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Sheng-Joue Young (✉ youngsj@nuu.edu.tw)

National United University

Yi-Hsing Liu

National Cheng Kung University

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High selectivity to ethanol gas sensor based on ZnO nanosheets decorated with Ag nanoparticles by aqueous solution and photochemical deposition

Sheng-Joue Young^{a,}, Yi-Hsing Liu^b*

^a Department of Electronic Engineering, National United University, Miaoli 36063, Taiwan

^b Institute of Microelectronics and Department of Electrical Engineering, Center for Micro/Nano Science and Technology, Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 701, Taiwan

*E-mail: shengjoueyoung@gmail.com; youngsj@nuu.edu.tw

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ABSTRACT

We demonstrated the fabrication of Ag NPs decorated ZnO NSs on a glass substrate using the aqueous solution and photochemical deposition method. The synthesis process is room temperature. This two-dimensional ZnO NSs can increase the performance of gas sensors due to increase the surface-to-volume ratio. Through increasing the surface-to-volume ratio of nanostructures, it is possible to increase the absorption portion of the target gas. In addition, noble metal NPs attached to the ZnO nanostructure can also increase the performance of gas sensors because Ag NPs act as strong electron acceptors, it will be induced enhanced electron depletion

layer. As a result, the Ag NPs decorated ZnO NSs gas sensor has high selectivity to ethanol, as well as improved gas sensing performance to ethanol as compared to ZnO.

1 INTRODUCTION

In recent years, the development of gas sensors is very mature, because the harmful or toxic gases, whether human or the environment will cause damage. Volatile organic compounds (VOC) are almost always present in the indoor environment, which the indoor air quality related. When exposed to VOC in the environment, it can cause health effects and cause so-called sick construction syndrome for human ^{1,2}. Zinc Oxide (ZnO), itself is an n-type semiconductor material. It has some unique physical, chemical, optical, and electrochemical characteristics, such as wide and direct band-gap (3.37eV), piezo electric characteristic, large exciton binding energy (60meV), thermal stability at room temperature, non-toxicity, manufacturing ease, and low cost ^{3,4}. Among of them, the various morphologies of ZnO include nanodiscs, nanowires (NWs), nanotubes, nanorods (NRs), nanoplates, nanopins, and nanosheets (NSs) have also been fabricated ⁵⁻¹¹. ZnO nanostructure have many synthetic methods, such as hydrothermal method (HTM), chemical vapor deposition (CVD), aqueous solution methods (ASM), pulsed laser deposition (PLD), electrochemical deposition (ECD), and electron-beam lithography (EBL) ^{8, 12-19}. Currently, ZnO nanostructures have been applied to optical and electronic devices, such as field-effect transistors (FETs), UV photodetectors (UV PD), light emitting diodes (LEDs), glucose sensors, varistors devices, gas sensors ²⁰⁻²⁸.

Many metal oxide semiconductor sensors including SnO₂, ZnO, WO₃, In₂O₃, and Fe₂O₃ have applied in detecting toxic and VOCs gas. ZnO has good sensitive to toxic and VOCs gas gases because of its excellent performance for chemically and thermally aspect ²⁹. As is well known, the

surface morphology and structure can affect performance of the gas sensor, so that bulk materials are too difficult to achieve highly sensitive properties. To improve the performance of gas sensors, we can proceed from structure of metal oxide semiconductor. For example, adjust structure defects or fabricate composite structure, including decorating noble palladium, platinum, aurum, silver (Ag) nanoparticles on the surface of metal-oxide semiconductor³⁰⁻³³. These factors can be changed gas sensing performance, such as sensitivity of detecting gas, force on the detection of target gas, decreasing detection response/recovery times and power consumption for sensor operating temperature^{34,35}. Hsueh et al. reported that Pt modified ZnO NWs-based ammonia sensors exhibited a better response than pure ZnO NWs³⁶. Zou et al. reported that Au modified ZnO microwires-based ethanol sensors exhibited a better response than pure ZnO microwires³⁷. However, the price of noble metals above is more expensive.

