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The effect of annealing on ZnO:Al thin film growth on preparatory glass substrate by dc magnetron sputtering

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Abstract. Al doped ZnO (or ZnO:Al) thin films were deposited onto a preparatory glass substrate using dc magnetron sputtering. The effect of annealing time was 0, 30 and 50 minutes onto the structural, morphological, optical properties and electrical properties of the ZnO:Al films have been investigated. Thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) and I-V measurements, respectively. XRD measurement showed that each sample had an amorphous structure. The morphology of the film was more homogeneous when annealed in 50 minutes. PL characterization showed two emission peaks, namely blue emissions at a wavelength of 447 nm and red emissions at a wavelength of 752 nm. ZnO:Al film with an annealing time of 50 minutes had a higher blue emission PL intensity than other films.

1. Introduction

The semiconductor oxide material is very potential for the manufacture of optoelectronic devices. Zinc oxide (ZnO) has a direct energy band gap of 3.37 eV and exciton binding energy at 60 meV at room temperature. ZnO is a semiconductor oxide material which has excellent thermal stability compared to other materials, for example, gallium nitride which has 25 meV binding energy [1]. Therefore, ZnO material is suitable for optoelectronic applications in wide band gap devices such as light-emitting diodes, color-sensitive solar cells, sensors, and detectors [2]. The electrical properties of ZnO can be increased through doping with cations of trivalent metal, usually using B, Al, or Ga element [3]. Group III elements generally have a higher valence with ionic size smaller than Zn^{2+} host cations. The substitution of the group III element dopant into host Zn site will produce excess electrons which will contribute to the addition of electrical conductivity of the ZnO material [5]. Among group III elements, aluminum metal is the best element to be used as a doping material because it has high electron mobility. Thus, it is expected that aluminum doping can increase the number of carrier electrons in ZnO material [6, 7]. Al doped ZnO (or ZnO:Al) which has a high concentration of electron carrier is very potential for applications in transparent conductor oxide (TCO) for applications in solar cells [8].

The growth of ZnO thin films has been carried out by various methods, including pulse laser deposition (PLD) [9], metal organic chemical vapor deposition (MOCVD) [10], pyrolysis [11], dip coating [12], electro-deposition [13], and sputtering [14]. In this study, ZnO:Al thin films were grown using the dc magnetron sputtering method under consideration that dc magnetron sputtering was able to produce good quality thin films with simple process and low production costs.

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Efforts to improve the quality of ZnO:Al thin films have been carried out, i.e. by performing annealing after the film growth process [15, 16]. Through the annealing process after the growth of thin films, it is expected to improve the atomic structure of the ZnO film. Post-growth annealing treatment of ZnO with dc magnetron sputtering was carried out in previous studies with optimal annealing temperature at 300°C [17]. In this study, ZnO:Al thin films were deposited on the preparatory glass substrate (low price and easily purchased) by dc magnetron sputtering. Furthermore, ZnO:Al thin films annealing process was carried out in a vacuum sputtering chamber at 300°C with various annealing time.

This paper focuses on the effect of annealing time on structure, morphology, optical properties and electrical properties of ZnO:Al thin films. The photoluminescence and the electrical properties of the ZnO:Al films are discussed in detail and emphasized the practical application of the ZnO:Al film.

2. Methods

ZnO:Al thin films in this study were grown with homemade dc magnetron sputtering. ZnO:Al target used was made from ZnO (MW09023 USA with 99.99% purity) and Al_2O_3 powder (USA MA01950 with 99.999% purity), with ratio of Al_2O_3 mole fraction of 3%. The target mass total of ZnO:Al was 10 grams. The complete stages of target making could be seen in the previous paper [17]. A preparatory glass was used as substrate for ZnO:Al thin films growth. The preparatory glass substrate preparation was done by cutting the preparatory glass with a size of approximately (1x1) cm^2. After that, the substrate was immersed in methanol to remove oil impurities on the surface of the substrate for 15 minutes in an ultrasonic bath. The substrate was then immersed in acetone for 10 minutes in an ultrasonic bath. Finally, the substrate was sprayed with nitrogen gas to keep the substrate dry and clean. In addition, ZnO:Al thin films were grown with deposition parameters as shown in Table 1.

The ZnO:Al film was grown at 400°C and then it was annealed in a vacuum chamber at 300°C with an annealing time of 0, 30 and 50 minutes, respectively. Then X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL) analysis at room temperature were carried out to investigate the structural, morphological and optical properties of thin films, respectively. I-V measurements were also carried out to study the electrical properties of films. Electrical resistivity was determined by measuring sheet resistance with a two point probe method.

