

The effect of CdCl₂ treatment on the structural properties and electrical conductivity types of ZnTe thin films

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Abstract:

This paper reports the successful surface treatments of p- and n-ZnTe thin film semiconducting layers prepared by electrodeposition technique. The surface treatment was carried out by using a chlorine precursor which is CdCl₂. The initial experiment carried out by applying CdCl₂ treatment to ZnTe layers of approximately 1200 nm showed that the CdCl₂ treatment did not introduce additional Cd-related phase to the ZnTe layers as revealed by the X-ray diffraction (XRD) measurements carried out on glass/FTO/p-ZnTe and glass/FTO/n-ZnTe mono-layers. The electrical conductivity type as determined from photo-electro-chemical (PEC) cell measurement also showed that after applying CdCl₂ aqueous solution for the treatment of p- and n-ZnTe layers grown on conducting glass substrates, the type remains unchanged.

Keywords: p-ZnTe, n-ZnTe, mono-layers, CdCl₂ surface treatment, structural, electrical

1. INTRODUCTION

ZnTe is a II-VI binary compound semiconductor with an optimum bandgap of 2.26 eV at room temperature [1]. The energy bandgap corresponds to a wavelength of approximately 549 nm which lies in the green portion of the electromagnetic (EM) spectra. This makes ZnTe a suitable candidate in the fabrication of green light emitting diodes (LEDs) [2]. For over a long period of time, intrinsic ZnTe layers have been generally accepted to be p-type only in electrical conduction [3] but recent researches have demonstrated the possibility of the ZnTe semiconductors to possess n-type electrical conduction without the introduction of extrinsic dopants [4]. Various researches have been conducted on the usage of ZnTe as a p-type window layer to other binary and ternary compound semiconductors [5,6]. However, not much work has been done on its suitability as an absorber material especially to CdS [7]. This is because its wide bandgap nature enables it to be more useful as window layers rather than as absorber layers [8]. However, the energy bandgap of ZnTe layers can be engineered to make it suitable as an absorber layer. The electroplating technique used in this work is one of the available techniques which allow the bandgap of a semiconductor material to be easily tuned. The bandgap tuning can be achieved by controlling parameters such as the time of growth, the pH of the electrolyte [9],

temperature of the electrolytic bath, stirring rate, concentration of salts used in the electrolytes and growth voltage. The successful tuning of energy bandgap of ZnTe layers have been explained in one of our previous communications [10].

Due to the successful tuning of ZnTe energy bandgaps from the bulk energy value of ~2.26 eV to lower energy bandgaps, it is therefore possible to use the lower energy bandgap ZnTe thin film as a hetero-partner to other higher energy bandgap semiconductor materials. As reported by Olusola *et al.* [10], lower energy bandgap p-type ZnTe layers were used as hetero-partner to higher energy bandgap n-type CdS layers. As a result of the tunability of ZnTe bandgap, it is therefore possible for ZnTe when grown in the p-region to be an absorber layer to n-type CdS window material to form a p-n junction solar cell. Schottky barrier solar cells can likewise be fabricated if n-ZnTe is used as hetero-partner to n-CdS thin films. Due to the likeliness of ZnTe (either p- or n-type) to function as an absorber layer to n-CdS, it is therefore essential just like in CdTe to study the effect of surface treatment using chemicals containing Cl [11,12] on the structural and electrical properties of glass/FTO/p-ZnTe and glass/FTO/n-ZnTe before applying the chemical treatments in the n-CdS/p-ZnTe hetero-structure. For this reason, ZnTe layer of ~1200 nm was electroplated and used in this experiment. In this paper, XRD and PEC cell measurement techniques were used to examine what happens to the structural and electrical properties of ZnTe thin films when the top

surface of the layer is treated with chemicals containing Cl before annealing in air.

2. EXPERIMENTAL DETAILS

The ZnTe layers (both p- and n-type) were electroplated on conducting substrates made from fluorine-doped tin oxide (FTO) at different cathodic growth voltages. The preparation of the ZnTe electrolyte was carried out by adding 0.045 M ZnSO₄.7H₂O and 10 ml of dissolved TeO₂ in 800 ml of de-ionised water. Cathodic potentials of 1600 mV and 1650 mV were used in growing the p-ZnTe and n-ZnTe thin films respectively.

The p- and n-type ZnTe layers described in this work were explored under three conditions namely: as-deposited (AD), heat-treated (HT) and cadmium chloride (CC) treated ZnTe layers. The AD-ZnTe layers are the thin films grown without any surface heat treatment. The HT-ZnTe layers are the layers annealed at a temperature of 400°C for 10 minutes in air without the application of chemicals to the surface prior annealing. The CC-ZnTe layers are the ZnTe layers annealed at a temperature of 400°C for 10 minutes in air with the application of chemicals (CdCl₂ aqueous solution) to the surface prior annealing.

