



Comparison of the physical properties for CdS and CdS doped PVA thin films prepared by spray pyrolysis

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Abstract

Cadmium sulphide (CdS) and CdS doped with PVA semiconductor thin films were prepared by chemical spray pyrolysis technique. The thickness of the films was varied in the range (1.281, 1.367, 1.421, 1.485) μm and (1.722, 1.776, 1.873, 1.938) μm for CdS and PVA doped films respectively. This parameter has affected the physical properties of the specimens. The films were characterized by X-ray diffraction (XRD). XRD patterns were indicated the presence of hexagonal phase of CdS, and with the increase of film's thickness the grain size has increased. The optical absorption spectra showed that the CdS films have a direct band gap value of (2.4-2.55) eV and (2.425-2.75) eV for doped samples with PVA.

Keywords: CdS; PVA; Thin films.

PACS: 61.46.-w; 62.25.-g; 68.55.-a.

1. Introduction

CdS is a technologically useful material, as many devices based on CdS, including sensors have come up in the recent years [1]. CdS has been used as a window material in high efficiency thin film solar cells based on CdTe and Cu(In,Ga)Se₂(CIGS). Cadmium sulfide (CdS), due to its wide band gap (2.42 eV), photoconductivity, and high electron affinity, is known to be an excellent heterojunction partner for p-type cadmium telluride (CdTe), p-type copper indium diselenide (CuInSe₂), and/or Cu(In,Ga)Se₂(CIGS) [2,3]. CdS has also been used in other applications including electronic and optoelectronic devices [4-6]. In the past few decades, several techniques such as thermal evaporation [7], radio frequency sputtering [8], physical vapor deposition [9], pulsed laser evaporation [10], molecular beam epitaxy [11], electro deposition [12], spraypyrolysis [13], metal organic chemical vapor deposition [14], successive ionic layer adsorption reaction [15], screen printing [16], close spaced vapor transport [17], and chemical bath deposition(CBD)[18,19], have been used in the deposition of CdS thin films. Over the years, different cadmium sources have been used in this process, such as cadmium sulfate [9, 10], cadmium acetate [11-15], cadmium iodide/nitrate [16-19], and cadmium chloride [12, 19]. The effect of Cd source on the film properties has been drawn attention for some Kitaev et al. [18]found that when CdCl₂ was used as a Cd source, the CdS film thickness was higher than using Cd(CH₃COO)₂, CdSO₄, or Cd(NO₃).

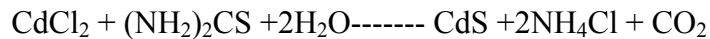
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One of the most promising techniques for producing large areas of inexpensive CdS film for terrestrial photovoltaic application is spray pyrolysis and here we followed this method to synthesize the CdS films and to study the effect of PVA doping due to its versatile physical properties and can filled industrial structure and film thickness on the optical and structural properties.

2. Experimental

2.1 CdS Films Preparation

The CdS thin films were prepared by taking a 0.1 M aqueous solution of thiourea and 0.1 M aqueous solution of cadmium chloride as starting solutions. Also CdS thin films were prepared from different number of spray (1 spray, 2 spray, 3spray, 4 sprays). The solutions were mixed thoroughly and final solution was sprayed onto heated substrates kept at temperature 400°C. The substrates were microscopic plane glass slides of area 2.5x 7.6 cm². The usual cleaning of the glass slides were first carried out. When the solution is sprayed the following reaction takes place at the surface of the heated substrate,



The yields a uniform growth of CdS films on the substrates. The duration for spraying was for a limited period which is about 4 second, and the distance from the heater to the end of the capillary tube is 20cm, then the yellow-orange deposit layer appeared on the substrate. After completing this experiment it was repeated with addition of PVA to the mixed solution.

The deposited CdS films are characterized by structural and optical properties under different growth conditions.

2.2 Techniques

Optical absorption measurements have been carried out using uv-visible spectrophotometer and XRD spectra for determining the structure of the films.

3. Results and Discussion

3.1 Structural Properties

As is well known, Cds can exist in two crystalline structures: the hexagonal (wurtzite) phase and the cubic (zinblende)phase .The patterns show a polycrystalline structure with mixed phase (cubic and hexagonal)]. Figure 1 and 2 show a comparative X-ray diffraction spectra of CdS films grown by spraypyrolysis processes on glass slide substrates. These spectra showed that the films have highly oriented crystallites with a preferential orientation along the c- axis (002) direction perpendicular to the substrate plane. The (002) diffraction line localized at 26.6 approximately, and the weak peak at approximately 24.8, 28.4, and, 43.7 which match with the (100), (101), and, (103) diffraction lines of hexagonal phase CdS, this result is in good agreement with other authors [20-23].

