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PREPARATION OF CdS:Fe THIN FILMS AND THE STUDY OF THEIR PHASE FORMATION AND OPTICAL PROPERTIES WITH POST-DEPOSITION ANNEALING

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Thin article discusses the results of the preparation and structural and optical characterization of chemical bath deposited CdS:Fe thin films. To achieve the deposition, chloride compounds of the principal precursors together with thiourea were used. The resulting thin films were characterized by using uv-vis spectrophotometer and X'Pert HighScore PW1710 PANalytical Diffractometer. Studies on the annealing effect reveal the inclusion of FeS phase and a blue shift in the band gap energy for the film annealed at 200^{o}C.

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1. Introduction

Large-area thin film semiconductors of metal-metal sulphides and selenides can be deposited on metals, glass and polymer substrates that are immersed in solutions containing metal complex ions and a source of sulphide or selenide. One such semiconductor material is CdS, which belongs to the II – VI compounds. In recent times, CdS thin films has gained considerable research attention and has become a promising candidate for various application especially in the technology for optical detectors, field-effect transistors and optoelectronic devices [1 –4]. CdS thin films are also widely used in the fabrication of solar cells [5]. Because of its optical properties, CdS is used in CdTe devices as an optical window [5, 6]. However, poor conductivity as low as $10^{-8}(\Omega m)^{-1}$ has been reported [7]. In order to overcome this problem, annealing and doping are used [7 - 9].

There are many methods to fabricate CdS thin films, such as successive ionic layer adsorption and reaction (SILAR) [10, 11], spray pyrolysis [12], CBD [13] etc. Chemical bath deposition (CBD) method is credited with numerous advantages such as the simplicity and availability of apparatus, easier composition control, low processing temperature, lower cost, easier fabrication of large area films, easy process of complex shaped substrates and possibility of using high purity starting materials. Consequently, many authors have employed this technique in depositing thin films of particular interest including oxides [14, 15], sulphides [16, 17], selenides [18], binary [19], ternary [20] as well as heterojunction [21] thin films. Beside, I.O. Oladeji et al reports that CBD produces CdS films with properties highly suitable for thin films CdTe or $Cu(InGa)Se_2$ solar cells [22].

In this report, chemical bath deposition technique was adopted for the deposition of thin films of CdS:Fe. One of the as-grown films was annealed in the oven at 200^{o}C for 1 hour and studied for the structural, optical and solid-state properties.

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2. Materials and method

Glass microscope slides were cleaned by degreasing them in dilute hydrochloric acid for 2 hours, washed in detergent solution, rinsed in distilled water and dried in oven at 30^{o}C above room temperature. The starting solution for the deposition of CdS:Fe thin films contains 1M $CdCl_2$ (cadmium chloride), 1M $SC(NH_2)_2$ (thiourea), 1M $FeCl_2$ (iron II chloride), while ammonia solution (NH_4OH) were added to maintain the pH value of the bath at 11. The PVP (polyvinyl pyrrolidon) solution, which were used to make up the volume of the bath to 50mls were prepared by adding 400ml of distilled water to 4.0g of solid PVP and stirred by a magnetic stirrer without heating until the solution becomes homogeneous. This process lasted for one hour. The $CdCl_2$, $FeCl_2$ solutions were mixed together at room temperature with continuous stirring. Then the NH_4OH solution was added until the required pH was obtained. The mixed solution was maintained at 55^{o}C in the oven. The clean glass substrates were immersed vertically into the bath and left for 4hrs. 20 mins. Finally, after deposition, the glass substrates were removed from the chemical bath and cleaned several times with distilled water, then dried in air atmosphere. One of the deposited films was annealed at 200^{o}C for 2hrs (sample D8) while the other was left unannealed (sample D7) and used as the control to study the effect of thermal annealing on the structural and optical properties of the films.

The structural properties of the films were studied by x-ray diffractometer with Cu K_{α} radiation (X'Pert HighScore PW1710 PANalytical). Optical properties of chemical bath deposited CdS:Fe thin films were measured at room temperature by using Unico – UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1100nm. Optical band-gaps of the samples were calculated from the absorption spectra.

