

Anomalous strain relaxation behavior of $\text{Fe}_3\text{O}_4/\text{MgO}$ (100) heteroepitaxial system grown using molecular beam epitaxy

S. K. Arora,^{a)} R. G. S. Sofin, and I. V. Shvets

Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), School of Physics, Trinity College Dublin, Dublin 2, Ireland

M. Luysberg

Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

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Strain relaxation studies in epitaxial magnetite (Fe_3O_4) thin films grown on MgO (100) substrates using high-resolution x-ray diffraction and cross-sectional transmission electron microscopy reveal that the films remain fully coherent up to a thickness of 700 nm. This thickness is much greater than the critical thickness t_c for strain relaxation estimated from mismatch strain. Anomalous strain relaxation behavior of $\text{Fe}_3\text{O}_4/\text{MgO}$ heteroepitaxy is attributed to the reduction in the effective stress experienced by the film due to the presence of antiphase boundaries (APBs) that enable the film to maintain coherency with the substrate at large thickness. However, the stress accommodation in the film depends upon the nature and density of the APBs. © 2006 American Institute of Physics.

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I. INTRODUCTION

Recently there has been a considerable interest in studying magnetic oxides due to their interesting fundamental properties and technological importance.^{1–3} These materials exhibit a rich complexity in magnetic and electronic properties due to strong cation-anion bonding, which is not found in metals. In addition, oxide surfaces are more complex than those of metals and semiconductors. There are added complexities due to the fact that some oxide surfaces are polar meaning that they are likely to reconstruct to reduce their surface Coulomb energy.⁴ Representative examples of investigations of two such magnetic oxide surfaces are Fe_3O_4 (100) and Fe_3O_4 (111).^{5,6} Out of the small number of known half metallic materials with high Curie temperatures (>300 K) more than half are oxides. These are manganese perovskites, spinel magnetite, and CrO_2 .^{1–3} Magnetite (Fe_3O_4) is a common and stable oxide. It has been actively studied due to its half metallic ferromagnetic nature, high Curie temperature (838 K), and also because of the metal-insulator transition at 120 K, known as Verwey transition, which is far from being fully understood.⁷ These properties make Fe_3O_4 a potential candidate for spin electronics devices such as spin valves or spin tunnel junctions and microwave resonant circuits. Recent attempts at using Fe_3O_4 for spin tunnel junctions are far from encouraging.^{8–10} To realize these applications, one requires good control over the stoichiometry and precise knowledge of the strain status of the films. The stoichiometry, strain, defect structure, etc., are expected to play a crucial role in determining the magnetotransport and magnetic properties of Fe_3O_4 films. MgO is an ideal substrate for epitaxy of magnetite due to the small lattice mismatch. Consequently, there are many investiga-

tions dealing with the growth of epitaxial thin films of Fe_3O_4 on MgO using a variety of deposition techniques.^{11–16} There are also a few reports concerning the growth of Fe_3O_4 on MgAl_2O_4 , sapphire, and Si and GaAs substrates.^{17–19} The strain state of the film depends on the differences in crystal structure symmetry and lattice mismatch between the film and substrate. It has been noted previously¹⁵ that the Fe_3O_4 films grown on MgO (100) show a sluggish strain relaxation behavior, relaxing partially well above the critical thickness of strain relaxation. Even for a thickness of $6.6\text{ }\mu\text{m}$ the relaxation was partial. However, no effort was made to understand the origin of this behavior.

The crystal structures of MgO and Fe_3O_4 have a cubic symmetry and are based on a face centered cubic (fcc) oxygen sublattice. MgO has a rocksalt structure with a lattice constant of 0.4213 nm and belongs to the $Fm\bar{3}m$ symmetry group. Fe_3O_4 exhibits an inverse cubic spinel structure with a lattice constant of 0.8397 nm and belongs to the $Fd\bar{3}m$ symmetry group.²⁰ The difference in the oxygen sublattice size of MgO and Fe_3O_4 gives a small lattice mismatch of 0.33%. There are two distinct forms of symmetry breaking in $\text{Fe}_3\text{O}_4/\text{MgO}$ heteroepitaxy. The first one is due to the fact that the lattice parameter of MgO is half that of Fe_3O_4 leading to a disruption of translation symmetry. The other one is due to the fact that the Fe_3O_4 ($Fd\bar{3}m$) crystal structure is lower in symmetry than that of MgO ($Fm\bar{3}m$). As a result, MgO unit cell rotated by 90° around an axis perpendicular to the interface falls in itself but the Fe_3O_4 one does not. This leads to the formation of antiphase boundaries (APBs).^{11–16} The differences in crystal structure and symmetry of MgO and Fe_3O_4 prompted us to look at the strain relaxation behavior of Fe_3O_4 films. This information will be very useful in the design of future spintronic devices and nanostructures based on magnetite.

