High sensitivity and low electric power consumption NO2 sensor using SnO2 thin film for smart detector design

Mengyuan Wang, Hui Huang*, Jialing Zhou
Dalian University of Technology, Dalian 116024, China.

*Corresponding author: huihuang@dlut.edu.cn

Abstract. In this research, SnO2 thin films were prepared by oxidizing the Sn thin films firstly, which was applied for NO2 sensing. The morphology, crystal structure and surface state of the film were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). By optimizing the preparation conditions of SnO2 thin films (i.e., oxidation temperature and thickness of the film), the response to 40 ppb NO2 was increased by 6 times and the response time was shortened by 1.5 times. The sensor shows low detection limit to NO2 at the concentration of 5 ppb at room temperature. It could be found that the high surface area to volume ratio and oxygen vacancy were considered to improving the sensing performance. The NO2 sensor fabricated by this method was available readily, high sensitivity and low power consumption (microwatt magnitude), which has great potential for commercial application.

Keywords: SnO2 film; Magnetron sputtering; NO2.

1. Introduction
With the development of industry and technology, air pollution has been widely concerned, a lot of poisonous and harmful gases are released into the air, and it causes environmental pollution as well as harmful to human health. For example, NO2 can cause acid rain, haze and photochemical smog. Environmental Protection Agency (EPA) has commented the concentration of noxious gases in air should far lower than the value determined by safety guidelines to provide necessary protecting for public safety. Thus, it was imperative to develop reliable and highly sensitive NO2 detector.

Chemiresistive sensors, especially metal oxide semiconductor (MOS) sensor has been researched widely in recent years because of its portability, easy integration and low cost compared with sensors based electrochemical and optical. Many kinds of MOS including WO3 [1], ZnO [2] and SnO2 [3] has been widely studied as sensing materials for NO2 detection. However, most of them should working at high temperature, which will affect the longevity, stability and application range of the sensor. Therefore, many studies have been done to reduce the working temperature of the sensor. One was to use UV illumination instead of heating to ensure the sensor work at lower temperatures. Saboor et al. [4] reported that Pd-SnO2 film response to NO2 was greatly increased by UV illumination. But the illumination method introduces UV source which increases the power consumption of the sensor and limits its integration. Another way to enhance the sensing properties was modulating the composition, morphology and defects of the materials. Wei et al. [5] reported SnO2 nanocrystals with abundant
oxygen vacancies has great response to NO₂ at room temperature. However, low detection limit is still a challenge when worked at room temperature. Thus, it is significantly to research a NO₂ sensor fabricated by a facile method with low detection limit and low power consumption.

In this paper, SnO₂ thin films with considerable amount of oxygen vacancies (20% analyzed by XPS) were prepared by oxidizing the Sn thin films for the first time. The SnO₂ films were applied for the NO₂ detection at room temperature. Oxidation temperature and the thickness of Sn film could affect the surface area to volume of the material, which greatly influence the response of NO₂. The sensor exhibited excellent properties with low detection limit (5 ppb) and low power consumption (<10 μW).

2. Materials and method

2.1. Materials and device preparation

SnO₂ thin films were prepared by sputtering Sn thin films on quartz substrates and then oxidation in dry air in a tubular furnace. The quartz substrate was cleaned with acetone, alcohol solution and deionized water respectively. The pre-sputtering for 15 min was needed to remove the residues on the surface of the Sn target. In order to investigate the influence of oxidation temperature on the performance of the sensor, the Sn metal layers with the thickness of 50 nm were sputtered at the substrates, and then oxidation at 600℃, 800℃ and 900℃ for 30 min to make SnO₂ thin films named S1, S2 and S3 respectively. Dry air was injected continuously during the oxidation process. In order to study the effect of the thickness of Sn on the performance of the sensor, we also prepared other thickness of Sn, such as 80 nm and 110 nm oxidized to SnO₂ at 800℃ for 30 min, and denoted as S2-1, S2-2. Ni/Au electrodes with the distance of 3mm were sputtering at all SnO₂ thin films to make gas sensor.

2.2. Characterization

The morphologies and grain size on the surface of SnO₂ thin films were characterized by Scanning Electron Microscope (SEM, NOVA NanoSEM). The crystal structure and phase of the films were characterized by X-ray diffraction analysis (XRD; Empyrean) (45 kV, 40 mA) in the range of 20-80° (2θ). The chemical state and form of Sn and O in the films were characterized by XPS (XPS, K-Alpha).

