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Metal Oxide Based Optical Fiber for Methane Gas Detection

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Abstract – Semiconductor metal oxide (SMO) as a sensing layer for gas detection has been widely used. Many researches have been performed to enhance the sensing performance including its sensitivity, reliability and selectivity. Electrical sensors that use resistivity as an indicator of its sensing are popular and well established. However, the optical based sensor is still much to explore in detecting gas. By integrating it with SMO, the sensor offers good alternative to overcome some drawbacks from electrical sensors.

Keywords: Gas Sensor, Metal Oxide, Methane

Introduction

Coalmines, water treatment plant and land fill sites always deal with methane (CH_4) emission. It is known that CH_4 will become highly combustible when mix with ambient air and could trigger massive explosion. Thus it is essential to monitor CH_4 emission to the atmosphere to ensure environmental safety (Mitra & Mukhopadhyay, 2007). Development and enhancement gas sensor has been explored for the past decades. Optimizing the sensor in term of its sensitivity, repeatability, reliability is very important as to benefit such mankind.

Typical gas sensor has been widely used is electrical based sensor. Basically, it uses semiconductor metal oxide as the sensing layer and integrates it with electrical probe to detect the analyte existence. Even so, this type of gas sensor prone to get distracted by electrical noise, unsuitable for volatile environment and has poor selectivity towards the analyte. On the other hand, optical fiber based sensor suggests better properties for instance robust, able to operate in volatile environment and resistance to electromagnetic interference (EMI). Generally, we could do some alteration on the optical fiber so it could improve the evanescent wave from the core through the cladding of the fiber. Optical fiber alteration can be done in several ways such as tapering, etching, microchannel cutting and a few more. The evanescent wave will interact with the sensing layer coated surrounding the optical fiber which reacted with the analyte (gas) (Pishdadian & Shariati Ghaleno, 2013).

Semiconductor Metal Oxide (SMO) as Gas Sensor

SMO offers chemical and thermal stability and provide excellent sensitivity to toxic gases and combustible hence good candidates for such detection. Much exploration on this sensitive layer has been carried out through decades and many improvements have been made as to obtain versatile characteristic of gas sensor. Improvement on material structure, doping, composite and chemical modification are important to enhance the sensing performance such as reliability, selectivity and sensitivity of the sensors.

Most common sensing layer of semiconductor metal oxide used for CH_4 detection are Zinc Oxide (ZnO) and Tin Oxide (SnO_2) (Bose et al., 2005; Gruber et al., 2003). Both of these SMO are non-stoichiometric independent of the preparation methods used. Generally the n-type semiconductor is non-stoichiometric associated with oxygen vacancy and metal excess acting as donor states providing conduction electrons (Mitra, Mukhopadhyay & Anoop, 2007). Nevertheless, the overall surface resistance of the films is significantly affected by chemisorption process whereby the oxygen from air gets into the grain boundaries. The chemisorbed oxygen traps conduction electrons and become negatively charged ions (O^{2-} , O^{-} or O^{2-}) on the surface (Schierbaum et al., 1991). Basically the process will result in an increase of the surface resistance.

The hydrocarbon gas such as CH_4 is a reducing gas. The trapped electrons are released when gas molecules and the negatively charged oxygen interact to produce H_2O and CO_2 (Bhattacharyya et al., 2008). For recovery process when the gas is removed out of the environment, the resistance of the surface will reduce. The mechanism explained above is for electrical gas sensor which already established and commercialized used. Recent works by George Fedorenko et al. has shown electrical based sensor using Pd/SnO_2 sensitive to CH_4 at elevated temperature of 350^{o}C. The nanosized Pd-containing SnO_2 was synthesized by a sol–gel technique. It was found that the highest sensor response of 1.41% Pd with the sensitivity of 12.4. The response time and recovery time measured are 6 s and 10 s. This study showed that the developed sensor is able to detect CH_4 with concentration range of 47–937 ppm (George et. Al., 2017). (Emil CORDOS et al. 2006) has also reported their work on resistive sensor using SnO_2 for CH_4 detection at operating temperature of 400^{o}C. The limit of detection was found to be at 1000 ppm of CH_4. The technical characteristics and detection method as well as the apparatus functional sketch were also studied.

