Effect of NaOH Concentration to the Growth of ZnO Nanorod Arrays

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***Abstract*— Tin (Sn)-doped zinc oxide (ZnO) films were synthesized using sol-gel immersion method where different concentration of sodium hydroxide (NaOH) were used during the synthesis process. The structural, optical, and current-voltage (I-V) characteristics of the films were investigated. From the FESEM images, it is observed that the density of the nanorods improved with the increment of NaOH concentrations. The average diameters of the nanorods reduced from 80 nm to 67 nm after the concentrations of NaOH were increased from 0 to 0.01 M. The optical measurement indicates that the synthesized films possessed good transmittance properties. 0.01 M of NaOH produced the highest bandgap energy of 3.26 eV compared to other films. In case of electrical properties measurement, 0.01 M NaOH produced the lowest resistance film. These results indicate that the addition of NaOH into acidic-based solution is crucial to control the growth of nanostructures.**

***Index Terms*—Nanorod, NaOH, Sn-doped ZnO**

I. Introduction

ZINC oxide (ZnO) is a well-known material in recent development of semiconducting devices. It is used in many applications such as in capacitors, leds, solar cells, and sensors [1, 2]. ZnO can be applied in many applications due to its' own characteristics such as high energy band gap, high exciton binding energy, easy to be fabricated, and low cost. Based on previous studies, fabrication of devices using intrinsic ZnO faces lot of problems such as high resistance film, poor carrier concentrations, and high density of defects [3]. Due to this, it is necessary to introduce extrinsic elements to the ZnO structure in order to improve its' properties. According to the previous study also, ZnO is very sensitive to the acidic-based media especially when it is involving solution-based preparation [4]. This is due to the solubility of ZnO in acidic solution. In order to avoid that, it is important to control the acidic level of the solution during the growth process. In this study, we have deposited Sn-doped ZnO nanorod array films using sol-gel immersion method. During the preparation of nanorod arrays, different concentrations of sodium hydroxide (NaOH) have been added into the solution. Their effects to the structural, optical, and electrical properties were investigated. The report on this kind of investigation is rarely reported by other researchers. Thus, it is worth to thoroughly investigate this part of research.

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II. Preparation Method

ZnO seed layer was prepared using spin coating technique. The preparation method was reported in previous report [5]. ZnO nanorod arrays were prepared using sol-gel immersion method. The reagents used are 14.87 g zinc nitrate ($(Zn(NO_3)_2 \cdot 6H_2O)$), 7.01 g hexamethylenetetramine ($C_6H_{12}N_4$), 0.18 g tin (IV) chloride ($SnCl_4 \cdot 5H_2O$), and sodium hydroxide (NaOH). The concentrations of NaOH were varied for 0.00125, 0.0025, 0.01, 0.05, and 0.1 M. First, the reagents were mixed into 500 ml of deionized water (DI), and then sonicated in sonication tank for 30 min at 50 °C. Then, the solution was aged for 3 h at room temperature. The solution was poured into Schott bottle, followed by placing the Schott bottle into water bath tank for nanorod growth for growth period of 1 h. Finally, the prepared samples were cleaned and annealed in 500 °C temperature for 1 h. The flow process can be observed in Fig. 1. For electrical properties measurement, the samples were placed with gold (Au) as electrodes and the complete structure of film can be perceived in Fig. 2. The samples were characterized using field emission scanning electron microscope (FESEM), ultraviolet-visible (UV-vis) spectrophotometer, and I-V measurement system.

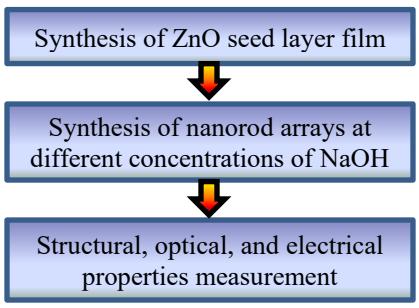

Fig. 1. Flow of synthesis and characterization process.

