**INFLUENCE OF FE DOPING ON CDS THIN FILMS****\*Munjaji E. Dudhamal, Jayesh R. Pawar and Rajesh A. Joshi\***

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**ABSTRACT**

The synthesis controlled optoelectronic and physicochemical properties of CdS thin films make it one of the potentially important semiconducting materials for application in various gadgets, sensors such as solar cell etc. The synthesis technologies includes physical as well as chemical approach, with an ultimate goal to control and modify the conductivity of materials for its applications, hence considering this

aspect, we have tried to study the Fe doping influence on photoconductivity of CdS thin films prepared using large area depositing, user friendly, cost effective chemical route on glass substrate. The synthesized as deposited and Fe doped CdS thin films characterized for evaluating the current density and conductivity using I-V characteristics, crystal structure, phase transition determined using X-ray diffraction (XRD) where peaks representing the planes (002), (101), (111), (110) and (200) confirms the formation of hexagonal phase of CdS thin films, while no specific separate peak confirming the formation of Fe doping is observed, except suppressing of (111) and (200) planes. Elemental composition and film morphology studied with the help of energy dispersive X-ray diffraction analysis (EDAX) equipped scanning electron microscopy (SEM) revealed and confirmed the expected and observed elemental composition; film morphology represents voids, rough and granular structural distribution over the substrate surface. Optical absorbance spectra revealed shift in absorbance peak from ~467 to ~495nm associated with band to band transition and spin orbit interaction on doping along with decrease in energy band gap from 2.19 to 2.04eV. The electrical properties revealed increase in electrical conductivity; this is also supported by an increment in current density upon Fe doping.

**KEYWORDS:** Chemical Bath Deposition, Thin film, Optoelectronic properties, Energy band gap, Photoconductivity, Doping influence.

## INTRODUCTION

Cadmium sulfide (CdS) thin films being semiconductor materials having great potential surface dependant opto-electronic properties which make it extremely useful as window layer accompanied with I-III-VI compounds to work as solar cell and other applications like light sensors, optical detectors etc.<sup>[1-3]</sup> As such thin films can be synthesized by different ways like physical and chemical which includes thermal, vacuum evaporation, chemical vapor deposition, spray pyrolysis, metal organic vapor-phase epitaxy, closed space sublimation, photochemical deposition, radio frequency sputtering, vapor transport deposition, electro deposition, pulsed laser ablation and chemical bath deposition etc.<sup>[4,5]</sup> but the thin films prepared by physical methods are having some shortcomings like compressed surface morphology, lower absorption coefficient and short path length etc, on the other hand films prepared by chemical route may results in uniformly distributed grains over the substrate surface having higher absorbance coefficient, good path length for charge transportation and charge separations etc. When materials considered for device grade applications, electrical properties like resistivity, conductivity plays very vital role hence these properties needs to be tailored, this can be done by adding some external materials like Fe as dopents.<sup>[6-8]</sup> Fe may behave as charge acceptor and thereby the photo-response characteristics of CdS film can be highly influenced, even the direct energy band gap may be decreased. Since Fe ions can replace either substitutional or interstitial cadmium ions in the CdS lattice hence it may take part in the process of charge separation and thereby increase the materials conductivity.<sup>[9,10]</sup>

Therefore considering the importance of conductivity alteration of CdS thin films for application as photo-sensor materials; we have tried to dope Fe using the user friendly, large area depositing chemical route on glass substrate. These as deposited and Fe doped CdS thin films characterized for X-ray diffraction pattern (XRD), Raman spectra, energy dispersive X-ray spectrum analysis (EDAX), scanning electron microscopy (SEM), UV-Vis absorbance spectroscopy and I-V for studying electrical properties under light illumination conditions respectively.

## EXPERIMENTAL

The CdS thin films synthesized onto glass substrates by using simple chemical bath depositions (CBD) technique with deposition temperature maintained at 80°C using cadmium

sulfate ( $\text{CdSO}_4$ ) and thiourea ( $\text{SC}(\text{NH}_2)_2$ ) as source of Cd and S respectively. The growth mechanism involved in the formation of CdS includes reaction between the cationic and anionic solution in an alkaline medium with deposition rate as a function of reaction bath temperature.<sup>[7,11]</sup> The aqueous solutions of two reactants were mixed, while pH was set at ~11 the reaction carried for 1hr to obtain yellowish-orange colored CdS thin film, while the Fe doping is carried out by the same simple method of adding controlled and calculated amount of  $\text{FeSO}_3$  solution, to obtain Fe doping in CdS thin films, very slight difference in physical appearance is observed compared to as deposited CdS thin films.<sup>[12]</sup>