^{a)}Author to whom correspondence should be addressed; FAX: +353-1-6083037; electronic mail: aroras@tcd.ie

II. EXPERIMENT

The Fe_3O_4 thin films of varying thickness (45–700 nm thickness) used in the present study were grown on (100) oriented MgO single crystal substrates (cut along the $\langle 100 \rangle$ direction within $\pm 0.2^\circ$) using an oxygen plasma assisted molecular beam epitaxy (MBE) system (DCA MBE M600) with a base pressure of 2×10^{-10} Torr. The substrates were cleaned *in situ* at 600 °C in 5×10^{-6} Torr oxygen for 2 h. Growth of the Fe_3O_4 films was carried out at a substrate temperature of 250 °C from a pure metallic Fe source by means of electron beam evaporation and oxygen-free radicals generated by an electron cyclotron resonance (ECR) plasma source. The plasma source was operated at 80 W power in an oxygen partial pressure of 1×10^{-5} Torr. Details of the growth conditions are published elsewhere.²¹ Reflection high energy electron diffraction (RHEED) (STAIB Instruments) was used to monitor the growth mode and growth rate (0.3 Å/s). For Fe_3O_4 films grown on MgO (100) surface, half-order streaks corresponding to the Fe_3O_4 film were observed after the growth of 2 ML (monolayer). The lattice constant of the Fe_3O_4 films as determined from the RHEED images was 0.84 ± 0.05 nm.

Magnetization measurements were performed using an alternating gradient field magnetometer (Micromag-3900, Princeton Measurements, USA) with a sensitivity of 10^{-8} emu. The magnetization versus field (M - H) loops were measured at room temperature by applying the magnetic field (maximum field of 1 T) in the film plane along the $\langle 100 \rangle$ direction. The diamagnetic contribution from the MgO substrate was subtracted from the measured data by performing a M - H loop of the MgO substrate of similar dimensions as that of thin film sample, in the same field range. The uncertainty in measuring the absolute value of magnetization for the films was about 1%.

For structural characterization of Fe_3O_4 thin films, high-resolution x-ray diffraction (HRXRD) measurements were performed using a multicrystal high-resolution x-ray diffractometer (Bede-D1, Bede, UK). Monochromatic $\text{Cu K}\alpha 1$ (1.540 56 Å) radiation with 20 arcsec beam divergence was obtained using four Si channel-cut crystals. The HRXRD in double or triple-axis configuration was performed to confirm the epitaxial relationship of the Fe_3O_4 /MgO heteroepitaxy. The in-plane ($a_{\parallel}$) and out-of-plane ($a_{\perp}$) lattice parameters were determined from the analysis of ω - 2θ rocking curves measured around the symmetric (200) and asymmetric (311) diffraction planes common to the substrate and thin film. When operated in triple-axis configuration, this instrument can detect lattice constant variations ($\Delta a/a$) as low as 2×10^{-6} and enables precise determination of the strain relaxation. The reciprocal space maps (RSMs) were obtained by performing a number of ω - 2θ scans for different ω offset values. The ω and ω - 2θ scan directions correspond to reciprocal lattice vectors $Q(x)$ and $Q(z)$ for a (hkl) plane, respectively.²²

To study the coherency of the interface between the Fe_3O_4 and MgO substrate and the morphology of the APBs transmission electron microscopy (TEM) was employed using cross-sectional and plan-view samples. Mechanical thin-

ning and Ar ion milling were applied to obtain electron transparent areas within the TEM specimen. Structural defects were identified by conventional TEM using a Philips CM 20 electron microscope operated at 200 kV. High-resolution images were obtained with a Philips CM 200 electron microscope, which was equipped with a CEOS double hexapole corrector. Adjusting a negative spherical aberration constant C_s of $-40 \mu\text{m}$ and using the optimum overfocus setting of the objective lens of 12 nm resulted in a directly interpretable bright-atom contrast and in minimized, subangstrom delocalizations.²³

III. RESULTS AND DISCUSSION

First we discuss the magnetization and resistivity measurement results in brief to show that the difference in crystal symmetry between the film and substrate has a significant influence on these properties. Magnetization measurements on different thickness magnetite films showed that it was possible to saturate the films of thickness greater than 120 nm with a moderate magnetic field (5–8 kOe). The saturation magnetization M_s measured at room temperature for the Fe_3O_4 films (>120 nm) on MgO substrates was found to be 475 emu/cm³ within the experimental uncertainty of 1%, which includes the error in thin film volume estimate. The observed values of M_s are in agreement with the M_s value for bulk magnetite (480 emu/cm³). For smaller thickness films, the magnetization (M) values attained for a 1 T field were lower than the saturation magnetization (M_s) of bulk magnetite, displaying a finite slope at higher fields. The observation of a reduced M and the inability to saturate epitaxial Fe_3O_4 films have been attributed to the presence of APBs.^{15,16} An increase in M and a reduction in the slope of the M - H curves at higher fields with increasing thickness suggest an increase in separation between the APBs. The magnetization results are in line with the previous reports.^{15,16} In addition to the magnetization measurements, resistivity as a function of temperature was investigated in these films. Resistivity values for these films measured at 300 K were found to decrease with an increase in thickness. For film thickness above 120 nm, the resistivity values were constant. The Verwey transition temperature for these films was found to be thickness dependent, being 108 K for the 45 nm film and 120 K for the 700 nm film. The resistivity results also support our conclusion that the separation between the APBs in Fe_3O_4 /MgO films is thickness dependent and it increases with an increase in film thickness. The magnetization and resistivity results are summarized in Table I.

