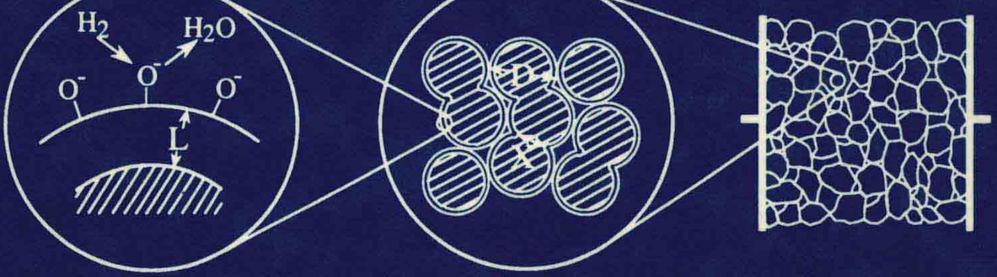
G. SBERVEGLIERI

editor

Gas Sensors



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Gas Sensors

Preface

There were two reasons that induced me to plan and to organize this book, the first was the lack of a text entirely devoted to the subject of gas sensors, notwithstanding some books devoted to the various kind of chemical sensors have recently been published. The second reason was the need of introducing the basic topics of gas detection mechanisms to a growing number of researchers active in research and development laboratories of industries and universities.

The field of chemical sensors is indeed in fast and consistent growth, as it is proved by the increased number of participants to the congresses that were recently held on this subject, namely the Third Meeting on Chemical Sensors (September 24 - 26, 1990, Cleveland), Transducers' 91 (June 24 - 27, 1991, S. Francisco) and EUROSENSORS V (September 30 - October 3, 1991, Rome).

Therefore, this book is mainly intended as a reference text for researchers with a MS degree in physics, chemistry and electrical engineering; it reports the last progresses in the R. & D. and in the technology of gas sensors.

I choose to deal specifically with the topic of gas sensors because these devices show a very large number of applications in the domestic and industrial field and they are characterized by a great effort of research and development.

The book limits itself to deal with the materials and the technologies that should be employed for the highly sensitive and selective detection of various gaseous species, neglecting the elaboration techniques of electrical signals supplied by the sensors like the pattern recognition; however, these topics can be found in specialized books.

The various topics were dealt in a complete way with regard to the working mechanisms and the preparation techniques of sensors, using an extensive number of references in order to orient the researchers which have not a specific knowledge in that field.

The last trends in the study of the material and in new technologies will be also outlined.

I wish to express my sincere thanks to the authors who accepted to write a contribution in this book, they are all people with a well recognized expertise in that field of chemical sensors. Moreover, I would thank Dr. Paolo Nelli for his help in the organization of the book.

I hope that this effort could be usefully exploited by all the people involved in the research and development of chemical sensors.

Brescia, June 1992

Prof. Giorgio Sberveglieri
Editor

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NEW APPROACHES IN THE DESIGN OF GAS SENSORS

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1. INTRODUCTION

During the past three decades, many solid-state sensor devices to detect gaseous components have been proposed based on various principles and materials. Several of them have grown to support our civil life in various respects. For example, semiconductor gas sensors using metal oxides, which detect inflammable gases in air such as CH_4, LPG and H_2, are currently used in a massive scale for gas leakage alarms in domestic houses. Oxygen sensors using stabilized zirconia have become indispensable for car emission control as well as metallurgical process control. Humidity sensors using ceramics or organic polymer electrolytes are very useful for automating food processing and air conditioning. These examples verify the high potentiality of gas sensors in the modern technologies related to safety, process control and amenity. Yet these achievements satisfy only a part of the ever-expanding demands for gas sensors.

In recent years, the number of gaseous species to be covered with gas sensors has increased dramatically. Toxic or bad-smelling gases frequently encountered in living circumstances such as H_2S and NH_3 as well as hazardous gases used for industrial processes such as AsH_3 and PH_3 have long been the targets of gas sensors. The detection of the various volatile gases or smells generated from foods or food materials has become increasingly important in food industries. These gaseous components are often present at very low levels and mixed with several disturbing gases. The recent global issues of energy and environment are increasing the necessity of those sensors which can detect air-pollutants in environments such as NOx, SOx and CO_2 or can be applied for the control systems of combustion exhausts from stationary facilities and automobiles. Various gas sensors should be developed for such new target gases. In addition, different sensors may be needed even for the same gas depending on the conditions of sensor operation. Dissolved oxygen in water or blood, for example, would be very difficult to measure with the stabilized zirconia oxygen sensor. Similarly the conventional humidity sensors are not suited for sensing the water vapor pressure of heated atmospheres such as those in industrial dryers.

