

# Effect of Annealing Temperature on CuGaO<sub>2</sub> Thin Films Deposited by RF Sputtering Technique

M. H. Abu Bakar<sup>\*1</sup>, L. M. Li<sup>1</sup>, K. A. Mohamad<sup>2</sup>, S. Sulaiman<sup>2</sup>, S. Salleh<sup>1</sup> and A. Alias<sup>1</sup>

<sup>1</sup>Faculty of Science and Natural Resources, Universiti Malaysia Sabah, 88999, Kota Kinabalu, Sabah

<sup>2</sup>Faculty of Engineering, Universiti Malaysia Sabah, 88999 Kota Kinabalu, Sabah

\*officialhafiz89@gmail.com

**Abstract** – A transparent p-type thin film CuGaO<sub>2</sub> was successfully deposited on the glass substrate by using RF sputtering deposition method and underwent different annealing temperature ranging from 200°C to 500°C and time ranging from 1 to 3 hour. The X-ray diffraction analysis shows (015) plane. The bandgap of the thin film is 3.3eV. The transparency of the thin film is around 70%. **Copyright** © 2015 Penerbit Akademia Baru - All rights reserved.

**Keywords:** RF sputtering, CuGaO<sub>2</sub> thin films, Annealing temperature, Annealing time.

## 1.0 INTRODUCTION

In realizing a transparent p-n junction devices such as diode [1], transistor [2], UV photodetector [3] and near-UV photodetector [4] many studies have been made to find and optimize a material that shows both transparent and electrical conductivity. But many of the studies that have been done are primarily about n-type transparent semiconductor such as ZnO [2], SnO<sub>2</sub> [5], In<sub>2</sub>O<sub>3</sub> [6] and there only a few studies have been made on the p-type transparent semiconductor. Until today there are several p-type TCO belong to delafosite such as CuAlO<sub>2</sub> [7], CuGaO<sub>2</sub> [8] and CuInO<sub>2</sub> [9] structure have been made and studied to improve their performance. Research done by A.Sivasankar [7] shows that the crystallinity of CuAlO<sub>2</sub> thin film is increase by increasing substrate temperature. The thin film properties is depending on the deposition condition and technique. This study has been made to study the effect of different annealing temperature and annealing duration on the CuGaO<sub>2</sub> thin film on glass substrate by using RF method.

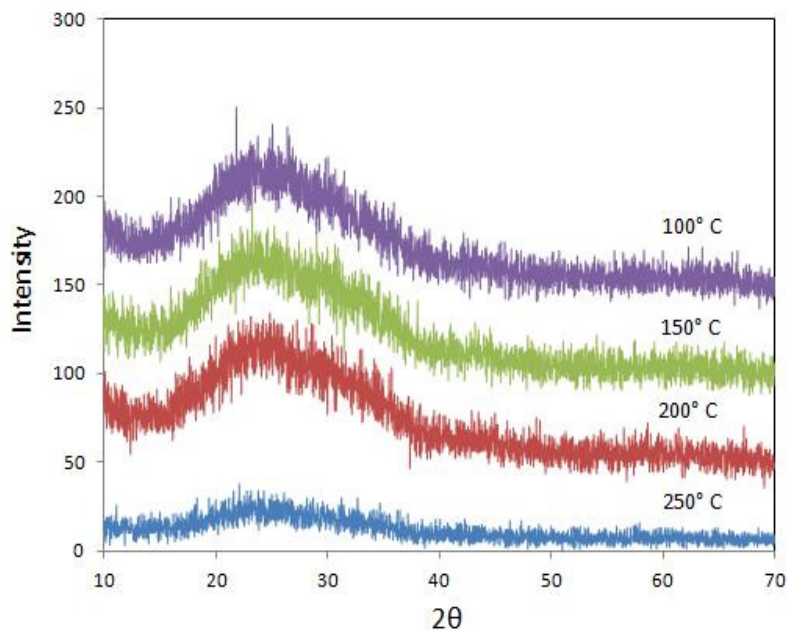
## 2.0 METHODOLOGY

The CuGaO<sub>2</sub> target disk with 99.99% purity is purchased from Stanford Material Corporation, plastic (PET), glass, distilled water, ethanol and acetone. The substrate from glass was cleaned for 3 minutes using distilled water, ethanol, acetone and distilled water in ultrasonic bath. The sample was dried by using nitrogen gas. The chamber was pumped until  $2.5 \times 10^{-5}$  Torr and the target were pre-sputtered for 10 minutes. The RF power was set to 100W and Argon gas flow was set to 10 sccm. The working pressure was  $2.5 \times 10^{-3}$  Torr and substrate rotation is 5 rpm. The CuGaO<sub>2</sub> thin film is deposited onto glass substrate at different substrate temperature

