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Tungsten Oxide-Based Semiconductor Sensor Highly Sensitive to NO and NO_2

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A sintered sensor element based on WO_3 was found to be very sensitive to NO and NO_2. The sensitivity, defined as the ratio of the resistance in the gases to that in air, was as high as 31 and 97 to 200 ppm NO and 80 ppm NO_2, respectively, at 300 °C. The element was well suited for sensing the gases at low levels. Satisfactory performances to NO and NO_2 were exhibited in the regions of 0-800 ppm and 0-200 ppm, respectively.

Nitrogen oxides, NO and NO_2, generated from combustion facilities and automobiles are air pollutants which give damages to human respiratory organs and nerves or cause acid rain, as now recognized world-wide. Their concentrations in air or exhausts are currently determined by means of spectroscopic analyzers based on chemical luminescence. Beside being costly, however, these analyzers are difficult to fit to feed back control systems. Thus there is a growing need for solid state sensors to detect the nitrogen oxides from the view point of emission control or air pollution monitoring. Several exploratory works have been carried out to develop such sensors by using semiconductive oxides,[1-3] solid electrolytes,[4] phthalocyanine,[5] and SAW devices.[6] The sensor using a semiconductive oxide is of particular interest from its structural simplicity and potential durability for operation under extreme conditions. As this type, a sensor using In^{3+}-doped TiO_2 has been commercialized.[1] Generally speaking, however, the semiconductor sensors so far reported are low or modest in sensitivity to either of NO and NO_2. It is of primary importance to exploit better sensing materials. In the course of an extensive search for more sensitive oxides, we have found that WO_3 can be an excellent sensing material for NO and NO_2, as described below.

The powder of WO_3 was prepared by pyrolyzing ammonium paratungstate ($(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$) at 600 °C for 5 h, followed by milling in a zirconia ball mill for 1 day. The powder was mixed with water into a paste, which was applied on an alumina tube substrate attached with two Pt coil electrodes 1.5 mm apart in between, and sintered at 600 °C for 4 h in air. The sintered body type element obtained is illustrated in Fig. 1. Gas sensing experiments were carried out in a standard flow apparatus equipped with a heating

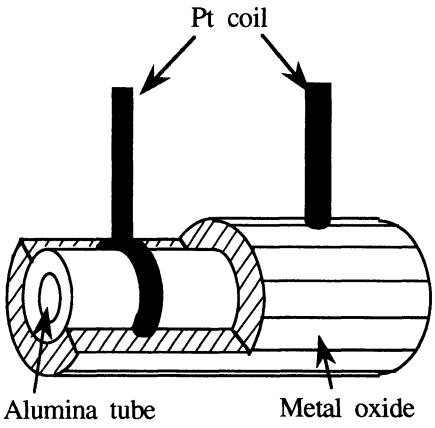

Fig. 1. Structure of sensor element used.

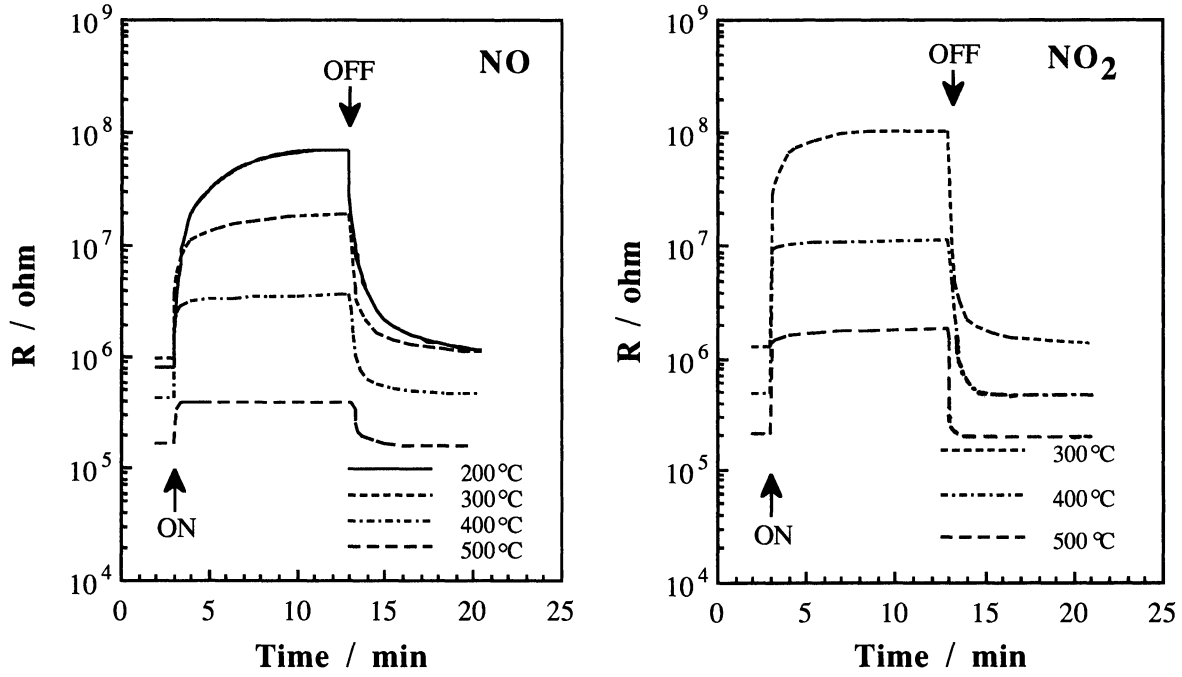

Fig. 2. Response transients of WO_3-based element to 200 ppm NO (left) and 80 ppm NO_2(right) at various temperatures.

