. The optical band gap of prepared and annealing thin films varied with the range (3.35 – 3.73) eV. The AFM results show homogenized grains after annealing at 200 ºC with surface roughness of 3.83 nm. Best values of dielectric were obtained for annealing samples.

1. Introduction

Semiconductors have gotten massive consideration in the previous decades because of their affected size dependent [1–4]. These materials have revealed admirable electronic and optical properties [5], and well chemical stability as compared to organic emitters [6,7]. Cadmium sulfide (CdS) (E_g = 2.42 eV) has a great interest in field of heterojunction (HJ) solar cells and characterized by many techniques [8]. It is suitable also for applications like visible radiation sensor [9]. Polycrystalline CdS are widely popular as window material in several (HJ) solar cells such as CdS/CdTe, CdS/CuS [10] for their favorable optical properties. Recently, CdS nanoparticles have been produced by numerous approaches including [11] sol–gel process [12], solid-state reaction, screen printing, hydrothermal method, electro deposition , molecular beam epitaxial (MBE) , physical vapor deposition, microwave etc,. Microwave can be defined as an electromagnetic radiation with the wavelength range of one millimeter to meter and frequency range (0.3–300) GHz [13]. As a result of properties of internal and volumetric heating, A thermal gradient through microwave processing can be prevented providing a uniform environment for chemical reaction [14]. This technique has been effectively utilized for the organic and metal clusters synthesis and the preparation of a range of Nano sized inorganic materials [15]. Microwave heating has the benefit of high-efficiency and fast formation of nanoparticles with a narrow size distribution comparing with conventional heating,. In case of thin films preparation, many approaches have been fabricated such as vacuum evaporation, molecular beam epitaxy, metal-organic vapor phase epitaxy, spray pyrolysis, chemical bath deposition etc. In this work, we used a chemical drop method, which is simple inexpensive and simple method for production of thin films. The CdS nanoparticles prepared by employed the microwave irradiation working at 20% power.

2. Experimental

Chemicals of analytical grade were utilized as received without additional purification. Cadmium chloride ($CdCl_3$, 0.1M), and thiourea [$CS(NH_2)_2$, 0.1M], were dissolved in 100 ml of 30% Ethylene glycol [$C_2H_6O_2$] after mix together in a reaction beaker. A domestic microwave oven (1100W/230V-50Hz) system for 20 min with power 20%, meaning that the microwave working in full power as pulse regime (each 30 s regime it works 6 s and does not works in 24 s.). At the end of reaction the precipitate was centrifuged, then washed several times with ethanol, then dried up at 60 ^{0}C in oven. Portion of the sample was ultrasonically by propanol for 2h, then the product ready for preparation thin films by dropping few drops on clean glass substrate and

leaved in air to dry. Two samples (one was prepared and the other annealing at 200 ^{0}C for 2h) were ready for distinguished by XRD (PW1840) model with radiation of (Cu-Kα) and wavelength of 0.154 nm. The sizes of the prepared sample were calculated by Debye–Scherer formula according to XRD peak broadening. (USB2000, Ocean Optics) double beam was used as UV-vis spectrometer with the range of (200-1100) nm. Digital Instruments of Nasoscope IIIa system in air was used to perform AFM images.

3. Results and Discussion

3.1 XRD studies

X-ray diffraction (XRD) patterns of as synthesis given in Fig. 1. Analysis of the diffractogram indicated of the sample exhibit peaks centered at 2θ = 24.75º, 26.50º ,28.10º and 36.65º, which correspond to hexagonal wurtzite phase structure of nanocrystals with highly three favorite orientations along (100), (101) and (002) planes. The peaks are satisfactory agree with the standard (JCPDS) file No. 41-1049 with lattice parameters a=4.145 Å and c=6.714 Å. X-ray diffraction verifies the phase singularity of the synthesized material, for example, there is no extra noticed peak matching with their binary system. Broad diffraction peaks verify the monocrystalline characteristics of the particles and can be utilized to compute the average crystallite size (G_s) using Scherrer's formula [16]:

$$G_s = \frac{0.9\lambda}{\beta \cos\theta}$$

Where λ is the wavelength of x-ray target, β is full width at half maximum (FWHM) and θ is Bragg angle in radiant. The approximated crystallite size of the nanocrystals using Scherrer's formula was calculated to be about 35 nm.