Figure 1(a) shows the ω - 2θ rocking curves (measured in triple-axis configuration at room temperature) for the (200) and (400) symmetric Bragg reflections of MgO and film, respectively, for different thickness (70–700 nm) Fe_3O_4 films. The horizontal axis in the figure is shown with reference to the Bragg angle of the (200) reflection for MgO substrate. The curves are shifted along the vertical axis for clarity. The bottom- and topmost curves belong to 70 and 700 nm thickness, respectively. The full width at half maximum (FWHM) of the film peak decreases with increasing film thickness, up to a thickness of 200 nm, and remains

TABLE I. Summary of the magnetization (M) at 1 T field, resistivity at 300 K, Verwey transition temperature, and observed and predicted strain relaxation values for the epitaxial magnetite films as a function of film thickness.

Thickness (nm)	M (1 T) (emu/cm ³)	Resistivity at 300 K (Ω cm)	Verwey transition temperature (K)	Observed percentage strain relaxation (%)	Strain relaxation predicted by FKR model (%)
45	440	0.015	108	0	0
70	465	0.010	114	0	0
120	472	0.0071	117.5	0	39
200	475	0.0069	118.2	0	62
400	473	0.0068	120	0	80
700	475	0.0069	120.5	0	88

constant for further increase in thickness. The FWHM for film peak was found to be 0.03° and 0.015° for 70 and 700 nm thick films, respectively. The FWHMs for the film peaks are comparable to that of the substrate (0.008° – 0.009°). The value of $a_\perp$ for the Fe_3O_4 thin films was determined from the separation of film-substrate peaks ($0.146\ 05^\circ$) and was found to be $0.837\ 17$ nm within the experimental accuracy ($\pm 0.000\ 05$ nm). Independent ω -rocking curves for film and substrate peaks indicated that the mosaic spread in the Fe_3O_4 thin films was comparable to that of the substrate. The ω - $n\theta$ ($n=5.18$) rocking curves (measured in double-axis configuration at room temperature) for the (311) asymmetric Bragg reflection of MgO which is common to the (622) reflection of the Fe_3O_4 film, in grazing exit geometry ($\omega=62.5685$, $2\theta=74.6582$), are shown in Fig. 1(b). A value other than 2 of the angular ratio $2\theta/\omega$ was required to detect the thin film peak through a single ω - $n\theta$ scan. This is due to the reason that the position of reciprocal lattice point (RLP) of thin film in the reciprocal space is not in a straight line with substrate RLP position due to the strain tilt. In addition to grazing exit (GE) geometry, asymmetric scans were also performed using a grazing incidence (GI) geometry. From the analysis of GE and GI asymmetric scans we obtained the in-plane and out-of-plane lattice parameters of the films. FWHMs of the film peaks were found to be 0.025° , 0.16° , 0.158° , and 0.158° for 70, 200, 400, and 700 nm thickness films, respectively. The $a_\parallel$ was found to be 0.8426 nm for all the films, within the experimental accuracy, exactly twice the substrate lattice constant. The values of $a_\perp$ are consistent with the values estimated through independent symmetric ω - 2θ scans. The HRXRD results show that the films grown on MgO remain fully coherent up to 700 nm thickness on the MgO (100) substrate. This was the largest thickness we could grow with the MBE due to the small growth rate ($0.3\ \text{\AA}/\text{s}$) used. Moreover, we were concerned with growing films under identical conditions to make sure that there were no variations in the film quality that could complicate the comparison of the strain relaxation behavior.

From the detailed structural characterization, we infer that the films grown on MgO substrates remain fully coherent up to 700 nm thickness. The lack of strain relaxation in $\text{Fe}_3\text{O}_4/\text{MgO}$ up to 700 nm thickness is a totally unexpected result. For Fe_3O_4 films on MgO (100) we expected a significant amount of strain relaxation at a thickness of 700 nm,

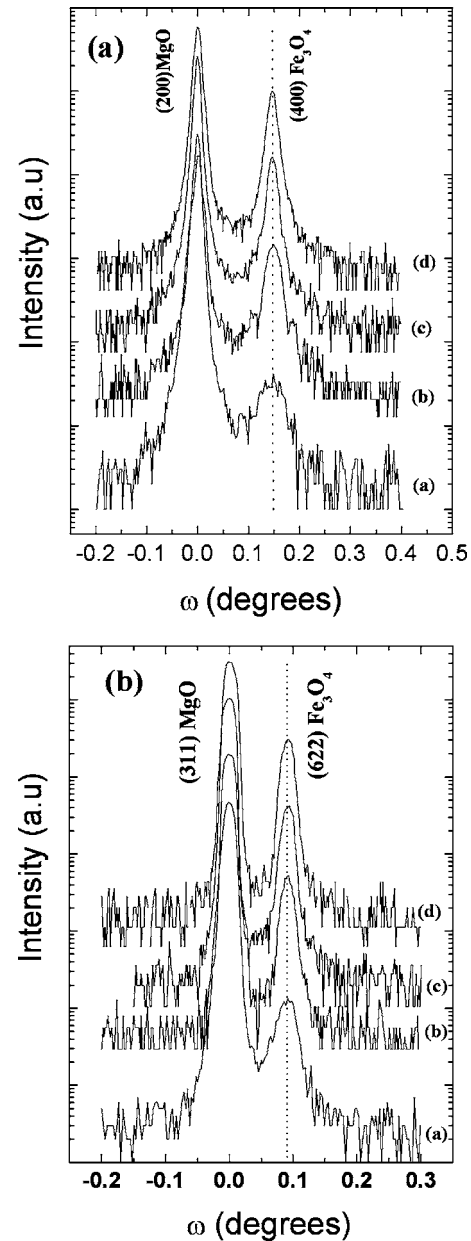


FIG. 1. The ω - 2θ rocking curves for different thickness Fe_3O_4 films of MgO (100) substrates measured for (a) symmetric (200) and (b) asymmetric (311) Bragg reflections common to substrate and thin film. Curves a, b, c, and d correspond to 70, 200, 400, and 700 nm film thickness, respectively, for both the figures. For asymmetric (311) Bragg reflection measurements, the grazing exit geometry was used. Curves are shifted on the vertical axis for clarity.

