Taguchi-type NO_x gas sensors based on semiconducting mixed oxides

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Mixtures of Al₂O₃–ZnO–V₂O₅ have been explored for use as active sensing materials in Taguchi-type NO_x sensors. The electrical resistance and Seebeck effect of these semiconducting oxide mixtures have been measured as a function of the composition. The sensitivity and selectivity of the sensor to NO and NO₂ gases against CO₂ were studied in order to find the optimal composition of the oxides. The presence of *p*–*n* junctions may play an important role in the conductivity and sensitivity of the sensor materials. The experimental results indicate that sensors based on mixtures of Al₂O₃–ZnO–V₂O₅ exhibit sensitive and fast response to 20 to 300 ppm of NO and/or NO₂ in the temperature range of 200 to 400°C, the sensitivity to NO is usually larger than that to NO₂. The sensors are almost insensitive to even 0.01 atm CO₂ gas. A preliminary discussion on the operation principle of the sensors is presented.

1. Introduction

Since the 1960s, when the high sensitivity of the electrical conductivity of some metal oxides like SnO₂, ZnO and Fe₂O₃ to the gaseous environment was found and proposed to be utilized for the detection of inflammable gases by Taguchi [1] and Seiyama [2,3], thin film semiconductor gas sensors have been developed and marketed worldwide. To date, the Taguchi-sensor for CO has found widespread application.

Because metal oxide gas sensors are usually sensitive to a variety of gaseous species in the atmosphere, a major drawback of these Taguchi-type sensors is the almost complete lack of selectivity, which has limited their use to non-quantitative applications. Several routes to improve their selectivity have been investigated, and these include the use of different metal oxides, varying the temperature of operation [4], and the introduction of additives to the oxide surfaces [5], for which usually known oxidation catalysts like Pd and Pt are being selected.

Varying degrees of success have been achieved using combinations of these methods.

Regarding metal oxide semiconductor NO_x sensors, many investigations have been reported [6–15]. Among these, the use of mixtures of two oxides was studied in Japan [14,15]. Table 1 summarizes the major results of this work. From table 1 it can be seen that a mixture of alumina and vanadium oxide exhibits a good selectivity to NO and NO₂ gases in a NO_x and CO_x containing atmosphere, while the sensitivity is not high. In contrast with this mixture, a mixture of alumina and zinc oxide exhibits very high sensitivity to NO_x, but if used as a NO_x detector, CO

Table 1
Sensitivity of metal oxide mixtures to NO, NO₂, CO, and CO₂ [15].

Sample	Temp. ^{a)} (°C)	Sensitivity ^{b)}			
		NO ^{c)}	NO ₂	CO	CO ₂
Al ₂ O ₃ –V ₂ O ₅	400	2.54	2.71	1.09	1.00
Al ₂ O ₃ –ZnO	400	5.37	6.39	7.08	1.09
V ₂ O ₅ –ZnO	400	2.41	2.61	2.00	1.00

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^{a)} Optimum temperature for NO and NO₂ detection.

^{b)} Sensitivity = R_{air}/R .

^{c)} NO, NO₂, CO and CO₂ concentration: 600 ppm.

will cause a rather strong noise signal. It seems that zinc oxide, which is a well-known semiconducting gas-sensing material, has a high sensitivity to various kinds of gaseous species. However, its selectivity is poor. The surface and adsorption properties of V_2O_5 , which is a well-known catalytic material, can be greatly modified by materials such as Al_2O_3 and SiO_2 . In the V_2O_5 - Al_2O_3 mixture, part of the V_2O_5 is assumed to react with Al_2O_3 to form AlVO_4 , which will give rise to new adsorption sites for NO/NO_2 [16]. Therefore, the effect of V_2O_5 - Al_2O_3 mixed oxides on the selectivity to NO_x gases seems to result from the creation of these new sites.

