Investigation on Temperature Dependence on C-V Characterization of ZnO-Cu_2O Thin Films

Zaw Htet Aung[1], San Yu Maw[2], Naing Naing Oo[3], Cho Cho Htay Aung[3], Win Win Thein[4]

Abstract

ZnO-Cu_2O thin films were fabricated by spin coating and chemical bath deposition methods onto ITO coated glass substrates. The ZnO thin films were annealed at 400 ºC to 600 ºC by interval 100 ºC. The ZnO-Cu_2O thin films were annealed at 150 ºC. The crystallographic structure of the thin films was examined by X-ray diffraction (XRD). XRD analysis showed the phase assignment and crystallographic properties of ZnO-Cu_2O thin films. The surface morphology is investigated by scanning electron microscopy (SEM), which revealed the crystalline nature of the film. Capacitance–Voltage (C-V) measurements were performed using LCR meter at frequency 100 kHz, in the dc bias voltage from -5 V to +5 V. The electrical properties such as built in potential and dopant concentration values were derived from C-V measurement.

Keywords: ZnO-Cu_2O, XRD, SEM, LCR, C-V

Introduction

A semiconductor is a material that has an electrical conductivity between a conductor and an insulator. In semiconductors, the highest occupied energy band, the valence band is completely filled with electrons and the next empty one is the conduction band. [Sagadevan S., (2013)]. The study of semiconducting thin films is being pursued with growing interest on account of their established and useful applications in many semiconductor devices such as solar energy converters, optoelectronics devices etc., [Geetha G., *et al*., (2016)].

The oxide nanoparticles synthesized by several methods appears more and more useful because these nanoparticles have good electrical, optical and magnetic properties that are different from their bulk counterparts [Muneer M., *et al*., (2012)].

Zinc oxide is a non toxic, abundant, low cost and n-type wide direct band-gap (3.2–3.4 eV) semiconductor (WBGS) that displays high optical transparency and luminescent properties in the UV and VIS region, good transparency, high electron mobility, strong room temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid crystal displays, energy-saving or heat-protecting windows, thin-film transistor and light emitting diode, solar cells, gas sensors, UV photo detectors heat mirrors, wave devices and bulk acoustic wave resonators etc [Omar Abd Elkader, (2012) & M.I. Khan *et al*., (2017)].

Cuprous oxide (Cu_2O) is naturally a p-type direct-bandgap semiconductor with a cubic crystal structure and a room-temperature bandgap energy of 2.17 eV, Cu_2O can be deposited using methods such as thermal oxidation, anodic oxidation, sputtering, solution growth, sol-gel, and electro-deposition [Jiang *et al*., (2014)].

Thin films, material layers with thicknesses between fractions of a monolayer and several micrometers, are ubiquitous today and can be found more or less everywhere. Thin films are applied to modify or enhance the surface of a material or to build functional devices such as light emitting diodes. A small selection of applications where thin films are used are;

[1] Lecturer , Department of Physics, Hinthada University
[2] Lecturer, Department of Physics, Technological University (Hinthada)
[3] Associate Professor, Department of Physics, Hinthada University
[4] Professor and Head, Department of Physics, Hinthada University

eyeglasses, microelectronics, drill bits and cutting tools, solar cells, mirrors, flat screens and windows. The properties of a film and thereby its area of application are, of course, mainly determined by the choice of material. But the structure of the film on a nanometer scale or micrometer scale, known as the microstructure, can also affect the film properties substantially [Daniel Magnfält, (2014)].

Experimental procedure of ZnO-Cu_2O Thin Films

Preparation of ZnO thin films

Zinc Oxide (ZnO) powder was prepared by sol–gel spin coating technique. To get the viscous solution, 3 g of ZnO was dissolved in 20 ml of methanol (CH_3OH) and 5 ml of Diethylene glycol $(HOCH_2CH_2)_2O$. Methanol was used as a solvent and Diethylene glycol was served as a stabilizer. The mixture was stirred using the magnetic stirrer for five days at 50 °C with 600 rpm. After stirring with magnetic stirrer, homogeneous ZnO solution was obtained.

