PERFORMANCE OF TiO_2 VIA SCREEN PRINTING TECHNIQUE

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PERFORMANCE OF TiO_2 VIA SCREEN PRINTING TECHNIQUE

by

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TABLE OF CONTENTS

ACKNOWLEDGEMENT i

TABLE OF CONTENTS ii

LIST OF TABLES iv

LIST OF FIGURES v

LIST OF SYMBOLS vi

LIST OF ABBREVIATIONS vii

ABSTRAK ix

ABSTRACT x

CHAPTER ONE: INTRODUCTION 1

  1.1 Background information 1

  1.1.1 Ethanol gas sensor 1

    1.1.2 Titanium dioxide (TiO_2) 2

    1.1.3 Fabrication of gas sensor via screen printing method 2

  1.2 Problem statement 3

  1.3 Research objectives 4

CHAPTER TWO: LITERATURE REVIEW 5

  2.1 Titanium oxide sensor 5

  2.2 Sensing mechanism 6

  2.3 Material for sensor platform 8

  2.4 Factors affecting the sensitivity of Tio_2 sensor 9

    2.4.1 Effect of composition of paste 10

    2.4.2 Effect of operating temperature 12

    2.4.3 Effect of binders 15

CHAPTER 3: MATERIALS AND EXPERIMENTAL METHODS 17

  3.1 Material and instrumentation 17

    3.1.1 Materials 17

3.1.2 Instrumentation 18

3.2 Sensing material preparation 18

3.2.1 Fabrication of gas sensor via screen printing preparation 18

3.3 Characterization of the TiO_2 thick film sensor 19

3.3.1 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) 19

3.3.2 X-Ray Diffraction (XRD) 19

3.4 Sensing performance 20

CHAPTER FOUR: RESULT AND DISCUSSION 22

4.1 Introduction 22

4.2 Characterization of sensing material 23

4.2.1 Scanning Electron Microscope (SEM) 23

4.2.2 Energy Dispersive X-ray (EDX) Analysis 25

4.2.3 X-Ray Diffraction (XRD) Analysis 27

4.3 Performance of TiO_2 sensor 29

4.3.1 Effect of composition of paste on sensitivity of TiO_2 sensor 30

4.3.2 Effect of operating temperature on sensitivity of TiO_2 sensor 32

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS 34

5.1 Conclusion 34

5.2 Recommendations 35

References 36

LIST OF TABLES

Pages

Table 2. 1 Classification according to the changes in the response of sensing element 6

Table 2. 2 Classification of metal oxides based on the conductivity type 6

Table 2. 3 Example of organic vehicle (binder + solvent) used in gas sensor 10

Table 3. 1 List of chemical used and their description. 14

Table 3. 2 List of equipment's availability 14

Table 4. 1 Chemical composition present in TiO2 in different composition of paste 23

Table 4. 2 XRD Data of TiO2 Nanoparticles (Theivasanthi and Alagar 2013) 25

LIST OF FIGURES

Pages

Figure 2. 1 Resistance in air as a function of temperature (Response properties of the MEMS sensor to ethanol) 12

Figure 2. 2 Transient responses to 50 ppm ethanol at 450^o, 500^o, and 550^o C (Response properties of the MEMS sensor to ethanol) 13

Figure 2. 3 Sensor responses to 50 ppm ethanol as a function of temperature (Response properties of the MEMS sensor to ethanol) 13

Figure 2. 4 Comparison of J-V characteristics of the DSSCs fabricated with two different pastes. 16

Figure 3. 1 Schematic diagram of the gas sensor rig. 17

Figure 4. 1 SEM image at 10.00 K x magnification for (a) TiO_2 film at mass ratio of [TiO_2] :[$(CH_2OH)_2$] = 3:7, (b) TiO_2 film at mass ratio of [TiO_2]:[$(CH_2OH)_2$] = 5:5and (c) TiO_2 film at mass ratio of [TiO_2]:[$(CH_2OH)_2$] = 6:4. 20

Figure 4. 2 EDX analysis for (a) TiO_2 film at mass ratio of [TiO_2]:[$(CH_2OH)_2$] = 3:7, (b) TiO_2 film at mass ratio of [TiO_2]:[$(CH_2OH)_2$] = 5:5and (c) TiO_2 film at mass ratio of [TiO_2]:[$(CH_2OH)_2$] = 6:4. 22

Figure 4. 3 XRD pattern of TiO_2 nanoparticles 24

Figure 4. 4 Transient response of the fabricated TiO_2 sensor. 26

Figure 4. 5 Sensitivity comparison at different composition of paste 27

Figure 4. 6 Sensitivity comparison at different operating temperature 29

LIST OF SYMBOLS

Symbol	**Description**	**Unit**
S	Sensitivity	percentage
R_a	Resistance of the film in air	Ohm
R_g	Resistance of the film upon exposure to ethanol	ohm
λ	X-ray wave length	length
β	Angular width of diffracted peak at half maximum radians for diffracted angle	length
D	Average particle size	nm
k	Scherrer constant	-

LIST OF ABBREVIATIONS

Cr	Chromium
La	Lanthanum
W	Tungsten
Mo	Molybdenum
Fe	Ferum
Pt	Platinum
Nb	niobium
TiO_2	Titanium dioxide
VOCs	Volatile organic chemicals
MOSFETs	Metal oxide semiconductor field effect transistor
H_2	Hydrogen gas
CO	Carbon monoxide
CH_4	methane
SMO	Semiconductor metal oxide
O_2	oxygen

MEMS	Micro-Electro-Mechanical Systems
ppm	Part per time
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-Ray
XRD	X-Ray Diffraction
DCCs	Dye-sensitized solar cells

