JOURNAL OF SOLID STATE CHEMISTRY **128,** 87–92 (1997)
ARTICLE NO. SC967159

Synthesis, Characterization, and Magnetic Properties of Fe_3O_4 Thin Films Prepared via a Sol–Gel Method

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Received February 5, 1996; in revised form September 16, 1996; accepted September 18, 1996

Different thickness Fe_3O_4 thin films, deposited on quartz substrates, have been directly synthesized via a sol–gel method. Homogeneous sols for preparing Fe_3O_4 thin films were obtained by interacting iron salts and polydentate ligands in ethanol. X-ray diffraction (XRD) and thermogravimetric analysis (TGA) identified the Fe_3O_4 phase and showed that there was no organic residue left in the films. A SQUID magnetometer was used to measure the coercive force of Fe_3O_4 thin films. The obtained coercive force of 30 Oe, measured from the trilayer thin film (275-nm thickness), showed the particles in the films were nanophase Fe_3O_4. A dramatic increase of coercivity of Fe_3O_4 thin films from 30 to 625 Oe and a demagnetization behavior, as the film thickness decreased from 275 to 120 nm, were observed on these films. © 1997 Academic Press

1. INTRODUCTION

Iron oxide based magnetic thin films are attractive materials for practical applications. Fe_3O_4 thin film is one of the promising material for magnetic devices. In the studies for preparing Fe_3O_4 thin films, several preparation methods have been reported (1–4). Since the high purity Fe_3O_4 phase is not very easy to obtain, vapor phase reactions, such as MOCVD and sputtering, are mainly used to prepare Fe_3O_4 thin films (5–9). The equipment and technology for preparing thin films by MOCVD and sputtering are relatively expensive and complicated. Searching for a wet chemical method to prepare high quality and large scale ferrite films has received a growing interest in recent years.

In most sol–gel preparation processes, metal alkoxides are used as metal sources. Since metal alkoxides are sensitive to moisture, it always needs careful control for the reaction processes for preparing thin films. In this report, we try to use a different sol–gel method to prepare iron ferrite thin films. Iron(II) and iron(III) salts were used as iron sources and polydentate ligands were used as chelating agents for preparing sols. In the sols, the formation of bonding of iron(III) to ethylene glycol [–(Fe–O)–R–O] has been reported (2). This result provides the possibility of a polymerization process, between metal ions and chelating agents, to occur to form oligomers in the sols. The polymerization reaction is described as

$$x\mathrm{Fe}^{2+} + y\mathrm{Fe}^{3+} + z\mathrm{HO}R\mathrm{OH} \rightarrow \text{–}(\mathrm{Fe}^{2+}\mathrm{O}R\mathrm{O}\text{–}\mathrm{Fe}^{3+}\text{–}\mathrm{O}R\mathrm{O})_n.$$

In the reactions, the "$O_{(II)}$" in $-\mathrm{Fe(III)}-\mathrm{O}_{(I)}-R-\mathrm{O}_{(II)}-$ is believed to have a chance to bond to different iron ions, such as iron(II) or even another iron(III) ions. Iron(II) and iron(III) are bonded to polydentate ligands and cause a homogeneous dispersion of iron(II) and iron(III) in the oligomers. It is expected that, during the drying process, the oligomers link to each other and form a xerogel film on the substrate. After sintering the xerogel films at high temperature, dense Fe_3O_4 films were formed on the substrates. It is believed that the oligomers, formed in the sols, are important prephase for Fe_3O_4 thin film preparations. The quality of the films will also be greatly affected by the homogeneity of the oligomers dispersed in the sols.

In the following studies, preparations of homogeneous sols and the formation of nanophase Fe_3O_4 films will be reported. Magnetic properties of different thickness Fe_3O_4 thin films were studied as well. This method of film preparation proved to be an easy way to prepare high quality and large scale Fe_3O_4 thin films.

