Effect Annealing Temperature on the Physical Properties of Cadmium Sulphide thin Films Deposited by using Thermal Evaporation Technique

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Abstract. This study measured some of the structural, electrical and optical properties of cadmium sulfide (CdS) thin films with thickness of 150 nm deposited on glass substrate by using thermal evaporation system under vacuum pressure 1x10⁻⁵ mbar. X-ray diffraction technology was used to analyses the structural properties of the CdS films. Results showed that the CdS films type cube polycrystalline structure and the preferred growth path was [111]. In evaluating DC conductivity, we observed two mechanism of activation energy. In the measuring Hall effect shows that the electrical conductivity of the CdS films is negative carriers (n-type). The result of the (AFM) measurements showed that the grain size and average roughness increased with annealing temperature increased. In optical properties it were found that transmittance 80% at RT that decreases with increasing annealing temperature. It also found that absorption coefficient, extinction coefficient and refraction index increased with increasing annealing temperature. Optical energy gap were found decreased with increasing annealing temperature as (RT, 150 and 300 C⁰) the results (2.4, 2.38 and 2.32 eV) respectively. The results electrical properties showed that the CdS thin films had two activation energy and Hall effect were found that the mobility increase with increasing annealing temperature.

1. Introduction
Cadmium sulfide (CdS) is one of the most suitable II – VI semiconductor materials for applications in solar cells technology. It is a direct band gap semiconductor having energy of 2.42 eV for single crystalline material at room temperature [1, 2]. It is n-type in electrical conduction and is widely used in the fabrication of electronic devices due to its unique optoelectronic features. Some of the applicable areas where CdS semiconductors have found optimum use fullness are: gas sensors [3–5], thin film field effect transistors [6], photo resistors [7], photo sensors [8–10]. The deposition methods and characteristics of cadmium sulfide semiconducting thin films has been received as considerable amount of interest due to their potential application in the area of electronic and opto-electronic devices fabrication such as solar cells [11, 12] thin film FET transistors, Light emitting diodes and photonic devices, CdS is employed to make nanocrystals, optical filters, and all optical switches [13, 14]. CdS can exist in two case of crystalline medications: the hexagonal (wurtzite) phase and the cubic (zincblende) phase [15]. Heat treatment is often used to tune the structure and properties of thin films such as CdS. It is because crystalline quality of the film plays an important role in the utilization of the CdS films for solar cell applications and thermal annealing leads to improve the crystalline quality of the films by the removal of strains, which can lead to the phase transition and thereby changing the band gap [16]. Also, such an annealing leads to phase transition from the metastable cubic phase to a stable hexagonal phase of CdS [17].

2. Experimental procedure
A Thermal evaporation technique was used to prepare CdS samples with high purity (99.999\%) on the glass substrates, before deposition, the samples were cleaned with alcohol and distilled water, dried with filtration paper and subjected to dry air current from a blower. Before deposition of the thin film, deposition electrodes from the aluminum material and using appropriate masks on the substrate using (Edward 306, coating unit) device under pressure \( 4 \times 10^{-5} \text{Torr} \), The distance between the samples and the boat was 20 cm. The thickness required (150 nm) for the prepared CdS films was calculated using the approximate weight method in accordance with the following
\[
m = 2\pi r^2 \rho t \quad \text{(1)}
\]
Where
That \( m \) is the mass of the material, \( r^2 \) is the distance between the boat/source and the Sample, \( \rho \) is the density of the material and \( t \) is the thickness of the film
Then, the samples put under oven with annealing temperature at 150°C and 300°C for 2 h.

3. Results and discussion
The results include the x-ray diffraction (XRD) of the CdS thin films, the findings of the electrical measurements (continuous conductivity and the Hall Effect) and the optical properties.

Structural properties
XRD
Studying the X-ray diffraction of the prepared CdS films with a thickness of 150 nm showed that the CdS films exhibit a cube-type polycrystalline structure. Moreover, grain size increases with rising annealing temperature because of the reduction in grain boundaries [18]. Figures (1) show the X-ray spectrum of CdS thin films.

