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Strain relaxation studies of the $\text{Fe}_3\text{O}_4/\text{MgO}(100)$ heteroepitaxial system grown by magnetron sputtering

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Abstract

Detailed strain relaxation studies of epitaxial magnetite, Fe_3O_4 , films on $\text{MgO}(100)$ substrates grown by magnetron sputtering reveal the accommodation of strain up to 600 nm thickness, a thickness far above the critical thickness (t_c) predicted by theoretical models. The results are in agreement with the suggestion that the excess strain in $\text{Fe}_3\text{O}_4/\text{MgO}(100)$ heteroepitaxy is accommodated by the presence of antiphase boundaries. The compressive strain generated by the antiphase boundaries compensates for the tensile strain within the growth islands, allowing the film to remain fully coherent with the substrate. Contrary to earlier findings, magnetization decreases with an increase in the film thickness. This vindicates the view that the structure of the antiphase boundaries depends on the growth conditions.

1. Introduction

Magnetite, Fe_3O_4 , is one of the transition metal oxides studied most extensively owing to its high Curie temperature (T_C), metal–insulator transition at low temperatures (~ 120 K) [1] and half-metallic nature [2]. Epitaxial films of magnetite hold promise for device fabrication. Strain in epitaxial magnetite films has a strong influence on the magnetic and magnetotransport properties. Although reports exist on the growth and characterization of thin films of magnetite on different substrates [3–11], the strain relaxation behaviour in $\text{Fe}_3\text{O}_4/\text{MgO}$ films grown by the sputtering technique has not been investigated in detail. The lattice mismatch between the film and substrate is -0.344% . In our previous study [12] on the strain relaxation behaviour of $\text{Fe}_3\text{O}_4/\text{MgO}(100)$ heteroepitaxial films grown by oxygen assisted molecular beam epitaxy (MBE), it was shown that the films remain in a fully strained state up to a much greater thickness than that predicted (~ 70 nm) from critical thickness models based on misfit strain [13, 14]. The anomalous strain relaxation behaviour was attributed [12] to the

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presence of antiphase boundaries (APBs). The APBs are natural defects occurring during the growth of an Fe₃O₄/MgO heteroepitaxial system [4, 5]. The oxygen atoms in both Fe₃O₄ and MgO are arranged in a face-centred cubic (fcc) lattice. The lattice constant of Fe₃O₄ ($a = 8.3987 \text{ \AA}$) is nearly twice that of MgO ($a = 4.213 \text{ \AA}$) due to the specific arrangement of Fe atoms at the vacant interstitial tetrahedral (A) and octahedral (B) sites. During the growth, the islands nucleate randomly and when they coalesce they can be shifted or rotated with respect to each other, forming antiphase boundaries. At some of these boundaries the angle subtended by the cation–anion–cation interaction is 180° and hence the superexchange interaction between the cations mediated by oxygen is antiferromagnetic. This results in a picture where large islands having ferromagnetic ordering within the islands are connected by regions (APBs) having antiferromagnetic and frustrated exchange. As a consequence the film's magnetization is not saturated even by a field of 7 T [4, 5].

It was further suggested [12] that the increased density of APBs leads to a fully strained state up to a much greater thickness. This conclusion was drawn for magnetite films grown by MBE. Now that the Fe₃O₄/MgO films grown with the sputtering technique possess larger densities of APBs than MBE grown films, the strain relaxation should be greatly suppressed in sputtered films. Here, we report a systematic study of the strain relaxation behaviour in Fe₃O₄/MgO(100) heteroepitaxial systems grown using the dc magnetron reactive sputtering technique to check the validity of our prediction.

2. Experimental procedure

Magnetite thin films with thickness ranging from 85 to 600 nm were grown under identical growth conditions on polished, (100) oriented MgO single-crystal substrates using dc magnetron reactive sputtering from a 99.95% purity Fe target in the presence of an argon–oxygen gas mixture. Prior to film deposition, the substrate was cleaned at 450°C in 1×10^{-5} mbar oxygen for 2 h. The base pressure of the system was 10^{-7} mbar. Deposition was performed at a substrate temperature of 400°C with the substrate–target distance kept at 12 cm. During deposition the Ar partial pressure was 0.2 Pa while the O₂ partial pressure was 0.01 Pa. The plasma power was kept at 50 W which gave a current of approximately 120 mA. The growth rate was monitored by a quartz-crystal balance (with a calibrated tooling factor) kept near the substrate and it was $\sim 100 \text{ \AA min}^{-1}$.

