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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF SOL-GEL DEPOSITED FLUORINE DOPED NANOCRYTALLINE CdS THIN FILMS

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ABSTRACT

In this study, pure and Fluorine (5,10 and 15 wt%) doped CdS thin films were prepared on glass substrate by sol-gel spin coating method dried at temperature 250 °C for 15 min. and annealed at temperature 450 °C for 2h. Structural properties, surface morphology of CdS and CdS: F thin films have been investigated with respect to the doping process. The X-ray diffraction (XRD) results point to that the structure of all prepared thin films are polycrystalline in nature and has a Hexagonal (Wurtzite) phase, CdS and CdO cubic phases was found related to annealing temperature and air ambient. The average grain size of CdS film was53.4 nm and increases as fluorine dopant concentration increase with maximum value of 97.3 nm for CdS:F (15wt%) so the pure and doped films have nanocrystalline structure. The introducing of fluorine does not affect the structural properties of the films. The Scanning Electron Microscopy (SEM) image for CdS and CdS:F thin films shows that smooth, uniform morphology and plated regularly. The stoichiometry of CdS:F prepared films confirmed by the energy dispersion x-ray spectroscopy (EDX) specta. Consequences of atomic force microscope (AFM) images for CdS and Cds:F thin films displayed smooth surface texture.

KEYWORDS: X-Ray Diffraction (XRD), X-Ray Spectroscopy (EDX), Atomic Force Microscope (AFM), Cds and Cds: F Thin Films

INTRODUCTION

CdS is one of II-VI compound semiconductor and has an energy band gap between 2.82- 2.5eV[1,2]. The Chalcogenide families are used as window and buffer materials for CdS/CdTe solar cells, and continue to be subject of enormous researches due to their potential applications in high-efficiency solar devices, where CdS thin film belonging to this family[1,3]. The important materials for application in optoelectronic devices such as photo-sensors, photo-conducting cells, transducers laser materials, optical wave guides and non-linear integrated optical devices[2,3]. Nanocrystalline Cadmium sulfide (CdS) thin film was synthesis by using an in expensive, easy sol-gel spin coating method on microscopic glass substrates [4,5]. Because of the short absorption length and trouble in forming a shallow thin film joint with a high conductivity surface layer CdS thin film solar cells are ordinarily made-up as hetero-structures. A wide variety of well-established deposition techniques including vacuum evaporation [2,3], E-Beam Technique[6], Chemical Bath deposition[1] spray pyrolysis [7], PLD [8,9], have been used to prepare CdSthin films. In this research pure and fluorine doped CdS thin films were synthesis on glass substrate with different dopant concentration by sol-gel spin coating technique and the structural, surface morphology and the optical properties were investigated with respect to the fluorine dopant concentration.

EXPERIMENTAL WORK

Sol-Gel spin coating technique was used to synthesis of pure and fluorine doped CdS thin film on glass substrates. Cadmium acetate dehydrate $Cd(CH_3COC_2)_2.2H_2O$,thiourea $(NH_2)_2CS$ and ammonium fluoride NH_4F were used as the source of Cd^{+2}, S^{-2} ions and fluorine dopant respectively. The glass slide were cleaned by distilled water in order to remove residuals and impurities from the surfaces, then they dipping in methanol for 5 min., and in acetone for one hour, then in deionized water for 10 min finally the substrates ultrasonically cleaned inside de-ionized water for 15 minutes and dried carefully by nitrogen gas. For synthesis of CdS thin films 10 ml of methanol is added to 2 gm (7.5mmol) of cadmium acetate in order to get a transparent solution, slow continuous stirring is required. 2gm of thiourea was dissolved in 50 ml of deionized water with stirring. Then the two solutions were mixed with stirring for half hour, adding 0.5 ml of glycerol to the mixturewith continuous stirring. Another solution of 0.57 ml triethylamine in 10 ml of methanol is prepared separately. The second solution has been mixed with the first solution of Cadmium and thiourea with continues stirring for one hour. Storing the final solution for 2 day at room temperature. The resulting solution have yellow colour completely during preparation and storing. The coating solution was dropped onto substrates and then the substrates were rotated at 1000 rpm for 30 second using Spin coater (model VTC-100). After the spin coating, the films were dried at 250 ˚C for 15 min. This coating/drying procedure was repeated for two times and then annealed at 450 ˚C temperatures in air for 2 h. The same procedure were used for synthesis CdS:F thin films by adding 0.1,0.2 and 0.3 gm (5,10,15 wt%) of NH_4F to the starting solution of cadmium acetate and thiourea. Structural properties and surface morphology of CdS:F have been investigated by using X-ray diffractometer (ADX-270) in 2θ range 20–70◦ and scanning electron microscopy and EDSX analysis using SEM (INSPECT-550). The surface texture of the prepared films is recorded by an atomic force microscopy AFM CSPM model AA3000.