![Fig (1): X-Ray spectrum of CdS thin film (a) at RT, (b) annealing at 150°C and (c) annealing at 300°C](image)

Atomic force microscopy (AFM)
The morphology of the surface of thin film must be investigated because of its influence on the efficiency of manufactured solar cells. This test determines the rates of granular size, surface roughness and square root roughness at different annealing temperature, as shown in Table (1). The images in two and three dimensions are shown in Figures (2). The AFM analysis indicates that grain size, root mean square (RMS), and average roughness increase with annealing temperature. This result is consistent with the study [19].
Fig (2): AFM photos CdS thin film (a) at RT, (b) annealing at 150°C and (c) annealing 300°C with two dimensions and three dimensions.

The table (1) shows the measurements of the atomic force microscope.

| sample | Annealing Temperature | Average Diameter nm | RMS Roughness nm | Ave Roughness nm |
|--------|-----------------------|---------------------|------------------|-----------------|
| CdS    | RT                    | 40.61               | 2.68             | 2.22            |
|        | 150°C                 | 50.83               | 6.19             | 5.27            |
|        | 300°C                 | 60.03               | 6.95             | 5.7             |

**Electric properties D.C electric conductivity**

The continuous conductivity of CdS films was measured by changing resistance with temperature to obtain information regarding the nature of the conductivity mechanism of the CdS films within the thermal range of (293k-433k). Then, the activation energy was calculated. Figures (3) show the relationship between the lnσ\text{d.c} of reverse temperature (1000/T) and the increase in continuous electrical conductivity with increasing temperature. This trend is one of the most important characteristics of semiconductors [20]. Evidently, the two types of activation energy corresponds to the results of the X-ray tests, that is, the films exhibit a polycrystalline structure and the activation energy can be calculated using the following equation[21]: The conductivity measurement indicates that continuous conductivity increases with annealing temperature as shown in Table (2).

σ\text{d.c}=σ\text{0} \exp (-E_a/kBT).......................... (2)
Fig (3): Change (Ln6) with (1000/T) of CdS (a) at RT, (b) annealing at 150C° and (c) annealing at 300C°

Table (2): activation energy of CdS thin film for various annealing temperatures

| Sample | Annealing Temperature | E1 eV | Range K | E2 eV | Range K | σRT Ω cm⁻¹ |
|--------|-----------------------|-------|---------|-------|---------|-------------|
| CdS    | R.T                   | 0.039 | 273-323 | 0.288 | 333-433 | 4.34 E-3    |
|        | 150C°                 | 0.013 | 273-323 | 0.208 | 333-433 | 0.138       |
|        | 300C°                 | 0.0107| 273-323 | 0.188 | 333-433 | 0.31        |

**Hall Effect**

Hall Effect measurements were performed at room temperature for pure CdS thin films to determine the type, concentration, and mobility of the majority of the charge carriers of these films. The pure CdS films are n-type, there by indicating that the majority of the charge carriers are the electrons, whereas the minority of the charge carriers are holes. This result may be attributed to the density of the Cd atoms, which act as a donors with a higher density than the S voids. From the measurement of the hall Effect, we observe that Mobility increases with annealing temperature as shown in Table (3). This trend is ascribed to an increase in grain size, which decreases grain boundaries.

Table (3): measurement of the Hall Effect of the CdS thin film for various annealing temperatures

| Sample | Annealing Temperature | RH cm²v | NH cm⁻³ | σHΩ cm⁻¹ | Type | H cm²/ν sec⁻¹ |
|--------|-----------------------|---------|---------|-----------|------|---------------|
| CdS    | R.T                   | -6.636 E+1 | 9.406 E+16 | 9.854 E-1 | n    | 6.539 E+1    |
|        | 150C°                 | -3.295E+4 | 1.895E+14 | 2.235E-3  | n    | 7.363E+1    |
|        | 300C°                 | -1.352E+7 | 4.616E+11 | 3.000E-5  | n    | 4.056E+2    |
Optical properties

The transmittance and absorbance of CdS films were recorded within the wavelength of (300-1100nm). Figure (10) shows transmittance as a function of the wavelength, it increases by increasing the wavelength. Pure CdS films exhibit good transparency in the visible and near-ultraviolet region where transmittance is approximately 80%. However, transmittance decreases with increasing annealing temperature as shown in figure (4). This result is consistent with researcher's result (Ragavendar et al) [22]

