ASM Sc. J., 11, Special Issue 2, 2018 for SANREM, 95-100

Electrical Characteristics of Doped ZnO/Cu_2O Heterojunction Diode by Sputtering Method

A.B. Abd Rahman[1*], A. Alias[3], F.L. Shain[1], W.Y. Lam[1], K.A. Mohamad[2]

[1]*Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Kota Kinabalu, Sabah, Malaysia*

[2]*Faculty of Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, Johor, Malaysia*

[3]*Faculty of Applied Science and Technology, Universiti Tun Hussein Onn Malaysia Pagoh, Johor, Malaysia*

Heterojunction thin films made from the combination of oxide semiconductor have attracted much attention due to its wide range of functional properties and plenty of potential application in optical and electronic devices. Zinc oxide (ZnO) semiconductor gains interest due to its versatile characteristics with wide direct band gap of 3.37 eV with added advantages to be used as in optoelectronics devices. In this paper, the electrical performances of heterojunction n-type ZnO (n-ZnO) and p-type cuprous oxide (p-Cu_2O) diodes will be compared with Al doped ZnO/Cu_2O and Ga doped ZnO/Cu_2O diodes. Heterojunction n-ZnO/p-Cu_2O diodes were fabricated by RF sputtering method. Pure ZnO ceramic target with 99.99% purity used as material target for ZnO thin films. A mixture of 3 wt% Al_2O_3 with 97 wt% ZnO and a mixture of 3 wt% Ga_2O_3 with 97 wt% ZnO used as target material for doped ZnO thin films. Several measurements such as resistivity, I-V curve, threshold voltage, series resistance and diode ideality factor were investigated. The overall results suggest that the doped heterojunction n-ZnO/p-Cu_2O diodes perform far better as compared to pure n-ZnO/p-Cu_2O.

Keywords: Doped Zn/Cu_2O, Thin Film, Heterojunction, Diode, Sputtering

I. INTRODUCTION

Zinc oxide (ZnO) gains interest due to its versatile characteristic which has large potential in various applications. One of the ZnO well known characteristic is wide direct band gap of 3.44 eV at low temperature and 3.37 eV which added advantages to be used as optoelectronics devices in blue and UV regions of the spectrum as fundamental element in liquid crystal displays, plasma displays panels, electronics paper displays, sensors, and photovoltaic panels. In addition, due to the large band gap, pure ZnO is colourless and transparent clear which is added advantages as transparent conductive oxide (Klingshirn, 2007; Tan *et al.*, 2005). However, controlling the conductivity of ZnO, doping is the main issue and a few suggestions were reported to overcome the issue related to ZnO conductivity as oxide semiconductor material.

There are two types of dopants that are used to improve the conductivity of ZnO, which is

---

*Corresponding author's e-mail: abubakar.rahman@ums.edu.my

Aluminium and Gallium. Al doped ZnO films deposited using magnetron sputter at lower temperature shows a good characteristic. While Ga doped ZnO is high oxidation resistance during deposition, exhibit better electronics stability in humidity and also suitable for stabilization of ZnO lattice system (Pugalenthi *et al.*, 2015; Gorrie *et al.*, 2010; Park, 2006; Yu *et al.*, 2005; Fathollahi & Amini, 2001; Zhang *et al.*, 1999; Park *et al.*, 1999).

Heterojunction thin films, which formed by using the combination of several oxide semiconductors have attracted much attention due to its wide range of functional properties and wide range of potential application in optical, magnetic device and also electronics devices. Combinations of p-type and n-type oxide semiconductor which brought together in close contact creating a depletion region where the p-type holes will recombine with n-type free electron hence create a heterojunction, which can be applied a basic application of electronic devices. One of the common applications of p-n heterojunctions is diode. A device composed of p-type semiconducting cuprous oxide (Cu_2O) with an energy band gap of 2.1 eV and n-type semiconductor ZnO with energy band gap of 3.4 eV have attracted attention as p-n junction thin film diode. Application of p-Cu_2O/n-ZnO thin films diode in various field such as solar cell, and light emitting diode increase potential of p-Cu_2O/n-ZnO thin films diode (Klingshirn, 2007). The p-Cu_2O/n-ZnO junctions have been constructed using several thin film deposition technique such as sol gel, spray, chemical vapor deposition and also magnetron sputter.

ZnO and Cu_2O heterojunction paired gains attraction due to the alignment of the conduction band edge of these two semiconductor materials added with their potential in solar cell and other optoelectronics devices. In this work, the electrical performance of heterojunction n-ZnO/p-Cu_2O diodes will be compared with Al doped ZnO/Cu_2O and Ga doped ZnO/Cu_2O diodes.

