Modified multimode polimer optical nanofiber for volatile organic compound sensing in room temperature

F. ABDURRAHMAN[a,b], N. ARSAD[a,*], A. ASHRIF, A. BAKAR[a], GAN KOK BENG[a], S. SHAARI[b]
[a]*Department of Electrical, Electronic and System Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan, Malaysia*
[b]*STKIPBina Bangsa GETSEMPENA. Aceh, Indonesia*

An intrinsic fiber-optic sensor to detect volatile organic compounds (VOCs) at room temperature is described. The sensor consists of a multimode fiber coated with a zinc oxide (ZnO) nanoparticle layer. The ZnO layer is deposited on the fiber surface after etching a portion of the fiber cladding to increase the evanescent interaction between the light and ZnO layer. Adsorption of VOCs on the ZnO layer changes its refractive index, resulting in a light intensity change. The interaction process of the light carried by the fiber with the VOCs is observed in absorption spectra. The sensor responds to methanol and acetone vapor concentration ranging from 5%-50%.

(Received September 21, 2018; accepted June 14, 2019)

Keyword: Fiber intrinsic sensor, Chemical etching, Evanescent, Sensor probe

1. Introduction

Volatile organic compound such as methanol, acetone, and ethanol effortlessly evaporates[1], and these compound have permissible exposure limit in the open air, ground and surface of water. An appropriate sensor is needed to monitor the evaporation of VOCs can potentially harm human respiratory system and cause other diseases and in some cases pose a fire risk[2].

Numerous electronic sensors to measure VOC contamination have been developed [3]. Nevertheless, such sensors still struggle to sense target chemicals that evaporate easily at room temperature. Most electronic sensors are equipped with intergrated heater circuit to generate heat around 200-400 ^{o}C to enhance the sensitivity of the material deposited on the sensor[4]. However, Sensing materials such as zinc oxide (ZnO) and copper oxide deposited on electronic sensors need a source to generate power, and interfered by electromagnetic field interference[5].

Plastic optical fibre (POF) are an excellent choice for use in sensors for determination of certain chemical vapour indoors [6] or inside a fabrication chamber because of their excellent and ease of cladding modification. POFs are also less brittle than silica fibers, and tolerate a low operating power. polymethilmethacrylate (PPMA) is a polymer that commonly used in polymer fiber optics. Sensors with a PPMA-based POF as an intrinsic probe are attractive because of flexibility, low density and low weight with 1195Kg m^{-3} compared to silica fiber optic [7].

Fiber optic media have been produced as a sensors for VOCs at room temperature. The sensor have the ability to operate remotely without any electrical source to generate power. To enhance the performance of the sensor, Fiber optic have been doped with various material to obtain nanofiber probe such as polyaniline PANI [8], Indium tin oxide [9], ZnO doped with Ce, Li and Al[10], CU-doped Zno [11] carbon nanotube [12] and graphene [13, 14] have been used to enhance the sensitivity of sensors. For example, an ammonia sensor based POFwith diameter 600 µm and length of 1cm coated with PANI doped with ITO has been reported [15] detection by this sensor is based on surface plasmon resonance; the refractive index of the coating material changes upon ammonia exposure. In other work, an intrinsic POF sensor for VOCs with graphene oxide was used to sense the presence of VOCs at room temperature without any carrier gas flowing trough the interaction area of the sensor [16].

Currently, fiber optic intrinsic sensor have drawn much attention because of their simple fabrication technique, which involves removal of cladding or core shape modification [17]. The Geomotrical shape of a sensor is a crucial aspect to achieve good performance of sensor [18]. Improvement of the fiber etching method enables modification of the cladding process to produce intrinsic modification cladding of fiber optic. Reproducibility of fiber sensor with etching method is important to achieve consistent sensor performance. This is because performance depends on the geometrical shape of the fiber; specifically, its core diameter and length [19].

ZnO is able to enhance the binding energy in photonics field of research [20], and is widely used in numerous chemical compound as dopant, and sensing material to attain high sensitivity. During fabrication a sensor probe, depositing a material onto fiber is challenging step in using common deposition methods like dip coating, chemical bath deposition chemical vapor deposition and drop casting[21] in this work dip-coating is chose to obtain a good coating of ZnO on the surface of fiber.

