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A row of four Shimadzu spectrophotometers is shown. From left to right: a small benchtop model, a larger benchtop model with a sample holder, a large floor-standing model with a front-loading sample compartment, and a tall, narrow floor-standing model with a top-loading sample compartment.

Preparation and the magnetic properties of Co- γ -Fe₂O₃ perpendicular magnetic films on NiO underlayer

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The NiO underlayer, which had $\langle 100 \rangle$ orientation, with NaCl-like structure could be prepared onto the glass substrate by reactive rf sputtering at ambient temperature. The CoO/Fe₃O₄ multilayers were grown epitaxially on the underlayer at 200 °C; the Fe₃O₄ and CoO on the NiO grew along the $\langle 100 \rangle$ axis independent of the bilayer thickness Λ , though those on the glass substrate did not show the $\langle 100 \rangle$ orientation for $\Lambda > 100$ Å. Followed by annealing of the multilayers in air at 280–350 °C, the $\langle 100 \rangle$ -oriented Co- γ -Fe₂O₃ perpendicular magnetic films were obtained. The (400) of the Co- γ -Fe₂O₃ on the (200) of the NiO has tensile stress at the interface because of the smaller (400) spacing than the (200) spacing normal to the film plane. Therefore, the (400) spacing measured parallel to the film plane (2.072 Å) was smaller than that of bulk, 2.086 Å. The magnetic properties of the Co- γ -Fe₂O₃ films on the NiO, Co- γ -Fe₂O₃/NiO, obtained above were evaluated. The squareness compensated by a demagnetization coefficient of Co- γ -Fe₂O₃/NiO were more than 0.94, though those of the Co- γ -Fe₂O₃ on the glass substrate, Co- γ -Fe₂O₃/glass, were about 0.85. The anisotropy energy of Co- γ -Fe₂O₃/NiO was estimated 3.3×10^6 ergs/cm³, which value was larger than that of Co- γ -Fe₂O₃/glass (2.5×10^6 ergs/cm³). Coercivity of the perpendicular hysteresis loop of Co- γ -Fe₂O₃/NiO increased with Co contents and could be controlled in the region of 0.8–5.0 kOe, although H_c of Co- γ -Fe₂O₃/glass were 5.0 kOe constantly. The columnar grains of the Co- γ -Fe₂O₃, whose diameter is 300–500 Å, grew continuously along the columnar grains of NiO.

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I. INTRODUCTION

Continuous thin films composed of γ -Fe₂O₃ with a spinel crystal structure have been noted as magnetic recording media because of their high chemical stability, corrosion resistance, large coercivity, and durability due to high hardness. In particular, the perpendicular magnetic films, e.g., the Os doped γ -Fe₂O₃ films obtained by the annealing of the films in an external magnetic field,¹ have been investigated for high-density recording media.

In our previous studies, we have found the preparation method to obtain the Co containing γ -Fe₂O₃, Co- γ -Fe₂O₃, perpendicular magnetic films by control of the crystalline orientation.² For the CoO/Fe₃O₄ multilayers of the bilayer thickness $\Lambda < 80$ Å on the glass substrate, the multilayers indicate $\langle 100 \rangle$ orientation, and $\langle 100 \rangle$ -oriented Co- γ -Fe₂O₃ films can be obtained by annealing of the multilayers in air at 400 °C. The Co- γ -Fe₂O₃ films have a large perpendicular magnetic anisotropy energy, which is induced with the preferential crystalline orientation of $\langle 100 \rangle$ axis.

In the present study, we researched the underlayer that promotes $\langle 100 \rangle$ orientation of the Co- γ -Fe₂O₃. Numerous works show that cubic spinel type crystal can be grown epitaxially on cubic NaCl-like structural materials such as rock salt,^{3,4} single-crystal MgO,^{5,6} CoO on rock salt,⁷ and NiO on single-crystal MgO.⁸ From this point of view, we tried to prepare $\langle 100 \rangle$ -oriented NiO films on the glass substrate, not on the single-crystal substrates, as the underlayer. Furthermore, the magnetic properties of the Co- γ -Fe₂O₃ films prepared onto the NiO underlayer were investigated in comparison with the Co- γ -Fe₂O₃ films on the glass substrate. The microstructures of the Co- γ -Fe₂O₃ films on the NiO were also investigated.