In the present study, we have explored the use of a mixture of three oxides in order to find an optimal composition in the system Al_2O_3 - ZnO - V_2O_5 , which has both high sensitivity and good selectivity to NO_x against CO and CO_2 .

2. Experimental procedures

Semiconducting mixtures of Al_2O_3 - ZnO - V_2O_5 with different compositions can be prepared either by a wet chemical method using co-precipitation from the corresponding nitrates or by solid state reaction of the binary oxides. In this study, solid state synthesis was employed to prepare the mixed oxide semiconductor materials.

The powders of mixed oxides were calcined at 450°C for five hours and then pressed into pellets which were sintered at 500°C for three hours. Platinum electrodes were sputtered to one of the faces of the pellets using a mask. The sensor element provided with the electrodes was finally assembled on a glass substrate as shown in fig. 1.

The electrical resistance of the semiconductor sensor elements was measured at room temperature in air using a dc voltage supply and a 150B Microvolt Ampere meter. The voltage drop over the sensor element was measured with a 197 Multimeter DMM. The Seebeck effect of these semiconductor materials was measured in order to determine the type of semiconductivity by applying a temperature gradient between the two electrodes and detecting the thermoelectric potential using a Nanovoltmeter TE 925.

The semiconductor sensors were exposed to dif-

Fig. 1. Schematic diagram of the semiconductor NO_x sensor element: 1, 2. Electrode leads; 3. Pt sputtered electrodes; 4. oxide semiconductor; 5. glass substrate.

Fig. 2. Sensor testing system: 1, 2, 3. Mass flow meters; 4. nano-voltmeter; 5. standard resistance; 6. standard battery; 7. thermocouple; 8. sensor element; 9. heater; 10. reactor.

ferent NO_x -containing ambients with or without oxygen in the sensor testing system as shown in fig. 2. The sensitivity and selectivity of the sensor elements to NO and NO_2 gases against CO_2 were measured at different temperatures.

3. Results and discussion

3.1. Composition and Seebeck effect of the semiconductors

The composition and Seebeck effect data of the different compositions of the mixtures of Al₂O₃–ZnO–V₂O₅ are presented in table 2. The sign of the Seebeck coefficient, S , provides a simple, direct test of the dominant charge carrier. The semiconducting materials denoted S5, S6 and S7 have the equimolar composition of ZnO–V₂O₅, Al₂O₃–V₂O₅ and Al₂O₃–ZnO, respectively, corresponding to the specimen in table 1. S1, S2 and S3 are the equimolar combinations of S6 and S7, S5 and S6, S5 and S7, respectively. S4 comprises an equimolar composition of the three oxides. It is apparent that the composition of the mixtures determines the type of the dominant charge carrier. The Seebeck coefficient is greatly affected by the defect structure of the materials, the nature and level of the dopants, and in case of oxidic semiconductors the oxygen partial pressure. ZnO is a well-known n -type semiconductor, but when different amounts of p -type V₂O₅ and/or inert Al₂O₃ are added, both p -type (S4 and S5 in table 2) and n -type (S1, S2, S3, S7 in table 2) semiconductors are obtained.

It is easily understood that a mixture of p -type and inert materials eventually represents a p -type semiconductor (S6), and mixing n -type with inert materials will yield n -type material (S7). In addition, it is known that the electrical conductivity of V₂O₅ is higher than that of ZnO, so when equal amounts of V₂O₅ and ZnO are mixed, the p -type conducting is dominating as indicated in S4 and S5. However,

the doping level of Al₂O₃ can influence the sign of Seebeck coefficient which is seen by comparing S1 and S4. A higher amount of ZnO in the mixture reasonably gives n -type as is observed in S3. However, the result of sample S2 is difficult to explain: a higher V₂O₅ content (even higher than that of S4) in the three-oxide mixture still results in n -type conductivity. While it is known that grain boundary interfaces play an important role in the electrical property variations of dispersions, a quantitative interpretation depends on insights into the microstructure – particle size relations.