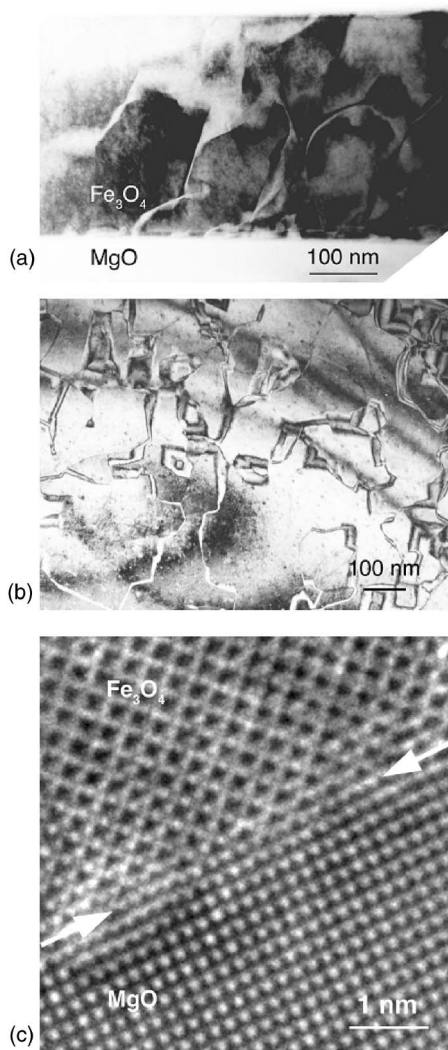


FIG. 2. (a) Cross-sectional TEM image of 400 nm Fe₃O₄/MgO recorded under two beam conditions for (2–20) spinel diffraction showing the presence of APBs in the Fe₃O₄ film. (b) Plan-view electron micrograph taken with (220) two beam imaging conditions showing the network of APBs. (c) High-resolution cross-section TEM image in (100) orientation taken with a $C_s = -40 \mu\text{m}$ and at overfocus. Accordingly, white atom contrast is obtained. Arrows mark the Fe₃O₄-MgO interface.

which is much greater than the estimated value of critical thickness t_c (60 nm) for strain relaxation on the basis of widely used Matthews and Blakeslee's (MB) model.²⁴

Further, to check the coherency of the interface we performed TEM studies on these Fe₃O₄ films. Figure 2(a) shows a cross-sectional TEM bright field image of an Fe₃O₄-MgO interface. According to the (220) two beam imaging conditions chosen, APBs are characterized by distinct contrast fluctuations. The network of APBs is observed to be denser close to the interface. The typical separation between APBs within the upper part of the film is about 100 nm. This is also confirmed by the plan-view image, which shows the upper part of the film [Fig. 2(b)]. Again (220) two beam imaging conditions were applied to visualize the APBs. Due to their inclination towards the electron beam, some of the APBs display a fringe contrast. Apart from the APBs no structural defects such as dislocations were observed, no matter which imaging condition was chosen. The high-resolution electron

micrograph [Fig. 2(c)] displays the interface between the MgO substrate and the Fe₃O₄ film. A white atom contrast was obtained according to the negative C_s imaging conditions chosen. The interface was observed to be completely coherent.

The network of APBs is formed during the coalescence of the initial spinel nuclei.^{11,12,15} While the oxygen sublattice of different islands coalesces without forming any defects, various arrangements of cations in the spinel islands result in the formation of APBs. In our case, the systematic variation of separation between APBs, across the film thickness, is contrary to previous reports.^{12,25} Earlier reports suggested that the separation between APBs increases with film thickness and is uniform for a given thickness. However, the results reported by them^{12,25} refer to a plan-view configuration; therefore, the information related to the size in the growth direction is not accessible. The size evolution of structurally shifted domains is not an uncommon feature and has been reported previously by other researchers for the case of GaAs/Si and GaAs/GaAs.^{26,27} The driving force for the reduction of the density of APBs can be the minimization of the total energy which implies a minimization of the APB area. Another possibility to explain the size evolution is the fusion of two APBs on different $\langle 110 \rangle$ planes, e.g., if two APBs grow along the $\langle 011 \rangle$ and $\langle 01\bar{1} \rangle$ directions, they may merge at some thickness depending on their separation at the point of nucleation. This issue will be addressed in a separate report.