RESULTS AND DISCUSSIONS

Structural and Morphological Properties

Structural Properties of CdS Thin films

The X-ray diffraction patterns of CdS thin film deposited at temperature 450 ^oC is shown in figure (1). The CdS thin film is found to have polycrystalline nature and grown in the hexagonal (wurtzite) crystal structure and also get cubic structure. The latter implies that the cubic to hexagonal transition on heating is a size-driven one causedby sintering and average grain growth this good agreement with [5,6]. It is observed that the main peaks appeared at 2Θ = 24.100°,29.402°, 42.20^o, 55.340° and 59.622 which are belong to (100), (101), (110),(004) and (104) planes, respectively.

The preferred orientation is (104) at 2Θ = 59.622º. The observed diffraction patterns are well agreement with the standard data for the CdS JCPDS card (41-1049) which indicate that CdS thin film is polycrystalline structure and exhibit hexagonal (wurtzite) phase. From figure (1) another phase grown in the cubic (zinc blende) crystal structure can be found at (200) and which belong to CdSat 2Θ = 33.375º (JCPDS card No. 21-0829). The structural data for CdS films are in good agreement with the earlier report presented by R. Demir (by CBD) [1], A. Abdolahzadeh (by Sol-Gel) [10],J. Herna´ ndez-Borja (by CBD)[11] and Adnan Nazir (by CSS technique) [12]. The diffraction peaks related to cubic CdO at 2Θ=38.285º (JCPDS card 05-0640) have been appeared (Figure 1). The presence of oxide phase is due to high temperature process and air ambient where some authors have reported the presence of CdO at the surface of CdS [10,13,14].

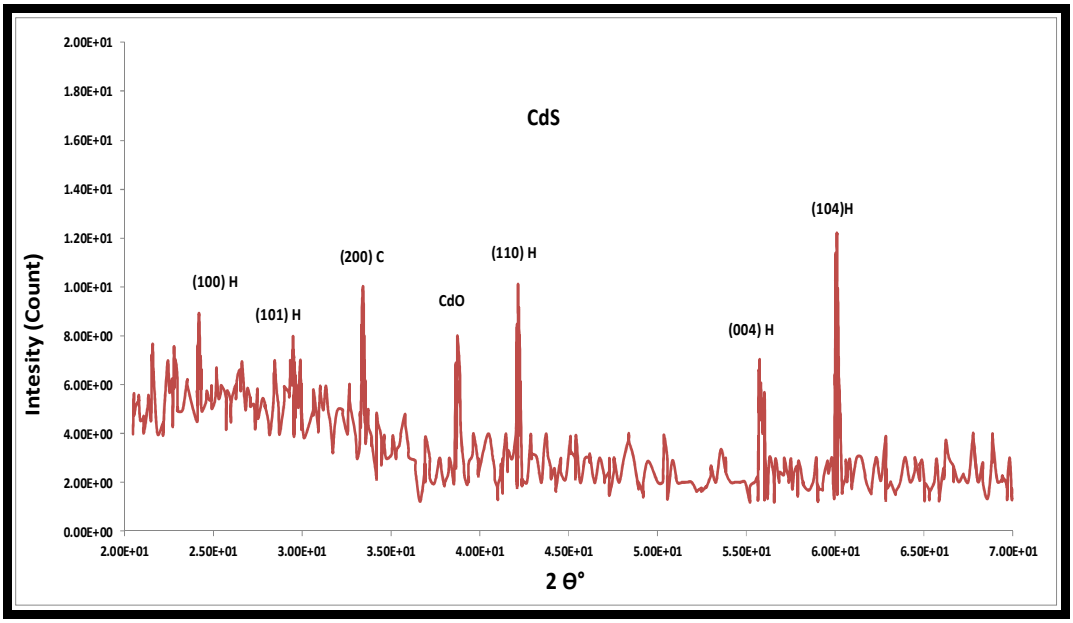


Figure1: X- Ray Diffraction Pattern Of Cds Thin Film

Figure (2) shows the X-ray diffraction pattern of CdS:F thin film doping by 0.1 gm (5%)Fluorine and have been annealed at 450 ºC for 2h. Four sharp peaks in the hexagonal phase were observed belong to (002), (200),(201)(004) and (104), planes at (2Θ=26.460º), (2Θ=50.503º), (53.103º), (55.181º), and (2Θ=61.720º) respectively. These values are compared with the (JCPDS Card No.41-1049) for CdS and it is matched with simple differences. Another phase grown in cubic crystal structure can be found at (200) which belong to CdS at 2Θ=33.281ºcompared with the card (JCPDS Card 21-0829). Cubic crystal structure can be found belonging to the plane (200) which refer to CdO at 2Θ=38.558º as discussed previously which compared with the (JCPDS Card No.05-0640). From the figure it can be clearly seen that peaks with doping process became sharper and more intense. From the figure it is clear that the fluorine dopant did not affect the crystal structure of CdS tin films and this result was in a good agreement with the result of authors Adel H. Omran [15] and SalihYılmaz [16].