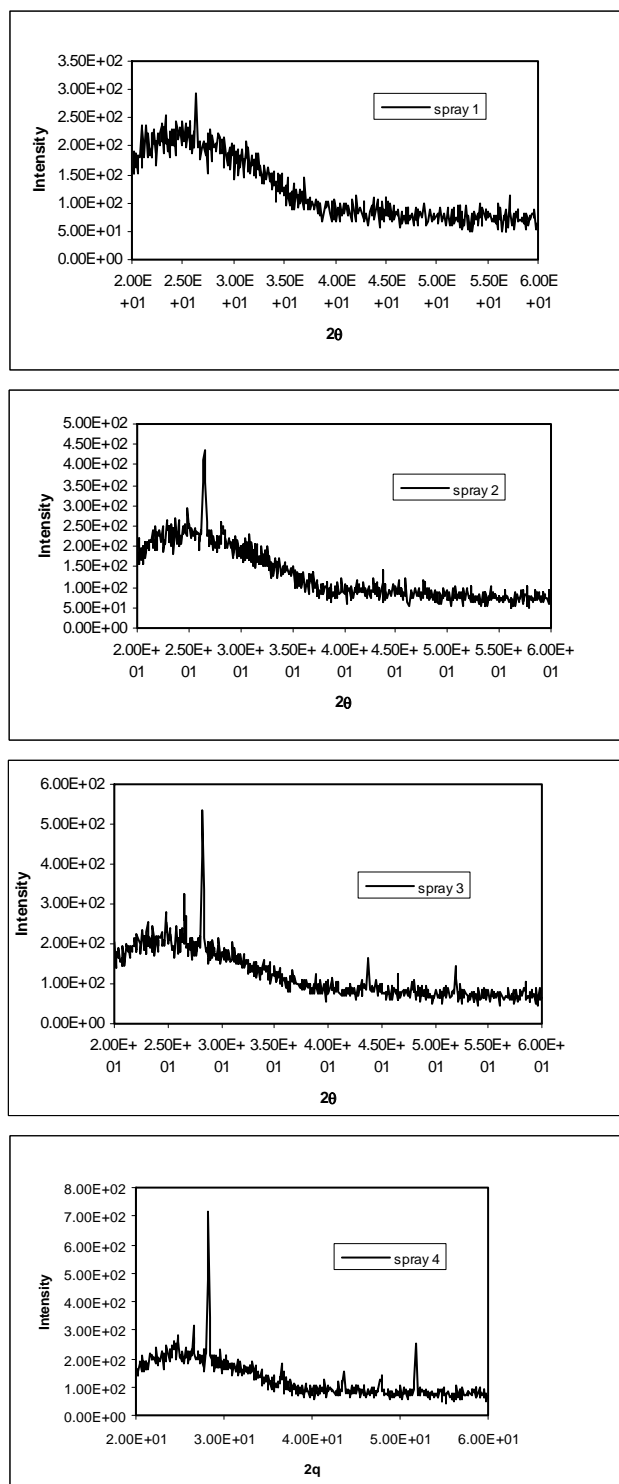


Figure 1: X-ray diffractograms of sprayed CdS films with different thickness.

