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ORIGINAL ARTICLE

Nanorods ZnO Thin Film Performance as Transparent Heater

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ABSTRACT – Transparent heaters have been used for various applications. In this research, a transparent heater made from ZnO nanorods has been successfully fabricated. ZnO nanorods were produced by using the chemical bath deposition method.The results of the XRD investigation showed that the ZnO_0.015 and ZnO_0.025 samples contained three and five ZnO peaks, respectively, with a hexagonal wurtzite crystal structure. The crystallite size increased along with the increase in the solution concentration from 71.198 nm to 82.924 nm. The morphological characterization of the samples using FE-SEM showed that ZnO_0.025 sample had a better surface covarege than ZnO_0.015 sample. The average diameters of ZnO_0.015 and ZnO_0.025 are 127.130 and 146.756 nm, respectively. The transmittance value decreased along with the increase of solution concentration which is from 55% to 53%. The value of the band gap energy decreased as the concentration of the seed solution increased from 3.25 eV to 3.20 eV. The resistivity values of ZnO_0.015 and ZnO_0.025 are 1.126 x 10^{-4} and 0.824 x 10^{-4}Ωcm, respectively. From these results it appears that ZnO_0.025 sample has a more optimal performance as a transparent heater compared to ZnO_0.015 sample.

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INTRODUCTION

Transparent conductors have been used for various applications such as flat panel displays [1], [2], photovoltaic [3], and light emitting diodes [4]. Another application of transparent conductors that is interesting to study is transparent conductors as a transparent heater [5], [6]. The characteristics that must be possessed by a transparent conductor to be effective as a transparent heater (TH) are; absorption coefficients in the ultraviolet (UV), visible (VIS) and near-infrared (NIR) regions must be low and has low resistivity or high conductivity (σ) values in order to generates heat at a relatively low voltage, despite being transparent.

Until now, researchers have used a variety of methods for producing a thin film of a transparent conductor oxide applications. The method of thin film fabrication used in this study is the chemical bath deposition method. This method consists of three steps, namely, preparation of seed solution, making layer of the seed by using spin coating technique, and growing a layer of seeds.

Some types of materials developed as transparent heaters are fluorine doped tin oxide (SnO_2:F or FTO) [7]–[9] dan *indium tin oxide* (ITO) [10], silver [11]–[14], Cu nanowire [15], graphene [16], single-walled carbon nanotubes (SWCNT) [17], [18] and multi-walled carbon nanotubes (MWCNT) [19], [20]. Another material used as a TH is Zinc Oxide (ZnO). ZnO has good transparency, low UV absorption, wide band gap energy, high stability in hydrogen plasma, and is non-toxic. Tonbul *et al*. has succeeded in making transparent heaters of aluminum doped ZnO by ultrasonic spray pyrolysis method [21]. Meanwhile, Jayathilake, *et al*. has fabricated a thin layer of ZnO co-doped Al and Ga using aerosol assisted chemical transport (AACT) method for TH application [22]. TH as a windows heater application has also been successfully made from ZnO doping Ga with rf-magnetron sputtering method [23]. However, research on ZnO materials in one-dimensional nanostructures, especially in the form of nanorods as transparent heaters has not been widely developed yet. Therefore, in this study the researchers do the fabrication of ZnO nanorods using chemical bath deposition (CBD) method. This study will also carry out and analyze the basic characteristics of ZnO nanorods and its performance as a TH.

The hypothesis in this study is that the thin layer of ZnO nanorods produced by CBD method will produce good electrical conductivity and good optical properties. Good conductivity and good optical properties are important characteristics in transparent heating technology. One of the factors that affects the electrical conductivity and optical properties of the thin layer ZnO nanorods is the concentration of the seed layer. The higher the concentration of the seed solution used, the higher the conductivity value is. Increasing the amount of concentration used effectively improves the coverage of the ZnO nanorods on the substrate. Thus, it allows each nanorod to connect with each other and form more conductive pathways for electron movement. In addition, the increasing concentration of the seed solution used is able to increase crystallinity and increase the average grain size (crystallite) so that the mobility of the carriers are greater which directly affect the increase in the conductivity value of the sample. Another study conducted by Iqbal *et al*. reported that the electrical conductivity of the ZnO nanorods thin film was influenced by the orientation of the rods to the substrate. The better the orientation of the rod to the substrate, the better the conductivity value will be.

