Extremely low coercivity in Fe₃O₄ thin film grown on Mg₂TiO₄ (001)

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We report very different magnetic properties of 40 nm-thick Fe₃O₄ thin films grown on tailored spinel substrate Mg₂TiO₄ (001) and on general substrate MgO (001). The sample on Mg₂TiO₄ (001) shows a very sharp Verwey transition with narrow hysteresis of only 0.5 K and a high transition temperature up to 126 K and, in particular, an extremely small coercivity as low as around 7 Oe from the Verwey transition to room temperature. This low coercivity is close to that of the single crystal bulk but several times smaller than that of the sample on MgO (001). Our work gives a first example of the magnetic properties in Fe₃O₄ thin film having higher Verwey transition than that of the single crystal bulk, which not only greatly expands our understanding about Fe₃O₄ but also provides a very good candidate for spintronic applications with quite low energy consumption.

I. Introduction

Magnetite (Fe₃O₄) is one of the most studied transition-metal oxides over the past several decades because of its rather unique and interesting set of magnetic and electrical properties, such as high Curie temperature (Tc = 858 K), relatively high saturation magnetization, small coercivity field and theoretically predicted half-metallic character. These properties make Fe₃O₄ very attractive for room temperature spintronic applications. Especially, Fe₃O₄ is a highly correlated material that undergoes a first-order metal–insulator transition (known as the Verwey transition) at TV = 124 K, but the mechanism of this transition is still unclear though tremendous amount of work has been done. However, the unique properties, which are relevant for various device applications, have been very difficult to realize in thin film form due to the existence of growth defects (such as the anti-phase boundaries (APBs)) and chemical-off stoichiometry. The inevitable presence of APBs in Fe₃O₄ thin films generally results in some unusual magnetic and transport properties, such as unsaturated magnetization in high magnetic fields, superparamagnetic behavior for epitaxial ultrathin films, unsaturated negative magnetoresistance, and very low Verwey temperature and quite broadened transition. Therefore, previous work of Fe₃O₄ thin films grown on MgO, MgAl₂O₄, SrTiO₃ or Al₂O₃ substrates, which only show lower TTV than that of the bulk due to the existence of microstructure defects. Therefore, to study the magnetic properties in Fe₃O₄ thin film with higher TTV than that of the bulk will greatly extend our understanding about the magnetite. To experimentally achieve this goal, based on the work in ref. 27, we carefully chose and made a new non-magnetic spinel substrate Mg₂TiO₄ (001) with small lattice mismatch +0.51%. We expect that the Fe₃O₄ thin film grown on this substrate will present higher TTV than that of the bulk and exhibit quite different magnetic properties from that of the films grown on the general substrates.

In this work, we report very different magnetic properties of 40 nm-thick Fe₃O₄ thin films grown on Mg₂TiO₄ (001) and MgO (001) substrates. It is found that the sample on Mg₂TiO₄ (001) displays a very sharp Verwey transition with narrow hysteresis of 0.5 K and a high TTV of 126 K, and remarkably an extremely small coercivity as low as around 7 Oe from Verwey transition to room temperature. This low coercivity is close to that of the single crystal bulk but several times smaller than that of the sample on MgO (001), which makes Fe₃O₄/Mg₂TiO₄ (001) a very good candidate for spintronic applications with quite low energy consumption.
II. Experiments