In order to meet such a need for various gas sensors, one has to have a concept of gas sensor design. Generally speaking, a gas sensor should possess two basic functions, i.e., a function to recognize a particular gas species (receptor function) and another to transduce the gas recognition into a sensing signal (transducer function). In many cases, the gas recognition is carried out through gas-solid interactions such as adsorption, chemical reactions and electrochemical reactions. On the other hand, the way of transduction is heavily dependent on the materials utilized for the gas recognition. For example, the gas recognition by semiconducting oxides is conveniently transduced into a sensing signal through the electrical resistance changes of the sensor elements, while capacitance can be used for the elements using dielectric materials. Electromotive force, resonant frequency, optical absorption or emission, etc. can also be utilized as sensing signals for other types of sensor material. The receptor and transducer functions are not always separated so explicitly in some sensors like those using semiconducting oxides or solid electrolytes. Nevertheless, the two functions are governed by

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different factors so that it is possible to modify or improve each function separately. This would provide a base for designing gas sensors. That is, good sensing characteristics would be obtained only when both functions are promoted sufficiently. The promotion of the receptor function is especially important for increasing the selectivity to a particular gas, while that of the transducer function is important for increasing the sensitivity.

The authors have long been engaged in the development of various gas sensors using semiconducting oxides, solid electrolytes, and piezoelectric quartz crystals. Our basic belief is that the receptor function is inherent to the solid surface used so that it can be altered or modified extensively with an introduction of a new material or with the modification of the surface with foreign additives, while the transducer function is more dependent on technological or extrinsic factors such as the structure of sensor devices and the microstructure of the materials used. Thus materials science is very important for the development of gas sensors. In this chapter, we wish to demonstrate how such design principles have worked for developing gas sensors using the three types of sensor material.

2. DESIGN OF GAS-SELECTIVE SEMICONDUCTOR SENSORS

Oxide semiconductor gas sensors are provided with porously sintered elements (resistors) of polycrystalline semiconducting oxides such as SnO_2 and ZnO. Inflammable gases as well as oxidative gases are detected from a change in the electrical resistance of the elements. As shown in Fig. 1, gas recognition (receptor function) is made through the adsorption or reaction of the gases on the surface of semiconducting oxides, while its transduction into a resistance change (transducer function) is controlled by microstructual factors of the semiconducting oxides, i.e., grain size (D) or neck size (X) relative to the depth of the surface space charge layer (L) [1]. It is well known now that the addition of noble metals like Pd and Pt is very useful for promoting the sensitivity and response rates of sensor devices to inflammable gases [2-6]. These metals apparently bring about advantageous effects on the receptor function, although the transducer function is also promoted by some noble metals (Pd and Ag) [7,8]. Such promoting effects can also be exerted by rather many oxide additives. That is, the surface of a semiconducting oxide can be modified with certain additives to become very susceptible to a particular gas. The resulting high gas selectivity, often accompanied by high gas sensitivity, can lead to a high performance sensor for the particular gas in problem. It is important, however, that the way of promotion can be different depending on the properties of the gases to be detected, since the surface processes of different gases, mostly catalytic oxidation processes, can be associated with different surface properties. Thus the modification of redox or acid-base properties of the oxide surface may be important depending on the gases. If the gas to be detected is specifically reactive to a certain substance, the substance may also be introduced on the surface as a foreign receptor. Some examples are described below.

The semiconductor sensor elements used here are mostly of a sintered block type shown in Fig, 2. Sensing materials (SnO_2, In_2O_3, WO_3) were applied and sintered on an alumina tube attached with Pt wire electrodes. Additives were added to the powder of the base sensing materials by impregnation methods. The loadings were usually set to 5 wt% for metal oxides and 0.4-0.5 wt% for noble metals. The gas sensitivity (S) was defined as the ratio of the stationary electrical resistance of each element in air (R_a) to that in the sample gas (R_g), i.e., $S=R_a/R_g$.

