Preparation and characterization of structural and optical properties of CdS thin film spin coating prepared

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Abstract. In this paper, a Cadmium sulphide (CdS) nanocrystal thin film has been prepared on glass substrate using the sol-gel method. As deposit and effect annealing films at an annealing temperature of 500°C for 1 hour were investigated and characterized. The characterization of prepared films included, structural properties using X-ray diffraction (XRD), Scanning electron microscope (SEM), Atomic force microscope (AFM), and optical properties using UV-Visible measurement. Based on XRD results the annealing reason increase in peak intensity due to the improvement in the crystallinity and the crystalline size decreased with increasing the annealing temperature in regrading of preferred diffraction peak (111) at 20 = 26 to be fourth more, this indicated a formation of cubic structure of the CdS nanocrystalline thin films as the predominant phase. When the dislocation density and strain initially decreased with increasing the annealing temperature due to the improvement of crystallization. SEM images revealed that the films have Nano sphere-based or cluster-like shape and the structure uniformly grown on the substrate have been observed with annealing temperature. Besides, the roughness, root mean square (RMS), and average diameter, decreased while the grain size increased with annealing temperature. The optical properties showed that the films have low absorption over the visible region and it's decreasing the annealing temperature which makes CdS is a promising material for optoelectronic application. The energy gap increases with a decrease in the size of the crystallites, while an energy gap value is somewhat larger than the typical value of bulk CdS. This may be due to the quantum confinement effect due to the nanometer crystallite size of the cadmium sulphide thin film. The first section in your paper.

Key words: CdS, Cadmium sulphide, nanocrystal thin film, sol-gel, spin coating.

1. Introduction
In the last few decennary, due to its uniqueness, semiconductor nanomaterials are attracting attention for their electrical, physical, mechanical and chemical properties. The quantum confinement Impact plays an important role in fine-tuning the optical and the electronic properties of semiconductor materials. Over the past three decades, Group II-VI based semiconductor nanomaterials have enticed great attention due to their potential applications in electronic and optoelectronic fields [1]. Cadmium sulphide is a very considerable II-VI semiconductor. It has a direct optical bandgap (2.4 eV at room temperature) [2]. Cadmium sulphide materials have high refractive index values in the range of 2.58–2.55 for the wavelength interval of 350–1600 nm [3], high mobility (0.1–10 cm² V⁻¹ S⁻¹), high absorption coefficient (10⁴-10⁵ cm⁻¹), and small exciton Bohr radius (2.5 nm). Cadmium sulphide thin film has been applied in varied fields, such as a light window, transistors, (LEDs) light-emitting diodes, and photocatalytic applications [4] [5]. The wide bandgap, low absorption loss, compact crystallographic cell structure, and electronic affinity makes CdS is a promising optoelectronic device [6]. In general, n-type semiconductor cadmium sulphide is conventionally utilized as a buffer layer for heterojunction solar cells with reason of tunable bandgap 2.4 eV and good transparency [7]. Nanoparticles of CdS doped with other semiconductor materials working as photosensor detection, (LED) Light emitting diodes, Semiconductor lasers [8], Thin films transistors, Photodetectors, Photosensitization, Photoluminescence, and Photocatalytic properties Solar cellular, and gas sensor [6]. These thin films are made by various physical and chemical methods, including vacuum evaporation, photochemical deposition, electrodeposition, molecular beam epitaxy, sputtering, spray
pyrolysis, metal-organic chemical vapour deposition, screen printing, chemical bath deposition, and sol-gel assisted spin coating method.[9][10]

In this study, we will investigate a simple spin coating technique for synthesizing cadmium sulphide thin films. The advantages of this technology are simplicity, low cost, non-vacuum, safety, and low operating temperature. Besides, this method can be easily scaled up for large area thin films of the same family. The structural, chemical analysis, morphological, optical, and conductive types of the prepared films were investigated [11]. In this paper, the cadmium sulphide thin films were created utilizing a simple spin coating technique and characterized its structural and optical properties were characterized.

