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Effect of copper on composition, structural and optical properties of copper doped ZnTe thin films

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ABSTRACT

Ultrathin (250 Å) initial deposit of copper on glass substrates were used for the subsequent deposition of ZnTe films under a pressure of 10^{-5} m.bar by thermal evaporation method. The decrease of atomic percentage of copper with increase of the ZnTe film thickness is confirmed by EDAX analysis. The phase change from hexagonal to cubic structure is observed by XRD analysis. The strain (ε), grain size (D) and dislocation density (ρ) were calculated and results are discussed. The transmittance and the optical bandgap energy were found decreases when increases of ZnTe film thickness. The optical transition of these films is found to be direct allowed. Copyright © 2013 VBRI press.

Keywords: Cu doped ZnTe; XRD; hexagonal phase; band gap; transmittance.

Introduction

Zinc Telluride (ZnTe) is one of the II-VI compound semiconductors which are having cubic structure. It is usually a p-type semiconductor and its lattice constant is 6.103 Å [**1**]. ZnTe being a wide and direct band gap of 2.26 eV at room temperature [**2**] with low electronic affinity of 3.53 eV [**3**]. It can absorb photons in the visible region without any phonon assisted mechanism that makes it useful in several electro-optic and opto-electronic applications [**4**]. The defects governing the electrical behavior of the pure material are due to Zn vacancies which can accept very few electrons [**5-8**]. As grown ZnTe films are highly resistive and their resistivity at room temperature is around 10^5 Ωm [**9**].

ZnTe thin films were used in tandem solar cell structure, which utilizes CdZnTe as the absorber material, and for the fabrication of CdZnTe/ZnTe quantum well structure. It has been extensively studied for applications of purely green light emitting diode and acts as a back contact material for CdTe in CdTe/CdS heterojunction solar cells [**10-13**], since it is expected to have a small valance band discontinuity with CdTe. It can be doped degenerately with copper [**14**], to obtain low resistance. These entire activities triggered in the studies of ZnTe films for device applications.

It has been observed that Cu is a more effective dopant in crystalline ZnTe than other Group 1B elements. Cu doped ZnTe films have been prepared by various methods, including thermal evaporation of ZnTe and Cu from two sources [**15**], RF and dc sputtering [**16,17**], electro-deposition [**18**], hot wall evaporation [**19**] and thermal evaporation [**20**]. This article proposes a new method for preparation of copper doped polycrystalline ZnTe thin films onto the glass substrates using thermal evaporation method. Besides this paper illustrates in detail how the composition, structure and optical properties varies based on copper concentration parameter.

Experimental

Substrate preparation

In the present work, Blue-Star glass slides have been used as substrates for the deposition of films. The glass substrates were first treated with sodium hydroxide (NaOH) solution. The alkaline agent dissolves fatty materials by saponification and renders them wet and keep the substrates into the distilled water. The second step is clean the substrates by the soap solution. After rinse with distilled water, the substrates were subjected to ultrasonic agitation for about 45 minutes in distilled water mixed with some drops of soap solution. The shock waves created in the agitator removes residues. The substrates were then dried in an oven for 45 minutes. Finally the substrates were cleaned with isopropyl alcohol. The isopropyl alcohol vapor condensed on the object to be cleaned and hence enhanced the removal of surface contaminants. Finally the substrates were then heated in an oven for about 45 minutes at a temperature of 100˚C.

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Film preparation

The deposition of copper and ZnTe were done in two separate deposition cycles. The deposition were carried out in vacuum better than 10^{-5} m.bar, inside a 12 inch vacuum chamber (HINDHIVAC 12A4D). Initially copper (99.99%, Aldrich) films of thickness (250 Å) were deposited over the well-cleaned glass substrates by vacuum evaporation technique. Then ZnTe (99.99%, Aldrich) films of thicknesses (650, 1400 and 3300Å) were deposited over the pre-deposited copper films (250 Å) at room temperature. A rotary drive was employed to maintain uniformity in film thickness and to get well diffusion of copper into ZnTe the samples were annealed in a hot air oven at 100˚C for 2 hours.

Measurements

Thickness of the films was measured by quartz crystal monitor ("Hind Hivac" Digital Thickness Montor Model–DTM–101), and verified by multiple beam interferometer (MBI) technique by forming Fizeau fringes [**21**]. Energy Dispersive Analysis of X-rays (EDAX) (JOEL 840 SEM/EDAX) was employed for the confirmation of composition of thin films. The structural aspects of the films were analyzed, using X-ray diffractometer with filtered CuKα radiation (λ = 1.5418 Å). The optical transmittance spectra of these films were recorded using a UV–VIS-NIR spectrophotometer (Jasco Corp., V-570) in the range 200 – 2500 nm with 1 nm resolution at room temperature.

