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Structural and electrical properties of brush plated ZnTe films

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Abstract

Zinc telluride thin films were deposited by the brush plating technique at a potential of -0.90 V (SCE) on conducting glass and titanium substrates at different temperatures in the range 30–90 °C. The films were polycrystalline in nature with peaks corresponding to the cubic phase. Direct band gap of 2.30 eV was observed. XPS studiers indicated the formation of ZnTe. Depth profiling studies indicated a uniform distribution of Zn and Te throughout the entire thickness. EDAX measurements were made on the films and it was found that there was a slight excess of Te. The carrier concentration was found to vary from 10^{14} – 10^{15} cm⁻³ with increase of substrate temperature. The mobility was found to vary from 5 to 60 cm² V⁻¹ s⁻¹.

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1. Introduction

Recently, there has been a growing interest in the II–VI family of semiconductors because of their potential use in a variety of solid-state devices such as solar cells, photodetectors, and light emitting diodes [1,2]. Particularly, ZnTe is of considerable interest in combination with other II–VI compounds in short wavelength, light-emitting diodes. In addition, p-type ZnTe has been used in high efficiency CdS/CdTe/ZnTe cells [1].

ZnTe thin films have been prepared by several techniques including molecular beam epitaxy (MBE) [3,4], electrodeposition [5], hotwall evaporation [6] and conventional vacuum evaporation [7]. To our knowledge there have been no reports on ZnTe films grown by brush plating technique. In this paper, structural, electrical and optical properties of brush plated ZnTe films are presented.

2. Experimental methods

ZnTe films were deposited on conducting glass and titanium substrates using an aqueous solution of 0.5 M ZnSO₄ and 50 mM TeO₂. The pH of the bath was adjusted to 2 by adding sulphuric acid. 10 ml of the precursor solution mixture was taken. Brush plating is one of the electrochemical methods of synthesizing thin films. This technique has been adopted for the first time to coat ZnTe film on conducting tin oxide and titanium substrates. It is a simple, convenient and low-cost method for obtaining large-area films. Details regarding equipments and solutions engaged in the deposition of metals and alloys are given by Norris [8,9]. Brush plating equipment includes power packs, solutions, plating tools, anode covers and auxiliary equipments. A schematic of brush plating system is given in Fig. 1. The stylus, consisting of a carbon rod wrapped in cotton wool served, as the anode. The cotton wool was held in position by a porous sleeve. The electrolyte bath contained 0.5 M ZnSO₄ and 50 mM TeO₂. The pH and temperature was maintained at 2.0 and 28 °C (room temperature) respectively

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Fig. 1. Schematic of the brush plating system.

throughout the experiment. Prior to plating, the stylus was wired to the power supply and the cotton wool was soaked in the electrolyte. The stylus was then brought into contact with the substrate and moved at uniform speed. An electrical current was found passing whenever the stylus was in contact with the substrate. This is associated with the acceleration of ions in the electrolyte trapped within the cotton wool which was subsequently reduced at the substrate to form ZnTe layer.

The brush anode viz., graphite electrode wound with cotton, was dipped in the solution and brushed over the cathode applying a potential of -0.90 V (saturated calomel electrode). The deposition potential was fixed on the basis of a previous report [10]. The deposition time was maintained as 15 min. The films were characterized by X-ray diffraction technique using a Phillips X-ray diffractometer and CuKa radiation, optical absorption studies were made using U 3400 Hitachi UV-vis-NIR spectrophotometer, X-ray photoelectron spectrocopy studies were made using a VG ESCALAB MKII spectrometer with MgKa radiation, energy dispersive analysis of X-ray (EDAX) measurements were recorded with the help of scanning electron microscope attached with an EDAX microanalysis unit and Atomic force microscopic studies were made using Molecular Imaging system. The thickness of the films was in the range of 1.5-2.5 µm with increase of substrate temperature. In the present study, to determine the electrical properties, including conduction type, of as-deposited ZnTe layers from an acidic electrolyte, resistivity and Hall effect measurements were carried out. The Hall effect measurement is a standard, reliable, and more direct method for obtaining the fundamental electrical properties of semiconductors. Nevertheless, limited numbers of Hall effect measurements on electrodeposited materials have so far been carried out. A possible reason for there being few reports is that the sample preparation for Hall effect measurements is difficult because the conducting substrate must be removed from the electrodeposited layer, while the layer is maintained intact. In the present work, we employed a method in which the ZnTe layer was transferred mechanically from the conducting substrate onto a non-conductive epoxy resin without the formation of cracks [11,12]. For Hall effect measurements, the ZnTe layers were transferred from the Ti substrate onto non-conductive epoxy resin by the following method. A sliced vinyl chloride pipe (thickness 3 mm, inner diameter 13 mm, outer diameter 18 mm) was placed on the ZnTe deposit so that the pipe, or ring, encircled the ZnTe-deposited area. Epoxy resin (torr seal; varian associates) was then poured inside the ring. After the epoxy had coagulated, the back of the substrate was fixed on a tight block with a quick-drying glue and the substrate was held vertically. Then, the epoxy with the ZnTe layer was removed from the substrate by tapping downward on the side of the ring with a mallet, in other words, by applying a shearing force between the ZnTe layer and the substrate. In this way, crack-free ZnTe layers on the non-conductive substrates could be obtained with high reproducibility. The transferred ZnTe layer was cut to a 6 mm square and four gold electrodes with a diameter of 1.5 mm were deposited on each corner by vacuum evaporation through an aluminum foil mask. Gold lead wires were attached to the gold electrodes with silver paste. This is similar to the process used for measuring the electrical properties of electrodeposited CdTe films[13]. The electrical properties of the ZnTe layers were examined at room temperature by resistivity and Hall effect measurements using the van der Pauw method. A magnetic field of 3.0 T was applied.

