Structural and Optical Properties of Gamma Irradiated CuGaO$_2$ Thin Film deposited by Radio Frequency (RF) Sputtering

M Duinong$^1$, F P Chee$^{1, *}$, S Salleh$^1$, A Alias$^2$, K A Mohd Salleh$^3$, S Ibrahim$^4$

$^1$ Faculty science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia.
$^2$ Department of Physics and Chemistry, Faculty of Applied Science and Technology, University Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, Malaysia
$^3$ Malaysia Nuclear Agency for Non-destructive Testing (NDT), Agensi Nuklear Malaysia, 43000 Kajang, Bangi Malaysia
$^4$ Malaysia Nuclear Agency, MINTec-SINAGAMA, Nuclear Agency Malaysia 43000 Kajang, Bangi, Malaysia

Email: fpchee06@gmail.com

Abstract. In space, semiconductor devices are vulnerable to various effect of high energy level of radiation causing single event upsets (SEU), damaging or altering the lattice structure. In this work, p-CuGaO$_2$ was selected due to its relatively wide bandgap and a visibility transmittance up to 80% as a potential semiconductor material capable of withstanding harsh radiation environment. p-CuGaO$_2$ thin films were deposited by RF powered sputtering on indium tin Oxide (ITO) substrates at 250$^\circ$C deposition temperature and annealed at 300 $^\circ$C. Structural morphology and optical properties of CuGaO$_2$ thin film were investigated before and after irradiation. The samples were irradiated using Cobalt-60, gamma-ray with a dose ranging from 10 kGy-200 kGy. The structural properties reveal that the CuGaO$_2$ films shows a diffraction peak at 2$\theta$=38.051$^\circ$ (012) before irradiation. The optical properties of deposited CuGaO$_2$ thin film, exhibits approximately 75% optical transmittance in the invisible region at pre-irradiation and post-irradiation results shows a decrease of optical transmittance of 55%. At a dose of 200 kGy, the band gap of CuGaO$_2$ is 3.62 eV which indicates that it is still within the acceptable range of a semiconductor properties. Early results of CuGaO$_2$ shows good mitigation towards irradiation thus indicating that CuGaO$_2$ thin film is capable of withstanding harsh radiation environment while retaining its semiconductor properties.

1. Introduction

In the current age, p-type Copper (Cu) based delfaossite oxide-based semiconductor is vital as it is a wide bandgap (II-IV) semiconductor group and due to its potential applications in semiconductor technology [1]. The basic chemical formula of a delafossite structure is given as CuMO$_2$, where the Cu element is a positive monovalent cation (Cu$^+$), where M is given as a trivalent cation (Ga$^{3+}$) and oxygen with a negative divalent anion (O$_2^-$). The structure of anisotropic delfaossite has a lattice dimension of 2.976 Å and 17.5 Å along the a and c axes respectively [2].
Similar to other types of Cu-based delafossite semiconductor, CuGaO$_2$ shows significant electrical and optical properties. Over the recent years studies on the effects of metal oxide based semiconductor is attracting considerable research attention due to its superiority over amorphous silicon based semiconductor as reported by Ramirez in 2013 [3-5].

Based on past reviews, a research was conducted on the radiation response of Cu (In,Ga)Se$_2$ (CIGS) thin films solar cells due to high energy electrons and protons [6]. The thin film solar cells were irradiated with electron energies ranging from 0.23 MeV to 3 MeV. Based on the research findings, the effects of electron irradiation, electron fluences that causes an efficiency degradation greater than 10% of the thin film solar cells are found to be a larger than $10^{16}$ cm$^{-2}$. The threshold value that causes the drop in the efficiency of the electron energies were found to be around 1 MeV.

In 2007, a research was conducted on the $\gamma$ ray interaction with copper-doped bismuth-borate glass [7]. The samples were irradiated with a $^{60}$Co gamma cell of 2000 Ci with a dose rate of 1.5Gy/s at 30°C. From the data obtained, the unirradiated samples gives strong UV spectrum extending from 200nm to 1000nm while, irradiated samples reveal minor changes evident from the increase in the intensities of the UV bands with visible absorption at 470 nm and a very broad band about 750nm indicating the exposure of $\gamma$ irradiation shows obvious retardation [7].

On the irradiation studies of Cu based semiconductor, there are very limited research on the effects of irradiation. In this research, a magnetron sputtering method was utilized in fabricating CuGaO$_2$ thin films as this technique is able to produce a stable and homogenous deposition rate, producing a high purity of quality film. The effects of Gamma-ray towards the structural and optical properties of CuGaO$_2$ thin film will be discussed in this paper.