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

Parameter	Description
Deposition	
Substrate	Preparatory glass substrate
Temperature	400°C
Argon pressure	500 mTorr
Plasma power	40 watts
Time	120 minutes
Annealing Process	
Condition	Vacuum (carried out in the chamber)
Temperature	300°C
Annealing time	0 ; 30 and 50 minutes

3. Results and Discussion

ZnO:Al thin films were grown on the preparatory glass substrate followed by annealing treatment with variations in annealing time of 0, 30 and 50 minutes. X-ray diffraction measurements (XRD) had been carried out to investigate the structure of ZnO:Al thin film and the results are shown in Figure 1. ZnO:Al films which were not carried out post growth annealing (annealing time 0 minutes) showed an amorphous atomic structure. After being annealed with variations of 30 and 50 minutes each time, the films also still showed curves with low intensity and were relatively flat, so that the samples had

amorphous properties. When viewed from an electron microscope (SEM) as shown in Figure 2, there appears a grained morphology of aggregates or an amorphous domain ZnO:Al with dimensional characteristics ranging from 100 to 150 nm. In addition, there are also changes in the surface morphology of the film when annealing was carried out with different annealing times. Films annealed for 50 minutes show a homogeneous amorphous domain with smaller characteristic dimensions than the previous sample.

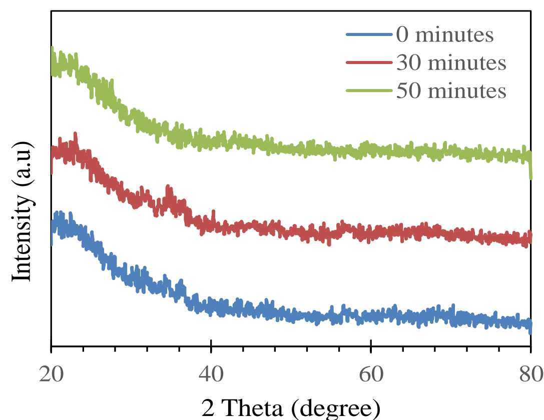

Figure 1. The result of XRD characterization of ZnO:Al thin films samples_with annealing time variation on annealing process.

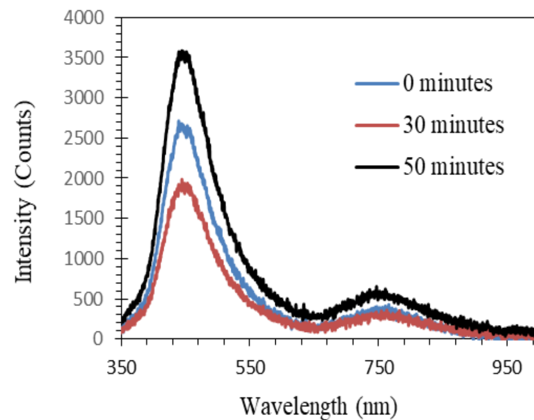

Figure 3. The room temperature PL versus wavelength spectra of the ZnO:Al thin films at excitation wavelength of 325 nm.

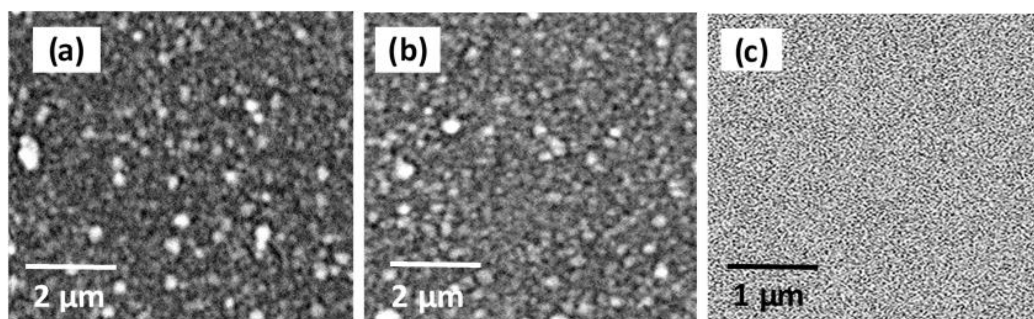

Figure 2. SEM image of ZnO:Al thin film samples with annealing time at annealing process: (a) 0 minutes, (b) 30 minutes, and (c) 50 minutes.

Photoluminescence (PL) studies had been carried out on non-doped ZnO thin films. Luminescence produced by ZnO thin films was very sensitive to the surface conditions of the film, and also depended on the method of growth and post-growth treatment. Also, the chemical composition, doping of impurities and the type of substrate could affect the luminescence of the film deposited on it. Photoluminescence of ZnO:Al was very sensitive to defects, which were caused by Al atoms which substituted zinc atoms or occupied interstitial sites. Figure 3 shows the PL room temperature spectrum obtained from ZnO:Al thin films on the preparation glass substrate at different annealing times (0, 30, 50 minutes). PL spectrum patterns of ZnO:Al thin films were similar to non-doped ZnO. All samples showed typical luminescent behavior with two emission bands, one visible band related to the blue region (the peak centered around 447 nm) and the other visible bands corresponding to the red region (the peak centered around 752 nm). The ultraviolet (UV) emission bands were not observed in our

experiments. The blue emission bands have a higher intensity compared to the red emission bands. The emission peaks in the visible region were seen to be related to the transition from various defect state called defect related deep-level emission (Figure 4). The deep-level emissions are usually associated with structural lattice defects and imperfections that act as strong recombination centers, so that the emission band is produced by the transition of donor-acceptor pairs [19]. These defects are intrinsic defects [20] such as zinc vacancies (V_{Zn}), oxygen vacancies (V_O), oxygen and zinc interstitial (O_i, Zn_i), and oxygen antisite (O_{Zn}). Intrinsic defects gave rise to acceptor levels or donor levels in the band gap; both cases greatly affect the luminescent nature of the film.

