NO_x Gas Sensing Properties of ZnO-based Varistor-type Gas Sensors

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Summary

Current (I)-voltage (V) characteristics of ZnO-based oxides have been investigated in air as well as in 100 ppm NO₂ and NO balanced with air at elevated temperatures. A pure ZnO exhibited a nonlinear I - V characteristic in air and its breakdown voltage shifted to a high electric field upon exposure to NO₂, but to a low electric field upon exposure to NO. Grain size of ZnO was increased slightly by the Bi₂O₃-based additive, which is essential for fabricating conventional varistors used as voltage-surge suppressors. In accordance with this change the sensitivities to NO₂ and NO were decreased, especially at 300°C. The Bi₂O₃-based additive containing Y₂O₃ was effective for reducing the grain size slightly, increasing the breakdown voltage in air and enhancing sensitivities, especially to NO₂ at 400°C and to NO at 300°C. The addition of Cr₂O₃ to the Bi₂O₃-based additive containing Y₂O₃ was more effective for reducing the grain size, but led to a deterioration of sensitivities to NO₂ and NO.

Keywords: varistor, ZnO, NO_x sensor, nonlinear I - V characteristic, breakdown voltage

1. INTRODUCTION

Gas sensor materials capable of detecting nitrogen oxides (NO_x, primarily NO and NO₂) with high sensitivity have attracted much interest in conjunction with the growing concern to the protection of global environments. Besides conventional sensor materials, such as semiconductors [1-3], conducting polymers [4,5] and solid electrolytes [6,7], the potential of sensor materials with a new method for detecting NO or NO₂ gas has also been tested [8,9].

Our previous studies have demonstrated a new gas-detection method, i.e. the use of gas-sensitive breakdown voltage, by employing porous ZnO- and SnO₂-based varistors [10-13]. The breakdown voltage of porous varistors shifted to a low electric field upon exposure to H₂ gas, whereas it shifted to a reverse direction in an atmosphere containing oxidizing gases such as O₃ and NO₂ in the temperature range of 300 to 600°C. Furthermore, it was found that the magnitude of the breakdown voltage shift, i.e. the magnitude of the sensitivity, was well correlated with gas concentration, and that the H₂ sensitivity was improved by controlling the composition of the Bi₂O₃-rich grain-boundary phase [14]. However, NO_x sensing properties of porous varistors have not been studied in detail.

The objective of the present study is to investigate the effect of the composition of the Bi₂O₃-rich grain-boundary phase on the NO and NO₂ sensing properties of porous ZnO-based varistors.

2. EXPERIMENTAL

2.1 Fabrication of Porous ZnO-based Elements

Besides a pure ZnO specimen, two series of specimens containing Bi₂O₃-based additive with and without Cr₂O₃ were prepared from a mixture of the following compounds: ZnO, Bi(NO₃)₃·5H₂O, Sb₂O₃, Co(NO₃)₂·6H₂O, MnCO₃, SiO₂,

Cr₂O₃ and Y₂O₃. The mixing ratios of these compounds were adjusted so as to achieve the final compositions of specimens listed in Table 1. The Bi₂O₃-based additive consisting of Sb₂O₃, Co₂O₃, MnO₂ and SiO₂ are essential for the fabrication of conventional varistors used as voltage-surge suppressors [15]. Only the amount of ZnO was reduced by the addition of 5.0 mol% Cr₂O₃ and in accordance with an increase in the Y₂O₃ content, while the amounts of other additives remained constant. Among the elements added to ZnO, Co and Mn are doped mainly in the ZnO grain and then reduce the ZnO bulk resistivity. On the other hand, other elements are known to form mixed oxide phases, such as spinel, pyrochlore and Bi-rich phases, and then to exist mainly at a grain boundary and/or a triple point. These mixed oxide phases control the grain growth of ZnO and then the microstructure of varistors [15]. Hereafter, the specimens without Cr₂O₃ are represented as ZYXXXX, while the specimens with 5.0 mol% Cr₂O₃ as ZCYXXXX. In both series, the last three letters of abbreviations XXX indicate the amount of added Y₂O₃ in mol%; e.g. ZY025 represents a specimen containing 0.25 mol% Y₂O₃.

