NO_x Sensing Properties of WO₃-based Semiconductor Gas Sensors Fabricated by Slide-off Transfer Printing

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NO_x sensing properties of semiconductor heterolayer sensors fabricated by slide-off transfer printing have been investigated. A WO₃ single layer sensor showed much higher sensitivity to NO₂ than that to NO. Loading of Ru or Pt on the surface of WO₃ led to a slight improvement of both the sensitivity and the response speed to NO, but the response speed to NO₂ was decreased especially by the Ru loading. In contrast, loading of Au improved notably the sensitivities and the response behavior to both NO₂ and NO. Stacking of a 0.5Pt-Al₂O₃ (0.5 wt% Pt-loaded Al₂O₃) layer over a 0.5Au-WO₃ layer showed little effect on the NO_x sensitivities, whereas double or triple stacking resulted in a remarkable enhancement of NO and NO₂ sensitivities at 350°C. However, the NO₂ sensitivity of these sensors was superior to the NO sensitivity. On the other hand, the NO₂ sensitivity of WO₃ was decreased by the stacking of a Pt-Al₂O₃ catalyst layer, whereas the NO sensitivity increased. Such changes in NO_x sensitivity became more significant when the loading amount of Pt in the catalyst layer increased from 0.5 to 1.0 wt%. As a result, it was found that the 1.0Pt-Al₂O₃/WO₃ heterolayer sensor exhibited comparable sensitivity to both NO₂ and NO at 350°C.

Key Words : Slide-off Transfer Printing, Semiconductor Gas Sensor, Heterolayer, WO₃, NO_x

1 Introduction

Numerous efforts have so far been directed to developing solid-state NO_x gas sensors by employing different kinds of sensor materials, including semiconductors,¹⁻⁴⁾ polymers^{5,6)} and solid electrolytes,⁷⁻⁹⁾ based on different sensing mechanisms. Recent R&D of NO_x gas sensors have three major trends. The first one is an approach to realize an extremely high NO₂ sensitivity by employing WO₃-based materials, and detection of dilute NO₂ in the range of 10-1000 ppb has been demonstrated.^{10,11)} The second one is aimed at improving NO sensitivity, *i.e.* enhancing selectivity to NO against NO₂, since NO is a dominant component among NO_x species in the emission gases from various combustion facilities. Such an approach has been conducted by employing a mixture of p- and n-type metal oxides, Co₂O₃ and Fe₂O₃, as a semiconductor gas sensor¹²⁾ and a Cr₂O₃(5 wt%)-loaded SnO₂ (5Cr₂O₃-SnO₂) as a varistor-type sensor (disc-type) consisting of micro p-n junctions.¹³⁾ The third one is to measure total NO_x by either oxidation of NO to NO₂ with a help of catalyst over sensor electrodes¹⁴⁾ or employing a sensor having NO sensitivity comparable to NO₂ sensitivity.

Our latest study directed to developing NO_x gas sensors can be classified into the last category mentioned above and have demonstrated that a 0.34 wt% Cr₂O₃-doped SnO₂ thick film sensor fabricated by a slide-off transfer printing method¹⁵⁾ showed almost comparable sensitivity to both NO and NO₂,¹⁶⁾ whereas its extremely slow recovery behavior needed to be improved. There-

fore, the aim of the present study was to improve especially NO sensing properties of the thick film sensors by employing hetero-layer structure, consisting of a sensing layer and a catalyst layer fabricated by the slide-off transfer printing method.

2 Experimental

WO₃ powder was prepared by pyrolyzing ammonium paratungstate ((NH₄)₁₀W₁₂O₄₁ · 5H₂O, Kishida Chem. Co., Ltd.) at 500°C for 5 h and subsequent crushing in a planetary-type ball mill for 30 min. Al₂O₃ powder was supplied from Taimei Chemical Ind. Co., Ltd. (TM-D, particle size: *ca.* 0.2 μm). For the loading of a noble metal (Au, Pt and Ru), the WO₃ or Al₂O₃ powder was impregnated with an aqueous solution of a given amount of HAuCl₄ · 4H₂O, H₂PtCl₆ · 6H₂O or RuCl₃ · 3H₂O, and then the solution was evaporated to dryness. The resulting solid was milled and heated at 400°C for 1 h in a hydrogen gas stream. These oxide powders loaded with noble metals were denoted as *n*M-AO (*n*: loading amount of a noble metal in weight %, M: Au, Pt and Ru, AO: WO₃ or Al₂O₃).

