Chapter VII

Copper Doped Zinc Telluride Thin Films
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7.1 Introduction

It has been realized long ago that large gap semiconductors are very difficult to obtain with desired conductivity [1], most of them being available with only one type of conductivity [2], even when large amounts of impurities are introduced in attempts to obtain the opposite type. This self compensation is common to all large gap materials ($E_g > 2$ eV) and has been extensively in particular in the highly ionic alkali halides and in the partly covalent II – VI compounds. Electrical and optical properties of semiconductors depend on the presence of impurities which induce bound states in the band gap. The characterization of these bound states is decisive for technological applications. This problem is particularly crucial for large gap semiconductors which are generally available with one type of conductivity. It has been already reported that the p-type conductivity of ZnTe originates mainly from $Cu_{Zn}$ [3], $Li_{Zn}$ [4] and for a smaller part from $Ag_{Zn}$ [1] rather than from intrinsic defects.

In order to obtain low resistance contact, it is necessary to prepare ZnTe films which are doped with a suitable acceptor impurity such as copper [5, 6]. There is evidence in literature of the preparation of ZnTe films doped with Cu
having suitable electronic properties, mainly due to the presence of copper in the ZnTe structure. Although copper is widely recognized to be an element able to increase the acceptor doping concentration of ZnTe window material, little work has been carried out on the modification of the crystallographic as well as optical properties of this compound in the presence of Cu contents. ZnTe and ZnTe:Cu are characterized by similar inter atomic distances in the cubic phase, as revealed by the overlapping of their reflection lines in the x-ray diffraction patterns; both shows p-type behaviour and resilience to conductivity type change in the presence of accepter suppressors [7]. The aim of the present study is to prepare copper doped zinc telluride films by electrochemical technique (both potentiostatic and galvanostatic modes). The influence of growth parameters upon the structure, optical, electrical and morphological properties of Cu doped ZnTe deposits are also studied.

7.2 Review of earlier work

The ability to grow compact and device quality semiconducting films using electrodeposition is of considerable technological interest. The as-deposited ZnTe semiconductor have their resistivities in the order of $10^8 \ \Omega\cdot cm$. ZnTe can be doped degenerately with copper to obtain low resistance films [8]. ZnTe crystals are grown by Bridgeman method using Te as solvent by Saminadayar et al [6]. Infrared measurements are made on ZnTe doped with Ag, Cu and Au acceptor impurities.
Observed transitions are discussed in the frame of the theory of Baldereschi. Anup Mondal *et al.* reported [9] the preparation of Cu-doped ZnTe films (<100 nm thick) by electrochemical method. Also, the CdTe/CdS solar cells using the ZnTe:Cu as the primary contact to the CdTe achieved efficiencies of 8.7% with low contact resistance was obtained by the same group. Aqili *et al.* reported [10] the two-sourced evaporation technique to yield ZnTe films and a drastic decrease in resistance was obtained when immersed in Cu (NO$_3$)$_2$ solution. The dependence of material properties of radio-frequency magnetron sputtered, Cu-doped, ZnTe thin films was reported by Gessert *et al.* [11]. Pistone *et al.* have synthesized thin film p-ZnCuTe by electrodeposition technique [12]. The alloying nature of ZnTe with copper results a material with different optical and electronic properties was also explained. Kobayashi *et al.* have obtained [13] the electrical and optical properties of Cu-doped high conductivity ZnTe thin films.

