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<td>Nagahama, Taro; Matsuda, Yuya; Tate, Kazuya; Kawai, Tomohiro; Takahashi, Nozomi; Hiratani, Shungo; Watanabe, Yusuke; Yanase, Takashi; Shimada, Toshihiro</td>
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Magnetic properties of epitaxial Fe$_3$O$_4$ films with various crystal orientations and tunnel magnetoresistance effect at room temperature

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Fe$_3$O$_4$ is a ferrimagnetic spinel ferrite that exhibits electric conductivity at room temperature (RT). Although the material has been predicted to be a half metal according to ab-initio calculations, magnetic tunnel junctions (MTJs) with Fe$_3$O$_4$ electrodes have demonstrated a small tunnel magnetoresistance (TMR) effect. Not even the sign of the tunnel magnetoresistance ratio has been experimentally established. Here, we report on the magnetic properties of epitaxial Fe$_3$O$_4$ films with various crystal orientations. The films exhibited apparent crystal orientation dependence on hysteresis curves. In particular, Fe$_3$O$_4$(110) films exhibited in-plane uniaxial magnetic anisotropy. With respect to the squareness of hysteresis, Fe$_3$O$_4$ (111) demonstrated the largest squareness. Furthermore, we fabricated MTJs with Fe$_3$O$_4$(110) electrodes and obtained a TMR effect of $-12\%$ at RT. The negative TMR ratio corresponded to the negative spin polarization of Fe$_3$O$_4$ predicted from band calculations. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4894575]

Half metals that have 100% spin polarization (P) at the Fermi level are key materials to fabricate spintronic devices because their high spin polarization enables very large magnetoresistance effects. The most impressive case is in magnetic tunnel junctions (MTJs) with epitaxial MgO tunnel barriers. As transport in MgO-MTJs is dominated by coherent tunneling of $\Delta$ electrons with 100% spin polarization, the tunnel magnetoresistance (TMR) ratio has reached 600% at room temperature (RT). Such a large TMR ratio has allowed us to fabricate highly functional spintronic devices like magnetoresistive random access memories (MRAMs). However, MTJs with MgO have stringent limitations where the crystal orientation should be bcc (001) due to band structure matching between MgO and the electrodes. Half metal is the solution to large TMR ratios without restricting the crystal structure or orientation. Thus, far, many oxide materials have been proposed as candidates for half metals, e.g., CrO$_2$, La$_{0.5}$Sr$_{0.5}$MnO$_3$, and Fe$_3$O$_4$. Of these materials, Fe$_3$O$_4$ has been considered to be the most promising as a half metal because of its high Curie temperature ($T_C$) of 858 K, which is an advantage in applications to spintronic devices that require high $T_C$. The crystal structure is an inverse spinel with Fe$^{3+}$ cations occupying tetrahedral sites (A sites) and Fe$^{3+}$ and Fe$^{2+}$ cations occupying octahedral sites (B sites). The magnetic couplings between A and B sites are antiferromagnetic and the couplings at A-A or B-B are ferromagnetic; consequently, it is a ferrimagnetic material. As Fe$_3$O$_4$ exhibits good electric conductivity at RT due to the hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ on the B sites, the conduction electrons are 100% spin polarized. As hopping is frozen on cooling, conductivity greatly decreases at low temperature, which is known as Verwey transition. The transition temperature, $T_V$, is 120 K. The saturation magnetization of bulk Fe$_3$O$_4$ is 510 emu/cc. According to Julliere’s formula, MTJs with Fe$_3$O$_4$ electrodes are expected to exhibit very high TMR ratios due to large spin polarization. To date, researchers have fabricated MTJs with Fe$_3$O$_4$ and measured magnetoresistance; however, the TMR ratios have been small. Although the reason for this is not completely understood, such small TMR ratios can be attributed to imperfect antiparallel magnetic states in MTJs. The magnetization process of Fe$_3$O$_4$ films should be improved to achieve clear parallel and antiparallel magnetic configurations. We prepared epitaxial Fe$_3$O$_4$ films with various crystal orientations, and investigated their crystalline qualities and magnetic properties. We also fabricated MTJs with Fe$_3$O$_4$ electrodes and observed a negative TMR effect of $-12\%$.

The Fe$_3$O$_4$ thin films were prepared with three crystal orientations of (001), (110), and (111) by using a molecular beam epitaxy (MBE) system. The sample structures were:

(1) an MgO(001) substrate/MgO (20 nm)/Fe$_3$O$_4$ (60 nm),
(2) an MgO(110) substrate/MgO (20 nm)/Fe$_3$O$_4$ (60 nm), and
(3) an Al$_2$O$_3$(0001) substrate/Pt (20 nm)/Fe$_3$O$_4$ (60 nm).

