Solid State Ionics 72 (1994) 338-343
North-Holland

SOLID
STATE
IONICS

NO_x sensing characteristics of $Bi_2Sr_2CaCu_2O_{8+x}$ and $Bi_2Sr_2CuO_{6+x}$ films

X.J. Huang and J. Schoonman

Laboratory for Inorganic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

The sensing behaviour of three kinds of Bi-based superconductor film, differing in microstructure, has been studied. The films comprise $Bi_2Sr_2CaCu_2O_{8+x}$ (BSCCO) with "open neck" contacts between grains, $Bi_2Sr_2CuO_{6+x}$ (BSCO) prepared by electronic beam evaporation and $Bi_2Sr_2CaCu_2O_{8+x}$ with "Schottky-barrier-limited" conductance. The sensitivity and selectivity to NO and NO_2 gases against CO and CO_2 have been investigated. The flow rate dependence of the NO_x sensitivity has been measured. The sensing behaviour of the third film to NO has been measured with both air and Ar as carrier gas. NO behaves as a reductant in air on the surfaces of $Bi_2Sr_2CaCu_2O_{8+x}$ and $Bi_2Sr_2CuO_{6+x}$. NO_2 is neither reductant nor oxidant under the same conditions. A qualitative sensing mechanism for NO_x on $Bi_2SrCaCu_2O_{8+x}$ and $Bi_2Sr_2CuO_{6+x}$ is proposed.

1. Introduction

The gas-detection concept of the semiconductor NO_x sensor is based on chemisorption and/or catalytic activity at the semiconductor surface, which causes resistance changes of the semiconductor due to electronic transfer between semiconductor and the chemisorbed gases. The chemisorption of chemical species on the surface of ceramic superconductors is expected to influence the charge carrier concentration in the surface layer, and even in bulk. Indeed, ceramic superconductors have been explored for use as active component in gas sensors [1].

According to our previous investigation [1], $Bi_2Sr_2CaCu_2O_{8+x}$ (BSCCO) and $Bi_2Sr_2CuO_{6+x}$ (BSCO) are two of the most promising materials for NO_x sensors. In this chapter, the focus is on the mechanism of the Taguchi-type sensors based on these ceramic superconductors.

As $YBa_2Cu_3O_7$, the structure of BSCCO contains many oxygen ion vacancies. The oxygen sorption-desorption occurs below 600°C [2]. Due to the existence of copper(III), and the presence of a bismuth with a valence higher than 3 in BSCCO, which has been confirmed by a series of experiments [3-5], BSCCO may possess a high chemical activity.

It has been reported that the Bi-Sr-Ca-Cu-O mixed oxides exhibit catalytic activity for the reaction of CO and NO, while selectivity to produce N_2 is good. In additions, these oxides are stable to moisture and CO_2 [6]. With regard to this catalytic activity, these oxides are expected to be suited as active sensor materials.

2. Experimental

2.1. Sample preparations

(A) Films of $Bi_2Sr_2CaCu_2O_{8+x}$ with "open neck" contacts between grains were prepared by melting the powders of the oxide directly on an Al_2O_3 substrate.

(B) Films of $Bi_2Sr_2CuO_{6+x}$ were prepared by electronic beam evaporation.

(C) Films of $Bi_2Sr_2CaCu_2O_{8+x}$ which conductance is "Schottky-barrier-limited". Films (A) and (C) were prepared as follows:

The starting material $Bi_2Sr_2CaCu_2O_{8+x}$ was prepared from a mixture of $Bi(NO_3)_3{\cdot}5H_2O$ (CMC), $SrCO_3$(>99%, BDH), $CaCO_3$(CMC), and $Cu(NO_3)_2{\cdot}3H_2O$(>99.5, Merck) with a molar ratio of Bi:Sr:Ca:Cu: =2:2:1:2. A thoroughly ground mixture is first pre-reacted at 820°C in air for 20 h, then reground and sintered at 850°C in air for another 20 h. Next the sintered material is ground to particles of 1 to 10 μm in diameter by ball-milling.

