



Effect of Temperature on Cu-doped p-ZnTe Thin-Films

G. Lastra ^{1*}, A. Olivas ^{2,3}, J.I. Mejía ³, M.A. Quevedo-López ³

¹PCeIM, Centro de Nanociencias y Nanotecnología-UNAM, CP. 22860, Ensenada, B.C. México.

²Centro de Nanociencias y Nanotecnología-UNAM, CP. 22860, Ensenada, B.C. México.

³Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas, 75080.

ABSTRACT

In this paper we study the effect of temperature in 150 (± 5) and 80 (± 5) nm p-ZnTe thin- films immersed in 60 mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}/150$ ml (H_2O) for 1 minute, and heated at 200 and 300 °C for 30 minutes. Active layers were deposited by pulsed-laser deposition (PLD) at room temperature. Electrical parameters in un-doped films were around 10^8 – 10^9 Ω and these values decreased to $\sim 10^3$ Ω when the films were immersed in a Cu solution. The Cu-doped samples heated at 300 °C showed a completely homogeneous doping. X-ray diffraction (XRD) patterns showed the orthorhombic structure at 200 and 300 °C.

Keywords

ZnTe; thin films; pulsed-laser deposition; Cu doping.

Academic Discipline And Sub-Disciplines

Science (Material Science)

SUBJECT CLASSIFICATION

Material Science (Semiconductor)

TYPE (METHOD/APPROACH)

Experimental

Council for Innovative Research

Peer Review Research Publishing System

Journal: JOURNAL OF ADVANCES IN PHYSICS

Vol. 10, No. 1

www.cirjap.com, japeditor@gmail.com

1. INTRODUCTION

Zinc telluride is a wide-bandgap II-VI compound semiconductor (2.26 eV) at room temperature. ZnTe is a promising material among II-VI group because it can be highly doped with p-type impurities ($> 10^{19} \text{ cm}^{-3}$) [1]. It is also the only p-type material from this group, due to zinc vacancy and acceptor impurities in the crystal. The application of *p*-ZnTe is solely to unipolar *p*-type devices. This compound has an electronic affinity of 3.53 eV and a work function of 5.75 eV [2,3]. Today, the most important application of this semiconductor is for optoelectronic devices such as green light emission diodes (LEDs) [4], heterojunction devices [5] and high-efficiency multi-junction solar cells [6]. Nowadays there is an effort in thin-film transistors (TFT) applications [7-9]. This last device is important to build complementary devices (CMOS) and flexible panels [7]. Also, ZnTe shows the zinc blende cubic phase, with main peaks (111), (220) y (311) [10, 11]. There exist many methods to deposit ZnTe, such as electrochemical deposition [12, 13], metalorganic vapor phase epitaxy (MOVPE) [14, 15], molecular beam epitaxy (MBE) [16] and pulsed-laser deposition (PLD) [17-20]. Here, we deposited *p*-ZnTe thin-films by PLD at room temperature and they were doped in Cu solution. This doping method is used due to its simplicity [21, 22].

2. EXPERIMENTAL

Electrical properties in 150 (± 5) and 80 (± 5) nm *p*-ZnTe thin-films were measured by circular transmission line method (CTLM). Active layers of *p*-ZnTe were deposited on HfO_2 substrate by PLD at room temperature, using an excimer laser (KrF, $\lambda = 248 \text{ nm}$) at energy density ($E_d = 0.78 \text{ J/cm}^2$) with an argon partial pressure of 20 mTorr and 10 Hz of laser frequency. After deposition the samples were immersed in 60 mg $(\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O})/150 \text{ ml}$ (deionized H_2O) for 1 minute. The solutions were kept at a temperature of 60 °C. Then, the films were cleaned in deionized water and dried by nitrogen. After drying, the samples were annealed at 200 and 300 °C for 30 minutes in a N_2 atmosphere (Thermco MiniBrute), Figure 1. After the heat treatment was completed, Au/Ni = (100/10 nm) were deposited on *p*-ZnTe films by e-beam evaporator (Temescal 1800). Sheet resistance, R_{SH} (Ω/\square); resistivity, ρ ($\Omega\text{-cm}$); contact resistance, R_c (Ω); specific contact resistance, ρ_c ($\Omega\text{-cm}^2$) and resistance, R (Ω) were measured by CTLM, where circles were developed by Lift-Off process, as shown in Figure 2. Previously to the formation of the CTLM pattern, samples were cleaned with acetone, isopropanol (IPA) and deionized water in ultrasonic bath for 3 minutes, then dried by nitrogen. The effects of temperature on *p*-ZnTe:Cu thin-films were displayed by plotting resistance vs distance. We measured circles from the CTLM pattern with inner circle radius (100, 150, 200, 250 and 300 μm) and distance “gap” (5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 μm). These measures were obtained by probe station, CASCADE microtech, and calculated by OriginPro 8.5 software. The effect of Cu doping on the structure of the films were studied by X-ray diffraction (XRD) using $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$), operated at 40 kV and 44 mA.

