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Influence of annealing time on the morphology and oxygen content of ZnO:Ga thin films

P Marwoto[1*], L Khanifah[1], Sulhadi[1], Sugianto[1], B Astuti[1] and E Wibowo[2]

[1]Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Semarang, Indonesia

[2]Department of Engineering Physics, School of Electrical Engineering, Telkom University, Indonesia

*Corresponding author: pmarwoto@mail.unnes.ac.id

Abstract. The effect of annealing time on the morphology and oxygen content of ZnO:Ga films has been deeply studied. ZnO:Ga films were grown with the use of the dc Magnetron Sputtering on the corning glass substrate. The films are grown with a plasma power of 30 watt, Argon gas pressure of 500 mtorr, and a substrate temperature of 300 °C for an hour deposition. The effect of annealing time on the morphology of ZnO:Ga films was observed by using Scanning Electron Microscope (SEM), whereas the oxygen content of the film was determined by Energy Dispersive X-ray (EDX) spectrometers. The SEM images showed that the ZnO:Ga film grown with an annealing time of 40 minutes possess relatively more homogeneous and compact morphology with smoother grain size than the ZnO:Ga films that deposited with annealing times of 30 and 50 minutes. The EDX results confirmed that this film possess lowest oxygen content (24.5 % of mass) but highest Ga content (1.7 % of mass) comparated to the ZnO:Ga thin films grown with another annealing times.

1. Introduction

The transparent conducting oxide (TCO) possess a fascinating characteristics to be applied as gas sensors, optical detectors, transparent electrodes, and solar cells [1, 2]. One of the most popular TCO that commonly used today is indium tin oxide (ITO). Nevertheless, ITO is considered as one of the toxic material and is it relatively expensive due to the scarcity of Indium element. Hence, it is necessary to develop a new TCO material that can substitute the ITO.

Zinc Oxide (ZnO) is a semiconductor material with a relatively high binding energy of 60 MeV [3], a direct band gap of about 3.37 eV, a significantly low fabrication cost, as well as a non-toxic material [4]. However, in a corrosive environment, ZnO is known to be quite unstable and poor electrical properties due to low carrier concentration charge [5]. The doping of Group IIIA elements such as: Boron (B), Indium (In), Aluminum (Al) and Gallium (Ga) on ZnO can enhance the level of stability and electrical conductivity to as high as 10^5 Ω.cm [6]. Among the doping materials, gallium (Ga) is considered as the best material choice owing to the fact that it holds an identical atomic radius as Zn [7] and the conductivity level measures higher than that of aluminum [8]. Besides, it is an element that has been evident to be less reactive and resistant to the oxidation. ZnO:Ga thin films exhibited relatively higher concentrations of the carrier mobility, as well as better thermal stability in comparison with un-doped ZnO thin films [9].

The characters of thin films are accredited to the fabrication and recrystallization processes [10]. The production of ZnO thin films can be carried out through various kinds of deposition techniques, such as sputtering techniques [11] pulsed laser deposition (PLD) [12], sol-gel [13], evaporation [14], electrolysis [15], and chemical vapor deposition (CVD) [16]. Dc Magnetron Sputtering has various advantages compared to other methods such as: it can be operated at low temperatures, it is able to grow thin films of materials that have a high melting point, it produces high quality films [1], it considered as simple deposition processes, and deposition costs are relatively low [16]. The previous studied [11] have shown that ZnO thin films with Ga(2%) doping have high crystal quality and optimum optical properties.

The parameters of the deposition and post-deposition process of ZnO films affect the internal composition being crystallinity and Zn-O bonding. The absent of oxygen in the ZnO film has a chance of resulting the crystal defects in the form of vacuities or interstitial oxygen. Annealing treatment is implemented in form of a recrystallization process to enable the atoms which have developed on the surface of corning glass substrate to restructure so it can cast films with a more uniform homogeneous morphology and crystal formation. However, in the post-deposition of annealing processes, it is impossible for oxygen to be released from the film surface, and this as a result influences the morphological structure and oxygen content of the film. Therefore, in this experiment, we examined the effect of annealing time on the films morphology and oxygen content of ZnO thin films that are doped by Ga element of 2%. The morphology of ZnO:Ga(2%) thin films were observed by using Scanning Electron Microscopy (SEM), while the oxygen content in the film was analyzed with the aid of Energy Dispersive X-ray (EDX).

