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Chemical Vapour Deposition of CdS Thin Films at Low Temperatures from Cadmium Ethyl Xanthate

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Abstract

Thin films of nanometer sized cadmium sulfide were directly prepared by aerosol-assisted chemical vapor deposition (AA-CVD) method, cadmium ethyl xanthate complex was used as precursor material at 225 ºC, 250 ºC and 275 ºC. The thermal decomposition of complex was characterized by thermal analysis, (thermogravimetric analysis (TGA) and a differential scanning calorimetry (DSC)). The prepared CdS thin films have been characterized by XRD and SEM- EDX analysis. TGA curves ensured that the rapid decomposition of $[Cd(S_2COEt)_2]$ gives a CdS in single step between 150 ºC and 200 ºC. XRD patterns confirmed that the CdS particles crystalized as a hexagonal crystallographic phase at low temperatures. The grain size of particles increased with increasing the preparation temperatures from 225 ºC to 275 ºC,. The spherical CdS nanoparticals were observed in SEM analysis.

Keywords: Chemical Vapour Deposition; Cadmium Sulfide, Thin Film; Low Temperature**s.**

1. Introduction

Cadimum sulfide is a yellow inorganic compound, employed in industry as a yellow pigment, it has thermal stability, good chemical stability and is easily soluble in acid solution but not soluble in water [1,2], beyond to II-VI semiconductor groups, used as N-type semiconductor, has Bohr radius of 2.4 nm^2 [3,4], has two common crystal structures with direct band gaps (E_g at 300 K): hexagonal (wurtzite) phase with 2.26 - 2.5 eV and cubic (sphalerite) phase with 3.5 eV [3,5]. All of these features have provided the cadmium sulfide qualifications for use in various fields, such as employed in photovoltaics and solar cell [6,7], in chemical sensor [8], in sensitive photo detectors [9], in light emitting diodes [10] and as photocatalyst [11]. Many procedures have been developed to produce CdS with divergent structures such as chemical precipitation method [12], sol-gel spin coating method [6], hydrothermal method [13], spray pyrolysis technique [14], solvothermal method [15], chemical vapour deposition method [16] and Chemical Bath Deposition Technique [17], among them chemical vapor deposition is a powerful technique for preparation high quality thin solid films. It is good method for control the thickness of the films and producing highly crystalline materials.

The goal of this work is to prepare the CdS thin film in one port step using aerosol-assisted chemical vapor deposition (AA-CVD) method at 225 ºC, 250 ºC and 275 ºC. Afterwards, the preparation process will conform by determining its characterizations by XRD, SEM- EDX analysis.

2. Experimental

A. Materials

Potassium ethyl xanthate $[KS_2COEt]$ cadmium chloride $[CdCl_2]$ and tetrahydrofuran (THF) were purchased from Sigma Aldrich. All of the chemicals were used as received without further purification.

B. Instruments

The thermal properties of $[Cd(S_2COEt)_2]$ complex was measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves, which were obtained by using a TA (Q50) and (Q10) TA Instruments systems under an inert atmosphere of dry nitrogen. The heating rate of the sample was 10 ºC/min. The morphology properties of films were determined using Scanning electron microscope

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images (SEM), that were obtained using a FEI Quanta 200 ESEM with an EDAX Genesis V4.61 for EDX analysis. The structure properties of the films were characterized by a grazing incidence X-ray diffraction (GIXRD) (Bruker D8 Advance diffractometer) using a Cu-Kα source (λ = 1.5418 Å, voltages = 40 kV, current = 30 mA).

C. Methods

Synthesis of cadmium (II)(O-ethylxanthate)

$[Cd(S_2COEt)_2]$ was synthesized by depending on a modified procedure, which was essentially prepared from a metal transition ethylxanthates precursor that described in literatures [18-20]. Potassium ethylxanthate (1.077 g, 0.00672 mol) in 100 mL of distilled water was added to a solution of cadmium (II) chloride (0.6159 g, 0.00336 mol) in 100 mL of distilled water also, the mixture was stirred for a further 30 min at room temperature. The product was filtered by vacuum filtration, washed three times with distilled water and dried in vacuum oven for 12h at 50 ^oC to give $[Cd(S_2COEt)_2]$.

Based on the results in **Table 1**, the melting point value and the chemical element analysis conform that the $[Cd(S_2COEt)_2]$ is successfully prepared, and these values are in agreement with the reported in reference [18].