![Fig (4): Transmission of CdS thin film](image)

Energy gap is one of the most important optical constants that depends on the physical properties of semiconductors to manufacture electronic devices, such as solar cells, optical detectors and optical diodes. The energy gap of the pure CdS films was calculated by plotting the relationship between \((\alpha h\nu)^2\) and \((h\nu)\) as shown in figure (13), and from the straight line extension of the curve and its intersection with the x-axis. The energy gap was found to be (2.4) ev at room temperature. When the annealing temperature increases to 150 C\(^0\) and 300 C\(^0\), the energy gap of the CdS thin film decreased to 2.38 ev and 2.32 ev, respectively. These values are close to those in a previous study [23].

![Fig (5): optical energy gap of CdS thin film with relationship between\((\alpha h\nu)^2\) and \((h\nu)\)](image)

Equation (3) shows that the coefficient of extinction is related to the absorption coefficient. Through this equation, the coefficient of extinction of the CdS films can be calculated as follows.

\[
\frac{\alpha}{4\pi} \frac{\lambda}{\alpha} = k
\]
Figure (6) shows the change in the coefficient of extinction as a function of wavelength.

The refractive index was calculated using equation (4). The refractive index is associated with the coefficient of extinction and reflectivity, there, the refractive index increases with annealing temperature as shown in figure (7).

\[ n = \left( \frac{4R}{(R-1)^2} \right)^{1/2} - k^2 - \frac{(R+1)}{R-1} \]

Fig (7): The refractive index as a function of the wavelength.

The interaction between light and medium charges is due to the absorption of energy in the material and the subsequent polarization of medium charges. This polarization is typically described as the complex dielectric constant of the medium [24] the real and imaginary dielectric constant of the CdS films were calculated using equations (5) and (6).

\[ \varepsilon_r = n^2 - k^2 \]  \hspace{1cm} (5)
\[ \varepsilon_i = 2nk \]  \hspace{1cm} (6)

Figures (8) indication that the dielectric constant in the real and imaginary parts generally decreases with increasing wavelength.
Fig. 8(a): The real dielectric constant as a function of the wavelength,(b): The imaginary dielectric constant as a function of the wavelength

4. Conclusions

The effect of annealing on the structure .optical and electrical properties of CdS thin films deposited by thermal evaporation technique were studied. The polycrystalline structure is a cubic type, and the dominant orientation of growth is [111] The AFM images of CdS thin films that fabricated at different substrate temperatures shows that the smoothness and uniform thickness. The average grain sizes were CdS films were increased with increasing of substrate temperatures. The films show a direct optical energy gap (Eg opt), and it decreases with the increase of annealing temperature . The optical transmittance varied with the annealing temperature extinction coefficient, refractive index and absorption coefficient show an increase when the annealing temperature increases. CdS films exhibit high continuous electrical conductivity that increases with annealing temperature The Continuous conductivity of CdS film is negative type