Table 1. Atomic percentage of Zn, Te and Cu for copper doped ZnTe thin films for thicknesses 650 Å and 3300Å.

Element	650 Å	3300 Å
Zn	59.33	59.03
Te	17.76	40.97
Cu	22.91	0.00

Results and discussion

EDAX analysis

The analyzed atomic percentage values of elements Zn, Te and Cu in the above films are presented in **Table 1**. From this **Table**, it is concluded that tellurium is replaced by copper. Due to this reason the atomic percentage of tellurium is decreased in ZnTe film of thickness 650 Å deposited on the pre-deposited copper film. But at higher ZnTe film thickness (3300 Å), the EDAX analysis shows zero atomic percentage of copper. From this, it is concluded that all the copper atoms were diffused into the ZnTe films without desorption from the substrate during the ZnTe deposition. This is also confirmed by XRD analysis.

XRD analysis

Fig. 1 shows the XRD patterns of ZnTe films with various thicknesses (650, 1000 and 3300 Å) deposited on the pre-deposited copper films of thickness (250 Å) on glass. ZnTe film of thickness 650 Å possesses hexagonal structure while on increasing the ZnTe film thickness up to 1000 Å, one of the dominant peaks (006) of hexagonal phase has diminished and cubic phase has been appeared. Further increasing the film thickness, all the peaks [(006), (009) and (0010] of hexagonal phase have diminished and those of only the cubic phase alone remain. No peaks for metallic Cu or any other compound such as Cu_2Te are observed.

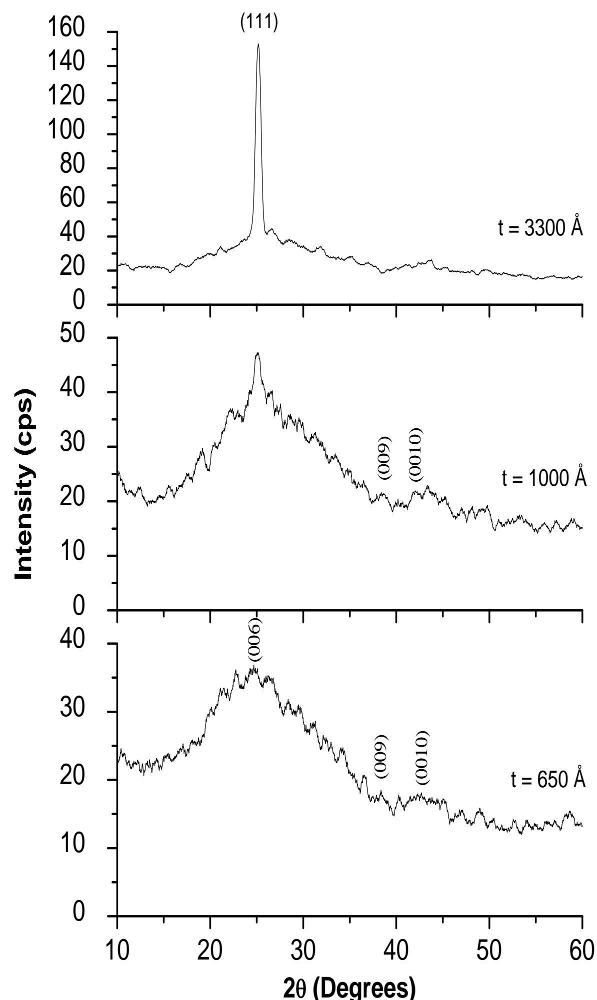

Fig. 1. X- ray diffractograms of vacuum evaporated copper doped ZnTe films.

Therefore, all the copper atoms diffuse into the ZnTe film during the deposition of ZnTe and influence the grain growth in the deposited ZnTe film. This phase change from hexagonal to cubic may be due to the decrease of copper composition and as well as the increase of ZnTe composition. In these structural changes in copper doped polycrystalline films it is obvious that the diffusion and location of copper atoms play an important role. It could be thought that most of the copper atoms locate in the grain boundaries for as-grown copper doped films. On increasing temperature, some of native copper atoms can diffuse into grains and be thermally ionized. The occupation of copper atoms in Zn sites of ZnTe lattice brings about the structural transition in copper doped ZnTe films [**22**]. The grain size

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(D) of the films is estimated using Debye Scherrer's formula [**23**],

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where, k is the constant = 0.94, λ - the wavelength of radiation, β - the full width half maximum of the corresponding peak of the XRD pattern and θ - the diffraction angle.

