Magnetic Properties of Ultrathin Magnetite Films Grown by Molecular Beam Epitaxy

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Magnetic properties as a function of film thickness (2–55 nm) for magnetite (Fe_3O_4) thin films grown on MgO (100) substrates show that the small thickness films ($\leq$ 5 nm) are ferromagnetic and possess magnetization values which are much greater than that of bulk Fe_3O_4. The inverse thickness dependence of the magnetization points to an interface related mechanism. Whereas, our detailed spin polarized density functional theoretical calculations suggests that there is only a marginal enhancement in the local spin moments of Fe-atom in the vicinity of the Fe_3O_4-MgO interface and it turns out that the noncompensation of spin moments between the two magnetic sublattices of spinel Fe_3O_4 is a major factor contributing to the enhancement of magnetization.

Index Terms—**Epitaxial layers, interface phenomena, magnetite, surfaces.**

I. Introduction

EPITAXIAL heterostructures of half metallic oxides such as magnetite, CrO_2 and rare Earth manganites have been the subject of great interest due to their potential applications in spintronics [1], [2]. Magnetite, Fe_3O_4, is an important half metallic oxide due to its high Curie temperature of 858 K and the presence of a metal-insulator transition at 120 K [3]. Various thin film growth techniques have been employed to grow epitaxial films of Fe_3O_4 on suitable substrates [4]–[8]. Transport and magnetic properties of epitaxial magnetite films have been investigated in detail [4]–[8].

Epitaxial Fe_3O_4 films grown on MgO substrate are reported to contain antiphase boundaries (APBs) [5]–[7]. Presence of these APB defects leads to the unusual magnetic properties of Fe_3O_4 films, in particular the nonsaturation of the magnetization, even at high field [5]–[7]. *Voogt et al.* [9] in their study on ultrathin epitaxial films (< 5 nm) of Fe_3O_4 on MgO showed a superparamagnetic behavior of the films, which they attributed to the 180° Fe-O-Fe superexchange interaction resulting in a frustration of the interdomain interactions. In general, saturation is believed to be more difficult for thinner films as the density of the APBs is greater.

From these investigations, it is clear that the magnetization property of magnetite thin films immensely depend on the method of preparation, nature of defects and the defect density. Although, the presence of APBs leads to a deterioration of magnetic properties, their presence is beneficial in attaining a greater magnetoresistance response in epitaxial films than in the single crystals, provided these nano-scale defects are appropriately manipulated [7], [10].

Though the physical properties of Fe_3O_4/MgO films have been studied in detail, magnetic properties of ultrathin films remain a controversial topic. A recent report by *Zhou et al.* [11] found that the ultrathin Fe_3O_4 films are ferromagnetic but their magnetization is reduced in comparison to the bulk values. They reported a magnetically inactive/dead layer of about 0.42 nm. In these investigations, no emphasis was given to the surface and interface magnetism which is expected to strongly influence the magnetic properties. In fact, the theoretical predictions on a (100) Fe_3O_4 surface using first principal calculations suggest either an increase or decrease in the magnetic moment of the surface layer which strongly depends on the surface reconstruction [12], [19]. All above factors motivated us to carefully examine the magnetic response of the films at small thicknesses. In this paper, we report a systematic study of the magnetic properties of well characterized Fe_3O_4 films (2–55 nm). We show that the films are ferromagnetic in the smaller thickness (< 5 nm) range and show a magnetic moment which is greater than the magnetic moment of bulk Fe_3O_4. We also compare the observed results with the theoretical calculations based on spin-polarized density functional theory for the Fe_3O_4-MgO (001) interface.

II. Experiment

Thin films of Fe_3O_4 were grown on (001) oriented MgO single crystal substrates using an oxygen plasma assisted molecular beam epitaxy (MBE) (DCA MBE M600, Finland) with a base pressure 5×10^{-10} Torr. Substrate temperature during growth was 523 K. Details of the growth procedure are given elsewhere [13]. The surface roughness of the substrates used in this study was < 0.4 nm as determined from the 5 μm $\times$ 5 μm area scans using an atomic force microscope, AFM, (Solver Pro, NT-MDT, Russia). After completion of growth, the films were cooled to room temperature (300 K) with a cooling rate of 10 K/min. Reflection high energy electron diffraction (RHEED) was employed to confirm the epitaxial growth and establish the growth mode. The presence of the RHEED intensity oscillations confirms that the films grew in a layer-by-layer mode with a growth rate of 0.3 Å/s.

