Influence of Growth Duration to the Zinc Oxide (ZnO) Nanorods on Single-mode Silica Fiber

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***Abstract*— Synthesizing Zinc Oxide (ZnO) nanorods by varying the growth duration will give effect to the morphology of ZnO nanorods which were grown by using microwave assisted hydrothermal method. The effect of different growth duration from 4 to 10 hours is investigated on the surface of bare silica optical fiber. The buffer coating of a silica fiber is stripped off for 5 cm to expose the area for the growth of ZnO nanorods. The ZnO nanorods were grown on the fiber by dipping the fiber into the prepared growth solution in a 90˚C microwave assisted hydrothermal synthesised. The physical characterization through field emission scanning electron microscopy (FESEM) results show the diameter of ZnO nanorods is about 75.0 - 93.8 nm and the length of ZnO nanorods ranges from 666.2 nm to 978.6 nm according to their growth duration. The uniform growth of 43.33 nanorods/(µm)2 reveals that the 10 hours of growth duration performs the highest density growth of ZnO nanorods. The amplified spontaneous emission (ASE) peaking at 1550 nm is used to investigate the effect on the light intensity in the optical fiber with coated and uncoated ZnO for optical characterization. The ASE spectrum shows that the light intensity decreases with the growth durations due to the light scattering effect.**

Index Terms— Growth durations; Hydrothermal technique; Optical fiber; ZnO nanorods.

I. INTRODUCTION

Fiber optic has gained tremendous interest for various applications such as in sensor, laser and communication. Due to its superior advantage which is immune to magnetic interference, fiber optics have suppressed over electrical devices. Fiber optics can be used in physical measurement (i.e. acceleration, temperature, strain, displacement, pressure) and chemical measurement (i.e. water pollutants, refractive index) [1]–[3].

According to National Science Foundation and National Nanotechnology Initiative (NNI), nanotechnology means the involvement of physical, chemical and biological system at scales ranging about 100 nanometers which then produce the application of technology [4]. Through the advancement of technology, nanomaterial plays an important role in the fabrication of sensors. One of the famous materials is Zinc Oxide due to its unique properties such as wide band gap (3.37 eV), with high excitation of binding energy (60 meV) [5] that allows efficient excitonic emission at room temperature. These properties are useful to be used in optoelectronics and sensor applications.

ZnO has varieties in structures which can be classified among new structure that have potential applications in many fields of nanotechnology. The structure of ZnO is depending

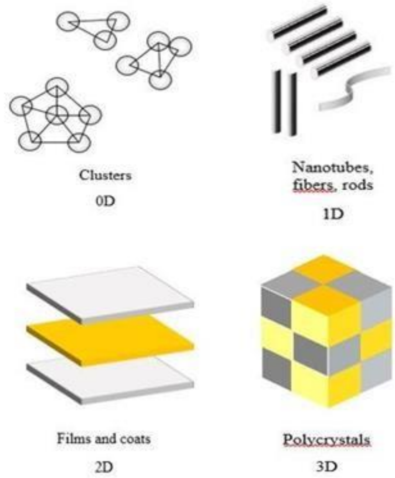

Figure 1: Illustrations of the 0D, 1D, 2D and 3D nanostructure

on their synthetization, for instance physical vapor deposition [6], vapor transport [7], and chemical vapor deposition [8]. However, these fabrication techniques require a relatively high temperature during the synthesis procedure. Amongst this method, hydrothermal is simpler, promise high yield of ZnO and the process can be controlled [9]. There are up to three dimensional structures which are one-[1D], two-[2D] and three-[3D] dimensional structures. Figure 1 shows the illustrations of the structures.

ZnO nanorod lies on the 1D structure group which exhibits many important applications such as in fiber optic sensors. For instance, ZnO nanorods in highly oriented and ordered arrays have been demonstrated to be important for sensing applications [10]–[13]. The advantage of one dimensional nanostructure is due to its ability to reduce the quantum confinement effects which is suitable for electronic and optical properties [14]. Referring to the refractive index, Zno has a higher refractive index which is approximately 2 compared to the silica which is 1.5. Due to this, it has potential application as an optical sensor. For instance, a humidity sensor based on ZnO nanorods coated on the silica fibers has been demonstrated and reported by Liu et al. It shows the enhancement of interaction between light coupled to the nanorods and the surrounding[15]. Konstantaki et al.

also reported an optically based sensor using ZnO nanorod as an out-cladding coating on the long period grating to sense ethanol [16]. In addition, Bora et al. also has reported the implication of ZnO nanorod based chemical vapor sensing by using multimode fiber by controlling the side coupling to the cladding [17]. It shows that the sensitivity of the sensor depends to the nature of the surface of the nanorods hence prove that the surface of the nanorod is important towards optical sensor application.