2.1 Ethanol vapor sensor

An ethanol vapor sensor can be used as a breath alcohol checker for car drivers and may also be used for brewing process control. Several oxides have been tested for the ethanol gas sensing, and relatively high sensitivity has been reported with evaporated SnO_2 [9], sintered α-Al_2O_3-SnO_2 [10], and sintered CaO-SnO_2 [11]. However, the sensing performances do not seem to be sufficient in sensitivity and response rate. We have found that the ethanol vapor sensitivity

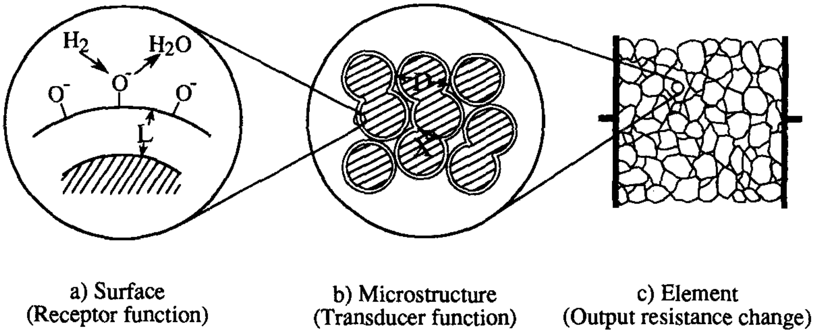

Fig. 1 Receptor and transducer functions of the semiconductor gas sensor. [Ref. 1]
D: particle size, X: neck size, L: thickness of space charge layer.

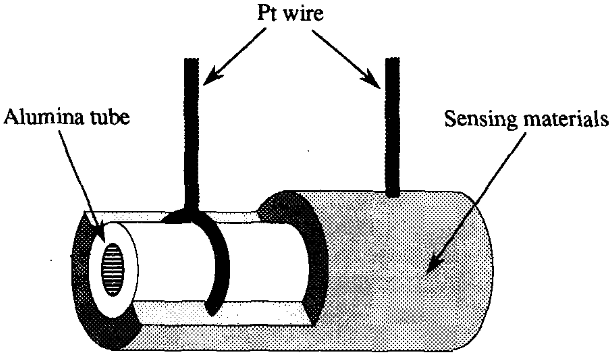

Fig. 2 Structure of sensor element.

of SnO_2(or In_2O_3)-based element increases tremendously with the addition of a basic oxide like La_2O_3 [12,13], and that the response rates can be promoted greatly by the addition of Pd or Pt [14]. The doubly promoted element thus shows excellent sensing performances for ethanol vapor in sensitivity, selectivity and response rate. Figure 3 compares the response transients of three SnO_2-based elements, pure SnO_2, La_2O_3(5 wt%)-SnO_2, and Pd(0.4 wt%)-La_2O_3(5 wt%)-SnO_2, to turning 1000 ppm C_2H_5OH in air on and off at 300 °C. It is apparent that the sensitivity (S) to ethanol vapor increases drastically with the addition of La_2O_3, though the simultaneous addition of Pd promotes S further. Also apparent is that the more important role of Pd is to promote the rates of response. The ethanol vapor sensitivity was very dependent on the operation temperature. The sensitivity of the La_2O_3-SnO_2 element to 1000 ppm C_2H_5OH, for example, was as high as 720 at 300 °C, but it decreased very rapidly on increasing the temperature to become 30 and 15 at 350 and 450 °C, respectively. The drastic promoting effect was thus exhibited only at 300 °C and below. The sensitivity of the respective elements to varying concentrations of C_2H_5OH at 300 °C is shown in Fig. 4. The doubly promoted elements have sufficient sensitivity to detect the breath alcohol at the critical concentration of 70 ppm, with a 70% response time of 1.5 min. It is emphasized that such promotion of the sensitivity with La_2O_3 is quite selective for ethanol vapor. The sensitivity to i-C_4H_{10}, for example, remains almost irrelevant with the addition of La_2O_3.

