High Sensitive Formaldehyde Gas Sensor Prepared by R.F. Induction Plasma Deposition Method

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The present work is concerned on developing high sensitive and high performance SnO_2 -based gas sensors for detecting indoor air pollutant formaldehyde gas. The film was deposited on an alumina substrate using R.F. Induction Plasma Deposition technique. Physical properties of sensing films were examined by SEM, XRD method. The sensors showed high sensitivity to typical HCHO gas at an extremely low gas concentration of 20 parts-per-billion (ppb) with quick response and recovery time at several minutes. The effect of the doping of various metallic additives on the gas-sensing properties and operating temperature dependency were also investigated in the work.

Keywords: high sensitive, SnO_2 , formaldehyde, Induction Plasma Deposition, metallic additives

1. Introduction

There has been an increasing attention on Sick Building Syndrome (SBS), which is a health issue of the occupants in building, especially in newly built houses and offices ⁽¹⁾. While the specific origin of the SBS remains unknown, it is believed to be caused by the chemical contaminants emitted from various indoor sources such as construction materials, furniture and biological contaminants ⁽¹⁾⁽²⁾. Formaldehyde (HCHO) is one of the typical chemicals strongly associated with the SBS. Long-term exposure to low levels of HCHO may cause respiratory difficulty, eczema and sensitization. Therefore, indoor HCHO level has been restricted at less than 80 parts-per-billion (ppb) averaged over 30 minutes in air by WHO ⁽²⁾⁽³⁾. The establishment of environmental standard of 80 ppb HCHO has stimulated the research activities of the development of HCHO detectable methods, and various sensors have been reported ⁽⁴⁾⁻⁽⁷⁾. However, most of these sensors still have several drawbacks in terms of sensitivity, selectivity and sampling time for the wide spread and routine application. For example, a colorimetric method, which showed relatively high sensitivity, needs at least 30 minutes or longer accumulation time for the detection 80 ppb HCHO ⁽⁶⁾⁽⁷⁾.

This paper is concerned on the development of high sensitive and rapid response HCHO sensor in air. SnO_2 -based gas sensor for detecting HCHO was fabricated using R.F. Induction Plasma Deposition (IPD) method. IPD technique has been used in various applications for material processing ⁽⁸⁾⁻⁽¹⁰⁾. It offers the advantages of the relatively large volume of reactive field and low velocity of discharge of induction plasmas compared to direct current (d.c.) and arc plasma deposition, which make it possible to expand the kinds of materials to be treated by the IPD method. Physical properties of sensing films were investigated by SEM and XRD method. The obtained sensors showed enough sensitivity at 20 ppb HCHO with quick response and recovery time at several minutes. Moreover, the influence of metal additives on the sensing properties

and the response to other causes of SBS such as toluene, xylene and carbon monoxide, were also described in the paper.

2. Experimental

Fig. 1 shows the sample structure. It is a thin film type structure fabricated on an alumina substrate. Deposition of the SnO_2 film was prepared with Thermal Spray Equipment (TAFE Incorporated). SnO_2 powders (99.99 % purity) mixed with 1 wt % polyvinyl alcohol were firstly prepared by granulation process to form average grain sizes about several tens of μm . Then the mixture of the powders were injected into a very high temperature plasma flame, where they were rapidly decomposed and ionized, and quickly cooled to form a coating on a polished alumina substrate ($3.5 \times 3.5 \times 0.8 \text{ mm}$). The thickness of generated sensing film was about $15 \mu\text{m}$. Au electrodes were formed on the front surface of the alumina substrate before the deposition as electrical contacts. Finally, the films were thermally treated for 100 minutes in air at temperature 800°C , and a free cooling was applied to samples after the heat treatment.

The principal operating parameters during IPD process such as plasma torch power, deposition distance, and powder feed rate have long been recognized as critical parameters. Many experiments under different deposition conditions were carried out to get desired properties of sensing coatings including our preliminary experimental discussions ⁽⁸⁾. Taking these results into consideration, the deposition conditions applied to the present

Fig. 1. Structure of the SnO_2 -based sensor

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Table 1. Typical RF induction plasma deposition conditions

Plasma power	84 kW (8.0 kV * 10.6 A)
Powder feed rate	2.7 g/min
Substrate Temperature	232 ~ 242 °C
Deposition Distance	650 mm
Deposition Time	205 sec

work were determined as shown in Table 1.