To synthesize the 1D structure which is nanorods, controlling the growth parameter is important. The growth parameter such us temperature growth, an annealing process, pH, deposition time and concentrations of the precursor can be varied depends on the desired structure. This is because, the morphology such as diameter, length and number of ZnO nanorods depend on how the synthesis is done [6], [7], [12], [13]. The hydrothermal technique uses a chemical phase approach which was achieved by using a chemical reaction to control the precipitation.

There is a lot of literature that has been reported on the growth of well-arrayed ZnO nanorods on flat surfaces such as Si [9], glass [18], carbon cloth [19], and Al foil [20]. However, due to a difficulty to coat on the curve surface, very limited literature discuss the well-arrayed nanorods on curve surface, for example around optical fibers. Previously, Fallah et. al. [21] grows zinc oxide nanorods onto a multimode plastic optical fiber surface and demonstrated side coupling to cladding modes. However, the multimode fiber will create high dispersion and attenuation rate plus the plastic optical itself cannot stand in high temperature. Thus, in this paper, we report the growth of well-arrayed, large-scale ZnO nanorods on single-mode silica fiber via the hydrothermal method and evaluates the influence of growth durations on the morphology of ZnO nanorods via physical and optical characterization. The well-arrayed nanorods are favorable for sensing applications as it has a large surface to volume ratio that is potentially promising for various novel optical sensing applications such as gas, temperature and humidity sensor.

II. Preparation Set-up

In this section, the set up for fiber preparation and ZnO nanorods fabrication will be discussed as well as a step for coating the fiber with ZnO nanorods.

A. Fiber preparation

Single-mode fiber with a core and a cladding diameter of 8µm and 125 nm, respectively is being used in this experiment. The buffer jacket which is a middle length of about 5 cm of fiber is stripped out. Isopropanol is used to clean the stripped region and followed by the steady flow of deionized (DI) water to prevent contamination.

B. Zinc Oxide Nanorods Fabrication

Zinc acetate dehydrate [$Zn(CH_3CHOO)_2.2H_2O$, Friendemann Schmidt Chemical] and Sodium Hydroxide [NaOH, Friendemann Schmidt Chemical] are the precursor used for seeding solution. Each of the solutions is mixed with 60 ml of ethanol. Another 60 ml of pure ethanol is mixed with Zinc Acetate dehydrate that has been mixed by 60 ml ethanol before. To acquire a constant pH, slowly added the solution of Sodium Hydroxide that has prepared before. The pH is important as it affects the morphology of the nanostructure of ZnO [22]. Then, slow bake the seeding solution for 3 hours to grow the ZnO particles. The white precipitate appears after 3 hours, which indicates the existence of ZnO nanoparticles in the seeding solution. To provide the first layer of ZnO on the fiber surface, the stripped SMF is dipped into the ZnO seeding solution while slowly stirring the solution for 30 minutes. Finally, the annealing process was done at 90 °C for 3 hours after seeding the ZnO layer. Growth solution is prepared by mixing the Zinc Nitrate hexahydrate ([$Zn(NO)_3]_2$, Sigma-Aldrich) and 1.4019 g of Hexamethylenetetramine [$(CH_2)NH_4$, Sigma-Aldrich] into the 1000 ml of deionized (DI) water. Stir the solution for 5 minutes. The ZnO nanorods will grow on the curve surface by dipping the fiber into the 500 ml of growth solution and put into the oven at 90˚C for 4 hours. The experiment was repeated for 6, 8, and 10 hours to investigate the differences in morphology of ZnO nanorods. Every 5 hours, the solution needs to be changed to maintain the growth rate.

III. Characterization of ZnO Nanorods

A physical and optical characterization was carried out in this work to observe the morphology of ZnO nanorods. The Field Emission Scanning Electron Microscopy (FESEM) was used to investigate the effects of growth duration on ZnO morphology. Each of the growth hours samples of coated fiber was used to confirm the presence of nanorods on the surface of bare silica optical fiber (SOF). The effects of different growth durations on length, diameter and density of ZnO nanorods were obtained.

