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Optical Sensing Performance of Multimode Polymer Optical Fiber (POF) Coated with ZnO towards Methanol Vapour

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Abstract. In this work, optical sensing performance of multimode polymer optical fiber coated with ZnO towards methanol vapour with different concentrations is studied. The etching process of the POF was carried out using chemical etching method. ZnO was synthesized with sol-gel method to obtain the sensitive material coating. The etched optical fiber was then dip-coated with ZnO and dried at 70oC to enhance the binding of the materials and to remove organic residue. Scanning Electron Microscope (SEM), and X-Ray poer Difraction (XRD) analyses were performed to characterize the ZnO layer. The measurements of optical performance were taken using a spectrophotometer in the optical wavelength in the range of 500–8000nm. The absorbance response of the ZnO coated etched fiber reduced proportionally, upon exposure to methanol vapour with concentration in the range of 5%–50%.

1. Introduction

The optical sensing is developed rapidly as asensor for most of all of the physical parameters of interest. Measurement of chemical contamination is required in a numerous of applications, including the water contamination, chemical, and food processing industry.[1] Thus, the chemical compound contamination measurement has been extensively studied over the last many years, and a remarkable progress in employing optical fiber sensor for the growth of volatile organic compound sensors has been developed.[2] However, potentially competent electronic based sensor as conventional technique e.g., capacitance based, wet-dry bulb and solid-state humidity sensors are also widely deployed and comprehensively practice in targeting the present of volatile organic compounds.[3-4]

ZnO instead of TiO2 as a sensitive material coating to sense the present of gas in various experiment has been utilized since 1962.[5-6] This material has been synthesized in various forms, such as single crystals, sintered pellets, thick layer, a thin layer, and heterojunction.[7] ZnO is expected to exhibit a high level of sensitivity, because the detection mechanism involves chemical absorption (chemisorption) followed by charge transfer to the surface that make a difference in the resistance of the detector element. Different methods were used to obtain a thin layer of ZnO,[8] eg, oxidation temperature, chemical deposition, electron beam evaporation, reactive evaporation activation, spray pyrolysis,[9] low pressure metal organic chemical vapor deposition (MOCVD) [10] and RF magnetron spray[11].

Ramza et.al conducted investigation on the coating modification of POF cladding by using ZnO powder and it is used the Fabry – Perot interferometer.[12] ZnO material is applied as the air pressure detector. The detection uses interferometer formation will produce the low response than the POF straight-line formation. The investigation shows that the initial swelling process size amount 0.000338 µm for the pointed of the vacuum pressure is 0 mBar and 1.181000 um for 104.8 mBar, even though sensor sensitivity is very small 1.1% due to thin coating process.

In recent times, research based on modified optical fiber has received greatly attention as an intrinsic sensor.[13] Modification cladding of the optical fiber was found to be more sensitive due to the manner of light propagation in the on the unclad portion of optical fiber core. A fraction of the optical power was found to propagate outside the tapered optical fiber core.[14] In other words, the evanescent field of the tapered fiber goes beyond the fiber physical boundary. Coating the tapered region with sensing layer lets the interaction of the layer with the evanescent field. When the VOCs interact with the sensing layer and change the layer properties, the evanescent field will also be affected.

Nowadays, many researchers implemented optical fiber detections scheme to sense the volatile organic compound using absorbance spectroscopy[15] and reflectance[16]. One of the most important thing to obtain a good sensitivity sensor performance is the use of material coating such as ZnO[17], PANI [18], Cerium oxide[19], and ITO[20].

However, mostly intrinsic detection of optical fiber sensor based on light absorption or light emission. This method selected due to its extreme sensitivity and good selectivity, namely 1000 times greater than that of most spectrophotometric measurement technique the advantage of this measurement technique is easy to operate[21].

