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Structural and morphological study on ZnO:Al thin films grown using DC magnetron sputtering

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Abstract. ZnO doped Al (ZnO:Al) thin film was deposited on corning glass substrate using DC magnetron sputtering method. Depositon process of the ZnO:Al thin films was kept constant at plasma power, deposition temperature and deposition time are 40 watt, 400°C and 2 hours, respectivelly. Furthermore, for annealing process has been done on the variation of oxygen pressure are 0, 50, and 100 mTorr. X-ray diffraction (XRD), and SEM was used to characterize ZnO:Al thin film was obtained. Based on XRD characterization results of the ZnO:Al thin film shows that deposited thin film has a hexagonal structure with the dominant diffraction peak at according to the orientation of the (002) plane and (101). Finally, the crystal structure of the ZnO:Al thin films that improves with an increasing the oxygen pressure at annealing process up to 100 mTorr and its revealed by narrow FWHM value and also with dense crystal structure.

1. Introduction

ZnO is a semiconductor material composed of class II-VI which has a wurzite hexagonal crystal structure. ZnO also includes on wide band gap material and a n-type seniconductor with direct optical band gap around 3.37 eV and exciton binding energy of 60 meV [1-2]. Its causes ZnO to be very suitable for wide band gap aplication such as light emitting diodes, dye sensitier solar cells, sensors, and detector [3]. Pure ZnO has a poorly structured unit that can be repaired by doping [4]. Al metal is the best element among other class III A elements can be used as a dopant material, which is based on the highest electron mobility of Al and doping Al provides high level carrier electrons [5]. Al contributes to width band gap ZnO with increasing concentrations of carriers known as the Burstein-Moss effect [6]. ZnO doping Al is highly potential to be applied as TCO [7].

Deposition of ZnO thin films can be carried out by various methods including metal oxide chemical vapor deposition (MOCVD) [8], sol-gel-dip-coating [9], pulsed laser deposition [10], electrodeposition [11], chemical spray pyrolysis [12-14]. Another method of ZnO thin film growth is using sputtering method [15]. Sputtering method based on the spreading was divided into two, namely radio frequency (RF) sputtering and direct current (DC) magnetron sputtering. In this study , ZnO :Al thin films was grown using DC magnetron sputtering method. Its because the advantage of DC magnetron sputtering method was produced a good thin film quality, simple process and a low cost production.

To obtain a good properties of ZnO:Al thin film can also performed using annealing process. In the previous work, the research based on the annealing effect has been done, that was obtained the optimum annealing temperature is 300°C [16]. Other parameter has effect on the crystallinity and structure of the film such as oxygen presuure during annealing process. Based on Kim *et al.*, [17], the entering of oxygen at the annealing process can increase the crystallinity, transmittance and improve surface morphology in thin films was obtained.

In this study annealing process will be carried out in the oxygen environment of thin film ZnO doping Al (3%) at a temperature of 300 with oxygen pressure variations ie 0 mTorr, 50 mtorr, 100 mtorr, 150 mtorr and 200 mTorr for 20 minutes [17].

2. Methods

In this experiment, the ZnO:Al target maked from compound of ZnO(MW09023 USA with purity 99.99%) and Al_2O_3 powder (MA01950 USA with piruty 99.999%) in total mass of 10 gram. The complete pellet-making mechanism can be seen in the previous paper [16]. The ZnO thin film deposition process is performed on a corning glass substrate. Corning glass substrate is cut to the size of approximately (1 x 1) cm^2. After that the substrate was immersed in the methanol to remove the oil impurities were attached on the substrate surface for 15 minutes in ultrasonic bath. Subsequently substrate was immersed in acetone for 10 min in ultrasonic bath. Finally the substrate is sprayed with nitrogen gas to keep the substrate dry and clean. Furthermore, parameter of ZnO: Al thin films grown as shown in Table 1.

Table 1. Deposition and annealing parameter of ZnO:Al thin films.

Parameter	Description
Deposition	
Temperature	400°C
Argon Pressure	500 mTorr
Plasma Power	44, 616 watt
Time	120 menit
Annealing Process	
Oxygen pressure	0, 50, 100 mTorr
Time	20 menit
Temperature	300°C

Furthermore, the characterization process of the ZnO:Al thin films was obtained has been done using X-ray diffraction (XRD) and Scanning electron microscope (SEM). XRD characteristics was used to determine the structure of the samples. Surface morphology of the films was obserb using SEM Phenom ProX.

3. Result and Discussion

ZnO:Al thin film was deposited on the corning glass substrate and annealed on oxygen environments with oxygen pressure variations has been performed. Crystallography structure of the ZnO:Al thin film was observed using X-ray diffraction (XRD) with a Cu-Kα radiation source (λ = 0.15406 nm). The XRD characteristics of the ZnO:Al thin films are shown in Figure 1.