The current-voltage characteristics of sensor responses were measured by a data acquisition system under repeated gas flow (500 sccm) between HCHO (diluted in dry air) and standard dry air (O₂: 20%, N₂: 80%) controlled by a Mass Flow Controller (SG-7S1, Aera Japan Ltd). The samples were set inside a temperature-controlled electrical furnace (ARF-40k, Asahi-Rika Co.). In order to investigate the temperature dependency of the sensors, the operating temperatures were varied from 250 to 350 °C. The sensitivity of the sample is defined as the change in sensor resistance in the HCHO gas atmosphere with respect to its resistance in air atmosphere as a function of test gas concentration. The sensitivity is calculated from

$$S = \frac{(Ra - Rg)}{Ra} \dots\dots\dots (1)$$

where Ra is the sensor resistance in air atmosphere and Rg is the sensor resistance in gas atmosphere.

The surface morphology of the films was observed with Hitachi S-4100 Scanning Electron Microscopy operating at 15.0 kV. X-ray diffraction was carried out to identify phases in the films with a Rigaku Geigerflex operating at 40 kV, 30 mA. A detailed description of the setting for these measurements has been reported in a previous paper ⁽⁸⁾. For the investigation of metal additives, different metals, In, Mg, Al, Ca, Zn, Cs, Ba, La, Ce, were introduced with 0.5 mol % concentration using impregnation method and they were annealed at 800°C.

3. Results and Discussion

3.1 Physical Properties The typical SEM images of generated sensing film annealed at 800 °C were shown in Fig. 2. As can be seen in this figure, the sensing film contained various size particles covering from several nanometers to hundred of nanometers. The smaller particles are seemed to be distributed on the surface of larger particles and the repetition of this structure of different size particles made the film porous. Fig. 3-A shows the XRD pattern of the sensing film obtained for 2θ scans between 25° and 55°, which showed predominant reflections from the crystallographic (110), (101) or (211) plane of cassiterite SnO₂. The secondary phases such as SnO and Sn₃O₄ have not been found in the films, which indicate that the films were composed of stoichiometric SnO₂ composition. Fig. 3-B is the XRD pattern of the sensor film before post-deposition heat treatment. It is noted that the peak intensities of the XRD pattern, especially for the (110), (101) or (211) plane, were lower than that of the annealed sample (Figure 3-A), which indicates that non-crystal structure remained in the as-grown film ⁽¹¹⁾.

3.2 Electrical characteristics Fig. 4 shows a time dependence of sensor response when the sensor was exposed to 200 ppb HCHO gas at 300 °C. As is clearly seen, the sensor

Fig. 2. SEM micrographs of the IPD SnO₂ film with (A)magnification 100k ; (B) magnification 10k

Fig. 3. XRD patterns of IPD SnO₂ sensing films: (A)annealed at 800 °C ; (B)without heat treatment

resistance decreased by the exposure to HCHO gas and returned to the initial value when the atmosphere was switched to the standard air. Both the response and recovery time were within several minutes. The resistance decrease may come from the oxidation of HCHO gas with oxygen adsorbed on the SnO₂ surface leading to a reduction of the barrier height of the SnO₂ grain boundaries of the surface or a reduction of the surface depletion layer depth of the

Fig. 4. Response curve of sensor prepared by IPD to 200 ppb HCHO

Fig. 7. Sensitivities vs. HCHO concentration for various operating temperatures

Fig. 5. Comparison of the sensitivities of as-deposited sensor and annealed sensor at 800°C

Fig. 8. Time response curve of indium-doped sensor operated at 300°C for various HCHO concentrations

Fig. 6. Time response of HCHO sensor for various HCHO concentrations

SnO₂ particles⁽¹²⁾⁽¹³⁾.

Although various parameters have influences on sensor properties for both physical and electrical aspects, plasma torch power and post-deposition heat treatment were found to be the most critical parameters to be carefully controllable to get high sensitive response. Fig. 5 showed the comparison of the sensitivity for various concentrations of HCHO gas between as-grown sample and annealed sample (800°C). As shown in this result, the post-deposition heat treatment enhanced the sensitivity. The desirable temperature for the heat-treatment was in the range 650°C -850°C although this is not optimized yet. As for the plasma torch power, relatively high power (50-90 kW) was found to be required to get good crystallized and high performance sensor film in the examined power range between 20-100 kW.

