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**FABRICATION OF THIN FILM TIN OXIDE GAS SENSORS
BY SOL-GEL TECHNIQUE**



Mr. Arporn Teeramongkonrasmee

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วิทยานิพนธ์นี้เป็นการศึกษาการประดิษฐ์หัวตรวจวัดแก๊สแบบฟิล์มบางของดีบุกออกไซด์โดยใช้เทคนิคโซล-เจล
สารละลายโซลของดีบุกออกไซด์ได้ถูกเตรียมด้วยกระบวนการสังเคราะห์ทางเคมี โดยมีดีบุกเตตระคลอไรด์และโซเดียมเอ
ทอไซด์เป็นสารเริ่มต้นหลักในการทำปฏิกิริยา ฟิล์มบางของดีบุกออกไซด์จะถูกเตรียมโดยการนำสารละลายโซลที่ได้จะนำไป
เคลือบลงบนแผ่นฐานรองที่เป็นกระจกด้วยเทคนิคการสปินโคตติง แล้วจึงเผาด้วยความร้อนที่อุณหภูมิ 550°C เป็นเวลา 1
ชั่วโมง เพื่อเปลี่ยนโครงสร้างให้เป็นดีบุกออกไซด์ จากการศึกษาพบว่าความหนาของชั้นดีบุกออกไซด์สามารถควบคุมใน
ลักษณะเชิงเส้นโดยการแปรจำนวนครั้งของการเคลือบ โดยมีความหนาของการเคลือบ 1 ครั้ง เท่ากับ 350 อังสตรอม

เพื่อให้การวิเคราะห์หาประสิทธิภาพการตอบสนองของหัวตรวจวัดแก๊สที่ได้ประดิษฐ์ขึ้นเป็นไปอย่างถูกต้อง
ได้มีการนำเสนอมงจรวดแบบใหม่ที่สามารถนำมาใช้คำนวณหาค่าความไวและค่าเวลาฟื้นตัวของหัวตรวจวัดแก๊สได้อย่างถูก
ต้องโดยไม่ขึ้นกับค่าของอุปกรณ์ภายนอกที่มาต่อ เช่น ค่าความต้านทาน ได้มีการเปรียบเทียบระหว่างวงจรมอนิเตอร์กับ
วงจรวัดแบบเดิมในแง่ของการวิเคราะห์ทางทฤษฎีและการทดลอง ผลที่ได้ชี้ให้เห็นว่าวงจรวัดแบบเดิมนั้นไม่เหมาะสมกับการ
ใช้หาค่าความไวในกรณีที่หัวตรวจวัดแก๊สมีลักษณะสมบัติของกระแสแรงดันแบบไม่เชิงเส้น ส่วนในกรณีของวงจรมอนิเตอร์
จะไม่พบปัญหาดังกล่าว นอกจากนี้เมื่อกำหนดให้แรงดันไบอัสของหัวตรวจวัดแก๊สมีค่าเท่ากันแล้วจะสามารถเปรียบเทียบค่า
ความไวและค่าเวลาฟื้นตัวของหัวตรวจวัดแก๊สได้อย่างถูกต้อง

โดยการใช้วงจรวัดแบบใหม่กับระบบวัดแก๊สแบบโพลาไรซ์อินเจกชันวัดลักษณะสมบัติการตอบสนองของหัวตรวจ
วัดแก๊สที่ได้ประดิษฐ์พบว่า ความหนาของฟิล์มบางดีบุกออกไซด์มีผลอย่างมากต่อค่าความไวของหัวตรวจวัดแก๊ส ความหนาที่
เหมาะสมของฟิล์มบางมีค่าอยู่ประมาณ 1000 อังสตรอม จากการวัดการตอบสนองที่มีต่อสารละลายของแอลกอฮอล์และ
แอมโมเนีย พบว่า หัวตรวจวัดแก๊สของดีบุกออกไซด์ที่ไม่มีการเติมสารเจือปนให้ค่าความไวสูงสุด การเติมสารเจือปนของทอง
แดงซัลเฟต ทองและเงินคลอไรด์จะทำให้ค่าความไวของหัวตรวจวัดแก๊สลดลง แต่การเติมเหล็กคลอไรด์มีแนวโน้มที่จะแสดง
ให้เห็นว่าความไวมีค่าสูงขึ้น การวิเคราะห์โดยใช้โมเดลของกฎการยกกำลังแสดงให้เห็นว่า หัวตรวจวัดแก๊สของดีบุกออกไซด์ที่
ไม่มีการเติมสารเจือปนจะสามารถตอบสนองแบบเชิงเส้นต่อแอลกอฮอล์ในช่วงความเข้มข้นร้อยละ 0.08-10 โดยปริมาตร และ
ต่อแอมโมเนียในช่วงความเข้มข้นร้อยละ 0.05 - 10 โดยปริมาตรสำหรับ อุณหภูมิการทำงานที่เหมาะสมของหัวตรวจวัดแก๊ส
คือ 250°C สำหรับการตรวจวัดแอลกอฮอล์และ 350°C สำหรับการตรวจวัดแอมโมเนีย

