



รายงานวิจัยฉบับสมบูรณ์

โครงการ

นาโนเซนเซอร์ก๊าซที่มีฐานเป็นโครงสร้างนาโนของสารประกอบซิงก์ออกไซด์
สัญญาเลขที่ DBG5380005

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ตุลาคม 2556

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สารบัญ

	หน้า
บทคัดย่อ ภาษาไทย	4
บทคัดย่อ ภาษาอังกฤษ	5
Executive summary	6
การดำเนินงานที่ผ่านมา	7
ผลที่ได้รับจากงานวิจัย	8
เอกสารอ้างอิง	15
Output ที่ได้จากโครงการ	16
จดสิทธิบัตร	16
ผลงานตีพิมพ์ทางวิชาการ	16
การนำเสนอผลงานทางวิชาการ	17
การเป็นวิทยากรบรรยาย	17
การเชื่อมโยงทางวิชาการกับนักวิชาการอื่นทั้งในและต่างประเทศ	18
รางวัลที่ได้รับ	18
ภาคผนวก เอกสารแนบ output ของงานวิจัย	20

บทคัดย่อ

ในงานวิจัยนี้ คณะผู้วิจัยได้ศึกษานาโนเซนเซอร์ก๊าซที่มีฐานเป็นโครงสร้างนาโนของสารประกอบซิงก์ออกไซด์ โดยมีวัตถุประสงค์หลักคือ เพื่อสร้างนาโนเซนเซอร์ก๊าซที่มีฐานเป็นโครงสร้างนาโนของสารประกอบซิงก์ออกไซด์ และศึกษาสมบัติการตรวจจับก๊าซ โดยต้องการพัฒนาสภาพไวให้มีค่าเพิ่มขึ้น ซึ่งการเตรียมโครงสร้างนาโนซิงก์ออกไซด์ใช้วิธี thermal oxidation ที่บรรยากาศปกติ ทำให้ได้โครงสร้างเป็น nanowire ที่มีขนาดเส้นผ่าศูนย์กลาง 40–300 นาโนเมตรและมีความยาวหลายไมโครเมตร จากนั้นได้นำ nanowire ที่ได้มาสร้างเป็นนาโนเซนเซอร์ ได้ใช้เทคนิคการเติมสารโลหะลงไปในสารประกอบซิงก์ออกไซด์ โดยใช้วิธีการเติมสารหลักอยู่สองอย่างคือวิธีการหยดสารละลายและวิธีสเปตเตอร์ริง ซึ่งสามารถสังเกตพบการเพิ่มขึ้นของสภาพไวของทั้งสองวิธี และพบว่าวิธีสเปตเตอร์ริงทำให้สภาพไวมีค่าสูงสุดถึง 478 ภายใต้ความเข้มข้นแอลกอฮอล์ 1000 พีพีเอ็ม เมื่อใช้เวลาสเปตเตอร์ริง 60 วินาที

ซึ่งการเพิ่มขึ้นของสภาพไวสามารถอธิบายได้โดยสมบัติอะตอมของโลหะในปฏิกิริยาการดูดซับเอทานอล และในปฏิกิริยาการดูดซับก๊าซออกซิเจนที่พื้นผิวของซิงก์ออกไซด์ ซึ่งสามารถอธิบายการเพิ่มขึ้นของสภาพไวและการขึ้นอยู่กับปริมาณของโลหะของสภาพไว ได้ตั้งสมการที่ทางคณะผู้วิจัยได้พัฒนาขึ้น ในรูปของตัวแปรความกว้างของชั้นปลอดพาหะ ดังนั้นสภาพไวสามารถออกแบบได้โดยการควบคุมความกว้างของชั้นปลอดพาหะผ่านทาง การควบคุมปริมาณของอนุภาคนาโนทองคำ ซึ่งทำได้ง่ายโดยการปรับเปลี่ยนเวลาการสเปตเตอร์ริง จากผลการทดลองนี้ สามารถนำไปต่อยอดประยุกต์ใช้ต่อไปทางด้านจุ่มอิเล็กทรอนิกส์

คำสำคัญ : ซิงก์ออกไซด์, โครงสร้างนาโน, นาโนเซนเซอร์, เทอร์มอลออกไซด์เซ็น

Abstract

In this work, we have investigated the nanosensors based on nanostructures of ZnO compounds. The main objectives of this work are to fabricate nanosensors based on nanostructures of ZnO compounds and investigate the ethanol sensing properties of nanosensors in order to enhance the sensor response. The ZnO nanostructures were prepared by thermal oxidation technique under normal atmosphere. Then, ZnO nanostructures exhibited the diameters of 40–300 nm with several micrometer lengths and were applied as nanosensors. The metal adding technique was used for enhancement of sensor response by metal impregnating and sputtering. The enhancement of sensor response due to metal adding on ZnO nanostructure sensors has been observed and found that the sputtering technique give the highest sensor response of 478 at sputtering time of 60 s under ethanol concentration of 1000 ppm. The sensor response enhancement can be explained by considering the catalytic effect on ethanol adsorption reaction and oxygen adsorption reaction. Consequently, the sensor response formula has been successfully developed and can describe the dependence of metal amount on sensor response in terms of the depletion layer width. As a result, the sensor response can be designed by controlling the depletion layer width via the amounts of gold nanoparticles, which can be simply performed by varying sputtering time. These results can be further explored for an implication in e-nose applications.

Keyword : Zinc oxide, nanostructure, nanosensor, thermal oxidation

Executive Summary

ในงานวิจัยนี้ มีวัตถุประสงค์หลักคือ เพื่อสร้างนาโนเซนเซอร์ก๊าซที่มีฐานเป็นโครงสร้างนาโนของสารประกอบซิงก์ออกไซด์ และศึกษาสมบัติการตรวจจับก๊าซ โดยต้องการพัฒนาสภาพไวให้มีค่าเพิ่มขึ้นรวมทั้ง เพื่อศึกษากลไกการดูดซับก๊าซของนาโนเซนเซอร์ ซึ่งการเตรียมโครงสร้างนาโนซิงก์ออกไซด์ใช้วิธี thermal oxidation ที่บรรยากาศปกติ ทำให้ได้โครงสร้างเป็น nanowire ที่มีขนาดเส้นผ่าศูนย์กลาง 40–300 นาโนเมตรและมีความยาวหลายไมโครเมตร จากนั้นได้นำ nanowire ที่ได้มาสร้างเป็นนาโนเซนเซอร์ และนำไปศึกษาสมบัติการตรวจจับไอเอทานอล พบว่า นาโนเซนเซอร์ มีสภาพไวที่ดีขึ้นกว่าเดิมจากเซนเซอร์ที่เตรียมจากฟิล์มบาง แต่ยังไม่สูงมากนัก จึงได้ใช้เทคนิคการเติมสารโลหะลงไปในสารประกอบซิงก์ออกไซด์ ซึ่งใช้วิธีการเติมสารหลักอยู่สองอย่างคือวิธีการหยดสารละลายและวิธีสปัตเตอร์ริง

วิธีการหยดสารละลายโลหะสามารถปรับปรุงค่าสภาพไวให้กับเซนเซอร์โครงสร้างนาโนซิงก์ออกไซด์ได้ ค่าสภาพไวสูงที่สุดมาจากเซนเซอร์ที่มีการเติมทั้งทองคำและแพลทินัมโดยมีค่าสภาพไวอยู่ที่ 85 เท่า ที่ความเข้มข้นของเอทานอล 1000 ppm ซึ่งสามารถอธิบายได้ว่าโลหะที่หยดลงไปมีสมบัติเป็นตัวเร่งปฏิกิริยาทั้งปฏิกิริยาการดูดซับเอทานอลและปฏิกิริยาการดูดซับออกซิเจน หลักฐานการเพิ่มขึ้นของค่า $k_{Eth}(T)$ และ $k_{Oxy}(T)$ สังเกตได้จากความต้านทานที่ลดลงในบรรยากาศเอทานอลและความต้านทานที่เพิ่มขึ้นในบรรยากาศปกติของเซนเซอร์หลังจากที่มีการเติมโลหะ

ถึงแม้ว่าวิธีการหยดสารละลายจะง่ายต่อการเตรียม แต่อย่างไรก็ตามการกระจายตัวของทองคำบนโครงสร้างนาโนซิงก์ออกไซด์นั้น พบว่ามีความไม่สม่ำเสมอเกิดขึ้นทำให้การเพิ่มขึ้นของค่าสภาพไวมีข้อจำกัด ดังนั้นการแก้ปัญหาเรื่องความไม่สม่ำเสมอดังกล่าวสามารถทำได้โดยการใช้เทคนิคสปัตเตอร์ริง แล้วนำไปเผาเพื่อให้เกิดเป็นอนุภาคนาโนทองคำ จากการทดสอบสมบัติการตรวจจับเอทานอล พบว่าการตอบสนองต่อไอเอทานอลของนาโนเซนเซอร์ก๊าซ ที่เติมอนุภาคนาโนทองคำ มีค่าสภาพไวที่เพิ่มขึ้นมากกว่าของนาโนเซนเซอร์ที่ไม่ได้เติมโลหะและของนาโนเซนเซอร์ที่เติมทองคำด้วยวิธีอื่น โดยที่ความเข้มข้น 1000 พีพีเอ็ม สภาพไวมีค่าเพิ่มขึ้น ตามเวลาการสปัตเตอร์ที่เพิ่มขึ้น และมีค่าสูงสุดถึง 478 ที่เวลาการสปัตเตอร์ 60 วินาที จากนั้นสภาพไวจะลดลงเมื่อเวลาการสปัตเตอร์เพิ่มขึ้น

ซึ่งการเพิ่มขึ้นของสภาพไวสามารถอธิบายได้โดยสมบัติคะตะลิสต์ของโลหะในปฏิกิริยาการดูดซับเอทานอล และในปฏิกิริยาการดูดซับก๊าซออกซิเจนที่พื้นผิวของซิงก์ออกไซด์ ซึ่งสามารถอธิบายได้ดังสมการที่ทางคณะผู้วิจัยได้พัฒนาขึ้น ในรูปของตัวแปรความกว้างของชั้นปลอดพาหะ รวมทั้งคณะผู้วิจัยได้พัฒนาต่อยอดสมการนี้เพื่อใช้อธิบายผลของปริมาณทองคำต่อสภาพไวของนาโนเซนเซอร์ได้สำเร็จอีกด้วย

ผลลัพธ์ที่ได้จากงานวิจัยนี้คือ ยื่นจดสิทธิบัตร จำนวน 1 เรื่อง การตีพิมพ์ผลงานทางวิชาการ จำนวน 6 เรื่อง การเขียนหนังสือ จำนวน 1 บท การเข้าร่วมประชุมเสนอผลงานทางวิชาการ จำนวน 7 เรื่อง การเป็น

วิทยากรบรรยาย จำนวน 6 ครั้ง การเชื่อมโยงทางวิชาการกับนักวิชาการอื่นทั้งในและต่างประเทศ จำนวน 2 หน่วยงาน และรางวัลที่ได้รับ จำนวน 5 รางวัล

การดำเนินงานที่ผ่านมา

1. ได้เตรียมสารประกอบซิงก์ออกไซด์ให้เป็นโครงสร้างนาโน เช่น nanowires, tetrapods โดยใช้เทคนิค thermal oxidation ตามเงื่อนไขการเตรียมต่างๆ
2. ได้ใช้เทคนิคการเจือสารโลหะ โดยเฉพาะทองคำ โดยวิธีการผสมระหว่างทองคำกับโครงสร้างนาโนซิงก์ออกไซด์ และการหดยดสารละลายทองคำลงบนโครงสร้างนาโนซิงก์ออกไซด์ รวมทั้งการใช้วิธีสปีดเตอริง แล้วนำไปเผาเพื่อให้เกิดเป็นอนุภาคนาโนทองคำ ลงในโครงสร้างนาโนซิงก์ออกไซด์ เพื่อทำให้การตอบสนองต่อไอเอทานอลดีขึ้น
3. ได้นำโครงสร้างนาโนของสารประกอบซิงก์ออกไซด์ที่เตรียมได้ไปตรวจสอบ และวิเคราะห์ด้วยวิธีต่าง ๆ ดังนี้
 - x-ray diffraction และ Transmission Electron Microscopy (TEM) เพื่อศึกษาโครงสร้าง
 - Scanning electron microscopy (SEM) เพื่อศึกษาพื้นผิวของโครงสร้างนาโน
 - Energy dispersive x-ray (EDX) เพื่อวิเคราะห์หาองค์ประกอบในโครงสร้างนาโน
 - Raman spectroscopy เพื่อศึกษาสมบัติทางแสง
4. ได้นำโครงสร้างนาโนของสารประกอบซิงก์ออกไซด์ที่เตรียมได้มาสร้างเป็นนาโนเซนเซอร์ก๊าซ และนำไปทดสอบสมบัติการตรวจจับไอเอทานอล
5. วิเคราะห์ผลการทดสอบสมบัติการตรวจจับก๊าซที่ได้ และสรุปผลการทดลอง

Output		ในกรณีล่าช้า (ผลสำเร็จไม่ถึง 100%) ให้ท่านระบุสาเหตุและการแก้ไขที่ท่านดำเนินการ
กิจกรรมในข้อเสนอโครงการ/ หรือจากการปรับแผน	ผลสำเร็จ (%)	
1. เตรียมนาโนเซนเซอร์จาก ZnO tetrapod และ ZnO tetrapod ที่เจือด้วย Au, Pt, Pd และตรวจสอบสมบัติการตรวจจับเอทานอล	100%	-
2. เตรียมนาโนเซนเซอร์จาก ZnO+TiO tetrapod และ ZnO+TiO ₂ tetrapod ที่เจือด้วย Au, Pt, Pd และตรวจสอบสมบัติการตรวจจับเอทานอล	100%	-
3. เตรียมนาโนเซนเซอร์จาก ZnO nanowire และ ZnO nanowire ที่เจือด้วย Au, Pt, Pd และตรวจสอบสมบัติการตรวจจับยูเรีย และเอทานอล	100%	-
4. เตรียมนาโนเซนเซอร์จาก ZnO nanoparticle และ ZnO nanoparticle ที่เจือด้วย Au, Pt, Pd และตรวจสอบสมบัติการตรวจจับเอทานอล	0%	ได้ทำการปรับแผนโดยจะไม่ทำการศึกษา nanoparticle แต่เน้นการศึกษาไปที่ nanowire และ

		tetrapod ซึ่งยังมีประเด็นให้ศึกษาอีกมาก
5. เตรียมนาโนเซนเซอร์จาก ZnO tetrapod และ ZnO tetrapod ที่เจือด้วย Au, Pt, Pd และตรวจสอบสมบัติการตรวจจับสนุเรีย	0%	ได้ทำการทดสอบเฉพาะสมบัติการตรวจจับสนุเรียเนื่องจามีปัญหาในการเซาระบบตรวจสอบสมบัติการตรวจจับสนุเรีย ซึ่งเฉพาะการตรวจสอบสมบัติการตรวจจับสนุเรียก็ยังมีประเด็นให้ศึกษาอีกมาก จึงได้มีการปรับแผน

ผลที่ได้รับจากงานวิจัย

เอทานอลเซนเซอร์ เป็นอุปกรณ์ชนิดหนึ่งที่ใช้ตรวจจับไอเอทานอล หรือแอลกอฮอล์ โดยอาศัยการเปลี่ยนแปลงสมบัติบางอย่างของสารเพื่อประยุกต์ใช้เป็นเครื่องวัดปริมาณแอลกอฮอล์ในลมหายใจ โดยปกติสารกึ่งตัวนำโลหะออกไซด์มักนิยมนำมาใช้ทำเอทานอลเซนเซอร์ ยกตัวอย่างเช่น SnO_2 , TiO_2 , WO_3 , ZnO เป็นต้น โดยการวัดความต้านทานที่เปลี่ยนไปของสารในสภาวะก๊าซ การที่จะบ่งบอกว่าก๊าซเซนเซอร์นั้นมีประสิทธิภาพดีหรือไม่ ตัวแปรที่สำคัญที่ใช้คือ สภาพไว (Sensitivity หรือ Sensor response) ดังนั้นจึงมีการพัฒนาเอทานอลเซนเซอร์ให้มีค่าสภาพไวที่สูงขึ้น โดยใช้เทคนิคต่างๆ มากมาย โดยเฉพาะการใช้นาโนเทคโนโลยีที่ทำให้สารมีโครงสร้างระดับนาโนเมตรมาทำเป็นเอทานอลเซนเซอร์แต่อย่างไรก็ตามการพัฒนาเอทานอลเซนเซอร์ให้มีค่าสภาพไวที่สูงมากๆ นั้นโครงสร้างนาโนจะต้องมีขนาดเล็กมาก [1] ซึ่งยากต่อการสังเคราะห์ให้ได้ในระดับที่ต้องการ

จากรายงานพบว่าเซนเซอร์ของนาโนซิงก์ออกไซด์ที่มีค่าสภาพไวสูงๆ นั้น ขนาดของโครงสร้างนาโนซิงก์ออกไซด์ต้องอยู่ในระดับเดียวกับความยาวเดอบาย (Debye length) หรือประมาณ 15 นาโนเมตร [2-3] ซึ่งเป็นการยากมากที่จะทำให้โครงสร้างนาโนอยู่ในระดับนี้ ดังนั้นการเติมโลหะต่างๆ เช่น ทอง [4-6], แพลททินัม [7], พัลลาเดียม [8-9] และเงิน [10] เพื่อเพิ่มสภาพไวให้กับเซนเซอร์จึงเป็นอีกทางเลือกหนึ่งในการพัฒนาเซนเซอร์ โดยโลหะดังกล่าวทำหน้าที่เป็นตัวเร่งปฏิกิริยาเคมีที่พื้นผิวระหว่างสารกึ่งตัวนำและแก๊สทำให้สามารถเพิ่มค่าสภาพไวได้

จากรายงานพบว่า การเติมทองเพื่อเพิ่มค่าสภาพไวให้กับเซนเซอร์นั้นสามารถทำได้หลายวิธีเช่น การผสมระหว่างทองกับโครงสร้างนาโนซิงก์ออกไซด์ [11] การหยดสารละลายทองคำลงบนโครงสร้างนาโนซิงก์ออกไซด์ [7, 12]

ดั่งนี้งานวิจัยในโครงการ “นาโนเซนเซอร์ก๊าซที่มีฐานเป็นโครงสร้างนาโนของสารประกอบซิงก์ออกไซด์” นี้ จะเน้นไปที่การเพิ่มสภาพไวของเซนเซอร์ก๊าซต่อไอเอทานอล ซึ่งเทคนิคหลักที่ใช้คือการเติมสารโลหะลงไปในสารประกอบซิงก์ออกไซด์ โดยใช้วิธีการเติมสารหลักอยู่สองอย่างคือวิธีการหยดสารละลายและวิธีสปัตเตอร์ริง ซึ่งจะได้กล่าวในรายละเอียดต่อไปดังนี้