What is the origin of this selective promotion by La_2O_3? To answer this question, 9 metal oxides other than La_2O_3 were tested for their effects [15]. Figure 5 summarizes the sensitivity of various SnO_2-based elements to ethanol vapor (1000 ppm) and i-C_4H_{10} (1000 ppm) as a function of electronegativity (X_i) of each metal cation added. Apparently many cations other than La^{3+}, such as Sm^{3+}, Sr^{2+}, Ca^{2+} and Gd^{3+}, also promote the ethanol vapor sensitivity. The effective promoters are the cations of alkali, alkaline earth or rare earth metals, all having X_i less than 9. The addition of basic oxides is thus essential for promoting the sensitivity to ethanol vapor, whereas the sensitivity to i-C_4H_{10} remains unpromoted with these oxides as also seen from Fig. 5. This suggests that the basic oxides influence the catalytic oxidation processes of ethanol vapor. It is known that ethanol vapor is oxidized through two reaction routes ; C_2H_5OH is dehydrogenated to $CH_3CHO + H_2$ on the basic surface or dehydrated to $C_2H_4 + H_2O$ on the acid surface, respectively, followed by the complete oxidation of the intermediates to CO_2 and H_2O. From a viewpoint of gas sensitivity, the dehydrogenation route is more favorable than the other, because both reaction intermediates, CH_3CHO and H_2, can interact with the semiconducting oxides in addition to that CH_3CHO has much higher molecular sensitivity than C_2H_4, the intermediate of the other route. As suggested from Fig. 5, SnO_2 itself is an acidic oxide in nature, so that the dehydration routes would prevails on the SnO_2 surface. When basic oxides are added, the increase in the basicity of the oxide surface would make the dehydrogenation route more preferable, giving rise to the promotion of the ethanol gas sensitivity. The origin of the promoting effect of La_2O_3 can thus be ascribed to an increase in basicity.

The doubly loaded element, Pd-La_2O_3-SnO_2, showed good sensing characteristics for ethanol vapor. However, the addition of La_2O_3 and Pd increased the electric resistance of the element to almost unpractical levels of ca. 10^8 Ω and above in air at 300 °C. To overcome this difficulty, the base semiconductor was changed from SnO_2 to In_2O_3 which has much smaller electric resistivity than SnO_2. Thick film type elements as shown in Fig. 6 were also fabricated by using a screen printing technique, in order to obtain quicker response rates. Table 1 summarizes the ethanol vapor sensing characteristics of various In_2O_3-based elements [13]. The ethanol vapor sensitivity (S) increased by one order of magnitude with the addition of La_2O_3 (sintered block type), whereas the simultaneous addition of Pd and La_2O_3 resulted in a further increase in S as well as shortening the 90% response time (thick film type). It is obvious that the doubly loaded thick film element, Pd-La_2O_3-In_2O_3, is superior to the sintered block type element, Pd-La_2O_3-SnO_2, in every respect of sensitivity, response rate, and compatibility to the electrical circuitry. It is remarked that, the same thick film element showed modest sensitivity values of ca. 30 or less to CO, H_2, CH_4, or i-C_4H_{10} (1000 ppm each) at 300 °C.

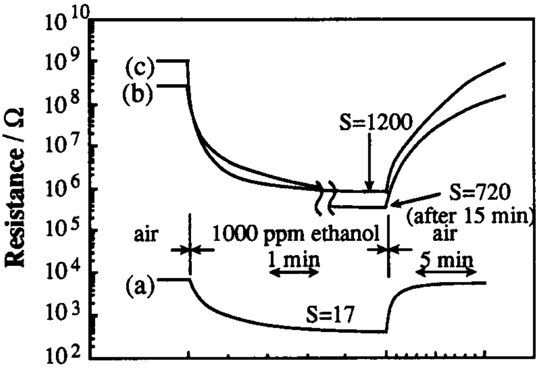

Fig. 3 Response transients of sensor elements to switching-on and -off 1000 ppm C_2H_5OH in air at 300 °C. ($S=R_a/R_g$)
(a) pure SnO_2
(b) La_2O_3(5 wt%)-SnO_2 (singly loaded)
(c) Pd(0.5 wt%)-La_2O_3(5 wt%)-SnO_2 (doubly loaded)

