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Semiconductor Sensors for Detecting TMA Gas

Sung Hyun Park, Hyek Hwan Choi and Tae Ha Kwon

Department of Electronics Engineering, Pukyong National University,
Pusan, 608-737, Korea

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ZnO thin films doped with Al_2O_3, TiO_2 and V_2O_5 with a thickness of about 100 nm were deposited on heated (250°C) SiO_2/Si substrates by RF magnetron sputtering. Sputtering deposition was carried out at a pressure of 10 mTorr in oxygen gas at a power of about 80 W. A ZnO thin film sensor with 4.0 wt% Al_2O_3, 1.0 wt% TiO_2 and 0.2 wt% V_2O_5 showed high sensitivity to 10 ppm trimethylamine at a working temperature of 250°C and to higher concentrations (160 ppm) at a working temperature of 300°C.

1. Introduction

A variety of gas sensors have been developed using metal oxide semiconductors such as SnO_2, ZnO and Fe_2O_3. The electrical conductivity of the sensors changes with exposure to various gases. The freshness evaluation of seafood has become an important issue from the viewpoint of quality control in the food industry. It is necessary to develop a nondestructive method for evaluating the freshness of seafood. It is known that ZnO thin film gas sensors have a high sensitivity to trimethylamine (TMA) gas which is emitted during the deterioration of seafood.[1–7] We have reported a gas sensor which is based on the electrical resistance change of sputtered ZnO thin films, which exhibits a high sensitivity and excellent selectivity for TMA gas.[8] Thus the sensor can be used to evaluate the freshness of seafoods. It was found that the sensitivity of the sensor to TMA, as well as to the odor from seafoods, is improved by doping impurity into the ZnO thin film. The detection of TMA gas is based on the electrical resistance change of the film.

Nanto *et al.*[7] deposited ZnO thin films containing various amounts of Al_2O_3 (0–5 wt%) on a glass substrate by magnetron sputtering. They achieved a sensitivity of 55 to 300 ppm TMA gas at a working temperature of 350°C. Egashira *et al.*[5] reported that a TiO_2 sensor

with 0.5 wt% Ru has a sensitivity of 450 to 300 ppm TMA gas at a working temperature of 550°C. Park and Kwon[8] showed that a ZnO thin film with 4.0 wt% Al_2O_3 and 1.0 wt% TiO_2 on a glass substrate has high sensitivity at a working temperature of 300°C.

In this study, ZnO thin film sensors were prepared by RF magnetron sputtering. These sensors were investigated with respect to the dependence of their sensitivity on the weight percent of ZnO, Al_2O_3, TiO_2 and V_2O_5 powder constituents and the working temperature of thin films. It is known that V_2O_5 has an excellent stabilizing effect and acts as a catalyst.[9] The sensitivity of the sensors to various gases was investigated at a working temperature of 250°C. The ZnO thin film doped with Al_2O_3, TiO_2 and V_2O_5 showed high sensitivity and selectivity for TMA gas.

2. Experiment

Three different targets were prepared using ZnO, Al_2O_3, TiO_2 and V_2O_5 powders with a purity of 99.99%. One target contained 4.0 wt% Al_2O_3 and 1.0 wt% TiO_2 (sensor A). The others contained 4.0 wt% Al_2O_3, 1.0 wt% TiO_2 and 0.2 wt% V_2O_5 (sensor B) and 4.0 wt% Al_2O_3, 1.0 wt% TiO_2 and 0.5 wt% V_2O_5 (sensor C). Disk-shaped targets were sintered for 10 h at 1000°C. The base material of the substrate was a p-type (100) silicon wafer with a thickness of 570 μm. Silicon dioxide was grown to a thickness of 3 μm on the substrate. Sputtering deposition was carried out at an RF power of 80 W at an oxygen gas pressure of 10 mTorr. ZnO films were prepared on substrates which were placed parallel to the target surface. The sputtering period was 10 min. The ZnO sensor films had the same compositions as those of the corresponding targets. Comblike Al/Au electrodes were deposited onto the ZnO thin films by thermal evaporation. Table 1 shows the sputtering conditions for the ZnO thin films.

The sensing characteristics of ZnO thin films were investigated by measuring their resistance as a function of gas concentration. The sensitivity K was defined as Ra/Rg, where Ra is the electrical resistance of the sensor in air and Rg is the resistance upon exposure to a gas.

Table 1
Sputtering conditions for the deposition of ZnO thin films.