Based on all considerations, PL emission analysis can be used to determine intrinsic defects that occur on ZnO:Al thin films, which are known to strongly affect electric transport properties within the lattice structure. The blue emission peak (447 nm or 2.81 eV) is the transition result from Zn_i and extended Zn_i state to the valence band, respectively [20]. Meanwhile, the red emission peak (752 nm or 1.6 eV) might be attributed to electronic transition from the near conduction band-edge to deep level oxygen vacancy (V_O) state. From the analysis of these two emission peaks, ZnO:Al thin films were grown on preparatory glass substrate by dc magnetron sputtering observed structural defects, namely zinc-interstitial (Zn_i) and oxygen vacancy (V_O).

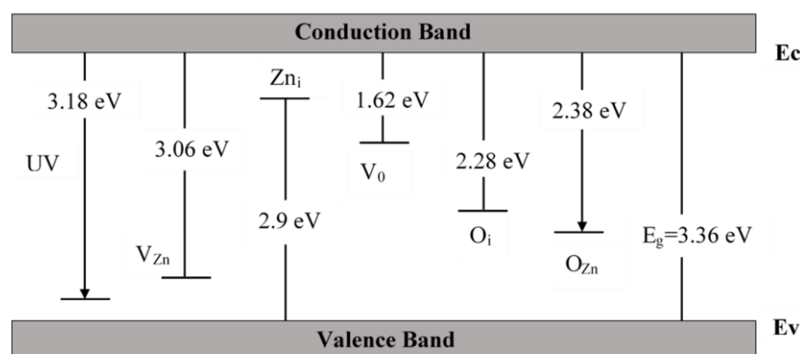

Figure 4. Schema of defect's level state and emission process in ZnO film [18].

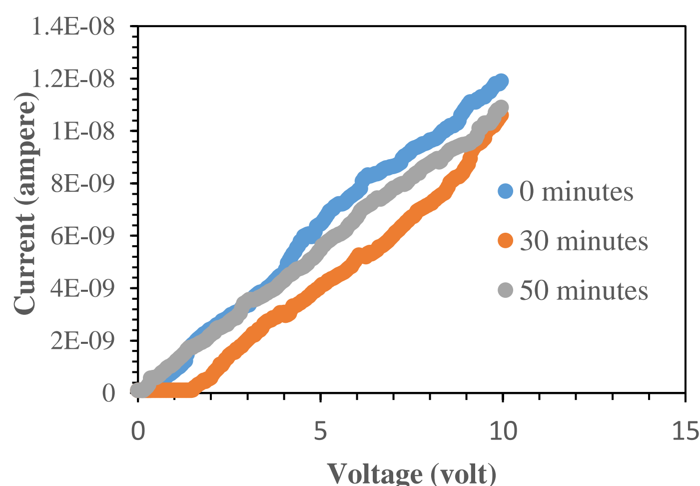

Figure 5. The electrical properties (I-V plots) examined by two probe method.

Table 2. Resistivity calculated from room temperature I-V measurements.

Duration of annealing (minutes)	Resistivity (Ωcm)
0	5.74 x 10^8
30	1.49 x 10^9
50	5.69 x 10^8

The room temperature I-V plots of the films are described in Figure 5. The ZnO:Al thin films grown on preparatory glass substrate exhibit ohmic conduction behavior, but resistivity of films grown on preparatory substrate appears to be very high as shown in Table 2. The high resistivity of this films due to the structure of films tend to be amorphous. The electrical properties of thin films are strongly influenced by atomic structure and grain boundary, which can disrupt the flow of electron. The annealing time seems to affect the resistivity of the film. Films are annealed for 50 minutes shows a lower resistivity value than other films. This shows annealing under vacuum conditions increases the amount of V_O and Zn_i, which act as electron donor. An increase in concentration of V_O increases the number of free electron, causing an increase in the conductivity.

4. Conclusion

ZnO:Al thin films had been grown on preparatory glass by dc magnetron sputtering. The effects of annealing time on films had been investigated. It_has been varied of 0, 30 and 50 minutes, respectively. XRD analysis revealed that the deposited thin film had amorphous structure with characteristics dimensions ranging from 100 to 150 nm. The films annealed for 50 minutes showed homogeneous domains of amorphous with a smaller characteristic dimensions than the previous sample. PL spectra showed high peak in the blue emission band and low peak in the red emission band. The intensity of blue emission and red emission peak increase when the film is annealed for 50 minutes, and the resistivity is lower due to zinc interstitial and oxygen vacancy contributions acting as intrinsic donors. ZnO:Al film with annealing at vacuum condition had a good optical properties in blue emission wavelength, and was applicable for optoelectronic devices such as blue light emitting diodes and laser.

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