STRUCTURAL AND THERMAL STUDY OF RUTHENIUM AND INDIUM DOPED CdSe THIN FILMS

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Abstract-

In present work, Ruthenium and Indium doped Cdse thin films were synthesized using the chemical bath deposition Technique on the fluorine doped tin oxide (FTO) substrate. The crystal structure and surface composition of the doped CdSe thin film are obtained by X-ray diffraction patterns, energy dispersive X-ray analysis, and FE-SEM images. The optical properties of obtained films were characterized by UV-visible spectral analysis. The UV- visible study reflects the transmittance and band gap in the range of 1.65 to 1.75 eV. Thermogravimetric analysis of doped CdSe in temperature region from zero to 1000 ⁰C confirms the weight loss of 10 % in the range from 200 to 250 ⁰C due to the removal of water contents from the film surface.

Keywords: - *Thin films, Chemical bath deposition, band gap, thermal stability.*

1. Introduction:-

In recent years, scientists and researchers shows their interest/curiosity towards the II-VI chalcogenide materials owing to the unique properties of thin films which get differ from the bulk material post doping scenario.(1-3) Cadmium selenide (Eg = 1.7 eV) is one of the binary semiconductors from II-VI group which has fascinated attention of many researchers due to its interesting properties and wide range of applications. Till date, scientific community explore different accepts of cadmium selenide (Cdse) nanostructure based thin films regarding to their basic properties and apply these properties for various applications like solar cells, optical detectors, dosimeters of ionized radiation, field effect transistors, and optoelectronic devices. (4-11) Especially, the n-type CdSe semiconductor (having bandgap 1.75 eV) has become quite interesting and significant because of its key applications to harness solar energy as well as uses in photodetection, optoelectronics, light amplifiers, and electrophotography devices. In general, the CdSe nanostructure based research has been extensively focused on influencing major features of electrical, optical, and structural properties of CdSe compounds (12,13). In present work, for synthesizing CdSe thin film the simple chemical bath deposition (CBD) technique was used for the synthesis of Ruthenium (Ru) and Indium (In) doped CdSe thin films simultaneously and yielding reproducible results for deposition of thin films of HgSe, CdHgS, etc. (14-16)

In the present investigation, efforts have been made to study of Pristine and doped (Ru and In) CdSe. These doped and undoped CdSe films were synthesized using CBD method and employed for structural elucidation (XRD and EDS), structural changes (TGA and UV- visible spectra), and morphology evolution (SEM). The preparation and properties are presented in this communication.

2. Experimental details

The Ru and In doped CdSe thin films have been synthesized on the fluorine doped tin oxide (FTO) substrate by CBD method. All the chemicals used were of analytical grade and used without any further purification.

Cadmium sulfate ($CdSO_4$), triethanolamine (TEA) (S.D. Fine), selenium powder (Aldrich), sodium hydroxide (NaOH), liquor ammonia, distilled water is used as solvent for the preparation of chemicals. The Sodiumselenosulphite was prepared by refluxing 5 gm selenium powder (Aldrich) with anhydrous sodium sulphite in 200 ml distilled water for about 9 hours use this final solution as stock solution for further reaction. For deposition purpose, 10 ml of 1 M $CdSO_4$ solution was taken in a beaker followed by the 5 ml of TEA solution was added to form a complex. Adjust the pH of the reaction mixture about 10.5±0.1 by adding 3ml NaOH (1 N) solution and 20 ml aqueous ammonia (14 N) solution in the complex prepare earlier. Make this resultant solution to 180 ml by the addition of distilled water. For doping purpose, add Ruthenium Chloride ($RuCl_3$) (Spectrochem) externally in different concentrations which varying from 0. 01mM (MiliMole) to 0.08 mM and add indium chloride ($InCl_3$) (Spectrochem) of 0.05 mM concentration was added to get the proper doping at the interstitial sites. This resultant mixture transfer in to fresh beaker and insert FTO coated glass substrates (approximately 75mm × 25mm × 2 mm in dimension) and cleaned repeatedly by double distilled water keep FTO vertically at 90º to each other to the substrate holder and which maintain at 70±5 rpm speed. Add stock solution of Sodiumselenosulphite slowly in the reaction mixture keep this reaction mixture in oil bath at 60ºC temperature for 90 min. After complete deposition the films were separated from substrate holder and washed several times with double distilled water and dried to get resultant films of Ru and In doped CdSe films. These thin films were used for further study.