Structural characterization of the sputtered Fe₃O₄/MgO(100) films was carried out in a multi-crystal high-resolution x-ray diffractometer, HRXRD, (Bede D1 system). In this system, monochromatic Cu K α_1 (1.54056 \AA) radiation with $12''$ beam divergence was obtained using four Si channel-cut crystals. In the triple-axis geometry, lattice constant variations ($\Delta a/a$) as low as 2×10^{-6} can be detected. This enables one to observe any change in the lattice parameter of the film precisely and hence the strain relaxation. The in-plane (a_{\parallel}) and out-of-plane (a_{\perp}) lattice parameters were determined from the analysis of ω – 2θ scans performed around the symmetric (200)/(400) and asymmetric (311)/(622) diffraction peaks common to the substrate and thin film.

Magnetization along the film plane was measured in a vibrating sample magnetometer (Princeton Measurements Corporation; model MicroMag 3900) with a sensitivity of $1 \mu\text{emu}$. The maximum field was $\pm 1 \text{ T}$ applied in steps of 2 mT. The diamagnetic contribution from the bare MgO substrate, having approximately the same dimension as the sample (thin film on MgO), was measured in the same field range and subtracted from the total magnetization measured. The uncertainty in measuring the absolute value of magnetization for the films was about 3–4%. This is inclusive of the error in the estimation of the volume of the film.

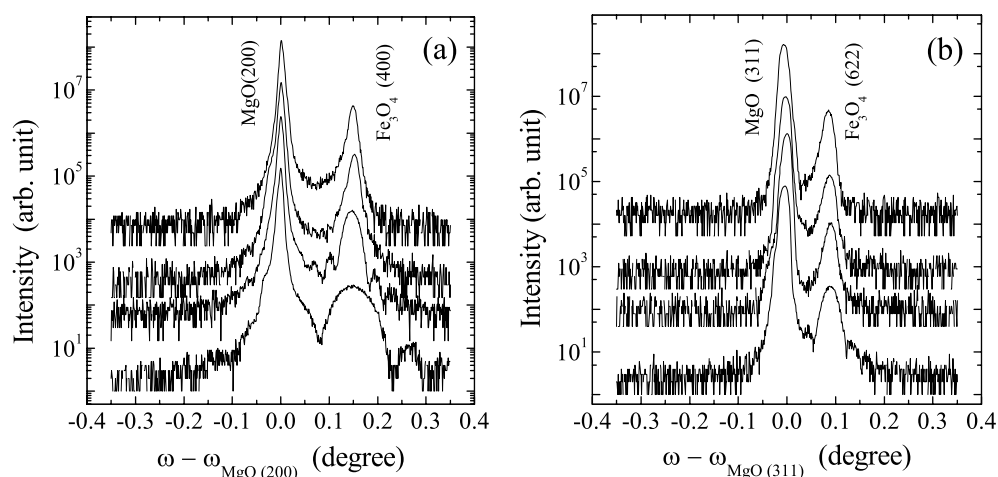


Figure 1. (a) Rocking curves taken around the (200) Bragg reflection of MgO which is common to the (400) reflection of Fe₃O₄ film and (b) rocking curves taken around the (311) Bragg reflection of MgO which is common to the (622) reflection of Fe₃O₄ film in grazing exit geometry. The bottommost curve relates to the 85 nm thick film and the curves above correspond to 200, 400 and 600 nm thick films, in ascending order.

Verwey transition temperatures of the Fe₃O₄/MgO(100) films were determined from the temperature variation of the resistance measured using the ac four-probe technique. Raman spectroscopy measurements were carried out using a Raman spectrometer (Renishaw) operated in a backscattering configuration. The spectrometer has an Ar-ion laser (model RL 633) operated at 514 nm wavelength and the laser power was set at 5 mW during the investigation of the samples.

