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Effect Of In-Doping On Structural And Optical Properties Of Zns Thin Film

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Abstract

In-doped ZnS thin film prepared by simplified 2-electrode electrochemical deposition technique. The solution 0.1N $ZnSO_4$ (Zinc sulphate), 0.1N $Na_2S_2O_3$ (Sodium thiosulphate) and 0.1N $InCl_3$ (Indium Trichloride) were used as precursor for Zn, S, and In ions respectively. The electrochemical behavior of Zn, S and In ions studied by using cyclic voltammetry method. As per XRD pattern In-doped ZnS film was found to be zinc blende crystal structure. Effect of In-doping on dislocation density and microstrain has been investigated by XRD data. The optical band gap energy varied between 3.87 -2.57 eV by increasing In-doping from 1% to 3%. Then optical band gap energy was found increases at increasing In-doping at 4%. The thin film sample ZnS: In (3%) has found highest transparency due to low refractive index at wavelength 785 nm in visible region.The electrical parameters such as resistivity, carrier concentration, mobility, hall coefficient were investigated by vanderpauw method of Hall Effect measuring system at doping percentage.

Keywords: In-doped ZnS thin film, electrodeposition,Structural Properties, Optical properties

Introduction:

ZnS is the chalcogenide semiconductor material of group II-VI. It has potential to use in solar cell photovoltaic device due to their wide optical band gap.ZnS exhibit zinc blende and hexagonal wurtzite crystal structures with band gap energy of 3.90 eV and 3.78 eV respectively [1-3]. ZnS is used in various optoelectronic devices like light emitting diode, sensors, dye synthesized solar cell, window layer in thin film solar cell [4-6].The various methods are employed to prepare ZnS thin film such as spray pyrolysis [7-8], chemical route [9], electrodeposition [10], chemical bath deposition [11], and sputtering [12]. The doping in ZnS can be tuned the energy band gap have been investigated from past few years [13]. Mn, Cu, In and Al-doped ZnS nanoparticles have been reported previously [14, 15]. Doping of ZnS is considered to improve the light absorption ability in visible light region. Till date very few researches works on optical and electrical properties of In-doped ZnS thin film have been carried out. The transition metals like Cu^{2+}, Ag^{2+}, Mn^{2+} and Pb^{2+} can be dope in ZnS crystal lattice for tunability of optical band gap.

Experimental details:

In-doped ZnS thin films were deposited by simplified 2-electrode electrodeposition techniques on FTO glass and stainless steel substrates. In order to obtain In-doped ZnS thin film different amount 1%, 2% and 3% correspond to 1ml, 2 ml and 3 ml of 0.1 M $InCl_3$ were added in 100 ml mixed electrolyte bath of 0.1 M $ZnSO_4$ and 0.1 M $Na_2S_2O_3$with successive steps as per fig 1.