The 40 nm-thick Fe$_3$O$_4$ thin films were grown on Mg$_2$TiO$_4$ (001) and MgO (001) substrates by using molecular beam epitaxy (MBE) in an ultrahigh vacuum system with a background pressure of $1 \times 10^{-10}$ mbar range. The substrates were annealed for 2 h at 600 °C in an oxygen pressure of $3 \times 10^{-7}$ mbar to obtain a clean and well-ordered surface structure before the deposition of Fe$_3$O$_4$. Standard samples were grown using an iron flux of 1 Å per minute, an oxygen background pressure of $1 \times 10^{-6}$ mbar, and a growth temperature of 250 °C. To determine the structural quality and chemical states, the films were analyzed in situ by using reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED) and X-ray photoemission spectroscopy (XPS). The RHEED patterns were taken at 20 keV electron energy, with the beam aligned parallel to the [100] direction of the substrate. The LEED patterns were recorded at electron energy of 88 eV. The thickness of the film was determined during growth from the oscillation period of the RHEED specular spot intensity. The XPS data were collected using 1486.6 eV photons (monochromatized Al K$_\alpha$ light) in normal emission geometry and at room temperature using a Scienta R3000 electron energy analyzer. The overall energy resolution was set to about 0.3 eV. The transport and magnetic properties of the Fe$_3$O$_4$ thin films were ex situ measured with a standard four probe technique using a physical property measurement system (PPMS) and superconducting quantum interference device (SQUID), respectively. High-resolution X-ray diffraction (HR-XRD) was employed for further ex situ investigation of the structural quality and the microstructure of the thin films. The XRD measurements were performed with a high resolution PANalytical X’Pert MRD diffractometer using monochromatic Cu K$_{\alpha 1}$ radiation ($\lambda = 1.54056$ Å).

Fig. 1  RHEED and LEED electron diffraction patterns of the following: the clean substrates Mg$_2$TiO$_4$ (001) (a) and MgO (b); 40 nm-thick Fe$_3$O$_4$ thin films grown on Mg$_2$TiO$_4$ (001) (c) and (e), and on MgO (001) (d) and (f), respectively. The (1 x 1) unit cell and the ($\sqrt{2} \times \sqrt{2}$)R45° superlattice are indicated by the red dashed square and solid square, respectively.
III. Results and discussions

Fig. 1 shows the RHEED electron diffraction patterns of clean substrates Mg2TiO4 (001) (a) and MgO (001) (b), the RHEED and LEED patterns of 40 nm-thick Fe3O4 thin films grown on Mg2TiO4 (001) (c and e), and on MgO (001) (d and f), respectively. The sharp RHEED streaks and the presence of Kikuchi lines (Fig. 1(c) and (d)), as well as the high contrast and sharp LEED spots (Fig. 1(e) and (f)) indicate a flat and well ordered (001) single crystalline surface structure of both samples. The characteristic $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction of Fe3O4 (001) can be observed, providing another indication for the high structural quality of the two Fe3O4 thin films. The $(1 \times 1)$ unit cell and the $(\sqrt{2} \times \sqrt{2})R45^\circ$ superlattice are indicated by the red dashed square and solid square, respectively (see Fig. 1(e) and (f)).

Moreover, it is found that the LEED pattern for the film on Mg2TiO4 (001) has 45° rotation as compared to the film on MgO (001), which should be due to the direction rotation of the substrate during its production process. Furthermore, to clarify the chemical states of the iron oxide, the thin films were in situ analyzed by XPS, as shown in Fig. 2(a)–(c). It is clear that the two samples exhibit the same wide scan spectra with binding energy from 1200 to 18 eV (Fig. 2(a)), Fe 2p core-level spectra (Fig. 2(b)) and valence band spectra (Fig. 2(c)), which demonstrates quite clean surface of the thin films and represents the typical signatures of Fe3O4 thin film.\textsuperscript{26,27,28,29} The structural quality of the thin films was further ex situ investigated by the high-resolution X-ray diffraction (HR-XRD). As shown in the Fig. 2(d), the long range 0–2θ XRD patterns do not present any phase other than Fe3O4, the (002)/(004) and (004)/(008) reflections correspond to MgO/Fe3O4 because of the lattice constant of Fe3O4 as twice as that of MgO (see the green color curve), and the (004) and (008) reflections are presented for both Mg2TiO4 and Fe3O4 for the red color curve. The two samples are in fully strained due to the small lattice mismatches.\textsuperscript{27,32} As the lattice mismatch of Mg2TiO4 (+0.51%) is larger than that of MgO (+0.33%), the tensile strain and also the lattice constant a (in-plane) are bigger for the former, and thus the lattice constant c (out-of-plane) of the Fe3O4/Mg2TiO4 (001) (8.343 Å) is smaller than that of the Fe3O4/MgO (001) (8.367 Å), corresponding to the relative shift of (004) and (008) peaks to the larger angles (see the red curve).

