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Magnetic study above the curie temperature of Υ-Fe_2O_3 in determining the dispersion nature of Co^{2+} ions in Co-modified Υ-Fe_2O_3 thin films†

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Abstract. Gamma (γ) iron oxide thin films containing 6 at% of cobalt atoms selectively dispersed at interstitial and octahedral locations have been prepared by a reactive chemical vapour deposition process. Such dispersion gives microscopic Co-trapped and Co-doped regions in γ-Fe_2O_3 matrix and introduces magnetocrystalline anisotropy leading to high coercivity values of 64–112 kA/m. Temperature dependence of coercivity and saturation magnetization for γ-Fe_2O_3 films confirm the dispersion model.

Keywords. Co-modified γ-Fe_2O_3 thin films; MOCVD; curie temperature; magnetocrystalline anisotropy; uniaxial anisotropy.

1. Introduction

Continuous thin films of γ iron oxide are preferred over particulate media. For supporting high density magnetic recording with higher values of coercivity (H_c) and mechanical strength as well as reduction in media noise, a further increase in H_c is required (Inagaki *et al* 1976). This can be done either by further reduction in the thickness of the film or by increasing the anisotropy in the media by using selective dopant or absorbant. Reduction in the film thickness is limited by the low value of saturation magnetization in the recorded bit leading to a poor value of S/N ratio. To increase anisotropy in the γ-Fe_2O_3 media, Co^{2+} ions are normally used either as dopant or absorbant (Tachiki 1960). In the uniformly doped Co-γ-Fe_2O_3 films, H_c value can be increased to 45 kA/m due to increase in magnetocrystalline anisotropy (Imaoka *et al* 1978). However, these films suffer from instability in magnetic parameters due to the strong dependence of H_c on temperature and high mobility of Co^{2+} ions inside γ-Fe_2O_3 matrix even at room temperature (Imaoka *et al* 1978). Meng *et al* (1987) used thermal diffusion of vacuum evaporated metallic cobalt film into the γ-Fe_2O_3 film. They obtained high coercivity of 192 kA/m which was attributed to uniaxial anisotropy in the media introduced by the formation of Co^{2+} rich γ-Fe_2O_3 layer at a specific depth in γ-Fe_2O_3 film. This film showed stability in the magnetic properties with H_c having no strong dependence on temperature (Meng *et al* 1987). Number of models are available in explaining the role of Co^{2+} in the doped or adsorbed media and the mechanism for increasing anisotropy in the media (Na *et al* 1993). The specific nature of dispersion of Co^{2+} ions in the spinel lattice of γ-Fe_2O_3 matrix is generally determined by the Mössbauer studies (Na *et al* 1993) where locations of Co^{2+} ions are determined at different stages of film growth along with usual magnetic M–H loop studies.

In view of the importance of thin magnetic films, we describe here a technique of cobalt dispersion in the γ-Fe_2O_3 matrix by varying the annealing temperature (T_A) while transformation of γ-phase takes place from Fe_3O_4 phase. The Co^{2+} ions are

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dispersed mostly in the interstitial sites in the spinel structure of γ-Fe_2O_3 at lower annealing temperature. As the annealing temperature increases the Co^{2+} ions get clustered mostly in the octahedral sites of spinel lattice (namely B sites) and show different kinds of anisotropy in the media as compared to that shown by the films annealed at lower T_A. This change in the nature of the magnetic anisotropy owing to the variation of dispersion nature of Co^{2+} ions has been studied above the curie temperature (T_c) of γ-Fe_2O_3 (i.e. 560°C) for Co-modified γ-Fe_2O_3 films annealed at different T_A. As cobalt has T_c of 800°C which is far above the T_c value of γ-Fe_2O_3 matrix (T_c = 560°C), an initial magnetization measurement at 600°C shows mainly the magnetization of cobalt along with a constant paramagnetic contribution of γ-Fe_2O_3 phase above its T_c. Paramagnetic contribution is common for all films annealed at

