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Structural phase diagram for ultra-thin epitaxial Fe₃O₄/MgO(001) films: thickness and oxygen pressure dependence

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Abstract

A systematic investigation of the thickness and oxygen pressure dependence for the structural properties of ultra-thin epitaxial Fe₃O₄ films has been carried out; for such films, the structural properties generally differ from those for the bulk when ≤ 10 nm. Iron oxide ultra-thin films with thicknesses varying from 3 nm to 20 nm were grown on MgO (001) substrates using molecular beam epitaxy under different oxygen pressures ranging from 1×10^{-7} torr to 1×10^{-5} torr. The crystallographic and electronic structures of the films were characterized using low energy electron diffraction and x-ray photoemission spectroscopy, respectively. The quality of the epitaxial Fe₃O₄ ultra-thin films was judged by magnetic measurements of the Verwey transition, along with complimentary XPS spectra. It was observed that the stoichiometry of ultra-thin films under 10 nm transform from the Fe₃O₄ phase to the FeO phase. In this work, a phase diagram based on thickness and oxygen pressure has been constructed to explain the structural phase transformation. It was found that high-quality magnetite films with thicknesses ≤ 20 nm formed within a narrow range of oxygen pressure. An optimal and controlled growth process is a crucial requirement for the accurate study of the magnetic and electronic properties for ultra-thin Fe₃O₄ films. Furthermore, these results are significant because they may indicate a general trend in the growth of other oxide films, which has not been previously observed or considered.

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I. INTRODUCTION

Magnetite (Fe_3O_4) has great potential for use in the new field of spintronics due to its interesting physical properties, e.g., ferrimagnetic and half-metallic behavior. Therefore, a basic understanding of these properties is essential for such applications. In addition to understanding the phenomena occurring at Fe_3O_4 surfaces, mastering the growth conditions of ultra-thin films of Fe_3O_4 with respect to the stoichiometry remains an important and very general challenge. One of the important issues of iron oxides is the mixed iron valence ($\text{Fe}^{2+}/\text{Fe}^{3+}$). Thus, iron oxides of different stoichiometry such as maghemite ($\gamma\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), and wüstite (FeO) can be formed and even transformed into one another under certain conditions. The structural, transport, and magnetic properties of the oxide films are strongly dependent on the oxygen content [1–4]. Furthermore, the ultra-thin film characteristic material properties are often changed due to finite size and/or interface effects between substrate and film. In particular, previous studies have reported that the structure of Fe_3O_4 films with thicknesses less than 10 nm is different from the bulk [5-6]. One important property of magnetite is that it has a metal/insulator transition at $T_V \approx 125$ K, known as the Verwey transition [7-8]. As the temperature is reduced below the Verwey temperature, the conductivity as well as the magnetization can decrease by as much as two orders of magnitude. This behavior is attributed to a charge ordering at the octahedral sites. The Verwey transition in magnetite films is very sensitive to the stoichiometry, which in turn depends on the deposition parameters such as the oxygen pressure [9–13]. Therefore, it is a useful indicator of the optimum growth conditions for high-quality magnetite thin films [14].

In this work, a comprehensive study of the effect of thickness and oxygen pressures on the structural properties of epitaxial Fe_3O_4 ultrathin films grown on MgO (001) substrates is presented. In order to get films of high quality, molecular beam epitaxy (MBE) under ultra-high vacuum was employed. The films were characterized *in-situ* by low energy electron diffraction (LEED) and x-ray photoemission spectroscopy (XPS) as well as ex-situ magnetic measurements.

The quality (stoichiometry) of the epitaxial Fe_3O_4 thin films was judged by magnetic measurements of the Verwey transition along with complimentary XPS spectra. In an earlier study, the optimum oxygen pressure during the growth of 20 nm Fe_3O_4 films was determined by observation of the Verwey transition [15]. This work explores further the effect of oxygen pressure on the stoichiometry of 20 nm Fe_3O_4 films as well as films with thicknesses less than 20 nm.

II. EXPERIMENT

The Fe_3O_4 films were grown by MBE on MgO (001) substrates under ultra-high vacuum with the base pressure lower than 3×10^{-10} torr. The MBE growth chamber also includes LEED and XPS for *in-situ* study of the surface structure of the films without breaking the vacuum. Before film deposition, the MgO (001) single crystal substrates were cleaned with acetone and methanol in ultrasonic baths followed by heating up to 300 °C in 2×10^{-7} torr of oxygen for 30 min in the ultra-high vacuum chamber. Afterwards, the high quality of the crystal surface of the substrate was confirmed by a sharp LEED pattern and XPS.