The mixture of raw materials was wet milled in a planetary-type ball mill for 30 min. The mixture was dried and then was calcined at 900°C for 1 h. The resulting solid was milled in a dry process for 10 min, mixed with 7 wt% the aqueous solution containing 5 wt% poly(vinylalcohol) solution, and then formed into discs of 5 mm diameter and about 1 mm thick. The disks were sintered at 900°C for 3 h in air. Both faces of a sintered disk were polished with an emery paper down to about 0.5 – 0.6 mm thick. Gold paste was applied (about 4.5 mm in diameter) to both faces of the disk, fired at 700°C for 30 min in air, and then served as electrodes for electrical measurements. A pure ZnO element was also fabricated in a manner similar to the above, except for the calcination and sintering conditions, 1200°C for 2 h and 900°C for 2 h, respectively.

2.2 NO_x Sensing Properties and Characterization of Porous ZnO-based Elements

Current (I)-Voltage (V) characteristics of ZnO-based elements were measured by scanning a dc electric field at a speed of 0.25 - 2.5 V/sec. To prevent the elements from local fusion due to Joule heating the measurement was stopped when the current flowing through the element reached 10 mA. These measurements were carried out at 300 - 700°C in air, 100 ppm NO and 100 ppm NO₂, the latter two being balanced with air. The breakdown voltage of an element is defined as an electric field at which the element conducts 10 mA, and the magnitude of the shift in the breakdown voltage induced by the presence of a sample gas is defined as gas sensitivity.

The effects of the addition of the Bi₂O₃-based additive and its composition on the microstructure of elements were studied by using a scanning electron microscope, SEM.

Table 1. Composition of specimens

Specimen	Final composition / mol%			
	ZnO	Bi ₂ O ₃ -based additive*	Cr ₂ O ₃	Y ₂ O ₃
Z	100	0	0	0
ZY000	97.3	2.7	0	0
ZY025	97.05	2.7	0	0.25
ZY033	96.97	2.7	0	0.33
ZCY000	92.3	2.7	5.0	0
ZCY025	92.05	2.7	5.0	0.25
ZCY033	91.97	2.7	5.0	0.33

* Bi₂O₃ : Sb₂O₃ : Co₂O₃ : MnO₂ : SiO₂ = 1.0 : 0.5 : 0.5 : 0.5 : 0.2 (molar ratio)

3. RESULTS AND DISCUSSION

3.1 NO_x Sensing Properties of a Pure ZnO Element

Figure 1 shows I - V characteristics of a pure ZnO element in air, 100 ppm NO₂ and NO at 400°C under different four scanning speeds. In this figure, the abscissa indicates the applied voltage divided by the element thickness. Nonlinear I - V characteristics were observed even for a pure ZnO element. This fact supports the concept that the existence of a physically separate, intergranular and insulating layer between two ZnO grains is not essential for the development of double Schottky barrier, as pointed out by several researchers [16, 17]. Of course, the existence of electron (majority of charge carriers in the case of ZnO) traps at the grain-boundary interface by any acceptor-like defect models and then the formation of a depletion layer in the grains are indispensable for developing the nonlinear behavior. The breakdown voltage shifts to a high electric field upon exposure to NO₂, in comparison with that in air, whereas to a low field in the case of NO, at every scanning speed. Such sensing properties are favorable for the discrimination between NO₂ and NO, but less advantageous in detecting the

total NO_x amount in a NO₂-NO gas mixture.

Possible reactions for the chemisorption of NO₂ and NO on ZnO and a Bi₂O₃-based intergranular phase are as follows.

Fig. 1. I - V characteristics of a pure ZnO element in air, 100 ppm NO₂ and 100 ppm NO at 400°C under different scanning speeds of applied dc electric field.

Fig. 2. Operating temperature dependence of (a) breakdown voltage in air and sensitivities to (b) 100 ppm NO₂ and (c) 100 ppm NO of a pure ZnO element.

