Growth, magnetic properties and the effect of cobalt addition in metal-organic chemical vapour deposited (MOCVD) gamma iron oxide thin films for magnetic recording applications

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Abstract. The present study aims at investigating MOCVD technique for the deposition of magnetic oxide thin films using volatile metal-organic compounds as source material. A three-step scheme has been described to form $\gamma\text{-Fe}_2\text{O}_3$ phase starting from $\alpha\text{-Fe}_2\text{O}_3$ films as-deposited in optically heated atmospheric cold wall CVD reactor. Growth of $\gamma\text{-Fe}_2\text{O}_3$ in a two-step process has been performed by depositing Fe_3O_4 phase directly by resistively heated low-pressure CVD (LPCVD) technique. Role of substrate temperature in controlling the oxidation leading to direct formation of metastable $\gamma\text{-Fe}_2\text{O}_3$ phase (single-step scheme) by atmospheric CVD technique has been described. A new mode of introduction of cobalt in the film, namely heterogeneous dispersion of cobalt in the $\gamma\text{-Fe}_2\text{O}_3$ matrix, has also been described. Crystallographic structure, microstructure and magnetic properties of the films have been studied in detail. Biaxial vector coil and high-temperature magnetic studies were carried out for determining the nature of anisotropy in the $\gamma\text{-Fe}_2\text{O}_3$ film. Growth of $\gamma\text{-Fe}_2\text{O}_3$ films in different schemes have been discussed from the studies of growth kinetics in a cold- and hot-wall-type reactor chambers.

Keywords. MOCVD; LPCVD; $\gamma\text{-Fe}_2\text{O}_3$; cobalt-modified $\gamma\text{-Fe}_2\text{O}_3$ films; magnetocrystalline anisotropy; uniaxial anisotropy; coercivity.

1. Introduction

Ferrimagnetic oxides with their moderate values of coercivity and remanent magnetization are ideal as magnetic recording materials for fabrication of magnetic recording media. The demand for long-life, reliable and high-density recording media has led to extensive research both in materials development, mostly in the preparation of oxide (Kishimoto *et al* 1979) and metallic thin film media (Iwasaki *et al* 1979), and in the innovation of new recording techniques (Abe and Gomi 1990). Ferrimagnetic oxides are possible with different crystallographic structures, e.g. spinel structure with one or two metallic ions in a formula unit, hexagonal magneto-plumbite structure and garnet structure. Magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) phases of iron oxide possess spinel structure and are commercially used as magnetic recording material (Hattori *et al* 1979). Particulate iron oxide is a widely used medium for the magnetic recording of both continuous audio signals and discrete digital signals in longitudinal mode of operation (Mee *et al* 1967). Thrust for higher density (Bate 1978) of data storage in case of digital recording has forced researchers to improve upon the magnetic properties, e.g. coercivity and remanent magnetization of the existing iron oxide media. Extensive studies have also been undertaken to develop new materials, viz. Co-modified iron oxides (Nakamura *et al* 1987) and hexagonal ferrites like barium ferrite (Kotnala 1992) with magneto-plumbite structure. However, in particulate media there are constraints on further improvement of the density of

digital recording. As density of recording increases, volume of the recorded bit decreases. Small volume of the recorded bit leads to higher noise owing to statistical fluctuations of the number of magnetic particles in case of particulate media (Bate 1978). In high-density recording, as the recorded bits come close to each other, demagnetization field of two adjacent magnetized zones increases (Chantrell and O'Grady 1992). In order to remove the demagnetization effect magnetic particles with higher coercivity are required, which is difficult to obtain in case of micron-sized particles (Bate 1965). This led researchers to develop thin films of those materials with very fine grain size in order to improve the signal-to-noise ratio and coercivity of the recording media.

Maghemite phase of iron oxide ($\gamma\text{-Fe}_2\text{O}_3$) is widely used for its superior recording characteristics and high mechanical strength (Inagaki *et al* 1976). $\gamma\text{-Fe}_2\text{O}_3$ is a metastable phase of iron oxide and is preferred over the Fe_3O_4 phase, as the latter has lower oxidation state. Fe^{2+} ions are oxidized gradually under atmospheric conditions causing distortion in recorded information (Meiklejohn 1986). $\gamma\text{-Fe}_2\text{O}_3$ films are prepared mostly in a three-step process where $\alpha\text{-Fe}_2\text{O}_3$ phase is deposited by different techniques (Dhara *et al* 1992a) as a first step. As-deposited films are reduced to Fe_3O_4 phase in a controlled H_2 ambient at low temperature ($\leq 350^\circ\text{C}$) and finally these reduced films are annealed ($250\text{--}450^\circ\text{C}$) in oxygen and/or air ambient to form $\gamma\text{-Fe}_2\text{O}_3$ phase. A two-step process for the preparation of $\gamma\text{-Fe}_2\text{O}_3$ phase is also reported (Heller 1976), where Fe_3O_4 phase is deposited directly by reactive r.f. sputtering in a controlled Ar/O_2 ambient and the as-deposited films are oxidized to obtain $\gamma\text{-Fe}_2\text{O}_3$ phase. Direct deposition of $\gamma\text{-Fe}_2\text{O}_3$ phase is also successfully reported (Ohta and Terada 1986) by pulsed reactive r.f. sputtering of iron target.