PRESTASI TiO_2 MELALUI TEKNIK PERCETAKAN SKRIN

ABSTRAK

Titanium dioksida (TiO_2) tulen yang berstruktur berlapis tunggal dengan mempunyai komposisi pes filem yang berbeza telah dibangunkan dengan menggunakan teknologi percetakan skrin pada substrat alumina. Komposisi pes filem TiO_2 adalah pada nisbah jisim [TiO_2]: [$(CH_2OH)_2$] = 3: 7, pes filem TiO_2 pada nisbah jisim [TiO_2]: [$(CH_2OH)_2$] = 5: 5 dan TiO_2 filem pada nisbah jisim [TiO_2]: [$(CH_2OH)_2$] = 6: 4. Pes yang digunakan untuk penyediaan filem diperolehi dengan menambah etilena glikol dimana ia adalah kenderaan organic bersama serbuk oksida. Sampel yang sudah siap dicampur akan dikeringkan pada suhu 100 ° C dan dipanaskan di dalam dapur leburan pada 350 ° C / 60 minit. Komposisi yang berbeza telah digunakan untuk mengkaji kesan komposisi pes ke arah sensitiviti. Sensor gas yang dibangunkan juga telah digunakan untuk menguji tindakbalas kepada suhu operasi yang berbeza (150 - 400 ° C). Hasil kajian menunjukkan bahawa suhu operasi optimum untuk sensor gas disintesis pada 200^oC. Secara strukturnya, kajian morfologi dan optik telah dijalankan menggunakan Mikroskop Elekton Mengimbas (SEM) menganalisis, pembelau XRD dan Serakkan Sinar X (EDX) analisis spektroskopi. Pencirian SEM menunjukkan kehadiran keliangan bagi zarah TiO_2 manakala EDX mengesahkan komposisi kimia TiO_x menjadi TiO_2. Hasil XRD menunjukkan bahawa peningkatan saiz crystallite sebagai peningkatan saiz zarah dan struktur TiO_2 adalah fasa anatase. Secara keseluruhan, sensor yang direka dengan menggunakan nisbah jisim [TiO_2]: [$(CH_2OH)_2$] = 5: 5 menggambarkan prestasi sensor yang terbaik dengan sensitiviti yang tertinggi. Penemuan ini telah dianalisis dan dibincangkan serta menghubungkaitkan keputusan eksperimen dengan analisis pencirian yang berkait rapat dengan sifat-sifat bahan sensor.

PERFORMANCE OF TiO_2 VIA SCREEN PRINTING TECHNIQUE

ABSTRACT

Nanostructured single layered of pure titanium dioxide, TiO_2 with different composition of paste thick films have been fabricated by screen printing technology on an alumina substrate. The composition of paste are the TiO_2 film at mass ratio of $[TiO_2]:[(CH_2OH)_2] = 3:7$, TiO_2 film at mass ratio of $[TiO_2]:[(CH_2OH)_2] = 5:5$ and TiO_2 film at mass ratio of $[TiO_2]:[(CH_2OH)_2] = 6:4$ .The pastes used for film preparation were obtained by adding an organic vehicle ethylene glycol, $(CH_2OH)_2$ to the oxide powders together. Samples were dried up to 100 °C and calcined at 350 °C/60 minutes. Different composition have been used to study the effect of composition of paste towards the sensitivity of sensor. The fabricated gas sensors were also used to test their responses to different operating temperatures (150 – 400 °C). The results showed that the optimum operating temperature for the synthesised gas sensor is at 200^o C. Structural, morphological and optical studies have been carried out using Scanning Electron Microscopy (SEM) analyses, X-Ray Diffraction (XRD) and Energy Dispersive X-Ray (EDX) analysis spectroscopy. The SEM characterization shows the presence of porosity for the TiO_2 particles while EDX confirms the chemical composition of TiOx to be TiO_2. The XRD result indicates that the crystallite size increases as the particle size increase and TiO_2 structure is anatase phase. Overall, the sensor fabricated by using mass ratio of $[TiO_2] :[(CH_2OH)_2] = 5:5$ illustrates the best sensing performance with the highest sensitivity. These findings were analysed and discussed by correlating the experimental results with the characterization analysis which were closely related to the properties of the sensing materials.

CHAPTER ONE: INTRODUCTION

1.1 Background information

1.1.1 Ethanol gas sensor

Ethanol gas sensor are important device that play role in preventing the damages caused by ethanol. Inhalation of high concentration of ethanol vapour can cause headaches, balance disorders, nausea, dizziness and confusion because ethanol produces high toxicity when taken by humans (Liao, Dai and Yang 2013) . According to M.Nirmala,, et al., (2011) demand for chemical sensors has been growing at a consistent rate in recent years due to their application in intelligent process management, environmental protection and medical diagnostics as well as in domestic and automobile sectors.

It is being applied in many fields such as control of fermentation processes, safety testing of food packaging and can also be fixed on vehicle steering wheels (Zhan, et al. 2013). Nowadays, ethanol sensors with stability and sensitivity are a favourable device and are used as a breathe alcohol checker to monitor vapours in human breath. However, the kind of sensors used as a breathe alcohol checker should have a very high sensitivity to ethanol vapour due to a lower-level ethanol vapour in human breathe. Moreover, ethanol is frequently a major breakdown product of foodstuffs, where bacteria or fungi develop. Ethanol sensor are necessary in this cases because it can be used to detect the spoilage and to take remedial measures (M.Nirmala,, A.Anu kaliani and C.Sanjeeviraja 2011).

Gas sensors based on semiconductor oxides have focused many research efforts in the last years. The most important advantages of such devices in front of the usual monitoring systems are their reliability, low cost, easy implementation and reduced size, being even compatible with microelectronic systems. Nevertheless, in order to improve the gas sensing performances several elements have been frequently incorporated as additives in the base titanium oxide, such as Cr, La, W, Mo, Fe, Pt or Nb (Ruiz, Cornet and Morante 2004) .

1.1.2 Titanium dioxide (TiO_2)

TiO_2 is a material with wide range of technological applications such as optical devices, sensors, catalysts and photocatalysts. In nature, T iO2 occurs in three forms - rutile, anatase and brookite. The most thermodynamically stable one from them is rutile, whereas brookite and anatase are metastable and transform to rutile on heating. Nano-crystalline titanium dioxide materials are a subject of great interest for their improved physical and chemical properties in comparison with its bulk. Because these properties are structure- and size-dependant, it is therefore important to develop new routes of synthesis by which the crystalline structure, the size and the shape of TiO_2 nanocrystals can be readily manipulated. In the recent years, many different methods have been developed and applied for the preparation of nano-sized TiO_2 particles. Methods such as sol-gel, microemulsion or reverse micelles and hydrothermal synthesis have all been used for the preparation of nano- TiO_2 particles (Cesnovar, et al. 2012).