In this article an intrinsic polimer optical fiber which consists of a modified multimode optical fiber POF coated with nano layer of Zinc oxide is developed. The diameter of the etched is 0.8 mm to prevent it from fracture. The instrinsic is produced by a repeatable process, in which a nanolayer of ZnO is placed on the bare core region after the fiber cladding is removed through mechanical etching. Mechanical etching allows the control of the etching process and high repeatability. The interaction of the sensor with VOCs is determined by changes of its evanescent field.

2. Experiment

2.1. Preparation of the etched multimode fiber

Multimode optical fiber, with core size of 0.8 mm and cladding thickness of 0.2 mm were used as intrinsic fiber sensors. The fiber sensor probe was fabricated by etching a length of 5cm in the middle of a fiber as an area to allow interaction between gas and the light within the evanescent field. Mechanical etching was performed using (Industrial Fiber optic, Inc. – IFCPK) sand paper and an abrasive aluminum oxide polishing film (Fiber instrument sale, Inc. - USA). This step was used to produce a precise, reproducible sensor probe. We employed mechanical etching because of chemical solvent as an etchant can influence the performance and durability of fiber optics exposed to vapor within a gas chamber. The waist diameter of the fiber will induce sensitivity because it controls the amount of light radiated to react with the chemical vapor present. The etching method must be properly selected to obtain a durable probe.

2.2. Preparation of zinc oxide nano layer

ZnO nanoparticles were synthesized by sol-gel method in which ZnO nanopowder (sigma adrich- US) (0.5M) was dissolved in ethanol (100.0 ml)and then constantly stirred for about 1 hour at temperature 70ºC. The solution was deposited on the etched fiber by dip-coating method. The fiber was dried on a hot plate at 60ºC to evaporate the solvent and remove the organic residue. This deposition and drying method was repeated four times to increase the thickness of the fibers. As shown in Fig. 2, the thickness of the coating increased after each dipping step. To confirm the structure of the material, X-ray diffraction (XRD) analysis was performed.

