

SENSING PROPERTIES OF COPPER OXIDE THIN FILM UPON EXPOSURE  
OF METHANE GAS IN AIR

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## ABSTRACT

Application of p-type semiconductor copper oxide thin films as methane gas sensors in air was investigated. A series of copper oxide thin film had been prepared. The thin films were fabricated by using direct current (DC) sputtering technique on Corning glass substrates at different deposition time (30 to 180 min at 30 min interval) hence different thicknesses of thin films were produced. The target used for the copper oxide thin film growth was metallic copper (99.99% purity). The thin film thicknesses were measured by using surface profiler (Dektak 3). Aluminum comb-like inter digital electrodes were deposited onto each substrate by thermal evaporation technique. Gas sensing characteristics mainly the resistance, sensitivity, response time and recovery time of copper oxide thin films upon exposure of methane gas in air were studied using gas sensing characterization system (GSCS) by varying the operating temperature starting from 100°C to 300°C with an increment of 50°C. The thicknesses of copper oxide thin films were in the range of 178 nm to 513 nm at a deposition rate of 2.20 nm/min. The films resistances were found to increase in the presence of methane gas, and decreased with the presence of synthetic air. The resistances of copper oxide thin films as a function of operating temperature at 100°C to 300°C were found to decrease with the increased of operating temperature. Sample S3 with film thickness 274 nm exhibited the highest sensitivity (3.29) for methane at operating temperature of 200°C with corresponding response time of 108 s and recovery time > 600 s. Whereas, for double array series, A2 (30 + 90 minute) showed the best sensitivity (2.01) with corresponding response time 86 s and recovery time > 600 s at operating temperature of 150°C. Accordingly, it can be concluded that single sample showed excellent sensitivity compared to double array series. Therefore, single sample was preferable as gas sensor for the detection of methane gas in air.

## ABSTRAK

Aplikasi semi konduktor jenis-p filem tipis kuprum oksida sebagai penderia gas metana dalam udara telah dikaji. Satu siri filem tipis kuprum oksida telah disediakan. Filem tipis telah difabrikasikan menggunakan teknik percikan arus terus (DC) di atas substrat kaca Corning pada masa pemendapan yang berbeza (30 hingga 180 min pada selang masa 30 min), maka filem tipis yang berbeza ketebalannya dihasilkan. Sasaran yang digunakan untuk pertumbuhan filem tipis kuprum oksida adalah logam kuprum (ketulenan 99.99%). Ketebalan filem tipis diukur dengan menggunakan pembukah permukaan (Dektak 3). Elektrod inter jejari berbentuk sikat telah dimendapkan ke atas setiap substrat dengan teknik penyejatan terma. Ciri penderia gas terutamanya rintangan, kepekaan, masa gerak balas dan masa pemulihan bagi filem tipis kuprum oksida terhadap dedahan gas metana dalam udara telah dikaji menggunakan sistem pencirian penderia gas (GSCS) dengan merubah suhu operasi daripada 100°C ke 300°C dengan tokokan 50°C. Ketebalan filem tipis kuprum oksida adalah dalam julat 178 nm sehingga 513 nm pada kadar pemendapan 2.20 nm/min. Rintangan filem didapati meningkat dalam kehadiran gas metana, dan berkurang dengan kehadiran udara sintetik. Rintangan bagi filem tipis kuprum oksida sebagai fungsi bagi suhu operasi pada 100°C ke 300°C telah didapati menurun dengan peningkatan suhu operasi. Sampel S3 dengan ketebalan filem 274 nm mempamerkan kepekaan tertinggi (3.29) terhadap metana pada suhu operasi 200°C dengan masa gerak balas bersamaan dengan 108 s dan masa pemulihan > 600 s. Manakala, siri tatasusun berganda, A2 (30 + 90 minit) menunjukkan kepekaan terbaik (2.01) dengan masa gerak balas bersamaan dengan 86 s dan masa pemulihan > 600 s pada suhu operasi 150°C. Oleh itu, boleh dirumuskan bahawa sampel tunggal menunjukkan kepekaan cemerlang dibandingkan dengan siri tatasusun berganda. Oleh itu, sampel tunggal adalah pilihan utama penderia gas untuk pengesanan gas metana dalam udara.

