Strain Relaxation Studies in Fe_3O_4/MgO (100) Hetero-epitaxial System Grown with Magnetron Sputtering

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Detailed strain relaxation studies on epitaxial magnetite, Fe_3O_4, films on MgO(100) substrates grown by magnetron sputtering reveal the accommodation of strain up to 600 nm thickness, a thickness much above the critical thickness (t_c) predicted by theoretical models. The results are in agreement with the suggestion that the excess strain in Fe_3O_4/MgO (100) hetero-epitaxy is accommodated by the presence of antiphase boundaries. The compressive strain generated by the antiphase boundaries compensate for the tensile strain within the growth islands, allowing the film to remain fully coherent with the substrate. Contrary to the earlier findings, magnetisation decreases with an increase in film thickness. This vindicates the view that the structure of the antiphase boundaries depend on the growth conditions.

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 out promise for device fabrication. Strain in epitaxial magnetite films has a strong influence on the magnetic and magneto-transport properties. Though there exist reports on the growth and characterisation of thin films of magnetite on different substrates [3-11], the strain relaxation behaviour in Fe_3O_4/MgO films grown by 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 Fe_3O_4/MgO (100) hetero-epitaxial 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) by critical thickness models based on misfit strain [13,14]. The anomalous strain-relaxation behaviour was attributed [12] to the presence of antiphase boundaries (APBs). The APBs are the natural defects occurring during growth in Fe_3O_4/MgO hetero-epitaxial system [4,5]. The oxygen atoms in both Fe_3O_4 and MgO are arranged in a face-centred cubic (fcc) lattice. The lattice constant of Fe_3O_4 (a=8.3987 Å) is nearly twice that of MgO (a=4.213 Å) 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 magnetisation is not saturated even by a field of 7 T [4,5].

It was further suggested [12] that the larger density of APBs leads to a fully strained state up to a much higher thickness. This conclusion was drawn for magnetite films grown by MBE. Now that the Fe_3O_4/MgO films grown with sputtering technique posses larger density of APBs than the 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 Fe_3O_4/MgO (100) hetero-epitaxial system grown using dc magnetron reactive sputtering technique to check the validity of our prediction.

Experimental Procedure

Magnetite thin films with the thickness ranging from 85 nm 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 Argon-Oxygen gas mixture. Prior to film deposition, the substrate was cleaned at 450° C in 1×10^{-5} m-bar oxygen for 2 hours. The base pressure of the system was 10^{-7} m-bar. Deposition was performed at a substrate temperature of 400° C with substrate-target distance kept at 12 cm. During deposition the Ar partial pressure was 0.2 Pa while the O_2 partial pressure was 0.01 Pa. The plasma power was kept at 50 W which gave a current of approximately 120 mA. Growth rate was monitored by a quartz-crystal balance (with a calibrated tooling factor) kept near the substrate and it was ~ 100 Å/min.

Structural characterisation of the sputtered Fe_3O_4/MgO(100) films was carried out in a multi-crystal high-resolution x-ray diffractometer, HRXRD, (Bede D1 system). In this system monochromatic $Cu_{K\alpha1}$ (1.54056 Å) 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 ($a_{||}$) 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.

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

Verwey transition temperatures of the Fe_3O_4/MgO(100) films were determined from the temperature variation of resistance measured using ac four-probe technique. Raman spectroscopy measurements were carried out using a Raman spectrometer (Renishaw make) operated in backscattering configuration. Ar ion laser operated at 514 nm wavelength with a 5 mW power was used to investigate the samples.

