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Structural optical and electrical properties of vacuum evaporated indium doped zinc telluride thin films

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ABSTRACT

ZnTe thin films were prepared on a glass substrate using thermal evaporation method under the vacuum of 10^{-5} Torr. Prepared films were doped with Indium by ion exchange process and the conductivity of the doped films was found to be increased by two orders of magnitude. AFM and XRD results indicated that ZnTe thin film possesses crystalline structure after doping. The optical energy gap (E_g) as calculated from the optical absorption spectra, was found to decrease with doping concentrations. The results of these studies are presented and discussed in this paper.

INTRODUCTION

Amongst the wide band gap II-VI semiconductor materials, Zinc Telluride (ZnTe) is the most attractive material and finds several applications in the field of device electronics[1-3]. Due to wide applications in the field of microelectronics and opto electronics, ZnTe thin films are extensively studied for electrical, optical and structural properties. Literature[4] reports that ZnTe exhibits improved photorefractive response when it is doped with vanadium. Recently, Aqili et al.[5], reports increase in conductivity of ZnTe thin films after doping with Ag. Several researchers have employed various doping techniques like co-evaporation, diffusion, ion-exchange process *etc.* to improve the properties of the films for device applications. However, due to simplicity, ion exchange process is now more commonly used to dope Ag and Cu to II-VI semiconductors[5]. Many researchers[6-8] have studied the structural, optical and electrical properties of ZnTe thin films, but properties of Indium doped ZnTe thin films has not been reported so far. Hence, we have carried out systematic investigations on structural, optical and electrical properties of thermally evaporated ZnTe thin films doped with Indium using ion exchange method.

EXPERIMENTAL

The ZnTe thin films were prepared using a vacuum coating unit (Hind High Vacuum Company, Bangalore) Model 12A4D. Pure ZnTe (Sigma Aldrich, 99.99%) was used as a source material for the evaporation. The material (~100mg) was placed into molybdenum boat with a small dimple at the center to act as a point source. The boat was heated indirectly by passing current through the electrodes. Cleaned glass slides were used as a substrate. These glass slides were cleaned with chromic acid, ultrasonic cleaner, soap water, distilled water and then with acetone. The source-substrate distance was maintained at 13.5 cm. Rotary drive was used to obtain the uniform coating. After reaching high vacuum (1×10^{-5} mbar) in the vacuum chamber, slowly current was applied to the electrodes to heat the substance. A source shutter was used to stop the deposition of the film on the substrate. When all the parameters (vacuum, rate of evaporation, substrate temperature, etc.) were optimized, then source shutter was removed and deposition of the film starts on the substrate. The rate of evaporation was maintained at ~1.4 Å/sec. All the films were prepared at room temperature. The rate of evaporation and thickness of the as-deposited films were measured using quartz crystal monitor ("Hind High Vacuum Company" Digital thickness monitor Model-DTM 101) fixed to the unit. The thickness of all the films was measured to be 170 nm.

As-deposited ZnTe films were cleaned with distilled water and annealed at 400K for 3 hours. These samples were immersed in the solution contained 1g ($In(NO_3).5H_2O$) in 1 liter (H_2O) for doping. The immersion time was varied from 5, 10, 15 min. The films after immersion were cleaned in distilled water bath and dried. Ion exchange takes place at the film surface, means high concentrating Indium layer forms on the surface of the film. Further these films were heated in a vacuum (1×10^{-3}mbar) at 400K for 3 hours to diffuse Indium atoms into the films.

X-ray diffraction (XRD) patterns were recorded on a Philips X-ray diffractometer (Model PW 1710) with Cu Kα radiation (λ= 1.54 Å). AFM measurements were carried out using a scanning probe microscope (SPM-Solver P47, NT-MDT, Russia) in contact mode. Rectangular cantilevers of silicon nitride (length 200 μm and width 40 μm) having a force constant of 3 N/m were employed for the measurement. Optical properties of the ZnTe thin films before and after doping were carried out using UV-VIS spectrophotometer (Shimadzu Model 1650-PC). Electrical properties of the prepared samples were measured using AUTOLAB PGSTAT 20. All characteristics were measured at room temperature.