RF Power	80W
Substrate	p-type Silicon
Substrate Temperature	250°C
Base Vacuum	1×10^{-6} Torr
Gas Pressure	10 mTorr (O_2)
Cooling	Air cooling

3. Results and Discussion

The sensitivity of a gas sensor is its most important feature and is defined as $K = Ra/Rg$. Figure 1 shows the sensing characteristics for three target materials as a function of TMA concentration at a working temperature of 300°C. Sensor B shows a higher sensitivity than sensor A and sensor C. Sensor B has a sensitivity of 355 to 60 ppm TMA gas. The sensing characteristic of sensor B is linear up to 40 ppm TMA gas. Figure 2 shows the sensitivities of the sensors to 160 ppm TMA gas for working temperatures in the range between 200°C and 400°C. The sensors exhibit the highest sensitivity at a working temperature of 300°C. The sensitivity decreases at higher temperatures. If the temprature is too low, the reaction to TMA gas is too slow to give a high sensitivity, whereas if the temperature is too high, the overall oxidation reaction proceeds so rapidly that the concentration of TMA gas at the surface becomes diffusion-limited and TMA gas concentration seen by the sensor approaches zero.[10] Figure 3 shows the sensing characteristics of sensor B for various gas concentrations (2 – 40 ppm) in the temperature range between 200°C and 400°C. The sensitivity decreases above 250°C. Figure 4 shows the TMA gas concentration dependence of the sensitivity of ZnO sensors at a working temperature of 250°C. The sensitivity increases rapidly to the concentration of 40 ppm and is saturated above 50 ppm at 250°C. Sensor B has particularly high sensitivity which is approximately linear up to 40 ppm, beyond which it rapidly saturates. Figure 5 shows the sensitivities of the sensors to 10 ppm

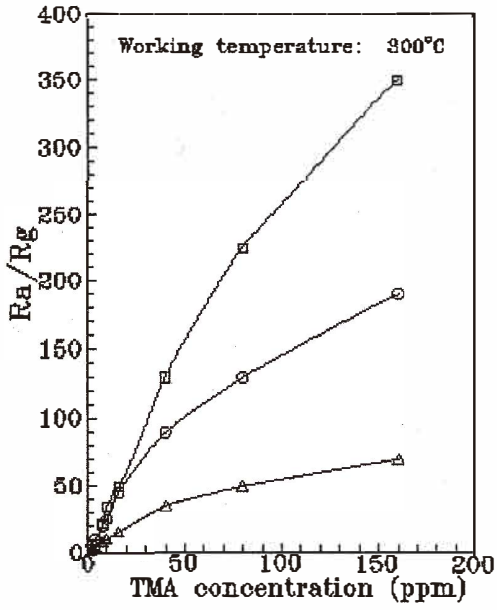

Fig. 1. TMA gas concentration dependece of the sensitivity of ZnO sensors at a working temperature of 300 °C (○: Sensor A, □: Sensor B, △: Sensor C).

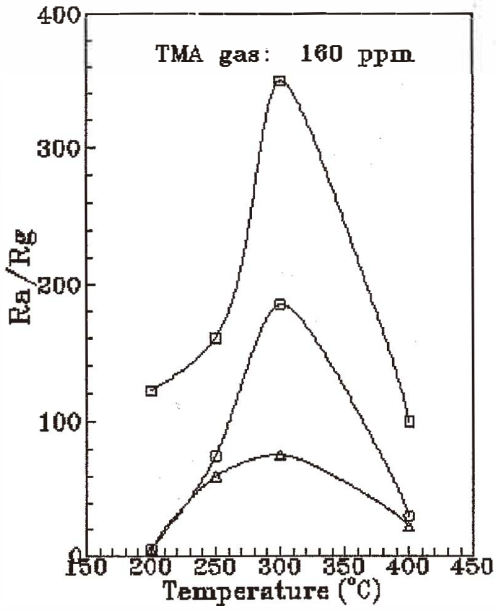

Fig. 2. The sensitivities of the sensors to 160 ppm TMA at working temperatures between 200 °C and 400°C (○: Sensor A, □: Sensor B, △: Sensor C).

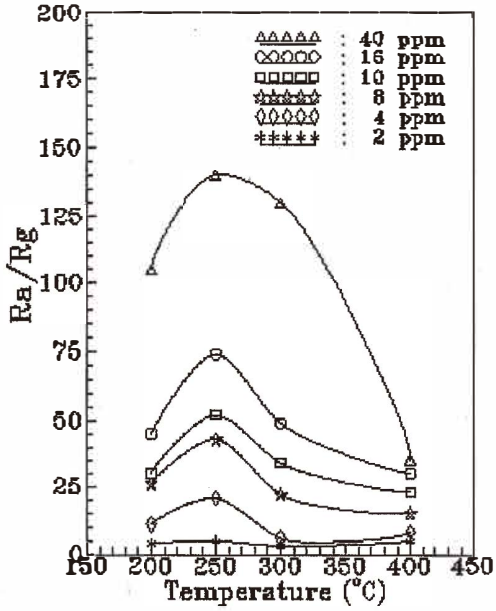

Fig. 3. The sensitivity of sensor B to various concentrations of gas at working tempratures between 200°C and 400°C.

