CHEMISTRY LETTERS, pp. 319-322, 1994.

Selective NO_2 Sensing Characteristics of Sc_2O_3 Mixed Nickel Copper Oxide

Nobuhito IMANAKA, Susumu BANNO, and Gin-ya ADACHI*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

Copper oxide and scandium oxide were mixed with p-type semiconducting nickel oxide and its NO_2 sensing performance was investigated. By mixing copper oxide with nickel oxide, the response of the oxide for NO_2 was improved. Further Sc_2O_3 mixing with nickel copper oxide greatly enhanced the sensing performance. Especially, the addition of scandium oxide into nickel copper oxide was considerably effective to sense only NO_2 in the nitrogen oxides existing atmosphere.

Nitrogen oxides have been becoming serious air pollutant gases. As the conventional detections, chemical luminescence and infrared analyses have been widely applied. However, the equipments of those methods are relatively large and expensive. In addition, it is quite difficult to measure the NO and the NO_2 content, individually. The inexpensive and accurate way of the detecting method has been strongly desired to be developed. As inexpensive and compact sensing devices, semiconductors,[1-5] solid electrolyte,[6-8] and phthalocyanine[9,10] have been tried to apply as a sensing element. In those methods, semiconductors have been extensively examined to use as a sensor material since they are easy to set up the sensor system with low cost. Most of the materials used are n-type semiconductors and respond not only to NO_2 but also to NO. Therefore, it is not possible to determine the accurate NO_2 content in the ambient atmosphere by using those n-type semiconductors as a sensing material.

Takasu et al.[11] have reported that NO shows an absolutely different oxidizing characteristics from oxygen on the surface of nickel-copper alloys. In this study, p-type semiconducting nickel oxide(NiO) was selected as a NO_2 sensing base material and copper oxide(CuO) was mixed to enhance the NO_2 sensing characteristics. In addition, Sc_2O_3 was further mixed with nickel copper oxide to improve the sensing performance.

An appropriate amount of NiO(purity: 99.9%) and CuO(purity:99.9%) was thoroughly mixed in an agate mortar. The mixture was pelletized and heated at 1000 ^{o}C for 2 h in air atmosphere. Scandium oxide mixed

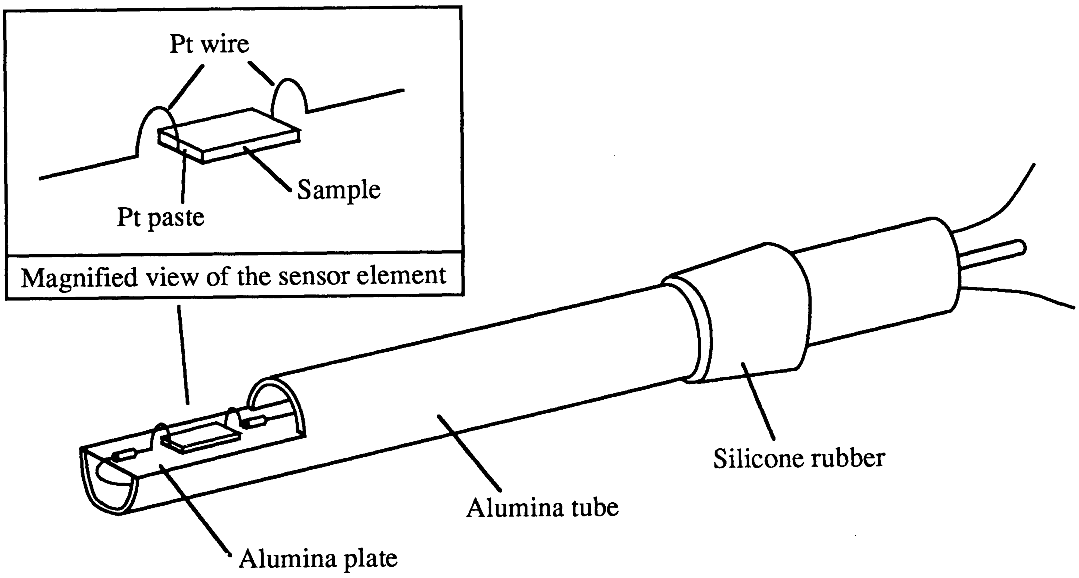

Fig. 1. Brief view of the sensor.

nickel copper oxide was also prepared in the same manner after Sc_2O_3(purity:99.9%) was mixed with the NiO and CuO mixture.

Figure 1 illustrates the brief view of the sensor setup. The sample was cut in a rectangular shape. Both sides of the sample were painted with Pt paste. Platinum wire was used as a lead and fixed with Pt paste. The sensor element was placed on an alumina plate. The resistivity measurement was carried out by passing a direct current(ca. 5 mA) between the two electrodes and the voltage between them was measured.