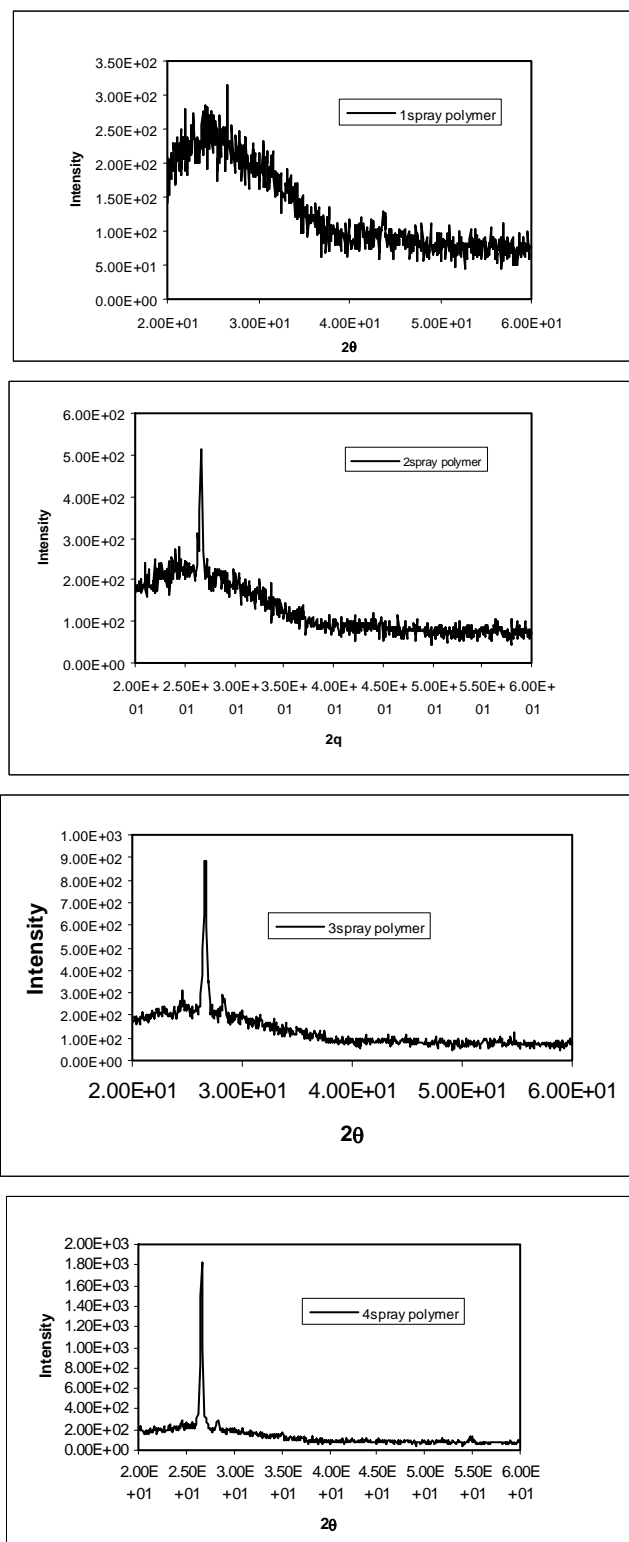


Figure 2: X-ray diffractograms of sprayed CdS films doped by PVA polymer with different thickness.

A comparison between the spectra of the films (with and without PVA) shows that there are more crystallization lines and more orientation of the crystal growth in the case of thicker film. The line (002) became stronger with increase thickness; (100), (101), and, (103) also appears with increase of the thickness. This means the thicker film has better crystalline

quality and the existence of polymer increase the crystalline of the films as indicated from XRD spectra.

The relative change of the full width at half maximum (FWHM) is shown in Figure 3. Increase thickness, a well crystallized film was obtained. Phase identification revealed that hexagonal CdS is formed. However Ashour [23] Battisha et. al [24], Lankaitis et al [25], and Ashour et al [26] using spraypyrolysis and different techniques, obtain a single phase of hexagonal phase of CdS thin films. Thus, the preparation conditions of this technique affect the resulting micro structural characteristics, such as crystallinity.

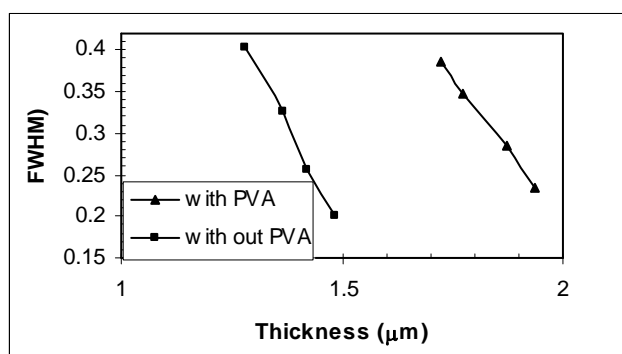


Figure 3: Effect of films thickness on the full width half maximum.