From the change of the breakdown voltage observed, it is anticipated that NO₂ forms negatively charged NO₂(ad) by capturing electrons in ZnO grain according to eq. (1), and therefore NO₂ acts as an oxidizing gas to enhance the height of the double Schottky barrier at ZnO-ZnO grain boundaries. Nitrite ions, NO₂⁻(ad), are also anticipated to be formed by the chemisorption of NO₂, but their formation according to eq. (2) result no change in the breakdown voltage. However, if NO₂ react with gaseous O₂ and then form NO₃(ad) according to eq. (3), enhancement of the height of the double Schottky barrier is also expected. Here, eq. (3) means an increase in the adsorption site for negatively charged species under the atmosphere containing gaseous NO₂.

In contrast, NO is anticipated to be chemisorbed positively according to eq. (4) and to act as a reducing gas under our experimental condition, while NO is known to act either a reducing gas or an oxidizing gas according to eq. (5) depending on adsorption conditions. If NO is oxidized with O(ad) according to eq. (6) and then the produced NO₂ move away from the surface immediately and/or chemisorbe according to eq. (2), a shift of the breakdown voltage to a low electric field can also be expected.

The behavior of an *I-V* characteristic in each environment is found to be dependent on the scanning speeds. The decrease in the scanning speed results in decreases both in the breakdown voltage in air and in the sensitivity, especially to NO, but an improvement of nonlinearity. The Joule heating was anticipated to be the main cause for such changes in *I-V* characteristics, since the effect of the Joule heating becomes significant at a lower scanning speed. Thus, *I-V*

Fig. 3. Scanning electron micrographs of ZnO-based elements: (a) pure ZnO, (b) ZY000, (c) ZY025, (d) ZY033, (e) ZCY000, (f) ZCY025 and (g) ZCY033.

Fig. 4. Operating temperature dependence of (a) breakdown voltage in air and sensitivities to (b) 100 ppm NO₂ and (c) 100 ppm NO of ZY series elements.

Fig. 5. Operating temperature dependence of (a) breakdown voltage in air and sensitivities to (b) 100 ppm NO₂ and (c) 100 ppm NO of ZYC series elements.

characteristics were measured at a scanning speed of 2.5 V/sec in the below so as to reduce the effect of the Joule heating.

The breakdown voltage of a pure ZnO element in air decreased with a rise in operating temperature, as shown in Fig. 2(a). In accordance with this change, sensitivities to 100 ppm NO₂ and NO decreased significantly with a rise in operating temperature, as shown in Figs. 2(b) and (c): the element became almost insensitive to NO₂ above 400°C and to NO above 500°C.

SEM observation of the fracture surface of a ZnO element has revealed that there is a wide distribution of ZnO particle size from sub- μm to ten μm , as shown in Fig. 3(a). All particles are sharply outlined and the average grain size is measured to be 7.0 μm by the intercept method.

3.2 NO_x Sensing Properties of ZY Series Elements

The breakdown voltage in air was decreased by the Bi₂O₃-based additive, i.e. the breakdown voltage of ZY000 was lower than that of pure ZnO at temperatures lower than 400°C, as shown in Fig. 4(a). Above 500°C, the effect of the Bi₂O₃-based additive on the breakdown voltage became obscure probably due to the significant contribution of the leakage current at high temperatures. Sensitivities to 100 ppm NO₂ and NO were also decreased by the Bi₂O₃-based additive, as shown in Figs. 4(b) and (c). SEM observation

of the fracture surface of ZY000 suggested the existence of a thin and continuous Bi₂O₃-rich grain-boundary layer, as shown in Fig. 3(b). Furthermore, the addition of the Bi₂O₃-based additive resulted in a narrower distribution of grains (compare Fig. 3(b) with Fig. 3(a)), and then led to an enlargement in average ZnO grain size to 9.0 μm . Sub- μm size particles are hardly observed in the case of ZY000. The enlargement of the ZnO grain size directly means a decrease in the number of ZnO-ZnO grain boundaries between two electrodes. The breakdown voltage of the element is the sum of a breakdown voltage per grain boundary and therefore is proportional to the number of grain boundaries [18]. Thus, the decrease in the breakdown voltage in air can be attributed undoubtedly to the decrease in the number of grain boundaries, even if a breakdown voltage per grain boundary, i.e. height of the double Schottky barrier at a grain boundary, remains unchanged irrespective of the grain sizes. But, it is anticipated that the height of the double Schottky barrier at a grain boundary decreases with an increase in grain size, since the contribution of the surface electron traps to the reduction of electrons in the bulk decreases with increasing grain size. Such effect is more significant in the neck part between two grains. This makes the grain boundary insensitive to gases inducing the changes in the electron-trap density. In air environment, possible chemical species acting as electron traps are oxygen adsorbates on grains and excess oxygen ions at grain