II. MATERIALS AND METHODS

The three samples of ZnO, Al doped ZnO and Ga doped ZnO films paired with Cu_2O were analyzed to study the electrical properties of those films as p-n junction diode. A n-type of ZnO, Al doped ZnO and Ga doped ZnO films were paired with p-type Cu_2O deposited on indium tin oxide (ITO) glass substrate and Cu were chosen as contact as shown in Figure 1.

These samples were fabricated by using RF magnetron sputtering method. Pure ZnO ceramic target with 99.99% purity was used as material target for ZnO thin films. A mixture of 3 wt% Al_2O_3 with 97 wt% ZnO and a mixture of 3 wt% Ga_2O_3 with 97 wt% ZnO was used as target material for doped ZnO thin films. These films were deposited onto ITO glass substrate. Prior to the deposition, the substrates were cleaned using an Ultrasonic Branson 3200 Cleaner by immersing the substrate in repeatedly three times in distilled water, ethanol, acetone and isopropyl alcohol respectively for 3 minutes and then the substrate was rinsed using distilled water before dried out using dry nitrogen gas. Sputtering was performed with RF power of 100 watt and the argon flow was set at 10 sccm. Table 1 summarizes the key parameters for setting-up deposition thin films using sputtering method.

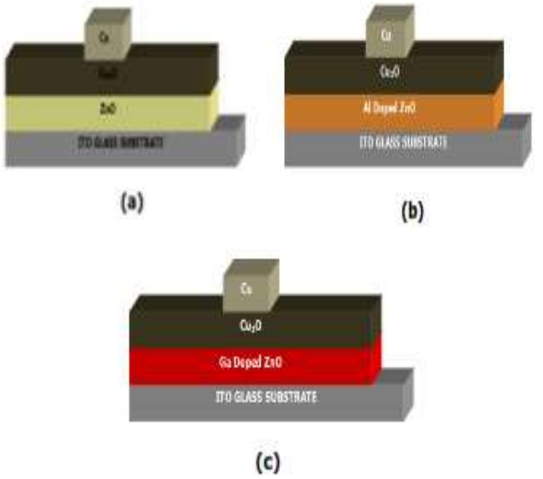


Figure 1: Diagram of p-n heterojuction of a) ZnO/Cu_2O b) $Al:ZnO/Cu_2O$ and c) $Ga:ZnO/Cu_2O$

Table 1: ZnO/Cu_2O PN Junction Deposition Parameter

Target (3 Inch)	Zinc Oxide (99.99%) Gallium Zinc Oxide (97/3 wt %) Aluminum Zinc Oxide (97/3 wt %) Cuprum Oxide (99.99%) Cuprum (99.99%)
Substrate	Indium Tin Oxide (2.54cm x 2.54cm x 0.1 cm)
Base Pressure	2.5 x 10^{-5} Torr
Deposition Time	40 minutes
Temperature	250℃
Ar Gas Flow Rate	10 sccm
RF Power	100 Watt

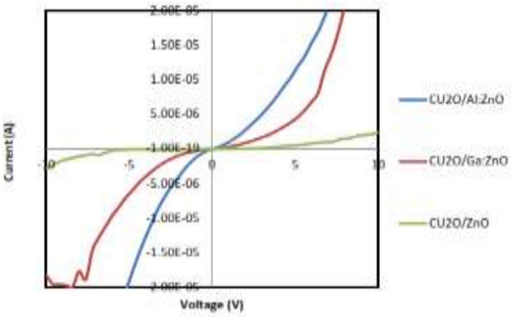
The resistivities for single layer deposited ZnO, Al doped ZnO and Ga doped ZnO were evaluated using the Keithley four point probe. The resistivity value gives the amount of resistivity and conductivity behavior for each sample. For the electrical evaluation, the current-voltage (I-V) characteristic of $Al:ZnO/Cu_2O$, $Ga:ZnO/Cu_2O$ and ZnO/Cu_2O p-n junction were measured by Keithley voltage source unit. The I-V characteristic is used to obtain and analyze few parameters related to diode electrical performance such as sheet resistance, barrier height and the ideality factor for each deposited p-n junction.