The effect of thickness on grain size (GS) of the obtained phase was also investigated. If the broadening is due only to the effect of crystallite size, grain size can be simply determined from the (002) diffraction line the Scherrer formula:

$$GS = k\lambda / \beta \cos \theta$$

Where β is the full width at half maximum (FWHM) of peak, λ is the wavelength of the X-ray, and k is the Scherrer constant (which generally depends on the crystallite shape) and equal to 0.94. The grain size calculated by Scherrer formula the XRD data, the small grain size, which is due to the evaporation of individual fine droplets during the sprayed process is undesirable for most semiconductor applications because of the barrier effects of grain boundary on the mobility in planar direction[27]. The grain size was found to be increase with increase films thickness (see Figure 4.), which is the same behavior as reported in [24]. These grain sizes for film doped by PVA are smaller than those without PVA, and thus the increasing of films thickness decreases the density of nucleation centers and under these circumstances, a smaller number of center start to grow, resulting in large grain. The results are summarizes in Table 1.

Table 1: Variation of thickness, FWHM, and grain size, of CdS films (with PVA, and without PVA) with different number of spray

Number of spray	Thickness(μm)		FWHM		Grain Size(nm)	
	With PVA	Without PVA	With PVA	Without PVA	With PVA	Without PVA
1SP	1.73	1.281	0.3856	0.4025	0.385	0.353
2SP	1.78	1.367	0.3485	0.3250	0.415	0.396
3SP	1.87	1.421	0.2854	0.2550	0.474	0.531
4SP	1.94	1.485	0.2334	0.2001	0.637	0.7164

Scanning electron microscope is a convenient technique to study the microstructure of the films and as it is now out of our reach, we will depend only on the information from the XRD.

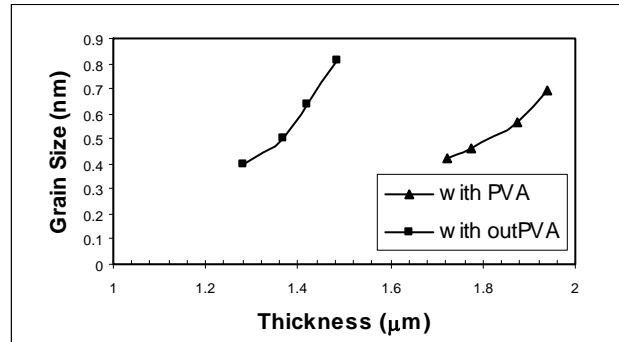
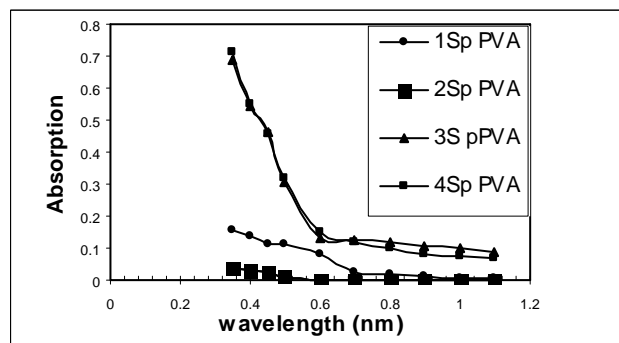


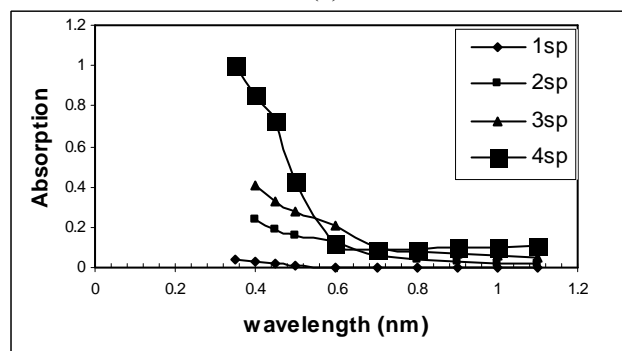
Figure 4: Effect of films thickness on the grain size.

3.2 Optical Properties

The optical properties of the spray pyrolysis CdS films (with and without PVA) are different to those produced by using other methods. Figure 5 and 6 presented the variation of the optical absorption and transmission as a function of the wavelength for films prepared at different thickness. The films with low thicknesses (with and without PVA) have a low absorption and high transmission while the films at high thicknesses have high absorption and low transmission. It can be observed that in general an increase in thickness improved the absorption or transmission. This improvement can be attributed to the perfection, stoichiometry of the films [23] depending on the film deposition conditions.