The micro strain (ε) and the dislocation density (δ) of the as grown films were estimated using the equations [**24, 25**]

$$\varepsilon = \left(\frac{\beta \cos\theta}{4}\right) \quad (2)$$

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

The grain size, strain and dislocation density are presented in **Table 2**. From this table, an appreciable increase in grain size is observed when comparing to the pure ZnTe films [**26**]. The observed phenomenon is due to the thin copper layer, which is known to be a good stimulator for grain growth in ZnTe films [**22**]. The decrease in grain size by increasing the ZnTe film thickness may be due to the decrease of copper composition and as well as the increase of ZnTe composition.

Table 2. Structural parameters and band gap energies of copper doped ZnTe thin films of different thicknesses.

Thickness (Å)	hkl	Grain size D (Å)	Strain ε 10^{-3} ($lin^{-2}m^{4}$)	Dislocation density δ 10^{14} (lin/m^2)	Band gap energy (eV)
650	006	816	0.425	1.502	2.17
	009	1002	0.346	0.996	
	0010	1715	0.202	0.340	
1000	009	532	0.651	3.533	2.15
	0010	952	0.364	1.103	
3300	111	196	1.769	26.030	2.00

Optical properties

Fig. 2 shows the transmittance spectrum of copper doped ZnTe films. It is clearly observed that these films have very low transmittance when compared to the pure ZnTe films [**26**]. This decrease in the transmission can be attributed to the introduction of impurity level between valance band and conduction band [**27, 28**]. The transmittance in the higher wavelength range is less than that of pure ZnTe films. This may be due to the fact that copper doped ZnTe films had higher carrier concentration than pure ZnTe films, as absorption in the near-infrared region is mainly due to free carriers [**29**]. This is in good agreement with the earlier investigation [**30**].

The decrease of transmittance at higher doping levels may be attributed to the increased scattering of photons by crystal defects created by doping. The free carrier absorption of the photons` may also contribute to the observed reduction in the optical transmission of heavily doped films [**31-33**].

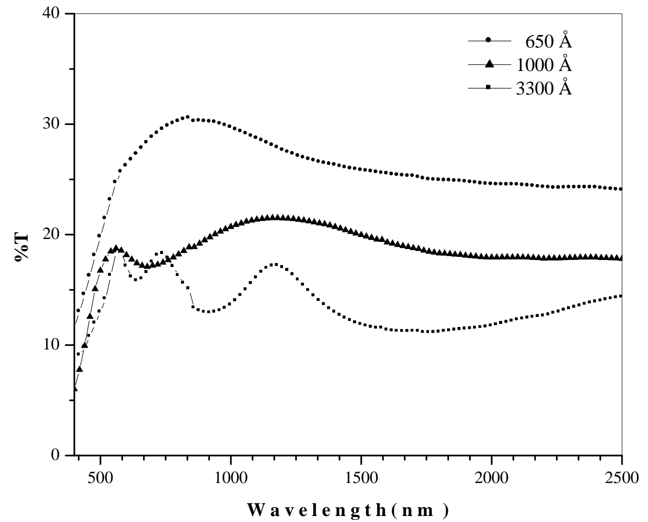

Fig. 2. Transmittance spectra of copper doped ZnTe films.

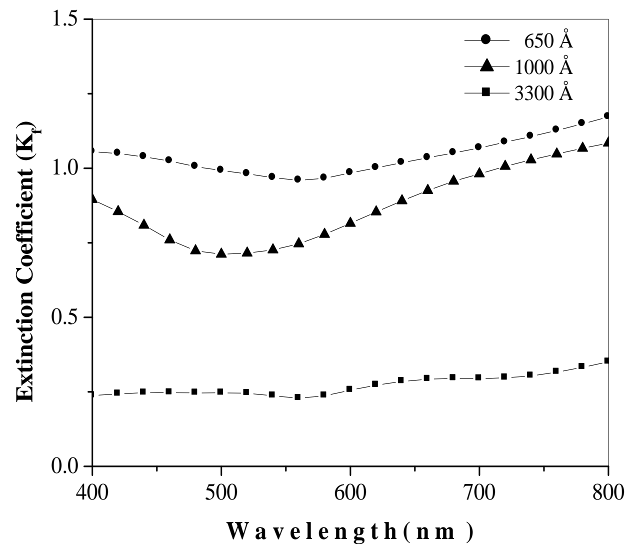

Fig. 3. Variation of extinction coefficient (k) on wavelength for copper doped ZnTe films.