which is 50-250°C. The samples that are heated at 250°C during deposition is annealed at different temperature ranging from 200°C to 500°C at different time ranging from 1 to 3 hour. Structural, optical properties and thickness of the films will be characterized using X-Ray Diffraction Philips Expert Pro and UV-Vis Spectrometer Lambda EZ210 and LS500 profilimeter, respectively.

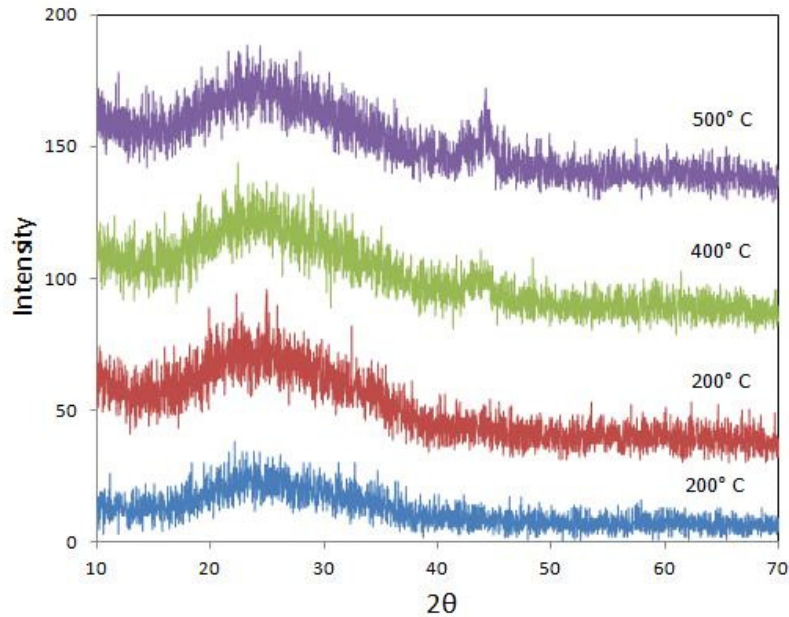
### 3.0 RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern for CuGaO<sub>2</sub> thin film deposited on glass substrate at 30 minutes at different substrate temperature. All the samples have thickness 300± nm. From the graph we can observe that there is no peak that related to the CuGaO<sub>2</sub> thin film and this is probably because the CuGaO<sub>2</sub> thin film is still amorphous state.



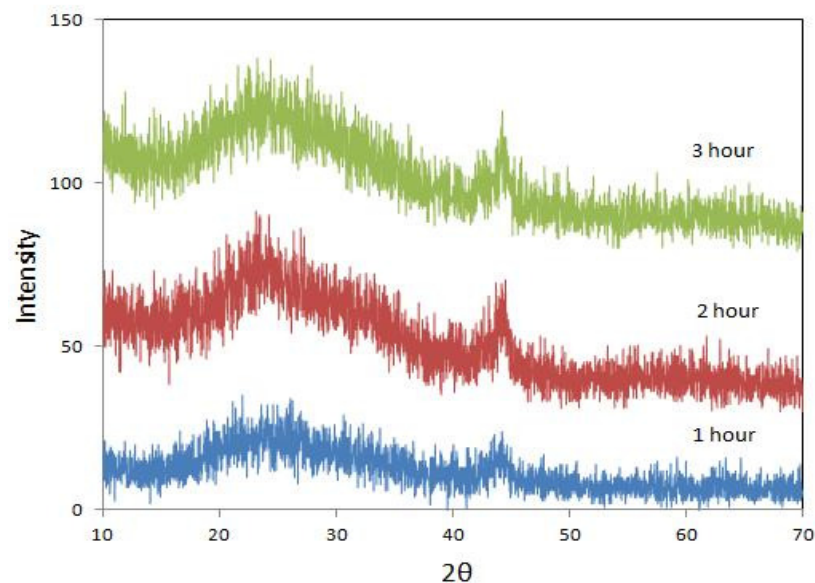
**Figure 1:** XRD pattern for CuGaO<sub>2</sub> deposited at different substrate temperature.