The single phase structural and epitaxial nature of the Fe_3O_4 films was characterized using a multi-crystal high-resolution X-ray diffractometer, HRXRD (Bede-D1, Bede, U.K.). Monochromatic $Cu_{k\alpha 1}$ (1.54056 Å) radiation with a 20 arcsec beam divergence was obtained using four Si channel-cut

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crystals. X-ray reflectivity investigations in these films revealed a small interface (0.3–0.5 nm) roughness between the Fe_3O_4-MgO interface. The surface roughness of these films was quite small (0.2–0.4 nm) as estimated from 5 μm $\times$ 5 μm area scans using an AFM. Magnetic properties of the films were examined by performing magnetization measurements using a vibrating sample magnetometer (Quantum Design-14 T Physical Property Measurements System) with a sensitivity of 5×10^{-7} emu. The magnetization verses field (M-H) loops were measured by applying the magnetic field (maximum field of 1 Tesla) in the film plane along the (001) direction. The diamagnetic contribution from the sample holder and MgO substrate was obtained from independent M-H loops and subtracted from the film's data. The uncertainty in measuring the absolute value of magnetization for the films is about 3%.

III. Results and Discussion

Prior to discussing the magnetization results we would like to mention that through detailed structural characterization using high-resolution X-ray diffraction, we have found that the Fe_3O_4 films maintain a one-to-one registry with the substrate. The in-plane and out-of-plane lattice parameter for the films as determined from the asymmetric (311) and symmetric (200) diffraction scans are 0.84266 ± 0.00005 nm (twice of the MgO lattice constant) and 0.83717 ± 0.00005 nm, respectively. Details of the structural characterization were published in an earlier report [13]. The unit cell volume, which is consistent with bulk magnetite, indicates that the films are stoichiometric. No evidence of the presence of any other iron oxide phase or unreacted Fe was found from our high resolution XRD and TEM studies [13]. In addition to the structural investigations, we also measured the Verwey transition temperature (T_v) in these films through magnetic measurements. All the films down to 2 nm thickness exhibited a T_v. Its value being 118 and 85 K for the 50 and 2 nm films, respectively. Presence of T_v in our films indicate that the stoichiometry of the films is quite close to Fe_3O_4.

Fig. 1 shows the magnetic hysteresis loops (HL) of Fe_3O_4 films (5, 15 nm thickness) measured at 300 K with an applied in-plane magnetic field. The 15 nm Fe_3O_4 films show a saturation behavior with a moderate magnetic field (8 kOe). For the 5 nm film, at large magnetic fields, the magnetization (M) exhibited a finite slope with the magnetic field. The magnetization values for the 5 and 15 nm Fe_3O_4 films are found to be 914 and 615 emu/cm^3, respectively. The coercivity (H_c) values for the same films are 70 and 220 Oe, respectively. For film thickness 20 nm or greater, we find that the magnetization values are quite close to the values for bulk Fe_3O_4 (509 emu/cm^3 for 55 nm film). In Fig. 2 we show the M (10 kOe) value measured at 300 K for different thickness Fe_3O_4 films. One can notice that the magnetization of the films increases substantially with the decrease in films thickness. Magnetization values for the thin films are significantly larger than that of bulk Fe_3O_4 (4 μ_B/f.u.). For example, for a 5-nm film, the magnetization is found to be 914 emu/cm^3 (7.7 μ_B/f.u.) at 10 kOe field. This behavior was repeatedly observed for the small thickness films (2–15 nm). As the film thickness increases, the magnetization decreases. This is a curious observation in a sense that much of the earlier published work related to ultra thin magnetite films suggested either the formation of a magnetically dead layer or

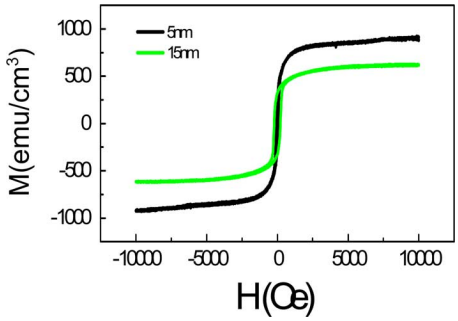

Fig. 1. Magnetization hysteresis (M-H) loops of Fe_3O_4 films measured at 300 K with an in-plane magnetic field.