Optical Fiber for Gas Sensing Application

Numbers of 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, Yoshino & Tanaka, 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, Y.L et al. 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.

Photonic Crystal Fiber (PCF) micro-taper has shown changes in wavelength shift in the range of 1546 – 1554 nm wavelengths when exposed to CH_4 gas (Monzon-Hernandez et al., 2008). The characteristics of CH_4 detection technique using near-infrared absorption spectroscopy was discussed in (Wang, Zhang & Zhang, 2013). The detection system is basically based on wavelength modulation and second harmonic (2f) signal detection technology. The CH_4 gas has a stronger absorption line at 1.66 μm where there is no water vapor and CO_2 absorption. The full width at half-maximum (FWHM) of CH_4 absorption cross section at near 1653.73 nm is about 0.06 nm, which is the absorption line of the detection system. The theoretical graphs for the absorption characteristics of D-fibre was used to monitor the presence of methane gas when the fiber transmits light in the 1.66pm wavelength band. Culshaw et al. has present their experimental works of 5m length of D-fiber is inserted into a test chamber. They have achieved resolutions of the order of l000 ppm of CH_4 with the signal levels available from the system. Both the measurement of integrated CH_4 concentration along the length of the fiber and distributed probing using time resolved interrogation of the gas concentration along the fibre length was discussed (Culshaw et al., 1992).

Semiconductor Metal Oxide Coated on Tapered Optical Fiber

There are several methods to modify the optical fiber such as micro-channelling, etching, and tapering (Fini, 2004). Tapering is a process of pulling the optical fiber by heating so that the size of the fiber becomes smaller. The important parameters in tapering are down and upper taper, length and waist diameter. This dimension profile will effect on how much the evanescent wave propagating from the core through the cladding layer. Figure 1 and 2 show how the optical fiber can be tapered and the equipment that can perform the tapering, respectively.

The basic principle of evanescent wave generation can be explained as follows. During light propagation with TIR, evanescent field is generated at the interface between the core and cladding which penetrates only a short distance but transfers energy to the cladding. The intensity of evanescent field decays exponentially away from the interface. The penetration depth, d_p of evanescent field in the cladding can be expressed in Equation 1 below,

$$\boldsymbol{d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 sin^2\theta - n_2^2}}} \qquad \textbf{(Eq. 1)}$$

In which 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. This evanescent field can be utilized for sensing application by removing the cladding so that a direct contact to the sample is formed (B. Renganathan et al. 2011).

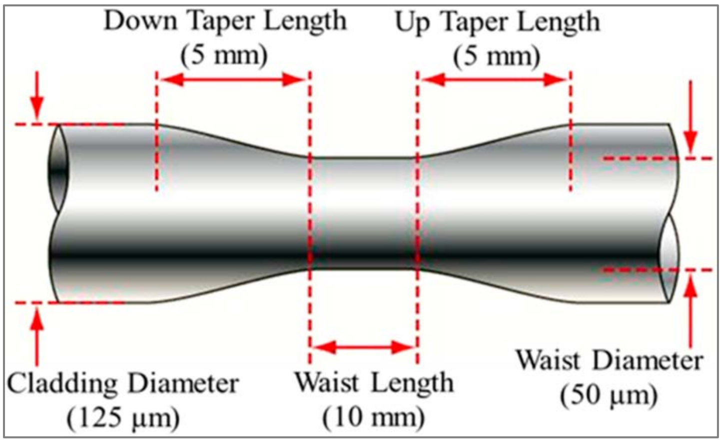

Figure 1: Tapered optical fiber parameters (Shabaneh, et al., 2014)