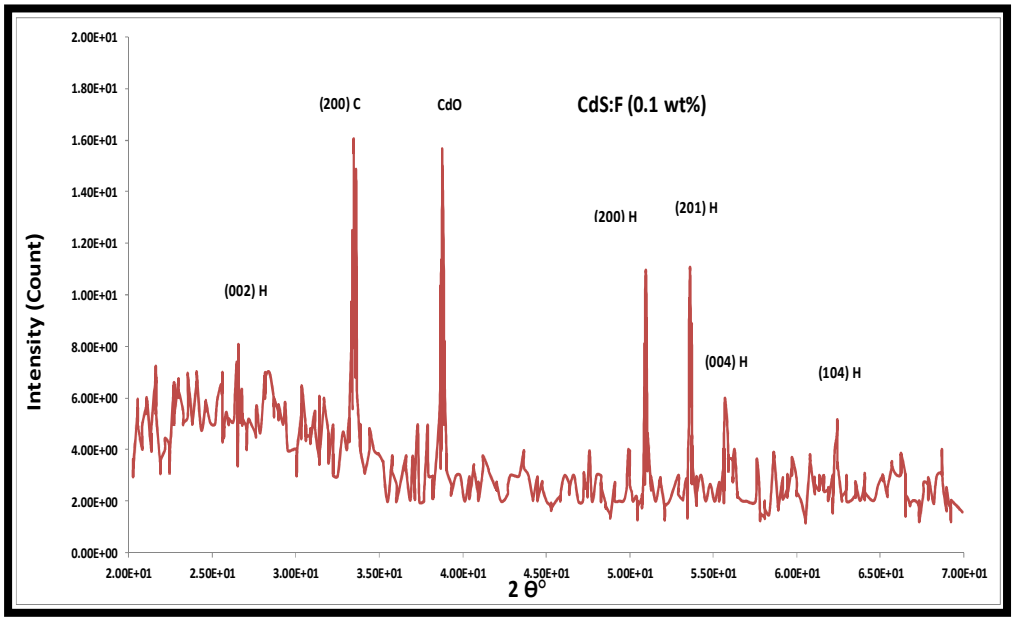


Figure2: X-Ray Pattern of Cds:F Thin Film with Doping with 0.1gm (5 %) Flourine

Figure (3) shows X-ray diffraction pattern of CdS:F thin film doping with 0.2 gm (10%) fluorine. It can be seen three peaks refer to (100), (004) planes and (202) plane at angles of (2Θ=25.191, 2Θ = 54.429º and 2Θ=57.260º) respectively comparing these values to the cards (JCPDS Card No.41-1049). Another phase grown in cubic crystal structure can be found at (200) which belong to CdS at 2Θ=33.279º compared with the card (JCPDS Card No.21-0829), and cubic crystal structure too can be found at(200) which belong to CdO at 2Θ=38.558ºcompared with the card(JCPDS Card No.05-0640). The appearance of CdS cubic phase can be attribute to the drying and thermal annealing process where it can be found at low temperature (about 250 ^{o}C) while the hexagonal phase grown-up at high temperature (more than 350^{o}C). The critical point for such phase transition is believed to be 300 ^{o}C, above which hexagonal phase predominates over cubic phase, this result are in a good agreement with the earlier report presented by [16,17,17,19,20,21]. From the figure the prefer orientation at (2Θ=57.260) of (004) of polycrystalline hexagonal phase of CdS: F as comparing these values to the cards (JCPDS Card No.41-1049).