Iron oxide thin films with thicknesses ranging from 3 nm to 20 nm were prepared under different oxygen pressure ranging from 1×10^{-7} torr to 1×10^{-5} torr using a reactive MBE method. For this purpose, pure iron was evaporated by thermal evaporation with a deposition rate of 3.33 Å/min at substrate temperature of 250 °C to avoid interdiffusion of magnesium ions from the substrate into the film [16]. The growth was terminated by immediately closing the Fe shutter and the oxygen leak valve, and pumping out the residual oxygen while keeping the sample at 250 °C for approximately 4 min until the chamber pressure was reduced to below 5×10^{-9} torr. The deposition rate was measured using a quartz crystal oscillator balance which was calibrated by XPS analysis. After deposition, the crystallographic and electronic structures of the films were studied by LEED and XPS (Mg-K α), respectively. These surface analysis techniques were used to distinguish between the iron oxide phases. Finally, the surfaces of samples were capped with a

very thin layer (2nm) of MgO, in order to avoid oxidation of the film and/or transformation to another iron oxide phase, e.g., γ -Fe₂O₃, prior to the magnetic measurements.

The magnetization measurements were carried out using a superconducting quantum interference device (SQUID) from Quantum Design. Measurements of the magnetization temperature dependence and the magnetization hysteresis loops were obtained with the magnetic field applied in-plane along the [001] direction of the film.

III. RESULTS AND DISCUSSION

A. Low Energy Electron Diffraction

Using oxygen pressures ranging from 1×10^{-7} torr to 1×10^{-5} torr, four series of films were grown with thicknesses 20 nm, 10 nm, 5 nm, and 3 nm. Low energy electron diffraction probes the surface crystal structure and is sensitive to the top two or three atomic layers. The LEED patterns of all films in this work were obtained with an electron energy of 137 eV. Figure 1 shows typical sharp and intense LEED patterns obtained from (a) a clean MgO (001) substrate and (b) an epitaxial 20 nm Fe₃O₄ (001) film grown at $p(\text{O}_2) = 7 \times 10^{-7}$ torr. An oxygen pressure of 7×10^{-7} torr was shown previously to be optimal for the growth of 20 nm Fe₃O₄ films [15]. The (1×1) unit cell and the ($\sqrt{2} \times \sqrt{2}$) $R45^\circ$ superlattice for the Fe₃O₄ (001) thin film are indicated by the larger (red) solid square and smaller (blue) solid square, respectively. The lattice parameter of Fe₃O₄ (8.39 Å) is nearly twice that of MgO (4.21 Å). All of the 20 nm films grown with oxygen pressures ranging from 3×10^{-7} torr to 1×10^{-6} torr showed the ($\sqrt{2} \times \sqrt{2}$) $R45^\circ$ surface reconstruction relative to the primitive surface unit cell of magnetite [17,18]. Figures 1(c) and 1(d) show the LEED patterns for an epitaxial 10 nm Fe₃O₄ (001) film grown at $p(\text{O}_2) = 7 \times 10^{-7}$ torr and an epitaxial 3 nm FeO (001) film grown at $p(\text{O}_2) = 7 \times 10^{-7}$ torr, respectively. The LEED pattern for the 10 nm film (Fig. 1(c)) shows the same surface structure as the 20 nm film (Fig. 1(b)), i.e., characteristic of single crystal magnetite; however, films under 10 nm, such as the 3 nm film shown in Fig. 1(d), did not. In Fig. 1(d), the (1×1) unit cell of FeO is indicated by the (red) dashed square. FeO has essentially the same basic structure and almost

same lattice constant (4.3 Å) as MgO (4.21 Å). Thus, the observation of this superstructure (1×1), as shown in Fig. 1(d), is a clear indication for the formation of a high-quality wüstite (FeO) surface. The LEED patterns clearly indicate that, for a fixed oxygen pressure (7×10^{-7} torr), reducing the film thickness to less than 10 nm results in a transformation to the FeO phase. Also, XPS and magnetic measurements support this conclusion (see below). The three different phases wüstite (FeO), magnetite (Fe₃O₄), and hematite (α -Fe₂O₃) can be distinguished by their diffraction patterns as they form different superstructures; however, it is hard to distinguish between γ -Fe₂O₃ (maghemite) and Fe₃O₄ with LEED because they have same superstructures and the lattice parameters are within the error bars of the measurements [19-22].