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This research is expected to be a reference in using nanorod ZnO which is one of 1-D materials to develop transparent heater technology.

EXPERIMENTAL METHOD

Materials and Instruments

The materials used in this study are zinc nitrate tetrahydrate ($N_2O_6Zn.4H_2O$/ZNT, Merck); hexamethylenetetraamine ($C_6H_{12}N_4$/HMTA, Merck); deionized water; technical ethanol; technical acetone; indium tin oxide glass (Sigma-Aldrich); and copper tape (Sigma-Aldrich).

Meanwhile, the tools used in this research are ultrasonic cleaner (GT Sonic VGT-1620QTD); muffle furnace; spin coaters; DC power supply, and thermocouple. The tools used for sample characterization are Field Emission Scanning Electron Microscope (FE-SEM JEOL JIB 4610F) for morphology analysis of the sample, X-Ray Dif-fraction (XRD, Shimadzu 7000) for crystal structure investigations, Ultraviolet-Visible (UV) Spectroscopy -Vis, Shimadzu 2450) for optical properties analysis, four point probe (Veeco FPP-500) for electrical properties analysis.

Method and Procedure

Procedure in this study was adopted from previous work whose done by Amalia *et al.* [24]. The procedure begins with the manufacture of seed solution. Preparation of seed solution was carried out by using an equimolar mixture of Zn-nitrate and HMTA (hexamethylenetetramine) at 0 °C temperature for about one hour with variations in solution concentration of 0.015 (ZnO_0.015) and 0,025 molar (ZnO_0.025). The next research procedure is making layer of the seed. The seed layer is made by using spin coating technique.

Each concentration of seed solution was dripped onto the ITO substrate and then allowed to stand for 10 minutes so that the seed solution was absorbed on the surface of the substrate. After that, the sample was rotated at 2000 rpm for 20 seconds. The coated substrate was then annealed in a muffle furnace at 200°C temperature for five minutes to increase the adhesion between the seed layer and the substrate.

That seed layer was then given the process of growing ZnO nanorods by using CBD method.The method of growing ZnO nanorods with CBD was done by hanging the substrate vertically in a glass beaker containing Zn-Nitrate and HMTA equimolar solutions with concentrations of 0.015 and 0.025 molar, at 90°C temperature for 3 hours.After that, the substrate was washed using deionized water and then dried in air. The results of this process will be continued with XRD, SEM, UV-Vis and fourpoint probe characterization processes, as well as testing the sample's performance as a transparent heater. This experiment has done in nanomaterials laboratories Metallurgy and Material Engineering, Universitas Indonesia.

RESULT AND DISCUSSION

The results of the crystal structure investigation using XRD on samples of ZnO_0.015 and ZnO_0.025 are shown in Figure 1. Based on the results of XRD analysis, the ZnO_0.015 sample there are threeZnO peaks with a hexagonal wurtzite crystal structure based on ICSD data located at angles of 2θ ~30,785°, ~35,349°, and 63,268°, each of which is a crystal plane. (100), (101), and (311). The peaks identified in this sample have low intensity. These results indicate that the resulted ZnO crystals have a low crystal density. In addition, two other confirmed peaks of ITO glass were detected.

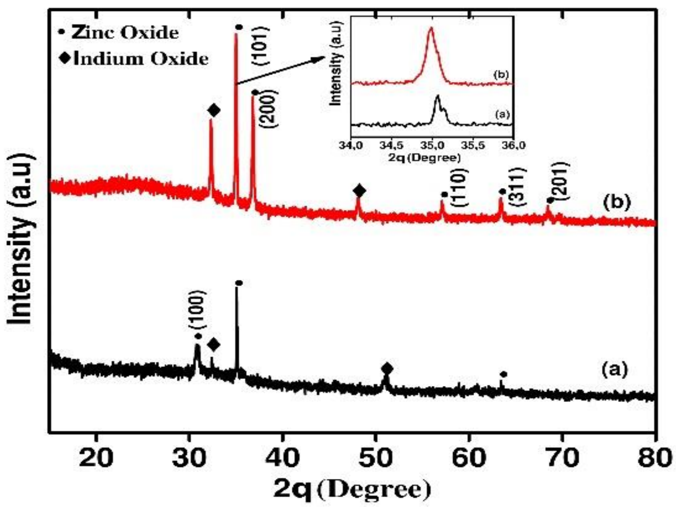

Figure 1. An XRD patterns of the Nanorods ZnO Thin Film with concentra-tion: (a) 0.015 and (b) 0.025 molar

Meanwhile, in the ZnO_0.025 sample, fiveZnO peaks with a hexagonal wurtzite crystal structure were detected, each of which is a crystal plane (101), (200), (110), (311), and (201) with a higher peak intensity than the ZnO_0.015 sample, especially at the peak of the crystal plane (101). Other diffraction peaks were confirmed as crystal planes of ITO.

