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Bi Surfactant Effect on the Magnetic Properties of Fe/Cr Multilayers Prepared by Sputter Deposition

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To obtain information about the correlation between interface structure and magnetotransport property in metallic multilayers, we have fabricated Fe/Cr multilayers with and without Bi as a surfactant by sputter deposition. From the observations of grazing incidence X-ray reflectivity and X-ray diffraction patterns, we confirmed that the interface structures of Fe/Cr multilayers with Bi are sharper than that of multilayers without Bi, which means that Bi operates as an effective surfactant. The magnetoresistance ratios of the multilayers prepared with Bi were larger than those of the multilayers without Bi.
Key words : Surfactant, Interface roughness, Magnetoresistance–multilayers, Crystal growth

1. INTRODUCTION

Understanding the epitaxial growth of thin metal films with an atomic scale is essential for the manipulation of the structure and interfaces of films to improve the quality of thin-film devices. The correlation between the interface structure and magnetic or electrical properties of metallic multilayers is not yet fully understood. It is recognized, however, that growth behavior of thin films greatly affects the properties of metallic multilayers. Consequently, knowledge of control the growth mode is necessary for understanding the basic properties of metallic multilayer. Numerous observations have been reported, indicating that interface roughness plays an important role in the giant magnetoresistance (GMR) effect. However, no clear picture has yet emerged and the reported data are contradictory. Petroff has reported that interfaces became rough by annealing in Fe/Cr multilayer prepared by MBE, and resulted in the increment of GMR [1]. However, Rencing has reported an opposite result that GMR of Fe/Cr multilayers with rough interfaces were smaller [2]. Therefore, it is important to get detailed information on the growth behavior and its effect on interface morphology.

One potential solution to this problem is the addition of a surfactant to the film [3,4]. The added material alters the kinetics and thermodynamics of growth, leading to higher quality films and multilayers. Surfactant epitaxy is a useful method for changing the thin film growth mode from 3D-island formation to layer-by-layer growth [3, 4]. Considerable surfactant effects in the growth of metals on metals have been reported by van der Vegt *et al.* [5]. Camarero *et al.* reported that a small amount of Pb deposited before the deposition of Co/Cu bilayers on Cu(111) reduces the amount of fcc twin formation, thereby improving the structural quality [6, 7]. Also surfactants have been shown to improve the spin valve devices by somehow altering growth mode [8–16].

Previously, using Bi as a surfactant, we found experimentally that the surfactant atoms induce both the layer-by-layer growth of Fe and Cr on Fe(100)-*c*(2×2)O reconstruction surface as well as a strong surface segregation effect of Bi during growth [17, 18]. Heteroepitaxial systems with surfactants are of greater interest for electronic devices, but there have been only a few examples of application for the metallic multilayers [19–22]. In this paper, we report the influence of Bi as a surfactant on the heteroepitaxial growth and magnetotransport properties of Fe/Cr metallic multilayers by sputter deposition.

2. EXPERIMANTAL

Buffer layers and Fe/Cr multilayers were grown by RF magnetron sputtering at room temperature. The base pressure was about 2.0×10^{-7} Torr, and the pressures during deposition were about 1.0, 1.0, and 5.0 mTorr for Fe, Cr, and Bi, respectively. A MgO(100) single crystal of 10×10 mm^2 was used as a substrate. The deposition rates were 0.9 ± 0.1, 1.0 ± 0.1, 3.0 ± 0.2 Å/s for Fe, Cr, and Bi, respectively. Fe buffer layers of 100Å were fabricated by evaporating Fe onto MgO(100) single crystals. The thicknesses of the Cr spacer layer were varied from 10 to 20 Å. In all multilayers, Fe layer thickness was fixed at 20 Å, and the each set of Fe and Cr was repeated 6 ~ 15 times. The thickness of Bi was varied between 3.0 Å and 10.0 Å. The surfactant Bi was evaporated only one time on the Fe buffer layer surface.