In this paper, ZnO was coated on tapered multimode polymer optical fiber (POF) sensor for sensing of different concentrations of methanol vapour using absorption detection method. POF was chosen due to easy handle modification process, compare to fiber optic silica, which needs sophisticated device to produce a tapered fiber and using harmful chemical solvent during modification process with wet chemical etching method as it describes in previous research [22] The sensitivity and the optical response of the ZnO coated and bare modified fiber sensor towards methanol were presented. Another section of your paper.

2. POF Cladding Modification Process

The overall sensor performance depends on producing of modification POF cladding that process with chemical etching procedure and good control procedure during intervention of chemical solvent to the cladding part in low temperature condition. The type of fiber used is the cylindrical type which contain of polymethylmethacrylate (PMMA) as the core and fluorinated polymer as the cladding. The POF core and cladding diameter is 980 µm and 20 µm. The fibers were etched at the middle part using pure acetone with 90% concentration inside the flat container with free strain condition; this is to avoid the breakage of POF during the etching process.

To ensure the output power of optical fiber after the chemical etching process is done by measuring propagation loss of POF using optical power meter (PM100- Thorlabs) a reduction in the light intensity in every measurement process indicated the removal of cladding because of the chemical etching process, and leaving only a bare core. The overall optical transmission of the etched optical fiber quantified in term of fractional power P (core), and P (caldding) in the core and cladding regions as propagating media.

$$\alpha_{vm} = \alpha_1 \frac{P_{Core}}{P} + \alpha_2 \frac{P_{Clad}}{P} \quad (1)$$

The experimental set up of POF loss propagation measurement is show in figure 1. The POF refractive index and number of modes shown by the light that remains at the fiber core. The amount of power increases significantly in the waist area of the etched fiber at the middle part, and the penetration depth of the evanescent field decays exponentially. The source of light that is being transmitted throughout the fiber can be done to determine the V number, as expressed in the following equation:

$$V = \frac{2\pi a_0}{\lambda} \sqrt{{n_{co}}^2 + {n_{cl}}^2} \quad (2)$$

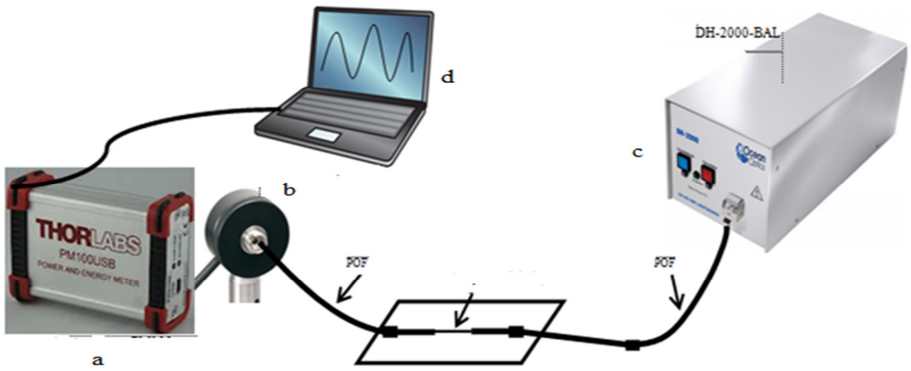

Figure 1. Experimental setup measurement of POF loss propagation of etching process:

(a) power meter (b) photo diode (c) broad band light source (d) computer.

3. Procedures and Materials

3.1. Materials

The schematic procedure of zinc Oxide synthesized is shown in figure 2. The syinthesized process of ZnO as coating layer on the fibers using sol–gel method is shown in figure 2. Solution has been prepared by dissolving 0.01 M zinc nitrate hexahydrate (Zn(NO3)2·6H2O) >98 % (*SIGMA-Aldrich*) and 0.01 M hexamethylenetetramine (HMTA) >99.0 % (*SIGMA-Aldrich*) in 100 ml Methanol and then constantly stirred on the hot plate for about 1 hour at temperature 70^{o}C to obtain a homogeneous solution of ZnO. Sol-gel method is choosing because this synthesized process is easy to operate in terms of fabricating a metal oxide material.