Figure 2 shows the XRD pattern for CuGaO<sub>2</sub> thin film at different annealing temperature ranging from 200°C, 300°C, 400°C, and 500°C. Because the glass melting point is around 550°C we limit the temperature for annealing at 500°C. All samples are deposited at 250°C substrate temperature and are annealed for 3 hours. For thin film annealed at 200°C there is no peak probably at this temperature the thin films is still in amorphous state because there is not enough thermal energy for the thin film to become crystalline. For the thin film annealed at 300°C, CuGaO<sub>2</sub> (015) peak is detected at 44°. The intensity of the CuGaO<sub>2</sub> (015) peak is increasing with increasing annealing temperature. This suggests that with increasing annealing temperature, the CuGaO<sub>2</sub> atom has enough thermal energy for the atom to arrange to form better crystalline. No other peak of CuGaO<sub>2</sub> is observed.



**Figure 2:** XRD pattern for CuGaO<sub>2</sub> annealed at different temperature

Figure 3 shows the XRD pattern for CuGaO<sub>2</sub> thin film annealing at 500°C at different time for 1, 2 and 3 hours. We chose 500°C because at this temperature the crystallinity of the CuGaO<sub>2</sub> is much better than the lower temperature. All samples are deposited with CuGaO<sub>2</sub> thin film at 250°C substrate temperature. From the graph we can observe that the CuGaO<sub>2</sub> (015) peak is increasing with increasing annealing duration. This shows that with increasing time the atoms of the CuGaO<sub>2</sub> thin film have enough energy to arrange and to form a better crystallinity. At 3 hour annealing time, the intensity of the XRD peak is maintain and probably because crystal structure of the thin film is already fixed in better arrangement.

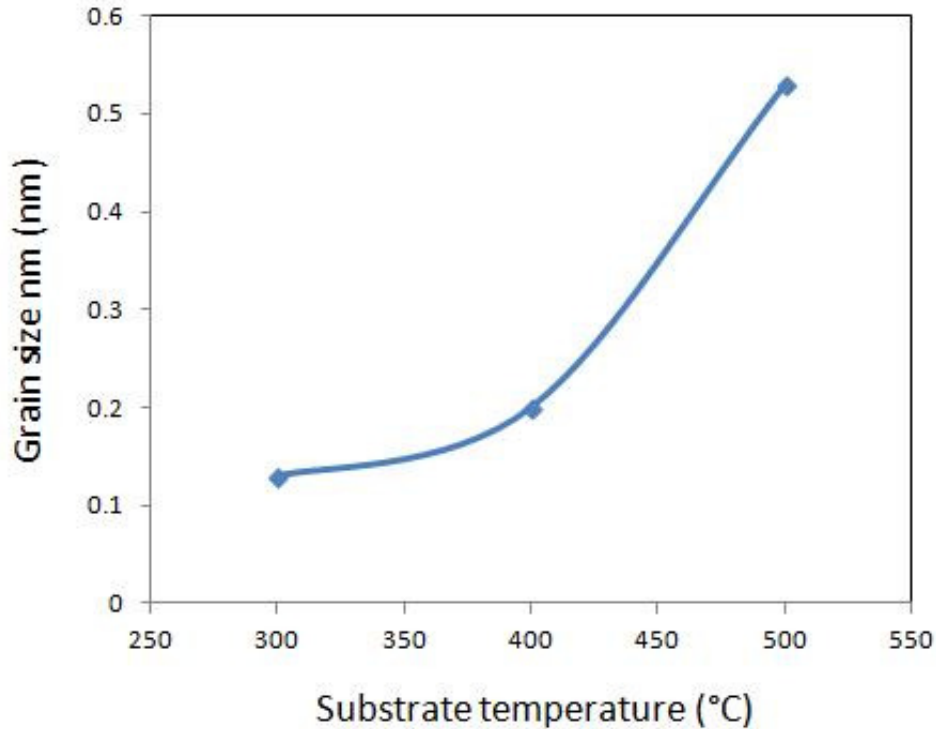


**Figure 3:** XRD pattern for CuGaO<sub>2</sub> annealed at different annealing time

The average grain size is determined L, is calculated by using Scherrer's equation [10]:

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where d represents the average grain size,  $\lambda$  is the wavelength of incident X-ray,  $\beta$  is the peak's FWHM and  $\theta$  is the Bragg angle. Figure 4 shows the variation of different grain size. The grain size is increasing with increasing annealing temperature from 0.13nm to 0.53nm.



**Figure 4:** Grain sizes of CuGaO<sub>2</sub> thin film for different substrate temperature

Figure 5 shows optical transmittance spectrum against wavelength for thin film annealed at 500°C for 3 hour. The transmittance of the samples that is annealed at temperature of 200°C, 300°C and 400°C is almost the same for wavelength range from 300 to 700nm. The transmittance for these samples approximately more than 75%. The transmittance of sample that is annealed at 500°C is slightly lower which is for a wavelength range from 400 to 500nm and 600 to 800nm.

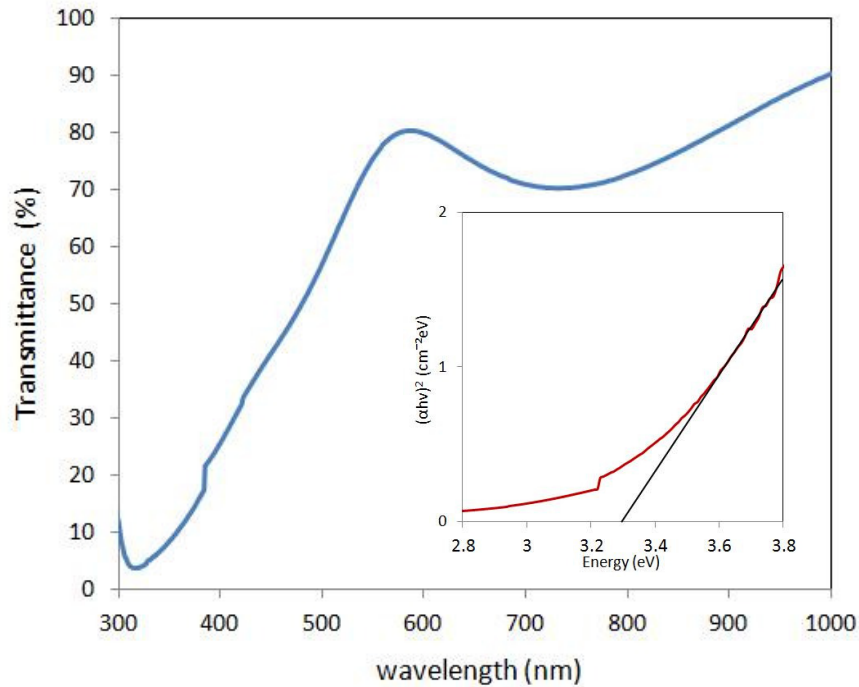
To further study the optical properties, we evaluated the optical band gap ( $E_g$ ) of the annealed film. The optical absorption coefficient ( $\alpha$ ) of the films can be calculated using the following equation [11]:

$$\alpha = \left(\frac{1}{n}\right) \ln \frac{1}{T} \quad (2)$$

where d is the film thickness and T is the transmittance of the film. The relation between optical absorption coefficient ( $\alpha$ ) and optical band gap ( $E_g$ ) can be written as

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (3)$$

where  $A$  is the absorption edge width parameter and  $h\nu$  represent the incident photon energy. The exponential  $n$  is  $1/2$  or  $2$  for direct allowed transition ( $E_{gd}$ ) or indirect allowed transition. The insert in Figure 5 shows estimation band gap for the CuGaO<sub>2</sub> thin film determined by the extrapolation of the linear part of the curve  $(\alpha h\nu)^2$  against  $h\nu$  graph. The estimated bandgap for CuGaO<sub>2</sub> is around 3.3eV which is compatible with research done by Hiroshi Yanagi [12].