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**LIST OF SYMBOLS**

$^{\circ}\text{C}$	Degree celcius
$\Omega$	Ohm
$\text{CH}_4$	Methane gas
CVD	Chemical vapor deposition
$d$	Film thickness
DC	Direct Current
GSCS	Gas sensing characterization system
$\text{M}\Omega$	Mega Ohm
mV	milivolt
nm	nanometer
ppm	part permillion
PVD	Physical vapor deposition
$R_a$	Sensor resistance in synthetic air
$R_g$	Sensor resistance in test gas of $\text{CH}_4$
$R_L$	Load resistance
$R_s$	Sensor resistance
$S$	Gas sensitivity
$t$	Time
$T$	Temperature
V	Voltage
$V_C$	Supplied voltage
$V_L$	Output voltage

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background of study**

In the extent of ecological pollution and industrial process control, medical diagnosis, agriculture and variety of other activities, the development of gas sensor for the early detection of chemical species, combustible and hazardous gases is in high demand (Hoa et al. 2010).

A sensor device produces an interface between the electronic equipment and the physical world by converting non-electrical physical or chemical quantities into electrical signals. The best sensing material is metal oxide semiconductor which offers an excellent sensor with several advantages (Liu et al. 2012).

Since thin film metal oxide semiconductor gas sensors have proven to be promising in this area of research, they have been extensively studied and have received very much attention due to their low cost and flexibility in production, the simplicity of their use, large number of detectable gases or possible application fields (Kanan et al. 2009). In the meantime they are pretty economical, vital, lightweight, durable and being a best deliver in both high sensitivity and quick

response time, these metal oxide semiconductors are favorably employed in a variety of different roles and industries (Fine et al. 2010).

## **1.2 Statement of problem**

As a concern to environmental and safety requirement, the development of methane sensor have been promoted to both high sensitivity and rapid response. Much technological effort has been made aiming at improvement of a simple, economical yet advantageous methane gas sensor for practical use. The most reported metal oxide methane sensor is the SnO<sub>2</sub> based (Ibrahim, 2005). While sensing properties of p-type methane sensor has scarcely been investigated. Thus this motivate this present study to develop a highly sensitive, fast response and fast recovery time gas sensor for detection of methane will be presented.

## **1.3 Objectives of study**

The objectives of the study are;

1. To synthesize copper oxide (CuO) thin film by using DC sputtering technique.
2. To investigate the effect of different CuO thin film thickness upon CH<sub>4</sub> (200ppm) exposure at operating temperature from 100°C to 300°C.
3. To determine the resistance, sensitivity, response time and recovery time of CuO thin film at selected operating temperatures.



#### **1.4 Scope of study**

The aim of this study is to present the detection properties of a single and array configuration of CuO-based sensing layer in the exposure of 200 ppm methane gas in air. Undoped CuO thin films were prepared from copper oxide metal target with purity 99.99% onto corning glass substrates by using DC sputtering technique. Different measurements were conducted to characterize the sensing properties. The Gas Sensor Characterization System (GSCS) was used to study the sensing parameters including sensitivity, response time and recovery time of CuO thin films at selected operating temperature upon 200ppm methane.

#### **1.5 Significant of the study**

Methane gas is one of the greenhouse gases that responsible for climate changes. The average level of the emission of methane recently had been reported rose unexpectedly. The source of the methane gas emission is not only concentrated at coal mining and industrial area but also from natural sources, agricultural as well as human activities (Anderson et al. 2012). Besides that, methane also produced in home septic and without being aware, methane gas leakage may unexpectedly occur in housing area. A research towards a better methane gas sensor which require a fast detection at low concentration in lower temperature will be an advantage to public safety.

## **1.6 Outline of thesis**

This thesis is structured as follows. In Chapter 1, the thin film gas sensor is briefly explained followed by the problem of statement, objectives, scope and significant of this study. The general reviews of metal oxide semiconductor gas sensor is stated in Chapter 2, including the development of methane gas sensor and gas sensing mechanism. Chapter 3 describes the experimental methodology which includes the technique used to fabricate copper oxide thin films, thickness measurement and the gas sensing characterizations. Results and discussion of the experimental work is presented in Chapter 4, followed by conclusion and suggestion of this study in Chapter 5.

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