Wet process-preparation of Re-doped WO₃ for wide range of NO₂ detection

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In order to reduce the electric resistance of the WO₃ sensing film fabricated from the ion-exchange method, lamellar-structured and Re-doped WO₃ was prepared through the acidification method. The mixed solution of Na₂WO₄ and Re₂O₇ was dropped into the mixed solution of H₂SO₄ and HCHO. Then the obtained gel was deposited on alumina substrate with Au electrode for thick film devices and calcined at 300°C. The size of the Re-doped WO₃ particles was smaller in one order in magnitude than that of the WO₃ by the ion-exchange method. The electric resistance of Re-doped WO₃ device in air showed minimum value at the 4 at% Re doping due to the increase in the donor density in the WO₃ crystal. As a result, the Re-doped WO₃ device exhibited low electric resistance less than 10⁸ Ω even in the 800 ppb NO₂. Such a low electric resistance device is suitable for the detection of the wide range of NO₂.

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1. Introduction

NO₂ is toxic gas for human, animal and plants and causes the deterioration of the environment through the acid rain and the photochemical smog. Therefore, the detection of NO₂ in the atmosphere is a great demand. In Japan, the environmental quality standard for NO₂ is strictly regulated below 40–60 ppb. Thus, the detection of NO₂ in ppb level is required. In the meantime, the detection of NO₂ in the range of ppb to ppm level is required for an automatic damper system in automobiles. Conventionally, the detection of NO₂ has been carried out through a spectrometry by means of a Salzmann reagent or a chemiluminescence. However, these spectrometric analyses need expensive and large-size apparatuses. Therefore, a compact and low-cost gas sensors such as semiconductor, potentiometric, amperometric and FET types have been developed for the continuous detection of NO₂.

Among them, semiconductor-type gas sensors have been regarded as one of the attractive gas sensors because of its high sensor response and simple electric circuits. For the NO₂ sensing material in the semiconductor gas sensor, Akiyama et al. have been reported that the spherical particle of WO₃ prepared by a pyrolysis of an ammonium paratungstate is one of the most candidate materials for the detection of NO₂. Then Choi et al. reported that the NO₂ gas sensor using lamellar structured WO₃ prepared by an ion-exchange method showed high sensor response compared to the sensor prepared by the conventional pyrolysis of an ammonium paratungstate. And they achieved successfully the detection of ppb-level NO₂, because lamellar structured WO₃ particles are consisted of nano-sized particles. However, the electric resistance of the sensing film prepared by the ion-exchange method was extremely high to exceed 10⁸ Ω even in the concentration range of ppb-level NO₂ and thus the electric resistance could not be measured by a simple bridge circuit due to the generation of the noise in the sensor signals. Therefore, it is necessary to reduce the electric resistance of the sensing film maintaining the lamellar-structured WO₃ particles to obtain the high sensitivity and wide range detection of NO₂. As a method for the decrease in the electric resistance of WO₃, some additives in the WO₃ particle have been reported. Bło et al. reported that the loading of Mn, Ta and Zr can prevent the WO₃ from the coagulation and thus the high sensitive detection of sub-ppm range NO₂ has been achieved. However, the decrease in the electric resistance of WO₃ by doping of WO₃ lattice has never been reported.

Therefore, in this study, we focused on the doping of Re⁶⁺ to the WO₃ lattice in order to reduce the electric resistance of the sensing film. Since the crystal structure of ReO₃ is similar to the crystal structure of WO₃ (corner-sharing octahedral structure), Re⁶⁺ may be successfully doped in the WO₃ lattice with constructing the corner-sharing octahedral structure of ReO₃. In addition, ReO₃ has the high electric conductivity due to the presence of the d conduction band. Therefore, by doping the Re⁶⁺ in the WO₃ lattice, it is expected that new energy level of ReO₃ is formed in the band gap of WO₃, and then the electric resistance of the WO₃ crystalline may be reduced. For the fabrication of Re⁶⁺-doped and lamellar-structured WO₃, an acidification of Na₂WO₄ with reduction of Re₂O₇ (HReO₄) were carried adopted. In this process, both the formation of lamellar structured WO₃·2H₂O and the reduction of HReO₄ to ReO₃ may be occurred at the same time. The lamellar-structured Re-doped WO₃ particles were obtained through the calcination. The Re-doped WO₃ particles were deposited on alumina substrate as a thick sensing film device and the electric resistance in the air and the air-diluted NO₂ was measured.

