A STUDY OF α -Fe₂O₃ ULTRAFINE PARTICLE FILMS

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Abstract- α -Fe₂O₃ thin films have been successfully fabricated onto silicon or ceramic by using PECVD method. The conditions for preparation of α -Fe₂O₃ films, which deposited from Fe(CO)₅ and O₂ in an r.f. flow discharge, have been discussed. The compositions and the structures of the thin films have been investigated by means of modern analysis techniques. The mean particle size of α -Fe₂O₃ ultrafine particle films were measured with the Mössbauer effect.

1. Introduction

The unusual magnetic behaviour of α -Fe₂O₃ has been the subject of numerous investigations. In recent years, semiconducting oxides, such as stannic oxide (SnO₂), zinc oxide (ZnO), and alpha-hematite (α -Fe₂O₃), have been widely applied for detection of various gas species, since sensors for poisonous gases are more and more in demand for safety and environmental protection. Some of these materials have already been put into practice as sensing elements. α -Fe₂O₃ has sepecially attracted much attention as a gas sensor material^[1]. Because α -Fe₂O₃ has generally good gas sensitivity and high chemical stability for detecting combustible gases such as CH₄, C₃H₈, i-C₄H₁₀, etc. However, little work has been carried out to elucidate the mechanism of the gas sensitive properties of the material from the standpoint of the microstructure of α -Fe₂O₃.

Thin film type gas sensors^[2] are now being developed and it is usually supposed that the chemisorption of the gas on the surface of a semiconductor leads to the addition or removal of localized charges on the surface. This can be detected by a change in conductivity of the film. Consequently, the crystallite size of the films is considered to be an important parameter for the gas sensitivity. The unique characteristics of the SnO₂ ultrafine particle films have been reported to be used for detecting humidity, C₂H₅OH and so on^[3]. In the present work, α -Fe₂O₃ typical ultrafine particle films which have the median particle size of several tens of angstroms are prepared by using plasma enhanced chemical vapour deposition (PECVD). The structure and composition of the films prepared by this method were then investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Mössbauer spectroscopy. The superferromagnetic transition was observed with Mössbauer spectroscopes. The Fe₂O₃-SnO₂-TiO₂ multilayer sensors have been fabricated for detecting C₂H₅OH and NO_x gas.

2. Experimental

Figure 1 shows the plasma deposition system utilized in this study.

Fig.1 Plasma enhanced chemical vapor deposition system

1. Bell jar	2. R.F.Coil	3. Substrate stand	4. Rotameter
5. TiCl_4	6. $\text{Fe}(\text{CO})_5$	7. To pump	8. Temp. Controller
9. Throttle	10. Heater	11. Thermometer	12. Gas cleaner
13. O_2 gas inlet	14. Wafer	15. Source inlet	

The plasma discharge chamber is a verticle transparent vitreous silica tube which can be maintained at low pressures under a sustained gas flow. The backgraound gas was oxygen. The flow rate of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) vapour was regulated by controlling the temperature of the glass flask containing the liquid source. The temperature of the silicon wafer or ceramic placed on the substrate stand was measured by a thermocouple. When necessary, the substrate wafers were heated externally with a planar electrical resistance heater introduced underneath the substrate stand.

The radio frequency power (at 1MHz) was applied to the gas through a copper coil of five turns fitting closely to the reaction chamber. In general, the power output was kept constant. The substrates were heated in the temperature range 25-350°C. The reaction gases were mixed to form the Fe_2O_3 films under varous deposition conditions by the plasma excited decomposition reaction.

The composition of the Fe_2O_3 films deposited on a sodium chloride or a silicon substrate was determined by infra-red absorption sepectroscopy.

The topography of film surfaces was investigated with a Hitachi (X-650) scanning electron microscope. To minimize charging approximately 10 nm of gold was sputtered onto the Fe_2O_3 film surfaces.

X-ray diffraction studies were performed with D/max-VA type X-ray diffractometer. The X-ray source was copper $\text{K}\alpha$ radiation (1.5 Å).