facility, through which dry air or a sample gas was let to flow at a rate of 200 cm^3/min. The sample gas was prepared by diluting the parent source of NO (1000 ppm in N_2) or NO_2 (200ppm in air) with dry air. The concentrations of NO and NO_2 were set in many cases to 200 and 80 ppm, respectively, as their typical levels in the exhausts, but in other cases they were varied in the ranges 0-800 ppm (NO) and 0-200 ppm (NO_2). On switching-on and -off the sample gas flow, the electrical resistance of the element was monitored and recorded by means of an electrometer at various temperatures. The gas sensitivity to NO or NO_2 was defined as R_g/R_a, where R_a and R_g are the resistance in air and the sample gas, respectively.

Figures 2 (a) and (b) show the response transients of WO_3 element to 200 ppm NO and 80 ppm NO_2 at various temperature, respectively. On turning-on NO or NO_2 flow, the resistance of the element increased rapidly to reach a steady state, while on turning-off it recovered the initial level also rather quickly. The 90%

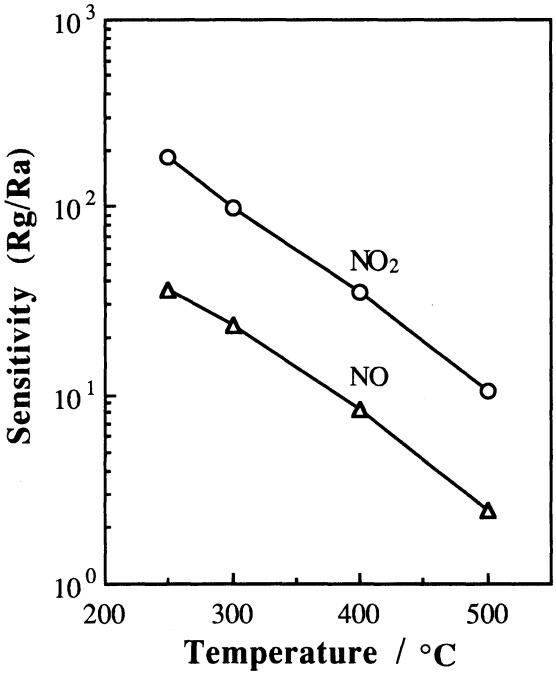

Fig. 3. The sensitivity of WO_3-based element to 200 ppm NO and 80 ppm NO_2 as correlated with the operating temperature.

response times to turning-on NO and NO_2 were 20 and 10 s at 300 °C, respectively. At 200 °C, no reliable response transient to 80 ppm NO_2 could be obtained with the present electrical circuitry because of the too high resistance level brought about by the NO_2 adsorption. At the same time, this means that the element becomes extremely sensitive to NO_2 at such low temperatures.

The sensitivity of the present sensor element to NO and NO_2 is shown as a function of operation temperature in Fig. 3. As just mentioned, the sensitivity to NO_2 (80 ppm) was very large, being 97 at 300 °C. Although it decreased rather steeply with increasing temperature, it still remained as large as 10 at 500 °C. The sensitivity to NO (200 ppm) was about one fifth of that to NO_2 (80 ppm) at each temperature tested. Nevertheless it is noted that the NO sensitivity levels marked by the present sensor at 400 °C and below are still quite excellent when one consider that the highest sensitivity attained by various semiconductor sensors to date is as low as 5 to 6 to both NO and NO_2 at 600 ppm.[3)]

The experiments mentioned so far have revealed that WO_3-based sensor element is very sensitive to the fixed concentrations of NO and NO_2. To evaluate the sensing properties of the element, experiments were extended to cover various concentrations of NO and NO_2. The results are summarized as sensitivity *vs.* concentration correlations in Fig. 4. As shown in Fig. 4(a), the element responded sensitively to the variations of NO concentration over the whole concentration range tested (0-800 ppm) at 200 °C. Combined with the sensitivity levels as high as 110, 200 and 340 at 200, 400 and 800 ppm NO, respectively, this assures that the element has sufficient capability of sensing the practical levels of NO in the exhausts at this temperature. A rise in temperature, however, caused the sensitivity to saturate at a smaller concentration region in addition to a steep loss of sensitivity. Because of such unfavorable effects, the reliable sensing range of NO decreased to approximately 0-200 ppm at 300 °C.

