Magnetoresistance and electronic structure of granular films with MgO or MgF\textsubscript{2} matrices

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Abstract. The magneto-transport properties and electronic structures of FeCo-MgO, FeCoB-MgO, FeCo-MgF\textsubscript{2} and FeCoB-MgF\textsubscript{2} granular films were investigated. From the X-ray photoelectron spectroscopy (XPS) measurements, it was recognized that the oxide layer formed on the surface of granules in FeCo-MgO. Especially Fe oxides were preferentially formed. By using (Fe\textsubscript{50}Co\textsubscript{50})\textsubscript{80}B\textsubscript{20}, the formation of Fe oxides on the granule surface was suppressed since B was oxidized instead of Fe. The MR ratio of FeCoB-MgO was approximately 2\%. By using MgF\textsubscript{2} matrix, the surface states of granules were drastically improved. XPS measurements indicated that an amount of metallic Fe in FeCoB-MgF\textsubscript{2} increased compared with FeCoB-MgO. Reflecting the improvement of surface states of granules, a large MR ratio of approximately 6\% was obtained in FeCoB-MgF\textsubscript{2}.

1. Introduction

Magnetic granular films, consisting of magnetic granules and insulating matrix, exhibit a large tunnel magnetoresistance (TMR) effect. The granular films have been attracted attention as one of promising candidates for magnetic sensor elements because of their technical advantages. The granular films can be generally prepared in one process, and various deposition techniques for preparation are developed, such as co-sputtering, reactive sputtering or tandem deposition. A high breakdown voltage is expected, since the granular films are regarded as a network of a large number of tunnel junctions. Furthermore, in the granular films, the TMR effects have been observed in wide resistivity range [1]-[6] from $10^{4} - 10^{10}$ $\mu\Omega$cm. The granular films are therefore expected to be integrated into various magnetic sensor devices.

The granular films employing various insulating matrices such as Al\textsubscript{2}O\textsubscript{3} [1], SiO\textsubscript{2} [2], MgF\textsubscript{2} [3], MgO [4] [5] and ZrO\textsubscript{2} [6] have been investigated so far, and it has been known that the TMR effects are influenced by the kind of insulating materials. Furthermore, since the TMR ratio of granular materials depends on the spin polarization of granules [7], the choice of magnetic materials is also an important factor to obtain a large TMR ratio. Recently, it has been reported that tunneling spin polarization (TSP) of FeCo increased by an addition of B, and (Fe\textsubscript{50}Co\textsubscript{50})\textsubscript{80}B\textsubscript{20} showed a large TSP of 49\% [8].

In this work, we made an attempt to investigate the influence of insulating and magnetic materials on TMR effects of granular films. MgO and MgF\textsubscript{2} were employed for insulating matrix, and Fe\textsubscript{50}Co\textsubscript{50} and (Fe\textsubscript{50}Co\textsubscript{50})\textsubscript{80}B\textsubscript{20} alloys were employed for the magnetic materials. The granular films were prepared by a tandem deposition method. The magneto-transport properties and electronic structure of granules were investigated. In this paper, our experimental results are presented.
2. Experimental

The tandem deposition method was employed to prepare the granular films by dc and rf magnetron sputtering. The base pressure was less than $4 \times 10^{-4}$ Pa. Fe$_{50}$Co$_{50}$ and (Fe$_{50}$Co$_{50}$)$_{80}$B$_{20}$ sputtering targets were utilized for the deposition of magnetic layer. Reactive sputtering in a gas mixture of Ar + O$_2$ was utilized for the deposition of the MgO under-layer. Depositions of other layers were carried out in an Ar atmosphere. The sputtering pressure was 0.8 Pa. Four kinds of granular films were prepared. The granular films with MgO/Fe$_{50}$Co$_{50}$/MgO structure are called FeCo-MgO. MgO/(Fe$_{50}$Co$_{50}$)$_{80}$B$_{20}$/MgO, MgF$_2$/Fe$_{50}$Co$_{50}$/MgF$_2$ and MgF$_2$/(Fe$_{50}$Co$_{50}$)$_{80}$B$_{20}$/MgF$_2$ are called FeCoB-MgO, FeCo-MgF$_2$ and FeCoB-MgF$_2$, respectively. The sample structure is shown in Fig. 1. The thickness of magnetic layer $d_{mag}$ was varied from 0.7 to 1.4 nm. The microstructures of samples were investigated by transmission electron microscopy (TEM). Depth profiling of X-ray photoelectron spectroscopy (XPS) was made in order to investigate the electronic structure of granules. Resistivity measurements were performed with the two-terminal method. The resistivity was calculated using nominal value of $d_{mag}$. MR measurements were carried out under the sweep of a magnetic field of ±15 kOe. The magnetic field was applied parallel to both the film plane and current direction. All measurements were carried out at room temperature.