Thus, in the present work, in order to develop a p-type semiconductor based on ZnTe but having larger absorption properties, conductivity and carrier concentration, Cu doped ZnTe films (ZnTe:Cu) are synthesized by both potentiostatic and galvanostatic electrodeposition. In particular, effects of Cu content in the ZnTe structure is investigated, together with the influence of growth parameters and post deposition treatments upon the morphological, electrical and optical properties of the films.
7.3 Experimental details

ZnTe thin films are grown by the electrodeposition technique on SnO$_2$:F substrates by potentiostatic and galvanostatic modes using an EG&G Princeton applied research Potentiostat/Galvanostat model 362, USA. Control of the electrodeposition process is in principle easier in the potentiostatic mode, since the growth process shows a form of cathodic inhibition. Nevertheless, this growth mode can be applied reliably, only if low-resistance cathodic substrates are employed. The deposition procedure for the preparation of ZnTe film is described earlier (Chapter III). Cu doped ZnTe films are obtained using CuSO$_4$ aqueous solution added in the deposition bath during the growth process. To produce stoichiometric films with uniform Cu doping, it is necessary to reduce the formation rate of free Cu compared to ZnTe. This could be obtained by adding triethanolamine, which acts as a complexing agent with CuSO$_4$ solution. This mixture is added in the acidic solution bath containing ZnSO$_4$ and TeO$_2$ to obtain ZnTe:Cu films. The concentration of the copper triethanolamine mixture was adjusted such that the formation of other compounds of Cu and Te are inhibited. The range of deposition parameters used to obtain homogeneous and uniform ZnTe and ZnTe:Cu films are, ZnSO$_4$ concentration: 0.15 to 0.25 M, TeO$_2$ concentration: 0.5 to 1 mM, CuSO$_4$ concentration: 0.05 to 1 mM, deposition potential: -0.7 to -1.1 V versus SCE, bath temperature: 30 to 90°C and solution pH: 3.5 ± 0.1.
Cyclic Voltammetry (CV) studies are carried out in standard electrochemical bath using the potentiostat. The type of semiconductivity of the ZnTe film is determined by measuring the potential difference between a hot and cold contact and are found to be p-type. The crystalline nature of the films are analyzed by X-ray diffraction using CuKα radiation (λ = 1.542 Å) by an XDS 2000™ machine from Scintag Inc., USA. The optical absorption properties are investigated with a UV-Vis-NIR spectrophotometer (Hitachi U 3400-20). The surface morphology of the deposits are analyzed using a scanning electron microscope (JEOL, JSM 840) unit.

7.4 Potentiostatic deposition

For most semiconducting devices, the formation of low resistance, metal-based, ohmic contacts were required for the establishment of a heavily doped region directly beneath the metal contact. If the surface layer is doped sufficiently high, current transport across the interface proceeds principally via tunneling at the Fermi level. Typically the resistivity of polycrystalline material is high due to grain boundary or surface scattering effects. In order to obtain low resistance contact, it is necessary to prepare ZnTe films, which are doped with suitable acceptor impurity like Cu, Ag or Au [14]. We carried out the following electrochemical experiment with a natural convection cell under potentiostatic mode to prepare the samples.
7.4.1 CV studies

Cyclic Voltammetry (CV) is a useful diagnostic tool for the study of electroactive species. Voltammogram is a plot between the applied scanning potential and the observed current density in the electrochemical system on carrying out the desired electrochemical reactions. Voltammogram gives an idea about the deposition potential range of individual elements and co-deposition potential range of all the elements put together, involved forming the compound semiconductor. Fig. 7.1 shows a typical cyclic voltammogram of a tin oxide coated electrode in electrodeposition bath between the potential range 0.4 and -1.1 V versus SCE. It is observed that, by scanning towards more negative potentials, the first cathodic wave appeared at -0.4 V versus SCE corresponds to the cathodic reduction of $HTeO_2^+$ to Te. Tellurium being nobler and it was expected to deposit first by the following charge transfer reaction:

$$HTeO_2^+ + 4e^- + 3H^+ \rightarrow Te + 2H_2O$$

A second cathodic wave observed at -0.78 V versus SCE may be ascribed to the formation of $ZnTe$ on the substrate by the following reaction:

