The Doping and Plasma Effects on Gas Sensing Properties of α-Fe_2O_3 Thin Film

J. Y. Choi and G. E. Jang[a]
Department of Materials Engineering, Chungbuk National University
San 48, Gesin-Dong, Cheongju 361-763, Korea,

[a]E-mail : gejang@chungbuk.ac.kr

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Pure and Sn or Pt doped α-Fe_2O_3 thin films were prepared on Al_2O_3 substrates by RF-magnetron sputtering method and the sensitivities were compared. It was found that pure α-Fe_2O_3 thin films did not exhibit much selectivity in CO and i-C_4H_{10} gases while it showed the high sensitivity in proportion to the gas concentration of C_2H_5OH gas. Pt-doped α-Fe_2O_3 showed to be alike sensing properties as pure α-Fe_2O_3 thin film in C_2H_5OH gas. However, Sn-doped α-Fe_2O_3 thin films exhibited the excellent sensitivity and selectivity in H_2 gas. After microstructure modification by plasma etching on pure α-Fe_2O_3 thin films, the gas sensing characteristics were dramatically changed.

Keywords : α-Fe_2O_3 thin film, Sensitivity, Selectivity, Plasma etching

1. INTRODUCTION

There has been considerable interest in recent years in hin film gas-sensing materials[1-3]. In comparison with conventional sintered bulk sensors, thin film gas-sensing naterials have good sensitivity, optimum operating emperature and selectivity due to an high surface exposed for gas adsorption[1,3]. Therefore, it is attrac-ive to prepare thin film gas sensors so as to improve the characteristics of commercialized sintered body gas ensors. In addition, sensors based on thin film gas-ensing materials are essential to the development and abrication of integrated gas sensors. Among the widespread use of thin film gas sensor, one of the most promising candidates is Fe_2O_3 based gas sensor[4-9].

This interest is connected with the properties of α-Fe_2O_3 which offered a high sensitivity to some reducing gases without the application of noble metal catalysts. Pure α-Fe_2O_3 with the corundum structure is a very stable oxide in nature and it was generally considered to have only poor gas sensitivity without adding any metal incorporation. However it was confirmed that a fine grained α-Fe_2O_3 thin film fabricated by thin film technology was especially sensitive to methane as well as alcohol. These results suggest that microstructure plays an important role in elucidating the basic sensing mechanism and largely influences surface electrical properties. Therefore a material with a high specific area seems to be quite suitable for future sensing device. So far a lot of research work has been carried out to improve the selectivity and sensitivity by applying catalyst or any processing technology[6-9].

We observed the sensing characteristics in reducing atmosphere were strongly dependent on the micro-structure and its doping elements. In this paper, especially, the doping and plasma effects on gas sensing properties of α-Fe_2O_3 thin films have been compared and discussed.

2. EXPERIMENTAL

2.1 Film deposition

RF magnetron sputtering method was applied to prepare pure and Pt or Sn doped α-Fe_2O_3 thin films on Al_2O_3 substrates. The base pressure was below 5×10^{-5} Torr and the working pressure was adjusted between $1\sim5\times10^{-2}$ Torr. The substrate was heated up to 500 ℃ and the applied RF power was 100~200 W. Ar ion etching was performed on the substrate for 20min prior to each experiment. The Ar ion etching not only cleaned the surface of the substrate but also improved the adhesion between the films and the substrates.

The flow rate of Ar and O_2 was controlled by the mass flow controller(MFC). The distance between substrates and gas ring was kept at 0.05 m. Finally, the films were deposited at room temperature and annealed at 350 °C for 72 hr in air atmosphere. The measured film thickness

was around 1.500 nm. After deposition α-Fe_2O_3 thin film was plasma etched or doped with Sn and Pt by RF or DC power for 30 sec to study the effect of micro-structure and surface reaction change on gas sensing characteristics.