II. EXPERIMENT

NiO films were prepared in Ar+O₂ mixed gas (O₂ pressure, P_{O_2} , was 0.07–0.09 mTorr) onto the glass substrate (HOYA N5) by reactive rf sputtering. The NiO film growth rate was 40 Å/min. CoO/Fe₃O₄ multilayers were prepared onto the NiO film and the glass substrate in Ar+O₂ mixed gas (P_{O_2} was 0.09–0.11 mTorr) at 200 °C by reactive rf sputtering. The multilayers growth rate was 40 Å/min. For the sputtering targets, Ni, Fe, and Co metal disks with 3 in. in diameter were used, respectively. In order to transform the multilayers to Co- γ -Fe₂O₃ films, the heat treatment was carried out in air at 280–350 °C for 1–3 h. The film thicknesses were measured with a surface roughness instrument. The crystal structures and Λ were examined by x-ray diffraction (Fe $K\alpha$). The magnetic properties were measured with a vibrating sample magnetometer at 20–75 °C. The composition and the depth distribution of composition in the films were analyzed by inductively coupled plasma atomic emission spectroscopy and electron spectroscopy for chemical analysis (ESCA), respectively. Microstructures of the Co- γ -Fe₂O₃ films on the NiO were observed by scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

NiO films prepared at 25 °C showed $\langle 100 \rangle$ orientation [Fig. 1(a)], though the films at 200 °C had $\langle 111 \rangle$ orientation. It revealed that the $\langle 100 \rangle$ -oriented NiO could be obtained at lower temperature than other NaCl-like structural oxide such as $\langle 100 \rangle$ -oriented MgO which were prepared at 310–750 °C.⁹ Figure 2 shows the relationship between the NiO film thickness, δ_{NiO} , and the intensity ratio, $I_{(200)}/I_{(111)}$, in the x-ray diffraction spectra of NiO. For the

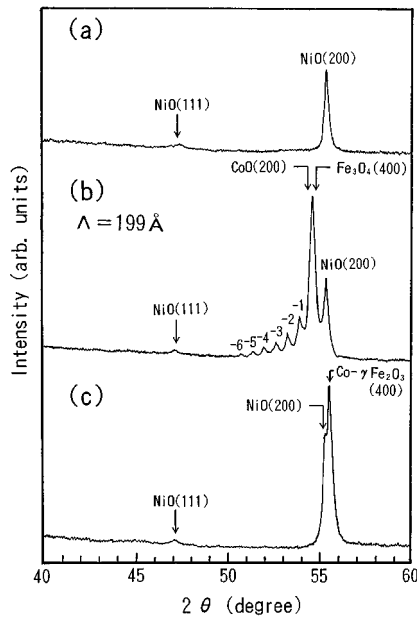


FIG. 1. X-ray diffraction spectra (Fe $K\alpha$) of $\langle 100 \rangle$ -oriented NiO film of 1200 Å in thickness prepared onto the glass substrate at 25 °C (a), CoO/Fe₃O₄ multilayer ([CoO(34 Å)/Fe₃O₄(165 Å)]₁₀) prepared onto the $\langle 100 \rangle$ -oriented NiO (b) and Co- γ -Fe₂O₃ on the $\langle 100 \rangle$ -oriented NiO obtained by annealing the multilayer at 350 °C for 2 h (c).

films of $\delta_{\text{NiO}} \geq 800$ Å, $I_{(111)}$ were the same value, about 10 cps, as shown in Fig. 1(a). It is assumed that there is random oriented initial growth layer of 800 Å in thickness, thus the films of $\delta_{\text{NiO}} \geq 1000$ Å were used as the underlayer in subsequent experiments.