0167-2738/94/$ 07.00 © 1994 Elsevier Science B.V. All rights reserved.

These powders are distributed homogeneously on Al_2O_3 substrates in amounts to make resultant films of less than 100 μm in thickness. The substrates were previously cleaned in acetone. The particles on the substrates are then melted at 950°C for 8 to 10 min. The film was polished to about 20–30 μm. These films (A) are then annealed at 850°C in air for 20 h. Poorly sintered thick films (C) were prepared by the same method except for the melting process. The sintering temperature used is 600°C. Thin films of $Bi_2Sr_2CuO_{6+x}$ were obtained with electron beam (EB) evaporation using a four-target BioRad turbocoater equipped with a quartz oscillator thin-film thickness monitor. Graphite crucibles were filled with the starting material of $Bi_2Sr_2CuO_{6+x}$ which was prepared by the same method as for $Bi_2Sr_2CaCu_2O_{8+x}$ with stoichiometry Bi:Sr:Cu = 2:2:1. As substrate an Al_2O_3 pellet was used. The distance between crucible and substrate was adjusted to be 8 to 10 cm. The substrate temperature during the evaporation process was between 200 and 400°C. The chamber was evacuated to 1×10^{-6} mmHg prior to deposition. The filament current and acceleration voltage were adjusted to be 7–8 mA and 3.5–4.0 kV in order to maintain an emission current in the range of 20–40 mA.

2.2. *Structure and microstructure*

The crystal structure of the films was identified by X-ray diffraction using Cu Kα radiation (Philips PW1840). A JEOL JSM-35 scanning electron microscope was used to observe the microstructure of the films.

2.3. *Electrical measurements*

Four gold electrodes were sputtered onto the surface to provide electrical contacts. The electrical resistivity of films (A) and (C) was measured by a standard four-probe Van der Pauw method. The electrical resistance of film (B) was measured using the two electrodes method with Ag paste electrodes. The films were exposed to different NO_x or CO_x-containing ambients in the sensor testing system described elsewhere [7]. The sensitivity and selectivity of the films to NO, NO_2 against CO and CO_2 were measured at different temperatures. The sensitivities of films (A) and (B) to NO and NO_2 were measured also at different gas flow rates.

3. Results and dicussion

The crystal structue of the films was confirmed by X-ray diffraction as the 2212 phase. The SEM photos show that there are wide necks between grains in film (A) and there is no such neck in films (B) and (C).

3.1. *The flow rate dependence of the sensitivity to NO_x*

The sensitivity of a sample to NO and other gases is defined as

$$S=\frac{R}{R_{\text{air}}}=\frac{\sigma_{\text{air}}}{\sigma}, \qquad (1)$$

where S denotes the sensitivity, R and σ denote the resistivity and conductivity of the sample when exposed to NO or other gases, while R_{air} and σ_{air} are the resistivity and conductivity of the sample in air as a reference, respectively.

Figs. 1 and 2 show the influence of the flow rate on the sensitivity of films (A) to NO and NO_2, respectively. The sensitivity to NO increases with total flow rate. The sensitivity to NO_2 decreases with total flow rate. The NO_2 sensitivity of BSCCO drops to −1 when the total flow rate reaches 250 ml/min.

Fig. 3 presents the flow rate dependence of the

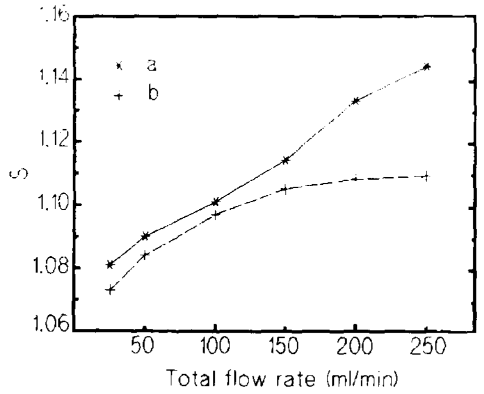

Fig. 1. Flow rate dependence of the sensitivity of a thick film of Bi–Sr–Ca–Cu(2212) to NO: (a) 352°C, (b) 399°C.

