



Chlorine Gas Sensing Properties of ZnO-CaO Ceramics

KEN-ICHI INOUE & MASARU MIYAYAMA

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan E-mail: tmiyaya@hongo.ecc.u-tokyo.ac.jp

Received March 21, 1997; Revised November 20, 1997; Accepted December 5, 1997

Abstract. The chlorine gas sensing properties of pure ZnO (PZ) and CaO-added ZnO (CAZ) ceramics with relative densities of 48–65% were investigated from 25–380°C in Cl₂ concentration range from 0.9 ppm to 20 ppm using air or N₂ as a carrier gas. In the entire temperature range, the conductivity of PZ and CAZ ceramics decreased by introducing Cl₂ gas. 3 mol% CAZ showed a Cl₂ sensitivity ($\sigma(0)/\sigma(\text{Cl}_2)$) of 10 for 0.9 ppm Cl₂ in air at 300°C, suggesting its usefulness for sensing of a low-concentration Cl₂ gas below 1 ppm. The CaO addition was found to decrease the Cl₂ sensitivity but to improve the recovery process after removing Cl₂ gas. These effects are attributed to changes in the amount and stability of adsorbed oxygen and to subsequent changes in Cl₂ adsorption behavior.

Keywords: zinc oxide, calcium oxide, chlorine gas sensor, gas adsorption

1. Introduction

Chlorine gas is used in various fields, e.g., as a raw material in chemical industries, a bleaching agent, a disinfectant of water, etc. Chlorine gas, however, is harmful to humans because of its strong oxidizing power. In order to protect humans and the natural environment from chlorine damage, sensing devices with high sensitivity and reliability are required in many fields. Several types of chlorine gas sensors using inorganic and organic compounds have been proposed; for example, a solid electrolyte type sensor using Cl⁻ ionic conductors such as PbCl₂-KCl [1,2] and BaCl₂-KCl [3,4], a ceramic heterocontact type sensor using SiC/ZnO [5,6], and an organic semiconductor type sensor using metal-phthalocyanines [7]. On the other hand, there are few studies on ceramic semiconductor type chlorine gas sensors [8]. Generally, simple sensor structure, durability, high sensitivity and rapid response are expected with ceramic semiconductor-type, compared with the other types of sensors.

In the present study, porous ceramics of pure zinc oxide (ZnO) (denoted as PZ hereafter) and calcium oxide (CaO)-added zinc oxide (denoted as CAZ

hereafter) were used as materials for semiconductor-type chlorine gas sensors. Chlorine gas sensing properties of these ceramics and the effects of CaO addition on the sensing properties were investigated. From these experimental results, the sensing mechanisms were also identified.

2. Experimental

2.1. Specimen Preparation

Powders of ZnO (99.99% pure, Kojundo Kagaku) and Ca(NO₃)₂·4H₂O (extra pure grade, Kanto Kagaku) were used as starting materials to prepare CAZ ceramics. Ca(NO₃)₂·4H₂O was weighed and dissolved in water. ZnO powder was added to the aqueous solution and mixed. The mixture was dried and calcined at 600°C for 5 h in air. The calcined powder was passed through a sieve, pressed into 5 × 15 × 3.5 mm plates at 49 MPa, and sintered at 700°C for 3 h in air. Calcining and sintering conditions for preparing PZ ceramics were the same as those for CAZ ceramics. The relative density of PZ and 3mol% CAZ ceramics were about 65 and 48% of

theoretical, respectively. The specimens were polished with a SiC abrasive paper (#400), washed with acetone, and then dried. Electrodes were applied by firing on Ag-In paste (Degussa Japan, J190 1588) at 500°C, on which epoxy resin was applied to prevent the electrodes from exposure to atmosphere.

2.2. Measurements

The microstructure of specimens was investigated with a scanning electron microscope (SEM; JEOL, JSMT330A). Pore distributions and pore surface area of specimens were measured by mercury intrusion porosimetry using a pore sizer (Shimadzu, Model 9320). Lattice constants of PZ and CAZ were calculated from X-ray diffraction (XRD) peaks using tungsten metal as a standard.

Figure 1 shows a schematic drawing of the measuring system used to study the chlorine gas sensing properties of the materials. A specimen on a holder was placed in an alumina chamber, in which dry air was flowed at 200 cm³/min as the carrier gas. In some cases, air with a desired relative humidity or dry nitrogen gas was used as the carrier gas. The relative humidity was controlled by changing the flow ratio of dry air and water-bubbled air. Electrical measurements were carried out by the two-probe direct-current method. A voltage was applied to the specimen and current changes due to the introduction of Cl₂ gas were monitored with an electrometer (Advantest, TR8652). The chlorine gas sensing properties were measured from 25–380°C for Cl₂ concentration in the range from 0.9–20 ppm in air or