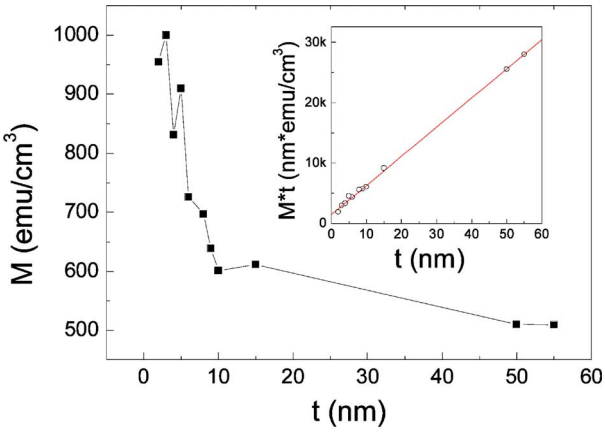

Fig. 2. Magnetization (M) measured at 300 K and 1 T filed as a function of film thickness. The inset shows M.t versus film thickness for Fe_3O_4 films.

the presence of superparamagnetism [9], [11]. In these earlier investigations, reduction in the magnetization was ascribed to the frustrated exchange at the APBs. We find that all the films down to 2 nm thickness exhibit a ferromagnetic behavior. Observation of a substantial (Giant) increase (95%) in magnetization for a 5-nm Fe_3O_4 films is in stark contrast to the earlier notion of a reduction in magnetization or a superparamagnetic behavior [5], [9], [11]. Lower surface roughness of the substrates is a key to the nonobservation of superparamagnetism as opposed to previous reports. We have found that the films grown on higher surface roughness than 0.4 nm leads to a greater surface and interface roughness which leads to a reduced magnetization or superparamgnetism depending on the film thickness. For 2 and 4 nm films, we find a slightly reduced magnetization as compared to 3 and 5 nm films, respectively, which can be attributed to the partial noncompensation of the spin moment of two magnetic sublattice of spinel Fe_3O_4 arising due to a small uncertainity in the films thickness (< 0.03 nm).

In order to understand the origin of the enhanced magnetization, we modeled our Fe_3O_4 films as consisting of a bulk-like Fe_3O_4 layer with a bulk saturation magnetization, M_s, and other thickness dependent contributions, M_i, (which are related to the interface, surface, and other contributions), then the magnetization M is given by

$$M = M_s + \frac{M_i}{t} \tag{1}$$

where t is the thickness of the film. The inset of Fig. 2, shows the thickness dependence of M(10 kOe) multiplied

by the Fe_3O_4 film thickness. Slope of the fit using (1) is 483 emu/cm^3 and agrees with the value of magnetic moment of bulk Fe_3O_4 (480 emu/cm^3). The positive intercept on the y axis (1483 nm.emu/cm^3) is the magnetic contribution to the film arising from thickness dependent contributions. Our data suggests that the earlier proposition of a dead layer model for the Fe_3O_4/MgO interface was an oversimplification [11]. The inverse thickness dependence of effective magnetization (M) given by the model (1) to separate out distinct bulk M_s and interface contributions is questionable, in particular for the case of Fe_3O_4 films on MgO (100) [11]. Apart from the interface- and surface-related contribution for ultrathin films, an additional thickness dependent magnetization contribution could result from a totally different origin, i.e., from the thickness dependence of antiphase domain size.