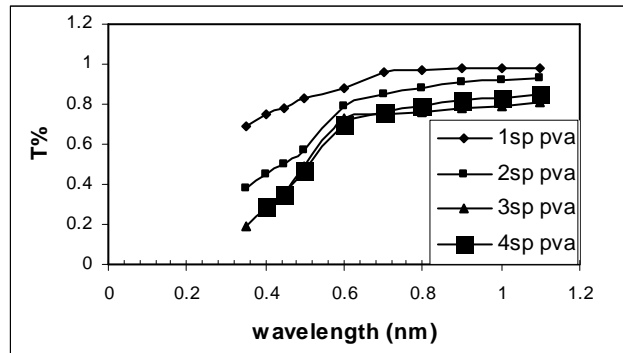


(a)

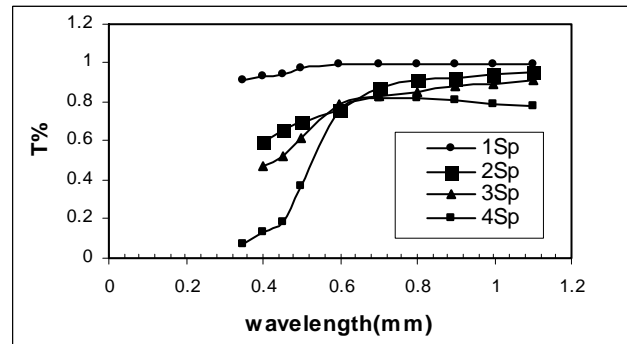


(b)

Figure 5: Absorption vs versus wavelength for CdS films sprayed at different thickness (a) with PVA (b) without PVA.



(a)



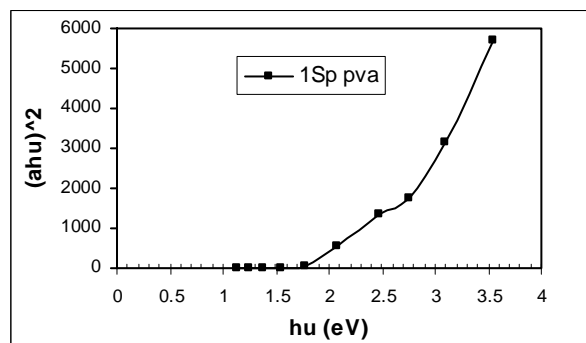
(b)

Figure 6: Transmittance vs versus wavelength for CdS films sprayed at different thickness (a) with PVA (b) without PVA.

The semiconductor band gap E_g was determined by analyzing the optical data with the expression for the optical absorbance α and the photon energy $h\nu$ [23] using the relation;

$$\alpha = K (h\nu - E_g)^{n/2} / h\nu$$

Where K is a constant and n is a constant which is equal to one for a direct-gap material. As shown in Figure 8 and 9. The plot of $(\alpha h\nu)^2$ versus $h\nu$ was analysed using the above equation. Extrapolation of the linear portion of the plot to the energy axis yielded the direct band gap value (2.425-2.75)eV for films with PVA and (2.4-2.55)eV for films without PVA, which agreement with the reported value by others [23-26].