3. Result and discussion-

3.1 Structural analysis

Fig. 1 shows the XRD pattern of the Ru and In doped CdSe thin fims. From the XRD spectral analysis it is clears that Ru and In doped CdSe thin films shows the crystalline nature.

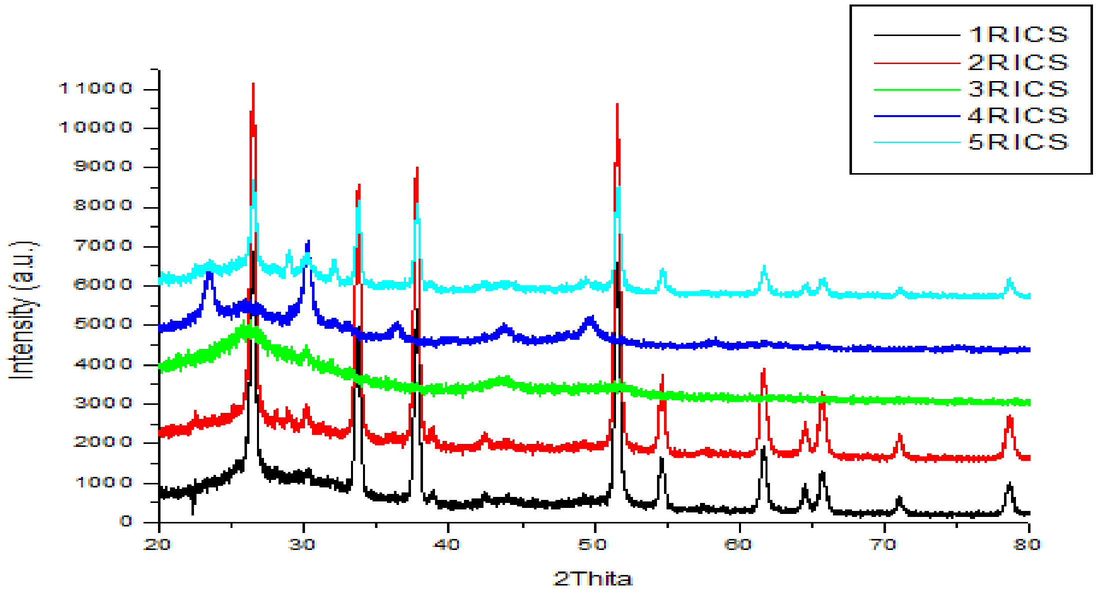

Fig 1. XRD pattern of Ru and In doped CdSe thin film

The peaks obtained at 26.666, 42.600 and 60.5214 is well match with (111), (220) and (311) respectively are matches with JCPDS card No 00-019-0191.which confirms the cubic nature of the material.(17) Slight shifting in the peak position confirms the Ru and In doping in CdSe.

3.2 Morphological and compositional analysis

Fig 2 a) illustrates FE-SEM images of Ru and In doped CdSe thin film. FE-SEM shows cubic structure of granules starts to grow on the surface. These cubical granules grows in different directions as well as in some places looks like larger in size. The uniform deposition of the material can be seen on the substrate.