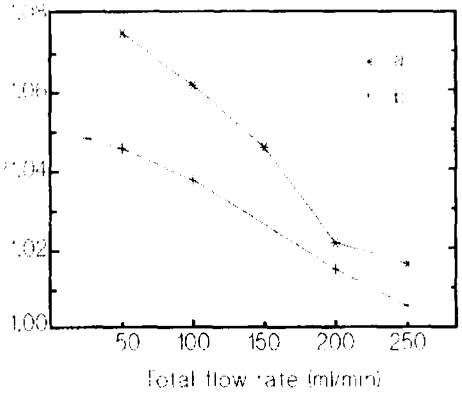

Fig. 2. Flow rate dependence of the sensitivity of a thick film of Bi-Sr-Ca-Cu(2212) to NO_2: (a) 352°C, (b) 399°C.

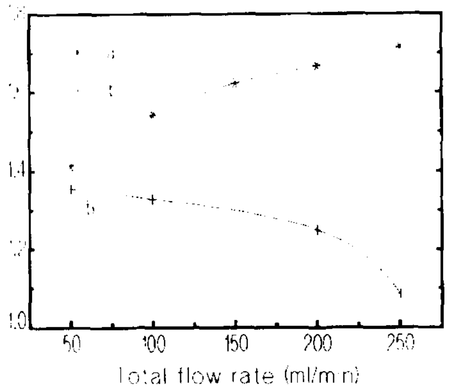

Fig. 3. Flow rate dependence of the sensitivity of a thin film of Bi-Sr-Cu(2201) to NO and NO_2: (a) NO, (b) NO_2.

sensitivity of a thin film of BSCO thin film to NO and NO_2. The sensitivity to NO increases while the sensitivity to NO_2 decreases with increasing flow rate.

3.2. The temperature dependence of the sensitivity to NO, NO_2, CO and CO_2

In all experiments discussed here, the flow rate of the gases is 200 ml/min. Fig. 4 shows the temperature dependence of the sensitivities to NO, CO and CO_2. The optimal temperature to detect NO and NO_2 is 350°C. The sensitivity of a thick film of BSCCO to CO_2 is quite low. This can be understood by considering that CO_2 cannot be oxidized or reduced under these experimental conditions. While under the same conditions, the oxidation of CO is permitted thermodynamically. CO behaves as a reductant as is also evident from other experiments [8,9].

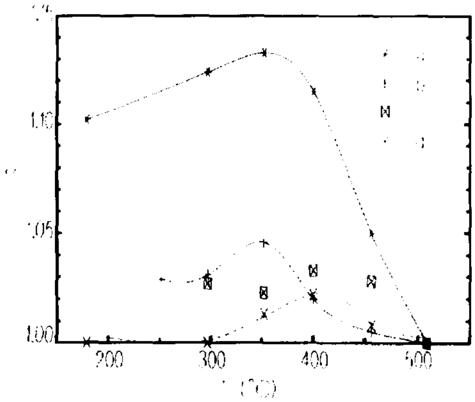

Fig. 4. Temperature dependence of the sensitivity of film (A) to NO, NO_2, CO, and CO_2 in air: (a) 500 ppm NO, (b) 500 ppm NO_2, (c) 500 ppm CO, (d) 1% CO_2.