B. X-ray Photoemission Spectroscopy

In order to identify the chemical state of the iron oxide, Fe 2p core-level XPS spectra were recorded for the iron oxide films grown under oxygen pressures ranging from 1×10^{-7} to 1×10^{-5} torr and with thicknesses from 3 nm to 20 nm. It is well known that the various iron oxides (γ -Fe₂O₃, Fe₃O₄, and FeO) can be distinguished from each other by their characteristic satellite peaks [23-26]. The Fe 2p_{3/2} satellite binding energy is different for the Fe²⁺ and Fe³⁺ valence states which occur for FeO and γ -Fe₂O₃, respectively; i.e., FeO and γ -Fe₂O₃ have clear satellite features at 715.5 eV and 719.1 eV, respectively. On the other hand, for stoichiometric Fe₃O₄, the presence of both satellites makes the distinct satellite peaks unresolvable.

Figure 2 shows the Fe 2p core-level XPS spectra for 20 nm iron oxide films grown with different oxygen pressures. The films grown at $p(\text{O}_2) = 1 \times 10^{-7}$ torr, 3×10^{-7} torr, and 5×10^{-7} torr have a weak satellite at 716.3 eV indicating the presence of excess Fe²⁺ ions as compared to bulk Fe₃O₄. For the film grown at the lowest oxygen pressure (1×10^{-7} torr) for the 20 nm series, the line shape of the Fe 2p spectrum looks different. The strong intensity of the Fe²⁺ satellite at 716.3 eV can be taken as an indication of the FeO phase and the feature at 707 eV indicates that metallic Fe clusters are present. In contrast, a satellite at 717.8 eV is observed for the films grown with $p(\text{O}_2) = 1 \times 10^{-6}$ and 4×10^{-6} torr, indicating presence of excess Fe³⁺ ions compared to bulk Fe₃O₄. This satellite indicates a shift of the film oxide phase from FeO toward γ -Fe₂O₃. The Fe 2p spectrum for the film grown with $p(\text{O}_2) = 7 \times 10^{-7}$ torr shows no sign of a satellite structure, which is taken as an indication of stoichiometric Fe₃O₄.

Figure 3 shows the Fe 2p core-level XPS spectra for the iron oxide films which were grown at $p(\text{O}_2) = 7 \times 10^{-7}$ torr with different thickness (20 nm, 10 nm, 5 nm, and 3 nm). Significant changes are observed with decreasing thickness from 20 nm to 3 nm. A satellite close to the Fe $2p_{3/2}$ main peak at 716.3 eV is observed for films ≤ 10 nm, indicating the presence of excess Fe^{2+} ions compared to bulk Fe_3O_4 . The intensity of this satellite, which is characteristic for the formation of Fe^{2+} ions in FeO, increases with decreasing thickness and the film transforms completely to the FeO phase when the thickness is ≤ 5 nm. Also, it can be seen in Fig. 3 that the Fe $2p_{3/2}$ main peak gradually shifts to lower binding energy with decreasing film thickness, also indicating the change in the structure of the films. The growth rate, oxygen pressure, and substrate temperature were identical for all of these films during deposition. Therefore, it can be concluded that the change in the stoichiometry from bulk Fe_3O_4 to FeO, is not related to one of the deposition parameters, but may be attributed to substrate-induced effects. This phenomena of initial formation of FeO during growth of very thin iron oxide layers has been reported for both metal substrates as well as oxide substrates [19, 27-30].

Figures 4 and 5 show the Fe 2p core-level XPS spectra for selected films with thicknesses 10 nm and 5 nm grown under various oxygen pressures, from 1×10^{-7} to 2.5×10^{-6} torr and from 7×10^{-7} to 1×10^{-5} torr, respectively. In Fig. 4, the Fe 2p XPS spectrum for a 10 nm film grown at 7×10^{-7} torr shows a weak satellite at 716.3 eV, suggesting an increase of the Fe^{2+} content associated with the presence of oxygen defects. For the 10 nm film grown at 1×10^{-6} torr, there is no sign of the Fe^{2+} and Fe^{3+} satellite structures. On the other hand, a satellite at 717.8 eV is observed for the film grown at 2.5×10^{-6} torr, indicating a presence of excess Fe^{3+} ions. This satellite behavior indicates a stoichiometric shift of the films from Fe_3O_4 toward the $\gamma\text{-Fe}_2\text{O}_3$ phase. At the low oxygen pressure from 3×10^{-7} torr to 1×10^{-7} torr, the line shape of Fe 2p spectra for the films looks much different and the feature at 707 eV can be taken as an indication that metallic Fe clusters are present. Since this (707 eV) feature is the main peak in the XPS spectrum for an Fe metal film, the Fe spectrum is plotted for reference in Fig. 4. In addition, a satellite structure for Fe^{2+} can be observed at 716.3 eV and the intensity of this satellite increases slightly with decreasing oxygen pressure, indicating an increasing Fe content. In conclusion, for

