Moisture-Insensitive Low-Concentration Oxidizing-Gas Sensor

Taku Horiguchim,[1, a] Yoshiki Sasak,[2, b] and Katsutoshi Saeki[1-2, b]
[1] Graduate School of Science and Technology, Nihon University
7-24-1 Narashinodai, Funabashi, Chiba 274-8501, Japan
[2] Colleges of Science and Technology, Nihon University
7-24-1 Narashinodai, Funabashi, Chiba 274-8501, Japan
E-mail: [a]cstu15017@g.nihon-u.ac.jp, [b]sasaki.yoshiki@nihon-u.ac.jp, [c]saeki.katsutoshi@nihon-u.ac.jp

Abstract: Gas detection by a given sensor is generally species-specific. For example, it is difficult to distinguish between oxidizing-gases like NO_2 and SO_2 because both gas molecules capture electrons in the response film of the sensor. We here propose a novel moisture-insensitive sensor consisting of a comb-shaped electrode on a Si substrate. We also suggest a new measurement method, using complex impedances, for distinguishing between NO_2 and SO_2 at low-concentrations. It is shown that this low-concentration oxidizing-gas sensor, fabricated on a Si substrate, is moisture-insensitive for humidities of 60% to 80%. Furthermore, it is possible to distinguish between NO_2 and SO_2 on the basis of the changes in the pattern of complex impedance.

1. Introduction

Harmful oxidizing-gases containing nitrogen oxides and sulfur oxides, and found in automobile exhaust gas, are ubiquitous and can affect humans, even at concentrations below 1 ppm. NO_2 in particular is harmful to people suffering from respiratory diseases. For example, a concentration of about 0.1 ppm can produce asthma in patients, while a concentration of about 0.2 ppm can be detrimental in children and patients with chronic bronchitis [1]. As a measure toward the prevention of such problems, accurate measurements of gas concentrations are highly desirable. It has recently been reported that the organic compound copper phthalocyanine (CuPc) adsorbs NO_2 and SO_2 [2-4]. In particular, these gases reportedly cause a change in resistance when adsorbed [5-6] and their concentrations can be measured using a response film and a comb-shaped electrode on an alumina substrate [7-8]. However, gas-concentration measurements are difficult to perform under conditions of high humidity using such an alumina gas sensor [9] because moisture adheres to the substrate. Furthermore, gas sensors are typically specific to one particular gas and cannot easily distinguish between oxidizing-gases like NO_2 and SO_2. In this present study, we propose a novel moisture-insensitive sensor consisting of a comb-shaped electrode on a Si substrate. We further suggest a new measurement method exploiting complex impedance for distinguishing between NO_2 and SO_2 in low-concentrations.

2. Sensor & Measurement system

Our proposed low-concentration oxidizing-gas sensor is depicted in Fig. l. A Si substrate, made from p-type Si wafer of thickness of 525 μm has a SiO_2 surface layer of thickness 65 nm produced by dry oxidation. The comb-shaped gold electrode, formed by lift-off, was designed with a tooth width and spacing of 50 μm. The 30-tooth electrode was covered with a 200-nm-thick CuPc response film deposited using a vaporation system.

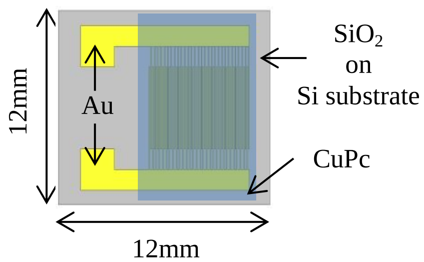


Fig.1 Proposed low-concentration oxidizing-gas sensor

Figure 2 outlines the measurement system for low-concentration oxidizing-gases. The sensor is placed in a thermostatic chamber held at 25°C but with variable humidity. The gas concentration is controlled by a *parmeater* using an air compressor. Air flow is first introduced for 5 minutes, then the oxidizing-gas enters with air flow from the *parmeater* for a further 10 minutes. Resistance was measured at a sampling interval of 10 seconds. The temperature of the thermostatic chamber was set to 50°C, and the sensor was allowed a recovery time in air flow of 30 minutes. Then, the temperature of the thermostatic chamber was set back to 25°C, and the composition of the flow gas was changed after a 30-minute air flow, to repeat the experiment.