Addition of cobalt in the formation of maghemite phase leads to the formation of Co-modified $\gamma\text{-Fe}_2\text{O}_3$ phase. Co^{2+} plays a crucial role in introducing anisotropy in the medium, which is likely to arise from the exchange coupling between Co^{2+} and Fe^{3+} ions as suggested first by Slonczewski (1958) and then later on by Tachiki (1960). Cobalt addition enhances anisotropy in the iron oxide media as seen from earlier reports (Nakamura *et al* 1987) where 0–6 at. wt.% of cobalt was used for the formation of Co-modified $\gamma\text{-Fe}_2\text{O}_3$ phase. In particulate media, cobalt can be introduced using several processes such as by Co-doping (Koster 1972), by Co-adsorption (Imaoka *et al* 1978) and by epitaxial surface deposition of Co-ferrite (Kishimoto *et al* 1979). Location of Co^{2+} ions in the lattice of $\gamma\text{-Fe}_2\text{O}_3$ determines the nature of anisotropy introduced in the medium and the stability of the medium. Co-doped $\gamma\text{-Fe}_2\text{O}_3$ medium shows the presence of uniaxial anisotropy and magnetic instability in the medium (Hayama *et al* 1980). This instability in the medium is ascribed to the movement of Co^{2+} ions in the Co-doped medium. The strong temperature dependence of coercivity confirms the uniaxial nature of anisotropy present in the medium. On the other hand, Co-adsorbed and epitaxial surface deposited media show magnetocrystalline anisotropy and magnetic stability in the media. Coercivity in case of Co-adsorbed medium shows insignificant temperature dependence (Meng *et al* 1987).

Perhaps the most basic change in the last fifteen years or so has been the use of continuous thin-film media of iron-based magnetic oxides instead of particulate media for the purpose of high-density digital recording and to increase signal-to-noise ratio at high density of recording. The most extensively used technique for processing these materials in thin-film form is reactive r.f. sputtering (Chen *et al* 1988) followed by post-deposition heat treatment. Alternative deposition techniques have, however,

received little or no attention. Among these, chemical vapour deposition (CVD) offers several advantages like high deposition rate capability and novel process controls which would be useful in obtaining the desired composition and structure. So far these iron and iron oxide-based thin films have been deposited by CVD techniques involving deposition from pure iron source using HCl transport (Babkin *et al* 1984) and by MOCVD technique employing metal-organic complexes of iron acetyl acetonate as the source material (Dhara *et al* 1992a). Thus while only isolated studies on CVD technique have been done, practically no detailed studies have been reported on undoped and cobalt-doped iron oxide.

Keeping the above perspective, the present study aims at studying the MOCVD technique for the deposition of magnetic oxide thin films using volatile metal-organic compounds as source material. The growth techniques of magnetic iron oxide films in three different possible schemes are discussed. A three-step scheme to form $\gamma\text{-Fe}_2\text{O}_3$ phase starting from $\alpha\text{-Fe}_2\text{O}_3$ films as-deposited by optically heated atmospheric chemical vapour deposition in a cold-wall CVD reactor using metal-organic complexes of Fe^{3+} (MOCVD) has been described. Growth of $\gamma\text{-Fe}_2\text{O}_3$ in a two-step process has also been performed by depositing Fe_3O_4 phase directly by resistively heated low-pressure MOCVD reactor. Direct deposition of $\gamma\text{-Fe}_2\text{O}_3$ films in a single-step scheme by atmospheric MOCVD technique has been described.

2. Experimental

Iron oxide thin films were deposited on glass substrates (Corning #7059) by CVD technique using ferric β -diketonates of acetyl acetonate or dipivaloylmethanate (DPM). Argon was used as the transporting gas. In the three-step and single-step schemes deposition was carried out in a cold-wall-type tubular optically heated atmospheric CVD reactor (figure 1). Substrates on graphite susceptor kept horizontal with respect to vapour direction were indirectly heated by tungsten halogen lamps. Precursors were evaporated by a secondary heater. Typical carrier gas flow rate was 1.5 l per min. Cobalt was added to iron oxide films by coevaporating cobaltus acetyl acetonate with ferric acetyl acetonate, used in those two schemes. Ferric acetyl acetonate $[\text{Fe}(\text{acac})_3]$ and cobaltus acetyl acetonate $[\text{Co}(\text{acac})_2]$ complexes were synthesized by refluxing FeCl_3 and CoSO_4 with acetyl acetonate and controlling pH

Figure 1. Schematic of optically heated CVD reactor.

Figure 2. Schematic of resistively heated CVD reactor.

to 5–6 with subsequent purification process of recrystallization and sublimation.

In the two-step scheme, deposition was performed in a hot-wall-type resistively heated low-pressure CVD (LPCVD) reactor chamber (figure 2). Substrates on steel susceptor inclined at 45° with respect to vapour direction were heated resistively in a separate zone followed by a mixer zone where evaporant from resistively heated source heating zone was fed into. More than one evaporation chamber facilitate the growth of multicomponent films. In the present study we have used only one evaporation chamber for the growth of iron oxide films. Metal-organic DPM complex of iron $[\text{Fe}(\text{DPM})_3]$ was used as precursor. $\text{Fe}(\text{DPM})_3$ was prepared by using FeCl_3 and HDPM in an alcoholic solution and purifying the precipitate by recrystallization and sublimation techniques.

Specific experimental conditions for deposition of iron oxide films in different schemes and Co-modified films are given below.

(i) *Three-step scheme:* The iron oxide films were deposited in the cold-wall-type atmospheric CVD reactor at a substrate temperature in the range of 350 – 450°C . Precursor $[\text{Fe}(\text{acac})_3]$ evaporation temperature was $\approx 190^\circ\text{C}$. As-deposited films were first reduced and then oxidized by annealing in H_2 and oxygen ambients respectively in a separate furnace. The reduction was performed in H_2 ambient at 350°C for 5 h. Oxidation was accomplished in oxygen ambient for 3 h at 350°C .

(ii) *Two-step scheme:* The iron oxide films were deposited in the resistively heated LPCVD reactor at a substrate temperature in the range of 500 – 550°C . Source $[\text{Fe}(\text{DPM})_3]$ evaporation temperature was $\approx 165^\circ\text{C}$. Films were deposited at a pressure of 0.5 torr of Ar which also acted as the carrier gas. The flow rate of Ar was kept constant and outlet port pumping rate was controlled to maintain the pressure for transporting $\text{Fe}(\text{DPM})_3$ vapour to the reaction zone. Thickness of the deposited films was measured by the stylus technique and varied between 800 and

Table 1. Film compositions with respect to cobalt content (at%) in the film.

