

EFFECT OF ZN CONCENTRATIONS ON ELECTRODEPOSITED ZNTE THIN FILMS

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ABSTRACT

Thin films of zinc telluride (ZnTe) have been deposited on glass/conducting glass substrates by low-cost aqueous electrodeposition (ED) method using different Zn²⁺ concentrations. The structural, optical and morphological properties of the resulting films have been characterized using X-ray diffraction (XRD), optical absorption and Scanning Electron Microscopy (SEM). It was confirmed by XRD technique that the deposited layers from the lower Zn concentration are more crystalline than those grown at higher Zn concentration with a strong peak observed at $2\theta = 24.05^\circ$, corresponding to (100) plane of hexagonal phase. Photoelectrochemical (PEC) studies revealed that the layers are p-type in electrical conduction. Optical absorption measurement was used for the bandgap determination of the deposited layers. The bandgap of the as deposited layers from the lower and higher concentration are in the range (2.28 - 2.45) eV and (2.65 - 2.78) eV respectively. The larger bandgap observed from the higher concentration may be due to the quantum effect which is confirmed by the absence of strong XRD peaks from these layers and/or inclusion of ZnO in the deposited layers.

KEYWORDS: ZnTe, Zn concentration, electrodeposition of semiconductors, thin films.

INTRODUCTION

Semiconductor compounds belonging to group II-VI family have a wide range of applications in the fabrication of solid-state devices such as thin film solar cells, infrared detectors, light emitting diodes (LEDs) and nuclear radiation detectors (Salem et al., 2008; Amutha et al., 2007; Merchant and Cocievera 1999; Bellakhder et al., 2001). ZnTe is a II-VI semiconductor with a wide and direct bandgap of (2.21 - 2.26) eV at room temperature and electron affinity of 3.53 eV (Mahalingam et al., 2002; Neumann-Spallart and Konigstein 1995). Thin film solar cells development needs at least two kinds of semiconducting layers; a wide bandgap window material and a narrow bandgap absorber material. The most common window material used to develop thin film solar cells based on CdTe and CuInGaSe₂ absorber materials is the n-CdS. Due to the toxic nature of Cd- and associated waste during growth of CdS using chemical bath deposition (CBD), ZnTe is an alternative environmentally benign compound that can be potentially used as window layer to replace the CBD-CdS currently used.

ZnTe is a p-type window material capable of producing higher potential barriers for electron transport in devices, and therefore gives higher V_{oc} values. The recent work reported in the literature (Dharmadasa 2009; Dharmadasa et al., 2005) on multi-layer graded bandgap solar cells based on AlGaAs/GaAs structures with p-type window materials have demonstrated highest V_{oc} (1100 - 1175 mV) and excellent FF (0.80 - 0.87) values. The development of ZnTe layers using electroplating enables the fabrication of next generation graded bandgap solar cells using low-cost materials.

The methods used to deposit ZnTe thin films includes isothermal close space sublimation (ICSS) (De melo et al., 2009), brush plating

(Murali et al., 2006), r.f and dc sputtering (Bellakhader et al., 2001), metal organic vapour phase epitaxy (MOVPE) (Nishio et al., 1999), electrodeposition (John et al., 2005; Islam et al., 2009; Mahalingam et al., 2002; Diso et al., 2011), pulsed laser ablation (Rouleau and Lowandes 1998), thermal evaporation (Bacaksiz et al., 2009), metal-organic chemical vapour deposition (MOCVD) (Mora-Ser et al., 2004) and molecular beam epitaxy (MBE) (Franta et al., 2004). This paper presents a summary of experimental results obtained on electrodeposited ZnTe (ED-ZnTe) using two different Zn²⁺ concentrations.

