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Research paper



Effect of Annealing Temperature of $Cugao_2$ thin Films by Using RF Magnetron Sputtering Technique on Optical and Structural Properties

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Abstract

Cu-based conductive oxide such as $CuGaO_2$ is seen to be a promising transparent p-type oxide material. The study of p-type semiconductor $CuGaO_2$ thin films have been carried out to investigate the effects of different parameters in providing the optimum result in achieving good optical transparency and conductivity of the thin film. The $CuGaO_2$ thin films were fabricated on quartz substrate via the Radio Frequency (RF) magnetron sputtering technique with varying substrate temperatures and different annealing temperatures. The p-type thin films were deposited at a temperature ranging from room temperature, 100°C, 200°C and 300°C. The samples were also annealed varying from temperature of 500°C, 600°C, 700°C and 800°C. The fabricated sample were characterized using X-ray diffraction (XRD), UV-Visible spectroscopy, and atomic force microscope (afm). XRD showed a peak at 2θ = 36.10° (012). The optical transparency values achieved from UV-Vis spectrometer were seen to be approximately 80% and the bandgaps were found to be in the range of 3.34-3.43 eV which is in line with the bandgap value from the research on $CuGaO_2$ thin films. From the afm, the mean surface roughness increases with increasing temperature and this is due to the increment of grain size. The highest grain size was observed at substrate temperature of 200°C.

***Keywords*:** *Annealing Temperature; $CuGaO_2$; RF Magnetron Sputtering; Thin Films.*

1. Introduction

The electronic industry has been well received by the current generation. Optoelectronics have intrigued the interest of many especially researchers due to its potential and demand in the marketplace. The basic electronic applications like LCD TV, mobile phones, electronic tablets and laptops have been the typical necessities in most societies we live in nowadays. Transparent Conductive Oxides (TCO) have been widely used not just due to its transparent properties but also their electrical properties in relevant devices which are commonly used in technological applications such as LEDs [1], flat panel displays [2], sensors [3] and transistors [4], which forms the basis of the optoelectronic industry. Most of the TCOs used are of the n-type semiconductors due to its good electrical properties such as SnO_2 [4], In_2O_3 [5] and ZnO [6]. In fabricating a TCO p-n junction diode, a good n-type and p-type TCO are needed. However, p-type conductivities are of several orders lower than the n-type semiconductors. The delafossite group was reviewed and showed potential in improving the p-type conductivities. Several p-types of the delafossite group such as $CuAlO_2$ [7] and $CuInO_2$ [8] and $CuGaO_2$ [3]. $CuGaO_2$ belongs to a p-type semiconductor group called the delafossite structure where is it has the formula of AMO_2 [9]. However, there were only few studies on the delafossite B-site cation Ga [2]. Previous studies emphasized on the effects of lower temperature post-treatment of the $CuGaO_2$ thin film, which were also limited with the use of glass that has a threshold of 550°C [10]. In this research, RF magnetron sputtering was used to deposit the $CuGaO_2$ thin films onto quartz with the effects of higher annealing temperature. The parameters involve different sputtering temperature and different annealing temperature in studying the effect on the thin film crystal structure. Post annealing improves the crystal structure of the $CuGaO_2$.

2. Research approach

$CuGaO_2$ target used in this experiment was of a purity of 99.99%, which was purchased from Stanford Material Corporation. The quartz substrates were cleaned using distilled water, acetone, methanol, ethanol and then distilled water again in an orderly manner for 15 minutes, all in an ultrasonic bath. Once the substrate was prepared, the deposition of $CuGaO_2$ thin films proceeded using RF magnetron sputtering. Pre-sputtering was first initiated before the fabrication of the samples. The pre-sputtering process was to eradicate contamination found on the target surface. The $CuGaO_2$ thin films were then deposited on quartz substrates at different sputtering temperature from room temperature, 100°C, 200°C and 300°C. Each sputtering process was 30 minutes long. Post annealing was performed with various temperatures on the samples of different sputtering temperature from 500°C, 600°C, 700°C and 800°C. Atomic force microscopy (afm) was used to

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evaluate the surface roughness. The structural and optical properties were characterized using X-Ray Diffraction Philips Expert Pro and UV-Vis Spectrometer Lambda EZ210.