Firstly, ITO coated glass substrates were cleaned with acetone and deionized water about 10 minutes. The ITO coated glass substrates were subsequently baked at 80 ºC for 10 minutes to evacuate moisture. ZnO sol-solution was then deposited onto the glass substrates by spin coating technique. When all the films were prepared and then they were placed in furnace and were annealed at temperature from 400 °C to 600 °C at interval 100 °C.

Preparation of ZnO-Cu_2O thin films

To get the Cuprous Oxide solution, 3 g of Cuprous Oxide (Cu_2O) and 20 ml of 2-Methoxyethanol ($C_3H_8O_2$) were mixed in the beaker. This solution was continuously stirred by a magnetic stirrer for 5 hrs with 600 rpm to become homogeneous. The ZnO thin films were placed into these solution and heated to 50 ºC for 1 hr by CBD. After deposition, the substrates were heated at 150 ºC for 30 minutes. Finally, ZnO-Cu_2O thin films were formed. ZnO-Cu_2O thin films were ready to be analyzed. The structural properties of thin films were studied by X-ray diffractometer (XRD). The surface morphology of ZnO-Cu_2O thin films were observed by using Scanning Electron Microscope (SEM) JEOL - JSM 5610 LV. The (C-V) measurement of ZnO-Cu_2O thin films was accomplished at 100 kHz, in the dc bias voltage from -5V to +5V.

Results and Discussion

XRD analysis of ZnO-Cu_2O Thin Films

XRD analysis was carried out to study the phase assignment and crystallographic properties of ZnO-Cu_2O thin films. It was performed using monochromatic CuK_α radiation (λ = 1.54056 Å) operated at 40 kV (tube voltage) and 30 mA. Specimen was scanned from 10° to 70° in diffraction angle 2θ with step-size of 0.02. The upper site of XRD spectrum represented the observed profile while the lower site indicated the standard ZnO and Cu_2O of JCPDS library file 1.

Figure (1), (2) and (3) showed the XRD patterns of ZnO-Cu_2O thin film at 400 °C, 500 °C and 600 °C. Form XRD plots, almost reflections were well-matched with the diffracted peaks of standard ZnO and Cu_2O of JCPDS. The ZnO peaks were found to be (1 1 1), (2 0 0), and (2 2 0) planes for all thin films. The Cu_2O peaks were found to be (1 1 0), (2 2 0) and (2 2 1) planes for all thin films. The films were crystallized in the cubical phase. The average lattice parameter of "**a**" axis for ZnO-Cu_2O thin films was observed as 4.2581 Å at

400 °C, 4.2651 Å at 500 °C and 4.2597 Å at 600 °C. The diameter of cubical shaped crystallite grain could be identified as crystallite size calculated by Debye-Scherrer equation:

$$G = \frac{0.9 \times \lambda}{B \times \cos \theta_B} \qquad (1)$$

Where G is crystallite size (Å), λ is wavelength of X-rays, B is FWHM of reflection and θ_B is Bragg's angle. The average crystallite sizes were found to be 41.643 nm at 400 °C, 42.508 nm at 500 °C and 54.135 nm at 600 °C in the Table (1).

Table (1) Crystallite sizes at different temperature of ZnO-Cu_2O thin films

No	**Temperature (°C)**	**crystallite size (nm)**
1.	400	41.643
2.	500	42.508
3.	600	54.135

