



## Electrochemical deposition and studies on CdCr<sub>2</sub>S<sub>4</sub> thin films

T. Mahalingam<sup>a,\*</sup>, S. Thanikaikarasan<sup>a</sup>, V. Dhanasekaran<sup>a</sup>, R. Mariappan<sup>a</sup>, P. Jayamurugan<sup>a</sup>, S. Velumani<sup>b</sup>, Jin-Koo Rhee<sup>c</sup>

<sup>a</sup> Department of Physics, Alagappa University, Karaikudi 630 003, India

<sup>b</sup> Centro de Investigación y de Estudios Avanzados del I.P.N. (CINVESTAV), Av. Instituto Politécnico, Nacional 2508, Col. San Pedro Zacatenco, 07360 México D.F., Mexico

<sup>c</sup> Millimeter-wave Innovation Technology Research Center, Dongguk University, Seoul 100 715, Republic of Korea

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### ABSTRACT

Cadmium chromium sulphide (CdCr<sub>2</sub>S<sub>4</sub>) thin films have prepared on indium doped tin oxide coated conducting glass (ITO) substrates from an aqueous electrolytic bath consists of CdSO<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> using potentiostatic electrodeposition technique. The deposited films are characterized using X-ray diffraction, scanning electron microscopy, energy dispersive analysis by X-rays and optical absorption techniques, respectively. X-ray diffraction pattern reveals that the deposited films possess polycrystalline nature with cubic structure. Surface morphology and film composition shows that the films with smooth surface and better stoichiometry are obtained under optimized deposition condition. The optical parameters such as band gap, refractive index and extinction coefficient are calculated from optical absorption measurements. The experimental observations are discussed in detail.

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### 1. Introduction

Thin films of diluted magnetic semiconductors attracts many researchers due to their wide range of applications in various fields [1–4]. Among them, ferromagnetic semiconductor systems have received much attention because of their applications in ‘spintronics’ [5,6]. CdCr<sub>2</sub>S<sub>4</sub> is found to be ferromagnetic semiconductor with a band gap value 2.4 eV which have found applications in various fields [7]. Thin films of CdCr<sub>2</sub>S<sub>4</sub> are usually crystallized in cubic structure (JCPDS-ICDD, 77-0677) with lattice constant ( $a = 10.24 \text{ \AA}$ ). Berger and Pinch studied the ferromagnetic resonance of CdCr<sub>2</sub>S<sub>4</sub> and CdCr<sub>2</sub>Se<sub>4</sub> single crystals [8]. Berger and Ekstrom have prepared CdCr<sub>2</sub>S<sub>4</sub> single crystals and studied their optical properties [9]. The preparation of CdCr<sub>2</sub>S<sub>4</sub> and HgCr<sub>2</sub>S<sub>4</sub> thin films by chemical bath deposition technique and their properties have been investigated by Mane et al. [10]. Salem and El-Ghazzawi have prepared CdCr<sub>2</sub>S<sub>4</sub> thin films using chemical deposition and studied their properties [11]. Investigation of published data indicates that huge amount of literature is available about the preparation and characterization of CdCr<sub>2</sub>S<sub>4</sub> single crystals but very few are available regarding thin films. Recently, electrodeposition technique appears to be attractive, due to its low cost and low temperature synthesise and the possibility to control the film thickness and morphology by readily

adjusting the electrical parameters as well as the composition of the electrolytic solution [12–14]. The preparation of CdCr<sub>2</sub>S<sub>4</sub> thin films on stainless steel substrates using electrodeposition technique and their structural, morphological, compositional and optical properties are investigated by Lade et al. [7]. To the best of our knowledge very few research reports are available concerning the growth and characterization of CdCr<sub>2</sub>S<sub>4</sub> thin films [7,10,11]. Hence, we have planned to carry out systematic investigation of CdCr<sub>2</sub>S<sub>4</sub> thin films obtained using electrodeposition technique. In the present work, CdCr<sub>2</sub>S<sub>4</sub> thin films have prepared on indium doped tin oxide coated conducting glass (ITO) substrates from an aqueous acidic bath containing CdSO<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The deposited films are subjected to X-ray diffraction, scanning electron microscopy, energy dispersive analysis by X-rays and optical absorption techniques, respectively. The effect of deposition potential on structural, morphological, compositional and optical properties of the films are studied and the results are discussed.