The total absorption coefficient was calculated from transmittance measurements with the aid of the expression [**34**]

$$\alpha = \left(\frac{4\pi k_f}{\lambda}\right)$$

The extinction co-efficient (k_f) can be calculated from the relation

$$k_f = \frac{2.303\lambda \log(\frac{1}{T_0})}{4\pi t}$$

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where T_0 is the transmittance and t the thickness of the film.

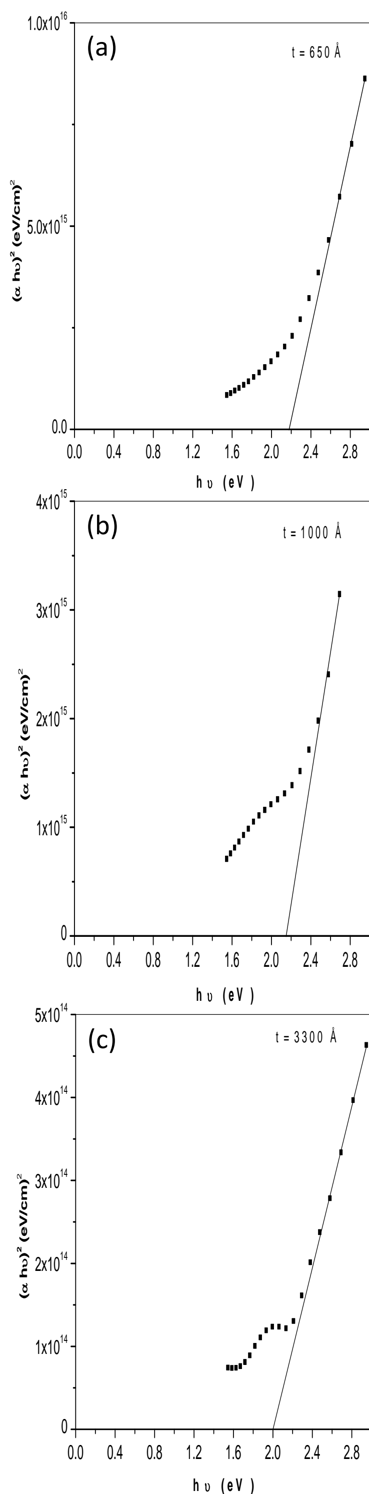

Fig. 4. The dependence of $(\alpha h\upsilon)^2$ vs hυ for copper doped ZnTe films of thickness (a) 650 Å, (b) 1000 Å and c) 3300 Å.

Fig. 3 shows the variation of extinction coefficient with wavelength for copper doped ZnTe thin films. A notable increase in extinction coefficient is observed near the fundamental absorption edge in the copper doped films whereas it decreases in pure films. This may be due to the presence of copper in those films. It is also noted that the extinction coefficient of the film decreases with decrease in copper composition. The electronic transition between valence and the conduction bands, is given by [**35**]-

$$\alpha h\upsilon = A\left(h\upsilon - E_g\right)^P$$

where the magnitude of the exponent 'p' characterizes the type of transition and takes the values 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively. In the above equation 'A' is a constant, 'E_g' the optical band gap and '$h\upsilon$' the energy of photon.

Fig. 4 shows $(\alpha h\upsilon)^2$ against the photon energy (hυ) for copper doped ZnTe films, indicating the possible optical transition is of direct-allowed type and the band gap energies are given in **Table 2**.

The direct band gap values these copper doped films decreased appreciably when compared to pure ZnTe films, which may be attributed to the segregation of impurities at the grain boundaries. Similar observation has been made by Pal et al for In doped ZnTe films [**36**]. The appreciable decrease in the band gap of copper doped films may also be caused by the presence of internal electric fields associated with the defects and by the changes in composition of the films.

Conclusion

Copper doped ZnTe thin films were deposited onto well-cleaned glass substrates by thermal evaporation. The decrease of atomic percentage value of copper with increase of the ZnTe film thickness is confirmed by EDX analysis. The X-ray diffraction analysis indicates that the films undergo a phase change from hexagonal to cubic structure. Copper doped ZnTe films have very low transmittance when compared to pure ZnTe films. A sharp increase in extinction coefficient is observed near the fundamental absorption edge. The optical transition of these films is found to be direct allowed.

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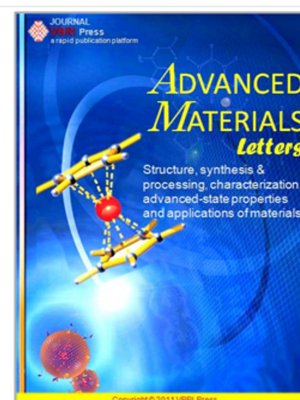

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