TITLE: Exchange Coupling and Spin-Flip Transition of CoFe2O4/alpha-Fe2O3 Bilayered Films

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EXCHANGE COUPLING AND SPIN-FLIP TRANSITION OF CoFe₂O₄/α-Fe₂O₃ BILAYERED FILMS

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ABSTRACT

CoFe₂O₄/α-Fe₂O₃ (ferrimagnetic / antiferromagnetic) bilayered films were prepared on α-Al₂O₃(102) single-crystalline substrates by helicon plasma sputtering. A well-crystallized epitaxial α-Fe₂O₃(102) layer was formed on the substrate, while CoFe₂O₄ grown on α-Fe₂O₃ (102) was a polycrystalline layer with a (100)-preferred orientation. The α-Fe₂O₃(102) films without CoFe₂O₄ layers clearly showed a spin-flip transition at about 400 K. The spins aligned perpendicular to the film plane at room temperature changed their direction within the film plane above 400 K. However the α-Fe₂O₃ base layers of CoFe₂O₄/α-Fe₂O₃ bilayered films did not show any spin-flip transition. The CoFe₂O₄ layer on α-Fe₂O₃ had a large in-plane magnetic anisotropy, while the spin axis of the α-Fe₂O₃(102) base layer was directed perpendicular to the film plane. The magnetization of ferrimagnetic CoFe₂O₄ layers was coupled perpendicularly to the spin axis of antiferromagnetic α-Fe₂O₃ layers due to the exchange coupling at the interface between CoFe₂O₄ and α-Fe₂O₃.

INTRODUCTION

Exchange coupling at an interface between ferromagnetic (FM) and antiferromagnetic (AFM) layers has received much attention mainly due to the technological applications in such devices as spin-valve sensors. It stabilizes a magnetic direction of the FM layer and functions as a bias field in the magnetic hysteresis loop. Recently, full micromagnetic calculations suggested the existence of the 90° FM - AFM coupling at the interface [1]. However the fundamental origin of exchange coupling between magnetic materials, especially magnetic oxide materials, is still unclear. α-Fe₂O₃ is one of candidates for the AFM materials fabricated in the spin-valve sensors [2,3]. The spin valves partly consisting of α-Fe₂O₃ have high thermal stability and large magneto-resistance ratio. By the way, one of the present authors found that epitaxial α-Fe₂O₃ (102) films on α-Al₂O₃(102) had an unique spin-flip transition [4]. The transition takes place at about 400 K, much higher than the Morin transition temperature (260 K) of the bulk crystal. The spin axis lying within a film plane above 400 K turns perpendicular to the film plane below the transition temperature.

There are a few studies on the exchange coupling between oxide materials with the FM/AFM bilayered structure [5]. Most of practical FM oxides are exactly ferrimagnetic. Microscopic spin configurations at the interface between oxide systems could be different from the ones between metallic systems. We prepared well-crystallized α-Fe₂O₃ and CoFe₂O₄ bilayered films by using helicon plasma sputtering technique [6]. CoFe₂O₄ is a typical ferrimagnetic material with an inverse spinel structure. Structural properties and magnetic interactions between ferrimagnetic CoFe₂O₄ (FM) and α-Fe₂O₃ (AFM) layers were discussed. If the exchange coupling at the CoFe₂O₄/α-Fe₂O₃ interface was strong enough, magnetic properties of the CoFe₂O₄ layer should be influenced by the spin-flip transition of the α-Fe₂O₃ layer or vice versa.
EXPERIMENT

Helicon plasma sputtering is a powerful technique to prepare high-quality multilayered films with sharp interfaces [7]. It has some advantages in comparison with conventional rf magnetron sputtering, such as high deposition rate stability and low plasma damage to the film surface. A helicon plasma cathode consists of a conventional rf magnetron cathode and a rf coil for a helicon wave. Fig. 1 shows a schematic drawing of the helicon plasma sputtering system we used. Two targets for helicon cathodes were made of sintered $\alpha$-Fe$_2$O$_3$ and CoO, respectively. The base pressure of the system was $10^{-7}$ Pa. Before sputter deposition an $\alpha$-Al$_2$O$_3$(102) substrate was annealed in vacuum at about 973 K for 1 hour in order to obtain a clean and well-ordered surface. $\alpha$-Fe$_2$O$_3$ base layers with the thickness of 100 nm were sputtered on the substrate at the substrate temperature of 673 K. CoFe$_2$O$_4$ layers with several thicknesses ranging from 25 to 200 nm were then deposited on $\alpha$-Fe$_2$O$_3$ at 773 K by simultaneous sputtering from both targets, to control the deposition rate ratio between $\alpha$-Fe$_2$O$_3$ and CoO. The deposited films were characterized by reflection high energy electron diffraction (RHEED), x-ray diffraction (XRD), scanning probe microscopy (SPM), vibrating sample magnetometer (VSM), conversion electron Mössbauer spectroscopy (CEMS), and energy dispersive X-ray spectroscopy (EDS).

