Electrodeposition and characterisation of ZnTe layers for application in CdTe based multi-layer graded bandgap solar cells

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Abstract

Zinc Telluride (ZnTe) thin films have been deposited on glass/conducting glass substrates using low-cost aqueous electrodeposition (ED) method. The structural, optical and morphological properties of the resulting films have been characterized using X-ray diffraction (XRD), spectrophotometry and Scanning Electron Microscopy (SEM). It has been confirmed by XRD technique that the deposited layers are nano- and polycrystalline mixture for as deposited layers. Photoelectrochemical (PEC) studies revealed that the layers are p-type in electrical conduction. Optical absorption measurement has been used for the bandgap determination of the deposited layers. The bandgap of the polycrystalline ZnTe layers are in the range (2.65 – 2.75) eV for the ZnSO\textsubscript{4} precursor, and (2.70 – 2.87) eV for the ZnCl\textsubscript{2} precursor instead of (2.21 – 2.26) eV reported for crystalline ZnTe. This increase may be due to the quantum effect which confirmed by the absence of strong XRD peaks from these layers and/or inclusion of ZnO in the deposited layers.

1. Introduction

The family of group II–VI semiconductors has been widely studied due to their stability of fundamental structural, electrical and optical properties for use in thin film solar cells, photodetectors and light emitting diodes (LEDs) [1-3]. Crystalline ZnTe has a direct bandgap of 2.21 to 2.26 eV at room temperature with low electron affinity of 3.53 eV [4, 5]. The development of thin film solar cells makes use of at least two kinds of semiconducting layers; a wide bandgap window material and a narrow bandgap absorber material. The two most researched absorber materials are CdTe and CuInGaSe\textsubscript{2}, and in both cases the majority of researchers use an n-CdS layer as a window material. Recent work on multi-layer graded bandgap solar cells based on AlGaAs/GaAs structures with p-type window materials has demonstrated their potential by producing high V\textsubscript{oc} (1100 - 1175 mV) and excellent FF (0.80 - 0.87) values [6, 7]. The use of p-type materials instead of n-type layers (CdS) as wide bandgap windows produce higher potential barriers for electron transport, yielding higher V\textsubscript{oc} values. The use of ZnTe as a window layer in solar cells can also reduce the toxic nature by replacing chemical bath deposited CdS layers currently used in thin film solar cells.

Various methods have been employed to deposit ZnTe thin films such as molecular beam epitaxy (MBE) [8], metal-organic chemical vapour deposition (MOCVD) [9], thermal evaporation [10], metal organic vapour phase epitaxy (MOVPE) [11], r.f and dc sputtering [12], isothermal close space sublimation (ICSS) [13], pulsed laser ablation [14], brush plating [15] and electrodeposition [5, 16-18]. This paper presents the results of attempts made to electrodeposit ZnTe layers from an aqueous solution, for use in thin film solar cells based on CdTe.

2. Experimental

2.1. Electrodeposition of ZnTe films

ZnTe thin films were cathodically electrodeposited onto glass/conducting glass substrates using two different chemical baths (i.e. using ZnSO\textsubscript{4} and ZnCl\textsubscript{2} precursors). The chemical compositions of the two baths are (0.15 M ZnSO\textsubscript{4}, 7H\textsubscript{2}O, 0.5 M Na\textsubscript{2}SO\textsubscript{4} and 3 ml TeO\textsubscript{2}) for ZnSO\textsubscript{4} and (0.15 M ZnCl\textsubscript{2} and 3 ml TeO\textsubscript{2}) for ZnCl\textsubscript{2} baths respectively. In both electrolytes the growth temperature and pH were ~78°C and 3.50 ± 0.01 respectively. Fluorine doped tin oxide (FTO) coated conducting glass...
substrates with the sheet resistance of 15 Ω/□ 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 analytical reagent grade 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.

2.2. Measurement Techniques

Cyclic voltammetry (CV) was performed using a Gill AC computeriser potentiostat (S/N 1313 ACM Instruments). With the information obtained from the voltammogram, ZnTe thin film deposition was carried out around -1600 mV for both chemical baths. After the deposition, the films were rinsed in distilled water and subsequently dried using nitrogen gas.

