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Role of Additives on Alcohol Sensing by Semiconductor Gas Sensor

Shigenori MATSUSHIMA, 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

Influences of various oxide additives on C_2H_5OH sensing properties of SnO_2-based elements were examined. The sensitivity and selectivity of the elements could be markedly promoted with the addition of basic oxides represented by La_2O_3. The promoting effect was estimated to be related with selectivity in oxidation reaction of C_2H_5OH.

Although semiconductor gas sensors based on SnO_2 have already been used in the many fields, modifications of the sensing properties such as the sensitivity and selectivity are still awaited to meet ever expanding demands for new applications. This type sensor detects inflammable gases in air from a change in electrical resistance of the gas sensing elements resulting from the adsorption and/or reaction of the gases on the semiconductor surface.[1] Therefore the sensitivities and selectivities for given objective gases are intrinsically determined by sensing materials and temperature, and there is no much room to alter them as far as pure SnO_2 is used. This situation has been overcome by use of modifiers. It has been known for the long time that small amounts of noble metals such as Pd and Pt, generally added to the elements, improve drastically the sensing properties especially to hydrogen or hydrocarbon.[2] Recent investigations have shown that metal oxides can also be effective modifiers for sensing several gases such as H_2S, CH_3SH and C_2H_5OH, though working mechanisms are not well understood.[3] This paper aims at elucidating the effects of metal oxide additives on the sensitivity and selectivity of SnO_2-based elements to C_2H_5OH gas and thus contributing to the development of a good alcohol sensor. There have been increasing demands for reliable alcohol sensors for use as a breath alcohol checker for a car driver or a monitor for alcohol gas in air. However, the demands have not been met fully by the several elements investigated so far such as $Sm_{0.5}Sr_{0.5}CoO_3+In_2O_3$,[4] SnO_2 film fabricated on hydroxyapatite,[5] and a catalytic combustion type element of $CaO-SnO_2$.[6]

SnO_2 powder was prepared from $SnCl_4$. The stannic acid, precipitated by adding ammonia to an aqueous solution of $SnCl_4$, was washed thoroughly with deionized water, dried at 100 °C, and calcined at 600 °C for 5 h in air. To prepare a metal-oxide loaded sample, the above SnO_2 powder was impregnated with an aqueous solution of an acetate of the chosen metal, followed by evaporation to dryness and calcination at 600 °C for 5 h in air. In this way, various oxides of

alkali, alkaline earth, rare earth, and transition metals were loaded. The loading was controlled to 5 wt% in all cases.

The sensor element fabricated is shown in Fig. 1. The SnO_2 powder loaded or unloaded with metal oxides was mixed with water and the resulting paste was applied 1.0 mm thick on an alumina tube (1.2 mmϕ) attached with two Pt coil electrodes 1.5 mm apart from each other. The element was sintered at 700 °C for 4 h in air. For gas sensing experiments, the element was set in a flow apparatus through which air or a sample gas was let to flow at a rate of 150 cm^3/min. The gas sensitivity (S) was defined as Ra/Rs, where Ra and Rs were the electric resistances of a chosen element in air and in a sample gas, respectively. The electric resistance was measured based on a conventional circuitry in which the element was connected with an external resistor in series. The output voltage across the external resistor at a circuit voltage of 10 V was used to evaluate the electric resistance of the element.

Figure 2 compares the responses of pure SnO_2 and La_2O_3-SnO_2 elements when gas flow was changed between air and a sample gas (1000 ppm C_2H_5OH + air) at 300 °C. As far as the gas sensitivity is concerned the effect of La_2O_3 doping is too obvious: the doped element showed a sensitivity as high as 724 to be compared with 17 of the undoped element. The La_2O_3 doping was a little effective to improve the rate of response. On switching to the sample gas flow, the 90% response times were not so much different between the two elements, while the recovery on switching back to the air flow was much faster with the doped element than with the undoped element.