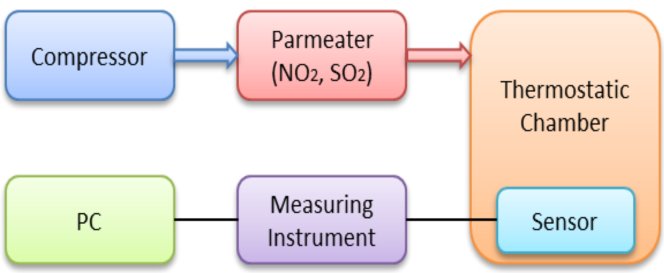


Fig.2 Measurement system

3. Moisture-insensitive characteristic

Figure 3 shows the humidity dependence of the sensor at different temperatures, measured using a high-resistance meter. There was no gas flow in this experiment. The vertical axis represents the output resistance, and the horizontal axis the humidity in the thermostatic chamber. The vertical axis is logarithmic because the sensor resistance changes significantly with temperature. Near room temperature (20°C to 30°C), the resistance changes by approximately 1 to 2 MΩ as the humidity varies from 40% to 80%. That is to say, the influence of the Si substrate is weaker than the variation of the calibration curve. This confirms that the Si substrate is moisture-insensitive.

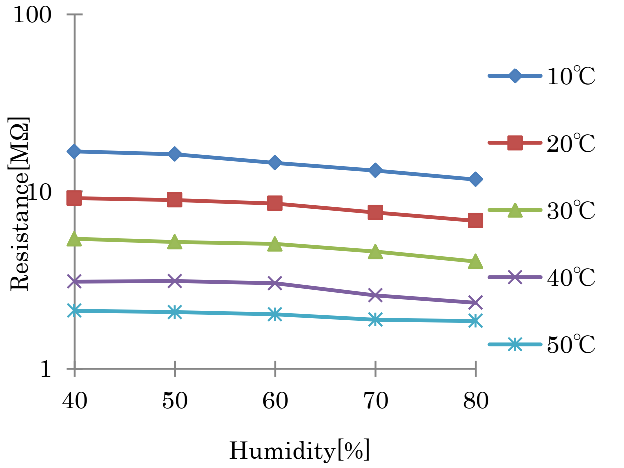


Fig.3 Humidity characteristics of the proposed sensor

Figure 4 plots the humidity dependence of the low-concentration oxidizing-gas sensor with the Si substrate. The NO_2 concentration is a variable parameter. The vertical axis represents the change in output resistance, and the horizontal axis the humidity in the thermostatic chamber. The measuring instrument was a DC resistance meter. For each NO_2 concentration, the change in DC resistance decreases by approximately 1.2 MΩ for a 10% increased in humidity. The effect of moisture on the substrate with the hydrophobic SiO_2 is small [9], indicating the possibility to measure an NO_2 concentration even when the humidity is increased. Furthermore, this figure shows that the change in DC resistance decreases because there is less attachment of NO_2 molecules to the response film, as NO_2 becomes dissolved in water vaper.