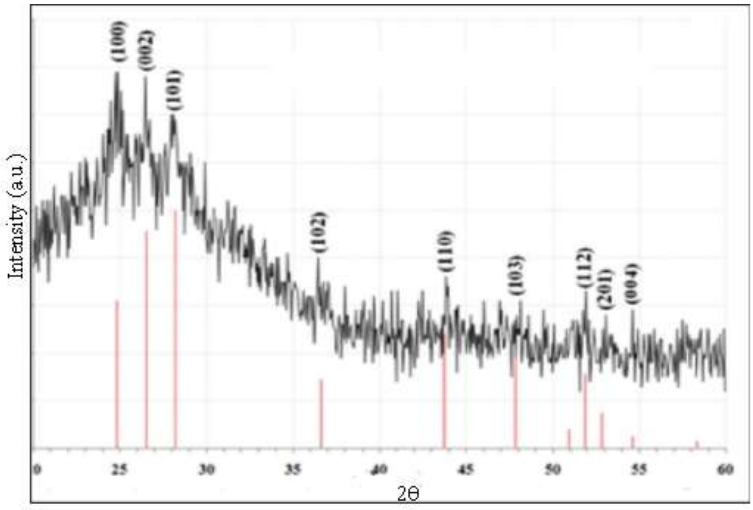

Figure 1:X-ray diffraction of CdS nanoparticles

Table 1: comparative between experimental and stander peaks

2θ (Degree)	d_{hkl} Exp. (Å)	FHWM	G_s (Å)	d_{hkl} Std. (Å)	hkl
24.75	3.594	0.62	163	3.586	(100)
26.50	3.361	0.66	150	3.360	(002)
28.10	3.173	0.70	140	3.164	(101)
36.65	2.450	0.72	138	2.452	(102)
43.85	2.063	0.80	124	2.071	(110)
48.15	1.888	0.80	126	1.900	(103)
51.90	1.760	0.70	151	1.763	(112)
53.05	1.725	0.70	152	1.733	(201)
54.60	1.679	0.86	118	1.679	(004)

3.2. Reaction Mechanism

Ethylglycol was presented as a decreasing agent matching with the proposed mechanism by Wan et al.[17]. In case of synthesizing copper sulfide hollow spheres in ethylene glycole solvent, acetaldehyde can be manufactured by dehydration of ethylglycol at very high temperature, where the acetaldehyde gives a hydrogen atom and performance as a decreasing agent, as illustrated in Equation.1 [23]. In addition, thiourea is added into the reaction too. Thiourea molecules give sulfur anions (S^{2-}), in ethylglycol solution as in Equation.3 [26]. Therefore, CdS nano size is regularly formed by the competitive reaction between Thiourea molecules and sulfur ions Cd^{2+}. Similarly, perform as a surface stabilizer causing the production of the homogeneous CdS

$$2HOCH_2CH_2OH) \rightarrow 2CH_3CHO \rightarrow CH_3OOCH_3 + 2H \quad \ldots\ldots (1)$$

$$CS(NH2)_2 \rightarrow H_2S + NH_2CN \quad \ldots\ldots(2)$$

$$H_2S \rightarrow H + HS \rightarrow 2H^+ + S^{2-} \quad \ldots\ldots(3)$$

$Cd^{2+} + S^{2-} \rightarrow CdS$ ……(4)

3.3. UV-Vis Spectrum

Figure (2) shows the wavelength dependence transmittance of CdS samples in wavelength range of 300nm-1100nm. The optical transmittance of the CdS film produced at room temperature was approximately 20% above wavelength ≈ 365nm while this value was increasing up to 60% when the sample was annealing at 200 ^{0}C which may due to the stress relief increasing in crystallization and the stability of the film. This result of transmittance obeyed with the results of Hasnat [18] using spray pyrolized method and Hani et al.[19] Using chemical bath deposition method. Below 350nm, there is a clear drop in the value of transmittance of the thin film because of the high effective absorbance of the thin films in this range.

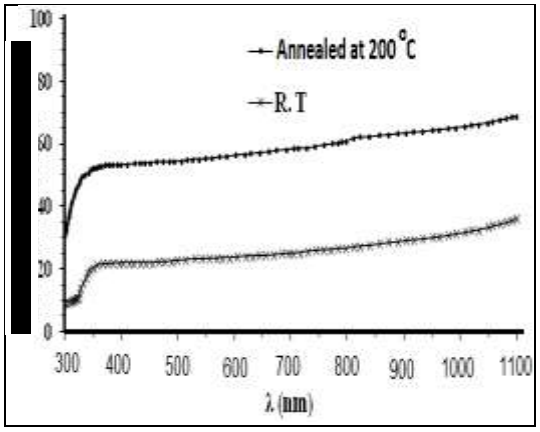

Figure 2: Relation between transmission and wavelength at UV-VIS region of CdS nanoparticles