### 2. Experimental details

The chemicals used in the present work were of analytical grade reagents (99.5% Purity, supplied from SD Fine, Mumbai, India). Thin films of CdCr<sub>2</sub>S<sub>4</sub> were deposited on ITO substrates from an aqueous acidic bath containing 0.03 M CdSO<sub>4</sub>, 1 M Cr<sub>2</sub>O<sub>3</sub> 0.3 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 0.05% H<sub>2</sub>SO<sub>4</sub> and 0.05% tartaric acid using potentiostatic cathodic electrodeposition technique. The first working solution of 0.03 M CdSO<sub>4</sub> was obtained by dissolving 5.7714 g of CdSO<sub>4</sub> in 250 cm<sup>3</sup> deionized water. The second working solution of 1 M Cr<sub>2</sub>O<sub>3</sub> was

\* Corresponding author. Tel.: +91 4565 230251.

E-mail address: [maha51@rediffmail.com](mailto:maha51@rediffmail.com) (T. Mahalingam).

obtained by dissolving 37.9975 g of  $\text{Cr}_2\text{O}_3$  in  $250\text{ cm}^3$  deionized water. The third working solution of  $0.3\text{ M Na}_2\text{S}_2\text{O}_3$  was obtained by dissolving 18.6135 g of  $\text{Na}_2\text{S}_2\text{O}_3$  in  $250\text{ cm}^3$  deionized water. Initially, the pH value of the electrolytic bath was  $3.5 \pm 0.1$ . By adding adjustable amount of NaOH the pH of the electrolytic bath was adjusted to  $5.5 \pm 0.1$ . If the pH value is low (below  $3.5 \pm 0.1$ ) there is rapid growth of films followed by its peeling out from the substrate. If the pH value is high (such as above  $6.5 \pm 0.1$ ) precipitation of  $\text{Na}_2\text{S}_2\text{O}_3$  occurs which yields films with poor quality. Hence the pH value was fixed as  $5.5 \pm 0.1$  to deposit  $\text{CdCr}_2\text{S}_4$  thin films. All the depositions were carried out using a PAR scanning potentiostat/galvanostat unit (Model 362, EG & G, Princeton Applied Research, USA) employing three electrode configuration with ITO substrate as working electrode, graphite plate as counter electrode and saturated calomel electrode (SCE) as reference electrode, respectively. The ITO substrates were treated for 15 min with ultrasonic waves in a bath of isopropanol and then rinsed with acetone. The SCE was kept closer to the working electrode by Luggin capillary arrangement. The pH of the electrolytic bath was maintained in the range between 3.5 and  $6.5 \pm 0.1$ . The bath temperature and deposition time were fixed as  $80^\circ\text{C}$  and 45 min, respectively. The deposition potential was fixed in the range between  $-550$  and  $-850\text{ mV}$  versus SCE.

Thickness of the deposited films was measured using stylus profilometer (Mitutoyo SJ 301). An X-ray diffractometer (XPERTPRO PANalytical, Netherland) with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.1540\text{ nm}$ ) was used to identify the crystalline nature and phases of the deposited films. The surface morphology and film composition were analyzed using an energy dispersive analysis by X-rays set up attached with scanning electron microscope (JEOL JSM 840). Optical absorption measurements of the deposited films was recorded using an UV–Vis–NIR spectrophotometer (HR-2000, M/S Ocean Optics, USA).