a 10 nm film thickness, the contribution of Fe^{2+} in the films gradually increases with decreasing $p(\text{O}_2)$ from 7×10^{-6} to 1×10^{-7} torr. Furthermore, it can be seen in Fig. 4 that the Fe $2p_{3/2}$ main peak of the films gradually shifts to lower binding energy with decreasing oxygen pressure, supporting the change in the structure of the films from Fe_3O_4 to the FeO phase. Figure 5 shows a selected series of Fe 2p core-level spectra for 5 nm iron oxide films grown with various oxygen pressures. Going from $p(\text{O}_2) = 7 \times 10^{-7}$ to 1×10^{-5} torr, the spectra shows that the surface structure changes from FeO to the $\gamma\text{-Fe}_2\text{O}_3$ phase. The films prepared at $p(\text{O}_2) = 2 \times 10^{-6}$ and 4×10^{-6} torr are nearly stoichiometric Fe_3O_4 , while the one grown at 1×10^{-5} is consistent with stoichiometric $\gamma\text{-Fe}_2\text{O}_3$. On the other hand, the films prepared with $p(\text{O}_2) = 7 \times 10^{-7}$ and 1.0×10^{-6} torr are consistent with stoichiometric FeO. The Fe $2p_{3/2}$ main peak also gradually shifts to lower binding energy with decreasing oxygen pressure.

C. Magnetization

As mentioned above, four series of films were grown with thicknesses 20 nm, 10 nm, 5 nm, and 3 nm, using oxygen pressures ranging from 1×10^{-7} torr to 1×10^{-5} torr. In order to determine the optimum oxygen pressure for the growth of fully stoichiometric Fe_3O_4 films for each thickness, the Verwey transition was investigated using magnetization measurements. The temperature dependence of the zero field cooled (ZFC) magnetization curve was measured for the various films. The measurements were made with magnetic fields ranging from 300 Oe to 1,000 Oe, applied in-plane along the [001] direction. The field value was selected to be the smallest value that yielded adequate signal.

Figure 6 shows the (ZFC) magnetization curves obtained during heating for the series of 20 nm films grown at the indicated oxygen pressures. A sharp Verwey transition was found at 121 K, close to the bulk value [31], in of the all films except the two grown under 1×10^{-6} and 4×10^{-6} torr oxygen pressure. However, the magnitude of Verwey transition decreases significantly as the oxygen pressure is decreased from 7×10^{-7} to 5×10^{-7} torr, and then 3×10^{-7} torr. The presence of the largest magnitude transition is used as additional evidence that film grown under $p(\text{O}_2) = 7 \times 10^{-7}$ torr is stoichiometric [32]. Therefore, $p(\text{O}_2) = 7 \times 10^{-7}$ torr is chosen as the optimal oxygen pressure for the growth of 20 nm Fe_3O_4 films at the deposition rate (3.33 Å/min) used in this study.

Magnetic hysteresis loops for the 20 nm iron oxide films were measured at 300 K by applying the magnetic field in the film plane along the [001] direction. All of these films exhibit a ferrimagnetic behavior. Figure 7(a) shows the total measured magnetic moment for the various films while Fig. 7(b) shows the film - only magnetization which is obtained by subtracting the MgO substrate contribution and dividing by the film volume. The saturation magnetization values at 300 K for 20 nm films grown at $p(\text{O}_2) = 3 \times 10^{-7}$ torr, 5×10^{-7} torr, and 7×10^{-7} torr were found to be 530 ± 30 emu/cm³, 470 ± 30 emu/cm³, and 480 ± 30 emu/cm³, respectively, comparable to the bulk value of Fe₃O₄ (480 emu/cm³). On the other hand, the saturation magnetization values for the 20 nm films grown at $p(\text{O}_2) = 1 \times 10^{-6}$ and 4×10^{-6} torr were found to be $\approx 300 \pm 30$ emu/cm³, which is closer to the saturation magnetization for γ -Fe₂O₃. In addition, these two samples did not show a Verwey transition and the XPS results also indicated that the composition was γ -Fe₂O₃.