3. Results and discussion

Fig. 2 shows comparisons of $d_{mag}$ dependence of resistivity. In Fig. 2 (a), it was recognized that the resistivity of FeCo-MgO increased with decreasing $d_{mag}$. An abrupt increase in resistivity around $d_{mag} = 1.1$ nm was observed between $d_{mag} = 1.1$ and 1.2 nm. This increase indicates the structural change of magnetic layer from continuous film to granular structure. When $d_{mag} < 1.1$ nm, apparent nonlinear dI-dV curves were obtained, indicating the tunnel conduction of the samples. FeCoB-MgO shows a gradual change of resistivity, and their resistivity is larger than that of FeCo-MgO. The tunnel conduction of FeCoB-MgO was confirmed in dI-dV measurements when $d_{mag} < 1.2$ nm. Fig. 2 (b) shows the comparison between FeCo-MgF$_2$ and FeCoB-MgF$_2$. The feature, that the granular films without B shows a sharp increase in resistivity around $d_{mag} = 0.9$ nm, is similar to that of FeCo(B)-MgO. The tunnel conduction of FeCoB-MgF$_2$ was also confirmed at $d_{mag} < 0.9$ nm for FeCo-MgF$_2$ and $d_{mag} < 1.1$ nm for FeCoB-MgF$_2$. Comparing the resistivity at the same $d_{mag}$, the resistivity of FeCoB-MgF$_2$ was smaller than that of FeCoB-MgO.
In order to discuss the structure and resistivity of granular films, TEM and XPS depth profile measurements were carried out. Fig. 3 shows a typical TEM micrograph of FeCoB-MgF$_2$. It is clearly seen that the granules are separated by MgF$_2$ matrix. The average diameter of granules was estimated to be 3.0 – 5.0 nm.

Figs. 4, 5, 6 show the depth profile spectra of FeCo-MgO, FeCoB-MgO and FeCoB-MgF$_2$, respectively. Each spectrum was measured after Ar ion etching every 30 seconds. The total etching time ($t_{etch}$) is indicated in the figures. In Fig. 4, the left and right panels correspond to the Co 2p and Fe 2p XPS spectra. The position and profile of the Co 2p peaks did not change by $t_{etch}$ variations. On the other hand, varying the $t_{etch}$ changed the profile of Fe 2p spectra. Two peaks can be seen at the Fe 2p peaks, especially at the 2p$_{3/2}$ peak. Peak positions are estimated to be 707-708 eV and 711-712 eV, respectively. Although the peak positions were slightly shifted from original positions by charge up effects, it is thought that these peaks correspond to metallic Fe and Fe$_2$O$_3$. The high peak intensity of Fe$_2$O$_3$ indicates oxidation of granules. As the $t_{etch}$ increased, the Fe$_2$O$_3$ peak decreased and then increased again, whereas the Fe peak increased and then decreased. These results indicate that the surface of granules is oxidized and the oxide layer is mainly composed of Fe$_2$O$_3$. In this work, Fe was selectively oxidized. The selective oxidation of Fe can be explained by the difference in heat of formation [9][10][11].