2. EXPERIMENTAL

2.1. Sols and Xerogel Films Preparations

Iron salts (iron(II) lactate (98%, Nacalai Tesque, Inc. (Japan)) and iron(III) nitrate nonahydrate (99%, Merck))

0022-4596/97 $25.00

were used as iron sources and organic polydentate ligands (ethylene glycol (99.5%, Merck) and citric acid monohydrate (99.5%, Merck)) were used as chelating agents to prepare the sols. Ethanol (95%, Nacalai Tesque, Inc. (Japan)) was used as solvent. Concentration of 1.0 *M* solutions of iron salts and organic chelating agents were mixed to prepare sols. The mole ratio of iron(II)/iron(III) = 1 : 2 for Fe_3O_4 preparation, was used to prepare the sols. The prepared sols were covered with parafilm and stirred with magnetic bar. A single phase sol was obtained after 10 h stirring. Sols were deposited on quartz substrates ($7 \times 2\ cm^2$) by a spinner. Xerogel films were obtained by vacuum drying the coated thin layer of sols at 40°C for 1 hr.

2.2. Viscosity Measurements

The relationship of viscosity vs solvent content of solutions and sol were studied to show the formation of oligomers in the sols. The solvent in solutions and sol was removed by vacuum oven at 40°C. The viscosity changes of solutions and sol were measured by a rotating viscometer (Brook Co.). The measurements of viscosities of solutions and sol were performed in a water bath at 20°C.

2.3. Fe_3O_4 Thin Film Preparations

A tube furnace with controlled atmosphere was used to prepare different thickness Fe_3O_4 films. These films, deposited on quartz substrates, were obtained by sintering the xerogel films at 450°C, under nitrogen atmosphere, for 3 h. Three different thickness films, from one to three layers of Fe_3O_4 films, were prepared by this method. Multilayer Fe_3O_4 thin films were prepared by deposition one on the other for two to three times.

2.4. Phase Identification of Fe_3O_4 Thin Films

The Fe_3O_4 phase was characterized on a Regaru D/MAX-IIIC diffractometer using Cu$K\alpha$ radiation. Since the films were so thin, a scanning rate of 5 s per step was used to obtain these XRD patterns.

2.5. Thermal Analysis of Fe_3O_4 Films

A Perkin–Elmer 7 Series thermal analysis system was used to study the thermal behavior of Fe_3O_4 films. The quartz substrates deposited with Fe_3O_4 films were cut into small pieces for TGA analysis. We used a three-step heating processes to study the thermal behavior of the Fe_3O_4 thin films; (a) purge the sample with oxygen gas for $\frac{1}{2}$ h at 30°C; (b) heat the film, with a 5°C/min heating rate, to 120°C and stay at the temperature for another $\frac{1}{2}$ h; and (c) heat the film again, with the same heating rate, to the final temperature of 600°C. A few pieces of quartz were used as blanks for TGA to compare the thermal behavior with that of Fe_3O_4 thin films.

2.6. Thin Film Thickness Measurements

Thicknesses of Fe_3O_4 thin films were measured by a surface texture analysis system (Dektak 3030 ST). Three different thickness Fe_3O_4 thin films were measured by this method. Thickness measurements were performed after part of the Fe_3O_4 thin films were carefully removed from the substrates with a small surgical knife. The scanning range on the thin films surface was 500 μm.

2.7. Surface Morphology Studies of Fe_3O_4 Thin Films

The surface morphology of the 120-, 200-, and 275-nm Fe_3O_4 thin films were examined by a scanning-electron microscope (JEOL JSM-840A SEM).

2.8. Magnetic Properties Measurements

The magnetic measurements have been carried out with a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design). Magnetization curves of the three different thickness films were directly measured from Fe_3O_4 films deposited on quartz substrates. The direction of the applied magnetic field was parallel to that of the substrates surface. The measurements were operated at 298 K in magnetic field from -1.0×10^4 to 1.0×10^4 Oe.