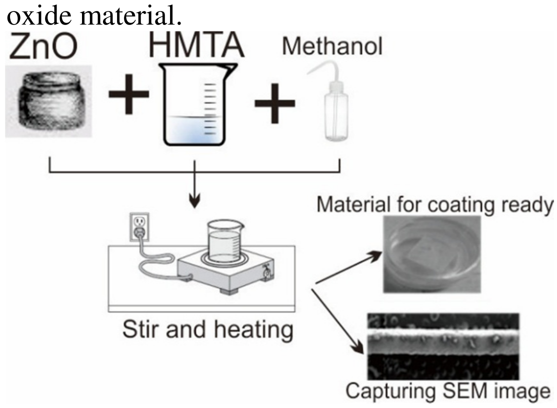

Figure 2. The synthesized process of ZnO as coating layer on the fibers using sol–gel method

3.2. Deposition method of ZnO

ZnO were deposited by dip coating method to produce a good coating material on the surface of polymer optical fiber as modified cladding probe sensor. After deposition process the fiber was dried on a hot plate at 60^{o}C to evaporate the solvent and remove the organic residue. This deposition and drying method was repeated several times to obtain evenly distributed coating material on the surface of modified cladding.

3.3. Characterization method
The synthesized of ZnO were characterized in detail by using X-ray diffraction (XRD) and scanning electron microscope (SEM) methods. For XRD characterization, the material was deposited on the glass substrate to obtain well-matched of ZnO diffraction peak. Moreover, SEM characterization was done to observe the evenness of coating materials on the surface of the POF.

The experimental setup to measure the absorbance spectrum of the previously prepared fibers is as shown in figure 3. A white light source (model: DH-2000-BAL Ocean Optics US) and a spectrometer (model: HR4000CG: UV-NIR) with full spectral output compromising a wavelength range of 200 nm to 1100 nm were used in this experiment. A personal computer was utilized as an interface to analyze the data generated from the spectrometer. As for the gas flow, it consisted of a vacuum pump, a digital pressure meter (model: HHP-90), a testing chamber, and a modified condenser.

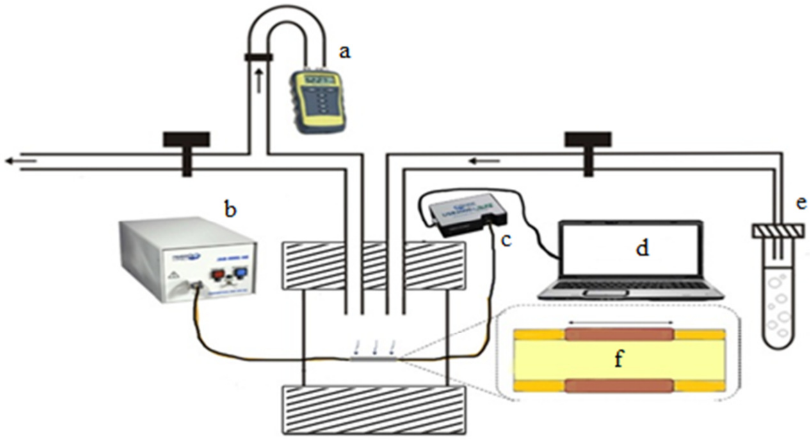

Figure 3. Experimental set up of absorbance measurement of methanol

Digital pressure meter (b) broad band light source (c) Spectrometer (d) computer

(e) Modified condenser (f) modified POF sensor

Air in the testing chamber was first pumped out using the vacuum pump. The pressure in the testing chamber was monitored using the digital pressure meter. Methanol vapor was then flows in to enter the testing chamber to interact with the sensor. As stated earlier in the theoretical section, the evanescence absorbance is affected by the fiber's parameters. Therefore, in this experiment the prepared fibers were prepared in 5 cm unclad section's length.