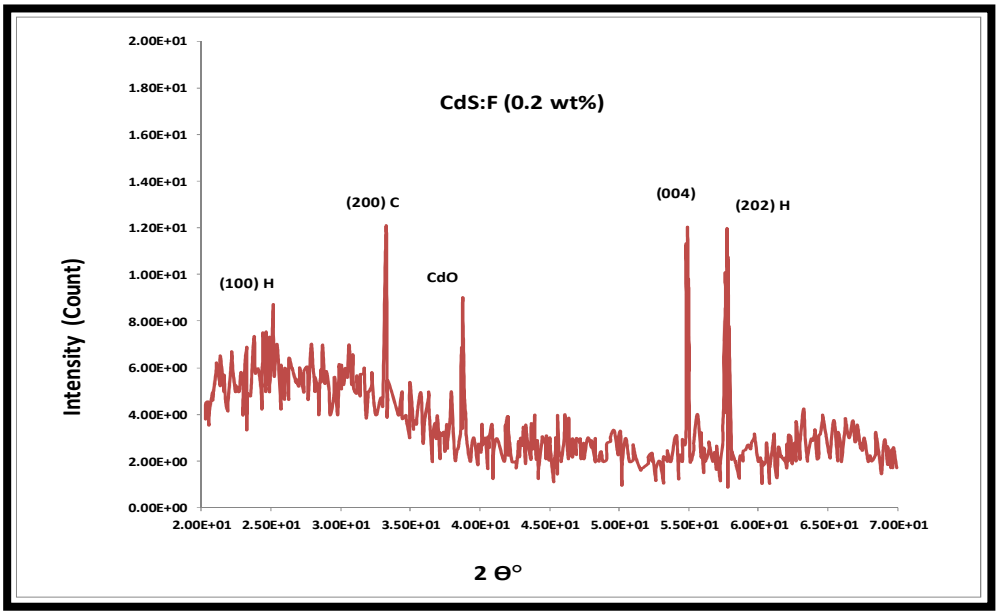


Figure 3: X-Ray Pattern of Cds Thin Film Doping with 0.2 gm (10) % Flour

Figure (4) shows the X- ray diffraction pattern of CdS:Fthin film doping with 0.3 gm (15%) fluorine and annealed at 450 ºC for 2hours. The peaks assigned to (100), (103),(202)and (104) planes at (2Θ=25.120º, 2Θ = 48.257º,2Θ=58.384º,2Θ=60.981º) respectively, with the orientations of polycrystalline hexagonal phase of CdS:F. Diffraction peaks indicates that the CdS:F thin film is preferentially oriented (100),(103),(202)and(104) planes. Another phase grown in cubic crystal structure can be found at (200) which belong to CdS at 2Θ=33.260º these result nearly closes to (JCPDS Card No.41-1049). As previously discussed another phase grown in cubic crystal structure can be found at(200) which belong to CdO at 2Θ=38.481 comparing with the card (JCPDS Card No.05-0640). From the figure it can be clearly seen that the preferential orientation peak with doping process became sharper and more intense. The average crystallite size is calculated and it is found to be increased from 53.4 for pure CdS, 78.8 nm for 0.1gm 5% fluorine, 89.5 nm for 0.2gm 10 fluorine to 97.3 nm for 0.3gm 15% fluorine, we found that when increase the doping ratio it is seen that average crystallite size of CdS thin film also increases by enhancing the crystallinty of the films [5]. This indicated that the doping processes will be reduced the crystal defects by giving the atoms of material enough energy to rearrange themselves in the lattice and overcome the random distribution inside material of thin films and the improvement of structural properties [22].

Several authors have reported the presence of CdO at the surface of CdS. A CdO cubic phase appeared after the annealing of the sample. The formation of oxide phase is due to air ambient and high temperature process and can be explained by a transformation of cubic CdS (unstable compared to hexagonal CdS) to give the CdO [10, 18, 14, 23].

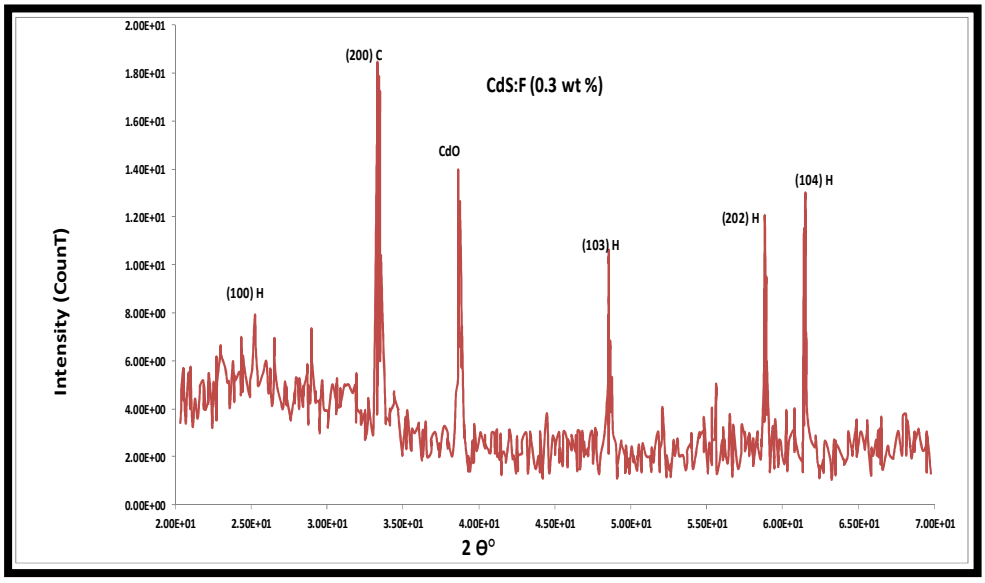
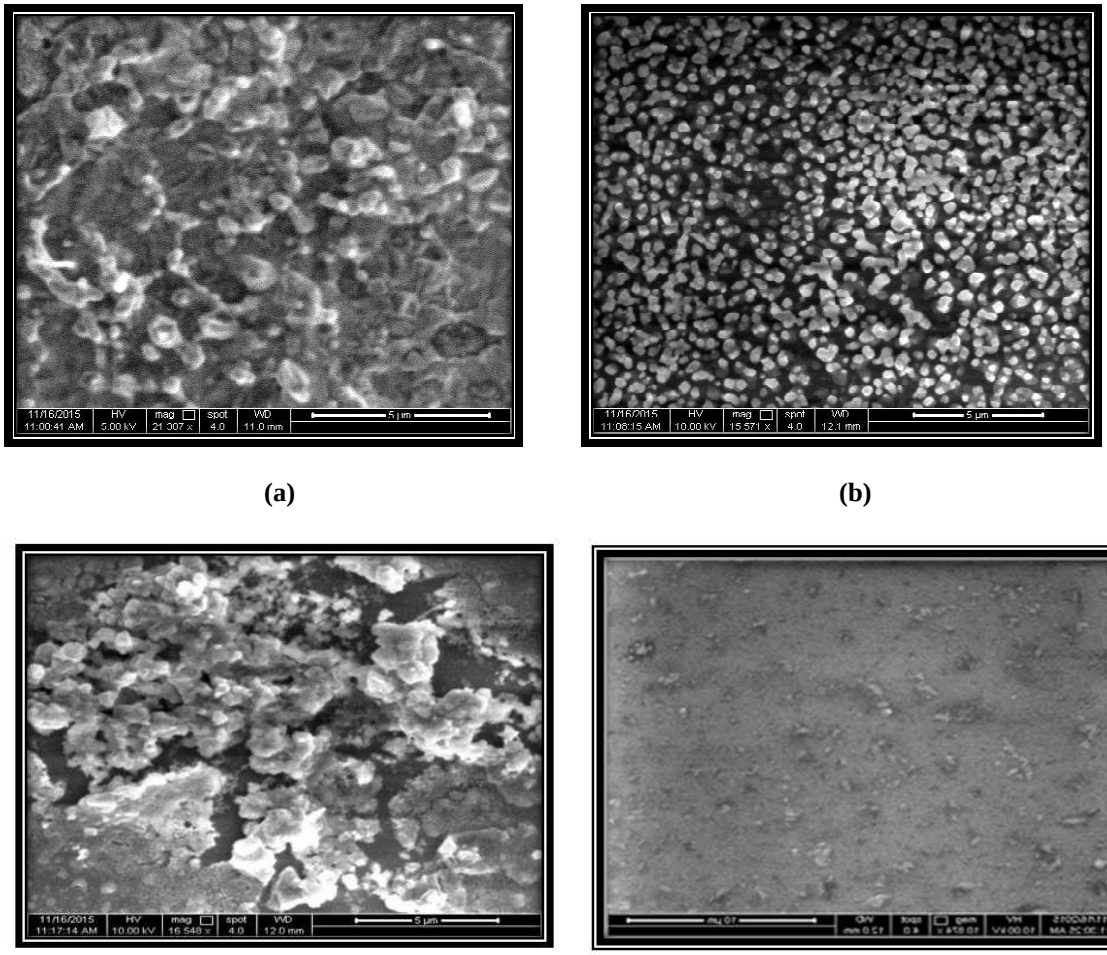


