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Properties of Cu-doped ZnTe thin films prepared by closed space sublimation (CSS) techniques

A. MAQSOOD, M. SHAFIQUE
Thermal Physics Laboratory, Department of Physics, Quaid-I-Azam University, Islamabad 45320, Pakistan
E-mail: tpl.qau@usa.net; tpl@qau.edu.pk

Zinc telluride, as one of group II–VI semiconductors, has been extensively studied for application as a purely green light emitting diode and as back contact for CdTe in CdTe/CdS heterojunction solar cells [1–5], since it is expected to have a small valance band discontinuity with CdTe and can be doped degenerately with copper [2–6], to obtain low resistance. Cu-doped ZnTe films have been prepared by various methods, including thermal evaporation of ZnTe and Cu from two sources [4, 5], RF and dc sputtering [2, 3], electro-deposition [6] and thermal evaporation [7].

In this work, we present some physical properties of the ZnTe doped with Cu by immersion in $Cu(NO_3)_2$-H_2O solution and the effect of immersion time and subsequent heating in vacuum on the preparation of such films.

ZnTe thin films were deposited on a soda lime glass substrate. The ZnTe material was sublimated from a graphite source. Mica sheet was used as an insulator between the source and the substrate. The distance between the sublimation source and the substrate could easily be changed for better uniform films. The source and the substrate were kept at temperature of 600 and 400 °C respectively. The ZnTe powder (99.99% purity) was used as a source for the evaporation of ZnTe on the substrate. Two K-type thermocouples were used to monitor the temperature of the source and the substrate during the evaporation process. The sublimation of the material was carried out at a pressure of $\sim 10^{-2}$ mb. The deposition time was 5 min. After deposition the films were kept at substrate temperature (400 °C) for ∼20 min. These parameters yield stoichiometric ZnTe films [8]. The films, prepared at the above mentioned deposition parameters, were treated chemically by immersion in low concentrated (0.4 g/1000 ml) $Cu(NO_3)_2$-H_2O solution at $80 \pm 2\,^{\circ}C$ for different periods of time. The films after immersion were cleaned in distilled water and then dried.

Quantitative chemical analysis of the samples was carried out by atomic absorption, using an inductively coupled plasma spectrometer.

The dc electrical resistivity of the cut films was measured by the Vander Pauw method at room temperature. The sheet resistance of as-deposited film was very high ($>10^6\ \Omega/\square$), while the resistivity of the films immersed in Cu solution reduced to less than 1 Ω-cm after annealing at 400 °C in vacuum for one hour. Fig. 1 shows the plot of Cu ratio (at.%) and resistivity as a function of immersion time. It is clear that the resistivity of the samples became saturated after a certain time, due to a Cu film on the surface of ZnTe film, which limits further ion exchange processes.

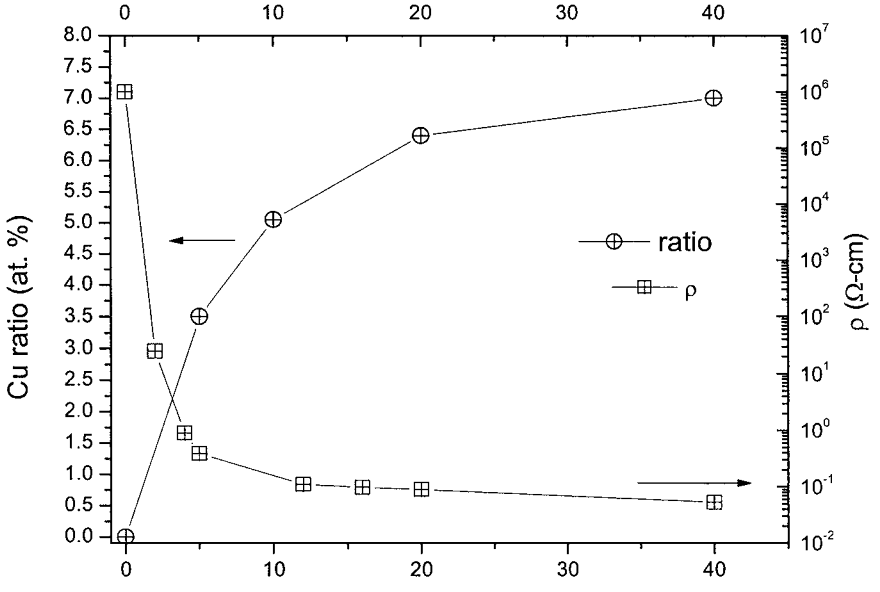

Figure 1 The dc electrical resistivity (ρ) and Cu ratio (at.%) as a function of immersion time.