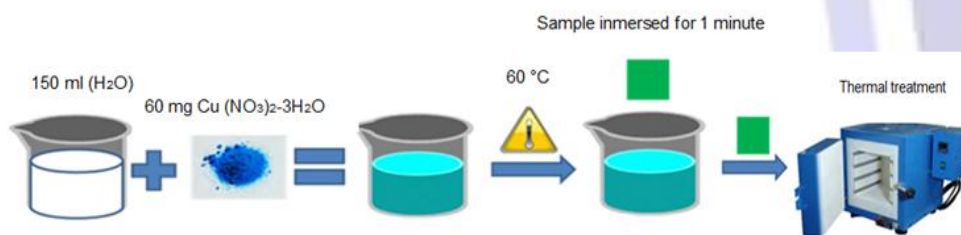


Fig 1. Copper-doped process of *p*-ZnTe thin-films.

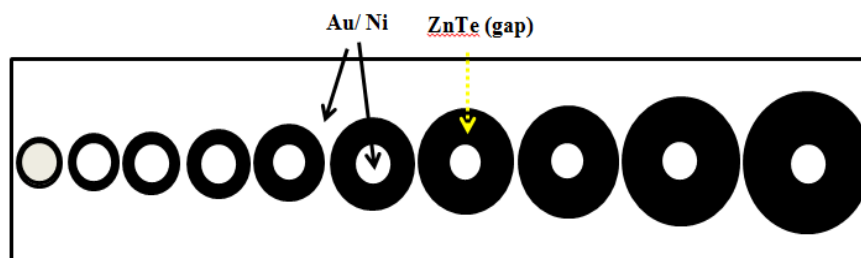


Fig 2. Circular Transmission Line Method by Lift-off process.

3. RESULTS AND DISCUSSION

3. Results and discussion

3.1. Electrical analysis

We measured 10 circles using two contacts on the probe station. We applied a range voltage from -0.5 to 0.5 V with an increase of 0.1 V, Figure 3. In this figure we can observe that there exists good ohmic contact between the Au/Ni and the semiconductor layers. Table 1 shows the electrical parameters for 150 (± 5) and 80 (± 5) nm *p*-ZnTe thin-films doped with

Cu measured by CTLM. Un-doped 150 (± 5 nm) active layers showed $R_{SH} = 1.77 \times 10^{10} \Omega/\square$, $\rho = 2.66 \times 10^5 \Omega\text{-cm}$, $R_C = 3.70 \times 10^6 \Omega$ and $\rho_c = 7 \Omega\text{-cm}^2$. Electrical values are higher in un-doped 80 (± 5 nm) samples in accordance with $R_{SH} = (\rho / t)$, where t is the thickness of semiconductor. However, these electrical parameters drastically decreased when they were immersed in 60 mg $(\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O})/150$ ml (H_2O) . These measures are similar for both thicknesses. Low specific contact resistance ($\sim 10^{-4} \Omega\text{-cm}^2$) means that there exists ohmic contact in the metal/semiconductor interface and this value is desirable for practical devices. This decrease in the resistance is probably due to the fact that ionized native Cu atoms occupy the Zn sites of ZnTe structure, which results in the increase of average carrier concentration (p type) and the increase of conductivity.