EXPERIMENTAL DETAILS

Electrodeposition of ZnTe films

Thin films of ZnTe were cathodically electrodeposited onto glass/conducting glass substrates using two different Zn²⁺ concentrations (i.e. 0.02M and 0.15M). ZnSO₄·7H₂O and TeO₂ have been used as the sources of Zn and Te ions respectively. In both electrolytes the growth temperature is the same (~87°C) while the pH values were 4.50 and 3.50 for 0.02M and 0.15M Zn²⁺ concentrations respectively. Fluorine doped tin oxide (FTO) coated conducting glass substrates with sheet resistance of 15 Ω/□ were used as substrates. These were cleaned in organic solvents (methanol and acetone), dilute HNO₃ and finally rinsed in glacial acetic acid. In between different solvents, the glass/FTO substrates were rinsed in de-ionized water. All chemicals used for electrodeposition were grade analytical reagent, of purity 5N (99.999%). A two-electrode system was used in this project in order to simplify the process and to eliminate an impurity source; the reference electrode.

A graphite anode and a glass/FTO cathode were used to pass an electric current through the electrolyte. The study of the electrodeposition mechanism was carried out using cyclic voltammogram.

Measurement Techniques

Cyclic voltammetry (CV) was performed using a Gill AC computerised potentiostat (S/N 1313 ACM Instruments). With the information obtained from the voltammogram, ZnTe thin film deposition was carried out beyond 1400 mV cathodic voltage for both chemical baths. After the deposition, the films were rinsed in distilled water and subsequently dried using nitrogen gas. X-ray diffraction measurements (XRD) were carried out using a Philips PW 3710 X-ray diffractometer using CuK_α radiation ($\lambda = 1.5416 \text{ \AA}$) in the range of $2\theta = (10 - 70)^\circ$ for the structural analysis of the deposited film. A Cary 50 Scan UV-Visible spectrophotometer (Varian) was used for optical bandgap measurements.

Photoelectrochemical (PEC) measurements using an electrolyte of $0.10\text{M Na}_2\text{S}_2\text{O}_3$ were carried out to determine the electrical conductivity type of the ED-ZnTe layers. A solid/liquid junction was formed by immersing glass/FTO/ZnTe in the electrolyte solution. The PEC signal was determined by the difference between voltages observed under illumination and under dark conditions. The magnitude of the PEC signal depends on the doping condition of the solid layer and hence, the width of the depletion region formed. The sign of the PEC signal determines the electrical conduction type. A Philips XL 30 ESEM-Field Emission Gun with accelerating voltage of 20 kV was used to study the surface morphology of the thin film layers.

RESULTS AND DISCUSSION

Voltammogram

Figure 1 (a) and (b) shows a typical cyclic voltammograms related to the electrodeposition of ZnTe thin films from two electrolytes. Te starts to deposit from $\sim 200 \text{ mV}$ cathodic voltage and deposition of Te-rich ZnTe compound is expected at $\sim 800 \text{ mV}$ to 1400 mV cathodic voltages. ZnTe thin films deposition takes place beyond 1480 mV cathodic voltage as can be deduced from these Figures. Two peaks were observed in the reverse direction which are attributed to the removal of metallic zinc and tellurium at $(1368 \text{ \& } 710) \text{ mV}$ and $(858 \text{ \& } 349) \text{ mV}$ cathodic voltages for 0.02M and 0.15M Zn^{2+} concentrations respectively. The pH is one of the key parameters necessary to be considered during the deposition of ZnTe layers. According to (Neumann-Spallart and Konigstein 1995; Mahalingam et al., 2002), at lower pH (3.50 ± 0.01), free tellurium is deposited and at comparatively higher pH (5.50 ± 0.01), the solution becomes cloudy due to the precipitation of TeO_2 or Cd(OH)_2 . Furthermore, the deposition

current density has a strong influence on the structure of the ZnTe thin films grown. It has been reported by (Neumann-Spallart and Konigstein, 1995) higher deposition current densities ($>400 \mu\text{Acm}^{-2}$) led to films with rough surfaces, whereas films deposited at lower current densities ($\approx 100 \mu\text{Acm}^{-2}$) had smooth surfaces.