XPS depth profile spectra of FeCoB-MgO are shown in Fig. 5. The left and right panels correspond to the Fe 2p and B 1s XPS spectra, respectively. The Co 2p XPS spectra were not shown here, since they showed almost the same feature as that of FeCo-MgO. Two peaks originated from Fe and Fe$_2$O$_3$ are seen in Fe 2p spectra. It is also confirmed that the almost the same $t_{etch}$ dependence of peak intensity as
that of FeCo-MgO. The difference in spectra is the peak intensity ratio of Fe / Fe$_2$O$_3$. These differences are clearly seen in the spectra with $t_{\text{etch}} > 90$ sec. The peak intensity ratios of FeCoB-MgO become larger compared with that of FeCo-MgO, indicating that metallic Fe increased owing to the addition of B. In B 1s XPS depth profile spectra, the peaks originated from B$_2$O$_3$ appeared, whereas the metallic B peak could not confirmed, suggesting a preferential oxidization of B. Thus, it is thought that the addition of B prevents Fe from oxidation. Although the surface of granules was oxidized in both FeCo-MgO and FeCoB-MgO, the composition of surface oxidized layer on granules seems to be different. It is thought that this difference had an influence on resistivity shown in Fig. 2 (a).

The XPS depth profile of FeCoB-MgF$_2$ is shown in the left panel of Fig. 6. Only Fe 2p spectra are presented. In the right panel, Fe 2p spectra FeCoB-MgO are presented for comparison. Two peaks can be seen at 707-708 eV and 712-714 eV, which corresponded to metallic Fe and Fe fluorides, respectively. Although two peaks can also be confirmed, the shape of spectra is quite different from that of FeCoB-MgO. In all spectra, Fe peaks were larger than fluorides peaks excluding the film surface ($t_{\text{etch}} = 0$), although the fluoride peaks become large with increasing $t_{\text{etch}}$. A large peak intensity ratio of Fe / FeFx suggest less influences of MgF$_2$ matrix on granule surfaces owing to the large heat of formation of MgF$_2$. Although the surface fluoride layer exists on granules in FeCoB-MgF$_2$, its thickness is expected to be much thinner than the surface oxide layer thickness of granules in FeCoB-MgO. In FeCoB-MgO, the electrons must tunnel through both thick surface oxide layer on granules and MgO matrix. Thus, FeCoB-MgO showed high resistivity compared with FeCoB-MgF$_2$ at the same $d_{\text{mag}}$.

**Figure 6.** XPS depth profile spectra of FeCoB-MgF$_2$, where $d_{\text{mag}} = 1.0$ nm (left panel). XPS spectra of FeCoB-MgO are also shown in right panel for comparison.

**Figure 7.** MR ratio of granular films as a function of $d_{\text{mag}}$. 
Fig. 7 shows MR ratio of granular films as a function of $d_{mag}$. For all kinds of granular films, MR ratio shows a maximum at a certain thickness. The maximum MR ratio of approximately 1 % was obtained in FeCo-MgO, whereas approximately 2 % was obtained in FeCoB-MgO. We infer that this increase in MR ratio results from a suppression of formation of Fe oxides on granules owing to the addition of B. Both in FeCo-MgF$_2$ and FeCoB-MgF$_2$, large MR ratios were obtained. The maximum MR ratio of FeCoB-MgF$_2$ reached of approximately 6 %. This drastic increase by using MgF$_2$ is due to an improvement of the surface state of granules, which confirmed from XPS depth profile measurements. The maximum MR ratio of in FeCo-MgF$_2$ is approximately 5.5 % which is slightly small compared with the maximum MR ratio in FeCoB-MgF$_2$. This difference may result from the difference in TSP between Fe$_{50}$Co$_{50}$ and (Fe$_{50}$Co$_{50}$)$_{80}$B$_{20}$.

4. Summary

We investigated the magneto-transport properties of FeCo-MgO, FeCoB-MgO, FeCo-MgF$_2$ and FeCoB-MgF$_2$ granular films. The electronic structure of granules was also investigated by the depth profiles of XPS.

From the XPS depth profiles, it was recognized that the oxide layer existed on the surface of granules in FeCo-MgO. On the surface of granules, Fe oxides were preferentially formed owing to its relatively high heat of formation. The maximum MR ratio of approximately 1 % was obtained. In FeCoB-MgO, surface oxidation of Fe was suppressed by the addition of B. Thus, the maximum MR ratio increased to 2 %. High intensity of metallic Fe peak was found in XPS spectra of FeCoB-MgF$_2$, indicating less influence of MgF$_2$ matrix on granules. The difference in surface states of granules in between FeCo-MgO and FeCoB-MgF$_2$ seemed to be due to the difference of heat of formations of insulating materials. A large MR ratio of approximately 6 % was obtained in FeCoB-MgF$_2$, reflecting the improvement of surface states of granules.

5. References

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