The mean particle size of the Fe_2O_3 ultrafine particles were determined from the Mössbauer spectroscopy analysis.

The thin film gas sensors were made of the ultrafine particle films. The sensing materials, the particle films of $\text{SnO}_2\text{-Fe}_2\text{O}_3$, were deposited onto the ceramic substrate with the gold-coated interdigital electrodes. Gas sensing properties of the devices were measured by the usual technique.

3. Results and Discussion

(1) Effects of the $\alpha\text{-Fe}_2\text{O}_3$ films deposition conditions

All experiments were carried out under continuous flow conditions and at the same pumping speed. $\alpha\text{-Fe}_2\text{O}_3$ films were formed in an r.f. plasma of $\text{Fe}(\text{CO})_5$ and O_2 at substrate temperatures between 25 and 350°C.

The relationship between deposition rate and deposition temperature is shown in Fig.2. It is evident from the figure that the deposition rate increases with temperature and the relationship is not linear. The reduction in activation energy due to plasma enhancement, allowed significant deposition rates at low temperatures.

Fig.2 Relationship between deposition rate and deposition temperature

The relationship between the thickness of film and deposition time is shown in Fig.3. The relationship is linear over the time range investigated and when extrapolated the line passes through the origin. In general, the deposition rate is between 0.05 and 0.08 μm/min for typical deposition conditions.

Fig.3 Film thickness versus deposition time

As expected, the exact deposition rate depended upon r.f. power, flow ratio of source gas flow rates, position of the substrate with respect to the coil and $\text{Fe}(\text{CO})_5$ inlet tube and so on.

The relationship between deposition rate and flow ratio of O_2 to $\text{Fe}(\text{CO})_5$ is shown in Fig.4. It is evident from the figure that a peak in deposition rate is obtained under these experimental conditions.

Fig.4 Deposition rate versus $\text{O}_2/\text{Fe}(\text{CO})_5$ flow ratio

(2) $\alpha\text{-Fe}_2\text{O}_3$ film structure analyses.

Fig.5 shows infra-red spectra of the Fe_2O_3 films. IR spectra of the films exhibit the bands at 580 cm^{-1} and 420 cm^{-1} , which may be attributed to Fe-O stretching vibrations.

Fig.5 Infrared absorbance spectra of $\alpha\text{-Fe}_2\text{O}_3$ films deposited onto silicon substrates

The absorption bands at $3340\text{--}3600 \text{ cm}^{-1}$ (variable) and at 1650 cm^{-1} are due to structural hydroxyl groups and water molecules on the surface. These peaks disappeared when the annealing temperature was increased. The IR spectra of the Fe_2O_3 films provides some essential information in determining the gas sensitive mechanism.

Fig.6 shows scanning electron micrographs of the $\alpha\text{-Fe}_2\text{O}_3$ films deposited onto

single crystal silicon substrates under various conditions. The mean particle sizes of the α -Fe₂O₃ films deposited at 100°C for 10 min [Fig.6(a)] are about 120 Å, and increased as the annealing temperature increased [Fig.6(b)]. The flow ratio of O₂ to Fe(CO)₅ (>10) and the substrate temperature (>250°C) may influence surface morphologies of the Fe₂O₃ films [Fig.6(c)].

a. Deposition temperature = 100°C for 10 min O₂/Fe(CO)₅ flow ratio = 5
 b. Annealing temperature = 300°C for 10 h.
 c. Deposition Temperature = 250°C for 10 min O₂/Fe(CO)₅ flow ratio = 10

Fig.6 Scanning electron micrographs of α -Fe₂O₃ films onto silicon substrates

Fig.7 shows X-ray diffraction results for three films deposited at 80°C and annealed at 200°C and 500°C for 10h. It shows that the sample grown at low temperatures displays no diffraction peaks [Fig.7(a)], indicating an amorphous state to X-rays, or the presence of very small crystallites. For the specimen isothermally annealed at 200 and 500°C after deposited at 100°C, the relative intensity of the peak in the diffraction pattern increases with increasing annealing temperature as shown in Fig.7(b) and (c). All the peaks can be attributed to the phase of α -Fe₂O₃.