Thickness measurement

The thickness of ED-ZnTe layers deposited for 60 minutes shows a value of $\sim 0.70 \mu\text{m}$ when measured using the Dektak technique. The theoretical estimate using Faraday's relation given by equation (1), gave the value $\sim 0.65 \mu\text{m}$.

$$T = \frac{1}{nFA} \times \frac{ItM}{\rho} \quad (1)$$

where, T is the thickness of the ZnTe film in cm, I is the deposition current density in mAcm^{-2} , t is the deposition time in seconds, M is the molecular weight in grams, n is the number of electrons transferred, F is the Faradays constant = 96485 C , A is the area of the deposited layers in cm^2 , and ρ is the density of ZnTe in gcm^{-3} .

Visual Appearance

Figure 2 shows the visual appearance of ZnTe layers deposited as a function of growth voltage. As shown in the Figure, at higher and lower cathodic voltages, the samples become dark which are attributed to the Zn and Te richness. In the intermediate voltages, the layers appear reddish brown, similar to that of bulk ZnTe material.

X-ray diffraction

The XRD investigations of ED-ZnTe grown at 1513 and 1560 mV from 0.02M and 0.15M Zn^{2+} concentrations are shown in Figure 3. The diffractograms show that at lower Zn concentration a strong peak is observed at $2\theta = 24.05^\circ$ which corresponds to preferred orientation along (100) plane of hexagonal phase. This peak agrees with the Joint Committee on Powder Diffraction Standard, JCPDS (01-075-2082) data on hexagonal ZnTe. Other peaks identified from the graphs are ZnO peak and (103) plane. At the higher concentration of Zn^{2+} the preferred orientation of ZnTe disappears with (102), (200) and (202) planes appearing in addition to the (100) plane. (Mahalingam et al., 2002) reported that ZnTe films crystallise at lower concentration and the results confirmed this observation. The values of d , D and Full width at half maximum (FWHM) of the strongest peak evaluated for results shown on panel 1 are presented in Table 1. Furthermore, due to the nature of the weak XRD peaks on panel 2 it is difficult to calculate these parameters.

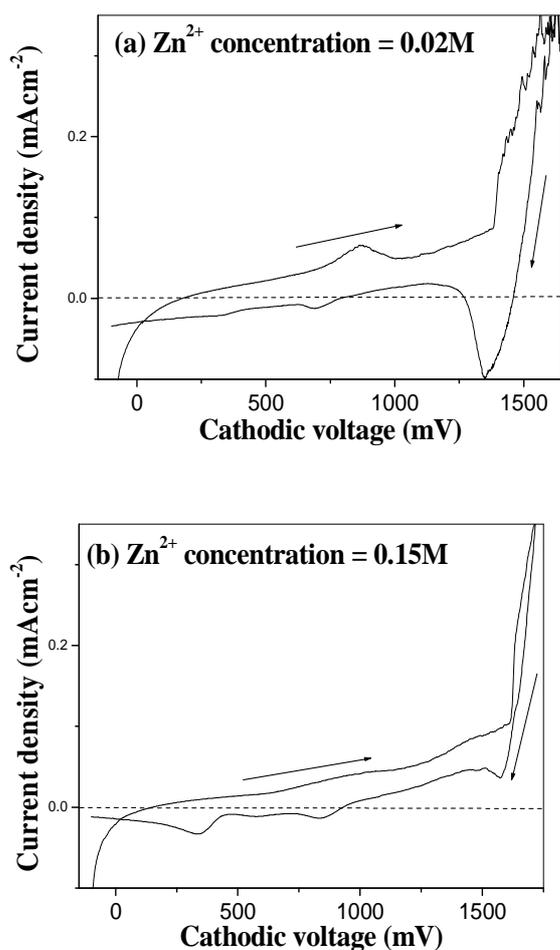


Figure 1: Typical voltammogram of electrolytic baths used for deposition of ED-ZnTe containing Zn^{2+} concentrations of (a) 0.02M and (b) 0.15M.