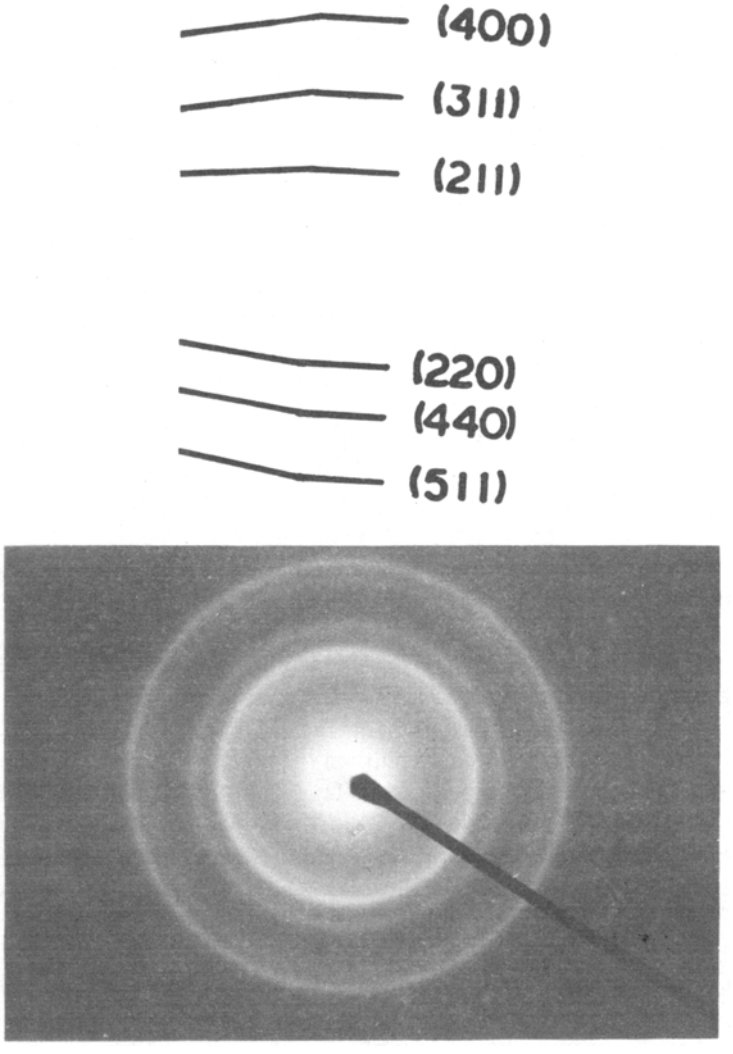

Figure 1. Electron diffraction pattern and its interpretation showing formation of γ-Fe_2O_3 phase in oxygen annealed films.

different temperatures, so any variation among them is identified as a change in the dispersion nature of Co^{2+} ions in the γ-Fe_2O_3 matrix (Beck 1971).

2. Experimental

Co-dispersed iron oxide thin films were deposited by chemical vapour deposition (CVD) technique by co-pyrolyzing a mixture of beta-ketonates of iron *tris* acetyl acetonate [$Fe(acac)_3$] and cobalt *bis* acetyl acetonate [$Co(acac)_2$] complexes onto cleaned glass (corning 7059) substrates. Cobalt concentration in the film was kept between 5–6 at%. For this a fixed weight of $Co(acac)_2$ complex was added to the source material corresponding to 6 at% of Co. The deposition was performed under atmospheric pressure using Ar as a carrier gas with the substrates preheated to 300–450°C. CVD deposited iron oxide films under varied conditions of substrate temperature and gas flow rate were found to be α-Fe_2O_3. This was established by detailed selected area electron diffraction (SAED) studies which were published earlier (Dhara *et al* 1992). In order to obtain γ-Fe_2O_3 phase, the films were reduced first at 350°C under an ambient of flowing H_2 for 5 h. These optimized conditions and results of Fe_3O_4 phase identification are reported elsewhere (Dhara *et al* 1992). The Fe_3O_4 films were oxidized over a period of 3 h at various temperatures between 250–450°C under controlled conditions and were found readily to convert to γ-Fe_2O_3. The typical SAED pattern for the oxidized film is shown in figure 1. Diffraction rings (figure 1) corresponding to (*hkl*) planes (210), (311), (444), (400), (511) along with superstructure line (211) indicate the presence of γ-Fe_2O_3 phase.

