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Low temperature acetylene gas sensor based on Ag nanoparticles-loaded ZnO-reduced graphene oxide hybrid

A.S.M. Iftekhar Uddin, Duy-Thach Phan, Gwiy-Sang Chung*

School of Electrical Engineering, University of Ulsan, 93 Daehak-ro, Nam-gu, Ulsan 680-749, South Korea

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ABSTRACT

This paper scrutinizes the fabrication of a chemiresistive type of acetylene (C_2H_2) gas sensor by synthesizing a silver (Ag)-loaded zinc oxide (ZnO)-reduced graphene oxide (Gr) hybrid via a facile chemical route. The as-synthesized hybrid was characterized in detail in terms of its structural, morphological and compositional properties. The physical properties of the hybrid exhibited a well-structured crystalline nature and mixed phases of Ag, Gr, and ZnO. The morphological characterization revealed that particle-like nanostructures of the ZnO and Ag mixer were well distributed and closely affixed onto the surface of thin-layer reduced graphene oxide sheets. At an optimum temperature of 150 °C, the 3 wt% Ag-loaded ZnO–Gr hybrid showed preferential detection of acetylene gas with a response value of 21.2 for 100 ppm gas concentrations. The fabricated sensor showed a low detection limit of 1 ppm, fast response and recovery times of 25 s and 80 s, respectively, and good repeatability. Experimental results also showed that the synthesized hybrid had a negligible relative humidity (RH) effect up to 31% RH, and then deteriorated significantly with increasing RH concentrations. After detailed examination, we conclude that an Ag-loaded ZnO–Gr hybrid could be an effective means of fabricating high-performance practical C_2H_2 sensors.

1. Introduction

Acetylene (C_2H_2) is a colorless, flammable unsaturated hydrocarbon gas with a distinctive odor, widely used as a fuel in oxyacetylene welding and cutting of metals, and as a raw material in various industrial and consumer products, such as acetaldehyde, synthetic rubber, paints, fabric and floor coverings, dry-cleaning solvents, and insecticide sprays. Generally, acetylene is not toxic, but when generated from calcium carbide, can contain toxic impurities such as traces of phosphine and arsine. Notable hazards are associated with its intrinsic instability, especially when it is liquefied, pressurized, heated or mixed with air. Consequently, the combustion of acetylene can produce a large amount of heat (its highest flame temperature is about 3300 °C), and it can explode with extreme violence if the absolute pressure of the gas exceeds 103 kPa (15 psi). Therefore, for environmental and safety purposes, the development of a highly effective C_2H_2 sensor has become increasingly important to meet the demands of accurate environmental monitoring, for early leakage warning and for avoiding incomplete combustion. However, information on C_2H_2 sensors is still very limited in the literature.

Most recently, Wang et al. [1] showed successful advancement in C_2H_2 sensing with a response of 17 (for 2000 ppm) at 250 °C by synthesizing nickel-doped zinc oxide (ZnO) nanofibers. Tamaekong et al. [2] reported a Pt/ZnO thick film-based C_2H_2 sensor at a working temperature of 300 °C with a sensor response of 43 (for 1000 ppm). Zhang et al. [3] hydrothermally synthesized a hierarchical nanoparticle (NP)-decorated ZnO microdisk-based C_2H_2 sensor with a large detection range (1–4000 ppm) and very high response (7.9 for 1 ppm) at 420 °C. Dong et al. [4] reported arc plasma-assisted Ag/ZnO composites for C_2H_2 sensing, which had a maximum response of 42–5000 ppm C_2H_2 at 120 °C. In addition, SnO_2 NPs [5], Pd–SnO_2 [6], Sm_2O_3–SnO_2 [7], Au/MWCNT [8], Ag/Pd–SiO_2 [9], etc, have been studied for C_2H_2 sensing. However, high working temperature, low sensitivity and synthesis-process complexity, are still a great challenge.

