Characterization of Multiphase in Fe_2O_3 Thin Film by PECVD

Bum-Jin Kim, Eun-Tae Lee, Gun-Eik Jang and

Yong-Sun Chung *

Department of Material Engineering, Chungbuk National University

Cheongju, Chungbuk 360-273, Korea

* Ceramic Materials Research Institute

Han Yang University, Seoul, Korea

Abstract

Fe_2O_3 thin films were prepared on Al_2O_3 substrate by PECVD(Plasma-Enhanced Chemical Vapor Deposition) process. The phase transformation of iron oxide film was determined as the substrate temperature and reduction-oxidation process. α-Fe_2O_3 was stable in deposition temperature ranges of 80~150℃. Fe_3O_4 phase was obtained by the reduction process of α-Fe_2O_3 phase in H_2 ambient. Fe_3O_4 phase was transformed into a γ-Fe_2O_3 thin film under controlled oxidation conditions at 280~300℃.

1.Introduction

In the Fe-O system, the three different polymorphic forms, FeO, Fe_3O_4 and Fe_2O_3, were exist. Also Fe_2O_3 has two typical modifications consisting of an α-Fe_2O_3 and γ-Fe_2O_3. Of theses, α-Fe_2O_3 and γ-Fe_2O_3 states are of technological interest owing to the possible application for reducing gas sensor because Fe_2O_3 need no noble metal catalysts as gas sensor materials[1,2]. However, there have not been many studies of preparation and characterization of iron oxide thin films in their different polymorphic forms. It is well known that these forms are easily transformed into one another through reduction-oxidaion process. Typically Fe_3O_4 films were formed by hydrogen reduction of α-Fe_2O_3 film and were oxidized to γ-Fe_2O_3 at 280℃[3,4]. Theses studies are mostly done by the bulk materials.

In this paper, thin film fabrication techenique by PECVD and transformation phenomena from α-Fe_2O_3 to γ-Fe_2O_3 phases are discussed in detail. And processing conditions and microstructure will be systematically investigated in terms of various processing parameters.

2. Experiment

Fe_2O_3 thin films were deposited by a PECVD process using the pentacarbonyl iron($Fe(CO)_5$). The source material has a melting point of -20℃, a boiling point of 102℃ and high saturation vapor pressure of 40mmHg at 30℃. Argon gas was used for as the carrier gas and plasma generation.

Fig. 1 shows the typical system of PECVD apparatus.

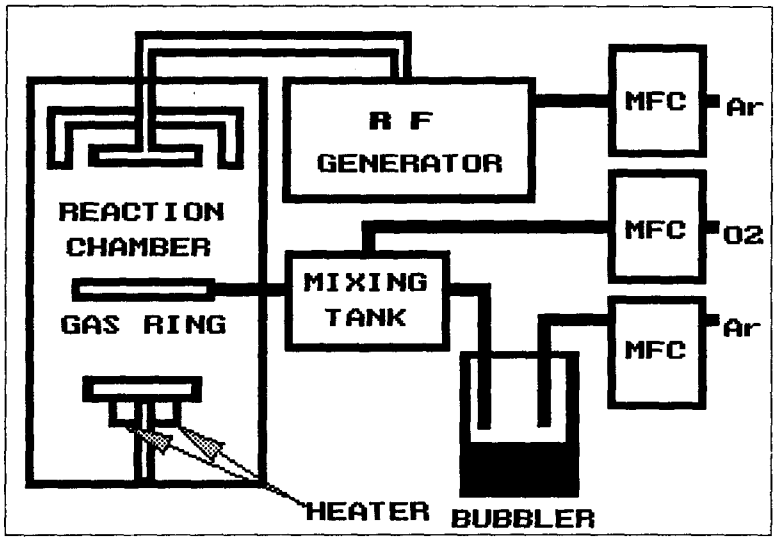

Fig. 1. Schematic diagram of PECVD systems

This experiment was divided into two processes in order to observe phase transformation phenomena from α-Fe_2O_3 to γ-Fe_2O_3. In the 1st process, initially the fabricated α-Fe_2O_3 were reduced to Fe_3O_4 and then this reduced Fe_3O_4 were oxidized to γ-Fe_2O_3. In the 2nd process, the fabricated Fe_3O_4 were oxidized to γ-Fe_2O_3.