2. Materials and Methods

The cadmium sulphide thin films nanostructures were grown by the sol-gel spin coating method at room temperature. (PEG) Polyethylene glycol200 [C\(_\text{2nH}_{4n+2}O_{n+1}\)] sol was prepared by mixing 0.6 ml of PEG, 0.5 ml of acetic acid [CH\(_2\text{COOH}\)] and 8.9 ml of ethanol [C\(_2\text{H}_5\text{OH}\)] under stirring for 1 hour. 1.3 Mol/L thiourea extra pure (CH\(_4\text{N}_2\text{S}\)) as a source of S and 1.3 Mol/L Cadmium Nitrate Tetra Hydrate Cd(NO\(_3\))\(_2\).4H\(_2\)O as a source of Cd and 15 ml ethanol accompanying 60 C° to get a solution. This solution was slowly added to the PEG sol with powerful stirring for 4 h until a homogeneous solution was obtained. As the reaction was started, the reaction system is gradually changed from transparent to light yellow. The final intended solution was stored at room temperature for at least 20 h to make sure that the mixing between all elements is satisfied. Then, the prepared solution was spin-coated on glass substrates at spinning speed 1500 RPM for 30 second on glass substrates were cleaned by Acetic acid and Ethanol. The precipitate collected from this step was dried on the hot plate at 100 C°. And annealed using a muffle furnace at 500 °C for 1 h these procedures have been exhibited in figure(1). The CdS thin film nanostructure was characterized using (XRD) X-Ray Diffraction, (AFM) Atomic Force Microscopy, (SEM) Scanning Electronic Microscopy, (UV–vis) Ultra Violet. XRD data was analyzed by the x’pert high score program.

Figure1. Schematic diagram of experimental procedure of prepared CdS thin film, procedure step
3. Results and Discussion

3.1. Structure and Morphology Characterization

Figure 2 show XRD patterns of the cadmium sulphide thin film as deposit and at an annealing temperature of 500 c which revealed that the diffraction peaks were at 2θ= 26.4, 43.8, 51.5 and 55 correspond to the crystal plane (111), (220), (311) and (222) respectively for as deposit) and the film has cubic structure and compound called cadmium sulphide which agree with (Reference code 01-089-0440) film show a strong preferential orientation at 2θ= 26.4 While, for a film after annealing process the diffraction peaks were at 2θ= 26.5, 30.6, 43.8, 51.9 and 54.4 correspond to the crystal plane (111), (200), (220), (311) and (222) the film have cubic structure and compound called Hawleyite which agrees with (Reference code 96-101-1252), the film shows a strong preferential orientation at 2θ= 26.5, moreover, a CdO cubic phase appeared after the annealing of the samples, indicated by the presence of diffraction peaks at 2θ = 33.0 and 38.5 correspond to the crystal plane (111), (220) (JCPDS card file no. 05-0640.), which formation of oxide phase is due to air ambient and high-temperature process given the CdO [11]. These results confirm that the deposition has proved more favorable as the intensities of peaks. The measured peaks are in good agree with others. the crystallinity of a cadmium sulphide thin film improve with annealing temperature which after annealing of cadmium sulphide thin films leads to improve the intensity of the diffraction peaks indicating the increase in a crystallinity of this films, the full width at half maxima (FWHM) increased from 0.3936 to 0.492 with annealing temperature. The increase of FWHM leads to a decrease in the crystallite size of the CdS thin films, the crystallization of the film improved with annealing which is related to the fact that the dislocation density and strain initially increases with the improvement of crystallization [12].

![Figure 2. The XRD patterns of the CdS thin film](image)

The crystallite size Dαω was calculated by using Debye-Scherrer’s relation [13] The lattice constants a and c of CdS structure can be calculated by using the unit cell program. The interplanar distance (d) is calculated using Bragg’s relation [14] Table 1 exhibit the values of interplanar distance, particle size, strain and dislocation density calculated using XRD patterns given in (figure 2) for different
XRD peaks which obtained lattice parameters 'a' & 'c' and the unit cell volume are in excellent agreement with the standard card values.