In the paper, the Ag NPs decorated ZnO NSs ethanol gas sensor was prepared on glass substrate by aqueous solution method and photochemical method. The physical, and electrical properties of the Ag NPs decorated ZnO NSs gas sensor were discussed. The both sensors gas sensing mechanism study among the ZnO and Ag NPs decorated ZnO NSs were performed. Our results indicate that Ag NPs decorated ZnO NSs sensor exhibited excellent performance for ethanol detection.

2 EXPERIMENTAL

In this work, the main precursor include silver nitrate (AgNO_3 , purity 99%), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, purity 99%), sodium hydroxide (NaOH) and sodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$) to fabricate Ag NPs decorated ZnO NSs on glass substrate. All experiments are used to distilled water as solvent. Before fabricating Ag NPs decorated ZnO NSs on glass substrate, a seed layer (ZnO) was deposited by radio frequency sputter. The seed

layer was prepared on glass substrate according to previously reported procedures ²². Then, the precursor solution was prepared for the synthesis of ZnO NSs, which the proportion of precursors were 0.1 M of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.4 M of NaOH. The two precursors were separately dissolved in 75 mL distilled water and stirring for 10 min. The ZnO/glass substrate is set on a self-made holder. The two precursors solution was poured slowly into a 150 mL beaker. After stirring for 1 min, the ZnO/glass substrate was immersed in the synthetic aqueous solution. During synthesis process, the synthesis solution kept stirring for 1 hr. Finally, the ZnO NSs was washed several times with distilled water. The ZnO NSs was prepared on glass substrate according to previously reported procedures ³⁸. Ag NPs was synthesized by using photochemical method at room temperature. The precursor solution was prepared by 0.5 mM of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ and 0.5 mM of AgNO_3 solution in distilled water stirring for 10 min. The sample was immersed in solution and irradiated under UV light (4W, 254 nm) for 15 min. After the completion of adsorption process, the sample was removed from synthetic solution and cleaned in distilled water. Finally, both samples were dried for 24 hr.

The ZnO and Ag NPs decorated ZnO NSs samples were measured by X-ray diffraction (XRD) on a Bruker D8 Discover diffractometer (source: $\text{Cu-K}\alpha$ radiation). The range of scanning is between 20° to 80° . The morphology of synthesis materials was investigated on a field-emission scanning electron microscope (SEM, Hitachi S-4800 type I). Then, the lattice and crystal of ZnO and Ag NPs were recorded on a high-resolution transmission electron microscope (HRTEM, Philips Technai-F20-G2 FEI-TEM). The two electron microscopes were carried on energy dispersive identification to analyze elemental composition of the sample. On the other hand, the element composition can also be verified by X-ray photoelectron spectroscopy (XPS).

The gas sensing measurement of ZnO NSs and Ag NPs decorated ZnO NSs sensors were carried on 10.6 L chamber. The chamber equipped with a heater, fan, mass flow controller and multimeter (MFC). Before measured gas sensor, the ZnO NSs and Ag NPs decorated ZnO NSs samples were coated silver paste to both ends of sample and dried in the oven at room temperature for 24 hr, which the sensor working area was 25 mm². Then, the sensor was placed on the heater in the chamber and connected to semiconductor multimeter analyzer (Keithley 2410). The schematic diagram of gas measurement system as shown [Figure 1](#). Before injecting the target gas, ZnO NSs and Ag NPs decorated ZnO NSs sensors were preheated until resistance stability of sensor. The working temperature is set in the range of 150 to 300 °C, which each measurement is interval at 30 °C. During measurement, the initial environment of chamber was filled air until resistance stability of sensor. Subsequently, the target gases were introduced to the chamber by MFC and recorded resistance and current value of sensors from semiconductor multimeter analyzer. The response (R) of ZnO NSs and Ag NPs decorated ZnO NSs sensors were defined as $R = I_{\text{gas}}/I_{\text{air}}$, where I_{air} and I_{gas} were initial air and injection of target gases current value, respectively.

