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Methane Gas Detection Using ZnO Coated on Tapered Optical Fiber

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Abstract: Zinc Oxide (ZnO) is one of the semiconductor materials used as a sensing layer for various detection purpose and one of them is to detect methane gas. In this work, an optical fiber sensor coated with ZnO was developed to detect methane (CH_4) gas. The ZnO layer was synthesized and deposited onto tapered optical fiber via drop cast method. The characterisation of synthesized ZnO was performed via SEM and EDX to verify the material properties. The developed sensor with 750 nm thickness of coated ZnO is then tested towards 0.5%, 0.75% and 1.0% concentration of methane gas at room temperature. The absorbance response observed during the sensing is correspond to the change of methane gas concentration. It was found that the sensor showed highest sensitivity when exposed to 1% concentration and lowest sensitivity for 0.5% of methane gas. The response and recovery time for 1% methane gas exposure was recorded to be around 2.0 minutes and 3.0 minutes, respectively. The developed ZnO sensor using optical fiber has showed sensitivity towards CH_4 gas at certain level of concentration.

Keywords: Gas Sensors, Optical Sensors, Sensing Material, Zinc oxide

1. Introduction

Methane gas when mixed with air can be highly volatile and could trigger explosion due to its inflammability properties. Continue monitoring methane is important especially in a confine and hot place such as coalmines and other field dealing with methane emission (Bhattacharyya et al., 2007). Therefore, the development of reliable and cost-effective methane gas sensor remains significant due to environmental safety issues. Currently, electrical sensor with semiconductor metal oxide for gas sensors is rapidly growing for such application. However, this type of sensor easily susceptible to electrical noise, unsuitable for volatile environment and has poor selectivity. On the contrary, optical based sensor using fiber optic offers better properties such as low cost, robust, sustainability in volatile and flammable environment and also resistance in electromagnetic interference. Modification of the optical fiber such as micro-channelling, etching and tapering would enhance the evanescent light to interact with the surrounding of the optical fiber. By coating optical fiber with a layer of sensitive material for gas detection, any changes of its properties will also alter the evanescent light passing through the layer (Pishdadian et al., 2013).

Semiconductor metal oxides exhibit chemical and thermal stability and high sensitivity to combustible and toxic gases and thus can be utilized as a sensing layer for such detection (Yi et al., 2011). For decades, extensive effort has been devoted to improving its performance such as sensitivity, selectivity, and reliability of the sensors. This includes by introducing optimized structure, doping, and chemical modification of the metal oxides (Paraguay et al, 2000; Korotcenkov, 2005). Typical semiconductor metal oxide gas sensor operates at high temperature (200^oC – 500^oC). which is quite unsuitable for a heated area for continue monitoring.

One of the semiconductor materials which has much attraction for its wide applications is Zinc Oxide (ZnO). It has been used for solar cells, chemical sensors, electrical and acoustic devices and luminescent purpose (Saito et al., 1985). ZnO is also known to be one of the earliest discovered and most used for applied oxide gas sensing material (Seiyama & Kato, 1962). It sensitives to various types of gasses at moderate to high operating temperature. Research on ZnO thin film sensors is growing rapidly and has shown detection towards hydrogen (H_2), carbon monoxide (CO) and methane (CH_4) (Nunes et al., 2001). Previous work reported mostly on electrical based sensor. For instance, investigation reported in (Nanto et al., 1993) where the ZnO was doped with Aluminium detecting trimethylamine gas. Cheng et al. has reported ZnO nanoparticles thin film able to detect volatile hydrocarbon gas with different concentration (Cheng et al., 2004). More works on electrical gas sensor published in (Bhattacharyya et al., 2018) where ZnO nanocrystalline with Palladium-Silver as a catalytic able to detect methane at 150^{o}C-250^{o}C operating temperature.

Several works has been performed to investigate further on capability of optical fiber as a gas sensor. Hideo Tai et al. have reported on their work using fiber optic evanescent wave to detect CH_4 (Tai et al., 1987). The optical response was detected at 3.392-um line of He-Ne laser with evanescent wave of 5% to 40% of the total propagating power is generated outside of the fiber. Even so, the 3.392-um source is quite costly for optical fiber gas sensor. Microstructure optical fiber also has been tested for CH_4 detection. (Hoo et al., 2010) has worked on multiple side-opening on the microstructure optical fiber to detect CH_4 gas. The source used was Near Infra-red region (N-IR) whereby approximately on 1665.48 nm, it has shown some response towards CH_4 (Hoo et al., 2010). The response time recorded was 3 s towards 5% of CH_4 concentration.