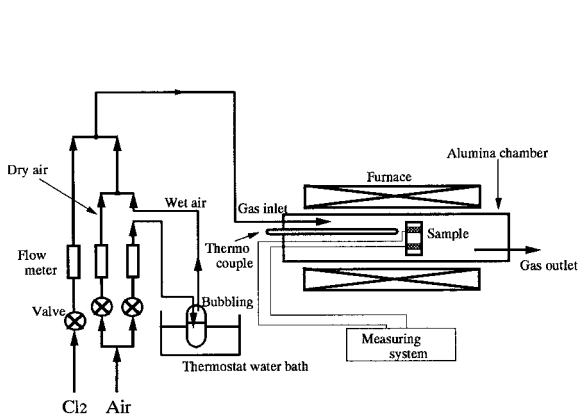


Fig. 1. A schematic drawing of the measuring system for chlorine gas sensing properties.

N₂. The Cl₂ gas sensitivity was defined as the ratio $\sigma(0)/\sigma(\text{Cl}_2)$, where $\sigma(0)$ is the conductivity in air or N₂, and $\sigma(\text{Cl}_2)$ is that in Cl₂ gas.

Temperature programmed desorption (TPD) for O₂ was carried out for powder samples prepared by grinding sintered bodies. Each sample was placed in a chamber and treated at 500°C for 5 h under vacuum conditions to desorb pre-adsorbed species. After introduction of O₂ gas (10 torr) for 30 min at room temperature, the chamber was evacuated to below 4×10^{-6} torr at room temperature, and the desorbed O₂ was analyzed by a mass spectrometer on heating at a rate of 20°C/min.

3. Results and Discussion

3.1. Microstructure

In XRD patterns of CAZ, diffraction peaks of CaO were observed in specimens with CaO content above 5 mol%, but peaks other than ZnO and CaO were not observed in specimens with CaO content up to 20 mol%. The lattice constant for the a-axis of CAZ was almost independent of CaO content, but that for the c-axis increased slightly up to 0.1 mol% CaO and was almost constant in the range from 0.1–20 mol% CaO, as shown in Fig. 2. These results indicate that the solubility limit of CaO in ZnO prepared by this condition is about 0.1 mol% and most of the added CaO is not dissolved into ZnO.

Figure 3 shows the results of SEM observations on the fractured surfaces of PZ and 3 mol% CAZ

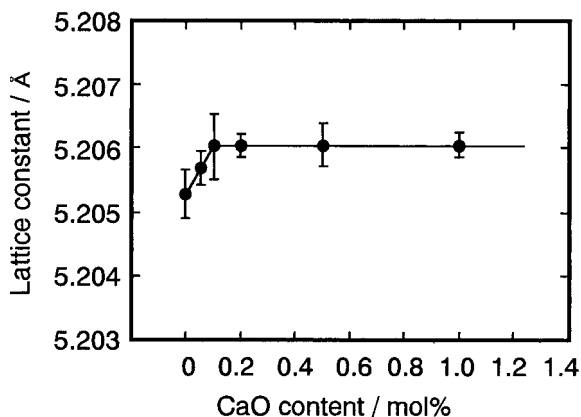


Fig. 2. Lattice constant for c-axis of CAZ ceramics sintered at 700°C for 3 h.

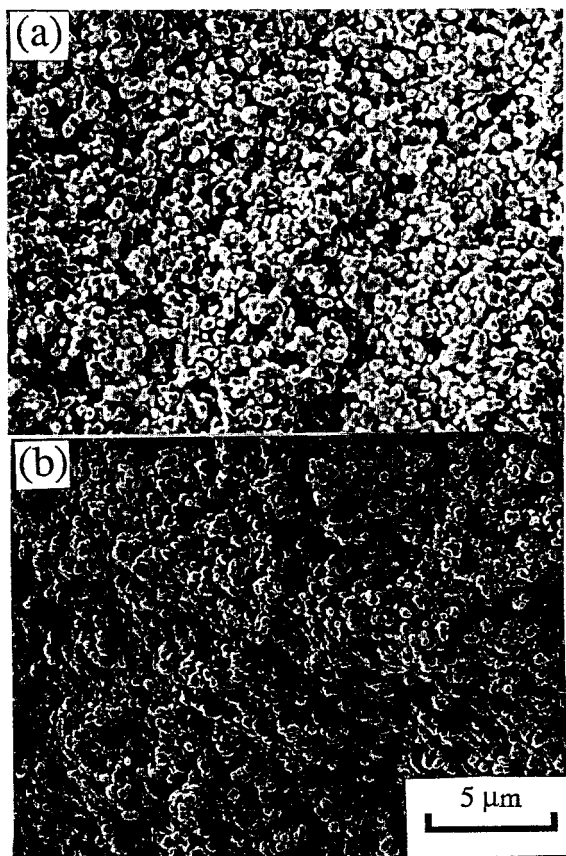


Fig. 3. SEM micrographs of (a) PZ and (b) 3 mol% CAZ ceramics sintered at 700°C for 3 h.

ceramics. The grain sizes of the specimens were found to be 0.5–1.0 μm and 0.3–0.8 μm for PZ and 3 mol% CAZ ceramics, respectively. The grain size of specimens became a little smaller with CaO additions and with increasing CaO content.