X-ray photoelectron spectroscopy (XPS) was used to determine the composition and depth profile of films. The XPS spectra were obtained on a PHI-QUANTUM-2000, using Al $K\alpha$ X-rays as the exciting source, at a beam diameter of about 0.5 mm. XPS depth profile can provide distribution information of chemical composition on the direction of perpendicular to the surface of films. A relatively low acceleration voltage, 1.0 keV Ar^+ ion beam, was used for Ar ion sputtering in order to increase the depth resolution.

The morphology of the surfaces after deposition was determined by AFM observations. AFM measurements were done in tapping mode using a JEOL JSPM-4200. The periodic compositional modulations and crystallographic structures of the samples were characterized by X-ray diffractions (XRD) and grazing incidence X-ray reflectivity (XRR) technique. Grazing incidence XRR measurements were performed by high resolution X-ray diffractometer using Cu $K\alpha$ radiation. The samples were mounted with a vertical sample stage and the scanning rates were 0.01°/min with a step of 0.005° controlled by a computer. The corresponding range of the scattering angle 2θ was from 0.4° to 5.2°. The measured data were fitted by computer in order to obtain the information of the interface root-mean square (rms) roughness.

Magnetoresistance (MR) at room temperature was measured using standard four-probe-technique with a constant current source and nanovoltmeter in an external field up to 1.5 T. The current and the magnetic field were applied parallel to the film plane. The $\Delta R/R$ data were normalized to the resistance at zero magnetic field.

3. RESULTS AND DISCUSSION

An effective surfactant must strongly float to the surface. To confirm the Bi surface segregation, XPS spectra of Bi were monitored. Figure 1 shows the Bi 4f spectra at different depths for (a) Fe and (b) Cr film on a glass substrate at room temperature. The thickness of the deposited Fe and Cr film is 100 Å. The surfactant Bi of 10Å was evaporated only one time on the glass substrate surface before Fe and Cr deposition. The metallic Bi 4f peaks situated at 157.0 and 162.3 eV, whereas the Bi oxide (Bi_2O_3) peaks situated about between 159 and 164 eV. As shown in Fig. 1, we can clearly see the Bi oxide 4f peaks, indicating that Bi floats up to the top of the Fe and Cr film surface. However, depth profiling measurements by Ar+-bombardment show that Bi is observed not only at the surface but aloso in the film.

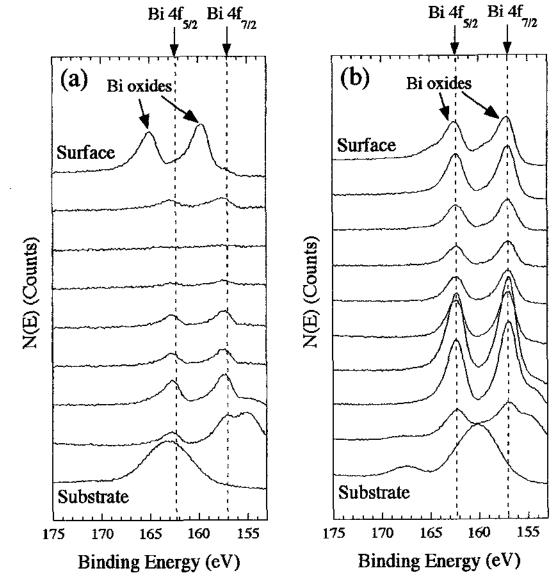

Fig. 1 XPS spectra of Bi 4f at different depths for (a) glass/Bi(10 Å)/Fe(100 Å) and (b) glass/Bi(10 Å)/Cr(100 Å) film at room temperature; the depth increment between successive curves is (a) 13.8 Å and (b) 12.2 Å, respectively.

We discuss here the surface segregation effect of Bi. Mae *et al.* reported that a smaller energy is necessary for the surfactant to be stable on the surface, and the difference in the atomic radius between the surfactant and the adatom plays an important role in the process of quick exchange of their positions [23]. Because the Bi atom has a larger atomic radius and a much lower surface energy compared with the Fe and Cr adatoms [24], Bi atoms are pushed out to the surface to relax the stress and to reduce the total energy of the system. The immiscibility of Bi with these adatoms has no influence on these surface segregation processes.

