Using co-sputtered platinum or palladium activated tungsten oxide films to detect reducing gases

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Abstract

WO\textsubscript{3}, activated by 1\% Pt or 1\% Pd, was deposited by radio frequency co-sputtering process. The as-sputtered films were thermally-treated at 450°C for 24h after co-sputtering. The microstructure, crystal structure and chemical composition of the as-sputtered and thermally-treated films were analyzed by SEM, XRD and XPS. The sensing characteristics of the Pt or Pd activated WO\textsubscript{3} films, as well as the pure WO\textsubscript{3} films, were characterized with 25-200 ppm H\textsubscript{2}, 25-200 ppm CO and 0.62-5 ppm NH\textsubscript{3} at 50-300°C in air with different humidity.

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1. Introduction

The main advantages of metal oxide sensors include simple construction, low cost, small size, high sensitivity and rapid response to low concentration gases, even to ppm and ppb level [1]. The characteristics of semiconductor gas sensors are determined by the reversible interactions of the gases with the material surface. Surface catalytic reactions result in a change of electrical conductivity of metal oxide layer, and catalytic noble metals are often used to strengthen these reactions in order to enhance the selectivity and the sensitivity of the sensors [2].

WO\textsubscript{3} is a well-established sensing material for oxidizing gases, especially for NO\textsubscript{2} and O\textsubscript{3}. It has been reported that noble metal (NM) activated WO\textsubscript{3} films show high sensitivity to low concentration H\textsubscript{2} [3] and other reducing gases. Platinum and palladium are proved to be two most promising NM to modify the

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sensing performance of WO$_3$ films [4]. The comparison of the two NMs activated tin dioxide (SnO$_2$) gas sensors to reducing gases was reported in [5]. There are different methods to prepare NM particles on WO$_3$ surface. NM additives can be added onto the WO$_3$ surface using post-deposition process, e.g. sputtering and thermal evaporation processes. NM additives can also be prepared by simultaneous deposition of WO$_3$. In a previous paper [6], we reported a straightforward process to prepare Pt activated WO$_3$ (Pt-WO$_3$) films, which were co-deposited using radio frequency sputtering. The 0.5%Pt-WO$_3$ films showed stable responses to H$_2$ after suitable heat-treatments. In this work, we used the same process to prepare Pt and Pd-WO$_3$ films. In order to compare the effect of catalytic particles on the sensing characteristics, Pt and Pd-WO$_3$ films as well as pure WO$_3$ films were deposited using the same deposition parameters. The effects of NM additives on H$_2$ sensing performance of WO$_3$ films were studied by resistance measurements. The cross-sensitivity of NM-WO$_3$ films to CO and NH$_3$ were also evaluated.

2. Experimental methods

The three types of films (pure WO$_3$, Pt-WO$_3$ and Pd-WO$_3$) were deposited in an r.f. sputtering device at room temperature, as schematically shown in Fig. 1. A sintered 35mm WO$_3$ disc was used as WO$_3$ target. A 12 mm$^2$ Pt/Pd chip was placed at the center of the WO$_3$ target surface. The r.f. power was maintained at 200W during the film deposition. The thickness of the films was 400 nm. More details about the deposition process can be found in [6]. All the films were directly annealed at 450°C for 24h after deposition. The surface morphologies of the films were characterized by SEM. XRD and XPS were performed to analysis the crystal structure and chemical compositions of the films. The sensing characteristics of the Pt/Pd-WO$_3$ films as well as the pure WO$_3$ films were measured in a Teflon chamber to measure the electrical resistance of films. More details about gas sensing measurement were given in [6]. Variable humidity of reference gas was used in this work. The moisture level was controlled by mixing dry air and wet air. When the resistance of the sensor was stable in reference air with given relative humidity and waiting for another 30 or 60 minutes, H$_2$, or CO or NH$_3$ was introduced in the reference air to get the desired concentrations of target gases. The gas sensing performance was tested in 25-200 ppm H$_2$, 25-200 ppm CO or 0.62-5 ppm NH$_3$ at 50 to 300°C. Sensor response is defined as $S=R_{air}/R_{gas}$, where $R_{air}$ and $R_{gas}$ are the film resistances in the absence and presence of target gas.

3. Results and discussion

The surface morphologies of the thermally-treated Pt-WO$_3$ and Pd-WO$_3$ films as well as the bare Al$_2$O$_3$ substrate were examined by SEM (image is not shown). The bare substrate is composed of 3-5 μm Al$_2$O$_3$ grains. Thin NM-WO$_3$ film can be observed on the Al$_2$O$_3$ grains. Fig. 2 shows the XRD patterns of the as-sputtered and thermally-treated Pt/Pd-WO$_3$ film. It can be found that the as-sputtered films present the amorphous structures. The peaks in Fig. 2(a) and 2(b) belong to the Al$_2$O$_3$ substrate and Au electrodes. After the thermal treatment at 450°C, the amorphous WO$_x$ in the films were transformed to well-crystallized WO$_3$.