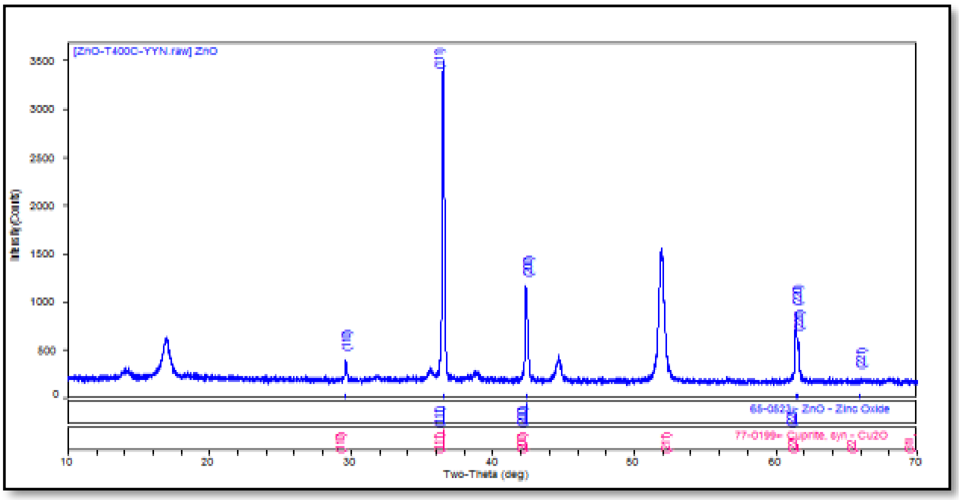

Figure (1) XRD pattern of ZnO-Cu_2O thin film at 400 °C

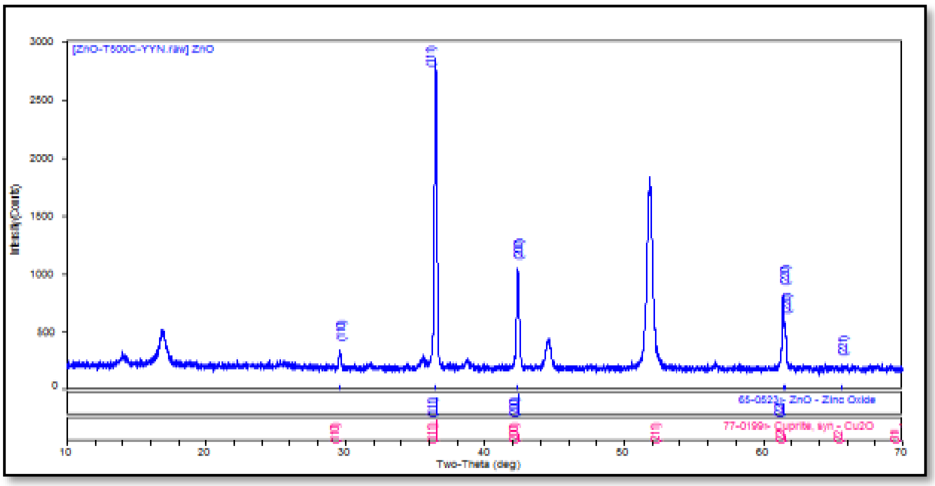

Figure (2) XRD pattern of ZnO-Cu_2O thin film at 500 °C

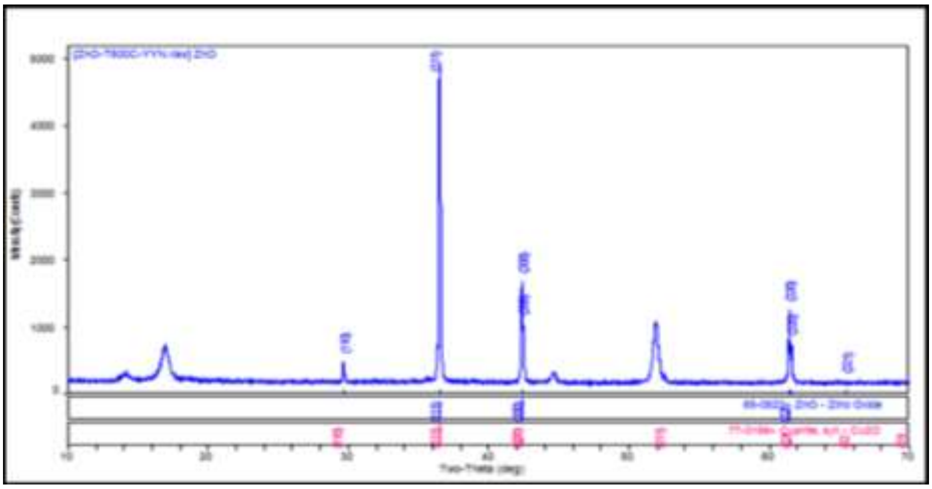

Figure (3) XRD pattern of ZnO-Cu_2O thin film at 600 ºC

SEM analysis of ZnO-Cu_2O Thin Films

The grain morphology of ZnO-Cu_2O thin films at 400 °C, 500° C and 600 °C was examined by scanning electron microscopy (SEM). Figure (4) showed the SEM photographs of ZnO-Cu_2O thin films at 400 °C, 500 °C and 600 °C. From the SEM images, they were found that its images exhibited spherical and cubical shape with average grain size estimated by well – known bar code system were about 5µm. The average grain size were found to be about 1.065 µm at 400 °C, 1.385 µm at 500 °C and 1.228 µm at 600 °C, respectively. The grains were uniformly distributed and non-cracking.