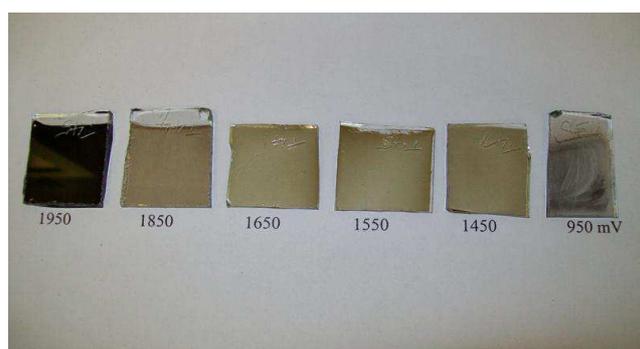


Figure 2: The appearance of as-deposited ED-ZnTe layers grown on glass/FTO substrate.

Table 1: Structural parameters of ED-ZnTe thin films (panel 1).

S/N	2 θ (Degrees)		Lattice spacing d (Å)		Crystallite size D (nm)	FWHM	hkl
	RP	OB	RP	OB			
1	24.029	24.050	3.7005	3.7761	4.4	0.334	100
2	24.029	24.050	3.7005	3.7305	8.8	0.169	100

N/B: 1 - as deposited, 2 - heat treated, RP - reported value from the JCPDS card, OB - observed value from the XRD Figure.

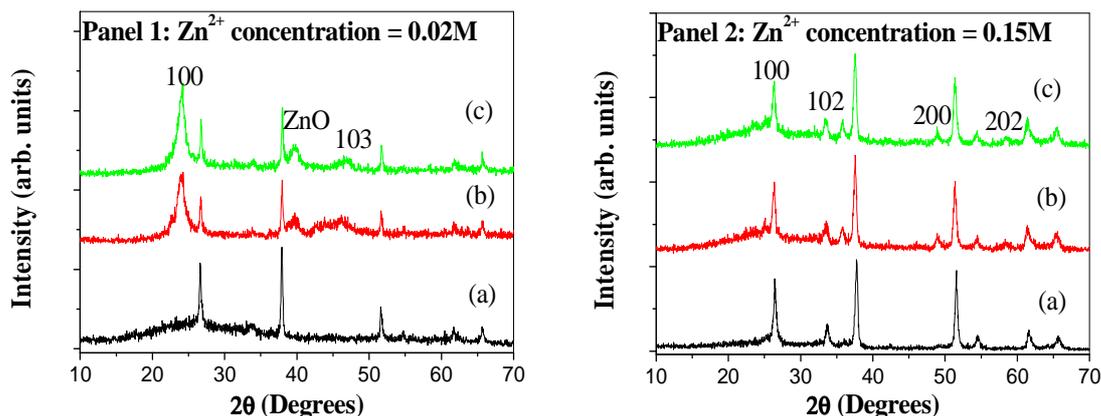


Figure 3: X-ray diffraction patterns of ED-ZnTe thin films grown at lower [panel 1; $V_g = 1513$ mV] and higher [panel 2; $V_g = 1590$ mV] concentrations of Zn^{2+} ; (a) glass/FTO, (b) as deposited and (c) heat treated ED-ZnTe.

From the Table, it was observed that crystallite size for heat treated sample increases and the FWHM decreases; this is attributed to coalescence of small crystals and formation of large grains. A further decrease in the lattice spacing is observed for the heat treated sample which is in agreement with the work in the literature (Lalitha et al., 2006). The observed lower value of d for heat treated sample is an evidence of removal of tensile strain by the heat treatment. The same trend is observed for FWHM; the crystallite size increases due to the increase in the grain sizes and the relaxation of excessive strains in the lattice.

Optical absorption

Optical absorption measurements were carried out in order to evaluate the bandgap. The absorption spectra of ED-ZnTe using 0.02M and 0.15M Zn^{2+} concentrations are shown in Figure 4. The bandgap energy, E_g , was estimated by plotting the square of absorbance (A^2) against photon energy ($h\nu$). The intercept on the energy

axis gives the values of the direct bandgap of the as deposited ZnTe; E_g as $\sim (2.32 - 2.50)$ eV and $(2.65 - 2.78)$ eV for 0.02M and 0.15M for Zn^{2+} concentration respectively.