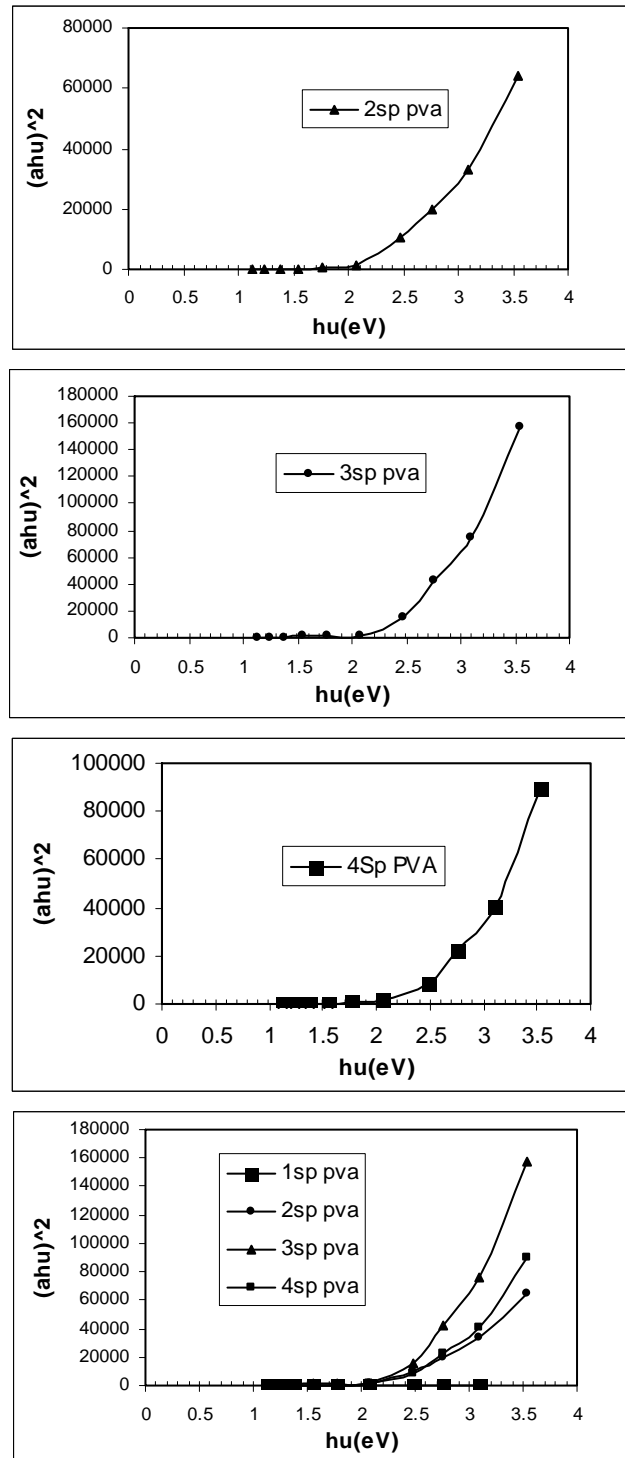


Figure 7: Variation of $(\alpha hu)^2$ with photon energy for films sprayed at various thickness with PVA.

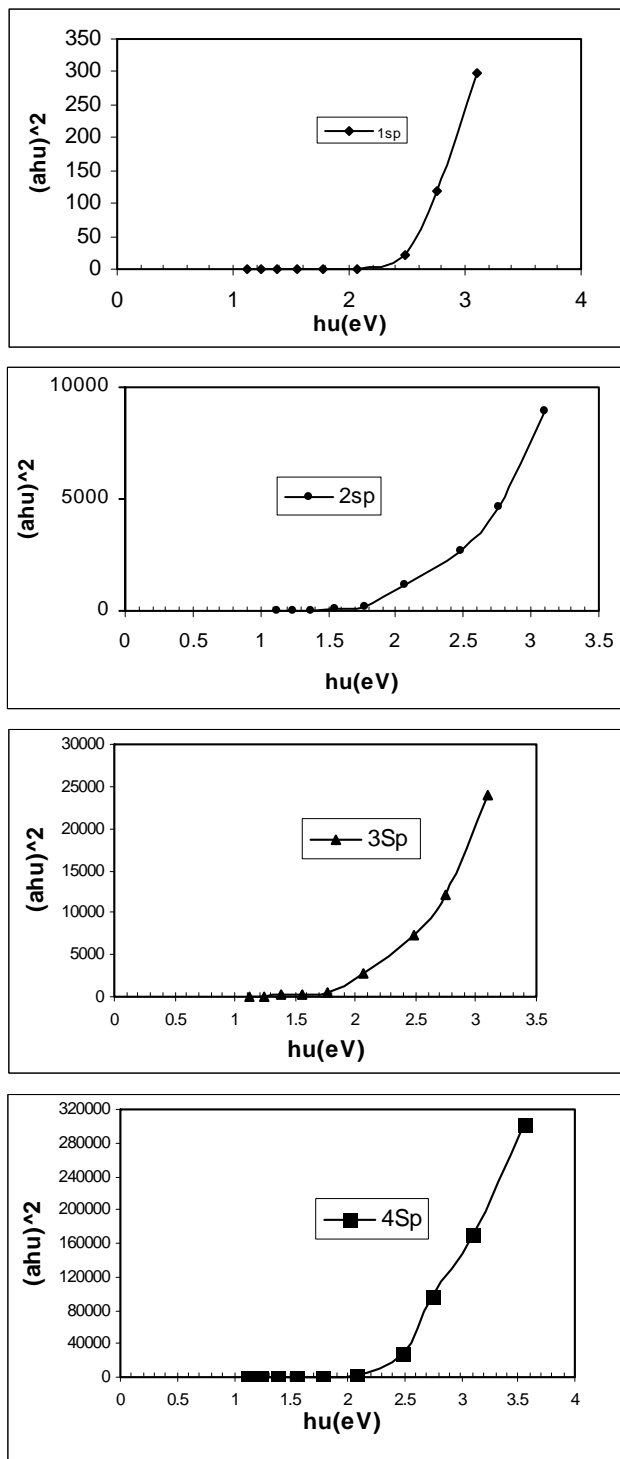


Figure 8: Variation of $(\alpha hu)^2$ with photon energy for films sprayed at various thickness without PVA.