1.1.3 Fabrication of gas sensor via screen printing method

Gas sensor fabrication major technologies usually used thick film technology because it have the ability to form a gas sensing layer with required composition and porosity. There are several approaches used to form a gas sensor. For example drop coating, tape casting and screen printing. But the most vital method is screen printing (Korotcenkov 2013).

Screen-printing is widely used in industry and the most widely used method for producing metal oxide semiconductor gas sensors commercially. Screen-printing involves pushing an ink through a porous layer or mesh, which is suitably masked to produce the required layout on the substrate. The ink essentially contains the material to be deposited, dispersed in a viscous vehicle and is printed on of the substrate. Once the ink is has been deposited, the print can be heated to remove the vehicle, leaving a solid material on the specific target area (Fine, et al. 2010).

1.2 Problem statement

Metal oxide sensors have been utilized for several decades as low cost methods for detecting combustible and toxic gases. However, issues with sensitivity, selectivity and stability have limited their use. It has been observed that the physical and sensing properties of tin oxide gas sensors are directly related to their preparation e.g. particle size, sensing film morphology, and film thickness as well as sensing film characteristics. Hence, in the present study, sol-gel method had been used to synthesize the TiO_2 nanoparticle and screen printing method had been used to develop the sensor. The nature of the gas response and how it is fundamentally linked to surface structure is being studied.

1.3 Research objectives

The present study has the following objectives:

i. To develop suitable sensing material of TiO_2 nanoparticles that can be used to detect VOCs.
ii. To analysed the screen printing technique used to fabricate thick-film sensor.
iii. To investigate the developed sensor response towards ethanol gas.

CHAPTER TWO: LITERATURE REVIEW

2.1 Titanium oxide sensor

Metal oxides are attractive materials for the fabrication of gas sensing devices because of their obvious advantages, such as low cost, production flexibility, and good thermal and chemical stability. The conductivity of metal oxide nanostructures changes with the surface adsorption and desorption of gas molecules. This change is caused by the electronic transfer that occurs upon the adsorption of gas molecules over the film surface. These conductivity changes strongly depend on the shape and the size of the nanostructures. Recently TiO_2 nanostructures with the different shapes have received extensive attention from the gas sensing research community due to their unique physical and chemical properties (Galstyan, et al. 2013).

There are many uses of titanium dioxide (TiO_2) which is act as an important multifunctional material in the photo-catalyst in solar cells, as a corrosion-protective coating, for the production of hydrogen, as an optical coating, as a gate insulator in MOSFETs, etc. TiO_2 also reported as the extraordinary sensitivity towards H_2 but they also shows a good sensing properties to CO, CH_4 and ethanol. Moreover, this sensor is a good candidate for gas sensing application because it being chemically very stable in high temperatures. However, the main disadvantage of these gas sensors is the inability to distinguish between gases, but it has been reported that the selectivity could be improved by dopants. The working principle of Semiconductor Metal Oxide (SMO) gas sensors is based on the change of their resistivity upon exposure to specific gas (Ohatkar, et al. May 2016).

TiO_2 has three polymorphs namely anatase, rutile and brookite. These different polymorphs influence the sensing properties. The anatase phase is preferred over rutile in gas sensing due to its higher photocatalytic activity. Anatase and brookite are thermodynamically metastable forms of TiO_2 which irreversibly convert to rutile at high temperatures. This anatase-to-rutile transition has a severe effect on the sensor's sensitivity. Therefore, it is essential to maintain the nanostructure in anatase phase to increase the device's sensitivity in gas sensing (Tan, Wlodarski and Kalantar-Zadeh October 2006).

2.2 Sensing mechanism

Considering the influence factors on gas sensing properties of metal oxides, it is necessary to reveal the sensing mechanism of metal oxide gas sensor. However, the detection mechanism is still in complex form and not yet fully understood. There are many parameters that affect the function of the solid state gas sensor for detection mechanism. These include the adsorption ability, electro physical and chemical properties, catalytic activity, thermodynamic stability, as well as the adsorption/desorption properties of the surface. However, it is believed that gas sensing by semiconducting metal oxide (SMO) devices involve two major key functions as receptor and transducer functions (Kanan, et al. 2009).

When a sensor is heated to a high temperature in the absence of oxygen, free electrons easily flow through the grain boundaries of the SMO film. At elevated temperatures, reactive oxygen species such as, O_2^- and O^- are adsorbed on the surface of metal oxide semiconductor. The sequence of processes involved in the adsorption of oxygen on the metal oxide surface can be described by the following formulae:

$$O_{2\ (gas)} \leftrightarrow O_{2\ (adsorbed)} \quad (1)$$

$$O_{2\ (adsorbed)} + e^{-} \leftrightarrow O_{2\ (adsorbed)} \quad (2)$$

$$O_{2\ (adsorbed)} + e^{-} \leftrightarrow 2O_{\ (lattice)} \quad (3)$$

During the adsorption of oxygen species on the surface of sensing element, capturing of electrons from conduction band and the associated decrease in the charge carrier concentration (e^-) leads to an increase in the resistance of the n-type sensing element until it attains equilibrium. Thus, the surface resistance increases and attains equilibrium during the chemisorption process. Any process that disturbs the equilibrium leads to a change in the resistance of metal oxide semiconductor. According to the conductivity behaviour of semiconductor metal oxide, the response varies. In n-type semiconductor, the majority charge carriers are electrons. When it interacts with a reducing gas an increase in conductivity occurs. On the other hand, an oxidizing gas depletes the charge carriers, leading to a decrease in conductivity. Table 2.1 clearly summarizes the response of the sensing element towards oxidizing and reducing gases and some n and p- type metal oxide semiconductor elements are listed in Table 2.2

Table 2. 1 Classification according to the changes in the response of sensing element

Classification	**Oxidizing gases**	**Reducing gasses**
n-type	Resistance increase	Resistance decrease
p-type	Resistance decrease	Resistance increase