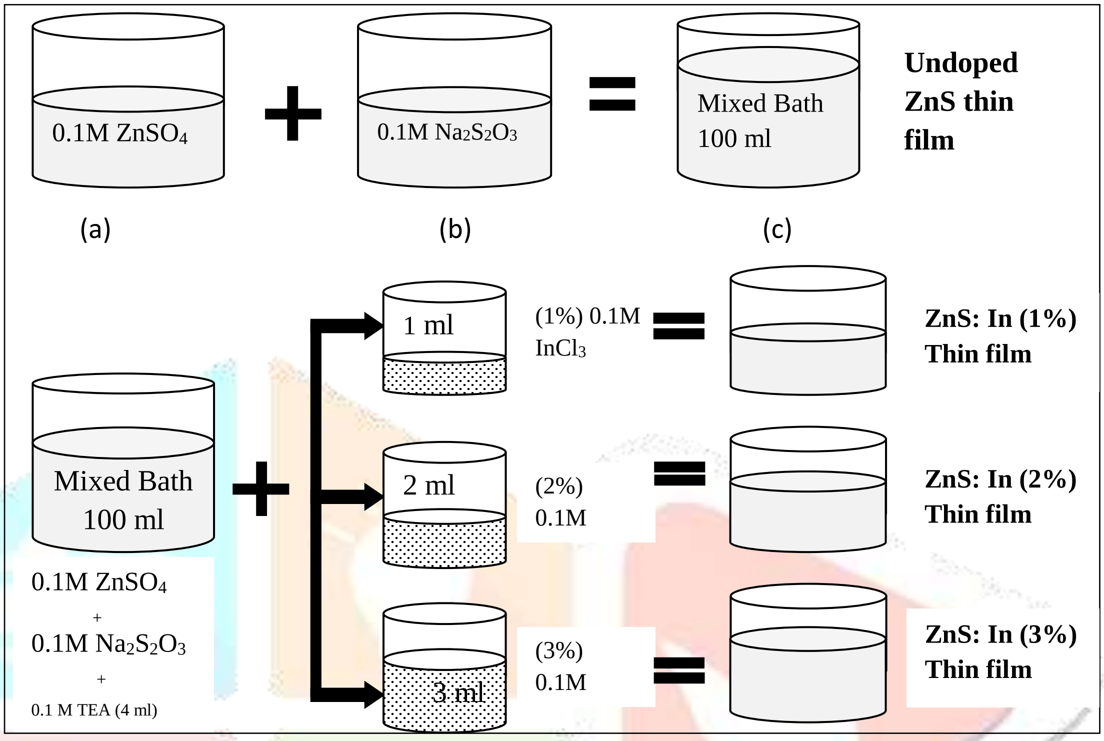

Fig.1 Illustrate the chemical abstract for preparation on undoped and In- doped ZnS thin

The deposing potential of In-doped ZnS thin film was investigated by cyclic voltammetry carried out. The simplified two-electrode electrochemical deposition shown in fig.2 was carried out for growth of In-doped ZnS thin film. In this set up, the graphite rod used as counter electrode and stainless steel or FTO glass substrate were used as working electrode. The distance between working electrode (substrate) and counter electrode (graphite rod) was adjusted at 1 cm during deposition carried out. 4% correspond to 4 ml (0.1 M Triethanolamine) was added in main electrolyte bath as complexing agent for well and adherent film formation. The pH of bath was adjusted at 3.5. In-doped ZnS thin film was deposited for 20 min after optimization of deposition time.