In order to look at the anomalous strain relaxation behavior of Fe₃O₄/MgO heteroepitaxy, first we present the details of the t_c prediction for this system. We consider the Fischer, Kuhne, and Richter (FKR) model²⁸ to estimate the critical thickness of a heteroepitaxial system above which the film exhibits strain relaxation. This model is a modified form of the MB model and takes into account the interaction between dislocations employing the image force approach. Critical thickness t_c estimated through this approach generally yields better agreement with experimental results. The critical thickness given by this model is

$$t_c = \frac{b \cos \lambda}{e} \left\{ 1 + \ln \left(\frac{t_c}{b} \right) \left[\frac{1 - \nu/4}{4\pi(1 + \nu)\cos^2 \lambda} \right] \right\}, \quad (1)$$

where b is the Burgers vector, e is the misfit strain [$e = (a_f - a_s)/a_s$] (a_f and a_s being the film and substrate lattice parameters), ν is the Poisson ratio, and λ is the angle between the Burgers vector and the direction in the interface, normal to the dislocation line. By using the experimentally obtained value of $\nu = 0.30$ (estimated by measuring $a_{\parallel}$ and $a_{\perp}$ from the asymmetric Bragg reflection performed in grazing exit and grazing incidence geometries) and Burgers vector values of 0.595 80 nm, this model gives a value of t_c of 70 nm for the Fe₃O₄/MgO system. Figure 3 shows the calculated equilibrium in-plane strain $\epsilon_{\parallel}$ using the FKR model for Fe₃O₄ films on MgO as a function of thickness along with the measured experimental data. It is evident from this figure that the observed and calculated values are not in agreement. For Fe₃O₄/MgO heteroepitaxy, no relaxation is observed up to 700 nm. This thickness is about an order of magnitude larger than predicted by the FKR model. In an earlier study, Mar-

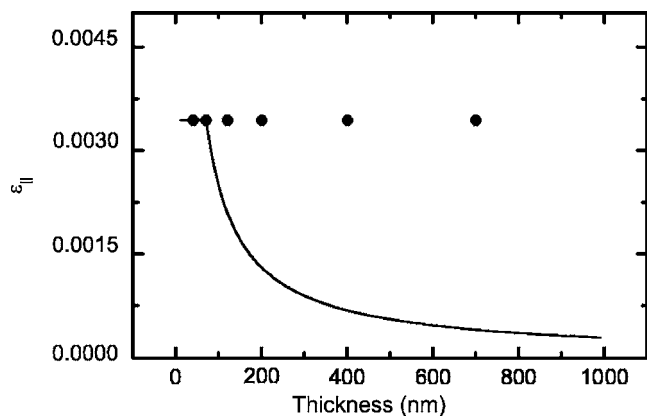


FIG. 3. Comparison of experimentally observed values of the in-plane strain $\epsilon_{||}$ with the FKR model predictions for the Fe_3O_4 films grown on MgO (100) substrates as a function of thickness. The solid line is the theoretical prediction and scattered points are experimentally observed values.

gules *et al.*¹⁵ have mentioned about the partial relaxation of strain in films much thicker than the critical thickness of strain relaxation. Even at $6.6\ \mu\text{m}$ thickness the films do not exhibit fully relaxed state. Although they noticed this feature, the issue of anomalous strain relaxation behavior was not addressed, as this was not the main focus of their investigations. Kale *et al.*¹⁸ explained some of the anomalous features observed in the magnetic properties of Fe_3O_4 films on MgO and MgAl_2O_4 substrates on the basis of critical thickness calculations. It was not clear from their investigations that whether the $\text{Fe}_3\text{O}_4/\text{MgO}$ films did exhibit anomalous or normal strain relaxation behavior as no details on the structural characterization were provided.

In order to understand the driving force that enables the film to maintain this large amount of elastic energy in $\text{Fe}_3\text{O}_4/\text{MgO}$ heteroepitaxy, we need to analyze the crystal structure differences between MgO and Fe_3O_4 . One could suggest that the structure of Fe_3O_4 accommodates the strain by deviation from stoichiometry. Such deviations should result in a lattice constant change. However, this explanation has to be discarded due to the fact that the volume of the magnetite unit cell in our films, which is sensitive to deviations from stoichiometry, remains constant. In addition to structural investigations the Verwey temperature of the films was also measured using the four-probe resistivity technique. As the Verwey temperature is highly sensitive to deviations from stoichiometry, its presence in all the films (Table I) further confirms that the films consist of stoichiometric magnetite.

Another reason for the lack of strain relaxation at much greater thickness in this heteroepitaxial system is possibly related to the difference between the crystal symmetries of the film and substrate, which lead to the formation of APBs. APBs can be formed due to the different translation and rotational symmetries of Fe_3O_4 and MgO. There are two kinds of APBs resulting from the disruption of translation symmetry. These correspond to half and quarter lattice constant shifts along the $[100]$ and $[110]$ directions, respectively. The third type of APBs results from the disruption of rotational

symmetry, which is equivalent to an out-of-plane shift by a quarter of a lattice period. The structure of these APB, is discussed in detail by Eerenstein *et al.*²⁵

