High Selectivity Hydrogen Gas Sensor Using Pd/ZnO Tapered Optical Fiber

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Abstract. Besides so many great potentials of hydrogen (H₂) applications, such as primary reagent used for the industrial chemical processes and a potential clean energy source in future, handling it can cause potential hazardous situations due to its highly flammable and explosive nature. Therefore, hydrogen leakage detection is crucial to control the chemical reaction process running smoothly, thereby ensure industrial manufacturing safety in routine life. For this reason, this paper will be reported on tapered optical fiber coated with Pd/ZnO that is sensitive and highly selective towards H₂ gas. The sensor developed comprises a tapered optical fiber and ZnO nanoparticles incorporated using a chemical bath deposition technique. The synthesized ZnO was inspected by FESEM, RAMAN, TGA and UV-VIS to confirm its material properties. The sensing response towards H₂, CH₄ and NH₃ was conducted to observe its sensitivity and selectivity towards the gases. It was found that the Pd/ZnO tapered optical fiber sensor demonstrated high selectivity and sensitivity on H₂ gas compared to CH₄ and NH₃ with 86.6% increment of response. The repeatability test was also conducted to re-confirm the reliability of the sensor developed. The test measured standard deviation of the number of cycles repeated which yield 0.02902 or 97.1% to produce the same output or responses. These results perhaps are useful, especially in the automotive industry for advanced combustion monitoring and emission control.

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor with a wide bandgap of the II-VI group. It is an inorganic compound with white color and insoluble in water. For past decades, ZnO has been comprehensively studied for its excellent chemical, electrical, physical and optical properties for various applications. This includes solar cell, gas sensor, photocatalyst, ultra-violet (UV) laser and light-emitting diode (LED) [1]. ZnO is favorable for gas sensor application because it can detect toxic and harmful substances [2] aside from its chemical sensitivity to volatile and other radical gases. Moreover, it is more abundant, low cost and non-toxic [3].

ZnO thin films can be easily synthesized and deposited on different substrates using various technique, for instance, hydrothermal, sputtering, spray pyrolysis, chemical/physical vapor deposition,
sol-gel and chemical bath deposition [4]. Many works reported on ZnO nanostructures such as nanobelts, nanowires, nanobridges, nanonails, nanorods, nanoribbons, nanotubes, and whiskers. This nanostructure is providing a superhigh surface-to-volume ratio that contributes to high sensitivity for chemical/gas sensing application [1]. Research on ZnO as a sensing layer for electrical gas sensor application is well established, particularly in detecting toxic gas and inflammable such as methane (\(\text{CH}_4\)), nitrogen dioxide (\(\text{NO}_2\)), carbon monoxide (\(\text{CO}\)) and hydrogen (\(\text{H}_2\)) [5].

Numerous works have been published and reported regarding ZnO as electrical sensors. ZnO nanostructures were grown by spray pyrolysis method by D.E. Motaung et al. [6] for \(\text{H}_2\) detection. The sensor developed is based on resistivity change when exposed to \(\text{H}_2\) at room temperature. The sensitivity of the ZnO nanoparticle sensor was more significant compared to columnar structures. Das et al. [7] reported Schottky diode type hydrogen sensor high performance using ZnO nanowires with platinum (Pt) as its electrodes. The sensor developed has shown good sensitivity and fast response of 2500 ppm \(\text{H}_2\) at room temperature. The recent development on gold nanoclusters assembled on ZnO nanostructures film for \(\text{H}_2\) gas sensor at low operating temperature was reported by Pichitchai Pimpang et al. [8]. The sensing material was prepared by thermal oxidation and deposited on a glass substrate with different temperature oxidation. The sensor has shown better response for Au assembled on ZnO as compared to without Au. The optimum response was obtained at 200 °C for 1% \(\text{H}_2\) concentration. It is well known that electrical sensor is vulnerable to electromagnetic interference (EMI) thus affecting the signal responses, and worst of all, possible sparks can trigger an explosion. On the contrary, optical sensors using optical fiber that has unique properties such as lightweight, immune to EMI and able to withstand a high temperature environment can be utilized as a gas sensor [9]. By modifying the cladding part of optical fiber, one can turn into a sensor that is sensitive to the surrounding.