The phenomenon of increasing the intensity of the diffraction peak with increasing concentration of seed solution was due to the fact that when the concentration of the solution was increased, the nucleation of ZnO became faster than the formation of ZnO nuclei in the early stages, then the nuclei gathered together forming ZnO crystallites. Based on the results of the crystallite size calculation using the Debye-Scherrer equation, the crystallite sizes for each sample were 71.198 and 82.924 nm. In general, the increase of crystal size was influenced by the concentration of HMTA used. HMTA will decompose when heated to form formaldehyde and ammonia. Ammonia reacts with water to produce OH^- which contributes to the crystallization of ZnO [25].

Figure 2 shows the morphology of the ZnO_0.015 and ZnO_0.025 sample structures. From the ZnO_0.015 sample, the coverage of the substrate surface growth orientation was not uniform and irregular. Meanwhile, from the ZnO_0.025 sample, the characteristic appearance of the thin film of ZnO nanorods was getting better and the growth of the nanorods was more uniform. The characteristic appearance of the thin film of ZnO nanorods which improved by increasing concentration of seedling solution could be related to the XRD pattern formed on the sample as shown in Figure 1. At a solution concentration of 0.025 M, the peak of the ZnO crystal formed was more dominant along with greater intensity than the concentration of the seed solution of 0.015 M. Meanwhile, the average diameter of ZnO nanorods for ZnO_0.015 and ZnO_0.025 samples were 127.130 and 146.756 nm. These results indicate that the concentration of the solution has an important role in the process of forming the morphology and size of the nanorod, due to increased Van der Waals forces in the seed solution. According to the Van der Waals force, the smaller the distance between the particles, the greater the attractive force between the particles. As a result, the size of the colloid in solution increases, resulting in a larger average diameter of the ZnO nanorods [26].

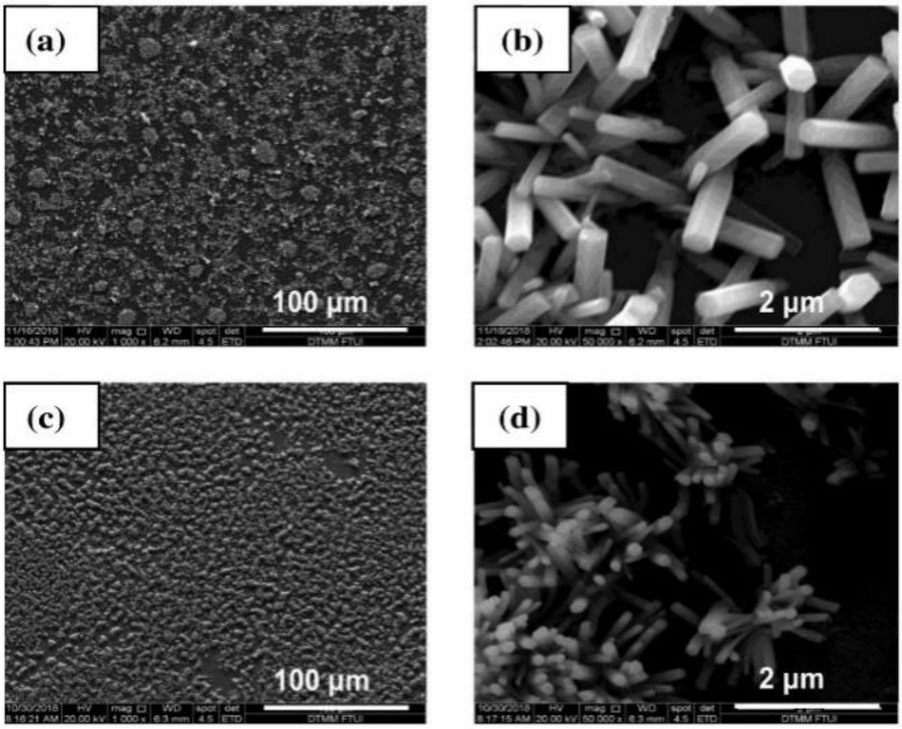

Figure 2. The FESEM images (at 1000 and 50000 magnification) of nano-rods ZnO thin film for (a), (b) 0.015 and (c), (d) 0.025 molar