3. Results and discussion

Structural studies were made using X-ray diffraction studies. Fig. 2 shows the XRD patterns of the films deposited at different substrate temperatures. Peaks corresponding to (111), (220) and (311) orientations of the cubic phase are observed. As the substrate temperature increases, the (111) orientation peak increases in intensity and the width of the peaks decreases as the temperature of the substrate temperature increases. The crystallite size was



Fig. 2. X-ray diffractogram of ZnTe films deposited at different temperatures (a) 30 $^{\circ}$ C, (b) 50 $^{\circ}$ C, (c) 90 $^{\circ}$ C.

calculated using Scherer's equation [14]. The crystallite size was found to increase from 40 nm to 100 nm as the sub-

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8

6

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Fig. 3. $(\alpha hv)^2$ vs. hv plot of ZnTe film deposited at a substrate temperature of 90 °C.

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6

8

2



Fig. 4. XPS spectrum of ZnTe films deposited at a substrate temperature of 90 $^{\circ}\mathrm{C}.$



Fig. 5. Depth profile of ZnTe film deposited at a substrate temperature of 90 $^{\circ}\text{C}.$



Fig. 6. EDAX spectrum of ZnTe films deposited at different substrate temperatures (a) 30 °C, (b) 50 °C, (c) 90 °C.



Fig. 7. Variation of carrier density and mobility with substrate temperature.

strate temperature increases from 30-90 °C. The lattice constant was estimated to be 0.610 nm for the films deposited at a substrate temperature of 90 °C. It is observed that the lattice constant is close to the value reported in the ASTM data [15].

Optical absorption spectrum of the films deposited on conducting glass substrates were recorded in the wavelength ranges 400–800 nm. Fig. 3 shows the $(\alpha hv)^2$ vs. hv plot for the films deposited at a substrate temperature of 90 °C. The plot is linear indicating the direct band nature of the films. Extrapolation of the linear region to the energy axis indicated a band gap of 2.30 eV. This value is similar to the value obtained on single crystals [16].

X-ray photoelectron spectroscopy indicated the formation of ZnTe. Fig. 4 shows the XPS spectrum of ZnTe films deposited at 90 °C. XPS studies indicated the Zn 3p and Te 3d peaks, which are in close agreement with the reported values for Zn and Te in ZnTe. Depth profiling was carried out at a sputter rate of 10 nm/min, this indicates a uniform distribution of Zn and Te throughout the thickness (Fig. 5). EDAX measurements yielded a composition of 49.5% Zn and 51.5% Te (Fig. 6). The value of the resistivity determined from the Van der Pauw method varied from $10^3-10^4 \Omega$ cm, similar to earlier report [17].

Hall measurements indicated the films to be p-type. Fig. 7 indicates the variation of mobility and carrier concentration with substrate temperature. The carrier concentration is found to vary from 10^{14} to 10^{15} cm⁻³ with increase of substrate temperature. The mobility is found to vary from 5 to 60 cm² V⁻¹ s⁻¹. The values of carrier concentration are lower than the earlier report on vacuum evaporated ZnTe films [17].

4. Conclusion

The results of this investigation indicate that films suitable for photoelectrochemical and photovoltaic devices can be deposited within a short period with small quantities of the precursors. Films with resistivities of the order of $10^4 \Omega$, carrier densities of $10^{14} \Omega$ cm and mobilities in the range 5–60 cm² V⁻¹ s⁻¹ can easily be obtained using the simple brush plating technique.

References

- [1] De Merchant J, Cocievera M. J. Electrochem. Soc. 1996;143:4054.
- [2] Ota T, Takahashi K. Solid State Electron 1973;16:1089.
- [3] Bicknell-Tassius RN, Kuhn TA, Ossau W. Appl Surf Sci 1989;36:95.
 [4] Gunshor RL, Koladziejski LA, Otsuka N, Datta S. Surf Sci 1986;174:522.
- [5] Arico AS, Silvestro D, Antonucci PL, Giordano N, Antonucci V. Adv Perform Mater 1997;4:115.
- [6] Link P, Schmidt T, Bauer S, Wagner HP, Leiderer H, Gebhardt W. J Appl Phys 1992;72:3730.
- [7] Pal U, Saha S, Chaudhuri AK, Rao VV, Banerjee HD. J Phys D: Appl Phys 1989;22:965.
- [8] Norris JC. Brush plating-Part I. Metal Finishing 1988;867:45.
- [9] Norris JC. Brush plating-Part II. Metal Finishing 1988;868:45.
- [10] Spallart Michael Neumann, Konigstein C. Thin solid films 1995; 265:33.
- [11] Von Windheim JA, Wynands H, Cocivera M. J Electrochem Soc 1991;138:3435.
- [12] Miyake M, Murase K, Hirato T, Awakura Y. J Electrochem Soc 2003;150:C413.
- [13] Miyake M, Murase K, Hirato T, Awakura Y. J Electroanal Chem 2004;562:247.
- [14] Guiner A. Theorie et Technique de la Radiocristallographie. Paris: Editions Dunod; 1969.
- [15] ASTM X-ray powder data 15-746, 19-1482, 4-554.
- [16] Sato K, Adachi S. J Appl Phys 1993;73:926.
- [17] Ibrahim AA, El-Sayed NZ, Kaid MA, Ashour A. Vacuum 2004; 75:189.