3. Results and discussion

HRXRD measurements in symmetric (400 reflection) and asymmetric (622 reflection) geometries were carried out on 85, 200, 400 and 600 nm thick Fe₃O₄/MgO(100) films. Figure 1(a) shows the rocking curves taken around the (200) Bragg reflection of MgO which is common to the (400) reflection of the Fe₃O₄ film. The rocking curves measured around the (311) Bragg reflection of MgO which is common to the (622) reflection of Fe₃O₄ film, in grazing exit geometry, are shown in figure 1(b). The bottommost curve relates to the 85 nm thick film and the curves above correspond to 200, 400 and 600 nm thick films, in ascending order. The curves are shifted along the ordinate for clarity. One observes that as the thickness of the film increases the full width at half-maximum (FWHM) of the film peak in the symmetric reflection (figure 1(a)) decreases while the intensity increases. MgO has the most intense peak and the Fe₃O₄ film peak is shifted by $\Delta\omega(\omega - \omega_{\text{MgO}(200)}) \sim 0.15^\circ$ with respect to the MgO peak. By adding the $\Delta\omega$ between the MgO peak and the Fe₃O₄ peak to the Bragg angle of MgO, θ_{MgO} , the Bragg angle for the 400 reflection of Fe₃O₄ film ($\theta_{\text{Fe}_3\text{O}_4}$) was calculated. The perpendicular lattice constant (a_{\perp}) of the film calculated from $\theta_{\text{Fe}_3\text{O}_4}$ was 8.3668 ± 0.0006 Å. The in-plane lattice constant (a_{\parallel}) of the film calculated from the rocking curves of the asymmetric reflection measured both in grazing incidence and in grazing exit geometry was 8.4266 ± 0.0007 Å. The in-plane lattice constant (a_{\parallel}) of the film is twice that of the MgO substrate, within experimental uncertainty. This indicates pseudomorphic growth

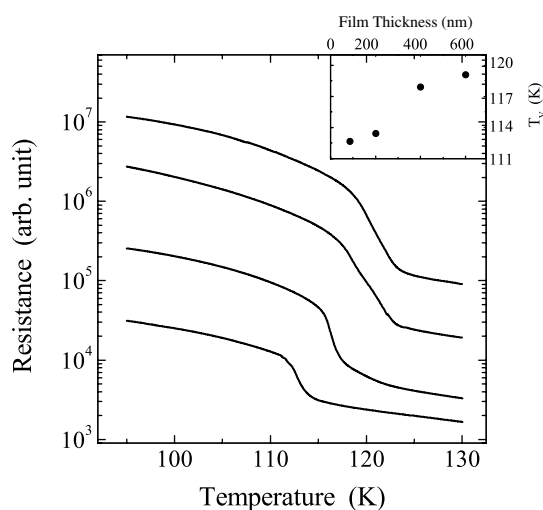


Figure 2. Variation of the resistance with temperature in the vicinity of the Verwey transition for Fe_3O_4 films. The curves are shown in ascending order with increasing film thickness. The inset shows the increase of the Verwey transition temperature, T_V , with an increase in the film thickness.

of Fe_3O_4 on MgO giving rise to an in-plane tensile strain. This shows that the films under investigation remain fully strained up to 600 nm. Due to experimental difficulty, epitaxial Fe_3O_4 films on MgO with higher thickness could not be fabricated.

To ascertain that the tetragonal distortion of the unit cell of the Fe_3O_4 films observed in this study is indeed due to strain and not due to deviations from stoichiometry, a detailed characterization of the films was carried out with (1) electrical resistivity measurements around the Verwey transition temperature (T_V) and (2) Raman spectroscopy measurements. All the films exhibit an increase in the resistivity around 115 K, a signature of the Verwey transition. Figure 2 shows the temperature variation of the resistance in the vicinity of the Verwey transition for all the films, with a shift along the ordinate for clarity. The curves are shown in ascending order with increasing thickness. T_V increases with an increase in the film thickness, as shown in the inset. The Verwey transition temperature, T_V , is a sensitive measure of the oxygen stoichiometry in magnetite films [15] and the occurrence of a Verwey transition in these films shows that the films are stoichiometric. The presence of peaks corresponding only to the Fe_3O_4 phase in the measured Raman shift on the films provides further evidence that the films do not contain iron oxide phases other than magnetite. The A_{1g} and T_{2g}^2 mode frequencies corresponding to the magnetite phase remain constant for all the films, within the error limits of the measurement, as shown in figure 3. For the sake of clarity the curves are shifted along the ordinate. The net volume of the regions around APBs is a small fraction of the total volume of the film and hence the contribution to the Raman scattered signal from these regions is small. Therefore, conventional Raman spectroscopy cannot distinguish the deviation from stoichiometry if any, in the regions around APBs. Further, the unit cell volume of the films calculated from a_{\parallel} and a_{\perp} obtained from the HRXRD measurements is the same as that of bulk Fe_3O_4 . This again suggests that the films are stoichiometric.