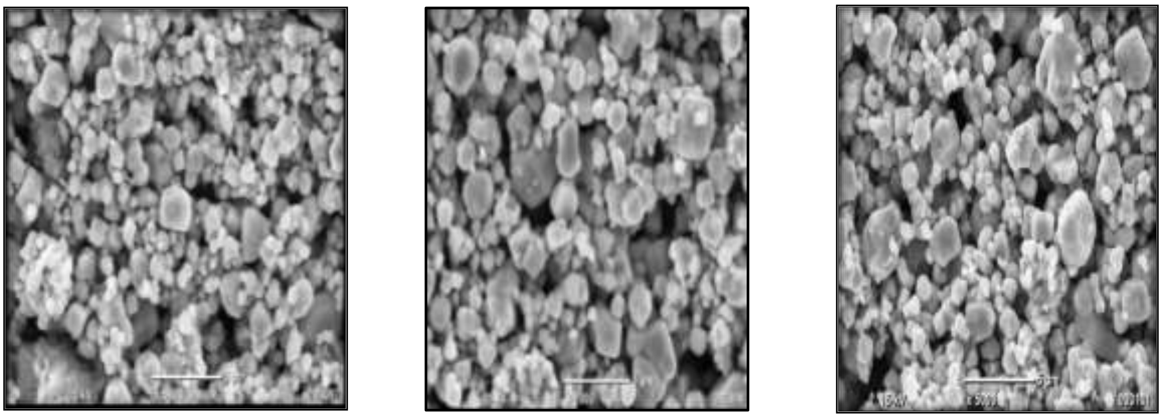

Figure (4) SEM image of ZnO-Cu_2O thin films at 400 ºC, 500 ºC and 600 ºC

$1/C^2$ –V analysis of ZnO-Cu_2O Thin films

In order to examine for more details in electrical behaviors of the ZnO -Cu_2O thin films, $1/C^2$ – V analysis was also studied in this work. The (C-V) measurement of ZnO -Cu_2O thin films was accomplished at 100 kHz, in the dc bias voltage from -5V to +5V. The slew-rate was set 0.5V for all cases. Measurements were performed at room temperature and the quantities of Schottky contact were estimated from the analysis of experiment results [Figures (1), (2) and (3)]. Reverse C-V characteristics exhibited a linear $1/C^2$ versus V plot.

The $1/C^2$-V characteristics were useful to determine the parameters such as build in potential (V_{bi}) and dopant concentrations in table (2). The build in potential calculation could be generally expressed as

$$V_{bi} = \frac{kT}{q} \ln\left(\frac{N_d N_a}{n_i^2}\right) \qquad (2)$$

Where k was Boltzmann constant, kT/q=25.86 mV at room temperature T = 300 K, N_d, N_a were donor and accepter concentrations and n_i was intrinsic carrier concentration (1.5×10^{16} cm^{-3}) [Funda P K et al, (2007)].

The $1/C^2$ – V characteristics obtained from the reverse bias or negative dc voltage region gave a straight line which was able to achieve V_{bi} value an intercept with voltage axis. In the assumption of an abrupt junction, the reverse capacitance of a p-n junction could be estimated as

$$\frac{1}{C^2} \alpha \ (V_{bi} + V) \qquad (3)$$

Where C was the reverse-bias capacitance and V was the reverse–bias voltage. The dopant concentration of ZnO-Cu_2O thin films in this work could be calculated by the following equations:

For slope estimate of $1/C^2$-V,

$$\text{slope} = \frac{\Delta \frac{1}{C^2}}{\Delta V} \qquad (4)$$

For acceptor concentration

$$N_a = \frac{2}{A^2 q \varepsilon_s \varepsilon_0} \times \frac{\Delta V}{\Delta \frac{1}{C^2}} \qquad (5)$$

For donor concentration,

$$N_d = \frac{n_i^2 \exp(qV_{bi} / kT)}{N_a} \qquad (6)$$

The slope calculation of $1/C^2$–V representation provided to determine the dopant concentration [P. M. Parameshwari1 *et al*., (2017)].