### 3. Results and discussion

#### 3.1. Film thickness

Thickness of the deposited films is controlled by separate variables such as (i) uniform growth (ii) surface morphology. Thickness of the deposited films is measured using stylus profilometer. By controlling the deposition potential and time, thickness of the deposited films could be controlled. Fig. 1 shows the variation of

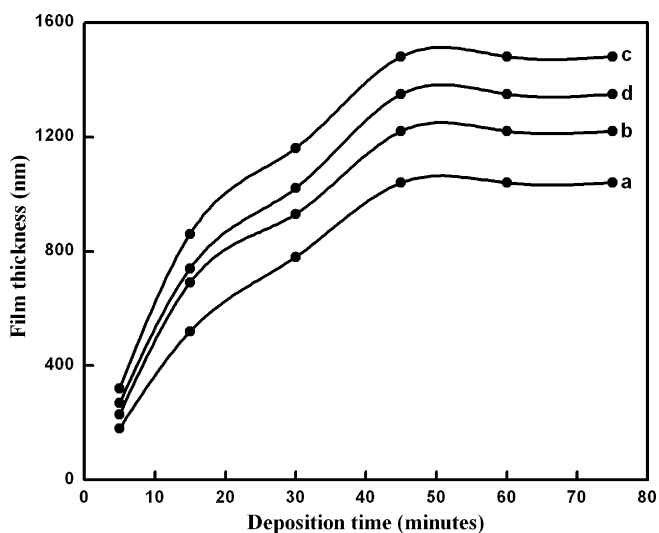


Fig. 1. Variation of film thickness with deposition time for  $\text{CdCr}_2\text{S}_4$  thin films prepared at various deposition potentials: (a)  $-550\text{ mV}$  versus SCE, (b)  $-650\text{ mV}$  versus SCE, (c)  $-750\text{ mV}$  versus SCE and (d)  $-850\text{ mV}$  versus SCE.

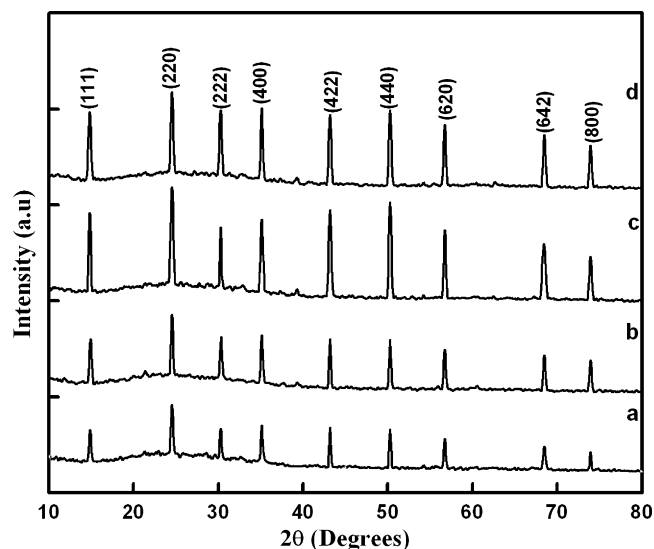


Fig. 2. X-ray diffraction pattern of  $\text{CdCr}_2\text{S}_4$  thin films prepared at various deposition potentials: (a)  $-550\text{ mV}$  versus SCE, (b)  $-650\text{ mV}$  versus SCE, (c)  $-750\text{ mV}$  versus SCE and (d)  $-850\text{ mV}$  versus SCE.