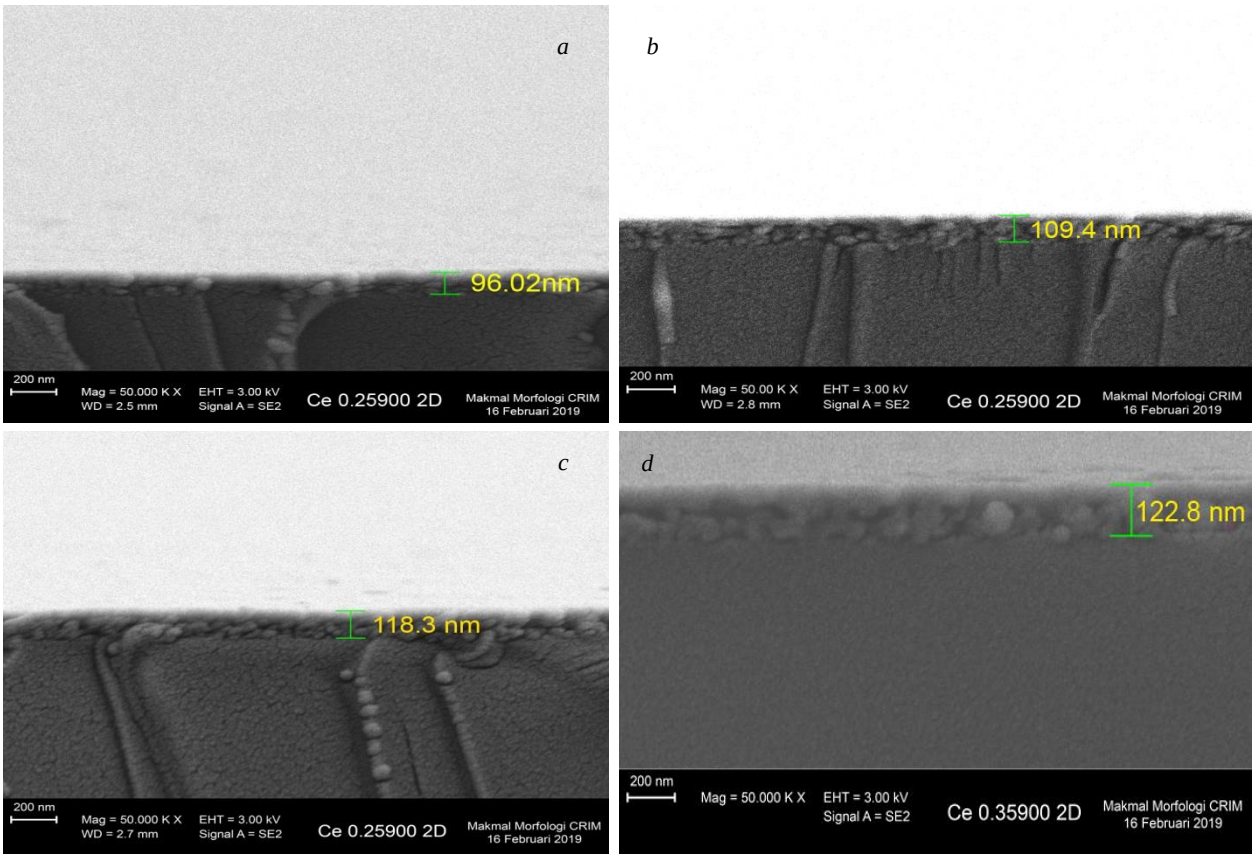

Fig. 1. Field emission scaning electron microscopy of the ZnO coating formed on the fiber core after different numbers of coating steps. The measured ZnO thickness was (a)98.02 nm (b) 109 nm (c) 118 nm (d) 122 nm

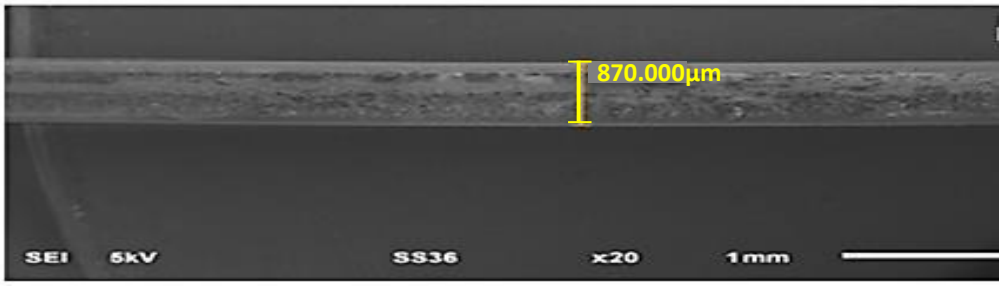

Fig. 2. Evanescent wave of the etched polymer optical fiber

2.3. VOC sensing experimental setup

The basic principle sensing of evanescent wave sensor is based on intrinsic fiber optic, involves measurement of the total internal reflection and propagation of light radiated beyond the core and cladding. The radiated light appears as a result of direct energy transfer from the optical absorption of the light propagated from the core to the material coating deposited on the core, which increases the excitation energy [8]. The penetration depth of an evanescent field is given by:

$$d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 sin^2\theta - n_2^2}} \quad (1)$$

where λ is the wavelength of transmiting light, θ is the incident angle at the surface of modified cladding, and *n1*, *n2* are the refractive index of core and cladding, respectively. The reflected light interact with the gas, which changes the light intensity resulting in a change of refractive index. The process result in a change of θ, which can be expressed as:

$$\theta_c = \mathrm{Sin}^{-1}\,(n_2/n_1) \quad (2)$$

3. Result

A stronger evanescent wave will increase the sensitivity of the response because θ increases sharply as it approaches the critical angle (θ_c).

