Mechanism of room temperature oxygen sensor based on nanocrystalline TiO₂ film

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Abstract. A titanium dioxide (TiO₂) thin film is proposed as the active layer for the detection of oxygen gas. The sensor is fabricated on silicon wafer using sol-gel dip coating technique with a constant withdrawal speed. The field emission scanning electron microscope image reveals that the film has a uniform structure while the x-ray diffraction analysis indicates that the film is anatase phase with tetragonal lattice structure. The film exhibit the highest intensity peak at (101) plane. The surface roughness measurement shows that the film has low surface roughness with small grain size. The electrical studies revealed that the resistivity is about 4.02 x 10⁻³ Ω.cm and the thickness of TiO₂ film is 127.44 nm. The gas sensor measurement showed that the sensor response of the film is about 4.21% at room temperature.

1. Introduction

Gas sensors have been widely used in many important areas such as automotive applications, environmental monitoring, industry and public safety. A chemical gas sensor is a device that can convert the concentration of a target gas into an electrical signal. There are different types of solid state gas sensors [1]. These sensors are based on catalytic combustion, electrochemical behaviour or resistance change in metal oxide semiconductor. Due to the advantages such as good thermal and chemical stability, low cost and easy production [2], metal oxide gas sensors have been widely used in the gas detection system. The performance of the gas sensors is significantly influenced by the structure and morphology of sensing material which is the metal oxide. The nanostructured metal oxide with different morphologies are suggested as the active layer for fabrication of gas sensors. It is necessary to reveal the sensing mechanism of the active layer in metal oxide gas sensor to fabricate and design the gas sensing materials with good performance. Brattein et al. [3] and Heiland [4] were introduced the reaction of the metal oxide materials with the presence of gases and demonstrate the result in the change of resistance in the early 1950’s. After that, Seiyama et al. [5] present the first
proposal for this type of device in 1962 and was patented by Taguchi [6]. The detection mechanism is complex and not yet fully understood due to various parameters that affect the function of the metal oxide gas sensors. The gas sensing by metal oxide believes to involve with two major parts which are receptor and transducer function [7]. The receptor function is the recognition of metal oxide with a target gas through a gas-solid interface resulting in an electronic change of the metal oxide surface. While the receptor function is the first part of the sensing process, the transducer function is a second process when the surface of the metal oxide senses the target gas, the electrical resistance of the metal oxide was changed. Other than measure the change of electrical resistance as the detection of this mechanism, it also could be detected by measuring the change of capacitance, work function, mass or reaction energy of the sensing material [8]. In oxygen atmosphere, oxygen is adsorbed onto the metal oxide surface, forming a potential barrier in the grain boundaries. A charged oxygen species, which trap electrons from the bulk material formed as a result of the interaction of atmospheric oxygen with the metal oxide surface. This charged oxygen species, repels other electrons from interacting with the bulk of the film, creating a region depleted of electrons which results in an increased potential barrier at the grain boundary [9].

Many metal oxides are suitable for detecting reducing, oxidizing or combustible gas by conductive measurement. From their electronic structure, the metal oxide that suitable for gas sensors can be determined. The range of the electronic structures of the metal oxides are divided into two categories [1,8,9]:

1. Transition metal oxides including Fe₂O₃, Cr₂O₃ and NiO
2. Non-transition metal oxides
   2.1 pre-transition metal oxides such as Al₂O₃, MgO
   2.2 post-transition metal oxides such as ZnO, SnO₂

Due to very large band gap energy, pre transition metal oxides are expected to be quite inert. This means it will cause difficulties for both electrons and holes to be formed. Furthermore, these types of metal oxides are seldom being selected as gas sensor due to their high resistance thus facing difficulties in electrical conductivity measurements. Among them, only metal oxides with d⁰ and d¹⁰ electronic configurations used in the gas sensor application. TiO₂ and V₂O₃ which are found in binary transition-metal oxides have d⁰ configuration while SnO₂ and ZnO found in post-transition metal oxides have d¹⁰ configuration [7,8].