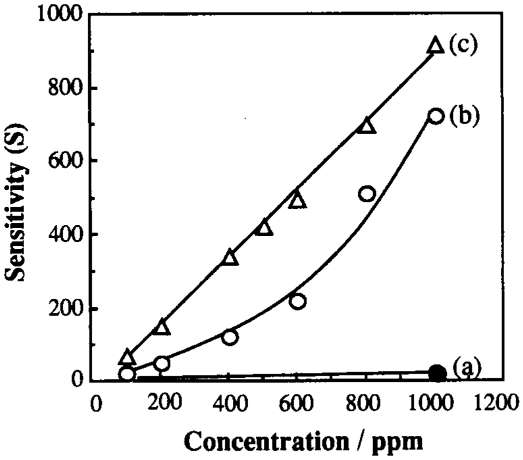

Fig. 4 The sensitivity of various elements to varying concentrations of C_2H_5OH at 300 °C.
(a) pure SnO_2
(b) La_2O_3(5 wt%)-SnO_2 (singly loaded)
(c) Pd(0.5 wt%)-La_2O_3(5 wt%)-SnO_2(doubly loaded)

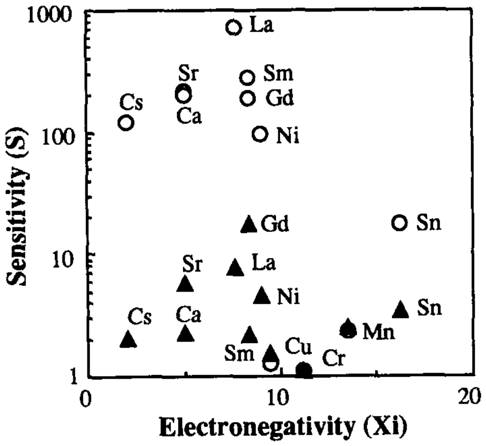

Fig. 5 The sensitivity of 5 wt% metal oxide loaded-SnO_2 elements as correlated with the electronegativity of loaded metal cations. The sensitivity to 1000 ppm C_2H_5OH (○) 1000 ppm i-C_4H_{10}(▲). [Ref. 12]

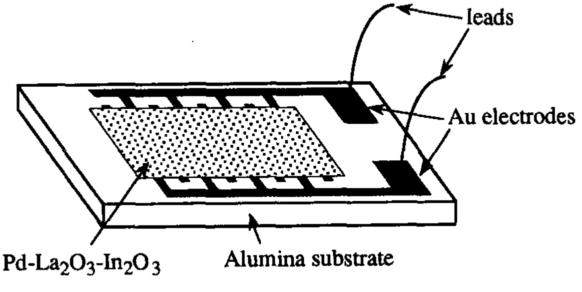

Fig. 6 Pd-La_2O_3-In_2O_3 thick film element with comb type Au electrodes. [Ref. 13]

Table 1. Ethanol gas sensing properties of In_2O_3 and SnO_2 based elements (300 °C) [Ref. 13]

Sensor material a)	Type b)	Electric resistance / Ω		Sensitivity	90% response time / min
		In air	In C_2H_5OH c)		
In_2O_3	SB	6.5×10^2	2.3×10^1	28	0.3
La_2O_3-In_2O_3	SB	4.9×10^5	1.5×10^3	340	3.1
Pd-La_2O_3-In_2O_3	TF	2.6×10^4	1.4×10^2	190	1.7
Pd-La_2O_3-In_2O_3	TF	1.6×10^6	1.1×10^3	1400	0.6
Pd-La_2O_3-SnO_2	SB	9.2×10^8	7.6×10^5	1200	3.1

a) Loading of the dopants : La_2O_3 5 wt%, Pd 0.5 wt%.

b) SB : sintered block type with distance between electrode of 3 mm,
TF : thick film type with distance between electrode of 0.3 mm.

c) 1000 ppm C_2H_5OH diluted with air.

2.2 H_2S sensor using CuO-SnO_2

Sulfides are typical components of bad smells generated from a human mouth, sewage or dump, and their sensing is needed for dentistry as well as for auto-ventilating a water closet. Semiconductor gas sensors to detect the simplest sulfide, H_2S, have been investigated in a few reports. The sensitivity and selectivity of SnO_2-based elements to H_2S are reportedly improved by adopting a quick cooling method [16] as well as by the addition of hydrophobic silica [17], ZrO_2 [18] or basic oxides to the elements [19]. An H_2S sensor using ZnO-SnO_2 has been commercialized as a breath checker which monitors bad smells of a breath [20]. We have found that the impregnation of SnO_2 with CuO is extremely effective for promoting the sensitivity to H_2S [21].