To analysis the surface composition of the films, XPS experiments were performed. The survey spectra and NM peaks are measured on the thermally-treated films. The films’ surface composed of tungsten, oxygen, small carbon contamination and small amounts of NM. The atom concentrations of NM in the films were calculated to be 1 at.%. The Pt in the films is metallic whereas Pd presents a mixture of oxide and metal. Peak synthesis for Pd3d-level spectrum of Pd atoms in Pd-WO$_3$ films was given in Fig. 3. The spectrum displays two doublets with first component Pd$^0$ and the second Pd$^{2+}$. According the result of peak synthesis, metallic Pd is around 30 % while the oxidized Pd is about 70 %.

Here H$_2$ sensing results of the NM-WO$_3$ films as well as the pure WO$_3$ films are studied. In Fig. 4, the sensor responses of the three films were measured at 225°C in 50% moist air as a function of H$_2$.
concentration in the range from 25 to 200 ppm. Pt and Pd activated WO$_3$ films show significant responses to H$_2$ at this condition whereas the pure WO$_3$ has no sense to H$_2$. The sensor response increases with the increase in H$_2$ concentration. The sensor responses to H$_2$ versus working temperature are plotted in Fig. 5. The maximum sensor response for Pt-WO$_3$ is at about 100°C and the maximum one for Pd-WO$_3$ is at 225°C. The Pd-WO$_3$ sensor exhibits a much narrower operating temperature range compared to Pt-WO$_3$. Although the Pt-WO$_3$ sensor showed a higher sensor response than Pd-WO$_3$ at low temperature range, the Pt-WO$_3$ sensor has a long response time below 200°C which is not practical in applications.

Fig. 1. scheme of radio frequency co-sputtering chamber, (1) substrate, (2) WO$_3$ target, (3) Pt or Pd chip, (4) throttle valve and (5) gas supply.

Fig. 2. XRD patterns of (a) as-sputtered Pd-WO$_3$ film, (b) as-sputtered Pt-WO$_3$ film, (c) thermally-treated Pd-WO$_3$ film and (d) thermally-treated Pt-WO$_3$ film.

Fig. 3. peak synthesis for Pd3d-level XPS spectra of palladium atoms in the thermally-treated Pd-WO$_3$ film.

Fig. 4. resistance response of three sensors to 25-200 ppm H$_2$ in 50% R.H. air at 225°C.

The sensing characteristics of the films to CO and NH$_3$ are also measured. The two NM activated films show different sensing behaviours to CO. The sensor response of Pt-WO$_3$ increased responses with the increase of CO concentration (1.4 to 2.3 when concentration increased from 25 to 200 ppm) whereas the response of Pd-WO$_3$ is insignificant (from 1.2 to 1.4). The pure WO$_3$ shows no response to CO. The two NM-WO$_3$ films have small responses to NH$_3$ when the NH$_3$ concentration is higher than 1.25 ppm whereas the pure WO$_3$ has no response. It can be concluded that the two NM-WO$_3$ films show the same responses to H$_2$ at 225°C while the Pd-WO$_3$ films has less response to CO and NH$_3$. Moreover, the Pd-WO$_3$ films give much narrower temperature range than Pt-WO$_3$. If the NM activated WO$_3$ films are chosen as sensing element for H$_2$ detection, the Pd-WO$_3$ is more suitable than the Pt-WO$_3$ film, due to Pd-WO$_3$ films exhibiting a narrower temperature range to H$_2$ as well as a better selectively to CO and NH$_3$. 

Fig. 5. XRD patterns showing the increase in 2 Theta (°) with increasing intensity.
Fig. 5. sensor response ($R_{\text{gas}}/R_{\text{air}}$) to 100 ppm H$_2$ in 50% R.H. air at temperatures ranging from 50 to 300°C.

For metal oxide gas sensor, humidity is always an important factor, which may influence the sensor performance. In this study, the effect of relative humidity on resistance response was studied. Fig. 6 shows that the relative humidity has an insignificant influence on resistance response. Although $R_{\text{air}}$ decreased a little with the increase of humidity, the sensor response keeps the same at different humidities. The reason for the decrease of the $R_{\text{air}}$ could be explained by the adsorbed water molecules on the film surface, which can release electrons to WO$_3$ and result in a decrease of film resistance.

4. Conclusions

The 1% Pt or 1% Pd activated WO$_3$ films are prepared using the co-sputtering process. The films present a well-crystallized WO$_3$ phase after a thermal treatment at 450°C for 24h. The XPS results reveal the Pt is in metallic state while 70% Pd is oxidized in the thermally-treated films. The Pt-WO$_3$ show higher sensor responses than Pd-WO$_3$ in the presence of H$_2$, CO and NH$_3$. The Pd-WO$_3$ shows maximum response at 225°C to the three gases whereas the optimised temperature varies for Pt-WO$_3$ films. The Pd-WO$_3$ sensor shows a much narrower sensing temperature range than Pt-WO$_3$ sensor.

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