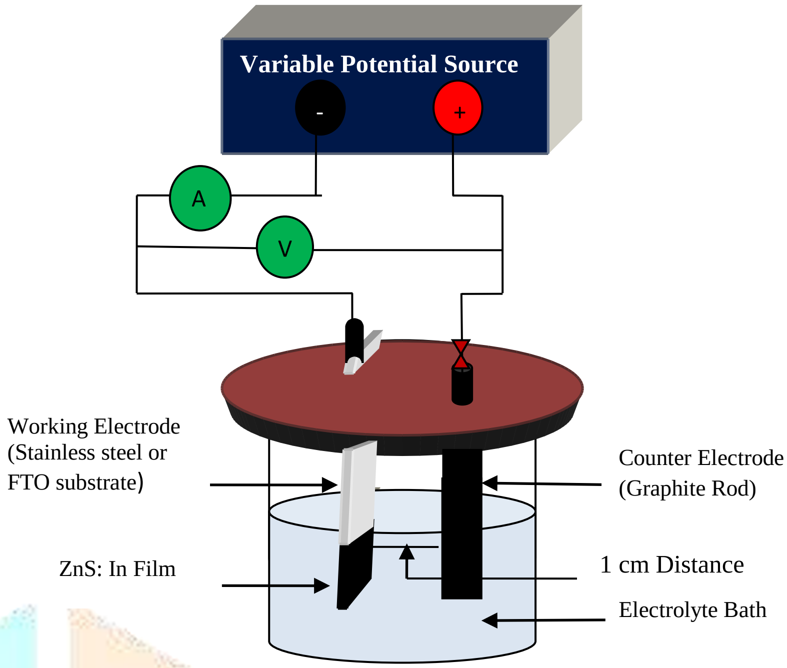

Fig.2 Schematic diagram of 2-electrode electrochemical deposition set up

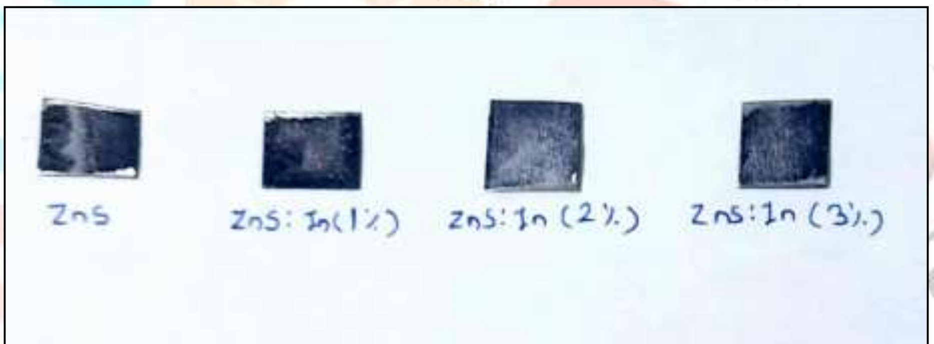

Fig.3 Illustrate the undoped –ZnS and In-doped ZnS thin films deposited by simplified 2-electrode electrochemical deposition method

The deposited films samples as given in fig.3 were characterized by X-ray diffraction with Cu Kα radiation (λ=1.542 A^0). The optical absorption and transmission spectra in the range 200-1100 nm were studied using UV-Visible spectrophotometer. Finally electrical parameters such as resistivity, carrier concentration, mobility, hall coefficient were estimated directly by using (ECOPIA equipment) vanderpauw method with Hall Effect measuring system.

Result and Discussion:

Cyclic voltammetry:

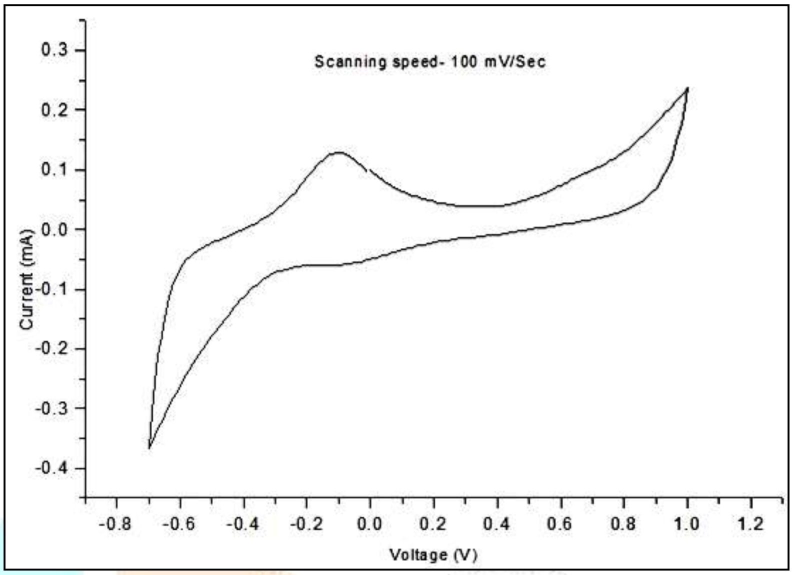

Fig.4 cyclic voltammetry of 0.1 N $InCl_3$ solution at scanning speed 100 mV/Sec

In fig.4 Anodic potential was reached at +1.0 V showed dissociation of In ion during forward scanning. During reverse scanning cathodic potential was reached at -0.7 V with respect to reference electrode Ag/AgCl indicates that In ions well deposited at -0.7V. To investigate the electrochemical behavior of ZnS mixed with In ions, the cyclic voltammetry have been studied. As per fig.5 it has been concluded that anodic potential such as +0.5 V due to dissociation of ions in bath during forward scanning. During reverse scanning cathodic potential was reached at -0.9 V. As we concluded that ZnS: In thin film well deposited at -0.9V cathodic potential with respect to reference electrode Ag/AgCl.