3. Magnetic properties

Magnetic properties were studied using a vibrating sample magnetometer (VSM) model DMS 1660. The magnetic properties of Co-dispersed iron oxide films in the γ-Fe_2O_3 form are strongly dependent on the oxidation annealing temperatures (T_A). Although, moderate annealing temperatures of 250°C are sufficient to transform the reduced Fe_3O_4 film into a γ-Fe_2O_3 phase, oxidation annealing between 300–450°C

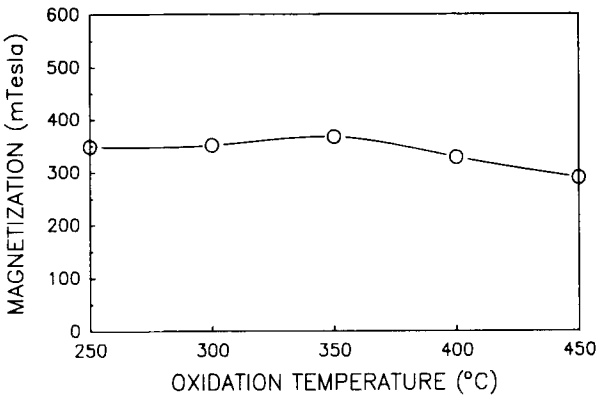

Figure 2. Variation of saturation magnetization with different oxidation annealing temperatures.

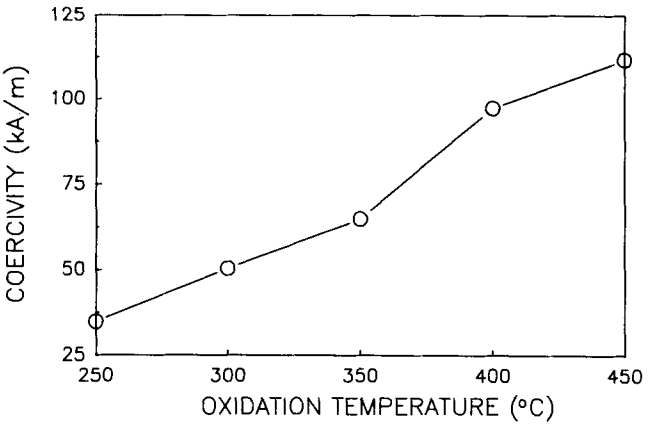

Figure 3. Variation of coercivity with different oxidation annealing temperatures.

had a significant effect on magnetic saturation and coercivity. M–H loop studies were performed at different temperatures individually for Co-modified γ-Fe_2O_3 films annealed at different T_A.

Saturation magnetization (M_s) values, measured at room temperature (T_{room}), of the Co-modified γ-Fe_2O_3 films annealed at different temperatures have been plotted in figure 2. M_s values of the films annealed at $T_A < 350°C$ showed no appreciable change indicating absence of the Co^{2+} ions in the octahedral (B) sites of the spinel iron oxide matrix. M_s values of the Co-modified γ-Fe_2O_3 films should have deteriorated if Co^{2+} ions with magnetic moment of $3\mu_\beta$/ion are introduced in the B sites replacing Fe^{2+} ions with magnetic moment of $4\mu_\beta$ of spinel lattice (Borelli *et al* 1972). On the other hand, M_s values showed a negative slope for the films annealed above 350°C indicating the increasing presence of Co^{2-} ions in the B sites of spinel lattice.

This variation in the slope of $M_s(T_A)$ plot above $T_A \geq 350°C$ indicate a possible change in the anisotropy in media. The change in the anisotropy can be studied by observing the variation of $H_c(T_A)$ plots. Figure 3 shows the variation of magnetic coercivity with the oxidation annealing temperature in the film plane. The incremental changes in the H_c show two distinct regions marked by different slopes indicating two different mechanisms of H_c enhancement. For the Co-dispersed γ-Fe_2O_3 film formed at 250°C, an initial high value of coercivity of 33·6 kA/m is obtained. This value further increases by a factor of two to 65·6 kA/m when oxidation is carried out at 350°C. It may be noted that these H_c values are quiet high in comparison with a minimum H_c of 45 kA/m obtained in past studies for Co-doped (Imaoka *et al* 1978), 50 kA/m for epitaxial Co-ferrites (Nakayama *et al* 1988) and 60 kA/m for Co-adsorbed particulates (Kishimoto *et al* 1979). Such high coercivity values obtained in our CVD prepared films are attributed to an increase in the anisotropy from the dispersion of Co^{2+} ions in the γ-Fe_2O_3 film where Co^{2+} locations differ from those at interstitial locations other than lattice sites of the spinel structure and at octahedral sites in the spinel structure, i.e. at Fe^{2+} sites (B-sites). This is better illustrated by the schematic diagram in figure 4. At low ($\leq 350°C$) oxidation temperature, films comprise of large grains containing Co^{2+} ions trapped at interstitials and smaller grains where Co^{2+} ions occupy the Fe^{2+} sites, as seen in figure 4a. This introduces an uniaxial anisotropy in the media. Thus, when