Figure 4 shows the magnetization curve for a representative film (thickness 600 nm) in the field range from -1 to $+1$ T measured at 300 K along with the enlarged view of the high-field region. The observed values of the magnetization for these films are comparable to the values reported [5] for films grown using the sputtering technique. There is a finite slope present in

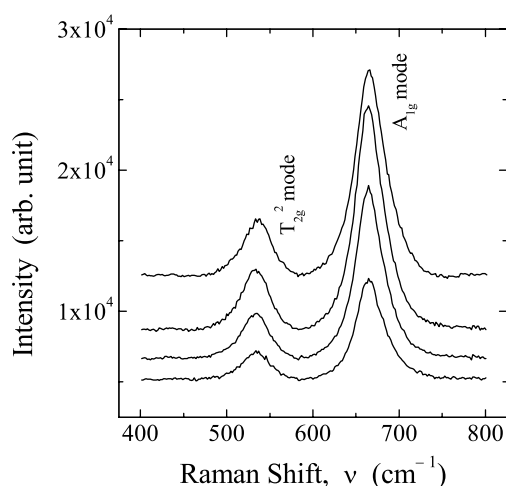


Figure 3. The Raman shift of Fe_3O_4 films for A_{1g} and T_{2g}^2 modes. The curves are shown in ascending order with increasing film thickness.

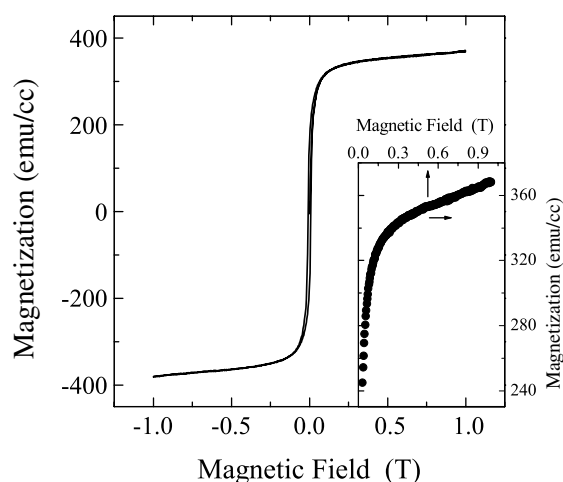


Figure 4. The magnetization curve for 600 nm thick film in the field range from -1 to $+1$ T, measured at 300 K. The inset shows an enlarged view in the high-field region.

the magnetization versus applied magnetic field ($M-H$) curve at 1 T field for all the films, which shows no sign of saturation. The reason for this is the presence of APBs in the Fe_3O_4 films [4, 5]. Although the presence of APBs in $\text{Fe}_3\text{O}_4/\text{MgO}$ thin films has been revealed by transmission electron microscopy [4, 9], scanning tunnelling microscopy [3] and magnetic force microscopy [9] studies, the exact structure of APBs is not yet clear. The regions around APBs could be stoichiometric or non-stoichiometric, as the APBs themselves are metastable defects. Any addition or removal of oxygen to the APB and also the rearrangement of atoms within the APB will modify the cation-anion-cation bond angle and hence the exchange interaction [16]. Even if a fraction of APBs contain 180° Fe-O-Fe chains, they would give rise to antiferromagnetic and frustrated exchange interactions across the APBs. When the magnetic field is applied along the film plane, the magnetic moments in the growth islands, within which