Table 1. X-ray diffraction parameter.

| Sample  | hkl   | FWHM [°2θ] | d-spacing | Crystallite size D | Dislocation δ | Strain € | lattice Constant a |
|---------|-------|------------|-----------|-------------------|---------------|-----------|-------------------|
| As deposit | 111 | 0.3939 | 3.46 | 5.1 | 0.0038 | 0.095 | 5.82 |
| Annealing | 111 | 0.4920 | 3.45 | 2.6 | 0.1479 | 0.119 | 5.83 |

The SEM image of the cadmium sulphide thin structure thin film is exhibited in Figure 3, which get it that the elements are Nanospheres or clusters-like shapes the structure uniformly grown on the entire surface of the substrate and exhibited that the CdS films are homogenous and well wrapped to the substrate without any cracks and pinholes at all samples.

Energy Dispersive X-ray Spectrometer, (EDAX) results are consistent with the formation of thin films of the cadmium sulphide deposited on silica glass substrates. This exhibit corresponds to a CdS thin film formation deposited on a layer of silica glass, which shown in Figure 4 and Table 2 when the suppose elements detected in the CdS thin film, the percentage of S, Cd, Si, and the small the portion In, Au, Na, Ca, Mg, And C elements are available in the thin film s.it is thought that these elements may probably result from the solution of the sol-gel and substrate.

Atomic force microscopy (AFM) The surface morphology of CdS thin film as-deposited and annealing temperature of 500 c are measured using AFM as shown in (Figure 5) which 3D images show the granular surface of the film surface with average and total grain increases from 256 to 829 of as deposit and annealing temperature 500 c which is due to the increase in grain boundary Movement, the average Roughness (Ravg) of the CdS thin films decreased from 26.6 to 5.64 nm, whereas the RMS roughness (Rq) values decreased from 36.6 to 8.15 nm of as deposit and annealing temperature 500 c as shown in Table 2 and figure (5). Therefore, The highest crystallinity, the lowest surface roughness, and the smallest particle size[15]
Figure 4. The EDAX of the CdS thin film structure

Table 2. roughness, RMS, avg. diameter and total grain of CdS thin films

| Substrate   | Roughness Avg. | Root mean square | Avg. diameter | Total grain |
|-------------|----------------|------------------|---------------|-------------|
| As-deposited | 26.6           | 36.6             | 139.74        | 256         |
| Annealing   | 5.65           | 8.15             | 115.53        | 829         |
3.2 Optical Properties

The learning of the optical properties absorption, transmission, and the energy gap (Eg) is important in understanding the behavior of semiconductor nanocrystals. The basic property of semiconductors is the separation of the energy gap 'tween the empty conduction band and the filled valence band. Photoexcitation of the electrons pass the energy gap is robustly allowed, which found The Absorption values decreased with annealing temperature and the Transmittance values increased with annealing temperature and As shown in the figure(6), all films are transparent in the visible region[16][17]. The optical performances of materials can be related to the surface roughness when The Energy gap of the films is determined from the energy gap evolution curves of the CdS thin films and the energy gaps were calculated from these curves which are found to be within 3.2–3.8 eV as shown in table 3 and figure (7)[18][12]. Therefore, The energy gap increases with the reduce of crystallite size[19] because of a decrease in the particle size and quantum size effect. This may be the reason for the decrease in particle size and turn increase in energy gap [20]. If the energy gap value is somewhat larger than the typical value for bulk CdS. This may be due to the quantum confinement effect due to the nanometer crystallite size of the cadmium sulphide thin film therefor It is well known that the bandgap energy depends on the particles Film size, crystal structure and strain [21] [22].
Table 3. The energy gaps and the values of crystallite sizes for the cadmium sulphide nanocrystalline films.

| Substrate  | Eg \((\text{Nanoparticle (Ev)})\) | Eg \((\text{Eg (bulk (Ev)})\) | Crystal size \((\text{nm)})\) | Reference |
|------------|----------------------------------|-----------------|-----------------|-----------|
| As-deposited | 3.2                              | 2.4             | 5.1             | [16]      |
| Annealing   | 3.8                              | 2.4             | 2.6             | [23]      |

