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Chemiresistive Sensor Based on One-Dimensional WO_3 Nanostructures as Non-Invasive Disease Monitors

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Abstract

In this study, a chemiresistive sensor based on one-dimensional WO_3 nanostructures is presented for application in non-invasive medical diagnostics. WO_3 nanostructures were used as an active gas sensing layer and were deposited onto a SiO_2/Si substrate using Pt interdigitated electrodes (IDEs). The IDE spacing was 5 μm and deposition was performed using RF sputter with glancing angle deposition mode. Pt IDEs fabricated by photolithography and dry etching. In comparison with thin film sensor, sensing performance of nanostructure sensor showed an enhanced response of more than 20 times when exposed to 50 ppm acetone at 400°C. Such a remarkable faster response can pave the way for a new generation of exhaled breath analyzers based on chemiresistive sensors which are less expensive, more reliable, and less complicated to be manufactured. Moreover, presented sensor technology has the potential of being used as a personalized medical diagnostics tool in the near future.

Keywords: Metal oxide gas sensors, Chemiresistive sensor, Exhaled breath analyzer, One-dimensional WO_3 nanostructures, Tungsten oxide (WO_3)

1. INTRODUCTION

Exhaled human breath contains several bio-markers that can be used as tools for diagnosing metabolic disorders such as lung cancer, kidney diseases, asthma, and diabetes [1-4]. Among these disorders, diabetes mellitus can be particularly dangerous since it causes chronic high blood sugar for a prolonged period and leads to inefficient wound healing among other complications [4]. Thus, diabetes should be quickly diagnosed as it requires daily management.

In general, exhaled breath contains as many as 300 different gaseous compounds including inorganic molecules such as NO, NH_3 or CO and volatile organic compounds (VOCs) such as acetone, ethane, and isoprene with concentrations ranging from ppb to ppm. Among these compounds, acetone exhalation is caused by fatty acid oxidation and ketoacidosis in diabetic patients due to lack of insulin [5]. Although a few VOCs are successfully detectable by table-top equipment by techniques such as gas chromatography-mass spectrometry (GC-MS) and proton transfer reaction-mass spectrometry (PTR-MS) [6,7], these techniques are not suitable for domestic use, which requires equipment with features such as portability, small form factor, low cost, real-time analysis, and large samples of collected exhaled breath. Chemiresistive sensors based on semiconductor materials offer an alternative to the abovementioned techniques since they offer long-term stability and high sensitivity owing to high electron concentration. Moreover, metal oxide thin films exhibit simple structures, simplicity of operation, low cost, and can be easily applied to semiconductor manufacturing. Chemiresistive sensors therefore offer great potential for detecting chemical compounds. However, metal oxides (Fe_2O_3, In_2O_3, WO_3, and TiO_2) thin film gas sensors poor sensitivity and selectivity [8]. To achieve sub ppb detection, metal oxide gas sensor needs the configuration of nanostructures such as nanowire, nanobelts, and nanorods for higher sensitivity and selectivity.

Herein, we synthesized the chemiresistive sensor based on one-dimensional WO_3 nanostructures by glancing angle deposition (GAD) using RF sputter. These nanostructure sensors have extremely fast response to acetone at elevated temperature. Consequently, highly sensitive properties of nanostructure WO_3

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sensors suggest their great potential for application in high performance exhaled breath analyzer as non-invasive disease monitors.

2. EXPERIMENTAL

2.1 Fabrication of Sensor

One-dimensional WO_3 nanostructure was assembled onto SiO_2/Si substrate with Pt interdigitated electrodes (IDEs) by off-axis RF sputtering with GAD mode [9]. Pt (150 nm thick) IDE patterns of 5 μm spacing were fabricated on a SiO_2/Si substrate using photolithography and dry etching. About 380 nm thin films were deposited onto pre-specified regions (1 mm×1 mm) by a shadow mask at room temperature. A polycrystalline WO_3 target with 2 inch thickness was utilized for the film deposition. The base pressure, working pressure, RF power, and gas flow rate were 2×10^{-6} mTorr, 3 mTorr, 350 W, and 30 sccm, respectively. The deposition rate was about 8.5 nm/min. To make the porous film, the sputtering deposition was carried out at a glancing angle (5°). The fabricated sensor was annealed at 500°C for 60 min in air to crystallize thin film and obtain the higher porous structure.