The APBs in Fe_3O_4 thin films have been revealed by scanning tunneling microscopy (STM), TEM, and magnetic force microscopy (MFM) studies.^{15,25,29,30} We suggest that the presence of APBs influences the strain relaxation behavior of the Fe_3O_4 films. Although the symmetry faults leading to APB formation are easy to figure out, the detailed structure of the APBs on the atomic level is unclear. At present, there is not enough experimental data to provide an understanding of the issue. The region around an APB could be nearly stoichiometric or substantially nonstoichiometric since the spinel structure itself contains a large amount of vacant *A* and *B* sites. Therefore, the total energy of the APB depends on its shape, size, number of erroneous bonds, nearest neighbor interaction, and the atomic arrangement in its vicinity. The APB is a static defect and one might expect that when the growth of the first monolayer of Fe_3O_4 is completed, these domains would grow vertically, so that the film thickness does not affect the density of the APBs. However, this is not the case as reported by others.²⁵

Our results suggest that the presence of APBs is responsible for the observed strain relaxation behavior. Before discussing the mechanism through which the APBs can participate in the film's strain relaxation, we would like to make a more general remark. It is reasonable to expect that the mechanical properties of a single APB are different for the two directions: along and perpendicular to the APB's plane. The growth of APBs is also known to be strongly anisotropic with respect to the film surface, i.e., the density of APBs with planes directed substantially perpendicular to the surface of the film is significantly different from that of the APBs with planes substantially parallel to the surface. Consequently, elastic properties of the film in the direction perpendicular to its surface are different from those along the surface. Therefore the entire film no longer has the elastic properties of a material with cubic symmetry but rather of one with a lower symmetry. In terms of the elasticity tensor ($E_{\sigma\mu\nu}$), the tensor of bulk magnetite has three components similar to that of any cubic material whereas the $\text{Fe}_3\text{O}_4/\text{MgO}$ film must have a greater number of components. Therefore the model of strain relaxation that fits well for cubic/isotropic material without APBs does not necessarily fit ones with lower symmetry of elasticity tensor. This suggests that the presence of APBs will affect the strain relaxation behavior in the $\text{Fe}_3\text{O}_4/\text{MgO}$ system. Our mechanism involves the consideration that there is no reason why APB should be based on a perfect oxygen sublattice. The models of APBs do invariably assume that the oxygen sublattice is stoichiometric and is in perfect match with that of the substrate. There is no justification for this assumption. On the contrary one should expect that this is not the case. We shall illustrate this point using several examples of APBs. Figure 4(a) shows the APB based on the $\frac{1}{2}[100]$ lateral displacement fault. The direction of the APB in this example is along $[010]$. Figure 4(a) shows the hypothetical "perfect" APB in which the anionic sublattice is perfect. In general, a perfect APB will be unstable due to charge pileup. Therefore, one could expect that the cations will be

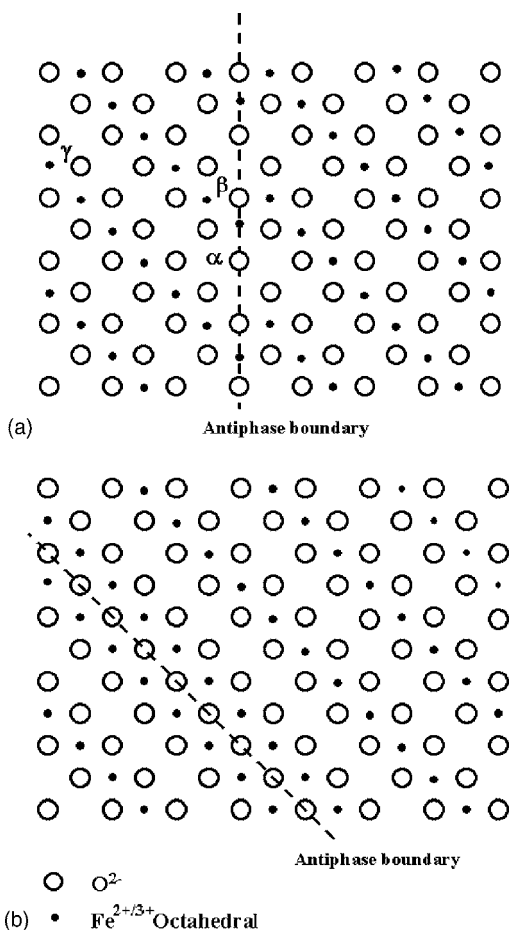


FIG. 4. Schematic diagram of an antiphase boundary formed in Fe_3O_4 films grown on MgO (100) substrate assuming a perfect oxygen sublattice; (a) with $\frac{1}{2}$ [100] shift vector along the [010] direction and (b) $\frac{1}{4}$ [100] shift vector along the $[1-10]$ direction.

redistributed to achieve a local charge neutrality. If one considers the details of the film growth process, it should be expected that on the contrary, some anion positions should be vacant. Indeed growth of the film implies that the MgO surface is showered by Fe atoms and they react with the oxygen in the environment of the chamber to form magnetite. With this mechanism in mind, the oxygen pressure in the chamber is adjusted to form the correct phase of iron oxide. The oxygen pressure required for the growth of a particular iron oxide is representative of the reactivity of iron on the surface. Now we can appreciate that the surface reactivities (affinity of oxygen) of the sites α and β are different. It is also different from the reactivity of the sites away from the APB (e.g., site γ). One should expect that the sites α are likely to remain vacant as they are located away from the Fe ions and thus oxygen affinity at these is reduced. Another example is shown in Fig. 4(b). This involves the APB formed by $\frac{1}{4}[110]$ lateral displacement fault that is directed along $[1-10]$. In this case the anions located directly at the APB have a different cationic coordination than those in the area away from the APB, again prompting a different reactivity. Moreover, even for the APB based on the same type of fault and having the same boundary direction, there are numerous possibilities for defects in the anionic lattice. Figure 5 shows two possible cases of the APB caused by a rotation fault and aligned along