2.2 Gas sensitivity measurement

The gas sensitivities of pure and Sn or Pt-doped α-Fe_2O_3 thin films to H_2, CO, i-C_4H_{10} and C_2H_5OH gases were measured in gas concentration range from 500 to 3000 ppm at operating temperature of 300 ℃ for this study. The inter-digital Pd-Ag electrodes were screen printed on a 8×4×0.4 mm^3 alumina substrate. Gas sensing characteristics were carried out by DC electrical resistance measurement in a gas flow system within a test chamber, which allowed the measurement of the sensitivity to various gases. The gas sensitivity, S(%), was defined as

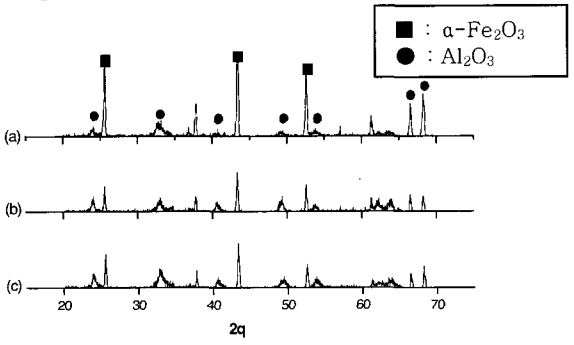
$$S\ (\%) = \frac{(Ra - Rg)}{Ra} \times 100 \quad (1)$$

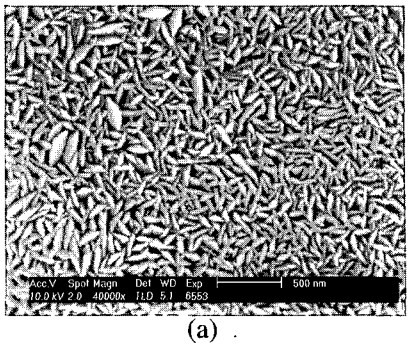
where Ra and Rg are the sensor resistances in clean air and in air containing testing gas, respectively.

3. RESULTS AND DISCUSSION

The film deposition was made based on Thornton model[10] in order to obtain the porous microstructure with fine crystalline. Figure 1 shows typical X-ray diffrac-tion patterns and SEM images of Fe-O thin films deposited by the RF power range of 100-200 W at room temperature.

As shown in Fig. 1, most prominent diffraction patterns revealed typical polycrystalline phases consisting of α-Fe_2O_3 and alumina phases and the thin film shows a fine morphology with a porous island structure regardless of RF powers. The best optimum condition to prepare the thin film for gas sensor was that RF power was 150 W and Ar pressure was 30 mTorr at room temperature. These films showed a uniform morphology with a porous structure and the average grain size was around 200 nm. To enhance the sensitivity and selectivity, Sn, or Pt doping and plasma etching were performed on the top of pure α-Fe_2O_3 surface.





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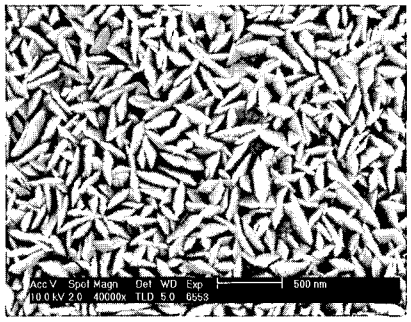

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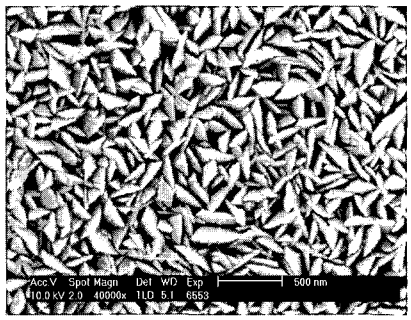
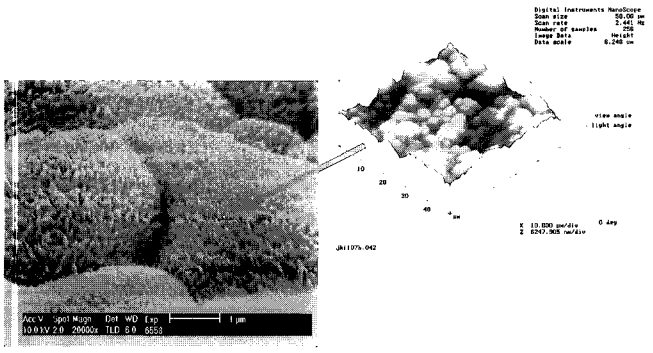


(c)

Fig. 1. The typical X-ray diffraction patterns and SEM images of Fe-O thin films deposited in the RF power range of 100-200 W at room temperature: (a) 100 W, (b) 150 W, and (c) 200 W.