Figure 6. The UV image of thin-film CdS structure

Figure 7. The energy gap of thin film CdS structure

4. Conclusion

The cadmium sulphide thin film was prosperously obtained by the spin coating technique annealing reason increase in peak intensity due to the improvement in the crystallinity If the energy gap value is somewhat larger than the typical value for bulk CdS. This may be due to the quantum confinement.
effect due to the nanometer crystallite size of the cadmium sulphide thin film. which makes the CdS is a promising material for optoelectronic application

References

[1] Z. R. Khan, M. Shkir, V. Ganesh, en S. Alfaify, “Linear and Nonlinear Optics of CBD Grown Nanocrystalline F Doped CdS Thin Films for Optoelectronic Applications: An Effect of Thickness Growth of Films”, 2018, doi: 10.1007/s11664-018-6437-9.
[2] A. Fernández-Pérez, C. Navarrete, E. Baradit, en M. Saavedra, “Modification of the junction parameters via Al doping in Ag / CdS : Al thin- film Schottky diodes for microwave sensors”, 2021.
[3] S. Yılmaz, I. Polat, M. Tomakin, en E. Bacaksız, “Transparent and conductive CdS:Ca thin films for optoelectronic applications”, Appl. Phys. A Mater. Sci. Process., vol 126, no 7, 2020, doi: 10.1007/s00339-020-03752-7.
[4] K. Karthik, S. Pushpa, M. M. Naik, en M. Vinuth, “Influence of Sn and Mn on structural, optical and magnetic properties of spray pyrolysed CdS thin films”, Mater. Res. Innov., vol 00, no 00, bl 1–5, 2019, doi: 10.1080/14328917.2019.1597436.
[5] M. Shkir et al., “A significant enhancement in visible-light photodetection properties of chemical spray pyrolysis fabricated CdS thin films by novel Eu doping concentrations”, Sensors Actuators, A Phys., vol 301, bl 111749, Jan 2020, doi: 10.1016/j.sna.2019.111749.
[6] L. Dhatcinamurthy, P. Thirumoorthy, L. Arunraja, en S. Karthikeyan, “Synthesis and characterization of cadmium sulfide (CdS) thin film for solar cell applications grown by dip coating method”, in Materials Today: Proceedings, 2019, vol 26, bl 3595–3599, doi: 10.1016/j.matpr.2019.08.219.
[7] S. Ullah, A. Bouich, H. Ullah, en M. Mollar, “Comparative study of binary cadmium sulfide (CdS) and tin disulfide (SnS2) thin buffer layers”, vol 208, no June, bl 637–642, 2020, doi: 10.1016/j.solener.2020.08.036.
[8] J. O. Emegha, J. Damisa, D. E. Elete, T. E. Arijaje, en P. Ogundile, “Growth and characterization of copper cadmium sulphide thin films”, 2021, doi: 10.1088/1742-6596/1734/1/012045.
[9] M. A. Islam, S. F. wa. M. Hatta, H. Misran, M. Akhtaruzzaman, en N. Amin, “Influence of oxygen on structural and optoelectronic properties of CdS thin film deposited by magnetron sputtering technique”, Chinese J. Phys., vol 67, bl 170–179, Okt 2020, doi: 10.1016/j.cjph.2020.06.010.
[10] J. Kovac et al., “Utilization of spray coated nano-crystalline cadmium sulfide thin film for photo-detector application Utilization of Spray Coated Nano-crystalline Cadmium Sulfide Thin Film for Photo-detector Application”, vol 030105, no October, 2020.
[11] N. Lejmi en O. Savadogo, “The effect of heteropolyacids and isopolyacids on the properties of chemically bath deposited CdS thin films”, Sol. Energy Mater. Sol. Cells, vol 70, no 1, bl 71–83, 2001, doi: 10.1016/S0927-0248(00)00412-8.
[12] I. Rathinamala, J. Pandiarajan, N. Jeyakumaran, en N. Prithivikumaran, “Synthesis and Physical Properties of nanocrystalline CdS Thin Films – Influence of sol Aging Time & Annealing Temperature”, vol 120, no 3, bl 113–120, 2014.
[13] Y. Al-douri et al., “Structural and optical insights to enhance solar cell performance of CdS nanostructures”, ENERGY Convers. Manag., vol 82, bl 238–243, 2014, doi: 10.1016/j.enconman.2014.03.020.
[14] S. Patra, P. Mitra, en S. K. Pradhan, “Preparation of nanodimensional CdS by chemical dipping technique and their characterization”, Mater. Res., vol 14, no 1, bl 17–20, Apr 2011, doi: 10.1590/S1516-14392011005000015.
[15] I. Bal, M. C. Baykul, en U. Saraç, “The effect of solution temperature on chemically manufactured cds samples”, Chalcogenide Lett., vol 18, no 1, bl 1–10, 2021.
[16] S. N. Vidhya en R. T. Karunakaran, “Structural, morphological, optical and diode properties
of chemical bath deposited nano-structured CdS thin films using EDTA as a complexing agent”, Mater. Sci. Pol., vol 37, no 3, bll 317–323, 2019, doi: 10.2478/msp-2019-0040.

