TiO2/B2O3 thick film gas sensor for monitoring carbon monoxide at different operating temperatures

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Abstract: TiO2/B2O3 gas sensor was fabricated on alumina substrate using screen-printing technology with thickness of sensing film in between of 3 – 5 µm. The sensing film of gas sensor was prepared by mixing the TiO2/B2O3 with organic binder. The morphology and structural element of sensing film was characterized using FESEM and x-ray diffraction. The gas sensor was exposed to 100 – 1000 ppm of carbon monoxide at different operating temperatures such as 100°C, 150°C, 200°C and 250°C. The result showed that the gas sensor behaved as n-type gas sensor and exhibited good response to various concentration of carbon monoxide at different operating temperatures. It also was found that highest sensitivity was achieved at 250°C, while optimal operating temperature was occurred at 150°C for TiO2/B2O3 gas sensor to the carbon monoxide.

1. Introduction

Metal-oxide gas sensor has received much attention because of its advantage such as good response and high selectivity to several gases. The need for gas sensor in detecting hazardous gas that colorless, odorless and tasteless such as carbon monoxide has become acute necessity due to health and environment safety. Low cost, nontoxic, chemical stable and wide band gap make Titanium dioxide (TiO2) as a practical material for gas sensing. TiO2 has been widely applied as a gas sensor to detect various type of gases such as hydrogen [1], carbon monoxide [2], nitrogen dioxide [3] and ammonia [4].

Carbon monoxide can impact to the human health in short-term or long term if human body was exposed to the limitation of carbon monoxide. According to the World Health Organization (WHO), exposure limit for carbon monoxide is 35 ppm for eight hour [5]. Previous studies showed that most material used in detecting carbon monoxide are TiO2 [2], [6], [7], tin dioxide [8], lutetium ferrite [9] and zinc oxide [10]. It was revealed that TiO2 can detect carbon monoxide at concentration below of 1000 ppm and reported that operating temperature of gas sensor for carbon monoxide usually occurred at 200°C.

In view of above, TiO2/B2O3 gas sensor was fabricated using screen-printing technique and exposed to various concentration of carbon monoxide at different operating temperatures (100°C, 150°C, 200°C and 250°C) to observe the sensitivity and optimum operating temperature of the gas sensor.
2. Materials and Method

Experimental work
TiO$_2$ (Aeroxide® P25), Boron oxide (B$_2$O$_3$) and m-xylene were obtained from Sigma-Aldrich. All chemicals were used as received without further purification. Initially, 90 w.t% of TiO$_2$ was mixed with 10 w.t% of B$_2$O$_3$ by stirring in one hour and followed by sonication in three hours using m-xylene as a medium. After that, the mixture was dried in an oven for 24 hours to produce a solid form. The solid material was grounded in a mortar to convert it into a powder. Then, the TiO$_2$/B$_2$O$_3$ powder was mixed with organic binder until homogeneous and viscous paste was obtained. Preparation of organic binder can be referred in Ref. [11]. To fabricate a gas sensor, TiO$_2$/B$_2$O$_3$ paste was printed on the alumina substrate using screen-printing technique and annealed in air at 500°C for 30 minutes. Next, an interdigitated electrode based on silver paste was deposited on the top of sensing film using screen-printing and annealed in air at 150°C for 30 minutes.

Experimental setup of gas sensor measurement
Measurement of gas sensor was conducted in a gas chamber. The gas chamber was connected to the source meter (Keithley 2450), mass flow controller, temperature controller, vacuum pump and a computer. Synthetic air (50 L/min) was used as a carrier gas and 100 – 1000 ppm of carbon monoxide was flowed to the gas chamber. Air was flowed in 600 sec and carbon monoxide was flowed in 1200 sec for each cycle to the gas chamber. Different operating temperatures was tested to the gas sensor such as 100°C, 150°C, 200°C and 250°C to find the highest sensitivity and optimum operating temperature.

3. Results and discussion

Characterizations of sensing film by FESEM and X-ray diffraction
Morphology of sensing film was characterized by FESEM (Brand: Thermo Fisher Scientific, Model: Nova Nanosem 230) at magnification of 200k at 10 kV. Figure 1 displays morphology of TiO$_2$/B$_2$O$_3$sensing film after annealing at 500°C in air. The diameter of TiO$_2$ nanoparticles in the range of 30 – 70 nm. It can be clearly seen that the uniformity of nanostructures, in which nanoparticles in spheres shape. This also suggests the homogeneity of the prepared paste.

![Figure 1. Morphology of TiO$_2$/B$_2$O$_3$sensing film after annealing at 500°C in air](image)

The X-ray Diffraction (XRD) (Brand: Philips, Model: PW 3040/60 MPD X’pert High Pro Panalytical) studies was carried out for thick film in 30 minutes, over a 2θ range between 20° and 80°. The XRD spectra of sensing film of TiO$_2$/B$_2$O$_3$gas sensor after annealing in air at 500°C is shown in Figure 2. The XRD spectra showed that TiO$_2$/B$_2$O$_3$thick film consists of anatase phases and rutile
phases. Anatase phase was attributed at $2\theta = 25.40^\circ$, $37.97^\circ$, $48.15^\circ$, $53.99^\circ$, $55.15^\circ$, $62.97^\circ$ and $70.25^\circ$, while rutile phase was attributed at $2\theta = 27.45^\circ$, $36.31^\circ$ and $69.01^\circ$.