Figure 2 represents the SEM (Scanning Electron Microscopy) micrographs and AFM (Atomic Force Microscopy) images of α-Fe_2O_3 thin film before and after plasma etching. The result of AFM measurement showed that plasma etched thin film had more rough surface structure than that of pure thin film. For the gas sensor application, it is obvious that high specific surface area with the porous island structure having fine grain size, which might offer more channels toward gases with a large contact area, is more favorable. In the case of α-Fe_2O_3 thin film doped with Sn or Pt, the result of EDS (Energy Dispersive Spectroscopy) and EPMA (Elec-tron Probe Micro Analysis) measurement confirmed Pt or Sn elements were uniformly dispersed in α-Fe_2O_3 matrix. Such a uniformly dispersed doping material is expected

to improve the gas sensing properties. The gas sensing properties of these fabricated specimens were investigated in terms of H_2, CO, i-C_4H_{10} and C_2H_5OH gases in concentration range from 500 to 3,000 ppm at an operating temperature of 300 ℃.



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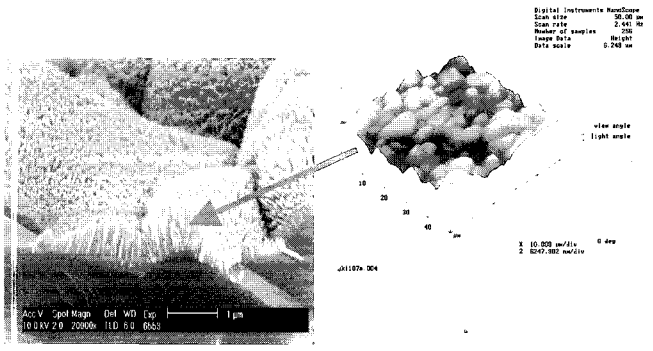
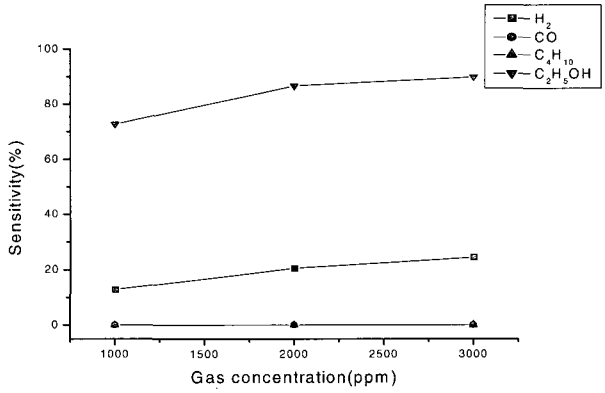


(b)

Fig. 2. SEM micrographs and AFM images of α-Fe_2O_3 thin film before and after plasma etching: (a) before and (b) after.

Figure 3 shows the gas sensitivity of α-Fe_2O_3 thin films depending on plasma etching conditions. It seems pure α-Fe_2O_3 thin film as in Fig. 3(a) does not show much selectivity for CO and i-C_4H_{10} gases while it demonstrates the maximum sensitivity of 89.8 % for C_2H_5OH. After plasma etching, the etched thin films, as in Fig. 3(b), reached to the highest, 92.8 % of sensitivity at 3000 ppm of C_2H_5OH environment as compared with that of pure α-Fe_2O_3 thin film under similar conditions. It was found that the gas sensitivity of α-Fe_2O_3 thin films to C_2H_5OH increased in proportion to the gas concentration. Moreover the selectivity of etched α-Fe_2O_3 thin film also shows the tendency of increase to H_2 from 24.4 to 62.5 % in 3000 ppm while the gas sensitivity to CO and i-C_4H_{10} gases was not improved significantly with increasing gas concentration. Therefore it was confirmed again that the sensing characteristics are dramatically changed depending on microstructure modification.