Cobalt (at%)	x in $\text{Fe}_{2-x}\text{Co}_x\text{O}_{3-s}$
0.0	0.0
0.5	0.02
2.0	0.09
4.0	0.17
6.0	0.26

1600 Å. As-deposited Fe_3O_4 films were annealed in O_2 ambient at 350°C for 3 h in order to form $\gamma\text{-Fe}_2\text{O}_3$ films.

(iii) *Single-step scheme*: Iron oxide films were deposited in the cold-wall-type atmospheric CVD reactor at a substrate temperature of 500°C. $\text{Co}(\text{acac})_2$ complex was added to the source $[\text{Fe}(\text{acac})_3]$ material corresponding to cobalt fraction ranging from 0.5 to 6 at%. Corresponding film compositions are described in table 1. In some experiments, the as-deposited films were reduced (350°C/5 h) in H_2 and then oxidized (350°C/3 h) in O_2 to confirm the presence of $\gamma\text{-Fe}_2\text{O}_3$ in those films.

(iv) *Cobalt modification in three-step scheme*: Cobalt modified iron oxide films were deposited in the atmospheric CVD reactor at a substrate temperature in the range of 350–450°C. $\text{Co}(\text{acac})_3$ was coevaporated with $\text{Fe}(\text{acac})_3$ at $\approx 190^\circ\text{C}$ to add 6 at% of cobalt in the film ($\text{Fe}_{1.78}\text{Co}_{0.22}\text{O}_{2.87}$). As-deposited films were reduced in H_2 ambient at 350°C for 5 h and subsequently oxidized at a temperature in the range of 250–450°C for 3 h.

The microstructures were analysed by transmission electron microscope (TEM) studies and crystallographic phases were detected by selected area electron diffraction (SAED) and X-ray diffraction studies. Magnetic properties were determined using a vibrating sample magnetometer (VSM: model DMS-1660).

3. Results and discussion

3.1 Compositional analysis

Figure 3 shows the depth profile of the 2500 Å (corresponding to etch time of 200 sec) iron oxide film as-deposited in the three-step scheme at $T_s = 450^\circ\text{C}$. 48 at% of oxygen and 45 at% of iron were found in the bulk of the film. Carbon stayed as an impurity, at a high level of 40 at% on the surface of the film. Carbon content went down to ≈ 7 at% after 15 sec of etching.

Figure 4 shows the depth profile of the 4000 Å iron oxide film as-deposited in the single-step scheme. The film composition was 44 at% of oxygen, 42 at% of iron and 6 at% of cobalt. Carbon stayed as an impurity, at an appreciably high 80 at%, on the surface of the film. Carbon content went down to ≈ 8 at% after 90 sec of etching.

Figure 3. Depth profile analysis of as-deposited iron oxide film grown in the first step of three-step scheme.

Figure 4. Depth profile analysis of as-deposited Co-doped iron oxide film grown in the single-step scheme.

3.2 Microstructure and crystalline phases

3.2a Structural evolution of γ - Fe_2O_3 phase from α - Fe_2O_3

Three-step scheme: We have studied the structural transformation of as-deposited α - Fe_2O_3 phase to γ - Fe_2O_3 phase by successive reduction and oxidation treatment. A detailed crystallographic structural analysis of the electron diffraction patterns of iron oxide films deposited under different conditions showed that as-deposited films always formed in the α - Fe_2O_3 phase, irrespective of the substrate temperature. As-deposited films generally consisted of nodular crystallites. These crystallites were well dispersed and at some places formed clusters. Clearly, this appears to be a consequence of the modified deposition mechanisms, discussed in the section dealing with the growth model.

When the as-deposited films were subjected to reduction–oxidation treatment in order to crystallize the γ -phase of Fe_2O_3 with the formation of an intermediate Fe_3O_4 phase after the reduction treatment, the morphology of the deposits did not undergo

Figure 5. Transmission electron micrograph showing microstructure of $\gamma\text{-Fe}_2\text{O}_3$ film grown in three-step scheme. Corresponding electron diffraction pattern is shown in the inset.

any significant change. Small increase in crystallite size was, however, observed which can be attributed to possible grain growth or homogenization. Figure 5 shows microstructures of the iron oxide thin film in the $\gamma\text{-Fe}_2\text{O}_3$ phase obtained after an oxidation at 300°C of the as-deposited films. Highly oriented crystallite structure could be characterized by diffraction spots in oxidized films (inset of figure 5). Analysis of the diffraction pattern of the $\gamma\text{-Fe}_2\text{O}_3$ film indicated that these films consisted of essentially the iron-rich $\gamma\text{-Fe}_2\text{O}_3$ phase. When interpreted in terms of the deposition mechanism in a cold-wall-type reactor chamber, it implies an insufficient oxidation of the Fe^{3+} ions depositing on the substrate from the pyrolysis of $\text{Fe}(\text{acac})_3$ complex. Characteristic diffraction rings were observed corresponding to diffraction from (220), (311), (400), (440) and (511) crystal planes of $\gamma\text{-Fe}_2\text{O}_3$ films. Derivation of the lattice parameter from the diffraction data yielded a value of $8.37\text{ \AA}$ which is in between the lattice parameters for iron oxide in stoichiometric Fe_3O_4 phase ($8.397\text{ \AA}$) and $\gamma\text{-Fe}_2\text{O}_3$ phase ($8.34\text{ \AA}$). An intermediate value of the lattice parameter of $\gamma\text{-Fe}_2\text{O}_3$ film indicates that these films were oxygen-deficient (Ohta and Terada 1986).