2. Methods

The Dc Magnetron Sputtering method was efficiently used to growth of ZnO:Ga(2%) thin film. The ZnO:Ga(2%) target was made from the mixture of both ZnO powder 99.999% and Ga_2O_3 powder 99.999% at the ratio of 98 wt% and 2 wt%, respectively. The procedures for making the target includes 3 hours of powder grinding, compaction of powder into 2.5 cm pellets, and then sintered at 750 °C for duration of 2.5 hours. The growth of film is performed on a 1x1 cm corning glass substrate that has been washed with acetone and methanol solutions making use of an ultrasonic bath. ZnO:Ga thin film was deposited on a 30 watt plasma power, Argon gas pressure of 500 mtorr, substrate temperature of 300 °C for 60 minutes. The film has been grown and annealed within a vacuum for 30, 40 and 50 minutes. Furthermore, the morphology of the ZnO:Ga film was examined with the use of a Scanning Electron Microscope (SEM), while its oxygen content was observed with an Energy Dispersive X-ray (EDX) characterization.

3. Results and discussion

The morphology of ZnO:Ga thin film with a variation of annealing time was observed with the use of SEM characterization with a magnification of 40,000 times as illustrated in Figure 1. Based on Figure 1, it can be seen that the ZnO:Ga thin film experiencing the change in morphological homogeneity along with the increasing annealing. The ZnO:Ga film with 40 minutes annealing time seems to have a more homogeneous, compact, and evenly distributed morphology compared to the ZnO:Ga films with 30 and 50 minutes annealing. In the annealing process, the energy given to the atoms making up a thin film is proportional to the temperature and the length of the annealing time. Both of these factors are able to influence the kinetic and thermodynamic processes that responsible to the rearranging the atoms distribution in the ZnO:Ga crystal [16]. A prolonged annealing time results in the detachment of the arranged atoms of thin films. This condition leads to the vacancy which affects the crystal structure and morphology of the thin films. While, too short the annealing time causes the rearrangement process of the atoms not properly conducted so that the less homogeneous morphology of ZnO:Ga film is formed.

It can be seen from Figure 1 that the grain boundaries of ZnO film are get large along the annealing treatments. The large of the grain boundaries of ZnO:Ga film that annealed for 50 minute can be caused by an interstitial defect in the grain boundaries area. The movement of an atom to the grain boundaries area causes the disturbing of the crystal growth (grain), leads to decreasing the crystal size and the grain boundaries of the film become larger. The large grain boundaries in a crystalline arrangement can increase the scattering properties of material [17]. As a result it reduces the material transmittance and create a barrier that resulting an increase of resistivity and decrease the conductivity of ZnO:Ga thin films.