X-ray diffraction spectrum of as-deposited CoO/Fe₃O₄ multilayer prepared for $\Lambda = 199$ Å onto the NiO underlayer is shown in Fig. 1(b). This indicates the multilayers are grown epitaxially on the NiO; The Fe₃O₄ and CoO on the NiO grew along the $\langle 100 \rangle$ axis independent of Λ , though those on the glass substrate did not show the $\langle 100 \rangle$ orientation for $\Lambda > 100$ Å.² The epitaxial growth of these crystals is attributed to good lattice match. The distances between the oxygen atoms in the fcc lattices of NiO, Fe₃O₄, and CoO along $\langle 100 \rangle$ direction were 2.089, 2.099, and 2.130 Å, respectively. These

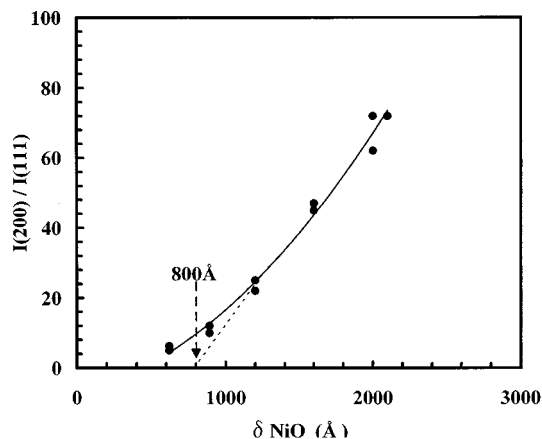


FIG. 2. Dependence of intensity ratio, $I_{(200)}/I_{(111)}$, in the x-ray diffraction spectra on film thickness, δ_{NiO} , of the NiO prepared at 25 °C.

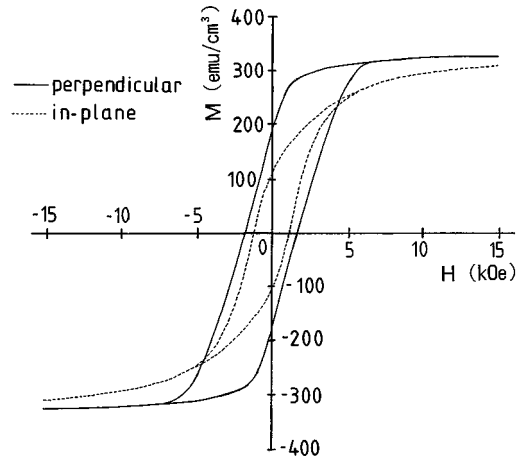


FIG. 3. Magnetic hysteresis loops of $\langle 100 \rangle$ -oriented Co- γ -Fe₂O₃ of 1300 Å in thickness with Co/Fe=0.03 on NiO underlayer.

dimensions represent a lattice mismatch between NiO and Fe₃O₄ of 0.48%, between Fe₃O₄ and CoO of 1.46%, all are within 1.5% of one another.

The Co- γ -Fe₂O₃ films obtained by annealing the multilayers on the NiO had $\langle 100 \rangle$ orientation as shown in Fig. 1(c). The (400) spacing of the Co- γ -Fe₂O₃ measured parallel to the film plane, $d_{(400)}$, was 2.072 Å. This value is smaller than that of bulk, 2.086 Å, because the (400) of the Co- γ -Fe₂O₃ on the (200) of the NiO has tensile stress at the interface due to smaller (400) spacing than (200) spacing normal to the film plane. Diffusion of Ni atoms in the NiO layer into the Co- γ -Fe₂O₃ was not observed.

The $\langle 100 \rangle$ -oriented Co- γ -Fe₂O₃ films on the NiO, Co- γ -Fe₂O₃/NiO, with the Co- γ -Fe₂O₃ film thicknesses varied from 500 to 2600 Å, were perpendicular magnetic films as shown in Fig. 3. The squareness compensated by a demagnetization coefficient of Co- γ -Fe₂O₃/NiO were more than 0.94, while those of the Co- γ -Fe₂O₃ on the glass substrate, Co- γ -Fe₂O₃/glass, were about 0.85. It is considered that a departure of the magnetic easy axis of Co- γ -Fe₂O₃/NiO from a perpendicular direction is smaller than that of Co- γ -Fe₂O₃/glass, reflecting the importance of

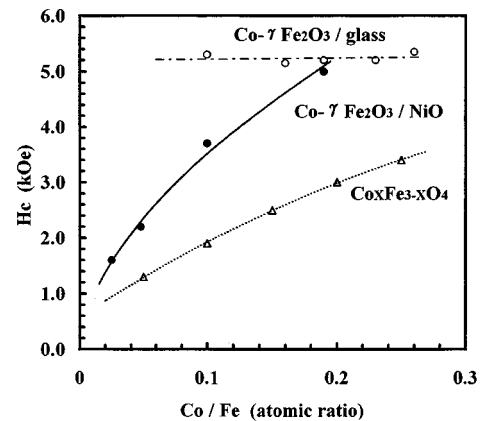


FIG. 4. Coercivity of the perpendicular hysteresis loop, H_c , vs atomic ratio for $\langle 100 \rangle$ -oriented Co- γ -Fe₂O₃ on NiO underlayer, $\langle 100 \rangle$ -oriented Co- γ -Fe₂O₃ on the glass substrate, and cobalt ferrite films.