III. RESULTS AND DISCUSSIONS

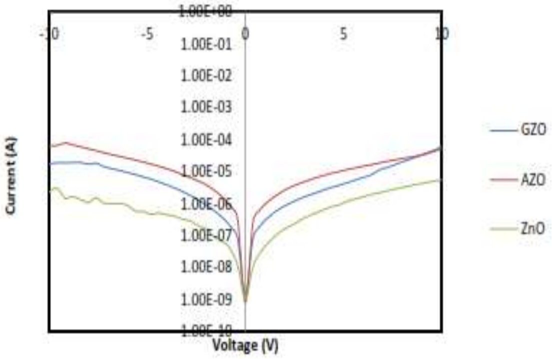
The comparison of the resistivity value for three different materials thin films were done in order to study the effect of dopant towards conductivity of the thin films. It is found that the resistivity of doped ZnO thin films; Al: ZnO 1.75 X 10^{-2} Ω cm and Ga: ZnO 1.25 X 10^{-2} Ω cm is lower than pure ZnO thin film 3.5 X 10^{-2} Ω cm as shown in Table 2. The present of dopant increase the population of electrons therefore improved the electron mobility and lowered the resistivity of the doped ZnO thin films. The difference of ionic radii between Al^{2+} and Ga^{2+} affect the resistivity between those two dopants. The ionic radii of Ga^{2+} is much closer to the ionic radii of Zn^{2+} thus reduce the films defects which in turn improve the electrical properties of Ga:ZnO thin films as compared to ZnO and Al:ZnO thin films.

Table 2 Comparison of resistivity Al: ZnO, Ga : ZnO and ZnO

	Al : ZnO	Ga : ZnO	ZnO
Resistivity	1.75 X 10^{-2} Ω cm	1.25 X 10^{-2} Ω cm	3.5 X 10^{-2} Ω cm



(a)



(b)

Figure 2: I-V characteristic of the Al:ZnO/Cu_2O, Ga:ZO/Cu_2O and ZnO/Cu_2O diode a) Linear scale b) Logarithmic

Figure 2 shows the I-V characteristics of Al:ZnO/Cu_2O, Ga:ZnO/Cu_2O and ZnO/Cu_2O thin films. Further analysis of electrical properties of Al:ZnO/Cu_2O, Ga:ZnO/Cu_2O and ZnO/Cu_2O were performed based on thermionic emission model current equation (I) which expressed as:

$$I = \exp(nkT/qV) - 1 \qquad (1)$$

where k is the Boltzmann constant, n is the ideality factor, T is the absolute temperature, q is the electronic charge, and V is the applied voltage. Then, the potential barrier height of the device is calculated by using the following relationship (Hussain *et al.*, 2012):

$$Is= AA^{**}T^2 \exp(-q\phi\ b/kT) \qquad (2)$$

where Is is the reverse saturation current, A is the device area, A^{**} is the Richardson constant, and $q\phi b$ is the potential barrier height. The plot of ln I as a function of V (ln I-V) used to extract the value of ideality factor. The values of ideality factor and potential barrier height are estimated and summarized in Table 3.

Table 3: Turn On Voltage (V_T), Saturation Current (I), Barrier Height, Series Resistance (Rs) and Ideality Factor of Al:ZnO/Cu_2O, Ga:ZnO/Cu_2O and ZnO/Cu_2O diode deposited by RF magnetron sputter.

p-n heterojunction	V_T(V)	I_0(A)	Barrier height (ΦB)	Rs (kΩ)	Ideality Factor (n)
Al:ZnO/Cu$_2$0	1.99	$8.41X10^{-10}$	1.77	22.80	12.31
Ga:ZnO/Cu$_2$0	1.52	$1.49X10^{-9}$	1.74	17.80	11.93
ZnO/Cu$_2$0	2.33	$1.12X10^{-9}$	1.75	30.00	14.50

The turn on voltage for all devices based on AZO/Cu_2O, GZO/Cu_2O and ZnO/Cu_2O, were estimated from the I-V characteristics in Figure 2. Turn on voltage for each sample is found to be 1.99 V, 1.52 V and 2.33 V for Al:ZnO/Cu_2O, Ga:ZnO/Cu_2O and ZnO/Cu_2O, respectively. The variation of turn on voltage is related to the decrease of the width of depletion region at the junction area. It is because of the increasing majority carrier injected by applied voltage. Addition of dopant increase the population of electrons therefore the electron mobility is significantly improved.

