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Gold-Loaded Tungsten Oxide Sensor for Detection of Ammonia in Air

Tomoki MAEKAWA, Jun TAMAKI, Norio MIURA, and Noboru YAMAZOE*
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816

Among various noble-metal loaded WO_3 sensor elements, the one loaded with Au showed the best NH_3 sensing performance in sensitivity and response rate at 450 °C. It could detect NH_3 in air over a wide concentration range from 5 ppb to 50 ppm. The optimum Au loading was 0.8 wt%.

Semiconductor gas sensors are now widely used for detecting small concentrations of combustible or toxic gases in air. Recently the detection of smelling components has become increasingly important for food industries, living environments, and medical treatments. The freshness of fishes, for example, can be monitored effectively by detecting the volatile amines of the fishes with gas sensors.[1-3] Among various smelling compounds, ammonia is a typical bad-smelling components generated from garbage or sewage. Currently NH_3 in air is analyzed by electrochemical methods after it is absorbed in aqueous solutions. Such methods are not well suited for rapid NH_3 sensing in addition to the maintenance problem of the analyzers. As solid-state NH_3 sensors, semiconductor devices using WO_3 pellet,[4] $Zn_xGeO_yN_z$,[5] Al doped ZnO,[6] AgCl,[7] and $Cr_{2-x}Ti_xO_3$[8] have so far been investigated, but none seem to be satisfactory in sensitivity and response rate for detecting NH_3 at low levels. We have found that a semiconductor sensor using WO_3 shows excellent NH_3 sensing properties, when promoted with Au, as described below.

The powder of WO_3 was prepared by pyrolyzing ammonium paratungustate ($(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$) at 600 °C for 5 h in air, followed by milling the product in a zirconia-ball mill for 1 day. The powder was loaded with noble metals (Ru, Rh, Pd, Ag, Pt, and Au) by mixing it with aqueous dispersions of respective colloidal metal particles (colloid concentration : 0.5×10^{-3} mol·dm^{-3}) for 5 h under agitation, followed by filtration, washing with deionized water, drying at 110 °C, and calcination at 600 °C for 5 h. The loadings of noble metals were fixed to 0.4 wt% unless noted otherwise. Porous sintered sensor elements were fabricated in the same way as described elsewhere.[9] The powder samples were applied on a alumina tube fitted with Pt wire electrodes and calcined at 700 °C for 4 h. The electrical resistances of the elements in dry synthetic air (R_a) and dry NH_3-air mixtures (R_g) were measured in the conventional flow apparatus. The gas sensitivity (S) was defined as R_a/R_g as usual.

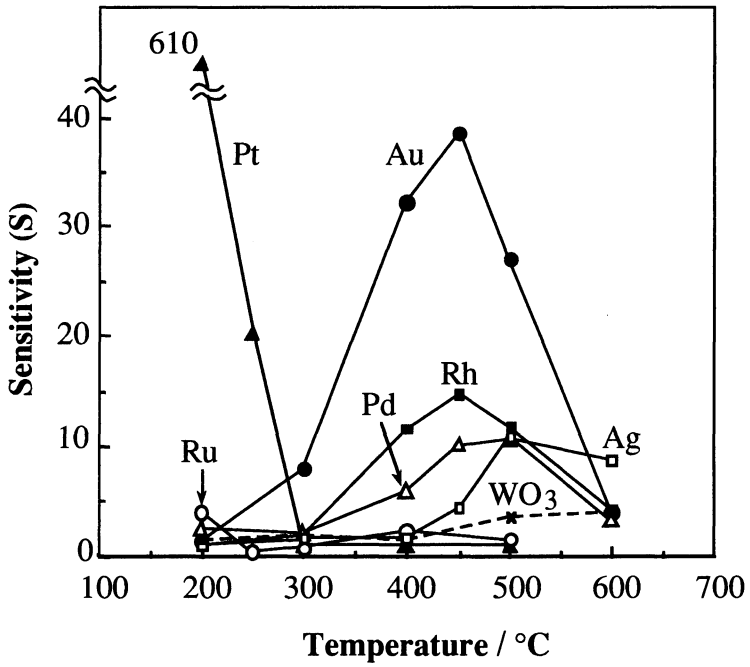

Fig.1. Sensitivity of various noble metal (0.4 wt%)-loaded WO_3 elements to NH_3 (50 ppm) in air at various temperatures.