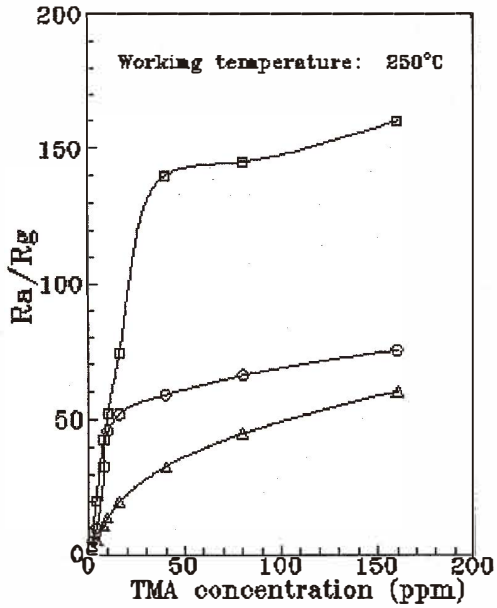

Fig. 4. TMA gas concentration dependence of the sensitivity of ZnO sensors at a working temperature of 250°C (○: Sensor A, □: Sensor B, △: Sensor C).

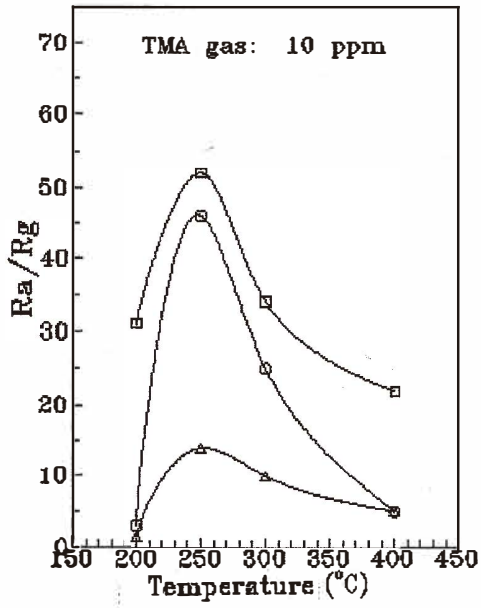

Fig. 5. The sensitivities of the sensors to 10 ppm TMA at working temperatures between 200°C and 400°C (○: Sensor A, □: Sensor B, △: Sensor C).

TMA gas in the working temperature range between 200°C and 400°C. The sensitivity of sensor B was 54 at a working temperature of 250°C but decreased at higher temperatures. In order to check the selectivity of sensor B. It was exposed to acetone, acetylene and ammonia gas at a working temperature of 250°C. The selectivities are shown in Fig. 6. The sensitivities of sensor B to acetone, acetylene and ammonia were 5, 8 and 15 at 160 ppm. Sensor B exhibits a high selectivity for TMA gas.

The results above suggest that sensor B operated at 250°C has excellent selectivity and high sensitivity to TMA gas of the added dopants, vanadium is shown to have an excellent stabilizing effect and V_2O_5 acts as a catalyst (sensitizer).[9] Although the use of 0.2 wt% V_2O_5 plays an important role in sensitivity improvement, the reason is unknown and is not theoretically systematized. We are now studying the effect adding very small weight percentages of V_2O_5. The more V_2O_5 is added in the target, the lower the sensitivity. We assume that the more V_2O_5 is added, the higher the barrier due to the stabilization effect becomes and therefore, fewer electrons can make the transition to conduction band, resulting in higher resistance of ZnO thin films.

The reproducibility of thin film sensors prepared under the same sputtering conditions was investigated and the variations of initial resistance (Ra) of thin film sensors were less than one order of magnitude.

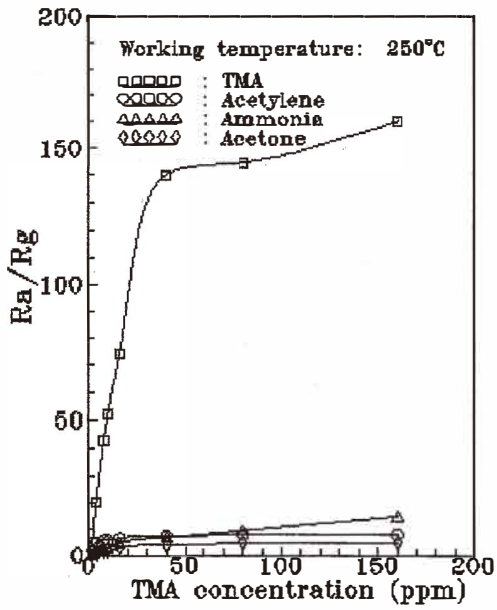

Fig. 6. The sensitivity of sensor B to various gases.

4. Conclusion

The sensing characteristics of ZnO sensors with various dopants were studied for various gases and operating temperatures. It was confirmed that a small amount of V_2O_5 (0.2 wt%) acted as an excellent sensitizer to TMA gas. A ZnO thin film sensor with 0.2 wt% V_2O_5 showed high sensitivity to 10 ppm TMA gas at a working temperature of 250°C, and to higher concentrations (160 ppm) at a working temperature of 300°C. It was shown that a sensor with 0.2 wt% V_2O_5 operating at 250°C could detect TMA gas with high sensitivity and good selectivity. We conclude that a ZnO thin film sensor with 4.0 wt% Al_2O_3, 1.0 wt% TiO_2 and 0.2 wt% V_2O_5, which gives measurements in terms of electrical resistance change, will be useful as a commercial TMA gas sensor

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