3.2b Structural transformation of as-deposited Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$

Two-step scheme: We have studied the crystallographic structure of as-deposited Fe_3O_4 and oxidized $\gamma\text{-Fe}_2\text{O}_3$ phase. Small-angle X-ray diffraction pattern of the as-deposited film (figure 6a) shows the peaks corresponding to (*hkl*) planes (220), (222), (311), (400), (511) and (440). These were interpreted to belong to magnetite (Fe_3O_4) phase. Observation of a weak fingerprint line from (222) plane provided

Figure 6. X-ray diffraction pattern of iron oxide films grown in two-step scheme for (a) as-deposited Fe₃O₄ and (b) oxidized γ-Fe₂O₃ phases.

further confirmation of the Fe₃O₄ phase in the as-deposited films. Lattice parameter calculated from this data was 8.48 Å. A comparison with standard lattice parameter value of 8.397 Å for stoichiometric bulk Fe₃O₄ phase shows that it is on the higher side. This indicates the presence of some oxygen deficiency in what was essentially a Fe₃O₄ film. The X-ray diffraction pattern of the oxidized film (figure 6b) shows the peaks corresponding to (220), (311), (511) and (440) reflections indicating formation of γ-Fe₂O₃ phase in the oxidized film. The lattice parameter calculated from diffraction data was 8.35 Å which is close to that reported for bulk γ-Fe₂O₃ phase (8.34 Å). Growth of stoichiometric γ-Fe₂O₃ phase on oxidation clearly established that as-deposited film contained mainly the Fe₃O₄ phase.

3.2c Direct growth of γ-Fe₂O₃ phase and its structural confirmation

Single-step scheme: In general, iron oxide films deposited at substrate temperature (T_s) between 300 and 500°C consisted of mainly α-Fe₂O₃ phase as revealed by the electron diffraction analysis. A direct growth of γ-Fe₂O₃ film occurs when the deposition is carried out at substrate temperature $T_s \geq 500^\circ\text{C}$. The electron diffraction pattern (inset of figure 7) consists of sharp rings and spots which clearly show that γ-Fe₂O₃ films are highly oriented with large crystallite size. In addition to diffraction

Figure 7. Transmission electron micrograph showing microstructure of as-deposited $\gamma\text{-Fe}_2\text{O}_3$ film grown in single-step scheme. Corresponding electron diffraction pattern is shown in the inset.

rings corresponding to (110), (220), (311), (400), (511) and (440) planes, characteristic superlattice diffraction from (211) plane clearly establishes that $\gamma\text{-Fe}_2\text{O}_3$ was the dominant growth phase. Microstructure of $\gamma\text{-Fe}_2\text{O}_3$ films (figure 7) is granular with well-compacted grains of average dimension $430 (\pm 80) \text{ \AA}$. The lattice constant of the $\gamma\text{-Fe}_2\text{O}_3$ phase in the as-deposited films as calculated from diffraction data was typically $8.375 \text{ \AA}$. This is somewhat higher in comparison with that for bulk $\gamma\text{-Fe}_2\text{O}_3$ ($8.34 \text{ \AA}$) which implies a deficiency in oxygen or the presence of minor components of less oxidized phases in what was essentially the $\gamma\text{-Fe}_2\text{O}_3$ film. In fact, additional lines in the diffraction pattern corresponding to (*hkl*) lines of (222) and (444) for Fe_3O_4 phase were also observed. To confirm that $\gamma\text{-Fe}_2\text{O}_3$ was the main growth phase, the as-deposited films were first reduced in hydrogen at 350°C for 5 h and then reoxidized at 350°C for 3 h in oxygen. Electron diffraction studies of films after hydrogen reduction show most of the main Fe_3O_4 diffraction rings including the fingerprint diffraction ring corresponding to the (222) reflection. The lattice parameter as calculated from diffraction analysis of the reduced film was $8.405 \text{ \AA}$ which agreed well with standard values for Fe_3O_4 phase in the reduced films. Electron diffraction data confirmed that, on reoxidation, as one should expect, these films reverted to the $\gamma\text{-Fe}_2\text{O}_3$ phase. This study clearly established that as-deposited films were $\gamma\text{-Fe}_2\text{O}_3$.

3.2d Structures of cobalt-modified iron oxide films

Under most general growth conditions undoped iron oxide films formed by CVD process are in the form of $\alpha\text{-Fe}_2\text{O}_3$ phase. Incorporation of Co^{2+} ions in the film during the growth stage does not have any effect on the crystallographic phase of the deposited film. Consequently no discernible improvement in the magnetic properties

Figure 8. Transmission electron micrograph showing microstructure of Co-modified $\gamma\text{-Fe}_2\text{O}_3$ film. Corresponding electron diffraction pattern is shown in the inset.

of the Co-modified iron oxide films were observed. Co-modified iron oxide films just as in the undoped case were required to be subjected to a H_2 reduction and controlled oxidation sequence in order to achieve the magnetic $\gamma\text{-Fe}_2\text{O}_3$ phase. Figure 8 shows microstructure and corresponding electron diffraction pattern for Co-modified $\gamma\text{-Fe}_2\text{O}_3$ films. Fine grain and generally defect-riddled microstructure of as-deposited film transformed to a compact granular structure in the Fe_3O_4 phase. A detailed study of the oxidation behaviour using electron diffraction pattern indicated that a large fraction of the reduced film was transformed to $\gamma\text{-Fe}_2\text{O}_3$ phase at a threshold oxidation temperature, T_{ox} , of 250°C . Oxidation at above the threshold temperature in the range $250^\circ\text{C} < T_{\text{ox}} < 450^\circ\text{C}$ was generally accompanied by considerable grain growth in the $\gamma\text{-Fe}_2\text{O}_3$ film. Directly reduced Fe_3O_4 film showed spinel structure as evidenced from the diffraction analysis. Oxidation of these films under steady-state conditions leading to transformation to $\gamma\text{-Fe}_2\text{O}_3$ phase was established by diffraction rings (inset of figure 8) corresponding to (111), (220), (311), (400), (511) along with superlattice reflections from the plane (211). The lattice parameter for a typical $\gamma\text{-Fe}_2\text{O}_3$ film is $8.34 \text{ \AA}$. This agrees well with the standard value of $8.339 \text{ \AA}$ for bulk $\gamma\text{-Fe}_2\text{O}_3$ suggesting that $\gamma\text{-Fe}_2\text{O}_3$ films were synthesized by controlled oxidation of Fe_3O_4 films.