2.1. Substrate cleaning

In cleaning the substrates, the sonicator is used to ensure an even and thorough wash of the substrates using acetone, isopropyl alcohol (IPA) and distilled water. Then, it is followed by using the nitrogen spraying method to dry the substrate prior sputtering [11].

In this research, the quartz slabs were cut into a 2.5 cm x 2 cm dimension before the cleaning process. The substrates then undergone a consecutive 15 minutes ultrasonic bath using distilled water, acetone, methanol, ethanol, and distilled water again. The substrates were then blown with nitrogen gas to dry in a clean chamber. The purpose of the alcohol is to ensure organic stains on the surface of the substrates are largely removed.

2.2. Radio frequency (RF) magnetron sputtering

$CuGaO_2$ target used in this experiment comes with a purity of 99.99%, which was purchased from Stanford Material Corporation. Throughout the process of handling the substrates, latex gloves must be worn to avoid further contamination on the surface of the substrates.

The sputtering chamber was then pumped until it reaches 7.0×10^{-6} Torr. The target was left to sputter for 10 minutes prior exposing the substrate to the process. Reason for the pre-sputtering process was to eradicate contamination found on the target surface. The RF power was set at 100 W and 80 sccm of argon gas was used as sputtering gas. The substrates were rotated at a speed of 5 rpm. In addition, the working pressure was approximately 4.0×10^{-3} Torr. The finishing touch was to have the samples annealed at 500°C, 600°C, 700°C and 800°C for three hours with a ramp rate of 100°C per minute.

2.3. UV-Vis spectroscopy analysis

The optical bandgap (E_g) can be obtained first by calculating the absorption coefficient (α) of the thin films by using the following equation:

$$\alpha = (1/d)ln(1/T) \quad (1)$$

where d is the film thickness and T is the transmittance of the film.

$$(ahv)^{1/n} = A(hv - E_g) \quad (2)$$

Where A is the absorption edge width parameter and hv which indicates the incident photon energy. The symbol n is either ½ or 2 depending if it is direct allowed transition or indirect allowed transition [12].

3. Results and Discussion

3.1. X-Ray Diffraction Spectroscopy (XRD)

Figure 1 shows the XRD pattern for the samples produced. The samples were then annealed at temperature of 500, 600°C, 700°C and 800°C. From Figure 1, we can observe that the peak is seen at approximately 2θ = 36.10 ° at annealing temperature of 800°C for all sputtering temperatures. Hence, the results shown indicates that the peak is achieved only at annealing temperature of 800°C at the orientation of (012) [13]. The rest of the XRD peaks are not significant from annealing temperature of 500, 600°C, 700°C, including the non-annealed samples (non-A). Reason being for no significant peaks is because the XRD graphs are in the amorphous state due to insufficient thermal energy in orientating the position of the atoms on the substrate surface for nucleation to happen [7].

