EFFECT OF ANNEALED TEMPERATURE ON NO₂ GAS-SENSING PERFORMANCES OF SnO₂ NANOWIRE SENSORS

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ABSTRACT

NO₂ gas is a highly toxic gas and emitted from vehicles such as motorcycles and internal engine transportations. It is one of the major reasons which cause air pollution in recent years, especially in big cities. Therefore, the development of NO₂ gas sensor for environmental monitoring has been gained research attention in the global. In this work, we report a simple and effective method to prepare SnO₂ nanowire gas sensors. The SnO₂ nanowires were directly grown on the unpolished Al₂O₃ substrate equipped with a pair of Pt-electrodes. The morphology and microstructure of as-grown nanowires have been investigated via X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The results indicated that the diameters and lengths of nanowires are about 60 – 100 nm and tens of μm, respectively. The gas-sensing performance of the SnO₂ nanowires sensors annealed at different temperatures have also investigated. The results revealed that the annealed temperatures of 400 °C and 500 °C do not affected on gas-sensing performance of SnO₂ nanowires sensors, while the annealed temperature of 600°C results in strong decrease in NO₂ gas response as compared with as-grown SnO₂ nanowires sensor.

Keywords: SnO₂, NO₂, gas sensors, nanowires.

1. INTRODUCTION

Recent years, the rapid growth of the number of vehicles in operation, the air pollutants emitted from these vehicles have contributed to air pollution, especially in large cities. The levels of pollution by CO, NO₂, SO₂, CO₂ and NH₃ have increased many times the level allowed standards. Therefore, the development of gas sensors for the detection of such gases has attracted considerable interest in recent years [1]. Many metal oxide semiconductors including ZnO, SnO₂, WO₃ and In₂O₃ have been applied for gas sensors [2]. Among them, SnO₂ has been emerged as one of the most promising candidate due to its high sensitivity [3], good selectivity [4] and low cost [5]. Many techniques for growing SnO₂ nanowires have been successfully
developed such as hydrothermal growth [6], pulse laser deposition [7], sol-gel [8], and chemical vapor deposition [9]. The most commonly used method for fabricating SnO$_2$ nanowires is tube furnace type thermal evaporation due to the simplicity, high-quality nanowires and low cost of this approach.

Nitrogen dioxide (NO$_2$) is highly harmful as an environmental pollutant which causes photochemical smog and acid rain. For environmental and safety reasons, gas sensors are required for monitoring concentration of NO$_2$ gas in air. In this work, we report the synthesis and physical characterizations of SnO$_2$ nanowires produced using thermal evaporation technique for gas sensor application. Besides, the gas-sensing performance of the SnO$_2$ nanowire sensors annealed at different temperatures have also investigated. The results show that the sensors exhibit good gas sensing performance to NO$_2$ gas. Especially, the sensors can detect NO$_2$ gas at low concentration range (ppb).

2. EXPERIMENTAL

The SnO$_2$ nanowires were grown by a chemical vapor deposition (CVD) system as shown in Figure 1. Pure Sn powder (Merck, 99.8 %) was placed in an alumina boat as the evaporation materials sources. The substrates with a previously deposited 10 nm Au catalyst layer were placed approximately 2–3 cm from the sources on both sides (up-stream and down-stream). The growth process was divided into two steps.

![Figure 1. Schematic diagram of CVD system to synthesis SnO$_2$ nanowires.](image)

Initially, the quartz tube was evacuated to 10$^{-2}$ Torr and purged several times with Ar gas (99.999 %). Subsequently, the quartz tube was evacuated to 10 Torr again, and the furnace temperature was increased from room-temperature to 750 °C in 20 minutes. After the furnace temperature reached the synthesized temperatures, oxygen gas was added to the quartz tube at a flow rate of 0.5 sccm, and the growth process was maintained for another 30 minutes. The as-synthesized SnO$_2$ nanowires were analyzed by X-Ray Diffraction (XRD, D8 Advance, Brucker, Germany), Field Emission Scanning Electron Microscopy (FE-SEM, S4800, Hitachi) and Transmission Electron Microscopy (TEM, JEM-100CX).