2. Materials and Methods

CuGaO$_2$ thin films were deposited on a commercially available Indium Tin Oxide (ITO) glass by Radio Frequency (RF) powered magnetron sputtering. The CuGaO$_2$ target disk with 99.99% purity, 3 inches diameter from Stanford Material Corporation was used. Preliminary steps include the cleaning of ITO substrate using distilled water, methanol, acetone for 10 minutes in an ultrasonic bath. The substrate was then rinsed in distilled water and dried with nitrogen gas. The magnetron sputtering chamber was pumped until $2.5 \times 10^{-5}$ Torr and the target were pre-sputtered for 15 minutes to remove surface impurities on the target disk. The deposition was carried out with an RF power set at 100 W, working pressure 9m Torr, a deposition temperature of 250 °C, an argon gas flow of 10 standard cubic centimeters per minute (sccm) and substrate rotation of 5 rotation per minute (RPM). Once the fabrication was completed, the samples were analysed using XRD where, the diffraction peak and full width half maximum will be incorporated into the Scherrer equation to calculate the grain size.

The grain size is obtained using Scherrer equation as shown in equation (1):

$$d = \frac{k\lambda}{\beta \cos \theta}$$  

(1)
K = shape factor constant

d = Average grain size

λ = the average wavelength of X-rays

β = FWHM

θ = Bragg angle

While the optical band gap of the thin film will be calculated using Beer’s law through the transmittance obtained from the UV-Vis spectrometer. (2):

\[ I = I_0 e^{-\alpha d} \]  
\[ \alpha = \frac{\ln(T)}{d} \]  
\[ (a\nu)^{1/n} = A(h\nu - E_g) \]  

\( I_0 \) = Initial intensity of light beam entering
\( I \) = Intensity of emitted radiation
\( \alpha \) = Optical Transmittance
\( d \) = Thickness of film
\( T \) = Transmittance
\( h \) = Planck’s constant
\( \nu \) = wavelength
\( E_g \) = Band gap

The structural design of the fabricated samples is as shown in Figure 1.

**Figure 1.** The structural design of p-CuGaO₂ on a substrate base of indium tin oxide.
On the optical properties, samples were analyzed using UV-Vis spectrometer Lambda EZ210. Fabricated samples were then irradiated with Cobalt-60 source utilizing JS10000 IR 219 tote irradiator system with an irradiation rate of 2 kGy/hr at MINTec-SINAGAMA. Samples were irradiated with an ionizing dose of 10 kGy, 50 kGy, 100 kGy, 150 kGy, and 200 kGy respectively. The structural and optical properties of the samples as post-irradiation were evaluated as well.

3. Results and Discussion

3.1 Structural Properties

Based on Figure 2, XRD analysis on the structural properties of pre-and post-irradiation of p-CuGaO$_2$ shows that the thin film retains its amorphous properties regardless of exposure towards radiation based on its broad wave. However, observable changes can be noticed at a total ionizing dose (TID) ranging from 50 kGy-200 kGy. The diffraction spectra with a lattice orientation of (006) is seen to have disappear indicating distortion of typical in the face centered cubic structure of the p-CuGaO$_2$ at higher radiation dose.

![Figure 2. X-ray diffraction (XRD) spectra of CuGaO$_2$ of un-irradiated and irradiated with a TID of 10 kGy, 50 kGy, 100 kGy, 150 kGy and 200 kGy respectively.](image)

Figure 3 shows the relation between changes in FWHM with the grain size of the sample with increasing TID. The results revealed that the full width half maxima (FWHM) of the samples increases with increasing ionizing dose. This indicates that the grain size diminishes as radiation dose was increased. At the highest TID of 200 kGy the sample shows a full width half maximum (FWHM) of 0.8089 with a grain size of 5.1286 nm, while un-irradiated sample shows a FWHM of 0.2749 with a grain size of 18.04 nm. This can be attributed to the strong effect of gamma-irradiation on the structure of p-CuGaO$_2$ and that FWHM is inversely proportional to grain size. However, at 150 kGy, there are no observable peaks. This indicates that the energy level of 150 kGy is at the maximum threshold of the CuGaO$_2$ thin film thickness. Based on the broad wave diagram obtained, the structural profile of the thin films was highly affected by gamma radiation, while at 200 kGy, the penetration depth of the energy exceeds the thickness threshold of the proposed thin film, where if the thickness of the semiconductor material is smaller compared to the projected range of the incident energy, the damage will be minimized [3].
Based on a research conducted by Al-Hamdani et al. (2014), it is shown that irradiating metal-oxide based semiconductor decreases the grain size which agrees to the findings in this research [8].