The structural and electrical conductivity type of the electroplated ZnTe thin films reported in this work were studied using X-ray diffraction (XRD) and photo-electro-chemical (PEC) cell measurements technique respectively. The XRD spectra were acquired using Philips PW3710 X'pert diffractometer that has Cu-K_α monochromator with wavelength of 0.154 nm. The XRD measurement was taken within the range of 2θ = (20–70)°. The experimental set-up used for the PEC cell measurements have been described in [13]. A detailed material characterisation of ZnTe thin films can be found in our recent publication [14].

3. RESULTS AND DISCUSSIONS

3.1. Effect of CdCl₂ surface treatment on the structural properties of p- and n-type ZnTe mono-layers

The first set of Cl treatments used for the ZnTe absorber layers was done using ZnCl₂ aqueous solution. Unfortunately, this treatment did not work out well because of the in-ability of the ZnCl₂ solution on the ZnTe surface to dry up with time; instead of the ZnCl₂ solution on the surface of the ZnTe layer to dry up, it was producing more of oily substance on the surface of the ZnTe thin films. The cause of this reaction is however not known as at the time

this research was carried out. For this reason, the experiment was discontinued and another Cl source which is CdCl₂ was made use of. The application of CdCl₂ treatment on top of the ZnTe absorber layers proved successful as the solution dried up quickly without forming oily substance on top of the material. Also, the ZnTe absorber layer survived heat-treatment after annealing with CdCl₂ treatment in air.

Figure 1 shows the XRD spectra of as-deposited (AD), heat-treated (HT) and cadmium chloride (CC) treated p-type ZnTe layers. The heat-treatment was carried out at 400°C for 10 minutes in air. The result shows that the preferred orientation occurs along the (100) plane for the p-ZnTe layers; other ZnTe peaks observed are summarised in Table 1. The XRD spectra shows that by applying CdCl₂ treatment to the ZnTe layers, no additional phase was introduced into the ZnTe thin films as a result of this treatment. All the peaks observed in the AD-ZnTe layers were equally observed in the HT- and CC-treated layers. This shows the possibility of applying the usual CdCl₂ treatment to ZnTe layers without changing the material structure or introducing additional/unwanted/detrimental phase to the semiconductor material.

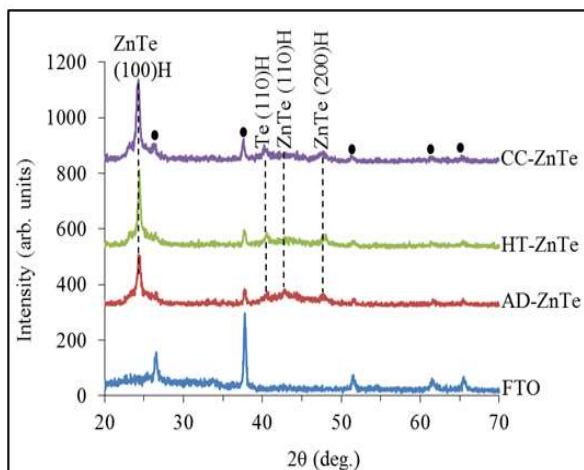


Figure 1. XRD spectra of as-deposited p-ZnTe layers, heat-treated and CdCl₂ treated p-ZnTe layers at 400°C, 10 minutes in air (Note: The black dots in the figure represent the FTO peaks)

Table 1. Summary of XRD data for as-deposited, heat-treated and CdCl₂ heat-treated p-ZnTe layers at 400°C, 10 minutes in air

Sample ID	Angle (2θ) ^o	d-Spacing (Å)	Crystal Structure	Chemical Formula	Plane of orientation (h k l)	Reference Code Matching
JZ 88A (AD-ZnTe)	24.45	3.64	Hexagonal	ZnTe	(100)	01-080-0009
	40.35	2.24	Hexagonal	Te	(110)	00-001-0727
	42.83	2.11	Hexagonal	ZnTe	(110)	01-080-0009
	47.78	1.90	Hexagonal	ZnTe	(200)	01-080-0009
JZ 88B (HT-ZnTe)	24.39	3.65	Hexagonal	ZnTe	(100)	01-080-0009
	40.53	2.22	Hexagonal	Te	(110)	00-001-0727
	47.98	1.89	Hexagonal	ZnTe	(200)	01-080-0009
JZ 88C (CC-ZnTe)	24.14	3.69	Hexagonal	ZnTe	(100)	01-080-0009
	40.32	2.23	Hexagonal	Te	(110)	00-001-0727
	47.57	1.91	Hexagonal	ZnTe	(200)	01-080-0009

The XRD results illustrated in Figure 1 contradict the reports given by Mohanty *et al.* [15] that ZnTe converts to CdTe and ZnO after treating the top surface of ZnTe thin film of ~140 nm with CdCl₂ treatment. The results and explanations given by Mohanty *et al.* cannot therefore be generalised. The reason for ZnTe reducing to CdTe and ZnO after CdCl₂ treatment may be due to several factors such as concentration of CdCl₂ solution used for surface treatment, growth conditions, heat-treatment temperature with duration and thickness of the ZnTe layers being used for their experimental investigations [15].