Aerosol-assisted chemical vapor deposition AA-CVD of $[Cd(S_2COEt)_2]$

A 0.3 g of cadmium ethyl xanthate was dissolved in (20 mL) of THF as precursor solution, the aerosol droplets of the precursor solution were carried to the reactor tube by a flow of argon (140 cm^3 min^{-1}). This employed procedure is modified from references [21]. The suggested chemical equations for thermolysis of $[Cd(S_2COEt)_2]$ are following [22] equations (1) to (3).

$$[Cd(S_2COEt)_2] + \text{heat} \rightarrow Cd(SCO)_2(SH)_2 + 2(CH_2CH_3) \quad \ldots\ldots(1)$$

$$Cd(SCO)_2(SH)_2 + \text{heat} \rightarrow Cd(SH)_2 + 2(SCO) \quad \ldots\ldots(2)$$

$$Cd(SH)_2 + \text{heat} \rightarrow CdS + H_2S \quad \ldots\ldots(3)$$

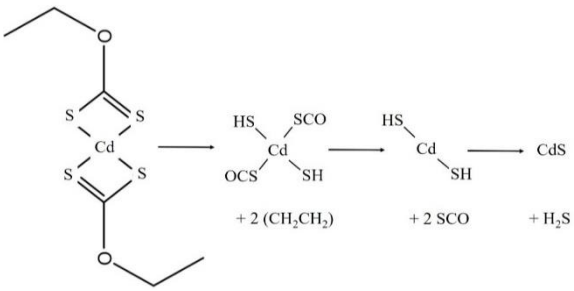
Table 1
The Melting point values and chemical element (C.H.S) analysis for $[Cd(S_2COEt)_2]$.

Sample	M.P / ^oC	Chemical element (C.H.S) analysis		
			Analytical Calculated values for C6H10CdO2S4	Practical (Found)values for C6H10CdO2S4
$[Cd(S_2COEt)_2]$	156-160 ^oC	C	20.3	20.1
		H	2.84	2.82
		S	36.14	36.10

3. Results and Discussion

A. Thermal decomposition of $[Cd(S_2COEt)_2]$

According to **Figure (1a)**, the decomposition of $[Cd(S_2COEt)_2]$ was studied using TGA and DSC. The decomposition of $[Cd(S_2COEt)_2]$ was produced CdS in a rapid single decomposition step between 150 ^oC and 200 ^oC. The residue weight (41.1 %) is closed to calculate value for residual CdS (40.7 %). The DSC curve in **Figure (1b)** explains one endothermic peak, which indicates to that the melting point of the $[Cd(S_2COEt)_2]$ compound was 155 ^oC and the enthalpy of melting (ΔH_M) in the range of -223 mJ. A thermal decomposition mechanism for the xanthate complexes occurs via the Chugaev elimination reactions [22,23], the decomposition profile of $[Cd(S_2COEt)_2]$ is shown in **Scheme1**.



Scheme1. The decomposition mechanism of $[Cd(S_2COEt)_2]$ compound.

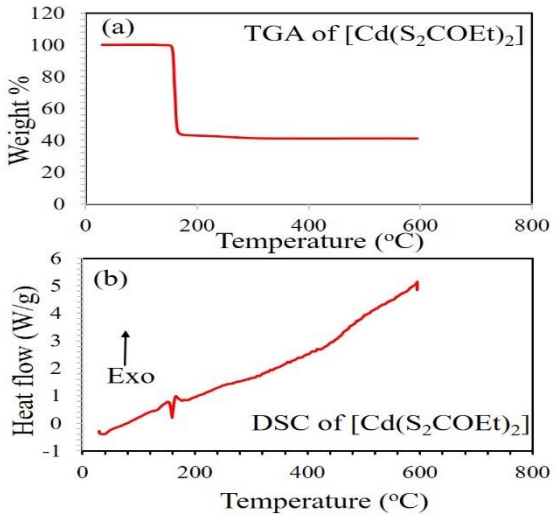


Figure 1. (a) Thermosgram and (b) Differential scanning calorimetric curves for the decomposition of $[Cd(S_2COEt)_2]$ compound.