$$Zn^{2+} + Te + 2e^- \rightarrow ZnTe$$

The current increased rapidly as the substrate potential increased cathodically more than -0.8 V versus SCE and this observation may be attributed to the high concentration of zinc ions present in the bath. The anodic sweep exhibited a
Fig. 7.1 Cyclic voltammogram of F:SnO₂ coated glass cathode in 0.18 M ZnSO₄, 0.6 mM TeO₂ and 0.08 mM CuSO₄ with solution pH 3.5 ± 0.1, scan rate 10 mV s⁻¹.
peak at -0.64 V versus SCE corresponds to elemental zinc stripping. The cathodic current increased further, crossed the forward sweep and exhibited a large anodic peak at -0.18 V versus SCE. This corresponds to stripping of tellurium. The results of the CV experiments led us to select a potential range of -0.85 to -1.1 V versus SCE for the preparation of ZnTe thin films. The CV plot related to the deposition of Cu and Te shows the reduction of TeO₂ and CuSO₄ in the potential -0.03 V (SCE) according to the reaction:

\[ \text{CuSO}_4 + e^- \rightarrow \text{Cu}^0 + \text{SO}_4^- \]

The small peak present at -1.08 V versus SCE is related to the oxidation of Cu. When the Cu content in the bath increases, the peak intensity also increases. It is observed that the concentration of Zn and Cu in the bath changes, there is a proportional change in the Zn/Cu ratio in the deposit. To establish the stoichiometric doping of Cu with ZnTe, lower concentration of Cu in the bath (0.08 mM) is selected.

7.4.2 Structural studies

The X-ray diffraction pattern of a typical ZnTe film deposited at 90°C in the asdeposited and doped condition is shown in the Fig.7.2. It is observed that, the XRD of undoped ZnTe film (Fig.7.2a) is found to be polycrystalline with preferential orientation along the (111) plane, the other secondary peaks visible are (200), (220), (311) and (331). All the peaks are associated with cubic ZnTe and no
Fig. 7.2 XRD patterns of ZnTe (a) and ZnTe:Cu (b) films deposited at 90°C bath temperature in potentiostatic mode. The inset shows the fit used to determine the lattice parameter.
major zinc or tellurium peaks are found. The observed relative intensities of the X-ray peaks for the ZnTe sample are compared with the JCPDS values (15-746). The lattice parameter $a$ is determined from Bragg's formula for the cubic system and using the angles 12.59, 14.59, 20.90, 24.73 and 33.37° (inset of Fig.7.2). The lattice constant calculated from XRD trace is found to be 6.09 Å, which agrees well with the bulk value of ZnTe (6.085 Å) in accordance with the reports on hot-wall evaporation [15]. The grain size of the as-deposited ZnTe film was estimated (45 nm) from half intensity width studies and using the Debye-Scherrer formula [16].

Structural analysis of Cu doped ZnTe films deposited at 90°C bath temperature is shown in Fig.7.2b. The XRD shows a cubic structure with a preferred orientation along the (111) plane. No major difference is observed in X-ray patterns of the as-deposited and Cu doped samples. In doped films, the sharpness of the peak increases which in turn decreases the FWHM. The grain size is calculated (56 nm), showing that, for Cu doped films, there is an increase in grain size, which improves the crystalline quality of the film. Due to the small quantity of Cu incorporated in the deposition bath (0.08 mM), the Cu peaks were not seen in XRD.

7.4.3 Optical characterization

The transmittance spectra of a typical ZnTe and Cu doped ZnTe film deposited at 90°C are shown in Fig.7.3. The optical band gap is determined from the absorption coefficient using the relation:

$$
\text{Absorption coefficient} = \frac{1}{\text{Transmittance}}
$$
Fig. 7.3 Transmission spectra of the ZnTe and ZnTe:Cu films deposited at 90°C in potentiostatic mode. The inset shows the plot of $(\alpha \nu)^2$ against $h\nu$ for ZnTe and ZnTe:Cu.


\[(\alpha h\nu)^2 = K(h\nu - E_g)\]

