Thick-film ammonia gas sensor with high sensitivity and excellent selectivity

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Abstract—A highly sensitive ammonia gas sensor using thick-film technology has been fabricated and examined. The sensing material of the gas sensor is FeOx-WO_3-SnO_2 oxide semiconductor. The sensor exhibits resistance increase upon exposure to low concentration of ammonia gas. The resistance of the sensor is decreased, on the other hand, for exposure to reducing gases such as ethyl alcohol, methane, propane and carbon monoxide. A novel method for detecting ammonia gas quite selectively utilizing a sensor array consisting of an ammonia gas sensor and a compensation element has been proposed and developed. The compensation element is a Pt-doped WO_3-SnO_2 gas sensor which shows opposite direction of resistance change in comparison with the ammonia gas sensor upon exposure to ammonia gas. Excellent selectivity has been achieved using the sensor array having two sensing elements.

Index Terms—Ammonia gas sensor, Oxide semiconductor, Sensor array, Selectivity

I. INTRODUCTION

Air pollution from various offensive odors has been a serious problem in modern life. Ammonia gas is one of the offensive odors to be eliminated from our working and living environments, and the detection of ammonia gas has become extremely important for the environmental protection. For that reason it is very useful to develop ammonia gas sensors of low cost, high sensitivity and good selectivity.

Several oxide semiconductor ammonia gas sensors have been proposed and developed. Maekawa et al. [1, 2] showed the Au-loaded WO_3 sensor had high sensitivity at low concentration of ammonia gas in air. Takao et al. [3] investigated the sensing properties of the In_2O_3-doped MgO ammonia sensor and examined some double layer sensors with a catalyst on the sensing layer. The resistance of all these n-type oxide semiconductor gas sensors is decreased by exposure to ammonia gas.

However, Nanto et al. [4] reported the Al-doped ZnO thin film ammonia gas sensor displayed resistance increase upon exposure to ammonia gas, whereas it exhibited resistance decrease to reducing gases.

Since reducing gas like H_2 and oxidizing gas like NO_X can be produced by the decomposition or oxidation reaction of ammonia gas [3-6], resistance change of oxide semiconductor sensors may be interfered. It is very difficult, therefore, to make ammonia gas sensors with high sensitivity and good selectivity operating in living environments.

In this paper, we report on an FeOx-WO_3-SnO_2 oxide semiconductor thick-film gas sensor which shows resistance increase upon exposure to low concentration of ammonia gas, and on a novel method for detecting ammonia gas quite selectively utilizing a sensor array consisting of an ammonia gas sensor and a compensation element.

II. EXPERIMENTAL

The ammonia gas sensor has been prepared using thick-film technology [7,8]. Fig. 1 presents the schematic view of our ammonia gas sensor and sensor package. The sensing element consists of a sensing layer, a heater and a pair of electrodes formed on an alumina substrate. The processing steps are:

(i) mixing powders of WO_3 and SnO_2;
(ii) paste preparation: thoroughly mixing sensing materials with organic vehicle by three-roll mill;
(iii) formation of a heater and a pair of electrodes with platinum paste (fired at 1100°C for 1 h);
(iv) formation of a 5 μm thick sensing layer (fired at 800°C for 30 min);
(v) coating of an $FeCl_3$ aqueous solution (0.05 M) on a sensing layer (fired at 600°C for 30 min);
(vi) wire bonding and packaging.

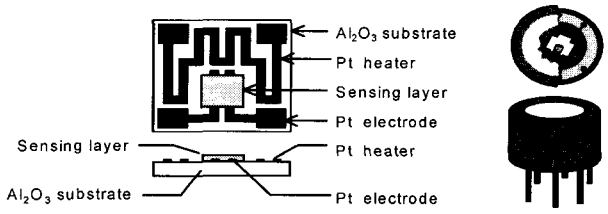

Fig. 1 Schematic view of the ammonia gas sensor and sensor package.