3.2. Temperature dependence of the sensor resistance

In the sensor testing system as shown in fig. 2, the voltage drop V_0 is measured and this parameter is used to calculate the resistance R of the sensor element with

$$R = \frac{E_0 - V_0}{V_0} R_0. \quad (1)$$

Here R_0 denotes a standard resistance, E_0 the output voltage of the dc voltage supply, and V_0 , the voltage drop over R_0 . Fig. 3 presents the resistance of the 7 sensor elements as a function of temperature.

In general, the conductance of the 7 sensors increases with temperature. It is seen that from about 90°C until 270°C, the magnitude of the conductance of the semiconductors follows the sequence S1 < S3 < S7 < S5 < S2 < S4 < S5. The differences in the temperature dependence of the sensor materials are probably due to their differences in composition

Table 2
Composition and Seebeck effect of Al₂O₃–ZnO–V₂O₅ semiconductors.

Sample	Al ₂ O ₃ (mol%)	ZnO (mol%)	V ₂ O ₅ (mol%)	$S=dV/dT$	Type
S1	50	25	25	–	n
S2	25	25	50	–	n
S3	25	50	25	–	n
S4	33	33	33	+	p
S5	0	50	50	+	p
S6	50	0	50	+	p
S7	50	50	0	–	n

Fig. 3. Temperature dependence of the resistance of sensors based on mixtures of Al_2O_3 - ZnO - V_2O_5 , (+) S1, (Δ) S2, ($\circ$) S3, (+) S4, (Δ) S5, ($\bullet$) S6 and (∇) S7.

and microstructure. The results seem to indicate that four effects play an important role.

(1) The data for sample S6 which is based on a mixture of Al_2O_3 and V_2O_5 , reveal that V_2O_5 exhibits a high electric conductivity. The higher conductivities are found for mixtures with the larger V_2O_5 contents.

(2) The data for sample S7 which is a mixture of Al_2O_3 and ZnO , reveal that ZnO exhibits a low electric conductivity. The higher conductivities are found for mixtures with the smaller ZnO contents.

(3) As has been mentioned before, dispersing an inert oxide into a conducting matrix has a marked influence on the electrical properties, and usually there is a maximum of conductivity with 30–40% of Al_2O_3 doping. The influence of this effect is seen by comparing the data for S1, S4 and S5. When Al_2O_3 is added to a mixture of equal amounts of V_2O_5 and ZnO (S4) and 33% Al_2O_3 reveals highest conductivity and 50% of Al_2O_3 doping in S1 has an obvious effect of decreasing the conductivity.

(4) Although the phase analysis has not been carried out by XRD, SEM and thermal analysis, it is believed that there are separate phases of ZnO , V_2O_5 and Al_2O_3 present in the specimens S1 to S4, since the sintering temperature was as low as 500°C . Therefore, at all the grain boundaries of p -type V_2O_5 and n -type ZnO , the formation of p - n junctions is assumed. The presence of p - n junctions decreases the conductivity in the way that it gives rise to charge barriers which will block the conduction pathway and

increase the activation energy. The reason for S1 being the poorest conducting material instead of S7 can be the effect of p - n junctions. Without the influence by p - n junctions in S1, S7 would have had the lowest conductivity because compared with S1, it comprises a larger amount of the poor conductor ZnO , the same amount of Al_2O_3 , and no highly conducting material V_2O_5 .

3.3. Sensitivity as a function of NO concentration

The sensitivity of the sensor elements to NO or other gases is defined as

$$\text{Sensitivity} = \frac{\sigma}{\sigma_{\text{air}}} = \frac{R_{\text{air}}}{R}, \quad (2)$$

where σ and R are the conductivity and resistance of the sensor element on exposure to NO or other gases, respectively, while σ_{air} and R_{air} denote the conductivity and resistance of the sensor element in air as a reference, respectively.