The resistivity as a function of temperature $\rho(T)$ of 40 nm-thick Fe3O4 thin films grown on Mg2TiO4 (001) and MgO (001), and of single crystal bulk is shown in Fig. 3(a). It is found that the $\rho(T)$ curves present a clear first-order Verwey transition. The Fe3O4/MgO (001) sample displays a low $T_v$ with a big hysteretic loop of about 4 K whereas the Fe3O4/Mg2TiO4 (001) sample exhibits a higher $T_v$ (126 K) than that of the bulk with very narrow hysteresis of only 0.5 K, which demonstrates that

Fig. 2 XPS spectra of 40 nm-thick Fe3O4 thin films grown on Mg2TiO4 (001) and MgO (001): wide scan spectra (a), Fe 2p core-level spectra (b) and valence band spectra, as well as Ag for reference (c); (d) X-ray diffraction patterns for the Fe3O4 thin films on Mg2TiO4 (001) and MgO (001). Only the (004) and (008) reflections of Fe3O4 can be observed for the two samples.
the Fe₃O₄/Mg₂TiO₄ (001) sample has quite few microstructural defects and the tensile strain pushes the Tᵥ over that of the bulk. The temperature dependence of magnetization M(T) of 40 nm-thick Fe₃O₄ thin films on Mg₂TiO₄ (001) and MgO (001) are exhibited in Fig. 3(b) and (c), respectively. It is obvious that a sharp jump of magnetization takes place at Verwey transition. The in-plane magnetic hysteresis loops at Tᵥ for the thin films on Mg₂TiO₄ (001) and MgO (001) are displayed as insets of (b) and (c), respectively. Remarkably, this extremely small Hᵥ at 127 K to our knowledge, is the smallest value in Fe₃O₄ thin films so far, which is close to that of the single crystal bulk but several times smaller than that reported in thin films grown on MgO, MgAl₂O₄, SrTiO₃ or Al₂O₃. Moreover, near the Hᵥ, a clear incoherent reversal of magnetization with magnetic field for 126 K while a rapid jump of magnetization with magnetic field for 127 K are observed, see the sharp peak of d(M/M₀)/dH under 127 K in the inset (right) of Fig. 4(a).

The in-plane Hᵥ as a function of temperature for 40 nm-thick Fe₃O₄ thin films on Mg₂TiO₄ (001) and MgO (001) are plotted in Fig. 4(c). A sharp change of Hᵥ occurs at their Verwey transitions for the two samples, respectively. Especially, the Fe₃O₄/Mg₂TiO₄ (001) sample keeps nearly constant Hᵥ of only about 7 Oe above its Tᵥ. As a contrast, the values of Hᵥ are much larger for the Fe₃O₄/MgO (001) sample, ranging from 140 Oe at 130 K to 90 Oe at 300 K and still about two times bigger than that of the Fe₃O₄/Mg₂TiO₄ (001) sample at low temperatures (T < Tᵥ). Furthermore, the two samples present the perpendicular anisotropic behavior, that the in-plane and out-of-plane correspond to the easy and hard axis, respectively (see Fig. 4(b)), and the anisotropic field is about 5 kOe, similar to that reported in previous work. It has been known that the microstructural defects (such as the APBs) greatly affect the transport and magnetic properties of Fe₃O₄ thin films, the APBs were claimed to act as pining centers for the magnetic domain walls, thus the substantial enhancement of Hᵥ for the Fe₃O₄/MgO (001) film should be

Fig. 3 Resistivity as a function of temperature for 40 nm-thick Fe₃O₄ thin films on Mg₂TiO₄ (001) and MgO (001), and of single crystal bulk Fe₃O₄ (a). Inset: temperature dependence of dlog(ρ)/dT near the Tᵥ for the samples on Mg₂TiO₄ (001) (up) and MgO (001) (down), respectively; zero-field-cooling (ZFC) and field-cooling (FC) magnetization of the samples on Mg₂TiO₄ (001) (b) and MgO (001) (c), respectively. The dM/dT versus temperature around the Tᵥ for the thin films on Mg₂TiO₄ (001) and MgO (001) are displayed as insets of (b) and (c), respectively.