Figure 4 (a) clearly shows the progressive sharpening of the absorption edge, which is due to the lower concentration of Zn^{2+} sources. This result goes together with the XRD spectra presented on panel 1 of Figure 3. The minimum value of 2.32 eV from the lower concentration is very close to the reported bandgap of crystalline ZnTe layer (2.21 - 2.26) eV (Mahalingam et al., 2002; Neumann-Spallart and Konigstein 1995). The larger value observed in the films with a higher concentration of Zn in the bath indicates that the layers formed consist of nano-crystals, producing larger bandgap values due to quantum effects. This increase could also be due to incorporation of ZnO ($E_g = 3.08 - 3.26$) eV (Dharmadasa 2009; Dharmadasa et al., 2005) and hence reducing the crystallinity of the deposits.

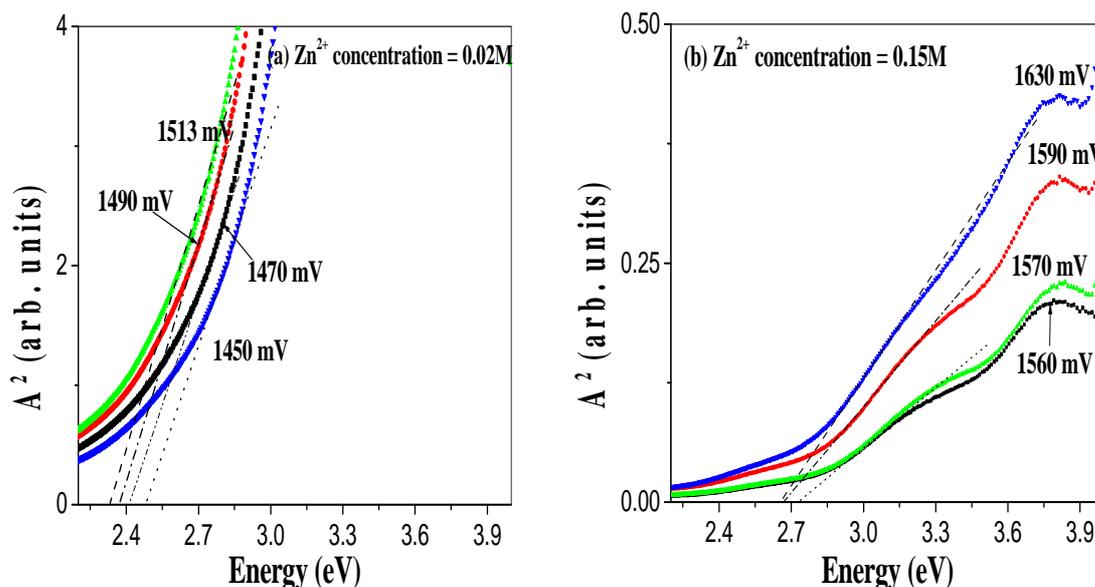


Figure 4: Optical absorption edges for as deposited ED-ZnTe for Zn^{2+} concentrations (a) 0.02M and (b) 0.15M

Photoelectrochemical (PEC) studies

PEC signal measurements were carried out on all the samples from the two concentrations and the results are shown in Figure 5. PEC studies provide vital information on electrical

conductivity type and hence help in design and fabrication of electronic devices using these films. These results indicate that all ED-ZnTe layers grown at the selected voltages were p-type in electrical conduction.