Figure 3 shows the gas sensitivities of the above two elements to 1000 ppm C_2H_5OH and 1000 ppm i-C_4H_{10} as a function of temperature in the range of 300 -

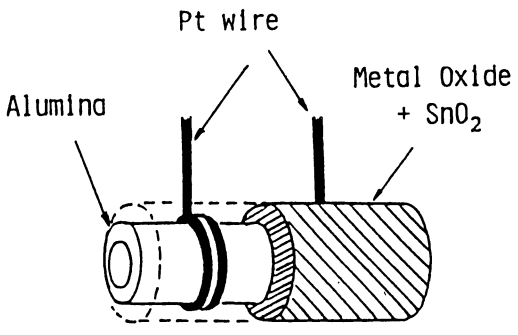

Fig. 1. Schematic view of gas sensor element.

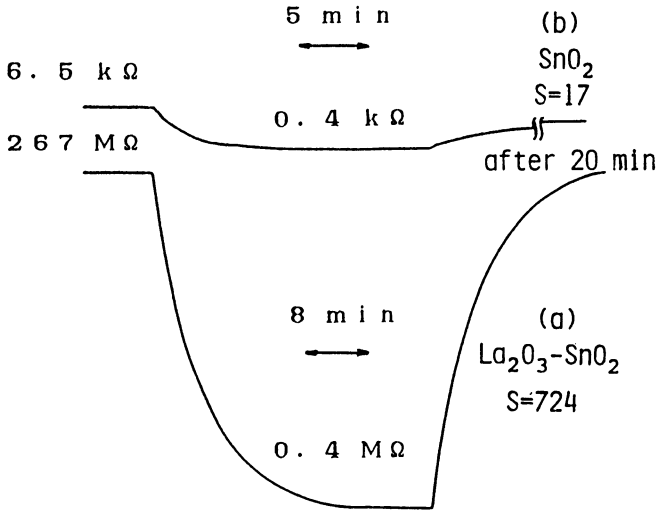

Fig. 2. Responses of La_2O_3-loaded SnO_2 element (a) and pure SnO_2 element (b) to 1000 ppm C_2H_5OH in air at 300 °C.

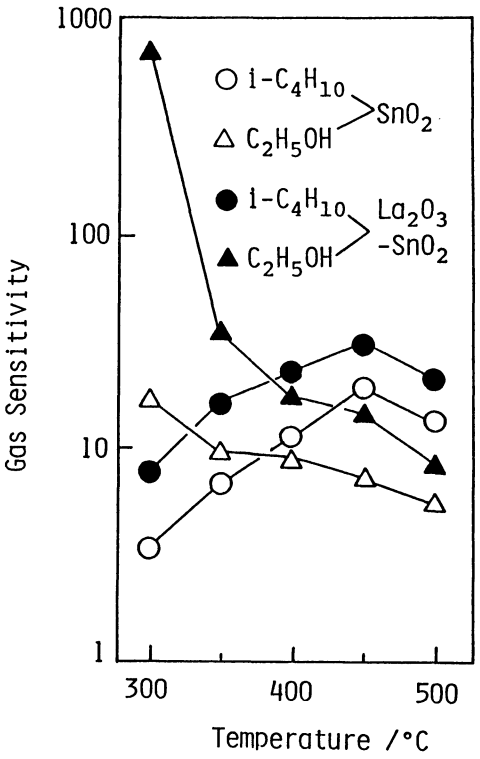

Fig. 3. Temperature dependences of gas sensitivities of La_2O_3 loaded- and unloaded-SnO_2 elements to 1000 ppm i-C_4H_{10} and 1000 ppm C_2H_5OH in air.

500 °C. In general the gas sensitivity is known to depend sometimes markedly on temperature. For alcohol gas, the sensitivity tends to decrease with increasing temperature. It is seen that La_2O_3 doping increases the alcohol gas sensitivity particularly at lower temperatures like 300 °C. It is also observed that no such marked enhancement of the sensitivity was exerted for the sensing of i-C_4H_{10}. This implies that La_2O_3 doping enhances the selectivity to C_2H_5OH over i-C_4H_{10} at lower temperatures.

To understand such doping effects the same experiments were extended to the samples doped with other various metal oxides. As a result, the promoting effects were found to be very much dependent on the metal oxides doped.