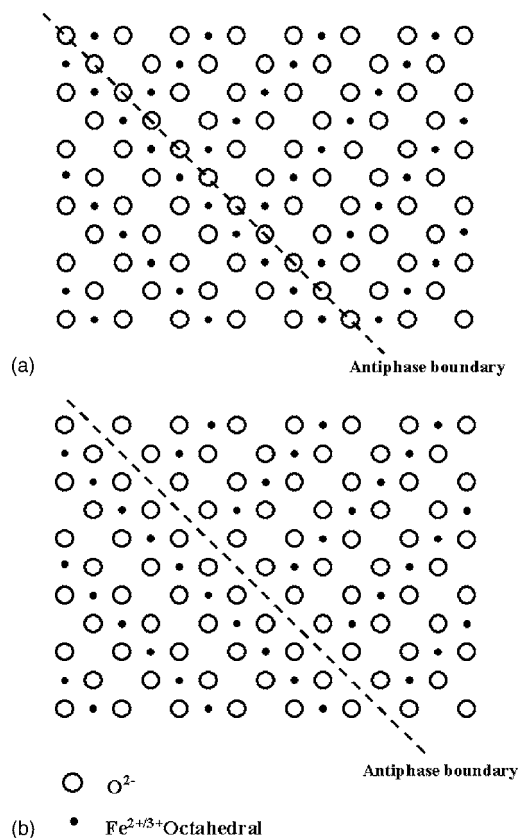


FIG. 5. Schematic diagram of a rotational-type antiphase boundary aligned along the [110] direction showing two different possibilities of (a) higher coordination for anions at the boundary and (b) lower coordination for anions at the boundary.

[110]. One can appreciate that in the case of Fig. 5(a) the coordination number of anions at the APB is greater than that away from the APB. The situation is reversed in the case of Fig. 5(b). At present there is not enough experimental data to provide atomic scale information on the APB structure; however, it is clear that the common assumption of the perfect oxygen lattice is unlikely to be correct. One should further expect that APB with vacant oxygen sites develops a compressive strain in the film. Such a compressive strain should have a strong implication on the strain relaxation behavior in the Fe_3O_4 /MgO (100) heteroepitaxial system. Therefore, the film containing APBs can be represented by areas having a different sign of strain, i.e., the domains under an in-plane tensile strain due to lattice mismatch, joined by the boundaries imposing a compressive strain onto the domains. This alteration of areas within the film having opposite kind of stress will reduce the overall strain experienced by the film and decrease the free energy of the system. It enables the system to maintain the fully strained state much above the t_c . It has been noted previously^{31,32} that in thin films containing structurally shifted domains, a compressive strain develops at the domain boundaries. This is a situation similar to the one in superlattice heterostructures where one can grow an overlayer of large mismatch on a substrate by growing it in alteration with the layer of another material that compensates for the mismatch strain. The effective stress experienced by the film will be strongly influenced by the density of APBs and their orientation and size. Therefore, depending on the

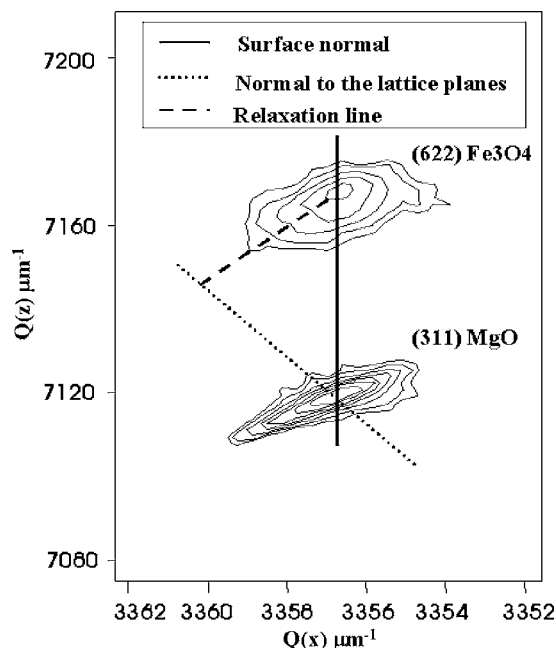


FIG. 6. Reciprocal space maps around the (311)/(622) Bragg reflection in grazing exit geometry for 700 nm thick Fe_3O_4 thin films on MgO (100) substrate. The vertical line shows the direction normal to the growth plane and the dashed line shows the direction of relaxation. The direction normal to the (311) planes is also shown. Along the x axis $Q(x)$ is plotted [$a_{\parallel} = \sqrt{2} \times 10^4 / Q(x)$] and $Q(z)$ along the y axis [$a_{\perp} = 3 \times 10^4 / Q(z)$].

density of the APBs and their type, one can observe a pattern of strain relaxation critical thickness for the films containing APBs.

We could further propose that the composition of the APB and the number of defects in it could be affected by the strain. For example, it is known that the affinity of the Fe surface to oxygen is affected by the value of stress in the Fe film.³³ One would therefore expect that the stoichiometry of the APB and the number of defects and vacancies in the film may be effected through the feedback mechanism. The feedback could be either positive or negative, thereby creating additional defects in the APBs, which, respectively, act to reduce or increase the overall strain in the film.