In order to explore the dependence of the optimal oxygen pressure for growth of high quality (stoichiometric) Fe₃O₄ films on the film thickness, systematic measurements of the magnetization over a temperature range which includes the Verwey transition were carried out. Figure 8 shows zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves for four different film thicknesses (20 nm, 10 nm, 5 nm, and 3 nm) with an oxygen pressure 1×10^{-6} torr. The Verwey transition was only observed in the 10 nm film and occurred at $T_V \approx 115$ K. This result clearly shows that the optimal oxygen pressure depends on the film thickness. Figures 9 and 10 show representative ZFC/FC curves for the 10 nm films ($p(\text{O}_2) = 2 \times 10^{-7}$ torr to 2.5×10^{-6} torr) and 5 nm films ($p(\text{O}_2) = 1 \times 10^{-6}$ torr to 1×10^{-5} torr), respectively. It can be seen that, using the Verwey transition as a judge of the stoichiometry, the thinner 5 nm films require a greater oxygen pressure for the growth of high-quality Fe₃O₄ epitaxial films. In summary, the Verwey transition appeared for films grown with oxygen pressure ranging from 3×10^{-7} torr to 7×10^{-7} torr, 7×10^{-7} torr to 1×10^{-6} torr, 2×10^{-6} torr to 1×10^{-5} torr, and $\approx 4 \times 10^{-6}$ torr for thickness 20 nm, 10 nm, 5 nm, and 3 nm, respectively. However, the Verwey transition is progressively broadened with decreasing thickness.

D. Phase diagram

The analysis of the formation of epitaxial ultra-thin iron oxide films with thickness varying from 3 to 20 nm under different oxygen pressures ranging from 1×10^{-7} torr to 1×10^{-5} torr, which was presented in the previous section, is graphically summarized with the phase diagram presented in Fig. 11. The phase diagram shows the three regions of different iron oxide phase, FeO, Fe₃O₄, and γ -Fe₂O₃. It is clear that optimal oxygen pressure for formation ultra-thin films depends on the thickness, and high-quality, single-phase Fe₃O₄ is obtained only within a narrow window as shown with the dashed lines. At a given thickness, the phase of the film strongly depends on the oxygen concentration which is given by its partial pressure. The reaction between oxygen and iron decreases with decreasing film thickness. Therefore, to obtain stoichiometric ultra-thin films of Fe₃O₄ with thicknesses less than 20 nm, it is necessary to increase the oxygen concentration by increasing the oxygen pressure.

IV. SUMMARY AND CONCLUSIONS

In summary, epitaxial Fe₃O₄ ultra-thin films were grown on MgO (001) substrates. The impact of film thickness and oxygen deposition pressure on the phases which form upon crystallization was explored. At a given oxygen pressure, the film stoichiometry is correlated with the film thickness. For films with thickness $10 \text{ nm} \leq t < 20 \text{ nm}$, the iron oxide films grow in an intermediate structure and stoichiometry between Fe_{1- δ} O and Fe₃O₄. At 20 nm film thickness, the films have a structure and stoichiometry that mainly consists of Fe₃O₄ with properties that are bulk-like. Below 10 nm, the films have the structure and stoichiometry of FeO. The results of LEED, XPS, and magnetic measurements all indicate a gradual change in structure for the ultra-thin Fe₃O₄ films with decreasing thickness. From these results it can be concluded that the growth of high-quality Fe₃O₄ ultra-thin films is strongly favored in a relatively narrow window of oxygen pressure.

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Figure Captions

Figure 1: Low energy electron diffraction patterns (for an electron energy of 137 eV) for: (a) a clean MgO (001) substrate and (b) an epitaxial 20 nm Fe₃O₄ (001) film grown on an MgO (001) substrate under an oxygen pressure $p(\text{O}_2) = 7 \times 10^{-7}$ torr. The (1×1) unit cell and the ($\sqrt{2} \times \sqrt{2}$) $R45^\circ$ superlattice for the Fe₃O₄ (001) thin film are indicated by the larger (red) solid square and smaller (blue) solid square, respectively. (c) An epitaxial 10 nm Fe₃O₄ (001) film and (d) an epitaxial 3 nm FeO (001) film, both grown under $p(\text{O}_2) = 7 \times 10^{-7}$ torr. The (1×1) unit cell of FeO is indicated by the (red) dashed square.