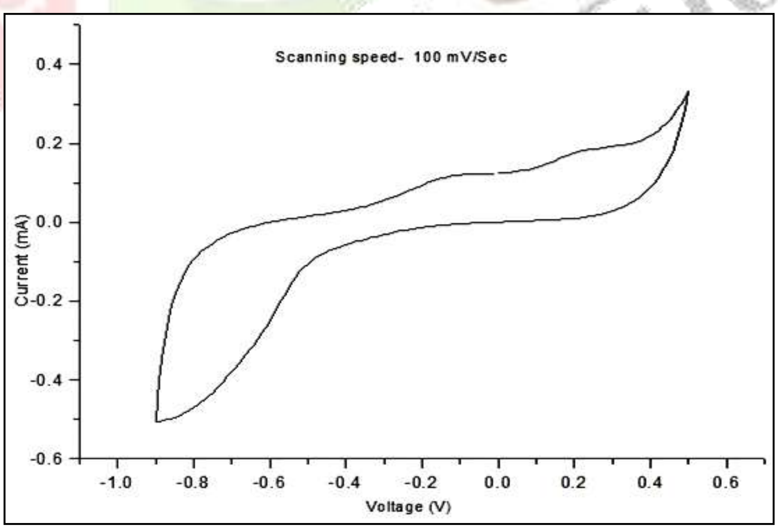

Fig.5 cyclic voltammetry of 0.1 N $ZnSO_4$, 0.1 N $Na_2S_2O_3$ and 0.1 N $InCl_3$ mixed electrolyte bath at scanning speed 100 mV/Sec

Structural characterization:

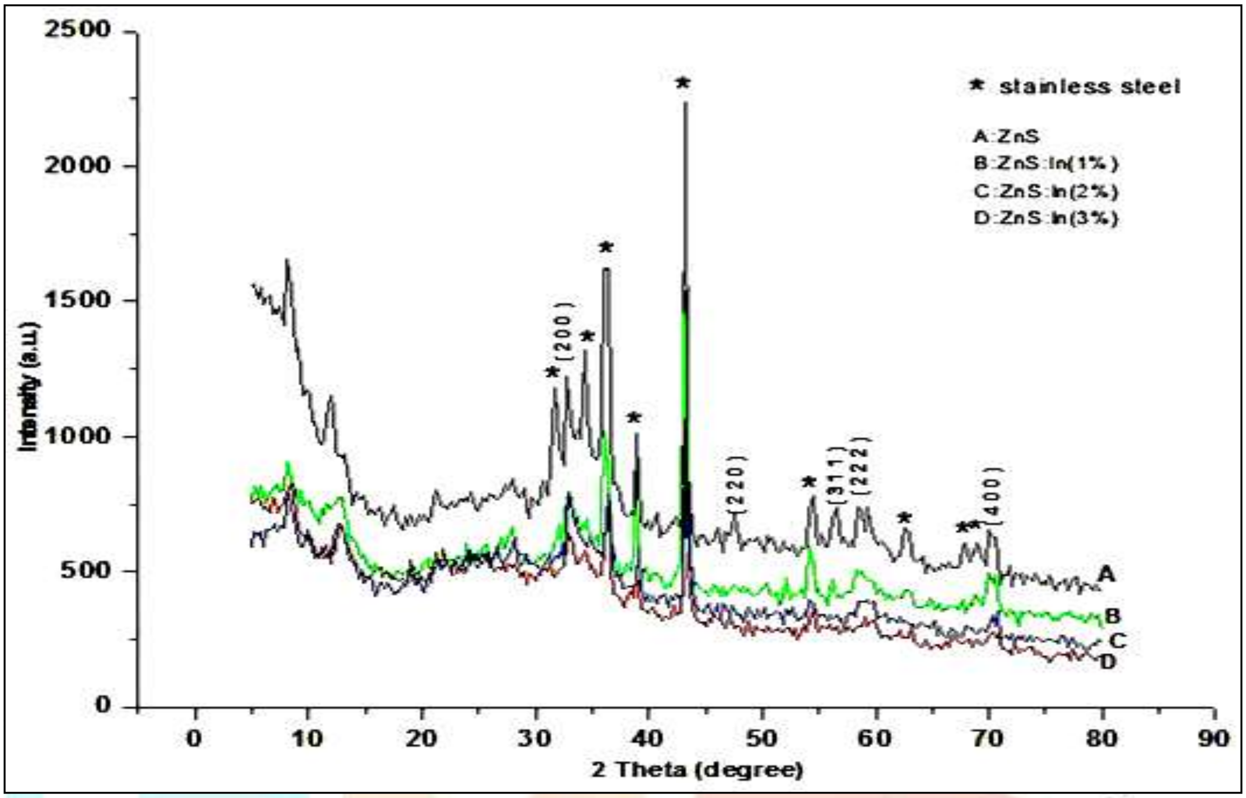

Fig.6 XRD pattern of (A) Undoped ZnS thin film (B) ZnS: In (1%) (C) ZnS: In (2%) (D) ZnS: In (3%).