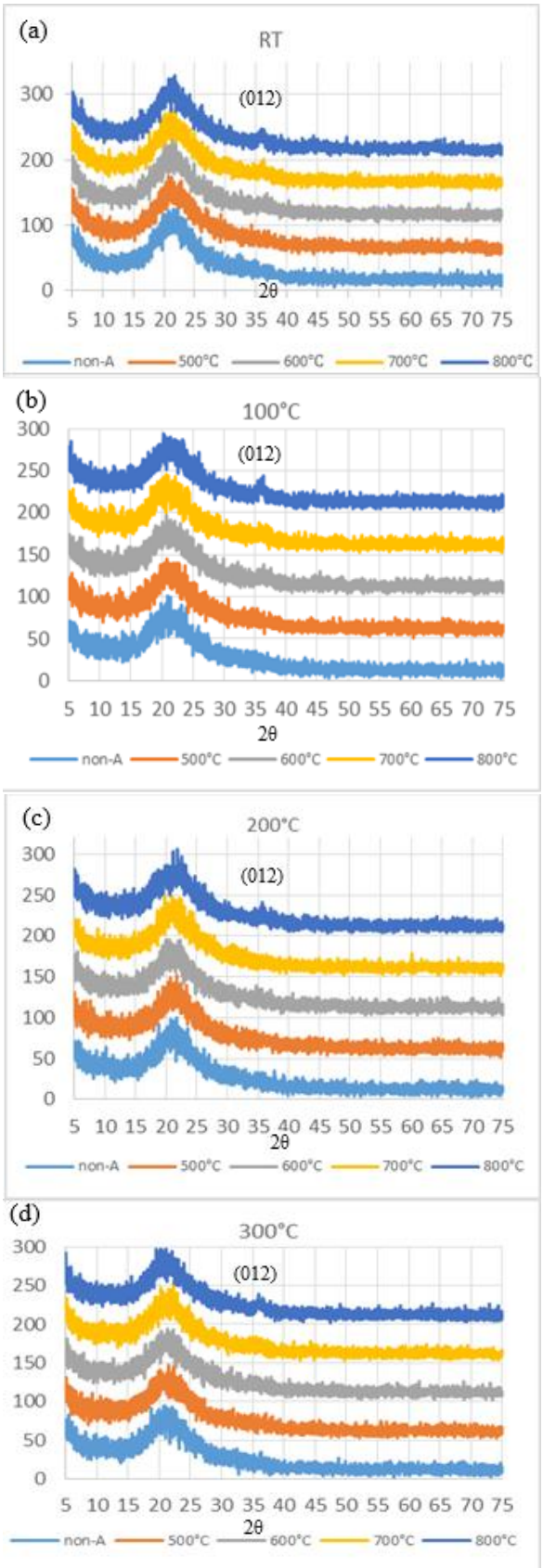


Fig. 1: XRD patterns of the thin films for sputtering temperature of (a) Room Temperature (RT), (b) 100°C, (c) 200°C and (d) 300°C with various annealing temperature from 500, 600°C, 700°C and 800°C, including a non-annealed sample (non-A)

Table 1: Grain Size of $CuGaO_2$ thin films of different sputtering temperature with post annealing temperature of 800℃

Substrate Temperature (℃)	FWHM	Grain Size (nm)
RT	0.26457	5.5
100	0.095833	15.2
200	0.075077	19.4
300	0.24875	5.9

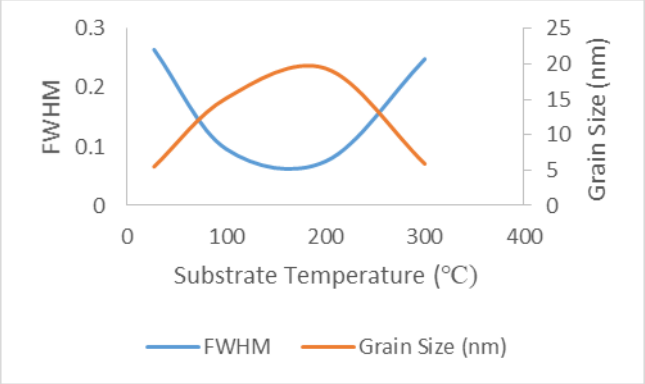


Fig. 2: Grain size for $CuGaO_2$ thin film deposited at room temperature (RT), 100°C, 200°C and 300°C with annealing temperature of 800℃

Since the XRD patterns for annealing temperature 800°C showed significant peaks, hence the samples of annealing temperature 800°C was studied specifically. The grain size of the thin films were seen to be increasing with temperature from room temperature (RT) towards 200°C before dropping sharply at 300°C. At lower substrate temperature, the atoms deposited are condensed and stuck in the region, forming small nuclei and clusters which leads to the smaller grain size. At higher substrate temperature, the mobility of the surface atoms and the cluster formation have increased, hence the larger grain size [14].