RESULTS AND DISCUSSION

Typical XRD and RHEED patterns of $\alpha$-Fe$_2$O$_3$ films deposited on $\alpha$-Al$_2$O$_3$ (102) single-crystalline substrates are shown in figs. 2(a) and (b), respectively. Epitaxial relationship between the $\alpha$-Fe$_2$O$_3$ layer and the $\alpha$-Al$_2$O$_3$ substrate can clearly be seen in both XRD and RHEED patterns. The XRD pattern had only a reflection from the film indexed as $\alpha$-Fe$_2$O$_3$(204) at the side of an intense $\alpha$-Al$_2$O$_3$(204) reflection. The sharp streak lines in the RHEED pattern indicated an atomically flat surface of the layer. Both $\alpha$-Fe$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ have a corundum structure with a small lattice misfit of $+5.8\%$. This could be a reason why the well-crystallized and atomically flat $\alpha$-Fe$_2$O$_3$ layers were epitaxially formed on the $\alpha$-Al$_2$O$_3$ substrates.

![Figure 1. Schematic drawing of helicon plasma sputtering system we used. The helicon cathodes consist of conventional rf magnetron cathodes and rf coils.](image)
Figure 2. (a) XRD and (b) RHEED patterns of an $\alpha$-Fe$_2$O$_3$ film deposited on an $\alpha$-Al$_2$O$_3$ (102) substrate.

Figs. 3(a) and (b) are typical XRD and RHEED patterns of CoFe$_2$O$_4$/Fe$_2$O$_3$ bilayered films, respectively. The XRD pattern of the CoFe$_2$O$_4$/Fe$_2$O$_3$ bilayered film had two reflections from the CoFe$_2$O$_4$ layer indexed as CoFe$_2$O$_4$(311) and (400) in addition to the reflection from the $\alpha$-Fe$_2$O$_3$ (204) base layer. The relative peak intensity ratio of CoFe$_2$O$_4$(400) to (311) was considerably large, in comparison with that of the CoFe$_2$O$_4$ bulk pattern with random orientation [8]. The CoFe$_2$O$_4$ layer formed on $\alpha$-Fe$_2$O$_3$(102) had strong (100)-preferred orientation. In crystallographic aspects, the $\alpha$-Fe$_2$O$_3$(102) surface has a pseudo-square structure though the $\alpha$-Fe$_2$O$_3$ crystal has hexagonal corundum structure. The CoFe$_2$O$_4$(100) layer with cubic spinel structure could be formed on the $\alpha$-Fe$_2$O$_3$ (102) base layer. However the lattice misfit between them is very large, about $-17\%$. The RHEED pattern of CoFe$_2$O$_4$ on $\alpha$-Fe$_2$O$_3$(102) was spotted and complicated. The CoFe$_2$O$_4$ layers in bilayered films were poly-crystallized and had (100)-preferred orientation. Moreover, chemical formula of the CoFe$_2$O$_4$ layer analyzed by EDS was Co$_{0.7}$Fe$_{2.3}$O$_4$.

The spin direction of $\alpha$-Fe$_2$O$_3$ layers on $\alpha$-Al$_2$O$_3$(102) was easily determined by CEMS. The CEMS spectrum of $\alpha$-Fe$_2$O$_3$ generally exhibited six lines due to the nuclear Zeeman splitting from a large internal magnetic field. Relative peak intensity ratio of the sextet is expressed theoretically as a function of an angle ($\theta$) between the $\gamma$-ray direction and the spin direction

$$3: \frac{4\sin^2 \theta}{1+\cos^2 \theta} : 1:1: \frac{4\sin^2 \theta}{1+\cos^2 \theta} : 3.$$
CEMS spectra of an \( \alpha-Fe_2O_3 \)(102) film deposited on \( \alpha-Al_2O_3 \)(102) measured at (a) 423 K and (b) room temperature.

**Figure 4.** CEMS spectra of an \( \alpha-Fe_2O_3 \)(102) film deposited on \( \alpha-Al_2O_3 \)(102) measured at (a) 423 K and (b) room temperature.