3. Results and discussion

3.1 Structural Analysis

X-ray diffraction (XRD) is an efficient tool for the structural analysis of crystalline materials. The XRD studies was carried out on the samples using X'Pert HighScore PW1710 PANalytical Diffractometer, using the CuK_{α} radiation of wavelength $\lambda = 1.5408$Å. The results are presented in figure 1. The existence of identifiable peaks in the diffractograms suggests that the films are highly crystalline in nature. However, the figures show that high temperature annealing has significant influence on the films deposited. Table 1 summarises the result from XRD analysis.

Table 1: Comparison of the results from XRD analysis of the film annealed at 200^{o}C and the as-grown film

Annealing Temp.	Position (2θ)	d-spacing	Compound Name	Chemical Formula	Ref. code
As-grown	26.74	3.33384	Hawleyite	CdS	00-042-1411
,,	29.01	3.07797	Sulfur	S	00-020-1227
,,	44.43	2.03701	Iron	Fe	01-085-1410
200^{o}C	42.84	2.11052	Austenite	Fe	00-052-0513
,,	26.38	3.37758	Cadmium Sulfide	CdS	01-089-0440
,,	47.17	1.92677	Iron Sulfide	FeS	00-049-1632
,,	39.08	2.30449	Sulfur	S	00-020-1227
,,	48.22	1.88564	Cadmium	Cd	00-001-1175

Table 1 shows that annealing the as-grown film in the oven at 200^{o}C influences the structure of the film deposited, leading to the appearance of peaks attributed to FeS and cadmium

metal. The peaks are also broader and more intense. The grain size (D) of the films under study was determined by measuring the full width at half maximum (β) using the well known Scherrer formula: $D = k\lambda/\beta\cos\theta$, where k is a constant taken to be 0.94, λ the wavelength of X-ray used (λ = 1.5408Å) and θ is the Bragg's angle. Using Scherrer's formula, the grain sizes were found to be of the order of 29.26nm and 39.23nm for the as-grown film and the film annealed at 200°C respectively. The number of crystallites per unit area (*N*) of the films was calculated from the formular, $N = t/D^3$, where t is the thickness of the film. The dislocation density (δ), defined as the length of dislocation lines per unit area, has been estimated using the equation, $\delta = 1/D^2$ [33]. The calculated structural parameters are summarized in table 2.

Table 2: Structural Parameter of CdS:Fe thin films

Annealing Temp. (°C)	Thickness (t) (nm)	Grain Size (D) (nm)	Number of Grains Per Unit Area (N) ($x10^{14}$)	Dislocation Density (δ) (line/m^2) ($x10^{14}$)
As-grown	403	29	165.24	11.89
200	393	39	66.25	6.57