Table 2. 2 Classification of metal oxides based on the conductivity type

Type of Conductivity	**Metal oxides**
n – type	ZnO, MgO, CaO, TiO_2, WO_3, SnO_2, In_2O_3, Al_2O, Ga_2O_3, V_2O_5, Nb_2O_5, ZrO_2
p– type	Y_2O_3, La_2O_3, CeO_2, Mn_2O_3, NiO, PdO, Ag_2O, Bi_2O_3, Sb_2O_3, TeO_2

The interaction of atmospheric oxygen with the SMO surface forms charged oxygen species, which trap electrons from the bulk of the material. The layer of charged oxygen at the surface 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 boundaries. This impedes the flow of electrons and thus increases the resistance. When the sensor is exposed to an atmosphere containing a reducing gas, the SMO surface adsorbs the gas molecules and lowers the potential barrier, allowing the electrons to flow easily and thus reducing the electrical resistance. In this manner, the sensors act as variable resistors whose value is a function of gas concentration (Kanan, et al. 2009).

2.3 Material for sensor platform

In recent days, researchers consider non-silicon Micro-Electro-Mechanical Systems (MEMS) micro heater as a platform for metal oxide semiconductor gas sensor. These sensor is necessary to accelerate chemical reactions on the surface of the catalytic or semiconductor sensing layer and for promoting dynamic equilibrium conditions because it can be operate at high temperature. Typical working temperature of the sensors ranges from approximately 150 to 450 ^{o}C. The application of bulk or thick film heaters of the sensors leads to relatively high heating power consumption (>150 mW), and only the use of MEMS micro hotplates makes possible the long-term autonomous operation of small (e.g. pocket-size) gas analytic instruments using semiconductor or thermocatalytic sensors (Vasiliev, et al. 2016).

The choice of the sensing film is important for the receptor function (the reactions between the gas and the metal oxide surface), but the choice of the transducer and the operation mode can affect the response of the complete device. Furthermore, not only the proper design of the transducer but also a proper choice of bonding and packaging is needed to provide a final sensor device for practical applications. The material used as substrate can be chosen; alumina- or silicon-based substrates, e.g., are the most used for gas sensors. If the bulk substrate is conductive then an additional insulating layer must be provided. Alumina substrates have its own advantages which is it has high thermal conductivity that is suitable in designing a good sensor (Kita, et al. 2014).

2.4 Factors affecting the sensitivity of TiO_2 sensor

A good gas sensor devices have several unique advantages such as low cost, small size, measurement simplicity, durability, ease of fabrication, and low detection limits (< ppm levels). In addition, most sensors tend to be long-lived and somewhat resistant to poisoning. For these reasons, they have rapidly grown in popularity, becoming the most widely used gas sensors available these days (Kanan, et al. 2009). In order to get the ideal chemical sensor, there are several parameters that are important to enhance the sensitivity of gas sensor. The factors that may affect the sensitivity of TiO_2 sensor are composition of paste, thickness of the film, and operating temperature.

Sensitivity is defined as:

$$S = R_a/R_g$$

Where, R_a = represents the electrical resistance in air

R_g = represents the electrical resistance in VOC vapour

It was measured by monitoring the output voltage V_{out}. All gas-sensing experiments were conducted under laboratory conditions at room temperature with a relative humidity of 40%.

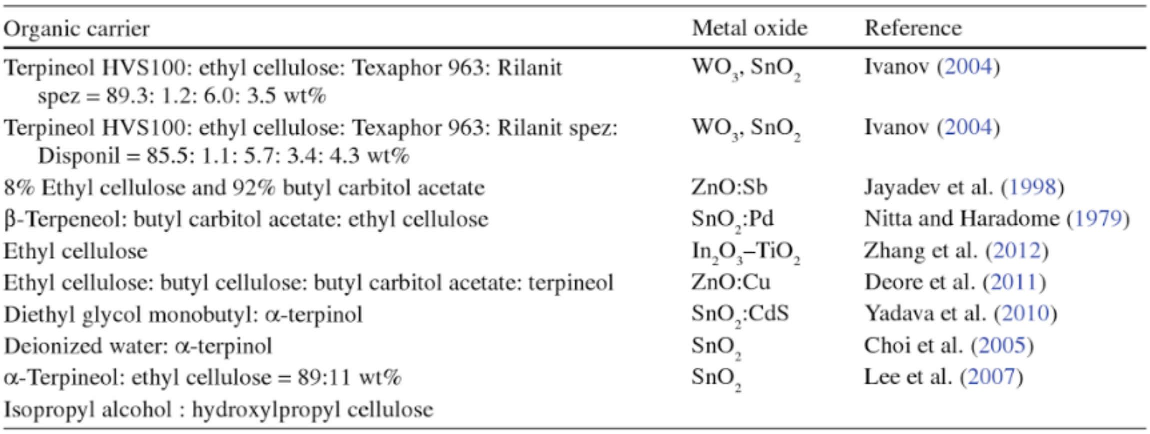
2.4.1 Effect of composition of paste

The conductive paste (silver paste, aluminium paste, and silver-aluminium paste) needed for the above process generally contain a conductive substance such as a silver powder or an aluminium powder, a glass powder, an organic vehicle, and other additives, Where the organic vehicle includes a binder and a solvent. The organic vehicle functions to impart the conductive paste with a good compatibility and rheological property, for example, to impart the conductive paste with suitable viscosity, good wettability and sintering property, and allow the powder in the conductive paste to be in a stable dispersion state (Hsu and Kaohslung 2013).

Organic vehicle is a blend of volatile solvents and polymers or resins together with a surfactant which need to provide a homogenous suspension of the particles that is suitable for the printing of the film configuration. The vehicle is a temporary that should be removed during the microstructure of the deposits is formed. The composition of the paste determine the shelf life of the paste, drying rate on the screen, the change in printability with ambient temperature and their cosmetic appearance. The cooperative effects and the relationship between the properties (density, wettability, surface energies, viscosity, etc.) of the organic vehicle and inorganic constituent of the paste contribute to the static and dynamic properties of the paste.

