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The magnetic behavior and structure of Fe_3O_4/MgO multilayers have been investigated with Mössbauer spectroscopy in field, magnetization measurements, and scanning tunneling microscopy. It is shown that detailed structural knowledge of the size of the structural domains and the width of the antiphase boundaries are indispensable in understanding the magnetization behavior of the films and the contradictory results reported in the literature. © *1999 American Institute of Physics.* [S0021-8979(99)75508-8]

In view of the possible technological importance of half-metallic Fe_3O_4 (magnetite) in, for example, all oxide tunnel junctions, there has been an increasing number of studies addressing the magnetization behavior of thin films of Fe_3O_4/MgO. However, not all of these studies are in agreement with each other and some contradictory observations are reported. In a recent study extremely high saturation fields, up to 70 kOe, were observed in 500–10 000 Å thick sputtered Fe_3O_4 films.[1] It was suggested that this was related to the presence antiphase boundaries (APBs), which are formed as a consequence of the nucleation of Fe_3O_4 on MgO.[2–4] The superexchange interactions across the APBs are assumed to align the net moment of adjacent domains antiparallel, which explains the observed high saturation fields. In contrast, 10–500 Å thick films produced by means of molecular beam epitaxy (MBE) display much lower saturation fields.[5]

A second issue in this field is the question whether or not a magnetically inactive or ''dead'' interface layer in the order of 10 Å is present in these layers. From neutron reflectrometry,[6] the thickness dependence of the magnetic moment,[5] Mössbauer spectrometry,[7] and also from the resistivity[8] and the magnetocrystalline anisotropy,[9] such a ''dead'' layer was reported. Nevertheless, in another study[4] Fe_3O_4/MgO multilayers with an Fe_3O_4 layer thickness below 53 Å were characterized by Mössbauer spectroscopy and magnetization measurements, showing no surface effects. In these thin films the presence of APBs are believed to result in a frustration of the superexchange interactions between the domains, permitting the magnetic moments of the domains to fluctuate more or less freely in a superparamagnetic manner.

In this article a study is presented of a set of MBE-grown Fe_3O_4/MgO layers for which magnetic and structural properties from magnetization, Mössbauer, and scanning tunneling microscopy (STM) measurements, are combined.

A set of four multilayers with the following composition was MBE grown at Philips Research Laboratories: MgO(100)+4×(300 Å Fe_3O_4+30 Å MgO)+30 Å NiO, in which each Fe_3O_4 layer was enriched with two parts of $^{57}Fe_3O_4$, positioned symmetrically at 0, 25, 75, and 125 Å distance from the MgO interfaces; see the illustration in Fig. 1(a). The total enriched thickness is 50 Å per Fe_3O_4 layer, which ensures that the observed Mössbauer signal arises mainly from the enriched parts of the multilayer.

Figure 1(b) shows the conversion electron Mössbauer spectroscopy (CEMS) spectra at room temperature of the multilayers as a function of the position of the enriched $^{57}Fe_3O_4$ part relative to the MgO interface. The spectra consist of two Zeeman splitted sextets, which partly overlap at positive velocities corresponding to Fe^{3+} (A sites) and $Fe^{2.5+}$ (B sites). The hyperfine fields for the A and B sites are 48.6 and 45.7 T and the isomer shifts are 0.25 and 0.64 mm/s, respectively, which is in agreement with the literature. The relative intensities of the A- and B-site spectrum are 36%:64%, which corresponds to almost perfectly stoichometric Fe_3O_4.[10] Hyperfine fields, isomer shifts, and intensity

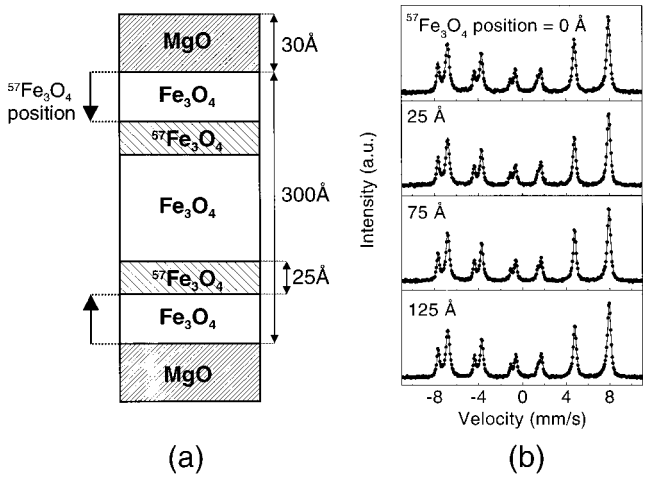

FIG. 1. (a) Schematic drawing of the multilayer structure and (b) Mössbauer spectra with no external applied field as a function of the position of the enriched part of the Fe_3O_4 layers.