Table 1 shows the deposition conditions of α-Fe_2O_3.

Table 1. Deposition conditions of α-Fe_2O_3

Plasma gas (sccm)	99	Deposition time (min.)	10	Bubbler temperature (℃)	30
Ar carrier gas (sccm)	10	Substrate temperature(℃)	80, 150, 250, 350	r.f power (watts)	100
O2 flow(sccm)	5				

Fe_3O_4 films were formed by a post-deposition reduction process in hydrogen. It is known that Fe_3O_4 is formed relatively at lower temperature than 300℃[5]. The reduction temperature was kept at 300℃. Reduction was accomplished in a 10:1 mixture of Ar:H_2 for various periods from 0.5 to 3h. The γ-Fe_2O_3 films were oxidized to Fe_3O_4 at 300~340℃.

In the 2nd process, Fe_3O_4 was deposited by PECVD. These films were deposited with various temperature ranges from 150℃ to 350℃. Table 2 shows deposition conditions of Fe_3O_4 thin film.

Table 2. Deposition conditions of Fe_3O_4 film

Plasma gas (sccm)	99	Deposition time (min.)	10	Bubbler temperature (℃)	30
Ar carrier gas (sccm)	10	Substrate temperature(℃)	150, 250, 350	r.f power (watts)	100

The as-deposited Fe_3O_4 films were oxidized by annealing for various periods of time ranges from 0.5 to 3h at 280~300℃.

3. Results and Discussion

The film properties were characterized by XRD, AES, SEM, AFM and BET for phase identification and surface characterization.

Fig. 2 shows the X-ray diffraction patterns of α-Fe_2O_3, Fe_3O_4 and γ-Fe_2O_3 phase. Based on X-ray experiment, inclusion of excess oxygen in the PECVD process leads to the formation of iron oxide films containing dominant α-Fe_2O_3 phase. Especially α-Fe_2O_3 phase was stable in deposition temperature ranges of 80~150℃.

In the Fig.2 (b) the XRD patterns showed that the α-Fe_2O_3 films were reduced to Fe_3O_4 films.