3 RESULTS AND DISCUSSION

Currently, there are very many techniques for photochemical reduction of Ag NPs.^{39,40} In our case, the method is use sodium citrate as a reducing agent. The citrate ions can effectively reduce silver ions. And then it can be increased reduction rate for silver ions by irradiated with ultraviolet light. The citrate-assisted mechanism of photochemical reduction of Ag⁺ can be expressed as ^{41, 42}:

It was formed CO_2 , acetone-1,3-dicarboxylate, H^+ ion, and electrons when the sodium citrate dissolved in deionized water and expose to the UV light. According to the literature, the citrate solvent and Ag ion are easily formed complex⁴³. The Ag ion can receive many electrons because the complexation provides transform pathway when expose UV light. In reduction process, there are two behaviors what the Ag atoms nucleate into Ag NPs, such as homogeneously and heterogeneously nucleation. Homogeneously nucleation form usually in the solution. Heterogeneously nucleation form by citrate ions as the stabilizer or heterogeneous structure surface such as ZnO. According to the literature, homogeneous nucleation requires a large surface activation energy, which indicates that heterogeneous nucleation is more effective nucleation than homogeneous nucleation⁴⁴.

Figure 2 show the morphology images of ZnO NSs and Ag NPs decorated ZnO NSs. It can be found that the ZnO NSs exhibit flaky and dense staggered. In addition, the Ag NPs were uniformly distributed on the surface of ZnO NSs as shown top view image. The size of ZnO NSs was about 1.87 μm (average height), 14 nm (average thickness) and the size of Ag NPs was approximately between 35 to 55 nm through scanning electron microscope preliminary estimates. The elemental composition analysis was using EDX spectrum for Ag NPs decorated ZnO NSs sample as shown inset Figure 2. The result indicated that the consist of Zn, O and Ag for Ag NPs decorated ZnO NSs, which the respective Ag content of the sample is 1.88% atoms ratio.

Figure 3 shows each crystal phase of ZnO NS and Ag NPs decorated ZnO NSs. For ZnO NSs, the peaks were located on 31.88, 34.46, 36.36, 47.63, 56.61, 62.88 and 67.95, respectively (each peak is 2 theta angle). These peaks correspond to crystal phase of ZnO wurtzite structure from JCPDS Card (number: 36-1451) database comparison, including (002), (100), (101), (102), (110), (103), and (112) phase. For Ag NPs decorated ZnO NSs, the peaks were located on 33.14° and

44.16°, respectively. The two peaks correspond to crystal phase of Ag from JCPDS Card (number: 04-0783) database comparison, including (111) and (200) phase. Among them, the intensity of (002) phase is highest. The result imply that the ZnO NSs preferentially grow along the c-axis direction. It was worth noting that ZnO NS and Ag NPs decorated ZnO NSs samples was not observed other crystal phase.

Figure 4 shows element composition of Ag NPs decorated ZnO NSs from XPS measurement. In Figure 4 (a), the mainly element composition including Zn, O, Ag and C, respectively. Among them, the binding energy of Zn2p spectrum is Zn 2p_{1/2} (1042.19 eV) and Zn 2p_{3/2} (1019.11 eV) as shown Fig 4 (b). The result indicating that the sample exist in Zn element and form Zn²⁺^{45, 46}. In Figure 4 (c), the binding energy of O1s spectrum is 527.93 eV and 529.136 eV. According to past report, the O1s spectrum contain binding of material and environment, such as lattice oxygen of ZnO and oxygen of hydroxyl^{47, 48}. In Figure 4 (d), the two peaks of Ag 3d_{5/2} (365.25 eV) and Ag 3d_{3/2} (371.24 eV) are typical binding energy in Ag 3d spectrum⁴⁹. These element compositions analysis can prove Ag NP exist in the surface of ZnO NSs.