The light source from a 1550 nm Amplified Spontaneous Emission (ASE) was emitted into the fiber and the output of light intensity was observed through Optical Spectrum Analyzer (OSA) as shown in Figure 2. Optical characterization has been done to analyze the effect of light scattering of ZnO nanorods coated on the stripped surface of the fiber with four different growth durations of 4, 6, 8 and 10 hours.

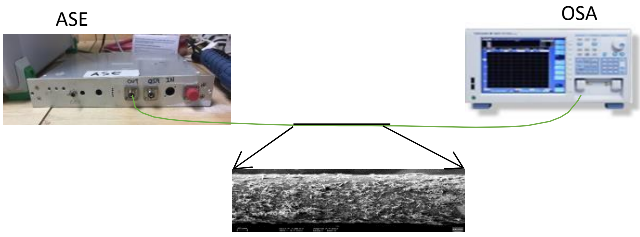

Figure 2: Optical characterization for light scattering by ZnO nanorods, which were coated onto a silica optical fiber

IV. Result and Discussion

Figure 3a-b shows the coated ZnO onto the SOF after 2 and 10 hours of growth duration, respectively. The red box shows the coating area of ZnO. It was observed that the ZnO was successfully coated on the curve surface by looking with our naked eyes and confirmed that the thickness of the coated ZnO nanorods is higher in 10 hours compared to 2 hours. However, the morphology of ZnO nanorods must be observed using FESEM and the changes in length, diameter and density were taken. Figure 4a-e shows the growth of ZnO nanorods on SOF for (a) 2, (b) 4, (c) 6, (d) 8 and (e) 10 hours at magnification of 10.0 kX. It was observed that ZnO nanorods have successfully grown on the curve surface of the fiber for the all growth durations with the effects on length, diameter and density on ZnO nanorods can be clearly seen.

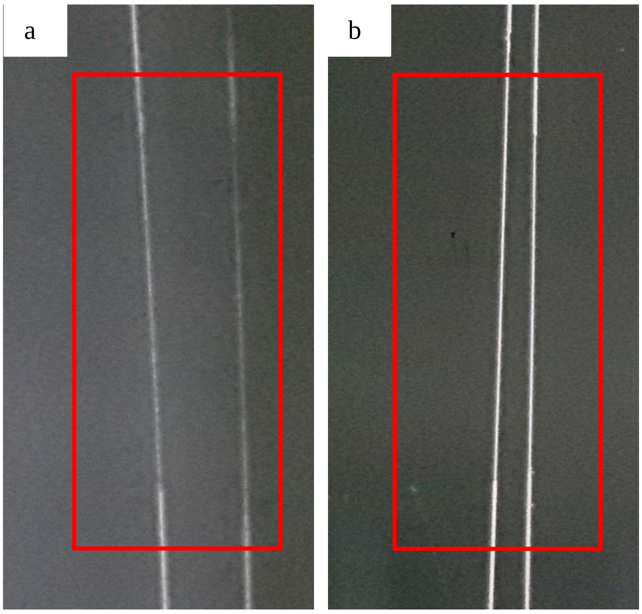

Figure 3: Bare surface of SOF coated with ZnO at a deposition time of a) 2 hour and b) 10 hour