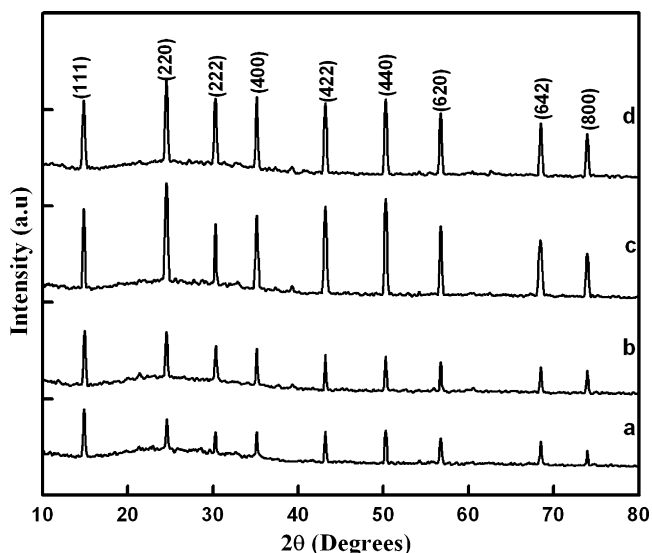
film thickness with deposition time for  $\text{CdCr}_2\text{S}_4$  thin films prepared at various deposition potentials ranging from  $-550$  to  $-850\text{ mV}$  versus SCE. It is observed from Fig. 1 that films with lower thickness is obtained at lower potential such as below  $-750\text{ mV}$  versus SCE. The films prepared at higher potential such as above  $-750\text{ mV}$  versus SCE thickness of the deposited films decreases due to the process of hydrogen evolution [14]. Hence, the films prepared in the potential region between  $-550$  and  $-750\text{ mV}$  versus SCE are found to be uniform and dense. It is observed from Fig. 1a that film thickness increases linearly with deposition time tend to attain its maximum value at a deposition time of 45 min. Further increasing deposition time above 45 min thickness of the films remains constant upto 75 min, thereafter it decreases slightly not shown in Fig. 1. Similar trend is noted for films prepared at various potentials. The maximum value of film thickness is obtained for films prepared at a deposition potential  $-750\text{ mV}$  versus SCE and at a deposition time of 45 min. Similar behaviour exhibited for  $\text{Cu}_2\text{O}$  thin films reported earlier [15].

#### 3.2. Structural studies

##### 3.2.1. Effect of deposition potential

X-ray diffraction pattern recorded for  $\text{CdCr}_2\text{S}_4$  thin films prepared on ITO substrates at various deposition potentials ranging from  $-550$  to  $-850\text{ mV}$  versus SCE is shown in Fig. 2. X-ray diffraction results represents that the deposited films possess polycrystalline nature with cubic structure with lattice constant ( $a = 10.24\text{ \AA}$ )

The diffraction peaks of  $\text{CdCr}_2\text{S}_4$  are observed at  $2\theta$  values of angles 14.82, 24.51, 30.27, 35.12, 43.17, 50.27, 56.72, 68.47, 73.92 corresponding to the lattice planes (111), (220), (222), (400), (422), (440), (642) and (800), respectively. The different peaks in the diffractogram are indexed and the corresponding values of interplanar spacing 'd' are calculated and compared with standard values [16]. It is observed from the diffractogram that all the identified peaks are from  $\text{CdCr}_2\text{S}_4$  and no additional peaks corresponding to Cd, Cr and S are present. Fig. 2 represents that the degree of crystallinity of the deposited films increases while increasing the deposition potential from  $-550$  to  $-750\text{ mV}$  versus SCE, thereafter the degree of crystallinity decreases slightly. The height of (220) peak is found to be higher than all other peaks in the diffractogram indicates that the crystallites are preferentially oriented



**Fig. 3.** X-ray diffraction pattern of  $\text{CdCr}_2\text{S}_4$  thin films prepared at various solution pH values: (a)  $3.5 \pm 0.1$ , (b)  $4.5 \pm 0.1$ , (c)  $5.5 \pm 0.1$  and (d)  $6.5 \pm 0.1$ .

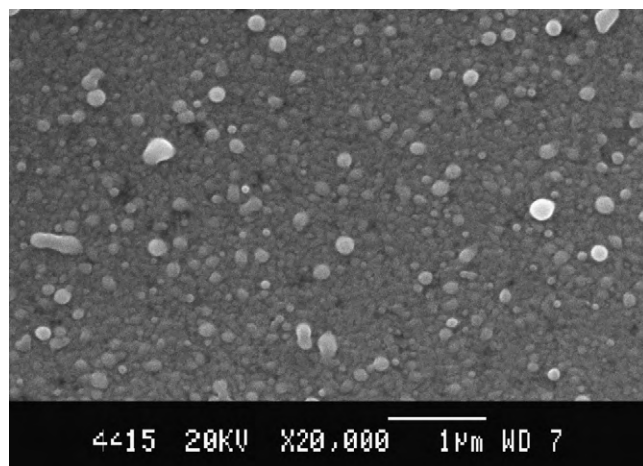
along (2 2 0) plane. It is observed from Fig. 2a–c that the height of (2 2 0) and all other planes are found to increase while increasing the deposition potential upto  $-750$  mV versus SCE, thereafter the height of all the peaks are decreases slightly as shown in Fig. 2d. The appearance of sharp and more intense diffraction peak at a deposition potential  $-750$  mV versus SCE represents the formation of films with better crystallinity. The crystallite size of the deposited films is calculated using Debye–Scherrer formula given in Eq. (1) [12].