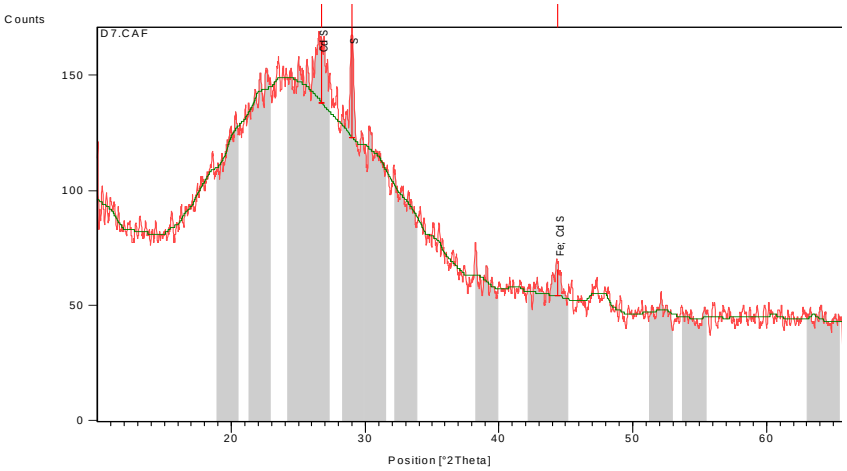

Fig.1a: XRD pattern of the as-grown film

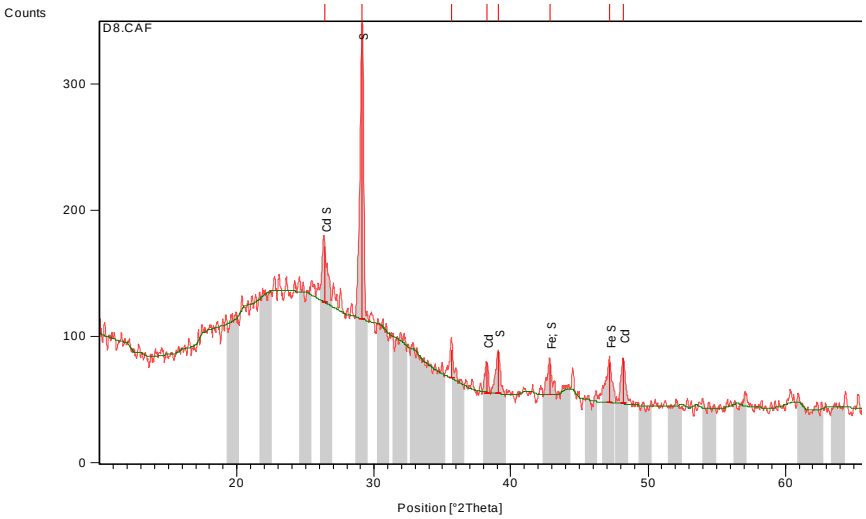

Fig.1b: XRD pattern of the film annealed at 200°C

3.2 Optical Analysis

The optical absorption spectra of the films deposited onto glass substrate were studied in the wavelengths range of 200 – 1100nm. The variation of absorbance, transmittance and reflectance with wavelength for the sample annealed at 200^{o}C and the as-grown film are shown in figs. 2-4. A close observation of these figures shows that thermal annealing has profound effect on these properties. The optical studies show that the annealed film is absorptive within the visible spectrum, while the as-grown film transmits most of the radiation incident on it. The values of the absorption coefficient, refractive index and extinction coefficient depend upon radiation energy as well as the annealing temperature, as shown in figs. 5-7.