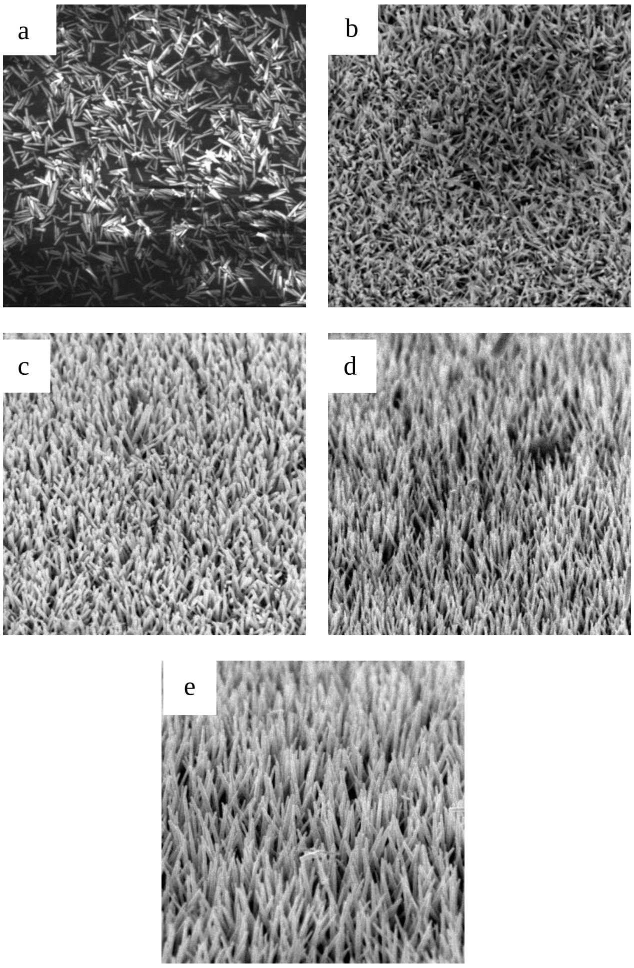

Figure 4: 10.0 kX FESEM images of ZnO on the surface of SMF fibers for (a) 2 (b) 4 (c) 6 (d) 8 and (e) 10 hours of growth durations.

Figure 5 shows the bare surface of the 10-hour growth duration at 5.0 kX magnification inserts with 50.0 kX magnification. The calculation of length and diameter of the ZnO nanorods has been shown to be 978.6 nm and 84.8 nm, respectively. These results were summarized in Table 1 with the density of ZnO nanorods for four different growth durations.

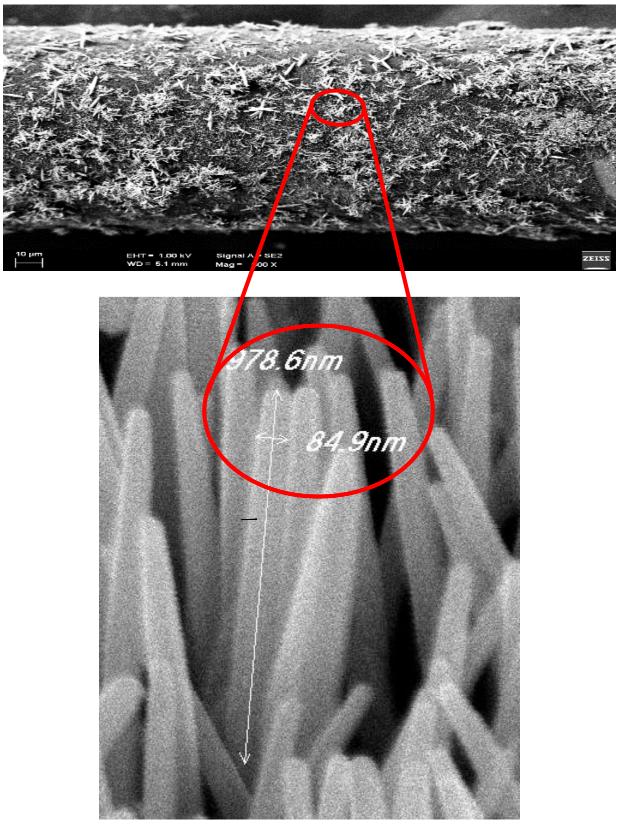

Figure 5: Bare surface of the 10-hour growth duration at 5.0 kX magnification insert with 50.0 kX magnification

At growth duration of 4 hours, the length, diameter and density of nanorods were estimated to be around 84.4 nm, 666.2 nm, and 27.12 nanorods/(μm)^2, respectively. The length, diameter and density of nanorods increased to 84.9 nm, 978.6 nm, and 43.33 nanorods/(μm)^2, respectively as the growth duration increased to 10 hours. Based on the trend, the diameter of ZnO nanorods at 4 hours was slightly same at 10 hours' deposition time.

Referring to table 1, the length was increased by increasing growth duration. The increase in length is due to the thermal decomposition by Hexamine (HMT) and $Zn(NO_3)_2$ precursor in the growth solution.

Table 1
Density of ZnO nanorods for four different growth durations

Time (hrs)	Diameter (nm)	Length (nm)	Density (nanorods/(μm)^2)
4	84.4	666.2	27.12
6	93.8	676.0	33.90
8	75.0	898.9	37.29
10	84.9	978.6	43.33

The length, diameter and density parameters are smaller at shorter growth duration due to the un-optimized thermal decomposition of HMT and $Zn(NO_3)_2$, which responsible for the ZnO nanorods formation. The small concentrations of ions lead to a slower nucleation rate that induces smaller rods growth. The Zn^{2+} will react with hydroxyl ion releases by

HMT in the process of thermal degradation to form ZnO [23]

Both materials act as a source of Zn^{2+} and OH^- respectively. However, the diameter of the nanorods starts to fluctuate at the growth durations of 8 hours. Because of HMT that is known as a non-polar chelating agent, OH^- ions adsorb on the lower energetic non-polar facets of the ZnO crystal [17].