The sensitivity (S) of various SnO_2-based elements loaded with 5 wt% metal oxides to 50 ppm H_2S at 200 °C is shown as a function of the electronegativity (X_i) of loaded metal cations in Fig. 7. S tends to increase with a decrease in X_i of the cations added, in agreement with the suggestion that, since H_2S is an acidic gas, S increases with increasing the basicity of the additives [19]. It is noteworthy, however, that CuO gives an extraordinarily high S value which deviates far from this general tendency. The H_2S sensing transient of the CuO-SnO_2 element is compared with that of an unpromoted element in Fig. 8. Both elements responded to turning 50 ppm H_2S on with a rather sluggish increase in electrical resistance, reaching a steady state in about 40 min. On turning H_2S off, CuO-SnO_2 element recovered the initial level in only 1 min, showing a switching-like characteristics. Its sensitivity to 50 ppm H_2S is seen to be as extremely high as 35,000, compared with only about 8 of the unpromoted element. The same element was hardly sensitive to the other inflammable gases of CO, i-C_4H_{10}, C_2H_5OH and H_2 (1000 or 800 ppm) at 200 °C. These remarkable sensing properties, i.e., extremely high sensitivity and selectivity to H_2S and switching-like recovery, are quite unique to CuO-SnO_2 element.

Strong dependence of the H_2S sensitivity on temperature was also a feature of CuO-SnO_2 element. Figure 9 shows the electrical resistances of the element in air (R_a) and in 50

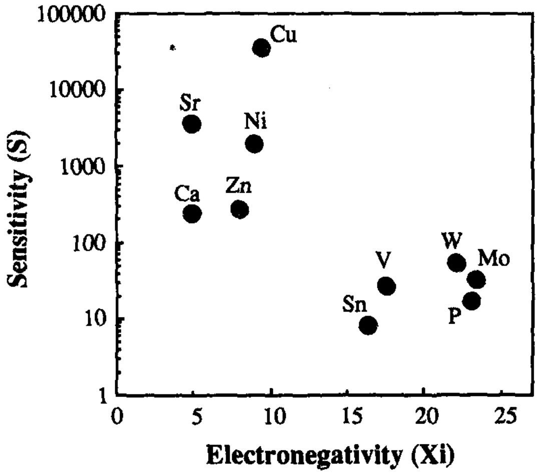

Fig. 7 Gas sensitivity of metal oxide loaded-SnO_2 elements to 50 ppm H_2S at 200 °C as a function of electronegativity of the loaded metal cations. [Ref. 21]

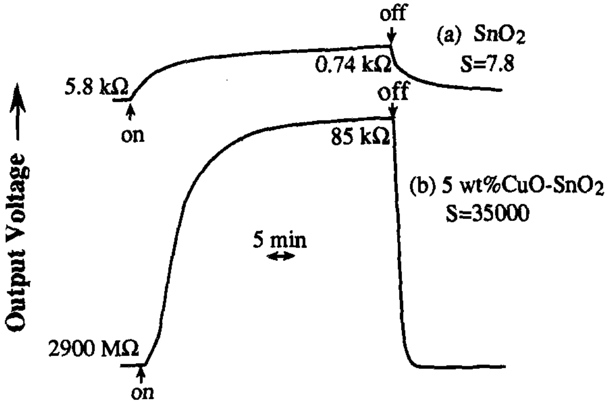

Fig. 8 Response transients of CuO-loaded (5 wt%) and unloaded SnO_2 elements to 50 ppm H_2S at 200 °C. [Ref. 21]

ppm H_2S (R_g) as well as the resulting gas sensitivity (S) as a function of temperature. R_a was very high (3×10^9 Ω) up to 300 °C and decreased gradually at higher temperature. On the other hand, R_g was low (ca. 10^5 Ω) up to 200 °C but then it increased drastically to high values (10^8 Ω) at 250 °C and above. As a result, S was extremely high (35000-40000) up to 200 °C, and then decreased to no more than 10 at 300 °C and above. XPS investigation revealed that such unique behavior of R_g and S was associated with the formation of CuS [22]. That is, CuO was readily converted to CuS on exposure to the H_2S-containing atmosphere at 200 °C or below, while CuO was restored on turning-off H_2S.