There is lesser number of works published on the optical fiber-based gas sensor using ZnO. Besides, only one work that used cerium (Ce), lithium (Li) and aluminum (Al) doped nanocrystalline ZnO on cladding modified optical fiber for gas ammonia (\(\text{NH}_3\)), ethanol (\(\text{C}_2\text{H}_5\text{OH}\)), and methanol (\(\text{CH}_3\text{OH}\)) (ranging from 0-500 ppm). It was discovered that the spectral intensity was linearly increased with concentration for ammonia but not for methanol and ethanol. The Ce doped ZnO has shown more sensitivity towards these gasses compared to Al and Li doped zinc oxides [8]. Another work on side-polished single-mode optical fiber (SMF) grown with ZnO nanostructures fabricated by A. Og. Dikovska et al. [11] for ammonia sensing. Rana Tabassum and Banshi D. Gupta [12] reported their work on \(\text{H}_2\) sensor utilizing palladium (Pd) and ZnO coated on multimode plastic-clad silica optical fiber. The sensor used a surface plasmon resonance approach to detect the shift in resonance wavelength upon \(\text{H}_2\) exposure. Yahya et al. has reported \(\text{H}_2\) responses for different thickness of ZnO coated onto tapered optical fiber [13]. Pd has been opted as a coating layer due to its high catalytic activities, making it ideal for \(\text{H}_2\) sensing and other combustible gases A very thin layer of catalytic metal integrated with metal oxide promotes chemical reactions by reducing the activation energy between the layer and the gas [14-15]. In this work, the selectivity and sensitivity of the developed sensor towards different gases were conducted.

2. Methodology

The optical fiber used is multimode type that is tapered using Vytran GPX-3400 optical glass fiber processor. The tapering process heat the optical fiber and stretch to the preferred dimension profile. For this work, the dimension profile is fixed to waist diameter of 20-um, up/down taper of 2-mm and 10-mm in length.

Chemical bath deposition technique is adopted to deposit ZnO onto the tapered optical fiber. Firstly, the process starts with surface activation on the tapered optical fiber before growing the ZnO nanostructures. The surface activation used potassium permanganate (KMnO₄) mixed with droplets of \(n\)-butanol. Then, the tapered optical fiber is dipped into the deposition solution and later placed in the water bath with a temperature of 85 °C for 10 min. For synthesizing ZnO, a solution was prepared by mixing 1 ml of 1 M zinc sulfate (\(\text{ZnSO}_4\)) as a precursor with 1.5 ml of 4 M ammonium hydroxide (\(\text{NH}_4\text{OH}\)). Subsequently, 2 ml of ethanolamine (\(\text{C}_2\text{H}_7\text{NO}\)) as a complexing agent was added into the
solution. The mixture later sonicated for 10 min to ensure the solution dispersed homogeneously. Finally, 15.5 ml of DI water was filled in the deposition solution and stirred well. The deposition solution was then placed in the water bath and the activated tapered optical fiber was dipped in the solution for 20 min. Next, the samples were annealed at 200 °C for an hour. The Pd coating was done using DC sputter with 5 nm thickness. The ZnO synthesized was characterized Field Emission Scanning Electron Microscope (FESEM), Raman Scattering, Thermogravimetric Analysis (TGA) and UV-Vis Spectroscopy (UV-Vis).

Figure 1 shows the gas sensing setup comprises of HL-2000 Ocean Optics USA tungsten halogen light source, spectrophotometer to observe the optical absorbance spectrum ranging 200 nm to 1100 nm, sealed gas chamber equipped with heater, gasses cylinder (H₂, CH₄, NH₃ and pure synthetic air) and Alborg controller. The sensor sample is placed in the gas chamber as to conduct the testing.