The XRD pattern of Undoped and In-doped ZnS thin films are shown in fig 6 After XRD analyzed it has been observed that the undoped ZnS thin film showed high crystallinity and exhibit all the peaks (200), (220), (311), (222) and (400) of Zincblende cubic or sphalerite phase similar to standard database (JCPDS No.05-0566). The stainless steel (316L) substrate was used for deposition of material and obtained other peaks of stainless steel are similar to standard database (JCPDS No.33-0397). It is confirmed the other peaks are of stainless steel. The XRD result showed that ZnS film is formed with sphalerite structure without secondary phase of InS has been found. The undoped ZnS sample exhibit high crystallinity as compared to In-doped ZnS. With increase in percentage of In from 1 to 3% has influenced the crystallinity of ZnS thin film. The intensity reduces also affected by percentage of dope material. This is due to change in electronic density or point defect in the crystallographic position. The guest ions in lattice leads to changes on scattering factor. 'In' ions are distributed in ZnS lattice and samples B, C and D exhibit change in intensity of peaks due to size of dope material.

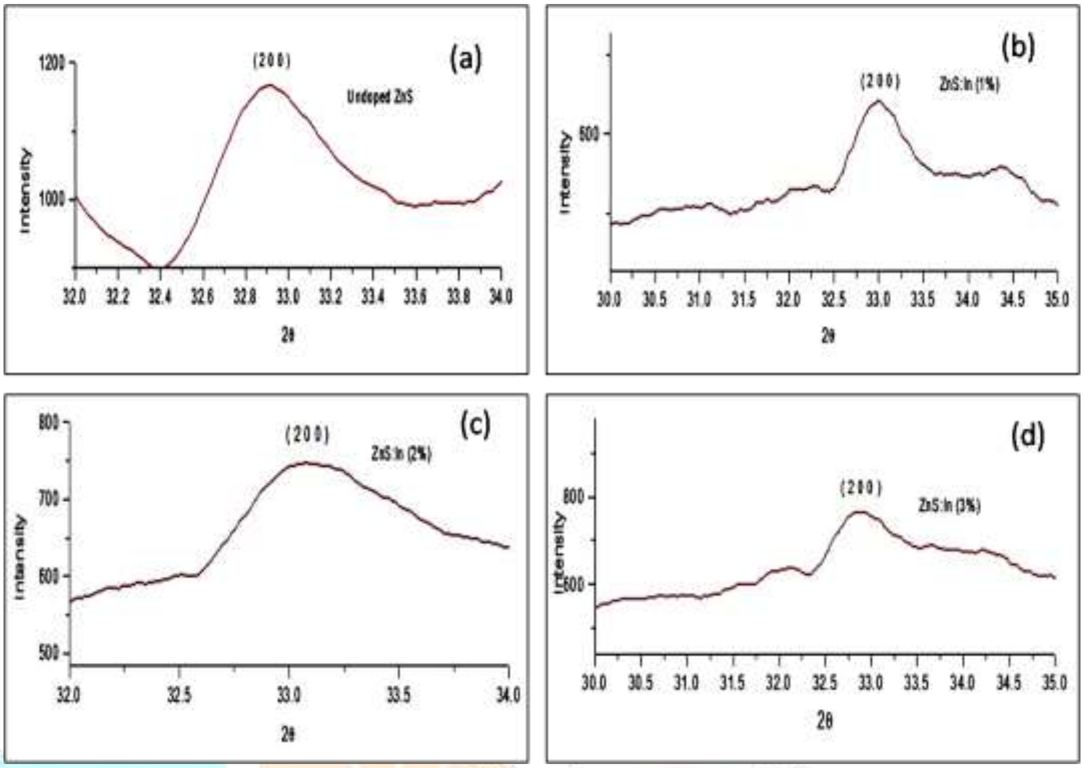

Fig.7. Illustrate the preferred orientation plane (200) of a) Undoped ZnS b) ZnS: In (1%) c) ZnS: In (2%) and d) ZnS: In (3%) for estimation of lattice constant