Investigation of the optical properties of the ZnO_0.015 and ZnO_0.025 samples is shown in Figure 3. The transmittance value decreased along with increasing concentration of the seed solution used. The transmittance value of ZnO_0.015 is 55%. Meanwhile, ZnO_0.025 has a 53% transmittance value. The decrease in transmittance value occurs due to the increase in the thickness of the film. Generally, increasing the thickness of the film causes more molecules involved in the absorption of the given light energy, thus less energy fraction can be passed, so that the resulting transmittance degree becomes smaller. In addition, the higher the thickness of the film will cause an increase in oxygen vacancies which causes a decrease in the percentage of transmittance. The band gap energy (Eg) value decreased as the concentration of the seed solution increased, which were 3.25 and 3.20 eV, respectively. With the lower the value E_g, excitation of electrons from the valence band to the conduction band will be more easy. These results have similar to research that has been done by Abdulrahman *et al.* [27].

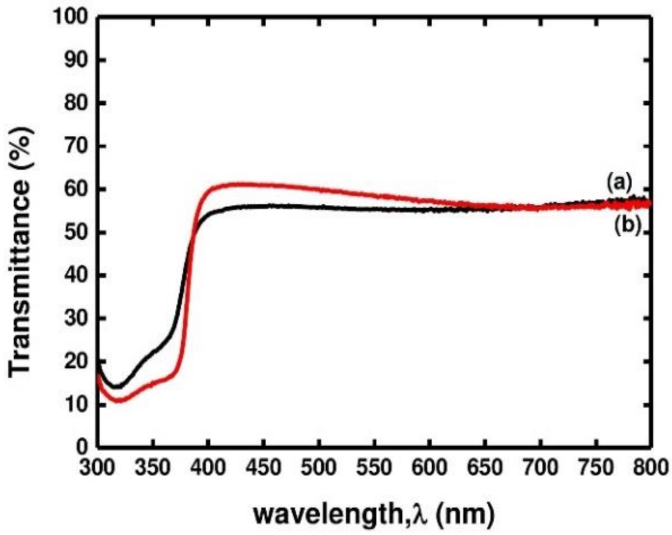

Figure 3. Optical transmissions spectra of nanorods ZnO thin films for (a) 0.015 and (b) 0.025 molar

Characterization of the electrical properties of the ZnOnano-rods thin layer seen from the resistivity value. The resistivity value of ZnO_0.015 is greater than the resistivity value of ZnO_0.025, which is 1.126×10^{-4} and $0.824 \times 10^{-4} \Omega$cm, as shown in Figure 4. This result was due to the increase in mobility carrier as the concentration of the solution increased. Mobility depends on several factors, one of which is the texture of the coating. The coating texture of the sample improves along with the increasing of solution concentration as shown from the FESEM.