The AFM images of the surface of MgO(100)/Fe(100 Å)/Bi(x Å)/Fe(20 Å)/Cr(20 Å) bilayer film are shown in Fig. 2. The rms roughness in Fig. 2(a) and 2(b) is 1.84 Å and 1.47 Å, measured over an area of 1000 × 1000 nm^2. When 3.0 Å of Bi (Fig. 2(b)) is used as a surfactant, the AFM image indicates more a uniform distribution of film thickness. From this results, Bi surfactant might play an important role to reduce the interface roughness.

We examined the effect of Bi on the interface structure in MgO(100)/Fe(100 Å)/Bi(x Å)/[Fe(20 Å)/Cr(16 Å)]$_6$/Cr (20 Å) multilayers by using XRR measurements.

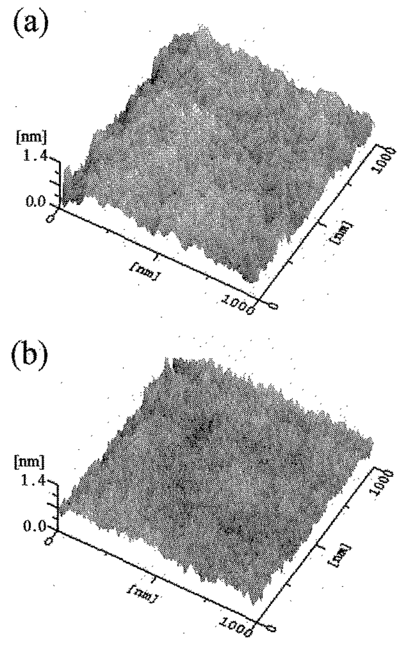

Fig.2 AFM images of the surface of MgO(100)/Fe(100 Å)/Bi(x Å)/Fe(20 Å)/Cr(20 Å) bilayer film (a) without Bi surfactant and (b) with Bi (x = 3.0 Å).

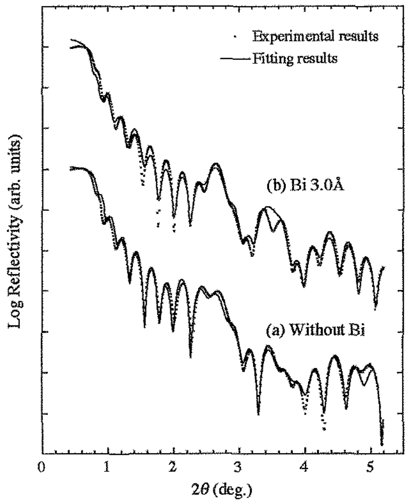

Fig.3 X-ray reflectivity curves of [Fe(20 Å)/Cr(16 Å)]$_6$ multilayer (a) without Bi surfactant and (b) with 3.0Å of Bi. Shown are the experimental data (points) and the simulated fitting data (lines).

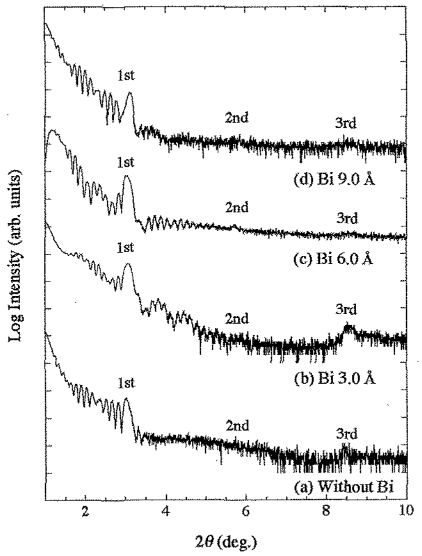

Fig.4 A set of low-angle X-ray diffraction patterns of MgO(100)/Fe(100 Å)/Bi(x Å)/[Fe(20 Å)/Cr(15 Å)]$_{15}$/Cr (20 Å) multilayers (a) without Bi, with (b) 3.0 Å, (c) 6.0 Å, and (d) 9.0 Å of predeposited Bi, respectively.