3.4. Energy Band Gap

The energy band gap could be obtained from spectroscopy measurements [20]. We found the following results. Fig.3 display $(\alpha h\nu)^2$ as a function of hν, where α is the absorbent coefficient of the film. By plotting the figure between $(\alpha h\nu)^2$ and photon energy $(h\nu)$ provides the value of direct energy band gap. The extrapolation of the straight line to $(\alpha h\nu)^2$ gives the value of energy band gap. Two band gaps were recorded one at 3.35 eV for original prepared sample and the other at 3.73 eV after annealing at 200 ^{0}C. Those results are greater than the value of bulk and thin film for CdS reported. This shift in energy bang gap attributed to the structure of (CdS)n clusters ($2 \leq n \leq 5$) as informed by [21]and they found the structure of CdS monomers and (CdS)n clusters shaped at the initial stages of (Cd^{+2} ions and S^{-2} ions) reaction as in Fig.4. They found the band gap at n=3 was 3.69 eV and when n=4 the band gap was 3.29 eV. That mean in our work the n have the values of 3 and 4. This results also in agreement with the results of Zeng [14].

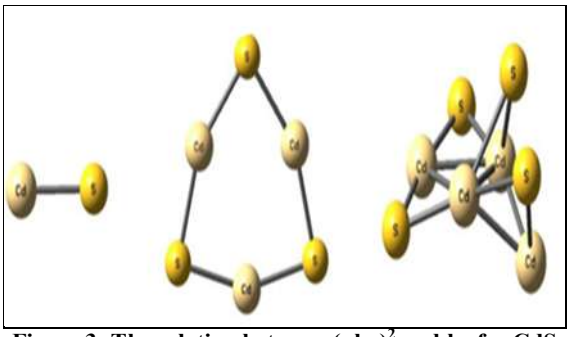

Figure 3: The relation between $(\alpha h\upsilon)^2$ and hν for CdS nanoparticles.

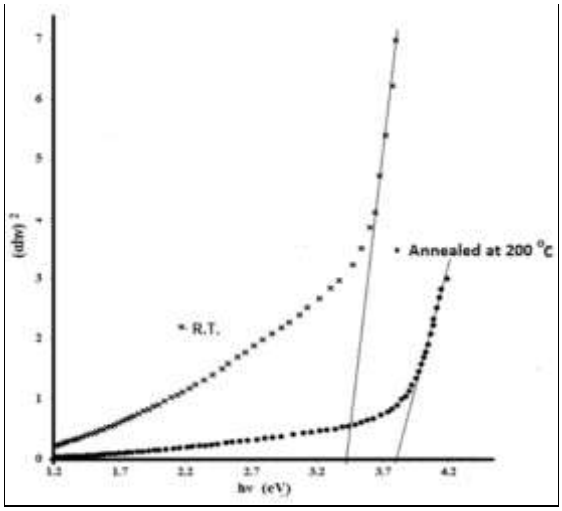

Figure 4: Coordination of (CdS)n cluster with n=1,3 and 4[21]

3.5. Dielectric properties

Dielectric properties of real and imaginary parts of the dielectric constant were illustrated in Figures 5 and 6.The real part is dependable of reducing the speed of light in material while the imaginary part acts as absorb energy from electric field because of the dipole motion. It is quite clear the effect of temperature on the results. After 340 nm, the ε_r value increases in case of original prepared sample and decreasing for annealing one. A good result was obtained for ε_i values in case of annealing sample to give all the values below 1.

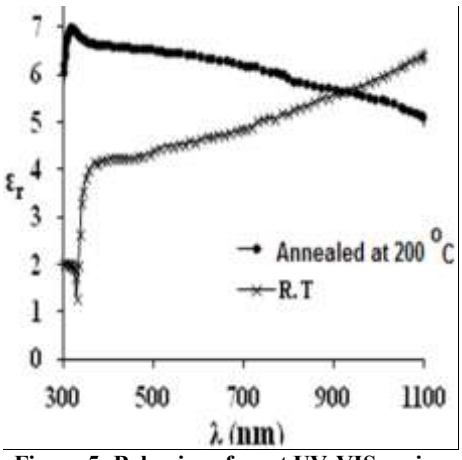

Figure 5: Behavior of ε_r at UV-VIS region

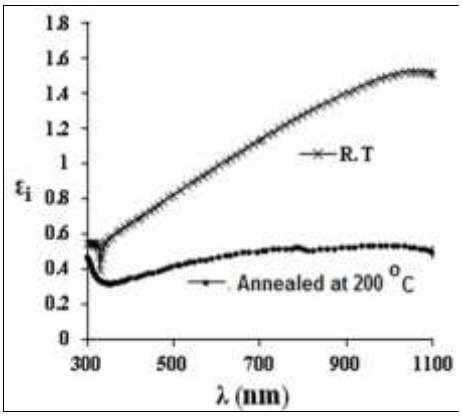

Figure 6: Behavior of ε_i at UV-VIS region

3.6. Atomic force microscopy

Atomic force microscopy AFM has been utilized to analysis the surface morphology of the CdS films. The matching AFM image are showed in Fig.7-a related to room temperature. A weak crystalline are formed and does not indicate a high particular structure and exhibits a low surface roughness 1.3 nm. As temperature increases, 200 ^{0}C , CdS film crystallization occurred then AFM images of the film grow up at a granulated structure, with low surface roughness 3.83 nm, Fig.7-b, comparing with literatures.