Results and Discussion

HRXRD measurements in symmetric (400) and asymmetric (622) geometries were carried out on 85 nm, 200 nm, 400 nm and 600 nm thick Fe_3O_4/MgO(100) films. Fig. 1 (a) shows the rocking curves taken around the (200) Bragg reflection of MgO which is common to the (400) reflection of Fe_3O_4 film. The rocking curves measured around the (311) Bragg reflection of MgO which is common to the (622) reflection of Fe_3O_4 film, in grazing exit geometry, are shown in Fig. 1(b). The bottom most curve belongs to the 85 nm thick film and the curves above correspond to 200 nm, 400 nm 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 (Fig. 1(a)) decreases while the intensity increases. MgO has the most intense peak and the thin film peak is shifted by $\Delta\omega$ ~0.15° with respect to the MgO peak. By adding the $\Delta\omega$ between the MgO peak and the Fe_3O_4 peak to the Bragg angle of MgO, θ_{MgO}, the Bragg angle for 400 reflection of Fe_3O_4 film (θ_{Fe3O4}) was calculated. The perpendicular lattice constant ($a_\perp$) of the film calculated from θ_{Fe3O4} 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 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 of Fe_3O_4 on MgO giving rise to 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 Fe_3O_4 films observed in this study is indeed due to strain but not due to deviations from stoichiometry, a detailed characterisation of the films was carried out with (1) electrical resistivity measurements at 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. The values of T_V as a function of film thickness are shown in Fig. 2. T_V increases with the increase in film thickness. Verwey transition temperature, T_V, is a sensitive measure of oxygen stoichiometry in magnetite films [15] and occurrence of Verwey transition in these films shows that the films are stoichiometric. Presence of peaks corresponding only to Fe_3O_4 phase in the measured Raman shift on the films adduce further evidence that the films do not contain iron oxide phases other than magnetite. The A_{1g} and T_{2g}^2 mode frequencies remain constant, within the error limits of the measurement and the peak-position fitting procedure, as shown in Fig. 3. 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.

Fig. 4 shows the Magnetisation curve at 300 K for a representative film (thickness 600 nm) in the field range from −1 T to 1 T measured at 300 K along with the exploded view of the high-field region. The observed values of magnetisation for these films are comparable to the values reported [5] on films grown using sputtering technique. There is a finite slope present in the magnetisation Vs 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. Though the presence of APBs in the Fe_3O_4/MgO thin films have 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 interaction across APBs. When the magnetic field is applied along the film plane, the magnetic moments in the growth islands, within which 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 anisotropy field (~ 0.6 T). Nevertheless, the long-range ferromagnetic order in the film is impeded by the antiferromagnetic and frustrated exchange interaction across APBs. More and more energy is to be supplied to overcome the frustration at the APBs. This manifests as the finite slope in the magnetisation curve even at high field.

The room temperature magnetisation measured at 1 T, $M_{1T,300 K}$, as a function of film thickness is shown in Fig. 5. $M_{1T,300 K}$ decreases with an increase in film thickness. This is contrary to the earlier findings [6,9] that the magnetisation increases with the film thickness. It was found [11] that the growth islands enlarge in size as the film thickness increases thereby increasing the magnetisation. In our previous study on films grown by MBE [12] it was found that the size of growth islands increases with an increase in film thickness. The observed decrease in magnetisation with the increase in film thickness in this study could be due to either (1) an increase in the density of APBs or (2) an increase in the fraction of APBs inducing antiferromagnetic

and frustrated exchange or an increase in both, with an increase in film thickness. The exact reason is not known as the structure and morphology of the APBs depend on the growth conditions. The MBE-grown films [12] have room temperature magnetisation values measured at 1 T field ranging from 410 emu/cc to 470 emu/cc, depending on the growth conditions. The slope of the magnetisation curve at 1 T field for MBE-grown film is smaller than that obtained for the sputtered films under investigation. This implies that the sputtered films have higher density of exchange frustrated regions than in 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 hetero-epitaxy. 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 below the critical thickness t_c, to minimise the free energy. However, due to the formation of APBs the excessive tensile strain can be accommodated in the film. Our model suggests that within the APBs there exists a tensile strain while there is a compressive strain at the domain 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 thicknesses much above 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. Film containing APB is a situation similar to the super-lattice hetero-structures where one can grow a material of large mismatch over a substrate by growing it in alteration with a layer of another

material which essentially compensates for the mismatch strain experienced by the film.