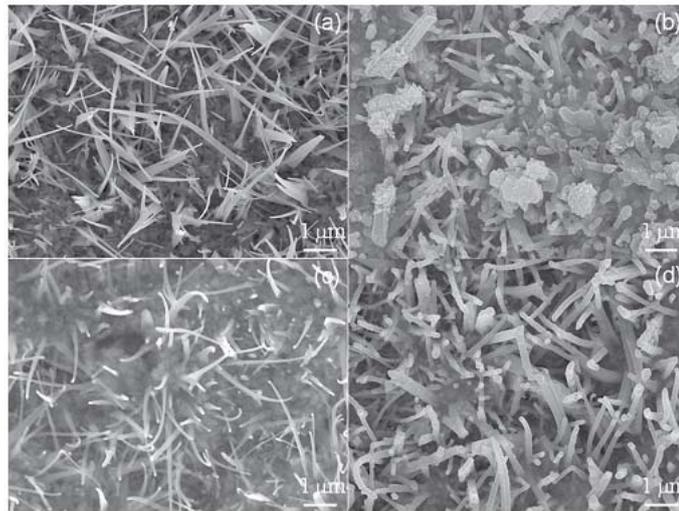
1. วิธีการหยดสารละลาย

โครงสร้างนาโนซิงก์ออกไซด์ถูกเตรียมโดยกระบวนการเทอร์มอลออกซิเดชันภายใต้บรรยากาศปกติ ผงสังกะสีที่มีความบริสุทธิ์ 99.9% ถูกทำให้ระเหยลงบนพื้นผิวอะลูมินาที่ความดัน 4×10^{-5} Torr จากนั้นนำฟิล์มไปออกซิไดซ์ที่อุณหภูมิ 500°C เป็นเวลา 24 ชั่วโมง ภายใต้บรรยากาศปกติ หลังจากนั้นนำไปหยดด้วยสารละลายทองคำและแพลททินัม สารละลายทองคำถูกเตรียมโดยกระบวนการทางเคมีซึ่งถูกรายงานในงานก่อนหน้านี้[5] ส่วนสารละลายแพลททินัมถูกเตรียมมาจาก 0.5-mM Hydro-gen hexachloroplatinate (IV) Hydrate, $\text{Cl}_6\text{H}_2\text{Pt} \cdot \text{aq}$ (38% Pt, Fluka) ในสารละลายอะซิโตน

หัวตรวจจับก๊าซเอทานอลที่สร้างจากโครงสร้างนาโนซิงก์ออกไซด์จะถูกเรียกว่า ZnO sensor ขณะที่เซนเซอร์ที่ถูกเติมด้วยสารละลายทองคำและแพลททินัมด้วยปริมาณ 0.1 mL บนพื้นที่ $5 \times 5 \text{ mm}^2$ จะถูกเรียกว่า ZnO: Au sensor และ ZnO: Pt sensor ตามลำดับ ยิ่งไปกว่านั้นเซนเซอร์ที่ถูกเติมทั้งสารละลายทองคำ 0.1 mL และสารละลายแพลททินัม 0.1 mL จะถูกเรียกว่า ZnO: Au+Pt sensor หลังจากนั้นเซนเซอร์ทั้งหมดถูกนำไปอบที่อุณหภูมิ 300°C เป็นเวลา 48 ชั่วโมง สภาพพื้นผิวถูกตรวจสอบด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด เซนเซอร์ทั้งหมดถูกนำไปวัดโดยวางฮีตเตอร์ไว้ด้านล่าง ส่วนด้านบนจะมีการติดขั้วแบบ interdigital electrode ด้วยทองคำ ลักษณะการตรวจจับก๊าซเอทานอลของ ZnO: Au sensor, ZnO: Pt sensor และ ZnO: Au+Pt sensor ถูกทดสอบด้วยบรรยากาศของเอทานอลที่ความเข้มข้น 50, 100, 500 และ 1000 ppm ตามลำดับ และอุณหภูมิที่ใช้ทดสอบอยู่ในช่วง $280\text{--}400^{\circ}\text{C}$

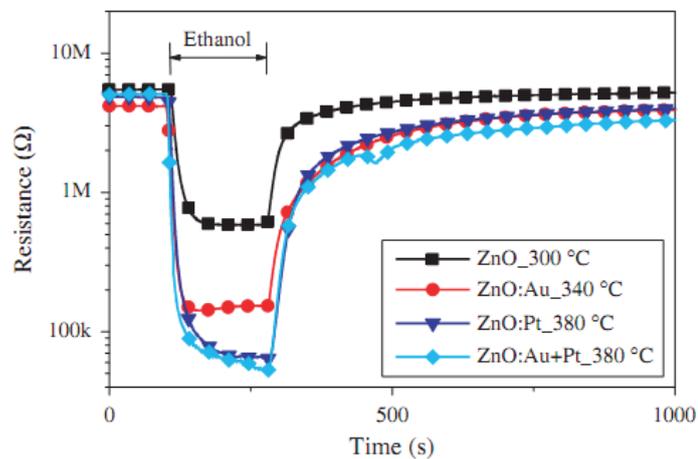
ผลการทดลอง

หลังจากกระบวนการเทอร์มอลออกซิเดชันพบว่าสีของฟิล์มเปลี่ยนจากสีเทาเป็นสีขาวแสดงให้เห็นว่ามีการเปลี่ยนแปลงจากสังกะสีเป็นซิงก์ออกไซด์โดยปฏิกิริยา $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$ จากภาพถ่ายจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดที่กำลังขยาย 10000 เท่า พบว่าโครงสร้างนาโนซิงก์ออกไซด์ที่สังเคราะห์ได้มีขนาดตั้งแต่ 40–300 นาโนเมตร และมีความยาวหลายไมครอน ดังแสดงในรูปที่ 1 (a) หลังจากหยดด้วยสารละลายโลหะพบว่าโครงสร้างนาโนของ ZnO: Au, ZnO: Pt และ ZnO: Au+Pt มีลักษณะที่แตกต่างกันเมื่อเปรียบเทียบกับ ZnO ดังแสดงในรูปที่ 1 (b)–(d) ลักษณะเหล่านี้เป็นผลเนื่องมาจากความเป็นกรดของสารละลายโลหะที่ถูกหยดไปในซิงก์ออกไซด์ ขนาดของโครงสร้างนาโนซิงก์ออกไซด์ที่เปลี่ยนไปมีค่าอยู่ในช่วง 50–350 นาโนเมตร, 50–270 นาโนเมตร และ 80–300 นาโนเมตร สำหรับโครงสร้างนาโนของ ZnO: Au, ZnO: Pt และ ZnO: Au+Pt ตามลำดับ



รูปที่ 1 ภาพถ่ายจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดของ (a) ZnO (b) ZnO:Au (c) ZnO:Pt และ (d) ZnO:Au+Pt

เซนเซอร์ของ ZnO ที่อุณหภูมิ 300°C, ZnO:Au ที่อุณหภูมิ 340°C, ZnO:Pt ที่อุณหภูมิ 380°C และ ZnO:Au+Pt ที่อุณหภูมิ 380°C มีการเปลี่ยนแปลงความต้านทานเมื่ออยู่ในบรรยากาศปกติและบรรยากาศของเอทานอลที่ความเข้มข้น 1000 ppm ดังแสดงในรูปที่ 2 ซึ่งความต้านทานลดลงเมื่อมีการปล่อยก๊าซเอทานอล นอกจากนี้ยังสังเกตได้ว่าอุณหภูมิที่ดีที่สุดในการตอบสนองต่อก๊าซเอทานอลของเซนเซอร์ ZnO:Au, ZnO:Pt และ ZnO:Au+Pt สูงกว่าของเซนเซอร์ ZnO



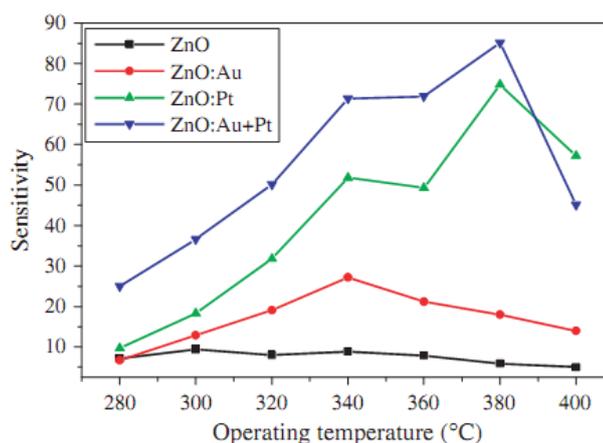
รูปที่ 2 การเปลี่ยนแปลงความต้านทานในบรรยากาศปกติกับบรรยากาศของก๊าซเอทานอลที่ความเข้มข้น 1000 ppm ของเซนเซอร์ ZnO ที่อุณหภูมิ 300°C, ZnO:Au ที่อุณหภูมิ 340°C, ZnO:Pt ที่อุณหภูมิ 380°C และ ZnO:Au+Pt ที่อุณหภูมิ 380°C

จากรูปที่ 3 ค่าสภาพไวจะเป็นฟังก์ชันกับอุณหภูมิและพบว่าการหดยดด้วยสารละลายโลหะจะสามารถปรับปรุงค่าสภาพไวให้สูงขึ้นได้ โดยเซนเซอร์ของ ZnO:Pt และ ZnO:Pt+Au มีค่าสภาพไวสูงที่สุด ซึ่งสภาพไวของเซนเซอร์ ZnO:Pt และ ZnO:Pt+Au ที่อุณหภูมิเหมาะสมมีค่าเป็น 27, 75 และ 85 ตามลำดับ ขณะที่สภาพไวของเซนเซอร์ ZnO มีค่าเป็น 9 เท่า

การปรับปรุงค่าสภาพไวของโลหะถูกอธิบายโดยสมการที่ (1) ซึ่งได้รายงานไปก่อนหน้านี้ [6]

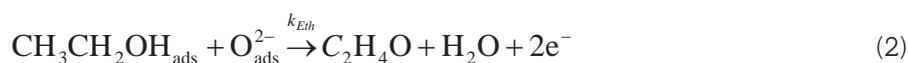
$$S = \frac{R_{air}}{R_{gas}} = \frac{\Gamma_{\tau} k_{Eth}(T) [O_{ads}^{ion}]^b}{n_0} C_g^b + 1 \quad (1)$$

โดยที่ Γ_{τ} คือค่าคงที่, $k_{Eth}(T)$ คือ reaction rate constant ในปฏิกิริยาการดูดซับเอทานอลที่เกิดขึ้นระหว่างออกซิเจนสปีชีส์กับเอทานอลที่อุณหภูมิเหมาะสม, $[O_{ads}^{ion}]^b$ คือความหนาแน่นของออกซิเจนสปีชีส์, C_g^b คือความเข้มข้นของเอทานอล, และ n_0 คือความหนาแน่นของอิเล็กตรอนของเซนเซอร์ในอากาศ



รูปที่ 3 ค่าสภาพไวเป็นฟังก์ชันกับอุณหภูมิของเซนเซอร์ ZnO, ZnO:Pt และ ZnO:Pt+Au ภายใต้ความเข้มข้นของเอทานอลที่ 1000 ppm

การปรับปรุงค่าสภาพไวเนื่องมาจากการเติมโลหะถูกอธิบายจากสองตัวแปรคือ reaction rate constant ($k_{Eth}(T)$) และความหนาแน่นของออกซิเจนสปีชีส์ ($[O_{ads}^{ion}]^b$) สำหรับตัวแปรแรกโลหะทำหน้าที่เป็นตัวเร่งปฏิกิริยาในปฏิกิริยาการดูดซับเอทานอล ทำให้ค่า reaction rate constant ($k_{Eth}(T)$) เพิ่มขึ้น ดังแสดงในปฏิกิริยาที่ (2)



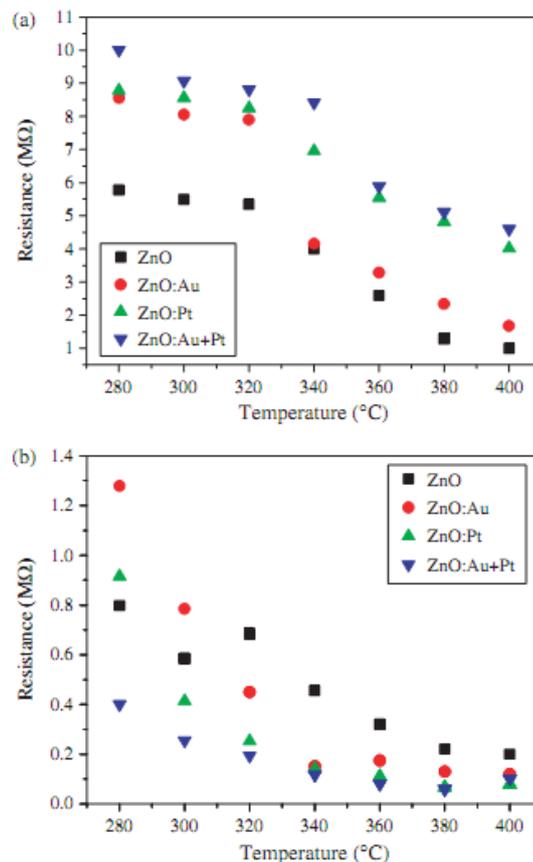
ดังนั้นเมื่อพิจารณาจากสมการที่ (1) จึงทำให้สภาพไวมีค่าเพิ่มขึ้น หลักฐานดังกล่าวถูกยืนยันจากการเปลี่ยนแปลงความต้านทานในเอทานอล

สำหรับรูป 4 (b) ความต้านทานภายใต้เอทานอลของเซนเซอร์ที่มีการเติมโลหะมีค่าต่ำกว่าของเซนเซอร์ ZnO เนื่องจาก reaction rate constant ($k_{Eth}(T)$) ในปฏิกิริยาการดูดซับเอทานอลมีค่าสูงขึ้น

สำหรับตัวแปรที่สอง โลหะที่เติมลงไปทำหน้าที่เป็นตัวเร่งปฏิกิริยาในปฏิกิริยาการดูดซับออกซิเจนทำให้เพิ่ม reaction rate constant ($k_{Oxy}(T)$) ในปฏิกิริยาดังกล่าว ดังแสดงในปฏิกิริยาที่ (3)



การเพิ่มขึ้นของ reaction rate constant ($k_{Oxy}(T)$) ในปฏิกิริยาการดูดซับออกซิเจนทำให้เกิดการเพิ่มขึ้นของความหนาแน่นของออกซิเจนสปีชีส์ ($[O_{ads}^{ion}]^b$) เมื่อพิจารณาจากสมการที่ 1 จึงทำให้สภาพโวลมีค่าสูงขึ้น หลักฐานที่ยืนยันถึงการเพิ่มขึ้นของ reaction rate constant ($k_{Oxy}(T)$) ในปฏิกิริยาการดูดซับออกซิเจนสังเกตจากความต้านทานของเซนเซอร์ในบรรยากาศปกติ ดังแสดงในรูปที่ 4 (a) ซึ่งพบว่าความต้านทานภายใต้บรรยากาศปกติของเซนเซอร์ที่มีการเติมโลหะมีค่าสูงกว่าของเซนเซอร์ ZnO อันเนื่องมาจากการเพิ่มขึ้นของ reaction rate constant ($k_{Oxy}(T)$) ในปฏิกิริยาการดูดซับออกซิเจน ดังนั้นจึงสรุปได้ว่าโลหะที่เติมลงไปในเซนเซอร์สามารถปรับปรุงค่าสภาพโวลได้ ซึ่งเป็นผลมาจากสมบัติการเป็นตัวเร่งปฏิกิริยาของโลหะในปฏิกิริยาการดูดซับเอทานอลและปฏิกิริยาการดูดซับออกซิเจนที่พื้นผิว



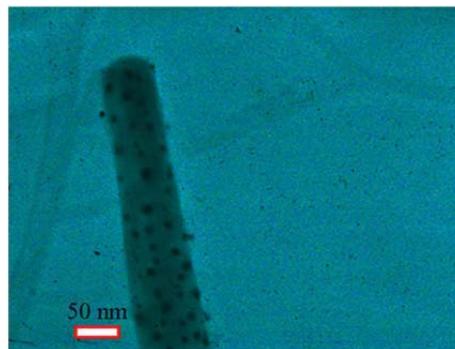
รูปที่ 4 ความต้านทานกับอุณหภูมิของเซนเซอร์ทั้งหมดภายใต้ (a) บรรยากาศปกติ (b) บรรยากาศของเอทานอล

สรุปผลการทดลอง

การหาค่าสสารละลายโลหะสามารถปรับปรุงค่าสภาพไวให้กับเซนเซอร์โครงสร้างนาโนซิงก์ออกไซด์ได้ ค่าสภาพไวสูงที่สุดมาจากเซนเซอร์ที่มีการเติมทั้งทองคำและแพลททินัมโดยมีค่าสภาพไวอยู่ที่ 85 เท่า ที่ความเข้มข้นของเอทานอล 1000 ppm ดังนั้นสามารถอธิบายได้ว่าโลหะที่หาค่าสสารละลายโลหะไปมีสมบัติเป็นตัวเร่งปฏิกิริยาทั้งปฏิกิริยาการดูดซับเอทานอลและปฏิกิริยาการดูดซับออกซิเจน หลักฐานการเพิ่มขึ้นของค่า $k_{Eth}(T)$ และ $k_{Oxy}(T)$ สังเกตได้จากความต้านทานที่ลดลงในบรรยากาศเอทานอลและความต้านทานที่เพิ่มขึ้นในบรรยากาศปกติของเซนเซอร์หลังจากที่มีการเติมโลหะ

2. วิธีสัปดาห์เตอริง

ถึงแม้ว่าวิธีการเติมโลหะด้วยวิธีหาค่าสสารละลายจะง่ายต่อการเตรียม แต่อย่างไรก็ตามการกระจายตัวของโลหะบนโครงสร้างนาโนซิงก์ออกไซด์นั้น พบว่ามีความไม่สม่ำเสมอเกิดขึ้นทำให้การเพิ่มขึ้นของค่าสภาพไวมีข้อจำกัด ดังนั้นการแก้ปัญหาเรื่องความไม่สม่ำเสมอดังกล่าวสามารถทำได้โดยการใช้เทคนิคสัปดาห์เตอริง โดยปกติแล้วทองคำเมื่อถูกสัปดาห์เตอริงลงบนโครงสร้างนาโนซิงก์ออกไซด์นั้นจะถูกเคลือบในลักษณะของ bulk หรือฟิล์มบาง (thin film) จึงไม่ค่อยมีสมบัติการเป็นตัวเร่งปฏิกิริยาที่ดี แต่ถ้านำไปเผาด้วยความร้อนพบว่าทองคำมีการหดตัวจนมีขนาดอยู่ในระดับนาโน เกิดเป็นอนุภาคนาโนทองคำดังแสดงในรูปที่ 5 ทำให้สมบัติการเป็นตัวเร่งปฏิกิริยาของอนุภาคนาโนทองคำนี้จะดีขึ้นกว่าเดิมมาก