**Figure 5:** Optical transmittance spectrum of CuGaO<sub>2</sub> thin film annealed at 500°C for 3 hour (insert show determining of direct bandgap)

#### 4.0 CONCLUSION

In this research we have successfully deposit CuGaO<sub>2</sub> thin film on glass substrate by using RF sputtering deposition method in a controlled Argon atmosphere. The crystallinity of the thin film is increase with increasing annealing temperature and annealing duration. We annealing at 500°C because at higher temperature the glass substrate start to deformed. The optical transmittance is almost the same for each sample which is more than 70% .The thin film show direct optical band gap of 3.3eV for thin film annealed at 500°C for 3 hours.

#### REFERENCES

- [1] H. Yanagi, K. Ueda, H. Ohta, M. Orita, M. Hirano, H. Hosono, Fabrication of all oxide transparent p-n homojunction using bipolar CuInO<sub>2</sub> semiconducting oxide with delafossite structure, Solid State Communications 121 (2002) 15-18.
- [2] J.D. Jin, Y. Luo, P. Bao, C. Brox-Nilsen, R. Potter, A.M. Song, Tuning the electrical properties of ZnO thin-film transistors by thermal annealing in different gases, Thin Solid Films 552 (2014) 192–195.

- [3] S.-Y. Tsai, M.-H. Hon, and Y.-M. Lu, Fabrication of transparent p-NiO/n-ZnO heterojunction devices for ultraviolet photodetectors *Solid-State Electronics* 63 (2011) 37–41.
- [4] H. Hosono, H. Ohta, K. Hayashi, M. Orita, M. Hirano, Near-UV emitting diodes based on a transparent p–n junction composed of heteroepitaxially grown p-SrCu<sub>2</sub>O<sub>2</sub> and n-ZnO, *Journal of Crystal Growth* 237-239 (2002) 496–502.
- [5] M.-M. Bagheri-Mohagheghi, M. Shokooh-Saremi, Optical and structural properties of li-doped SnO<sub>2</sub> transparent conducting films deposited by the spray pyrolysis technique: a carrier-type conversion study, *Semiconductor Science and Technology* 19 (2004) 764–769.
- [6] M.H.Z. Maha, M.-M. Bagheri-Mohagheghi, H. Azimi-Juybari, M. Shokooh-Saremi, The structural, thermoelectric and photoconductive properties of sulfur doped In<sub>2</sub>O<sub>3</sub> thin films prepared by spray pyrolysis, *Physica Scripta* 86 (2012) 055701.
- [7] A.S. Reddy, H.H. Park, G.M. Rao, S. Uthanna, P.S. Reddy, Effect of substrate temperature on the physical properties of dc magnetron sputtered CuAlO<sub>2</sub> films, *Journal of Alloys and Compounds* 474 (2009) 401–405.
- [8] T. Mine, H. Yanagi, K. Nomura, T. Kamiya, M. Hirano, H. Hosono, Control of carrier concentration and surface flattening of CuGaO<sub>2</sub> epitaxial films for a p-channel transparent transistor, *Thin Solid Films* 516 (2008) 5790-5794.
- [9] M. Sasaki, M. Shimode, Fabrication of bipolar CuInO<sub>2</sub> with delafossite structure, *Journal of Physics and Chemistry of Solids* 64 (2003) 1675–1679.
- [10] R.-S. Yu, H.-H. Yin, Structural and optoelectronic properties of p-type semiconductor CuAlO<sub>2</sub> thin films, *Thin Solid Films* 526 (2012) 103–108.
- [11] Y. Zhang, Z. Liu, D. Zang, L. Feng, Structural and opto-electrical properties of Cu–Al–O thin films prepared by magnetron sputtering method, *Vacuum* 99 (2014) 160–165.
- [12] H. Yanagi, H. Kawazoe, A. Kudo, M. Yasukawa, H. Hosono, Chemical design and thin film preparation of p-type conductive transparent oxides, *Journal of Electroceramics* 4 (2000) 407-414.