Figure 1 also shows a further improvement in the crystallinity of CC-ZnTe layers after annealing as a result of increase in the peak intensity. For the p-type ZnTe layers of ~1.2 μm, a peak was also observed whose d-spacing value matches that of elemental Te. These peaks occurred at 40.35°, 40.53° and 40.32° for AD-, HT-, and CC-ZnTe layers respectively. As shown in Table 1, these peaks have hexagonal crystal structure and occurred along (110) plane. The observed d-spacing values for the elemental Te seen in AD-, HT-, and CC-treated p-ZnTe layers are 2.24, 2.22 and 2.23 respectively; these values closely correspond to the reported d-spacing value of elemental Te with reference code 00-001-0727. The XRD results reveal the possibility of having p-ZnTe thin films due to the presence of elemental Te. It is worthwhile to know that the inclusion of extra 0.030 M to the initial 0.015 M concentration of Zn precursor used by Olusola *et al.* [10] did not eliminate the

presence of elemental Te peak when the ZnTe layer is grown in the p-region.

Figure 2 shows the XRD spectra of AD, HT and CC treated n-type ZnTe layers. The n-ZnTe layers were subjected to the same heat-treatment conditions like p-ZnTe layers. The XRD results showed that the highest peak of the n-ZnTe mono-layers occurred along the (100) plane just like the p-ZnTe layers; other ZnTe peaks observed are summarised in Table 2. As revealed from the XRD spectra, Cd-related peaks were not introduced into the material after annealing the n-ZnTe layers treated with CdCl₂. As shown in Figure 2, the peak with the highest intensity was observed along the same (100) plane for AD-, HT- and CC-treated n-ZnTe layers

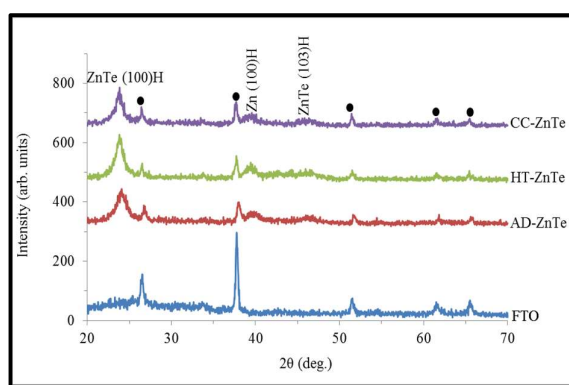


Figure 2. XRD spectra of as-deposited n-ZnTe layers, heat-treated and CdCl₂ treated n-ZnTe layers at 400°C, 10 minutes in air (Note: The black dots in the figure represent the FTO peaks)

Table 2. Summary of XRD data for as-deposited, heat-treated and CdCl₂ heat-treated n-ZnTe layers at 400°C, 10 minutes in air

Sample ID	Angle (2θ) ^o	d-Spacing (Å)	Crystal Structure	Chemical Formula	Plane of orientation (h k l)	Reference Code Matching
JZ 78A	24.04	3.70	Hexagonal	ZnTe	(100)	01-080-0009
(AD-ZnTe)	39.77	2.27	Hexagonal	Zn	(100)	00-001-1244
	45.98	1.97	Hexagonal	ZnTe	(103)	01-080-0009
JZ 78B	23.95	3.72	Hexagonal	ZnTe	(100)	01-080-0009
(HT-ZnTe)	39.47	2.28	Hexagonal	Zn	(100)	00-001-1244
	46.53	1.95	Hexagonal	ZnTe	(103)	01-080-0009
JZ 78C	23.75	3.75	Hexagonal	ZnTe	(100)	00-019-1482
(CC-ZnTe)	39.31	2.29	Hexagonal	Zn	(100)	00-001-1244
	46.72	1.94	Hexagonal	ZnTe	(103)	01-080-0009

A peak was observed in n-type ZnTe layers of approximately 1.2 μm whose d-spacing matches that of elemental Zn. The peak was found to be of hexagonal crystal structure along (100) plane. For this peak not to be confused with that of elemental Te, the reference codes for both elemental Zn and Te were compared side by side with the results observed from the XRD measurement analysis and the results are illustrated in Tables 3 and 4. As shown in Table 3, the observed peak positions and d-spacing values for elemental Zn observed in AD-, HT-, and CC-treated n-ZnTe layers match closely with the reference peak positions and d-spacing values of elemental Zn respectively. The observed d-spacing values range from 2.27-2.29 for the three semiconductor materials under present investigation. This therefore clearly shows that the presence of peak with the d-spacing values ranging from 2.27-2.29 corresponds to that of elemental Zn. This again confirms the possibility of having n-ZnTe due to the presence of elemental Zn leading to Zn-richness.