3.2. UV-Visible Spectroscopy (UV-Vis)

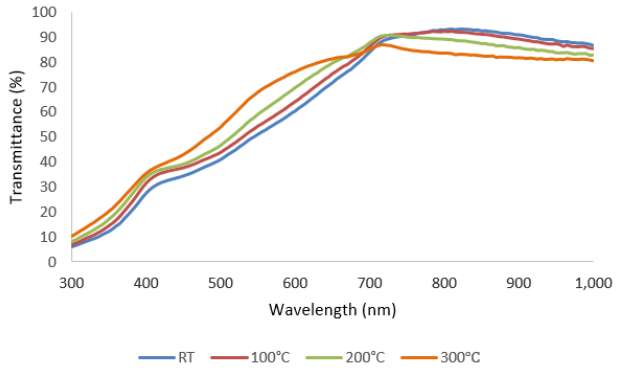


Fig. 3: Optical transmittance for $CuGaO_2$ thin film deposited at room temperature (RT), 100°C, 200°C and 300°C with annealing temperature of 800℃

Transmittance of the $CuGaO_2$ thin film is approximately 80%. Due to good structual homogeneity and crystallinity of the film, hence the high transparency [15]. As the sputtering temperature increases, it is observed that the absorption edge of $CuGaO_2$ thin film shifts to the shorter wavelengths. Reason for the better transmittance at higher temperature is due to better crystal arrangement than that of the lower temperature and also because light passing through the thin films are less scattered [10].
The plot of $(ahv)^2$ versus hv of the thin films are as shown below. The extrapolating of the linear line helped determine the optical band gap from the graph.

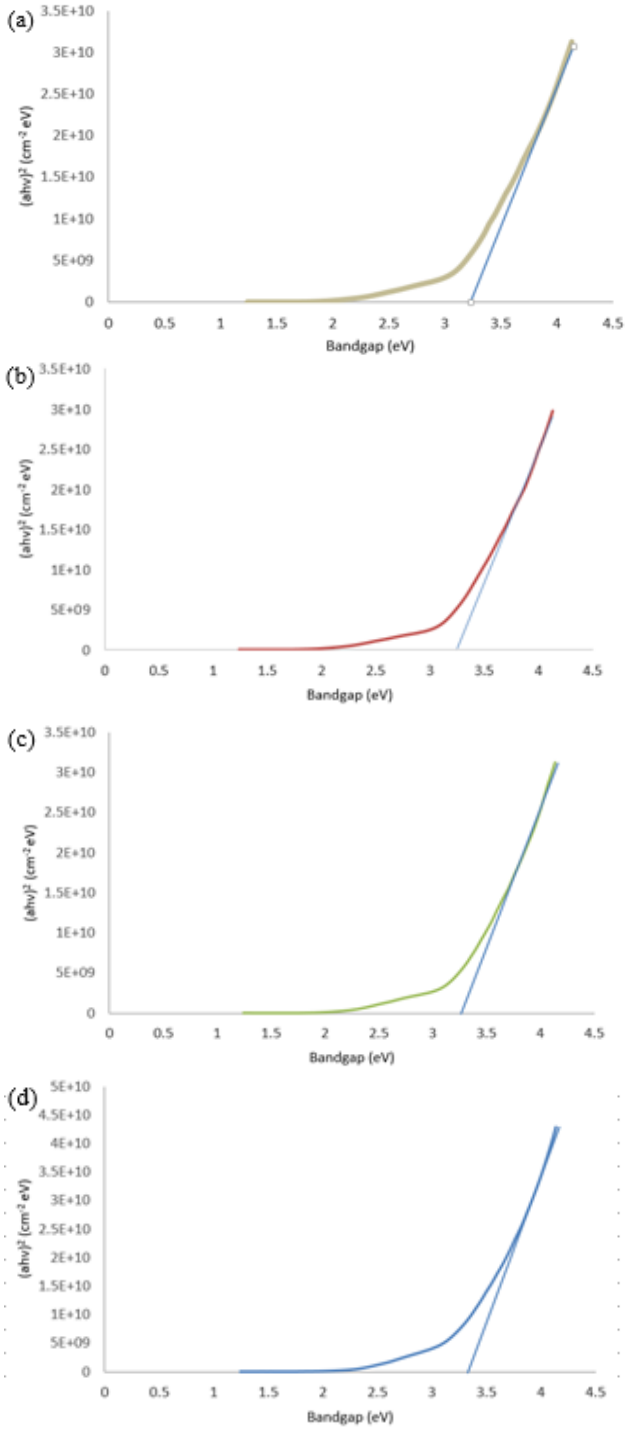


Fig. 4: Tauc plots of $CuGaO_2$ thin films at temperature (a) room temperature, (b) 100°C, (c) 200°C and (d) 300°C with annealing temperature of 800℃ to determine the bandgap

Table 2: Bandgaps of $CuGaO_2$ thin films of different sputtering temperature with post annealing temperature of 800℃

Substrate Temperature	Bandgap (eV)
Room Temperature	3.34
100℃	3.35
200℃	3.40
300℃	3.43

he bandgaps were determined from the calculation using Tauc equation and observation from the Tauc plots. As the substrate temperature increases, so does the bandgap of the substrates. This is a Moss-Burstein effect where the bandgap of the film is increased as the absorption edge is pushed to higher energy state due to some states close to the conduction band being populated.