Figure 4 shows the pore size distribution of pure and CAZ ceramics. The total pore volume was found to increase with the CaO addition to a value about twice that of PZ. The average pore diameter was 0.21 μm for PZ and 0.22–0.26 μm for ZnO added with 1–10 mol% CaO, respectively. In the above CaO content range, the pore size distribution did not change appreciably. The total pore surface area, estimated from the pore size distribution, was 1.8 m^2g^{-1} for PZ and 3.0–3.3 m^2g^{-1} for 1–10 mol% CAZ ceramics, respectively. From these results, it was concluded that the effect of CaO additions was to retard

sintering of ZnO and to increase specific pore surface area.

3.2. Chlorine Gas Sensing Properties

Figures 5 (a) and (b) show the typical conductivity changes of pure and 3 mol% CAZ ceramics when 20 ppm Cl_2 gas was introduced in dry air at 300°C. The conductivity decreased substantially by introducing Cl_2 gas. The Cl_2 sensitivity ($\sigma(0)/\sigma(\text{Cl}_2)$) was about 500 and about 80 for PZ and 3 mol% CAZ, respectively. The response speed was higher for CAZ than for PZ, and the 90% recovery time (the time required for recovery to the 90% value of the initial conductivity after removing Cl_2 gas) was about 50 min and about 20 min for PZ and 3 mol% CAZ, respectively. It was found that the effect of CaO additions was to decrease Cl_2 gas sensitivity but to improve response speed, especially in the recovery process after removing Cl_2 gas.

Since the sensitivity and the recovery process are important factors for practical use of these materials as gas sensors, their CaO content dependence was studied. Figure 6 shows the dependence of sensitivity and 90% recovery time on CaO content to Cl_2 gas (20 ppm). By addition of CaO above 1 mol%, although the Cl_2 gas sensitivity was decreased, the recovery was improved compared with that of PZ. For CaO contents above 5 mol%, the conductivity changes induced by Cl_2 gas were not stable and reproducible. The addition of 0.05 mol%, which is below the solubility limit, decreased the Cl_2 gas

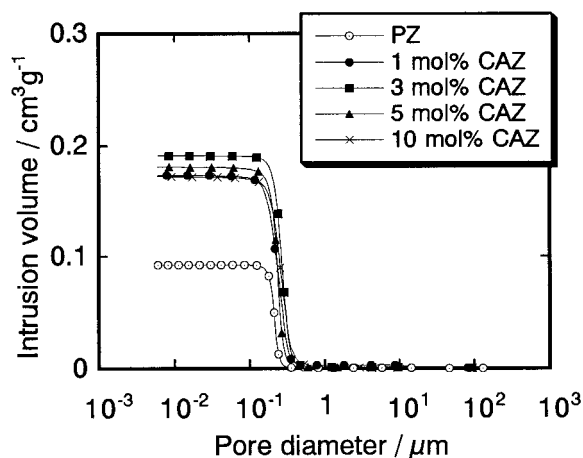


Fig. 4. Pore size distributions of PZ and CAZ ceramics sintered at 700°C for 3 h.

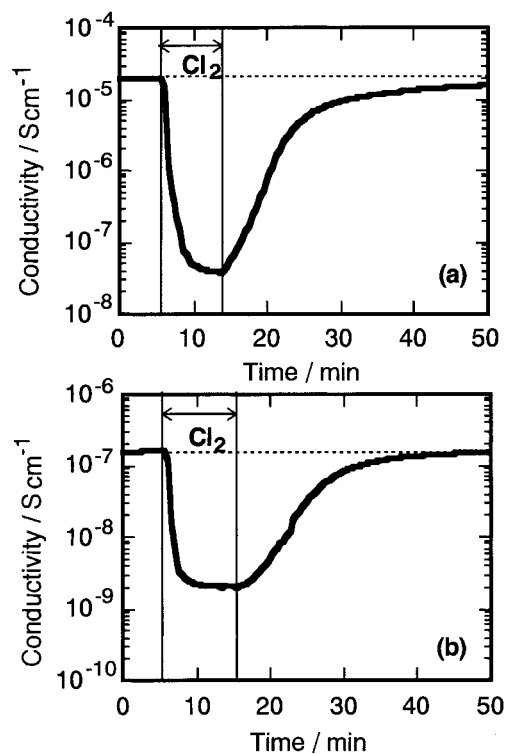


Fig. 5. Typical conductivity changes of (a) PZ and (b) 3 mol% CAZ ceramics by 20 ppm Cl_2 gas in dry air at 300°C .

sensitivity, but did not improve the recovery. It is assumed that the CaO, not dissolved in ZnO, is responsible for the improvement of the recovery process. Based on these results, 3 mol% CAZ was chosen as the material for the following measurements.