$$D = \frac{0.9\lambda}{\beta \cos \theta_B} \quad (1)$$

where  $\lambda$  is wavelength of  $\text{CuK}\alpha$  target used ( $\lambda = 0.1540$  nm),  $\beta$  is Full Width at Half Maximum of the peak in radian,  $\theta_B$  is Bragg diffraction angle at peak position in degrees. The crystallite size of the films prepared in the potential range between  $-550$  and  $-850$  mV versus SCE are found to be in the range between 32 and 43 nm. Similar behaviour exhibited for  $\text{Cu}_2\text{O}$  thin film reported earlier [15].

### 3.2.2. Effect of solution pH

The solution pH value is one of the important parameter which determine the structure and stoichiometry of the deposited films. The electrochemical deposition of  $\text{CdCr}_2\text{S}_4$  thin films are carried out at various solution pH values in the range between 3.5 and  $6.5 \pm 0.1$ . If the solution pH value is lesser than  $3.5 \pm 0.1$  the formation of films may be hindered due to the process of hydrogen evolution reaction. The process of hydrogen evolution gives poor quality films. If the solution pH value is greater than  $6.5 \pm 0.1$ , precipitation of electrolytic bath occurs which in turn yield poor quality films. Hence the solution pH value is fixed in the range between 3.5 and  $6.5 \pm 0.1$  in order to prepare good quality films. X-ray diffraction pattern recorded for  $\text{CdCr}_2\text{S}_4$  thin films prepared at various solution pH values is shown in Fig. 3. It is observed from Fig. 3 that the diffraction peaks of  $\text{CdCr}_2\text{S}_4$  are found at values of angles 14.82, 24.51, 30.27, 35.12, 43.17, 50.27, 56.72, 68.47, 73.92 corresponding to the lattice planes (1 1 1), (2 2 0), (2 2 2), (4 0 0), (4 2 2), (4 4 0), (6 4 2) and (8 0 0), respectively. The different peaks in the diffractogram are indexed and the corresponding values of interplanar spacing 'd' are calculated and compared with standard values [16]. It is observed from Fig. 3a, that the films deposited at pH value around  $3.5 \pm 0.1$  exhibit the peaks of  $\text{CdCr}_2\text{S}_4$  with preferential orientation along (1 1 1) plane. If the pH value of the electrolytic bath is increased



**Fig. 4.** SEM picture of  $\text{CdCr}_2\text{S}_4$  thin films obtained at a deposition potential of  $-750$  mV versus SCE.

to  $4.5 \pm 0.1$  the peak height of (1 1 1) plane decreased and there is slight increment in peak height of (2 2 0) plane. The films deposited at pH value  $5.5 \pm 0.1$  is found to exhibit well defined crystallites with preferential orientation along (2 2 0) plane. Further increasing the pH value above  $5.5 \pm 0.1$ , the intensity of all the peaks are found to decrease as shown in Fig. 3d. It is also observed from Fig. 3a–d there is no change in crystal structure, but there is change in preferential orientation of the plane from  $3.5 \pm 0.1$  to  $5.5 \pm 0.1$  is observed. Similar behaviour is exhibited for  $\text{Cu}_2\text{O}$  thin films reported earlier [17]. Hence, the solution pH value is fixed as  $5.5 \pm 0.1$  for further studies. The sizes of the crystallites are found to be in the range between 20 and 43 nm for films obtained at different pH values.