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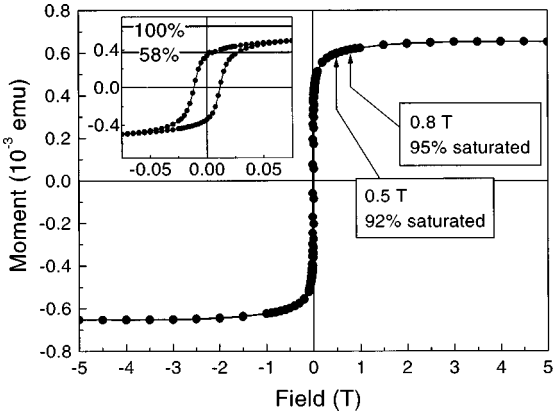

FIG. 2. Magnetization loop at room temperature of the multilayer with the enriched part in the middle of the Fe_3O_4 layer. The inset shows the magnetization at low fields with the saturation magnetization (100%) and the remanence (58%).

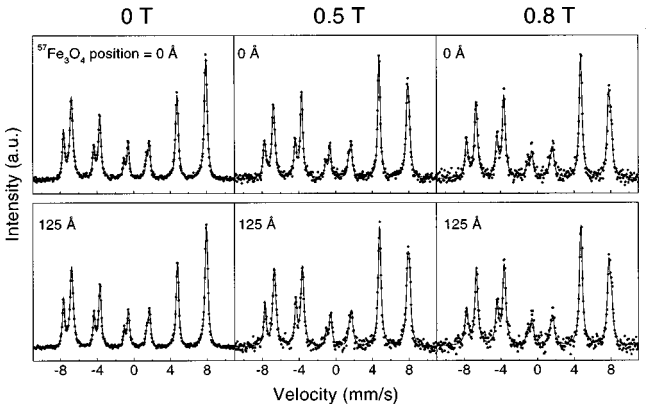

FIG. 3. Mössbauer spectra in external fields of 0, 0.5, and 0.8 T in the plane of the layers for the enriched part at the interface and in the middle of the Fe_3O_4 layers.

ratios are independent of the enriched layer position, which means that within experimental accuracy there is no indication for a magnetically different layer near the interfaces with MgO. In a way, this is surprising since one expects that the magnetic symmetry break at the interfaces disturbs the delicate balance of the ferrimagnetic ordering. Apparently, if such an effect is present, the current 25 Å probe layer is too thick to sense the resulting changes. Alternatively, the concept of a ''dead'' layer of constant thickness on top of a perfectly aligned ferrimagnetic array might be too simple and the interface effect may propagate through the whole layer. In that case the interface effect results in a homogeneous magnetization which gradually decreases when the thickness is reduced to only a few elementary Fe_3O_4 cells. Nevertheless, one also has to realize that the observation time period of the CEMS measurements of about 10^{-8} s is short compared to the dc magnetization measurement time ($\approx$1 s), allowing the possibility that slow fluctuations of the magnetic spins at the interface are of influence on the measured saturation magnetic moment. Additional experiments are needed to confirm this. In the remainder of this article we will focus on the field dependence of the magnetization as observed in the magnetization and CEMS measurements and its relation to the structural domains and the APBs.

The relative intensities for the individual lines in one sextet is $3{:}X{:}1{:}1{:}X{:}3$. For all the zero-field spectra X is approximately 2, which means that the magnetic moments either make an angle of 54.7° with respect to the film normal (along the $\langle 111\rangle$ direction) or that they are randomly out-of-plane distributed. In Fig. 2 the magnetization hysteresis loop measured with a superconducting quantum interference device (SQUID) with the field along the $\langle 100\rangle$ direction is shown of the multilayer with the enriched part in the middle of the Fe_3O_4. For all the samples the magnetization curves are identical. The magnetization is not saturated up to fields of at least 1.5 T, which is too high to explain in terms of a competition between the different anisotropy contributions, as already was pointed out by Margulies *et al.*[1] for sputtered Fe_3O_4 layers. At fields of 0.5 and 0.8 T, 92% and 95% of the saturation moment is reached (relative to the saturation moment for fields higher than 3 T). The inset of Fig. 2 is a magnification of the magnetization loop at low fields which shows a remanence of 58%. This perfectly corresponds to the magnetic moments not randomly distributed but pointing in the easy $\langle 111\rangle$ directions since its projection along $\langle 100\rangle$ yields a remanence of 57.7%.

Figure 3 shows the CEMS spectra of the multilayers with the enriched part at 0 and 125 Å from the MgO interfaces for applied fields of 0, 0.5, and 0.8 T in plane along the $\langle 100\rangle$ direction. The signal-to-noise ratio for the spectra in field is somewhat less than without field due to the disturbing influence of the field on the conversion electron paths. Nevertheless, it is again evident that no significant difference can be observed between the spectra for the enriched layer at the interfaces and in the middle, which also holds for the spectra with the probe layer at 25 and 75 Å from the MgO interfaces (not shown). The relative intensities of the lines in both sextets $3{:}X{:}1{:}1{:}X{:}3$ increases from $X=2$ without applied field to $X=3$ in an applied field of 0.5 T and up to $X=3.3$ in an applied field of 0.8 T. From these relative line intensities the angle θ between the incoming γ rays and the magnetization direction can be calculated, yielding $\theta=54.7°$, $\theta=67.8°$, and $\theta=72.0°$ for 0, 0.5, and 0.8 T, corresponding to relative in-plane magnetization components of 58%, 93%, and 95%, respectively, in almost perfect agreement with the magnetization loop of Fig. 2.