The images of the atomic force microscope, Fig.7-a, showed the presence of black point-like interspersed with the deposited atoms, which represent point defects that may be caused by the oxygen vacancy that accompanying the deposition process, same result with [24,25], or may represent impurities deposited on the surface during the preparation of films. Figure 7-b shows the disappearance of most those spots This may be due to the fact that the annealing process has greatly contributed to reducing the defects of oxygen vacancies and rearranging the atoms in crystalline form.

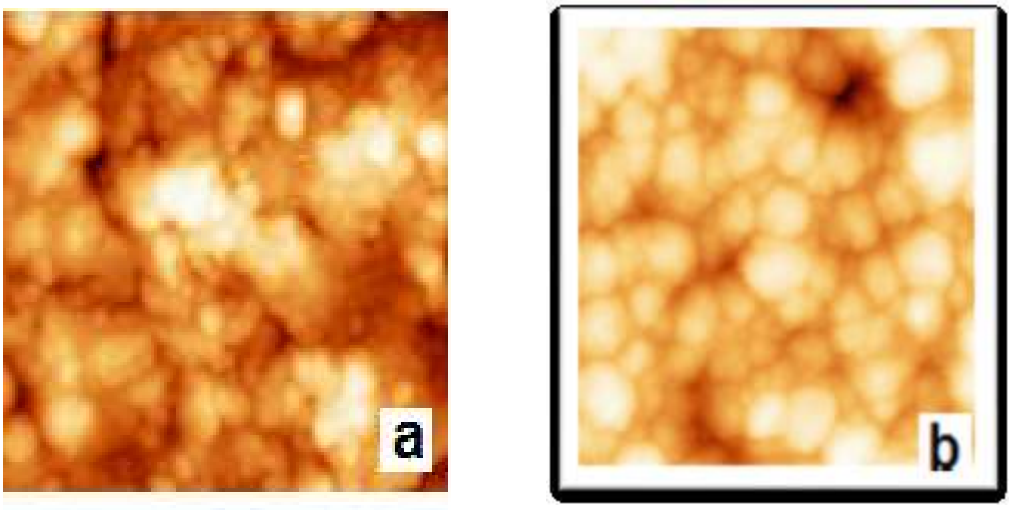

Figure 7: Evolution of the AFM images (a) at room temperature and (b) at 200 °C.

Conclusions

We have shown that CdS prepared by microwave radiation can form thin films on glass substrates by chemical drop technique. Results of x-ray showed particles near 35 nm in size of uniform crystal shape structure after annealing. UV–VIS spectra observed that the transmission spectra shift towards shorter wavelength. Shift in energy gap attributed to the configuration of $(CdS)_n$ clusters ($2 \leq n \leq 5$) for the structure of CdS monomers and (CdS)n clusters formed at the initial stages of the (Cd^{+2} ions and S^{-2} ions) reaction due to the microwave radiation time. Both ε_r and ε_i have a good result for annealing thin film. Atomic force microscopy shows a roughness value of 3.83 nm with high crystallization. All the results were obeyed the literature data.

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توصيف أغشية كبريتيد الكادميوم الرقيقة المحضرة بطريقة التقطير الكيميائي

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الملخص

باستخدام تقنية بسيطة تم إنماء أغشية كبريتيد الكادميوم (CdS) النانوية. تم تشكيل مسحوق من جسيمات نانوية كأغشية رقيقة باستخدام تقنية التقطير الكيميائي. لُدنت النماذج المحضرة عند درجة حرارة 200 ºC ثم أجريت فحوصات الاشعة السينية وطيف الاشعة فوق البنفسجية–المرئية وصور مجهر القوى الذرية إضافة الى بعض خصائص العزل الكهربائي. أشارت النتائج إلى نقاوة عالية من أغشية CdS النانوية تم الحصول عليها بنجاح ذات تركيب بلوري سداسي الشكل بحجم 35nm باستخدام اتساع خط طيف الأشعة السينية. فجوة الطاقة البصرية للأغشية المحضرة والملدنة تباينت ضمن المدى (3.73 - 3.35) eV. أظهرت نتائج مجهر القوى الذرية تجانسا في الحبيبات المترسبة بعد تلدينها بدرجة حرارة 200 ºC وبمعدل خشونة للسطح بمقدار 3.83 nm. أفضل نتائج العزل الكهربائي تم الحصول عليها كانت للنماذج الملدنة.