Thus far, titanium dioxide (TiO₂) has been used in a wide range of applications such as hydrogen generation by water splitting, dye-sensitized solar cells and photocatalytic water purification [10]. TiO₂ is n-type semiconductor and in sensor technology, it is frequently considered as a promising material for gas detection system. This is due to its non-toxic properties, commercial availability at low cost, chemical and thermal stability. Furthermore, n-type semiconductor have possibility to work at at lower oxygen partial pressure [1]. TiO₂ has different phases which are present in different post-annealing temperature in sol-gel technique. The phases are rutile, anatase and brookite. Anatase and brookite phases are metastable which irreversibly convert to rutile phase at high post-annealing temperature.

2. Experimental details

2.1. Precursor solution
Firstly, 10 ml titanium (IV) butoxide (Sigma Aldrich 97 %) and 10 ml glacial acetic acid were dissolved in ethanol at room temperature. Introduction of ethanol prior to glacial acetic acid induces immediate precipitation due to highly reactive alkoxides. Therefore, glacial acetic acid which has been added as a stabilizing agent for hydrolysis was initially stirred with ethanol followed by the addition of titanium (IV) butoxide. Deionized water was added to the solution under continuous stirring. Finally, diluted hydrochloric acid was added. The mixture was stirred and heated to 40 °C for about 10 minutes.
Then, the solution was continuously stirrer at a constant speed for 3 hours to complete the reaction and avoid from agglomeration. A yellow transparent solution was obtained from this process.

2.2. Film fabrication

The film was deposited at room temperature with sol-gel dip coating using (PTL-MM01 Desktop Dip Coater) on silicon substrate at a withdrawal speed of 10 mm.min\(^{-1}\). Prior to the sol-gel dip coating process, a silicon substrate was cleaned by diluted hydrofluoric acid to remove the native oxide. In order to obtain a uniform coating, the substrate was slowly dipped and withdrawn from a beaker containing precursor solution with constant withdrawal speed. Three stages were included in the sol-gel dip coating process:

1. The substrate was immersed into the precursor solution.
2. The substrate was left for 5 minutes in the solution and was starting to vertically withdrawn from the solution at 10 mm.min\(^{-1}\).
3. The thin layer of film was deposited on the substrate itself during the substrate was withdrawn from the solution. The moving substrate during the withdrawal process entrains the liquid in a viscous boundary layer that splits in two at the free surface, which cause the outer solution is returned to the beaker. The withdrawal speed determines the thickness of the coating film, which can be expressed by Landau-Levich equation [11]:

\[
    h = 0.94 \frac{(\eta \nu)^{2/3}}{\gamma^{1/6}(\rho \gamma)^{1/2}}
\]

Where \( h \) is film thickness, \( \eta \) is withdrawal speed, \( \nu \) is viscosity, \( \gamma \) is liquid-vapour surface tension, \( \rho \) is liquid density and \( g \) is gravitational acceleration. From this equation, higher withdrawal speeds resulting in increasing of film thickness. To improve the adhesion of film on silicon substrate, the film was preheated on a hot plate at 100 °C for 10 minutes after the dip coating process. The film was then annealed at 400 °C to improve the structural quality of the film. The fabrication process of the TiO\(_2\) thin film was according the flow in figure 1.

![Figure 1. Schematic diagram of the experimental methodology of TiO\(_2\) thin film.](image)

2.3. Film characterization

The film on silicon substrate was characterized for phase analysis using x-ray diffraction (XRD) (Panalytical : X'Pert\(^3\) Powder) with Cu- K\(\alpha\) radiation source at setting of 40 mA and 40 kV and a step
size 0.03° 2θ. 2 theta of the diffraction pattern was collected in the range of 20-70°. The surface morphology of the film was characterized using field emission scanning electron microscope (FESEM)(Jeol : JSM-7600F) with an accelerating voltage of 15 kV. Approximate film thickness was measured using surface profiler (KLA Tenkor : Alpha-Step IQ) with 10000 µm scan length and 50 µm scan speed. The thickness measurement was repeated three times and the average of film thickness was taken as a reading. To measure the resistivity, four point probe (Lucas-Signatone : Pro 4-G00 integrated with the Keithley 2400 series source meter) was used. The measurement system allows to measure high resistance range up to 100 MΩ per square. The surface roughness of the film was characterized using Atomic force microscopy (AFM)(Park Systems : Park XE-100) using non-contact mode AFM. A low force exerted on the sample (10^-12) using this contact. The scan size image of the film was taken 1x1 µm and the scan rate was 0.9 Hz.