As per fig.7 the peak of preferred plane (200) of sample d) ZnS: In (3%) slightly shifted to smaller diffraction angle from angle of diffraction at same plane of undoped ZnS thin film. Consequently, lattice constant slightly increases. The lattice constant 'a'was calculated by using equation

$$a = d\sqrt{h^2 + k^2 + l^2} \qquad (1)$$

Where, d is interplanar spacing and h, k, l are miller indices planes. The lattice constant for preferred orientation (200) of undoped ZnS thin film sample A was estimated about 5.424 Å. For In-doped ZnS thin film samples b, c and d the lattice constant 'a' were found 5.424 Å, 5.424 Å and 5.443 Å respectively. The lattice parameter increases due to incorporation of 'In' ions on zinc ion sites. Because ionic radius of indium ion is higher than ionic radius of zinc. Consequently, lattice constant are slightly increases.

The crystallite size was estimated by using the Debye Scherrer formula as given below

$$D=\frac{0.9\lambda}{\beta cos\theta} \qquad (2)$$

Where 'D' is the crystallite size, λ=1.5405 Å, 'β' is the full width at half maximum and 'θ' is the angle of diffraction. The crystallite size of Undoped ZnS, ZnS: In (1%), ZnS: In (2%) and ZnS: In (3%) samples were estimated about 34.46 nm, 26.97 nm, 22.08 nm and 23.44 nm respectively for favored orientation (200). The crystallite size of sample ZnS: In (3%) was foundan increase due to radius of dopant ions is greater than host ion. The dislocation density (δ) was estimated by using Williamson smallman equation given below.

$$\delta = \frac{1}{D^2} \, (3)$$

Where D is crystallite size,

The microstrain (ϵ) was determined by using following equation.

$$\epsilon = \frac{\beta}{4\tan\theta} \, (4)$$

Where, β is full width at half maximum,

Table.4.6 Shows estimated values of average crystallite size, Dislocation density and microstrain of a) undoped ZnS thin film b) ZnS: In (1%), c) ZnS: In (2%) and d) ZnS: In (3%) thin films.

Thin film Samples	2θ for plane (200)	d-spacing	Lattice constant a (A^0)	FWHM	Average Crystallite Size (nm)	Dislocation density(δ)x 10^{-3}(nm^{-2})	Microstrain (ϵx10^{-3})
Undoped ZnS	32.90	2.7120	5.424	0.251	34.46	0.8421	211.35
ZnS: In (1%)	33.00	2.7120	5.424	0.321	26.97	1.3747	270.93
ZnS: In (2%)	33.08	2.7120	5.424	0.392	22.08	2.0511	330.07
ZnS: In (3%)	32.90	2.7216	5.443	0.369	23.44	1.8200	312.50

Optical Characterization:

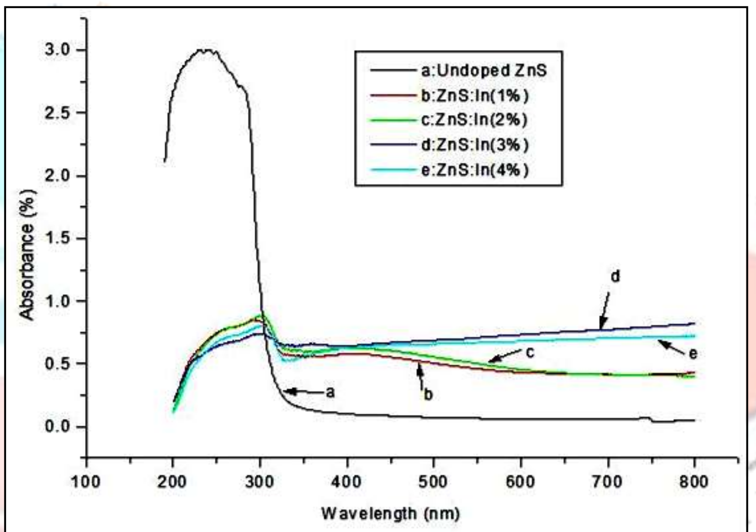

Fig.8.Optical absorption spectra of a) Undoped ZnS thin film b) ZnS: In (1%) c) ZnS: In (2%) d) ZnS: In (3%) e) ZnS: In (4%)