In the last few years, among widely investigated metal oxide groups, ZnO has attracted considerable interest in sensing applications to detect volatile and toxic gases due to its high conductive electron mobility and good adsorption characteristics under the working conditions of the sensors [10–15]. However, drawbacks like low sensitivity, poor selectivity and high working temperature limit practical applications in the gas-sensing area (i.e., flammable

* Corresponding author. Tel.: +82 52 259 1248; fax: +82 52 259 1686.
E-mail address: gschung@ulsan.ac.kr (G.-S. Chung).
URL: http://home2.ulsan.ac.kr/user/gschung (G.-S. Chung).

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and explosive environments). Therefore, to overcome the shortcomings and to enhance sensing characteristics, researchers have been focusing on metal oxide–metal oxide and metal–metal oxide compositions with numerous synthesis techniques [16–20].

Interestingly, inherent catalytic properties of metal aggregates, dispersed into a metal oxide matrix, modify the surface reactions and greatly enhance the charge carrier separation of the oxide matrix. This phenomenon helps to boost the sensing mechanism, and hence improve sensing performance [21]. Among numerous metals, Ag has attracted immense interest, due to its promising catalytic properties, in the development of photocatalysis [22,23], catalytic oxidation [24], chemical and gas sensing [25,26], etc. A number of Ag–ZnO nanostructure-based high-performance gas sensors have been reported [25,27–30]. Moreover, two-dimensional graphene has concerned much attention since its discovery due to its excellent electrical, chemical and optical properties. Most recently, Fowler et al. [31] discussed chemically derived graphene as a highly sensitive chemical sensor due to its extraordinary carrier mobility. Besides the synergistic interplay between graphene and metal–metal oxide composition, graphene as a template plays a vital role in enhancing the physical properties and sensing performance of the composite materials [19,32–34].

In this context, this paper is focused on the fabrication of a C_2H_2 sensor based on an Ag-loaded ZnO-reduced graphene oxide (Gr) hybrid via a facile chemical route in order to enhance C_2H_2 sensing performance at low operating temperatures. To the best of our knowledge, an Ag-loaded ZnO–Gr hybrid nanostructure-based acetylene gas sensor has not yet been reported in the literature. The fabricated sensor was evaluated systematically in terms of response, response/recovery times and selectivity toward C_2H_2. The humidity effect on the fabricated sensor was also studied in this work. The main aim of this work is to fabricate an effective, high-performance C_2H_2 sensor that can operate at low temperature.

2. Experimental

2.1. Synthesis and characterization

All the chemicals used in the experiment were of analytical grade and obtained from Sigma Aldrich, Dongwoo Fine-Chem., and Dae Jung Chem. & Inds. Co. Ltd. Graphene oxide (GO) was prepared according to the process provided by Hummers and Offeman, and Phan et al. [35,36]. ZnO powder was prepared through a solvothermal method using 4 M of $Zn(NO_3)_2{\cdot}6H_2O$ and 8 M of sodium hydroxide (NaOH) in ethanol, at 120 °C for 8 h and dried at 60 °C. The Ag-loaded ZnO–Gr hybrid was synthesized via a chemical route. In a typical process, an appropriate amount of silver nitrate ($AgNO_3$) was added to the ZnO–GO at 2:1, followed by continuous stirring for 30 min. Hydrazine monohydrate was then used in the mixer as an agent to reduce GO to reduced graphene oxide (Gr) and Ag^+ to Ag atoms at a temperature of 110 °C for 8 h. Various samples were prepared by varying the weight percent (0–5 wt%) of $AgNO_3$ to ZnO, referred to as ZnO–Gr/Ag%: ZG–Ag0, ZG–Ag1, ZG–Ag3, ZG–Ag5.