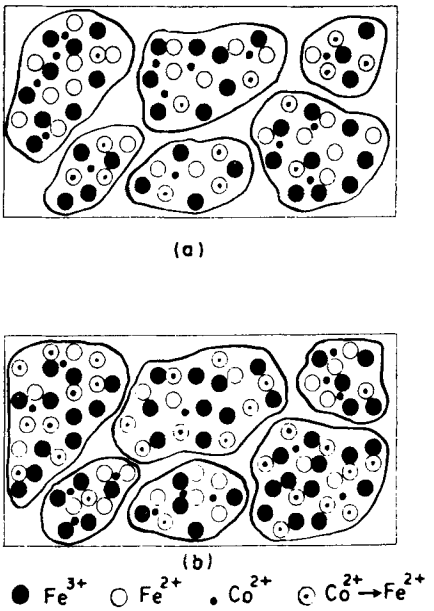

Figure 4. Schematic illustration depicting the nature of microstructural anisotropy in Co–γ–Fe_2O_3 films based on heterogeneous lateral dispersion of cobalt at interstitial and octahedral sites for films oxidized at temperatures (T_{ox}): (**a**) 250°C $\leqslant T_{ox} \leqslant$ 350°C and (**b**) $T_{ox} \geqslant$ 350°C.

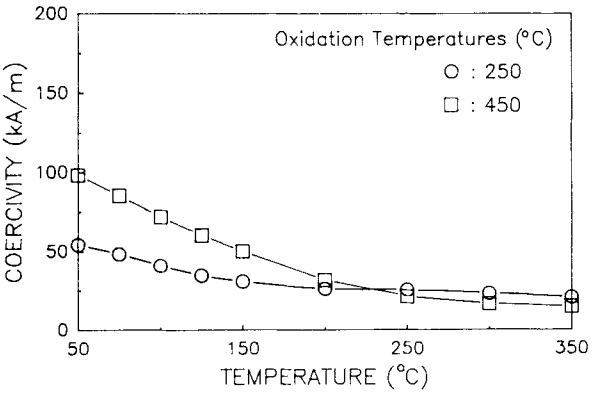

Figure 5. Temperature dependence of H_c for Co–γ–Fe_2O_3 films formed by oxidation at (**a**) 250°C and (**b**) 450°C.

γ-Fe_2O_3 phase is realized by oxidizing Fe_3O_4 film at temperatures between 250 to 350°C, considerable enhancement in H_c values up to 112 kA/m are achieved. As the oxidation temperature is increased over 350°C, a higher thermal energy available during this high temperature oxidation results in introduction of Co^{2+} ions in the B sites of spinel γ-Fe_2O_3 matrix (figure 4b). The film now comprises of large granular regions where Co^{2+} ions are substituted at Fe^{2+} site while the region where Co^{2+} ions are still trapped are smaller. This conclusion is based on the study of saturation

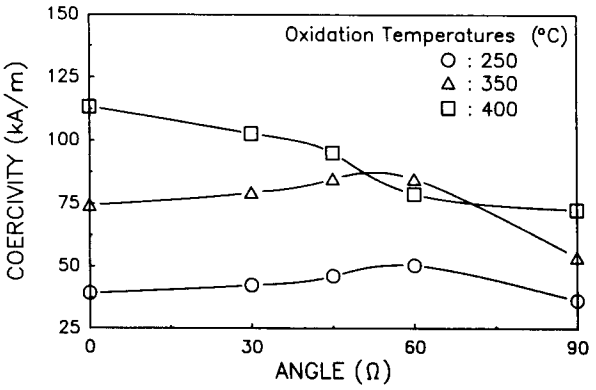

Figure 6. Variation of in-plane coercivity (H_c) at different orientational angles (Ω) of the films w.r.t. field direction.

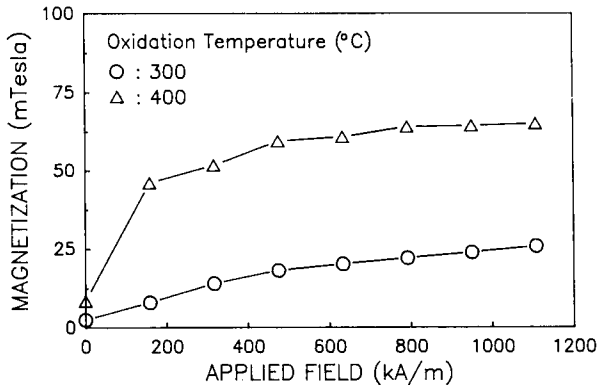

Figure 7. Initial magnetization studies at 600°C for the films annealed at (**a**) 300°C and (**b**) 400°C.

magnetization which reduces with oxidation temperature above 350°C (figure 2). This reduction is due to increase in number of Co^{2+} ions at the cation vacancy sites (Borelli *et al* 1972). Such relocation of Co^{2+} ions enhances the magnetocrystalline anisotropy in the film, resulting in a rapid increase in H_c (||) values (figure 3).