We could observe E_g for films doped with PVA is higher than their values for films without PVA (Table 2) i.e there is a blue shift of the absorption edge. This difference is due to the existence of PVA and the band gap is increased due to an interstitial between PVA and CdS states within the prepared structure in agreement with Devi et al results [28]. They synthesizes nanocrystalline CdS thin films in PVA matrix and also reported a direct band material relation similar to the above to obtain the energy gap. As presented in Table 2, the

values of energy gap which obtained in this work are approximately equal to the range of values of Devi et al [28]. They found that the increment in the value of energy gap is inversely proportional to the square of the crystallite size and the value of the band gap in our work increases with decrease of crystallite size in qualitative trends with their findings. In this work, however, the increment in the value of energy gap is in general indirectly proportional to the crystallite size (Table 1) and the value of the band gap in this work increases with the decrease of the crystallite size.

Table 2: Band gaps for CdS nanocrystalline films (with and without PVA) for different numbers of spray

Number of spray	Band gaps (E_g) eV	
	With PVA	Without PVA
1SP	2.425	2.4
2SP	2.5	2.45
3SP	2.65	2.5
4SP	2.75	2.55

Existing polymer is suggested to be used for improving the efficiency of photovoltaic devices such as the solar cell. In addition the organic polymers may provide lighter weight, flexible and cheaply produced as alternative to the conventional bulk semiconductor solar cells

This work is to be followed by Conductivity measurement, C -V characteristic measurement and SEM & AFM measurement.

Comparing with the other methods that are used to synthesis semiconductors thin films, CBD is relatively simple, cost effective, produce high quality thin films cover wide area as well as it is low energy method [29]. It is also widely used to grow nanocrystalline thin films or other type of nanostructure such as nanoflowers [30-31].

There are, however, two important advantages for CdS-polymer nanocomposites, the first that the polymer matrix can make nanometer scale CdS clusters and lead to improving the stability, dispersion and mechanical strength of the materials. The second advantage is that the surface of the CdS nanoparticles could be modified by the polymeric matrix via the interactions between the two components [32].

4. Conclusion

The content of this paper can be summarized by the following statement;

1. CdS films were fabricated by spray pyrolysis using a solution of cadmium chloride and thiourea.
2. The films were deposited onto glass substrates at different thickness.
3. The films with different thickness, with, and, without PVA were found to have influenced the phase and preferred orientation of the films.
4. The films prepared at low thickness have the least crystalline quality, and as increase the thickness; the quality of crystallinity improved.
5. The existence of PVA increases the quality of crystallinity.
6. Increase thickness increase in grain size.
7. Optical properties of CdS thin films were studies using absorption and transmittance spectra.
8. The films have good optical quality properties larger grain size and are well suited for solar cell applications.

The optical gap was calculated and shown a good agreement with other results which suggest that the method of spray pyrolysis for the deposition of CdS thin films should be further considered towards the application and fabrication of a solar cell.