The gas-sensing properties were then measured with a standard flow rate of 400 sccm for both dry air balance and analytic gases. During sensing measurement, resistance of the sensors was continuously measured using a Keithley 2700 instrument interfaced with a computer while the dried air and analytic gases were switched on/off in each cycle. Sensors response was defined as $S = R_g/R_a$, where $R_g$ and $R_a$ are resistances of sensor in target gas and dry air, respectively.
3. RESULTS AND DISCUSSION

3.1. Material characterizations

Figure 2(a) shows the XRD pattern of SnO$_2$ nanowires. It can be seen from the diffraction patterns that there are typical peaks for tetragonal tin dioxide, which are (110), (101), and (211) planes. All the peaks are well indexed to the tetragonal structure with lattice constants $a = 4.73$ Å, $c = 3.18$ Å, which are in good agreement with those in the standard data card (JCPDS Card No. 77–0452).

The morphologies of the SnO$_2$ fabricated by thermal evaporation were characterized by FE-SEM and TEM images and the results were indicated in Figure 3(b-d). It can be seen that the SnO$_2$ nanowires were successfully synthesized at the temperature of 750°C on Al$_2$O$_3$ substrate (Figure 3b). The high magnification of FESEM and TEM images of the SnO$_2$ nanowires (Figures 3c and 3d) are revealed a smoothness and uniformity along the surface of the wire axis. Uniform SnO$_2$ nanowires were produced on a very large area of the substrate. The average diameters and lengths of the SnO$_2$ nanowires ranged from 60 to 100 nm, and from 50 to 150 µm, respectively.

![Figure 2](image-url)

*Figure 2. Materials characterizations: (a) XRD pattern; (b,c) FE-SEM and (d) TEM image of the SnO$_2$ nanowires fabricated by thermal evaporation.*

3.2. Gas sensing properties

In order to investigate gas-sensing performance of the SnO$_2$ nanowire sensors, a dynamic gas-sensing test was performed. The NO$_2$ gas-sensing properties of as-grown SnO$_2$ nanowire sensor are summarized in Figure 3. A good response-recovery characteristic was obtained under sensing temperature range of 150 – 250°C and 0.1-1 ppm NO$_2$ gas. As can be seen, the sensor
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could detect NO$_2$ gas at low concentrations (su-ppm). However, the highest response was obtained at working temperature of 150 °C, in which the sensor resistance increased rapidly upon exposure to target gas and reached saturation within few minutes. The response ($R/R_a$) increased from about 10 to 160 when target gas concentration increased from 100 to 1000 ppb. The resistance of sensors exhibited a upward trend when exposure to NO$_2$ gas, because SnO$_2$ material is known as an n-type semiconductor with free electrons as carriers due to the vacancy of oxygen, while NO$_2$ is a oxidation gas. Thus, when NO$_2$ was adsorbed on the surface, the NO$_2$ molecules accepted the electron from the tin oxide nanowires, decreased the carrier density, and resulted in the increase sensors’ resistance [10].

![Graph](image.png)

Figure 3. The NO$_2$ gas response of the as-growth SnO$_2$ at different temperatures: (a) 250 °C, (b) 200 °C, (c) 150 °C and (d) The response with different gas concentration.