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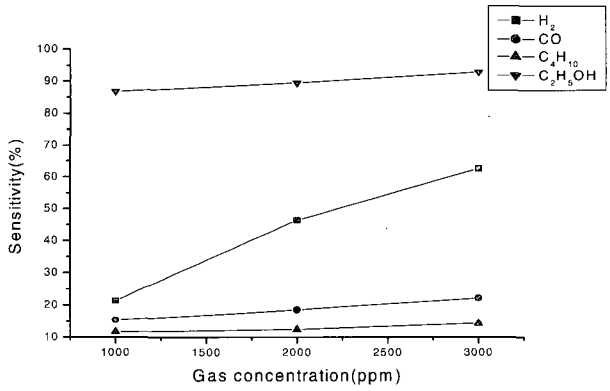
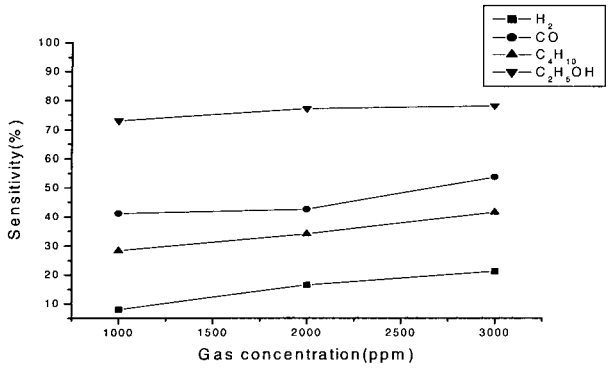


(b)

Fig. 3. The gas sensitivity of α-Fe_2O_3 thin film depending on plasma etching conditions: (a) before plasma etching and (b) after plasma etching.

Figure 4 shows the gas sensitivity of α-Fe_2O_3 thin film depending on doping elements. Pt-doped α-Fe_2O_3 as in Fig. 4(a) showed to be alike sensing properties as pure α-Fe_2O_3 thin film in C_2H_5OH gas. One of the noticeable changes in Pt-doped thin films was that the sensitivity to i-C_4H_{10} gas increased slowly as a function of gas concentration, i.e., from 28.3 % at 1000 ppm to 41.5 % at 3000 ppm concentration. On the other hand, the Sn doped thin films to i-C_4H_{10} gas only revealed only 7 % sensitivity at 1000 ppm and 12 % sensitivity at 3000 ppm, respectively. However Sn doped α-Fe_2O_3 thin films demonstrate an excellent sensitivity to H_2 gas, i.e., 90.4 % sensitivity at 3000 ppm gas concentration.



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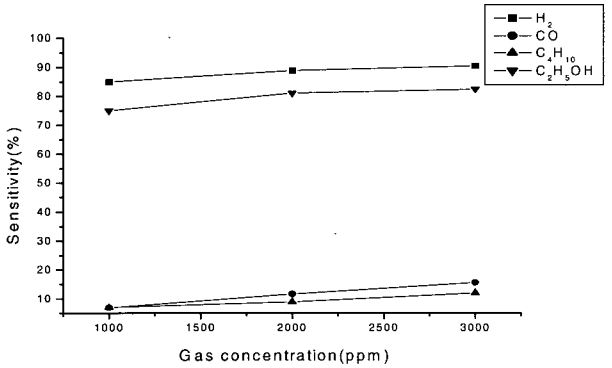

(b)

Fig. 4. The gas sensitivity of α-Fe_2O_3 thin films depending on doping elements: (a) Pt-doped and (b) Sn-doped.

4. CONCLUSION

Pure and Pt or Sn doped α-Fe_2O_3 thin films were prepared by the RF magnetron sputtering technique. The sensing characteristics of the thin films after doping with Sn, or Pt and plasma etching were studied in terms of various reducing gases and with different gas concentrations. In this study, we arrived at the following conclusions.

1) The best optimum condition to prepare the thin film for gas sensor was that RF power was 150 W and Ar pressure was 30 mTorr at room temperature. These films showed a uniform morphology with a porous structure and the average grain size was around 200 nm.

2) It seems that pure α-Fe_2O_3 thin film does not show much selectivity for CO and i-C_4H_{10} gases while it demon-strates the maximum 89.8 % of sensitivity for C_2H_5OH with excellent selectivity.

3) After plasma etching, the etched thin films reached the highest, 92.8 % of sensitivity at 3000 ppm of C_2H_5OH concentration as compared with that of pure α-Fe_2O_3 thin film. It was found that the gas sensitivity of α-Fe_2O_3 thin films to C_2H_5OH was increased in proportion to the gas concentration. Therefore it was confirmed again that the sensing characteristics are dramatically changed depending on microstructure modification.

4) Pt doped α-Fe_2O_3 showed to be alike sensing properties as pure α-Fe_2O_3 thin film in C_2H_5OH gas. However Sn-doped α-Fe_2O_3 thin film exhibited an excellent sensitivity and selectivity for H_2 gas.

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