References

- [1] A. Ashour, R. D. Gould and A. A. Ramadan, *Phys. Stat. Sol.* **125** (1991) 541
- [2] A. Ashour, *Turk J Phys.* **27** (2003) 551
- [3] A. Davis, K. Vacearo, H. Dauplaise, W. Waters and J. Lorenzo, *J. Electrochem. Soc* **146** (1999) 1046
- [4] Aguilar-Hernandez, G. Contreras-Puente, A. Morales-Acevedo, O. Vigil-Galan, F. Cruz-Gandarilla, J. Vidal-Larramendi, A. Escamilla-Esquivel, H. Hernandez-Contreras, M. Hesiquio-Garduno, Arias-Carbajal, M. Chavarria-Castaneda and G. Arriaga-Mejia, *Semicond. Sci. Technol.* **18** (2003) 111
- [5] C. Dai, L. Horng, W. Hsieh, Y. Shih, C. Tsai and D. Chuu, *J. Vac. Sci. Technol. A.* **10** (1992) 484
- [6] C. Tsai, D. Chuu, G. Chen and S. Yang, *J. Appl. Phys.* **79** (1996) 9105
- [7] C. Voss, Y. Chang, S. Subramanian, S. Ryu, T. Lee and C. Chang, *J. Electrochem. Soc.* **151** (2004) C655
- [8] F. A. Kasim, M. A. Mahdi, J. J. Hassani, S. K. J. Al-Ani and S. J. Kasim, *Int. J. Nanoelectronics and Materials* **5** (2012) 57-66
- [9] G. Kitaev, A. Uritskaya and S. Mokrushin, *Russ. J. Phys. Chem.* **39** (1965) 1101
- [10] G. Laukaitis, S. Lindoor, S. Tamulevicius and M. LeskelTM, *Applied Surface Science* **185** (2001) 134
- [11] H. Uda, H. Yonezawa, Y. Ohtsubo, M. Kosaka and H. Sonomura, *Sol. Energy Mater. Sol. Cells* **75** (2003) 219
- [12] I. K. Battsha, H. H. Afify, G. Abd El-Fattah and Y. Badr, *Fizika* **248** (2002) 253
- [13] I. Oladeji, L. Chow, C. Ferekides, V. Viswanathan and Z. Zhao, *Sol. Energy Mater. Sol. Cell* **61** (2000) 203
- [14] M. A. Mahdi and S. K. J. Al-Ani, *Int. J. Nanoelectronics and Materials* **5** (2012) 11-24
- [15] M. A. Mahdi, Asmiet Ramizy, Z. Hassan, S. S. Ng, J. J. Hassan and S. J. Kasim, *Chalogen. Lett.* **9** (2012) 19
- [16] M. A. Mahdi, S. J. Kasem, J. J. Hassen, A. A. Swadi and S. K. J. Al-Ani, *Int. J. Nanoelectronics and Materials* **2** (2009) 163-172
- [17] M. Conteras, M. Romero, B. To, F. Hasoon, R. Noufi, S. Ward and K. Ramanathan, *Thin Solid Films* **403/404** (2002) 204
- [18] M. Ilieva, D. Dimova-Malinovska, B. Ranguelov and I. Markov, *J. Phys. Condens. Matter* **11** (1999) 10025
- [19] M. Sasagawa and Y. Nosaka, *Electrochim. Acta* **48** (2003) 483
- [20] O. Vigil-Galan, J. Larramendi, I. Riech, G. Rodriguez, A. Iribarren, J. Aguilar-Hernandez and G. Contreras-Puente, *Semicond. Soi. Technol.* **17** (2002) 1193

- [21] O. Vigil-Galan, J. Ximello-Quiebras, J. Aguilar-Hernandez, G. Contreras-Puente, A. Cruz-Orea, J. Mendoza-Alvarez, J. Cordona-Bedoya, C. Ruiz and V. Bermudez, *Semicond. Soi. Technol.* **21** (2006) 76
- [22] P Raji, C Sanjeeviraja and K Ramachandran, *Bull. Mater. Sci.* **28** (2005) 233
- [23] P. Boieriu, R. Sporcken, Y. Xin, N. Browning and S. Sivananthan, *J. Electron. Mater.* **29** (2000) 718
- [24] R. Birkmire, B. McCandless and S. Hegedus, *Int. J. Sol. Energy* **12** (1992) 145
- [25] R. Buckley, J. Woods, *J. Phys. D. Appl. Phys.* **6**, 1084, 1973
- [26] R. Devi, P. Purkayastha, P. K. Kalita and B. K. Sarma, *Bull. Mater. Sci.* **30** (2007) 123
- [27] R. Naciri, H. Bihri, A. Rahioui, M. Abd-Lefdil and C. Messaoudi, *Revue des Energies Renouvelables CER 07 Oujdo* (2007) 165
- [28] S. Al Kuhaimi, *Vacuum* **51** (1998) 349
- [29] Shadia J. Lkhmayies and Riyad N. Ahmad-Bitar, *American Journal of Applied Sciences* **5** (9) (2008) 1141
- [30] Shadia J. Lkhmayies and Riyad N. Ahmad-Bitar, *GCREEDER* (2009) Amman-Jordan, March 31st- April 2nd 2009
- [31] Y. Ma, A. Fahrenbruch and R. Bube, *Appl. Phys. Lett.* **30** (2000) 423
- [32] Y. Y. Ma and R. H. Bube, *J. Electrochem. Sci.* **124** (1977) 1430