Structural, Morphology and Optical properties of Ag-doped Nanostructured CdS thin films

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Abstract

Chemical Spray Pyrolysis (CSP) method is employed to deposit CdS and Silver (Ag)-doped CdS films. The effect of Ag doping at 1, and 3 wt-% levels is considered. The principal X-ray diffraction peak was along (020) plane. Maximum grain size was observed at the (CdS:3% Ag) films. The dislocation density parameter increased from 53.04 to 37.08, whereas the strain(%) parameter decreases from 25.23 to 21.10. Atomic force Microscope (AFM) images indicate a polycrystalline structure, and reveal that the undoped CdS and doped CdS:Ag films have discontinuous surfaces with spherically grains decreased from (58.05 to 45.77 nm) with the increase of doping from 0% to 3%. Root-mean square (Rrms) roughness of surface is about (9.81-5.42) nm. Also, there was a clear decrement in transmittance as Ag increment. The optical energy bandgap $E_g$ has been decreased from 2.47 to 2.37 eV due to increase in Ag content. The absorption coefficients with photon energy increase with increasing concentration doping in Ag.

Keywords: CdS, spray pyrolysis, Ag doping, structural, AFM, optical properties, bandgap.

1. Introduction

Cadmium Sulfide (CdS) semiconductor material has solid hexagonal or cubic crystal with $E_g$ of 2.42 eV [1, 2]. It is utilized as window material while the electrical and optical properties can be easily manipulated by adding some different materials such as silver or indium atoms [3]. The growth of CdS thin films by CSP is progressed, by ion condensation of Cd$^{2+}$ and S$^{2-}$ ions on the substrate and homogeneous growth [4]. The optoelectronic properties of CdS thin films have been improved by doping with Ag$^{2+}$ ion having ionic radius (1.15Å) greater than that of Cd$^{2+}$ (0.97Å), similar investigation have been drawn with Pb$^{2+}$ ion [5]. Many methods are employed to prepare CdS thin films including vacuum evaporation [6], MBE [7], sputtering [8], printing [9], laser ablation (LA) [10], electro-deposition [11], SILAR [12], CBD [13], chemical spray pyrolysis [14-19], CVD [20] etc. CSP was selected for this research because it is costless, extremely clear and large area films with simple doping procedure. Previous studies focus on obtaining high quality CdS films by manipulating the parameters of CSP method, like deposition time, temperature, pH value and by varying the concentrations of various reagents as well as their complexing agents. In this work, Ag -doped CdS thin films at doping levels of 0, 1, and 3 wt-% have been studied.
2. Materials and Methods

The chemical sources of cadmium and sulphur ions to prepare CdS thin films were 0.01M Cd [C₂H₂CdO₄, MW=266.53] and 0.01M thiourea [CH₄N₂S, MW=76.12] respectively. Silver trichloride [(AgCl₃, MW=185.72] was used as a source of Ag ions. The molar ratio of dopant (AgCl₃) was changed from 0 to 3%. The foregoing are the prerequisites for preparation: The temperature of the substrate was 400°C, the space between spout and base was 29 cm, the spraying time was increased by 60 seconds to prevent cooling, the spray rate was 4ml/min, and the carrier gas was Nitrogen. The gravimetric approach was used to determine the film thickness, which was 300 ± 30 nm. XRD analysis was done by (SHIMADZU XRD-6000), while AFM analysis was done by (AA3000 SPM) to evaluate film topography. Absorbance spectra were recording utilizing Shimadzu spectrophotometer Model: UV-1800).

3. Results and Discussions

The XRD pattern of as prepared samples of CdS films doped with various weight content of Ag was recorded in the region of 2θ (20– 80)° and displayed in Figure(1) that shows peaks at 2θ= 26.25°, 36.99°, 57.30° and 63.30°, correspond to the (001), (020), (012) and (130) reflection planes of CdS with the standard data file JCPDS (43 -0985) which confirm that CdS crystals with relatively pure phases are obtained, The main peak was along (020) plane.

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Average crystallite size for the preferred reflection of (020) plane was calculated using the Scherrer formula (1) [21-24].

\[ D = \frac{0.9\lambda}{\beta\cos\theta} \]  \hspace{1cm} (1)

where λ is the wavelength of X-rays, β and θ are (FWHM) and Bragg’s angle respectively. D values were 13.73 to 16.42 nm with Ag level as seen in Table. 1

The dislocation density (δ) in thin films were obtained via the relation [25-28]:

\[ \delta = \frac{1}{D^2} \]  \hspace{1cm} (2)

The dislocation density (δ) has been found to vary from 53.04 to 37.08 with Ag concentration as listed in Table. 1

The strain (ε) gives information about material structure, and obtained by employing the following equation [29-32]:

\[ \varepsilon = \frac{\beta\cos\theta}{4} \]  \hspace{1cm} (3)

The strain (ε) has been found to vary from 25.23 to 21.10 with Ag concentration as listed in Table. 1

Figure (2) performs D, β, δ and ε vs. Ag content.
Figure 1. XRD-styles of deposited films.