These as-deposited and Fe doped CdS thin films are characterized for structural, elemental, morphological, optical and electrical properties. The structural analysis was performed using X-ray diffraction (XRD) patterns recorded on Bruker AXS, German (D8 Advanced) diffractometer in scanning range of  $20\text{-}60^\circ$  ( $2\theta$ ) using  $\text{Cu K}\alpha_1$  radiations with wavelength of  $1.5405 \text{ \AA}$ . Elemental composition and surface morphology studied from scanning electron microscopy associated energy dispersive X-ray spectrum facility obtained on JEOL-JSM-5600. Optical absorbance spectra are recorded using UV-Vis spectrophotometer in the range 400 to 1100nm over Elico model SL-177. I-V response measured under illumination to  $100\text{mW}/\text{cm}^2$  light source and the data acquired on Lab-Equip I-V measurement setup.

## RESULTS AND DISCUSSION

### *X-ray diffraction (XRD)*

Fig. 1 shows the X-ray diffraction pattern (XRD) of the as deposited and Fe doped CdS thin films, from the profile it can be revealed that the films are polycrystalline in nature, while three prominent peaks can be seen corresponding to (111), (220) and (311) planes which are in good agreement with standard JCPDS data card 65-2887.<sup>[13]</sup> The preferential orientation along the (111) plane is associated with rising of small peaks in doped thin films indexing (100) and (101) (JCPDS card 77-2306) which could be attributed to hexagonal phase modifications and improvement in crystallinity of the particles. Even on doping the diffraction peaks shows very small shift which can be correlated to variation in lattice parameters, this may be due to the smaller ionic radius of Fe (0.064 nm) compared to Cd (0.096 nm).<sup>[14]</sup> Hence, doping of Fe leads to the structural phase transformation, this can be correlated to the fact that number of available diffracting planes decreases with decrease in size which ultimately leads to the broadening of the diffraction peaks.<sup>[15]</sup> The average

crystallite size calculated using Debye Scherrer formula is found to be ~27nm and ~35 nm for as deposited and Fe doped thin films respectively.<sup>[16]</sup>

### ***Compositional analysis***

Fig. 3(a) and 3(b) corresponds to energy dispersive X-ray analysis spectra (EDAX) obtained from as deposited and Fe doped CdS thin films respectively, used for the elemental composition analysis of the material ingredients. From the spectrum it is observed that the elemental proportion of cadmium (Cd) and sulphur (S) in the as deposited and Cd, S and Fe in the doped thin films corresponds and confirms the expected stoichiometry of the elements.<sup>[1,14]</sup> Non observation of any other peak in the spectra corresponds that no other external impurity is present in the materials.

### ***Surface morphology***

Fig. 4(a) and 4(b) represents the scanning electron microscope (SEM) images of as deposited and Fe doped CdS thin films respectively, which shows uniform distribution of grains all over the substrates. The granular size observed to be smaller and fine in case of as deposited samples while morphology of the doped thin films shows relatively larger grains with presence of some voids, such differentiations can be correlated to growth of fewer defects and stresses resulting in larger grains. Since the method followed in the present article includes ion exchange mechanism, hence the doped species fixes itself either at interstitial sites and/or substitution sites.<sup>[19]</sup> The acquisition of position depends on size of atoms and vacant sites available, this phenomenon may be explained with interstitial-substitution diffusion with touch and go mechanism. Such morphology can be useful when considering the material for surface related operations like physical and/or chemical sensors etc.

### ***Optical analysis***

The as deposited and Fe doped CdS thin films characterized for understanding the electronic transition using optical absorbance analysis techniques represented by Fig. 5 which reveals, significant variation in optical properties upon Fe doping. From the optical absorption spectra, it is observed that the absorbance coefficient increases in doped thin films comparative to as deposited. The absorption peaks obtained in the optical spectra of as deposited sample can be correlated to band to band transitions while on Fe doping the variations may have been observed due to alloy fluctuation, defects absorption, Fe intra-ion absorption and large exchange interaction of electrons in conduction and valence bands with the d electrons of Fe.<sup>[16,20]</sup> This spin orbit interaction between Fe and S can be expected to be

main cause for observed shift in absorption band edge. Effect of this orbital hybridization can be understood by drawing energy band gap of as deposited and Fe doped thin films, as represented in inset of Fig. 5 which shows plot of  $(\alpha h\nu)^2$  versus  $h\nu$  for calculation of energy band gap ( $E_g$ ). Decrease in energy band gap from 2.19 to 2.04eV is observed for as deposited and Fe doped CdS thin films respectively which can be attributed to increased  $p$ - $d$  interaction on doping. According to energy band theory the upper valence band is formed by  $p$ - $d$  hybridization involved in band formation.<sup>[14]</sup> The strength of  $d$ - $p$  interaction depends inversely on energy of separation between Cd and S, therefore the repulsive interaction pushes the anti-bonding  $p$ - $d$  states that constitute valence band maxima (VBM) to higher energies.