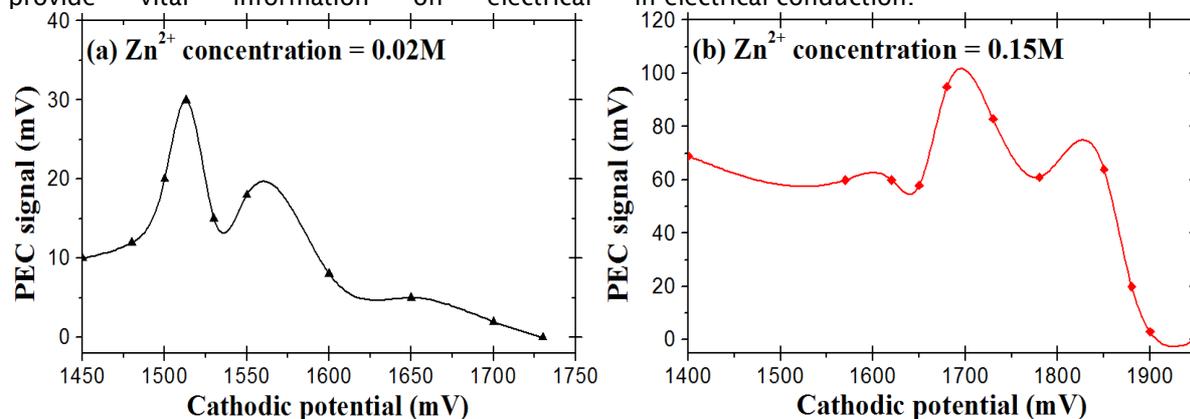


Figure 5: PEC signal as a function of growth voltage for as deposited ED-ZnTe layers for Zn^{2+} concentrations (a) 0.02M and (b) 0.15M.

It should be noted that Na_2SO_4 has been used as a supporting electrolyte to grow ZnTe. The presence of sodium in the electrolyte could act as a p-type dopant in ZnTe producing always p-type ZnTe layers.

Scanning Electron Microscopy (SEM) studies

SEM studies were carried out to investigate the surface morphology and uniformity of ED-ZnTe layers. The SEM micrographs of as deposited ED-ZnTe layers are shown in Figure 6 (a) and (b) from two different Zn^{2+} concentrations. The appearance indicates the uniform distribution of grains size of ~15 nm and ~10 nm from lower

and higher concentrations of Zn^{2+} respectively. Reproducibility of the films is one of the main challenges facing most of the growth techniques. In this work, the main difficulties are the right control of parameters such as pH, tellurium addition, temperature of the electrolytic bath, deposition potential etc.

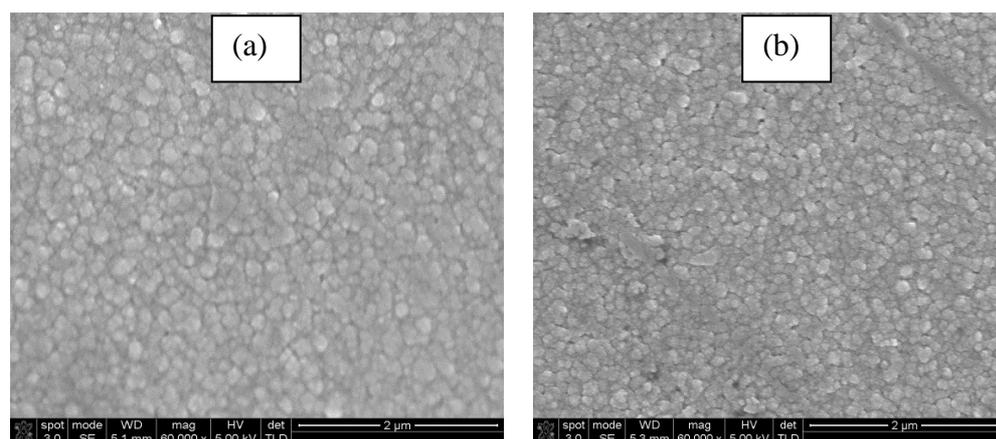


Figure 6: SEM images of ED-ZnTe grown on glass/FTO substrates for Zn²⁺ concentrations (a) 0.02M $V_g = 1513$ mV and (b) 0.15M $V_g = 1590$ mV.

CONCLUSIONS

ZnTe layers have been electrodeposited using an aqueous electrolyte and a two-electrode system. The layers obtained have excellent adhesion properties with a uniform Brick-red appearance. XRD studies show that at lower concentration a strong peak is observed at $2\theta = 24.05^\circ$ which corresponds to preferred orientation along (100) plane of hexagonal phase, but when the concentration increases the (100) planes becomes very weak. Optical absorption measurement provides minimum bandgap of the as deposited ZnTe as ~ 2.28 eV and 2.65 eV for

0.02M and 0.15M of Zn²⁺ concentrations respectively. PEC studies indicate p-type electrical conduction for electrodeposited ZnTe layers.

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