2.2 Characterization

Field emission scanning electron microscopy (FE-SEM, SU-70 Hitachi) was used to examine the morphology and microstructure of the fabricated sensors array at 15 kV accelerating voltage. The gas sensing properties were measured by external heating in a box furnace. The resistance changes of the sensor were monitored by a voltage source meter (Keithley, 2635A) and then the sensor resistance was measured under a DC bias voltage of 1V and a constant flow rate of 500 sccm. The data files were recorded to a computer through the use of LabVIEW over the GPIB interface.

3. RESULTS AND DISCUSSIONS

3.1 Fabrication of Sensor

Fig. 1(a) shows FE-SEM image of a WO_3 thin film directly deposited by GAD on SiO_2/Si substrate with IDE patterns of 5 μm spacing. The dimensions of overall sensor substrate are 1 cm ×1 cm with pre-specified regions (1 mm×1 mm) as sensing layer. This sensor substrate did not include an integrated heater, and for sensing test was attached to micro heater at the bottom of sensor.

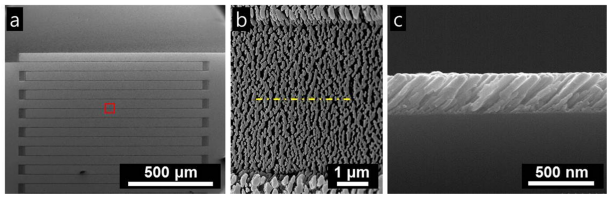

Fig. 1. (a) Plain-view FE-SEM image of active layer (1 mm×1 mm) with Pt IDEs, (b) magnified view of red square area in image "a" showing highly porous WO_3 nanostructure between Pt IDEs, and (c) Cross-sectional FE-SEM image of 45°-inclined one-dimensional nanostructure.

The WO_3 thin film was uniformly formed both on the Pt IDEs and on the SiO_2 surface (Fig. 1(b)). A closer look at the WO_3 film between the Pt IDEs shows a highly porous film with nanostructure elements. Due to self-shadowing effects by vapor flux, a WO_3 film deposition by GAD results in a porous film with 1D nanostructure. The cross-sectional FE-SEM image in Fig. 1(c) shows a highly porous film with finger-like 1D nanostructure. In comparison with compact thin film, the obtained porous metal oxide thin film had a larger specific surface area which makes these one-dimensional WO_3 nanostructure thin films suitable for the effective diffusion and adsorption of gas molecules through the overall film.

3.2 Sensor Measurements

Highly sensitive sensing properties of the nanostructure WO_3 sensor is demonstrated in Fig. 2(a), which displays responses of the sensor to 50 ppm acetone (CH_3COCH_3) as a function of temperature ranging from 200 to 450°C (R_a/R_g ratios for the reducing gases, where R_g and R_a denote the sensors' resistance in the presence and absence of a test gas, respectively). The acetone is a known VOC that lead to relatively very high gas responses by metal oxide gas sensors at high temperature. The response to acetone climaxed around 400°C, while sensitivity to acetone was very low at low temperature. This result is consistent with previous reports that the optimum detection temperature for acetone is a lot higher than those for the NO_x [10]. For this reason, the WO_3 has been known as suitable material with the high selectivity for acetone at high temperature. This selectivity is enhanced in this study as a result of highly porous finger-like nanostructure which caused effective diffusion and absorption of gas molecules.