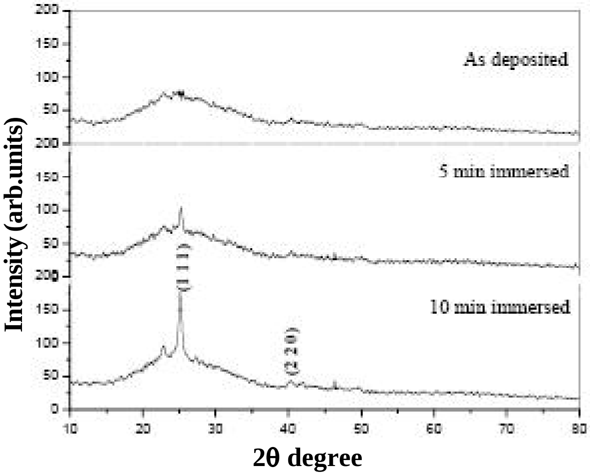

Figure 1: XRD graph of (a) As-deposited (b) 5 min immersed (c) 10 min immersed ZnTe thin film

TABLE 1: XRD parameters of ZnTe thin films doped with indium

Sample name	d(Å)	D(Å)	$\varepsilon 10^{-3}$ (lin^{-2} m^{-4})	δ 10^{15}(lin/m^2)
5min immersed	3.54512	130	3.04	5.86
10min immersed	3.53373	148	2.44	4.545

RESULTS AND DISCUSSIONS

Structural properties

XRD patterns of ZnTe films before and after doping are presented in figure 1. It is observed that as-deposited film prepared at room temperature possesses broad peak indicating amorphous structure. The presence of intense peak at 2θ = 25.21 degree in (111) direction for indium doped films reveals that these films are crystalline in nature. The 2θ values observed in the XRD and those of JCPDS (01-0582) data were found in fair agreement between them. Doped films were found to exhibit two diffraction peaks associated with (111) and (220), of which the intensity of (111) orientation is predominant. The lattice parameters of the films were calculated using the Bragg's formula[9]:

$$2d\sin\theta = n\lambda \quad (1)$$

The grain size of the crystallites were calculated from the XRD using Scherer's relation,

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (2)$$

Where k = 0.94 is a constant, λ- the wavelength of radiation, β- the full width half maximum and θ - the diffraction angle. The micro strain (ε) and the dislocation density (δ) of doped films were estimated using the equations and are presented in TABLE 1.

$$\varepsilon = \frac{(\beta \cos\theta)}{4} \qquad (3)$$

and

$$\delta = \frac{1}{D^2} \qquad (4)$$

From the TABLE 1 it is observed that the grain size increases which intern decreases strain and dislocation density. But there are no noticeable peaks in XRD indicating presence of In into the samples.

It appears that the process of annealing after immersion in indium nitrate solution facilitates the grain growth in ZnTe thin films, which decreases the number of grain boundaries. As a result, an improved microstructure and morphology are created. Grain growth in similar materials is well known and reported for solid state re-crystallization method[10,11]. The intensity variation in is due to reorientation of the planes after immersion and annealing.

Surface morphology of the as-deposited ZnTe thin film is shown in figure 2a. It shows a smooth surface indicating amorphous nature of the film. This result supports the XRD characteristics of the as-deposited ZnTe thin film. Figure 2b. shows the morphology of the ZnTe thin film doped for 10 min. A large number of grains can be seen, which indicates the crystalline nature of the film. It is obvious because the films were annealed before and after doping with Indium. Due to the heat treatment grain growth will takes place which gives the crystallinity and good surface morphology. These results are in good agreement with XRD characteristics.