$$CuO + H_2S \rightarrow CuS + H_2O \qquad (1)$$

$$CuS + (3/2)O_2 \rightarrow CuO + SO_2 \qquad (2)$$

The CuS state was indicated by the appearance of an XPS signal of S2p at 161.8 eV. XPS investigation also disclosed an important fact that the binding energies BEs of $Sn3d_{5/2}$ and $O1s_{1/2}$ levels for the CuO-SnO_2 system were significantly lower than those for pure SnO_2, while the differences disappeared when CuO was converted to CuS. This indicates that the addition of CuO increases the work function of SnO_2, while the conversion to CuS brings back the normal surface of SnO_2. Based on these findings, the H_2S sensing mechanism can be explained as follows. CuO is assumed to be dispersed as fine particles on the surface of SnO_2 grains. Since CuO and SnO_2 are p- and n-type semiconductors, respectively, a p-n junction is formed at each interface between CuO and SnO_2. The junctions deprive the SnO_2 grains of conduction electrons and thus increases the work function of SnO_2 and the electrical resistance of the element. On exposure to H_2S, CuO is converted to CuS which is a metallic conductor. This will destroy the p-n junctions, leading to the drastic decrease of the electrical resistance, and hence the extremely high sensitivity to H_2S. When air flow is resumed, CuS is transformed back to CuO. If this reaction is very fast, the recovery can be very quick, giving rise to switching-like behavior as observed. It is additionally stated that the conversion of CuO to CuS in the H_2S-containing atmosphere becomes increasingly difficult with increasing temperature, as investigated by XPS. This is the reason for the loss of the high H_2S sensitivity at 250 °C and above.

The sensitivity to H_2S at 200 °C depended on the loadings of CuO as well as on the loading methods. As shown in Fig. 10, it was possible to attain the sensitivity exceeding 10^4 to 5 ppm H_2S with some elements, though the response was rather slow at such small concentrations. It appears that the CuO-SnO_2 element would be able to detect H_2S at ppb levels if further improvements are carried out.

2.3 NOx sensor using WO_3

Nitrogen oxides, NO and NO_2 (denoted NOx), generated from combustion facilities and automobiles are representative air pollutants. Currently their concentrations in air or exhausts are determined by means of spectroscopic analyzers based on infra-red absorption and chemical luminescence. Beside being bulky and expensive, these analyzers are difficult to use for *in situ* monitoring of NOx or for feed-back control of NOx. Several studies have been carried out to develop solid-state NOx sensors using semiconducting oxides [23-25], solid electrolytes [26], phthalocyanine [27], and SAW devices [28]. Semiconductor sensors appear to be well suited for the NOx-controlling systems from their durability under extreme conditions, and a sensor of this type using In^{3+}-doped TiO_2 [23] has been commercialized. However, these sensors are still low or modest in the sensitivity to either of NO and NO_2. It is of primary importance to explore better sensing materials. In this respect, we have found that WO_3 can be an excellent sensing material for NO and NO_2 [29].

Figure 11 shows the response transients of the WO_3 sensor element to turning -on and -off 200 ppm NO or 80 ppm NO_2 at various temperature above 250 °C. The electrical resistance of the element increased upon contact with NO and NO_2. Since WO_3 is n-type semiconductor,

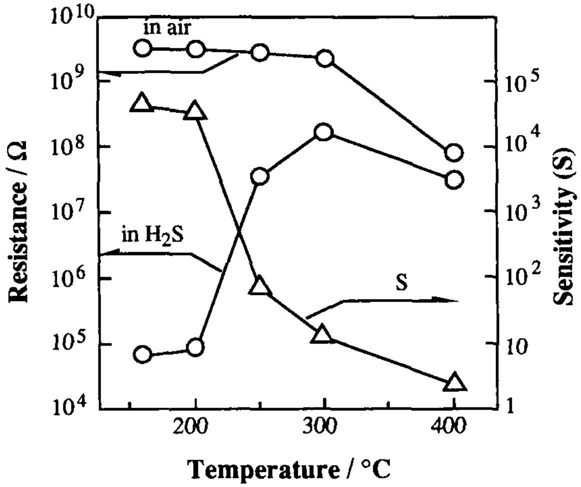

Fig. 9 The electrical resistances and the H_2S sensitivity of CuO (5 wt%)-SnO_2 element as correlated with operation temperature (H_2S : 50 ppm). [Ref. 21]