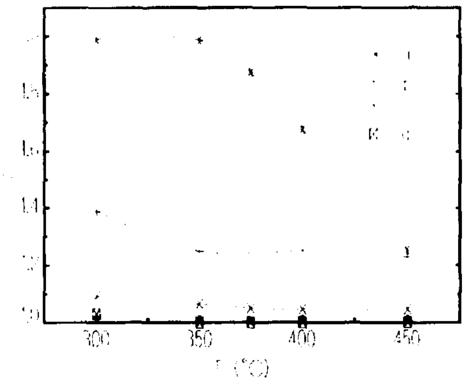

Fig. 5. Temperature dependence of the sensitivity of film (B) to NO, NO_2, CO, and CO_2 in air: (a) 500 ppm NO, (b) 500 ppm NO_2, (c) 500 ppm CO, (d) 1% CO_2.

The sensitivity of a thick film of $Bi_2Sr_2CaCu_2O_{8+x}$ to 500 ppm NO was almost one order of magnitude greater than that to 500 ppm CO, and 1% CO_2. Therefore the selectivity against CO and CO_2 is expected to be sufficient.

The temperature dependence of the sensitivity of films (B) and (C) to NO_x and CO_x is shown in figs. 5 and 6. Films (B) and (C) exhibit selectivity to NO against CO_x.

3.3. Discussion on the sensing mechanisms

While we do not wish to be limited to any particular theory, it is accepted that the sensing mecha-

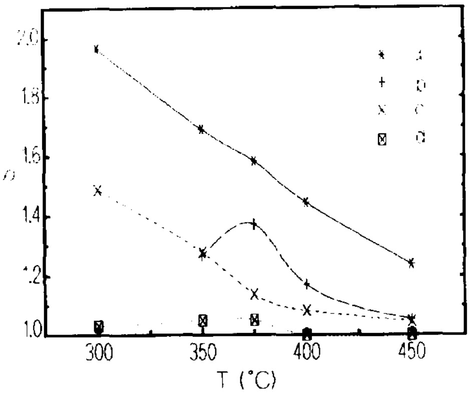

Fig. 6. Temperature dependence of the sensitivity of film (C) to NO, NO_2, CO, and CO_2 in air: (a) 500 ppm NO, (b) 500 ppm NO_2, (c) 500 ppm CO, (d) 1% CO_2.

nism is based on a chemisorption phenomenon. The mechanisms of redox processes at the surface of perovskite oxides are topotactic in nature, thus accounting for the reversible loss and uptake of lattice oxygen, or for the concomitant creation and annihilation of oxygen ion vacancies and electronic charge carriers rendering these systems as attractive oxidation catalysts [10].

The amount of gas adsorbed, and thus the effect on the resistivity, depends on the NO concentration. The sensor responds to the gas until a concentration is reached at which chemisorption sites are substantially saturated, and a maximum number of defects is effected.

In general, NO behaves as an oxidizing species at the surface of *n*-type materials [11–13]. However, according to the thermodynamic data [14], both the decomposition to N_2O or N_2 and oxidation of NO to NO_2 are possible under these experimental conditions. For decomposing NO on the catalyst in air, van den Bleek et al. [15] proposed that NO should be coordinated as NO^-. When NO is adsorbed on the surface of *n*-type materials, one electron transfer from the conduction band to an anti-bonding orbital of NO leads to the formation of an anion,

$$[:\underset{\cdot}{\overset{\cdot}{N}}\overset{\pi}{-}\underset{\cdot}{\overset{\cdot}{O}}:]^{-}\,.$$

The formation of NO^- can be accounted for *n*-type materials. At the surface of a *p*-type semiconductor, one or more electrons may transfer to the semiconductor, and NO^- shall not be formed. Hence, the prerequisite for NO decomposition is not satisfied. Therefore, NO does not decompose.

While a chemical species which behaves as a reducing agent chemisorpted on the surface of semiconducting materials, the conductivity of *p*-type materials will decrease and that of *n*-type materials will increase. CO acts as an electron donor, i.e. as an occupied surface state. On adsorption CO injects electrons into the material's conduction band, and hence increases the conductance [16,17].

$$G_{gas} \leftrightharpoons G^{+}_{surf} + e^{-}_{bulk}\,. \tag{2}$$

By way of redox reactions combustible gases participate in a defect reaction which affects the bulk semiconductor's stoichiometry. The concentration of the material's bulk conduction band electron relates the reducing gas concentration [18,19]

$$G_{gas} + MO_{2bulk} \leftrightharpoons P_{gas} + (MO)^{++}_{bulk} + 2e^{+}_{bulk}\,. \tag{3}$$

CO acts as a reducing agent under these experimental conditions. When it is adsorbed on the surface of the 2212 phase material, the conductivity of the material decreases.