The temperature dependence of magnetization M(T) of 40 nm-thick Fe₃O₄ thin films on Mg₂TiO₄ (001) and MgO (001) are exhibited in Fig. 3(b) and (c), respectively. It is obvious that a sharp jump of magnetization takes place at Verwey transition. The Tᵥ of Fe₃O₄ films on Mg₂TiO₄ (001) and MgO (001) are displayed as insets of (b) and (c), respectively. Furthermore, it is found that the FC curve of Fe₃O₄/Mg₂TiO₄ (001) film shows much larger magnetization change at Tᵥ than that of Fe₃O₄/MgO (001) film (see Fig. 3(b) and (c)). Although the bulk Fe₃O₄ keeps ferrimagnetic below Tᵥ ~ 860 K, yet the easy (hard) axis changes from [111] to [100] with changing from cubic Fd3m to monoclinic Cc. Usually, the bulk Fe₃O₄ exhibits a very sharp variation of magnetization at Tᵥ under small magnetic field. In Fe₃O₄ thin films, however, the presence of microstructural defects can negatively affect the rotation of the magnetic axis. Therefore, the Fe₃O₄/Mg₂TiO₄ (001) film having fewer microstructure defects is more sensitive to the applied magnetic field, and the much larger magnetization change at Tᵥ can be observed.

It has been reported that the coercivity field (Hᵥ) significantly enhances with the Fe₃O₄ transforming from high-temperature cubic spinel structure to low-temperature monoclinic structure due to the abrupt increase in magnetocrystalline and magnetostriiction constants. In the plane magnetic hysteresis loops at 126 K (at Tᵥ) and 127 K (just above Tᵥ) in applied field of 50 kOe of the 40 nm Fe₃O₄/Mg₂TiO₄ (001) film is shown in Fig. 4(a). It is observed that the Hᵥ sharply decreases from 213 Oe at 126 K to only 6 Oe at 127 K (see the inset (left) of Fig. 4(a)).

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induced from this effect. As a result, by using a tailored spinel substrate we can obtain exceptionally high quality Fe₃O₄ thin film, with getting rid of the microstructure defects, it is the first time for us to observe the magnetic properties in Fe₃O₄ thin film having higher Tᵥ than that of the single crystal bulk, which enlarges our understanding about the Fe₃O₄. Furthermore, this Fe₃O₄/Mg₂TiO₄ (001) thin film with extremely low coercivity will bring in quite low energy consumption in spin valves or spin tunnel junctions.

IV. Conclusion

In summary, we have studied the magnetic properties of 40 nm-thick Fe₃O₄ thin films grown on Mg₂TiO₄ (001) and on MgO (001). We found that the Fe₃O₄/Mg₂TiO₄ (001) film shows a very sharp Verwey transition with narrow hysteresis and high Tᵥ up to 126 K, and especially an extremely small Hᵥ as low as about 7 Oe from the Verwey transition to room temperature. This small Hᵥ is close to that of the single crystal bulk but several times smaller than that of the films grown on general substrates. Our work not only gives a first example of the magnetic properties in Fe₃O₄ thin film having higher Verwey transition than that of the single crystal bulk but also provides a very good candidate for spintronic applications in quite low energy consumption.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors would like to thank Prof. Liu Hao Tjeng, Dr Chun-Fu Chang and Dr Alexander Komarek for useful discussion. This work has been supported by the Max Planck-POSTECH Center for Complex Phase Materials, and the National Basic Research Program of China (No. 2017YFA0206302), and the National Nature Science Foundation of China under projects 51590883 and 51331006, and as a project of the Chinese Academy of Sciences with grant number KJZD-EW-M05-3.

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