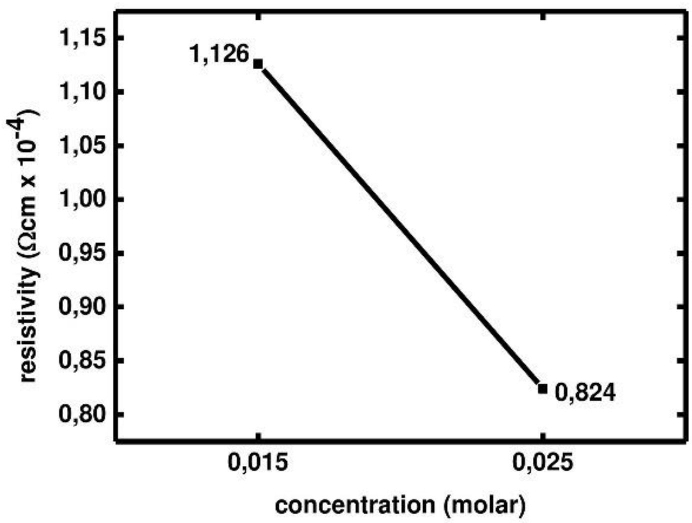

Figure 4. Resistivity of nanorods ZnO thin film with different concentration

The performance of the sample ZnO_0.015 and sample ZnO_0.025 are shown in Figure 5. When both samples were given an initial voltage of 7 volts for 60 seconds, the surface temperature increased through time. However, at the 60 seconds, the surface temperature of the ZnO_0.015 sample is smaller than that of the ZnO_0.025 sample. An increase in the input voltage of 9 volts for 60 seconds for each sample shows that the ZnO_0.025 sample has a higher surface temperature than the ZnO_0.015 sample.The surface temperature of the sample occurs due to the presence of an electric field on the surface of a thin layer of ZnO nanorods after an electric voltage is applied. The electric voltage accelerates the movement of charge carriers (electrons), so that the heat energy generated due to collisions between electrons and atoms in the layer is getting bigger which is indicated by an increase in surface temperature through time. These results show that the ZnO_0.025 sample has a more optimal performance as a transparent heater than the ZnO_0.015 sample. However, compared to the results of research conducted by Jayathilake *et al.*, the performance of transparent heaters based on ZnO nanorods obtained is still relatively low. In the study conducted by Jayathilake *et al.*, transparent heaters were fabricated by ZnO-based materials doped with aluminum and gallium [22].

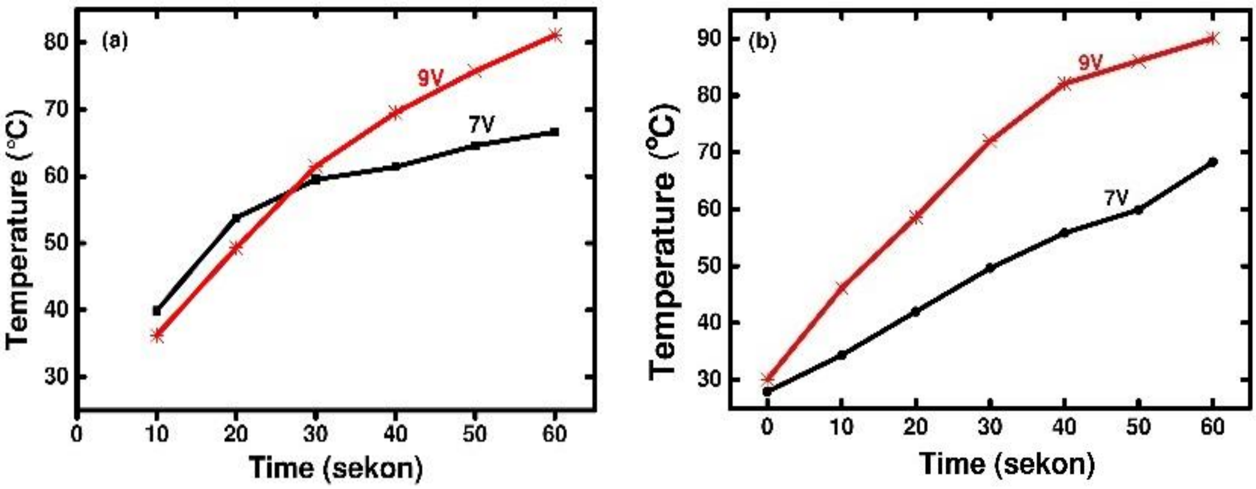

Figure 5. Temperatures measured as a function of time for the nanorods ZnO thin film with concentration (a) 0.015 and (b) 0.025 molar

CONCLUSION

A thin film of ZnO nanorods has been successfully fabricated by using the chemical bath deposition method. The crystallite size and the average diameter of ZnO nanorods increased along with increasing solution concentration from 71.198 nm to 82.924 nm and from 127.130 nm to 146.756 nm, respectively. Investigation of the optical characteristics of the samples showed a decrease in transmittance from 55% to 53% as the increasing concentration of the seed solution used. The samples were investigated for use as transparent heaters; Maximum temperatures of 65^{o}C and 80^{o}C were reached after applying 7 and 9 V, respectively, for one min at the sample with 0.015 M concentration. Meanwhile, maximum temperatures of 70^{o}C and 90^{o}C were reached after applying 7 and 9 V, respectively, for one minute at the sample with 0.025 M concentration.

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