Table 1. The obtained structural parameters $E_g$ and grain size of CdS films.

| Samples         | (hkl) Plane | $2\theta$ ($^\circ$) | FWHM ($^\circ$) | $D$(nm) | $E_g$(eV) | Dislocations density ($\times 10^{14}$)(lines/m$^2$) | Strain $\times 10^4$ |
|-----------------|-------------|----------------------|-----------------|--------|----------|-------------------------------------------------|-----------------------|
| Undoped CdS     | 020         | 36.99                | 0.61            | 13.73  | 2.47     | 53.04                                           | 25.23                 |
| CdS: 1% Ag      | 020         | 36.95                | 0.56            | 14.96  | 2.42     | 44.68                                           | 23.17                 |
| CdS: 3% Ag      | 020         | 36.90                | 0.51            | 16.42  | 2.37     | 37.08                                           | 21.10                 |
Figure 2. FWHM (a) D (b) δ (c) ε (d) of grown films.

Figure 3. shows AFM images of the of Undoped CdS and doped CdS:Ag films prepared by SPT. Figure 5 (a2, b2 and c2) shows three dimensional AFM images. Surface morphology of Undoped CdS and doped CdS:Ag films as noticed from the AFM micrographs assure that the spherical shape grains are uniformly distributed with average grain size of about (58.05-45.77) nm and average roughness (Ra) of surface was about (8.66-3.48) nm. Rrms was about (9.81-5.42) nm. The Data in Table 2 clarify AFM parameters PAFM indicating a high smooth surface.

Table 2. PAFM of grown films.

| Thin films  | Particle size Average nm | Ra (nm) | Rrms (nm) |
|-------------|--------------------------|---------|-----------|
| Undoped CdS | 58.05                    | 8.66    | 9.81      |
| CdS: 1% Ag  | 47.95                    | 7.84    | 7.59      |
| CdS: 3% Ag  | 45.77                    | 3.48    | 5.42      |
Samples optical properties were measured by means of UV-visible spectroscopy. When $I$ and $I_0$ are the measured intensities of outgoing and incoming waves, respectively, the Transmittance ($T$) is given by \( \% 100\% \) [33-37]:

$$T\% = \frac{I}{I_0} \times 100\% \quad (4)$$

Then absorbance ($A$) was calculated using [38-41]

$$A = \log_{10}(\frac{I}{I_0}) \quad (5)$$

Optical characteristics were investigated to study the influence of Ag doping levels. The transmission spectra are presented in Figure. 3. The optical transmittance decreases with increase in Ag concentration. The diagram shows that transmittance is maximum at (\(\lambda=550\text{nm}\)) transmission and with Ag incorporation to the CdS thin films decreases the transmittance and it reaches the value of 75\% at 3\% Ag doping. A reduction in absorption is achieved rising in transmittance. This may attribute to increase in levels near the band edges and increase the carrier concentration [42].
Figure 4: Transmittance with wavelength for CdS thin films and different doping of Ag concentration.

Figure 4 illustrates absorption coefficient ($\alpha$), the result shows that ($\alpha$) steadily increases with increasing photon energy for all samples. As photon energy increases, electrons with energy similar to that of band gap will interfere with photon. Consequently, a vast amount of electrons will interfere with the photon, causing the photon to be absorbed. Higher absorption coefficient materials absorb photons more readily, which excite electrons into the conduction band. Because of the decreased ($\alpha$) of the deposited Ag:CdS thin film, it is ideal for the construction of solar cells. $\alpha$ can be evaluated from the absorbance (A) according to (6) [43-46]:

$$\alpha = 2.3026 \frac{A}{t}$$

(6)

where $t$ is film thickness.
The bandgap energy of these prepared semiconducting films. Figure 6 offers the plot of $(\alpha h\nu)^2$ versus $h\nu$, where the best match line intersects the energy axis, yielding bandgap energy. Absorption coefficient plots of pure CdS and Ag:CdS films, in general, display a straight line section, showing that it is a direct semiconductor. The result of that the band gap $E_g$ shows in figure 5 of undoped and doped thin film. The decreased as increasing of Ag concentration for the 1% doped $E_g = 2.47eV$ and for the 3% doped $E_g = 2.42eV$, while $E_g = 2.37eV$ for the undoped sample. Decreases in $E_g$ can be traced mainly to defect-induced band tailing caused by the development of localized energy states along band edges. [47]. Rendering to inter-band absorption theory, the optical absorption coefficient for the direct allowed transition is given in Eq.7 [48-51].