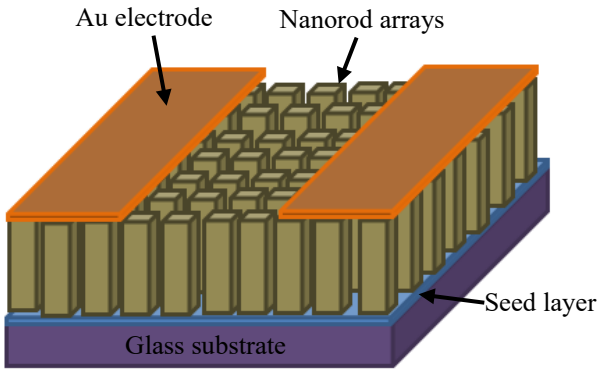

Fig. 2. Configuration of Sn-doped ZnO nanorod array films after deposited with Au electrodes.

III. Result and Discussion

A. Structural Properties

Fig. 3 shows the surface morphology of the ZnO films at different concentrations of NaOH. The images were taken at 50,000 × magnifications. Fig. 3(a) shows the surface morphology of 0 M (without NaOH). The nanorods possessed hexagonal shape with diameter of the nanorods varies from 50 to 110 nm. Fig. 3(b) displays the surface of sample with 0.001 M of NaOH. It is observed that the nanorod sizes slightly reduced compared to 0 M sample. The diameter of the nanorods ranged from 43 to 105 nm. Fig. 3(c) depicts the surface morphology of 0.01 M NaOH. Compared to 0 and 0.001 M, this sample possessed the smallest average diameter of 67 nm, with the diameter size varies from 40 to 70 nm. In addition, the density of nanorods also increased with the addition of 0.01 M of NaOH into the ZnO solution. The formation of ZnO and also the substitution of Sn atoms into ZnO lattice in form to form SnO_2 can be described in the given equation [6, 7]:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (1)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (2)$$

$$Sn^{4+} + 4OH^- \rightarrow Sn(OH)_4 \quad (3)$$

$$Sn(OH)_4 + 2OH^- \rightarrow [Sn(OH)_6]^{2-} \quad (4)$$

$$[Sn(OH)_6]^{2-} \rightarrow SnO_2 + H_2O + 2OH^- \quad (5)$$

On the basis of previous study, the implementation of sodium-based compound capable of acting as the chelating agent to enhance the growth of SnO_2 [8]. Due to higher formation energy and bond enthalpies of SnO_2 compared to ZnO [9, 10], it is considerably difficult for Sn^{4+} to occupy the Zn^{2+} sites. In addition, the amount of $SnCl_4.5H_2O$ which used as the source of Sn doping is relatively small. Thus, we expected that the addition of NaOH may enhance the kinetic formation of SnO_2 in ZnO crystal. From the images, the reduction of nanorods diameter may be due to the increment of successful doping of Sn^{4+} into ZnO lattice. When Sn^{4+} ions replaced the Zn sites in ZnO structure, the crystal structure may be shrunk. This is due to smaller ionic radius of Sn^{4+} compared to Zn^{2+} [11]. Due to this, smaller diameter of nanorods was produced. Furthermore, this leads to the enlargement of surface area of the film.

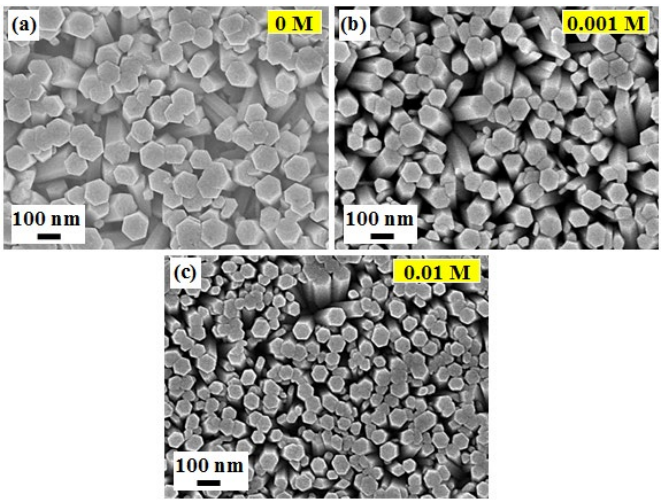

Fig. 3.Surface morphology of Sn-doped ZnO nanorod arrays at (a) 0 (without NaOH), (b) 0.001, and (c) 0.01 M of NaOH.