Figure 2 presents the NO_2 sensing characteristics of the sensor with the variation of the Ni/(Ni+Cu) ratio. Here, S denotes the sensitivity to nitrogen dioxide(NO_2) and Ra and Rb are the resistivity of the sensor element with NO_2 at 50 ppm and 200 ppm in the ambient atmosphere, respectively. The response to NO_2 was very small in the case of NiO or CuO alone. However, with the increase of the CuO amount in the nickel copper oxide, the sensitivity toward NO_2 went up and a maximum response was obtained at the NiO :CuO ratio around 2. Here, the CuO mixing with NiO results in the formation of the Ni(Cu)O solid solution as reported in Ref. 12. From an X-ray powder diffraction analysis, it was found that the oxide with the Ni/Cu ratio of 2 is not a single phase but the $Ni_{0.8}Cu_{0.2}O$ solid solution and CuO mixture. Further Sc_2O_3 mixing of 5 mol% considerably enhanced the sensitivity of the $Ni_{0.8}Cu_{0.2}O$ and CuO mixture shown as the closed square in Fig. 2. Scandium oxide mixing did not make a solid solution with Ni(Cu)O but formed $Sc_2Cu_2O_5$. Therefore, the Sc_2O_3 mixed nickel copper oxide is composed of four compounds such as $Ni_{0.8}Cu_{0.2}O$, CuO, $Sc_2Cu_2O_5$, and

Sc_2O_3. The formation of the $Sc_2Cu_2O_5$ compound is appreciably effective to increase the NO_2 sensing properties of the element.

Figure 3 shows a typical response of the sensor output for the Sc_2O_3(5 mol%) mixed nickel copper oxide. The time necessary for a 90% response was about 8 min. In a direction to increase or decrease the NO_2 content, almost the same sensor output was obtained at a certain NO_2 concentration. From this result, it becomes clear that continuous and repeatable response can be obtained.

Figure 4 presents the variation of the sensor's resistivity change with the nitrogen oxides(NO_2 or NO) gas concentration. With the increase of the NO_2 gas concentration, the resistivity of the element monotonously decreased. On the contrary, the sensor output was almost constant during the variation of the NO gas content, while the nickel copper oxide without Sc_2O_3 responded both NO and NO_2. This result clearly indicates that the Sc_2O_3 mixing with nickel copper oxide contributes greatly to the enhancement of the selective NO_2 sensing in the NO and NO_2 coexisting atmosphere.

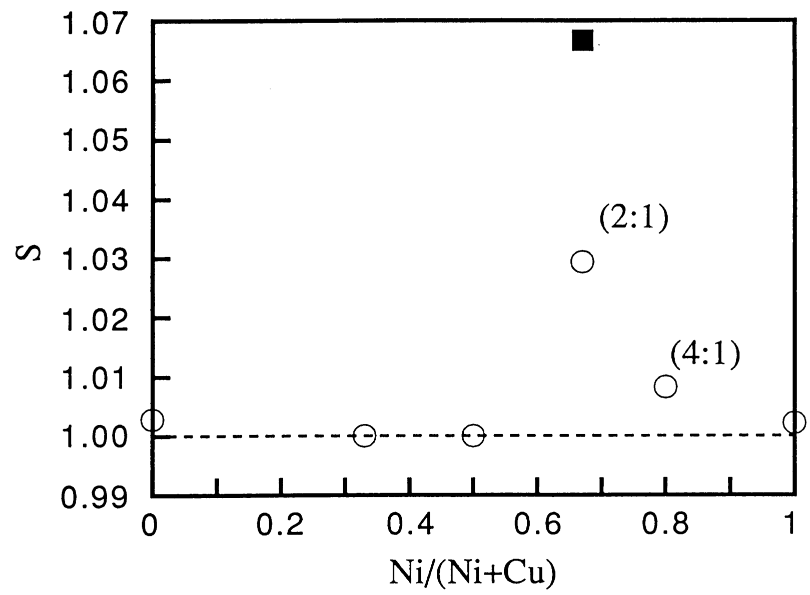

Fig. 2. NO_2 sensing characteristics of the sensor with the Ni/(Ni+Cu) ratio at 500 °C. S is equal to Ra/Rb. Closed square is the case for Sc_2O_3(5 mol%) mixed Ni-Cu-O(Ni/Cu=2).