Further, due to the anisotropic stress accommodation by APBs, as the density of APBs decreases with film thickness, the in-plane strain that is induced by them according to our model changes with thickness: the upper part of the film close to the surface and its lower part close to the interface have different strain values. This must be reflected in small changes of in-plane and out-of-plane lattice constants along the film thickness and therefore, smearing of the diffraction peaks. As evident from the broadening of the FWHM for thin film peak observed in triple-axis geometry (311) rocking curves, FWHM was found to be 0.0064° and 0.0077° for 400 and 700 nm thickness, respectively. To extract this information in detail, one needs to carry out a RSM for an asymmetric Bragg reflection. Broadening of RLP can provide information regarding the absence or presence of strain or compositional gradients. In Fig. 6, we show a reciprocal space map for the 700 nm Fe_3O_4 film on MgO measured for the (311) Bragg planes in grazing exit geometry ($\omega = 62.5685$, $2\theta = 74.6582$). The reciprocal lattice vectors $Q(x)$

and $Q(z)$ represent the in-plane (110) and out-of-plane (100) directions, respectively. The position of the intense substrate peak is adjusted to the bulk MgO ($a = 0.4213$ nm) position. From the position of the thin film reciprocal lattice point in the RSM along the $Q(x)$ and $Q(z)$ directions, we find that the in-plane lattice parameter of the film is 0.8426 nm, and it is exactly twice the substrate lattice constant. In Fig. 6 we have also shown the direction of the relaxation line. The relaxation line can be calculated analytically and it depends on the surface orientation and the elastic properties of the layers as well as the Bragg reflection considered.²² From the figure it is clear that the layer RLP broadens in the direction of the relaxation line. The broadening along the relaxation line is indicative of the presence of a strain gradient in the layer without affecting the stoichiometry. However, if a composition gradient was present in the layer then one expects broadening of the RLP towards the substrate RLP.

To check the assumption of our model that the stress compensation depends on the APB density, we have grown another (set 2) of films of 400 and 700 nm thickness to obtain a different density of APB. These films were grown under slightly different growth conditions than those used for the previous set of samples to obtain a significantly different value of APB density. Magnetization measurements on the second set of films yielded reduced magnetization values (410 and 430 emu/cm³ for 400 and 700 nm films, respectively), suggesting that these films had a significantly larger density of APBs than the first set of films. The second set of films showed 12% and 16% relaxations for 400 and 700 nm thickness, respectively. The observed relaxation values are still lower than the value of strain relaxation predicted for 400 and 700 nm thickness in $\text{Fe}_3\text{O}_4/\text{MgO}$ heteroepitaxy. This result demonstrates the link between the APBs and the status of strain relaxation. However, since the details of the structure of the APB and their exact orientation are not known at present, it is not possible to make any definitive suggestions on the functional relationship between the APB density and the strain relaxation behavior. We have summarized the observed values of magnetization, resistivity, and calculated and observed strain relaxation values in Table I for the Fe_3O_4 films grown on MgO substrates. Our model of stress accommodation by APBs in epitaxial magnetite films also explains the lack of relaxation in much thicker films by Margulies *et al.*¹⁵

Another possibility for the failure of critical thickness predictions in the case of $\text{Fe}_3\text{O}_4/\text{MgO}$ is possibly related to the impediment of dislocation movement by the large Peierls force that creates an activation barrier.³⁴ There are modified forms of MB model, which attempt to explain the large critical thickness for low misfit heterostructures grown at low temperatures.³⁴ The effect of this is to raise the critical thickness at low growth temperatures. By extrapolation of this argument, it is possible that high growth temperature or post-growth treatment could reduce the Peierls barrier and therefore reduce the critical thickness that will approach the MB model prediction. Chidambarrao *et al.*³⁵ have obtained a good agreement between the calculated critical thickness based on the above considerations and the observed values for the Si-Ge/Si system. Liu *et al.*³⁶ have shown that low

temperature grown pseudomorphic InGaAs/GaAs heterostructures can be relaxed by a high temperature postgrowth treatment, which reduces the Peierls barrier. In our case postgrowth high temperature annealing or high temperature growth, which could shed light on this aspect, is not feasible due to the reason that at higher temperatures Mg diffuses into Fe_3O_4 and forms a MgFe_2O_4 phase.³⁷ This will alter the lattice mismatch and hence the critical thickness. Therefore, we have not attempted to explore this issue. Moreover, our study suggests that the strain relaxation behavior depends on the density of APBs.

IV. CONCLUSIONS

From the strain relaxation studies of epitaxial Fe_3O_4 thin films grown on MgO (100) substrates we infer that the films grown on MgO (100) substrate remain fully coherent up to much greater thickness than predicted by the FKR model (~ 70 nm). The observed strain relaxation behavior is attributed to the differences in the crystal structure symmetry between MgO and Fe_3O_4 . Due to the lower crystal symmetry of the spinel structure of Fe_3O_4 compared to that of MgO, APBs are formed and lead to the formation of areas within the film that have opposite sign of stress. The stress compensation by the APBs reduces the effective stress experienced by the films. The reduction in effective stress experienced by the film depends strongly on the nature and density of APBs.

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