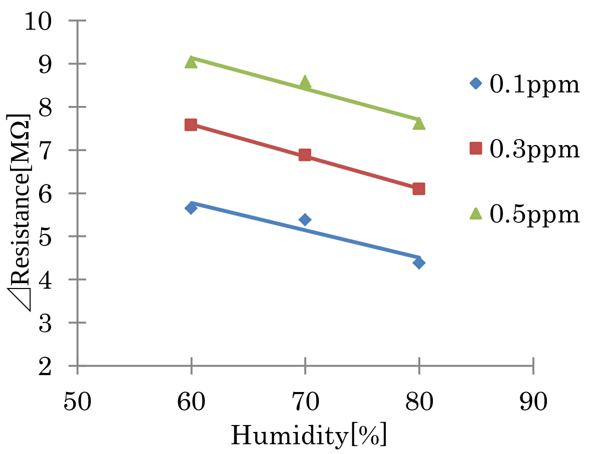


Fig.4 Humidity characteristics of the low-concentration oxidizing-gas sensor

4. Measurement using complex impedance

Figure 5 shows a Nyquist diagram measured using an LCR meter, when either pure air or NO_2 was injected. The vertical axis represents reactance, and the horizontal axis resistance. The red and blue symbols denote air and 0.5 ppm NO_2, respectively. The difference between the two Nyquist plots shows that NO_2 can be measured using complex impedance.

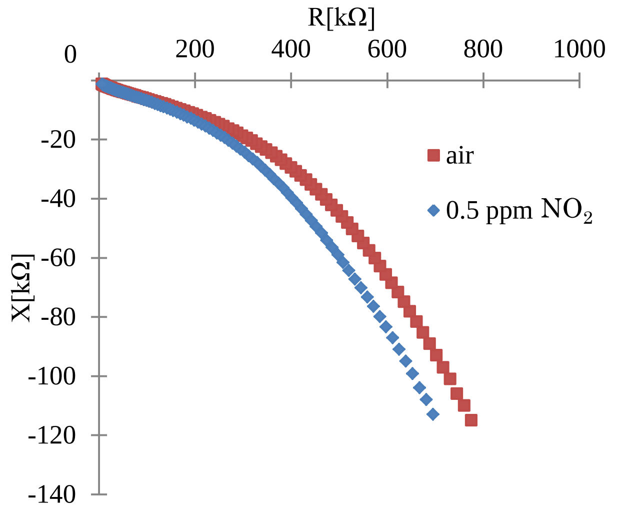


Fig.5 Nyquist diagram for injected air or 0.5 ppm NO_2

Figure 6 shows the difference in the complex impedance between pure air and NO_2, measured as a function of frequency and based on the type of plots shown in Fig. 5. The right and left vertical axes represent the changes in reactance ⊿X and resistance ⊿R, respectively. The horizontal axis represents frequency. When the frequency is increase, ⊿X increases and ⊿R decreases. At high frequencies, both ⊿X and ⊿R approach zero. Stable measurements are therefore feasible at the logarithmically intermediate frequency 2.5 kHz. This is therefore the appropriate frequency for concentration measurements.