The WO_3 sensor elements loaded or unloaded with various noble metals were tested for sensing characteristics to 50 ppm NH_3 in air at various temperatures. Figure 1 shows the resulting gas sensitivity of each element. The pure WO_3 element showed low NH_3 sensitivity of less than 5 to 50 ppm NH_3 in the whole temperature range examined, as was also seen with the elements using other metal oxides. The addition of various noble metals to the element was found to be effective for promoting the NH_3 sensitivity at temperatures above 300 °C. The sensor elements loaded with Au, Rh, Pd, and Ag gave volcano-shaped sensitivity-temperature relations, each having a maximum at 450 - 500 °C. The highest NH_3 sensitivity was exhibited by Au-WO_3 element at 450 °C. The promoting effects were in the order, Au > Rh > Pd $\simeq$ Ag, while Ru was almost ineffective. It may be noted that Pt-WO_3 element seemingly showed a very high sensitivity (610) at 200 °C. However, the response to turning-on NH_3 was so slow at such a low temperature that the high sensitivity could not be of practical importance for developing an NH_3 sensor. These results indicate that Au-WO_3 element is the most promising as an NH_3 sensor among the tested elements. In the field of catalysis, Au-supported catalysts such as Au/α-Fe_2O_3, Au/Co_3O_4, and Au/NiO have been reported to be highly active for the oxidation of CO.[10] However, the present promoting effects do not seem to be directly related with such catalytic activity. Further investigations are necessary for understanding the prominent promoting effect of Au.

Figure 2 depicts the response transients of Au-WO_3 element to NH_3 in air at 450 °C. The electrical resistance in air (8.9×10^5 Ω) was low enough to be compatible with the practical circuitry ordinarily used. On exposure to 50 ppm NH_3 (a), it decreased quickly to reach a steady value of 2.3×10^4 Ω within 20 s. The recovery time on turning-off NH_3 was

about 1 min. The decrease in electrical resistance on exposure to NH_3 suggests that NH_3 consumes the adsorbed oxygen of the element in the same way as other combustible gases do.

From a practical viewpoint, an NH_3 sensor should be sensitive enough to sub-ppm NH_3 because NH_3 give us an unpleasant smell at such low levels. The sensitivity of Au-WO_3 element was tested for dilute NH_3 down to 5 ppb. As shown in Fig. 3, an almost linear relationship was observed between the logarithm of the sensitivity and that of the NH_3 concentrations ranging from 5 ppb to 50 ppm at 450 °C. It is noteworthy that Au-WO_3 element is fairly sensitive to dilute NH_3, exhibiting the sensitivity of 2.3 for 5 ppb NH_3. The response rates became somewhat slower as NH_3 concentration decreased : 90% response and 90% recovery took 2 and 3 min, respectively, for 5 ppb NH_3 (Fig. 1(b)). In this way Au-WO_3 element was shown to be able to detect extremely low levels of NH_3 in air.

So far the loading of Au was fixed to 0.4 wt%. In order to know the optimum Au loading, the loadings were varied from 0 to 1.2 wt%. Figure 4 depicts the electrical resistances of the elements in air (R_a) and in 50 ppm NH_3 (R_g) as well as the resulting NH_3 sensitivity at 450 °C as a function of Au loading. The NH_3 sensitivity reached a maximum value of 68 at 0.8 wt% Au. Quite interestingly R_a increased steeply with an increase in Au loading to be maximum at 0.8 wt% Au. This suggests that Au exerts an interaction with WO_3 which eventually deprives WO_3