3.3. Atomic Force Microscopy (AFM)

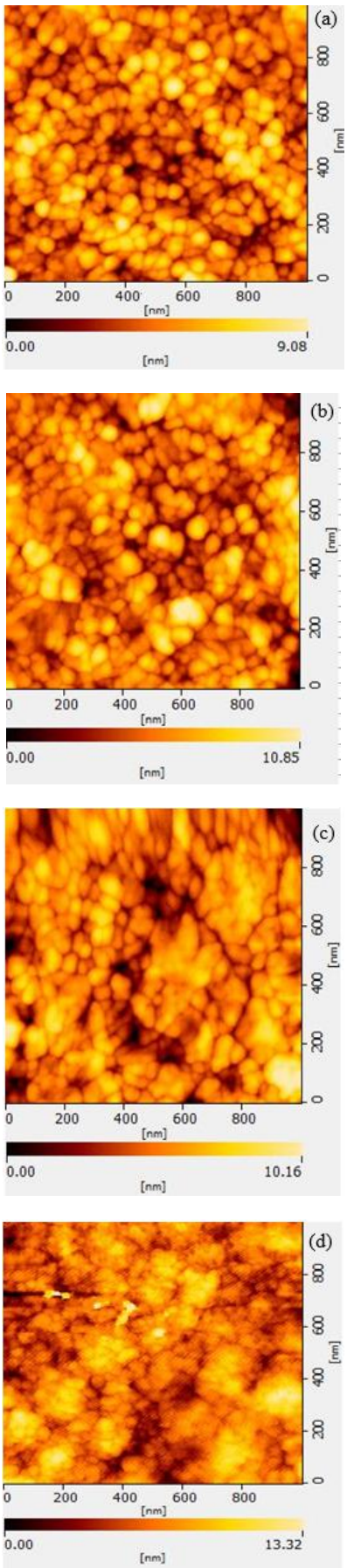


Fig. 5: AFM for $CuGaO_2$ thin film deposited at (a) room temperature (RT), (b) 100°C, (c) 200°C and (d) 300°C with annealing temperature of 800°C

Table 3: Mean roughness of $CuGaO_2$ thin films of different sputtering temperature with post annealing temperature of 800℃

Substrate Temperature	Average Surface Roughness (nm)
Room Temperature	5.170×10^{-3}
100℃	2.357×10^{-3}
200℃	4.830×10^{-1}
300℃	2.348×10^{-1}

As observed from Figure 5 of the different sputtering temperatures, as the temperature is increased from room temperature (RT), 100°C, 200°C and 300°C, the grain-like particles becomes more "fused" as they are closely packed and densely arranged. This possible phenomenan may be due to the nature of the rhombohedral structure of the faces of the $CuGaO_2$ crystal [16]. Hence, we observed from the average surface roughness in Table 3 that as the substrate temperature increases, the average surface roughness also increases with increasing grain size [17].

4. Conclusion

It is seen that there was no significant peak for the annealed thin films except that of the 800°C on the quartz substrate. This is likely due to the thin films being in an amorphous state. The transmittance were seen to be approximately 80% as the absorption edges of $CuGaO_2$ thin films shift to the shorter wavelengths. The optical bandgaps were measured in the range from 3.34 eV to 3.43 eV. The grain-like particles become more closely packed and the average surface roughness increases with increasing sputtering temperature.

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References

[1] Tsukazaki A, Ohtomo A, Onuma T, Ohtani M, Makino T, Sumiya M, Ohtani K, Chichibu SF, Fuke S & Segawa Y (2004), Repeated Temperature Modulation Epitaxy for p-type Doping and Light-Emitting Diode Based on ZnO. *Nat. Mater*. 4, 42-46.