A typical sensing performance curve of a sensor based on the one dimensional WO_3 nanostructures detecting 50 ppm acetone at 400°C is shown in Fig. 2(b). Upon exposure to reducing acetone,

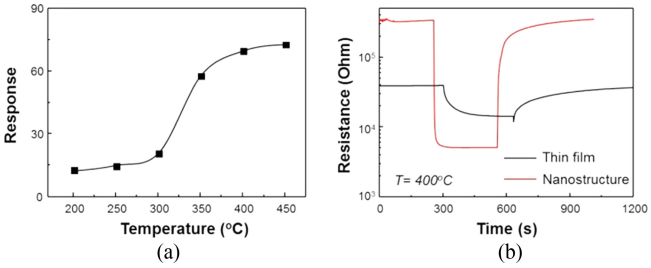

Fig. 2. (a) Gas responses to 50 ppm of acetone (CH_3COCH_3) over the temperature range of 200 to 450°C and (b) sensing performances of the nanostructured WO_3 sensor and a sensor based on WO_3 thin film to 50 ppm acetone at 400°C.

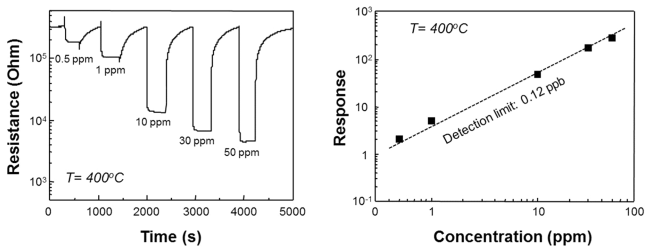

Fig. 3. (a) Dynamic sensing transients of the nanostructure WO_3 sensor to 0.550 ppm acetone at 400°C and (b) response of the two sensors as a function of acetone concentration. Theoretical detection limit of sensors is presented.

the sensor quickly responds with decrease in resistance, which confirms that the WO_3 film is an n-type semiconductor. Compared with the reference thin film sensor, the developed sensor exhibited extremely high responses to acetone. Moreover, for 50 ppm, the response to acetone was about 70, which was noticeably higher than pre-reported results [10]. However, if thin film sensor arrays are exposed to high humidity (> 80%), the sensitivity of the sensor can be reduced due to the interaction between adsorbed molecules and decrease of the depletion area on the surface.

As shown in Fig. 3(a), the response curve of the nanostructured WO_3 sensor to 0.550 ppm acetone at 400°C is stable gas performance with relatively fast response time and full recovery time. Even at low concentration of 500 ppb., the nanostructure WO_3 sensor showed clear response. To the best of our knowledge, the obtained response is the highest value ever reported for metal oxide thin film sensors. Based on the response change with the acetone concentration, the response values (R_a/R_g) of the sensors are plotted in logarithmic scale (Fig. 3(b)). The linear relationship between the response value and the concentration demonstrates the feasibility of the sensor for real applications.

By applying a linear least-squares fit to the data, the theoretical detection limit of the sensor is estimated to be as low as 0.12 ppb. These results suggest that the porous nanostructure is responsible for the high response of the sensor. We also believe that the narrow necks regions (1030 nm) between finger-like nanostructures are changed to the full depletion area (space charge layer) by acetone adsorption, which in conjunction with 30 nm Debye length of WO_3 play a critical role in the remarkably enhanced sensing properties of the sensor. The detection limit of the nanostructured WO_3 sensor to acetone is much lower than the ambient air quality standard levels for acetone (1 ppm) in European Union, the Unites States, and Korea [11-13]. Furthermore, these sensors are sufficient for diagnosing diabetes (standard: 1.8 ppm) as a non-invasive disease monitor [4]. This illustrates the promising potential of these sensors for applications in the ultrahigh sensitive acetone detection in ppb.-level as part of a breath analyzer for diabetes diagnostic probe.

4. CONCLUSIONS

In this work, we fabricated the chemiresistive sensor based on one-dimensional WO_3 nanostructures deposited by GAD using RF sputter. This sensor showed an ultrahigh selectivity to acetone at elevated temperature. The detection limit of acetone was determined to be as low as 0.12 ppb. We expect that the sensor produced by RF sputter can be manufactured with low complexity and the final product be low cost and more reliable than similar sensor produced via wet process. Consequently, highly sensitive sensing properties of nanostructure WO_3 sensor suggest the possibilities of application in high performance exhaled breath analyzer as a personal medical diagnostics tool to diagnose diabetes.

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