The potential barrier height calculated for ZnO, Al doped ZnO and Ga doped ZnO is found to be 1.75, 1.77 and 1.74 respectively. The value of barrier height influence the number of majority carrier. Presence of Al and Ga as dopant in ZnO influence the carrier concentration which affect the energy band bending and decrease the depletion region width of diode. ZnO/Cu_2O have the higher ideality factor of 14.5 compare to 12.31 for Al:ZnO/Cu_2O and 11.93 for Ga:ZnO/Cu_2O. These three devices have relatively high ideality factor compared with an ideal diode due to the influenced by the recombination factors of electron at the depletion region which affect the electron mobility (Birkmire & Eser, 1997). Another factors contribute to the higher ideality factor is condition of pn heterojunction surface which lead to imperfections during the combination of pn junction therefore influence the electrical properties of diode (Mahmood *et al.*, 2013). Among the three devices, series resistance for ZnO/Cu_2O is the highest, which is 30 kΩ, followed by Al:ZnO/Cu_2O with 22.80 kΩ and 17.80 kΩ for Ga:ZnO/Cu_2O. Both Al doped ZnO and Ga doped ZnO have lower series resistance from ZnO which is related to the presence of Al^{3+} and Ga^{3+} ions in Al doped ZnO and Ga doped ZnO films.

IV. CONCLUSION

In summary, the pn heterojunction ZnO/Cu_2O, Al doped ZnO/Cu_2O and Ga doped ZnO/Cu_2O diodes were successfully fabricated using sputtering deposition method. The resistivity of both doped diodes Al:ZnO and Ga:ZnO was found to be lower than pure ZnO thin film. The present of dopant has increased the population of electrons consequently the electron mobility is higher and the resistivity of the doped ZnO thin films become lower. The ideality factor of these three devices were high due to the influenced by the recombination factors of electron at the depletion region which limit the electron mobility as current carrier. As for overall comparison, the Ga:ZnO/Cu_2O was found to be the best among the three heterojunction diodes which having lower threshold voltage, lower barrier height, lower series resistance and lower ideality factor.

V. ACKNOWLEDGMENT

This research was funded by project code SBK0264-TK-2016. The author would like to thank University Malaysia Sabah for the hospitality provided.

[1] Klingshirn, C. F., ZnO . (2007). Material, Physics and Applications', Chem Phys Chem, 8(6), pp. 782-803.

[2] Tan, S. T., Chen, B. J., Sun, X. W., Fan, W. J., Kwok, H. S., Zhang, X. H., & Chua, S. J.(2005). Blueshift of Optical Band Gap in ZnO Thin Films Grown by Metal-Organic Chemical-Vapor Deposition. Journal of Applied Physics, 98,1-5.

[3] Gorrie, C. W., Sigdel, A. K., Berry, J. J., Reese, B. J., Van Hest, M. F. A. M., Holloway, P. H., & Perkins, J. D. (2010). Effect of Deposition Distance and Temperature on Electrical, Optical and Structural Properties of Radio-frequency Magnetron Sputtered Gallium doped Zinc Oxide. Thin Solid Films, 591, 190-196.

[4] Pugalenthi, A. S., Balasundaraprabhu, R., Gunasekaran, V., Muthukumarasamy, N., Prasanna, S., & Jayakumar, S. (2015). Effect of Thickness on the Structural, Optical and Electrical Properties of RF Magnetron Sputtered GZO Thin Films .Materials Science in Semiconductor Processing, 29, 176-182.

[5] Yu, X., Ma, J., Ji, F., Wang, Y., Cheng, C., & Ma, H. (2005).Thickness Dependence of Properties of ZnO:Ga Films Deposited by RF Magnetron Sputtering', Applied Surface Science, 245(1-4), pp. 310-315.

[6] Zhang, S., Wei, S., & Zunger, A. (1999). Elements of Doping Engineering in Semiconductors', AIP Conference Proceedings.

[7] Park, J. H. (2006). Deposition-Temperature Effects on AZO Thin Films Prepared by RF Magnetron Sputtering and Their Physical Properties, 49,584-588.

[8] Fathollahi, V., & Amini, M. M. (2001). Sol-gel Preparation of Highly Oriented Gallium doped Zinc Oxide Thin Films, 235-239.

[9] I. Hussain, M. Y. Soomro, N. Bano, O. Nur, and M. Willander. (2012). Interface trap characterization and electrical properties of Au-ZnO nanorod Schottky diodes by conductance and capacitance methods. Journal of Applied Physics 112, 064506.

[10] Birkmire, Robert W. (1997). Polycrystalline Thin Film Solar Cells: Present Status and Future Potential, Annual Review of Materials Science, 27, 625-653.

[11] Mahmood, M. R. (2013). Electrical Properties Dependence on Substrate Temperature of Sputtered ZnO Nanoparticles Thin Films on Teflon Substrates. Journal Applied Science, 795, 403-406.