The sensitivity to NO concentrations in oxygen-free ambients has been studied for all above mentioned sensors. S1 was expected to be the most promising sensor material with both high sensitivity and selectivity to NO detection, since S1 is an equimolar mixture of the highly selective mixture Al_2O_3 - V_2O_5 , and the highly sensitive material Al_2O_3 - ZnO as indicated in table 1. Fig. 4 gives an example of the sensitivity of this sensor as a function of NO concentration at a fixed operating temperature of 290°C . For NO concentrations up to 350 ppm, S1 yields a linearly increasing response. However, in the NO

Fig. 4. Sensitivity of sensor S1 as a function of NO concentration at 290°C .

concentration range of 350 to 1200 ppm, the sensitivity as defined by eq. (2) first dropped to 2 and then gradually decreased. This result shows that sensor S1 can be used for NO detection as NO_x sensor for NO concentration of 0 to 350 ppm.

Other sensor elements reveal similar results, in that a maximum of sensitivity exists at about 300 ppm of NO. To understand this observation, it is necessary to consider the sensing mechanism of this type of NO_x sensors. Although the operating principle of semiconductor CO sensors has been extensively discussed in the literature, e.g. [17], the sensing mechanism of semiconductor NO_x sensors is not well understood.

In semiconductor CO sensors, the operation model comprises the surface reaction between associatively adsorbed CO from the ambient gas with chemisorbed CO₂⁻, followed by the return of the electron from the CO₂⁻ to the conduction band, owing to the exothermic reaction energy of the CO oxidation, and the subsequent thermal desorption of the neutral sorbed CO₂. Therefore, the electrical conductivity of the *n*-type semiconductors increases with exposure to CO and oxygen, while that of *p*-type semiconductors decreases when CO and oxygen are present. However, the sensing mechanism of semiconductor NO_x sensors is much more complicated. For instance, NO or NO₂ can be easily chemisorbed as such at the surface of the *p*-type or *n*-type semiconductors like oxygen, indicating that oxygen is not needed in the chemisorption of NO_x sensors as in semiconductor CO sensors. Furthermore, the element N has multiple valences, NO can be reduced or oxidized to different states, e.g. N₂, N₂O, N₂O₃, NO₂, N₂O₄ and N₂O₅. In other words, it can be a reducing or oxidizing gas depending on the sensing material and the operating conditions such as temperature and oxygen partial pressure.

It is well known that *n*-type semiconductors have higher resistance in an oxygen or NO_x (NO and NO₂) ambient as compared to that in vacuum [13]. This is because if an electronegative molecule such as oxygen or NO_x is approaching the semiconductor surface and its electron affinity A is larger than the semiconductor work function W_ϕ , the molecule will tend to pick up an electron from the semiconductor conduction band and become chemisorbed at the surface. The net result of the chemisorption of the

acceptor-type gas such as oxygen or NO_x on *n*-type semiconductors is a decrease in electron concentration in the conduction band near the semiconductor surface, and hence a decrease in the conductance parallel to the surface. The chemisorption of NO_x leads to band bending. Irreversible effects occur for large band bending at high NO_x partial pressures which lead to dissociation of NO₂, and subsequent reactions of atomic oxygen with the oxide lattice [19]. Therefore, in case of high concentrations of NO_x, the desorption of the chemisorbed NO_x can be very difficult, and it can be the reason for the decreasing sensitivity at higher NO concentrations as shown in fig. 4. Since sensor S1 is a three phase mixture of *p*-type V₂O₅, *n*-type ZnO and alumina, with an over-all *n*-type conductivity as mentioned above, the sensing mechanism could be quite complicated. It may contain the chemisorption of NO₂ and oxygen at the surface of ZnO as NO₂⁻ and O⁻, respectively, but it may also contain the chemisorption of NO on V₂O₅ as NO⁺. Furthermore, it may resemble the surface reaction model of CO sensors, i.e. NO is associatively adsorbed to react with the chemisorbed oxygen to form NO₂. Another possible sensing mechanism is the effect of *p*-*n* junctions which will be discussed in the following section. The sensing behaviour may be the net result of the possible mechanisms. One may expect that at high NO concentrations, the chemisorption of NO_x on ZnO will be the dominant mechanism in the sensing process. This leads to a decrease of the conductivity, and hence a lower sensitivity.

