Humidity Effects on the Growth of ZnO Nanorods using Hydrothermal Method

Mohd Hafiz Jali¹,², Hazli Rafis Abdul Rahim³, Haziezol Helmi Mohd Yusof¹,³, Md Ashadi Md Johari¹,⁴, Siddharth Thokchom⁵, Sulaiman Wadi Harun¹

¹Department of Electrical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
²Faculty of Electrical Engineering, Universiti Teknikal Malaysia Melaka, 76100 Melaka, Malaysia
³Faculty of Electronic and Computer Engineering, Universiti Teknikal Malaysia Melaka, 76100 Melaka, Malaysia
⁴Faculty of Electrical and Electronic Engineering Technology, Universiti Teknikal Malaysia Melaka, 76100 Melaka, Malaysia
⁵School of Technology, Assam Don Bosco University, Guwahati, Assam,781017, India

Abstract. The effects of ZnO nanorod samples with different growth times samples to the morphological structures and output light intensity are reported. The proposed structure comprises of silica microfiber integrated with Zinc Oxide (ZnO) nanorods coated glass surface. The silica microfiber is tapered into constant waist diameter of 10 µm using flame brushing technique. While the glass surface is coated with ZnO nanorods using hydrothermal method for 6 hours, 9 hours, 12 hours, 15 hours and 18 hours growth times. The samples are exposed to the different humidity levels ranging from 35%RH to 85%RH to observe the effect of the morphological structures such as length, diameter and density and the output light intensity. The resulted measurements provide the correlation between the growth time during the synthesis process to the ZnO nanorods physical structure as well as the output light intensity in different humidity levels. It utilizes the unique features of the scattering and surface absorption of the microfiber and ZnO nanomaterials coated glass surface to alter the output light intensity. The reported results may contribute to the optimal ZnO nanorods growth time for humidity sensing applications.

1. Introduction

Microfiber exhibits numerous characteristics such as strong optical confinement, large evanescent field, configurability and flexibility which make them promising element for physical sensing [1]. Large evanescent field propagating outside the microfiber turn them into a very sensitive medium to a change in the surrounding refractive index (RI) [2]. The surrounding material's refractive index would increase as the power fraction propagating in the evanescent field. Thus, the evanescent wave coupled with other waveguides such as metal, and semiconductor forming near-field interaction with its surrounding. Thus, high fractional evanescent field allow great responses towards physical sensing [3-5].
ZnO nanomaterial has high exciton binding energy (~60 meV at room temperature), wide band gap (3.37 eV), higher surface-to-volume ratio, direct charge transport along ZnO arrays and chemically reactive surface [6]. Thus, it becomes desirable material for various applications such as resonators [7], biosensors [8] and medical devices [9]. Due to a higher RI as compared to silica fiber, guided light couple into ZnO nanorod waveguides [10]. Furthermore, high concentrations of oxygen vacancies create active sites for water molecules adsorption for humidity sensor [6]. Despite a number of coating techniques for ZnO nanorods growth such as physical vapour depositions [11], chemical vapour depositions [12] and vapour transport [13], hydrothermal synthesis method has been used because it is inexpensive since it avoid the use of high temperature and complex vacuum environment.

Optical device has superiority compare to electronic counterpart due to it abilities to be used in harsh conditions such as higher pressure and temperature level as well as in flammable environments [14, 15]. The sensing works when the sensitive material interact with the evanescent field surrounding it and changes the transmitted output power [15]. Normally the sensitive material is directly coated which make the handling process of the become complicated and weaken the performance of the microfiber [16, 17]. In this paper, the microfiber has been integrated with ZnO nanorods coated glass as a potential structure for humidity sensing. It eases the interaction between ZnO coating layer and the evanescent wave from the microfiber with easy fabrication process, low cost and simple structure. The effect of the physical growth of the ZnO nanorods to the light transmission behaviour at different humidity level also explained in this work. The demand for optical sensor in many fields has attracted researchers to explore numerous sensing structure for physical sensing [18].

2. Theoretical Analysis

ZnO nanorods parameter such as diameter, density and length are highly relied on the growth time. The light intensity propagates over a distance $L$ of the coated region is formulated by first order scattering model [19]. $C_{sc}$ is the scattering cross section of one nanorod ($C_{sc} = \alpha/\rho_v$). $\rho_v$ is the average rods density per unit volume, $\rho_v = \rho_a/J$ where $\rho_a$ is the average number of nanorods per unit area and $J$ is the average rods length. $\alpha$ is the scattering coefficient ($\alpha = -\ln(I/I_o)/L$) over the length of the sensing region, $L$. Where $I$ is the intensity of the light leaving the medium after interaction of sensing region with the analyte, $I_o$ is the intensity of the light entering the medium before interaction of sensing region with the analyte. Therefore, the average intensity is described in equation (1).

$$I_{ave} = -C_{sc}\rho_v I_o L$$

Figure 1 illustrates the proposed structure for humidity sensing. RI of ZnO becomes larger compare to the microfiber when exposed to humidity when air medium is replaced by water molecules due to chemisorbed process on the ZnO nanorods surface [20]. When the light source (I) transmitted through the coating region, the output light intensity ($I_o$) will significantly reduce. This is because when the effective index of the ZnO nanorods and surrounding medium increases, the forward scattering coefficient increase and reduce the light transmission along the microfiber [21].
3. Material, fabrication and characterization

3.1. Glass substrate and microfiber preparation

Preparation of microfiber and ZnO nanorods coated glass has been described in the previous work [22]. Hydrothermal synthesis technique is used to grow ZnO nanorods onto glass substrates (Heathrow Scientific LLC, USA) for 6 hours, 9 hours, 12 hours, 15 hours and 18 hours. Single mode fiber (Corning SMF-28, USA) with 125 µm diameter was tapered into waist diameters of 10 µm with tapered length of 2 cm using flame brushing technique as shown in Figure 2. It is realized by controlling several elements such as motor speed, fiber stretching length, and flame movement. The length and diameter of the microfibers were verified and measured using microscope (Medilux-12) with 20X magnification.