Table (2) Built in potential (V_{bi}) and dopant concentration (N_a and N_d) values derived from the analysis of $1/C^2$-V characteristics of ZnO-Cu_2O thin films at different temperatures

ZnO-Cu_2O thin films	**V_{bi} (V)**	**$N_a(cm^{-3})$**	**$N_d(cm^{-3})$**
400 ° C	0.62	1.834E+30	3.13E+12
500 ° C	0.74	1.445E+31	4.10E+13
600 ° C	0.84	5.974E+30	4.73E+15

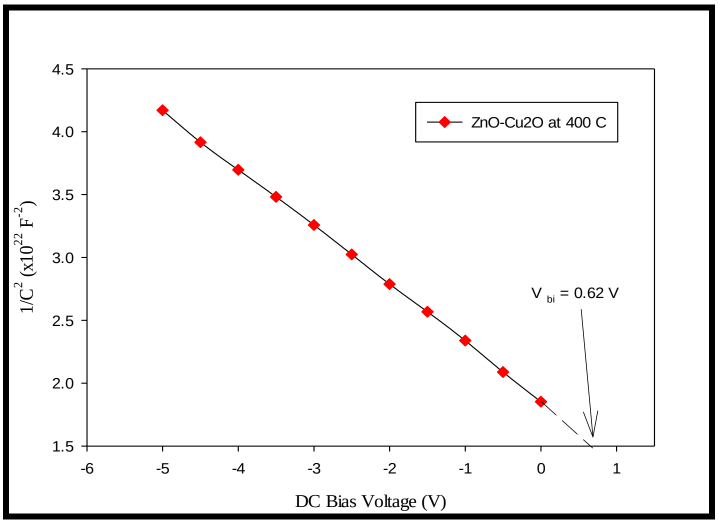

Figure (5) $1/C^2$-V Characteristic of $ZnO-Cu_2O$ thin film at 400°C

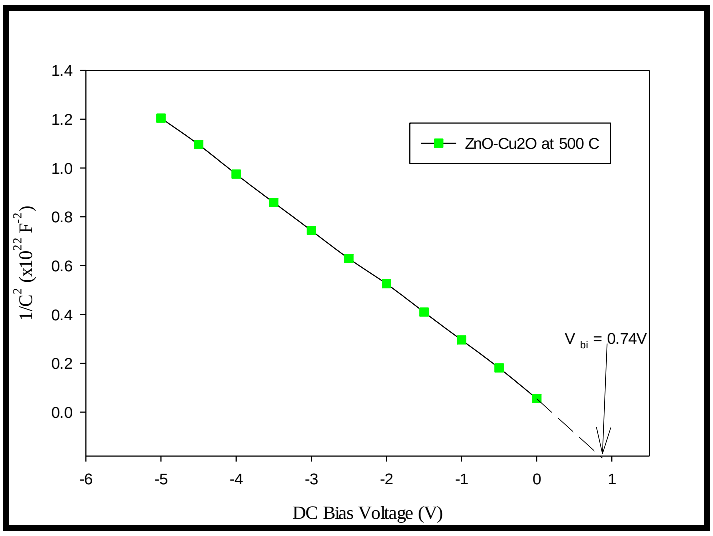

Figure (6) $1/C^2$-V Characteristic of $ZnO-Cu_2O$ thin film at 500°C

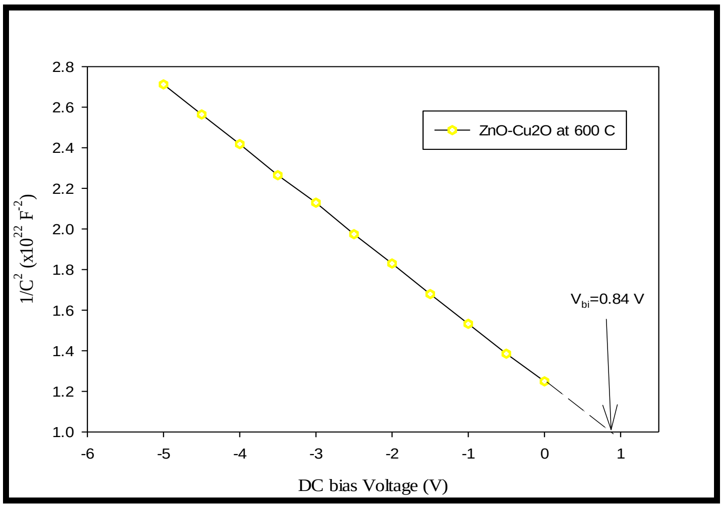

Figure (7) $1/C^2$-V Characteristic of $ZnO-Cu_2O$ thin film at 600°C

Conclusion

Zinc oxide (ZnO) thin films were deposited by the spin coating method onto ITO coated glass substrates. Cuprous oxide (Cu_2O) thin layers were deposited onto ZnO/ITO thin layers by chemical bath deposition method. From XRD analysis, it is obsrerved that the average crystallite sizes of the thin films were increased with the increase of annealing temperature. From SEM investigation, the shapes of grain of the ZnO-Cu_2O thin films were spherical and cubical feature and grain sizes were measured to be 1.065 μm at 400°C, 1.385 μm at 500°C and 1.228 μm at 600°C. Carrier concentration was found to be 1.834E+30 cm^{-3}, 31.445E+31 cm^{-3} and 5.974 E+30 cm^{-3} for acceptor, and 3.13 E+12 cm^{-3}, 4.10 E+13 cm^{-3}, and 4.73E+15 cm^{-3} for donor. Built in potential (V_{bi}) of ZnO-Cu_2O thin films was found to be 0.62 V, 0.74 V and 0.84 V. In semiconductor electrochemistry, a Mott–Schottky plot describes the reciprocal of the square of capacitance ($1/C^2$) versus the potential difference between bulk semiconductor and bulk electrolyte. In many theories, and in many experimental measurements, the plot is linear. From $1/C^2$-V Characteristics of ZnO-Cu_2O thin films are observed and implied Mott-Schottky relation.