None of these works demonstrate ZnO coated on tapered optical fiber for methane detection, which makes its potential as gas sensor can be explored further. In this paper, tapered optical fiber coated with ZnO thin film has been successfully developed for methane gas detection. The sensor has shown optical (absorbance) response towards high concentration of methane at room temperature.

2. Methodology

Before ZnO coating process takes place, the multimode (MM) optical fiber is tapered using Vytran GPX-3400 optical glass fiber processor. Tapering is a process of pulling the optical fiber while heating it with the graphite filament to get taper dimension profile as preferred. For this work, the MM optical fiber from a standard of 125-um diameter was tapered, to waist diameter of 40-um, 2-mm up/down taper and 10-mm in length. The tapered region is the modification of the optical fiber as to enhance the evanescent light emits from the core of the fiber. Fig. 1 illustrates tapered optical fiber with sensing layer coated onto the tapered region.

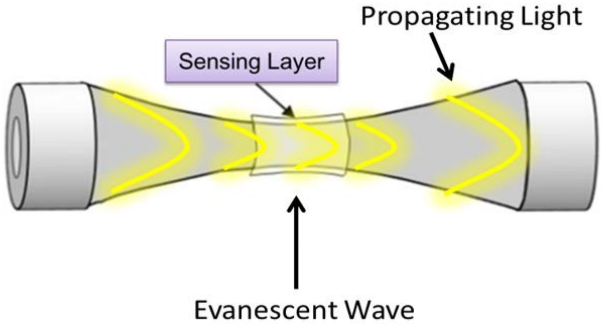

Fig 1. Tapered optical fiber

The evanescent wave generation happen at the interface between the core and cladding when the light propagates with Total Internal Reflection (TIR). The evanescent field penetrates only a small distance but transfer energy to the cladding. The intensity of evanescent field decays exponentially away from the interface. The Eq. (1) shows the penetration depth, d_p of evanescent field in the cladding (Yahya et al., 2018).

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

Whereby, θ is the angle of incidence, n_1 and n_2 are the refractive index of core and cladding respectively, and λ is the wavelength of the light. By removing the cladding of the fiber, the evanescent field can be utilized for sensing application so that a direct contact to the sample is formed (Renganathan et al., 2011).

Preparation of ZnO using sol-gel method follows accordingly. Zinc Nitrate ($Zn(NO_3)_2$) of 0.01 M in aqueous solution was mixed with 0.01 M of Hexamethylenetetramine (HMTA-$C_6H_{12}N_4$) in a 100 ml of deionized (DI) water. The solution was then stirred for 2 hours at 60°C until it became a clear homogeneous solution. The chemical reaction has produced ZnO when hydroxyl ions (from HMTA degradation) react with Zn^{2+} ions (Lokman et al., 2015). To coat ZnO, simple procedure of drop cast method was performed. The fiber was dipped in the ZnO solution for 5 minutes and then dry for another 5 minutes on the hotplate. The process was repeated for 5 times to increase its coating layer thickness. The sensor fabrication process can be summarized in Fig. 2.