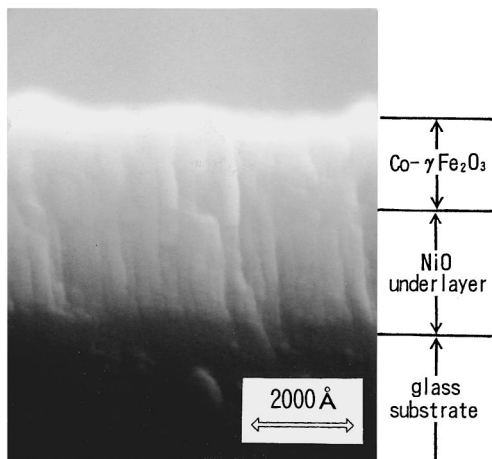


FIG. 5. SEM observation of cross section of $\langle 100 \rangle$ -oriented $\text{Co-}\gamma\text{-Fe}_2\text{O}_3$ film on NiO underlayer obtained by annealing at 300°C for 2 h.

the $\langle 100 \rangle$ orientation. For the films having the coercivity of perpendicular hysteresis loop, H_c , of 5.0 kOe, the anisotropy energy of $\text{Co-}\gamma\text{-Fe}_2\text{O}_3/\text{NiO}$ was estimated $3.3 \times 10^6 \text{ ergs/cm}^3$ from the initial in-plane magnetization curve, which was larger than that of $\text{Co-}\gamma\text{-Fe}_2\text{O}_3/\text{glass}$ ($2.5 \times 10^6 \text{ ergs/cm}^3$), because of the tensile stress described above. H_c of $\text{Co-}\gamma\text{-Fe}_2\text{O}_3/\text{NiO}$ increased with Co contents and could be controlled in the region of 0.8–5.0 kOe, although those of $\text{Co-}\gamma\text{-Fe}_2\text{O}_3/\text{glass}$ were 5.0 kOe constantly (Fig. 4). Additionally, the same H_c could be obtained from $\text{Co-}\gamma\text{-Fe}_2\text{O}_3/\text{NiO}$ films with about one-third the Co content of the cobalt ferrite films prepared onto the glass substrate.¹⁰ It seems that the larger H_c for $\text{Co-}\gamma\text{-Fe}_2\text{O}_3/\text{NiO}$ relative to the cobalt ferrite is caused mainly by a higher extrinsic stress-induced anisotropy due to the larger tensile stress. Temperature dependence of H_c , dH_c^*/dT (here dH_c^* is dH_c divided by H_c measured at room temperature), for

$\text{Co-}\gamma\text{-Fe}_2\text{O}_3/\text{NiO}$ was $-0.266\%/^\circ\text{C}$ which was smaller than Co-surface modified $\gamma\text{-Fe}_2\text{O}_3$ powder used for magnetic tapes, $-0.32\%/^\circ\text{C}$.¹¹

SEM observation of the cross section of $\text{Co-}\gamma\text{-Fe}_2\text{O}_3/\text{NiO}$ is shown in Fig. 5. The columnar grains of the $\text{Co-}\gamma\text{-Fe}_2\text{O}_3$, whose diameter is 300–500 Å, grew continuously along the columnar grains of the NiO.

$\text{Co-}\gamma\text{-Fe}_2\text{O}_3/\text{NiO}$ have the possibilities to be a high-density magnetic recording media, e.g., $\text{Co-}\gamma\text{-Fe}_2\text{O}_3/\text{NiO}$ have a large coercivity, a chemical stability, and high hardness tolerable for sliding contact use with no overcoat, i.e., “0” spacing. Further investigations are now in progress.¹²

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