3. RESULTS AND DISCUSSIONS

3.1. Formation of Sols

Homogeneous sols were prepared by dissolving iron salts and polydentate ligands in ethanol. The lines A, B, and C from Fig. 1 are viscosity curves measured from three solutions prepared by separately dissolving iron(III) nitrate, ethylene glycol, and citric acid in ethanol. No obvious viscosity changes were seen as the solvent of these three solutions were slowly removed. Line D shows the viscosity curve measured from the sol prepared by mixing iron salts (iron(II) lactate and iron(III) nitrate) and chelating agents (ethylene glycol and citric acid) in ethanol. In the figure, only line D shows a dramatic viscosity increase as the solvent is slowly removed. A polymerization reaction occurred between the iron ions and the chelating agents to form oligomers in the sol. The viscosity increase is believed to be caused by the increasing interaction of oligomers, leading to the higher viscosity of the sol. A red light laser scattering was seen from the sols, which also showed the formation of oligomers. In the sols, iron(II) and iron(III) ions were well mixed. They were bonded to polydentate ligands and were randomly dispersed in the oligomers. Since the iron ions

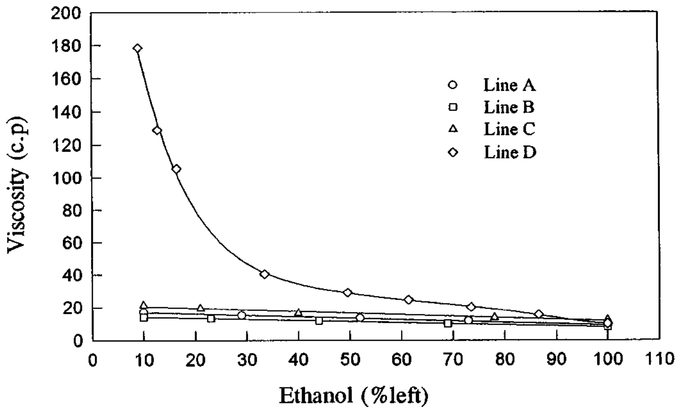

FIG. 1. Viscosity vs solvent content curves; line A, solution of iron(III) nitrate; line B, solution of ethylene glycol; line C, solution of citric acid; line D, sol prepared by dissolving iron(II) lactate, iron(III) nitrate, ethylene glycol, and citric acid in ethanol.

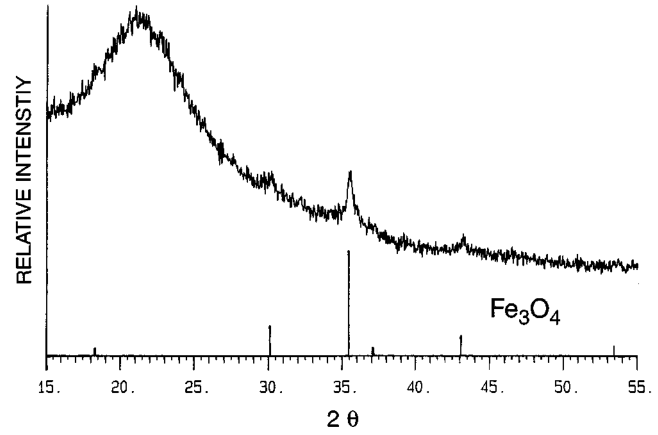

FIG. 2. XRD pattern of Fe_3O_4 thick film.

(iron(II) and iron(III)) are directly bonded to oxygen atoms and the distance between iron(II) and iron(III) is within molecular range, it increases the possibility of the oligomers to form Fe_3O_4 during a sintering process.