The sensitivity to NO_2, on the other hand, was still excellent even at 400 °C, as shown in Fig. 4(b). The

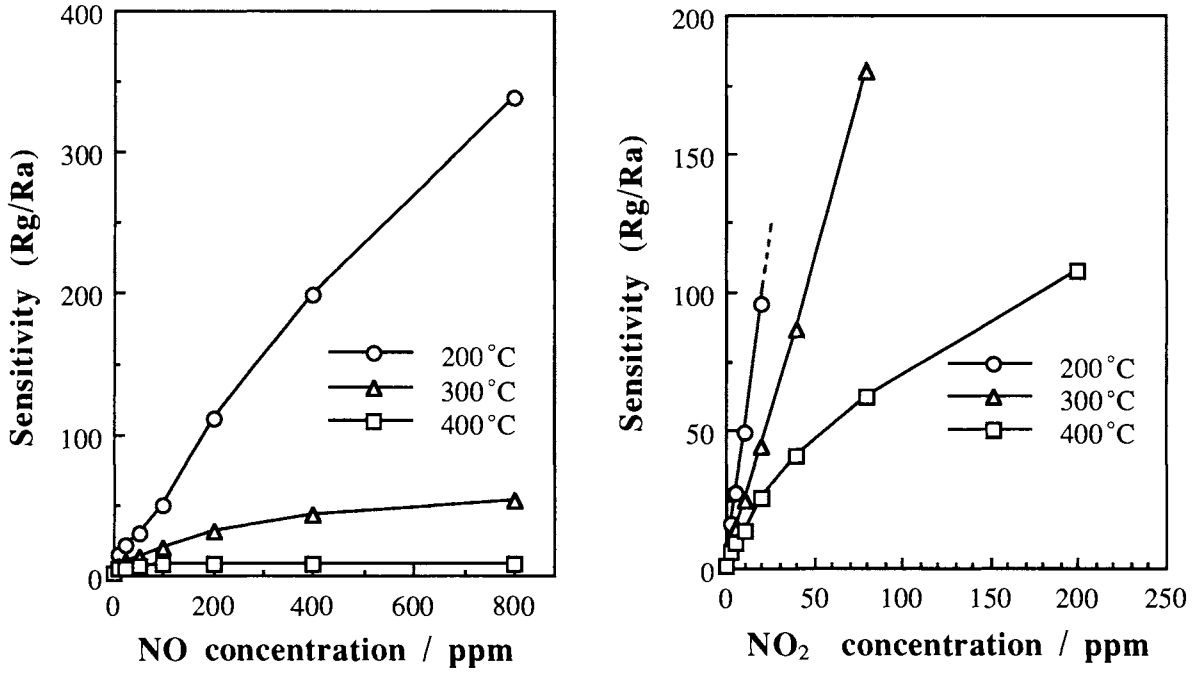

Fig. 4. Sensing capability of WO_3-based element to the variation of gas concentration for NO (left) and NO_2 (right) at various temperature.

Table 1. Sensitivity (R_g/R_a) of WO_3-based element to various gases (300 °C)

Gas	NO	NO_2	CO	H_2	CH_4	i-C_4H_{10}
Conc./ppm	200	80	1000	1000	500	1000
Sensitivity	23	97	0.50	0.60	0.81	0.14

practically important concentration range of NO_2 in the exhausts (0-100 ppm) seems to be safely covered by the present element at 300 or 400 °C. At 200 °C, however, the acceptable NO_2 concentration was less than 40 ppm in the present circuitry because the element became too resistive when exposed to NO_2 at 40 ppm and above. These results indicates that the present element is suited for detecting low concentrations of NO_2 especially at low temperatures such as 200 and 300 °C.

The exhausts of combustion facilities usually include various inflammable gases which may interfere with the detection of NO and NO_2. As a preliminary test, the element was exposed to several inflammable gases at 300 °C. Table 1 summarizes the response of the element to tested gases. As expected, the resistance of the element decreased on exposure to an inflammable gas, leading to a sensitivity value (R_g/R_a) less than unity. In this expression, therefore, the actual sensitivity to an inflammable gas should be evaluated from the reciprocal of the indicated value. The values show that the element is not so sensitive to CO, H_2 and CH_4 but rather sensitive to i-C_4H_{10}. Even the response to 1000 ppm i-C_4H_{10}, however, is far less than that to 200 ppm NO or 80 ppm NO_2. Nevertheless, this indicates that some hydrocarbons at high levels can interfere with the present sensor and further investigations are necessary to solve this problem.

As stated above, WO_3-based element responds to NO and NO_2 by sharp increases of its resistance. Since WO_3 is an n-type semiconductor, this means that NO and NO_2 form anionic adsorbates on the surface of WO_3 particles under the present conditions. These gases are known to give various types of adsorbates on the oxide surface depending on the experimental conditions.[7] Elucidation of the adsorbed state of NO and NO_2 would be indispensable for understanding the sensing mechanism of the present sensor.

In conclusion, WO_3-based element has excellent sensing properties to NO and NO_2 with high sensitivity and quick response rates. With its sensitivity being far superior to the other oxides reported so far, WO_3 seems to be very promising material applicable to semiconductor sensors for NO and NO_2.

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