B. X-ray diffraction analysis

The nano-structure for the prepared CdS as thin film has been investigated using XRD technique. Based on achieved three clear peaks from **Figure 2**, the prepared CdS thin films in different temperatures are being as hexagonal CdS phase at 24.8º, 26.5º and 28.1o, which assigned to (100), (002) and (101) planes, (JCPDS-89-2944 and JCPDS-067776) respectively [24-26]. At 47.26º, the relative sharp peak with (220) plane beyond also to as hexagonal CdS phase (JCPDS Card No.-75-1546) [27]. The mean crystal size for CdS thin films peaks were calculated in **Table 2** with using Debye-Scherrer Equation [28-33].

$$L=\frac{k\,\lambda}{\beta\,Cos\,\theta} \qquad (4)$$

Where, L is the mean crystal size in (nm), λ is the wavelength of the instrument source (Cu k_α) in (nm), β is the full width at half maximum intensity in (mathematically transfer from degree to radian) [34], θ is the Bragg diffraction angle and k is shaped constant (0.94 for spherical shape [35]).

Referring to results in **Table 2**, the prepared CdS thin films are nanoparticles, and the increment in temperature from 225 ºC to 275 ºC lead to increase in the mean crystal size magnitude, which demonstrated the agglomerate of particles that occurred with increased the temperature via preparation process [36].

Table 2: The Mean Crystallite Sizes of CdS thin films at different temperatures.

Samples	Mean Crystallite Sizes/ nm
CdS thin film at 225 ºC	8.442
CdS thin film at 250 ºC	8.320
CdS thin film at 275 ºC	9.431

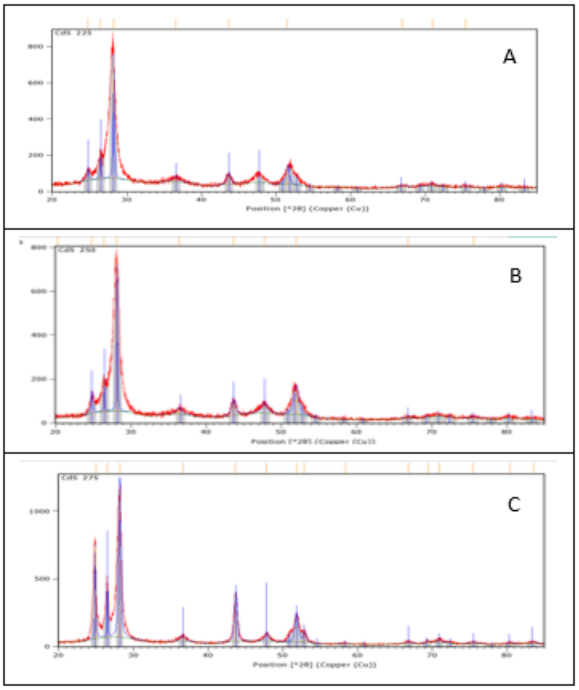


Figure 2. Powder X-ray diffraction patterns of CdS thin films prepared by Aerosol-assisted chemical vapor deposition AA-CVD of $[Cd(S_2COEt)_2]$ complex at (A) 225 °C, (B) 250 °C and (C) 275 °C.

C. SEM-EDX analysis

The SEM images and EDX analysis in **Figure 3** were performed. The shape of all prepared CdS thin films samples is found to be spherical. The packs positions in EDX analysis were illustrated at (2 – 4) keV; and that confirmed the CdS thin films are growing successfully at low temperature in ranged 225 ºC to 275 ºC using CVD process. These results are in good agreement with that reported in literatures [37,38]. The maximum percentage of summation weight for Cd and S atoms is obtained at 275 ºC and equal to 94.466% with less error in %, which shown in **Table 3**.

Table 3: The weight percentage of Cd, S and CdS in prepared samples at 225 ºC, 250 ºC and 275 ºC.

Samples	Elements	series	$[wt.-\%]_{Experiment}$	[norm. wt.-%]	[norm. wt.-%]	Error in %
Sample 1 at 225 ºC	Sulfur	K-series	18.64291414	22.87592183	50.97552615	0.981564
	Cadmium	L-series	62.8528799	77.12407817	49.02447385	3.39634
		Sum of wt. CdS %	81.49579404	100	100	
Sample 2 at 250 ºC	Sulfur	K-series	16.3128995	22.29646017	50.14709226	0.995902
	Cadmium	L-series	56.85072995	77.70353983	49.85290774	3.438636
		Sum of wt. CdS %	73.16362944	100	100	

Sample 3 at 275 ºC	Sulfur	K-series	21.19155	22.43282271	50.34342966	0.820393
	Cadmium	L-series	73.27517	77.56717729	49.65657034	3.284376
		Sum of wt. CdS %	94.46673	100	100	