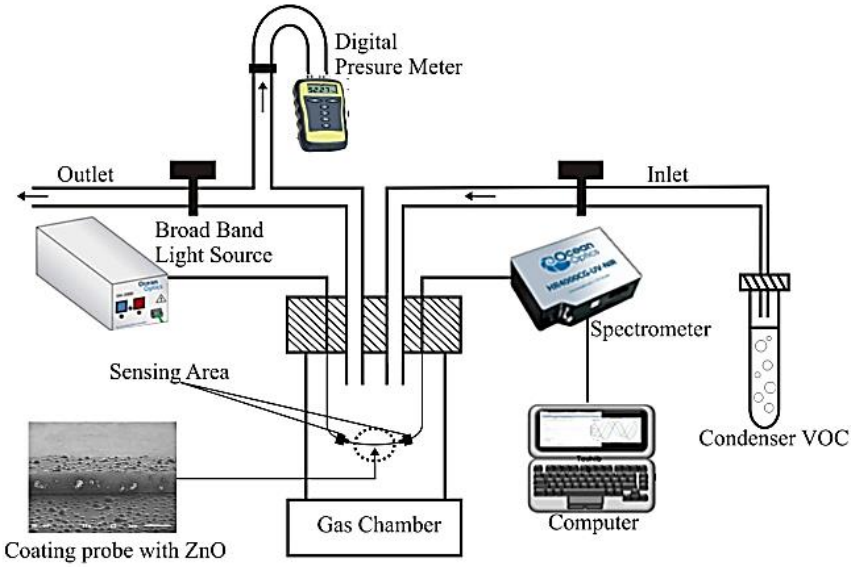

Fig. 3. Experimental setup for VOC sensing using a ZnO- nano layer coating on a nano fiber

To measure the performance of the modified fiber sensor, it was placed in a gas chamber and connected to a light source(Ocean optics - USA, DH-200-BAL), element CCD aray detector (Toshiba A364) as receiver connected to a spectrometer (Model HR400, Ocean Optics -USA) as absorbance spectral measurement. The experimental process setup shown above in Fig.3. The VOCs within the condenser are carried by dehydrated air from the vacum pump through the inlet tube that directly attached inside the sensing area within the chamber test. A light source with broadband wavelength range transmited the light and measured by spectrometer coupled to the end of fiber probe. The spectral Data of absorbance were analyzed by spectra suite software. A digital pressure meter was used to measure the air pressure within the chamber during the experiments.

The field-emission scanning electron microscopy (FESEM) image in Fig. 4 (a) shows the cross section of

POF after mechanical etching and subsequent ZnO deposition. Fig. 4 (b) illustrates a cross section of the fiber surface at 500x magnification, while Fig. 4 (c) shows the particles image of ZnO, and Fig. 4 (d) displays the thickness of the coating at 50x magnification the desposition process produced a nanolayer of ZnO coating the fiber. The fiber could not be subjected to an annealing process because the polymer fiber was only heat resistant 70ºC.