From the foregoing CEMS and magnetization measurements we can conclude that the magnetization points along the $\langle 111\rangle$ directions in zero field and cannot be saturated in fields up to at least 0.8 T. As was shown recently[2] this can be explained by the presence of structural domains separated by APBs. The moments of two adjacent domains are antiferromagnetically coupled which leads to frustration when, for example, three domains meet.

The experimental evidence for the existence of APBs in our films we have obtained from STM. In Fig. 4 we present a 1200×1200 Å^2 STM image of MgO(100) + 400 Å Fe_3O_4, grown under exactly the same conditions as the multilayers. Broad plateaus (different gray shades) of several hundreds of angstroms wide are visible, separated by monoatomic steps of 2 Å high, corresponding to the distance between two ad-

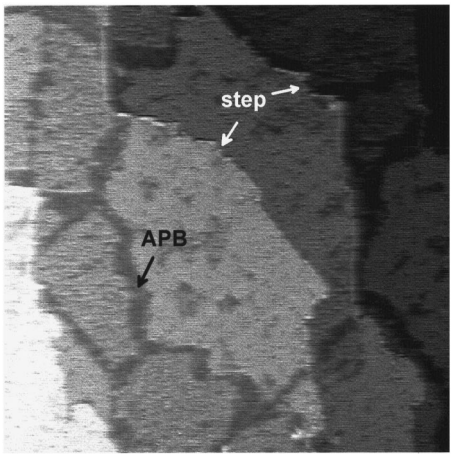

FIG. 4. STM image of a $1200\times1200\ \text{Å}^2$ region of MgO(001)+400 Å Fe_3O_4. Large terraces with steps of 2 Å high can be seen. Broad APBs are visible on the terraces, which in some cases extend over steps and form large structural domains.

jacent planes of oxygen or equivalent iron atoms. On these terraces broad lines are observed which are the APBs separating two regions of the same height rotated over 90° (for detailed pictures of the APBs see Gaines *et al.*[3]). The fact that the APBs extend in some cases across steps indicates that the APBs are not induced by the steps but are an intrinsic feature related to the nucleation of Fe_3O_4 on MgO. The large structural domain in the middle of Fig. 4 has a width of 550 Å and a length of 1100 Å, which is comparable to the size of the domains observed by Margulies *et al.*[2] From STM it is difficult to obtain an average grain size, but recent transmission electron microscope pictures[11] of a 2000 Å thick MBE-grown layer show that the average domain size is in the order of 3000 Å, which is an order of magnitude larger than the domains observed by Margulies *et al.* We do not know, however, whether the average domain size in this 2000 Å thick film is the same as in our 300 and 400 Å thick films.

Most striking in our films is the width of the APBs, which is in the order of 10–100 Å, because in the models of Margulies *et al.*[2] and Voogt *et al.*[4] it was assumed that the oxygen lattice is continued at an APB, which is clearly not the case. Since the APBs are strongly disordered regions with numerous stacking faults, the magnetic state of this region is not clear,[3] which means that the antiferromagnetic superexchange interaction across the APBs is probably strongly suppressed or even absent. It is even not unlikely that also magnetostatic interactions between domains contribute to the frustration of the magnetization.[12] This also explains why different saturation fields are observed in different studies, because the specific preparation conditions may very well determine the width of these APBs and, therefore, the strength of the antiferromagnetic coupling across the boundaries. Detailed knowledge of the size of the domains and the width of the APBs via STM is, therefore, essential. To quantify the impact of APBs on the magnetization behavior further, we have described the approach to saturation of our layers according to $M\propto 1-b/H^n$, describing a macroscopic antiferromagnetic chain, similar to Margulies *et al.*[2] From the magnetization curve shown in Fig. 2 we obtain $n=0.5$, as expected for a competition between Zeeman and exchange energies and $b=8.8\ \text{Oe}^{1/2}$. Saturation is reached faster than for the films of Margulies *et al.*,[2] which is in agreement with the broad APBs observed in our films and a larger average domain size as compared to the films of Margulies *et al.*

In conclusion, CEMS measurements of Fe_3O_4/MgO do not show a significant difference between bulk layers and interface layers. The magnetic moments point along the ⟨111⟩ directions in zero field according to CEMS and gradually align along the field consistent with the experimentally observed magnetization, which can be understood by frustration of the moments due to the presence of antiferromagnetic exchange interactions across APBs.

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