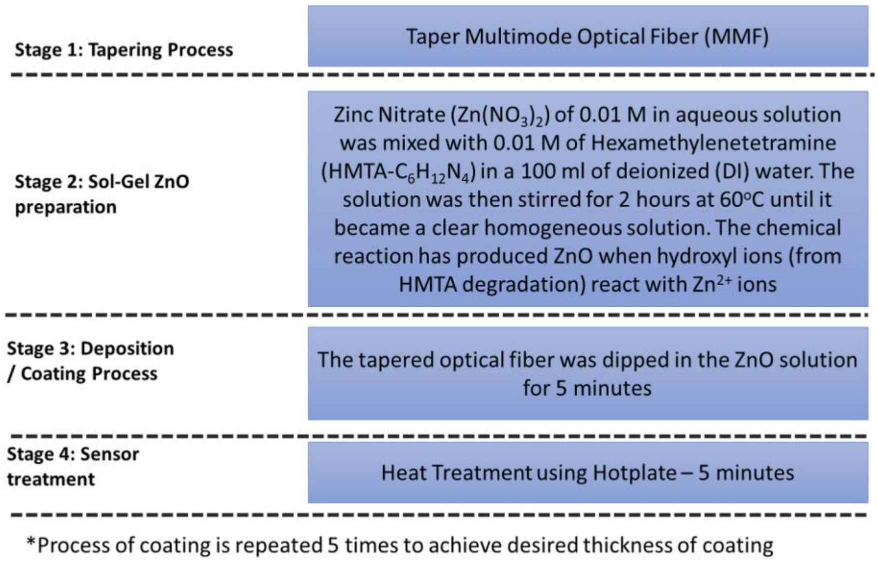

Fig. 2. Sensor fabrication process

To inspect the morphology of the ZnO coating, characterisation was carried out via Scanning Electron Micrograph (SEM). The CH_4 gas testing setup is illustrated in Fig. 3. Tungsten halogen was used as a light source and spectrophotometer USB4000 VIS-NIR to observe changes in absorbance spectrum ranging 200 nm to 1100 nm wavelength. The developed sensor sample was placed in the sealed gas chamber and the purging gas was controlled via computer software which regulates the concentration of CH_4 diluted in pure synthetic air. The test was performed between 0.5% to 1.0% concentrations of CH_4 and the absorbance measurement and dynamic response of the sensor was recorded.

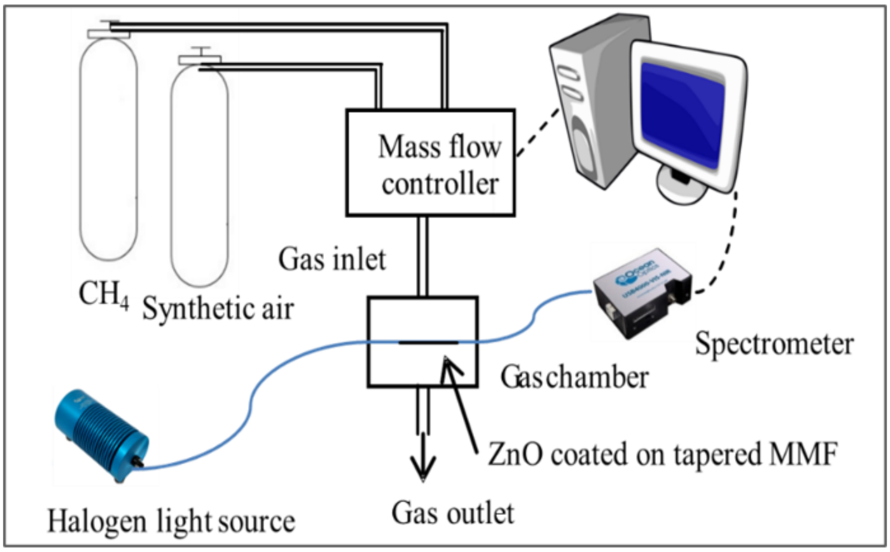

Fig. 3. Gas sensing experimental setup

3. Results and Discussion

The surface morphologies of ZnO deposited onto tapered optical fiber was inspected using SEM as demonstrated in Fig. 4. From the images, it was found that the ZnO thin film deposited was an amorphous structure. The layer appeared to be dense, compact and has a uniform coating. On the surface it was observed that the layer has random cracked pattern probably due to layer per layer coating. To measure the thickness, the coated fiber is diced to inspect the layer coated. It was found that the thickness is averagely about 750 nm.

To verify the ZnO synthesised, EDX measurement was conducted and the result is displayed in Fig. 5. Clearly the peaks indicate the existence of zinc (Zn) and also oxygen (O) elements on the sample. Note that the silicon (Si) is from the glass substrate used to hold the sample during the measurement.