Figure 4 depicts the gas sensitivities of various doped elements to 1000 ppm C_2H_5OH (a) and 1000 ppm i-C_4H_{10} (b) as a function of the electronegativity of each loaded metal-cation. It is seen that the high sensitivities to C_2H_5OH tend to be conducted by addition of basic oxides containing alkali, alkaline earth, or rare earth metals, though considerably large scattering of the plots does not allow quantitative discussion. This tendency coincides fairly well with the finding on a contact combustion-type elements based on SnO_2 that the alcohol sensitivity was improved by the addition of CaO and other alkali or alkaline earth metal oxides.[6] The acid-base properties of elements hardly affected the sensitivities to i-C_4H_{10} as shown in Fig. 4(b).

It is well known that there are two processes in the oxidation of C_2H_5OH, i.e., a process initiated with oxidative dehydrogenation to CH_3CHO (1) and another initiated with dehydration to C_2H_4 (2). The selectivity for the two reactions is

$$C_2H_5OH + (1/2)O_2 \longrightarrow CH_3CHO + H_2O \quad (1)$$

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O \quad (2)$$

known to be influenced by acid-base properties of oxide surface, that is, the dehydrogenation proceeds preferentially on the oxide surface with strong basicity, while the dehydration is favored on the acidic surface.[7] This reaction selectivity seems to be deeply related with the strong promoting effects of basic oxide additives on the alcohol sensitivity of SnO_2-based elements. It has been

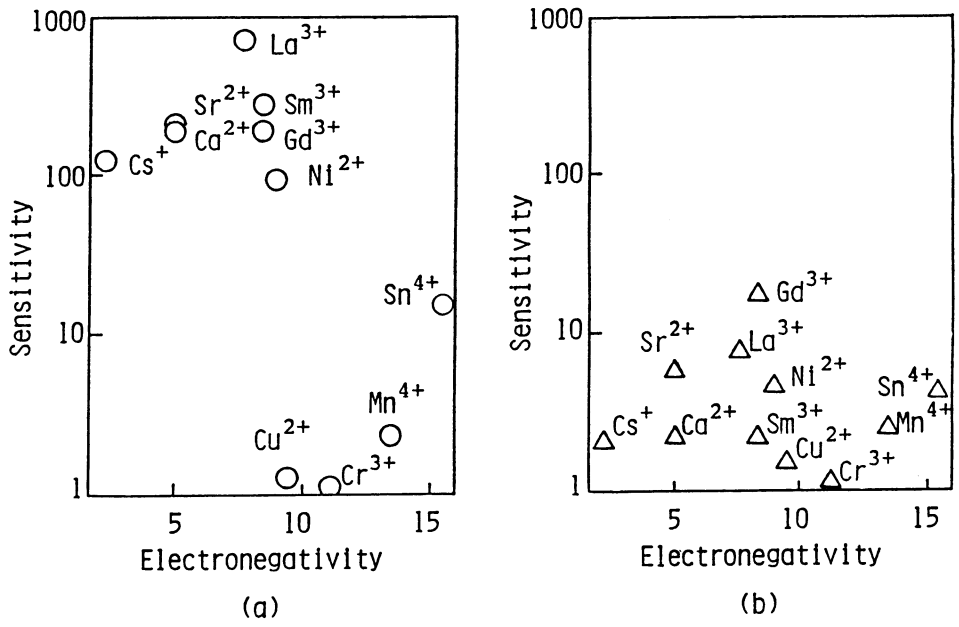

Fig. 4 Gas sensitivities of 5 wt% metal oxide loaded-SnO_2 elements to 1000 ppm C_2H_5OH (a) and 1000 ppm i-C_4H_{10} (b) in air at 300 °C as correlated with the electronegativities of loaded metal cations.

shown that, of the above two intermediates from C_2H_5OH, CH_3CHO has higher molecular sensitivity than C_2H_5OH, while C_2H_4 does lower sensitivity than C_2H_5OH.[8] Therefore the selection of the oxidative dehydrogenation root on the basic surface would inevitably increase the alcohol sensitivity of the SnO_2-based elements.

In conclusion, basic oxide additives such as La_2O_3 markedly promote the sensitivity and selectivity of SnO_2-based sensor to C_2H_5OH. The effects are likely to be related with changes in reaction selectivity in the oxidation of C_2H_5OH.

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