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}}$$ (7)

where $A$ is a constant.
Figure 6. $(\alpha h \nu)^2$ against $h \nu$ of intended thin films.

The values of the extinction coefficient $K$ are calculated utilizing the following eq.8 [52-55]:

$$ K = \frac{a \lambda}{4\pi} \quad (8) $$

where $\lambda$ is the wavelength of the light.

Figure (7) depicts the variance of $K$, showing that $k$ increased and reached a high limit at 540 nm. The extinction coefficient increases and falls in direct proportion to light absorption; in the case of polycrystalline films, extra absorption of light occurs at the grain boundaries. This results in $k$ being non-zero for photon energies less than the fundamental absorption edge. [56]. The extinction coefficient value is increasing with the increasing Ag doping concentration at the wavelength range of 500-550nm. The incorporation of Ag$^{2+}$ ions to replace Cd$^{2+}$ gives rise to donor levels in the band gap of CdS material.
The refractive index $n$ can be obtained via following equation [57-60]:

$$n = \left[ \frac{4R}{(R - 1)^2} - k^2 \right]^\frac{1}{2} - \frac{(R + 1)}{(R - 1)}$$ (9)

Figure 7 shows the refractive index plot vs. wavelength. As seen in Fig. 8, all the films have maximum $n$ at 550nm. $n$ values decrease with increasing wavelength. As seen in Fig. 7, the values of $n$ change with doping of Ag and exhibit highest value at 3% Ag:CdS thin film is the highest value, compare to lowest value at of CdS film. This increased in $n$ values can be attributed to improvement of optical properties. A high $n$ parallel to a high $R_a$ and a smaller grain size, all of which help to minimize the effective mean free path due to increased surface scattering. [61].
Figure 8. Refractive index for CdS with different doping concentration of CdS: Ag thin films versus wavelength.

4-Conclusion

A low cost simple CSP method was utilized to grow CdS and Ag:CdS thin films. XRD analysis assures that the increase of Ag content improve the (020) preferential orientation. $D$ increases from 13.73 nm to 16.42 nm as Ag content increase, whereas the dislocation density parameter increased from 53.04 to 37.08, and the strain decrease from 25.23 to 21.10.

AFM images show the average diameter size was about (58.05-45.77) nm and root-mean square (rms) roughness of surface is about (9.81-5.42) nm. Effect of crystallite size attributed to the change in concentration of Ag doping.

The pure film gives maximum 85 % transmittance and the high doping gives 75% transmittance. The band gap changes from (2.47-2.42)eV with increasing Ag doping concentration. The absorption coefficient has a gradual increase in value with increase doping in Ag. The refractive index values change with doping of Ag to reach the highest value at 3% CdS:Ag.