Where \(\alpha\) is the absorption coefficient, \(h\nu\) is the photon energy, \(K\) is a constant which is related to the effective masses associated with the valence and conduction bands, \(E_g\) is the energy gap between the bottom of the conduction band and top of the valence band at the same value of wave vector. An energy band gap of 2.26 eV for ZnTe and 2.23 eV for ZnTe:Cu is obtained by extrapolating the linear part of the curves \((\alpha h\nu)^2\) versus \((h\nu)\) are shown in the inset of Fig.7.3. It is hypothesized that Cu introduces some additional energy levels in the ZnTe band gap close to the valence band edge, with a consequent reduction of the energy associated with direct transition. Due to doping of Cu in ZnTe films, the optical transmission is reduced due to free-hole absorption. The variation of refractive index \((n)\) as a function of wavelength is shown in Fig.7.4. It is observed that the refractive index of Cu doped ZnTe film is higher than that of the undoped ZnTe sample; this may be attributed to an increase in packing density and the crystallinity of the films. Both doped and undoped films exhibits an exponentially decreasing \(n\) values, as the wavelength increases. Similar behaviour has been reported for two-sourced evaporated copper doped ZnTe thin films [17].

7.4.4 Electrical properties

The electrical studies of ZnTe films are performed using a four-probe Van der Pauw technique. ZnTe films are found to be highly resistive in the range
Fig. 7.4 Variation refractive index with wavelength (potentiostatic mode) for a typical ZnTe and ZnTe:Cu films deposited at bath temperature 90°C.
1.5× 10$^5$ to 5.5× 10$^8$ Ω-cm when the bath temperature is varied from 30 to 90°C. The electrical behaviour of the undoped and Cu doped ZnTe films are shown in Fig.7.5. It has been mentioned earlier that ZnTe films were always found to be p-type owing to acceptor levels associated with Zn vacancies present in the film. As the deposition temperature increases (30 to 90°C) the resistivity of the film decreases from 10$^5$ to 10$^3$ Ω-cm. Such intrinsic ZnTe semiconductors are of little importance in various fields due to its higher resistivity. These limitations are overcome by adding a small and measured amount of chemical impurity to the intrinsic semiconductor. This added impurity is very small of the order of 1 atom per million atoms of the pure semiconductor, the resistivity of the film get reduced due to the production of more charge carriers. The electrical properties are altered and most of the charge carriers originate from impurity atoms. Hence, the resistivity of Cu doped ZnTe film reduces from 10$^5$ to 10$^3$ Ω-cm in the temperature range 30 to 90°C.

Due to the thickness restriction and the fact that as Hall effect instrument does not have the required high input impedance, we could not measure the carrier density for ZnTe films. However, the decrease in resistivity for copper doped films may be due to the increase in hole density. At higher bath temperatures ZnTe films with improved crystallinity is obtained which in turn may reduce grain boundary scattering with a consequent reduction in the resistivity of the films. A decrease in resistivity, attributed to the ionized dopant, was followed by an increase
Fig. 7.5 Variation of resistance with bath temperature (potentiostatic mode) for a typical ZnTe and ZnTe:Cu films.
in resistivity due to more effective scattering of carriers as the dopant concentration increased further.

7.4.5 Morphological studies

Fig. 7.6 illustrates the surface morphology determined by scanning electron microscope for an undoped and Cu doped ZnTe sample. A typical ZnTe film deposited at potential -1.0 V versus SCE with bath temperature 90°C (Fig. 7.6a) shows globular surface morphology. Some regions are found to possess brighter contrast than the under layer indicating the occurrence of loosely adhering surface particles. The tendency of the ZnTe surface to accumulate loosely adhering particles increased for thicker deposit. Since ZnTe films are highly resistive, the electrodepositing ions may find it increasingly unfavourable to discharge on ZnTe covered surface, once it becomes sufficiently thick. The Cu doped ZnTe surface morphology shown in Fig. 7.6b exhibits a flake-like appearance. This is in sharp contrast to the undoped surface where a mixed dendritic as well as granular surface morphology is observed.