They are also usually blend of cellulose-type resin or cellulose acetate and solvents like terpineol, ethyl cellulose or ethylene glycol. Several example may be seen in Table 2.3. The ratio of the inorganic to organic part in the paste has usually been kept at (70-75)/ (25-30). These simple vehicle perform well with many solid systems in a variety of printing conditions and environment.

Table 2. 3 Example of organic vehicle (binder+solvent) used in gas sensor



Organic carrier	Metal oxide	Reference
Terpineol HVS100: ethyl cellulose: Texaphor 963: Rilanit spez = 89.3: 1.2: 6.0: 3.5 wt%	WO_3, SnO_2	Ivanov (2004)
Terpineol HVS100: ethyl cellulose: Texaphor 963: Rilanit spez: Disponil = 85.5: 1.1: 5.7: 3.4: 4.3 wt%	WO_3, SnO_2	Ivanov (2004)
8% Ethyl cellulose and 92% butyl carbitol acetate	ZnO:Sb	Jayadev et al. (1998)
β-Terpeneol: butyl carbitol acetate: ethyl cellulose	SnO_2:Pd	Nitta and Haradome (1979)
Ethyl cellulose	In_2O_3–TiO_2	Zhang et al. (2012)
Ethyl cellulose: butyl cellulose: butyl carbitol acetate: terpineol	ZnO:Cu	Deore et al. (2011)
Diethyl glycol monobutyl: α-terpinol	SnO_2:CdS	Yadava et al. (2010)
Deionized water: α-terpinol	SnO_2	Choi et al. (2005)
α-Terpineol: ethyl cellulose = 89:11 wt%	SnO_2	Lee et al. (2007)
Isopropyl alcohol : hydroxylpropyl cellulose		

According to Hsu & Kaohslung, May 7, 2013 the binders commonly used in the art include polymethacrylates, ethyl cellulose, an alkyd resin, and the like. The solvents commonly used in the art include glycol ether-based organic solvents such as ethylene glycolmonobutyl ether acetate and diethylene glycol monobutylether, or terpene-based solvents (for example, ot-terpineol), and the like. The viscosity of the organic vehicle used in the art is adjusted with a solvent, so as to facilitate coating operations. Moreover, the solvents should not be so volatile because they might leave a hard unprintable paste on the screen mesh but at the same time they will evaporate early in the drying phase of the process. (Korotcenkov 2013). However, as a large quantity of the solvent evaporates in the drying process after the printing, the environment will be contaminated, which is inconsistent with the concept of environmental protection. In addition, the drying process requires a long time, which becomes one of bottlenecks in increasing production capacity (Hsu and Kaohslung 2013).

2.4.2 Effect of operating temperature

Typically, temperature dependence of a metal-oxide sensor signal to the presence of a given analyse possesses a bell shape with a maximum at a certain temperature. This dependence arises due to several reasons. First of all, as mentioned above, the charge of oxygen species adsorbed at the oxide's surface depends on temperature .Second, since the oxidation reaction is an activated process, its rate increases with temperature. Finally, all adsorption, desorption, and diffusion processes are temperature dependent (Bochenkov and Sergeev 2010).

According to research article, VOC detection using oxide materials is based on a resistance change from a reaction between oxygen adsorbed on the oxide surface and VOCs (surface combustion). The electron depletion layer thickness on the oxide surface is decreased by removing adsorbed oxygen, which decreases electrical resistance. Thus, the surface chemical reaction is transduced to a resistance change, which is used as a sensor signal. Among the materials studied, the TiO_2 nanotube-based sensing films were highly sensitive, selective, and stabile for detecting VOCs, such as toluene, formaldehyde, and ethanol, at high temperatures (e.g., 450–550 ^{o}C). The highly porous morphology from the unique anisotropic TiO_2 nanotube shape provides effective gas diffusion paths. This unique morphology efficiently changes the electrical resistance of the sensing films through a VOC reaction with adsorbed oxygen deep inside the films. High temperature operation of TiO_2-based sensors is advantageous because it prevents severe interference from small combustible gases, such as CO and H_2. An additional advantage of high temperature operation is prevention of carbon deposits at the sensing layer after VOC combustion, which typically produces a significant decrease in the recovery speed.

The research was then be evaluated by prepare gas sensor devices based on metal oxides which operated at elevated temperatures (e.g., greater than 250–300 ^{o}C). The operating temperature was controlled using the micro heater. Sample gases (50 ppm in dry air) were prepared by mixing commercial ethanol and toluene gases with synthetic air. Figure 2.1 shows the device resistance in air at different temperatures (450, 500, and 550 ^{o}C). The device resistance in air was decreased by increasing the operating temperature.

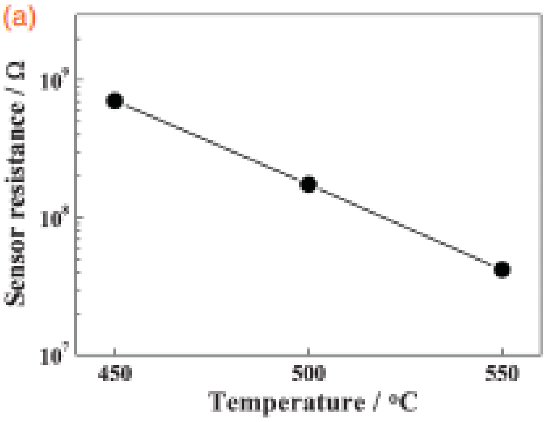


Figure 2. 1 Resistance in air as a function of temperature (Response properties of the MEMS sensor to ethanol)

Figure 2.2 shows the transient responses to ethanol (50 ppm) at 450, 500, and 550 ^{o}C. The resistance quickly and immediately decreased after the sensor was exposed to air containing ethanol, which is typical for n-type semiconductors that respond to reducing gases. The resistance returned to the original value upon switching the gas atmosphere from air containing ethanol to air without ethanol. The results demonstrate that the MEMS device responded and recovered well at these temperatures.