If NO acts as an oxidizing species, a dissociative chemisorption of NO with the participation of free and trapped electrons in oxygen ion vacancies can be hypothesized [20]:

$$e^{-} + V_{O}^{\cdot\cdot} + NO(g) \rightarrow O_{O}^{\times} + N_{ads} \tag{4}$$

accompanied by the successive reactions:

$$2N_{ads} \rightarrow N_2(g)\,, \tag{5}$$

$$N_{ads} + NO_{ads} \rightarrow N_2O(g)\,. \tag{6}$$

The conductivity of *p*-type materials will increase. In this study, no such effect was found. Although NO_2 behaves as an oxidant on the surface of *p*-type phthalocyanine [21–24], it did not act as an oxidizing agent on BSCCO and BSCO.

Ishihara et al. [25] found that NO behaves as a reductant on the surface of *p*-type Cr_2O_3–Nb_2O_5, and as an oxidant on the surface of *n*-type oxides.

According to the results of Kishida et al. [26], a clean surface of a 2212-phase single crystal is stable without any adsorption of O_2 gas.

There are a few cases where reduction and oxidation of the semiconductor has been the process assumed for a candidate gas sensor. Setter [27] used cobalt oxide to detect CO, proposing a redox model in which a lattice oxygen is exchanged during the oxidation of CO on cobalt oxide. Göpel et al. [28] observed the existence of oxygen ion vacancies formed on a TiO_2 defect surface. This vacancy is formed by a high-temperature treatment, or by a low-temperature exposure of the defect surface to CO, whereby CO_2 formation occurs upon reaction with an adjacent lattice oxygen. This reaction even proceeds at 300 K.

For the conversion of NO to NO_2, the reaction reads

$$NO+\tfrac{1}{2}O_2=NO_2\,. \qquad (7)$$

The equilibrium constant K can be calculated from the data for the Gibbs energy [14], i.e.

$$\ln K=-\Delta G/RT\,. \qquad (8)$$

From this relation we obtain for the partial pressure of NO_2 at different temperatures, i.e.

$$P_{NO_2}=\frac{K\sqrt{P_{O_2}}}{1+K\sqrt{P_{O_2}}}\,[P_{NO}+P_{NO_2}]\,. \qquad (9)$$

When the mixed gas is fed into the reactor and arrive at the surface of the sample, the equilibrium can be reached if the flow rate is low enough.

When the flow rate of the NO_2-air mixture is too high, the conversion ratio of NO_2 to NO is very low. A sensitivity close to 1 means that the material has no sensitivity to NO_2. The NO_2 sensitivity which is measured is due to NO formed by NO_2 conversion. NO causes the resistivity of the sample to increase. Considering that BSCCO 2212 phase is a p-type material, and NO shows reductive behaviour in air, the conversion almost reaches equilibrium at low flow rate. Then the sensitivity to NO and NO_2 will not differ much. When the flow rate increases, the conversion decreases. Then the sensitivity to NO increases, and that no NO_2 decreases.

3.4. Discussion on the difference of the sensitivity among films

It is apparent that the sensitivity of film (A) is lower than that of film (B) and film (C) under the same conditions.

The main reason is proposed to be a microstructural effect. There are three kinds of grain boundaries, i.e.

(i) "closed neck" contacts where the depletion zone is formed by overlap of two surfaces. Here the conductivity is 'Surface-trap limited'.