The powders prepared were mixed with 5 wt% ethyl silicate and an appropriate amount of a printing oil (Goo Chem. Co., Ltd., OS-4530) as an organic binder by using a three-roller mill (Degussa Japan Co., Ltd., EXAKT M-35) or a hybrid mixer (Keyence Corp., HM-500) to give paste stuffs with good homogeneity and viscosity suitable for screen printing. The paste stuffs were screen-printed using a 100 mesh screen on a sheet of mount paper with

Fig. 1 SEM photographs of cross-sectional views of (a) WO_3 and (b) $0.5\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ fabricated by slide-off transfer printing.

gum, which was dextrin, soluble in water. Then an organic lacquer (Degussa Japan Co., Ltd., 80450) as a cover coat was screen-printed over the oxide layer using a 26 mesh screen to obtain slide-off transfer sheets. The oxide films were separated from the mount paper by soaking them in water, and then were transferred on alumina substrates, on which interdigitated Pt electrodes (the gap between electrodes: $500\text{ }\mu\text{m}$) had been printed, followed by drying at 80°C for 30 min. This process repeated by employing different oxide films in fabricating heterolayer sensors. The heterolayer sensors are represented as $\text{AO}(m)/\text{BO}$ (AO and BO: an upper and lower oxide layer, respectively, m : the number of stacking of the upper oxide layer). The sensors fabricated were fired at 800°C for 2 h in air, and were preheated at 700°C for 48 h to stabilize their gas-sensing characteristics prior to gas sensitivity measurement. Surface and cross-sectional views of the heterolayer sensors obtained were observed by a scanning electron microscope (SEM, Hitachi, S-2250 N).

The sensitivity of the sensors to 100 ppm NO_2 and 100 ppm NO in air was measured in a flow apparatus in the temperature range of $250\sim 500^\circ\text{C}$. The sensitivity (R_g/R_a) was defined as the ratio of the sensor resistance in a sample gas (R_g) to that in air (R_a).

3 Results and Discussion

3.1 Microstructure of heterolayer sensors

Figure 1 shows cross-sectional views of a WO_3 single layer and $0.5\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ heterolayer sensor observed by SEM. In both sensors, no large voids or cracks were found at the interface among the oxide layers and the alumina substrate. Then, the films exhibited good adhesive properties to each other as well as to the alumina substrate during the repeated slide-off transfer printing and the subsequent heat treatment. Microstructure of the $0.5\text{Pt-Al}_2\text{O}_3$ layer was revealed to be very uniform, but large agglomerated secondary particles, different in

size and shape, with a rather rough surface were observed for the WO_3 layer, probably due to the grain growth of WO_3 fine particles. The total thickness of the heterolayer sensor shown in Fig. 1(b) was about $32\text{ }\mu\text{m}$ and was in good accordance with the sum of the thickness of an individual film ($0.5\text{Pt-Al}_2\text{O}_3$ layer: ca. $12\text{ }\mu\text{m}$, WO_3 layer: ca. $20\text{ }\mu\text{m}$) prepared separately.

3.2 NO_x sensing properties of M- WO_3 single layer sensors

Figure 2 shows response transients of WO_3 and 0.5M-WO_3 ($\text{M}=\text{Au}$, Pt and Ru) to 100 ppm NO_2 and 100 ppm NO at 350°C . WO_3 exhibited a resistance increase upon exposure to both NO_2 and NO, but much higher sensitivity to NO_2 than that to NO. In addition, the response speed to NO_2 was much faster than that to NO, whereas the recovery speed to NO_2 was comparable to that to NO. Loading of 0.5 wt% Pt or Ru on WO_3 led to much higher NO sensitivity and faster response behavior than those of WO_3 . However, NO_2 sensitivity of 0.5Pt- and 0.5Ru-WO_3 was comparable to that of WO_3 , whereas their NO_2 response speed was deteriorated, in comparison with that of WO_3 . On the other hand, among the sensors tested, 0.5Au-WO_3 showed the highest NO_2 and NO sensitivities and the fastest NO_2 and NO response. Figure 3 shows the operating temperature dependences of the sensitivities to 100 ppm NO_2 and 100 ppm NO of WO_3 loaded with and without a 0.5 wt% noble metal. The NO_2 sensitivity showed its maximum at $300\sim 350^\circ\text{C}$ for every sensor. The NO sensitivity of WO_3 was minimized at 350°C in the temperature range studied, but the loading of a noble metal resulted in sensitivity enhancement and then maximum sensitivity appeared at $300\sim 350^\circ\text{C}$ for all the 0.5M-WO_3 sensors. The NO and NO_2 sensitivities of the 0.5M-WO_3 sensors showed almost the same temperature dependence, while the NO_2 sensitivity was superior to the NO sensitivity over the whole temperature range. This behavior may arise from oxidation of NO to NO_2 on the surface of the noble metal microparticles, and therefore the resistance increase may come from the adsorption of NO_2 on the WO_3 surface. The observed change in NO_2 and NO sensing properties induced by the noble metal loading approximately coincides with those reported by other researchers. For example, Penza *et al.*