This may reduce the Zn^{2+} ion on non-polar facets, explaining the reason of why the diameter of the nanorods grows slower compared to the growth in length. HMT agent also plays an important role in the morphology of the ZnO because of the shape-inducing polymer surfactant [24] resulting at 10 hours, the shape is more like needle compares to 6 and below. The reactions of formation ZnO nanorods are explained in the following chemical reactions:

$$C_6H_{12}N_{14} + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \quad (3)$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \quad (4)$$

Based on Figure 6, it is shown through the optical characterization the relation between the light intensity at 1550 nm and the growth time. It is evidence that 10 hours' growth duration provides the high loss because of the scattering effect. Due to the high density of ZnO nanorods coated on the surface of the bare fiber, which effectively affects the modification of the cladding hence contributes to the changes in refractive index outside the core. Some light will propagate out to the surrounding along the transmission because of the refractive index at the outside is higher compared in the core [25].

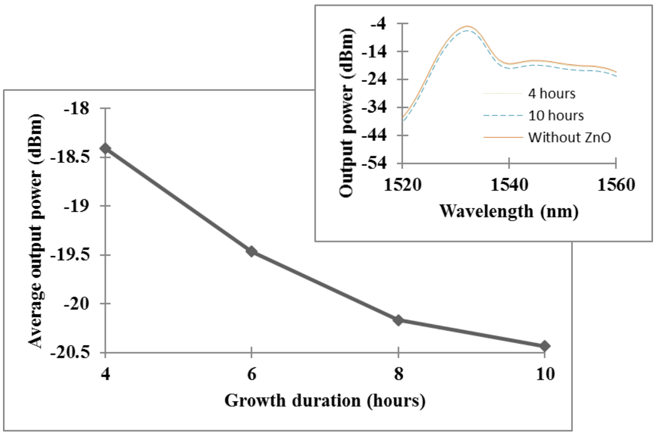

Figure 6: The average output power at 1550 nm for different growth durations and the inset shows the relation between the output power with uncoated, 4 and 10 hour growth time.

The coated ZnO nanorods have been used to test the ability to be a temperature sensor device. Figure 7 shows the output transmission power for a temperature sensor in a range of 30 °C to 80 °C at 8 hours of growth duration. It shows that the output power increased to 40 °C and saturated at 50 °C to 70 °C, and decreased to 80 °C. The loss is reported to increase with an increase in temperature. This is due to the thermal effect that caused the transmission of light scattered out more rather than transmit into OSA [26].

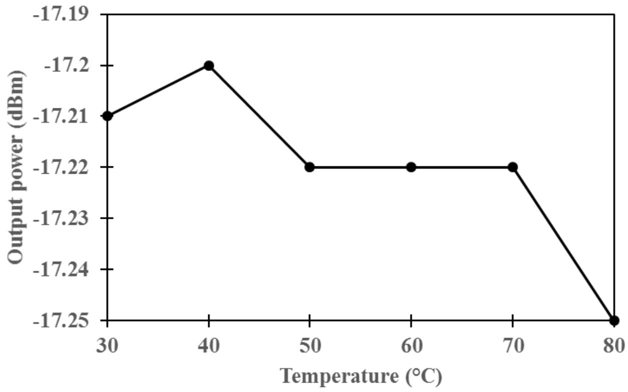

Figure 7: Output power for sensing the temperature at range 30°C to 80°C at 8 hours duration.

V. Conclusion

The ZnO nanorods coated on the stripped surface of silica fiber was successfully prepared by using the hydrothermal method. The effect on the morphology of the ZnO nanorods influence by the growth durations was successfully investigated in terms of its physical and optical characterization. Results from FESEM shows that the length and density of the nanorods are increasing as the growth durations increased which was due to the thermal decomposition of HMT and $Zn(NO_3)_2$ precursor whilst the diameter fluctuate at the period of above 8 hours. These effects significantly alter the light intensity propagated in the fiber due to the interaction between the light scattering effect and the ZnO nanorods. Based on the optical characterization, the output power exhibits a decrease in intensity as the growth durations increased. The sample of 8 hours of growth duration has successfully been used to test for the temperature sensor at a range of 30 °C to 80 °C.

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