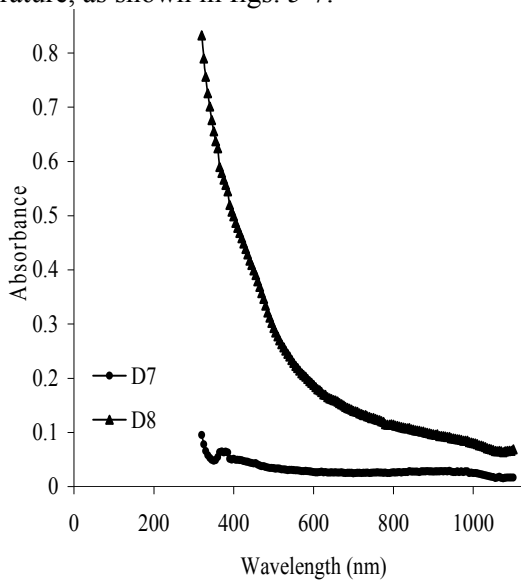

Fig. 2: Plot of absorbance vs. wavelength for CdS:Fe thin films

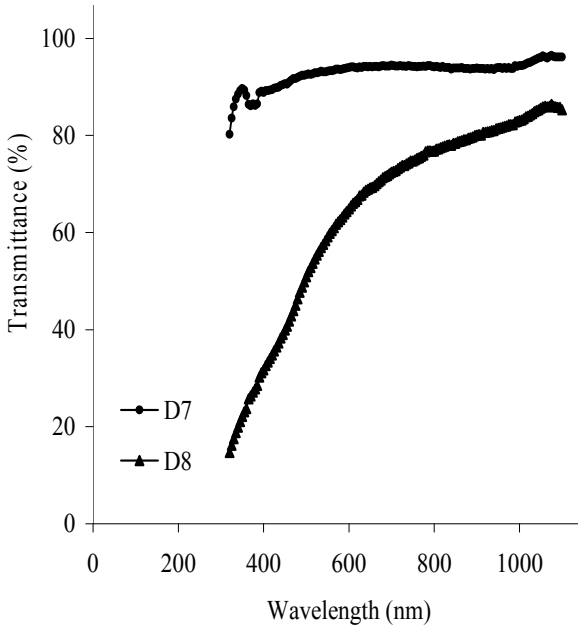

Fig. 3: Plot of transmittance vs. wavelength for CdS:Fe thin films

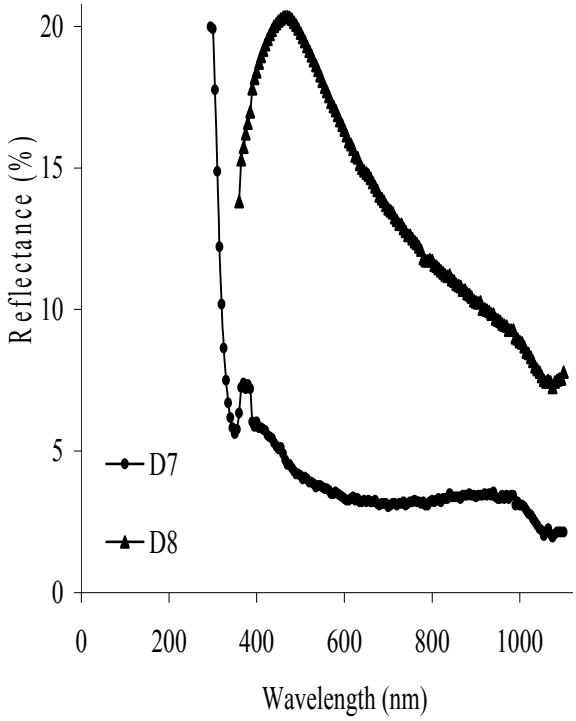

Fig. 4: Plot of reflectance vs. wavelength for CdS:Fe thin films

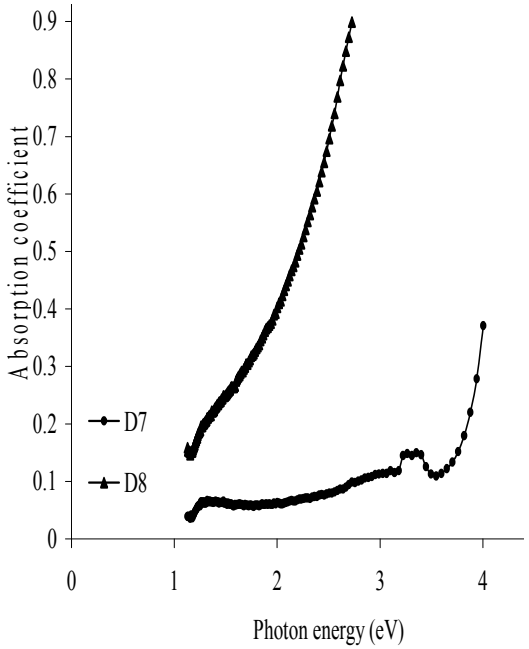

Fig. 5: Plot of absorption coefficient vs. photon energy for CdS:Fe thin films

The interpretation of experimental results is most often performed with the help of formula derived for three-dimensional crystal model. The band gap, E_g was calculated using the following relation [24]:

$$\alpha = A(h\nu - E_g)^n / h\nu$$

Where A is a constant, hν is the photon energy and α is the absorption coefficient, while n depends on the nature of the transition. For direct transitions n = ½ or ⅔, while for indirect ones n = 2 or 3, depending on whether they are allowed or forbidden, respectively.

The band gap E_g was determined from the variation of $(\alpha h\nu)^2$ with $h\nu$ (fig. 8). The linear nature of the plot indicates the existence of direct transition. The band gap was determined by extrapolating the straight portion of energy axis at $\alpha = 0$. The band gap was found to be 2.3eV and 2.6eV for the as–grown and the annealed films respectively. This result shows the high dependent of the band gap of CdS:Fe thin films on the annealing temperature. However the increase in the band gap with annealing temperature in this film represent a deviation from observations and suggestions that better quantum confinements take place at higher annealing temperature. That is, particle size decreases with annealing temperature, resulting in higher band gap energy [25]. In this case, there is an increase in both crystallite size and band gap energy.