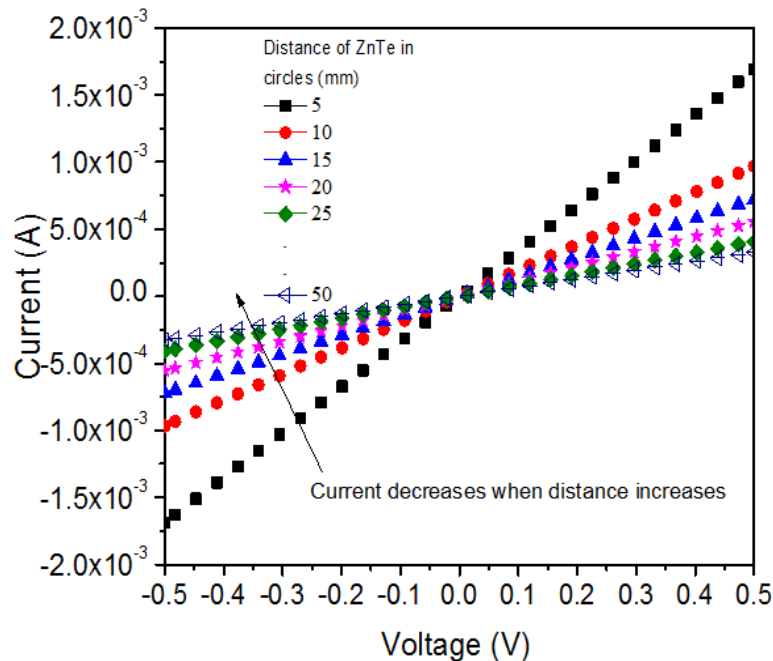


Fig 3. Current-voltage (I-V) curves measured by CTLM .

Table 1. Electrical parameters for p-ZnTe:Cu thin films heated at 200 and 300 °C for 30 minutes.

Thickness (nm)	Thermal treatment (°C)	Time of thermal treatment (min)	Sheet resistance (Ω/\square)	Resistivity ($\Omega\text{-cm}$)	Contact resistance (Ω)	Specific contact resistance ($\Omega\text{-cm}^2$)
150*	-	-	1.77×10^{10}	2.66×10^5	3.70×10^6	8
150	200	30	3.84×10^4	0.50	31	1.00×10^{-4}
150	300	30	4.83×10^4	0.72	20	2.00×10^{-4}
80*	-	-	3.55×10^{10}	2.66×10^5	6.75×10^6	10
80	200	30	6.54×10^4	0.59	19	6.30×10^{-4}
80	300	30	4.34×10^4	0.39	21	1.20×10^{-4}

*Undoped p-ZnTe thin films

An important goal of Cu doping is having a homogeneous ZnTe:Cu surface (i.e. A doping Cu homogeneous p -channel ZnTe thin film transistor (TFT) is necessary). Figure 4 depicts how the resistance of the films decreased when they were doped with copper. Also, this graph provides information about homogeneity of the doping. If a linear increase in resistance is shown, it means that resistance of the ZnTe is homogeneous over the entire surface. High values of resistance around 10^9 – $10^9 \Omega$ were demonstrated in un-doped layers, Figure 4 (a). However, resistance of the samples decreased to $10^3 \Omega$ when they were doped in Cu solution, and then annealed at 200 and 300 °C for 30 minutes, as shown in Figure 4 (b) and (c), respectively. Resistances of 5×10^2 to $3.5 \times 10^3 \Omega$ are extracted by measuring the inner circle radius and distance of gap, Figure 4 (b). Also, we can see that the Cu doping is not homogeneous over the film at 200 °C. However, we have a completely homogeneous Cu doping surface at 300 °C like un-doped ZnTe.