In the temperature range of $25\text{--}380^\circ\text{C}$, the conductivity of PZ and CAZ ceramics decreased by exposure to Cl_2 gas. Figure 7 shows conductivity changes of 3 mol% CAZ ceramics induced by 20 ppm Cl_2 gas in dry air at various temperatures. As the temperature decreased, the Cl_2 gas sensitivity increased, but the recovery time also greatly increased. The 90% recovery time was about 20 min at 300°C , but the conductivity did not recover to the 90% value even after 40 min after Cl_2 gas removal at 230°C . At temperatures below 70°C , the conductivity was almost unchanged after removing the Cl_2 gas. As above, 300°C was assumed to be the most appropriate temperature for Cl_2 gas sensing using 3 mol% CAZ ceramics.

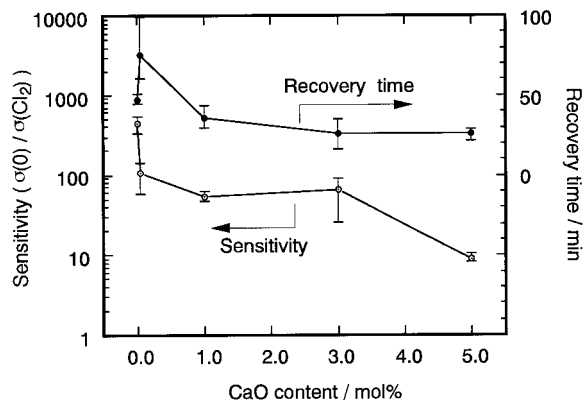


Fig. 6. Dependence of gas sensitivity and recovery time on CaO content in dry air plus 20 ppm Cl_2 at 300°C .

Figure 8 shows response curves to 2.5–20 ppm Cl_2 gas in dry air at 300°C for 3 mol% CAZ ceramics. Reproducible conductivity changes and good recovery were observed. Figure 9 shows logarithmic plots of Cl_2 gas sensitivity as a function of Cl_2 gas concentration. The plots showed an almost linear dependence of the logarithm of sensitivity on the logarithm of Cl_2 gas concentration. The slopes of the plots were about 1 and about 0.6 for PZ and 3 mol% CAZ, respectively. The sensitivities of PZ and 3 mol% CAZ became closer for lower Cl_2 concentrations. Since the sensitivity reached 10 even for 0.9 ppm Cl_2 , the 3 mol% CAZ ceramics was found to be applicable for sensing low-concentration Cl_2 gas below 1 ppm. When N_2 was used as a carrier gas, the Cl_2 gas sensitivity increased by more than 1 order of magnitude compared with that in air, in both PZ and 3 mol% CAZ, but the Cl_2 dependence (the slope of the plot) was maintained in each specimen.

3.3. Sensing Mechanisms

The decrease in conductivity of n -type semiconducting ZnO by introduction of Cl_2 gas is attributed to the following mechanisms; model 1: Chlorine molecules are adsorbed on the ZnO surface as negatively charged ions, trapping electrons from ZnO [9–11], and model 2: the Cl_2 gas and water vapor in the atmosphere react to produce hypochlorous acid (HClO) with high oxidizing power, and this hypochlorous acid forms an insulating layer on the ZnO surface [5,6]. The second model has been proposed for SiC/ZnO heterocontact type Cl_2 gas

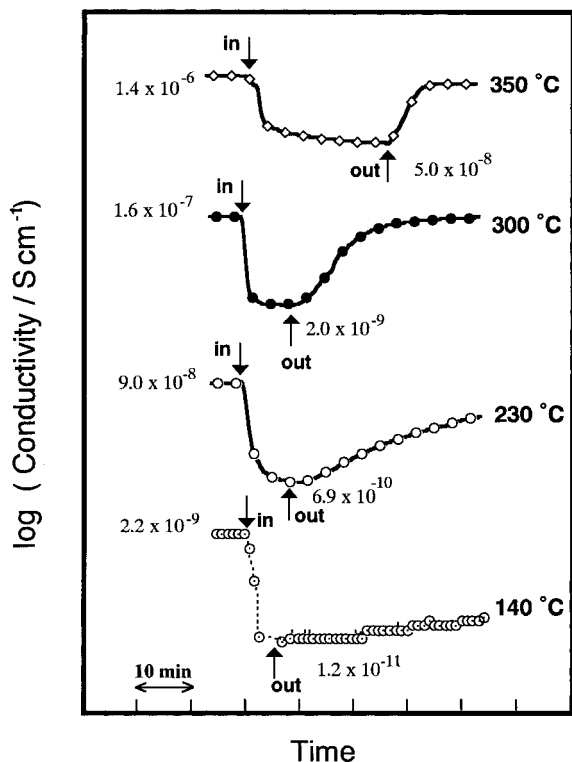


Fig. 7. Conductivity response curves to 20 ppm Cl₂ gas in dry air at various temperatures for 3 mol% CAZ ceramics. Numbers indicate conductivities in S cm⁻¹.

sensors operated at room temperature [5,6]. When the second model is adapted, it is expected that the Cl₂ gas sensitivity is affected by humidity in the atmosphere. Figure 10 shows the dependence of 20 ppm Cl₂ gas sensitivity on relative humidity in air at 300°C. The Cl₂ gas sensitivity was found to be hardly affected by the humidity in both PZ and CAZ ceramics.