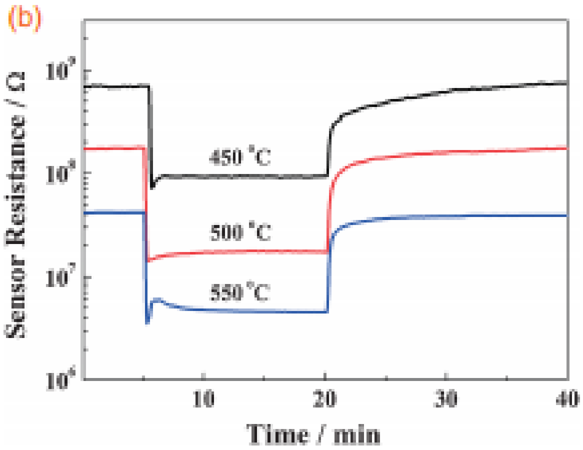


Figure 2. 2 Transient responses to 50 ppm ethanol at 450^{o}, 500^{o}, and 550^{o} C (Response properties of the MEMS sensor to ethanol)

Figure 2.3 shows the sensor response (S) to ethanol (50 ppm) at 450, 500, and 550 ^{o}C. The sensor response decreased with increasing operating temperature, likely due to efficient ethanol combustion on the sensing layer surface at higher temperatures. However, it exceeded 10 at 450 ^{o}C, which is evidence of good sensitivity to ethanol despite the small sensing area. The level of sensitivity is comparable to other MEMS-based gas sensors. The good sensor response to ethanol at a low concentration observed herein is a promising feature of this sensor (Kida, et al. 2013).

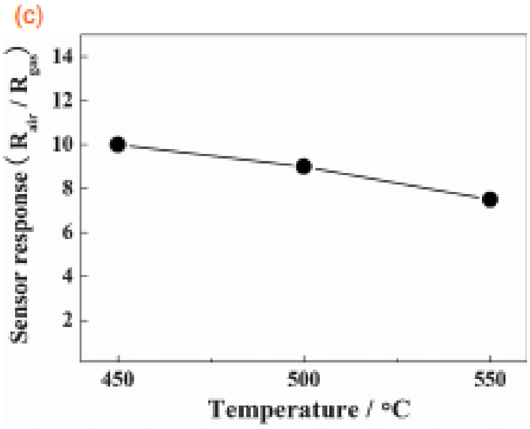


Figure 2. 3 Sensor responses to 50 ppm ethanol as a function of temperature (Response properties of the MEMS sensor to ethanol)

2.4.3 Effect of binders

Binders are commonly employed to deposit titanium dioxides films to improve the mechanical strength of the film. In order to study the effect of organic binders on their TiO2 films, a simple method of preparation of screen printable TiO_2 paste from commercial anatase TiO_2 nanopowder using two different organic binders i.e. polyvinylpyrrolidone and ethyl cellulose was tested. As reported in the journal, to make strong bonding between the TiO_2 nanoparticles and the alumina surface, the presence of hydroxides (-OH) groups can play a vital role. The hydroxide groups will increase the chemical bonding of each. Moreover, by adding DI water, paste provides more hydroxide groups on the surfaces and helps in reducing the inter-particle aggregations. It can cause less shrinkage in the film during high temperature calcination. Thus, the bonding between TiO_2 particles and the alumina surface will be stronger. By adding acetic acid, the rate of aggregation of particles is inhibited, due to its adsorption on the surface of TiO_2 .This is because acetic acid and water are necessary to obtain more homogeneity in the paste.

Furthermore, Figure 2.4 shows the J-V performance variations of different DSSCs fabricated using TiO_2 pastes made with various PVP binder concentrations. When compared to the paste without binder, TiO_2 photoanodes fabricated from the TiO_2 paste with PVP binder showed an improved current density. However by increasing the quantity of PVP in binder solution, it was found that the efficiency was decreasing. Even though, the adhesion of TiO_2 particles was improved, on sintering, it was observed that the porous structures of the film was reduced considerably, which resulted to the poor dye adsorption and hence the poor efficiency. Due to this problem, ethyl cellulose was introduced as the binder and dye adsorption issue was resolved. As a results, due to the better TiO_2 film formation with increased porous structures in the photoanode, TiO_2 paste made with ethyl cellulose binder showed better open circuit voltage and fill factor compared that of TiO_2 paste made with PVP binder (D, et al. October 2016).

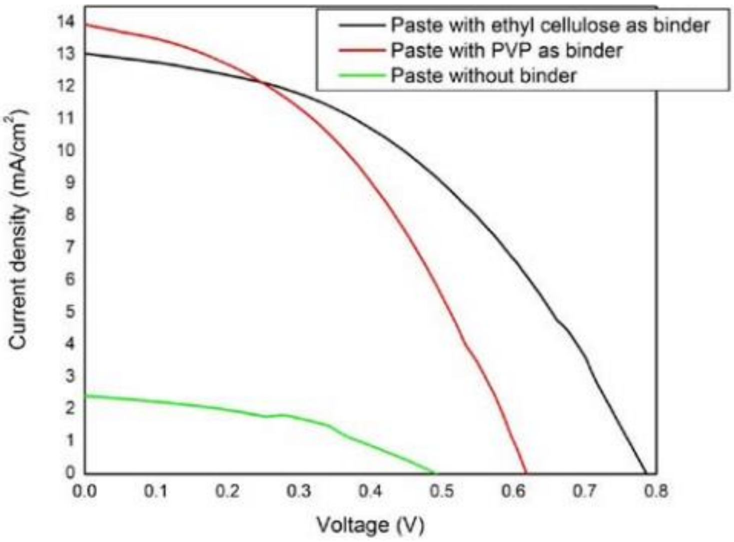


Figure 2. 4 Comparison of J-V characteristics of the DSSCs fabricated with two different pastes.

CHAPTER 3: MATERIALS AND EXPERIMENTAL METHODS

3.1 Material and instrumentation

3.1.1 Materials

The materials used for fabrication and testing of the sensor are listed in Table 3.1 below:

Table 3. 1 List of chemical used and their description.