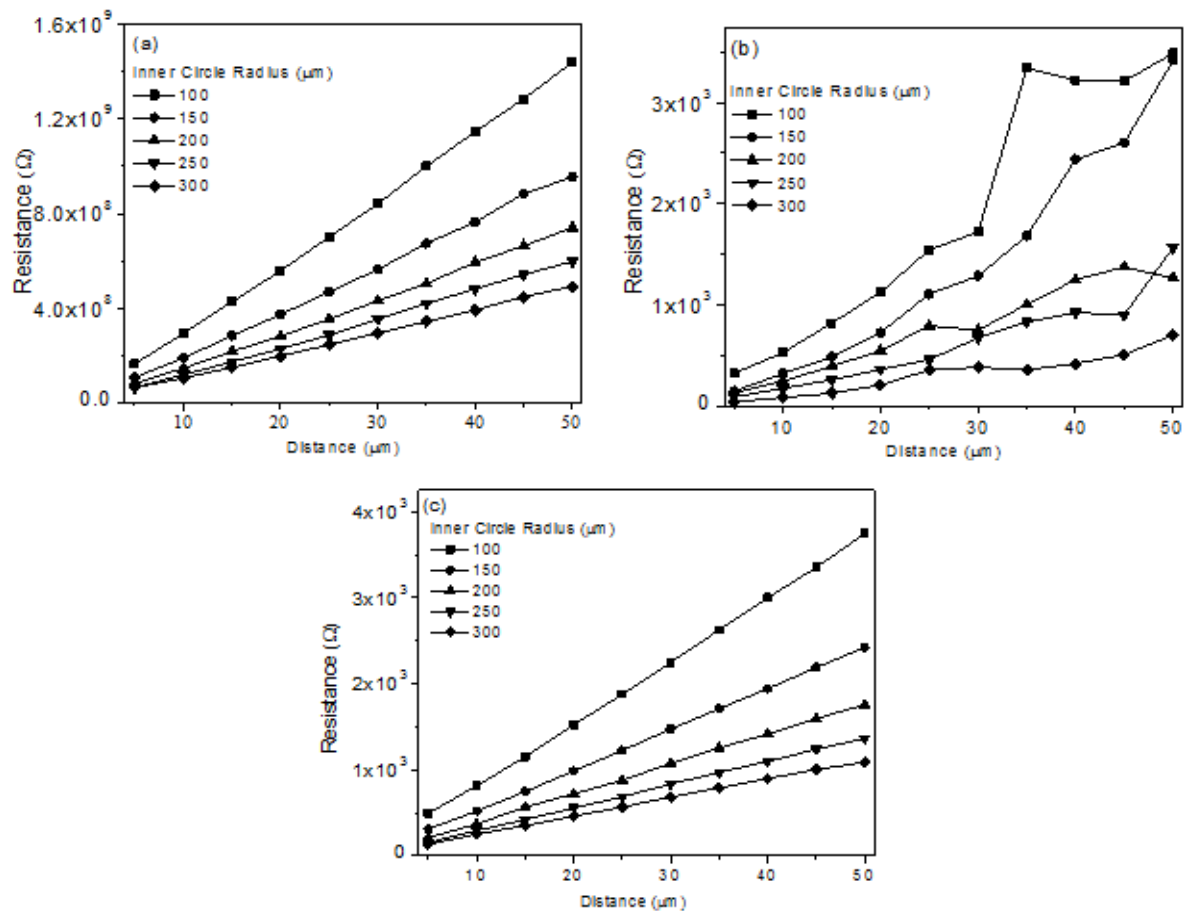


Fig 4. Effect of copper-doped p -ZnTe surface heated at (a) Un-doped film, (b) 200 °C and (c) 300 °C for minutes.

3.2. X-ray analysis

Figure 5 shows X-ray diffraction (XRD) patterns of the undoped/doped p -ZnTe thin-films, where doped films were heated at 200 and 300 °C for 30 minutes. It is observed that the un-doped (150 nm) sample presents the cubic phase (C) with dominant peaks belonging to the (111), (220) and (311) planes [10]. These relative intensity X-ray peaks for the ZnTe semiconductor were compared with the JCPDS card (015-0746). Then the sample was immersed in the copper solution for 1 minute, and then heated at 200 °C for 30 minutes. At this temperature, some copper atoms are thermally ionized causing the orthorhombic (O) phase of CuTe to appear as we are able to identify it on the 27.5 signal of 2θ corresponding to the plane (052). At 300 °C, the intensity of the orthorhombic peak increased, and the cubic (200) plane corresponding to ZnTe cubic phase appeared, Figure 5 (a). Figure 5 (b) shows the XRD diffraction for 80 nm ZnTe samples. These films also presented orthorhombic peaks as figure 5 (a), but with weaker intensities.