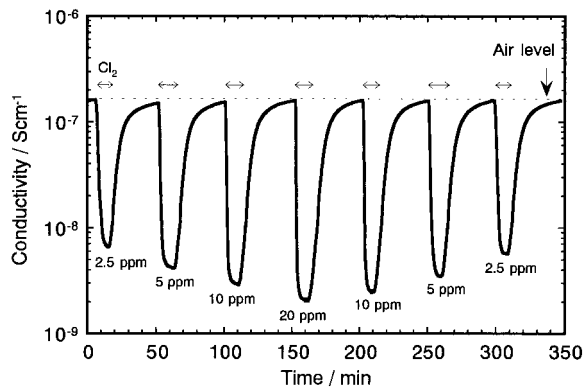


Fig. 8. Conductivity response curves to varying Cl₂ concentrations for 3 mol% CAZ ceramics in dry air at 300°C.

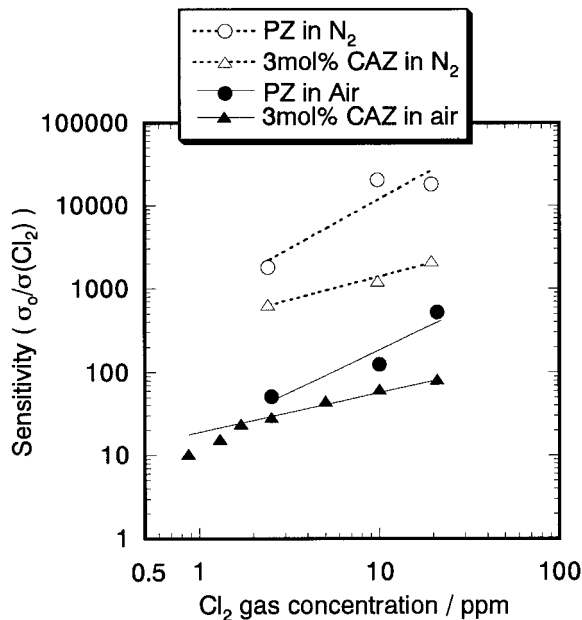


Fig. 9. Logarithmic plots of Cl₂ gas sensitivity as a function of Cl₂ gas concentration in dry air and N₂ at 300°C. The solid lines indicate the estimated sensitivity using Eqs. 5 and 10.

Accordingly, the effect of HClO is assumed to be negligibly small in the present system at 300°C.

As stated above, the Cl₂ gas sensitivity in N₂ was more than one order of magnitude larger than that in air in both PZ and 3 mol% CAZ. Generally, it is well known that oxygen molecules are adsorbed on ZnO surfaces in air, trapping electrons. Likewise, chlorine molecules adsorbed on ZnO surfaces should trap

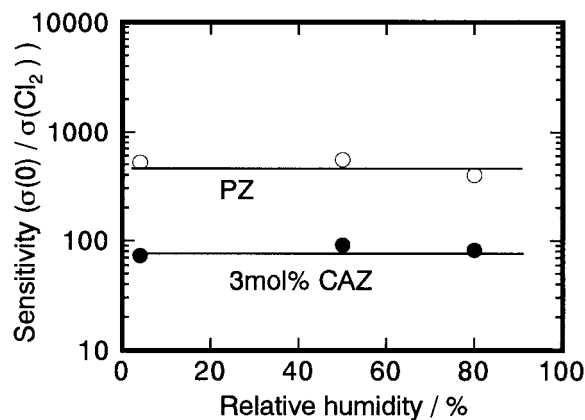


Fig. 10. Dependence of 20 ppm Cl₂ gas sensitivity at 300°C on relative humidity in air. Humidity is expressed as the relative humidity at 25°C.

electrons due to the strong electronegativity of the chlorine atom. The enlargement in sensitivity in N_2 compared with that in air indicates that chlorine and oxygen are competitively adsorbed on ZnO surfaces. Consequently, the first model can be adapted in this system.

The CaO addition decreased the Cl_2 gas sensitivity, but improved the recovery, as shown Figs. 5(a) and (b). Concerning adsorbed oxygen on metal oxides, each type of adsorbed oxygen is known to give different slopes in plots such as Fig. 9 [12]. From the difference in the slopes of such plots between for PZ and for 3 mol% CAZ, we assume that CaO additions effect the adsorption behavior of Cl_2 . Since a competitive adsorption is assumed between O_2 and Cl_2 , it is expected that the change in form of Cl_2 adsorption is related with the change in form of O_2 adsorption.

