Optimization of ZnO nanorods growth duration for humidity sensing application

Mohd Hafiz Jali, Hazli Rafis Abdul Rahim, Haziezol Helmi Mohd Yusof, Md Ashadi Md Johari, Siddharth Thokchom, Sulaiman Wadi Harun

1. Introduction
Zinc oxide (ZnO) nanomaterial has wide band gap (3.37 eV), high exciton binding energy (~60 meV at room temperature), direct charge transport along with ZnO arrays, higher surface-to-volume ratio and chemically reactive surface [1]. It became desirable material for various applications such as biosensors [2], resonators [3] and medical devices [4]. Guided light couple into ZnO nanorod waveguides due to higher refractive index (RI) as compared to silica fiber [5]. Moreover, high concentrations of oxygen vacancies create active sites for water molecules adsorption for humidity sensor [1]. Even though numbers of synthesis techniques for ZnO nanorods coating process such as chemical vapour depositions [6], physical vapour depositions [7] and vapour transport [8] has been implemented, hydrothermal synthesis method has been selected because it is inexpensive and avoid the use of complex vacuum environment and high temperature.
Another major component for the proposed sensor is microfiber. It demonstrates unique properties such as large evanescent field, strong optical confinement and configurability which make them promising element for physical sensing [9]. Evanescent field propagates outside the microfiber make it a very sensitive medium to a change in the surrounding refractive index (RI) [10]. 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, a high fractional evanescent field allows great responses towards physical sensing [11-13].

There are numerous advantages of an optical device as compared to electronic counterpart such as can be employed at a higher pressure and temperature level as well as in flammable environments [14, 15]. The sensing works when the sensitive material interacts 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]. 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 the easy fabrication process, low cost and simple structure. In this paper, the optimization approach of the ZnO nanorods growth duration for the proposed sensor has been explained in this work. The demand for an optical sensor in many fields has attracted researchers to explore numerous sensing structure for physical sensing [18].

2. Sensing mechanism

Figure 1 illustrated the sensing mechanism of the proposed sensor. When the proposed sensor is exposed to the humidity, the water molecule chemisorbed onto the ZnO nanorods surface due to weak hydrogen bonding and the air medium is replaced by humidity. This cause the refractive index of the ZnO becomes higher as compared to the microfiber. Thus, the interaction between the evanescent field and nanorods surface occur which highly reliance on the refractive index and the extinction coefficient [19]. The evanescent wave absorbance depends on the concentrations of the analyte if other parameters remain constant [20]. The effective index between the surrounding medium and ZnO nanorods would increase as the humidity level increase. More light coupling into the ZnO nanorods waveguides due to the increment of the forward scattering coefficient which reduce the light transmission through the sensing region [21].

![Figure 1. Proposed humidity sensor structure.](image_url)
3. Material, fabrication and characterization

3.1. Glass substrate and microfiber preparation
Microfiber and ZnO nanorods coated glass has been prepared according to our previous work [22]. ZnO nanorods have been grown onto glass substrates (Heathrow Scientific LLC, USA) using hydrothermal synthesis technique 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 a 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 a microscope (Medilux-12) with 20X magnification.

![Microfiber with diameter around 10 µm.](image)

3.2. Characterization & experiment
In order to view the physical structures of ZnO nanorods growth and determine the chemical content of the samples, Field emission Scanning electron microscopy (FESEM) and Energy dispersive X-ray (EDX) was performed. Figure 3 depicted the experiment setups. 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 used as a light source and connected to an optical spectrum analyser (OSA) (Anritsu: MS9710C) for output power measurement. The output spectrum was measured in the bandwidth between 1500 to 1600 nm measured in dBm. The humidity level was increased 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 close 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 shows the EDX elemental analysis of the ZnO nanorods samples consist of only zinc and oxygen. Figure 5 shows the FESEM images of the nanorods density on the glass surface at different growth times at 20.00 kX magnifications. The average nanorods density decrease monotonically with the increment of growth time because the diameter of the nanorods increases as shown in the graph in figure 6. It would affect the forward and backward scattering into the nanorods which lead to variation light transmission behaviour inside the microfiber. Thus, the output light intensity would change with respect to difference nanorods structure.

Figure 3. Experimental setup to observe the effect of humidity level.

Figure 4. EDX elemental analysis shows the samples only consist of zinc and oxygen.
Figure 5. FESEM images of the ZnO nanorods density at different growth duration.

Figure 6. Average nanorods density at different growth hours duration.

Figure 7 shows the output power difference when the proposed sensor was exposed at maximum humidity and minimum humidity level. Output power fluctuated according to the difference nanorods morphological structure during the exposure to different humidity level [23]. The output power difference of the 12 hours sample has the highest value because larger light absorption into the nanorods. This is due to the sample has the best trade-off between the diameter and density which allow more light to absorb into the ZnO nanorods sample. Figure 8 shows the trendline of every growth time samples. It
shows that the output power of 12 growth time sample reduced tremendously as compared to other samples. The linearity of 9 hours, 12 hours and 15 hours growth time samples have more than 95% which show an acceptable result for sensing application as depicted in figure 9. The 12 hours growth time sample has the highest sensitivity with 0.0316 dBm/%RH compared to the other samples as shown in figure 10. Thus, the 12 hours 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.

Figure 7: Output different from every growth time samples.