In order to gain additional insights into surface/interface related contributions to the magnetization, we carried out a spin-polarized density functional theoretical calculations for a series of Fe_3O_4-MgO (001) interfaces with different slab thicknesses based on either A (tetrahedral)- or B (octahedral)-layer nucleation and their relative positions on the MgO (001) surface and compare them with those for bulk Fe_3O_4. The interface model was constructed according to the stacking sequence shown in Fig. 3 for the [001] direction. All calculations were performed using the VASP code with the projector augmented plane wave (PAW) method using generalized gradient approximation (GGA) [14]. We use 300 eV for the plane wave energy cutoff, and $6 \times 6 \times 2$ grid for $\mathbf{k}$-point integration. All structural relaxation calculations are performed until the forces on the atoms become less than 20 meV/atom. From the calculations for Fe_3O_4-MgO interface, we infer that the interface of Fe_3O_4 with B-site nucleation is energetically most stable. We performed a detailed band structure calculation for three different slab thicknesses corresponding to 1, 1.5, and 2 unit cell thick Fe_3O_4 layers on MgO. Fig. 4 illustrates the layer structure used for *Model-1-1*. *Fe-O* layer in the structure used for the calculations *Fe-O* layers are the Fe_B-type layer as shown in Fig. 4. The model-1-1 consist of 5 Fe_B-type, 4 Fe_A-type layers and 5 MgO layers. The slab is surrounded by a 1-nm vacuum layer on either side of the slab. Details of the parameters used in the calculation and results are summarized in Table I. The magnetic moments of Fe atoms in Fe_B layer in the vicinity of Fe_3O_4-MgO interface are comparable to that obtained for bulk Fe_3O_4 from a similar calculation. However, an increase in polarization of some of the oxygen atoms (as large as 0.36 μB) in the vicinity of interface was noted. These calculations suggest that the spin moment contribution from the Fe_3O_4-MgO interface is not enough to explain our observation of an enhanced magnetization. It has been shown that inclusion of electron correlations via on-site Coulomb interaction (U) in DFT calculation is important to understand magnetic properties and charge ordering phenomena in magnetite [15], [16]. A recent GGA +U study [17] suggest that the electron correlation effects influence the magnetization and shows an enhanced magnetization (by a few percent) for B-terminated Fe_3O_4 (100) surface. It is clear from the above discussion that the inclusion of the electronic correlation effects will not influence the results of DFT calculation presented in this study.

To explore the mechanism of magnetization enhancement in Fe_3O_4 films, we consider a noncompensated structure, i.e., one

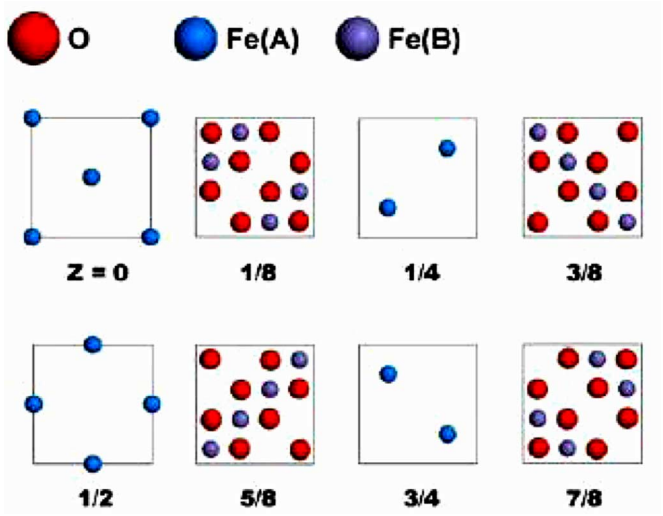

Fig. 3. Schematic illustration of the layered structure of Fe_3O_4 along the Z direction used for the DFT calculations, where the layers with $z = 0, 1/4, 1/2, 3/4$ represent A-termination and the layers with $z = 1/8, 3/8, 5/8, 7/8$ represent B-termination of Fe_3O_4 (001) surface.

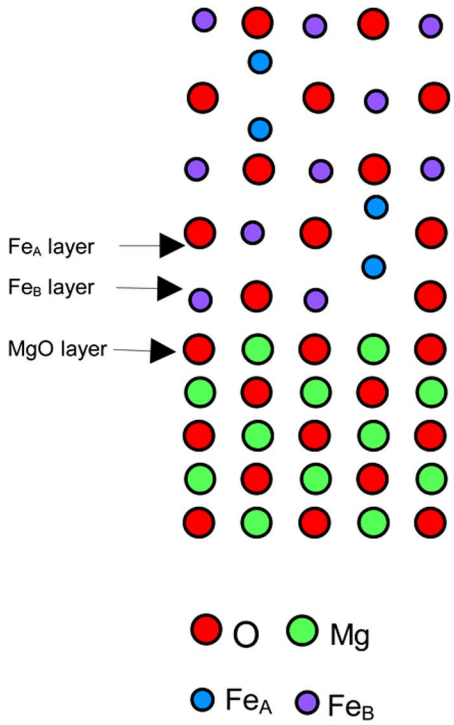

Fig. 4. Schematic illustration of the Model-1-1 used for the DFT simulations. The model utilizes 5-Fe_B type, 4 Fe_A type and 5 MgO layers. The Mg atoms are represented with the green spheres.