Figure 4: X-Ray Pattern of Cds:F Thin Film Doping with 0.3 gm (15%) Fluorine

Surface Morphological Analysis

The surface morphology of the deposited CdS thin films is very helpful to study the surface morphology of the CdS thin films [24]. The Sol-gel spin coating CdS thin films are characterized by scanning electron microscopy (SEM) analysis and EDX measurements. SEM and EDX is a promising technique for the topography and surface elements analysis study of samples, as it gives important information regarding the growth mechanism, shape and size of the grains.

Figure (5a) shows SEM images of CdS substrate include large and small grain size and have an irregular shape when CdS thin film deposed at 450 ºC. The morphology of the films display a dense uniform and homogenous surface with a fine partical size the roughness and coarse scales are low in thin film sample this result similar with M. M. Ismail, and *et*l [24]. However, when CdS thin film doping with 0.1 gm (5%) of Fluorine the SEM images show a homogeneous and smooth uniform surface with no detectable micro-cracks and the morphology of the prepared films indicates that the size of the particles is increased with the increasing of the doping ratio as show in the figure, it having perfectly spherical grains with well-defined grain boundaries and this result with the literature [5] as shown in figure (5b). Figure (5c) shows CdS thin films and when doping with 0.2 gm (10%) of fluorine become granular structure with low homogeneity than it pure and doping by 0.1 gm (5%) of fluorine and it consist of nanocrystalline grains with uniform coverage of the substrate surface. The agglomerations of particles there is randomly oriented morphology with increase in grain size has be observed which agree with [10]. Figure (5d) shows CdS thin films when doping with 0.3 gm (15%) Fluorine and the results shows smooth and uniform distributed surface morphology shows a dense and homogenous surface with very fine particle size confirming, the roughness and coarse scales are low in this sample [25,16]. It is seen that the cluster of particles has formed batches on the surface of the sample which is evident for surface morphology which can be correlated with XRD pattern. When the Fluorine concentration increased to 0.3 gm (15%), the coalescence improved more so that the inter-cluster spaces disappeared and the grain size enhanced slightly. This result confirms the XRD data. The observed differences among the microstructures of the samples can presumably be attributed to the addition of the Fluorine, [25].



(a) **(b)**

(c) **(d)**

Figure 5: SEM Images of (a) CdS, (b) CdS:F (0.1gm5%), (c) CdS:F(0.2gm10%), and (d) CdS:F(0.3gm15%) Thin Films

In material characterization, it is important to determine how an element is distributed laterally and to find the inclusion on the surface. This is most conveniently done by using a focused probe of x-rays that is scanned above the surface and the characteristic elemental single are used to products an element map of the surface, [23].

The EDX of CdS thin film which can confirm the existence of elements (Cadmium, Sulphid) which constitute thin film structure. From the figure (6)it can be observed ratios of these elements and can be observed convergence in the mixing ratios of Cadmium and Sulphide and this proves that the CdS pure and mixing ratio of the 0.1gm 5%, 0.2 gm 10% and 0.3 gm 15% fluorine. Figure (6-a, b, c, d) shows EDX of CdS thin film deposited at 450 ºC. In addition to Cd, S. Elemental weights (wt.% 87.8, 12.72) of Cd, S elements in the CdSthin films.