### 3.3. Morphological and compositional analyses

The surface morphology of  $\text{CdCr}_2\text{S}_4$  thin films has been analyzed using scanning electron microscope. Fig. 4 shows the SEM image of  $\text{CdCr}_2\text{S}_4$  thin films prepared at a deposition potential  $-750$  mV versus SCE. It is observed from Fig. 4 that the film surface is found to be smooth and covered with tiny spherically shaped grains. The grains are distributed over the entire surface of the film. The unreacted sulphur could be seen at few places on the surface of the film. The sizes of the grains are found to be in the range between 0.12 and  $0.22 \mu\text{m}$ . The average size of the grains is found to be  $0.16 \mu\text{m}$ .

The quantitative analysis of  $\text{CdCr}_2\text{S}_4$  thin films has been carried out in order to determine the relationship between deposition potential and film composition. After etching the film surface, a quantitative determination of  $\text{CdCr}_2\text{S}_4$  thin films has been analyzed using energy dispersive analysis by X-ray spectroscopy. Fig. 5 shows the variation of Cd, Cr and S content with deposition potential for  $\text{CdCr}_2\text{S}_4$  thin films obtained at various deposition potentials. It is observed from Fig. 5 that the content of Cd and S decreases and the content of Cr increases while increasing the deposition potential from  $-550$  to  $-850$  mV versus SCE. The atomic molar ratio (Cd:Cr:S) for  $\text{CdCr}_2\text{S}_4$  thin films obtained at deposition potential  $-750$  mV versus is found to be 1.09:1.83:4.08: indicates the nearly stoichiometric formation of  $\text{CdCr}_2\text{S}_4$  thin films. This result is consistent with X-ray diffraction analysis of the sample with phase corresponds to  $\text{CdCr}_2\text{S}_4$ . Similar result exhibited for  $\text{CdCr}_2\text{S}_4$  films reported earlier [7].

### 3.4. Optical properties

The optical absorption of  $\text{CdCr}_2\text{S}_4$  thin films has been analyzed without accounting for reflection and transmission losses. The nature of transition involved is determined from

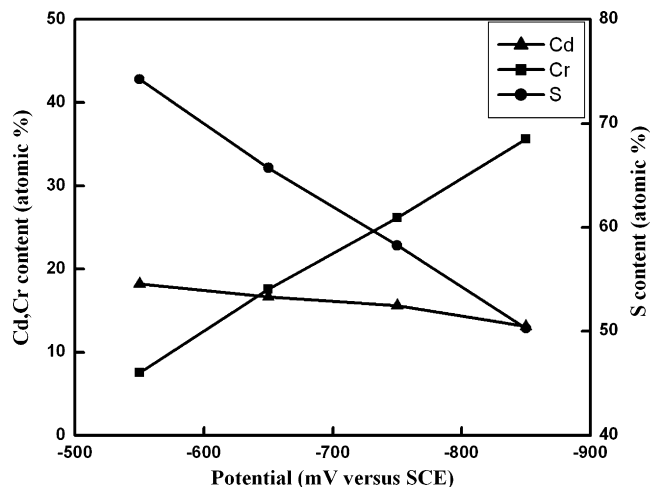


Fig. 5. Variation of Cd, Cr and S content with deposition potential for films obtained at various deposition potentials.