3.4. Temperature dependence of sensitivity and response time

The temperature dependence of the sensitivity of sensor S3 to 330 ppm NO is presented in fig. 5 as an example. Similar results have been obtained for other sensors. The sensitivity of the sensor elements to both low and high NO concentrations can be enhanced by increasing the operating temperature in the temperature range of 25 to 425°C. However, as reported in ref. [15], a decrease of sensitivity with an increasing temperature in the range of 400 to 600°C was observed. Furthermore, a TPD (temperature programmed desorption) study revealed [15] that NO and NO₂ show a maximum adsorption on the sur-

Fig. 5. Temperature dependence of the sensitivity of sensor S3 at $P_{\text{NO}} = 330$ ppm.

face of $\text{Al}_2\text{O}_3\text{--V}_2\text{O}_5$. Therefore, it is reasonably expected that 400°C is the optimal operating temperature for $\text{Al}_2\text{O}_3\text{--V}_2\text{O}_5$ based NO_x sensors.

In addition, the response is faster at higher operating temperatures, so the response of the sensors can be promoted by increasing the operating temperature. In general, the response time of this type of sensor is much shorter than that of the $\text{Ag}^+\text{--}\beta\text{--alumina}$ based NO_x sensors [18]. However, the operating temperature of the sensors is limited by the thermal stability of the active materials. The present composites of three oxides are stable up to 500°C . At higher temperatures the materials will melt.

3.5. Selectivity to NO and NO_2 against CO_2

The interference of CO_2 in the detection of NO and NO_2 was primarily investigated by measuring separately the sensitivity to NO, NO_2 and CO_2 . The effect of CO has not been studied because of safety reasons of the used gas sensor testing system. Table 3 describes the experimental results of the sensitivity to CO_2 in comparison with the sensitivity to NO and NO_2 at fixed working temperatures in the range of $284\text{--}325^\circ\text{C}$. It appears that all the sensors are practically insensitive to CO_2 even if the CO_2 concentration is as high as 0.01 atm. Therefore, a high concentration of CO_2 in the gas to be analysed will not interfere with the detection of NO and NO_2 . It is also noticed that the semiconductor sensors are more sensitive to NO than to NO_2 , which is in disagreement with the reported results in table 1. This result

Table 3
Sensitivity of the mixed oxides.

Sample	Operating temp. ($^\circ\text{C}$)	Sensitivity ^{a)}		
		NO ^{b)}	NO_2	CO_2
S1	290	2.25	1.42	0.97
S2	325	1.74	1.32	1.00
S3	295	1.25	1.18	1.01
S4	284	3.17	1.16	0.99
S5	306	4.22	1.81	1.00
S6	325	2.80	1.60	0.94
S7	325	2.23	1.00	1.03

^{a)} Sensitivity = R_{air}/R .

^{b)} NO, NO_2 : 100 ppm, CO_2 : 0.01 atm.

is also quite different from the situation in the solid electrolyte based NO_x sensors (ref. [18]), since for the Nernst-type NO_x sensor, it is NO_2 rather than NO that reacts with the solid electrolyte. It, therefore, appears that the combined use of the semiconductor and solid electrolyte NO_x sensors provides the possibility to detect NO and NO_2 separately.

3.6. Effect of $p\text{--}n$ junction on sensitivity

As mentioned above, since the sensing materials contain p -type V_2O_5 and n -type ZnO, it is reasonable to expect that at the interface of p -type and n -type semiconductor grains, $p\text{--}n$ junctions will form and these may play an important role in the gas sensing mechanism. Similar to the CO sensing mechanism with a CuO/ZnO heterojunction in ref. [20], a model for selective NO gas sensing based on a $\text{V}_2\text{O}_5/\text{ZnO}$ $p\text{--}n$ junction is proposed as follows:

(1) NO and O_2 are selectively adsorbed on p -type V_2O_5 and n -type ZnO, respectively.