The optical properties of samples were carried out by UV-Visible spectrophotometer with wavelength scanning in the range 200 nm to 800 nm. As per fig.8 it has been found that the absorption edges shifted to longer wavelength with increasing In-content in the range 0 - 3% in ZnS thin films. It is observed that sharp rise in absorbance occurs between 321 nm to 330 nm with increasing In-doping 0-3%. But the absorption edge again decreases to smaller wavelength about 324 nm when increasing In-doping 3-4% in ZnS. This is due to increasing specific surface area of ZnS nanostructure due to microstrain with increasing doping.

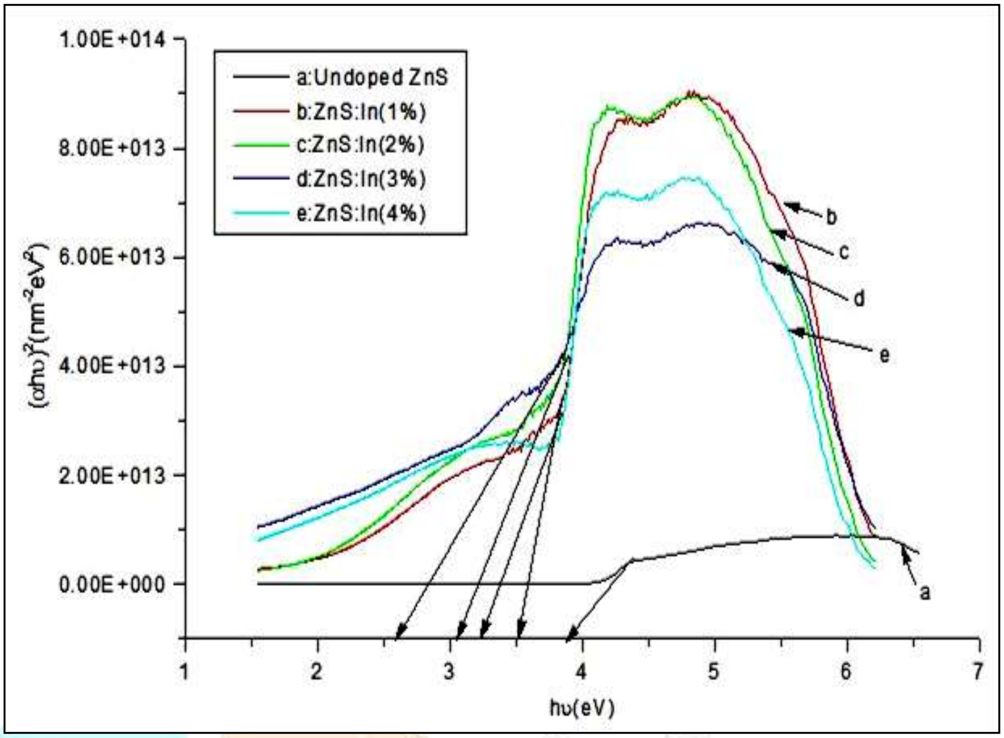

Fig. 9 Energy Band Gap of a) Undoped ZnS thin film b) ZnS: In (1%) c) ZnS: In (2%) d) ZnS: In (3%) e) ZnS: In (4%)

To estimate band gap energy of Un and In-doped ZnS thin films samples by tauc plot shown in fig.9. The tauc plot hν versus $(\alpha h\nu)^2$ by using following equation

$$(\alpha\ h\nu)^{1/n} = A(h\nu- E_g) \quad (5)$$

Where, α is absorption coefficient, h is Planck's constant, ν frequency of light, A is constant and E_g is band gap. The band gap energy of Un and In-doped ZnS thin films samples were estimated by tauc plotting graph $(\alpha h\nu)^2$ versus hν by intercept of straight-line portion of $(\alpha h\nu)^2$ versus hν-on-hν axis. The band gaps energy was found about 3.87 eV, 3.51eV, 3.05 eV, 2.57 eV and 3.23 eV of undoped ZnS, ZnS: In (1%), ZnS: In (2%), ZnS: In (3%) and ZnS: In (4%) respectively.The band gap energy decreases with increasing In-doping (0-3%) in ZnS thin film. But In-content increases in higher amount at 4% the energy band gap increased. The incorporation of In ions in to ZnS lattice due to this increase of specific surface area of ZnS nanostructure and reducing crystallinity of ZnS thin film.