with an odd number of *Fe-O* planes. If a unit cell is not complete, one expects an increase in the magnetic moment due to noncancelation of the magnetic moments between A- and B-site Fe^{3+} ions. We call this mechanism a noncompensation effect. It is clear that the noncompensation of spin moments due to an odd number of layers will enhance the magnetization of the surface layers and its effect will vanish for larger thickness samples. To estimate the effect of noncompensation we used a supercell

TABLE I
SUMMARY OF LATTICED PARAMETER, FILM THICKNESS SPIN POLARIZATION, TOTAL MAGNETIC MOMENTS OF THE CELL, AND AVERAGE MAGNETIC MOMENTS OF Fe_A AND Fe_B ATOMS FOR Fe_3O_4 CRYSTAL AND OUR LOWEST ENERGY Fe_3O_4(001)/MgO(001) INTERFACE MODEL WITH DIFFERENT THICKNESS OF Fe_3O_4 FILMS. NUMERAL IN THE END OF MODEL'S NAME INDICATES THE THICKNESS OF $Fe_3O_4^4$ LAYER IN UNITS OF UNIT CELL SIZE

Results \ Model	Bulk	Model-1-1	Model-1-1.5	*Model-1-2*
# of Atoms	56	74	104	*134*
# of Fe_A	8	4	6	*8*
# of Fe_B	16	10	14	*18*
Film Thickness (nm)	--	0.8394	1.2591	*1.6788*
a (nm)	0.8394	0.59529	0.59529	*0.59529*
b(nm)	0.8394	0.59529	0.59529	*0.59529*
c(nm)	0.8394	2.10275	2.93803	*3.77993*
Spin-polarization	1	0.816	0.906	*0.931*
Total M (μ_B)	31.591	27.089	34.993	*42.834*
Average $M_{FeA}(\mu_B)$	-3.430	-3.402	-3.413	*-3.420*
Average $M_{FeB}(\mu_B)$	*3.531*	*3.410*	*3.667*	*3.632*

model with a slab thickness equivalent to 50 Fe-O layers and find that the spin moment/f.u. is substantially larger due to noncompensated surface layer; e.g., its value being 6.6 μB/f.u. for the fifth *Fe-O* layer and 5 μB/f.u. for fifteenth *Fe-O* layer. The value of magnetizations decreases rapidly for a thicker slab and for a fiftieth *Fe-O* layer, we find that the magnetization is comparable to the value for bulk Fe_3O_4, i.e., $\sim$4 μB/f.u. For an even number of layers or fully compensated Fe_3O_4 slabs, magnetization is only slightly larger than the bulk value indicating that the surface effects are marginal in this case. From these results we infer that the noncompensation is the main factor for magnetization enhancement for thin Fe_3O_4 films. The orbital moment contribution from surface atoms also has to be ruled out as this is an effect comparable to the interface polarization effect. The uncompensated spin and extra charge associated with the surface might also lead to a much more profound change in the magnetic moment of the entire film. It may affect the antiferromagnetic exchange (J_{AB}) between the A- and B-layers underneath the surface, i.e., intersublattice exchange interaction. Slight decrease in the magnetization of 2 and 4 nm layers can be explained due to partial noncompensation which can arise either due to a small error in thickness of the film or roughness related effects. If we consider the noncompensation model along the growth direction and at the APBs, we can explain about 23% enhancement for a 5-nm film. The estimate related to the APBs assumes: (a) domain size is 5 nm $\times$ 5 nm; (b) it is possible to overcome the AFM exchange by the application of magnetic field [18]; and (c) at the boundary stacking condition for the spinel structure, i.e., ABAB... is not satisfied.

IV. CONCLUSION

From our study, we infer that the magnetite films, in particular at small thicknesses (< 5 nm) are ferromagnetic and they possess magnetization values which are much larger than the values for bulk Fe_3O_4. We find that the noncompensation of spin moments between the two magnetic sub-lattices of the spinel Fe_3O_4 along the growth direction and at the APBs is one of the major factors contributing to magnetization enhancement. Other possibilities such as influence of nonstoichiometry and noncompensation on the magnetic exchange interactions can not be completely ruled out.

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