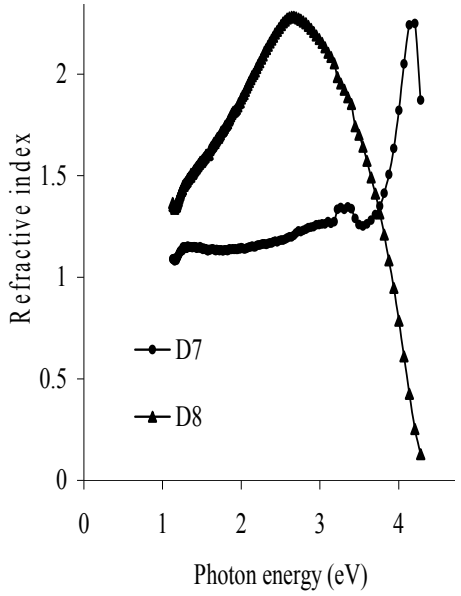

Fig. 6: Plot of refractive index vs. photon energy for CdS:Fe thin films

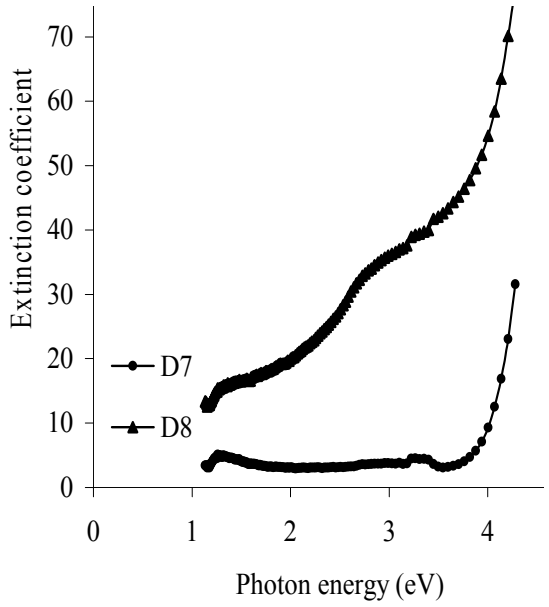

Fig. 7: Plot of extinction coefficient vs. photon energy for CdS:Fe thin films

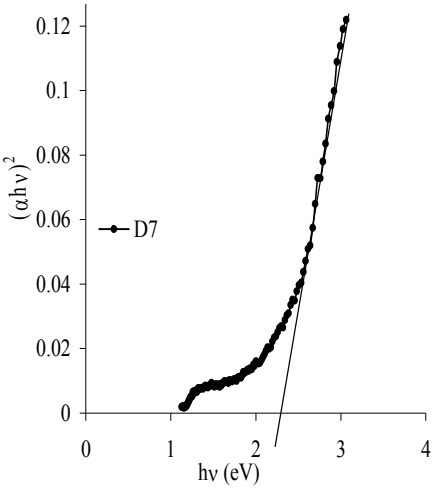

Fig. 8a: Plot of ($\alpha h\nu$) vs. $h\nu$ for as-grown CdS:Fe thin films

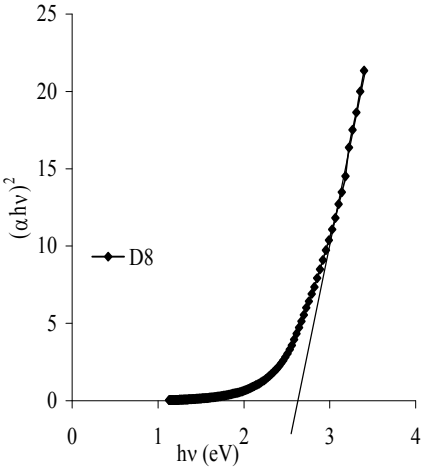

Fig. 8b: Plot of ($\alpha h\nu$) vs. $h\nu$ for CdS:Fe thin films annealed at 200^{o}C

4. Conclusions

Thin films of CdS:Fe have been successfully deposited using chemical bath deposition technique at 55^{o}C. The structural characterization reveals the co-existence of FeS with the parent CdS:Fe film when annealed at 200^{o}C. Similarly, the optical results show the influence of thermal annealing on the transmittance, absorbance as well as the reflectance of the films. The observed value of the band gap energy for as-grown film was 2.3eV, which increased to 2.6eV when annealed at 200^{o}C for 2hrs. The properties of high absorbance in the VIS and wide band gap energy exhibited by the annealed film makes the film suitable as window layers for solar cell application.