2.4. Gas sensor measurement technique
The prepared film was placed in a custom-made sealed chamber having the capacity volume of 2.01x10^-3 m^3. Gas flow to the chamber was controlled by a mass flow controller (Sierra Instrument, Smart Track 50 Series). The sensor was tested in the room temperature at oxygen flow rate of 500 sccm (square cubic centimeter per minute). The gas sensing behavior of the film was evaluated by measuring the relative change in resistance with and without exposure of oxygen gas. The data are collected using the precision digital multimeter (Fluke 8846 A). Before starting sensing experiments, the chamber was purged with Argon gas for 5 minutes to remove any possible contaminations. The measurement setup shown in figure 2.

![Figure 2. Experimental setup for gas sensor testing.](image)

3. Characterization of TiO₂ thin film

3.1. Structural properties
The x-ray diffraction (XRD) pattern of nanostructured TiO₂ film fabricated using sol-gel dip coating was demonstrated in figure 3. Measurement with XRD reveals that anatase with tetragonal lattice structure is the only crystalline phase present in this film. The highest peak intensity at 20 of 25.2° corresponding to (101) reflections of the TiO₂ anatase phase. Additionally, five strongest intensity diffraction peaks of anatase are indicated in the figure 3 at 38.0° (004), 48.1° (200), 54.0° (105), 55.1° (211) and 62.8° (204). All the indicated anatase peaks are present in the experimental pattern with approximately correct integrated intensity proportions according to the standard anatase nanocrystalline structure (Inorganic Crystal Structure Database (ICSD) file no.98-015-4604). The anatase peaks demonstrate that the crystallization has occurred in the film. Based on figure 3, the film exhibits the highest intensity of XRD diffraction peak at (101) plane, therefore the calculation of
crystallite size was highlighted at (101) plane. The average crystallite size was estimated from full width at half maximum (FWHM) of the XRD peak using Scherrer’s equation [12]:

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

where \( D \) is the crystallite diameter in nm, \( k \) is the shape constant (0.9), \( \lambda \) is the wavelength of the x-ray radiation in nm, \( \theta \) is the Bragg angle in degrees and \( \beta \) is the observed peak width at half-maximum peak height. The calculated crystallite size for (101) plane at 2\( \theta \) of 25.2988° are as equation (3). The crystallite size of the TiO\(_2\) film is 30.64 nm.

\[ D = \frac{(0.9)(0.154060 \text{ nm})}{(0.2657 \times \frac{\pi}{180} \text{ rad} \cos \frac{25.2988^\circ}{2})} = 30.64 \text{ nm} \]  

![Figure 3. XRD spectrum of TiO\(_2\) thin film.](image)

3.2. Surface morphology

FESEM image was presented in figure 4. It can be seen that the film has a porous structure. Previous studies show that a material with porous structure gives higher sensitivity due to an increase in the surface area for the gas interaction [13]. To get better understanding of the particle distribution and further details on the surface properties of TiO\(_2\) thin film, the fabricated film was further observed with AFM surface imaging analysis. From this measurement, additional knowledge can be obtained such as grain size, surface roughness and three dimensional (3D) views of the TiO\(_2\) thin film. Figure 5 presents 3D AFM image of the TiO\(_2\) thin film. The colour scale in AFM image represents the different height values of the film in the image. Brigh colour indicates for higher height values while dark colour indicates lower height values. The particle distribution of the film on the substrate is almost even and uniform in manner with small grain size. \( R_q \) is defined as the standard deviation of the surface height values from the mean height while \( R_a \) is defined as the roughness average. The results of AFM data are presented in table 1. From the results, the film has a low surface roughness, indicating a possibility that the film was smooth. Furthermore, a low surface roughness represents good homogeneity of the film.
Table 1. AFM roughness parameters of the TiO$_2$ thin film.