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References

[1] Pankove J I Optical Processes in Semiconductors Dover Publication 1971.
[2] Romeo A Terheggen M Abou-Ras D Bätzner D L Haug, F-J Kälin M Rudmann D and Tiwari A N 2004 Research and Applications 12 (2-3) 93–111.
[3] Perna G Capozzi V Ambrico M Augelli V Ligonzo T Minafra A et al 2004 Thin Solid Films 453/454 187–94.
[4] Khallaf H I Oladeji O Chai G and Chow L 2008 Thin Solid Films 516(21) 7306.
[5] Anbarasi M Nagarethinam V S Baskaran R et al. 2016 Pac Sci Rev 18 72–77.
[6] Trajic J Glic M Romcevic N Romcevic M Stanisic G Hadzic B Petrovic M and Yahia Y S 2015 Sci. Sintering 47 145.
[7] Boieriu P Sporken R Xin Y Browning N and Sivananthan S 2000 J. Electron. Mater. 29 718.
[8] Kumar V Sharma D K Bansal M K Dwivedi D K Sharma T P 2011 Sci. Sinter 43 335.
[9] T.M. Khan, T. BiBi, SOP Trans. Appl. Phys. 1, 48 (2014).
[10] Zhang Y Ma H Wu D Li R Wang X Wang Y Zhu W Wei Q and Du B 2016 Biosens Bioelec 77 936.
[11] Kim W Baek M Yong K 2016 Sens. Actuat. B 223 599.
[12] Wilson K and Ahamed M 2016 Appl. Surf. Sci. 361 277.
[13] Yilmaz S Atasoy Y Tomakin M and Bacakisz E 2015 Superlat. Microstruct 88 299.
[14] Hassan E S Eltayef A K Mostafa S H Salim M H and Chiad S S 2019 Journal of Materials Science: Materials in Electronics 30(17) 15943-15951.
[15] Qader K Y Hadi E H Habubi N F Chiad S S Jadan M and Addasi J S 2021 International Journal of Thin Films Science and Technology 10 (1) 41-44.
[16] Hassan E S Khudhair D M Muhammad S K Jabbar A M Dawood M O Habubi N F and Chiad S S 2020 Journal of Physics: Conference Series 1660(1).
[17] Salloom H T Hadi E H Habubi N F Chiad S S Jadan M and Addasi J S 2020 Digest Journal of Nanomaterials and Biostructures 15(4) 1189-1195.
[18] Qader K Y Ghazi R A Jabbar A M Abass K H and Chiad S S 2020 Journal of Green Engineering 10(10) 7387-7398.
[19] D. Barreca, A. Gasparotto, C. Maragno, E. Tondello, J. Elec Electrochem. Soc. 151, G428 (2004).
[20] Habubi N F Mishjil K A and Chiad S S 2013 Indian Journal of Physics 87(3) 235-239.
[21] Hassan E S Mubarak T H Abass K H Chiad S S Habubi N F Rahid M H Khadayeir A A Dawod M O and Al-Baidhany I A 2019 Journal of Physics: Conference Series 1234(1) 012013.
[22] Khadayeir A A Hassan E S Chiad S S Habubi N F Abass K H Rahid M H Mubarak T H Dawod M O and Al-Baidhany I A 2019 Journal of Physics: Conference Series 1234 (1) 012014.
[23] Muhammad S K Hassan E S Qader K Y Abass K H Chiad S S and Habubi N F 2020 Nano Biomedicine and Engineering 12(1) 67-74.
[24] Chiad S S and Mubarak, T H 2020, International Journal of Nanoelectronics and Materials 13 (2) 221-232.
[25] Ali R S Sharba K S Jabbar A M Chiad S S Abass K H and Habubi N F 2020, NeuroQuantology 18(1) 26-31.
[26] Dawood M O Chiad S S Ghazai A J Habubi N F and Abdulmunem O M 2020 AIP Conference Proceedings 2213 (1) 020102.
[27] Hassan E S Mubarak T H Chiad S S Habubi N F Khadayeir A A Dawood M O and Al-Baidhany I A 2019 Journal of Physics: Conference Series 1294(2).
[28] Khadayeir A A Hassan E S Mubarak T H Chiad S S Habubi N F Dawood M O and Al-Baidhany I A 2019 Journal of Physics: Conference Series 2019 1294 (2)

[29] Chiad S S Noor H A Abdulmunem O M and Habubi N F 2019 Journal of Physics: Conference Series 1362(1).

[30] Ghazai A J Abdulmunem O M Qader K Y Chiad S S and Habubi N F 2020, AIP Conference Proceedings 2213 (1) 020101.

[31] Othman M S Mishjil K A Rashid H G Chiad S S Habubi N F and Al-Baidhany IA 2020 Journal of Materials Science: Materials in Electronics 31(11) 9037-9043.

[32] Nasr. I. Najm, Hanan K. Hassun, Bushra K. H. al-Maiyaly, Bushra H. Hussein, and Auday H. Shaban, “Highly selective CdS:Ag heterojunction for photodetector applications,” AIP Conference Proceedings 2123, 020031 (2019).

[33] Jandow N N Othman M S Habubi N F Chiad S S Mishjil K A and Al-Baidhany I A 2020 Materials Research Express 6 (11) 2020.

[34] Abdulmunem O M Jabbar A M Muhammad S K Dawood M O Chiad S S and Habubi N F 2020 Journal of Physics: Conference Series 1660 (1).

[35] Hussin H A Al-Hasnawy R S Jasim R I Habubi N Fand Chiad S Journal of Green Engineering, 10(9)7018-7028.

[36] Al Rawas A S Slewa MY Bader B A Habubi N F and Chiad S S 2020 Journal of Green Engineering10 (9) 7141-7153.

[37] Hassan E S Qader K Y Hadi E H Chiad S S Habubi N F and Abass K H 2020 Nano Biomedicine and Engineering 12(3) 205-213.

[38] Chiad S S Noor H A Abdulmunem O M Habubi N F Jadan M and Addasi J S 2020 Journal of Ovonic Research 16 (1) 35-40.