Chemicals/ Reagents	**Assay**	**Supplier**	**Purpose of use**
Ethylene Glycol ($C_2H_6O_2$)	-	-	-As solvent to dissolve TiO_2 powder to make a paste
Titanium Oxide (TiO_2)	-	-	-For fabrication process
Purified air	20.8% O_2 79.2 % N_2	Malaysia	-Simulated air as feed gas, VOC carrier gas
Ethanol Gas (C_2H_5OH)	98.5 %	Alpha G.P.R Chemicals	-For testing process

3.1.2 Instrumentation

The equipment used for fabrication and testing of the sensor are listed in Table 3.2 below:

Table 3. 2 List of equipment's availability

Availability	**Equipment**	**Model**
School of Chemical Engineering	Analytical balance	Shimadzu AY 220
	Hot plate stirrer	Favorit
	Furnace	Carbolite ELF 11/63
	BET Surface Area Analysis	Micromeritics ASAP 2020
	Scanning Electron Microscope Q	Quanta FEG450
School of Material Engineering	X-ray Diffraction	Philips PW 1710

3.2 Sensing material preparation

The purpose of this study was to develop a suitable sensing material of nanoparticles that can be used to detect VOCs under different conditions.

3.2.1 Fabrication of gas sensor via screen printing preparation

The paste were set to satisfy TiO_2 film at mass ratio of $[TiO_2]:[(CH_2OH)_2]$ = 3:7 , TiO_2 film at mass ratio of $[TiO_2]:[(CH_2OH)_2]$ = 5:5 and TiO_2 film at mass ratio of $[TiO_2]:[(CH_2OH)_2]$ = 6:4 . To obtain thick films, this suspension was then screen printed onto an alumina plate. The coated alumina plate were dried at 100 °c for 10mins and subsequently calcinated at 350 °c for 1 h. It was coated for 3 layers. Finally, the gas sensor were aged at 200°c for 24 h to improve stability and repeatability.

3.3 Characterization of the TiO_2 thick film sensor

3.3.1 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

In this study, electron microscope (Quanta FEG450, USA) was used to conduct SEM analysis at room temperature. The sample powders were placed on a carbon double sided tape with the aluminium stub at the base and coated with gold for electron reflection. The prepared samples were then vacuumed for 5-10 min before observations and analyses were made at different magnifications.

On the other hand, EDX is an auxiliary segment of SEM to check the existence of elemental compositions in the sensor powders. The analysis was carried out by using an Oxford X-Max EDX microanalysis system with an operating voltage in the range of 0.1–30 kV.

3.3.2 X-Ray Diffraction (XRD)

In this study, XRD analysis was carried out using a Philips Goniometer PW 1820 diffractometer, PW 1710 diffraction controller and X-ray generator PW 1729 operated at 40 kV and 120 mA. The resulting analysis was described graphically as a set of peaks with % intensity on the y-axis and the goniometric angle on the x-axis. From the graph, crystallite phases are identified by comparing it with Standard Powder Diffraction Files from International Centre for Diffraction Data (ICCD). The diffractometer was used with monochromatized Cu-Kα radiation ($\lambda = 0.154056$ nm) and taken in the range of 10 - 90° (2θ) with a step size of 0.01°.

3.4 Sensing performance

A gas sensing experimental rig is set up as shown in the schematic diagram in Figure 3.1. The equipment used includes purified air and ethanol vapour storage tanks, control valves, mixer, gas chamber, heater, thermocouple, electrometer and temperature controller. In the gas chamber, the sensor is connected to an electrometer by a pair of clips. The heater is allowed to heat up to 150 °C and the temperature is measured by a thermocouple. The purified air inlet valve is opened and its flow rate is set to 300 ml/min while the ethanol vapour inlet valve is opened with its concentration being set to the desired concentration using mass valve controller. A computer which is equipped with the software Xlogger is connected to the electrometer and is used for data acquisition, storage and plotting in real time for the analysis of sensitivity of gas sensor. After the operating temperature reaches steady state, a constant voltage of 5 V is supplied. The DC resistance of the gas sensor is measured for every second by the electrometer. The data collected is transferred into the computer and saved. The sensitivity analysis is calculated automatically by the software. The sensor performance testing is repeated at operating temperature of 200 °C, 300 °C and 400 °C.

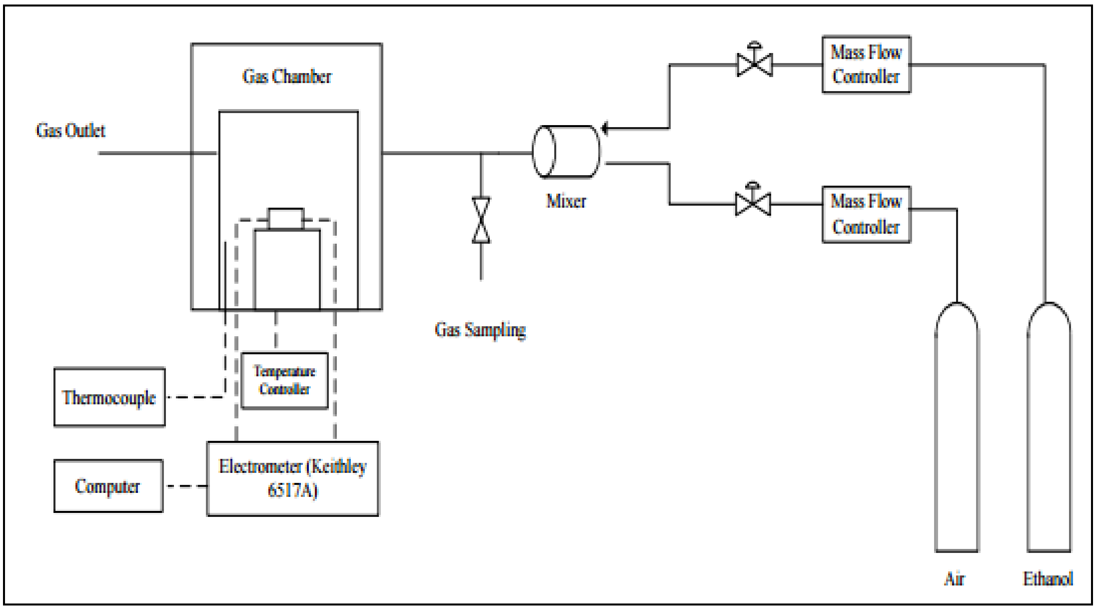


Figure 3. 1 Schematic diagram of the gas sensor rig.