3.2. *Characterizations of Fe_3O_4 Thin Films*

The iron oxide thin film phase identifications were performed. The XRD pattern of Fe_3O_4 thicker film ($\sim$480 nm), prepared via the sol–gel method at 450°C identified the polycrystalline phase of Fe_3O_4 (Fig. 2). The three x-ray diffraction peaks at $2\theta = 30.16°$, $2\theta = 35.46°$, and $2\theta = 43.12°$ correspond to (220), (311), and (400) diffraction planes of Fe_3O_4. The broad diffraction peak at $2\theta = 21.52°$ corresponds to the background of the quartz substrate. According to literature, γ-Fe_2O_3 transforms to α-Fe_2O_3 at temperatures higher than 350°C (10). Since there is no α-Fe_2O_3 diffraction peak observed in the x-ray pattern, the phase of the obtained magnetic film is proved to be Fe_3O_4. It showed the sol–gel method is a successful method for preparing Fe_3O_4 films. The XRD pattern of 120-nm Fe_3O_4 thin film showed a very weak diffraction peak at $2\theta = 35.46°$ (Fig. 3a). As the film thickness increased, from one to three layers of Fe_3O_4, the intensity of the diffraction peak increased as well (Fig. 3b and 3c). Since the films were so thin, Fe_3O_4 thin films showed only one diffraction peak at 2θ near 35.46°. These XRD patterns proved that the obtained thin films were Fe_3O_4 films. Figure 3d shows the diffraction pattern of an oxidized Fe_3O_4 film. The diffraction peak at $2\theta = 33.62°$ corresponds to the phase of α-Fe_2O_3.

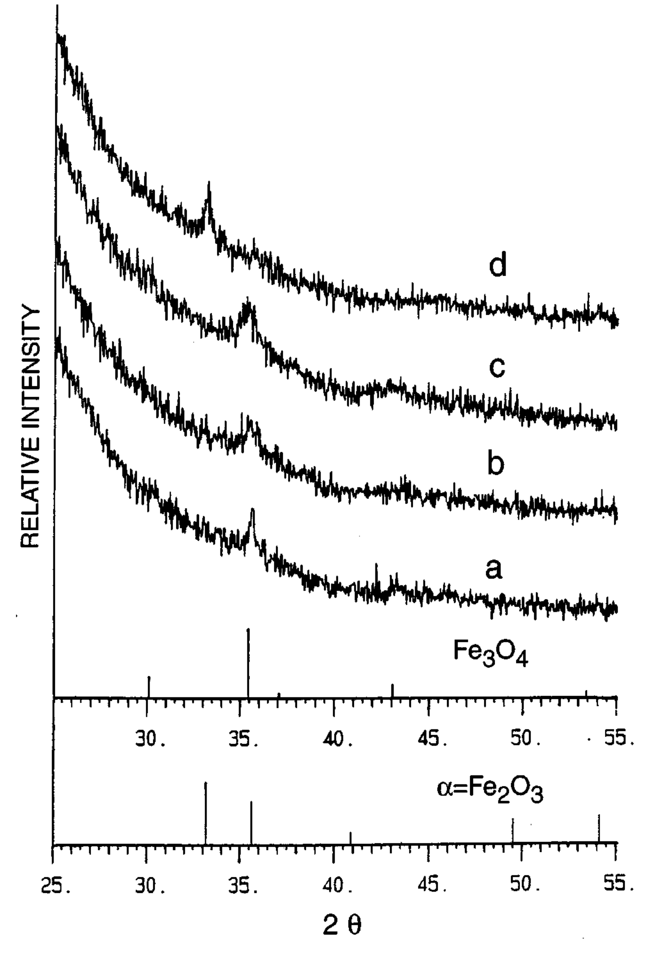

FIG. 3. XRD patterns of (a) 120-nm Fe_3O_4 thin film, (b) 200-nm Fe_3O_4 thin film, (c) 275-nm Fe_3O_4 thin film, and (d) α-Fe_2O_3 thin film.

Oxidization reaction of magnetite, $4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$, will gain in weight during the reaction. Thermogravimetric analysis was used to further verify the thin film phase of Fe_3O_4. TGA curve of Fe_3O_4 thick film (curve (a) Fig. 4) shows the weight gain process which corresponds to oxidization of Fe_3O_4 to α-Fe_2O_3. The oxidization temperature was lower than that of commercial Fe_3O_4 powder. It is believed to be caused by the ultra fine grain size of Fe_3O_4 in the films. The weight gain process not only shows the