B. Optical Properties

Fig. 4 depicts the optical properties of the films analyzed using UV-vis. The transmittance properties of the films were measured at wavelength of 300 – 800 nm. The films provided good transmittance properties at visible region, and sharp drop when the light reaching UV region. The average transmittance of the film with different NaOH concentrations varies from 75% to 90%. The highest transmittance possessed by 0.01 M sample while the 0 M (without NaOH) possessed the lowest average transmittance at visible region. The improvement of optical transmittance with the addition of 0.01 M of NaOH may be explained by the improvement of film uniformity produced by the sample. Due to high density of nanorods, the scattering effect occurred (reflection and refraction) during

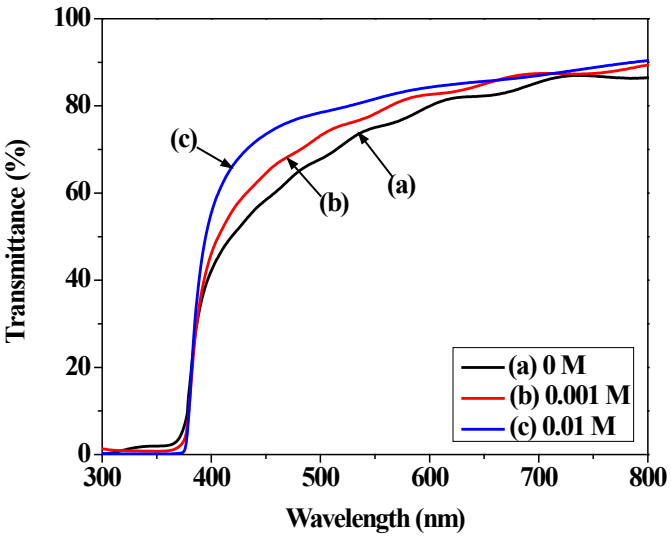

Fig. 4.Transmittance properties of Sn-doped ZnO nanorod arrays at different concentration of NaOH.

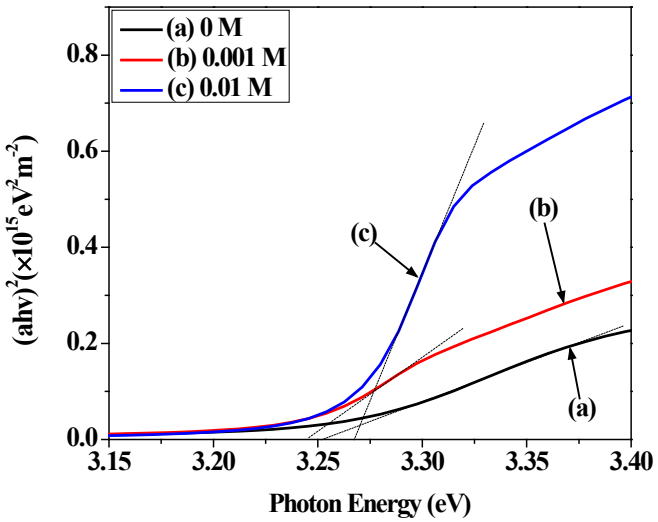

Fig. 5.Tauc's plot for energy gap estimation of the Sn-doped ZnO nanorod array films.