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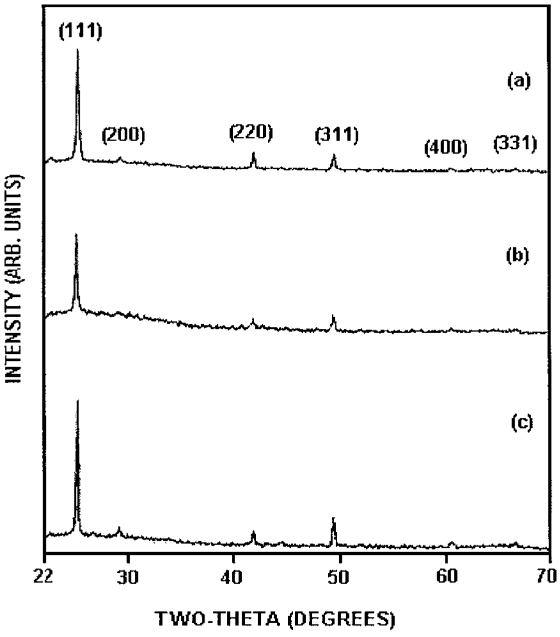

Figure 2 Indexed X-ray diffraction pattern of the (a) as-deposited film, (b) Cu-doped film for 20 min, and (c) Cu-doped annealed at 400 °C for 1 h.

The structure of the films was studied by X-ray diffraction (XRD) using Cu K_α radiation. Fig. 2 shows the XRD pattern of as deposited film (a), Cu-doped (b, c) and annealed films (c). The structure is composed of purely cubic phase with $\langle 111 \rangle$ as preferred orientation. The orientation was little affected by chemical treatment as shown in Fig. 2b. An ordered structure was again achieved on annealing the film at 400 °C for 1 h.

The transmission spectra (in the range 400–2000 nm) have been recorded by Perkin-Elmer, Lambda 19, UV-VIS/NIR spectrometer with UV-Winlab software. Fig. 3 shows the transmission of as-deposited and Cu-doped ZnTe films at room temperature. It is clear that transmission decreases with the increase of immersion time of films in the solution. This decrease in the transmission can be attributed to the introduction of impurity level between valance band and conduction band [9, 10]. The emission and absorption of specific frequencies can be related with the presence of dopant and imperfections, which provide localized energy levels in the forbidden energy gap.

These localized energy levels may be acceptor or donor levels depending on the dopants. In high absorption or low transmission regions [11, 12], the following relation is used for the dependence of transmittance (T) on absorption

$$T \approx e^{-\alpha}$$

where α is the absorption co-efficient and is given by $\alpha = -(1/d)\ln T$, d being the thickness of the film. The band gap is determined by using the well known dependence $\alpha \sim (h\nu)^{-1}(h\nu - E_g)^{1/2}$, where α is defined above, $h\nu$ is the phonon energy and E_g is the optical band gap. By extrapolating α^2 versus the incident photon energy ($h\nu$) plot. The band gap can be obtained. The plot of α^2 vs. $h\nu$ (Fig. 4) shows that the direct optical band gap of the films is 2.24 eV for un-doped and 2.21 eV in case of film immersed in the solution for 20 min. This shifting of the optical energy band gap towards the low energy region can be associated to the introduction of the impurity level between the conduction band and valance band.

The experimental results showed that the dc electrical resistivity of as-deposited film was very high ($>10^6$ Ω-cm). The resistivity of the films decreased with the increase of immersion time in the $Cu(NO_3)_2$ solution due to ion exchange of Cu ion with ZnTe film surface. A reduced value of about 0.5 Ω-cm was obtained for the film immersed for 40 min in the solution. The XRD studies showed well orientated cubic structure of as-deposited films. The immersion of ZnTe films in the $Cu(NO_3)_2$ solution affected the intensity of the peaks to some extent. On annealing, the pattern became identical to as-deposited film. The transmission spectra showed a decrease of transmission with an increase of immersion time, and a slight shift in the optical band gap.

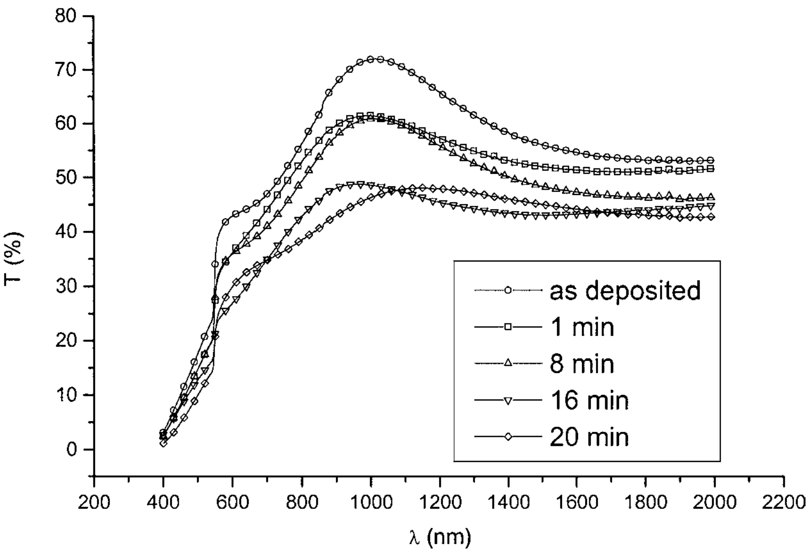

Figure 3 Transmission spectra of ZnTe thin films as a function of wavelength at room temperature.