References
[1] O. toma, R. Pascu, M. Dinescu, C. Besleaga, T.L. Mitran, N. Scarisoreanu, S. Antohe, 2011, Chalcogenide Letters, Vol. 8, No. 9, p. 541 – 548.
[2] C. Wu, J. Jie, L. Wang, Y. Yu, Q. Peng, X. Zhang, J. Cai, H. Guo, D. Wu, Y. Jiang, 2010, Nanotechnology, Vol. 21, 505203.
[3] A. Giberti, D. Casotti, G. Cruciani, B. Fabbri, A. Gaiardo, V. Guidi, C. Malagu, G. Zonta, S. Gherardi.2015, Sensors Actuators, B Chem., Vol. 207, 504–510.
[4] X. Jiao, L. Zhang, Y. Lv, Y. Su,2013, Sensors Actuators, B Chem., Vol. 186, 750–754.
[5] W. Kim, M. Baek, K. Yong, 2016, Sensors Actuators, B Chem., Vol. 223, 599–605.
[6] B. Mereu, G. Sarau, E. Pentia, V. Draghici, M. Lisca, T. Botila, L. Pintilie, 2004, Mater. Sci. Eng. B, Vol.109, 260–263.
[7] H. Sezen, A. A. Rockett, S. Suzer, 2012, Anal. Chem. 84, 2990–2994.
[8] B. G. An, H. R. Kim, M. J. Kang, J. G. Park, Y. W. Chang, J. C. Pyun, 2016, Anal. Chim. Acta, Vol. 927, 99–106.
[9] X. Li, C. Hu, Z. Zhao, K. Zhang, H. Liu,2013, Sensors Actuators, B Chem., Vol.182, 461–466.
[10] X. Li, Q. Yang, H. Hua, L. Chen, X. He, C. Hu, Y. Xi, J.2015, Alloys Compd., Vol.630, 94–99.
[11] Sung-Gi Hur and Eui-T K, Ji-Hong L, Geun-Hong K. 2008, Characterization of photoconductive CdS Thin films prepared on glass substrates for photoconductive-sensor applications. J. Vac. Sci. Technol. B, Vol. 26, 4: 1334-1337.
[12] Yasmeen Z D, Salah Q H, Saba J H, Najiba A H. 2015, Effect of Substrate Temperature on the Morphological and Optical Properties of Nanocrystalline ZnO Films Formed By DC Magnetron Sputtering. Journal of Applied Physics, Vol. 7, 1: 59-63.
[13] Demir R, Gode F. 2015, Structural, optical and electrical properties of nanocrystalline CdS thin films Grown by chemical bath deposition method. Chalcogenide Letters; Vol. 12, 2: 4350.
[14] Ashok Ch, Venkateswara K R, Shilpa Ch Ch, Rajendar V Lakshmi R N. 2014, Fabrication and Characterization of CdS Thin Films for the Solar Cell Applications. International Journal of Chem. Tech. Research; Vol. 6, 6:3367-3370.

[15] Oladiran A A, Oluwaseun A, Kolawole S Y. 2012, Study of optical and crystallographic properties of CBD grown CdS thin films. IJRRAS; Vol. 12, 3

[16] Han, Junfeng, et al. 2011 "Optimized chemical bath deposited CdS layers for the improvement of CdTe solar cells." Solar Energy Materials and Solar Cells, Vol. 95, 3: 816-820.

[17] Mishra S, Ingale A, Roy UN, Gupta A. 2007, Study of annealing-induced changes in CdS thin films Using X-ray diffraction and Raman spectroscopy. Thin Solid Films, Vol. 516:91-98.

[18] Metin, Hulya, Mehmet Ari, Selma Erat, Semra Durmuş, Mehmet Bozoklu, and Artur Braun. 2010. "The Effect of annealing temperature on the structural, optical, and electrical properties of CdS films." Journal of Materials Research, Vol.25, no. 1 : 189-196.

[19] Lee S, Lee ES, Kim TY, Cho JS, Eo YJ, Yun JH, Cho A. 2015, Effect of annealing treatment on CdS/CIGS thin film solar cells depending on different CdS deposition temperatures. Solar Energy Materials and Solar Cells. Vol. 1; 141:299-308.

[20] Choubey, Ravi Kant, Dipti Desai, S. N. Kale, and Sunil Kumar. 2016, "Effect of annealing treatment and deposition temperature on CdS thin films for CIGS solar cells applications." Journal of Materials Science: Materials in Electronics, Vol. 27, no. 8: 7890-7898.

[21] Mao, Ling-Feng, H. Ning, Changjun Hu, Zhaolin Lu, and Gaofeng Wang. 2016,"Physical modeling of activation energy in organic semiconductor devices based on energy and momentum conservations." Scientific reports, Vol. 6 : 24777.

[22] Mariappan, R., PonnuSwamy, V., Ragavendar, M., Krishnamoorthi, D., & Sankar, C. 2012, The effect of annealing temperature on structural and optical properties of undoped and Cu doped CdS thin films. Optik-International Journal for Light and Electron Optics, 123(12),1098-1102.

[23] Metin, H., and R. Esen. 2003, "Annealing studies on CBD grown CdS thin films." Journal of Crystal Growth, Vol. 258.1-2 : 141-148.

[24] NAFTALY, M., et al. 2016, Dielectric constants of bulk ferroelectric PZT measured by terahertz time-domain Spectroscopy. Advances in Applied Ceramics, Vol. 115. 5: 260-263