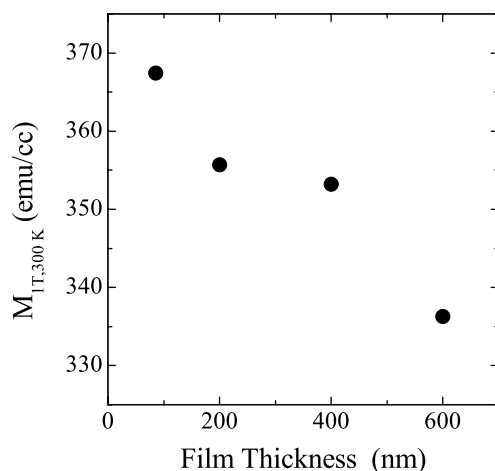


Figure 5. The room temperature magnetization measured at 1 T field, $M_{1T,300K}$ (emu cm⁻³), as a function of the film thickness.

the ferromagnetic interaction prevails, start aligning along the applied field direction. The growth islands constitute the major volume of the film and hence the film shows ‘technical saturation’ around the magnetocrystalline anisotropy field (~ 0.03 T) [5]. Nevertheless, the long-range ferromagnetic order in the film is impeded by the antiferromagnetic and frustrated exchange interaction across the APBs. More and more energy is required to overcome the frustration at the APBs. This is manifested as the finite slope in the magnetization curve even at high field.

The room temperature magnetization measured at 1 T, $M_{1T,300K}$, as a function of the film thickness is shown in figure 5. $M_{1T,300K}$ decreases with an increase in the film thickness. This is contrary to the earlier findings [6, 9] that the magnetization increases with film thickness. It was found [11] that the growth islands enlarge in size as the film thickness increases, thereby increasing the magnetization. In our previous study on films grown by MBE [12] it was found that the size of growth islands increases with an increase in the film thickness. The observed decrease in magnetization with the increase in film thickness in this study could be due to (1) an increase in the density of the APBs, (2) an increase in the fraction of APBs inducing antiferromagnetic and frustrated exchange or (3) an increase in both, with an increase in film thickness. The exact reason is not known as the structures of the APBs depend on the growth conditions. The MBE-grown films [12] have room temperature magnetization values measured at 1 T field ranging from 410 to 470 emu cm⁻³, depending on the growth conditions. The slope of the magnetization curve at 1 T field for MBE-grown films is smaller than that obtained for the sputtered films under investigation. This implies that the sputtered films have a higher density of exchange frustrated regions than the MBE-grown films.

Accommodation of the excessive strain in the epitaxial magnetite films on MgO could be understood on the basis of APBs which are stacking faults naturally occurring during island growth mode in heteroepitaxy. During the epitaxial growth there develops an excessive strain along the surface of the film increasing the free energy of the film. As a result, one expects the film to develop misfit dislocations and start relaxing the strain at a thickness even below the critical thickness t_c , to minimize the free energy. However, due to the formation of APBs the *excess* tensile strain can be accommodated in the film. Our model suggests that within the growth islands there exists a tensile strain while there is a compressive strain at the antiphase

boundaries, cancelling out the excess contribution to the free energy of the film. This enables the film to retain the registry with the substrate at thickness values much greater than t_c . It has been noted previously [17, 18] that in thin films containing structurally shifted domains, a compressive strain develops at the domain boundaries. Films containing APBs is a situation similar to the superlattice heterostructures where one can grow a material of large mismatch over a substrate by growing it in alternation with a layer of another material which essentially compensates for the mismatch strain experienced by the film.

4. Conclusion

By a detailed investigation of the Fe₃O₄/MgO(100) heteroepitaxial system, anomalous strain accommodation up to 600 nm film thickness was observed. Alternating tensile and compressive strains generated within, respectively, the growth islands and the antiphase boundaries account for the anomalous strain accommodation in the films. Tailoring films with a higher density of APBs would eventually lead to the growth of thicker films in heteroepitaxy. It was found, contrary to the earlier findings, that in sputtered Fe₃O₄ films the magnetization decreases with an increase in the film thickness. The increase in magnetization with film thickness for films grown by MBE on identical substrates is contrary to our observations on sputtered films. This indicates that the structure of the APBs is sensitive to the growth conditions. The extent to which APBs frustrate the pattern of the exchange field depends on the type of the APBs and their structure, which in turn depends on the growth conditions and film thickness.

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