Figure 8. Trendline of every growth time samples at when %RH increases
5. Conclusion
This report demonstrated the optimization technique of the ZnO nanorods growth time for the proposed sensor. This study is essential to understand the relationship between difference nanorods physical structure and the light scattering behaviour inside it. The best growth time sample was found to be 12 hours growth time sample. The output power reduced tremendously when humidity level increase due to light leakage from the microfiber which absorbs into the nanorods. The linearity and sensitivity also show the highest result as compared to the other samples. The outcomes of this work provide an optimal ZnO nanorods growth time samples for humidity sensing application.

Acknowledgements
The authors would like to acknowledge the University of Malaya, Universiti Teknikal Malaysia Melaka and Ministry of Education, Malaysia for their financial support. (PJP/2018/FKEKK(4B)/S01616).
References

[1] Ismail A S, Mamat M H and Mahmood M R 2017 Nanostructured Materials-Fabrication to Applications: InTech)

[2] Chiavaiali F, Baldini F, Tombelli S, Trono C and Giannetti A 2017 Biosensing with optical fiber gratings Nanophotonics 6 663-79

[3] Irawati N, Rahman H, Ahmad H and Harun S 2017 A PMMA microfiber loop resonator based humidity sensor with ZnO nanorods coating Measurement 99 128-33

[4] Quy C T, Hung C M, Van Duy N, Hoa N D, Jiao M and Nguyen H 2017 Ethanol-sensing characteristics of nanostructured ZnO: nanorods, nanowires, and porous nanoparticles Journal of Electronic Materials 46 3406-11

[5] Voss T, Svacha G T, Mazur E, Müller S, Ronning C, Konjhodzic D and Marlow F 2007 High-order waveguide modes in ZnO nanowires Nano letters 7 3675-80

[6] Wu J J and Liu S C 2002 Low-temperature growth of well-aligned ZnO nanorods by chemical vapor deposition Advanced materials 14 215-8

[7] Kong Y, Yu D, Zhang B, Fang W and Feng S 2001 Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach Applied Physics Letters 78 407-9

[8] Huang M H, Wu Y, Feick H, Tran N, Weber E and Yang P 2001 Catalytic growth of zinc oxide nanowires by vapor transport Advanced Materials 13 113-6

[9] Jali M H, Rahim H R A, Johari M A M, Hamid S S, Yusof H H M, Thokchom S, Wang P and Harun S W 2019 Optical characterization of different waist diameter on microfiber loop resonator humidity sensor Sensors and Actuators A: Physical 285 200-9

[10] Lim K, Harun S, Arof H and Ahmad H 2012 Selected Topics on Optical Fiber Technology: InTech

[11] Lou J, Wang Y and Tong L 2014 Microfiber optical sensors: A review Sensors 14 5823-44

[12] Chen G Y, Ding M, Newson T and Brambilla G 2013 A review of microfiber and nanofiber based optical sensors The Open Optics Journal 7

[13] Wu X and Tong L 2013 Optical microfibers and nanofibers Nanophotonics 2 407-28

[14] Lokman A, Arof H, Harun S W, Harith Z, Rafaie H A and Nor R M 2016 Optical fiber relative humidity sensor based on inline Mach–Zehnder interferometer with ZnO nanowires coating IEEE Sensors Journal 16 312-6

[15] Ascorbe J, Corres J, Arregui F and Matias I 2017 Recent developments in fiber optics humidity sensors Sensors 17 893

[16] Bhatia V, Campbell D K, Sherr D, D’Alberto T, Zabaronek N, Ten Eyck G A, Murphy K A and Claus R O 1997 Temperature-insensitive and strain-insensitive long-period grating sensors for smart structures Optical Engineering 36 1872-7

[17] Yao Q, Meng H, Wang W, Xue H, Xiong R, Huang B, Tan C and Huang X 2014 Simultaneous measurement of refractive index and temperature based on a core-offset Mach–Zehnder interferometer combined with a fiber Bragg grating Sensors and Actuators A: Physical 209 73-7

[18] Misra S K, Pandey N K, Shakya V and Roy A 2015 Application of undoped and Al 2 O 3-doped ZnO nanomaterials as solid-state humidity sensor and its characterization studies IEEE Sensors Journal 15 3582-9

[19] Azad S, Sadeghi E, Parvizi R, Mazaheeri A and Yousefi M 2017 Sensitivity optimization of ZnO clad-modified optical fiber humidity sensor by means of tuning the optical fiber waist diameter Optics & Laser Technology 90 96-101

[20] Punjabi N, Satija J and Mukherji S 2015 Sensing Technology: Current Status and Future Trends III: Springer) pp 25-45

[21] Yusof H H M, Harun S W, Dimyati K, Bora T, Mohammed W S and Dutta J 2018 Optical dynamic range maximization for humidity sensing by controlling growth of zinc oxide nanorods Photonics and Nanostructures-Fundamentals and Applications 30 57-64

[22] Jali M H, Rahim H R A, Ashadi M J M, Thokchom S and Harun S W 2018 Applied microfiber evanescent wave on ZnO nanorods coated glass surface towards temperature sensing Sensors and Actuators A: Physical 277 103-11
[23] Azad S, Sadeghi E, Parvizi R and Mazaheri A 2017 Fast response relative humidity clad-modified multimode optical fiber sensor with hydrothermally dimension controlled ZnO nanorods *Materials Science in Semiconductor Processing* **66** 200-6