As shown in Fig. 2, the measurement of the gas sensing properties was carried out in a system fully controlled by a personal computer. Under the applied circuit voltage of 5 V, the resistance of the sensor was calculated from the voltage across a load resistor connected in series with the sensor. The sensitivity was defined as R_g/R_a, where R_a and R_g are the resistance of the sensor in air and upon exposure to ammonia gas, respectively. The temperature of the

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sensor was controlled using a platinum heater of the sensor and calibrated by an infrared thermometer (Horiba IT340).

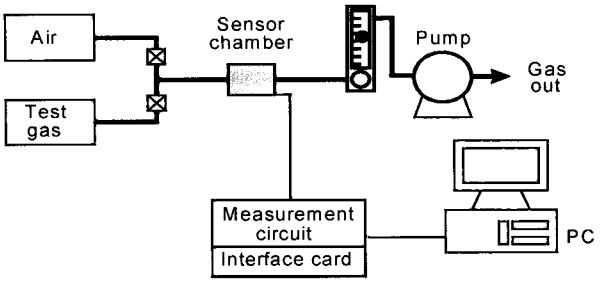

Fig. 2 Schematic view of the measurement system.

III. RESULT AND DISCUSSION

The sensing material of the sensor is iron oxide dispersed WO_3 (5 wt.%)-SnO_2 oxide semiconductor. It was confirmed with an X-ray diffraction analysis that iron oxides such as Fe_2O_3 and Fe_3O_4 were formed on the sensing layer by the thermal oxidation of Fe^{+3} ion.

Fig. 3 illustrates the transient resistance change of the sensor to 10 ppm of ammonia gas at an operating temperature of 330°C. The best result in sensitivity has been obtained at 330°C among the various operating temperatures tested ranging from 200 to 400°C. The sensor shows resistance increase to low concentration of ammonia gas. In general, the resistance of tin oxide-based n-type oxide semiconductor decreases by exposure to reducing gases, while the resistance increases to oxidizing gases. Since reducing gas like H_2 and oxidizing gas like NO_X can be produced by the decomposition or oxidation reaction of ammonia gas [3-6], the resistance change of the oxide semiconductor gas sensor by ammonia gas can probably be interfered. At the present stage, the exact sensing mechanism of the ammonia gas sensor is not yet clear. It seems, however, the phenomenon of the resistance increase is induced by oxidizing species like NO_X. The additive materials such as iron oxide and tungsten oxide would act as a catalyst and accelerate the formation of oxidizing species.

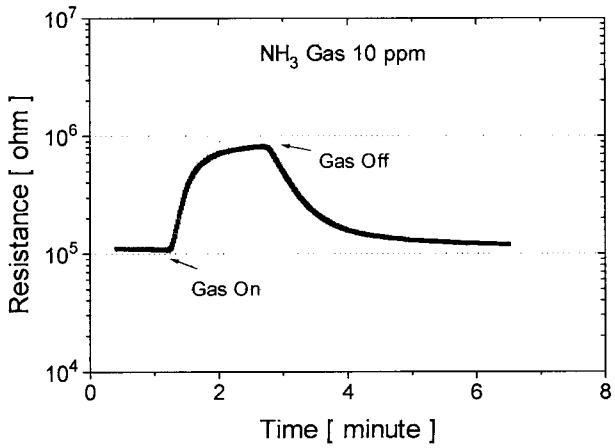

Fig. 3 Transient resistance change of the sensor upon exposure to 10 ppm ammonia gas at the operating temperature of 330°C.