3.3 Magnetic properties

3.3a M – H loop characteristics

(i) *Three-step scheme:* As-deposited iron oxide films, irrespective of deposition temperature, were weakly ferromagnetic being essentially in the $\alpha\text{-Fe}_2\text{O}_3$ phase. These

Figure 9. Characteristic M - H loops of reduced Fe_3O_4 and oxidized $\gamma\text{-Fe}_2\text{O}_3$ films grown in three-step scheme. Magnetic properties are shown in the inset.

films on reduction to the Fe_3O_4 phase showed a saturation magnetization ($\mu_0 M_s$) value of 310 mT, remanent magnetization (M_r) value of 181 mT, and coercivity (H_c) value of 18 kA/m (figure 9). On oxidation to form $\gamma\text{-Fe}_2\text{O}_3$ phase the M_r and H_c values of the films increased to 270 mT and 61 kA/m. Squareness ratio ($\text{SQ} = M_r/M_s$) of the Fe_3O_4 film was 0.58. After oxidation, the SQ for $\gamma\text{-Fe}_2\text{O}_3$ films increased to a considerably high value of 0.76. The coercive squareness (S^*) which provides a measure of slant of the M - H loop and is given by

$$S^* = 1 - \left(\frac{M_r}{H_c} \right) \left(\frac{1}{\text{slope at } H_c} \right),$$

has also been measured to be 0.30 for the $\gamma\text{-Fe}_2\text{O}_3$ films. Enhancement in M_r , H_c and SQ parameters in $\gamma\text{-Fe}_2\text{O}_3$ is attributed to introduction of strong anisotropy in the film. It is apparent that the changes in the microstructure of the film could also be responsible for it. This is discussed in the growth model section.

(ii) *Two-step scheme:* Figure 10 shows a comparison of typical hysteresis loops for the as-deposited Fe_3O_4 and oxidized $\gamma\text{-Fe}_2\text{O}_3$ films. Increase in H_c from 93 kA/m for as-deposited Fe_3O_4 film to 122 kA/m for oxidized $\gamma\text{-Fe}_2\text{O}_3$ film is attributed to anisotropy introduced by redistribution of Fe^{3+} and vacancies among octahedral and tetrahedral sites of spinel lattice. $\gamma\text{-Fe}_2\text{O}_3$ showed M_r and SQ values of 102 mT and 0.80 respectively.

(iii) *Magnetic properties of directly deposited Co-doped $\gamma\text{-Fe}_2\text{O}_3$ films—single-step scheme:* The magnetic properties of the directly deposited $\gamma\text{-Fe}_2\text{O}_3$ films were in general superior to the conventionally formed $\gamma\text{-Fe}_2\text{O}_3$ films through a reduction-oxidation process. This is attributed to the fractional variations in the partial presence of Fe_3O_4 phase in $\gamma\text{-Fe}_2\text{O}_3$. Figure 11 shows characteristic M - H loop of $\gamma\text{-Fe}_2\text{O}_3$ films containing 6 at% of cobalt directly deposited at substrate temperature of $\approx 500^\circ\text{C}$. The inferred magnetic parameters are shown in the inset. Typically the H_c values of directly deposited $\gamma\text{-Fe}_2\text{O}_3$ films ranged from 119 to 237 kA/m depending upon the cobalt concentration in the film with highest H_c of 237 kA/m. This film showed M_r , SQ and S^* values of 281 mT, 0.83 and 0.60,

Figure 10. Characteristic $M-H$ loops of as-deposited Fe_3O_4 and oxidized $\gamma\text{-Fe}_2\text{O}_3$ films grown in two-step scheme. Magnetic properties are shown in the inset.

Figure 11. Characteristic $M-H$ loops of iron oxide films containing 6 at% cobalt for directly deposited $\gamma\text{-Fe}_2\text{O}_3$ at $T_s = 500^\circ\text{C}$ and as-deposited $\alpha\text{-Fe}_2\text{O}_3$ films at $T_s = 400^\circ\text{C}$. Magnetic properties are shown in the inset.

respectively, which are higher than those of the r.f. sputtered films (Ohta and Terada 1986).

High coercivity values of directly deposited $\gamma\text{-Fe}_2\text{O}_3$ at $T_s = 500^\circ\text{C}$ underwent a deterioration upon reduction due to transformation to a Fe_3O_4 phase. Reoxidation to $\gamma\text{-Fe}_2\text{O}_3$ phase improved the properties but these remained inferior to those of the directly as-deposited film. In contrast, the $\alpha\text{-Fe}_2\text{O}_3$ films formed at a lower deposition temperature of 400°C showed considerable improvement in H_c values as reduction led to growth of Fe_3O_4 phase. These results confirmed the formation of $\gamma\text{-Fe}_2\text{O}_3$ phase as concluded from the crystallographic studies.

In order to explore the nature of the anisotropy introduced by cobalt in these films, biaxial vector coil measurements were performed (Ouchi and Iwasaki 1988). To carry out biaxial magnetic measurements, two orthogonal sets of sensing coils were used in VSM. The magnetization vectors at different film orientation angles (Ω) between 0 and 180° with respect to the direction of applied magnetic field (H_a) were determined by measuring the parallel (M_x) and perpendicular (M_y) components

Figure 12. Variation of magnetization (M_Y) perpendicular to applied field direction at different orientation angles (Ω) for Co-doped γ - Fe_2O_3 films grown in single-step scheme.

of magnetization. From these sets of data, the magnetization in the plane of the film (M_L) and that perpendicular to the film plane (M_Y) could also be computed as a function of Ω . Anisotropy energy (K) in the film can be calculated from these data. These measurements have shown that the direction of anisotropy lies in the film plane. Variation of M_Y with Ω has been studied for γ - Fe_2O_3 films with 0.5–6 at% cobalt (figure 12). Symmetric variation of M_Y was observed for the films in the 0–90° and 90–180° range which indicated magnetocrystalline anisotropy arising from the cobalt present in the film.