![Figure 2. XRD spectra of TiO$_2$/B$_2$O$_3$ sensing film after annealing at 500°C in air](image)

**Figure 2.** XRD spectra of TiO$_2$/B$_2$O$_3$ sensing film after annealing at 500°C in air

***Characteristic of TiO$_2$/B$_2$O$_3$: Gas Sensor to Various Concentrations of Carbon Monoxide at Different Operating Temperatures***

Figure 3 presents response of TiO$_2$/B$_2$O$_3$: gas sensor to various concentrations of carbon monoxide at different operating temperatures. It showed that the gas sensor behaved as n-type gas sensor, where the current increased when exposed to the carbon monoxide and current decreased when exposed to the carrier gas. The gas sensor also exhibited good response to 100 – 1000 ppm of carbon monoxide at different operating temperatures of 100°C, 150°C, 200°C and 250°C. It can be seen that, the current of gas sensor started to increase in 600 sec and followed by decrement and stabilization in the following 600 sec when exposed to the carbon monoxide. Other than that, the gas sensor was stable in 600 sec during air was flowed.

![Figure 3. Response of TiO$_2$/B$_2$O$_3$: gas sensor to various concentrations of carbon monoxide at different operating temperatures](image)

(a)  (b)
Figure 3. Response of TiO$_2$/B$_2$O$_3$ gas sensor at different operating temperatures (a) 100°C, (b) 150°C, (c) 200°C and (d) 250°C

Sensitivity of gas sensor was calculated using $S = I_g/I_a$, where $I_g$ is current under carbon monoxide and $I_a$ is current under air. The values of sensitivity at different concentrations of carbon monoxide is shown in Figure 4. The $I_g$ value was taken at saturated current because this value showed large difference at various concentrations of carbon monoxide, while $I_a$ value was taken during flow of air at initial condition. It can be observed that the sensitivity of gas sensor increased as operating temperature increased. The highest sensitivity for 100 – 1000 ppm of carbon monoxide was achieved at operating temperature of 250°C, while the optimal operating temperature for this gas sensor was occurred at 150°C. Large difference of current was observed for each concentration of carbon monoxide at 150°C, where it produced large difference of sensitivity. Besides, among different operating temperatures, the graph of sensitivity for 150°C behaved as linear graph compared to the others, where this result suggest that optimal operating temperature for TiO$_2$/B$_2$O$_3$ gas sensor was occurred at 150°C.

Mechanism of TiO$_2$/B$_2$O$_3$ Gas Sensor to Carbon Monoxide

The mechanism of gas sensor was based on the adsorbed oxygen on the surface of sensing material at different operating temperatures. During exposure to air, oxygen molecules adsorbed on the oxides surface and ionized to oxygen species such as $O_2^-$, $O^-$ and $O^{2-}$. This reaction is showed in (eq. (1) to eq. (3)) [12]. At operating temperature less than 150°C, $O_2^-$ was produced, while $O^-$ works at temperature of 150°C to 400°C and $O^{2-}$ only works at operating temperature larger than 400°C [13].

\[
\begin{align*}
O_2^+ + e^- & \rightarrow O_2^- \quad (1) \\
O_2^- + e^- & \rightarrow O^- \\
O^- + e^- & \rightarrow O^{2-}
\end{align*}
\]
When carbon monoxide was flowed to the surface of gas sensor, the ionized oxygen react with molecules of carbon monoxide and produce carbon dioxide (eq. (4) to eq. (6)) [12].

\[ 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 + e^- \]

\[ \text{CO} + \text{O} \rightarrow \text{CO}_2 + e^- \]

\[ \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + 2e^- \]

Figure 5 presents the sensing mechanism of gas sensor based on grain size of metal-oxide to the carbon monoxide at optimal operating temperature. At operating temperature of 150°C, \( \text{O}^- \) was produced on the metal-oxide surface. Adsorbed oxygen increases the resistance of metal-oxide by trapping the electrons from the surface and increase the depletion region. Thus, larger grain size of TiO\(_2\) nanoparticles and larger band gap were observed. When carbon monoxide was flowed to the metal-oxide surface, the ionized oxygen will combined with carbon monoxide and released the carbon dioxide. At this stage, smaller grain size and lower band gap were obtained. Other than that, conduction band also become larger, thus reduced resistance of gas sensor was observed.

4. Conclusions

TiO\(_2\)/B\(_2\)O\(_3\) gas sensor was successfully fabricated in this work using screen-printing technique and exposed to various concentrations of carbon monoxide at different operating temperatures. The gas sensor showed good response to 100 – 1000 ppm of carbon monoxide at different operating temperatures such as 100°C, 150°C, 200°C and 250°C. The highest sensitivity was achieved at 250°C, while optimal operating temperature was occurred at 150°C for TiO\(_2\)/B\(_2\)O\(_3\) gas sensor.

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