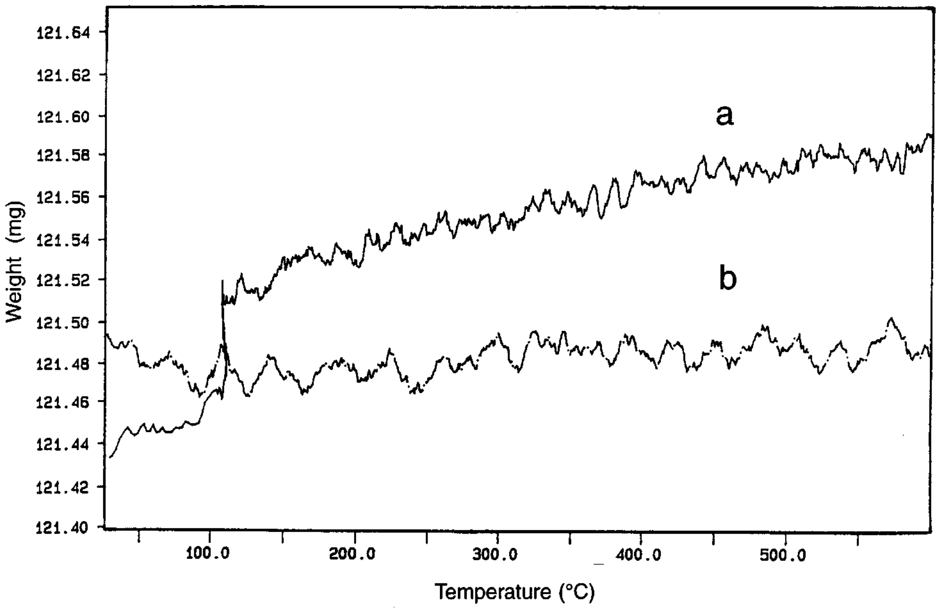

FIG. 4. (a) TGA curve of Fe_3O_4 film which was deposited on quartz substrate, (b) TGA curve of quartz substrate only.

obtained magnetic iron-oxide is Fe_3O_4, instead of γ-Fe_2O_3, but also shows that the Fe_3O_4 thin films do not have organic residue in the films.

Average thickness and roughness of Fe_3O_4 thin films were measured and are reported in Table 1. The average thickness of the three Fe_3O_4 films varied from around 120 to 275 nm. The average roughness of these films, measured to within a 100-μm scanning range, was smaller than 50 Å. The thickness variations of 120-, 200-, and 275-nm films, measured at two end points of a 100-μm scanning region, are 3.8, 2.0, and 2.1 nm respectively. These show that the thickness of these three films were rather uniform.

Surface morphology of these films were examined by SEM photographs. Figures 5, 6, and 7 show SEM photographs of surface morphology of 120-, 200-, and 275-nm Fe_3O_4 thin films. According to SEM, the Fe_3O_4 deposits were separated into small and uniform domains. The diameter of each domain is around 0.2 to 0.3 μm. The separation of these domains is believed to be caused by the difference of thermal expansion coefficient between Fe_3O_4 and quartz substrate. For different thickness films, the domain separation may cause an uncertainty in volume that is deposited on the unit substrate surface area. As the film thickness increased from 120 to 270 nm, no obvious surface morphology changes were seen on SEM photographs.

Table 1
Thicknesses of Fe_3O_4 Thin Films Prepared via Sol–Gel Method

Layers of Fe_3O_4 films	One layer	Two layers	Three layers
Average thickness	120.0 μm	200.0 μm	275.0 μm
Average roughness	3.7 μm	4.7 μm	3.2 μm

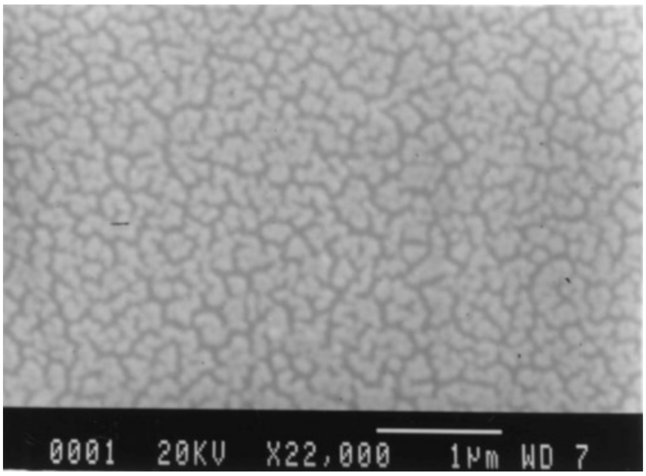

FIG. 5. SEM photograph of 120-nm Fe_3O_4 thin film.