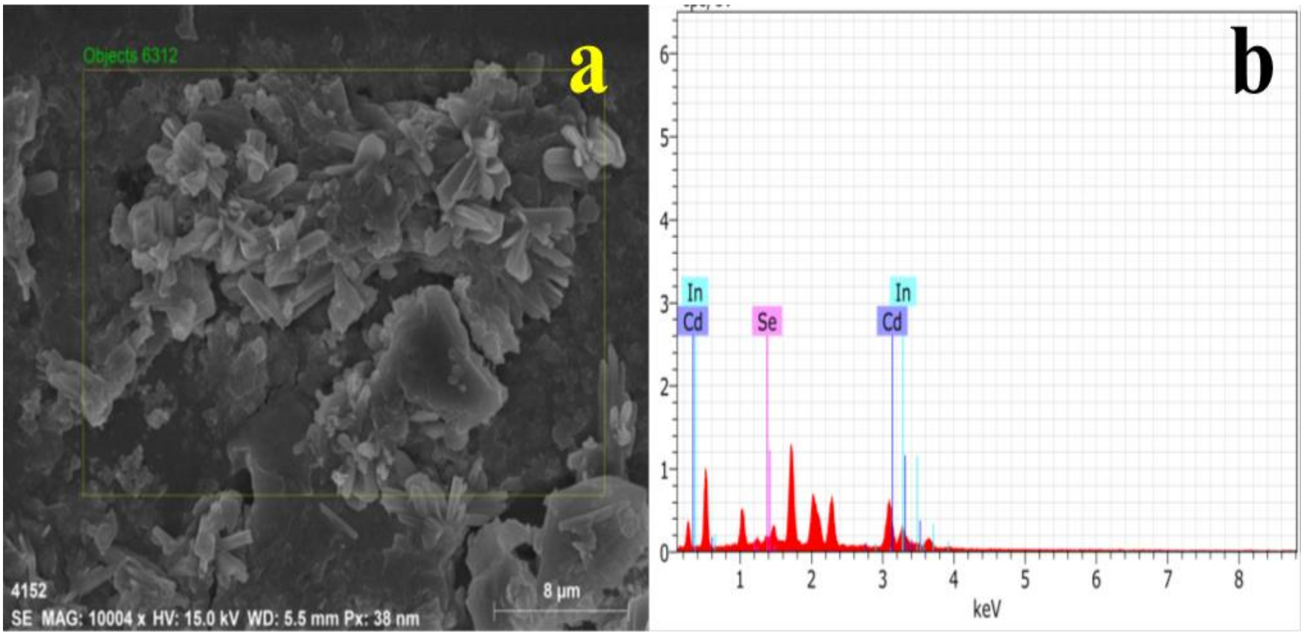

Fig 2. a) FE-SEM images, and b) EDX spectra of Ru and In doped CdSe thin film

The crystallite size (*D*) of the films was calculated from the Debye-Scherrer's formula from the full-width at half-maxima(FWHM) β of the peaks expressed in radians (17)

$$D = K\lambda/\beta \cos\theta$$

where, the constant *k* is the shape factor (taken as 0.94), λ is the wavelength of X-rays (1.5406 A^{o} for CuKα), and θ is the Bragg's angle. The average grain sizes of the deposited films, estimated according to the Debye–Scherrer's formula is D=26. These values calculated from XRD measurements are compatible with SEM pictures. Fig. 2b) shows EDX spectra of Ru and In doped CdSe thin film. In EDX spectra as expected it shows Cd and Se peaks as we are taking concentration of Cd and Se based materials high as compared to doping materials. Along with this other peaks are also present it is due to doping of materials in CdSe which confirm the doping of Ru and In.

3.3 Optical absorbance spectra and Thermogravimetric analysis

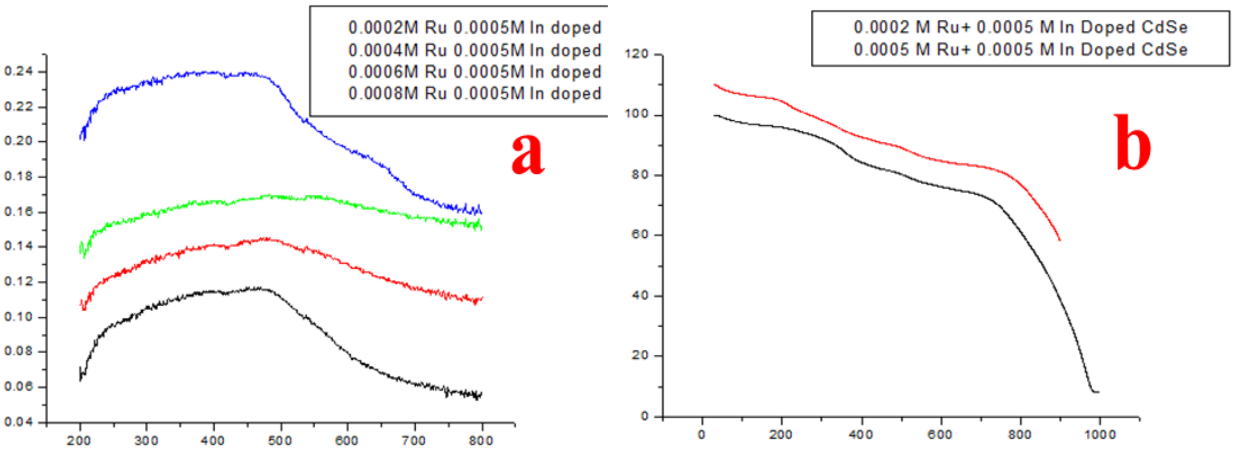

Fig 3. a)UV-*vis* absorption spectra, and b) Thermogravimetric analysis of Ru and In doped CdSe thin film