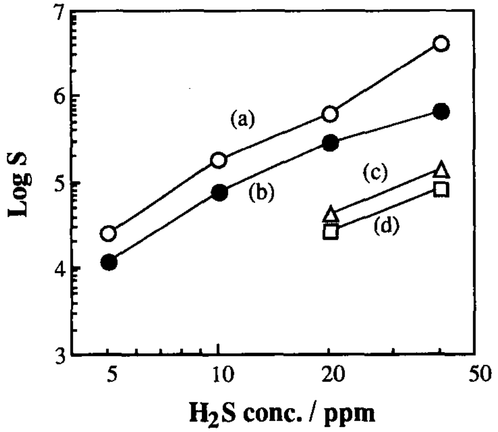

Fig. 10 Sensitivity-concentration profile for H_2S detection observed on CuO(5 wt%)-SnO_2 elements prepared from various starting Cu salts at 200 °C.
(a) $CuCl_2 \cdot 2H_2O$, (b) $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$,
(c) $Cu(CH_3COO)_2 \cdot H_2O$, and (d) $Cu(NO_3)_2 \cdot H_2O$.

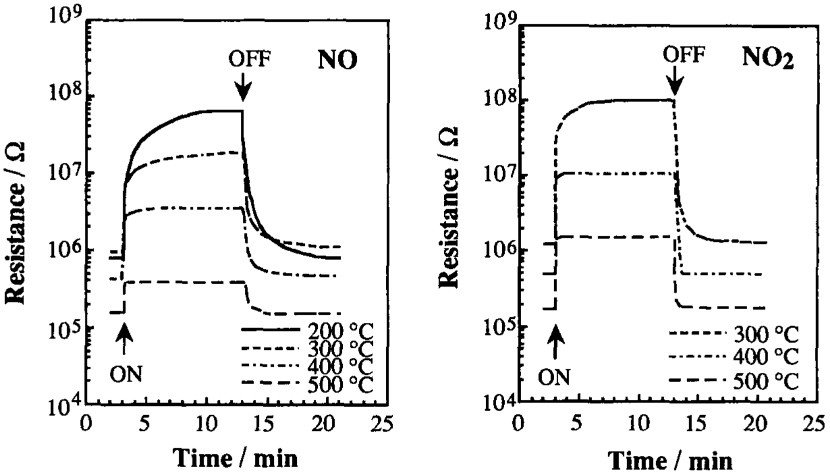

Fig. 11 Response transients of WO_3 element to 200 ppm NO (left) and 80 ppm NO_2 (right) at various temperatures. [Ref. 29]

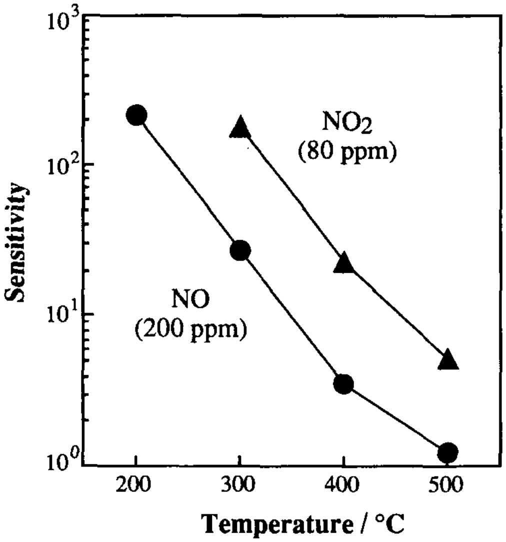

Fig. 12 Temperature dependence of sensitivity (R_g / R_a) of WO_3 element to 200 ppm NO and 80 ppm NO_2 in air. [Ref. 29]