3. Results and Discussion

The surface morphology of the ZnO coated on tapered optical fiber was examined using FESEM as illustrated in figure 2. Image (a) and (b) show the optical fiber before and after ZnO coating. It can be seen that ZnO coating is well coated around the optical fiber. The morphology of the synthesized ZnO observed to be nanoflowers structure (c) ranging from 60 nm to 150 nm in size (d). The nanostructure size is really important as it will provide a high surface area to volume ratio which yields a large number of surface atoms. This will lead to insufficiency of surface atomic coordination and high surface energy. Thus, the surface becomes highly active. This will also promote further adsorption of gas molecules when sensing.
Figure 2. FESEM image of (a) bare optical fiber, (b) optical fiber coated with ZnO and (c) nanoflowers structure of ZnO (d) particle size distribution

Figure 3 shows Raman spectra of synthesized ZnO sample, excited with a 532 nm laser. A few peaks were identified from the spectrum at 323 cm$^{-1}$, 438 cm$^{-1}$, 570 cm$^{-1}$ and 1099 cm$^{-1}$. $A_1$ and $E_1$ modes are polar and split into transverse optical ($A_1$TO and $E_1$TO) and longitudinal optical ($A_1$LO and $E_1$LO) components. In contrast, $E_2$ mode comprises two modes of low (heavy Zn sub-lattice vibration) and high frequency (oxygen atoms vibration) phonons. The peak at 323 cm$^{-1}$ and 570 cm$^{-1}$ correspond to acoustic overtone and $E_1$ low mode vibration. The peak at 438 cm$^{-1}$ corresponds to $E_2$ high mode dominates in the non-resonant Raman scattering spectra indicating good crystal quality. It is also found that peak 1099 cm$^{-1}$ is due to the acoustic combination of $A_1$ and $E_2$. The peaks stated above are significant, suggesting that the ZnO has good crystallinity and high purity. Based on [16], good crystallinity will provide more surface area, hence, strong gas molecules-sensing layer interaction.
Figure 3. Raman spectra of synthesized ZnO, excited with a 532 nm laser.

TGA measurement was performed in a dynamic nitrogen atmosphere with sample sizes of 21 mg and a heating rate of 10 °C/min. The TG plot in figure 4 displays a weight loss of 0.27% (0.059 mg) between 30 °C and 200 °C, due to the evaporation of the water absorbed on the material’s surface. The loss of weight continues about 1.89% between 200 °C to 530 °C, indicating the loss of intercalated water and hydroxyl ions physically adsorbed in the material. The temperature tested was 30 °C to 600 °C in which the total weight loss of the sample was only 0.477 mg from the initial value of 21 mg. The loss is insignificant, showing the thermal stability and high purity of synthesized ZnO nanostructures [17].

Figure 4. TG curves of the synthesized ZnO

The absorbance spectrum obtained from the UV-Vis measurement is used to plot \((a\nu^2)\) versus \(\nu\) so the optical band gap can be calculated. The optical band gap \((E_g)\) value can be measured by taking the tangent to the curve cross the \(\nu\) axis, as demonstrated in figure 5. From the graph, the estimated optical band gap for the synthesized ZnO is 3.1 eV. It was reported in [18] that narrowing the optical band gap will provide a high concentration of oxygen deficiency. This deficiency served as the active sites for adsorbed oxygen to interact with the targeted gas molecules. Hence, the sensitivity of the sensing material can be increased.
The sensing responses are monitored through optical absorbance that exhibits when the developed sensor was exposed to 1% of H2, CH4 and NH3 gasses. The cumulative change in the absorbance can be integrated over a specific wavelength range, defining the dynamic responses. Figure 6 shows for both ZnO and Pd/ZnO sensors on the cumulative absorbance response against operating temperature when exposed to 1% of H2. The ZnO sensor only exhibits a low absorbance response at 200 °C, and the absorbance change decreases as temperature increases. On the other hand, the Pd catalyst coated on top of the ZnO layer has provided some gas sensing enhancement. Pd/ZnO tapered optical fiber sensor exhibits absorbance change even at low temperature. It was found that the optimum operating temperature that displays the maximum absorbance response is at 180 °C. Not only the absorbance change has increased, but also the optimum operating temperature also has decreased to the lower point with the effect of Pd as a catalyst in H2 sensing.