CHAPTER FOUR: RESULT AND DISCUSSION

4.1 Introduction

The detection of ethanol gas has been conducted using titanium dioxide, TiO_2 based thick film gas sensor. TiO_2 was selected to be the sensing material due to extraordinary sensitivity towards H_2 but they also shows a good sensing properties to CO, CH_4 and ethanol. Moreover, this sensor is a good candidate for gas sensing application because it being chemically very stable in high temperatures (N. Ohatkar, et al. May 2016). In order to understand more about the TiO_2 sensing performance, screen printing method was being used to fabricate the gas sensors with different composition. The influence of average crystallite size towards the sensing performance of the gas sensor was studied.

In this study, titanium dioxide sample powders were characterized using few methods which are X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Energy Dispersive X-Ray (EDX) analysis. XRD is being used for phase identification of the crystalline titanium oxide sample. Besides that, the topography of the surface of titanium oxide sample film were studied using SEM analysis while the existence of elemental compositions of the sensing material powders were checked by using EDX analysis to ensure titanium oxide was synthesized successfully.

Overall, this chapter is divided into 3 main sections which are characterization of sensing materials, studies on the effect of operating temperature of the sensor towards ethanol gas and the composition of paste via screen printing technique.

4.2 Characterization of sensing material

4.2.1 Scanning Electron Microscope (SEM)

The SEM images of titanium dioxide are shown in Figure 4.1 (a-c). It can be observed due to their composition of titanium dioxide TiO_2 and ethylene glycol, $(CH_2OH)_2$ as a binder. In figure 4.1 (a) the mass ratio of $[TiO_2]$:[(CH_2OH) $_2$] = 3:7 showed that there are large area between the fine particles and agglomeration exist. Figure 4.1 (b) which is for the mass ratio of $[TiO_2]:[(CH_2OH)_2] = 5:5$ showed almost similar morphology of fine particles, but the area become narrower to each other and agglomeration less exist. After applying higher composition of TiO_2 and $(CH_2OH)_2$ which give mass ratio of $[TiO_2]:[(CH_2OH)_2] = 6:4$ in figure 4.1 (c), particles become closer and form a strong bond between each other. The agglomeration tends to not exist in this figure 4.1 (c). Thus, this result obtained further confirmed that the increase in composition of paste will contribute to the low agglomeration and smooth surface and uniform over the large area.

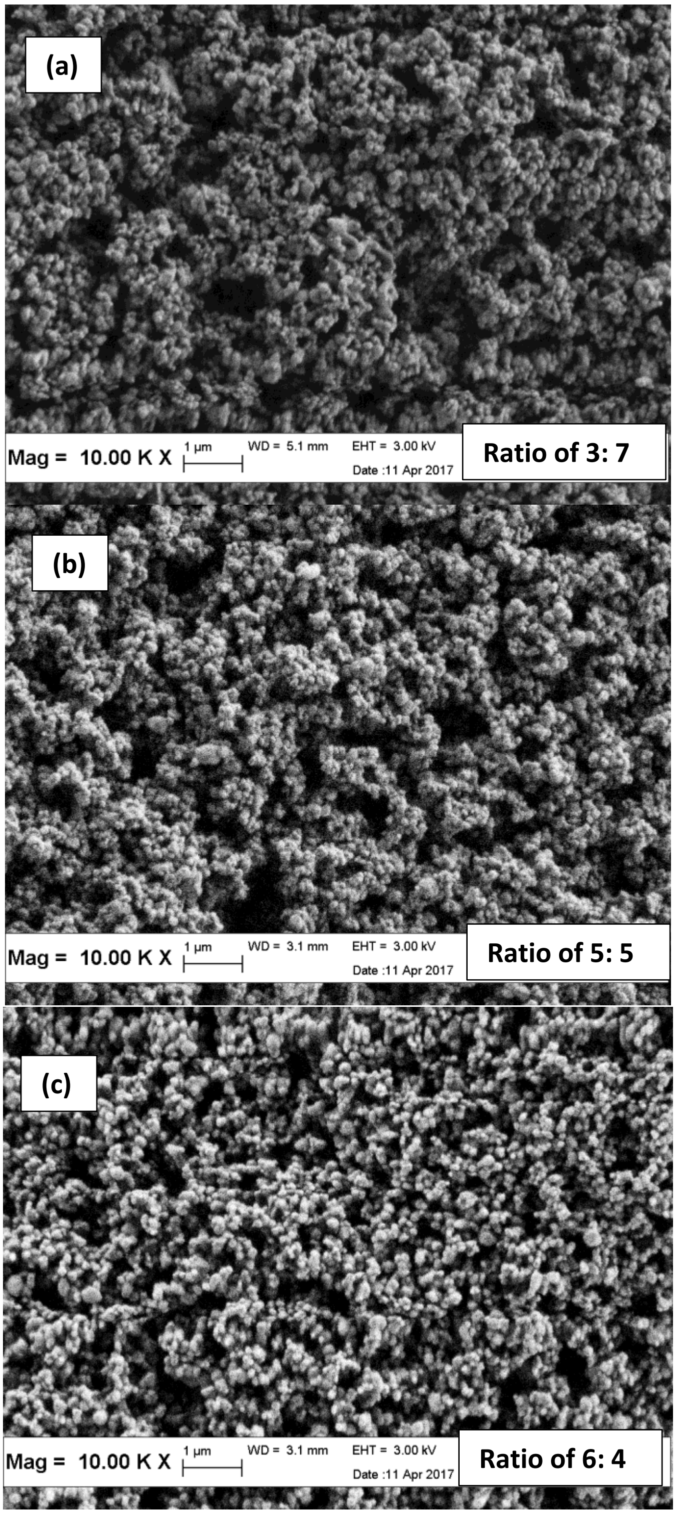


Figure 4. 1 SEM image at 10.00 K x magnification for (a) TiO_2 film at mass ratio of $[TiO_2]:[(CH_2OH)_2] = 3:7$, (b) TiO_2 film at mass ratio of $[TiO_2]:[(CH_2OH)_2] = 5:5$and (c) TiO_2 film at mass ratio of $[CH_2OH)_2] = 6:4$.