Fig. 6 showed the response curve of the sensor prepared with plasma deposition power 84 kW and post-deposition annealing temperature 800°C. The gas sensor was examined to detect HCHO at a concentration range from 20 to 200 ppb in order to meet the environmental standard. It is clearly seen that the gas sensor has achieved high sensitivity at extremely low HCHO concentration down to 20 ppb with quick response and recovery time in several minutes. Fig. 7 shows the sensitivity as a function of HCHO concentrations for various measurement temperatures. The sensitivity showed almost linear dependence to the HCHO concentrations with maximum response at around 300 °C. It is obvious that the measurement temperature is also an important parameter to be taken into consideration for the sensor design.

3.3 Sensitivity Improvement by Metal Doping In our succeeding research, it was found that specific metal doping into SnO₂ film effectively worked to enhance the sensitivity for HCHO detection⁽¹⁴⁾⁽¹⁵⁾. Different metals, Mg, Al, Ca, Zn, In, Cs, Ba, La, Ce, were introduced into as-deposited film with 0.5 mol % concentration aqueous solution using impregnation method. The films were then thermally treated for 100 minutes in air at temperature 800 °C, and a free cooling was applied to samples after the heat treatment.

Fig. 8 showed time response of an metal Indium doped sensor for various HCHO gas concentrations and Fig. 9 is the comparison of the sensitivities between undoped and In-doped sensors. It is obvious that In-doped sensor showed higher sensitivity than that of the undoped sensor with similar response and recovery time. Fig. 10 showed the comparison of the sensitivities for sensors doped with different metal additives. Comparing with the undoped

Fig. 9. Sensitivities to HCHO at various concentrations for undoped and indium-doped sensors

Fig. 10. Sensitivities to 40 ppb HCHO for various metal introduced sensors in comparison with the undoped sensor

Table 2. Sensitivities upon exposure to various SBS causes

Gas	Concentration	Sensitivity
formaldehyde	1ppm	0.5
toluene	1ppm	0.09
xylene	1ppm	0.12
CO	100 ppm	0

one, the sensors doped with Ca, Zn, Cs, Ba, La metals showed better sensitivities. On the contrary, the sensor doped with Mg, Al and Ce metals have less sensitivities. Although the mechanisms of the metal additives and the performance should be investigated in detail in our future work, these results suggest that high sensitive and high selective sensing film for detecting HCHO gas may be designed by taking into consideration of different metal doping effects.

3.4 Selectivity of the Sensor by Detecting other Causes of SBS

For a sensor to be useful, it is necessary that it is selective to a particular gas with negligible sensitivity to other gases. Table 2 shows the sensitivities of the undoped sensor upon exposure to various causes of SBS such as toluene, xylene, and CO gases, which may co-exist with HCHO in contaminated air, to examine whether other SBS causing reagents interfere with the determination of HCHO. The sensor showed almost no or extremely small response to toluene, xylene, and CO at ppb-level gas concentration, so the tested concentration of formaldehyde, toluene, and xylene was set at 1 ppm, and the CO concentration at 100 ppm. The sensor showed lower sensitivity to typical VOCs

toluene and xylene compared to HCHO, but displayed no response to CO gas in the concentration range used in this experiment.

4. Conclusion

R.F. Induction Plasma Deposition method was successfully applied to get porous structure SnO₂ film involving different size particles from several nanometers to hundreds of nanometers. The SnO₂ film displayed sufficient sensitivity to HCHO gas with a concentration of less than 20 ppb with response and recovery time less than several minutes. Although it was still a preliminary study, the plasma deposition power and the post-deposition heat treatment were found to have significant effects on the properties of the sensing film.

It was also found that In-doped SnO₂ gas sensor showed better sensitivity toward HCHO detection, which indicated that some metal addition had positive effect on the gas-sensing characteristics. Both the undoped and In-doped sensors showed enough sensitivity to detect HCHO gas covering environmental standard, so the fabricated sensors are promising for monitoring indoor air environments. However, the sensors also had responses to typical VOCs such as toluene and xylene although their sensitivities were lower than HCHO, and the improvement of the selectivity of the sensors is now under progress in our study.

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