Effect of V$_2$O$_5$ coating on NO$_2$ sensing properties of WO$_3$ thin films

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Abstract

WO$_3$-based thin film micro-gas sensors coated with V$_2$O$_5$ layers were fabricated and NO$_2$ gas sensing characteristics were measured. The silicon-based substrate embedded with Pt interdigitating electrodes and heater was prepared by MEMS technology. Vanadium pentoxide (V$_2$O$_5$) was sputtered on the WO$_3$ thin film at room temperature. All the films were annealed in air at 600 $^\circ$C for 4 h. The effect of the thickness of V$_2$O$_5$ layers on NO$_2$ response has been investigated. The coating with a 20 nm V$_2$O$_5$ layer made the WO$_3$ thin film more sensitive to NO$_2$. In addition, reversible response behavior could be achieved. SEM photographs revealed that the WO$_3$ thin film with the 20 nm V$_2$O$_5$ coating layer showed porous structure.

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1. Introduction

Nitrogen oxide NO$_x$ (NO or NO$_2$) is mainly released from combustion facilities and automobiles. It can cause diseases of respiratory system and is the main reason of acid rain, photochemical smog [1]. Therefore, the effective methods to detect nitrogen oxides are highly demanded to reduce the noxious effects on environment and human beings.

NO$_2$ is the main gas to be detected because NO is easily oxidized to NO$_2$ in atmosphere. There have been lots of efforts on developing a variety of NO$_2$ gas sensors such as electrochemical sensors [2], SAW sensors [3], and polymer sensors [4]. Recently, metal oxide semiconductor NO$_2$ gas sensors have been studied extensively because of their simple fabrication processes and low cost. Especially, WO$_3$ is one of good materials for NO$_2$ sensing due to its high sensitivity and good selectivity to low concentration NO$_2$ gas [5].

Moreover, thin films are the most suitable for the production of micro gas sensors [6]. Several methods have been used to prepare WO$_3$ thin films, including sol–gel [7], sputtering [8] and thermal evaporation [9]. Many researches have studied on the structural properties and sensing characteristics of WO$_3$ thin films. As reported by Akiyama et al. [10], a WO$_3$ thin film has high sensitivity and short response and recovery time to low concentration NO$_x$. It has been reported that the sensitivity of the WO$_3$ thin film to NO$_2$ was enhanced by the addition of metals, such as Au, Al or Pt [11]. Our previous work has established that the WO$_3$ thin film prepared by dc magnetron sputtering and annealed in air at 600 $^\circ$C for 4 h was monoclinic and showed high sensitivity to low concentration of NO$_2$ [12].

In this paper, micro NO$_2$ gas sensors were fabricated with WO$_3$-based thin films on silicon-based substrates. Vanadium pentoxide (V$_2$O$_5$) was sputtered on the WO$_3$ thin film as an additive. The effect of the thickness of V$_2$O$_5$ layer on the NO$_2$ response has been investigated in order to develop a thin film sensor that is more sensitive to NO$_2$.

2. Experimental

WO$_3$-based thin film micro NO$_2$ sensors were fabricated on silicon substrates. The structure and the preparation of the
Table 1: Sputtering conditions of WO₃ thin film and the layer of V₂O₅

<table>
<thead>
<tr>
<th>Film</th>
<th>Target composition</th>
<th>Sputtering gas</th>
<th>Sputtering pressure (Pa)</th>
<th>Substrate temperature</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO₃</td>
<td>99.9% W metal</td>
<td>70% Ar:30% O₂</td>
<td>0.5</td>
<td>300 °C</td>
<td>200</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>99.9% V₂O₅</td>
<td>70% Ar:30% O₂</td>
<td>1.0</td>
<td>Room temperature</td>
<td>510 ± 200</td>
</tr>
</tbody>
</table>

substrate have been described in detail in Ref. [12]. A WO₃ thin film was deposited by dc sputtering. The layers of V₂O₅ in different thickness were deposited by RF sputtering on the WO₃ thin film. Finally, the films were annealed in air. All the thin films were figured with shadowing mask and the area is 0.5 mm × 0.5 mm. Table 1 shows the sputtering conditions of the WO₃ thin film and the V₂O₅ layer.