To measure the high-resolution morphology image through FEI-TEM, the sample need to prepare pre-work. First, we used a scalpel to scrape the Ag NPs decorated ZnO NSs from glass substrate. Second, the powder of Ag NPs decorated ZnO NSs was put into glass bottle and pour 1 mL of ethanol. Then, the glass bottle place into ultrasonic oscillator and shake for 30 minutes. Finally, the solvent dripped onto the copper mesh and dried at 80°C several times. Fig 4 show high-resolution morphology images of Ag NPs decorated ZnO NSs. The low-magnification TEM image can be observed that Ag NPs decorated surface of ZnO NSs as shown Figure 5 (a). Also, one can see that each NP is well decorated onto the NS surface. Among them, the lattice spacing of ZnO NS is 0.264 nm and the d spacing is corresponding to the (002) plane. On the other hand,

t the lattice spacing of Ag NP is 0.247 nm and the d spacing is corresponding to the (111) plane. The selected area electron diffraction (SAED) pattern indicates that the sample exhibit the two crystal phases of ZnO NS and Ag NPs. [Figure 5 \(b\)](#) and [figure 5 \(c\)](#) shows the mapping images of the Ag NPs decorated ZnO NSs through EDX spectroscopic of transmission electron microscope. The mapping images corresponding to three elements (Ag, Zn, and O) from the sample, which Ag NPs contain approximately 8.707 % of Ag atomic. This result can be further indicated that the Ag NPs was decorated on the surface of ZnO NSs.

It is important factor which the operating temperature of metal oxide gas sensors because operating temperature of sensor directly affect the sensor performance. Thus, we design different operating temperature to find the optimal working conditions of the sensor. [Figure 6 \(a\)](#) shows different operating temperature (150, 180, 210, 240, 270 and 300°C) response of the two sensors exposed to 100 ppm ethanol vapor. The response of ZnO NSs sensor was 1.223, 1.516, 1.52, 1.576, 1.425 and 1.732, respectively. The response of Ag NPs decorated ZnO NSs sensor was 1.117, 2.012, 4.914, 6.57, 28.78 and 18.8, respectively. It can be clearly seen that the Ag NPs decorated ZnO NSs sensor has the highest response at operating temperature of 270°C, then decrease gradually. Therefore, the optimal operating temperature for both sensors were set at 270°C.

[Figure 6 \(b\)](#) shows the different ethanol concentration dynamic responses curve of the ZnO NSs and Ag NPs decorated ZnO NSs gas sensor with exposed to 50, 100, 200, 300, 500, 700 and 1000 ppm. The responses of the ZnO NSs sensor was 1.177, 1.318, 1.468, 1.729, 1.875, 2.08 and 2.199, respectively. The responses of the Ag NPs decorated ZnO NSs sensor was 19.064, 28.784, 49.785, 66.17, 102.694, 126.43 and 160.05, respectively. It can be also seen that the Ag NPs decorated ZnO sensor provides high response sensitivity than pure sensor, and the sensitivity rapidly increases with increasing ethanol concentration. As shown [Figure 6 \(c\)](#), the dynamic

response/recovery curve in seven period, which the ZnO NSs and Ag NPs decorated ZnO NSs ethanol gas sensor at 270 °C (ethanol as 100 ppm). It can be observed that each cycle is very stability and reproducibility.

To explain the working mechanism of the Ag NPs decorated ZnO NSs gas sensor, we have prepared some models to explain these phenomena as shown [Figure 6 \(d\)](#). When sample exposed to the atmosphere, the surface of ZnO NSs will adhere to ambient gas molecules, including oxygen, water vapor and other gas. As the increase in operating temperature, larger amount oxygen species (O_2^- , O^- , O^{2-}) are adhered on the surface of ZnO NSs. These oxygen molecules captured electrons and generated an electron depletion layer from surface of ZnO NSs. With increasing exposure time, the carrier concentration of ZnO NSs gradually decreased due to oxygen molecules captured electrons, resulting in the resistance of ZnO NSs increased [50, 51](#). When injecting the target gas (ethanol vapor), ethanol molecules occupied and reacted the oxygen molecules position from the surface of ZnO NSs, resulting in more electrons enter ZnO NSs after the reaction and the captured electron electrons released to conduction band from oxygen molecules [52, 53](#). The two process reduced the width of electron depletion layer and decreased resistance of ZnO NSs. The related reactions process can be expresses as follows:

It can act as a catalytic activity to target gases and oxygen for a noble metal decorated on ZnO NSs. Among them, oxygen species (O_2^- , O^- , O^{2-}) can be lightly adsorbed on the surface of Ag NPs, resulting in many electrons to be captured from the conduction band of ZnO. As mentioned above, oxygen molecules captured electrons and generated an electron depletion layer from surface of ZnO NSs ⁵⁴. After Ag NPs adsorption, the electron depletion layer will also increase from the surface of Ag/ZnO. From results observed the current value of Ag NPs decorated ZnO NSs sensor is lower than ZnO NSs sensor before the target gas is not injected. (In the atmosphere) as shown Fig5 (c). After injecting the ethanol vapor, ethanol molecules occupied and reacted the oxygen molecules position from the surface of Ag/ZnO NSs, resulting in electron depletion layer narrowed. This phenomenon cause electrons more easily back to ZnO NSs. On the other hand, a part of the ethanol gas will chemically react with oxygen gas and more electron enter ZnO NSs in reaction process. From results observed the current value of ZnO NSs and Ag NPs decorated ZnO NSs significant increase. Although, the current value of Ag NPs decorated ZnO NSs sensor did not surpass ZnO NSs sensor. But the overall on/off ratio significant increase (as response define $R = I_{gas}/I_{air}$).

To compare with other types of reducing gas, we analyze four types of VOC gases, including methanol, acetone, ethanol and isopropanol. Figure 7 shows the different VOC gases response value for the ZnO NSs and Ag NPs decorated ZnO NSs sensor. The concentration of each gas sensing is injected into 100 ppm in chamber and the operating temperature is 270 °C. The results show that ethanol gas gain the highest response value among all VOC gases (28.784). Table1 shows the different material of ethanol gas sensing performances comparing than Ag NPs decorated ZnO NSs (this paper). These results imply that the Ag NPs decorated ZnO NSs has

excellent selectivity for ethanol gas than VOC gases. Moreover, noble metal can effectively improve the performance of gas sensing.

4 CONCLUSION

In the work, the Ag NPs decorated ZnO NSs had been synthesized on ZnO/glass substrate through two simple steps for chemical solution and photochemical deposition synthesis. The low and high magnification electronic images confirmed that the Ag NPs were distributed on the surface of ZnO NSs. The average length and diameter of ZnO NSs were found to be 1.87 μm and 14 nm. The size of the Ag NPs was 35 nm to 55 nm. To investigate the optimum operating temperature sensor, it can be clearly seen that the Ag NPs decorated ZnO NSs gas sensor has the highest response at operating temperature of 270°C. The Ag NPs decorated ZnO NSs gas sensors responded towards the ethanol gas concentration of 50 and 1000 ppm with the sensor responses of 19.064 and 160.05, respectively. As a result, the Ag NPs decorated ZnO NSs gas sensor has high selectivity to ethanol, as well as improved gas sensing performance to ethanol as compared to pure ZnO.

FIGURES:

Figure 1. Schematic diagram of homemade gas measuring system.

Figure 2. SEM images of ZnO NSs and Ag NPs decorated ZnO NSs.

Figure 3. XRD pattern of the ZnO NSs and Ag NPs decorated ZnO NSs

Figure 4. XPS spectrum of (a) full spectrum, (b) Zn 2p, (c) O 1s, and (d) Ag 3d in Ag NPs decorated ZnO NSs.

Figure 5. (a) Low, high-magnification TEM image and SAED pattern of Ag NPs decorated ZnO NSs. (b) EDX spectrum and (c) Mapping images (Zn, O, Ag) of Ag NPs decorated ZnO NSs.