The model for dispersion of Co^{2+} ions at B-sites and interstitial sites and variation in its extent with oxidation temperature as developed above has been confirmed by measurement of coercivity dependence on temperature (figure 5). According to our proposed model (figure 4), films oxidized at higher temperature should contain more amount of Co^{2+} ions at B-sites than that in case of the films oxidized at lower temperature. If all the Co^{2+} ions were at the B-site of the spinel structure, as in case of Co-doped γ-Fe_2O_3, the coercivity should show a strong dependence on the temperature (Tachiki 1960). As seen from figure 5, the Co-modified γ-Fe_2O_3 formed by oxidation at higher (> 350°C) temperature shows a relatively stronger dependence of coercivity on temperature than that for the films which are oxidized at lower ($\leqslant 350$°C) temperatures. For γ-Fe_2O_3 film grown by oxidation at 250°C, a relatively weaker dependence of coercivity with temperature is observed. This clearly indicates that in the films annealed at T_A of 250°C Co^{2+} ions are dispersed in the interstitial sites of

γ-Fe_2O_3 matrix showing presence of uniaxial anisotropy in the media. On the other hand, for films annealed at a temperature of 450°C, a strong temperature dependent coercivity was observed indicating presence of magnetocrystalline anisotropy in the media owing to a large fraction of Co^{2+} ions present at the B-sites of these films, as in Co-doped case.

A further confirmation of the Co-dispersion model is provided by the studies of variation of coercivity of the Co-modified γ-Fe_2O_3 films with the orientation angle Ω as obtained from magnetic measurements where M -H loops were measured at room temperature with film plane oriented at different angles with respect to applied field. This is presented in figure 6. The H_c values for γ-Fe_2O_3 film formed at low oxidation temperatures (250–350°C) exhibit a peak at 60° in a variation with film orientation Ω. This anisotropic nature is attributed to uniaxial anisotropy present in the film due to γ-Fe_2O_3 regions with Co-trapped at interstitial sites. As the oxidation temperature is increased, the uniaxial anisotropy progressively reduces. As a result, a monotonous decrease in the coercivity for film oxidized at 400°C and disappearance of the coercivity maxima in figure 6 was observed, indicating presence of magnetocrystalline anisotropy in these films (Lu and Charap 1992).

At 600°C temperature, γ-Fe_2O_3 films exceed the T_c value and become paramagnetic while cobalt remains ferromagnetic at that elevated temperature as cobalt has T_c around 800°C. So magnetic studies of Co-modified γ-Fe_2O_3 films at a temperature of 600°C shows mainly the ferromagnetic contribution of cobalt species on a paramagnetic background of γ-Fe_2O_3 matrix. A comparative study has been shown in figure 7 where initial magnetization at temperature 600°C was plotted for films annealed at T_A of 300°C and 400°C. Higher value of M_s was observed for films annealed at T_A of 400°C ($T_A > 350$°C) than that observed for films annealed at T_A of 300°C ($T_A < 350$°C). This indicates the formation of Co^{2+} clusters in the films annealed at T_A above 350°C (Beck 1971). Such clustering of Co^{2+} ions introduces magnetocrystalline anisotropy in those films, as evidenced from our earlier discussion on H_c (T) and H_c (Ω) plots in figures 5 and 6, respectively. In comparison, the films annealed at $T_A \leqslant 350$°C with dispersed Co^{2+} ions show uniaxial anisotropy.

4. Conclusions

In conclusion magnetic studies at different temperatures have demonstrated a new mode of Co incorporation in γ-Fe_2O_3 thin film which considerably enhances the magnetic properties in the films. In this mode the Co^{2+} ions are mainly dispersed in the interstitial locations other than the lattice sites of the spinel structure in the γ-Fe_2O_3 matrix for films annealed below 350°C, showing weak temperature dependent uniaxial anisotropy which is akin to Co-adsorbed media. For films annealed at $T_A > 350$°C, Co^{2+} ions get clustered at octahedral (cation B) sites of spinel lattice showing doped nature of Co^{2+} ions in the γ-Fe_2O_3 with strong temperature dependent magnetocrystalline anisotropy.

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