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2. Experimental

2.1 Preparation of Re-doped WO₃ particles

The preparation procedure of the Re-doped WO₃ particle is shown in Fig. 1. First of all, a desired proportion of Re₂O₇ was added to a solution of 0.104 mol dm⁻³ Na₂WO₄. In the aqueous solution, Re₂O₇ seems to exist as a water soluble species of HReO₄. Then the mixed solution of HReO₄ and Na₂WO₄ was dropped through a burette into the mixed solution of 2.0 mol dm⁻³ of H₂SO₄ and 15 ml of HCHO. After aging at 30°C for 24 h, yellow-colored precipitate was obtained in the solution. Then the obtained gel was washed with DI-water by centrifugation (10000 rpm) several times in order to remove the Na⁺.

2.2 Sensor fabrication and measurement

Sensor devices were fabricated by a screen-printing method. The gel obtained was pasted on alumina substrates attached with a pair of comb-type Au electrodes (at a space of 90 µm between the electrodes) through patterned-screens to fabricate sensor devices. Then, the devices were heat-treated at 300°C for 2 h in air. The morphology of the Re-doped WO₃ particles was observed using a FE–SEM (JSM–6340F, JEOL Ltd.). The sensor device thus fabricated was settled in a quartz tube and heated by an electric furnace for sensing property measurements. The sensor device was connected with a standard resistor in series, and the voltage across the standard resistor was measured at an applied voltage of dc 4 V to evaluate the electric resistance of the device. The electric resistance of the devices in air and in air containing target gas (0–1000 ppb NO₂) was measured in the temperature range of 150 to 300°C. Sensor response (S = Rgas/Rair) was defined as the ratio of the electric resistance in target gas (Rgas) to in air (Rair).

3. Results and discussions

3.1 Morphology of Re-doped WO₃ particles

Figure 2 shows FE–SEM images of Re-doped WO₃ by an acidification of Na₂WO₄ with a reduction of HReO₄. The contents of Re are (a) 0 at%, (b) 4 at%, (c) 8 at%.

Fig. 1. Preparation procedure of Re-doped WO₃ by an acidification of Na₂WO₄ with a reduction of HReO₄.

Fig. 2. FE–SEM images of the non- and Re-doped WO₃ by an acidification of Na₂WO₄ with a reduction of HReO₄. The contents of Re are (a) 0 at%, (b) 4 at%, (c) 8 at%. 
electric resistance has recorded a minimum at 4 at%. Furthermore, the electric resistance increased with further increasing in the Re doping. In order to understand the tendency between the electric resistance and the doping amount of Re in the range of 0 to 8 at%, the activation energy for the conduction of electrons was calculated from the dependence of the electric resistance on the operating temperature. Figure 4 shows the dependence of the activation energy on the doping amount of Re. It was found that the activation energy was decreased with increasing the doping amount of Re in the range of 0 to 4 at%. The decrease in the activation energy is not due to the change in the morphology and the size of the Re-doped WO₃ particles as shown already in Fig. 2. In this case, the decrease in the activation energy may be derived from the increase in the donor density due to the generation of the energy level of ReO₃ in the WO₃ band gap. On the other hand, the activation energy of 8 at% Re-doped WO₃ was higher than that of the neat WO₃. In the case of the 8 at% Re doping, it seems that a part of the Re could not doped in WO₃ lattice, and the excess Re was segregated onto the WO₃ particles as ReO₃. However the reason why the segregated ReO₃ particles gave high activation energy is not clear. Further study is necessary to elucidate the detailed mechanism.