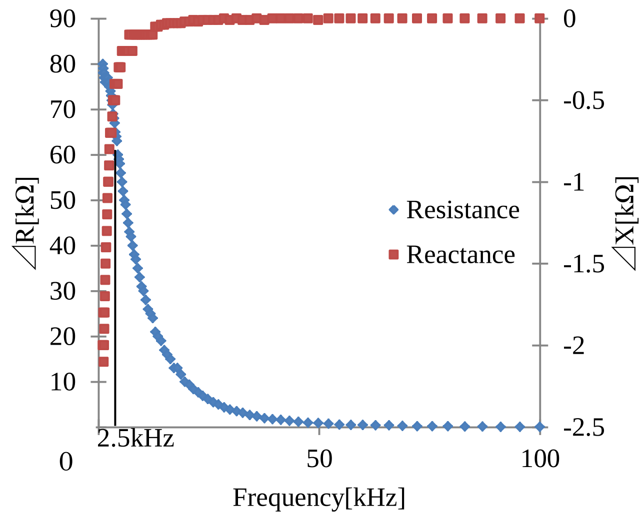
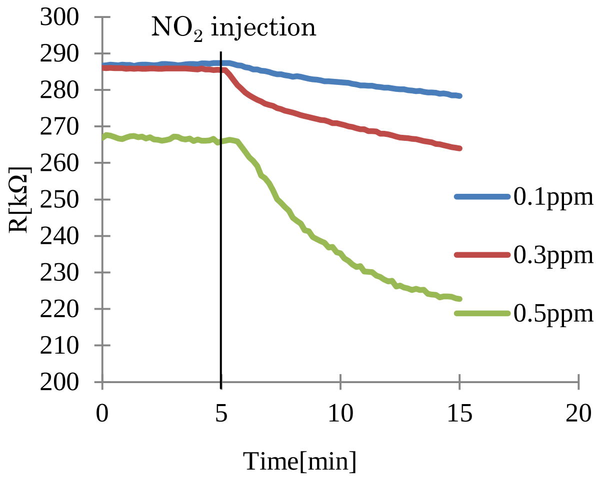
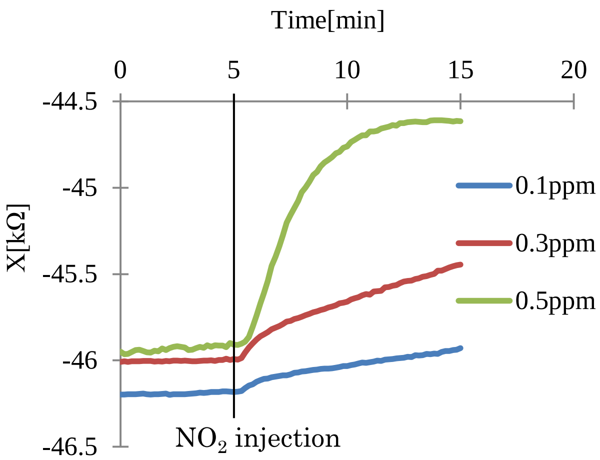


Fig.6 Difference in complex impedance for injected air or NO_2

Figure 7 shows the time responses of the NO_2 measurement. The horizontal axis represents time and the vertical axes in (a) and (b) represent, respectively, the change in resistance R or reactance X. After injecting NO_2, the changes in resistance and reactance vary depending on the NO_2 concentration. As the resistance decreases, the reactance increases. This observed therefore shows it is possible to detect an NO_2 concentration using complex impedance.



(a) Resistance



(b) Reactance

Fig.7 Time responses of NO_2 measurements

Figure 8 shows calibration curve with the standard deviations corresponding to each NO_2 concentration. The vertical axis represents the change in reactance ⊿X and the horizontal axis the change in resistance ⊿R for gas containing NO_2. Standard deviations were calculated from 9 measurements for each gas composition. This figure suggests that the proposed measurement method, based on complex impedance, can measure low-concentrations of NO_2 with a precision of 0.2 ppm.

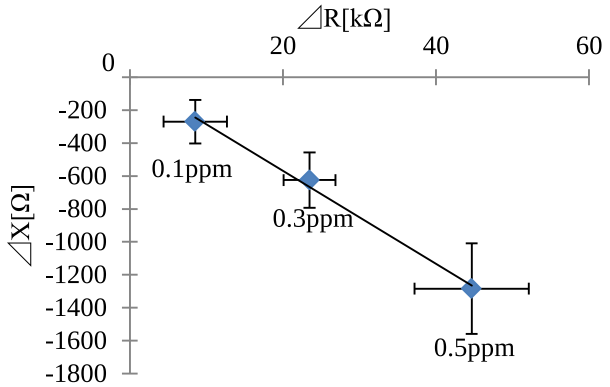
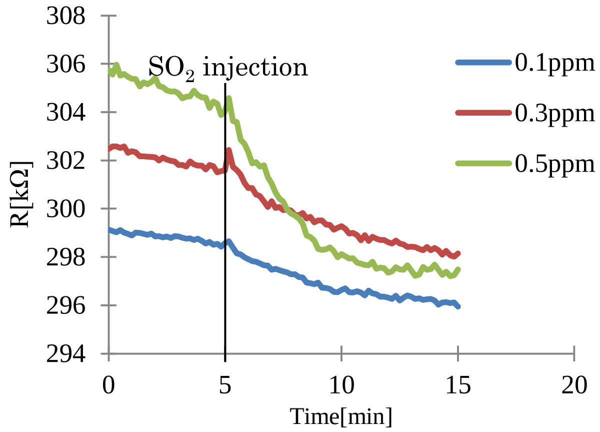
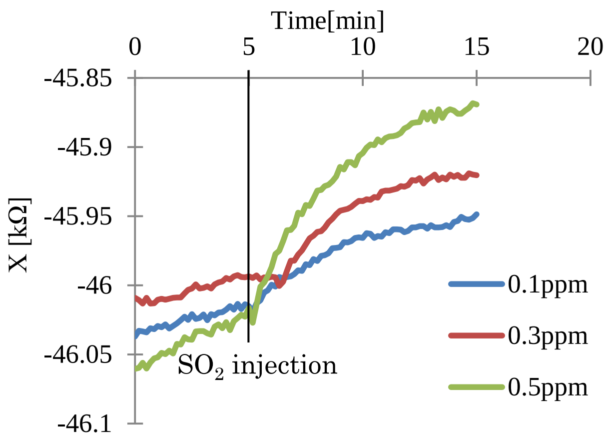