(iv) *Magnetic properties of heterogeneously dispersed Co-modified iron oxide films:* Figure 13 shows typical hysteresis loops for the reduced Fe_3O_4 and γ - Fe_2O_3 films. The remanent magnetization, coercive force and squareness ratio of the γ - Fe_2O_3 films were observed to be 220 mT, 65 kA/m and 0.60 respectively. These values are higher than those for Fe_3O_4 films. S^* parameter close to 0.40 was obtained for both films.

As discussed earlier extensive transformation of Fe_3O_4 film to γ - Fe_2O_3 phase takes place even at a moderate temperature of 250°C. However, it was found that oxidation at higher temperature (> 250–450°C) had profound effect on the magnetic properties of Co-modified γ - Fe_2O_3 films. The transformation of Fe_3O_4 film to γ - Fe_2O_3 phase by 250°C oxidation did not significantly improve the M_r value which changed from 156 mT for Co-modified Fe_3O_4 to 161 mT for Co-modified γ - Fe_2O_3 . Clearly, therefore, Co^{2+} ion positions in the γ -phase are not affected much during the 250°C oxidation process. The magnetic properties of Co-modified iron oxide films in the γ - Fe_2O_3 form were strongly dependent on the oxidation temperatures. Figure 14 shows the variation of magnetic coercivity in the film plane [$H_c(\parallel)$] and perpendicular to the film plane [$H_c(\perp)$] with the oxidation temperature. The incremental changes in the $H_c(\parallel)$ show two distinct regions marked by different slopes indicating two different mechanisms of H_c enhancement. For the Co-modified γ - Fe_2O_3 film formed at 250°C, an initial high value of coercivity of 33 kA/m was obtained. This value further increased by a factor of two to 65 kA/m when oxidation was carried out at 350°C. It may be noted that these H_c values were quite high in comparison with a minimum H_c of 44 kA/m obtained in earlier studies for Co-doped, 49 kA/m for epitaxial Co-ferrites and 59 kA/m for Co-adsorbed iron oxide. Such high coercivity values obtained in our CVD prepared films are attributed to an increase in the

Figure 13. Characteristic M - H loops of Co-modified iron oxide films for reduced Fe_3O_4 and oxidized $\gamma\text{-Fe}_2\text{O}_3$ films. Magnetic properties are shown in the inset.

Figure 14. Dependence of coercivity (a) in the plane and (b) perpendicular to the plane of the $\gamma\text{-Fe}_2\text{O}_3$ film on oxidation temperature.

anisotropy from microstructured Co-inclusions in the $\gamma\text{-Fe}_2\text{O}_3$ film where Co^{2+} locations differ from those at octahedral sites in the spinel structure and those which are trapped at interstitial locations other than lattice sites of the spinel structure.

Biaxial magnetic measurements were done to understand the above observation of Co-dispersion in $\gamma\text{-Fe}_2\text{O}_3$ matrix. Figure 15 shows the changes in the M_Y component with Ω at an applied field (H_a) of 4 kOe. An increase in M_Y (at 90°) was observed when the oxidation temperature was kept at 350°C . Fe^{2+} to Fe^{3+} transformation and redistribution of Fe^{3+} and vacancies among tetrahedral and octahedral sites of spinel lattice were responsible for increase in average saturation values (Dhara *et al* 1992b). Asymmetric nature of the M_Y curve in the 0 - 90° and 90 - 180° regions indicated that anisotropies of different physical nature were present in the film. As discussed earlier, heterogeneous nature of the Co^{2+} dispersions involving Co^{2+} at octahedral (magnetocrystalline) and interstitial (uniaxial) sites may be partly responsible for this behaviour. Completely different behaviour of M_Y in case of $\gamma\text{-Fe}_2\text{O}_3$ film oxidized at 400°C was observed. Not only was the net value

Figure 15. Variation of magnetization (M_y) perpendicular to applied field direction at different orientation angles (Ω) for Co-modified $\gamma\text{-Fe}_2\text{O}_3$.

Figure 16. Variation of anisotropy energy at different orientation angles (Ω) for Co-modified $\gamma\text{-Fe}_2\text{O}_3$ films.

of M_y (at 90°) lower but the angular dependence was more symmetrical (sinusoidal). The $\gamma\text{-Fe}_2\text{O}_3$ film at this oxidation temperature showed strong magnetocrystalline anisotropy as a result of increase in number of Co^{2+} ions at cation sites. Consequently a reduction in extent of Co^{2+} heterogeneity might have led to this behaviour. Anisotropy energy showed a maximum at 271 J/m^3 for a film oxidized at 400°C . A film with an oxidizing temperature of 250°C showed a value of 264 J/m^3 (figure 16). On the other hand, films annealed at 350°C showed a low anisotropy value of 81 J/m^3 . A confirmation of the heterogeneity model is provided by the studies of variation of coercivity of the Co-modified $\gamma\text{-Fe}_2\text{O}_3$ films with the orientation angle Ω as obtained from vector magnetic measurements. This is presented in figure 17. The H_c values for $\gamma\text{-Fe}_2\text{O}_3$ film formed at low oxidation temperatures ($250\text{--}350^\circ\text{C}$) exhibited a peak at Ω of 60° . This anisotropic nature is attributed to microstructure-related anisotropy present in the film due to the presence of strong magnetostatic interaction (Lu and Charap 1992) in $\gamma\text{-Fe}_2\text{O}_3$ regions with Co^{2+} trapped at interstitial and Co^{2+} at octahedral sites. As the oxidation temperature was increased, the microstructure-related

Figure 17. Variation of in-plane coercivity (H_c) at different orientation angles (Ω) for Co-modified γ - Fe_2O_3 films.

Figure 18. Variation of magnetization with applied field for Co-modified γ - Fe_2O_3 films.

contribution to anisotropy progressively decreased. As a result, a monotonous decrease in the coercivity for film oxidized at 400°C and disappearance of the coercivity maximum in figure 17 was observed. This clearly indicates that contribution to anisotropy is dominated by magnetocrystalline type due to migration of interstitially trapped Co^{2+} to cation sites (Speliotis and Judge 1991).