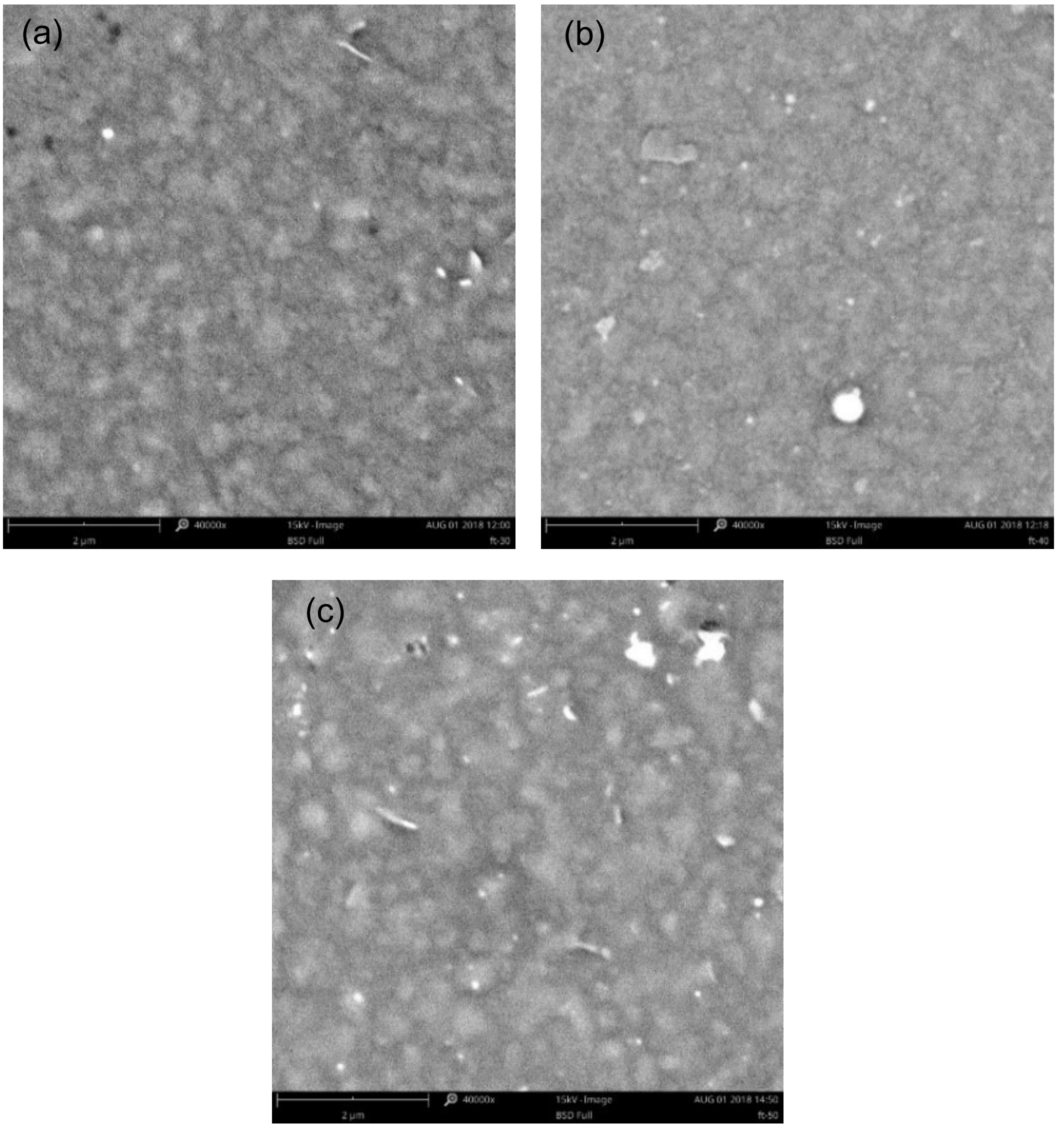

Figure 1. SEM image of ZnO thin films with variation of annealing time (a) 30 minutes, (b) 40 minutes, and (c) 50 minutes.

The EDX results as showed in Figure 2 confirmed that ZnO:Ga thin films for all variations of annealing time contain elements of zinc (Zn), gallium (Ga), oxygen (O), silicon (Si), and aluminum (Al). Based on laboratory data gathered from TedPella.Inc (Microscopy Products for Science and Industry), it has been established that Si and Al are constituent elements of corning glass that is employed as substrate. Hence, it can be concluded that the constituents of ZnO:Ga thin films are Zn, Ga, and O elements. The content percentage of each element of the film for three annealing time variations is illustrated in Table 1.

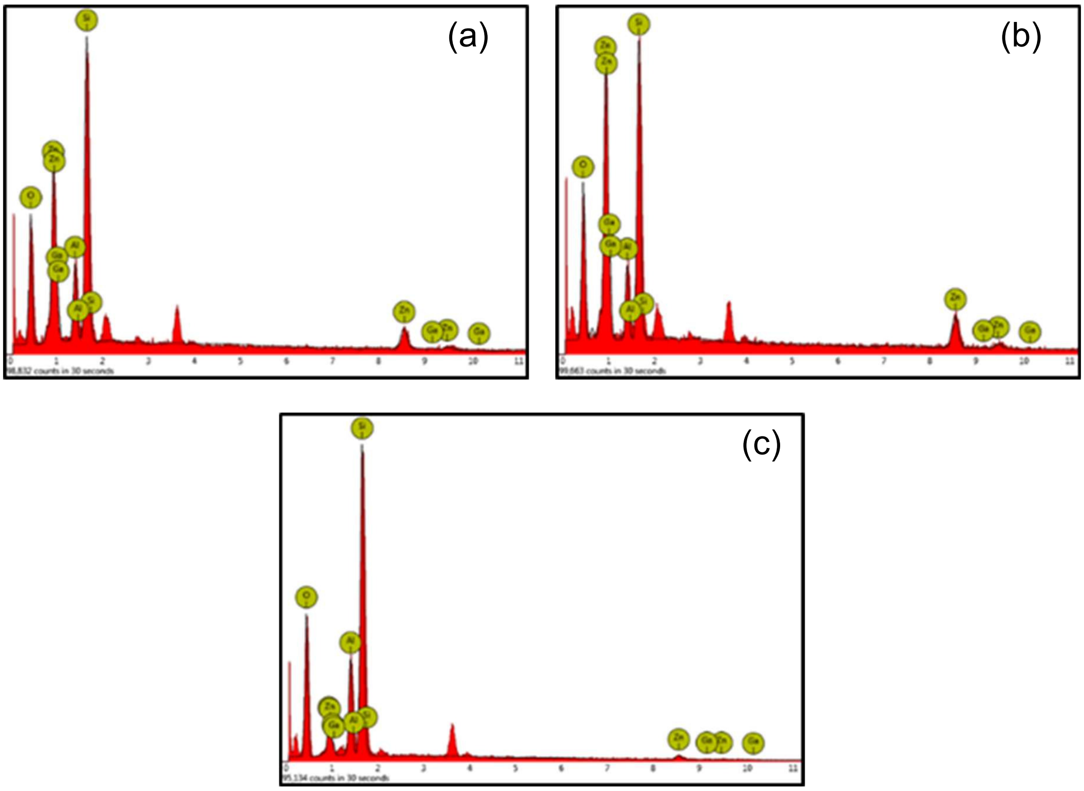

Figure 2. The EDX spectrum of ZnO:Ga thin films with variation of annealing time. (a) 30 minutes, (b) 40 minutes, and (c) 50 minutes.