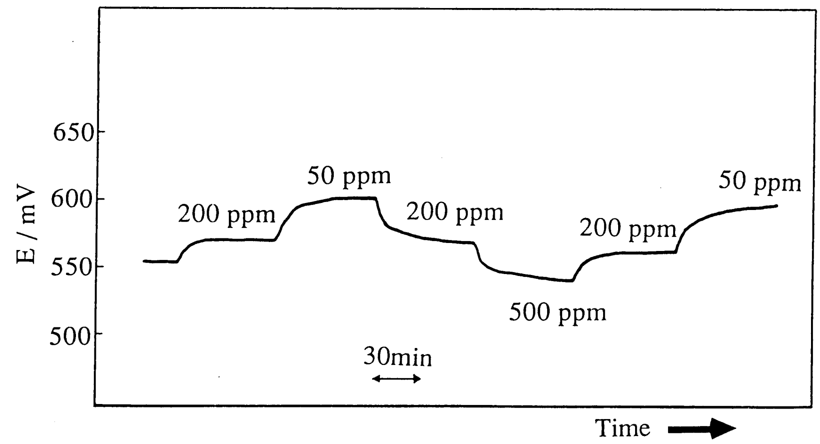

Fig. 3. A typical response of the sensor output at 600 °C.

In conclusion, copper oxide mixing with p-type semiconducting NiO made a two phase mixture of the $Ni_{0.8}Cu_{0.2}O$ solid solution and CuO and the response to NO_2 of the Ni-Cu-O compound was appreciably improved. Further Sc_2O_3(5 mol%) mixing with the Ni-Cu-O compound greatly enhanced the sensing performance. In addition, the oxides with Sc_2O_3 responded only to NO_2 and demonstrated to be one of candidates to selectively sense the accurate NO_2 content in the nitrogen oxides existing atmosphere.

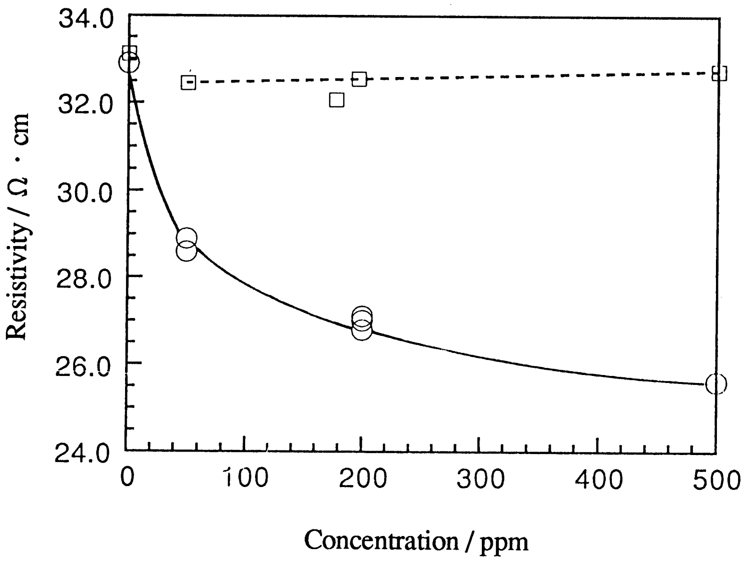

Fig. 4. The variation of the sensor's resistivity with the NO(□) or the NO_2(○) content at 600 °C.

References

1) S. Chang, *IEEE Trans. Elec. Dev.*, **ED-26**, 1875 (1979).

2) T. Inoue, K. Satake, A. Kobayashi, H. Ohkoshi, T. Nakahara, and T. Takeuchi, *Digest of the 12th Chem. Sens. Symp.*, **1991**, 129.

3) M. Akiyama, J. Tamaki, N. Miura, and N. Yamazoe, *Chem. Lett.*, **1991**, 1611.

4) S. Matsushima, D. Ikeda, K. Kobayashi, and G. Okada, *Chem. Lett.*, **1992**, 323.

5) S. Matsushima, K. Kobayashi, and G. Okada, *Denki Kagaku*, **61**, 680 (1993).

6) Y. Shimizu, Y. Okamoto, S. Yao, N. Miura, and N. Yamazoe, *Denki Kagaku*, **59**, 465 (1991).

7) S. Yao, Y. Shimizu, N. Miura, and N. Yamazoe, *Chem. Lett.*, **1992**, 587.

8) S. Yao, Y. Shimizu, N. Miura, and N. Yamazoe, *Chem. Lett.*, **1993**, 193.

9) T.A. Jones, B. Bott, and S. C. Thorpe, *Sens. Actuators*, **17**, 467 (1989).

10) S. Dogo, J. -P. Germain, C. Maleysson, and A. Pauly, *Thin Solid Films*, **219**, 251 (1992).

11) Y. Takasu, Y. Matsuda, S. Maru, and N. Hayashi, *J. Phys. Chem.*, **79**, 1480 (1975).

12) J. Bularzik, P. K. Davies, and A. Navrotsky, *J. Am. Ceram. Soc.*, **69**, 453 (1986).

(Received November 4, 1993)