4. Results and Discussion

4.1. X-Ray Difraction
The result of the synthesized material coating was evaluated by X-ray diffraction (XRD) (D8 Advance, Bruker AXS Germany) and results are shown in figure 4. A series of characteristic peaks were observed which obtain well-suited with bulk wurtzite hexagonal. As compared with the FWHM of the peaks pattern, and proof the material coating revealed on the fiber surface was ZnO. The width peak of the ZnO is the widest among other material that used in this study. Meanwhile, the

highest intensity around 2300 is achieved by layered hydroxide zinc nitrate (LHZN). Due to the ZnO material has the smallest crystallize than others, so this material can be used properly to the POF. The d-spacing of each peak is then obtained by solution of the Bragg equation for the appropriate value of λ. Once all d-spacings have been determined, automated search/match routines compare the *d*s of the unknown to those of known materials. Due to each material has a unique set of d-spacings, matching these d-spacings provides an identification of the unknown sample. A systematic procedure is used by ordering the d-spacings in terms of their intensity beginning with the most intense peak.

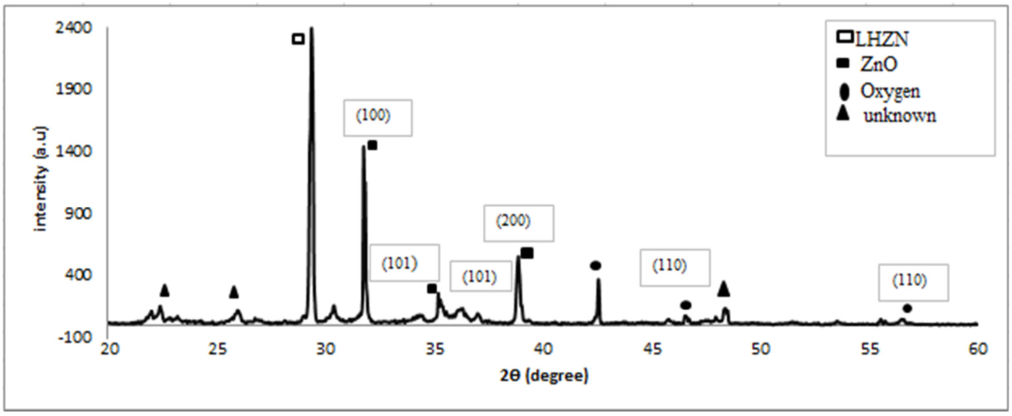

Figure 4. Typical XRD pattern of ZnO nanoparticles synthesized using solgel method (JCPDS 36-1451)

4.2. SEM

Coating of fiber intrinsic sensor was observed using scanning electron microscope, to obtain a good coating surface of modified part, as interaction area between the interactions of methanol vapour and light that radiated beyond the core, during the experimental to sense the present of VOC vapour. The SEM depicted in figure 5 shows the coating material that evenly distributed onto POF. The coating material distributed equally is crucial to ensure a good performance of sensor.