Conclusion

By a detailed investigation of $Fe_3O_4/MgO(100)$ hetero-epitaxial system the anomalous strain accommodation up to 600 nm film thickness was observed. Alternating tensile and compressive strain generated within, respectively, the growth islands and the antiphase boundaries account for the anomalous strain accommodation in the films. Tailoring films with higher density of APBs would eventually lead to the growth of thicker films in hetero-epitaxy. It was found, contrary to the earlier findings, that in sputtered Fe_3O_4 films the magnetisation decreases with an increase in film thickness. The increase in magnetisation with the film thickness that is contrary to our observations on films grown by MBE on identical substrates indicates that the structure of the APBs is sensitive to the growth conditions. The extent to which APBs frustrate the pattern of exchange field depends on the type of APBs and their structure, which in turns depends on the growth conditions and film thickness.

Acknowledgment

References

[1] E J W Verwey and P W Haayman, Physica (Amsterdam) 9 (1941) 979

[2] A Yanase and K Siratori, J. Phys. Soc. Jpn. 53 (1984) 312

[3] J M Gaines, P J H Bloeman, J T Kohlhepp, C W T Bulle-Lieuwma, R M Wolf, A

Reinders, R M Jungblut, P A A van der Heijden, J T W M van Eemeren, J aan

de Stegge and W J M de Jonge, Surface Science, 373 (1997) 85

[4] D T Margulies, F T Parker, M L Rudee, F E Spada, J N Chapman, P R Aitchison

and A E Berkowitz, Phys. Rev. Lett. 79 (1997) 5162

[5] D T Margulies, F T Parker, F E Spada, R S Goldman, J Li, R Sinclair and A E

Berkowitz, Phys. Rev. B 53, (1996) 9175

[6] G Q Gong, A Gupta, Gang Xiao, W Qian and V P Dravid, Phys. Rev. B 56 (1997)

5096

[7] S B Ogale, K Ghosh, R P Sharma, R L Greene, R Ramesh and T Venkatesan,

Phys. Rev. B 57 (1998) 7823

[8] R Hohne, CA Kleint, A V Pan, M K Krause, M Ziese and P Esquinazi, J. Mag.

Mag. Mater. 211 (2000) 271

[9] J F Bobo, D Basso, E Snoek, C Gatel, D Hrabovsky, J L gauffier, L Ressier, R

mamy, S Visnosky, J Hamrl, J Tillet and A R Fert, Eur. Phys. J. B 24 (2001) 43

[10] W Eerenstein, T T M Palstra, S S Saxena and T Hibma, Phys. Rev. Lett. 88

(2002) 247204

[11] W Eerenstein, T T M Palstra, T Hibma and S Celotto, Phys. Rev. B 68 (2003)

014428

[12] Stress accommodation by antiphase boundaries in epitaxial magnetite thin films,

S K Arora, R G S Sofin and I V Shvets, communicated to Euro. Phys. Letters

[13] A Fischer, H Kuhne and H Richter, Phys. Rev. Lett. 73 (1994) 2712

[14] J W Mathews and A E Blakeslee, J. Crys. Growth 27 (1973) 118

[15] R Aragón, R J Rasmussen, J P Shepherd, J W Koenitzer and J M Honig, J. Mag. Mag. Mater. 54-57 (1986) 1335

[16] Y Zhou, Xuesong Jin and I V Shvets, J. Appl. Phys. 95 (2004) 1

[17] A Biswas, M Rajeswari, R C Srivastava, Y H Li, T Venkatesan, R L Greene and A J Millis, Phys. Rev. B 61, (2000) 9665
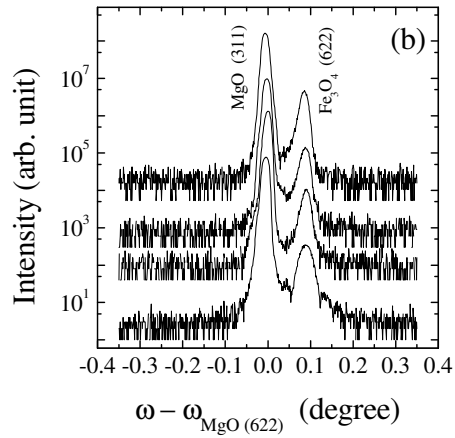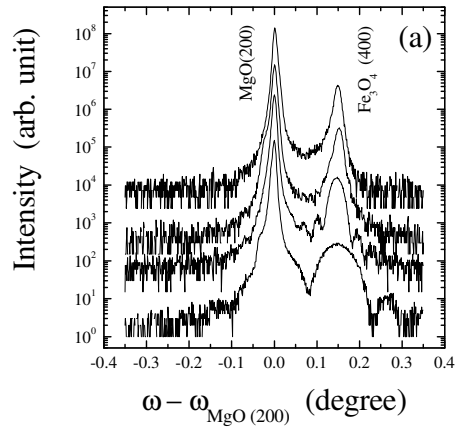
[18] R Koch, D Winau and K H Rieder, Phys. Scr. T49B (1993) 539