Fig. 2 Response transients of (i) WO_3 , (b) 0.5Au-WO_3 , (c) 0.5Pt-WO_3 and (c) 0.5Ru-WO_3 to (a) 100 ppm NO_2 and (b) 100 ppm NO at 350°C .

Fig. 3 Operating temperature dependence of the sensitivities to (a) 100 ppm NO_2 and (b) 100 ppm NO of WO_3 and 0.5M-WO_3 ($\text{M} = \text{Au}, \text{Pt}$ and Ru).

reported that the sensitivities as well as the response and recovery speed to NO and NO_2 of WO_3 -based sensors (*ca.* 300 nm thick) were improved notably by the loading of Pd, Pt or Au.⁴⁾ The response speed to NO in the present study was also improved by the loading, irrespective of the kind of noble metals. However, only the loading of Au led to an improvement of the response speed to NO_2 . The opposite effect of the Pt and Ru loading on the sensitivity and response speed to NO_2 observed in the present study may arise from the difference in thickness of the sensing layer between Penza's and our study, though the detail is not clear at present.

3.3 Stacking effect of $n\text{Pt-Al}_2\text{O}_3$ catalyst layer on NO_x sensing properties of WO_3 -based sensing layer

Further attempts were made to improve NO_x sensing properties of a 0.5Au-WO_3 sensing layer by stacking a $0.5\text{Pt-Al}_2\text{O}_3$ catalyst layer in a pile. Figure 4 depicts the effect of the stacking of the $0.5\text{Pt-Al}_2\text{O}_3$ catalyst layer on the operating temperature dependences of the sensitivities to 100 ppm NO_2 and 100 ppm NO of 0.5Au-WO_3 . Little change in sensitivities to NO_2 and NO as well as their operating temperature dependence was induced by the stacking of a $0.5\text{Pt-Al}_2\text{O}_3$ catalyst layer, *i.e.* both 0.5Au-WO_3 and $0.5\text{Pt-Al}_2\text{O}_3(1)/0.5\text{Au-WO}_3$ exhibited the maximum sensitivity to NO_2 and NO at 300–350 °C, while the sensitivity to NO_2 was about ten times as large as that to NO for both sensors. When the stacking was repeated, *i.e.* in the case of $m=2$ and 3, the NO_2 sensitivity increased below 350 °C, compared with that for $m=0$ or 1, and the NO sensitivity showed a clear maximal value at 350 °C and increased with increasing the number of stacking of the $0.5\text{Pt-Al}_2\text{O}_3$ layer ($R_g/R_a = \text{ca. } 42$ at $m=1$,

Fig. 4 Operating temperature dependence of the sensitivities to (a) 100 ppm NO_2 and (b) 100 ppm NO of $0.5\text{Pt-Al}_2\text{O}_3(m)/0.5\text{Au-WO}_3$ ($m = 1-3$).

ca. 83 at $m=2$ and *ca.* 102 at $m=3$). The NO_2 sensitivity at 350 °C also increased with increasing the number of the stacking ($R_g/R_a = \text{ca. } 350$ at $m=1$, *ca.* 460 at $m=2$ and *ca.* 670 at $m=3$). However, comparable NO and NO_2 sensitivity could not be achieved even at 350 °C. Thus, these sensors are not suitable for total NO_x sensing.