(ii) "Schottky-barrier limited" conductivity may occur in a porous medium. Within the grains the conductivity behaves ohmic, while the contacts act as a Schottky barrier, which arises from trapped charge in the surface states. Here the gas sensitivity is independent of grain size. The conductivity is limited by charge transport across the barrier, and is proportion to $\exp(-eV_s/kT)$. The conductivity activation energy eV_s is affected by the charge and fractional coverage of the surface species and is, therefore, a function of the composition of the gaseous ambient.

(iii) "Open neck" contacts occur in well-sintered films. In this situation, the neck is wider than the space charge regions. Now two different situations may be distinguished. In one situation the conductivity of the surface layers exceeds that of the bulk, i.e. the surface-trap-limited regime. In the case of film (A), the scanning electron micrographs reveal the width of the neck to be much larger than that of the depletion layer, which is usually of the order of 100 Å. In addition, the electrical conductivity of the central-part of the neck exceeds that of the depletion layers. In this situation the conductance is "bulk-trap-limited". The variation of the width of the central part of the neck due to the introduction of reducing gases is rather small compared to the total width of the neck. The conductivity change is small, and, therefore, the sensitivity is low. If the width of the neck approaches twice the Debye length when the grain size is reduced, the conductivity will change substantially when reducing gases are introduced. This results from a rather large relative change of the width of the central part of the neck. If the width of the central part of the neck is less than twice the Debye length, the conductance will become "surface-trap-limited". The conductance depends on the carrier density in the surface layer, and this conductivity will change when reducing gases are introduced. Therefore, the sensitivity will be high. Xu et al. [29,30] have shown that the sensitivity of tin oxide to hydrogen depends on the grain size. For an n-type material in reducing atmosphere, the conductance becomes "surface-trop-limited", because the conductance of the surface is much higher than that of the bulk. When the width of neck is comparable with twice the Debye length, the resistance becomes "surface-trap-limited". For *p*-type material, a high sensitivity results only when the width of the neck approaches, or is less than twice the Debye length. Sensors with a high sensitivity using submicron powders or ultra thin films are subject of further research. Another approach is the synthesis of poorly sintered thick films as active sensor material as the case of film (B) and film (C). Their conductances are "Schottky-barrier-limited", and they show high sensitivity.

4. Concluding remarks

CO behaves as a reductant at the surfaces of $Bi_2Sr_2CaCu_2O_{8+x}$ and $Bi_2Sr_2CuO_{6+x}$ in air. NO also behaves as a reductant under the same conditions. NO_2 is neither a reductant nor an oxidant under the same conditions. The sensitivity to CO is much lower than that to NO. CO_2 and NO_2 behave neigher as a reductant nor as an oxidant. Their sensitivities are quite low. The NO_2 sensitivity is due to NO formed by decomposition of NO_2.

Based on the experimental facts, a qualitative sensing mechanism for NO_x on $Bi_2Sr_2CaCu_2O_{8+x}$ and $Bi_2Sr_2CuO_{6+x}$ is proposed. The principle sensing reaction is

$$NO(g)+O_O^{\times}+2h^{\cdot}\rightarrow(NO_2)_{ad}+V_O^{\cdot\cdot}\,.$$

The lattice oxygens in the surface layer are involved in the sensing reaction. The difference in the sensitivity of the three kinds of films is attributed to a grain size effect.

References

[1] X.J. Huang, L.Q. Chen and J. Schoonman, Solid State Ionics 57 (1992) 7.

[2] N. Miura, H. Suzuta, Y. Deshimaru, Y. Shimizu, H. Sakashita and N. Yamazoe, Mol. Cryst. Liq. Cryst. 184 (1990) 189.

[3] L.Q. Chen, X.J. Huang, T.E. Hui, Y.Z. Huang and J.Q. Bi, Progress in High Temperature Superconductors, Vol. 22, eds. Z.X. Zhao, G.J. Cui and R.S. Han (World Scientific, Singapore, 1989) p. 382.