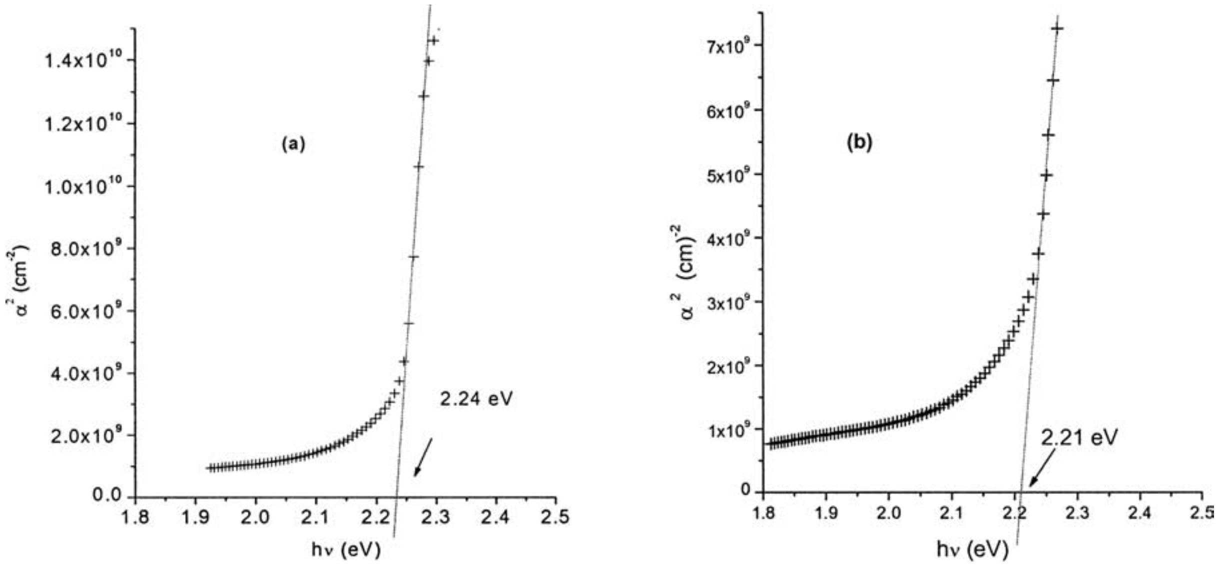

Figure 4 Plot of (α^2) as a function of $h\nu$: (a) as deposited and (b) Cu-doped film for 20 min.

Acknowledgments

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References

1. D. RIOUX, D. W. NILES and H. HOCHST, *J. Appl. Phys.* **73** (1993) 8381.
2. T. A. GESSERT and T. J. COUTTS, in Proceedings of the 12th NREL Photovoltaic Program Review (1993) p. 345.
3. T. A. GESSERT, A. R. MASON, R. C. REEDY, R. MASTON, T. J. CUTTS and P. SHELDON, *J. Electron. Mater.* **24** (1995) 1443.
4. J. TANG, D. MAO, L. FENG, W. SONG and J. U. TREFNY, in Proceedings of the 25th PVSC (Washington, DC, 1996) p. 952.
5. L. FENG, D. MAO, J. TANG, R. T. CULINS and J. U. TRENFNY, *J. Electron. Mater.* **5** (1996) 1442.
6. N. B. CHAURE, J. P. NAIR, R. JAYAKRISHAN, V. GANESAN and R. K. PANDEY, *Thin Solid Films* **324** (1998) 78.
7. S. I. KOBOYASHI and N. SAITO, *Jpn. J. Appl. Phys.* **19** (1980) 1199.
8. A. K. S. AQILI, Z. ALI, A. MAQSOOD, I. A. QAZI, A. HAQ, M. AHMED and M. ABBAS, in Proceedings of the 6th International Symposium on Advanced Materials (Islamabad, 1999) p. 525.
9. D. K. SCHRODER, "Semiconductor Material Device Characterization," 2nd edn. (Wiley, New York, 1998).
10. R. M. ROSE, L. A. SHEPARD and J. WULFF, "The Structure and Properties of Materials," Vol. 4 (John Wiley and Sons Inc., New York, 1967).
11. J. C. MANCIFACIER, J. GASIOT and J. P. FILLARD, *J. Phys. E: Sci. Instrum.* **9** (1976) 1002.
12. J. C. MANCIFACIER, M. D. MURCIA and J. P. FILLARD, *Thin Solid Films* **41** (1977) 127.

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