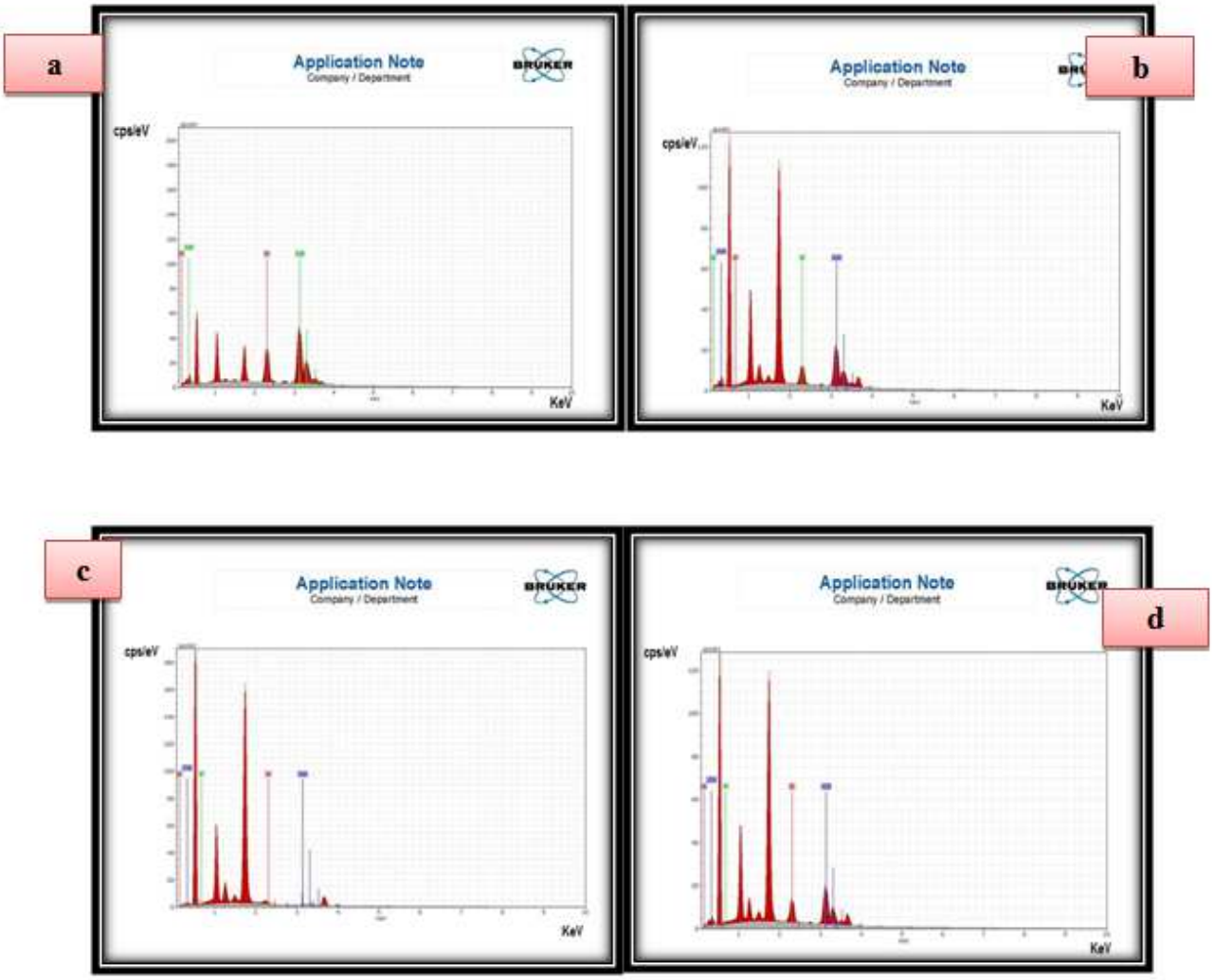


Figure 6: EDX Images of (a) CdS, (b) CdS: F (0.1gm 5%), (c) CdS:F(0.2gm 10%), and (d) CdS:F(o.3gm 15%) Thin Films

Surface Texture Analysis

Atomic force microscopes (AFM) are well suited for visualize the surface texture of the deposited CdS thin films, especially when the surface feature sizes are far below one micron. Figure (7a) shows the AFM images of a pure CdS the thin films and figure (7 b,c,d) CdS:F thin films, with doping ratios (0.1,0.2,0.3) gm (5,10,15)% of the fluorine dopant and annealing at 450ºC for two hour. The results investigated show that deposited CdS thin films with different doping rates exhibits different surface texture. The smooth surface texture is observed in the deposited CdS thin films.