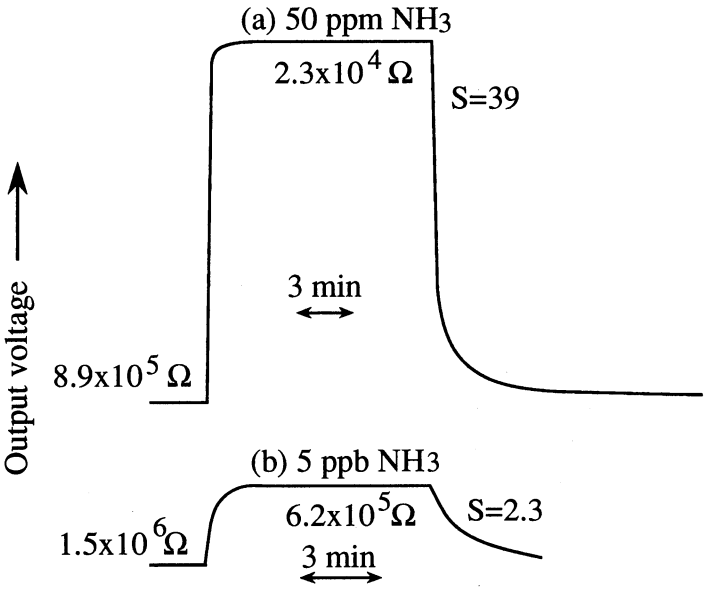

Fig. 2. Response transient of Au(0.4 wt%)-WO_3 element to NH_3 in air (450 °C).

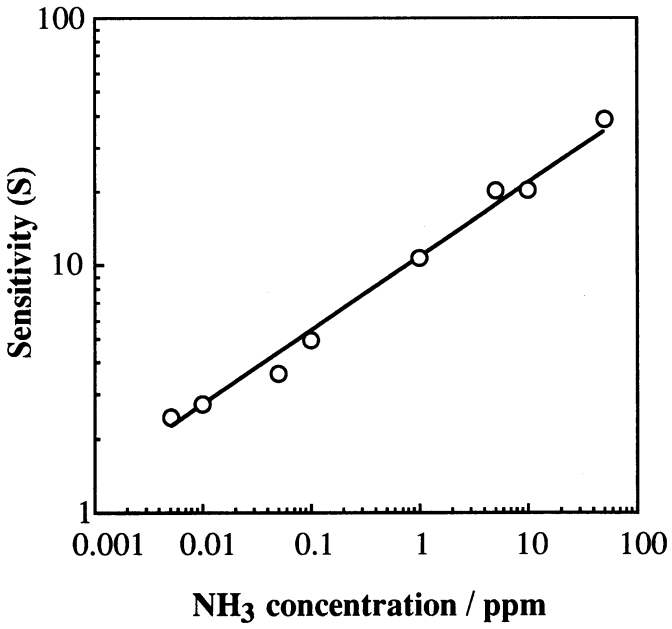

Fig. 3. Sensitivity of Au(0.4 wt%)-WO_3 element as correlated with NH_3 concentration (450 °C).

particles of conduction electrons in air. In the NH_3 containing atmosphere, on the other hand, major part of the deleted electrons are given back to WO_3, to allow the electrical resistance to decrease down to R_g. It follows that the promoting effect of Au would be ascribed to the electronic interaction between Au and WO_3. Such a promoting mechanism has been proposed for the detection of combustible gases with Pd-SnO_2 and Ag-SnO_2 elements.[11]

In conclusion, Au-loaded WO_3 elements exhibited excellent sensing properties to NH_3 in air at 450 °C. The elements were sensitive to dilute NH_3, being able to detect 5 ppb NH_3 in air.

We are grateful to Toda Kogyo Co. Ltd. for donation of noble-metal colloidal samples.

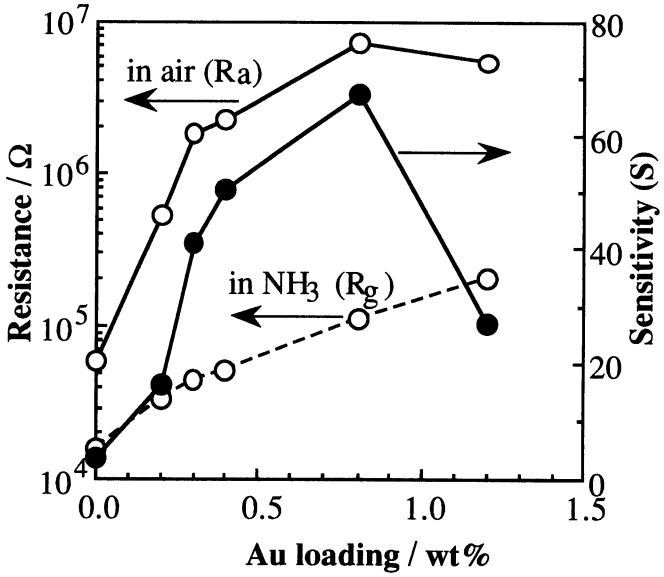

Fig. 4. Several characteristics of Au-WO_3 elements as a function of Au loading (450 °C). NH_3 concentration:50 ppm in air.

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