[4] H.K. Liu, S.X. Dou, K.H. Song, C.C. Sorrell, K.E. Easterling and W.K. Jones, J. Solid State Chem. 87 (1990) 289.

[5] K. Kurusu, H. Takami and K. Shintomi, Analyst 11 (1989) 1341.

[6] N. Mizuno, H. Toyama, M. Tanaka, M. Yamato and M. Misono, Bull. Chem. Soc. Japan. 64 (1991) 1383.

[7] X.J. Huang, PhD Thesis (Delft University of Technology, 1993).

[8] T. Arakawa, K. Takada, Y. Tsunemine and J. Shinokawa, Sensors Actuators 14 (1988) 215.

[9] H. Windischmann and P. Mark, J. Electrochem. Soc. 126 (1979) 627.

[10] P.P. Edwards, M.R. Harrison and R. Jones, Chem. Brit. 23 (1987) 962.

[11] S.C. Chang, Proc. Int. Meeting Chemical Sensors, eds. T. Seiyama, K. Fueki, J. Shiokawa and S. Suzuki (Kodansha and Elsevier, Tokyo, 1983) p. 78.

[12] T. Ishihara, K. Shiokawa, K. Eguchi and H. Arai, Sensors Actuators 19 (1989) 259.

[13] J. Lagois, H.P. Oepen and W. Hagen, NTG-Fachber. 93 (Sens. Technol. Anwend.) (1986) 93.

[14] I. Brain and O. Knacke, in: Thermochemical Properties of Inorganic Substances (Springer, Berlin, 1973).

[15] C.M. van den Bleek, J.W. Eek, J. Reedijk and P.J. van den Berg, I. Chem. E. Symp. Series No. 57 (Control Sulphur Other Gaseous Emmis.) (1979) R1-R14.

[16] G. Heiland, Sensors Actuators 2 (1982) 343.

[17] S.R. Morrison, Sensors Actuators 2 (1982) 329.

[18] E.M. Logothetis, K. Park, A.H. Meitzler and K.R. Laud, Appl. Phys. Lett. 26 (1975) 209.

[19] T.Y. Tien, H.L. Stadler, E.E. Gibbons and P.J. Zacmanidis, Am. Chem. Soc. Bull. 54 (1975) 280.

[20] P.K. Clifford, in: Proc. Intern. Meeting on Chemical Sensors, eds. T. Seiyama, K. Fueki, J. Shiokawa and S. Suzuki (Kohansha and Elsevier, Tokyo, 1983) p. 135.

[21] B. Bott and T.A. Jones, Sensors Actuators 5 (1984) 43.

[22] S. Pizzini, G.L. Timo, M. Beghi, N. Butta and C.M. Mari, Sensors Actuators 17 (1989) 481.

[23] T.A. Jones, B. Bott and S.C. Thorpe, Sensors Actuators 17 (1989) 467.

[24] T.A. Jones and B. Bott, in: Proc. 2nd Intern. Meeting Chemical Sensors, eds. J.L. Aucouturier, J.S. Cauhape, M. Destriau, P. Hagenmuller, C. Lucat, F. Menil, J. Portier and J. Salardenne (Elsevier Sequoia, Lausanne, 1986) p. 167.

[25] T. Ishihara, K. Shiokawa, K. Eguchi and H. Arai, Chem. Lett. (1988) 997.

[26] S. Kishida, H. Tokutaka, H. Fujimoto, K. Nishimori and N. Ishihara, Japan. J. Appl. Phys. 28 (1989) L1389.

[27] R. Setter, J. Coll. Interface Sci. 65 (1978) 432.

[28] W. Göpel, G. Rocker and R. Feierabend, Phys. Rev. B 28 (1983) 3427.

[29] C. Xu, J. Tamaki, N. Miura and N. Yamazoe, Denki Kagaku 58 (1990) 1143.

[30] C. Xu, J. Tamaki, N. Miura and N. Yamazoe, Sensors Actuators B 3 (1991) 147.