a. Deposition temperature = 80°C for 10 min
 b. Annealing temperature = 200°C for 10 h
 c. Annealing temperature = 500°C for 10 h

Fig.7 X-ray diffraction spectra of α -Fe₂O₃ films deposited onto silicon substrates

Mössbauer spectra of α -Fe₂O₃ have been measured to examine on the mean partial sizes of α -Fe₂O₃ ultrafine partial films. Mössbauer spectra recorded as a function of increasing particle size for α -Fe₂O₃ are shown in Fig.8(a,b,c,). According to the report of W. Kundig et.al. [8], Fig.8(a) represents an average particle size of 50 Å at 80°C and gives a spectrum consisting of only the quadrupole-split center line. The average particle size is so small that the behaviour is completely

superparamagnetic.

Fig.8 Mössbauer spectra of $\alpha\text{-Fe}_2\text{O}_3$ as a function of the average particle size

As the two specimens isothermally deposited at 100°C are annealed at 200°C and 400°C for 10h., the particle size increases. In going from samples A to C, the Zeeman lines become progressively more preponderant over the quadrupole-split center line. In sample C the average particle size has increased with annealing temperature and almost corresponds to a pure ferromagnet. Therefore, the $\alpha\text{-Fe}_2\text{O}_3$ films deposited at lower temperature (<80°C) are attributed to the ultrafine particle films.

The experimental results indicate that the internal magnetic fields (H_f) of sample C, quadrupole splitting and isomer shift are calculated as 516 K O_e , 0.326 mm sec^{-1} and 0.444 mm sec^{-1} , respectively. Then the thin films at 400°C for 10h are the phase of $\alpha\text{-Fe}_2\text{O}_3$.

(3) Gas sensing properties of the $\alpha\text{-Fe}_2\text{O}_3$ films.

Ordinary $\alpha\text{-Fe}_2\text{O}_3$ does not show a sensitivity to reducible gases, but $\alpha\text{-Fe}_2\text{O}_3$ prepared from iron sulphate solution has a gas sensitive property. Truly thin film gas sensors, deposited by PECVD method, have generally shown poor gas sensing properties at 250°C. We have used multilayer structures which overcome these problems. The two structures used are shown in Fig.9(a,b).

Fig.9 Schematic drawing of the multilayer thin film sensors

We suggest that the use of ferric oxide with covered a thin layer of SnO_2 or TiO_2 , greatly improves the reversibility and long-term stability. High sensitivity and high selectivity of thin film gas sensors have been obtained to NO_x and C_2H_5OH in this work.

4. Conclusions

Alpha-hematite films have been fabricated successfully by using the plasma enhanced chemical vapour deposition method and the effects of reaction factors are discussed in this work. An r.f. plasma of O_2 and $Fe(CO)_5$ can be used to deposit α - Fe_2O_3 films onto the single crystal silicon substrate or the ceramic at temperature ranging from 25 to 350°C. The surface micrographs of the α - Fe_2O_3 films have been observed by scanning electron spectroscopy. The structures and compositions of α - Fe_2O_3 films are investigated by means of infra-red spectra techniques and X-ray diffraction methods.

The average particle size of the α - Fe_2O_3 ultrafine particle films have been measured by Mössbauer spectroscopy. It indicates that the mean particle size of α - Fe_2O_3 films is 50 Å for deposition temperatures less than 80°C and the thin films are totally superparamagnetic in structure. The results obtained in this study can be applied to the development of a thin film gas sensing device of great sensitivity. They may also provide useful suggestions for explaining the gas sensing mechanism. Finally good sensing properties of Fe_2O_3 - TiO_2 - SnO_2 multilayer thin film sensors have been obtained for detecting NO_x and C_2H_5OH gas.

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