| Roughness parameter                  |       |
|--------------------------------------|-------|
| Average grain size, (nm)             | 23.0  |
| Root mean square roughness, Rq (nm)  | 0.371 |
| Roughness average (nm)               | 0.295 |

3.3. Electrical properties

The resistivity of the film was measured using four point probe. From the four point probe measurement, the resistivity is calculated using the formula as follows:

\[
\rho = 2\pi s \frac{v}{I}
\]  

(4)

where \(\rho\) is resistivity, \(s\) is spacing between probe, \(v\) is the voltage and \(I\) is the current. It is easier to interpret the data measured by the four point probe than results gathered by two point probe because in two point probe the contact resistance can be large and strongly depend on the pattern and materials of the electrode. The four point probe contains four probe in a linear arrangement which are made to contact with the sample during measurement of the film. The current is made to flow between the outer probe, and the voltage is measured between the two inner probe without drawing any current. The resistivity of the film measured in this work was $4.02 \times 10^{-3} \ \Omega \cdot \text{cm}$ with thickness of the film 127.44 nm.

4. Gas sensing mechanism

A definition of sensor response was interpreted in different way for different studies [14–16]. In this work, gas response was measured as the ratio between the change of resistance when exposed to target gas and the resistance in air [17]. The \(R_g\) is denoted as resistance in target gas and \(R_a\) is denoted as resistance in air. The sensor response, \(R\) can be expressed as below:

\[
R (\%) = \frac{R_g - R_a}{R_a} \times 100
\]

(5)
Based on the flow rate of the gas flow, \((Q = 500 \text{ cm}^3\text{min}^{-1})\) and the volume of the gas chamber \((V = 2010 \text{ cm}^3)\), we believe that the time constant where the mixing process of the gas is \((t = V/Q \sim 4 \text{ minutes})\). The calculated sensor response for this film is about 4.21 %.

![Figure 6. Response curve of oxygen gas sensor.](image)

The change of the electrical resistance shows that the film has good response for detecting oxygen gas. The film behaves as n-type semiconductor with increase of resistance in a presence of oxidizing gas (oxygen gas) as shown in figure 6. \(O_2^-\) is believed to be dominant charged oxygen species at the operating temperature below 150 °C [18]. Figure 7 (a) and (b) schematically show the structural and band model of gas sensor mechanism when exposed to oxygen gas. In figure 7 (a), atmospheric oxygen is adsorbed onto the surface of the TiO₂ film, forming a potential barrier at the grain boundaries. The charged oxygen species \((O_2^-)\), which trap the electrons from the TiO₂ film are formed when the atmospheric oxygen interact with the surface of the TiO₂ film. These prevent the flow of electrons and thus increased the resistance. When the sensor exposed to oxygen gas which is classified in oxidizing gas, the charged oxygen species increased more which resulting in higher potential barrier as shown in figure 7 (b), prevent the electrons to flow, and thus increasing the electrical resistance. This mechanism explained the increases of the film resistance when oxidizing gas such as oxygen gas exposed to the n-type semiconductor (TiO₂ film).

![Figure 7. Schematic diagram for oxygen sensor response toward TiO₂ film in (a) air (b) the presence of oxygen gas.](image)

5. Conclusion
The sol-gel dip coating has been used to fabricate TiO₂ thin film with withdrawal speeds of 10 mm.min⁻¹. The film was deposited on silicon substrate and XRD pattern shows that the film is anatase phase. The crystallite size calculated from scherrer equation is 30.64 nm and observation from FESEM image shows that the film has porous structure. The AFM results show that the film has an average grain size of 23 nm while the surface roughness is 0.371 and 0.295 for root mean square and average
roughness, respectively. The measurement of four point probe shows that the film has low resistivity which is 4.02 x 10^{-3} \, \Omega \cdot \text{cm with film thickness of 127.44} \, \text{nm. The change of the electrical resistance of the film when exposed to oxygen gas was experimentally investigated and shows that the film behaves as n-type semiconductor when exposed to oxidizing gas. The calculated sensor response of this film is 4.21\%.}

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