The results are shown in Fig. 3. The total number of bilayers of Fe/Cr multilayers was set to 6 in consideration for the ability of calculation of computer. The dotted line is the measured data, and the solid line is the fitting curve by means of a nonlinear least-squares curve fitting technique. The slope of the Fe/Cr multiplayer prepared without Bi was steeper, which means that this multilayer has rougher interfaces than the multilayer prepared with 3.0 Å of Bi. From fitting the curves, the value of rms interface roughness of Fe/Cr multilayer with Bi (3.6 Å) is smaller than that of Fe/Cr multilayer without Bi (4.1 Å). From the AFM and the analysis of grazing incidence XRR measurements, we conclude that the Fe/Cr multilayers prepared by Bi surfactant epitaxy have sharp interfaces.

Since one should increase the total number of bilayer of Fe/Cr multilayers to get a large MR ratio, we have fabricated MgO(100)/Fe(100 Å)/Bi(x Å)/[Fe(20 Å)/Cr(15 Å)]$_{15}$/Cr (20 Å) multilayers. We examined the effect of the Bi surfactant on the structures of interface using X-ray diffraction. From high-angle X-ray diffraction patterns, we confirmed that all the samples have a (100) orientation along the growth direction (not shown). Figure 4 shows a set of low-angle X-ray diffraction patterns of [Fe(20 Å)/Cr(15 Å)]$_{15}$ multilayers (a) without Bi, with (b) 3.0 Å, (c) 6.0 Å, and (d) 9.0 Å of predeposited Bi. The finite-size peaks resulted from interface of X-ray refractions from the film surfaces and the film-substrate interface appear for the Bi surfactant-mediated multilayers. Especially, the sample of Fe/Cr multilayer with 3.0 Å of predeposited Bi exhibit clear Bragg peaks up to the third order and clear-cut finite-size peaks between the Bragg peaks. However, the Bragg and finite-size peaks of without Bi sample have a considerably reduced intensity and are visibly broadened. The broadening of Bragg peaks and the loss of higher-order finite-size peaks is characteristic of increased layer roughness [25][26]. Therefore, we consider that the Bi surfactant decreased interfacial roughness and made interfaces

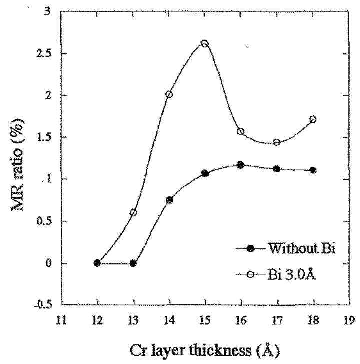

Fig.5 Magnetoresistance ratios vs Cr spacer layer thickness at room temperature for MgO(100)/Fe(100 Å)/$[Fe/Cr]_{15}$/Cr (20 Å) multilayers without Bi (closed circle) and with 3.0 Å of predeposited Bi (open circle), respectively. In all multilayers, Fe layer thickness was fixed at 20 Å.

more flat.

The MR ratios vs Cr spacer layer thickness at room temperature for the $[Fe/Cr]_{15}$ multilayers are shown in Fig. 5. In all multilayers, Fe layer thickness was fixed at 20 Å. The MR ratios of the multilayers prepared with Bi are larger than those of the multilayers without Bi. Especially, when the thickness of Cr layer is 15Å, the MR ratio has increased from 1.06 % to 2.61 % with 3.0 Å of Bi predeposition, corresponding to an enhancement over two times compared to the structure without Bi deposition. As shown in Fig. 4, the Bi surfactant decreased interfacial roughness of $[Fe/Cr]_{15}$ multilayers. These results imply that the sharpness of interfaces mediated by Bi surfactant can be related to the large GMR effect.

4. CONCLUSIONS

We have investigated the effect of a Bi surfactant layer on the interface structures and the magnetotransport properties of Fe/Cr multilayers prepared by sputter deposition. From the XPS measurements, the surface segregation of Bi during the growth of sputtered film is confirmed. From the measurements of X-ray diffraction and grazing incidence X-ray reflectivity, we confirmed that the Fe/Cr multilayers prepared with Bi surfactant had sharp interfaces. The magnetoresistance ratio of the multilayers prepared with Bi were larger than those of the multilayers without Bi. We conclude that the increase in MR is caused by the changes of the sharpness of interfaces mediated by Bi surfactant.

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