The samples were studied using a Cary 50 Scan UV-Visible spectrophotometer (Varian) for investigating the optical properties and for estimation of bandgap values. The bandgap energy, E_g was derived from Stern relation [4, 5, 15, 18] using:

$$\alpha = \frac{k(h\nu - E_g)^n}{h\nu}$$

(1)

where, $\nu$ is the frequency, $h$ is the Planck’s constant and $n$ takes the value of either 1 or 4. The value of $n$ is 1 and 4 for direct and indirect transitions respectively.

Photoelectrochemical (PEC) measurements using an electrolyte, 0.10 M Na₂S₂O₃, 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.

X-ray diffraction measurements (XRD) were carried out using a Philips PW 3710 X-ray diffractometre using CuKα radiation ($\lambda = 1.5418$ Å) in the range of $2\theta = (10 \rightarrow 70)\degree$ for the structural analysis of the deposited film. The X-ray generator tension and current were 40 kV and 40 mA respectively. 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.

3. Results and Discussion

3.1. Voltammogram

Typical cyclic voltammogram related to the electrodeposition of ZnTe (ED-ZnTe) thin film are shown in Figure 1 (a) and (b). These figures indicate that the formation of ZnTe compound takes place beyond 1620 mV, cathodic voltage. Two peaks were observed in the reverse direction which are attributed to the removal of Zinc and Tellurium at (-1078 & -300) mV for ZnCl₂ precursor and (-993 & -391) mV for ZnSO₄ precursor respectively. pH is among the key parameters necessary to be considered for the deposition of ZnTe layers. According to references [5, 17], at lower pH (3.50 ± 0.01), free tellurium was deposited and at comparatively higher pH (5.50 ± 0.01), the solution became cloudy due to the precipitation of TeO₂ or Cd(OH)₂. Furthermore, the influence of deposition current densities is important on the properties of deposited ZnTe thin films. It is found that [5], higher deposition current densities (>400 μAcm⁻²) led to the films with a rough surfaces, whereas films deposited at lower current densities (<100 μAcm⁻²) had a smooth surfaces.
3.2 Visual appearance

ZnTe films of about 0.4 µm thick were deposited in about 40 minutes while the solution is moderately stirred. Figure 2 (a) and (b) shows the visual appearance of ZnTe layers deposited as a function of growth voltage ($V_g$) for ZnSO$_4$ and ZnCl$_2$ baths respectively. As shown in the Figures, 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.

3.3 Thickness measurement

The thickness of ED-ZnTe layers deposited for 40 minutes shows a value of ~0.40 µm when measured using the Dektak technique. The theoretical estimate using Faraday's relation given by equation (2), gave the value ~0.35 µm.

$$T = \frac{1}{nFA} \times \frac{ItM}{\rho}$$  \hspace{1cm} (2)

where, $T$ is the thickness of the ZnTe film in cm, $I$ is the deposition current density in mAcms$^{-2}$, $t$ is the deposition time in seconds, $M$ is the molecular weight in grams, $n$ is the number of electrons transferred, $F$ is the Faraday's constant = 96485, $A$ is the area of the deposited layers in cm$^2$, and $\rho$ is the density of ZnTe in gcm$^{-3}$.

The thickness estimated using the two methods gives similar values of the same order of magnitude for the electrodeposited films.
3.4. Optical absorption

Optical absorption experiments were carried out using three different ZnTe layers grown at different cathodic voltages as shown in Figure 3 (a) and (b). The values of $E_g$ were determined by plotting the square of absorbance ($\alpha^2$) against photon energy ($h\nu$). The bandgap of crystalline ZnTe layer is $(2.21 – 2.26)$ eV [4-5], but the bandgap obtained for ED-ZnTe layers is higher than those reported values. The larger values in the range $(2.65 – 2.75)$ eV for ZnSO$_4$ precursor and $(2.70 – 2.87)$ eV for ZnCl$_2$ precursor, 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 [19, 20].