Fig.8 Calibration curve with standard deviations for each NO_2 concentration

Figure 9 plots the corresponding time responses for SO_2 measurements. The horizontal axis represents time and the vertical axes of (a) and (b) the changes in resistance R and reactance X respectively. After injecting SO_2, the changes in resistance and reactance also vary depending on the SO_2 concentration. As the resistance decreases, the reactance increases, confirming that it is possible to measure SO_2 concentrations using complex impedances. However, the extent of change in complex impedance is less than with NO_2.



(a) Resistance



(b) Reactance

Fig.9 Time responses of SO_2 measurements

Figure 10 plots the calibration curve with standard deviations for each SO_2 concentration. The vertical and horizontal axes represent, respectively, the changes in reactance ⊿X and resistance ⊿R for the SO_2 measurements. The standard deviations were again calculated using 9 measurements for each gas composition. This figure confirms the ability of the proposed method to measure low SO_2 concentrations with precision of 0.2 ppm, using complex impedance.

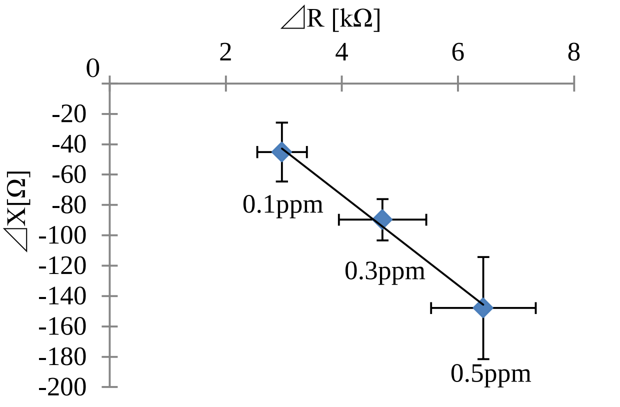


Fig.10 Calibration curve with standard deviations for each SO_2 concentration

Figure 11 summarizes the extents of change in complex impedance for the different concentrations of NO_2 or SO_2. The black and blue axes represent the changes in reactance and resistance, respectively, while the red axis represents the gas concentrations. This figure highlights the possibility to distinguish between the two gaseous species on the basis of the patterns in the complex impedance measurements.