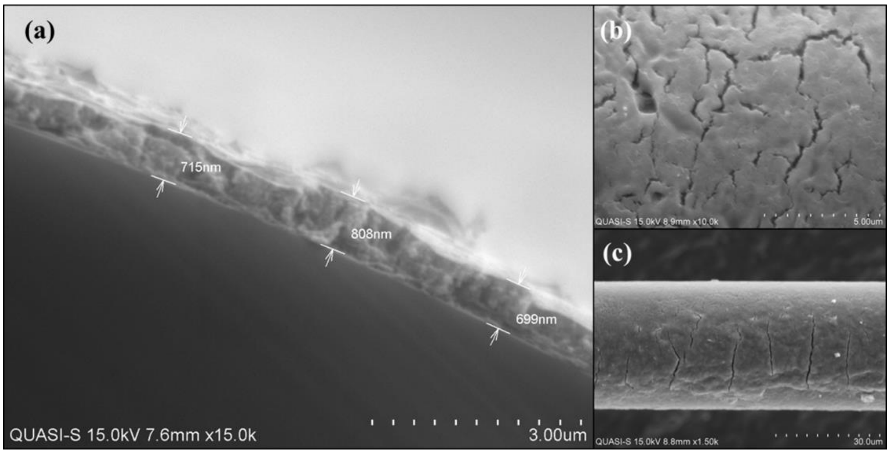

Fig. 4. SEM image of a) Cross-sectional image of ZnO coated, (b) surface morphology of ZnO, (c) ZnO coated on the tapered optical fiber

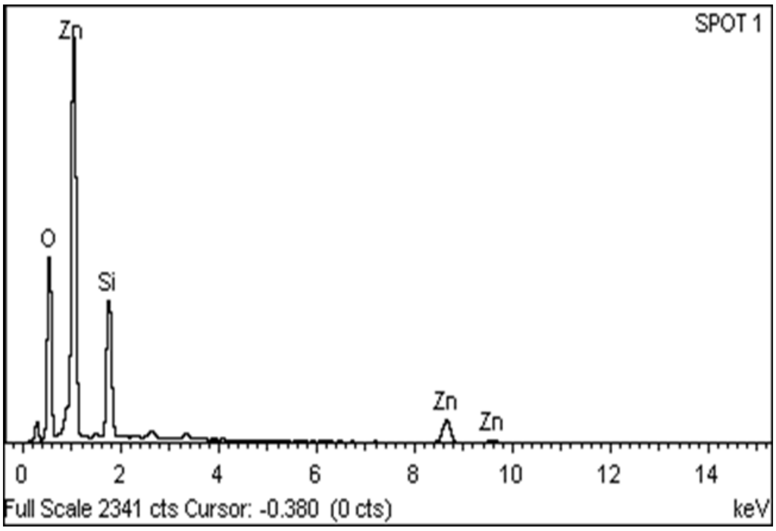

Fig. 5. EDX peaks of synthesized ZnO

Fig. 6 presents the absorbance response of ZnO coated tapered optical fiber towards different concentration of CH_4 at room temperature. The pure synthetic air and CH_4 gas were alternately purged during the testing for 15 minutes and 10 minutes, respectively. At 0.5% concentration of CH_4, there was no absorbance change spotted but at 0.75% of CH_4, there was a slight increase on the absorbance spectrum between 500 nm to 800 nm range. The significant change of absorbance can be seen when 1.0% of CH_4 was exposed to the ZnO sensor.

The absorbance difference observed can be explained through this mechanism. It starts with the chemisorption of oxygen on the ZnO surface. The oxygen molecule attracts an electron from the conduction band of ZnO and forms O_2^- at room temperatures. ~~These O_2^- ions get adsorbed on the ZnO surface forming ZnO:O_2^- species through strong ZnO-O_2^- interaction.~~ Through strong ZnO-O_2^- interaction, ZnO:O_2 species are formed with O_2^- ions adsorbing on the ZnO surface.When the analyte CH_4 breaks down into C-H_3 and H^+, this hydrogen radical reacts with the adsorbed O_2^- producing H_2O and by product CO_2 (Allsop et al., 2017). This process has changed the electrical properties of the ZnO and altered the absorption of light, ~~hence~~ consequently changing the ~~the change in~~ absorbance magnitude. During the recovery process, the sensing layer of ZnO ~~was exposed~~ was exposed with synthetic air. The flow in/out of adsorbed oxygen and desorbed H^+ ions ~~in/out~~ of the sensing layer ~~hence~~ causing the absorbance spectrum to return~~s~~ to its original baseline (Yahya et al., 2020).