Table 1. Percent of mass of element content of ZnO:Ga thin films.

Annealing Time (minutes)	Elements (%)				
	Zn	O	Ga	Si	Al
30	31.2	28.2	1.5	30.7	8.4
40	39.7	24.5	1.7	26.6	7.4
50	8.4	43.1	1.4	36.1	11.1

The EDX results showed that the Zn and Ga elements increase with the annealing time of 30 to 40 minutes, and diminished with an annealing time of 40 to 50 minutes. Conversely, the percentage of O element is decreases along the annealing time of 30 to 40 minutes, and then increase once the annealing time is increased to 50 minutes. An increased of Ga content leads to the increase of the charge carrier concentration and conductivity of thin film [11]. It due to the partial substitution between Ga^{3+} and Zn^{2+} ions; the Ga^{3+} ions donating one free electron on the ZnO:Ga thin films [17]. The small oxygen content in thin films can indicate the presence of oxygen vacancies in the crystal arrangement. In contrast, the excess oxygen content can cause defects in the film and lead to degradation of the quality of crystals [18]. The high amount of oxygen element in the ZnO:Ga film that was annealed for 50 minutes indicates the presence of oxygen interstitial in the crystal, thus disrupting the nucleation and crystal growth process. As a result, the ZnO:Ga film grown with rough morphology with the contrast grain boundaries as confirmed by SEM image in Figure 1.

4. Conclusion

The ZnO:Ga thin films have been successfully grown by using dc Magnetron Sputtering. The ZnO:Ga films were treated by annealing treatment after deposition process. It can be seen that the film treated by the annealing time of 40 minutes possess relatively more homogeneous, and compact morphology compared to the ZnO:Ga films deposited with annealing times of 30 and 50 minutes. This film possess lowest oxygen content (24.5 % of mass) but highest Ga content (1.7 % of mass). The high concentration of Gallium content with low Oxygen consideration is supposed might enhanced the conductivity of ZnO:Ga thin film.

References

[1] Noh W-S, Lee J-A, Lee J-H, Heo Y-W, and Kim J-J 2015 *Ceram Int* **42** 4136
[2] Chen S, Warwick M E A and Binions R 2015 *Sol Energy Mat Sol Cells* **137** 202
[3] Yu L, S Liu, B Yang, J Wei, M Lei and X Sahu B B, Jeon G Han, Masaru H and Keigo T 2015 *J Appl Phys* **117** 023301
[4] Efafi B, S Soraya M, Mohammad H Majles Ara, Bijan G and Hamid R Mazandarani 2017 *Mater Lett* **195** 52
[5] Young S J, C C Yang and L T Laia 2017 *J Electrochem Soc* **164** B3013
[6] Buyanova I A, Wang X J, Wang W M, Tu C W and Chen W M 2009 *Superlattices Microstruct* **45** 4
[7] Su W F, C W Chen, J J Wu and Y Y Lin 2016 U S Pat US 9.269,840 B2
[8] Amara S and Mohamed B 2014 *J Mater Sci: Mater Electron* **26** 3
[9] Young S J, C C Yang and L T Laia 2017 *J Electrochem Soc* **164** B3013
[10] Awang R, Siti N H M Daud, Chi C Yap, Mohammad H H Jumali and Z Zalita 2013 *Sains Malaysiana* **42** 1663
[11] Kumarasinghe P K K, A Dissanayake, B M K Pemasiri and B S Dassanayake 2017 *Mat Sci Semicond Process* **58** 51
[12] Maller R, Porte Y, Alshareef H N and McLachlan M A 2013 *J Mat Chem C* **04** 149
[13] Marwoto P, Wibowo E, Suprayogi D, Sulhadi, Aryanto D and Sugianto 2016 *Am J Appl Sci* **13** 1394
[14] Yu L, Liu S, Yang B, Wei J, Lei M, Fan X2015 *Mat Lett* **141** 79
[15] Chen S, Carraro G, Barreca D and Binions R 2014 *Thin Solid Films* **584** 316
[16] Wang Y, W TangW and Zhang L 2015 *J Mat Sci and Tech* **31** 175
[17] Wang G-G, Zeng J , Han J-C, and Wang L-Y 2013 *Mat Lett* **137** 307
[18] Abdallah B, Jazmati A K and Refaai R 2017 *Mat Res* **20** 607