[17] M. V. V. Prasad, K. Thyagarajan, en B. R. Kumar, “Effect of post-annealing temperature on linear and non-linear optical properties of sol-gel spin coated CdS thin films”, vol 7, no 3, bll 182–189, 2019.

[18] M. Thambidurai, … N. M.-C., en undefined 2009, “preparation and characterization of nanocrystalline CdS thin films.”, search.ebscohost.com, Toegang verkry: Nov 02, 2020. [Online]. Available at: http://search.ebscohost.com/login.aspx?direct=true&profile=ehost&scope=site&authtype=crawler&jrnl=15848663&AN=45003340&h=nlDAKn9xtzV%2FwTOhfJOpqCAWK%2BL5CWoOYDLZwSEmVIRiumwVCVHW6dBozsoNxBaMzL1TLHTZcIpTGWCD9A%3D%3D&crl=c.

[19] R. Devi, P. Purkayastha, P. K. Kalita, en B. K. Sarma, “Synthesis of nanocrystalline CdS thin films in PVA matrix”, Bull. Mater. Sci., vol 30, no 2, bll 123–128, Apr 2007, doi: 10.1007/s12034-007-0022-9.

[20] Ahmed Alaa Kandoh et al 2021 IOP Conf. Ser.: Earth Environ. Sci. 790 012073
[21] Salam Hussein Ewaid et al 2021 IOP Conf. Ser.: Earth Environ. Sci. 722 012008
[22] M. Dhanam, D. P. Devasia, B. Kavitha, en B. Maheswari, “Structural and optical analysis of CdS nanocrystals prepared by low temperature thermolysis”, Dig. J. Nanomater. Biostructures, vol 5, no 3, bll 587–592, 2010.

[23] M. Thambidurai et al., “Nanocrystalline CdS thin films prepared by sol-gel spin coating”, vol 102, no 100, bll 584–586, 2011.

[24] Salam Hussein Ewaid et al 2021 IOP Conf. Ser.: Earth Environ. Sci. 790 012075
[25] A. Info, “Preparation of Nanocrystalline CdS Thin Films by a New Chemical Bath Deposition Route for Application in Solar Cells as Antireflection Coatings”, vol 3, no 2010, bll 82–90, 2011.

[26] Ewaid, S.H.; Abed, S.A.; Al-Ansari, N. Water Footprint of Wheat in Iraq. Water 2019, 11, 535.

[27] N. P. I. Rathinamala, N. Jeyakumaran, “PREPARATION AND CHARACTERIZATION OF CdS NANO-FILMS VIA SOL – GEL METHOD AT DIFFERENT ANNEALING TIME”, vol 37, no 37, bll 47–51, 2016.