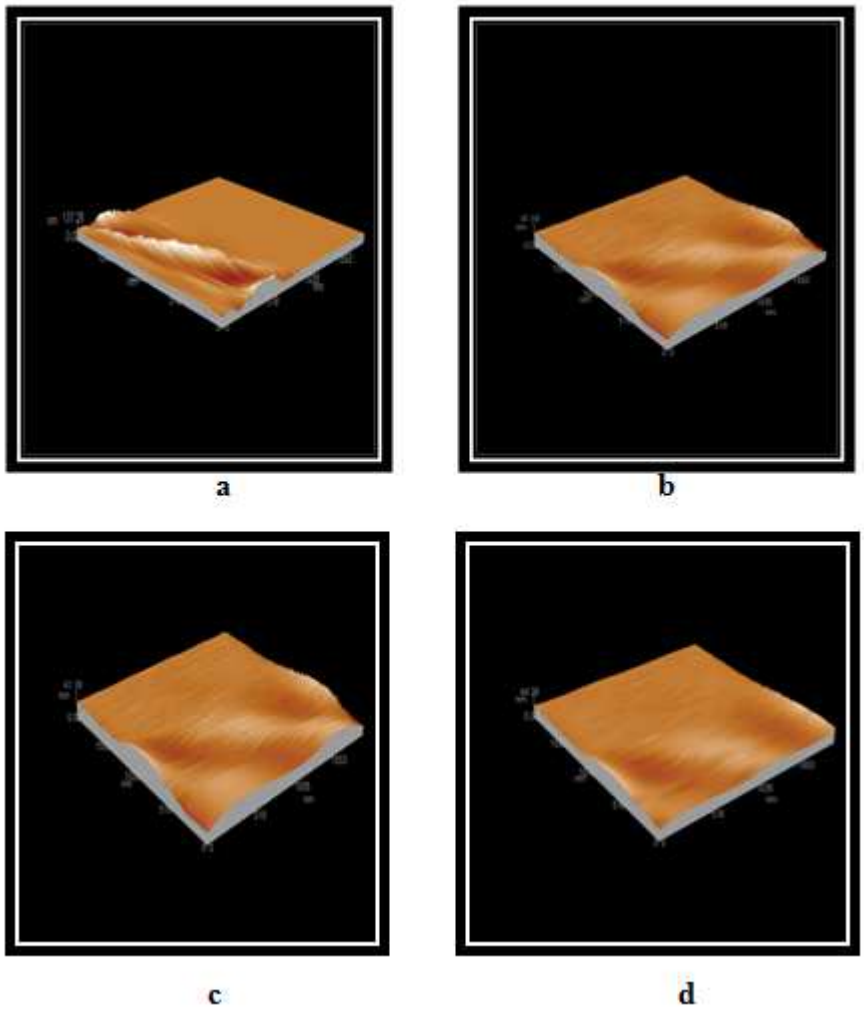


Figure 7: AFM Images of (a) CdS, (b) CdS:F(0.1gm5%), (c)CdS:F(0.2gm10%), and (d) CdS:F(0.3gm15%) Thin Films

CONCLUSIONS

Pure and Fluorine doped CdS thin films have been successfully deposited by sol-gel spin coating technique. Reliant on the obtained results, it can be determined and concluded that:

- The XRD results show that CdS and CdS:Fthin films were polycrystalline in nature with Hexagonal wurtzite structure. The CdSphase is confirmed by X-ray diffraction in the deposited films. It has been seen that the fluorine-doping causes growing up the average grain size with improved the crystallinty of the films.
- The SEM images display the granular structure and uniform morphology of CdS and CdS:Fthin films. Whereas the EDXS analysis confirms the stoichiometry of the prepared films.
- The AFM images display that the smooth surface texture is observed in the deposited of CdSthin films.
- These consequences show that low-cost sol-gel processing is a suitable practical method for preparing CdS thin film.