รูปที่ 5 รูป TEM bright field ของโครงสร้างนาโนซิงก์ออกไซด์เมื่อถูกสัปดาห์เตอริงทองคำด้วยเวลา 20 วินาที แล้วนำไปเผาเพื่อให้เกิดเป็นอนุภาคนาโนทองคำ

จากการทดสอบสมบัติการตรวจจับเอทานอล พบว่าการตอบสนองต่อไอเอทานอล ที่ความเข้มข้น 100–1000 ppm ของนาโนเซนเซอร์ก๊าซ ที่เติมอนุภาคนาโนทองคำ มีค่าสภาพไวที่เพิ่มขึ้นมากกว่าของนาโนเซนเซอร์ที่ไม่ได้เติมโลหะและยังมีค่ามากกว่าของนาโนเซนเซอร์ที่เติมทองคำด้วยวิธีอื่น

นอกจากนี้ปริมาณของอนุภาคนาโนทองคำในปริมาณที่ต่างกันส่งผลต่อค่าสภาพไวของเอทานอลเซนเซอร์ด้วย โดยสภาพไวจะมีค่าเพิ่มขึ้นตามปริมาณทองคำจนถึงค่าหนึ่ง ซึ่งคณะผู้วิจัยได้พัฒนาต่อยอดสมการเติม เพื่อใช้อธิบายผลของปริมาณทองคำต่อสภาพไวของเอทานอลเซนเซอร์ดังสมการที่ (4)

$$S = \left(\frac{\Gamma_t k_{Eth}(T) (\Phi n_d w (V_m / V_s))^b \exp(m^2 / 2)}{n_d} \right) \frac{D^2}{(D - 2w)^2} C_g^b + 1 \quad (4)$$

เมื่อ

Γ_t คือ ค่าคงที่

$k_{Eth}(T)$ คือ ค่าคงที่ปฏิกิริยาที่อุณหภูมิ T

Φ คือ อัตราส่วนของพื้นที่ผิวต่อปริมาตร (Surface-to-volume ratio)

V_m คือ ปริมาตรของสาร

V_s คือ ปริมาตรของระบบ

n_d คือ ความหนาแน่นของอิเล็กตรอนไดโอด

C_g คือ ความเข้มข้นของเอทานอล

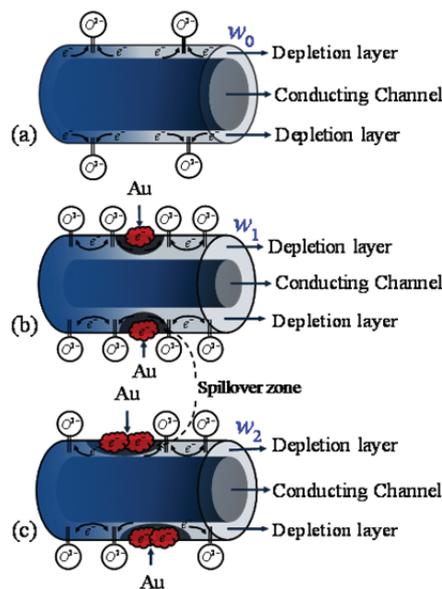
D คือ ขนาดเส้นผ่านศูนย์กลางกลางอนุภาคของสารที่นำมาทำเซนเซอร์

w คือ ความหนาของชั้นปลอดพาหะของสาร

$m = w/L_d$ ขณะที่ L_d คือความยาวเดอบาย

เลขยกกำลัง b คือ ตัวบ่งชี้ชนิดของออกซิเจนไอออน โดยที่มีค่าเท่ากับ 0.5 และ 1 เมื่อออกซิเจนไอออน เป็น O^{2-} และ O^- ตามลำดับ

จากสมการนี้พบว่าสามารถใช้อธิบายการเพิ่มขึ้นของค่าสภาพไวอันเนื่องจากการเติมอนุภาคนาโนทองคำ โดยอนุภาคนาโนทองคำนี้มีผลทำให้เกิดการเพิ่มขึ้นของ $k_{Eth}(T)$ และเกิดการเพิ่มขึ้นของความหนาชั้นปลอดพาหะ ซึ่งตัวแปรทั้งสองนี้แปรผันตรงกับค่าสภาพไว ดังนั้นจึงทำให้ค่าสภาพไวมีค่าเพิ่มขึ้นเมื่อมีการเติมอนุภาคนาโนทองคำลงไป



รูปที่ 6 แผนภาพแสดงอนุภาคนาโนทองคำที่เกาะบนพื้นผิวของซิงออกไซด์เมื่อ (a) ไม่มีอนุภาคนาโนทองคำ (b) มีอนุภาคนาโนทองคำในปริมาณที่เหมาะสม (c) มีอนุภาคนาโนทองคำในปริมาณที่มากเกินไป

ปริมาณอนุภาคนาโนทองคำที่ถูกเติมลงไปนั้นส่งผลต่อค่าสภาพไวของเซนเซอร์ โดยพิจารณาจากการเปลี่ยนแปลงความหนาของชั้นปลดพาหะดังแสดงในรูปที่ 6 ดังนั้นการควบคุมความหนาในชั้นปลดพาหะของโครงสร้างนาโนซิงก์ออกไซด์สามารถทำได้ง่ายโดยวิธีการสับเตอริงทองคำและส่งผลให้สภาพไวมีค่าเพิ่มขึ้น จากผลเหล่านี้สามารถนำเอทานอลเซนเซอร์ไปประยุกต์ใช้เป็นจมูกอิเล็กทรอนิกส์ได้ (e-nose)

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6. เป็นวิทยากรบรรยาย เรื่อง ZnO nanostructures for ethanol sensors and dye-sensitized solar cells ให้นักศึกษาในกระบวนวิชา 210496 seminar in material science ประจำปีการศึกษาที่ 1/2553 เมื่อวันที่ 23 มิถุนายน 2553 มีนักศึกษาลงทะเบียน 53 คน

การเชื่อมโยงทางวิชาการกับนักวิชาการอื่นทั้งในและต่างประเทศ

1. มีความร่วมมือกับ อ.ดร. นิยม ไชยสิทธิ์ มหาวิทยาลัยพะเยา จ.พะเยา ในการทำวิจัยเกี่ยวกับ ZnO nanosensor

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รางวัลที่ได้รับ

1. ผศ.ดร.สุภาพ ชูพันธ์ ได้รับโล่ประกาศเกียรติคุณ เป็นผู้มีความวิจัยที่ได้รับการอ้างอิงในวารสารวิชาการระดับนานาชาติ (ฐานข้อมูล Scopus) รวมในช่วง 5 ปี ระหว่าง พ.ศ. 2549–2553 ประจำปี 2554 สูงสุดอันดับที่ 3 คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่ ให้ไว้ ณ วันที่ 28 ธันวาคม 2554

2. ผศ.ดร.สุภาพ ชูพันธ์ ได้รับโล่ประกาศเกียรติคุณ เป็นผู้มีความวิจัยที่ได้รับการอ้างอิงในวารสารวิชาการระดับนานาชาติ (ฐานข้อมูล Scopus) รวมในช่วง 5 ปี ระหว่าง พ.ศ.2550–2555 ประจำปี 2555 สูงสุดอันดับที่ 2 คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่ ให้ไว้ ณ วันที่ 26 ธันวาคม 2555

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เอกสาร reprint ทั้งหมดที่เป็น output ของงานวิจัย

สิทธิบัตร

ผลงานตีพิมพ์ทางวิชาการ

Ethanol Sensing Characteristics of Sensors Based on ZnO:Al Nanostructures Prepared by Thermal Oxidation

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Abstract— ZnO and ZnO:Al nanostructure were synthesized and fabricated as ethanol gas sensors. For FE-SEM images, the diameter and length measured at the middle of the wire-like structure were in range of 100-500 nm and several micrometers, respectively. From TEM analysis, it was suggested that the ZnO:Al nanostructure grew along $(1\bar{1}20)$ direction on $[0001]$ plane. The Raman spectra of ZnO and ZnO:Al nanostructures can confirm existence of defect effects due to oxygen vacancies and Zn interstitials of ZnO. Besides, it also suggested that the ZnO:Al nanostructures had $(1\bar{1}20)$ direction perpendicular to the surface. The ethanol sensors based on ZnO:Al nanostructure sensors can be improved when compare with pure ZnO nanostructure sensor at the ethanol concentrations of 50-1000 ppm. The highest sensitivity of 32 was obtained in ZnO:Al nanostructure sensors with Al 1% by mol compared to 14 of pure ZnO nanostructure sensor at optimum temperature of 300°C. The sensitivity improvement of ZnO:Al sensors can be explained by an increase of oxygen vacancy-related defects which increase the surface depletion layer width as described in sensitivity equation. The larger surface depletion layer width results in higher the potential barrier height at the contacts and finally, sensitivity improvement.

I. INTRODUCTION

ZnO is a promising n-type semiconducting oxide that has potential for gas sensor with excellent sensing toward various gases such as LPG, methanol, and ethanol. The ethanol sensing properties based on ZnO sensors have been extensively studied due to potential in fabricating high-performance ethanol sensors [1] for application as an alcohol breath analyzer [2-3]. An important parameter in ethanol sensor study is sensitivity which calculated from the ratio of the resistance in air and the resistance in air-mixed gas. Typically, the sensitivity of sensors based on bulk and thin film of ZnO is low. Thus, several approaches, for example, using nanostructure, adding noble metal, and doping for defect formation have been studied in order to improve the sensitivity.

There has been a report on the sensitivity improvement of ethanol sensor based on Al-doped ZnO nanomaterial [4]. The Al-doped ZnO sensors exhibited excellent sensing properties of sensitivity (~ 200), response time (~ 8 s) and recovery time (~ 10 s) at ethanol concentration of 3000 ppm and working temperature of $\sim 290^\circ\text{C}$ for the sample annealed at 500°C with 2 at.% Al_2O_3 . The sensitivity improvement was explained by using effective specific surface model.

The sensitivity improvement of sensors based on Al-doped ZnO film toward methanol has also been reported and explained by low lattice disorder [5].

Moreover, the sensitivity improvement of sensors based on Al-doped ZnO nanotetrapods has been reported [1] and explained in terms of the enhanced modulation of conductance caused by the preferential adsorption of the ethoxy on the oxygen vacancies.

In this work, we have reported on the sensitivity improvement by controlling the defect in ZnO nanostructure using Al doping. The effect of oxygen vacancies arising from Al doping on ethanol sensing properties of ZnO nanostructures sensor was investigated. Besides, we have proposed a generalized formula to describe the sensitivity improvement of ZnO nanostructure sensors due to Al doping.

II. EXPERIMENTAL DETAILS

ZnO:Al nanostructures were synthesized on alumina substrates via thermal oxidation technique with no catalyst. Zn (purity 99.9%) and Al (purity 99.9%) starting powder was mixed and ground at Al content of 1-3% by mol. Then, Zn:Al powder mixture was mixed with polyvinyl alcohol (PVA) to form the paste. The paste was screened as a thick film onto the alumina substrate and then, sintered at the temperature 600°C for 24 h under a normal atmosphere. The surface morphology of ZnO:Al nanostructures were characterized using the field emission scanning electron microscopy (FE-SEM). The optical properties were investigated by Raman spectroscopy using a JY T64000 triple monochromator Raman spectrometer (Horiba Jobin Yvon SAS, France) with a backscattering optical configuration. An excitation source was an argon laser

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at a wavelength of 514.5 nm. The crystal structure was characterized by transmission electron microscopy (TEM) using a JEOL JEM-2010 transmission electron microscope.

For sensor fabrication, gold inter-digital electrodes were pasted onto the sensor area and a heater was put underneath the alumina substrate. The heater was made from nickel-chromium coil with resistance of 35–40 Ω which could be controlled the operating temperature in the range of 280–360°C. The sensors properties were measured using volt-ampometric technique at the bias constant voltage of 5 V at the ethanol concentration of 50-1000 ppm. The sensitivity was studied as the ratio of the resistance in air and the resistance in ethanol-air mixed gas (R_a/R_g).

III. RESULTS AND DISCUSSION

Surface morphology

The nanostructures have been successfully synthesized on alumina substrate at the temperature of 600°C for 24 h under normal atmosphere. For comparison, FE-SEM images of ZnO:Al nanostructure of Al content 1% by mol, 2% by mol, and 3% by mol with high magnification were shown in Fig. 1 (a), (b), (c), (d), (e), and (f), respectively.

It can be seen that the morphology of ZnO:Al nanostructures for all cases exhibited similar wire-like structures. The diameter and length measured at the middle of the wire-like structure were in a range of 100-500 nm and several micrometers, respectively. Also, the bending tips of ZnO:Al nanostructures were observed in all samples.

A TEM bright field of ZnO:Al nanostructure with Al content of 1% by mol was shown in Fig. 2 (a). The corresponding selected area diffraction pattern (SADP) (inset) can be indexed as only hexagonal phase indicating alloying of ZnO:Al nanostructure. From trace analysis, it was found that the growth direction of ZnO:Al nanostructure grew along $(1\bar{1}\bar{2}0)$ on $[0001]$ plane. Moreover, Fig. 2 (b) shows a high-resolution TEM image of a single crystalline ZnO:Al nanostructure grown at 600°C which the lattice fringes were spaced 0.52 nm apart.

The Raman spectra of ZnO and ZnO:Al nanostructures were shown in Fig. 3. The peaks at around 332 and 438 cm^{-1} were observed and can be attributed to E_{2H} - E_{2L} and E_{2H} vibrational modes. While the observed peaks at 385 and 583 cm^{-1} can be attributed to $A_1(\text{TO})$ and $E_1(\text{LO})$, respectively.

According to Raman selection rule for a back scattering configuration of wurtzite hexagonal structure [6], $A_1(\text{LO})$ and E_2 are allowed modes for c-axis perpendicular to the surface. But $A_1(\text{TO})$, $E_1(\text{TO})$, and E_2 are allowed modes for $(1\bar{1}\bar{2}0)$ direction perpendicular to the surface. Thus, the observation of $A_1(\text{TO})$ peak (no $A_1(\text{LO})$ peak) suggested that the $(1\bar{1}\bar{2}0)$ direction is perpendicular to the surface which was in good agreement with the growth direction from TEM analysis.

In addition, $E_1(\text{LO})$ is normally a forbidden peak from Raman selection rule. However, $E_1(\text{LO})$ peak at 583 cm^{-1} was observed in our cases and generally, can be related to the formation of defects due to oxygen vacancies and Zn interstitials of ZnO [6-8]. So, the intensity ratio of $E_1(\text{LO})$ to E_2 can be used to indicate degree of defects due to the oxygen vacancies and Zn interstitials of ZnO. From the Raman spectra, the intensity ratio of $E_1(\text{LO})$ to E_2 of ZnO:Al

nanostructures with Al content of 0, 1, 2, and 3% by mol was 0.132, 0.150, 0.140, and 0.136, respectively. It can be seen that the defects were higher for ZnO:Al nanostructures due to Al doping.

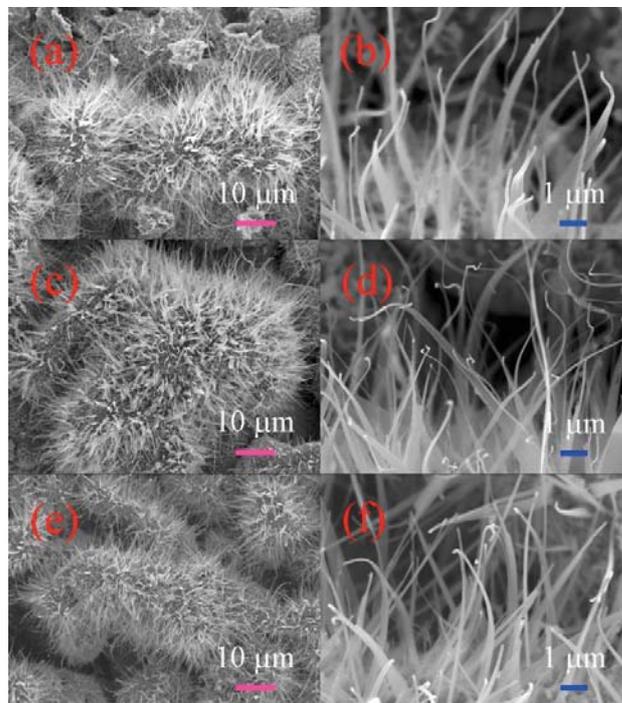


Fig. 1. FE-SEM images of (a), (b) ZnO:Al 1% by mol, (c), (d) ZnO:Al 2% by mol, (e), (f) ZnO:Al 3% by mol.

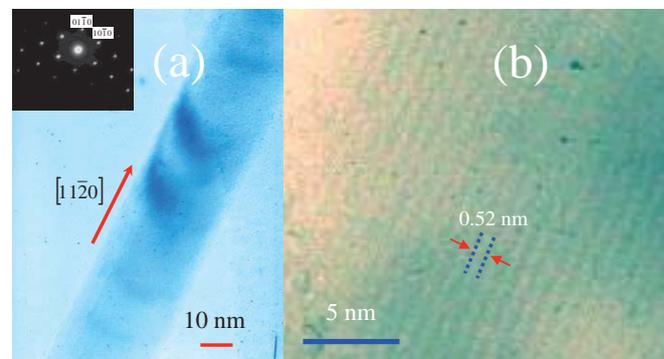


Fig. 2 (a) TEM bright field of ZnO:Al nanostructure. Inset showed the SADP of a single crystalline ZnO:Al nanostructure and (b) HRTEM image of ZnO:Al nanostructure with the lattice fringes of 0.52 nm.

Ethanol sensing characteristics

For optimum temperature determination, the sensitivity based on ethanol sensor at ethanol concentration of 1000 ppm was plotted between the sensitivity versus the operating temperature as shown in Fig. 4. The sensitivity was high at the operating temperature of 280-300°C and it was low at the operating temperature in range of 300-380°C. So, the optimum temperatures were about 300°C for all sensors.