As seen in Table 4, the d-spacing values for elemental Te observed in AD-, HT-, and CC-treated p-ZnTe layers correspond closely with the reported d-spacing values of elemental Te with reference code 00-001-0727. This again shows the tendency of having p-ZnTe due to the presence of elemental Te thus leading to Te-richness.

Table 3. Comparison of the reference codes of elemental Zn and Te with the data obtained from XRD measurements for n-type ZnTe thin film semiconductors

XRD Parameters	Elemental Zn	Elemental Te	Elemental Te	AD-ZnTe (JZ 78A)	HT-ZnTe (JZ 78B)	CC-ZnTe (JZ 78C)
	Reference	Reference	Reference	Observed	Observed	Observed
2θ (deg.)	39.31	38.44	40.61	39.77	39.47	39.31
D (Å)	2.29	2.34	2.22	2.27	2.28	2.29
hkl	100	102	110	100	100	100
code matching	00-001-1244	00-001-0727	00-001-0727	00-001-1244	00-001-1244	00-001-1244
Crystal Structure	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal

Table 4. Comparison of the reference codes of elemental Zn and Te with the data obtained from XRD measurements for p-type ZnTe thin film semiconductors

XRD Parameters	Elemental Zn	Elemental Te	Elemental Te	AD-ZnTe (JZ 88A)	HT-ZnTe (JZ 88B)	CC-ZnTe (JZ 88C)
	Reference	Reference	Reference	Observed	Observed	Observed
2θ (deg.)	39.31	38.44	40.61	40.35	40.53	40.32
D (Å)	2.29	2.34	2.22	2.24	2.22	2.23
hkl	100	102	110	110	110	110
code matching	00-001-1244	00-001-0727	00-001-0727	00-001-0727	00-001-0727	00-001-0727
Crystal Structure	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal

3.2 Effect of CdCl₂ treatment on the electrical conductivity type of ZnTe mono-layers

PEC cell measurements were equally done for both p-type and n-type ZnTe layers of ~1200 nm. The result shows that for p-type material; after CdCl₂ treatment, the material remains p-type and for n-type material, the material remains n-type after CdCl₂ treatment. As illustrated in Figure 3, an increase was observed in the PEC signals of the as-deposited p-ZnTe semiconductor materials after heating in air without and with CdCl₂ treatment. In the n-region, the magnitude of the PEC signals tends towards p-type material after heating ordinarily in air and with CdCl₂ treatment. This very phenomenon was also observed in n-CdTe after annealing the CdTe without and with CdCl₂ treatment [16,17]. This experimental result shows that there is no type conversion after treating both materials with CdCl₂; hence the material tends to be more stable even after CdCl₂ treatment.

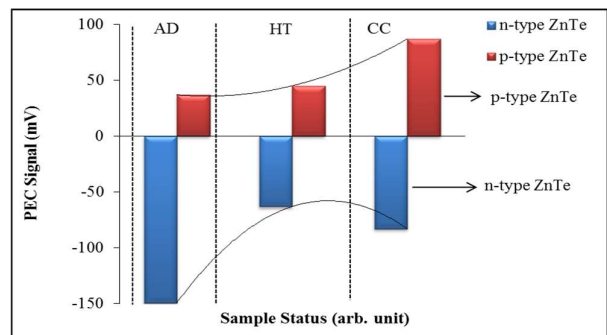


Figure 3. Effect of CdCl₂ treatment on the electrical conductivity type of p-, and n-ZnTe mono-layers.

Conclusion

The material characterisation results presented in this paper revealed that heat-treated and chemically treated ZnTe layers possess better material quality than as-deposited ZnTe layers. As seen from the XRD results, both p- and n-type ZnTe layers have hexagonal crystal structures with a common preferred orientation along (100) plane. Likewise, the inclusion of CdCl₂ for surface treatment did not introduce Cd-related phase into the p- and n-type ZnTe structures. From the electrical conductivity type measurements, no type conversion took place after treating both p- and n- ZnTe semiconductor materials with CdCl₂ thus revealing the stability of the semiconductor material after CdCl₂ treatment. Research work is on-going to use the chemically treated p-ZnTe layers as hetero-partner to n-CdS window layers so as to fabricate photo-voltaic cells with the device structure glass/FTO/n-CdS/p-ZnTe/Au.

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