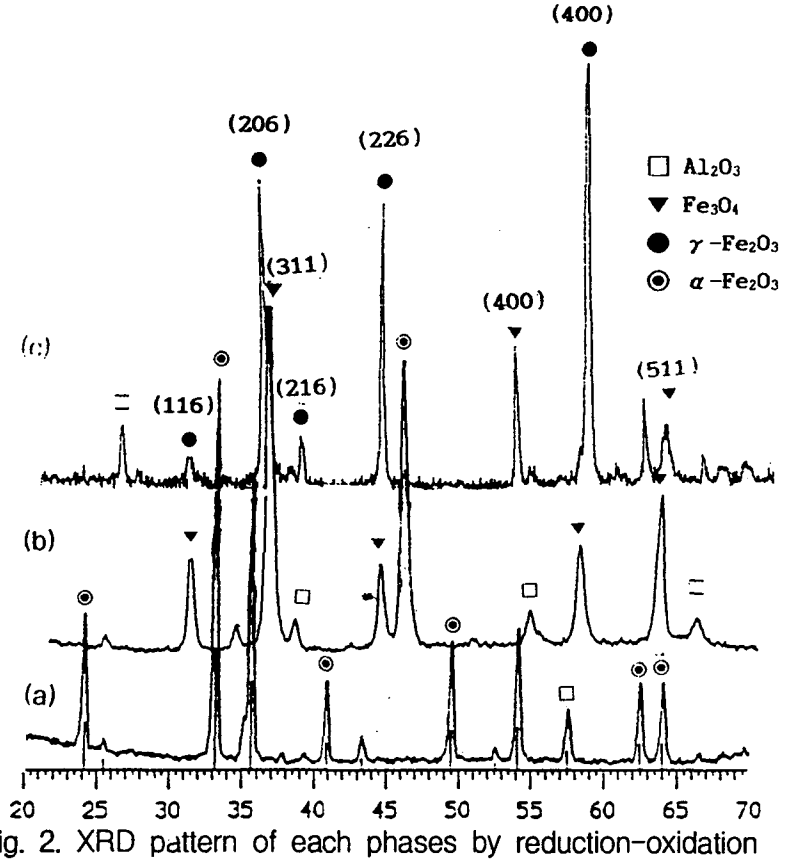

Fig. 2. XRD pattern of each phases by reduction-oxidation

(a) as-deposited α-Fe_2O_3 phase (b) reduced Fe_3O_4 phase (c) oxided γ-Fe_2O_3 phase

The result indicated that hydrogen reduction for 2h at 300~340℃ caused the transformation from α-Fe_2O_3 to Fe_3O_4.

The Fig.2 (c) showed that the Fe_3O_4 films were oxidized to γ-Fe_2O_3 films and the α-Fe_2O_3 phase was not detected in the reduced-oxidized films.

Fig.3 shows the X-ray diffration pattern of as-deposited Fe_3O_4 and oxidized γ-Fe_2O_3 phase. The result of XRD pattern in Fig.3 indicated that γ-Fe_2O_3 was transformed into a Fe_3O_4 by oxidation process and Fe_3O_4 and γ-Fe_2O_3 were exixsted as coexistent phase.

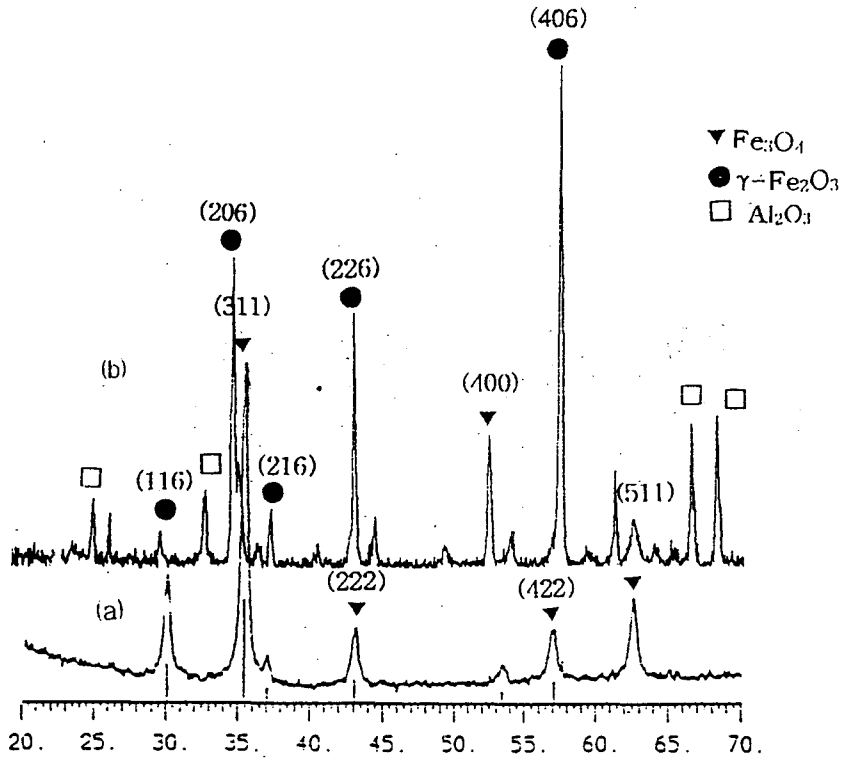

Fig. 3. XRD pattern of each phases
(a) as-deposited Fe_3O_4 phase (b) oxidized γ-Fe_2O_3 phase

The Auger Electron Spectra line shapes of a Fe_2O_3 thin films before argon sputtering and after 2 min. of sputtering are shown in Fig 4. The carbon and sulfur peak existed before sputtering. However, C and S was not detected in sputtered films. In the result, The fabricated films had the composed of Fe and O without impurity