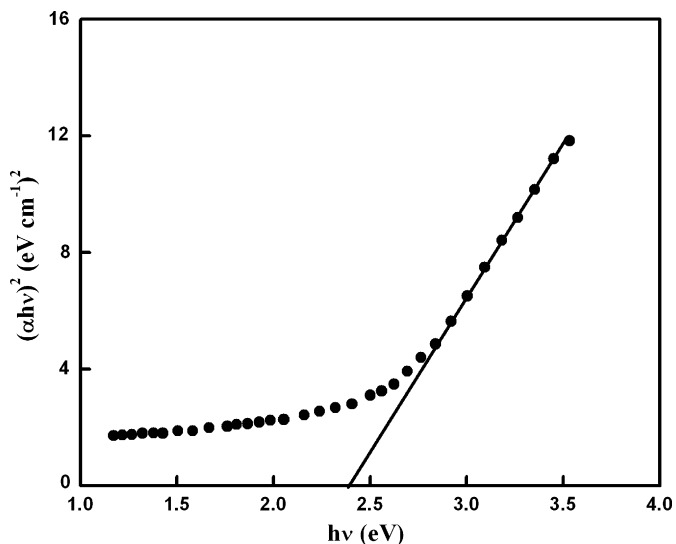


Fig. 6. Plot of  $h\nu$  versus  $(\alpha h\nu)^2$  for  $\text{CdCr}_2\text{S}_4$  thin films prepared at a deposition potential of  $-750$  mV versus SCE.

the absorption coefficient values using the following relation [14].

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where  $\alpha$  is the absorption coefficient in  $\text{cm}^{-1}$ ,  $h\nu$  is the photon energy,  $A$  is an energy dependent constant and  $E_g$  is the energy gap. For allowed direct transition  $n=1/2$  and for allowed indirect transition  $n=2$ . From the calculated values of absorption coefficients, a plot of  $h\nu$  versus  $(\alpha h\nu)^2$  is drawn for  $\text{CdCr}_2\text{S}_4$  thin film prepared at a potential value  $-750$  mV versus SCE and shown in (Fig. 6). The linear portion of the graph is extrapolated to the energy axis ( $X$ -axis) which is shown in Fig. 6. The intersection point gives the band gap energy of the material. The estimated value of band gap is found to be  $2.38$  eV. The band gap value of material obtained in this work is quite closer to the value reported earlier [7]. The refractive index and extinction coefficient are calculated for films obtained at a deposition potential  $-750$  mV versus SCE in the wavelength range between  $350$  and  $1100$  nm. Fig. 7 shows the variation of refractive index and extinction coefficient with wavelength for  $\text{CdCr}_2\text{S}_4$  thin films. It is observed from

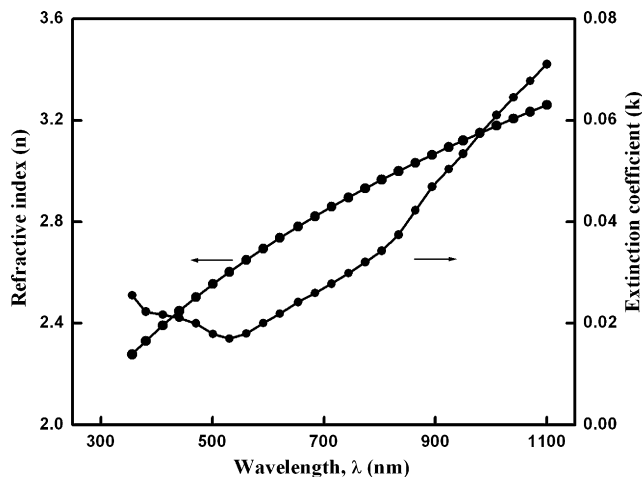


Fig. 7. Variation of refractive index ( $n$ ) and extinction coefficient ( $k$ ) with wavelength ( $\lambda$ ) for  $\text{CdCr}_2\text{S}_4$  thin films.

Fig. 7 that the value of refractive index increases and extinction coefficient decreases upto  $530$  nm, thereafter both of them increases.

#### 4. Conclusions

Thin films of  $\text{CdCr}_2\text{S}_4$  have been deposited on ITO substrates at various deposition potential and solution pH values using potentiostatic electrodeposition technique. X-ray diffraction pattern of the deposited films reveals the formation of films with polycrystalline nature with tetragonal structure. It is also observed that the crystallites are found to exhibit most prominent reflection along  $(220)$  plane. The pH effect on structural properties shows that there is change in most prominent reflection from  $(111)$  to  $(220)$  for films obtained at various solution pH values. Surface morphology and film composition shows that films with better quality and stoichiometry are obtained at a deposition potential  $-750$  mV versus SCE. The band gap value of the material obtained in this work is found to be  $2.38$  eV which is in close agreement with the value reported earlier. The value refractive index and extinction coefficient are found to be  $2.6$  and  $0.017$ .

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