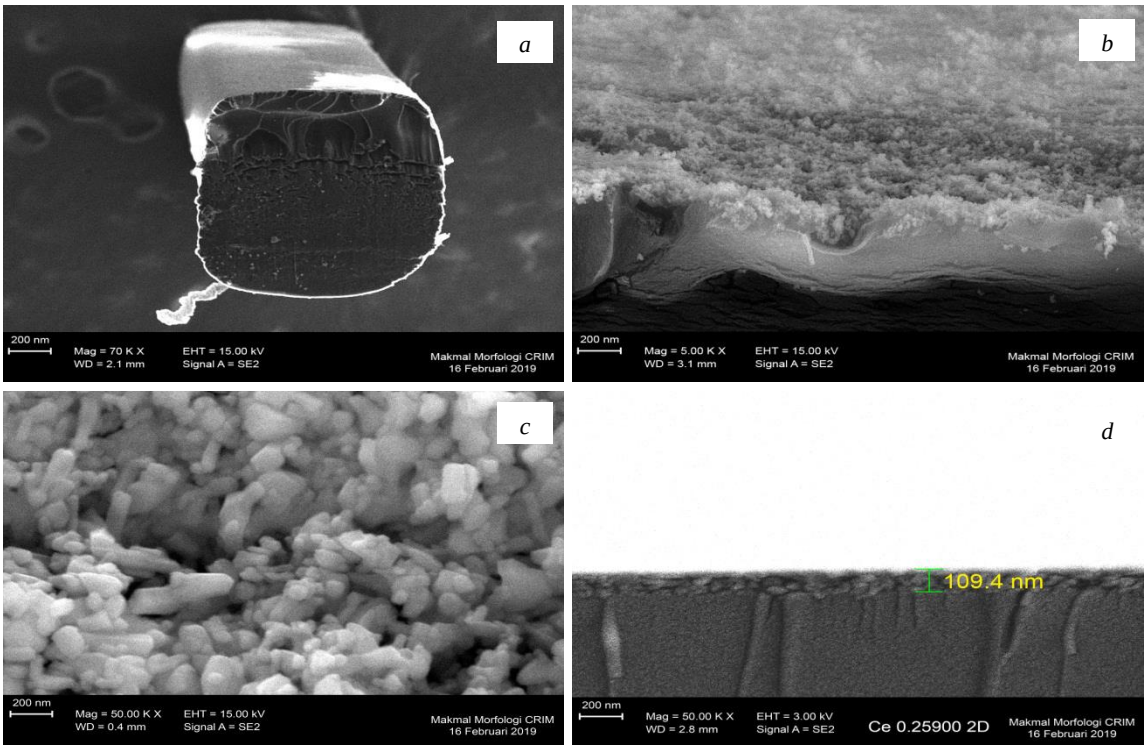

Fig. 4. Field emission scanning microscopy images of the optical fiber sensor.(a) cross section of POF after mechanical etching, (b) cross section of the fiber surface at 500x magnification (c) particles size of ZnO (d) the thickness of the coating at 50.00 KX magnification

3.1.2. X-ray diffraction

The XRD pattern of the coated fiber (Fig. 5) shows that the nanolayer on the fiber surface was ZnO. The material characterized by XRD was treated at 70 ºC to observe the material coating on the surface POFs.

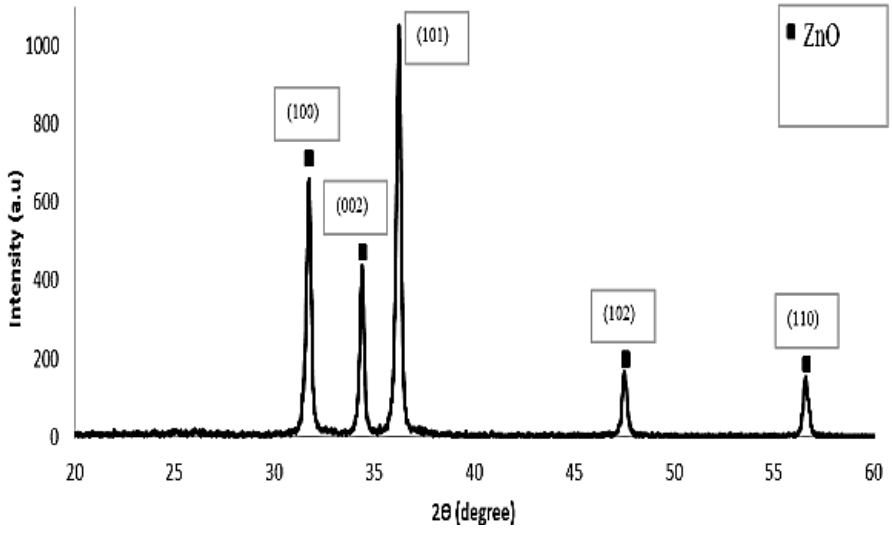

Fig. 5. XRD patern of the ZnO coating on the fiber senso

3.1.3. Sensor absorbance response

Fig. 6 present the absorbance of the fiber optic intrinsic sensor to various concentrations of methanol ranging from 5%-50%. The absorbance of methanol occurred at wavelengths between 500nm to 800nm, and the maximum interaction between light and vapor gas in the evanescent field was 533nm. A greater evanescent wave field was observed from the area with modified cladding than surrounding unmodified region. The interaction between the ZnO nanolayer on the modified fiber and different concentrations of methanol transforms the optical characteristic of the coating layer; that is, the sensor responds to methanol.