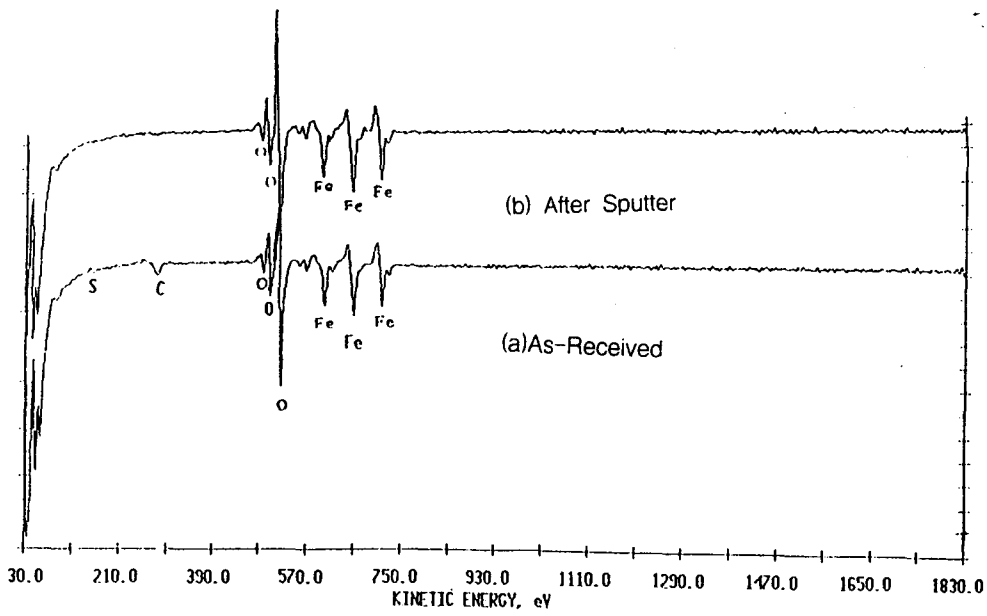

Fig. 4. The Result of AES peak
(a)As-Received (b) After Sputter

Fig. 5 shows the SEM microstructure of the fabricated films. The fabricated thin films had the porous island structure with a large specific surface area. The result suggested that the fabricated thin films might be used as gas sensor material.

Fig. 5. SEM Microstructure of the film

4. Conclusion

In this study, α-Fe_2O_3 phase was observed in deposition temperature at 80~150℃. In the systematic transformation, as-deposited α-Fe_2O_3 phase is transformed into a Fe_3O_4 phase under controlled reduction conditions in H_2 ambient for 2.5h at 300~340℃ and the reduced Fe_3O_4 was oxidized to γ-Fe_2O_3 at 280~300℃. The result of XRD pattern showed that Fe_3O_4 and γ-Fe_2O_3 was coexistent phase.

The result of AES indicated that the fabricated films had the composed of Fe and O without impurities but C and S in the surface.

The fabricated films have a large specific surface area and expect the application as gas sensor matrials.

References

1) Y. Nakatani and M. Matsuoka, Sintered α-Fe_2O_3 gas sensor, Proc. 1st sensor symp, Tsukuba, Japan, June 18~19, 1981. pp.63~68.

2) Kazuhiro Hava and Noriyuki Nishida, H_2 sensors using Fe_2O_3-based thin films, sensors and Actuators B, 20(1994) 181~186.

3) Yoshihiko NAKATANI and Michio MATSUOKA, Some Electrical Properties of γ-Fe_2O_3 Ceramics, Japanes Journal of Applied Physics Vol.22, No. 2, February, 1983 pp.233~239.

4) S. Hattori, Y. Ishii, M. Shinohara and T. Nakagawa, IEEE Trans. Mag., Vol. MAG-15, p1549.1979

5) Yoshichika BANDO, Shigeo HORII and Toshio TAKADA, Reactive Condensation and Magnetic Properties of Iron Oxide Films, Japanes Journal of Applied Physics Vol. 17, NO. 6, June, 1978 pp. 1037~1042