Fig. 4 indicates the sensitivity versus ammonia gas concentration at the operating temperature of 330°C. In low gas concentration region ranging from 5 to 50 ppm,

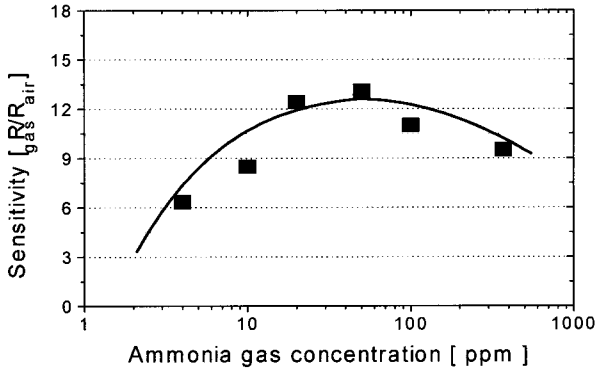

Fig. 4 Sensitivity vs. ammonia gas concentration at the operating temperature of 330°C.

the sensitivity increases with increasing gas concentration. In high region ranging from 50 to 500 ppm, however, the sensitivity is decreased. It seems from the result of Fig. 5 that reducing species and oxidizing species can be produced simultaneously by the decomposition or oxidation reaction of ammonia gas on the sensing layer. In the high region, the concentration of reducing gas like H_2 produced by the decomposition of ammonia gas would be increased and it would in turn interfere the resistance change of the sensing layer. This result of the sensitivity versus ammonia gas concentration is similar to that of the Al-doped ZnO thin film ammonia sensor [4].

Since the tolerance level of ammonia gas for human is about 25 ppm [4], it is necessary that the sensor respond to concentrations below this threshold. It can be seen from Fig. 3 that the sensitivity is high enough to use practically for the detection of ammonia gas.

Fig. 5 shows the resistance change of the sensor to various interfering gases. The sensor was exposed to ethyl alcohol, methane, propane, carbon monoxide and nitrogen dioxide. As mentioned earlier, the resistance of the n-type oxide semiconductor is generally decreased by reducing gases. As seen in Fig. 5, the sensor displays resistance decrease upon exposure to high concentrations of the interfering reducing gases, whereas it indicates resistance increase to ammonia and nitrogen dioxide gases. It shows good selectivity to the interfering reducing gases accordingly.

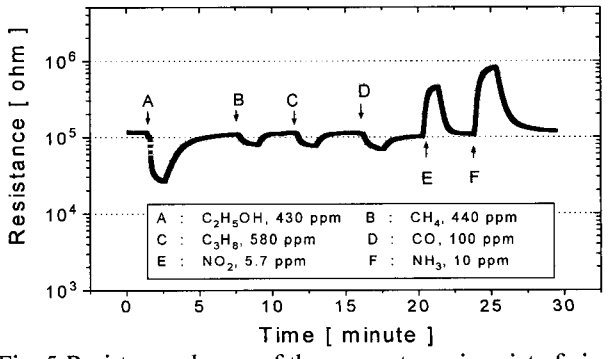

Fig. 5 Resistance change of the sensor to various interfering gases at 330°C.

In order to achieve excellent selectivity to numerous interfering gases, a novel method utilizing a sensor array consisting of the above-mentioned ammonia gas sensor and a compensation element has been developed. The measurement circuit and the structure of the sensor array are presented in Fig. 6. The compensation element is a sensor for reducing gases. The sensing material of the compensation element is Pt-doped WO_3 (5 wt.%)-SnO_2 oxide semiconductor. The processing steps are exactly same as the FeOx-WO_3-SnO_2 ammonia gas sensor except Pt coating. A $H_2PtCl_6(6H_2O)$ aqueous solution was used to form Pt layer. Details on the fabrication and characterization of the sensor will be reported elsewhere. The compensation element is connected in series with the ammonia gas sensor in the sensor array equipped with a heater. The resistance of the compensation element is decreased by reducing gases and slightly decreased by ammonia gas as well. As seen in Fig. 6, the resistance ratio ($X = R_S/R_C$) can be calculated by measuring the output voltage V_{out}, where R_S and R_C are the resistance of the ammonia gas sensor and the compensation element, respectively.