the illumination of light may be reduced [3]. This led to better transmission of light particle across the film. As mentioned earlier, the substitution of Sn^{4+} ions into ZnO lattice reduced the average diameter size. Due to this, we expect that the thickness of the film may also reduce as reported in previous studies [3, 12]. This may also lead to the enhancement of optical transmittance. Bandgap energy was estimated from Tauc's plot as shown in Fig. 5. The Tauc's plot is obtained from the given equation [13]:

$$ahv = A\left(hv - E_g\right)^n \tag{1}$$

The estimated energy gap of 0, 0.001, and 0.01 of NaOH are 3.24, 3.24, and 3.26, respectively. The E_g values slightly increase when the NaOH concentrations reached 0.01 M. This shifting may be related to the increment of Sn element in ZnO crystal induced from the increment of nanorod array densities. According to Burstein-Moss effect, the addition of carrier

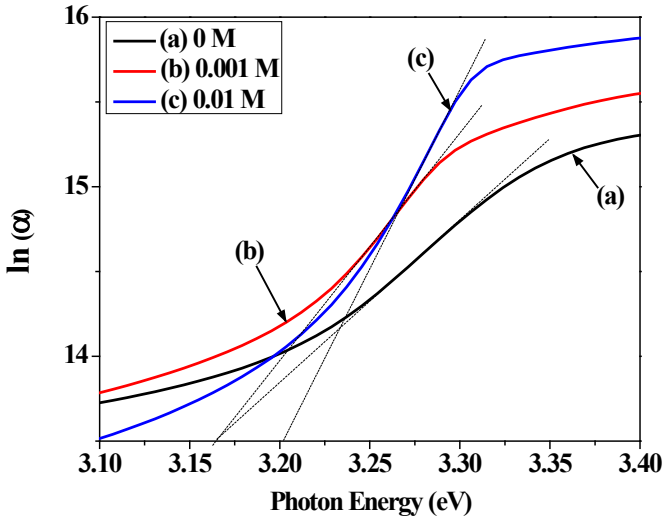

Fig. 6. Plot of ln α versus photon energy (hv) of Sn-doped ZnO nanorod array films.

causes band filling and pushes the Fermi level into conduction band [14]. This may induce broadening in energy gap. Thus, it leads to increment of energy gap. Urbach energy which represents the width of the band tails of localised state can be determined as followed [15]:

$$a(v) = \alpha^0 e^{\left(\frac{hv}{E_u}\right)} \tag{2}$$

where α^0, E_u, and v are constant, Urbach energy and the frequency, respectively. The plot for E_u estimation is shown in Fig. 6 and the estimated E_u are 111, 67, and 44 eV for 0, 0.001, and 0.01 M NaOH, respectively. From the result, it is indicates that the increment of NaOH concentration induced smaller width of band tail, which may be reflected to the decrement of structural defect in the ZnO lattice. This behavior can be seen from the improvement of nanorods uniformity in FESEM images which improved after the addition of higher concentration of NaOH.

C. *Electrical Properties*

Electrical properties of the films were measured using I-V measurement system. The result is shown in Fig. 7. The result was taken at ambient temperature. The bias voltage has been varied from -5 V – 5 V. The measurement displayed that the films possessed Ohmic behavior. In addition, we observed that the film with 0 M NaOH has the lowest current signal while sample with 0.01 M NaOH provide the highest current signal. Based on the data, we estimated the film resistances using Ohm's law (V=IR). From the calculation, the resistance of 0, 0.001, and 0.01 M of NaOH are 1.15, 0.84, and 0.60 MΩ, respectively. The resistance plot is shown in Fig. 8. From the plot, it is clearly observed that the film resistance significantly reduced at higher concentration of NaOH (0.01 M). From the analysis, there are several possibilities that caused the