Acknowledgements

We would like to thank Pro-Rector Dr. Nilar Myint and Pro-Rector Dr. Mar Lar, Hinthada University, for their kind permission to carry out this research work. Our deepest gratitude is expressed to Department of Physics, University of Yangon and Universities' Research Centre (URC), Yangon which supported us in completing this research.

References

Elkader O.A., (2012). "Preparation and characterization of nanostructured zinc oxide thin films", American Institute of Physics, 1482, 539-542

Funda P K *et al*., (2007). "Current-Voltage (I-V) and Capacitance-Voltage (C-V) Characteristics of $Au/Bi_4Ti_3O_{12}/SnO_2$ Structures", G.U. Journal of Science, 20(4): 97-102

Geetha G *et al*., (2016). "Investigations on the Synthesis, Optical and Electrical Properties of TiO_2 Thin Films by Chemical Bath Deposition (CBD) method" , Mat . Res., 19 (2)

Jiang *et al*., (2014). "Microstructure and optical properties of nanocrystalline Cu_2O thin films prepared by electrodeposition", Nanoscale Research Letters, 9,219

Khan M.I. *et al*., (2017). "Characterizations of multilayer ZnO thin films deposited by sol-gel spin coating technique", Results in Physics, 7, 651–655

Magnfält D., (2014). "Fundamental processes in thin film growth", Linköping Studies in Science and Technology, 1592

Muneer M *et al*., (2012). "Synthesis and Catalytic Activity of TiO_2 Nanoparticles for Photochemical Oxidation of Concentrated Chlorophenols under Direct Solar Radiation", Int. J. Electrochem. Sci., 7, 4871 – 4888

Parameshwari1 P.M. *et al.*, (2017). "Current-Voltage and Capacitance-Voltage measurements on $Al/Cd_{0.8}Zn_{0.2}S$ Schottky barrier diodes subjected to 8 MeV electron beam irradiations", International Journal of Pure and Applied Physics. 13(1) 133-142

Sagadevan S., (2013). "Semiconductor Nano materials, Methods and Applications: A Review", Nanoscience and Nanotechnology, 3(3), 62-74