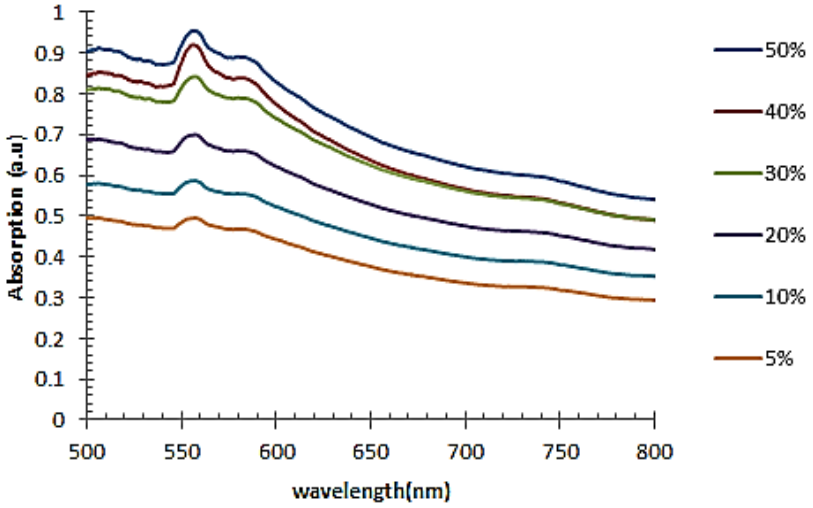

Fig. 6. Response of the sensor to methanol

When methanol vapor flowed through to the interaction area, chemical reactions occurred between methanol and oxygen molecules, resulting in the formation of formic acid and water vapor in conjunction with the realease of electrons into the coating material [4].

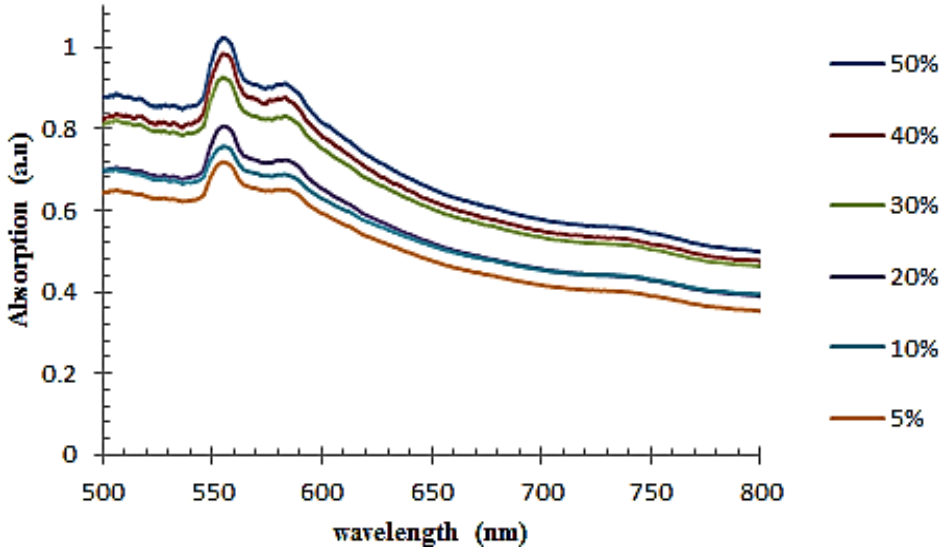

Fig. 7. Response of the sensor to acetone

Fig. 7 depicts the absorbance spectra of POF intrinsic sensor coated with ZnO nanolayer exposed to different concentrations (5 % - 50 %) of acetone at room temperature. The absorbance response of acaetone also occured in wavelength range 500-800nm, and the measured absorption peak maximum was in 550 nm. This response occurred because of the photon traversed through the porous ZnO nanolayer on the sensor.