From figure 7, it was observed that there is no distinguish absorbance increase when the sensor is exposed to CH4 and NH3. However, a distinct absorbance increase can be seen from the initial condition of synthetic air to 1% H2 exposure at 700 to 1000 nm range of wavelength. This absorbance change is due to H2 adsorption onto the ZnO sensing layer in which the Pd thin layer dissociates H2 into H+ and reacts with chemisorbed oxygen (O− and O2-) hence producing H2O molecules [19]. The generated
electrons reduced the $\text{Zn}^{2+}$ in the center of ZnO crystal lattice to $\text{Zn}^+$. Therefore, any changes in sensing layer properties will also change the absorption of light, thus changing absorbance magnitude.

![Figure 7](image5.png)

**Figure 7.** Absorbance response versus wavelength of Pd/ZnO coated tapered optical fiber sensor when exposed to 1% concentration of (a) CH$_4$, (b) NH$_3$ and (c) H$_2$ at 180 °C operating temperature.

The Pd/ZnO sensors were tested towards different gases to examine their selectivity performance. The gasses selected were ammonia (NH$_3$) and methane (CH$_4$). The measurement was performed by exposing the sensor to synthetic air and selected gas alternately at 180 °C operating temperature. Figure 8 shows the dynamic responses of cumulative absorbance increase when these gasses exposed to the sensor. Note that an increase of 2.435 upon exposure of 1% H$_2$, 0.237 and 0.133 for CH$_4$ and NH$_3$, respectively. It was observed that the absorbance increase for H$_2$ is 86.8% that is distinguishable compared to CH$_4$ and NH$_3$, which are 8.45% and 4.74%, respectively. The sensor developed has shown high selectivity towards H$_2$ gas and less sensitive to NH$_3$ and CH$_4$. According to [20], CH$_4$ gas is a stable gas that requires very high energy to dissociate H from C. High operating temperature is needed to enhance the sensitivity towards this gas. The sensor is less sensitive towards NH$_3$, probably because of Pd coating since the Pd is more suitable in dissociating the H$_2$ gas. This confirms that the produced sensors portray a good selectivity for H$_2$ compared to the cases of NH$_3$ and CH$_4$. 

![Figure 8](image6.png)
Figure 8. (a) Dynamic response for Pd/ZnO coated tapered optical fiber sensor when exposed to 1% concentration of H₂, NH₃ and CH₄ at 180 °C and (b) comparison bar graph for selectivity test.

Figure 9. Four (4) cycles repeatability test for 1% of H₂.

Figure 9 displays the repeatability of the Pd/ZnO tapered optical fiber sensor when exposed to four (4) cycles of 1% concentration of H₂ gas. From the graph, it is observed that the sensor able to exhibit the same output response for every cycle tested. The repeatability is measured by the standard deviation of the number of cycles repeated, which yield 0.02902 or 97.1% to produce the same output or responses.

4. Conclusion
The developed Pd/ZnO tapered optical fiber sensor has shown high selectivity towards H₂ gas (86.8%) compared to CH₄ (8.4%) and NH₃ (4.7%), respectively. On top of that, the developed sensor showcases good repeatability to produce the same responses with a standard deviation of 0.02902 or 97.1%. The synthesized ZnO exhibits nanoflowers structures with good crystallinity and purity based on material characterization performed. Hence, the increase of the film surface area provided strong gas molecules-sensing layer interaction. The narrowing optical band gap contributes to a high concentration of oxygen deficiency. This deficiency served as the active sites for adsorbed oxygen to interact with the targeted gas molecules. As a result, the sensitivity of the sensing material can be increased too. The future work can be improved further by incorporating other nanomaterials onto a gas sensor platform in this work. The selectivity towards other gases can be achieved by merely integrating a chemo resistive type of semiconducting metal oxide sensors to the developed sensor.
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