Fig. 1: (a) Rocking curves taken around the (200) Bragg reflection of MgO which is common to the (400) reflection of Fe_3O_4 film and (b) rocking curves taken around the (311) Bragg reflection of MgO which is common to the (622) reflection of Fe_3O_4 film in grazing exit geometry. The bottom most curve belongs to the 85 nm thick film and the curves above correspond to 200 nm, 400 nm and 600 nm thick films, in ascending order.
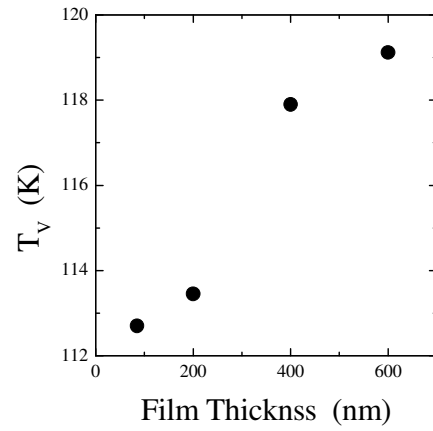
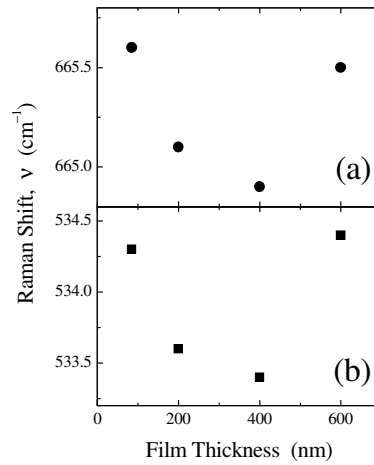Fig. 2. Variation of the Verwey transition temperature, T_V, with film thickness.

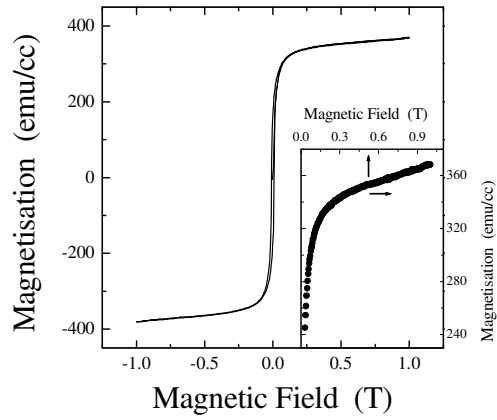Fig. 3. Raman shift of the films as a variation of film thickness for (a) A_{1g} and (b) T_{2g}^2 modes

Fig. 4. Magnetisation curve for 600 nm thick film in the field range from − 1 T to + 1 T, measured at 300 K. The inset shows the exploded view in the high-field region.
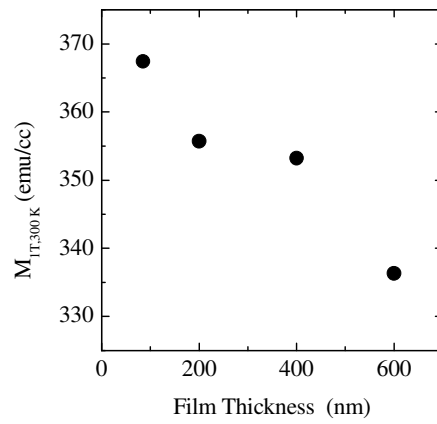

Fig. 5. Room temperature magnetisation measured at 1 T field, $M_{1T,300 K}$ (emu/cc) as a function of film thickness.