Figure 11 shows TPD spectra of O_2 for PZ and 3 mol% CAZ powders prepared by grinding those ceramics sintered at $700^\circ C$ for 3 h. In this measurement, both powders were ground so as to have almost the same specific surface area as confirmed using a pore sizer. Two peaks were observed at about $100^\circ C$ and $350^\circ C$. The peak at about $100^\circ C$ could be due to physisorbed oxygen and O_2^- , and the peak at about $350^\circ C$ to O^- and O^{2-} . It was found that the peak at $350^\circ C$ becomes larger with 3 mol% CaO addition. Since the measurement temperature of Cl_2 sensing properties is $300^\circ C$, it is concluded that the amount of adsorbed oxygen is larger for 3 mol% CAZ than that for PZ at that temperature.

Figure 12 shows the temperature dependence of

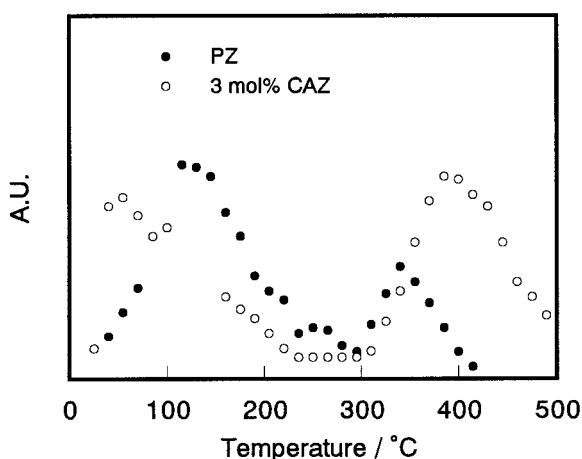


Fig. 11. TPD spectra of O_2 for PZ and 3 mol% CAZ.

conductivity in air for PZ and CAZ ceramics. The heating rate was $1^\circ C/min$ in this measurement. These ceramics showed decreases in conductivity with increasing temperature and then minima in the temperature range of $220\text{--}320^\circ C$. This decrease of conductivity is known to be caused by an increase in the charge of adsorbed oxygen [13]. The temperature, at which the conductivity minimum is observed, shifted from 285 to $310^\circ C$ by the CaO addition. For PZ, $300^\circ C$ is in the region that the conductivity is increasing above the minimum. This indicates that the high temperature forms of adsorbed oxygen begin to desorb from PZ surfaces below $300^\circ C$. On the other hand, the conductivity is still decreasing at $300^\circ C$ for 3 mol% CAZ, indicating that the adsorbed oxygen in the high temperature forms are less desorbed from 3 mol% CAZ at $300^\circ C$. The above results suggest that the adsorbed oxygens are being stabilized by the CaO addition.

According to reports on halogen adsorption on metals and metal oxides, chlorine molecules are adsorbed dissociatively in most cases [9–11]. On the 3 mol% CAZ surface, since adsorbed oxygens are assumed to be stabilized by CaO additions, it is expected that dissociative adsorption of chlorine occurs without oxygen desorption as,

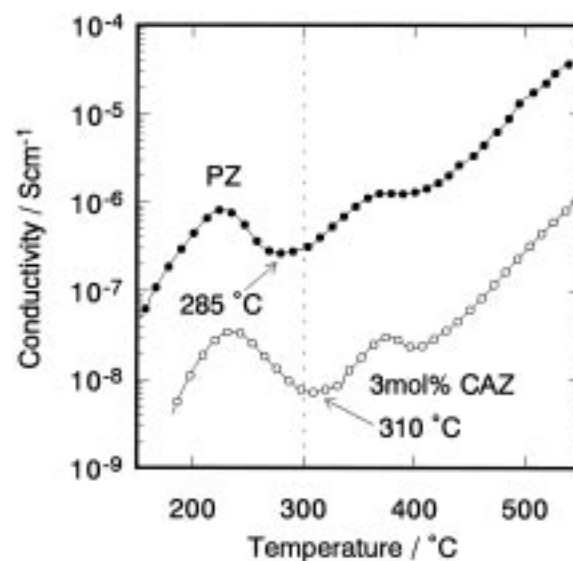
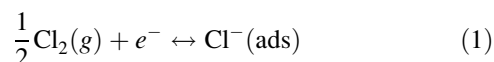


Fig. 12. Temperature dependence of conductivity for PZ and 3 mol% CAZ.