7.5 Galvanostatic deposition

Enhancement of Zn ion vacancies within the lattice can be achieved by means of doping. Hence effort is taken to reduce the resistivity of the film through doping. Reduction of ZnSO₄ concentration in the electrolyte reduces the resistivity
Fig. 7.6 SEM picture of representative ZnTe (a) and ZnTe:Cu (b) films deposited at bath temperature 90°C through potentiostatic mode of deposition.
of the film from $10^8$ to $10^5$ ohm-cm. Further, reduction in resistivity is achieved by
doping the electrolyte with CuSO$_4$. This causes decrease in resistivity of the film of
the order of $10^3$ ohm-cm. The asdeposited and Cu doped ZnTe films are analysed
using XRD, optical, electrical and surface morphological studies and the results are
discussed below.

7.5.1 Structural characterization

ZnTe thin films are cathodically deposited through galvanostatic mode
under the following condition: Cathodic current density: 1.6 mAcm$^{-2}$, Solution pH:
3.5 ± 0.1, Bath temperature: 80°C, Concentration of ZnSO$_4$: 0.15 M, Concentration
of CuSO$_4$: 0.07 mM, Concentration of TeO$_2$: 0.5 mM, Plating duration: 45 minutes.
Fig.7.7 shows the XRD traces of ZnTe and Cu doped ZnTe prepared through
galvanostatic mode. The most intense peak is observed due to the (111) plane, while
additional smaller peaks are also observed. It should be mentioned here that, with
increasing deposition temperature the (111) peak sharper at the expense of the other
smaller peaks. The lattice constant calculated from the XRD traces of the films is
6.085 Å. It compares well with the bulk value of 6.089 Å for cubic structure. The
films are polycrystalline in nature. At lower current densities (<1.5 mAcm$^{-2}$) some
Te peaks are observed and further they disappear as the current density increases.
It may be remarked that electrodeposited tellurium often exhibit a dendrite
Fig. 7.7 XRD patterns of ZnTe(a) and ZnTe:Cu(b) films deposited at 80°C bath temperature in galvanostatic mode of deposition.
morphology. If this happens, the area of the electrodeposited films may continuously change leading to a rise in the overall current density.

XRD analysis of the Cu doped ZnTe films deposited at 80°C indicates that the films demonstrate preferred orientation along (111) plane. Although XRD analysis of the Cu doped films are similar to that of un-doped films, but the Cu doped films do not indicate the possible presence of any phase change for room temperature depositions. Presently, it cannot be established, if this difference is due to the presence of Cu or to the differences in deposition parameters. In order to identify possible Cu-Te phases, comparisons of XRD data have been performed between doped and un-doped films, as well as among films deposited at different deposition conditions. This analysis has revealed several small peaks in the doped films that do not correspond to published ZnTe powder data (i.e., $2\theta \approx 43.5^\circ$ and $\sim 45.3^\circ$). Although comparisons with available powder data suggest that the unidentified peaks could result from Cu-Te phases, these indications are not conclusive, because the peaks also correspond well to the likely presence of metallic Te, Zn or Cu [18]. The grain size calculations are noted as 38 nm, whereas for un-doped films it is 27 nm.

7.5.2 Optical studies

Optical properties are of much importance for the semiconducting thin films. The measurement of absorption of a sample provides a satisfactory way to
determine the form of the absorption edge. The absorption edge and energy band gap can be determined from the optical absorption measurements. The band gap of the un-doped and Cu doped ZnTe films are experimentally determined from the optical absorption data, using the linear relationship between \((ah\nu)^2\) versus \((h\nu)\). The corresponding linear plots are shown in Fig. 7.8. The asdeposited ZnTe film showed higher optical absorption than the Cu doped film. The direct energy gap was determined by the intersection of the linear regression with the energy axis. The calculated values of the direct band gaps are found to be 2.25 eV for asdeposited films and 2.21 eV for Cu doped ZnTe films. The direct energy gap obtained for undoped ZnTe film is in good agreement with literature [7, 19]. It is hypothesized that copper introduces some additional electronic levels in the ZnTe band gap close to the valence band edge, with a consequent reduction of the energy associated with the direct transition.