2.3. Gas-Sensing Measurement

Static test system including gas inlet and outlet as well as external circuit interface was used for NO₂ detection. The NO₂ was injected by standard calibrated syringe from the gas inlet. We defined the concentration of NO₂ to be tested \( C_{NO₂} \) was calculated according to the formula:

\[
C_{NO₂} = \left( \frac{V_{NO₂}}{V_b} \right) \times 100\% \tag{1}
\]

Which \( V_{NO₂} \) is the volume of injected NO₂ (the concentration is 10 ppm) and \( V_b \) is the volume of the box (the volume is 2 L). All sensors were tested NO₂ in the concentration range of 5-80 ppb under air atmosphere.

The response of the sensor (S) is defined as follow:

\[
S = \left( \frac{|R_g - R_a|}{R_a} \right) \times 100\% \tag{2}
\]

Which \( R_g \) and \( R_a \) is the resistance of SnO₂ thin film in test gas and air. Response and recovery time are defined as the time required for the sensor resistance change rate to reach 90% of the total change rate.
3. Results and discussion

3.1. Morphological characterization

Figure 1(a-d) shows the top-view SEM morphology of SnO$_2$ films (S1, S2, S3), respectively. It was observed that the SnO$_2$ film had an unidentified morphology. The film was smooth and dense when oxidated at 600°C and the grains size are ~140 nm. At the oxidation temperature of 800°C and 900°C, the film shrink into particles with grains size of ~120 nm. With the particle size decreased, the surface area to volume ratio increased, which was beneficial for the gas molecules adsorption on the surface of the film.

![Figure 1. SEM images of SnO$_2$ films oxidized at different temperature of 600°C (a, S1), 800°C (b, S2) and 900°C (c, S3).](image1)

Figure 2(a-d) shows the surface morphology of the SnO$_2$ film fabricated with different thickness (50 nm, 80 nm and 110 nm), which oxidized at 800°C. Their particle sizes are ~120 nm, ~140 nm and ~170 nm, respectively. With the increase of the thickness, the size of the particles increases obviously results in a corresponding rise of surface area to volume ratio, which was conducive to the adsorption of gas molecules.

![Figure 2. SEM images of SnO$_2$ films prepared by oxidizing Sn of different thicknesses of (a, S2) 50 nm, (b, S2-1) 80 nm, and (c, S2-2) 110 nm.](image2)

3.2. Crystal structure characterization

XRD pattern of SnO$_2$ film with the thickness of 50 nm oxidized at 800 °C was shown in Figure 3. The characteristic diffraction peaks at 26.6°, 29.9° and 51.6° corresponding to the crystal planes of (110), (111) and (103), which could be attributed to the tetragonal cassiterite structure of SnO$_2$ (corresponding to JCPDS 41-1445).
3.3. Chemical state analysis

Chemical factors have more influence on the gas sensing response than physical factors [5], so we analyze the XPS of the sample carefully. The survey XPS spectra at Figure 4 (a) shows the element of Sn, O and C. The position of other peaks was calibrated by setting the C 1s peak position at 284.8 eV. As shown in Figure 4(b), the diffraction spectrum of O 1s could be divided into three peaks. The peak near 530 eV could corresponding to Sn-O bound as crystal lattice (O_L), while located near 531.1 eV was associated with oxygen vacancies (O_V). The peak located at 532.4 eV was related to the state of chemisorbed oxygen (O_C). The oxygen vacancy of 20% was much higher than that described in other literature [6], which abundant oxygen vacancies were beneficial for the NO₂ molecule adsorption on the film surface. On the other hand, oxygen vacancies were behaved as the donors in SnO₂ thin film, which increase the electron density in the conduction band. Hence, the film exhibits an N-type conductivity.

3.4. Gas-sensing property

In the process of fabrication SnO₂ thin films, the oxidation temperature and thickness of Sn film have influenced the performances for NO₂ detecting. Figure 5(a-b) shows the NO₂ response of SnO₂ films.
fabricated at different oxidation temperature of 600℃-900℃. As shown in Figure 5(a), with the NO₂ concentration in the testing chamber increased from 5 ppb to 80 ppb, the resistance of SnO₂ film enhanced. Figure 5(b) shows the relationship between performance and oxidation temperature. The response of sample S2 to 40 ppb of NO₂ was 3.73, while the response of sample S1 and S3 are 2.86 and 0.62 respectively. And the response time were 270 s, 293 s, and 402 s, respectively. It was worth noting that when oxidation at 900℃, the resistance of the film was increased by near 100 orders of magnitude than that of the oxidation at 800℃, which may be related to the discontinuity of the film with the response decrease sharply.