When the reaction of Eq. (1) is in an equilibrium state, the concentration of adsorbed chlorine ion $[\text{Cl}^-(\text{ads})]$ is given by the law of mass action using the chlorine partial pressure P_{Cl_2} and the electron concentration n , as

$$[\text{Cl}^-(\text{ads})] = K_1 P_{\text{Cl}_2}^{0.5} n \quad (2)$$

where K_1 is the equilibrium constant. The charge neutrality condition is

$$[\text{Cl}^-(\text{ads})] + n = n_0 \quad (3)$$

where n_0 is electron concentration in air. Since the electron concentration trapped by chlorine ions ($n_0 - n$) is equal to $[\text{Cl}^-(\text{ads})]$, the following equation is obtained assuming the electron mobility is constant,

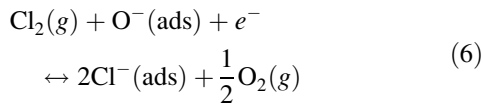
$$\begin{aligned} [\text{Cl}^-(\text{ads})] &= n_0 - n \\ &= k(\sigma(0) - \sigma(\text{Cl}_2)) \end{aligned} \quad (4)$$

where $\sigma(0)$, $\sigma(\text{Cl}_2)$ are conductivity in air and in Cl_2 , respectively, and k is constant. From Eqs. (2) and (4), the following equation is obtained

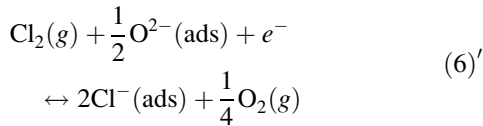
$$\frac{\sigma(0)}{\sigma(\text{Cl}_2)} = K_1 P_{\text{Cl}_2}^{0.5} + 1 \quad (5)$$

Accordingly, the slope in the logarithmic plot of Cl_2 gas sensitivity and P_{Cl_2} becomes 0.5 for 3 mol% CAZ.

On the other hand, for PZ, since the adsorbed oxygens in the high temperature forms are not stable at 300°C, the dissociative adsorption of chlorine accompanied by desorption of adsorbed oxygen is assumed and following reactions can be expected,



or,



When assuming Eq.(6), the law of mass action gives

$$[\text{Cl}^-(\text{ads})]^2 P_{\text{O}_2}^{0.5} = K_2 P_{\text{Cl}_2} [\text{O}^-(\text{ads})] n \quad (7)$$

where $[\text{O}^-(\text{ads})]$ is the concentration of adsorbed oxygen ion in Cl_2 atmosphere and K_2 is the equilibrium constant. The charge neutrality condition is

$$\begin{aligned} [\text{Cl}^-(\text{ads})] + [\text{O}^-(\text{ads})] + n \\ = [\text{O}^-(\text{ads})_0] + n_0 \end{aligned} \quad (8)$$

where $[\text{O}^-(\text{ads})_0]$ is the concentration of adsorbed oxygen in air. The concentration of electron trapped by chlorine ions ($n_0 - n$) and that of desorbed oxygen ion ($[\text{O}^-(\text{ads})_0] - [\text{O}^-(\text{ads})]$) are the same and they are the half of the adsorbed chlorine concentration. Accordingly, the next equation is given,

$$\begin{aligned} [\text{Cl}^-(\text{ads})] &= 2(n_0 - n) \\ &= 2([\text{O}^-(\text{ads})_0] - [\text{O}^-(\text{ads})]) \end{aligned} \quad (9)$$

When $\sigma(0) \gg \sigma(\text{Cl}_2)$ and then $\{1 - \sigma(\text{Cl}_2)/\sigma(0)\}^2 \sim \{1 - 2\sigma(\text{Cl}_2)/\sigma(0)\}$ can be assumed, Eq. (10) can be given from Eqs. (7) and (9), as

$$\frac{\sigma(0)}{\sigma(\text{Cl}_2)} = \frac{K_2 P_{\text{Cl}_2}}{4 P_{\text{O}_2}^{0.5}} \left\{ \frac{[\text{O}^-(\text{ads})_0]}{n_0} - 1 \right\} + 2 \quad (10)$$

In high P_{Cl_2} range where $\sigma(0) \gg \sigma(\text{Cl}_2)$ can be assumed, Eq. (10) gives

$$\frac{\sigma(0)}{\sigma(\text{Cl}_2)} \propto P_{\text{Cl}_2} \quad (11)$$

From Eq. (11), the slope in the logarithmic plot of Cl_2 gas sensitivity and P_{Cl_2} becomes 1. In case of Cl_2 adsorption by Eq. (6)', the same dependence could be obtained.

The sensitivity was also estimated using Eqs. (5) and (10) by assuming $K_1 = 1.80 \times 10^4 \text{ atm}^{-1}$ for CAZ, and $K_2 = 2.42 \times 10^6 \text{ atm}^{-0.5}$, $[\text{O}^-(\text{ads})_0] = 10^3 \text{ cm}^{-3}$ for PZ. The value of $6.25 \times 10^{11} \text{ cm}^{-3}$ was used for n_0 of PZ, which was calculated from the measured conductivity in air of $2.50 \times 10^4 \text{ S cm}^{-1}$, the elemental charge of $1.60 \times 10^{-19} \text{ C}$ and the electron mobility of $200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [15]. The estimated sensitivities for PZ and CAZ in air were shown as the solid lines in Fig. 9. The Cl_2 concentration dependence of sensitivity for PZ and CAZ, obtained from the above Cl_2 adsorption equations, are almost in accordance with those obtained experimentally as shown in Fig. 9. The enhancement of sensitivity in N_2 can be explained by the competitive adsorption of chlorine and oxygen at high P_{O_2} . This P_{O_2} dependence is indicated in Eq. (10) for PZ. The long recovery time after removing Cl_2 observed in PZ is assumed to be due to the chlorine desorption accompanied by the oxygen adsorption, as

indicated by Eq. (6) and (6)'. From the above results, we conclude that the change of chlorine gas sensing properties by CaO addition is attributed to increases in the amount and stability of adsorbed oxygen.