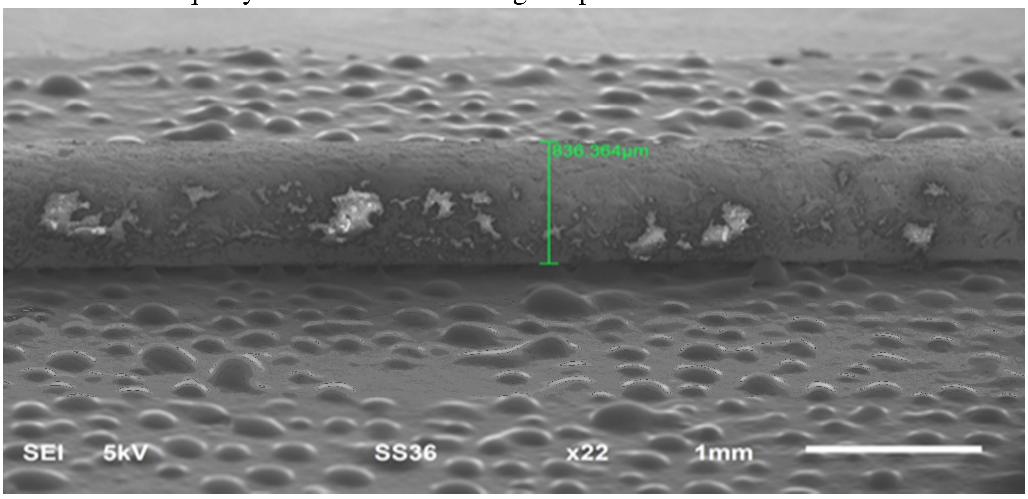

Figure 5. SEM image of POF coated with ZnO

The thickness of deposition material shown in figure 6. The deposition of ZnO on the POF surface was repeated to ensure ZnO coating formed on the fiber core after different numbers of coating steps. The measured ZnO thickness was (a) 118nm (b) 134 nm (c) 149.06 nm. The thickness layer that uses as the sensor is 149.06 nm during the test inside the chamber.

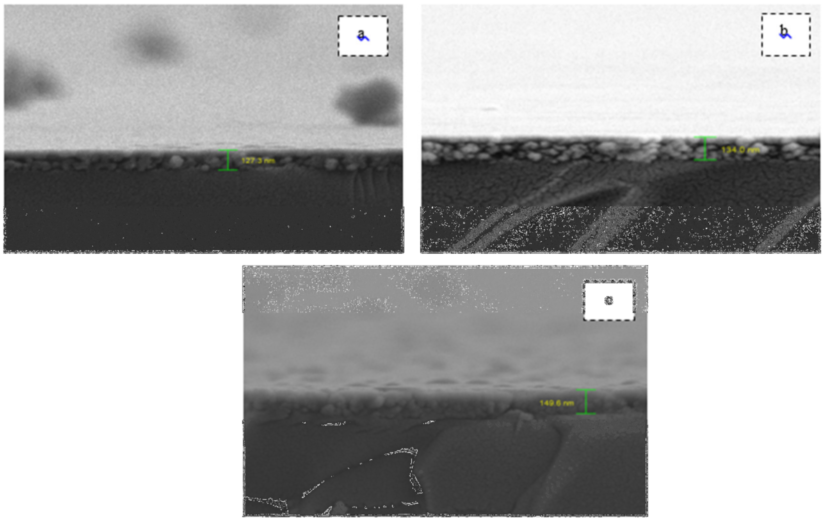

Figure 6. Scanning electron microscopy of the ZnO (a) 118nm (b) 134 nm (c) 149.06 nm

4.3. *POF intrinsic sensor detection of methanol vapour*

The light that radiates outside the core as a result of evanescent field wave is expected to react to the methanol vapour, and when the reaction occurs at the surface of the etched POF there will be a change to the internal reflection and intensity of the propagating light inside the fiber due to changes in the refractive index of the air around the core of fiber. Modified POF as intrinsic sensor were exposed to the methanol vapour and the results depicted in figure 7. The absorption spectrum coefficients graph showing the absorption of methanol. spectral characteristic of light ranging from 500 nm to 800 nm. The sensor was exposed to the different concentration of methanol vapor ranging from 5% to 50% as it shows in depicted graph the amount of absorption increases with increasing concentration of methanol vapour. This condition implies that the modified cladding possesses sensitive reaction as it is able to effectively detect the presence of the volatile organic compound inside the test chamber.