Figure 5(c-d) shows the NO₂ response of SnO₂ film with different thickness of 50 nm-110 nm. From Figure 5(c), it could be seen that the response of SnO₂ to NO₂ gradually decreases with the increase of the thickness of Sn film. As demonstrated in Fig. 5(d), when the thickness of the Sn film increased from 50 nm to 110 nm, the response to 40 ppb NO₂ decreased from 0.89 to 3.73, and the response time increased from 270 s to 413 s. This was attributed to the increase of particle diameter on the film surface and the decrease of the surface area to volume.

In addition, cycle measurement for 40 ppb NO₂ and selectivity of the S2 were shown in Figure 6. As shown in Figure 6 (a), it was clear that the sensor has good repeatability. Once NO₂ injected, the resistance of the film increased and recovered to its baseline when NO₂ was replaced by air. As shown in Figure 6 (b), it was clear that the sensor shows good selectivity to 100 ppm CH₄, CO, NH₃ and H₂.
3.5. Gas-sensing property

The gas sensing mechanism of MOS could be represented as follows: gas molecules adsorption and desorption on the surface of materials, and the conductivity of materials changed which output as an electrical signal. When the NO\textsubscript{2} injected in the testing chamber, the gas molecules could capture electrons from SnO\textsubscript{2} film at low operating temperature causing the depletion increased. As shown in formula (3):

\[
\text{NO}_2(g) + e^- \rightarrow \text{NO}_2^-
\] (3)

Thus, the sample S2 has the greatest response to NO\textsubscript{2} for its largest surface area to volume among all the samples (except the sample S3). It seems that the oxidation temperature of 800°C was the cut-off point of device performance. Once the oxidation temperature increased to 900°C, the resistance of the film increases by 1000 times sharply with the sensor performance declined dramatically. This phenomenon may attribute to the NO\textsubscript{2} molecules could capture small number of electrons with the electrons in the SnO\textsubscript{2} film decreased.

Additionally, NO\textsubscript{2} gas sensing response of SnO\textsubscript{2} thin film was also related to the abundant oxygen vacancy content. The oxygen vacancies could increase the NO\textsubscript{2} adsorption and enhance the charge transfer\cite{6}. The excellent performance of the sample S2 could be attributed to the considerable amount of oxygen vacancy (20%).

4. Conclusions

In summary, SnO\textsubscript{2} films used for NO\textsubscript{2} detection have been deposited on quartz substrate by oxidation methods was proposed for the first time. The NO\textsubscript{2} sensor fabricated by this method was readily available, high sensitivity and low power consumption. By optimizing the oxidation temperature and the thickness of the Sn film, the response to NO\textsubscript{2} was increased by 6 times and the response time was shortened by 1.5 times. The SnO\textsubscript{2} film shows low detection limit of 5 ppb to NO\textsubscript{2}. In the end, the gas sensing mechanism was discussed, which considered has relation with the surface area to volume and oxygen vacancy of the film.

References

[1] Kamble, C., M. Panse and A. Nimbalkar, Ag decorated WO\textsubscript{3} sensor for the detection of sub-ppm level NO\textsubscript{2} concentration in air. Materials Science in Semiconductor Processing. 103 (2019) 104613.
[2] Wang, J., et al., On-chip grown ZnO nanosheet-array with interconnected nanojunction interfaces for enhanced optoelectronic NO₂ gas sensing at room temperature. Journal of Colloid and Interface Science. 554 (2019) 19-28.

[3] Fang, J., et al., Gas sensing properties of NiO/SnO₂ heterojunction thin film. Sensors and Actuators, B: Chemical. 252 (2017) 1163-1168.

[4] Saboor, F.H., et al., Enhanced NO₂ gas sensing performance of bare and Pd-loaded SnO₂ thick film sensors under UV-light irradiation at room temperature. Sensors and Actuators, B: Chemical. 223 (2016) 429-439.

[5] Wei, Y., et al., SnO₂ nanocrystals with abundant oxygen vacancies: Preparation and room temperature NO₂ sensing, Journal of Alloys and Compounds. 681 (2016) 43-49.

[6] Y. Xiong, W. Lu, D. Ding, L. Zhu, X. Li, C. Ling, Q. Xue, Enhanced room temperature oxygen sensing properties of LaOCl-SnO₂ hollow spheres by UV light illumination, ACS Sensors. 2 (2017) 679-686.