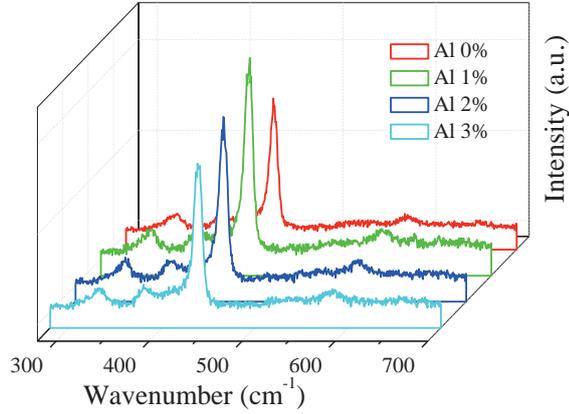


Fig. 3 Raman spectra of ZnO:Al nanostructures with Al content of 0, 1, 2, and 3% by mol.

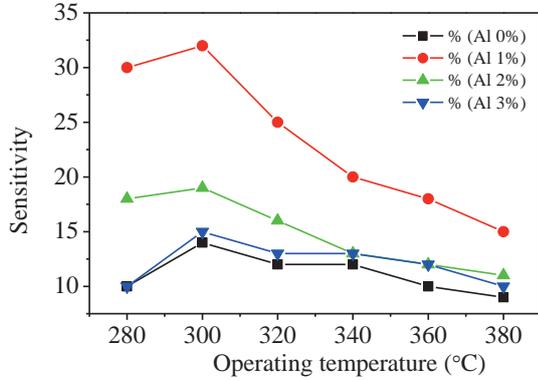


Fig. 4 Relation between sensitivity versus the operating temperature at the ethanol concentration of 1000 ppm.

From the resistance response and recovery characteristics as shown in Fig. 5, it was found that the sensitivity of ZnO:Al nanostructure sensors were higher than that of pure ZnO nanostructure sensors. The highest sensitivity of 32 was obtained in ZnO:Al nanostructure sensors with 1% Al by mol compared to 14 of pure ZnO nanostructure sensor at optimum temperature of 300°C. Thus, the sensitivity improvement was clearly achieved by Al doping.

Moreover, the sensing characteristics can also determine the oxygen species on ZnO nanostructure surfaces by using an equation of sensitivity (S) [9-12]:

$$S = 1 + aC^b \quad (1)$$

where C represents ethanol concentration, a and b are constant.

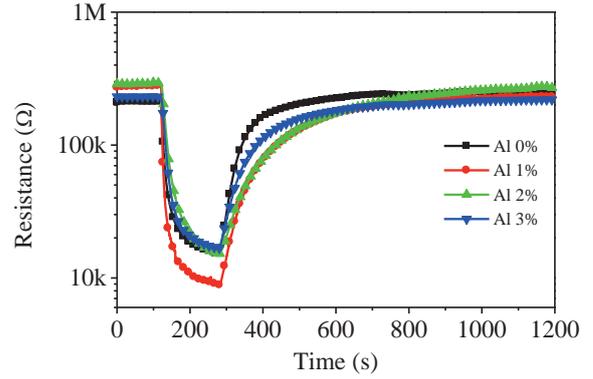


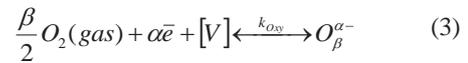
Fig. 5 Resistance response and recovery characteristics of ZnO:Al sensors at the temperature of 300°C.

The value of the constant depends on the sensor material and the type of gas sensor which exposed to at the operating temperature. The value of the constant b is normally around either 0.5 or 1, depending on the charge state of the surface ion. It was reported that for b of 0.5 the adsorbed surface oxygen ion is O^{2-} and for b of 1, the adsorbed surface oxygen ion is O^- . The b value can be determined from equation (1) which can be rewritten as:

$$\log(S - 1) = \log a + b \log C \quad (2)$$

It can be seen that $\log(S-1)$ has linear relation with $\log C$ having a slope of b value. Thus, b value can be obtained from a slope value of a plot between $\log(S-1)$ and $\log C$. Fig. 6 show linear relation of $\log(S-1)$ and $\log C$ at the optimum operating temperatures for pure ZnO nanostructures and ZnO:Al nanostructure sensors. The b values obtained from the slope in Fig. 6, were 0.46, 0.37, 0.41, and 0.30 for pure ZnO sensor, ZnO:Al 1%, 2%, and 3% by mol, respectively. It can be seen that b value of all sensors were closed to 0.5 suggesting the oxygen ion species on ZnO:Al nanostructure surface were still O^{2-} similar to pure ZnO.

In order to explain the sensitivity improvement due to Al doping, let consider the oxygen adsorption reaction that can be represented in general equation as [12]



where $O_2(gas)$ is an oxygen molecule in ambient atmosphere, \bar{e} is density of conduction electron at the surface, k_{Oxy} is the reaction rate constant or reaction rate coefficient, $O_{\beta}^{\alpha-}$ is a chemisorbed oxygen species, $[V]$ is the defect effect such as oxygen vacancy or zinc interstitial, $\alpha = 1$ for singly ionized forms, $\alpha = 2$ for doubly ionized forms, $\beta = 1$ for atomic forms, and $\beta = 2$ for molecular forms.

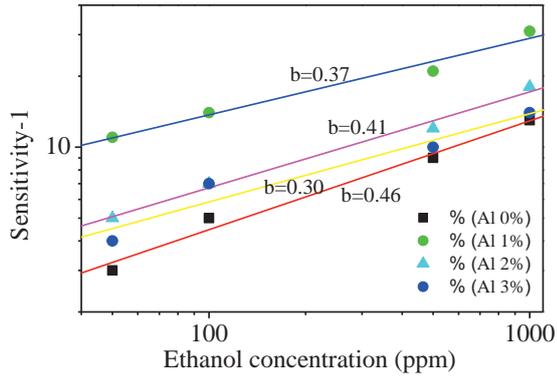


Fig. 6 Plot of $\log(S-1)$ versus $\log C$ of pure ZnO and ZnO:Al nanostructure sensors at the optimum temperature.

At the chemical equilibrium, equation (3) can be generally deduced by mass action law as:

$$\sigma = k_{Oxy} [V][e]^2 P^{1/2} \quad (4)$$

where σ is density of O^{2-} per unit area, $[V]$ is a defect density, $[e]$ is density of conduction electron at the surface, and P is a partial pressure of oxygen molecule. Moreover, if there are no electron-trapping sites other than the adsorbed oxygen ion O^{2-} on the surface, the depletion layer width (w) can be related to density of O^{2-} per unit area (σ) as [13]:

$$\sigma = n_d w \quad (5)$$

where n_d is a density of donor electrons. It can be seen that the defect density is linearly dependent on the depletion layer width. From our previous work [14], the sensor sensitivity in this case is described as

$$S = \left(\frac{\Gamma_i k_{Eth}(T) (\Phi n_d w (V_m / V_s))^b \exp(m^2 / 2)}{n_d} \right) C_g^b + 1 \quad (6)$$

where Γ_i is proportional constant, $k_{Eth}(T)$ is a reaction rate constant between adsorbed oxygen species and ethanol vapor which depends on the operating temperature, m is the reduced depletion depth which is defined by $m = w/L_d$, L_d is a Debye length, Φ is a ratio of surface area per volume of material (V_m), and V_s is the system volume, C_g is the ethanol concentration.

The sensitivity improvement of ZnO:Al sensors can be explained by using equation (6). As seen in Raman results, Al doping in ZnO structure increased the oxygen vacancy-related defects. The increase of oxygen vacancy-related defects (high $[V]$ in equation (4)) due to Al doping increases the surface depletion layer width. Thus, the larger surface depletion layer results in higher sensitivity as seen in equation (6).

It should be noted that the depletion layer width also depends on the height of the potential barrier at the contacts [13]. So, the larger the depletion layer width implies that the higher the height of the potential barrier at the contacts.

IV. CONCLUSIONS

ZnO and ZnO:Al nanostructure were synthesized and fabricated as ethanol gas sensors. From characterization, the diameter of the wire-like structure was in range of 80-600 nm

with the growth direction along $(11\bar{2}0)$ on $[0001]$ plane. The Raman spectra of ZnO and ZnO:Al nanostructures can confirm existence of defect effects due to oxygen vacancies and Zn interstitials of ZnO. The ethanol sensors based on ZnO:Al nanostructure sensors can be improved when compare with pure ZnO nanostructure sensor at the ethanol concentrations of 50-1000 ppm. The sensitivity improvement of ZnO:Al sensors can be explained by an increase of oxygen vacancy-related defects which increase the surface depletion layer width as described in sensitivity equation. The larger surface depletion layer width results in higher the potential barrier height at the contacts and finally, sensitivity improvement. Thus, the doping for defect formation is a promising technique for the sensitivity improvement.

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Control of depletion layer width via amount of AuNPs for sensor response enhancement in ZnO nanostructure sensor

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ABSTRACT

The ethanol sensing characteristics in ZnO nanostructure sensors with Au coating by sputtering technique were investigated. The enhancement of sensor response due to gold nanoparticles (AuNPs) on ZnO nanostructure sensors has been observed and explained by considering the catalytic effect on ethanol adsorption reaction and oxygen adsorption reaction. Consequently, the sensor response formula has been developed based on the adsorption reactions. In addition, the dependence of gold amount on gas sensor response was systematically investigated. It was found that under the ethanol concentration of 1000 ppm, the sensor response increased as the sputtering time increased, exhibited maximum value of 478 at sputtering time of 60 s, and then, decreased at longer sputtering time. Based on the results, the developed formula can describe the dependence of gold amount on sensor response in terms of the depletion layer width. As a result, the sensor response can be designed by controlling the depletion layer width via the amount of gold nanoparticles (AuNPs), which can be simply performed by varying sputtering time. These results can be further explored for their an implication in e-nose applications.

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1. Introduction

Gas sensors based on metal-oxide semiconductors such as ZnO [1–4], SnO₂ [5], TiO₂ [6], WO₃ [7], Fe₂O₃ [8], and In₂O₃ [9] have great potential applications in environmental monitoring, chemical process controlling, and personal safety [10]. In particular, gas sensors based on ZnO nanostructures have been widely investigated due to the feasibility for ultrahigh sensitive sensors in ppb-level detection. However, ethanol sensors based on ZnO nanostructure typically exhibit low sensor response unless the nanostructure size is smaller than the value of Debye length (less than 15 nm) [11,12], which is not easy to achieve. Thus, the techniques for sensor response enhancement have been intensively studied. Adding noble metals, such as gold (Au) [13–15], platinum [16], palladium [17,18], and silver [19], is one of the techniques commonly used to improve the sensor response. Typically, the noble metal acts as a catalyst to modify surface reactions of metal oxide semiconductors to enhance gas sensing and results in higher sensor response than that of pure ZnO.

From our previous reports, the approaches of mixing gold with ZnO nanostructure [13] and impregnating by dropping gold

solution on ZnO nanostructure [14,15] have been studied and the enhancement of sensor response have been observed in both cases. These two methods are simple and easy for fabrication, but it is difficult to control metal uniformity and metal size distribution which affects performance of the sensors.

These problems can be overcome by using sputtering technique. Normally, as-sputtered gold on ZnO nanostructure is found to form thin gold layer. However, heat treatment of the thin gold layer can lead to the formation of a stable population of gold nanoparticles which uniformly disperse on the ZnO surface [20]. There are several reports on using sputtering technique for metal adding. For example, Li et al. coated gold by sputtering technique on ZnO nanorods with diameters down to 15 nm and found an increase in the sensor response and decrease in the response time [21]. Also, Santhaveesuk et al. have reported the sensor response enhancement of ZnO tetrapods (T-ZnO) and ZnO tetrapods mixing with TiO₂ (T-TiZnO) using gold coating by sputtering technique [22]. However, there is still no report of a systematic study on the relation between gold amount and gas sensing properties. Moreover, there is still no sensor response formula that describes the effect of mechanism of gold nanoparticle on the surface of ZnO nanostructure sensor.

In this work, we have systematically investigated the gold amount dependence on gas sensor response. The sensor response enhancement due to gold nanoparticles on ZnO nanostructure

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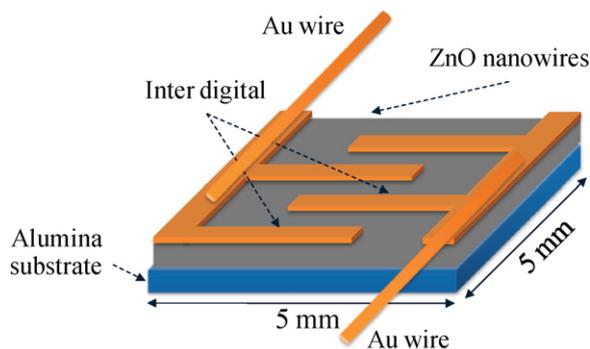


Fig. 1. Schematic diagram of ethanol sensing characteristic measurement.

sensors have been explained by catalytic effect on ethanol adsorption reaction and oxygen adsorption reaction. Furthermore, an explicit sensor response formula has been proposed according to this explanation. Also, we have demonstrated that the sensor response can be designed by control of depletion layer width via amount of gold nanoparticles and this can be simply performed by varying sputtering time.

2. Experimental

2.1. ZnO nanostructure preparation

ZnO nanostructures were prepared by thermal oxidation technique with no catalyst on alumina substrates [15]. Zn powder was evaporated on alumina substrate without substrate heating. In brief, Zn powder (purity 99.9%) with 0.3 g was placed on an alumina boat that was inserted in the chamber under pressure of 5×10^{-5} torr and the heating current was set to approximately 30 A. The distance between boat and substrate was about 10 cm. After evaporation process, a gray Zn thin film was formed on the alumina substrate with a thickness of 3 μm . Next, it was sintered to form a ZnO nanostructure at the temperature of 500 °C for 24 h under normal atmosphere. The ZnO nanostructures were characterized by using field emission electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS). Finally, the gold nanoparticles on the surface of the ZnO nanostructure were observed by using transmission electron microscopy (TEM), (JEOL JEM-2010).

2.2. Ethanol sensor fabrication

Ethanol sensors were fabricated by using ZnO nanostructure with an area of about $5 \times 5 \text{ mm}^2$ as shown in Fig. 1. Sensors based on pure ZnO nanostructure were called S00. Adding metal on the surface of ZnO nanostructure was performed by sputtering technique. ZnO nanostructures were coated with gold at sputtering time of 10–100 s by using SPI-module™ sputter coater and the direct current (DC) of 18 mA. The distance between the gold target and ZnO nanostructure was about 5 cm. Then, the as-sputtered gold on ZnO nanostructure was heated at the temperature of 400 °C in air for 24 h in order to form AuNPs. Finally, the Au-coated ZnO nanostructures were used for fabricating ethanol sensors which were called S10–S100 according to sputtering time.

The sensors were fabricated by putting gold paste as interdigital electrodes on the top of the sensor surface and putting a heater underneath the alumina substrate. The heater for the sensor was made from nickel–chromium which could control temperature in the range 280–380 °C. The operating temperature was measured by thermocouple placed on the middle of the sensor. The characteristics of the sensor were studied in a gas flow chamber. The electrical

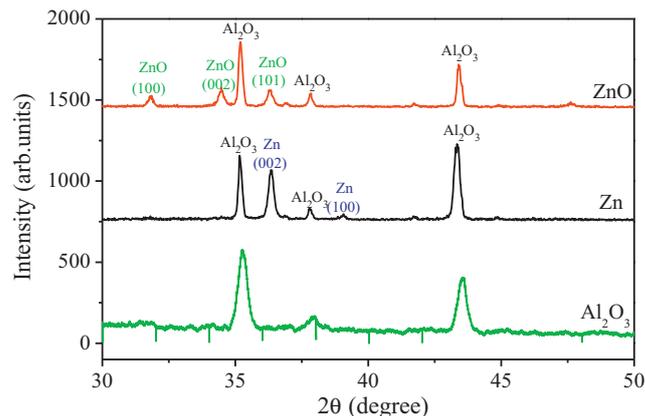


Fig. 2. X-ray diffraction pattern of thin film after sintering at 500 °C for 24 h compared with Zn film and alumina substrate.

measurements were performed by using a volt-ampereometric technique. A constant bias voltage of 5 V was applied to the sensor. The sensors were heated at the temperature of 300 °C for 24 h before testing. After that, the current and voltage signals were monitored and recorded through a desktop computer. From these signals, the sensor's resistance was then determined with the active gas at various concentrations (50, 100, 500, and 1000 ppm).

Ethanol vapor with various concentrations was generated from ethanol solutions by using alcohol simulator (GUTH laboratories Inc., Harrisburg USA) which simulated the alcohol concentration similar to an exhaled human breath. The sensor response is defined as the ratio of the electrical resistance of sensor in air (R_a) and in ethanol–air mixed gas (R_g).

3. Results and discussion

3.1. Characteristics of ZnO nanostructure and Au-coated ZnO nanostructure

After the evaporation process, the obtained thin film had gray color on alumina substrates. After sintering at 500 °C for 24 h, the gray color of the film changed to white color suggesting a change of Zn to ZnO via the chemical reaction $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$ which can be confirmed from XRD pattern as shown in Fig. 2. It can be seen that peaks in XRD pattern of the film after sintering can be indexed for only ZnO peaks and Al_2O_3 substrate. The growth mechanism of ZnO nanostructure by thermal oxidation process has been proposed in our previous report [23].

The morphology of ZnO nanostructure on alumina substrates was observed from FE-SEM as shown in Fig. 3(a). It was found that the nanostructures exhibited the wire-like structure with diameter of 40–200 nm and length of several microns. The thickness of ZnO nanostructure on alumina substrates was about 3 μm . For Au-coated ZnO nanostructure, the morphology looked similar to ZnO nanostructure as shown in Fig. 3(b)–(d) at the sputtering time of 20, 60, and 100 s, respectively. Nevertheless, gold nanoparticles (AuNPs) could not be observed on ZnO nanostructure surface although this may be due to low magnification of the FE-SEM images.

However, AuNPs on ZnO nanostructure surface could be observed from the TEM bright field image of Au-coated ZnO nanostructure at the sputtering time of 20 s as shown in Fig. 4. It can be seen that the AuNPs (black spots) adsorbed on ZnO nanostructure surface with particle size less than 15 nm. It should be noted that after the heat treatment the gold nanoparticles were observed as similar to those in other reports [20].