(2) Due to the chemisorption of the gaseous molecules, charge transfer from the semiconductor bulk to the chemisorbed species will take place, i.e. electrons will transfer from ZnO to oxygen to form O^- and holes from V_2O_5 to NO to form NO^+ .

(3) NO_2 will be produced by the reaction of NO^+ on V_2O_5 and O^- on ZnO. Consequently, the charge carriers recombine at the interface of the $p\text{--}n$ junction.

(4) The formed NO_2 molecules will be released from the interface to leave empty adsorption sites for other NO and O_2 molecules.

Through this process, electrical current passes from V₂O₅ to ZnO only under forward bias (V₂O₅⁺, ZnO⁻) of the *p-n* junction. In our sensing materials, the presence of a large number of micro *p-n* junctions with different orientations is expected. Hence the *p-n* junctions under forward bias in the electrical field will give rise to extra current passing from V₂O₅ to ZnO, then increase the conductivity and sensitivity of the sensors. Of those *p-n* junctions under reverse bias no such increase of the sensitivity shall be observed. Hence, the sensitivity may increase with the number of *p-n* junctions.

The observation shown in table 3 that the sensitivity to NO is usually larger than that of NO₂ can be explained by the effect of the *p-n* junction. Since N₂O₅ is a thermodynamically unstable compound, a sensing mechanism based on the *p-n* junctions is not expected for NO₂.

If we take into account the number of *p-n* junctions which is determined by the amounts of *p*-type V₂O₅ and *n*-type ZnO in the different sensor elements, their particle sizes and also the amount of Al₂O₃ which is related to the number of adsorption sites, the sensitivity sequence for NO and NO₂ in table 3 can be discussed.

The numbers of *p-n* junctions in sensors S1, S2 and S3 are supposed to be the same because they all have 25% V₂O₅ + ZnO, the maximum numbers of *p-n* junctions in S4 and S5 are 33% and 50%, respectively. Therefore, the sensitivity of S4 to NO is larger than that of S1, S2 and S3, the sensitivity of S5 to NO being the largest. S6 and S7 follow a different mechanism because no *p-n* junctions can be formed in these materials. The influence of adsorption sites on the sensitivity is revealed by the fact that S1 has a higher sensitivity than S2 and S3, both for NO and NO₂. It is also considered that the *p*-type sensors (S6 and S2 with more *p*-type semiconductor) generally give higher sensitivity than the *n*-type sensors (S7 and S3 with more *n*-type material) as suggested in table 3.

3. Conclusions

(1) The semiconductor NO_x sensor materials with different compositions of Al₂O₃, V₂O₅ and ZnO were prepared. The resistance and Seebeck coefficient of

the sensors were studied as a function of oxide composition and temperature.

(2) The sensors with different compositions reveal fast and sensitive response to 20 to 300 ppm NO. At higher NO concentrations, the sensitivity gradually decreases. In the temperature range up to 400°C the sensitivity increases with increasing operating temperature.

(3) All the sensors containing V₂O₅ are sensitive to NO₂, and usually the sensitivity to NO₂ is lower than that to NO. All the sensors are essentially insensitive to CO₂, suggesting that the interference of CO₂ in NO and NO₂ detection will not be a problem.

(4) Several possible sensing mechanisms were discussed preliminarily and the relation between sensitivity and compositions of the different sensor elements was explained based on the sensing mechanisms and the effect of *p-n* junctions. This Taguchi-type NO_x sensor is promising for NO and NO₂ detection as an alternative to the Ag⁺-β"-alumina solid electrolyte based NO_x sensors at higher temperatures and lower NO_x concentrations, although the sensing mechanism is not yet understood in detail.

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