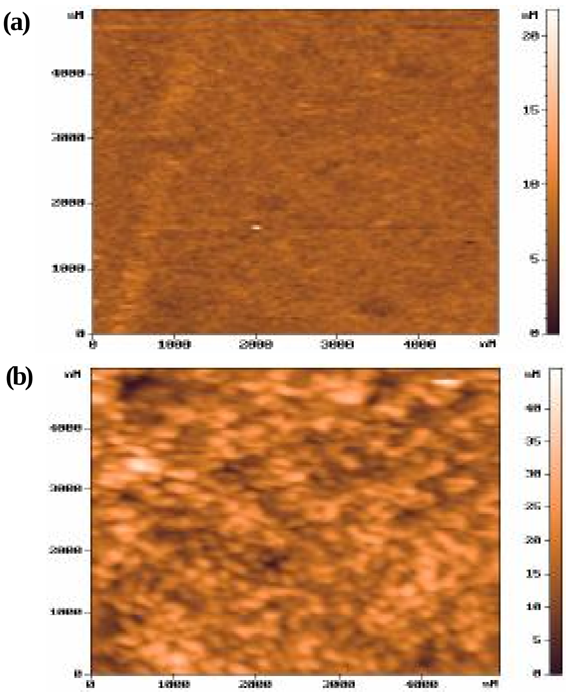

Figure 2: AFM photograph of (a) As- deposited (b) doped ZnTe thin film

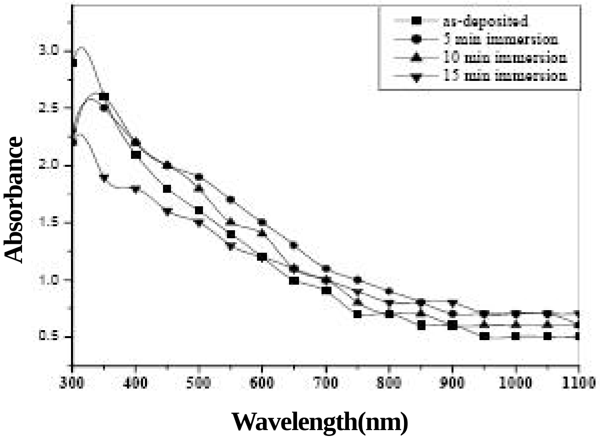

Figure 3: Optical absorbance spectra of ZnTe thin films

Optical properties

The absorbance spectra of the ZnTe thin films before and after doping are shown in figure 3. The spectra reveal that all the films show more absorbance in ultraviolet region. There is a slight decrease in the absorbance for the doped films due to incorporation of indium atoms into the ZnTe films. All the films show good absorbance in the visible range.

From the absorbance data, the absorption coefficient was calculated using Lambert law:

$$\ln\left(\frac{I_0}{I}\right) = 2.303\,\text{Abs} = \alpha d$$

Abs is optical absorbance, I_O and I are intensities of the incident and transmitted radiation respectively α is absorption coefficient and d is thickness of the films (cm). Optical band gap (E_g) was determined by analyzing the optical data with the expression for the optical absorption coefficient α and the photon energy $h\nu$ using the relation

$$\alpha = k(h\upsilon - Eg)^{n/2} / h\upsilon$$

Where k is a constant, the value of n is equal to one for a direct-gap material, and four for an indirect-gap material. Plots of $(\alpha h\nu)^2$ versus $h\upsilon$ were drawn using the

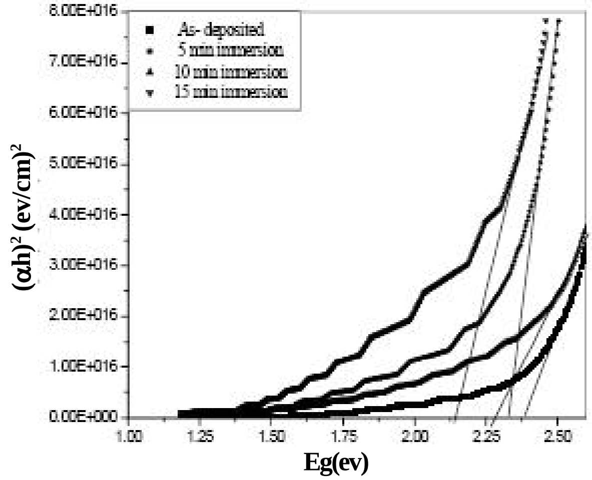

Figure 4: Plots of $(\alpha h\upsilon)^2$ vs. $h\nu$ for ZnTe thin films

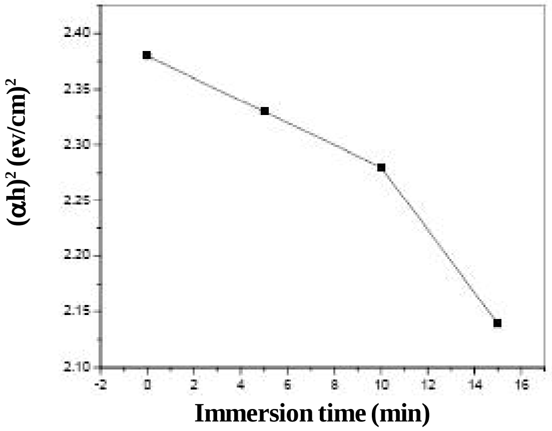

Figure 5: Plots of Eg vs. immersion time for ZnTe thin films

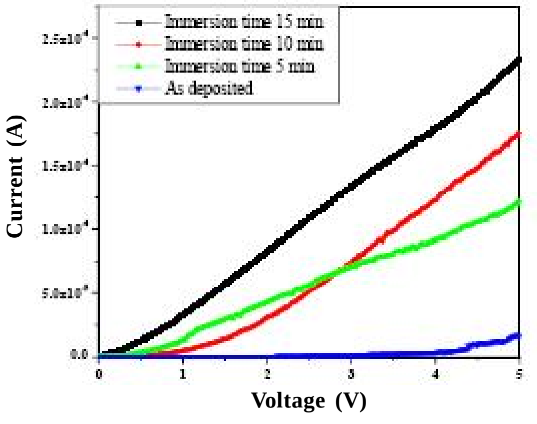

Figure 6: I-V Characteristics of ZnTe films before and after Doping

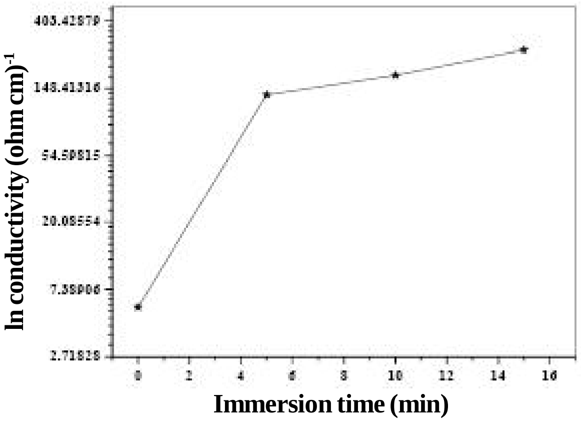

Figure7: Variation of conductivity with doping concentration of doped ZnTe thin films