3.2 Optical Properties

Based on the analysis obtained from the UV-Vis spectrometer, the optical translucency becomes darker with increasing total ionizing dose (TID). The transmittance of unirradiated CuGaO$_2$ is about 75% while irradiated sample shows a decrement in transparency with increasing dose. The changes in the optical transmittance is as shown in Figure 5. This result is due to the formation of color centers. Oxygen vacancies are known as colour centres, or F centres (from Farbe, the German word for colour) [4]. It is believed that ionizing radiation causes structural defects, leading to a change in their density upon exposure to gamma-rays. The formation of colour centres has been associated with an increase in electrical conductivity, in which free electrons are produced as a result of band-to-band transitions and trapping of these electrons in oxygen ion vacancies. The translucency of the thin film is as shown in Figure 4.

From the optical transmittance, the direct band gap of CuGaO$_2$ thin films can be calculated using the intercept of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) plot. Utilizing Beer’s Law equations (2). Based on the calculated data, as ionizing dose is increased, the optical band gap is decreased.
Figure 6 shows the band gap changes. The band gap observed for 10 kGy, 50 kGy and 100 kGy, 150 kGy and 200 kGy are 3.85 eV, 3.74 eV, 3.68 eV, 3.68 eV and 3.62 eV respectively. Based on research, the optimum band gap for p-CuGaO$_2$ is 3.72 eV.

The changes in band gap is due to the increment of the separation between the valence and conduction band. However, the band gap for CuGaO$_2$ still retains its semiconductor properties even after irradiation.

Figure 5. Optical Transmittance of CuGaO$_2$

Figure 6. Optical Band Gap of CuGaO$_2$
4. Conclusion

It was observed that all the prepared CuGaO$_2$ thin films (pre-irradiation) were light-yellow to the eye and has a good transparency of 75%. The colour of the films become darker with irradiation due to the formation of colour centres. No observable change is noticed at 10 kGy and shows the same translucency with the unirradiated samples. TID ranging from 50 kGy to 200 kGy shows a decrease in the optical transmittance. Morphological structure of the thin films was significantly affected based on irradiation towards the grain size calculated at 200 kGy. Most of the radiation-induced defects are due to oxygen vacancies that to a certain extent cause degradation in the stoichiometry of the layers, however the spectra of CuGaO$_2$ remains unchanged.

5. References

[1] Al-Jawhari H A 2015 A review of recent advances in transparent p-type Cu$_2$O-based thin film transistors. *Mat. Sci. Semicond. Process.* **40** 241–252
[2] Yu R S and Lee Y C 2018 Effects of annealing on the optical and electrical properties of sputter-deposited CuGaO$_2$ thin films. *Thin Solid Films.* **646** 143–149
[3] Arshak K and Korostynska O 2004 Preliminary studies of properties of oxide thin/thick films for gamma radiation dosimetry. *Mat. Sci. Eng.: B.* **107**(2) 224–232.
[4] Arshak K and Korostynska O 2006 Response of metal oxide thin film structures to radiation. *Mat. Sci. Eng.: B.* **133**(1-3) 1–7.
[5] Ramirez J I, Li Y V, Sun K, Basantani H and Jackson T N 2013 ZnO thin film transistors for extreme environment applications. *Int. Semicond. Device Res. Symp. (ISDRS).*
[6] Jasenek A, Rau U, Weinert K, Schock H W and Werner J H 2003 Radiation response of Cu (In, Ga) Se$_2$/solar cells. *3rd World Conference on Photovoltaic Energy Conversion, 2003. Proceedings of IEEE.* **1** 593–598
[7] El-Batal F H 2008 Gamma ray interaction with copper-doped sodium phosphate glasses. *J. Mat. Sci.* **43**(3) 1070–1079
[8] Al-Hamdani N A, Al-Alawy R D and Hassan S J 2014 Effect of gamma irradiation on the structural and optical properties of ZnO thin films. *IOSR J. Comp. Eng.* **16**(1) 11–16.

Acknowledgments

The authors are thankful to Ministry of Higher Education (MoHE) and Universiti Malaysia Sabah for the financial support through Fundamental Research Grant Scheme (FRG0448-STG-1/2016), Skim Dana Khas (SDK0075-2019) and UMSGreat 2017 (GUG0131-1/2017).