In this study, we investigated the effect of annealed temperature on gas sensor response. The SnO$_2$ nanowires were annealed at 400 °C, 500 °C and 600 °C in 5 hours and measured at operating temperature of 150, 200 and 250 °C and NO$_2$ gas concentrations of 100, 250, 500 and 1000 ppb NO$_2$ gas. The transient response of the three sensors was shown in Figure 4(a-c). Apparently, the annealed SnO$_2$ nanowire sensors exhibited a good response-recovery characteristic. The gas response as a function of gas concentration was shown in Figure 4(d-e). It can be seen clearly that the annealed temperature strongly depends on the gas response. In more details, the responses of the sensor annealed at 400, 500 and 600 °C upon exposure to 1000 ppb NO$_2$ at 200 °C are 68, 60 and 25, respectively. As compared with the as-grown SnO$_2$ nanowires, the sensors annealed at 400 and 500 °C have similar response. When annealed temperature increased up to 600 °C, the response is significantly decreased. This could explain further study for plausible explanation.
Figure 4. The transient response of SnO₂ nanowire sensors annealed at 400 °C (a), 500 °C (b) and 600 °C (c). The response as function of gas concentration measured at 200 °C (d), 150°C (e) and 250 °C (f).

The effect of source materials amount on gas sensing properties was shown in Figure 5. The results indicated that using 100 mg g of Sn powder to fabricate the on-chip sensor based on SnO₂ nanowires gave the highest response (around 25), while the sensor grown from 30 mg only gave the response of nearly 8 and the one grown from 150 mg had a response of about 13. Using 150 mg Sn powder resulted in a thicker layer of SnO₂ nanowires, thus making the adsorption of NO₂ onto the surface of the nanowires more difficult. In the case of using 30 mg source material, the as-grown layer was too thin, therefore the sensitivity was not as high as the sensor fabricated from 100 mg Sn powder.

Figure 6. The transient response of SnO₂ nanowires grown from 30 mg (a), 100 mg (b) and 150 mg (c) Sn powder upon exposure to 500 ppb NO₂ at 200 °C and comparison response of the three sensors (d).
4. CONCLUSION

The SnO$_2$ nanowires were synthesized directly on the Al$_2$O$_3$ substrate equipped with electrodes by thermal evaporation route. This is a potential method that can be applied for mass-production of SnO$_2$ nanowire gas sensor. The SnO$_2$ nanowire sensor has exhibited good sensing performance to NO$_2$ gas. It can detect the concentration of NO$_2$ at ppb levels. Therefore, it is potential candidate to develop gas sensors for monitoring toxic and flammable gases.

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REFERENCES

TÓM TẮT

ẢNH HƯỞNG CỦA NHIỆT ĐỘ Ủ DẾN TÍNH CHẤT NHÁY KHÍ NO₂ CỦA CẢM BIẾN DÂY NANO SnO₂

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Trong những năm gần đây tình trạng ô nhiễm môi trường do khí NO₂ sinh ra từ các phương tiện giao thông đang trở thành một vấn đề quan tâm đến các nhà khoa học trên thế giới. Do đó, việc phát triển cảm biến khí NO₂ để kiểm soát chất lượng không khí đang thu hút sự quan tâm của các nhà khoa học trên thế giới. Trong nghiên cứu này, chúng tôi giới thiệu quy trình chế tạo dây nano SnO₂ bằng phương pháp bốc bay nhiệt từ bột Sn ở 750 °C. Hình thái, cấu trúc và tính chất của vật liệu được khảo sát bằng nhiễu xạ điện tử tia X (XRD), hiển vi điện tử phát xạ trường (FE-SEM). Kết quả chế tạo vật liệu chỉ ra rằng, dây nano SnO₂ có đường kính khoảng 60 - 100 nm và chiều dài tới vài chục micro - mét. Tính chất nhạy khí NO₂ của cảm biến trên cơ sở dây nano SnO₂ xử lý nhiệt ở các nhiệt độ khác nhau cũng được khảo sát. Kết quả khảo sát cho thấy, khi xử lý nhiệt ở 400 °C và 500 °C không ảnh hưởng đến đặc trưng nhạy khí của cảm biến dây nano SnO₂. Tuy nhiên, khi xử lý ở nhiệt độ 600 °C làm suy giảm khả năng đáp ứng của cảm biến với khí NO₂.

Từ khóa: SnO₂, NO₂, cảm biến khí, nhạy khí, dây nano.