Following the deposition of MgO or Pt buffer layers, Fe$_3$O$_4$ thin film was formed by reactive deposition at a temperature ($T_{sub}$) of 300 °C in an O$_2$ atmosphere of 4 × 10$^{-4}$ Pa. Then, the films were annealed at 600 °C for 30 min in an O$_2$ atmosphere. The partial pressure of O$_2$ gas was 1 × 10$^{-4}$ Pa during annealing. All the samples were fabricated under the same growth conditions to enable the quality of Fe$_3$O$_4$ films to be compared. Epitaxial growth was observed with reflection high energy electron diffraction (RHEED) and the surface morphology was observed with atomic force microscopy (AFM). We also investigated the magnetization process at RT with a vibrating sample magnetometer (VSM).

Figs. 1(a) and 1(b) show the RHEED patterns of Fe$_3$O$_4$(100) before and after O$_2$ annealing at 600 °C for 30 min. The electron beam was incident along [100]. Fig. 1(c) is an AFM of Fe$_3$O$_4$(100) after annealing. A streak RHEED pattern can be observed in Fig. 1(a) meaning the
Fe₃O₄ film grew epitaxially. In addition, p(1 × 1) surface reconstruction was observed. The streak pattern sharpened after annealing at 600 °C in the O₂ atmosphere, as can be seen from Fig. 1(b). A step-terrace structure can be confirmed from the AFM in Fig. 1(c). The roughness average, Rₐ, was 0.12 nm, and the terrace width was 200 nm.

Figs. 1(d)–1(f) show the RHEED patterns and AFMs of Fe₃O₄(110) grown on MgO(110). The incident electron beam direction was [−110]. A spotty pattern was obtained before annealing due to the island growth of Fe₃O₄ (110). However, the surface flatness was improved dramatically by O₂ annealing at 600 °C, as can be seen from the RHEED pattern in Fig. 1(e). The surface in the AFM of Fe₃O₄(110) after annealing in Fig. 1(f) had anisotropic shapes along [100], which seemed to originate from the anisotropy of the MgO(110) substrate. Rₐ was estimated to be 0.39 nm.

Finally, Figs. 1(g)–1(i) show RHEED patterns and AFMs of Fe₃O₄(111). The direction of the incident electron beam was [11−20] Fig. 1(g) shows RHEED patterns of as-deposited Fe₃O₄(111). It shows streak patterns that indicate a flat surface and surface reconstruction. Terrace and step structures can be observed in the AFM of Fe₃O₄(111) after annealing in Fig. 1(i); however, islands with a diameter of 200 nm and height of several tens of nanometers were observed on the surface (not shown) in the AFM of a large area. The Rₐ was estimated at 2.40 nm, which was one order of magnitude larger than the other crystal orientations. The large roughness could be attributed to the lattice mismatch between Fe₃O₄ and the Pt buffer layer. As the lattice constant of Fe₃O₄ was 0.8397 nm and that of MgO was 0.421 nm, the lattice mismatch was about 0.3%. However, as the lattice constant of Pt was 0.392 nm, Fe₃O₄ lattice mismatch to the Pt buffer layer was 6.6%. Such large lattice mismatch could give rise to a larger surface roughness for Fe₃O₄(111) than that for Fe₃O₄(100).

The magnetization curves at RT for the Fe₃O₄ films are plotted in Fig. 2. The magnetic field was applied in plane. The diamagnetic components of the substrates were subtracted under the assumption that the magnetizations of the Fe₃O₄ were saturated at 5 kOe, which is the maximum field of VSM. The magnetization curve of Fe₃O₄ (100) is in Fig. 2(a). The saturation magnetization (Mₛ) was 330 emu/cc, the remanent magnetization (Mᵣ) was 100 emu/cc, and the coercive field (Hₑ) was 80 Oe. The remanent magnetization ratio (Mᵣ/Mₛ) was 0.30. Fig. 2(b) plots the magnetization curves of Fe₃O₄ (110) where the directions of the magnetic field were [001] and [−110]. The saturation magnetization was 185 emu/cc for both magnetic field directions. Mₛ, Hₑ, and Mᵣ/Mₛ in the magnetic field along [001] were 30 emu/cc, 210 Oe, and 0.16, and those for [−110] were 100 emu/cc, 780 Oe, and 0.54. The magnetization process strongly depended on the directions of the magnetic field, viz., the squareness and Mᵣ/Mₛ were larger for the [−110] magnetic field than those for [100]. Fig. 2(d) plots the dependence of the coercivity of Fe₃O₄ (110) film on the magnetic field measured with a MOKE system (Hₑ= 2 kOe). The Hₑ of the Fe₃O₄ (110) film indicated apparent uniaxial anisotropy. Nevertheless, the films had an anisotropic shape along the [100] direction, as shown in Fig. 1(f), and the films had a larger remanent ratio in the [−110] direction. Therefore, the anisotropy in Fig. 2(b) was attributed to the magnetocrystalline anisotropy in Fe₃O₄. Saturation magnetization was 390 emu/cc, remanent magnetization was 290 emu/cc, and coercivity was 300 Oe in the magnetization curve of Fe₃O₄ (111). The remanent magnetization ratio was approximately 0.74, which was the largest value in the three crystal directions. The magnetic process was almost independent of the field directions. These values are summarized in Table I. All the films exhibited smaller saturated magnetizations than the value for bulk Fe₃O₄ of 510 emu/cc. The reason for this is that the external field was not sufficient to saturate the
magnetic moments in the Fe$_3$O$_4$ films. According to previous studies, Fe$_3$O$_4$ thin films contain considerable numbers of antiphase boundaries (APBs)\textsuperscript{15} that make the Fe$_3$O$_4$ hard to saturate magnetically due to antiferromagnetic coupling at the APBs.