Figure 1. Proposed structure for humidity sensing

Figure 2. Microscopic view of microfiber with diameter around 10 µm
3.2. Characterization & experiment

Field emission Scanning electron microscopy (FESEM) and Energy dispersive X-ray (EDX) was conducted to view the morphology of ZnO nanorods growth and determine the chemical constituent of the samples. Figure 3 illustrated the test setup of the experiment works. The microfiber was laid on the ZnO nanorods coated glass surface and placed inside a sealed chamber (22 x 12 x 12 cm). Amplified Spontaneous Emission (ASE) from an erbium doped fiber amplifier (EDFA) was launched at one end of the microfiber and the other end was connected to an optical spectrum analyser (OSA) (Anritsu: MS9710C) for intensity measurement. The output spectrum was measured in the bandwidth between 1500 to 1600 nm measured in dBm. The humidity level was increases from 35%RH to 85%RH at almost constant room temperature, 27°C. The probe of %RH meter (Hygrometer RS 1365, Sensitivity: 1%) was placed as close as possible to the samples to monitor the actual humidity level around the sample’s surface. The readings were recorded several times to verify the stability and repeatability of the experiment results.

4. Result and discussion

Figure 4 depicted the EDX elemental analysis of the coating samples consist of only zinc and oxygen. It can be observed that ZnO nanorods growth time varies the morphological structures such as length, diameter and density. Figure 5 shows the FESEM images of the nanorods length on the glass surface at different growth times at 20.00 kX magnifications. Based on Figure 6, it was found that the average nanorods length rise monotonically with the increment of growth time. While Figure 7 shows the FESEM images of the nanorods diameter on the glass surface at different growth times at 20.00 kX magnifications. The average nanorods diameter was also increases monotonically with the increment of growth time as shown in Figure 8. Whereas for density, the FESEM images of the nanorods on the glass surface at different growth times at 20.00 kX magnifications is shown in Figure 9. Based on Figure 10, it was found that the average nanorods density decrease monotonically with the increment of growth time. These physical structure variations would affect the forward and backward scattering into the
nanorods which contributed to difference light transmission behaviour inside the microfiber. Thus the output light intensity would change with respect to variance nanorods structure.

**Figure 4.** EDX elemental analysis revealed the samples only consist of zinc and oxygen

![Image of EDX analysis]

**Figure 5.** FESEM images of the ZnO nanorods length

(a) 6 hours  (b) 9 hours  (c) 12 hours  (d) 15 hours  (e) 18 hours
Figure 6. Average nanorods length at different growth time duration

Figure 7. FESEM images of the ZnO nanorods diameter

Figure 8. Average nanorods diameter at different growth times duration
Figure 9. FESEM images of the ZnO nanorods density

Figure 10. Average nanorods density at different growth hours duration
Based on results in Figure 6, Figure 8 and Figure 10, average intensity at different level of humidity is calculated using equation (1). Output intensity fluctuates according to the difference nanorods morphological structure during the exposure to different humidity level [23]. Based on Figure 11, average intensity of the 12 hours sample reduced significantly due to light leakage in almost all humidity concentration level. The intensity was found to be varies in a small magnitude at low %RH and further reduced at higher humidity level. This is due to refractive loss which is negligible at low %RH because there is only slight refractive index (RI) difference between sensing material and analyte molecule. Thus most change is due to the evanescent wave absorbance phenomenon at low humidity level. While at high concentration, the changes is predominantly due to refractive loss that occurred because of significance RI difference between two medium [24]. Besides that, this result also represents the correlation between intensity and nanorods structure. As aforementioned in Figure 6, Figure 8 and Figure 10, nanorods lengths and diameters increased when the growth time increased that lead to reduction of the nanorods’s density. As a matter of facts, backward scattering would dominate with shorter rods and lower rod density. Thus, the response reduced with lower nanorods length and smaller density of nanorods [21]. Hence, the best trade-off between these parameters needs to be figure out experimentally. Based on the results in Figure 11, it was found that 12 hours grow time sample produce significant sensing response in almost %RH. Thus, the 12 growth time was an optimal sample for humidity sensing application because it exhibits the highest light absorption inside ZnO nanorods which was the utmost criteria for the proposed sensing mechanism. As for comparison on the similar studies, Rahim et al. has performed light side coupling based on ZnO nanorods spiral coating pattern on the plastic optical fiber. He also found that the 12 hours growth time sample produce highest light side coupling with reduced leakage due to backscattering [25].

Figure 11: Average intensity of every growth time samples at different humidity level

5. Conclusion
We have successfully investigated the effects of humidity on the morphological structures of ZnO nanorods and the output power intensity. This study is essential to understand the relationship between difference nanorods physical structure and the light scattering behavior inside it. The best trade-off
between the diameter, length and density is found to be achieved by the sample of 12 hours grow time. The average intensity reduced significantly in almost all humidity level due to light leakage from the microfiber. The results of this work provide an optimal ZnO nanorods growth time for humidity sensing application. Future works can be done to specifically evaluate the sensing performances of the proposed structure using the optimal sample.

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7. References
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