Figure 6. (a) shows the response of the ZnO NSs and Ag NPs decorated ZnO NSs gas sensor measured at 150°C to 300°C exposed to 100 ppm ethanol vapor. (b) the responses value of the ZnO NSs and Ag NPs decorated ZnO NSs gas sensor when exposed to 50, 100, 200, 300, 500, 700, 1000 ppm ethanol vapor, and (c) Typical dynamic response/recovery curve in seven period, which the pure and Ag NPs decorated ZnO NSs ethanol gas sensor at 270 °C (ethanol as 100 ppm). (d) shows the possible gas-sensing mechanism of ZnO NSs and Ag NPs decorated ZnO NSs in the air ambient and ethanol, respectively.

Figure 7. Response of the pure and Ag NPs decorated ZnO NSs sensor was measured in different gases, including methanol, acetone, isopropyl and ethanol vapor. The concentration of each gas is fixed to be 100 ppm and the operating temperature is 270 °C .

TABLE 1 COMPARISON OF ETHANOL SENSING PERFORMANCES OF DIFFERENT ZnO GAS SENSORS

nanostructure	C ₂ H ₅ OH concentration (ppm)	Working temperature (°C)	Sensor response (R) $I_{\text{gas}} / I_{\text{air}}$	Ref
ZnO NWs	500	300	~10	[29]
Au-ZnO MWs	10	15	~2	[37]
Au-ZnO NWs	10	300	1.65	[55]
Pd-ZnO nanostructures	500	300	280.7	[56]
Au-ZnO nanostructures	500	300	73	[56]

AUTHOR INFORMATION

Corresponding Author

Sheng-Joue Young—*Department of Electronic Engineering, National United University, Miaoli 36003, Taiwan; E-mail: shengjoueyoung@gmail.com; youngsj@nuu.edu.tw*

Yi-Hsing Liu—*Institute of Microelectronics and Department of Electrical Engineering, Center for Micro/Nano Science and Technology, Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 701, Taiwan; E-mail: yhliu0870@gmail.com*

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

NSs, nanosheets, NWs, nanowires, NRs, nanorods, NPs, nanoparticles, MWs, microwires, VOC, volatile organic compound,

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Figures

Figure 1

Schematic diagram of homemade gas measuring system.

Figure 2

SEM images of ZnO NSs and Ag NPs decorated ZnO NSs.

Figure 3

XRD pattern of the ZnO NSs and Ag NPs decorated ZnO NSs

Figure 4

XPS spectrum of (a) full spectrum, (b) Zn 2p, (c) O 1s, and (d) Ag 3d in Ag NPs decorated ZnO NSs.

(a)

(b)

(c)

Figure 5

(a) Low, high-magnification TEM image and SAED pattern of Ag NPs decorated ZnO NSs. (b) EDX spectrum and (c) Mapping images (Zn, O, Ag) of Ag NPs decorated ZnO NSs.

Figure 6

(a) shows the response of the ZnO NSs and Ag NPs decorated ZnO NSs gas sensor measured at 150 °C to 300 °C exposed to 100 ppm ethanol vapor. (b) the responses value of the ZnO NSs and Ag NPs decorated ZnO NSs gas sensor when exposed to 50, 100, 200, 300, 500, 700, 1000 ppm ethanol vapor, and (c) Typical dynamic response/recovery curve in seven period, which the pure and Ag NPs decorated ZnO NSs ethanol gas sensor at 270 °C (ethanol as 100 ppm). (d) shows the possible gas-sensing mechanism of ZnO NSs and Ag NPs decorated ZnO NSs in the air ambient and ethanol, respectively.

Figure 7

Response of the pure and Ag NPs decorated ZnO NSs sensor was measured in different gases, including methanol, acetone, isopropyl and ethanol vapor. The concentration of each gas is fixed to be 100 ppm and the operating temperature is 270 °C.