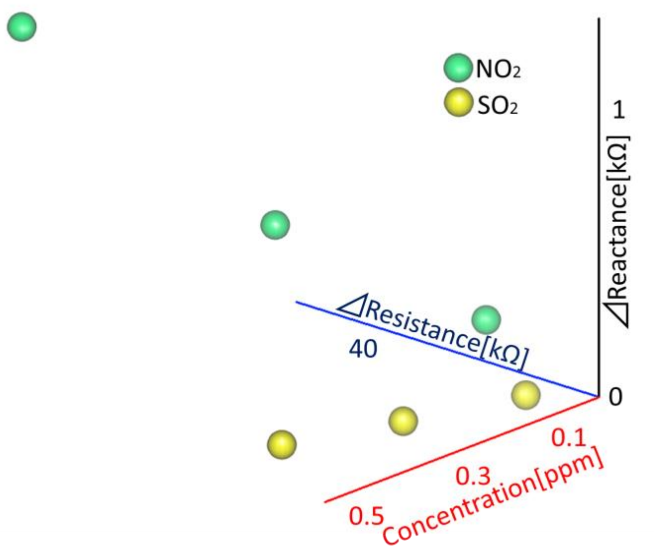


Fig.11 The changes in the complex impedance for different NO_2 and SO_2 concentration

5. Conclusion

We proposed a novel moisture-insensitive sensor consisting of a comb-shaped electrode on a Si substrate. We also suggested a new measurement method, based on complex impedances, for distinguishing between low-concentrations of NO_2 and SO_2.

It is thus shown that this low-concentration oxidizing-gas sensor on a Si substrate is moisture-insensitive for humidities ranging from 60% to 80%. Furthermore, it is possible to distinguish between NO_2 and SO_2 on the basis of the patterns in the changes in complex impedances.

Future work will consider the implementation of a signal-processing unit including an amplifier on the same Si substrate.

References

[1] J Orehek, J P Massari, P Gayrard, C Grimaud, J Charpin, “Effect of short-term, low-level nitrogen dioxide exposure on bronchial sensitivity of asthmatic patient”, The Journal of Clinical Investigation, Vol.57, No.2, 301–307, 1976.

[2] M. von Schickfus, R. Stanzel, T. Kammereck, D. Weiskat, W. Dittrich, “Improving the SAW gas sensor: device, electronics and sensor layer”, Sensors and Actuntors B, Vol.19, 443-447, 1994.

[3] Katsutoshi Sugiyama, Katsutoshi Saeki, Minoru Saito, Yoshifumi Sekine, “A Study on Gas Sensors Using a SAW Device”, Circuits and Systems, 459-462, 2014.

[4] Youwang Hu, Jiwen Xiang, Xiaoyan Sun, Chengzhi Xu, Shu Wang, and Ji’an Duan, “Sensitivity Improvement of SAW NO_2 Sensors by p-n Heterojunction Nanocomposite Based on MWNTs Skeleton”, IEEE Sensors Journal, Vol.16, No.2, 287-292, 2016.

[5] Chul Park, Dong Hyun Yun, Sung-Tae Kim, Yung Woo Park, “Enhancement of the NO_2-sensing capability of copper phthalocyanine bymeasuring the relative resistance change”, Sensors and Actuators, Vol.30, 23-27, 1996.

[6] N. Padmaa, Aditee Joshi, Ajay Singh, S.K. Deshpande, D.K. Aswal, S.K. Gupta, J.V. Yakhmi, “NO_2 sensors with room temperature operation and long term stability using copper phthalocyanine thin films”, Sensors and Actuators, Vol.143, 246–252, 2009.

[7] Shuizhu Wu, Fang Zeng, Fengxian Li, Yinlan Zhu , “Ammonia sensitivity of polyaniline films via emulsion polymerization” European Polymer Journal, Vol.36, 679-683, 2000.

[8] N.S.Baik, G.Sakai, N.Miura, N.Yamazoe, “Hydrothermally treated sol solution of tin oxide for thin-film gas sensor” Sensors and Actuators, Vol.63, 74–79, 2000.

[9] Masato Takeuchi, Gianmario Martra, Salvatore Coluccia, Masakazu Anpo”, Evaluation of Hydrophilic/Hydrophobic Properties and Wettability of Oxide Surfaces”, Journal of The Surface Science Society of Japan, Vol.30, No.3, 148-156, 2009.