ภาควิชา วิศวกรรมไฟฟ้า

สาขาวิชา วิศวกรรมไฟฟ้า

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ลายมือชื่อนิสิต อ.ดร. มานะ ศรีบุษยศักดิ์

ลายมือชื่ออาจารย์ที่ปรึกษา ดร. Toyosaka Morizumi

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ARPORN TEERAMONGKONRASMEE : FABRICATION OF THIN FILM TIN OXIDE GAS SENSORS BY SOL-GEL TECHNIQUE. DISSERTATION ADVISOR : ASSC. PROF. MANA SRIYUDTHSAK, D. Eng. DISSERTATION CO-ADVISOR : PROF. TOYOSAKA MORIIZUMI, D. Eng. 161 pp. ISBN 974-331-253-6.

In this dissertation, a systematic study involving the fabrication of thin film SnO₂ gas sensors by sol-gel technique had been carried out. The sol solution of SnO₂ was prepared by chemical synthesis process. Tin tetrachloride and sodium ethoxide were used as the fundamental reactants. The synthesis sol had been coated on the glass substrate by spin coating technique to form thin films. The coated films were then subjected to anneal at 550 °C for 1 hour to change their structure to SnO₂. It was found that the thickness of SnO₂ films could be linearly controlled by varying the number of coatings. The thickness of each coating was about 350 Å.

In order to analyze the gas sensing performance quantitatively, a novel gas measuring circuit was proposed. This circuit could be used to calculate sensitivity and recovery time without depending on the external circuit components such as resistance. The performance of this proposed circuit had been compared with that of the conventional circuit in both theoretical and experiment aspects. The results indicated the conventional measuring circuit is not suitable for calculating gas sensitivity in the case which a semiconductor gas sensor under test has a nonlinear *I-V* characteristic. For the proposed circuit, this nonlinear property did not cause any problem in calculating sensitivity. Moreover, the gas sensing performance of various gas sensors could be compared quantitatively if the bias voltage of all gas sensors were set to the same value.

The characterization of the fabricating gas sensors had been performed on a flow injection system combining with the proposed measuring circuit. The sensitivity of gas sensor had been found to be strongly dependent on the film thickness. The experiments showed that the optimum thickness was about 1000 Å. From the gas response tests to alcohol and ammonia solutions, it was found that the unmodified SnO₂ gas sensor gave the highest sensitivity. The addition of some modified substances such as CuSO₄, AgNO₃ and Au reduced the gas sensitivity. However, there was a tendency to increase sensitivity by adding FeCl₃. By using the power law model to analyze the change of sensitivity with sample concentration, it was found that the unmodified SnO₂ gas sensor could be used to detect alcohol and ammonia in the range of 0.08 - 10 and 0.05 - 10 % by volume respectively. The optimum operating temperature was 250°C for alcohol detection and 350°C ammonia detection.

ภาควิชา.....วิศวกรรมไฟฟ้า.....

ลายมือชื่อนิติศ..... *Arporn Teeramongkonrasmee*.....

สาขาวิชา.....วิศวกรรมไฟฟ้า.....

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List of Symbols and Acronyms

Acronyms

CVD	Chemical vapor deposition
EB	Electron beam evaporator
GasFET	Gas sensitive field effect transistor
HC	Hydrocarbon
HP	Hydrophobic silica
TEM	Transmission electron microscope
TM	Trimethylchlorosilane
XPS	X-ray photoelectron spectroscopy

Fundamental constants

ϵ_0	Permittivity in free space	$8.854 \times 10^{-12} \text{ F m}^{-1}$
k	Boltzmann constant	$1.381 \times 10^{-23} \text{ J K}^{-1}$
q	elementary charge	$1.602 \times 10^{-19} \text{ C}$

Symbols

ϵ	Dielectric constant
θ	Surface coverage
σ	Conductivity
ϕ	Work function
α	Non-linear coefficient
τ	Time constant
C	Capacitance
C_s	Sensor capacitance
d	Density
D	Grain diameter

Symbols (continued)

D_{av}	Estimated grain size
E	Energy
E_c	Conduction band edge
E_F	Fermi energy level
E_v	Valence band edge
G	Conductance
I	Current
I_o	Reverse saturation current
n	Electron concentration
N_A	Acceptor concentration
N_D	Donor concentration
N_s	Surface charge density
p	Hole concentration
P	Pressure
R	Resistance
R_s	Sensor resistance
S	Sensitivity
S_{av}	Specific surface area
T	Absolute temperature
t_r	Recovery time
V	Potential
V_{in}	Voltage source
V_o	Contact potential
V_s	Voltage across gas sensor
W	Thickness of space-charge layer