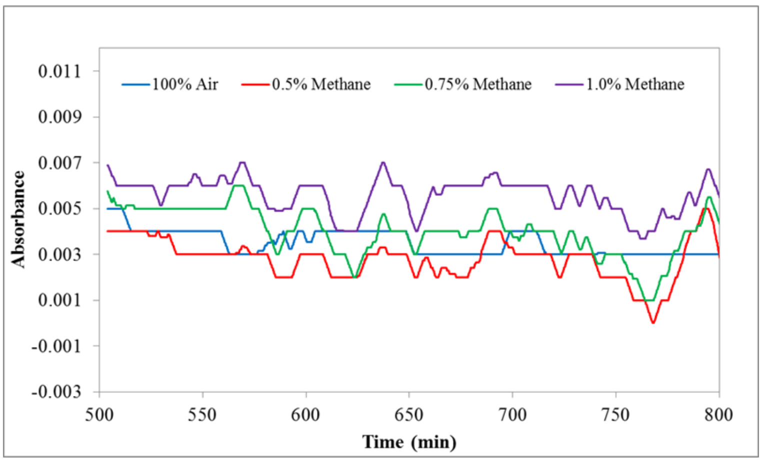

Fig. 6. Absorbance response versus wavelength when ZnO sensor exposed to CH_4 at room temperature

Fig. 7 shows the dynamic response of ZnO coated tapered optical fiber sensor when exposed to 0.5%, 0.75% and 1.0% concentration of CH_4. It was found that the absorbance changes only occur when exposed to 0.75% and 1.0% of CH_4 concentration. At 0.5% of CH_4, there is no change detected at all. It is believed that due to ZnO amorphous structure that is dense with no porosity has made active surface area of the ZnO to react with the analyte became less. On the other hand, when the CH_4 concentration is increase, molecules of H^+ from the broken bond of CH_4 surpluses on the surface and reacted to the chemisorbed oxygen on the surface of ZnO (Yang et al., 2019). ~~It is also noted that the baseline of the responses drifted when higher concentration of H_2 was introduced.~~ It is noteworthy to mention that when higher concentration of H_2 was introduced, the baseline responses drifted from initial baseline. This is due to more H^+ ions trapped in the amorphous structure of ZnO. The response and recovery time recorded for 1% exposure of CH_4 are 2.0 minutes and 3.0 minutes, respectively.

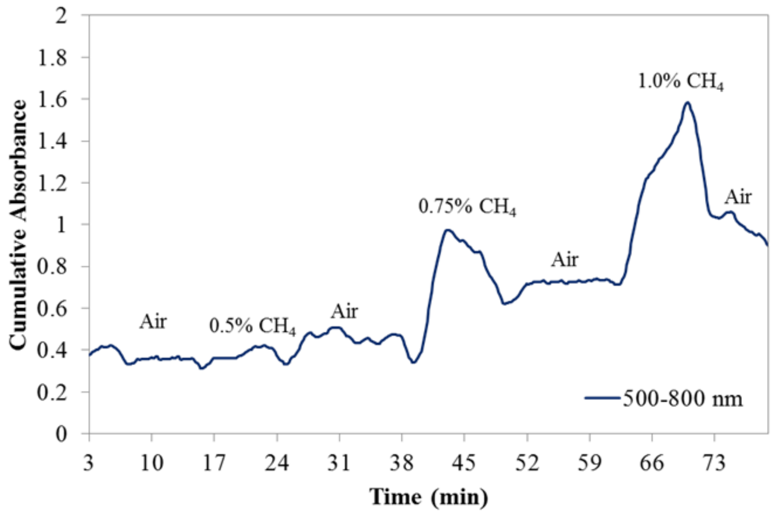

Fig. 7. Dynamic response of ZnO sensor when exposed to 0.5%, 0.75% and 1.0% concentration of CH_4 gas

4. Conclusion

CH_4 gas sensing using ZnO coated on tapered optical fiber have been successfully presented in this paper. From the SEM and EDX characterisation, the ZnO coating layer exhibit uniform thin film amorphous structure with thickness of 750 nm averagely. The sensor response was detected at room temperature for higher concentration (0.75% and 1.0%) of CH_4 gas compared to the lower concentration (0.5%). This sensor has shown potential gasochromic properties for CH_4 gas sensing application

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