Fig. 3 a) demonstrates UV-*vis* absorption spectra of Ru and In doped CdSe thin film. UV-*vis* absorption spectra taken in the range of 200 nm to 800 nm. All the absorption spectras are nearly identical in nature, they show absorption peak in the range of 450nm to 500 nm. Peaks are shifted as Ru concentration increase from 0.02 mM to 0.08 mM and also increases in absorption as Ru concentration increases. It shows that as Ru concentration increases show good optical response to materials. Thermogravimetric analysis (TGA) in temperature region from zero to 1000 ºC is shown in Fig. 4 b). From TGA analysis it confirms the weight loss of 10 % in the range from 200 to 250 ºC from Ru and In doped CdSe material. Weight loss in material is due to the removal of water contents from the film surface. A weight loss of approximately 10 % has been observed in the temperature range of 750 to 900 ºC which is due to the loss of organic surfactant used during the synthesis of Ru and In doped CdSe.

3.4Electrochemical measurements

Electrochemical measurement such as CV (Current –Voltage) measurement of Ru and In doped CdSe thin film shown in fig. 4.

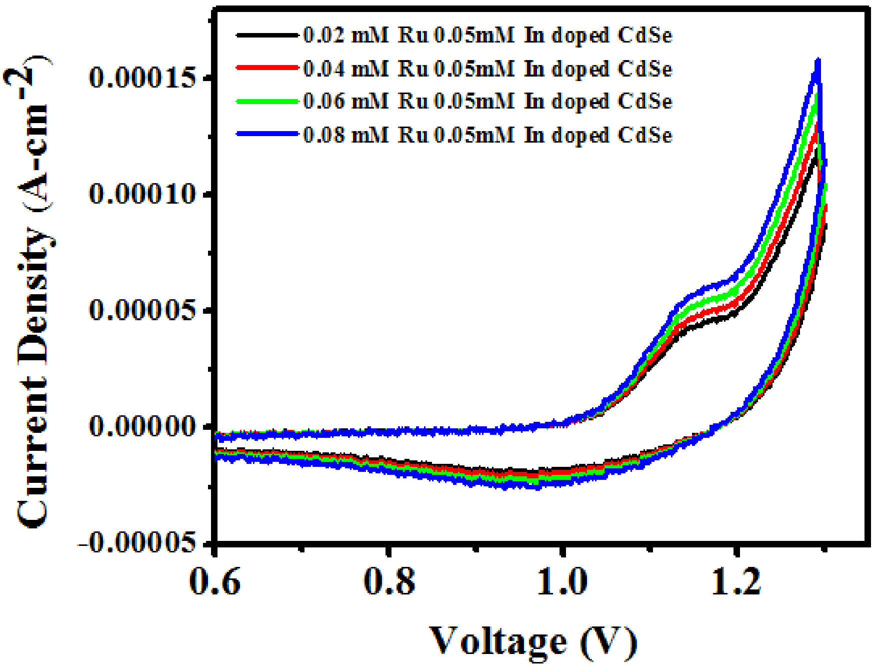

Fig. 4 CV measurement of Ru and In doped CdSe thin film

CV measurements of Ru and In doped CdSe thin film was carried out in 0.5 M aqueous solution of Sodium sulfite (Na_2SO_3) as the electrolyte using three-electrode system at 10 mV s^{-1} sweep rate (with wide window 0.6 to 1.3 V). From Fig. 4 it is observed that with increase in Ru precursor concentration area under the curve increased as well as the redox peaks were evidently seen. Also the value of maximum current (I_{max}) increased from 4.3 X 10^{-5} A cm^{-2} (for 0.02 mM Ru 0.05 mM In doped CdSe) to 5.55 X 10^{-5} A cm^{-2} (for 0.08 mM Ru 0.05 mM In doped CdSe).

4. Conclusion: -

The Ru and In doped CdSe thin films were prepared by using the chemical bath deposition method. Formation of film was confirmed by XRD spectra which matches with JCPDS card no. 00-019-0191. The formed films were crystalline, cubic in structure, and stable to the temperature. The optical study reveals that the band gap is up to 1.67 eV. The cubic rod formation due to Ru and In doping in CdSe. The low concentration of Ru and In doping has been stated in terms of substitution dissolution of Ru and In ions in the bulk of CdSe. Cyclic voltammograms shows increases in I_{max} value as increase in Ru doping concentration.

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