References

[1] S. Eitssayeam, U. Intatha, K. Pengpat and T. Tunkasiri, J. Materials Science **40**, 3803 (2005).
[2] K.V. Zinoviev and O. Zelaya-Angel, Mater. Chem. Phys. **70**, 100 (2001)
[3] H. Zhang, X. Ma and D. Yang, Mater. Lett. **58**, 5 (2004).
[4] K.H. Jurgen Buschow, R. W. Cahn, M.C. Flemings, B. Ilschner, E. J. Kramer and S. Mahajan, in ‘‘Encyclopedia of Materials: Science and Technology’’, Vo.2 (Elsevier, 2001) p. 873
[5] J. Britt and C. Ferekids; Appl. Phys. Lett. **62,** 2851 (1993).

[6] P.K. Nair, O. Gomez Daza, A. Arias-Carbajal Readigos and M.T.S. Nair; Semicond. Sci. Technol. **16,** 651 (2001).
[7] R.S. Mane and C.D. Lokhande; Mater. Chem. Phys. **65**, 1 (2000).
[8] H. Metin and R. Esen; J. Cryst. Growth **258,** 141 (2003).
[9] C.D. Lokhande; Mater. Chem. Phys. **26**, 405 (1990).
[10] A. Ates, M.A. Yildirim, M. Kundaki and M. Yildirim, Chinese J. of Phys. **45(2)** (2007).
[11] A.U. Ubale, R.J. Dhokne, P.S. Chikhlikar, V.S. Sangawar, D.K. Kulkarni; Bull. Mater. Sci. **29(2)** (2006)
[12] S.J. Ikhmayies, R.N. Ahmed-Bitar; American J. of Applied Sciences, **5(9)** 56 (2008)
[13] E. Cetinorgu, C. Gumus, R. Esen; Thin Solid Films, **515** (2006)
[14] M. Ristova, J. Velevska; Solar Energy Materials and Solar Cells, 71 (2002).
[15] H.M. Pathan, W.Y. Kim, K.D. Jung. O.S. Joo; Applied Surface Science, 246 (2005).
[16] P.U. Asogwa, S.C. Ezugwu, F.I Ezema, R.U. Osuji; Chalcogenide Letters. **6(7)**, 287 (2009)
[17] S.C Ezugwu, F.I. Ezema, R.U. Osuji, P.U. Asogwa, B.A. Ezekoye, A.B.C. Ekwealor, C. Chigbo, M. Anusuya, M.M. Beevi; Optoelectronics and Advanced Materials-Rapid Communications, 3(6) (2009)
[18] F.I. Ezema, A.B.C. Ekwealor, R.U. Osuji; Turk J. Phys. **30**, 157 (2006)
[19] F.I. Ezema, P.U. Asogwa, A.B.C. Ekwealor, P.E. Ugwuoke, R.U. Osuji; J. of the University of Chemical Technology and Metallurgy, **42(2)**, 217 (2007)
[20] S.C. Ezugwu, F.I. Ezema, R.U. Osuji, P.U. Asogwa, A.B.C. Ekwealor, B.A. Ezekoye; Optoelectron. Adv. Mater.-Rapid Comm., **3(2)**, 141 (2009)
[21] P.U. Asogwa; The Pacific J. of Sc. and Tech. 10(2) (2009)
[22] J.O. Oladeji, L. Chow, J.R. Liu, W.K. Chu, A.N.P. Bustamante, C. Fredrickson, A.F. Schult; Thin Solid Films, 359.
[23] K. Ravichandran, G. Muruganantham, B. Sakthivel and P. Philominathan; J. of Ovonic Research, **5(3),** 63 (2009)
[24] P.P. Hankare, A.H. Manikshete, D.J. Sathe, P.A. Chate, K.C. Rathod, Mater. Chem. Phys. **113** 183 (2009)
[25] P.U. Asogwa, S.C. Ezugwu, F.I. Ezema, Superficies y Vacio **23(1)** 18 (2010)