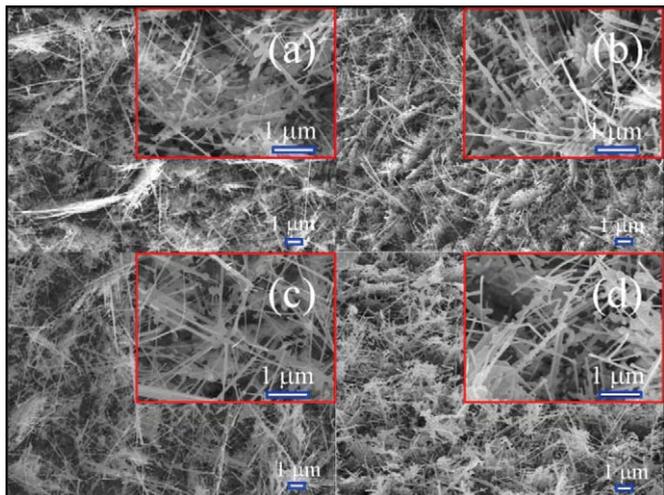


Fig. 3. FE-SEM images of (a) pure ZnO nanostructure, (b) ZnO nanostructure coated with Au for 20 s, (c) 60 s, and (d) 100 s, respectively.

The chemical composition of Au-coated ZnO nanostructure was investigated by using EDS. The EDS spectra are shown in Fig. 5(a)–(c) for sputtering time of 20, 60, and 100 s, respectively. The peaks of Au, Zn, and O signals are clearly observed. The peak at around 2.1 keV which corresponds to M_{α} energy level of gold, is clearly observed, suggesting gold particle on ZnO nanostructure surface. The average atomic percent of Au is 0.64%, 1.83%, and 13.19% at sputtering time of 20, 60, and 100 s respectively, indicating different amounts of gold for different sputtering time.

The coating amount of Au on ZnO nanostructure was confirmed by measuring the Au thickness coating on glass substrate using Rutherford Backscattering Spectrometry (RBS) and fitting the RBS spectrum with results from the simulation program SIMNRA [22]. The sputtering rate was derived from the measured Au thickness and found to be about 0.47 nm per second. Moreover, RBS can determine area concentration of gold which can indicate gold amount dependence on sputtering times which is a linear relationship between Au atom concentration and sputtering time as shown in Fig. 6.

3.2. Ethanol sensing characteristics

The resistance response and recovery characteristics of S60 sensor exposed to ethanol concentration of 1000 ppm at the operating

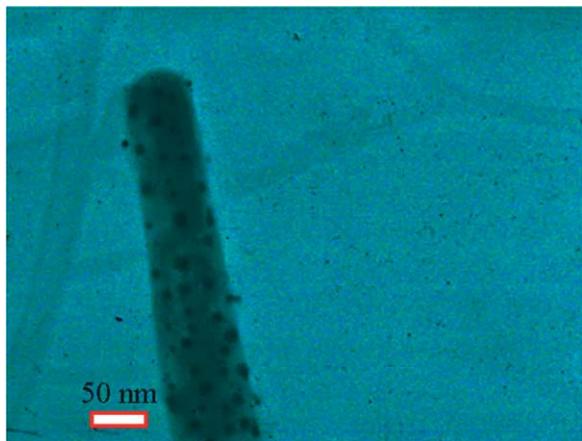


Fig. 4. TEM bright field image of ZnO nanostructure coated with Au at the sputtering time of 20 s.

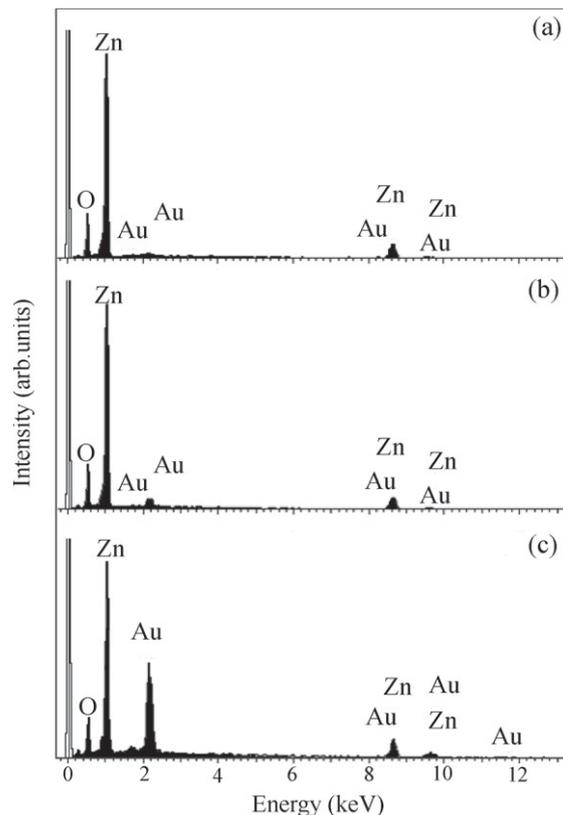


Fig. 5. EDS spectra of ZnO nanostructure coated with gold at the sputtering time of (a) 20 s, (b) 60 s, and (c) 100 s, respectively.

temperature in range of 280–380 °C are shown in Fig. 7(a). The resistance of the sensor dropped sharply in ethanol atmosphere and recovered to the initial value after removing ethanol vapor. All sensors exhibited similar resistance response and recovery characteristics with different resistance value. In Fig. 7(b), the sensor responses at 1000 ppm ethanol are plotted as a function of operating temperature. It can be seen that all the sensors exhibited the highest sensor response at 300 °C. Therefore, this is the optimum operating temperature for all the sensors.

Fig. 8(a) shows the sensor response of S00–S100 exposed to the ethanol concentration of 1000 ppm at the optimum temperature of 300 °C. It was found that the sensor response of S10–S100 sensors (with Au-coating sensors) was higher than that of S00 sensor (without Au-coating sensor). The sensor response of S00 sensor is about

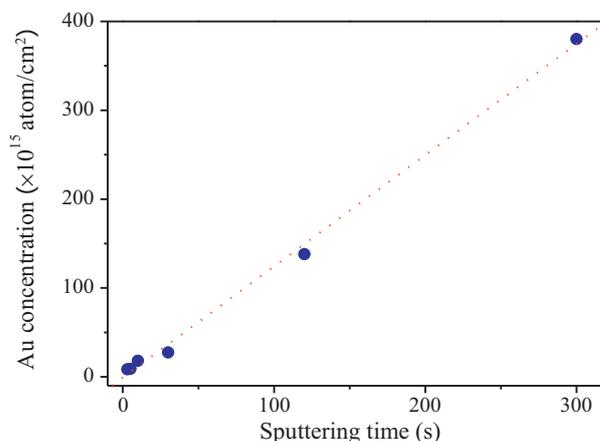


Fig. 6. Linear relationship between Au atom concentration and sputtering time.

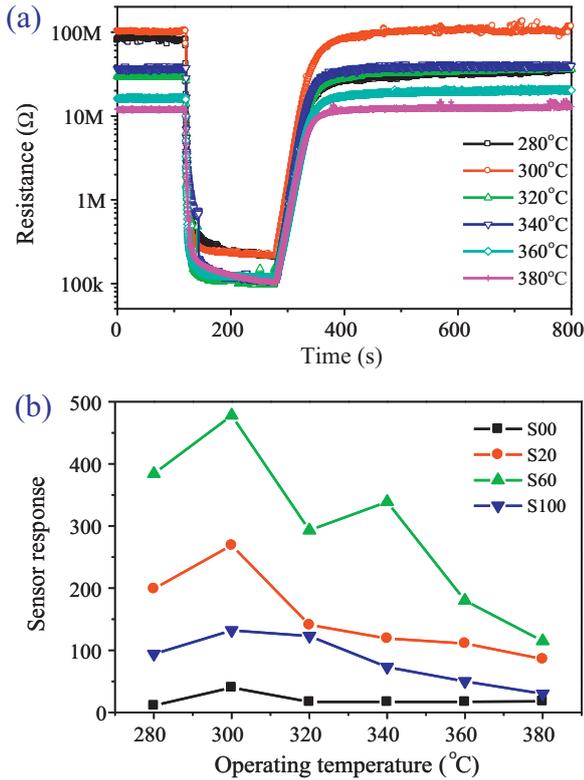


Fig. 7. (a) Resistance response and recovery characteristics of S60 sensor exposed to ethanol concentration of 1000 ppm at different operating temperatures, (b) the sensor response versus the operating temperature of sensors under ethanol concentration of 1000 ppm.

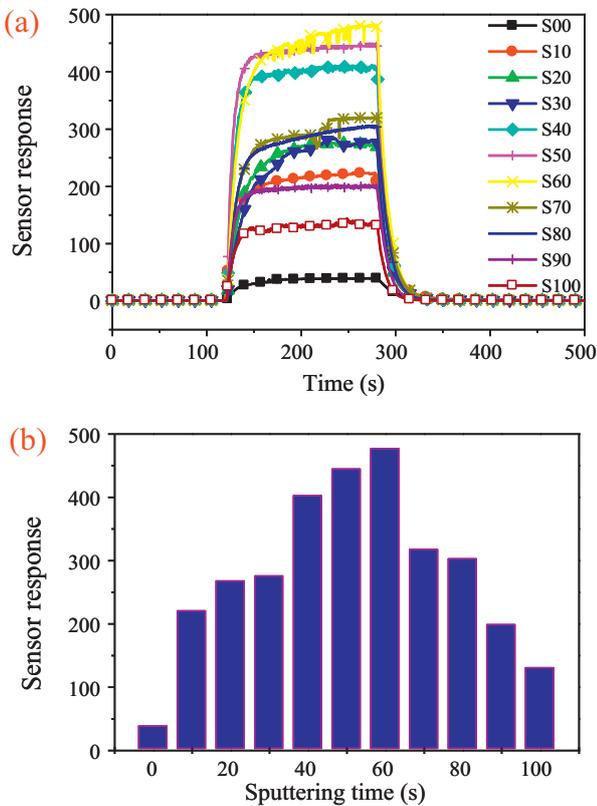


Fig. 8. Sensor response of S00–S100 (a) versus time and (b) versus sputtering time under ethanol concentration of 1000 ppm at the optimum temperature of 300 °C.

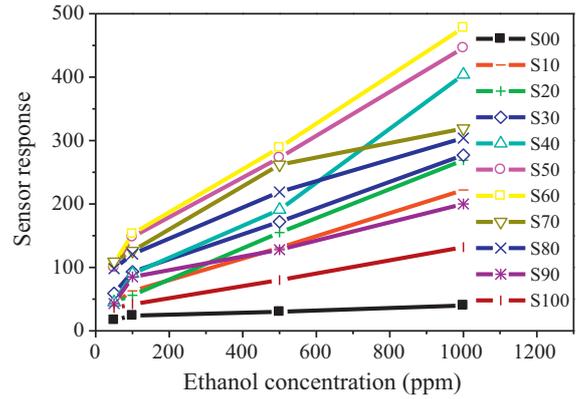


Fig. 9. Sensor response versus ethanol concentration at the optimum temperature of 300 °C.

40 while the sensor responses of S10–S100 sensors are 222, 269, 277, 404, 446, 478, 319, 304, 200, and 132 respectively, as seen in Fig. 8(b). The highest value of sensor response was obtained from S60 sensor. It can be seen that the sensor response increased at short sputtering time, reaches maximum value at 60 s, and then decreases for longer sputtering time. The sputtering time dependence on sensor response will be discussed in detail later.

Fig. 9 shows the relation between the sensor responses versus ethanol concentration at the operating temperature of 300 °C with ethanol concentration in the range of 50–1000 ppm. Clearly, the sensor response depends on ethanol concentration but the relation is not linear. This will be discussed in more detail in the next section.

3.3. Oxygen adsorption on ZnO surface

Normally, the oxygen adsorption reaction on the surface is of two types, depending on the operating temperature [24]. When ZnO nanostructure is heated at low temperature (100–200 °C), oxygen molecules (O_2) in air adsorbed onto the surface of the ZnO nanostructure forming oxygen ion molecules O_2^- . At high temperature (250–350 °C), oxygen molecules in air are dissociated to become oxygen ions with single or double negative electric charge due to the attraction of an electron from the conduction band of the ZnO nanostructure. Thus, the oxygen adsorption reaction can be represented as:



where $O_2(\text{gas})$ is an oxygen molecule in ambient atmosphere, \bar{e} is an electron on the surface that is depleted from the conduction band of the ZnO nanostructure, $O_{\beta}^{\alpha-}$ is a chemisorbed oxygen species, $\alpha = 1$ for singly ionized forms, $\alpha = 2$ for doubly ionized forms, $\beta = 1$ for atomic forms, and $\beta = 2$ for molecular forms.

From Eq. (1), oxygen adsorption on the ZnO nanostructure surface has various species that depend on the operating temperature. The oxygen species on the surface can be obtained from fitting with experimental data. Usually, gas adsorption on the surface can be empirically represented as [25–27]:

$$S = 1 + aC^b \quad (2)$$

where C represents ethanol concentration. The sensor response (S) is characterized by the constant a and b . The value of the constant depends on the sensor material and the type of gas sensor. The value of the constant b is normally around either 0.5 or 1, depending on the charge state of the surface ion. It was found that the adsorbed oxygen ion is O_2^- for b of 0.5, the adsorbed oxygen ion is O^- for b

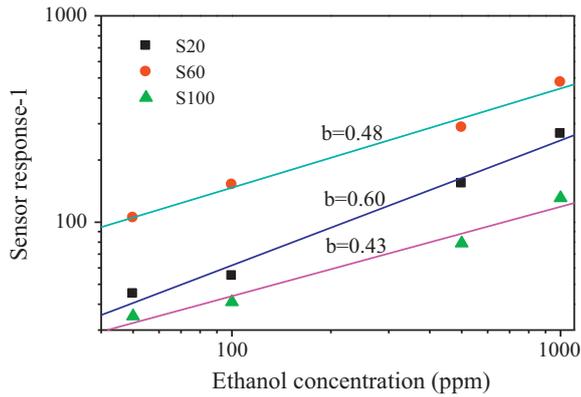


Fig. 10. Plot of $\log(S-1)$ versus $\log C$ of S20, S60, and S100 at the optimum temperature.

of 1 [14,25]. So Eq. (2) can be rewritten as in Eq. (3) in order to find oxygen adsorption species on the surface.

$$\log(S-1) = \log(a) + b\log(C) \quad (3)$$

It can be seen that $\log(S-1)$ has a linear relation with $\log C$ having a slope of value b . Thus, the b value, which represents oxygen ion species on the surface of ZnO sensors, can be obtained from a plot of $\log(S-1)$ versus $\log C$.

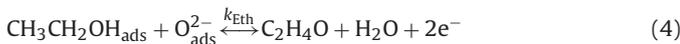
From our results, the b value was obtained from a linear fit of $\log(S-1)$ and $\log C$ as shown in Fig. 10. It can be seen that the b value of all sensors was nearly 0.5 suggesting the oxygen ion species on ZnO nanostructure surface were O^{2-} .

3.4. Explanation of sensor response enhancement

The sensor response enhancement due to AuNPs on ZnO nanostructure sensors can be explained by the effect of catalyst on ethanol adsorption reaction and effect of catalyst on oxygen adsorption reaction. It is well-known that Au exhibits an excellent catalytic ability, especially for Au NPs [20,28,29]. Therefore, Au coating would result in the higher reaction rate constant for both ethanol adsorption reaction and oxygen adsorption reaction.

3.4.1. Effect of catalyst on ethanol adsorption reaction

Let us consider ethanol adsorption reaction as given by:



This reaction can be used to derive sensor response formula which does not account for depletion layer effect as [24]:

$$S = \frac{R_{air}}{R_{gas}} = \frac{\Gamma_\tau k_{Eth}(T) [O_{ads}^{ion}]^b}{n_0} C_g^b + 1 \quad (5)$$

where Γ_τ is proportional constant, $k_{Eth}(T)$ is a reaction rate constant between adsorbed oxygen species and ethanol vapor which depends on the operating temperature, $[O_{ads}^{ion}]$ is adsorbed oxygen species concentration, C_g is the ethanol concentration, and n_0 is the electron concentration of sensor in air.

Since the reaction rate constant $k_{Eth}(T)$ is directly proportional to the sensor response, as seen in Eq. (5), AuNPs coating on ZnO surface sensor will result in the higher sensor response through increasing of electron concentration at the surface, as seen in Eq. (4). This explanation is similar to our previous report [22]. The evidence for having higher $k_{Eth}(T)$ is observed from the sensor resistance in the ethanol ambient. It is clearly seen in Fig. 11 that the sensor resistance in the ethanol ambient of Au-coated ZnO nanostructure sensor is lower than that of pure ZnO nanostructure sensor,

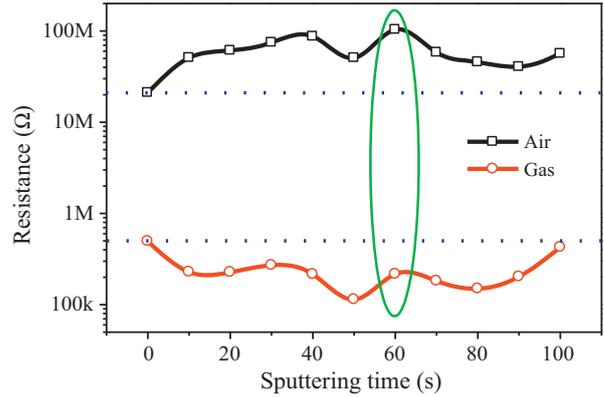


Fig. 11. Sensor resistance as a function of the sputtering time for all sensors in air and ethanol-air mixed gas at the operating temperature of 300 °C under ethanol concentration of 1000 ppm.

indicating the higher reaction rate constant $k_{Eth}(T)$ between adsorbed oxygen species and ethanol vapor.

3.4.2. Effect of catalyst on oxygen adsorption reaction

Let us consider the oxygen adsorption reaction as given in Eq. (1). In the previous section, we stated that oxygen ion specie was O^{2-} for ZnO sensor. Thus, Eq. (1) can be rewritten by substituting with $\beta = 1$ and $\alpha = 2$ as given in Eq. (6)



The chemical reaction from Eq. (6) is the reversible reaction including reaction constant, and equilibrium constant of oxygen adsorption reaction (k_{Oxy}) which is defined as $k_{Oxy} = k_a/k_d$, k_a and k_d for oxygen adsorption and desorption reactions, respectively. At equilibrium condition, it can be deduced by using the mass action law that

$$k_a [e]^2 P^{1/2} = k_d \sigma \quad (7a)$$

$$\sigma = k_{Oxy} [e]^2 P^{1/2} \quad (7b)$$

where σ is density of O^{2-} per unit area, $[e]$ is density of conduction electron at the surface, and P is a partial pressure of oxygen molecule.