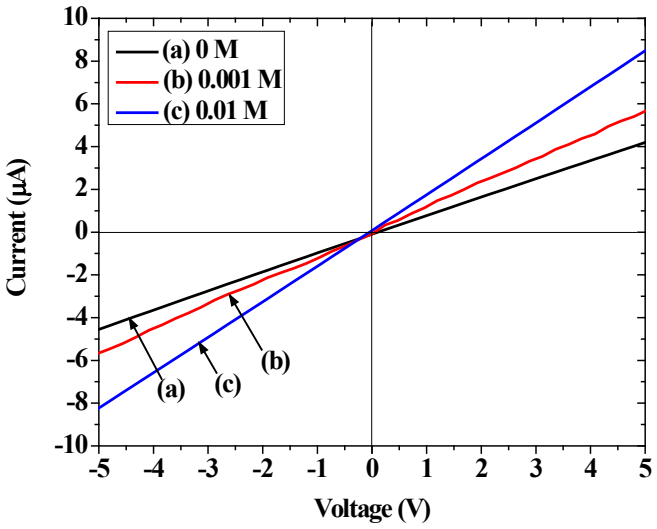

Fig. 7. I-V plot of Sn-doped ZnO nanorod arrays at different concentrations of NaOH.

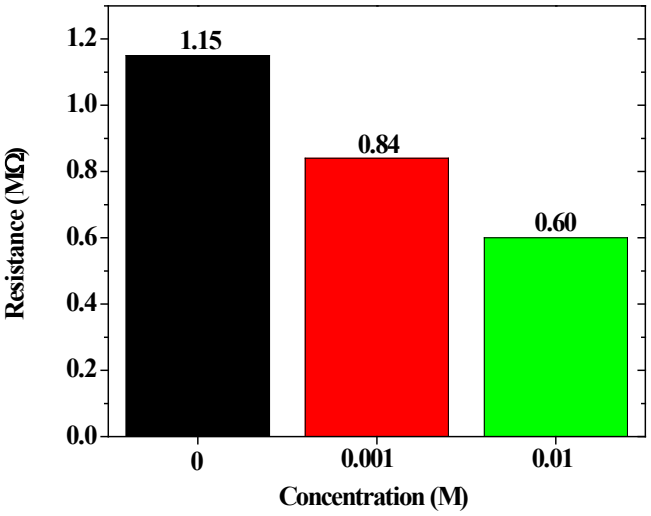

Fig. 8. Plot of resistivity of Sn-doped ZnO nanorod arrays at different concentrations of NaOH.

reduction of film resistance. First is related to the improvement of nanorod densities at high concentration of NaOH which can be observed in FESEM images. When the nanorod densities increased, the possibility of doping element to be substituted into the ZnO lattice also increased. Due to this, more free carrier can be generated into the film. Thus, the resistance of film is reduced. In addition, Wang et al. reported that the appearance of Na^{2+} ions capable of assisting the substitution of Al^{3+} ions into ZnO lattice [16]. Based on this study, it is expected that the Na^{2+} ions which generated from NaOH compound capable of acting as the catalyst to enhance the Sn^{4+} substitution into ZnO lattice. The other possibility is related to unintentional doping of Na^{2+} ions into ZnO lattice which donated from the NaOH compound. This will also increase the concentration of free carriers in the film. Both of this reason may explain the reduction of film resistance when the concentration of NaOH increased.

IV. Conclusion

Sn-doped ZnO nanorods were synthesized using sol-gel immersion method. Three different concentration of NaOH were added during the synthesis process to reach 0, 0.001, and 0.01 M of concentrations. From the FESEM result, it is observed that the density of nanorods on the film increased when the concentration of NaOH increased. Besides, the average diameter also decreased with the increment of NaOH. For optical properties, the films displayed good transmittance at visible region with average transmittance around 75% to 90%. In addition, the increment of NaOH concentration up to 0.01 M has increased the E_g and reduced the E_u to 3.26 eV and 44 eV, respectively. For I-V characteristic, 0 M of NaOH produced the highest film resistance of 1.15 MΩ while 0.01 M of NaOH produced the lowest film resistance of 0.60 MΩ. All of these analyses indicate that the addition of NaOH into Sn-doped ZnO solution during the synthesis proses is very crucial. This addition capable of improving the surface area, better optical properties, and excellent electrical properties.

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