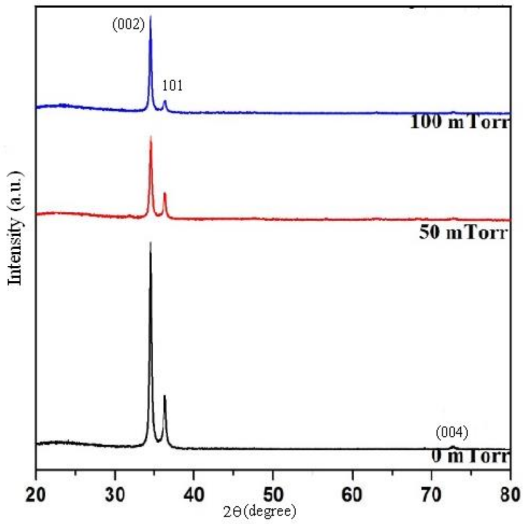

Figure 1. The result of XRD characterization of ZnO:Al thin film samples with oxygen pressure variation on annealing process.

The data was obtained from the diffractogram results then compared with JCPDS data (04-015-4060) in order to identify the orientation of growing crystal structure on the substrate. Based on Figure 1, shows the diffraction peak of a ZnO:Al thin film was attributed a polycrystalline structure. The structure of this polycrystalline film is similar to the previous researcher [7]. The diffraction peak of ZnO:Al thin film with oxygen pressure variation in the observed annealing process corresponds to the dominant plane of (002) and (101). This indicates that the ZnO:Al thin film has a polycrystalline structure with the wurtzite hexagonal phase [18]. The hexagonal structure shows that uniform grain growth is perpendicular to the surface of the substrate [19]. The peak intensity of the ZnO:Al diffraction decreases with the increases oxygen pressure applied to the annealing process. This is due to the reduction of kinetic energy in the reactive compound with increased oxygen concentration in the chamber that limits the diffusion of the surface of the atom [20]. Crystal plane (002) and (101) can be applied on photo anoda single layer and double layer on Dye-Sensitized Solar Cell (DSSC), respectively [21]. Furtehrmore, based on XRD characterization data is also used to determine full width at half maximum (FWHM), lattice parameter, *d*-spacing and crystal size was summarized in Table 2.

Table 2. XRD analysis results of ZnO:Al thin film with a variation of oxygen pressure at the peak of orientation (002).

Oxygen Pressure (mTorr)	2θ (°)	FWHM (°)	Crystallite Size (nm)
0	34.48	0.40	20.09
50	34.52	0.42	18.99
100	34,48	0.37	21.66

Table 2 shows that Bragg angle,2θ, FWHM, and crystallite size of the (002) plane. Based on the Table 2, its clear that the 2θ of the ZnO:Al thin film samples was shifted to the large 2θ, when the sample was increased oxygen pressure at annealing process from 0 mTorr up to 50 mTorr. Its caused by decreasing of interplanar distance on the atoms [22]. Furthermore, the quality of ZnO: Al thin film also can be seen from the FWHM value. Thin films with small FWHM values indicate that the film has a good crystal quality [1]. The FWHM value of ZnO:Al thin film was increased up 0.02^{o} when the oxygen pressure increases from 0 mTorr to 50 mTorr. The size of the crystal of ZnO:Al thin films at 0 mTorr and 50 mTorr oxygen pressures decreased 20.09 nm to 18.99 nm, but when the oxygen pressure was increased to 100 mTorr, the crystallite size increase to 21.66 nm. This similar to the Huang *et al* [23], which is the size of the crystal increases when the oxygen was applied on the annealing process rather than vacuum or annealing without oxygen. ZnO:Al thin film processing in the oxygen environment causes the incorporation of oxygen in the film, which then compensates for vacancies [19]. It is expected that the oxygen void decreases with annealing in the oxygen environment due to the incorporation of oxygen in the film. Therefore, studies of films that are annealed under different oxygen pressure conditions are essential for obtaining high quality thin films. The largest crystal size was found in the ZnO:Al thin film at 100 mTorr oxygen pressure as inverse to the smallest FWHM values [24].

The small crystallites size will reduce the grain boundary size. Grain boundary is the surface or area that connects between two grains of a single crystal. The crystal size change and the FWHM film value state the level of the lattice strain in the film. The smaller FWHM value causes the smaller of the lattice strain level in the film. The presence of lattice strains in the film indicates the occurrence of stress in the film. Stress in the film was affected in the quality of the thin film crystal was obtained. The value of the lattice strain and stress of the ZnO:Al thin film grown is shown in Table 3.

Table 3. The value of lattice strain and stress of ZnO:Al thin film with oxygen pressure variation on the annealing process.