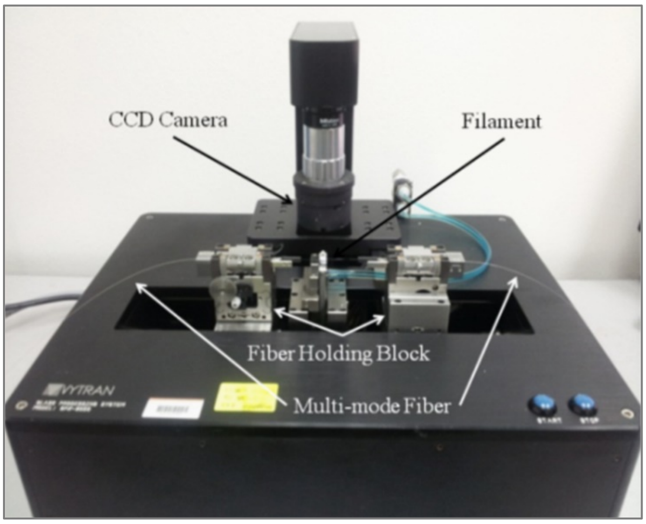

Figure 2: Optical Fiber Tapering Equipment (Vytran) (Shabaneh, et al., 2014)

The tapered optical fiber can be coated with SMO as for sensing layer to react with the analyte (gas). A few studies were carried out on optical fiber coated with SMOs. J. Ou et al. has performed investigation on nano-platlet Tungsten Trioxide (WO_3) coated on optical fiber for hydrogen (H_2) gas sensing. The reflectance response has shown good sensitivity with less than 60 s for response and recovery time (Ou, et al., 2010). Another optical fiber sensor coated with SMO was reported by Nor Akmar et al. where MnO_2 nanostructures coated onto tapered optical fiber for H_2 detection. The studies include the effects of thin layer palladium coated on MnO_2 and annealed sensor sample towards H_2 sensing performance. The testing was conducted at elevated temperature of 240°C. It was found that the absorbance response of the annealed Pd/MnO_2 on optical fiber has increased to 65% as compared to 20% for the as-prepared Pd/MnO_2 upon exposure to 1% H_2 in synthetic air (Nor Akmar et al., 2017).

Aidong Yan et al. have performed studies on fiber optic sensors for methane measurements based on evanescent optical interactions. The porous Pd-SnO_2 thin film was synthesized by block copolymer template scheme and coated on D-shaped fiber as functional sensing materials. The sensor has shown good repeatability at evaluated temperature of 500°C. The result indicates that the sensor can readily measure CH_4 concentration between 1% and 50% (Aidong Yan et al., 2016). Recent work published by (Thomas Allsop et al., 2018) on optical sensing using single mode optical fiber coated with ZnO to detech CH_4 at room temperature. The operation of the device is basically upon the interaction of near-infrared localized surface plasmons generated by platinum regions within a matrix of ZnO. The sensor yields an equivalent refractive index spectral sensitivity of 1.8 x 10^5 nm/RIU.

The proposed sensing mechanism is when the electron donated from CH_4 dissociation is received by metal oxides centre of crystal lattice. The metal oxides ions are reduced to a lower state which changes the electronic state of the metal oxides. This change will affect the optical properties of the evanescent wave that probing the interaction of sensing layer of metal oxides and the CH_4 molecules. To the current status, there is no study published on the tapered optical fiber coated with SMO for CH_4 detection. Therefore, it is a good opportunity to explore on the potential SMO such as ZnO and SnO_2 to be coated on the tapered fiber for CH_4 sensing. Absorbance, reflectance and transmission of the optical responses can be studied for a new discovery and potential towards CH_4.

Conclusion

This articles review on CH_4 detection using optical fiber coated with semiconductor metal oxide as a sensing layer. The modification on the optical fiber is essential to obtain as much as evanescent wave can penetrate through the cladding layer of the optical fiber. The sensing layer which interacts with the analyte (gas) to be coated on the modified (tapered) optical fiber will exhibit optical responses such as absorbance, reflectance and transmission. The previous work done on this field is quite limited and there is so much potential area that can be explored further.

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