above equation. Extrapolation of the linear portion of the plot to the energy axis yielded the direct band gap value as shown in figure 4. Shift of optical band gap with Indium concentrations was observed and band gap decreases with increase in the indium concentrations. Due to an ion-exchange, in the indium nitrate solution, incorporation of Indium into ZnTe films might be possible. Incorporation of indium introduces inter-band energy levels in the band gap of ZnTe thin films, which was responsible for slight shift in the energy gap.

Figure5 shows the decrease in energy gap with immersion time. Conduction band edge decreases with increase in the doping concentration. Optical band gap of as deposited film was found to be 2.37 eV (Theoretical 2.24 eV) where as for 15 min immersed film it was found to be 2.139 eV. It can also be attributed to the more number of accepters after incorporation of Indium atoms into the ZnTe thin films. This is due to the change in the conduction band edge[12].

Electrical properties

As-deposited and doped ZnTe thin films were cut into 1 cm × 1 cm square, electrical contacts were made with silver. The I-V characteristics of as deposited samples and indium doped (for different immersion times) samples are presented in figure 6. It was observed that the highest forward current at constant voltage can be obtained at 15 min immersion, which means the highest conductivity. As-deposited ZnTe film shows maximum current of about 0.1μA at 5V whereas the films immersed for 5 min will shows the current of 0.001μA This large increase in the current is due increase in carrier concentrations after incorporation of In-atoms into the ZnTe films which is explained further in structural properties.

The variation of bulk conductivity of these films with increase in immersion time is as shown in figure 7. The conductivity of the In doped ZnTe thin films increased about two orders of magnitude that of undoped films. The conductivity v/s immersion time graph shows rapid increase in conductivity for doped samples compared to un-doped samples and becomes linear above 5 min immersion. This behavior can be attributed to the incorporation of Indium atoms that act as donor sites, which in turn increase mobility and carrier concentration, hence decreasing the barrier height at the grain boundaries, resulting in less impedance for the carrier transport. Similar types of report have been given for CdTe thin films[13].

CONCLUSIONS

ZnTe thin films were prepared using thermal evaporation method and successfully doped with Indium using ion exchange process. XRD characteristics reveal that ZnTe thin films become crystalline after doping and annealing at 150^{0}C. The morphology of the films as studied by AFM supports the XRD results. Optical band gap of the doped films decreases with increase in doping concentrations, which confirms the incorporation of indium atoms into the ZnTe thin films. There was a two order of magnitude enhancement in the in the conductivity of the doped films.

REFERENCES

[1] P.J.Dean; J.Luminescence.,**18**,19 **(1979)**.
[2] L.Svob, Y.Marfaing; Sol.Stat.Commun., **58**, 307 **(1986)**.
[3] M.S.Vingradov, D.L.Vasilevski; Inorg.Mat., **21**, 156 **(1985)**.
[4] M.Ziari, W.H.Steier, P.M.Ranon; App.Phy.Lett., **60**, 1052 **(1992)**.
[5] K.S.Akram, Aqili, Asghari Masqood, Zulfiqar Ali; App.Sur.Sci., **191**, 280 **(2002)**.
[6] Petr klapetek, Ivan Ohlidal, Alberto Montaigne-Ramil, Alberta Bonanni, David Stifter, Helmut Sitter; Jp.J.App.Phys., **42**, 4706 **(2003)**.
[7] Q.Guo, M.Ikejira, M.Nishio, H.Ogawa; Sol.Stat. Commun., **100**, 813 **(1996)**.
[8] A.A.Ibrahim; Vacuum., 81, 527 **(2006)**.
[9] R.Amutha, A.Subbarayan, R.Sathyamoorthy, K. Natarajan, S.Velumani; J.New.Mat. Electrochem. Sys., **10**, 27 **(2007)**.
[10] R.Triboulet; Crys.Res.Techn., **38**, 215 **(2003)**.
[11] S.Hassani, A.Lusson, Tromson-Carli, R.Triboulet; J.Crys.Grow., **249**, 121 **(2003)**.
[12] Ali, N.Abbas Shaha, A.Masqood; Sol.Stat.Elect., **52**, 205 **(2008)**.
[13] W.F.Mohammed, M.A.S.Yousif; Renewable Energy., **26**, 285 **(2002)**.