Stacking of a $0.5\text{Pt-Al}_2\text{O}_3$ or $1.0\text{Pt-Al}_2\text{O}_3$ catalyst layer on a pure WO_3 sensing layer was also tested to improve NO_x sensing properties of the WO_3 single layer sensor. Figure 5 shows the operating temperature dependences of NO and NO_2 sensitivities of two heterolayer sensors ($0.5\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ and $1.0\text{Pt-Al}_2\text{O}_3/\text{WO}_3$). For comparative purpose, the data of WO_3 in Fig. 3 were again plotted in Fig. 5. As stated previously, WO_3 exhibited an extremely high NO_2 sensitivity of *ca.* 210 at 350 °C, but at the same temperature the NO sensitivity was *ca.* 2 at most. Stacking of a $0.5\text{Pt-Al}_2\text{O}_3$ catalyst layer resulted in a decrease in NO_2 sensitivity, but in an increase in NO sensitivity at 350 °C. When an $1.0\text{Pt-Al}_2\text{O}_3$ catalyst layer was employed, such changes in NO_2 and NO sensitivities at 350 °C became more significant. Namely, the $1.0\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ heterolayer sensor showed comparable sensitivity to both NO and NO_2 ($R_a/R_g = \text{ca. } 30$ for NO , and *ca.* 47 for NO_2) at 350 °C. Thus, $1.0\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ showed the most suitable NO_x sensing properties as a total NO_x sensor, among the sensors tested. The response transients to 100 ppm NO and NO_2 of $1.0\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ at 350 °C are shown in Fig. 6. The response to NO was rather slow, in comparison with that to NO_2 , but the sensor exhibited similar recovery behavior for both NO and NO_2 , although the recovery behavior needed to be fur-

Fig. 5 Operating temperature dependence of NO_x sensitivities of WO_3 , $0.5\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ and $1.0\text{Pt-Al}_2\text{O}_3/\text{WO}_3$. Open and filled symbols show the sensitivities to 100 ppm NO_2 and 100 ppm NO , respectively.

Fig. 6 Response transients of $1.0\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ to (a) 100 ppm NO_2 and (b) 100 ppm NO at 350°C .

ther modified in future.

Xue *et al.* have reported that $2.0\text{Pt-Al}_2\text{O}_3$ showed the maximum NO conversion to NO_2 (67%) at 350°C in the temperature range studied.¹⁷⁾ The temperature dependence of the NO sensitivity observed with $0.5\text{Pt-Al}_2\text{O}_3(m)/0.5\text{Au-WO}_3$ and 0.5 or $1.0\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ approximately followed the temperature dependence of the NO conversion reported. Thus, it is considered that NO is oxidized to NO_2 in the $\text{Pt-Al}_2\text{O}_3$ catalyst layer and the WO_3 -based sensing layer responds to the resulting NO_2 . In the atmosphere containing NO_2 , on the other hand, it is expected that NO_2 was reduced partially to NO toward a thermodynamic equilibrium in the $\text{Pt-Al}_2\text{O}_3$ layer. Such oxidation and reduction behavior of NO and NO_2 in the $\text{Pt-Al}_2\text{O}_3$ layer may be responsible for the comparable sensitivity to both NO_2 and NO observed with the $1.0\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ sensor at 350°C .

4 Conclusion

A WO_3 single layer sensor showed much higher sensitivity to NO_2 than to NO . Among the noble metals tested, loading of Au on WO_3 improved notably the sensitivities and the response speed to both NO_2 and NO . Stacking of a $0.5\text{Pt-Al}_2\text{O}_3$ layer over a 0.5Au-WO_3 layer showed little effect on the NO_x sensitivities, whereas double or triple stacking of the $0.5\text{Pt-Al}_2\text{O}_3$ layer resulted in a remarkable enhancement of NO and NO_2 sensitivities at 350°C . However, the NO_2 sensitivity of these sensors was superior to the NO sensitivity. On the other hand, the NO_2 sensitivity of WO_3 was decreased by the stacking of a $\text{Pt-Al}_2\text{O}_3$ catalyst layer, whereas the NO sensitivity increased. Such changes in NO_x sensitivity became more significant when the loading amount of Pt in the catalyst layer increased from 0.5 to 1.0 wt%. As a result, it was found that the $1.0\text{Pt-Al}_2\text{O}_3/\text{WO}_3$ heterolayer sensor exhibited comparable sensitivity to both NO_2 and NO at 350°C and that it was the most suitable candidate as a total NO_x sensor among the sensors tested.

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