CEMS spectra of an \( \alpha-Fe_2O_3 \)(102) film without a \( CoFe_2O_4 \) covering layer are shown in fig. 4 as a function of the temperature. The spectra had the intensity ratio of nearly 3:0:1:1:0:3 at 300 K and 3:4:1:1:4:3 at 423 K. The spin axis of the \( \alpha-Fe_2O_3 \)(102) film was abruptly changed from the perpendicular direction (\( \theta=0^\circ \)) to the in-plane direction (\( \theta=90^\circ \)) at about 400 K.

Besides the intensity ratio of the CEMS spectra of the \( CoFe_2O_4/\alpha-Fe_2O_3 \)(102) bilayered film did not show any temperature dependence, even when the \( \alpha-Fe_2O_3 \)(102) layer was covered by a very thin, 25 nm-thick, \( CoFe_2O_4 \) layer. All spectra of the \( \alpha-Fe_2O_3 \)(102) base layer had the intensity ratio of about 3:0:1:1:0:3 as shown in fig. 5. The \( \alpha-Fe_2O_3 \) layer covered by \( CoFe_2O_4 \) did not show the spin-flip transition. The spin direction in \( \alpha-Fe_2O_3 \) was fixed perpendicular to the film plane over the all temperatures.

In-plane and out-of-plane magnetization curves of the \( CoFe_2O_4/\alpha-Fe_2O_3 \) bilayered films were also measured at various temperatures. Figs. 6(a) and (b) show room temperature magnetization curves of the 200 nm-thick \( CoFe_2O_4 \) films without and with the \( \alpha-Fe_2O_3 \)(102) base layers, respectively. No uniaxial magnetic anisotropy nor exchange bias field was induced in the \( CoFe_2O_4 \) layers, when they did not have the \( \alpha-Fe_2O_3 \) base layers. \( CoFe_2O_4 \) is known to have a large magnetocrystalline anisotropy along the \( <100> \) direction [8]. The \( (100) \)-oriented \( CoFe_2O_4 \) layers could have domain structures magnetized along the in-plane \( [100] \) and \( [010] \) and the out-of-plane \( [001] \) directions. The large coercivity was, thus, observed in both in-plane and out-of-plane hysteresis loops.

On the other hands, the \( CoFe_2O_4 \) layers deposited on the \( \alpha-Fe_2O_3 \)(102) base layers had a large in-plane magnetic anisotropy. The exchange bias field of about 200 Oe was induced. The spin...
axis of the $\alpha$-Fe$_2$O$_3$ base layers was directed perpendicular to the film plane as discussed above. The magnetization of the CoFe$_2$O$_4$ (FM) layers was exactly coupled perpendicularly to the spin axis of the $\alpha$-Fe$_2$O$_3$ (AFM) layers. The 90° FM-AFM coupling observed in CoFe$_2$O$_4$/$\alpha$-Fe$_2$O$_3$ bilayered films was in good agreement with the theoretical result reported by Koon [1]. The large in-plane anisotropy of the CoFe$_2$O$_4$ layers was probably induced by the 90° coupling with the $\alpha$-Fe$_2$O$_3$ layers and it should suppress the spin-flip transition of the $\alpha$-Fe$_2$O$_3$ layers irreversibly.

**SUMMARY**

Exchange coupling between a ferrimagnetic CoFe$_2$O$_4$ layer and an antiferromagnetic $\alpha$-Fe$_2$O$_3$ layer was examined to prepare CoFe$_2$O$_4$/$\alpha$-Fe$_2$O$_3$ bilayered films. (100)-oriented CoFe$_2$O$_4$ layers were formed on well-crystallized epitaxial $\alpha$-Fe$_2$O$_3$(102) layers deposited on $\alpha$-Al$_2$O$_3$(102) single-crystalline substrates. The $\alpha$-Fe$_2$O$_3$(102) films without CoFe$_2$O$_4$ layers clearly showed the spin-flip transition at about 400 K. The spin axis lay within the (102) plane of $\alpha$-Fe$_2$O$_3$ at high temperatures but became almost normal to the plane at low temperatures. However the $\alpha$-Fe$_2$O$_3$(102) layers covered by CoFe$_2$O$_4$ layers did not show any spin-flip transition. The spin axis of the $\alpha$-Fe$_2$O$_3$(102) base layers was fixed on the perpendicular to the films. Magnetic hysteresis loops of CoFe$_2$O$_4$/$\alpha$-Fe$_2$O$_3$ bilayered films indicated that a large in-plane magnetic anisotropy and an exchange bias field were induced in the films. The 90° coupling at the interface between ferrimagnetic and antiferromagnetic materials was directly observed in the CoFe$_2$O$_4$/$\alpha$-Fe$_2$O$_3$ system fabricated entirely of oxides.
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