7.5.3 Electrical studies

Un-doped ZnTe film is found to have resistivity between \(10^5\) to \(10^8\) \(\Omega\)-cm, with a median around \(10^7\) \(\Omega\)-cm. This is consistent with the finding of others, who obtained resistivities of \(10^7\) to \(10^8\) \(\Omega\)-cm by metal organic chemical vapour deposition and \(10^5\) \(\Omega\)-cm using hot-wall vacuum evaporation [20] and MOVPE [21]. The p-type character of undoped ZnTe has been attributed to acceptor type Zn vacancies in ZnTe [20, 22]. Because, undoped thin film is very resistive.
Fig. 7.8 Plot of \((\alpha \gamma)^2\) against \(h\gamma\) for ZnTe and ZnTe:Cu films under galvanostatic mode of deposition.
(>1500 Ω-cm), a detailed electrical analysis of this (un-doped) material was not possible with the equipment used for this study i.e., the apparatus used for Hall measurements is not designed for measurement of high resistance samples. However, because the principle aim in this work is to investigate the effect of deposition conditions on the (more conductive) doped films, a more complete analysis of this material could be performed.

Fig.7.9 depicts the electrical behaviour of the as-deposited and Cu doped ZnTe films. It reveals that the Cu doped film is drastically decreased in the order of $10^3$ Ω-cm. By increasing the Cu content in the electro deposition bath, a sufficient decrease of sheet resistivity and an increase of major carrier concentration were observed for the deposits. It is thought that copper introduces a set of intermediate electronic levels close to the valence band edge. In general, the effect of additives on hole density mirrored the effect on resistivity. When the resistivity decreased, the hole density increased by a somewhat larger factor because the mobility decreased. The decrease in mobility with increased carrier density is due to increased scattering by the higher density of impurities.

7.5.4 Surface morphology

The scanning electron micrograph of the stoichiometric film in the as-deposited and Cu doped conditions is shown in Fig.7.10. The difference in contrast between the surface particles (lighter contrast) and the bulk (darker contrast) in
Fig. 7.9 Variation of resistance with bath temperature for a typical ZnTe and ZnTe:Cu film under galvanostatic deposition.
Fig. 7.10 SEM picture of representative ZnTe (a) and ZnTe:Cu (b) films deposited at bath temperature 80°C, through galvanostatic mode of deposition.
Fig. 7.10a indicates a porous surface for ZnTe films (0.41 nm). The grains are also not in good electrical contact with each other. On the contrary, an improved surface morphology with considerably reduced charging effects can be seen in Fig. 7.10b for ZnTe:Cu films. The average grain size in this film is also larger (0.48 nm). The actual structure is likely composed of fibrous, upright columns and these are artifacts of the arriving adatoms having insufficient surface mobility to find low-energy lattice sites [23]. Under higher annealing treatment (150°C), the films begin to indicate typical features of transitional growth, with the columnar structure being replaced with small grains separated by voids. As the annealing temperature is increased to 350°C, the microstructure becomes more granular and begins to indicate surface features consistent with three dimensional grain growths.

7.6 Conclusion

Cu doped ZnTe films were prepared by electrochemical method (both potentiostatic and galvanostatic modes) yielded stoichiometric and uniform films. A copper complex added to the bath allowed controllable p-type doping of the ZnTe films. Incorporation of Cu$^{2+}$ ions in the bath alters the density of carriers and consequently the barrier and the conductivity. The X-ray diffraction studies have not revealed any change in the film structure but the grain size of the Cu-doped film increases (56 nm). The optical studies of the Cu-doped films show a decrease in the transmission, an increase in the refractive index and also a slight shift in the optical
band gap. The SEM examination presents the globular and flake-like morphology for the as-deposited and Cu-doped ZnTe films. These films will be used as contact layers to the CdZnTe films in high efficiency tandem solar cell structures.
References