The dispersion of cobalt in ferrimagnetic γ - Fe_2O_3 matrix was studied by measuring magnetization (figure 18) at 600°C which is more than the Curie temperature (T_C) of γ - Fe_2O_3 but lower than that of ferromagnetic cobalt species ($T_C \approx 800^\circ\text{C}$) of films oxidized at 300°C and 400°C oxidized films. A higher magnetization value for the films oxidized at 400°C than that for the 300°C oxidized one indicated that clusters of cobalt were present in the former. On the other hand, lower value of magnetization for 300°C oxidized film indicated that cobalt is well dispersed through the entire volume of the specimen. These data lend further support to our earlier conclusions regarding Co-heterogeneity (Beck 1971).

3.3b Temperature dependence of coercivity

(i) *Two-step scheme*: Coercivity decreased almost linearly with increase in temperature for $\gamma\text{-Fe}_2\text{O}_3$ films deposited using the two-step scheme (figure 19). In the undoped iron oxide films, only the induced anisotropy, originating from the redistribution of Fe^{3+} ions and vacancies among octahedral and tetrahedral sites, remains in the film which is not strongly dependent on temperature. Curie temperature of the $\gamma\text{-Fe}_2\text{O}_3$ films oxidized from directly deposited Fe_3O_4 films was found to be 550°C .

(ii) *Nature of anisotropy in directly deposited Co-doped $\gamma\text{-Fe}_2\text{O}_3$ film—single-step scheme*: Temperature dependence of coercivity of the $\gamma\text{-Fe}_2\text{O}_3$ films deposited in the single-step scheme and containing 0.5–6 at% of cobalt was studied to find out the nature of anisotropy in the films introduced by Co^{2+} ions. Figure 20 shows the temperature dependence of H_c value of the films with 0.5–6 at% of cobalt content. Slopes were negative and its magnitude ranging from 10 to 19 (for $T \leq 200^\circ\text{C}$) in the $H_c(T)$ plot (figure 20) indicated that H_c of the films was strongly temperature-

Figure 19. Dependence of coercivity with temperature for $\gamma\text{-Fe}_2\text{O}_3$ film grown in two-step scheme.

Figure 20. Dependence of coercivity with temperature for Co-doped $\gamma\text{-Fe}_2\text{O}_3$ films grown in single-step scheme.

Figure 21. Dependence of coercivity with temperature for Co-modified $\gamma\text{-Fe}_2\text{O}_3$ films.

dependent. This suggests that magnetocrystalline anisotropy (Meng *et al* 1987) which has a strong inverse dependence on temperature is present in the directly deposited $\gamma\text{-Fe}_2\text{O}_3$ films. The magnitude of the slope had the lowest value of 10.55 for $\gamma\text{-Fe}_2\text{O}_3$ film containing 0.5 at% cobalt and this value increased with increasing cobalt content in the film as shown in figure 20. Curie temperatures (T_C) for these directly deposited $\gamma\text{-Fe}_2\text{O}_3$ films were also studied. It was found that the value of T_C decreased with increasing amount of cobalt in the $\gamma\text{-Fe}_2\text{O}_3$ matrix. Curie temperature of the film containing 0.5 at% cobalt was found to be 540°C and this value decreased to 480°C for the film containing 6 at% cobalt.

(iii) *Confirmation of cobalt heterogeneity in Co-modified films:* Temperature dependence of coercivity of the Co-modified $\gamma\text{-Fe}_2\text{O}_3$ films grown by oxidation of Co-modified Fe_3O_4 films at different annealing temperatures (250–450°C) were studied to find out the nature of anisotropy in the films introduced by Co^{2+} ions and the nature of cobalt dispersion in the $\gamma\text{-Fe}_2\text{O}_3$ matrix. Figure 21 shows the temperature dependence of H_c value of the films grown at oxidation temperatures 250, 300, 400 and 500°C. In the $H_c(T)$ plot (for $T \leq 200^\circ\text{C}$) relatively low magnitude of the slope, which were -1.8 ($T_{\text{ox}} = 250^\circ\text{C}$) and -2.9 ($T_{\text{ox}} = 300^\circ\text{C}$) for the $\gamma\text{-Fe}_2\text{O}_3$ films grown at oxidation temperature $< 350^\circ\text{C}$, indicated that H_c of these films was independent of temperature. This indicated that uniaxial anisotropy which is not affected by temperature, as found in case of Co-absorbed media, was present in the film suggesting dispersed nature of cobalt. Higher magnitudes of the slope of 4.2 ($T_{\text{ox}} = 400^\circ\text{C}$) and 8.6 ($T_{\text{ox}} = 500^\circ\text{C}$) for the $\gamma\text{-Fe}_2\text{O}_3$ films oxidized at temperature $> 350^\circ\text{C}$ suggest that magnetocrystalline anisotropy (Nakamura *et al* 1987) which has a strong inverse dependence on temperature was present in the $\gamma\text{-Fe}_2\text{O}_3$ films grown at $T_{\text{ox}} > 350^\circ\text{C}$, as shown in Co-doped films. Curie temperature study for the Co-modified $\gamma\text{-Fe}_2\text{O}_3$ films grown at oxidation temperature of 250°C and 400°C showed T_C values of 635°C and 405°C respectively.

4. Growth mechanism

4.1 Cold-wall CVD reactor

The gas-phase interactions of Ar, O_2 , $\text{Fe}(\text{acac})_3$ vapours were inhibited due to the cold-wall design of the reactor. Fragmentation of $(\text{acac})_3$ -ligand at substrate surface

leads to CH_3^+ radical and secondary reactions leading to its further dissociation into CO, CO_2 and H_2O . This depletes oxygen in the vicinity of the substrate. Mass spectrometric data have shown that these secondary reactions and hence oxygen depletion are strongly influenced by temperature (Reichert *et al* 1970). Both the rate of formation of CO_2 ($\approx$ rate of consumption of O_2) and volume fraction of CO_2 dramatically increase as the temperature increases from 485 to 515°C (Mellor 1946).