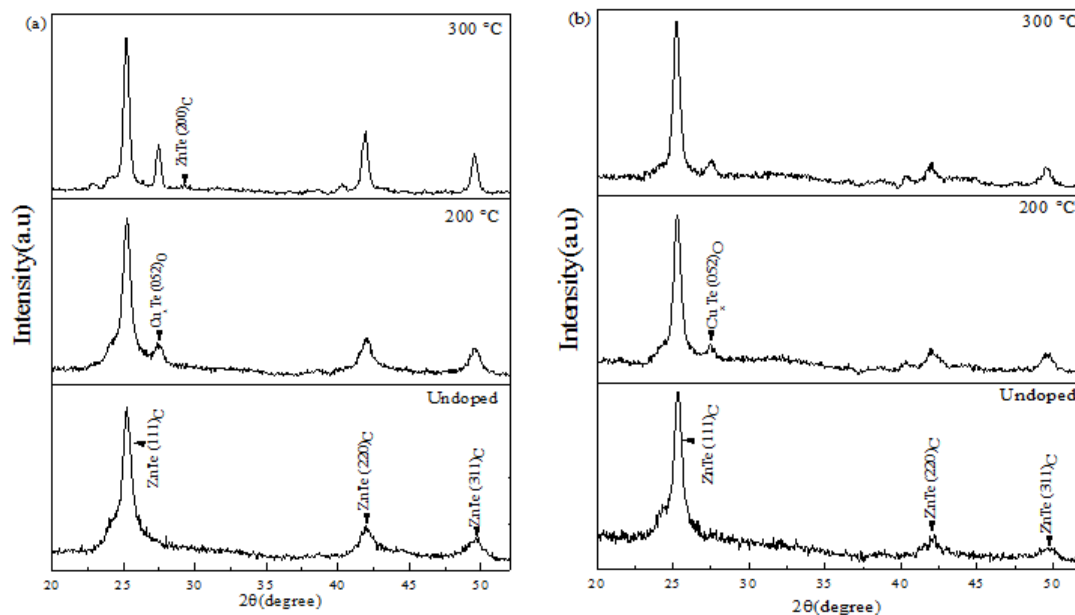


Fig 5. X-ray diffraction patterns of ZnTe:Cu films; (a) for 150 (± 5) nm and (b) 80 (± 5) nm for *p*-ZnTe thin-films heated at 200 °C and 300 °C for 30 minutes.

4. CONCLUSION

Electrical parameters of copper-doped *p*-ZnTe films drastically decreased when compared with un-doped thin-films. Also, we could observe that the Cu doping is not homogeneous at 200 °C. On the other hand, we have a completely homogeneous Cu doping surface at 300 °C. The XRD patterns showed that copper was diffused in the ZnTe crystalline structure at different temperatures (200 and 300 °C), however, is detectable in a 150 (± 5) nm thin-films.

ACKNOWLEDGMENTS

The authors would like to thank Norberto Como, Martha Rivas and J. Avila for their technical assistance. Financial support was received in the form of a grant from PAPIIT-UNAM IN108613, a sabbatical grant from DGAPA-UNAM to A. Olivas and a scholarship from Conacyt to G. Lastra.