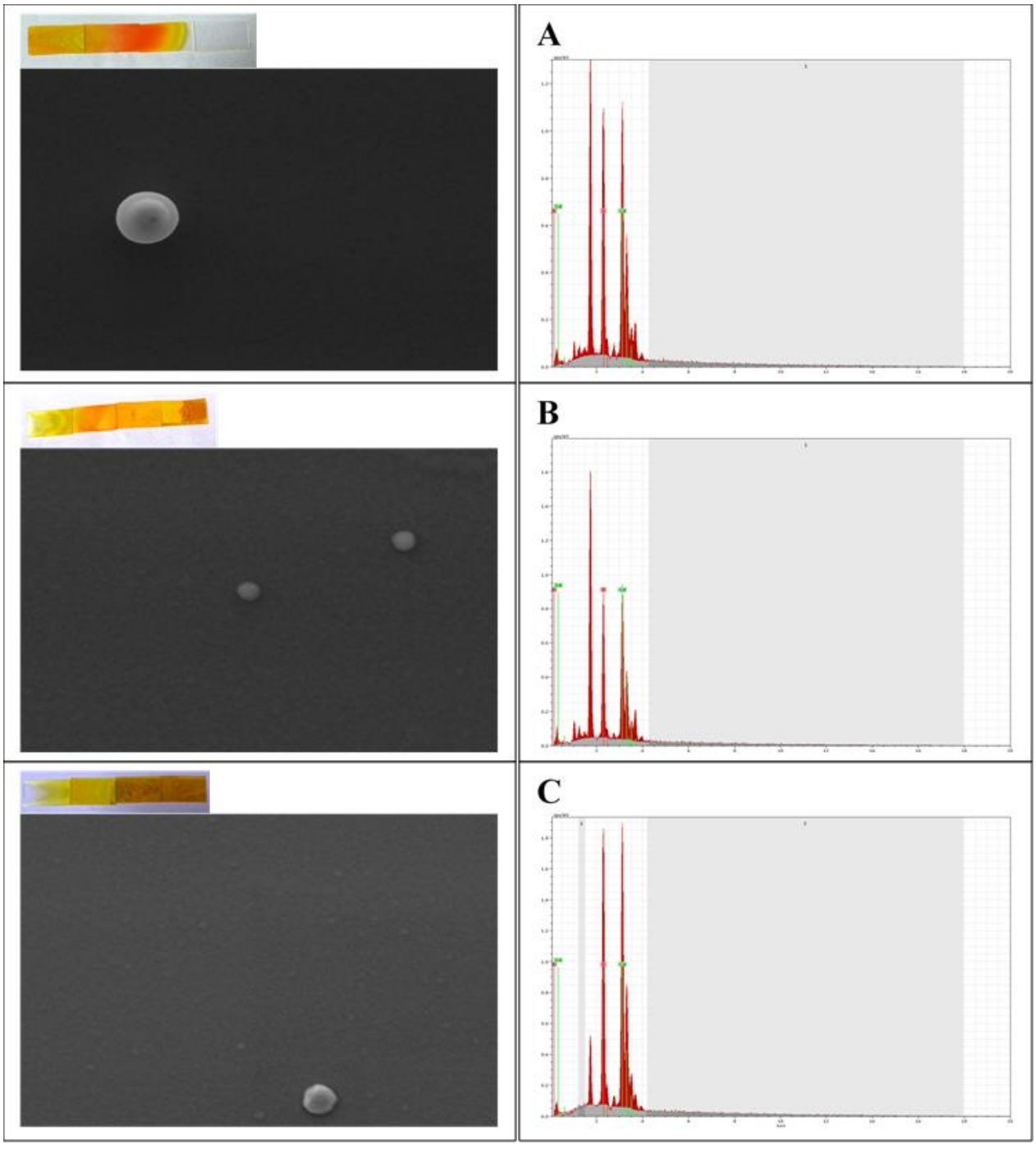


Figure 3. SEM-EDX for result of prepared CdS thin films at a) 225 ºC, b) 250 ºC and c) 275 ºC.

4. Conclusions

Chemical vapour deposition of cadmium ethyl xanthate has been successfully performed at low temperature during its pyrolysis, the decomposition **of** $[Cd(S_2COEt)_2]$ gives CdS Thin films on glass substrates at 225 ºC to 275 ºC. XRD data indicated that to the all prepared CdS thin films samples are polycrystalline. The SEM-EDX analysis that was obtained refers to all prepared samples having a **spherical** shape at low temperatures, and the maximum sum of wt. CdS % is found for sample 3 at 275 ºC . The process was easy to produce CdS films for photovoltaic application at low temperatures.

5. Conflicts of interest

"There are no conflicts to declare".

6. Formatting of funding sources

Self

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