3.3. *Magnetic Properties*

A SQUID magnetometer was used to study the magnetic properties of the three different thickness Fe_3O_4 thin films.

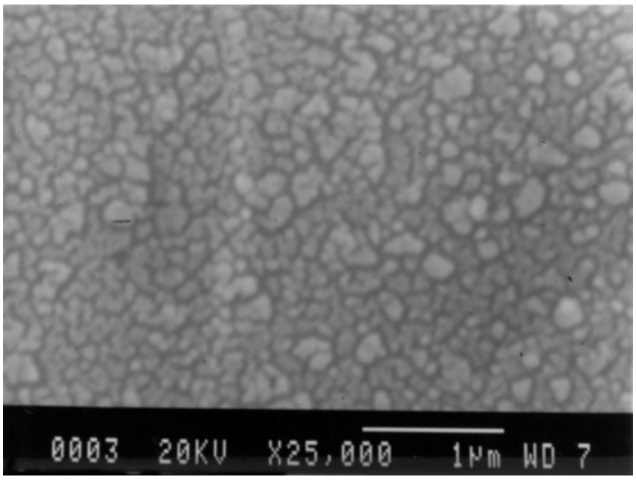

FIG. 6. SEM photograph of 200-nm Fe_3O_4 thin film.

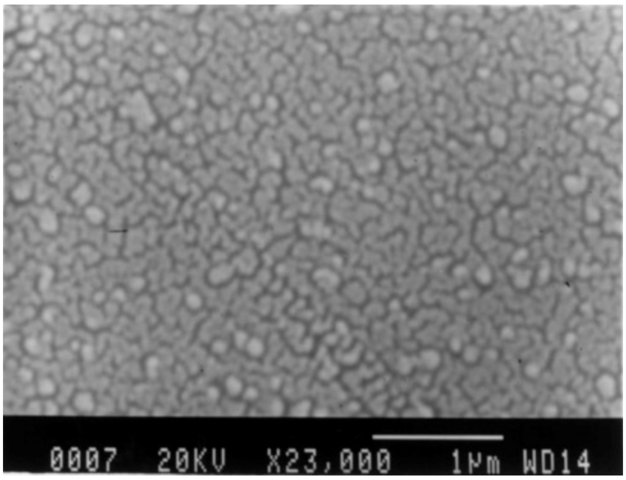

FIG. 7. SEM photograph of 275-nm Fe_3O_4 thin film.

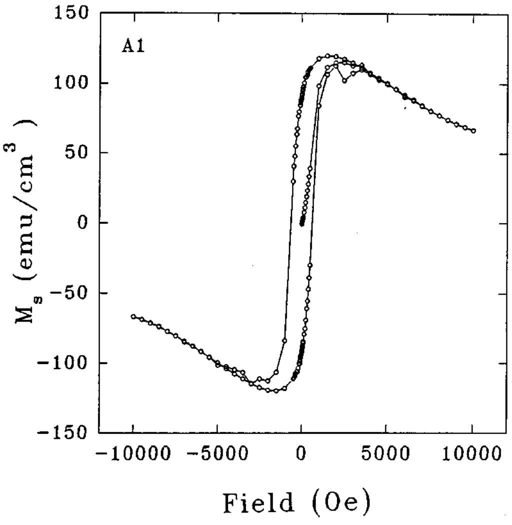

FIG. 8. The magnetization curve of 120-nm Fe_3O_4 thin film.