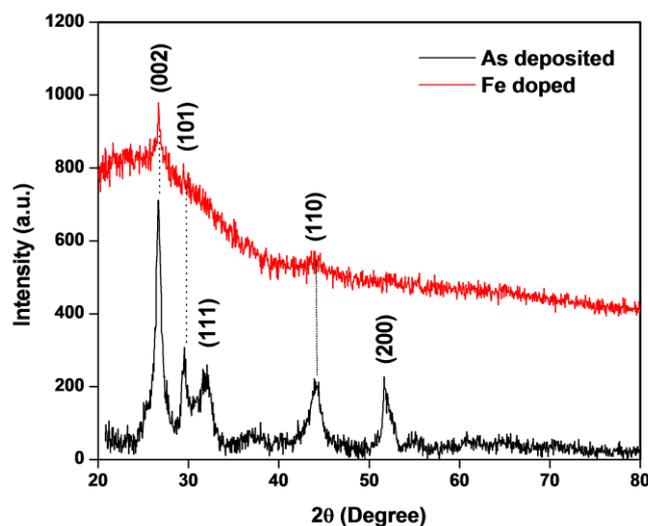


Figure 1: XRD pattern obtained from as deposited and Fe doped CdS thin films

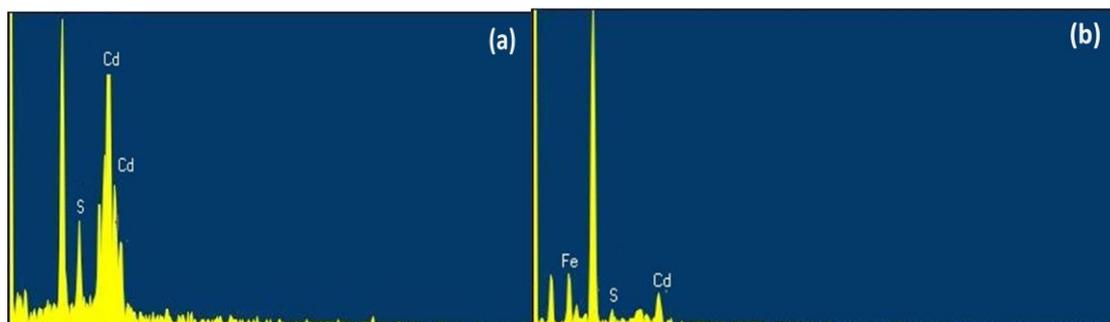


Figure 2 (a) and (b): Represents the EDAX spectra obtained from as deposited and Fe doped CdS thin films respectively.

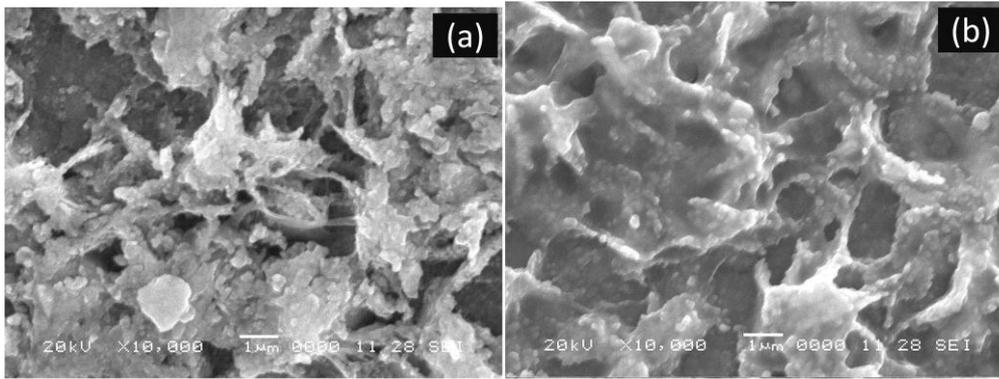


Figure 3 (a) and (b): Represents the SEM images obtained from as deposited and Fe doped CdS thin films respectively.