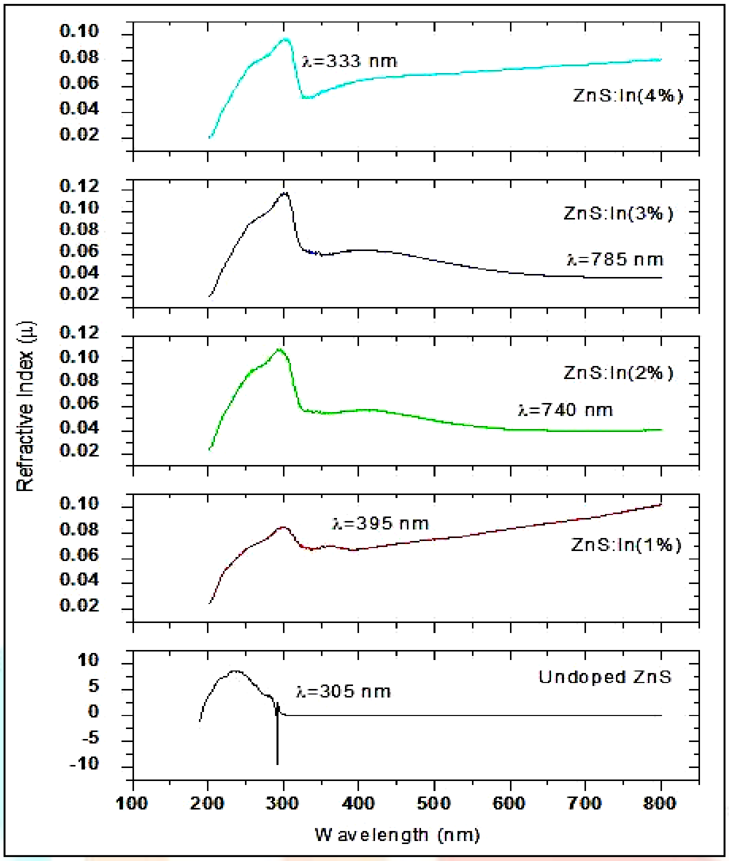

Fig.10 Illustrate the refractive Index of Un and In-doped ZnS thin film deposited on FTO glass

The refractive index of Un and In-doped ZnS thin films were estimated by using following equation

$$n = \frac{1}{T} + \sqrt{\frac{1}{T-1}} \qquad (6)$$

Where, n is refractive index, T is percent transmittance. The percent transmittance (Ts) was determined by using following equation

$$T = 10^{(-A)} X 100 \qquad (7)$$

Where, A is absorbance

As per Figure.10 the refractive index (n) decreased with increasing wavelength. The undoped ZnS thin film has high refractive index in visible region. But the refractive index decreases with increasing wavelength by increasing In-doping in ZnS thin film. Undoped ZnS, ZnS: In (1%), ZnS: In (2%), ZnS: In (3%) and ZnS: In (4%) has highest transparency due to low refractive index in the wavelength range 305 nm, 395 nm,740 nm, 785 nm and 333 nm respectively. The thin film sample ZnS: In (3%) has highest transparency due to low refractive index at wavelength 785 nm in visible region. which allow to use this film layer as an optical window or buffer layer in thin film solar cell device.

Conclusion:

Undoped ZnS and In-doped ZnS thin film was successfully growth by using simplified 2-electrode electrodeposition technique. In-doped ZnS thin film was well deposited at -9 V cathodic potential with respect to reference electrode Ag/AgCl. As per XRD pattern In-Doped ZnS thin film exhibit zinc blende crystal structure without formation of InS crystal phase. The optical band gap energy was regulated by In-doping in ZnS. The optical band gap energy was decreased 3.87-2.57 eV by increasing In-content in ZnS. The sample ZnS: In (3%) has highest transparency due to low refractive index at wavelength 785 nm in visible region which allow to used as window layer of buffer layer in thin film solar cell device.

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