In the three-step scheme, deposition was done keeping substrate temperature in the range of 350–450°C. In this temperature range, formation of $\alpha\text{-Fe}_2\text{O}_3$ phase was favoured owing to the relatively high oxygen supply near the substrate. As brought out from the microstructural studies, iron oxide films deposited in three-step scheme had a relatively lower density of nucleation centres. The growth of films occurred by a coalescence process resulting in the formation of larger grains and grain clusters. Such structural evolution was a consequence of high mobility of dissociated $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions or Fe atoms on the substrate surface and possibly due to their lower rate of oxidation (oxygen supply was high enough to form as-deposited $\alpha\text{-Fe}_2\text{O}_3$ films but at the same time low enough to form oxygen-deficient phases in the as-deposited films) to form iron-rich iron oxide. At flat orientation of the substrate, inevitably a low $\text{Fe}^{2+}/\text{Fe}^{3+}$ flux density favours a smaller number of nucleation sites and large grains as was indeed observed. The coexistence of dispersed stoichiometric $\gamma\text{-Fe}_2\text{O}_3$ grains and Fe-rich $\gamma\text{-Fe}_2\text{O}_3$ clusters caused inclusion of additional magnetic anisotropy in the film arising from microstructural variations. This anisotropy, referred to as the microstructure-induced anisotropy, was responsible for the observed high values of H_c and M_r parameters in the films. In terms of the mechanism of direct deposition of $\gamma\text{-Fe}_2\text{O}_3$, the presence of oxygen-deficient phases, confirmed by lattice parameter studies, was due to a controlled and slower oxidation kinetics. Since low deposition temperatures (350–450°C) favour $\alpha\text{-Fe}_2\text{O}_3$ phase, it seems that at higher deposition temperatures, intake of oxygen during formation of iron oxide was somehow depleted. Consequently, formation of Fe_3O_4 and its *in situ* oxidation to $\gamma\text{-Fe}_2\text{O}_3$ became possible. Reactive growth of iron oxide films in this technique was entirely due to pyrolysis of $\text{Fe}(\text{acac})_3$ complex upon interaction with the glass substrates held at high temperature of 500°C. A balance in the CO, CO_2 and O_2 for a direct growth $\gamma\text{-Fe}_2\text{O}_3$ films is, therefore, possible under certain experimental conditions only.

4.2 Hot-wall CVD reactor

In terms of the mechanism, it appears that the direct deposition of Fe_3O_4 , as confirmed by XRD analysis, was due to a controlled and slower oxidation kinetics. Reactive growth of iron oxide films in this technique is entirely due to pyrolysis of $\text{Fe}(\text{DPM})_3$ complex upon interaction primarily with the substrate held at high temperature and with the hot walls of the reactor. In principle, introduction of O_2 would have led to growth of $\alpha\text{-Fe}_2\text{O}_3$ phase which is a higher oxidation state of iron oxide. Fragmentation of the DPM ligand at hot wall leads to its further dissociation into CO, CO_2 and hydrocarbon species (Reichert *et al* 1970). These vapours, particularly CO and CO_2 , on coming in contact with the heated substrate surface where iron radical formation was taking place, provided an environment favourable for the growth of iron oxide films in a lower oxidation state, viz. Fe_3O_4 . Thus, a limited

supply of O_2 favoured formation of Fe_3O_4 phase thermodynamically. A direct deposition of Fe_3O_4 (magnetic) films therefore took place under certain experimental conditions only as described above.

As discussed earlier, $\gamma-Fe_2O_3$ phase was formed by the oxidation of Fe_3O_4 phase derived from the reduction of $\alpha-Fe_2O_3$ phase. By depositing Fe_3O_4 phase directly we are able to eliminate one process step in the way to form magnetically stable $\gamma-Fe_2O_3$ phase. In the LPCVD process described here, a direct formation of Fe_3O_4 phase is likely to be assisted by the controlled partial pressure of O_2 and gas-phase reaction as promoted by hot-wall-type reactor chamber.

5. Conclusions

- (i) In three-step scheme, high M_r , H_c and SQ values of 270 mT, 61 kA/m and 0.76 are observed in $\gamma-Fe_2O_3$ films. Microstructural anisotropy is introduced by the iron-rich clusters as promoted by cold-wall-type reactor chamber. As a result considerable enhancements in the magnetic properties of the film are realized.
- (ii) In two-step scheme, we have demonstrated a technique based on the chemical phase dissociation of Fe-organic complex for a direct growth of Fe_3O_4 thin films. High coercivity of 122 kA/m, remanence value of 102 mT and SQ value of 0.80 of the $\gamma-Fe_2O_3$ films of thickness $\approx 800 \text{ \AA}$ as obtained by oxidation of as-deposited Fe_3O_4 film are quite attractive for application in magnetic information recording. A two-step growth of $\gamma-Fe_2O_3$ films, achieved using a LPCVD technique described here, offers a considerable simplification of the process technology. The manifestation of the condition of the controlled oxidation kinetics required for the direct growth of Fe_3O_4 films is attributed to the secondary reactions during the pyrolysis of metal-organic compound.
- (iii) In single-step scheme, we have demonstrated a technique based on chemical phase dissociation of Fe-organic complex for direct growth of $\gamma-Fe_2O_3$ thin films which offers a great simplification of process technology. Typically the high coercivity value of 237 kA/m, M_r value of 280 mT, SQ and S^* values of 0.83 and 0.60 of these films obtained by adding 6 at% of cobalt make them most suitable for high-density magnetic information recording. Strong temperature dependence of coercivity indicated presence of magnetocrystalline anisotropy in the Co-doped $\gamma-Fe_2O_3$ films.
- (iv) Biaxial magnetic studies, magnetic studies at temperature higher than the Curie temperature of $\gamma-Fe_2O_3$ and temperature dependence of coercivity have demonstrated a new dispersion mode of Co-incorporation in $\gamma-Fe_2O_3$ thin film which considerably enhances the magnetic properties in the films. High values of M_r of 220 mT, H_c of 65 kA/m and SQ of 0.60 should be of considerable interest for the application of these films as recording media.

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