We fabricated the MTJs with Fe$_3$O$_4$(110) electrodes, and measured the tunnel magnetoresistance effect. The film structure was MgO(110)/NiO(110) (5 nm)/Fe$_3$O$_4$(110) (60 nm)/Al$_2$O$_3$ (2.4 nm)/Fe (5 nm)/Co (10 nm)/Au (30 nm). The NiO layer was inserted to suppress the diffusion of Mg from the substrates. Junctions of $10 \times 10 \mu m^2$ were fabricated by photolithography, Ar ion milling, and sputtering. The junctions demonstrated a clear TMR effect of $-12\%$ at RT, as shown in Fig. 3(a). The negative MR agreed with the \textit{ab-initio} calculations that predicted negative spin polarization in Fe$_3$O$_4$. According to band calculations, the majority band of Fe$_3$O$_4$ has a bandgap at the Fermi level, so that conduction electrons have minority spin, meaning negative spin polarization.\textsuperscript{6} On the other hand, the Fe electrode with the Al$_2$O$_3$ barrier was experimentally found to have positive spin polarization.\textsuperscript{21} Therefore, a negative MR ratio was expected in Fe$_3$O$_4$/Al$_2$O$_3$/Fe MTJs. To the best of our knowledge, these are the first experimental results of a negative MR ratio with an Al$_2$O$_3$ barrier and Fe$_3$O$_4$ electrodes.\textsuperscript{16–20}

The polarization of Fe$_3$O$_4$ deduced from the MR ratio based on Julliere’s formula was $-16\%$, in which the polarization of Fe/Al$_2$O$_3$ was assumed to be 40%.\textsuperscript{21} Although the polarization was much smaller than the predicted value, $-16\%$ is of the same order as the reported values using various barrier materials.\textsuperscript{22,23} With respect to the dependence on bias, the MR ratio had negative values in the range of $\pm 1$ V, and the absolute value basically decreased with large bias voltage. The MR ratio remained at about $-12\%$ in the small bias region, which may be associated with the electric structure of Fe$_3$O$_4$.

| Table I. Magnetic characteristics of Fe$_3$O$_4$ films with various crystal orientations. |
|---------------------------------|-----------------|----------------|-----------------|----------------|
| Fe$_3$O$_4$(100)               | 330             | 100            | 80              | 0.30           |
| Fe$_3$O$_4$(110) H/[001]       | 185             | 30             | 210             | 0.16           |
| Fe$_3$O$_4$(110) H/[–110]      | 185             | 100            | 780             | 0.54           |
| Fe$_3$O$_4$(111)               | 390             | 290            | 300             | 0.74           |

FIG. 2. Hysteresis curves obtained from VSM measurements at RT for epitaxial Fe$_3$O$_4$ films with various crystal orientations. (a) is Fe$_3$O$_4$(100), (b) is Fe$_3$O$_4$(110), and (c) is Fe$_3$O$_4$(111). Directions of magnetic fields are given in plots. (d) is the coercive field, where the $H_c$ of Fe$_3$O$_4$(110) film is a function of the direction of the magnetic field. The angle is defined relative to the $[-110]$.  

FIG. 3. (a) TMR curve for MTJ of MgO(110)/NiO(110) (5 nm)/Fe$_3$O$_4$(110) (60 nm)/Al$_2$O$_3$ (2.4 nm)/Fe (5 nm)/Co (10 nm)/Au (30 nm) at RT. Red, blue, and black lines are MRs with bias voltages of 10, 500, and 1000 mV. (b) Dependence on bias of TMR ratio. Direction of bias voltage is defined with respect to upper electrode.
Theoretical investigations into transport properties are necessary to interpret the dependence on bias in detail.

Fe$_2$O$_4$ epitaxial films with various crystal orientations were fabricated by reactive MBE and all the films grew epitaxially. The Fe$_2$O$_4$ (110) films exhibited clear uniaxial magnetic anisotropy that originated from crystal anisotropy. The squareness of the hysteresis curves strongly depended on the crystal orientation. A negative MR ratio of $-12\%$ was observed in the MTJs with Fe$_2$O$_4$(110) electrodes. Although the absolute value was small, the negative MR agreed with the theoretical predictions.

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