REFERENCES

- [1] S. Bhunia, D.N. Bose, "Schottky barrier studies on single crystal ZnTe and determination of interface index", *Journal of Applied Physics*, 2000.
- [2] H. S. Hajghassem, W.D. Brown, "Stable ohmic contacts to zinc telluride", *Microelectron. Reliab.*, 1987.
- [3] M. Nishio, Q. Guo, H. Ogawa, "Ohmic contacts to *p*-type ZnTe using electroless Pd", *Thin Solid Films*, 1999.
- [4] K. R. Murali, M. Ziaudeen, N. Jayaprakash, "Structural and electrical properties of brush plated ZnTe films", *Solid-State Electronics*, 2006.
- [5] K. R. Gowrish, V. Kasturi, G.K. Shivakumar, "Studies on vacuum deposited *p*-ZnTe/*n*-ZnSe heterojunction diodes", *Solid-State Electronics*, 2010.
- [6] T. A. Gessert, W. K. Metzger, P. Dippo, S. E. Asher, R. G. Dhere, M. R. Young, "Dependence of carrier lifetime on Cu-contacting temperature and ZnTe:Cu thickness in CdS/CdTe thin film solar cells", *Thin Solid Films*, 2008.
- [7] W. E. Bowen, W. Wang, J. D. Phillips, "Complementary Thin-Film Electronics Based on *n*-Channel ZnO and *p*-Channel ZnTe", *IEEE Electron Device Letters*, 2009.
- [8] G. Lastra, M. A. Quevedo-Lopez, A. Olivas, "Thin-Film *p*-type ZnTe Transistors by Photolithography", *Chalcogenide Letters*, 2014.
- [9] G. Lastra, P. A. Luque, M. A. Quevedo-Lopez, A. Olivas, "Electrical properties of *p*-type ZnTe thin films by immersion in Cu solution", *Materials Letters*, 2014.



- [10] J-q Zhang, L-h Feng, W. Cai, J-g Zheng, Y-p Cai, B. Li, L-l Wu, Y. Shao, "The structural phase transition and mechanism of abnormal temperature dependence of conductivity in ZnTe:Cu polycrystalline thin films", *Thin Solid Films*, 2002.
- [11] A. A. Ibrahim, "DC electrical conduction of zinc telluride thin films", *Vacuum*, 2006.
- [12] T. Mahalingam, V. S. Jhon, S. Rajendran, P. J Sebastian, "Electrochemical deposition of ZnTe thin films", *Semicond. Sci. Technol.*, 2001.
- [13] B. Bozzini, M. A. Baker, P. L. Cavallotti, E. Cerri, C. Lenardi, "Electrodeposition of ZnTe for photovoltaic cells", *Thin Solid Films*, 2000.
- [14] T. Tanaka, K. Hayashida, M. Nishio, Q. Guo, H. Ogawa, "Photoluminescence of Cl-doped ZnTe epitaxial layer grown by atmospheric pressure metalorganic vapor phase epitaxy", *Journal of Applied Physics*, 2003.
- [15] S. I. Gheyas, S. Hirano, M. Nishio, H. Ogawa, "Aluminum doping of ZnTe grown by MOVPE", *Applied Surface Science*, 1996.
- [16] A. Ichiba, M. Kobayashi, "Al and N co-doped ZnTe layers grown by MBE", *Journal of Crystal Growth*, 2007.
- [17] M. Oszwaldowski, T. Berus, J. Rzeszutek, P. Sidorchuk, J. Polit, E. Sheregii, J. Szade, "Pulsed laser deposition of II-VI semiconductor thin films and their layered structures", *Journal of Alloys and Compounds*, 2004.
- [18] A. Erlacher, M. Ambrico, G. Perna, L. Schiavulli, T. Ligonzo, H. Jaeger, B. Ullrich, "Absorption and photoconductivity properties of ZnTe thin films formed by pulsed-laser deposition on glass", *Applied Surface Science*, 2005.
- [19] A. Erlacher, A. R. Lukaszew, H. Jaeger, B. Ullrich, "Structural and surface analysis of thin-film ZnTe formed with pulsed-laser deposition", *Surface Science*, 2006.
- [20] B. Kotlyarchuk, V. Savchuk, "Investigation of ZnTe thin films grown by pulsed laser deposition method", *phys. stat. sol.*, 2007.
- [21] Akram K. S. Aquili, A. Maqsood, Z. Ali, "Properties of copper-doped ZnTe thin films by immersion in Cu solution", *Applied Surface Science*, 2001.
- [22] Akram K. S. Aquili, A. Maqsood, Z. Ali, "Properties of Ag doped ZnTe thin films by an ion exchange process", *Applied Surface Science*, 2002.