[2] R. Bruce G, Nathan A, Meagan AM, Xiaoli T & David PC (2005), Synthesis, microstructure, and electrical properties of the delaffosite compound $CuGaO_2$. *Journal of Alloys and Compounds* 391, 262-266.

[3] Alias A, Mohamad KA, Gosh BK, Sakamoto M & Uesugi K (2012), Fabrication of $CuGaO_2$ Films by Sol-gel Method for UV Detector Application. *IEEE-ICSE2012*. 2, 763–765.

[4] Presley RE, Munsee CL, Park CH, Hong D, Wager JF & Keszler DA (2004), Tin Oxide transparent thin-film transistors. *Journal of Physics D: Applied Physics* 37, 20.

[5] Sahm T, Gurlo A, Barsan N & Weimar U (2007), Properties of Indium Oxide Semiconducting Sensors Deposited by Different Techniques. *Particulate Science and Technology* 24, 441-452.

[6] Dhara, S, & Giri PK (2012), Stable p-Type Conductivity And Enhanced Photoconductivity From Nitrogen-doped Annealed ZnO Thin Film. *Thin Solid Films*. 520(15), 5000–5006.

[7] Reddy AS, Park HH, Rao GM, Uthanna S & Reddy PS (2009), Effect of Substrate Temperature on the Physical Properties of DC Magnetron Sputtered $CuAlO_2$ Films. *Journal of Alloys and Compounds* 474(1–2), 401–405.

[8] Sasaki M & Shimode M (2003), Fabrication of Bipolar $CuInO_2$ with Delafossite Structure. *Journal of Physics and Chemistry of Solids* 64(9), 1675–1679.

[9] Liu Q, Liu Z, Chen J, Feng L & Tian H (2011), First-principles Study of Structural, Mechanical, Electronic and Optical Properties of 3R- and 2H- $CuGaO_2$. *Physica B*. 406, 3377-3382.

[10] Abu Bakar MH, Lam ML, Mohamad KA, Sulaiman S, Salleh S & Alias A (2015), Influence of Substrate Temperature and Post An-

nealing of $CuGaO_2$ Thin Films on Optical and Structural Properties. *AIP Conference Proceedings* 1674(020019), 1-5.

[11] Saurabh K & Screenivas K (2016), Residual Stress and Defect Content in Magnetron Sputtered ZnO Films Grown on Unheated Glass Substrates. *Current Applied Physics* 16, 748-756.

[12] Haarindraprasad R, Hashim U, Gopinath SCB, Kashif M, Veeradasan P, Balakrishnan SR, Mishra YK (2015), Low Temperature Annealed Zinc Oxide Nanostructured Thin Film-Based Transducers: Characterization for Sensing Applications. *PLoS ONE* 10(7), 1-20.

[13] Chien-Yie T & Ching-Lien C. (2017), Improved Electrical Properties of p-type $CuGaO_2$ Semiconductor Thin Films through Mg and Zn Doping. *Journal of Ceramics International* 43, 2563-2567.

[14] Mohamed JR, Sanjeeviraja C & Amalraj L (2016). Influence of Substrate Temperature on Physical Properties of (111) oriented $CdIn_2S_4$ Thin Films by Nebulized Spray Pyrolysis Technique. *Journal of Asian Ceramic Societies.* 4(2), 191-200.

[15] Zhang L, Huang J, Tang K, Ren B, Zhang S & Wang L (2016), The Effects of Substrate Temperature on Properties of B and Ga Co-doped ZnO Thin Films Grown by RF Magnetron Sputtering. *Journal of Surface & Coating Technology* 20977, 1-5.

[16] Chien-Yie T & Ching-Lien C (2017), Growth and Characterization of sol-gel derived $CuGaO_2$ Semiconductor Thin Films for UV Photodetector Application. *Journal of Crystal Growth* 468, 662-665.

[17] Ghorannevis Z, Hosseinnejad MT, Habibi M & Golmahdi P (2015), Effect of Substrate Temperature on Structural, Morphological and Optical Properties of Deposited Al/ZnO Films. *Journal of Theoretical and Applied Physics* 9(1), 33-38.