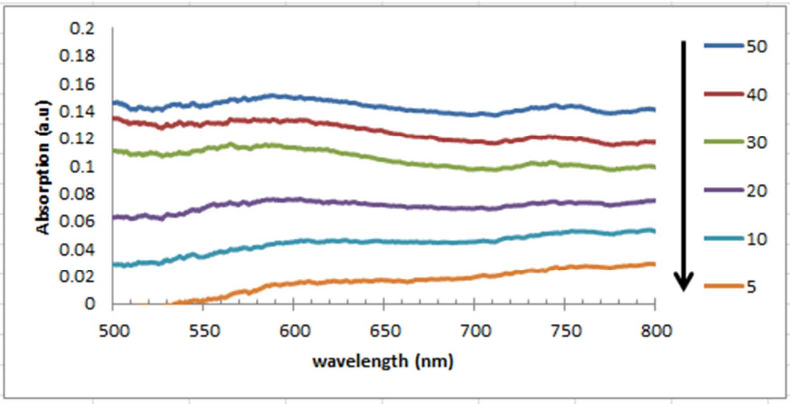

Figure 7. Absorbance Spectra of Methanol

Figure 8 depicted the response of the change in absorbance measurement during interaction of methanol vapor and intrinsic sensor inside the chamber test. This is proving the repeatability of the sensor by flowing in the methanol with the 30% and 40% concentration. When the gas flow in and interact with the sensor it will show the increment of absorbance and when the gas flow out the graph will show the decrement point of interaction. The stable result implies that ZnO adhered well onto surface of modified part of sensor. The good compatibility of the ZnO and optical fiber interface is contributed by electrostatic interaction between the oxide functional groups of ZnO and the polymeric material of the POF.

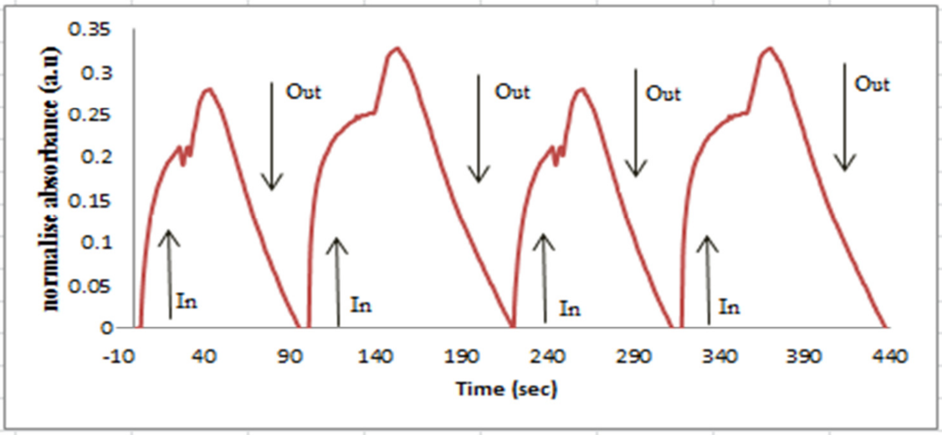

Figure 8. Response of the intrinsic sensor of POF to methanol vapour inside the testing chamber.

These results show that the proposed sensor coated with ZnO deposited on modified POF is suitable and shows better performance in measuring the presence of methanol in real time for future work the sensitive material that used as coating must be selected. The coating of synthesized material needed to obtain sensitive and transparent material. Furthermore, it can be processed without need any annealing process with high temperature to remove the organic residue in term of obtaining a good sensitive material. This is especially applied for sensor based on fiber optic with polymer material.

5. Conclusion

In this work, multimode POF intrinsic sensor coated with ZnO was developed. The sensor exhibit the present of methanol vapour inside the chamber test using absorbance spectroscopy measurement technique. The sensor exhibit repeatability response of the sensor to ensure a good performance in detecting the present of methanol vapour. The intrinsic sensor is a prospecting detector for air monitoring contamination in industry and environment. This sensor also can be used to detect another volatile organic compound which is easy evaporate in room temperature and can cause any harmful situation to human respiratory also another disease problem.

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