Oxygen pressure (mTorr)	Lattice strain (%)	Stress (GPa)
0	0,32	-0,75
50	0,34	-0,79
100	0,29	-0,70

Lattice strains shows that crystal has structure defects. The smaller lattice strain of the film meant the film was obtained has a good quality and the vice versa, the larger of the stress value affecting on the quality of the film as good quality. The increases of the stress is an affected of the decreases in oxygen atom on the chamber during annealing process [18]. A large stress value indicates the magnitude of the forces between the atoms of the crystal constituent. Stress is proportional to the magnitude of the bonding force between atoms, so the higher stress was produced high the bonding force between atoms. Negative stresses show the pressure on films that are impacted by the environment. The bonding force between atoms is proportional to the binding energy of crystals, this energy is needed to separate the atoms in the crystal. Vibration of the lattice which plays a role in the formation of energy in the crystal shows the homogeneity of the arrangement of atoms in the crystal. The atoms in this arrangement are not free to move due to the force. The atoms that make the crystal always vibrate (vibration) to the equilibrium position, so the higher value of the stress meants the arrangement of the atoms in the film more homogeneous.

For the surface morphology was analysed using scanning electron microscopy (SEM). Figure 2 present SEM images of the ZnO:Al thin films with different oxygen pressure at annealing process. The surface morphology of ZnO:Al thin films has rice grain-like appearance. Figure 2(a) shows the grain size of the films on average relatively small and homogeneous films on annealing without oxygen or oxygen pressure of 0 mTorr. The larger grain size with a rough surface morphology on annealing with oxygen pressure of 50 mTorr was observed in Figure 2(b). Also its can be shown the morphology of the crystalline grain become dense when the oxygen pressure was increased up to 100 mTorr. This finding is to be expected since a higher oxygen pressure at annealing process has enough time for oxygen from the environment to fill on the ZnO:Al structure. These results are consistent with reports Hsu *et al*.,[24], the texture of the film should be treated differently when oxygen pressure variation, the grain size is increased in certain oxygen pressure. Based on the report of Chen *et al*., [25], ZnO thin films by oxygen in the annealing process has a better crystal. The larger of grain size on the surface morphology of the crystals its means crystal has a good quality [22,26]. Based on the Figure 2, its also can be seen, for the crystal structure is not to be changed with increasing the oxygen pressure at annealing process. As a result, the variation of the oxygen pressure at annealing process causes enlargement of grain size and dense of the surface morphology of thin films.

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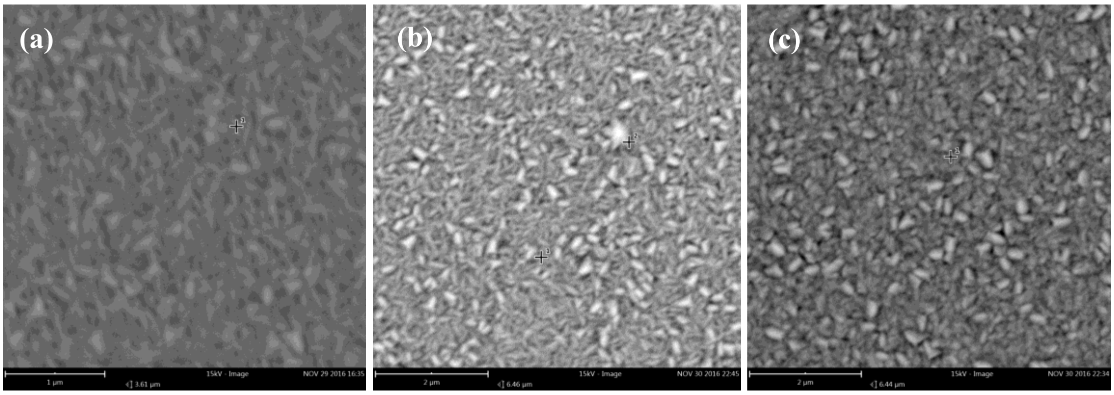

Figure 2. SEM images of ZnO:Al thin films with Oxygen pressure at annealing process : a) 0 mTorr, b) 50 mTorr, and c) 100 mTorr.

4. Conclusion

ZnO:Al thin films were deposited on corning glass by DC Magnetron sputtering. The effect of oxigen pressure on the anealing process on the structure and morphological properties of ZnO:Al thin films were studied by XRD, and SEM characterization. According to the XRD results reveal that the deposited thin films has a polycrystalline hexagonal wurtite structure with the dominant orientation of (002) and (101) plane. Among the ZnO:Al thin films, the ZnO:Al thin film annealed at oxygen pressure of 100 mTorr exhibit the small FWHM value or the crystallite size is larger means the quality of the film is good. That result also supported by SEM result. So, we suggest that the oxygen pressure of 100 mTorr is the most suitable pressure at annealing process for obtaining high quality of ZnO:Al thin films with good structure and morphologycal properties.

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