Fig. 7 illustrates the resistance ratio X of the sensor array for various test gases under the circuit voltage of 5 V and operating temperature of 330°C. The ammonia gas sensor and the compensation element present same way of resistance change upon exposure to many reducing gases (cigarette smoke, C_2H_5OH, C_3H_8 and CO). Upon exposure to 50 ppm of NH_3, on the other hand, the ammonia sensor and the compensation element show opposite direction of resistance change. Consequently, the value of X for 50 ppm of NH_3 is much higher than that of the rest of the test gases. In the case of NO_2, the value of X is also quite low because the ammonia sensor and the compensation element indicate same way of resistance change (not shown in Fig. 7). As shown in Fig. 7, excellent selectivity has been achieved using the sensor array having two sensing elements.

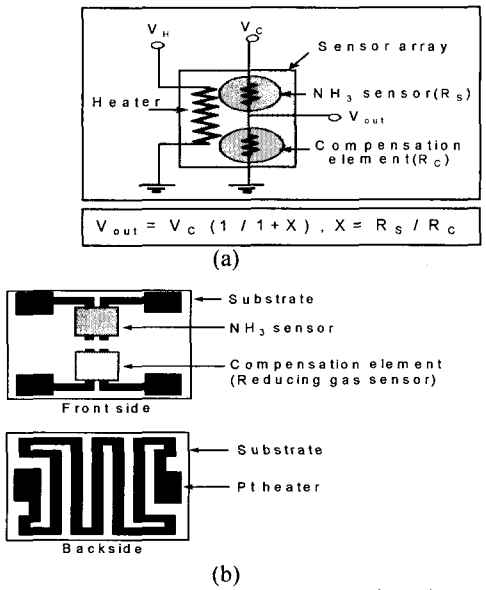

Fig. 6 (a) Measurement circuit (V_C: circuit voltage, V_H: heater voltage, R_S: resistance of the ammonia gas sensor, R_C: resistance of the compensation element). (b) Structure of the sensor array.

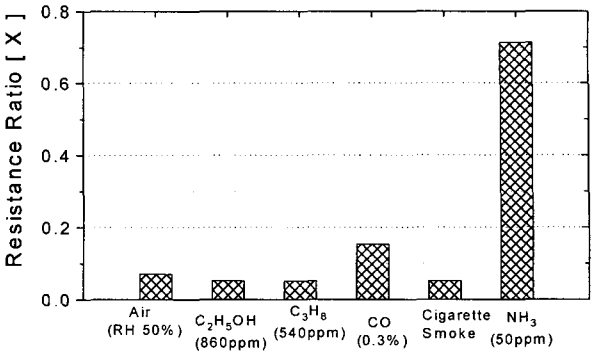

Fig. 7 Resistance ratio (X) of the sensor array under the circuit voltage of 5 V and operating temperature of 330°C.

IV. CONCLUSION

A highly sensitive thick-film ammonia gas sensor has been prepared and examined. The sensing material of the sensor is FeOx-WO_3-SnO_2 oxide semiconductor. The sensor shows resistance increase upon exposure to low concentration of ammonia gas. This is probably induced by oxidizing species like NO_X produced from the oxidation reaction of ammonia gas on the oxide semiconductor surface. The resistance of the sensor is decreased, on the other hand, for exposure to reducing gases such as ethyl alcohol, methane, propane and carbon monoxide. In order to improve the selectivity of the ammonia gas sensor, a novel method utilizing a sensor array consisting of an ammonia gas sensor and a compensation element has been proposed and developed. The compensation element is a Pt-doped WO_3- SnO_2 gas sensor which shows opposite direction of resistance change in comparison with the ammonia gas sensor upon exposure to ammonia gas. Excellent selectivity has been achieved using the novel method.

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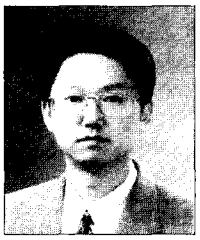

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