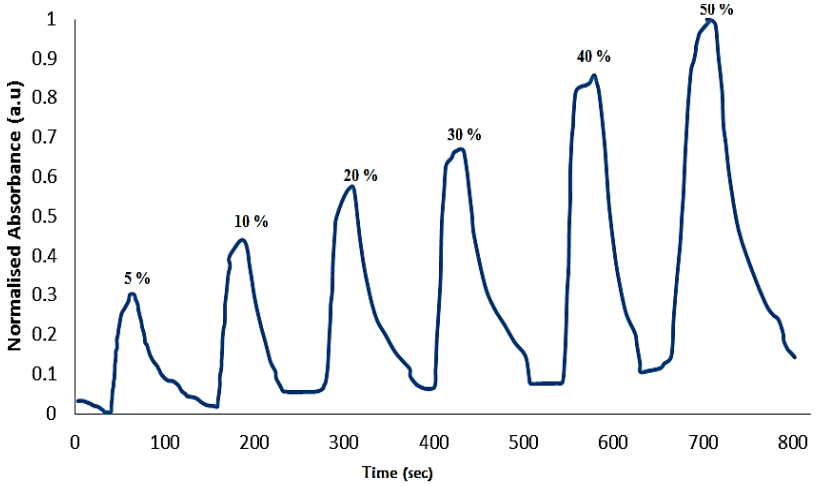

Fig. 8. Dynamic response of volatile organic compound toward different concentration

The dynamic response of the sensor towards different concentrations of VOCs inside the chamber test was measured, as shown in Fig. 8. The sensor response changes according to the different methanol concentration. This is likely caused by the change of the refractive index of the ZnO nanolayer as well as chemisorption of methanol onto ZnO nanolayer, as shown of peak absorbance response of wavelength .The absorbance of the sensor increases substantially as the response time lengthens. The dynamic absorbance sensor increased when the sensor was exposed to 5% VOC. The sensor absorbance recovered fully, returning to its baseline value upon exposure to air. Overall, the response time of the ZnO coating increased with VOC concentration, while the recovery time in air remained similar. The response and recovery of the developed sensor are stable. Furthermore, the sensor shows high sensitivity and repeatability. The repeatable behavior of the sensor was confirmed by measuring its absorbance response after exposure to another cycle of 5%, 10%, 20%,30%,40% and 50% of methanol. Similar results to those of the first cycle were obtained for the second cycle.

4. Conclusion

The VOC sensing of performance of fiber optic intrinsic sensor consisting of POF coated with a nanostructured ZnO layer was examined. The main objective of this research was to identify the effect of a ZnO nanolayer on the performance of a POF as a highly sensitive optical transducer. The performance of the sensor toward VOCs methanol was measured at room temperature. The fiber sensor was sensitive towards methanol and acetone with absorbance responses depending on the VOC concentration, and maximum absorption wavelength of 533 nm for methanol and 550 nm for acetone. The magnitude response of the sensor was similar for methanol and acetone of the same concentration. The result indicates the sensitivity of the sensor influenced by refractive index of the ZnO nanolayer. Nevertheless, the absorbance responses change depend on methanol and acetone concentration. The sensor response is originate from the chemisorption of both VOCs onto the ZnO nanolayer. The absorbance spectrum of the developed sensor increases when exposed to VOCs over the wavelength range of 500-800nm. A methanol concentration of 5% was sucsessfully detected by the sensor at room temperature with fast response and recovery times. The high sensitivity of this fiber sensor coated with a ZnO nanolayer towards VOCs indicated that it has potential for application in air contamination analysis, and bio sensor detection such as breath analyzers.

Acknowledgments

All authors are grateful to Photonics Technology Lab FKAB Universiti Kebangsaan Malaysia, The Ministry of Higher Education of Malaysia for the support and grant under DIP-2018-017 and CRIM laboratory - University Kebangsaan Malaysia laboratory for providing the laboratory facilities to carry out the research.

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*Corresponding author: noa@ukm.edu.my
fhayzar@gmail.com