![Figure 3: Optical absorption edges for as-deposited ED-ZnTe grown at different voltages on glass/FTO substrates from (a) ZnSO$_4$ and (b) ZnCl$_2$ containing baths.](image)

3.5. Photoelectrochemical (PEC) studies

The results of PEC investigation for ED-ZnTe layers are shown in Figure 4 (a) and (b). These results indicate that all ED-ZnTe layers grown at shown voltages were p-type in electrical conduction. PEC studies provide vital information on electrical conductivity type and hence help in fabrication of electronic devices using these films. It should be noted that Na$_2$SO$_4$ has been used as a supporting electrolyte to grow ZnTe in the ZnSO$_4$ bath. The presence of sodium in the electrolyte could act as a p-type dopant in ZnTe producing p-type ZnTe layers always. Furthermore, the presence of chloride ions in the ZnCl$_2$ bath did not change the electrical conductivity type even though chlorine could act as an n-type dopant.

![Figure 4: PEC signal as a function of growth voltage for as-deposited ED-ZnTe layers for (a) ZnSO$_4$ bath and (b) ZnCl$_2$ bath.](image)
3.6. **X-ray diffraction**

XRD studies were carried out for the best samples which show uniform reddish colour and the sharpest optical absorption edge. Figure 5 shows the XRD diffractogram obtained for glass/FTO substrate and as-deposited ZnTe layers from ZnSO₄ and ZnCl₂ baths. It is observed that there are no strong XRD peaks arising from both ZnTe layers. The only sign of peaks due to ZnTe are the ones appearing at \(2\theta = 35^\circ\) and \(47^\circ\) corresponds to (102) and (200) planes of hexagonal structure respectively. This confirms the existence of nano- or poly-crystalline ZnTe materials in these layers. In addition a broad hump has developed in the region of \((15 – 30)^\circ\), indicating that there is an amorphous material present in these layers. Therefore, these as-deposited layers seems to be a mixture of amorphous (nano-) and poly-crystalline ZnTe material.

![Figure 5: X-ray diffraction patterns of glass/FTO, and as-deposited ZnTe layers from ZnSO₄ and ZnCl₂ containing baths.](image)

3.7. **Scanning Electron Microscopy (SEM) studies**

SEM studies were carried out to investigate the surface morphology and uniformity of ED-ZnTe layers. The SEM pictures of as-deposited ED-ZnTe layers are shown in Figure 6 (a) and (b) from two different baths. The appearance indicates the uniform distribution of grains size of \(~10\) nm from ZnSO₄ bath and \(~15\) nm from ZnCl₂ bath.

![Figure 6: SEM picture of as-deposited ED-ZnTe layers from (a) ZnSO₄ and (b) ZnCl₂ containing baths.](image)
4. Conclusions

This initial work demonstrates that ZnTe layers can be electrodeposited using an aqueous electrolyte and a two-electrode system. The layers obtained have excellent adhesion properties with a uniform reddish appearance. Optical absorption measurement provides bandgap of $(2.65 \pm 0.05)$ eV for ZnSO$_4$ precursor and $(2.70 \pm 0.07)$ eV for ZnCl$_2$ precursor instead of reported bandgap of $(2.21 \pm 0.06)$ eV [4, 5] for crystalline ZnTe material, indicating that the layers consist of nanoparticles introducing quantum effects which increase the bandgap. The same effect could also be introduced by inclusion of possible component ZnO, in these layers. XRD studies, further confirms the nano- and polycrystalline nature of ZnTe layers grown by this method. PEC studies indicate the p-type electrical conduction for electrodeposited ZnTe layers. The work is continuing to further develop these material layers and incorporate them in multi-layer graded bandgap solar cell devices [6, 7] based on electrodeposited CdTe materials.

Acknowledgements

Pilkington Group Limited is thanked for providing glass/FTO substrates for this work and Vinay Patel is thanked for his contribution in carrying out SEM measurements. The main author (D. G. Diso) wishes to acknowledge the financial support given by Kano University of Science & Technology, Wudil – Nigeria.

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