Typically, the resistance of sensors including two parts: the resistance along a cylindrical nanowire and between nanowires. The resistance along the nanowire is due to surface depletion layer and conductive channel. The resistance between nanowires is due to potential barrier (band bending) between wires which depend on a size of nanostructure. Thus, let us consider a diameter of cylindrical nanowire D with a depletion layer width (w). It can be divided into three cases.

1. Under $D \gg 2w$ (large size)

In this case, the depletion layer width is much narrow compared to diameter of cylinder so the depletion layer has small effect on the electron density and in the wires. However, it does greatly affect the potential barrier of the contacts between wires. Thus, the resistance of the sensors is dominantly controlled by the potential barrier in this case [11].

The density of conduction electrons at surface $[e]$ is expressed in terms of surface potential as follows [30]:

$$[e] = n_d \exp\left(-\frac{qV_B}{kT}\right) \quad (8)$$

where n_d is density of donor electron, which is assumed to be constant throughout ZnO semiconductor and the relation between V_B and w is shown as:

$$w = \left(\frac{2\varepsilon}{qn_d} V_B \right)^{1/2} = L_D (2\beta V_B)^{1/2}, \quad V_B = \frac{(w/L_D)^2}{2\beta} \quad (9)$$

Here L_D is the Debye length defined by $L_D = (\varepsilon kT/q^2 n_d)^{1/2}$, and $\beta = q/kT$, where k and T are Boltzmann constant and temperature, respectively. By using Eq. (9), we can rewrite it as:

$$[e] = n_d \exp(-m^2/2) \quad (10)$$

where m is the reduced depletion depth which is defined by $m = w/L_D$. Since the resistance of the sensors is dominantly controlled by the potential barrier in this case, the sensor resistance R , can be considered to be inversely proportional to the electron density:

$$R = R_0 \exp(m^2/2), \quad R \propto \frac{1}{[e]} \quad (11)$$

where R_0 is the resistance under the flat band condition.

Moreover, if there are no electron-trapping sites other than the adsorbed oxygen ion O^{2-} on the surface, the depletion layer width (w) can be related to density of O^{2-} per unit area (σ) as [30]:

$$\sigma = n_d w \quad (12)$$

From Eq. (12), the larger depletion layer width results in higher density of O^{2-} per unit area (σ). Finally, density of O^{2-} per unit area (σ) and $[e]$ ($[e] = n_0$ in this case) can be inserted into sensor response formula [24] give:

$$S = \left(\frac{\Gamma_t k_{\text{Eth}}(T) (\Phi n_d w (V_m/V_s))^b \exp(m^2/2)}{n_d} \right) C_g^b + 1 \quad (13)$$

where Γ_t is proportional constant, $k_{\text{Eth}}(T)$ is a reaction rate constant between adsorbed oxygen species and ethanol vapor depends on the operating temperature, Φ is a ratio of surface area per volume of material (V_m), and V_s is the system volume, m is the reduced depletion depth which is defined by $m = w/L_D$, and L_D is Debye length, n_d is density of donor electron, which is assumed to be constant, w is the depletion layer width and C_g^b is the ethanol concentration.

From Eq. (13) (under $D \gg 2w$), it can be seen that the gas sensing mechanism is controlled by the potential barrier of the contact between wires. Furthermore, the potential barriers are independent of the cylinder size and therefore the sensitivity is independent of D .

2. Under $D > 2w$

In this case, the depletion layer has effect on both electron density in the wires and the potential barrier of the contacts between wires. Thus, the resistance of the sensors is controlled by surface depletion and the potential barrier in this case.

The conductance related to nanowire after oxygen adsorption is given as:

$$G = \frac{e\mu_0[e]\pi(D-2w)^2}{4l} \quad (14)$$

where μ_0 is the crystal electron mobility, l the distance between electrodes. Thus, the gas-sensing mechanism is dependent on both the width and height of the contact potential barriers [31,32].

Thus, the sensor resistance due to surface depletion layer and potential barrier is represented by:

$$R = R_0 \left(\frac{D}{D-2w} \right)^2 \exp(m^2/2) \quad (15)$$

From Eq. (12), (8) and using $[e] = n_0$, the sensor response formula [24] can be given as:

$$S = \left(\frac{\Gamma_t k_{\text{Eth}}(T) (\Phi n_d w (V_m/V_s))^b \exp(m^2/2)}{n_d} \right) \left(\frac{D}{D-2w} \right)^2 C_g^b + 1 \quad (16)$$

From this equation, it can be seen that the sensor response depend not only on the potential barrier between wires but also on the size of nanowire.

3. Under $D \leq 2w$

In this case, the depletion layer has effect only on electron density in the wires and can be regarded as fully depleted cylinders. The fully depleted cylinders are occurred when the Fermi level is totally controlled by surface states under nearly flat energy bands [31–33] and so potential barrier can be neglected. Thus, the resistance of the sensors is controlled only by surface depletion in this case.

Normally, the depletion layer width depends on Debye length as shown in Eq. (9). So, the sensor response of ZnO nanostructures is ultra high when their sizes are comparable or less than to Debye length (less than 15 nm) similar to the third case of $D \leq 2w$. However, in this work, we used AuNPs to increase the depletion layer width. Thus, the sizes of ZnO nanostructures can be larger in order to satisfy condition of $D \leq 2w$ or $D > 2w$ for enhancement of sensor response.

In addition, the depletion layer width can be approximately obtained from resistance in air and the resistance under the flat band condition (the resistance before oxygen adsorption) as in Eq. (15). For example, the depletion layer width is obtained to be 18.62 nm for S60 and 15.54 nm for S00. It is worth to noted that the depletion layer width of S00 is in agreement with that of pure ZnO in Wang's work (about 15 nm) [11]. Therefore, our sensors correspond to the case of $D > 2w$ and sensor response formula as in Eq. (16) was used to explain in our case.

From Eq. (16), it can be used to explain the enhancement of sensor response. It can be seen that an increase of k_{Oxy} due to catalytic effect of AuNPs leads to a decrease in density of conduction electron at the surface ($[e]$), as seen in Eq. (7), and the decrease of $[e]$ results in the larger depletion layer width (w), as seen in Eq. (15). Finally, the larger depletion layer width results in the enhancement of sensor response as seen in Eq. (16).

However, the sensor response decreases when gold sputtering time is more than 60 s. To explain the decrease of sensor response, let us consider a ZnO cylinder with diameter of D and having depletion layer width of w , as shown schematically in Fig. 13. As discussed earlier, the depletion layer width relates to density of O^{2-} per unit area (σ) and also equilibrium constant of oxygen adsorption reaction (k_{Oxy}), which should be proportional to the amount of Au nanoparticles.

3.4.3. Dependence of gold nanoparticle amount on depletion layer width

Since the sputtering time related to gold nanoparticle amount on ZnO nanostructures which is can be related to the depletion layer width as shown Fig. 12. So, let us consider gold amount dependence on depletion layer width in three cases. First, when there is no Au nanoparticle coating on the surface of the ZnO cylinder, as shown in Fig. 13(a). In this case, the depletion layer width (w_0) is very small when compared with the cylindrical diameter. The sensor response depends strongly on the ZnO morphologies via surface to volume ratio (Φ) parameter [24] and will be considered as a reference or control sensor.

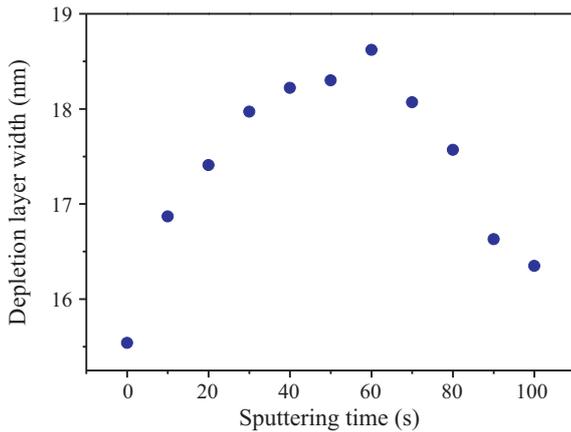


Fig. 12. Relation between depletion layer width and sputtering time.

Second, consider the case when there are some AuNPs on the surface of the ZnO cylinder, as shown in Fig. 13(b). As discussed before, AuNPs increase $k_{O_{xy}}$ due to catalytic effect on oxygen adsorption reaction. Then, the dissociation of oxygen molecules in air leads to oxygen ions adsorption by capturing electron to become oxygen ion species, O^{2-} [24]. ZnO nanostructure loses more conduction electrons at the surface (e^-) due to AuNPs spillover effect which causes a spillover zone at the neighborhood of AuNPs. Therefore, the depletion layer width is enlarged with suppression of the underlying conduction channel [34]. The larger depletion layer width (w_1) results in the enhancement of sensor response as seen in Eq. (16). Moreover, the larger depletion layer width results in increase height of the potential barrier at the contacts among the nanowires and consequently leads to resistance increase of the

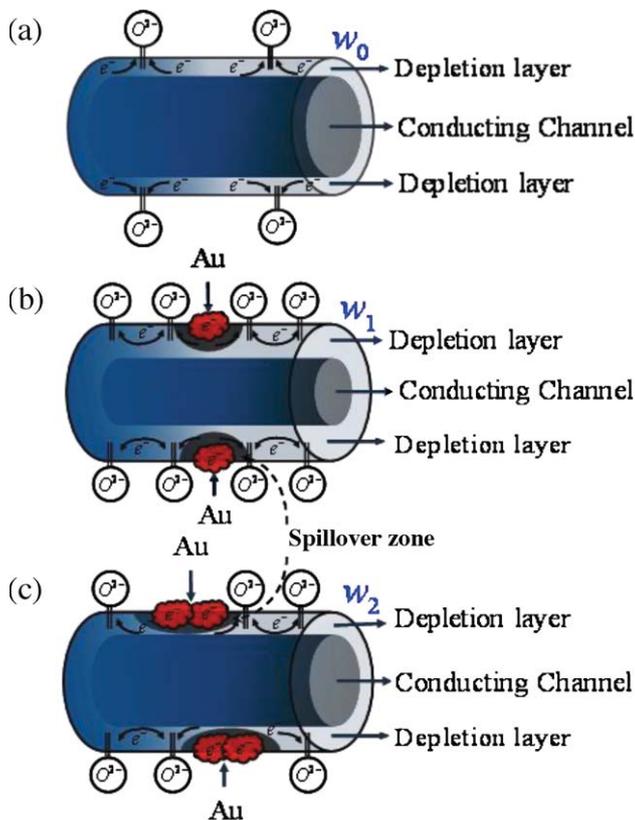


Fig. 13. Schematic diagrams of gold adsorbed on ZnO surface, (a) without gold, (b) with gold nanoparticle and (c) with large amount of gold nanoparticles.

nanowire sensors. It should be noted that the resistance of sensor coated with AuNPs (S10–S100) in air atmosphere showed higher resistance than pure sensor (see in Fig. 11) even though the sensor has a large amount of AuNPs on the surface.

Finally, at higher loading amounts of AuNPs, the over amount of AuNPs on the ZnO surface results in an overlap with the other AuNPs on ZnO surface as seen in Fig. 13 (c). The overlapped AuNPs leads to less capability of conduction electrons at the surface to capture adsorbed oxygen because there were not enough exposed surfaces of ZnO nanowires to receive dissociated oxygen adsorbs. And less exposed surfaces of ZnO nanowires also affected narrow depletion layer width (w_2) of the sensors [35,36]. Thus, at overloading amounts of AuNPs the depletion layer width is narrower instead of wider due to overlap effect. However, the sensor response in this condition is still higher than that of pure or reference sensor.

It can be seen that the dependence on depletion layer width with gold amount in three cases can be used to explain our results of sensor response dependence on sputtering time as shown in Fig. 8(b). Therefore, the sensor response can be designed by controlling of depletion layer width via the amount of AuNPs. It should be noted that it is easy to fabricate sensors with different sensing characteristics by using this sputtering technique. The sensors with different sensing characteristics are an essential component in electronic nose applications. Thus, these results can be further explored for their implications in e-nose applications.

4. Conclusion

AuNPs were successfully coated on ZnO nanostructure by sputtering technique to create ethanol sensors. The enhancement of sensor response due to AuNPs on ZnO nanostructure has been observed and explained by catalytic effect on ethanol adsorption reaction and oxygen adsorption reaction. Based on the adsorption reactions, a sensor response formula has been successfully developed for explanation. Also, the gas sensor response dependence on gold amount was successfully explained in term of the depletion layer width. Therefore, the sensor response can be designed by control of depletion layer width via the amount of AuNPs, which can be simply performed by varying sputtering time. The results have an implication in e-nose applications.

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Zinc Oxide Whiskers by Thermal Oxidation Method

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ABSTRACT

ZnO whiskers were grown in quartz tube by thermal oxidation method. Zinc powder was heated in a horizontal quartz tube with a furnace at a temperature of 700°C for 2 hr, under normal atmosphere. Three different kinds of the products can be obtained after the oxidation process. One is transparent whiskers located at the bottom of the quartz tube. Next is cotton-like bulk and the other is white, fluffy product. The products were characterized by field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS). It was found that the products composed of whiskers and tetrapod whiskers. The lengths and the diameter of whiskers were in the range of 10-240 mm and 0.20 - 4.60 mm, respectively while the percent of yield was up to 20% by weight. The lengths and the diameter of tetrapod whiskers were in the range of 3.15-10.63 mm and 0.13- 2.64 mm while the percent of yield was up to 68% by weight.

Keywords: zinc oxide, whisker, tetrapod, thermal oxidation.

1. INTRODUCTION

Recently, quasi one-dimensional (1D) nanostructures such as whiskers, wires, rods, belts, and tubes have received the great interest due to their very large surface-to-volume ratio and become the focus of intensive research owing to their unique applications in mesoscopic physics, fabrication of nanoscale optic and electronic devices [1]. ZnO is now receiving special attention for its potential applications in optical and electronic materials [2]. It is an n-type semiconductor with a direct band gap of 3.37 eV at room temperature close in properties to GaN ($E_g = 3.5$ eV at room temperature), which is widely used in the fabrication of blue light emitting diodes.

The strong exciton binding energy of 60 meV, which is much larger than that of GaN (25 meV) and the thermal energy at room temperature (26 meV) can ensure an efficient exciton emission at room temperature under low excitation energy [2-5]. ZnO can be grown into a variety of micro and nanostructures, such as tetrapod-shape, microrods, one-dimensional microtubes, thin film, nanobelts, nanowires, nanoneedles, nanotubes, nanorods, nanocables and whiskers [1, 6-14]. ZnO nanostructures are particularly adaptable and have various potential applications, such as gas sensors [15, 16], solar cells [17], field emitters [18] and the field effect

transistor (FET) [19]. Among them, ZnO whisker has attended due to ease of preparation and single crystalline properties.

ZnO whiskers have a hexagonal columnar shape (pencil-like structure) and ZnO whiskers, having tetrapod shape, consist of a ZnO core in the zinc blended structure form in which four ZnO arms in the wurtzite structure radiate. Each arm is well faceted with a hexagonal cross-section and is uniform in length and diameter [20]. Among kinds of ZnO whiskers, tetrapod whisker possesses good comprehensive properties, such as semiconductivity, wear resistance, vibration insulation and microwave absorption. Owing to the unusual geometry and single crystalline character, they can be widely applied as both devices and structural materials [21,22]. In particular, the introduction of ZnO tetrapod whiskers imparts antielectrostatic and antibacterial properties to polyacrylate-based composites. Tetrapod-polymer composites can be used in the fabrication of solar cells. Moreover, similarly other structures, ZnO whiskers have attractive gas-sensing and luminescent properties [2].

Due to these promising applications, ZnO whiskers can be prepared by several methods such as solvothermal [1], thermal evaporation [23], Metal Organic Chemical Vapor Deposition (MOCVD) [24], Pulsed Laser Deposition (PLD) [25] and thermal oxidation [15,16,21,22]. The thermal oxidation method is a simple, low cost and fast process. So in this work, ZnO whiskers were prepared with high yield by thermal oxidation of Zn powder.

2. MATERIALS AND METHODS

ZnO whiskers were prepared by thermal oxidation technique. In typical preparation processes, Zn powder mass (Ajax Finechem, quoted purity of 99.9%) was used at weight of 3, 3.5, 4, 4.5, 5, 5.5 and 6 g then the powder

was hand-grounded in agate mortar. After that, ZnO powder was put into the horizontal one-end sealed quartz tube (150 ml) to serve as the source materials. The quartz tube was then pushed into the central of a conventional tube furnace under normal atmosphere at 700°C. The gate of the furnace was closed without special sealing during the whisker generation process. After 2 hr. sintering, the quartz tube was taken out from the furnace into air for rapid cooling.

The obtained products were investigated by field emission scanning electron microscope for morphology and energy dispersive spectroscopy for chemical composition.

3. RESULTS AND DISCUSSION

Before heating, a typical color of zinc powder is grey. After heating process, Zn was oxidized with O₂ in normal atmosphere and transform to ZnO. It was observed that wall of the quartz tubes were covered with a white layer product and there were three different kinds of the products ranging from the bottom to the edge of the quartz tube. One is transparent columned whiskers located at the bottom of the quartz tube. Next is white, cotton-like bulk and other is white, fluffy product. It can be further classified in three portions according to morphologies and density, namely the first portion, the second portion and the third portion as showed in Figure 1.

The different morphologies of products in different portions due to the growth mechanism of the wire-like nanostructures including nanowires, nanorods, nanobelts and whiskers can be explained by the kinetics of anisotropic growth via a vapor-solid mechanism represented as:

$$P = B \exp\left(\frac{-\pi\sigma^2}{k_B^2 T^2 \ln(\alpha)}\right)$$

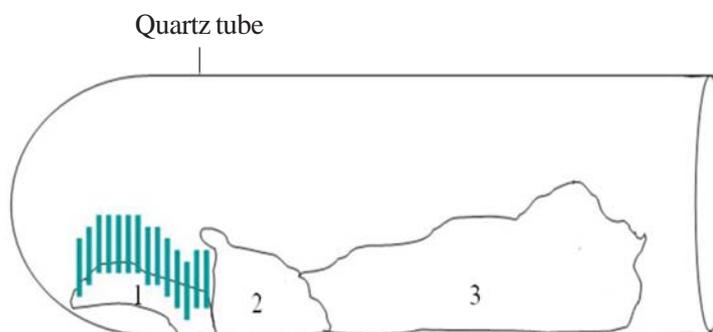
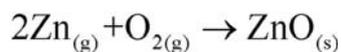


Figure 1. Schematic of the ZnO whiskers formed in different portion in the quartz tube.

where P is the nucleation probability on the surface of a whisker, B is a constant parameter, σ is the surface energy of the solid whisker, k_B is the Boltzmann's constant, T is the absolute temperature, and α is the supersaturation ratio between the actual vapor pressure and the equilibrium vapor pressure corresponding to temperature (usually, > 1) [26-28]. The supersaturation ratio play an important parameter in controlling morphology of wire-like and belt-like nanostructures[26]. Smaller supersaturation ratio promotes the growth of wire-like structures. In contrast, larger supersaturation ratio promotes two dimensional growths resulting in the formation of belt-like structures. However, the tetrapod whisker was not grown on substrate and the supersaturation ratio should be larger than belt-like structures for facilitate the three dimension nucleation resulting in the formation of tetrapod whiskers [28].