Phase transition analysis was carried out with an X-ray diffractometer (XRD) (Rigaku Ultima IV) with Cu $K\alpha$ ($\lambda = 0.154056$ nm) radiation with a 2θ scanning range of 10–80°. The surface morphology and the compositional analysis of the as-prepared samples were examined with field emission scanning electron microscopy (FESEM) using a JEOL JSM-7600F (accelerating voltage: 10 kV). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and an energy-dispersive spectrometer (EDS) were carried out using a JEOL JEM-2010F.

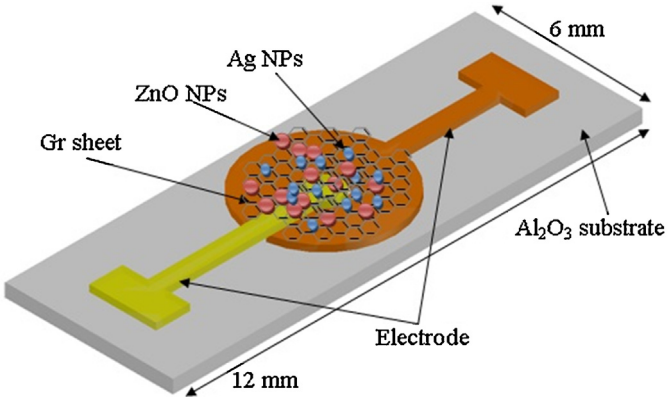

Fig. 1. Schematic diagram of the fabricated sensor device.

2.2. Gas sensing

For electrical and gas sensing measurements, a resistivity-type sensor device was fabricated as follows: two electrodes (dimension: 2 mm × 4 mm, thickness: 100 nm) were fabricated by depositing platinum (Pt) on 6 mm × 12 mm Al_2O_3 substrate by lift-off process. The spacing between two electrodes was 210 μm. The sensing material was then well dissolved in ethanol (1 mg/mL) and deposited on the center of the patterned electrodes using a spray-coating process. The device was dried at 100 °C on a hot-plate until on all solvent evaporates. This step was repeated for 3–4 times. Fig. 1 shows a schematic diagram of the fabricated sensor device. Finally, post-situ annealing in air was carried out with the sensor device at 400 °C for 30 min before gas sensing tests.

Gas sensing measurements were conducted at atmospheric pressure within a temperature range of 25–250 °C for various C_2H_2 concentrations in a sealed chamber using the flow-through technique. The fabricated sensor device was placed in an in-house gas sensor assembly (chamber), and a Keithley probe station (SCS-4200) with a bias voltage fixed at 1 V was used for all measurements and data acquisition. A programmable heater integrated with the sensor holder in the chamber was used to adjust the temperature. A computerized mass flow controller (ATO-VAC, GMC 1200) system was used to vary the concentration of C_2H_2 in synthetic air. The gas mixture was delivered to the chamber at a constant flow rate of 50 sccm (standard cubic centimeters per minute) with different C_2H_2 concentrations. The gas chamber was purged with synthetic air between each C_2H_2 pulse to allow the surface of the sensor to return to atmospheric conditions. The sensor response (S) was calculated using R_a/R_g, where R_a is the resistance of the sensor in the presence of synthetic air, and R_g is the resistance in the presence of C_2H_2 at certain concentrations. The response time and recovery time of the sensor are defined as the time to reach 90% of total resistance change.

3. Results and discussion

3.1. Crystal structure and morphology

The observed XRD patterns of pure ZnO, and 0–5 wt% Ag-loaded ZnO–Gr hybrids are displayed in Fig. 2. The characteristic diffraction peaks of the as-synthesized materials exhibited a well-structured crystalline nature and mixed phases of Gr and ZnO (Fig. 2(b)), and silver, Gr, and ZnO (Fig. 2(c–e)), respectively. Fig. 2a shows the diffraction peaks of pure ZnO. The diffraction peaks of ZnO (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), and (1 1 2) were endowed with a harmonious standard ZnO hexagonal wurtzite structure (JCPDS card No. 36-1451) and the peaks of Ag (1 1 1), (2 0 0) and (2 2 0)