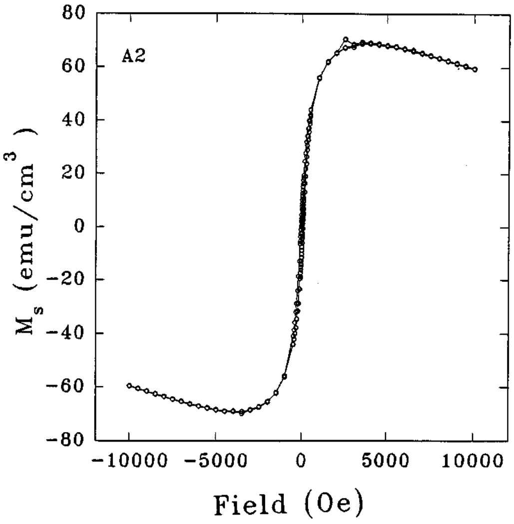

FIG. 9. The magnetization curve of 200-nm Fe_3O_4 thin film.

The applied magnetic field was from -1.0×10^4 to 1.0×10^4 Oe. The magnetic measurements were performed at room temperature. Figure 8 shows the hysteresis curve of Fe_3O_4 thin film with thickness of 120 nm. It shows a measured coercive force of 625 Oe with a saturation magnetization of 135 emu/cm^3. Figures 9 and 10 show the magnetic properties of bi- and trilayer thin films of Fe_3O_4, with thicknesses of 200 and 275 nm. The measured coercivity of these two films were 59 and 30 Oe, with saturation magnetization of 72 and 32 emu/cm^3. The low coercivity obtained in trilayer Fe_3O_4 thin films is believed to be caused by nanocrystalline Fe_3O_4 particles in the thin films. It was also found that as the film thickness decreased from 275 to 120 nm the coercivity of the films increased dramatically from 30 to 625 Oe. A demagnetization behavior was seen on these three films (Figs. 8–10). It showed that the saturation magnetization decreased with increasing applied magnetic field within high magnetic field range. This demagnetization behavior was seen only on very thin films and the demagnetization increased with decreasing film thinkness. These magnetic properties were seen on Fe_3O_4 thin films deposited on pyrex glass substrates as well. The causes of the demagnetization are still under study.

The obtained magnetic properties of Fe_3O_4 thin films show that magnetic properties of Fe_3O_4 are affected by both grain size and film thickness.

4. CONCLUSIONS

The sol–gel method shows it is a potential wet chemical method for preparing Fe_3O_4 thin films. Since the species

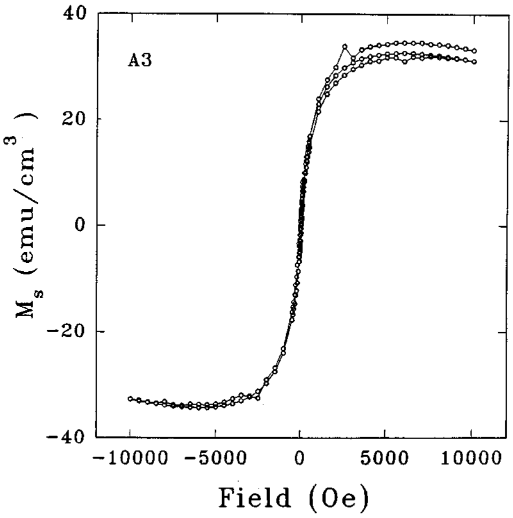

FIG. 10. The magnetization curve of 275-nm Fe_3O_4 thin film.

involved in the reactions are not sensitive to moisture and can be chemically controlled during the reactions, iron(II) and iron(III) salts can be directly used to prepare Fe_3O_4 thin films. The nanocrystalline particles of Fe_3O_4, formed in the films, cause the thin films to have distinct magnetic properties. It is believed that by changing reaction conditions even thinner and larger scale Fe_3O_4 thin films can be prepared by this method. It also shows that even more interesting magnetic properties will be seen on those thinner films.

ACKNOWLEDGMENT

This work was supported by the National Science Council of Taiwan, under Contract Numbers NSC82-0208-M-031-012-T and NSC83-0208-M-031-005.

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