The thickness of the films was controlled by deposition time and the deposition rate was calibrated using a surface profiler. WO₃-based thin films were characterized using SEM and XPS. The devices were mounted on 6-leads TO-8 metal encapsulations. The gas sensing properties of the films were measured using a static test system and dry air was adopted to clean the chamber before measuring the recovery properties. The response of the film to NO₂ is defined as 

$$\frac{\Delta R}{R_0}[13],$$

where \( R_0 \) is the resistance of the films in the air and \( \Delta R \) is the change of the resistance upon exposure to NO₂.

3. Results and discussion

An XPS spectrum of the WO₃ thin film with a 20 nm V₂O₅ layer was measured with the system of PHI-5300/ESCA. Fig. 1 shows the XPS spectrum of the film annealed in air at 600 °C for 4 h. After the correction of XPS peaks, the binding energy of W 4f was determined to be 35.62 eV. This value agrees well with literature value for W⁶⁺ [14]. V⁵⁺ peak of 517.45 eV was also detected on the film surface after annealing. The atomic percent at the film surface was W:V:O = 21:3:76, according to the area of the peaks. Thus, V₂O₅ remained on the surface of WO₃ thin film after the annealing.

The SEM photographs of WO₃-based thin films are shown in Fig. 2. It is obvious that the grain size of the WO₃ thin film annealed in air at 600 °C is smaller than that of the WO₃ thin film annealed in air at 400 °C (see Fig. 2a and b). Fig. 2c is the SEM photograph of the WO₃ thin film with the 20 nm V₂O₅ coating layer annealed in air at 600 °C for 4 h. More porous surface structure could be achieved by the coating with a 20 nm V₂O₅ layer.

The response of WO₃ and WO₃ with a 20 nm V₂O₅ coating layer to 10 ppm NO₂ as a function of operating temperatures is shown in Fig. 3. Both the films were annealed in air at 600 °C for 4 h. The V₂O₅ coating improved the response of the film to NO₂. This can be explained partly by the SEM photographs of WO₃-based thin films. High response is caused by the change of the surface structure. The more porous the film surface is, the more the adsorption gas. More work needs to be done to explain the mechanism of the V₂O₅ coating in detail.

The responses of the films had the same trend with the change of the operating temperature. The maximum response of the two films to NO₂ was obtained at the operating temperature of 250 °C. The V₂O₅ coating did not change the optimal
operating temperature. Therefore the optimal operating temperature of the film was found to be about 250 °C.

The thickness effect of the V2O5 layer on the response to NO2 has been investigated. The thickness of the V2O5 film was varied from 5 to 20 nm. Fig. 4 shows the variations in response of the films with NO2 concentrations. The WO3 thin films with thinner V2O5 coating layers exhibited poor NO2 response, comparable to that of the pure WO3 thin film over the whole NO2 concentration range tested. But, the WO3 thin film with the 20 nm V2O5 coating layer showed improved response, i.e. a response value of 8 at a NO2 concentration of 10 ppm. For comparative purpose, the 200 nm V2O5 thin film was prepared and then annealed in air at 600 °C for 4 h. The NO2 response of the pure V2O5 film measured is also cited in Fig. 4. It is obvious that the pure V2O5 thin film is not sensitive to NO2 at the operating temperature of 250 °C.

The response and recovery of WO3 thin film with the 20 nm V2O5 coating layer to 6 ppm NO2 is shown in Fig. 5. The film responds to NO2 reversibly and the response time of the film is short. The film resistance reaches the original level after recovery, but the recovery process takes rather longer time.

4. Conclusions

The grain size of WO3 thin film annealed at 600 °C is smaller than that of WO3 thin film annealed at 400 °C. Coating with the V2O5 layer changed the surface structure of WO3 thin film. The WO3 thin film with the 20 nm V2O5 coating layer annealed in air at 600 °C for 4 h was porous than that of the pure WO3 thin films. Coating with the 20 nm V2O5 layer improved the response of WO3 thin film to NO2.

References


Biographies

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