[39] Chiad S S Alkelaby A S and Sharba K S 2019 Journal of Global Pharma Technology 11(7) 662-665.

[40] Salam Hussein Ewaid et al 2020 J. Phys.: Conf. Ser. 1664 012143.

[41] Ahmed Sabah Al-Jasime et al 2020 J. Phys.: Conf. Ser. 1664 012141.

[42] Ewaid, S.H.; Abed, S.A.; Al-Ansari, N.; Salih, R.M. Development and Evaluation of a Water Quality Index for the Iraqi Rivers. Hydrology 2020, 7, 67.

[43] Hadi E H Abbsa M A Khadayeir AA Abood Z M Habubi N F and Chiad SS 2020 Journal of Physics: Conference Series 1664(1).

[44] Jadhav UM, shinde MS, Patel SN, Patil RS (2014). Structural, optical and electrical properties of nanocrystalline cadmium sulphide (CdS) thin films deposited by novel chemical route. Indian J. pure appl. Phys. 52:39-43

[45] Khadayeir A A Jasim R I Jumaah S H Habubi N F and Chiad S S 2020 Journal of Physics: Conference Series 1664(1).

[46] Hadi E H Sabur D A Chiad S S Habubi N F and Abass K H 2020 Journal of Green Engineering 10(10) 8390-8400.

[47] Ghazai A Qader K Fadhil H N Chiad S S and Abdulmunem O 2020 IOP Conference Series: Materials Science and Engineering 870 (1).

[48] Ahmed N Y Bader B A Slewa M Y Habubi N F and Chiad S S 2020 NeuroQuantology 18(6) 55-60.

[49] S. Chandramohan, T. Strache, S.N. Sarangi, R. Sathyamoorthy and T. Som, Mater. Sci. Eng. B, 2010, 171, 16.
[50] Chiad S S Abass K H Mubarak T H Habubi N F Mohammed M K and Khadayeir A A 2019 Journal of Global Pharma Technology 11(4) 369-375.

[51] Alkelaby A S Abass K H Mubarak T H Habubi N F Chiad S S and Al-Baidhany I 2019 Journal of Global Pharma Technology 11(4) 347-352.

[52] Khadayeir A A Abass K H Chiad S S Mohammed M K Habubi N F Hameed T K and Al- Baidhany IA 2018 Journal of Engineering and Applied Sciences 13 (22) 9689-9692.

[53] Habubi N F Oboudi S F and Chiad S S 2012 Journal of Nano- and Electronic Physics 4(4) 04008 (4).

[54] Latif D M A Chiad S S Erhayief M S Abass K H Habubi N F and Hussin H A 2018 Journal of Physics: Conference Series 1003(1) 012108.

[55] Jandow NN Habubi NF Chiad S S Al-Baidhany I Aand Qaeed MA 2019 International Journal of Nanoelectronics and Materials 12(1) 1-10.

[56] Chiad S S Habubi N F Abass W H and Abdul-Allah M H 2016, Journal of Optoelectronics and Advanced Materials 18 (9-10) 822-826.

[57] Sharba K S Alkelaby A S Sakhil M D Abass K H Habubi N F and Chiad S S 2020 NeuroQuantology 18(3) 66-73.

[58] J. C. Manifacier, J. Gasiot and J. P. Fillard, J. Phys. E. : Scientific Instruments, 9 (1989).

[59] Ahmed F S Ahmed N Y Ali R S Habubi N F Abass K H and Chiad S S 2020 NeuroQuantology 18 (3) 56-65.

[60] Habubi N F Abass K H Chiad S S Latif D M A Nidhal J N and Al Baidhany A I 2018 Journal of Physics: Conference Series 1003 (1) 012094.

[61] Muhammad S K Dawood M O Ahmed N Y Hassan E S Habubi N Fand Chiad S S 2020 Journal of Physics: Conference Series 1660(1).

[62] Hadi E H Sabur D A Chiad S S Habubi N F and Abass K H 2020 Journal of Green Engineering 10(10) 8390-8400.

[63] Rajashree C Balu A R and Nagarethinam V S 2014 Int. J. ChemTech. Res. 6(1) 347–360.

[64] Alfrdji, E. H. O. (2020). An Efficient Technique for solving Lane-Emden Equation. Al-Qadisiyah Journal Of Pure Science, 25(1), math 1-10.

[65] Alsabbagh, A. R. A. A., & Al-taai, E. A. (2020). ON THE STABILITY CONDITIONS OF 2D TIME FRACTIONAL DIFFUSION EQUATION . Al-Qadisiyah Journal Of Pure Science, 25(1), math 11-15.