boundaries (diffused into the grain boundaries) [19, 20]. The lower NO₂ and NO sensitivities of ZY000 than those of pure ZnO at 300°C are then attributed to larger ZnO grain sizes of ZY000. Of course, another possibility for the decrease in the breakdown voltage of the element is a decrease in the height of the double Schottky barrier at a grain boundary and hence a decrease in breakdown voltage per grain boundary induced by the Bi₂O₃-based intergranular phase.

Addition of Y₂O₃ was found to depress slightly the grain growth of ZnO, as was confirmed from the comparison of Fig. 3(b) with Figs. 3(c) and (d). The average grain sizes of ZY025 and ZY033 were 8.5 and 6.8 μm, respectively. Another feature of the microstructure is the existence of well-outlined sub-μm particles. Sensitivities to NO₂ and NO were increased by the addition of Y₂O₃. Especially, NO₂ and NO sensitivities of both ZY025 and ZY033 were higher than those of pure ZnO at 400 and 300°C, respectively, as shown in Figs. 4(b) and (c). Such sensitivity enhancement is first attributed to the decrease in grain size induced by the addition of Y₂O₃. But, the fact that ZY025 exhibited higher NO and NO₂ sensitivities than pure ZnO irrespective of larger average grain size suggests some sensitizing effects of the Bi₂O₃-base additive containing Y₂O₃, though the detail is not clear at present.

3.3 NO_x Sensing Properties of ZCY Series Elements

Addition of 5.0 mol% Cr₂O₃ to the Bi₂O₃-base additive was effective for suppressing anomalous ZnO grain growth, as shown in Figs. 3(e) - 3(g). From the comparison among Figs. 3(b) - 3(g), it is apparent that Cr₂O₃ is more effective for suppressing the ZnO grain growth than Y₂O₃. In this series, the number of very small particles increased with increasing Y₂O₃ contents. By excluding such small particles, average grain sizes of ZCY000, ZCY025 and ZCY033 were measured to be 3.0, 3.6 and 3.7 μm, respectively.

The breakdown voltage in air for every ZCY series element was higher than that of pure ZnO at every temperature, as shown in Fig. 5(a). But, the magnitude of the breakdown voltage enhanced was lower than that expected from the change in the grain size, especially in the cases of ZCY025 and ZCY033. By comparing Figs. 4(b) and (c) with Figs. 5(b) and (c), it is clear that ZCY series elements exhibit lower NO₂ and NO sensitivities than ZY series elements. Thus, the simultaneous addition of Cr₂O₃ to the Bi₂O₃-based additive containing Y₂O₃ was less effective for improving the NO₂ and NO sensitivities, whereas it resulted in a decrease in grain size. Furthermore, ZCY series elements were less sensitive to both NO₂ and NO than pure ZnO, with some exceptions, especially for NO₂ sensitivity at 400°C. The number of sensitive grain boundaries and/or sensitivity of a grain boundary are speculated to decrease probably due to the presence of small particles.

4. CONCLUSIONS

Pure ZnO exhibited nonlinear *I-V* characteristics in air as well as in 100 ppm NO₂ and NO balanced with air at elevated temperatures. Thus, it is confirmed again that the exis-

tence of a physically separate, intergranular and insulating layer is not essential for the development of double Schottky barrier at grain boundaries. All ZnO-based elements exhibited a shift in breakdown voltage to a high electric field upon exposure to NO₂ and to a low electric field upon exposure to NO under the condition studied. The addition of the Bi₂O₃-based additive containing Y₂O₃ led to a decrease in grain size and to enhancement in sensitivity to NO₂ and NO. Such sensitivity enhancement was first attributed to the increase in the number of grain boundaries. In addition, the Bi₂O₃-based additive containing Y₂O₃ was suggested to exhibit some sensitizing effects. The addition of Cr₂O₃ to the Bi₂O₃-based additive containing Y₂O₃ was more effective for reducing the ZnO grain size, but was less effective for improving the sensitivities to NO₂ and NO.

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