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REFERENCES

1. Zahraa Hussain Heyat "Studing the Effect Some Physical Properties of Cd $_2$SnO4 Thin Films Prepared by Sprying Pyrolysis Technique", M. S. C Thesis, Application Scince Department, University of Technology,(2008).
2. M. A. Olopad, A. M. Awobode, O. E. Awe and T. I. Imalerio, "Structural and Optical Characteristics of Sol-Gel Spin –Coated Nano Crystalline CdS Thin Film", Ijrras, Vol.15, No. 1, PP.120-124, (2013).
3. I. Rathinamala, J. P and iarajan and N. Jeyakumaran," Investigation on Structural and Optical Properties of CdS Film Fabricated by Spin Coating Technique for Optoelectronic Applications" Chem. Tech. Research, Vol.6,No.3, pp.1913-1915, (2014).
4. Raghu Patel, Naveen Chickmagalur Shivappa, ShailajaJeetendra, Ganesh Sanjeev, Murugaiya Sridhar and Mahesh Hampapatna Matt, "Optical and Structural Properties of CdS/ZnSe bi-Layer Thin Films Prepared by E-Beam Technique", International Journal of Material Scince and Applications, Vol.3, No.3, PP.116-120, (2014).
5. R. Benerjee, R. Jayakrishn and P. Ayynb,"Effect of the size-Induced Structure Transformation on the Band Gab in CdS Nanopartical", J. phy, No.12, P. P, (10647-10654), (2000).
6. F. S. Hashim, M. A. Habeeb, I. R. Ghanim," Effect of zinc on structural and some optical properties of CdS thin films", Chemistry and Materials Research, Vol.3 No.12, (2013).
7. R. Demir, F. Gode, “Structural, Optical and Electrical Properties of NanocrystallineCdS Thin Films Grown by Chemical Bath deposition method”, Chalcogenide Letters, Vol. 12, No. 2, 43 - 50, 2015.
8. A. Abdolahzadeh Ziabari and F. E. Ghodsi, "Growth, Characterization and Studying of Sol-Gel Derived CdS Nano crystalline Thin Films Incorporated in Polyethyleneglycol: Effect of Post-Heat Treatment", Solar Energy Materials and Solor Cells, Vol.105, PP.249-262, (2012).
9. J. Hernandez-Borja, Y. V. Vorobiev and R. Ramırez-Bon, “Thin film solar cells of CdS/PbS chemically deposited by an ammonia-free process”, Solar Energy Materials & Solar Cells, Vol. 95, 1882–1888, (2011).
10. Adnan Nazir, Andrea Toma, Nazar Abbas Shah, Simone Panaro, Sajid Butt, Rizwanur Rehman Sagar, Waseem Raja, Kamran Rasool, Asghari Maqsood, “Effect of Ag doping on opto-electrical properties of CdS thin films for solar cell applications”, Journal of Alloys and Compounds, Vol.609, 40–45, (2014).
11. Y. Al-Douri, Q. Kohasawneh, S. Kiwan, U. Hashim, S. B. Abd Hamid, A. H. Reshak, A. Bouhemadou, U. Ameri and R. Khenate, "Structural and Optical Insights to Enhance Solar Cell Performance of CdS Nanostructure", Energy Conversion and Management, Vol.82, 238-243,(2014).
12. S. Chun, Y. Jung, J. Kim, D. Kim, The analysis of CdS thin film at the processes of manufacturing CdS/CdTe solar cells, Journal of Crystal Growth**,** Volume 326, Issue 1, 152–156,(2011).

13. Adel H. Omran Alkhayatt and Shymaa K. Hussian," Fluorine highlydopednanocrystallineSnO2 thin films prepared by SPD technique", Materials Letters, Vol. 155, 109-113, (2015).
14. Salih Yılmaz, " The investigation of spray pyrolysis grown CdS thin films doped with flourine atom", Applied Surface Science, Vol.357, 873–879, (2015).
15. A. Abdolahzadeh Ziabari, F. E. Ghods, "Influence of Cu Doping and Post- Heat Treatment on the Microstructure, Optical Properties and Photoluminescence Features of Sol-Gel Derived Nanostructured CdS Thin Films", Journal of Luminescence, Vol.141, PP. 121-129, (2013).
16. Hani Khallaf, Guangyu Chai, Oleg Lupan, Lee Chow, S. Park, Alfons Schulte, "Characterization of gallium-doped CdS thin films grown by chemical bath deposition", Applied Surface Science. Vol. 255, 4129–4134, (2009).
17. B. Ghosh, Kamlesh Kumar, Balwant Kr Singh, Pushan Banerjee, Subrata Das, "Growth of CdS thin films on indium coatedglass substrates via chemical bath deposition and subsequent air annealing**,"** Applied Surface Science**,** Vol. 320, 309–314, (2014).
18. O. Zelaya-Angel, J. Alvarado-Gil, R. Lozada-Morales, H. Vargas, and A. Ferreira da Silva, " Band gap shift in CdS semiconductor by photoacoustic spectroscopy: Evidence of a cubic to hexagonal lattice transition, Applied Physics Letters, Vol. 64, 291–293, (1994).
19. Y. Al-Douri, Jamal H. Waheb, M. Ameri, R. Khenata, A. Bouhemadou and A. H. Reshak, "Morphology, Analysis and Properties Studies of CdS Nanostructures under Thiourea Concentration Effect for Photovoltaic Applications", Int. J. Electro chem. Sci., Vol.8, PP.10688-10696, (2013).
20. Jae-Hyeong Lee, Dong-Jin Lee, "Effects of CdCl2 treatment on the properties of CdS films prepared by r.f. magnetron sputtering", Thin Solid Films, Vol.515,6055–6059, (2007)**.**
21. AbdulwahabS. Z. Lahewil, Y. Al. Douri, U. Hashim and N. M. Ahmed, "Structural, Analysis and Optical Studies of Cadmium Sulphide Nanostructured", Procedia Engineering, Vol.53, PP. 217-224, (2013).
22. M. M. Ismail, H. H. Afify, M. ElShaarawy, N. M. H. Shash, A. Ashiry and I. K. Battisha, "Effect of Annealing Temperature on the Optical Properties of Nano-Structure CdS Embedded in Silica Gel Thin Film Prepared by Sol-Gel Technique, Australian Journal of Basic and Applied Scince, Vol.6, No.13, PP.530-535, (2012).
23. C. Gopinathan, T. Sarveswarran and K. Mahalakshmi, "Studies on CdS Nano crystalline Thin Films With Different S/Cd Ratio Prepared Using Chemical Bath Deposition Method", Adv. Studies The or. Phys., Vol.5, No.4, PP.171-183, (2011).