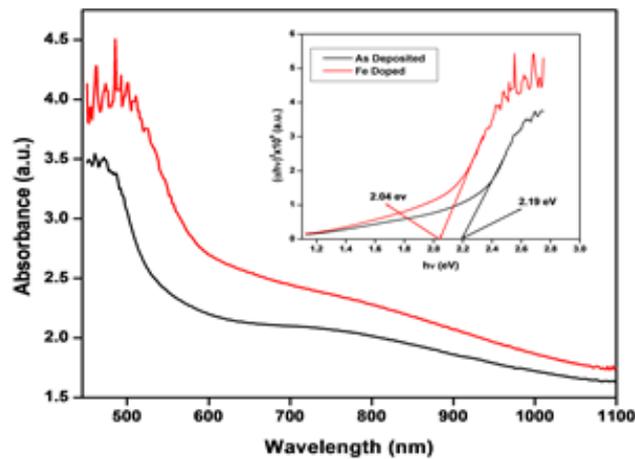


Figure 4: Shows the plot of wavelength against absorbance used for deriving the absorbance coefficient and inset figure represents the plot of energy against  $\alpha h\nu^2$  used for plotting the energy band gap of the materials.

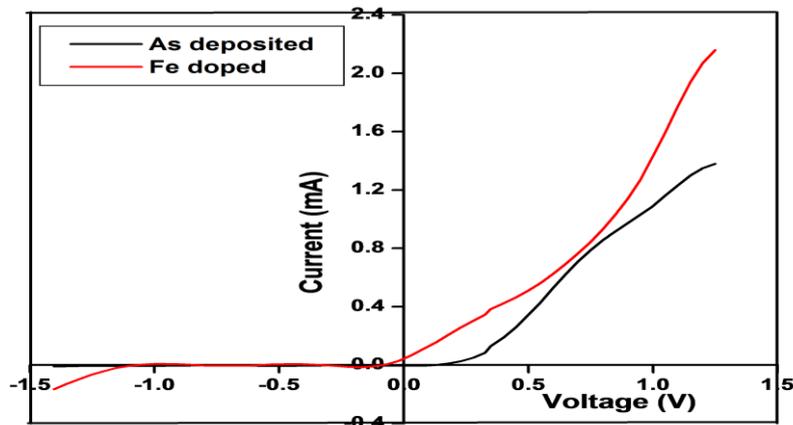


Figure 5: Plot of current (I) versus voltage (V) under illumination condition used for deriving the photoconductivity of the as deposited and Fe doped CdS thin films.

### *Electrical characteristics*

The charge transformations in as deposited and Fe doped CdS thin films are studied by using electrical properties derived from current voltage (I-V) characteristics as represented in Figure 6 and four probe techniques used for calculation of electrical charge carrier concentrations. I-V characteristics represent the Ohmic behavior of as deposited and Fe doped CdS thin films, the photoconductivity calculated in both cases corresponds to increase from 56% to 85% respectively, while the conductivity of Fe doped CdS thin film is observed to be higher than the as deposited CdS thin films, this increment in the conductivity can be related to the defect state induced charge transformation.<sup>[16]</sup> The chemical route synthesized as deposited thin films may contains surface defects, which consists of fine crystallites with higher surface area having well separated grain boundaries, this can generates disturbance for donor-acceptor transitions, where donor and/or acceptor defects are located at surfaces or grain boundaries.<sup>[21]</sup>

As Fe doping treatment is provided, chemical composition modifications and thereby Fe and Cd atoms replacement may have provided the path for swift electron hole pair generation and transportation.<sup>[22]</sup> So by the space charge limited theory compositional modification may lead to reduce trap levels in the material so upon illumination the generation of electron-hole pair may fulfill the trap levels and hence can result in increase in conductivity of the material.

### **CONCLUSIONS**

From the results obtained above it can be concluded that the CdS thin films and Fe doping can be achieved using the cost effective user friendly and large area depositing chemical bath technique. The XRD spectrum confirms formation of CdS and Fe doping in CdS thin films. Observance of Cd, S and Fe peaks in EDAX confirms expected and observed elemental composition in as deposited and Fe doped CdS thin films. The interstitial and substitutional replacement of ionic elements leads to optical band edge and energy band gap increments, while the conductivity of the materials observed to be increased upon Fe doping which is attributed to defect state and compositional modifications induced phenomenon.

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