In this work Zn in gas phase can be occurred when we heat Zn metal at 700°C which above melting point of it. The mechanism can be explained based on the thermal oxidation reaction which expressed as:



The O_2 for this reaction come from the residual O_2 inside the tube at the beginning and the O_2 which enter into the quartz tube from

the opened end. Then the O_2 concentration near the opened end of the tube is higher than the O_2 concentration far inside the tube therefore the supersaturation ratio of ZnO vapor near the opened end is larger than at the bottom. In this result the shape of products depend on the supersaturation ratio of ZnO vapor's zone in the quartz tube as can see from the SEM images in Figure 2 which the first portion is composed of ZnO whiskers with the hexagonal column (pencil-like structure). The diameter and length were in the range of 30-140 nm and 0.38-4.59 μm , respectively (Figure 2a). The second portion is white and quite dense. It consists of tetrapod whiskers which have the hexagonal cylinder legs. The leg-length of 7.34 ± 0.87 (6.17-9.21) μm and the diameter of 0.32-0.66 (0.49 \pm 0.09) μm (Figure 2b). We obtained two types of tetrapod whiskers in the third portion. In this portion, there is the highest concentration of O_2 lead to high probability of Zn vapor oxidized with O_2 . Large supersaturation ratio promotes tetrapod growth easily. The obtained tetrapod whiskers have 2 different kinds due to the growing time. That mean tetrapod whisker in the inner layer have been grown first and the growth is continuously. Thus, the tetrapod whiskers in the inner layer will be longer and bigger than that in the outer layer as showed in the figure that the outer

layer is white, fluffy which quite porous with a thickness of about 1-3 mm and it is composed of tetrapod whiskers which have the leg-length of 4.77 ± 1.46 (3.15-8.87) μm and the diameter of 0.66 ± 0.14 (0.43-0.97) μm at the base, 0.21 ± 0.05 (0.13-0.28) μm at the needle (Figure 2c). The inner layer

composed of tetrapod whiskers which have the hexagonal cylinder legs. The leg-length of 7.21 ± 1.64 (4.26-10.63) μm and the diameter of 1.50 ± 0.65 (0.67-2.64) μm (Figure 2d). By SEM observation, the tetrapod whiskers become shorter in leg-length and smaller in aspect ratio as from outside to inside.

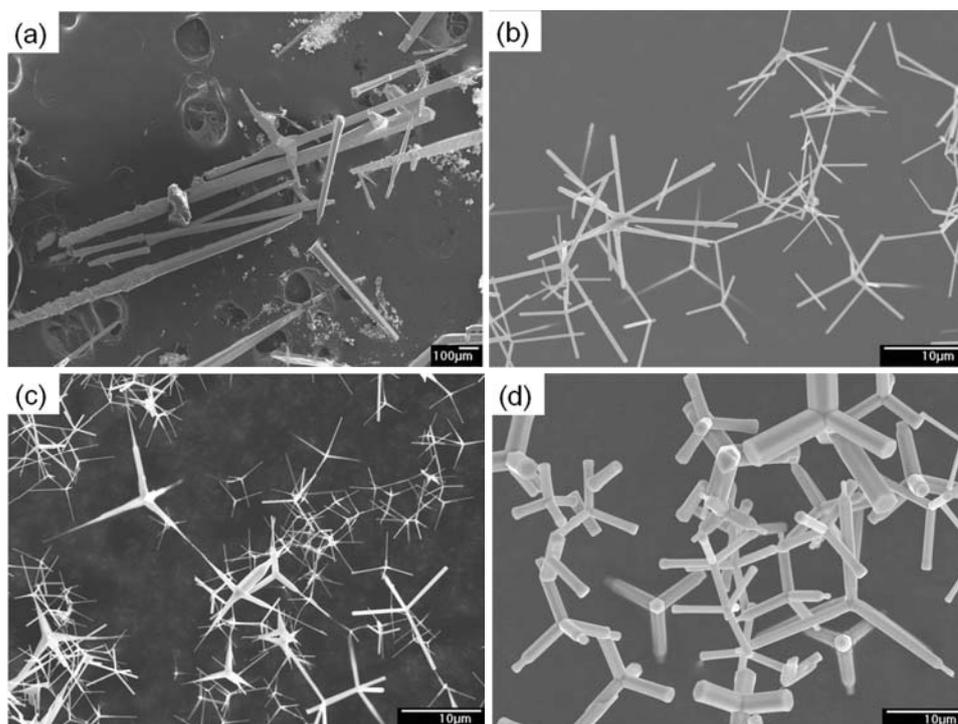


Figure 2. SEM images of ZnO whiskers in difference portions. (a) first portion, (b) second portion, (c) outer layer of third portion, d) inner layer of third portion.

Figure 3 showed EDS spectra of (a) whisker and (b) tetrapod whisker. The spectra were obtained by focusing electron beam in the top of whisker. The peaks at Zn and O signals indicated that Zn was oxidized with O and form ZnO whiskers. The atomic ratio of Zn and O from the EDS spectra of whisker and tetrapod whisker were 47.65 : 52.35 and 44.19 : 55.81, which was nearly 1:1 ratio. Thus, the obtained whisker could be considered as ZnO.

Figure 4 showed the effect of Zn powder weight on the producing yield. Producing yields of tetrapod whisker was high when the weights of Zn powder was used more than 3.5 g and it seem to be saturated. Producing yield of whiskers did not have a significant change with the change of Zn powder weight used. The obtained whiskers which prepared by thermal oxidation of Zn powder were almost hexagonal column shaped but the higher of weight of

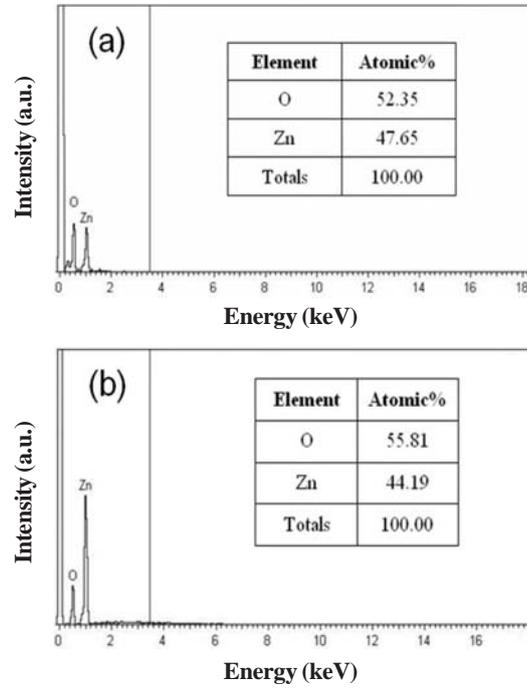


Figure 3. The EDS analysis of (a) whiskers, (b) tetrapod whiskers.

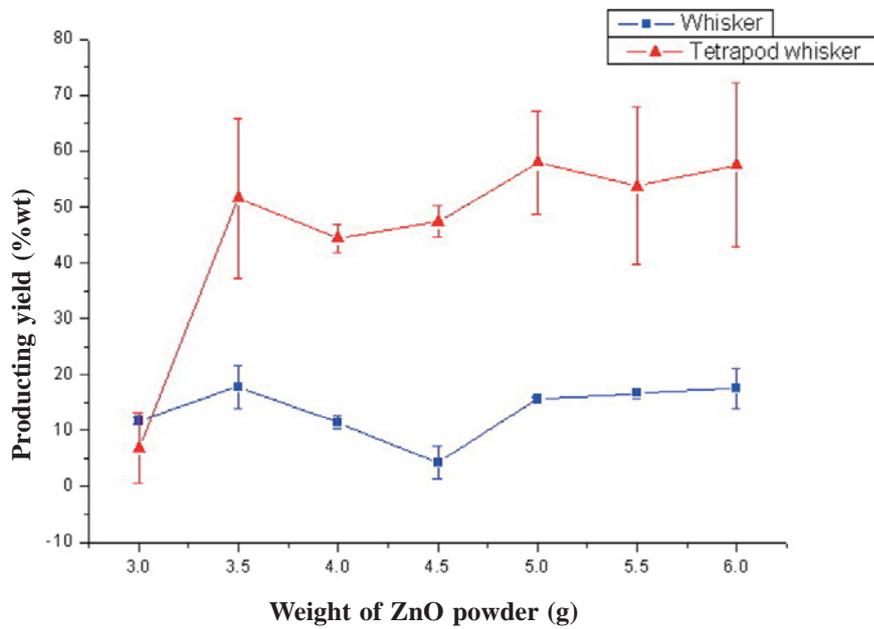


Figure 4. The effect of ZnO powder weight on the producing yield.

Zn powder led to less uniform of structure, as showed in Figure 5. Because of the high vapor pressure of Zn in the growth area, it

was found that a lot of fine particles were deposited on the surface of whiskers.

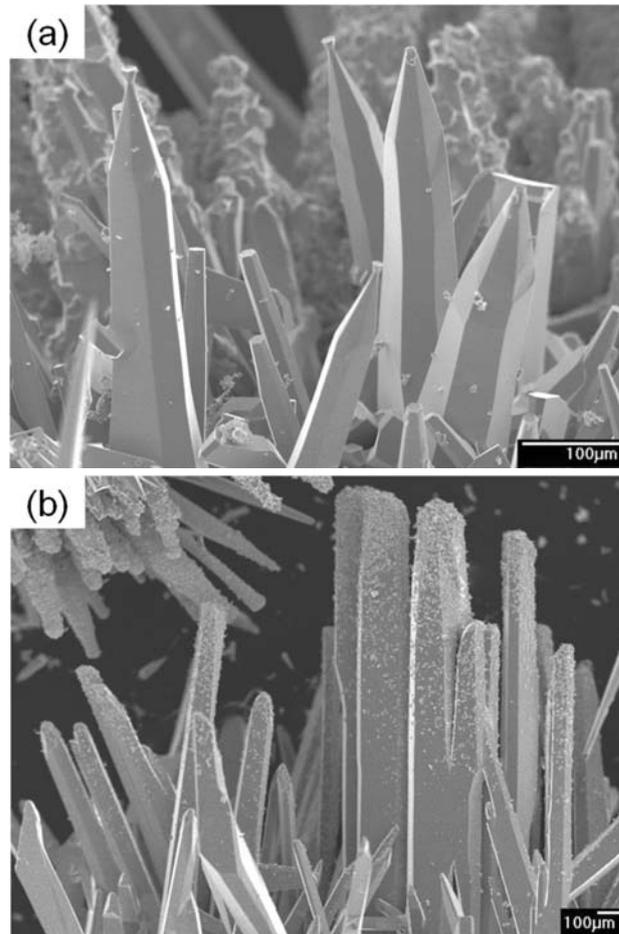


Figure 5. SEM images of ZnO whiskers which different ZnO powder weight used. (a) Zn powder 3.5 g, (b) Zn powder 5 g.

4. CONCLUSIONS

ZnO whiskers were successfully prepared by thermal oxidation method. From FE-SEM, the lengths of whiskers were in the range of 10-240 μm , the diameters were in the range of 0.20 - 4.60 μm while the percent of yield was up to 20% by weight. The lengths

of tetrapod whiskers were in the range of 3.15-10.63 μm , the diameters were in the range of 0.13- 2.64 μm while the percent of yield was up to 68% by weight. From EDS, it was suggested that the chemical component is ZnO. It was found that the higher of weight Zn powder led to less uniform of structure.

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Effect of Solution on Growth of Zinc Oxide Tetrapod by Thermal Oxidation Technique

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ABSTRACT

In this work, the effects of solution on the growth of zinc oxide tetrapod (*T*-ZnO) were investigated. *T*-ZnO nanostructures were prepared by the thermal oxidation technique of metal zinc powder mixed with different solutions such as methanol (CH₃OH), ethanol (C₂H₅OH) and hydrogen per oxide (H₂O₂). The mixtures were heated at the temperature of 1,000°C in normal atmosphere. A detailed field emission scanning electron microscopy (FE-SEM) showed that *T*-ZnO prepared by heating zinc and H₂O₂ gave the best tetrapod-like nanostructures. The length and diameter at the leg tip of *T*-ZnO is about 8.17 ± 1.17 μm and 47.8 nm, respectively. With this condition the highest percent yield of *T*-ZnO was about 4.82% by weight. Moreover, as determined by the energy dispersive spectroscopy (EDS), the atomic ratio of Zn and O was about 1:1. In addition, this study reveal that H₂O₂ acts as a strong oxidizing properties and has a role as a strong oxidizer to supply more reactive oxygen species to zinc in order to form *T*-ZnO.

Keywords: ZnO, tetrapod, thermal oxidation technique.

1. INTRODUCTION

Zinc Oxide (ZnO) is one of the promising metal oxide wide-band gap (3.37 eV) semiconductors [1]. It has potential applications in optoelectronics, catalysis, surface acoustic wave devices, microelectronics, biomedical devices, solar cells, and most widely applied as gas sensing materials [2-6]. Moreover, it can be grown into a variety shape both micro and nano crystal structures, such as microrods, one-dimensional microtubes, thin films, nanobelts, nanowires, nanoneedles, nanotubes, nanorods and tetrapods [7-15]. Recently,

tetrapod-shaped ZnO nanostructures (*T*-ZnO), having sharp legs with enhanced properties [16], have received the great interest due to their very large surface-to-volume ratio. Now, its applications are also expanding continuously [17].

T-ZnO can be synthesized by many techniques, Zhou et al. [18] synthesized *T*-ZnO whiskers which were prepared with high yield and good purity in a short reaction with otherwise shaped metallic zinc at 500-800°C under atmospheric pressure. Also, Guo-ping

et al. [19] synthesized *T*-ZnO whiskers and microrods in one crucible by thermal evaporation of Zn/C mixtures at 930°C in air without any catalyst. While Fu et al. firstly reported [4] the growth of *T*-ZnO microtubes which were synthesized from mixtures of high-purity Zn powder and activated carbon in a crucible at 930-940°C in air without the presence of any catalyst. Recently, we synthesized *T*-ZnO nanostructures by heating the mixture of zinc powder and hydrogen peroxide solution at 1,000°C under normal atmospheric pressure [20]. However, the synthesis of *T*-ZnO is still a subject of investigation, especially, in the case of heating zinc and solution which acts as a strong oxidizer to supply more reactive oxygen species to zinc in order to form ZnO nanotetrapods.

In this work, we reported the effects of solution on the growth of *T*-ZnO. The different solutions such as CH₃OH, C₂H₅OH and H₂O₂ were used as a supply more reactive oxygen species. The morphology and chemical reaction of *T*-ZnO for every case were discussed.

2. MATERIALS AND METHODS

ZnO nanotetrapods were prepared by a thermal oxidation technique. Zinc powder and different solutions such as methanol

(CH₃OH), ethanol (C₂H₅OH) and hydrogen peroxide (H₂O₂) were thoroughly mixed together at 10:1 ratio by weight heated at the temperature of 1,000°C in normal atmosphere. The detail sample and solutions are listed in Table 1. The horizontal furnace was heated inside the furnace. During the process, Zn and the mixtures evaporated to Zn vapor rapidly when put into a hot alumina crucible. The oxidation process of Zn at 1,000°C took for a few minutes under normal atmospheric pressure and the obtained products color changed from grey to white and fluffy product. After that, a crucible was pulled out from furnace and left it to cool down at room temperature. Finally, the morphology and composition of the obtained *T*-ZnO products were characterized by field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS), respectively.

3. RESULTS AND DISCUSSION

FE-SEM images of the synthesized *T*-ZnO at magnification of x2,000 and x50,000 (tip), respectively, are shown in Figure 1. Notice that the four-legs of the *T*-ZnO can be observed. Figure 1(a) also shows *T*-ZnO whiskers from pure Zn powder. The analyses of the leg tip of the *T*-ZnO

Table 1. The details samples and solutions in this work.

Conditions	The mixtures	
		Solutions
(1)	zinc powder (Ajax, 99.99% purity)	-
(2)		methanol (CH ₃ OH) (J.T. Baker, 100% purity)
(3)		ethanol (C ₂ H ₅ OH) (Merck, 99.9% purity)
(4)		hydrogen peroxide (H ₂ O ₂) solution (Merck, 30% concentration)

nanostructures were made. The results show that the length and diameter of the tetrapods are about 9.30-12.77 μm and ~ 67.13 nm, respectively. The average length of the tetrapods was 10.87 ± 1.13 μm and the diameter at the tip was normally less than 100 nm, having a hexagonal shape corresponding to hexagonal ZnO structure. In addition, figure 1

(b)-(d) show *T*-ZnO whiskers from Zn mixed with different solutions. The minimum and maximum of the length and diameter of the *T*-ZnO are summarized in Table 2. It should be noted that Zn powder mixed with solutions give the products which have secondary growth less than that of pure Zn powder. This result indicates that the smaller size and

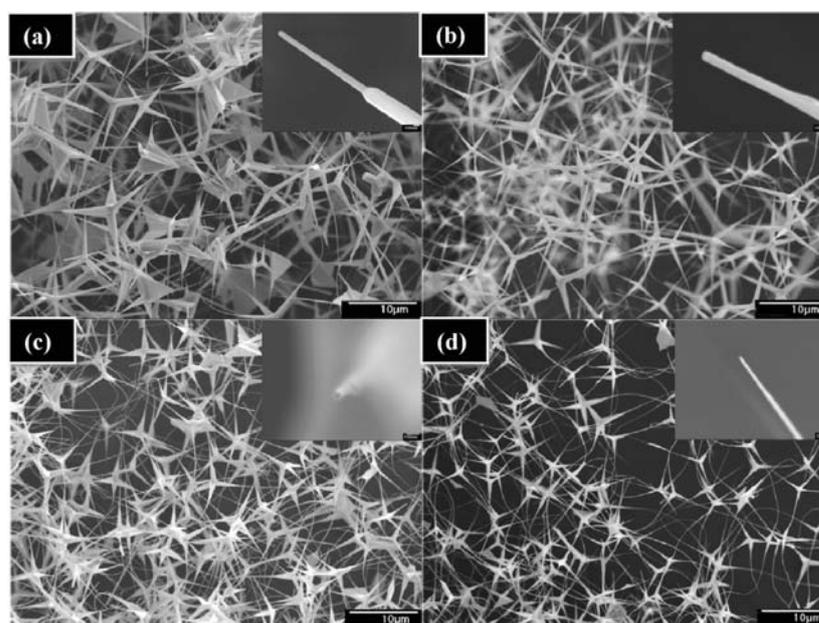


Figure 1. FE-SEM images with x2,000 magnification of *T*-ZnO from (a) pure Zn powder, (b) Zn+CH₃OH, (c) Zn+C₂H₅OH, and (d) Zn+H₂O₂. Insets are FE-SEM images at the tip with x50,000 magnification of *T*-ZnOs.