Figure 2: Fe 2p photoemission spectra obtained with Mg K α x-ray radiation for epitaxial 20 nm iron oxide films grown on MgO (001) substrates under different oxygen pressures. From the satellite peaks which characterize the Fe²⁺ and Fe³⁺ valence states, the iron oxide phases are identified.

Figure 3: Fe 2p photoemission spectra obtained with Mg K α x-ray radiation for epitaxial iron oxide films with various thicknesses (20 nm, 10 nm, 5 nm, and 3 nm) grown on MgO (001) substrates under $p(\text{O}_2) = 7 \times 10^{-7}$ torr. The satellite peak which characterizes the Fe²⁺ valence states is indicated.

Figure 4: Fe 2p photoemission spectra obtained with Mg K α x-ray radiation for epitaxial 10 nm iron oxide films grown on MgO (001) substrates under different oxygen pressures. The satellite peaks which characterize the Fe²⁺ and Fe³⁺ valence states are indicated. For reference, the photoemission spectrum for an Fe metal film is included.

Figure 5: Fe 2p photoemission spectra obtained with Mg K α x-ray radiation for epitaxial 5 nm iron oxide films grown on MgO (001) substrates under different oxygen pressures. The satellite peaks which characterize the Fe²⁺ and Fe³⁺ valence states are indicated.

Figure 6: Magnetic moment (emu) versus temperature (K) during heating for 20 nm iron oxide films grown on MgO (001) substrates under various oxygen pressures: (a) 4×10^{-6} torr, (b) 1×10^{-6} torr, (c) 7×10^{-7} torr, (d) 5×10^{-7} torr, and (e) 3×10^{-7} torr. The films were initially cooled in zero field. The Verwey transition appears strong for oxygen pressures 3×10^{-7} torr, 5×10^{-7} torr, and 7×10^{-7} torr; however, it is not visible for 1×10^{-6} torr and 4×10^{-6} torr.

Figure 7: (a) Total magnetic moment (emu) versus magnetic field (Oe), hysteresis loops, obtained at 300 K for the 20 nm films grown on MgO (001) substrates under oxygen pressures $p(\text{O}_2) = 3 \times 10^{-7}$ torr, 5×10^{-7} torr, 7×10^{-7} torr, 1×10^{-6} torr, and 4×10^{-6} torr. (b) Film magnetization (emu/cm³), obtained from the data in (a) corrected for the MgO substrate contribution.

Figure 8: Magnetic moment (emu) versus temperature (K) during heating, and subsequent cooling (ZFC and FC curves), for iron oxide films grown on MgO (001) substrates under 1×10^{-6} torr with various thicknesses (a) 20 nm, (b) 10 nm, (c) 5 nm, and (d) 3 nm. The Verwey transition appears strong for the 10 nm film.

Figure 9: Magnetic moment (emu) versus temperature (K) during heating, and subsequent cooling (ZFC and FC curves), for 10 nm iron oxide films grown on MgO (001) substrates under various oxygen pressures: (a) 2×10^{-7} torr, (b) 7×10^{-7} torr, (c) 1×10^{-6} torr, and (d) 2.5×10^{-6} torr. The Verwey transition appears strong for the film grown under $p(\text{O}_2) = 1 \times 10^{-6}$ torr.

Figure 10: Magnetic moment (emu) versus temperature during heating, and subsequent cooling (ZFC and FC curves) for 5 nm iron oxide films grown on MgO (001) substrates under various oxygen pressures: (a) 1×10^{-6} torr, (b) 3×10^{-6} torr, (c) 7×10^{-6} torr, and (d) 1×10^{-5} torr. The Verwey transition appears for $p(\text{O}_2) = 3 \times 10^{-6}$ torr, 7×10^{-6} torr, and 1×10^{-5} torr, but not for $p(\text{O}_2) = 1 \times 10^{-6}$ torr.

Figure 11: Film - thickness versus oxygen - growth pressure phase diagram for ultra-thin epitaxial iron oxide films on MgO (001) substrates.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure8

Figure 9

Figure 10

Figure 11