For the above estimation, the electron mobility was assumed to be independent of Cl₂ gas concentration. It is known that the mobility also changes by gas adsorption or reaction in fine-grain, porous semiconductor ceramics due to changes in the potential barrier at grain necks [14]. In the present specimens, this effect should more strongly contribute to the Cl₂ sensitivity in CAZ than in PZ, due to the smaller grain size in the CAZ. However, the measured Cl₂ concentration dependence of sensitivity was larger in PZ. Accordingly, a mobility change by Cl₂ gas seems to be small and not the dominant factor for the conductivity changes.

Introduction of reducing gases like CO and H₂ gave increases in conductivity for the CAZ, i.e., opposite to that in Cl₂ gas. The oxidizing gas NO₂ gave a decrease in conductivity, but its sensitivity was less than 12% of that for Cl₂ gas at the same concentration. Accordingly, the interference from other gases is negligible.

CAZ was found to have a high sensitivity for Cl₂ gas at concentrations below 3 ppm in air, required for practical Cl₂ gas sensors. Since the recovery time is not short, CAZ would be a better candidate as a Cl₂ gas sensor for detection of Cl₂ gas leakage rather than for continuous monitoring.

4. Conclusions

The following results were obtained from the present study,

1. The conductivity of PZ and CAZ ceramics were strongly decreased by Cl₂ gas in the temperature range of 25–380°C. As the measuring temperature decreased, the Cl₂ gas sensitivity increased but the recovery time following Cl₂ gas removal increased. The 90% recovery time of 3 mol%

CAZ was about 20 min at 300°C for 20 ppm Cl₂ in air.

2. The sensitivity of 3 mol% CAZ ceramics reached 10 even for 0.9 ppm Cl₂ in air at 300°C, suggesting its usefulness for sensing low-concentrations of Cl₂ gas.
3. The Cl₂ gas sensitivities of PZ and 3 mol% CAZ ceramics were independent of relative humidity in air at 300°C.
4. CaO additions decrease Cl₂ gas sensitivity but improve recovery times. It is assumed that the added-CaO stabilizes the adsorbed oxygens and restricts the oxygen desorption when Cl₂ molecules are adsorbed dissociatively on ZnO surfaces.

References

1. Y. Niizeki, S. Itabashi, Y. Onodera, and O. Takagi, *Denki Kagaku*, **54**, 948–953 (1986).
2. Y. Niizeki, O. Takagi, and S. Tushima, *Denki Kagaku*, **54**, 961–965 (1986).
3. H. Aono, E. Sugimoto, Y. Mori, and Y. Okajima, *Chem. Lett.*, 1039–1042 (1993).
4. H. Aono, E. Sugimoto, Y. Mori, and Y. Okajima, *J. Electrochem. Soc.*, **140**, 3199–203 (1993).
5. M. Miyayama, H. Yatabe, Y. Nakamura, and H. Yanagida, *J. Ceram. Soc. Jpn.*, **95**, 1145–1147 (1987).
6. R. Koyama, Y. Nakamura, M. Miyayama, and H. Yanagida, *Proc. Jpn. 1st International SAMPE Symp., Japan*, 375–380 (1989).
7. C. Nylander, *J. Phys. E: Sci. Instrum.*, **18**, 736–750 (1985).
8. A. Galdicas, Z. Martnas, and A. Šetkus, *Sensors and Actuators B*, **7**, 633–636 (1992).
9. P.E. Chandler, P.A. Taylor, and B.J. Hopkins, *Surf. Sci.*, **82**, 500–510 (1979).
10. L.A. Obvintseva, E.E. Gutman, Y.M. Bakshi, I.A. Myashikov, and A.I. Gel'bshtein, *Russ. J. Phys. Chem.*, **58**, 409–412 (1984).
11. P.A. Dowben, *CRC Crit. Rev. Solid State Mater. Sci.*, **13**, 191–210 (1987).
12. B.M. Arghropoulos and S. Teichner, *J. Catal.*, **3**, 477–487 (1964).
13. M. Takata and H. Yanagida, *J. Ceram. Soc. Jpn.*, **87**, 13–21 (1979).
14. H. Ogawa, M. Nishikawa, and A. Abe, *J. Appl. Phys.*, **53**, 4448–4455 (1982).