3.3 Electric resistance of Re-doped WO₃ sensing films in NO₂

The electric resistance of Re-doped WO₃ prepared by the acidification of Na₂WO₃ with reduction of HReO₄ was investigated. Figure 5 shows the dependence of the electric resistance on the NO₂ concentration for non- and Re-doped (4 at%) WO₃ devices. As a comparison, the properties of the WO₃ device fabricated by the ion-exchange method are also shown in the same figure. As shown in Fig. 5, the electric resistance of the device fabricated by the ion-exchange method exceeded 10⁸ Ω even in the 200 ppb NO₂. On the other hand, however, the electric resistance of the non-doped WO₃ devices fabricated from the acidification of Na₂WO₃ was lower than 10⁸ Ω. The reason for the decreasing in the electric resistance is because the conductive pass way in the sensing film increased by reducing the size of the lamellar particles. Moreover, the Re-doping into the lamellar structured WO₃ reduced the electric resistance in both NO₂ and air by one order in magnitude, because the donor density of WO₃ crystallite seems to be increased by forming new energy level in the band.

Fig. 3. Dependence of electric resistances in air on the doping amount of Re at the operating temperature of (a) 150°C, (b) 200°C, (c) 250°C.

Fig. 4. Dependence of the activation energy on the doping amount of Re.

Fig. 5. Dependence of electric resistances at 200°C on the NO₂ concentration for (a) the WO₃ device prepared by ion-exchange method, (b) the WO₃ device prepared by the acidification of Na₂WO₃, (c) the Re-doped WO₃ (Re: 4 at%) device prepared by the acidification of Na₂WO₃ with the reduction of HReO₄. In each samples, black and white plots indicate the electric resistances in NO₂ and air, respectively.

Fig. 6. Sensor responses as a function of NO₂ concentration for (a) the neat WO₃ device prepared by the acidification of Na₂WO₃ and (b) the Re-doped WO₃ (Re: 4 at%) device prepared by the acidification of Na₂WO₃ with the reduction of HReO₄.
gap of WO$_3$. On the other hand, the electric resistance of this device was also less than $10^8 \ \Omega$ even in the 800 ppb NO$_2$. Such a sensor device with low electric resistance may be suitable for the detection of the NO$_2$ concentration in the wide range of ppb-level to ppm-level.

Figure 6 shows sensor responses as a function of NO$_2$ concentration for neat WO$_3$ and Re-doped WO$_3$ sensors. The sensor responses of both samples were proportional to the NO$_2$ concentration. Such tendency is good agreement with the report of Yamazoe et al.\textsuperscript{16} They reported that the sensor response to NO$_2$ is theoretically proportional to the NO$_2$ concentration because small crystallites show volume depletion. In the case of volume depletion, it is also indicated that sensor response is proportional to the absorption equilibrium constant of NO$_2$ and inversely proportional to the crystallite size or donor density. In Fig. 6, the slope of the sensor response of the Re-doped WO$_3$ device can be seen to be larger than that of the neat WO$_3$ device, although the donor density of Re-doped WO$_3$ may be higher than that of neat WO$_3$. The inconsistency seems to be caused by the change of the absorption equilibrium constant or crystallite size. Such factors may be changed by doping Re into the WO$_3$ lattice. However the detailed investigation should be carried out in the future.

4. Conclusion

Lamellar-structured Re-doped WO$_3$ particles were prepared by the acidification of the Na$_2$WO$_4$ with the reduction of HReO$_4$ in order to reduce the electric resistance of the sensor device. As the result, the electric resistance in air has recorded a minimum at 4 at% Re doping although the morphology and the size of the Re-doped WO$_3$ particles were not dependent on the doping amount of Re. The decrease in the electric resistance seems to be caused by the increase in the donor density in the WO$_3$ crystal. The electric resistance of the Re-doped WO$_3$ device fabricated from the acidification of Na$_2$WO$_4$ with reduction of HReO$_4$ could be repressed under $10^8 \ \Omega$ even in the 800 ppb NO$_2$ and the sensor device showed a fairly good sensor response to NO$_2$.

References
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