Table 2. The minimum and maximum of length and diameter of *T*-ZnO synthesized from mixture of Zn with different solutions by using thermal oxidation technique.

Samples	Lengths (μm)		Average of Diameters (nm)
	Min-Max of Lengths (μm)	Average of Lengths (μm)	
(1) Zn	9.30-12.77	10.87 ± 1.13	67.13
(2) Zn + CH ₃ OH	8.73-13.85	11.00 ± 1.51	142.45
(3) Zn + C ₂ H ₅ OH	6.95-11.50	8.74 ± 1.20	64.95
(4) Zn + H ₂ O ₂	5.90-9.86	8.17 ± 1.17	47.80

the better shape of the tetrapods synthesized from mixture of Zn and H_2O_2 were obtained as displayed in Figure 1(d).

EDS spectrum of the *T*-ZnO from the mixture of Zn and H_2O_2 at $1,000^\circ C$ is shown in Figure 2. The spectra were obtained by focusing electron beam in the middle of

whisker, showing Zn and O signals. This indicates that the observed spectra agree well to ZnO element. To obtain an atomic composition ratio, the semi-quantitative analysis of the EDS spectrum was also made and the results showed the Zn:O composition ratio of about 50:50.

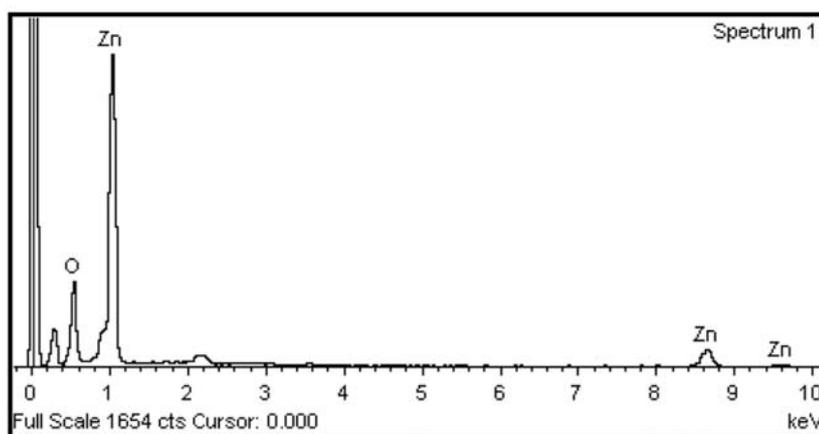


Figure 2. EDS spectrum of *T*-ZnO from the mixture of Zn with H_2O_2 solution at $1,000^\circ C$.

Table 3. The percent yield of *T*-ZnO by weight at different solutions.

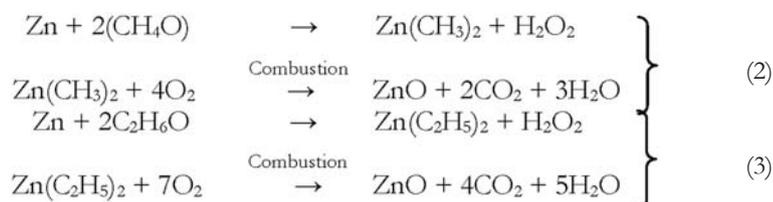
Samples	Weight of zinc powder (g)	The percent yield of ZnO tetrapod by weight
(1) Zn	2.00	2.83%
(2) Zn + CH_3OH	2.00	1.81%
(3) Zn + C_2H_5OH	2.00	2.58%
(4) Zn + H_2O_2	2.00	4.82%

The analysis of the percent yield of *T*-ZnO was selected from the best shape of all products which were then compared with Zn powder. The percent yield of *T*-ZnO by weight is summarized in Table 3. It can be seen that, sample (4) has the percent yield by weight more than other which was 4.82%.

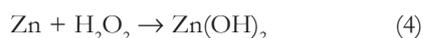
In addition, the ZnO nanostructures were produced due to the zinc oxidized by oxygen, which can be represented as



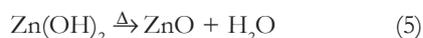
Alternatively, reaction products of organo-metallic compounds have a toxic substance from the burning of an organo-metallic compound provided by the combustion of dimethyl zinc ($Zn(CH_3)_2$) and diethyl zinc ($Zn(C_2H_5)_2$) from (2) and (3).



However, inhalations of zinc oxide fume particles produced by the combustion of zinc organo metallic compounds causes zinc metal fume fever [21]. This is an uncomfortable condition characterized by elevated temperature and “chills.” Typically, the chemical reactions between metallic zinc (Zn) and hydrogen peroxide (H_2O_2) solution are [22]



Then, $\text{Zn}(\text{OH})_2$ begins to decompose to form ZnO and water at around 100°C as follows [8, 10]:



From our previous research [20, 22], *T*-ZnO from the mixtures of Zn and H_2O_2 solution had a single-crystalline hexagonal structure with the lattice constants of $a=3.24 \text{ \AA}$ and $c=5.19 \text{ \AA}$ as determined by x-rays diffraction (XRD) measurements. The transmission electron microscopy (TEM) equipped with selected area electron diffraction accessory used for microstructures observations, showed that the legs of *T*-ZnOs grew along [0001] *c*-axis direction. However, it is important to note here that H_2O_2 solution acts as a strong oxidizer to supply more reactive oxygen species to Zn in order to form *T*-ZnO.

4. CONCLUSIONS

T-ZnO nanostructures were prepared by the oxidation reaction technique. The results of FE-SEM images and EDS spectra of *T*-

ZnO suggested that the best tetrapod-like ZnO nanostructures prepared by heating the mixture of zinc and H_2O_2 were formed with the highest percent yield of about 4.82% by weight. Therefore, H_2O_2 acts as a strong oxidizer to supply more reactive oxygen species to zinc in order to form *T*-ZnO.

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Enhancement of Sensor Response by Au Nanoparticles Doping on ZnO Tetrapod Sensor

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Abstract Zinc oxide tetrapods (*T*-ZnO) were synthesized using thermal oxidation technique from Zn powders mixed with hydrogen peroxide (H₂O₂). Through a detailed field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD) showed that the *T*-ZnO exhibited single crystalline hexagonal wurtzite structure. The leg tip of the *T*-ZnO was about 8.17±1.17 μm in length and 47.80 nm in diameter. The ethanol sensors, based on the *T*-ZnO and the *T*-ZnO doped with Au nanoparticles (Au/*T*-ZnO), were fabricated and investigated for the ethanol sensing properties. The ethanol sensor response of the *T*-ZnO and the Au/*T*-ZnO sensors was tested at the operating temperature of 260-360°C with the ethanol concentration of 50, 100, 500, and 1000 ppm. The results showed that the Au/*T*-ZnO sensors exhibited exceptionally higher sensitivity than the pure *T*-ZnO sensors for entire ethanol concentration with optimum temperature of 340°C and 320°C, respectively. This enhancement can be explained in terms of the electron concentration of sensor in air, n_0 and the reaction rate constant, k_{Eth} between the adsorbed oxygen species and the ethanol vapor due to the increase of effective surface for adsorption of ethanol on the surface. With an excellent catalytic ability, the Au nanoparticles doping on the *T*-ZnO sensors would result in higher reaction rate constant than the undoped *T*-ZnO sensors.

Introduction

Zinc oxide (ZnO) is one of the promising metal oxide wide-band gap (3.37eV) semiconductors [1] that have been widely applied as gas sensing materials [1-7]. Recently, ZnO tetrapod nanostructures have received the great interest due to their very large surface-to-volume ratio [7, 8]. However, *T*-ZnO sensors still have some limitations which limit its applicability in real-time applications [9]. Therefore, the gas sensing properties can be enhanced by doping a noble metal in oxide semiconductors [10]. These metal catalysts were added as coating on the sensor surface by doping and/or by mixing with raw materials [7, 10-12]. In this article, we have fabricated and examined the ethanol gas sensing properties of both undoped and Au nanoparticles-doped *T*-ZnO sensors.

Experimental

Zinc oxide tetrapods were synthesized using a thermal oxidation reaction technique [13]. It starts with Zn powders (99.9%, Aldrich) mixed with H₂O₂ solution (30% concentration, Aldrich). Its mix ratio of 1:10 by weight was heated at the temperature of 1000°C for a few minutes under normal atmospheric pressure.

In order to fabricate ethanol sensors based on the synthesized *T*-ZnO, the *T*-ZnO was mixed with polyvinyl alcohol (6% by weight) and then screened onto the alumina substrate with gold inter-digital electrodes. The sensing area was about 3.0 mm x 3.0 mm. The *T*-ZnO sensor was annealed at 550°C under normal atmosphere for 6 hr, and then cooled down naturally to room temperature. The effect of Au nanoparticles doping on the surface of the *T*-ZnO sensor was also

studied. The sensor was dropped with 0.05%mol Au nanoparticles and then, heated at 350°C for 3 hr. The *T*-ZnO and Au/*T*-ZnO sensors were also characterized by FE-SEM, EDS, and XRD, respectively and tested for ethanol sensing properties.

The ethanol sensor response was studied in a gas flow chamber under an ethanol vapor (50, 100, 500 and 1000 ppm) atmosphere at different temperatures. Typically, ethanol sensitivity or sensor response (S_g) is defined as R_{air}/R_{gas} [10, 12, 14, 15], where R_{air} is the electrical resistance of the sensor in air, and R_{gas} is its resistance in ethanol-air mixed gas.

Results and discussion

The synthesized product from Zn and H₂O₂ mixture having four-legs so called zinc oxide tetrapod structure as clearly observed in Fig. 1(a). The length of the *T*-ZnO is about 8.17±1.17 μm and the cross-sectional size, which is average of diameter at the tip of the leg is normally less than 50 nm. The inset in Fig. 1(a) shows the Au nanoparticles doping on the surface of the *T*-ZnO. The chemical composition of the Au/*T*-ZnO is shown in Fig. 1(b). The EDS spectrum indicates that the atomic composition ratio of Zn:O:Au is about 48.54:51.43:0.04% (1:1:0.05%). Both the *T*-ZnO and the Au/*T*-ZnO having a hexagonal shape correspond to hexagonal ZnO structure as shown in Fig. 1(c). The peak profiles show the pure hexagonal ZnO [9,10,13]. It is clearly seen that no Au peak is observed in the pattern. The disappearance of the Au peak may be due to the Au doping concentration being less than the detection limit of the XRD experiment. These results are in agreement with the FE-SEM results indexed as a hexagonal wurtzite structure of both *T*-ZnO and Au/*T*-ZnO. These fitted profiles show the hexagonal unit cell with $a = 3.2511 \text{ \AA}$ and $c = 5.0287 \text{ \AA}$.

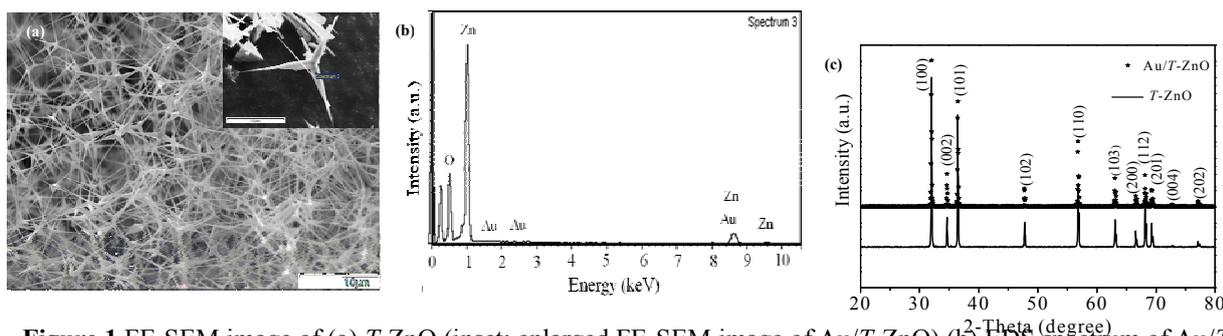


Figure 1 FE-SEM image of (a) *T*-ZnO (inset: enlarged FE-SEM image of Au/*T*-ZnO) (b) EDS spectrum of Au/*T*-ZnO and (c) diffraction patterns of *T*-ZnO and Au/*T*-ZnO.

The sensors were tested to ethanol concentration of 1000 ppm at temperatures of 260°C-360°C as shown in Fig. 2(a) and (b), showing cycles of a resistance-temperature response of the *T*-ZnO and Au/*T*-ZnO sensors, respectively. It is well-known that gas sensing mechanism of the most metal oxide semiconductor sensors is based on adsorption between oxygen ions on the surface of sensor and target gas [10, 14-15, 16].

The plots of the sensor response at different ethanol concentrations ranging from 50 to 1000 ppm were shown in Fig. 2(c) and (d). It is clearly observed that the resistance in air and its sensor response of the Au/*T*-ZnO sensor were higher than that of the *T*-ZnO sensor. The data revealed that the optimum sensitivity is about 44 and 87 at 320°C and 340°C for the *T*-ZnO and Au/*T*-ZnO sensors, respectively, suggesting that the enhancement of sensitivity becomes more evident at higher ethanol concentrations. Moreover, at the optimum temperature the Au/*T*-ZnO sensor exhibited the highest sensor response. It can be clearly seen that the Au/*T*-ZnO sensors exhibit higher sensor response than that of the undoped *T*-ZnO sensors for entire ethanol concentrations. The results demonstrated the ability of the Au doping to greatly improve the sensitivity of the *T*-ZnO based ethanol gas sensors. Due to size-dependent catalytic property and spillover effect, Au nanoparticles are very interesting for doping in ZnO gas sensor as compared with Au powder-doped ZnO sensor [7, 11, 17].

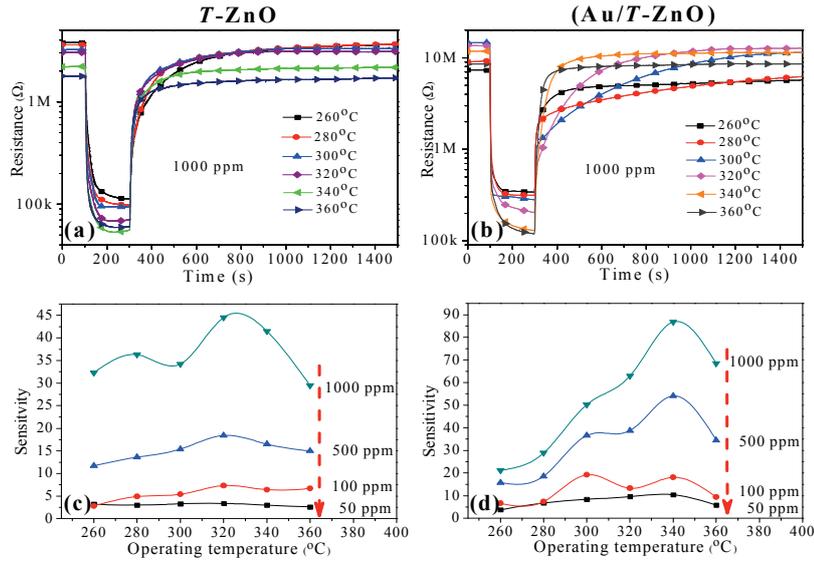


Figure 2 Resistance-temperature response of (a) *T*-ZnO sensor and (b) Au/*T*-ZnO sensor tested under the ethanol vapor of 1000 ppm at various temperatures. Sensitivity-temperature of (c) *T*-ZnO sensor and (d) Au/*T*-ZnO sensor at ethanol concentration of 50-1000 ppm.

The oxygen ions on the surface of the Au/*T*-ZnO are active with the ethanol molecule and give up the electrons from the surface back to the conduction band of ZnO semiconductor [16]. The enhancement of the sensor response can be explained by the sensor response formula for explaining the sensors based on ZnO [9-10, 16]:

$$S_g = \frac{R_a}{R_g} = \frac{\Gamma_t k_{Eth}(T) [O_{ads}^{ion}]^b}{n_0} C_g^b + 1 \quad (1)$$

where Γ_t is a time constant, $k_{Eth}(T)$ is a reaction rate coefficient between adsorbed oxygen ions with ethanol molecules that depends on the operating temperature, O_{ads}^{ion} is adsorbed oxygen species, C_g^b is the ethanol concentration and n_0 is the electron density of the sensor. Generally, temperature dependence of sensor response is controlled by two parameters; $k_{Eth}(T)$ and n_0 . Then these parameters increase exponentially with increasing temperature. However, sensor response is proportional to $k_{Eth}(T)$ but inversely proportional to n_0 .

In our case, Au nanoparticles could have effects on the sensor response through O_{ads}^{ion} , n_0 , and $k_{Eth}(T)$. The dispersion of the Au nanoparticles on the *T*-ZnO surface provides more active sites for oxygen adsorption due to the catalytic effect of the Au nanoparticles [12, 17]. Then the adsorbed oxygen captures electron in the *T*-ZnO to form oxygen ion. Therefore, the *T*-ZnO loses more carrier electrons, leading to lower electron concentration, n_0 , and causing a larger depletion layer at the *T*-ZnO surface. The less electrons and larger depletion layer on *T*-ZnO surface are also explained in terms of the formation of nano-Schottky barriers like junctions on the surface with higher potential barrier resulting in higher resistance [12, 17]. This resulted in higher resistance of the Au/*T*-ZnO sensor comparing to *T*-ZnO sensor in air. The increase of the adsorbed oxygen density and the decrease of electron concentration led to the enhancement of the sensor response of the Au/*T*-ZnO sensor.

Moreover, the Au nanoparticles also act as a catalyst for the reaction between adsorbed oxygen ions and ethanol molecules due to a reduction of activation energy [11]. Thus, reaction rate coefficient increases and results in enhancement of the sensor response. In terms of the reaction rate constant between the adsorbed oxygen species and the ethanol vapor, $k_{Eth}(T)$ in the effect can be explained by the following reactions:

