Magnetic Properties and Microstructure of Electrodeposited Co/Cu Multilayers

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ABSTRACT

Co/Cu multilayers were electrodeposited on a brass substrate with a target layer thickness of 4 nm in a single electrolyte, and their magnetic properties and microstructure were investigated. Cross sections of the samples were observed using field-emission scanning electron microscopy, and electron backscatter diffraction measurements were also conducted. Each sample was composed of columnar crystal grains vertical to the substrate, with each grain having a Co/Cu multilayered structure. During growth of the grains, the layers were bent regularly at specific boundary lines in the cross section and were thus composed of a zigzag multilayered structure. The magnetic properties were measured using a vibrating sample magnetometer. The saturation magnetization and coercivity were measured using a vibrating sample magnetometer. The saturation magnetization and coercivity were measured using a vibrating sample magnetometer. The saturation magnetization and coercivity were measured using a vibrating sample magnetometer. The saturation magnetization and coercivity were measured using a vibrating sample magnetometer. The saturation magnetization and coercivity were measured using a vibrating sample magnetometer. The saturation magnetization and coercivity were measured using a vibrating sample magnetometer. The saturation magnetization and coercivity were measured using a vibrating sample magnetometer.

1. Introduction

Single-bath multilayer electrodeposition is an important technique for the preparation of functional nanomaterials using a wet process. This technique is attracting significant interest as a method for improving the properties of electrodeposited films for industrial applications. The single-bath method uses the difference in the reduction potentials between two types of metal ions contained in a single electrolyte, and the electrodeposited composition can be varied by varying the substrate potential. Therefore, multilayers can be prepared inexpensively by appropriate modulation of the substrate potential in a single electrolyte. To perform this single-bath deposition precisely, we have developed a coulomb controller that controls the layer thickness in accordance with Faraday’s laws of electrolysis. This device was successfully demonstrated to improve the uniformity of Co/Cu multilayered structures electrodeposited on Si wafers. Furthermore, this device simplified the procedure of the single-bath method, so that its practicality was improved.

The Co/Cu multilayered structure is a popular system that can be obtained using the single-bath method. The reduction potentials of Co and Cu are both moderate in this method. Co–Cu is an equilibrium immiscible system that is expected to maintain stable and sharp interfaces between layers. Giant magnetoresistance (GMR) is one of the special features of Co/Cu multilayers. However, electrodeposited Co/Cu multilayers show relatively poor performance compared to physically deposited multilayers. Shima et al. electrodeposited Co/Cu multilayers onto Si wafers covered with a glass seed layer, and they reported that interlayer ferromagnetic coupling was caused by layer undulation around grain boundaries in Co/Cu multilayers and this phenomenon weakened the antiferromagnetic coupling required for large GMR. From another point of view, this implies the possibility that the magnetic properties of electrodeposited films may be controllable by multilayer electrodeposition.

The ability to control the magnetization of electrodeposited films would be very valuable for electronics applications. On the other hand, when nanometer scale multilayer electrodeposition is conducted on an ordinary polycrystalline metal surface, it is generally unclear as to what structure will be generated in the film, though industrial electrodeposition processes are generally conducted on polycrystalline metal surfaces. Thus, it is important to investigate the internal structure of multilayers electrodeposited on a polycrystalline metal surface and its effects on the multilayer properties so that this technique can be applied for improving general surface finishing processes.

We previously reported that when the layer thicknesses were <10 nm in electrodeposited Co/Cu multilayers on rolled brass, the crystal structures of Co and Cu were both fcc and the lattice constant was the same, being intermediate between those for individually electrodeposited fcc-Cu and fcc-Co films, and the surfaces of such multilayers were especially rough. These results suggested that the internal structure of the nano-Co/Cu multilayers in such a case is not simple. If multilayered structure is maintained in such electrodeposited films, the internal structure may influence the magnetic properties as a cause of the interlayer ferromagnetic coupling, although, these are uninvestigated. In this study, Co/Cu multilayers with layer thicknesses of <10 nm were electrodeposited on an ordinary metal substrate and the internal structure was investigated by cross-sectional observations. Furthermore, we investigated the effectiveness of this method for improving the magnetic properties.

2. Experimental

Figure 1 shows a schematic diagram of the electrodeposition setup. A conventional three-electrode configuration was used with a 0.3 dm³ glass beaker as the electrodeposition cell. A Pt plate was used as the counter electrode (CE) and a saturated Ag/AgCl type electrode was used as the reference electrode (RE). The substrate
Cu alloy and the alloy becomes almost pure Co at concentration, which results in a low concentration of Cu in the Co ing to the substrate potential. The electrolyte used has a low Cu deposited when the substrate potential is <0 mV vs. RE, whereas Co is electrodeposited when the substrate potential is <−700 mV vs. RE. Thus, the electrodeposited film becomes pure Cu or a Co–Cu alloy according to the substrate potential. The electrolyte used has a low Cu concentration, which results in a low concentration of Cu in the Co–Cu alloy and the alloy becomes almost pure Co at −950 mV vs. RE.

The substrate potential was modulated with a rectangular waveform using a coulomb controller connected to a potentiostat (HA-501G, Hokuto Denko); the electrolytic current was accurately monitored with the coulomb controller and the substrate potential was appropriately adjusted, as listed in Table 1, when the charge transported by the current reached set values. The set values of the charge were determined from theoretical calculations; the applied set values of charge were the products of the values listed in Table 1, the exposed area of the substrate, and the target layer thickness. Electrodeposition was conducted to give a total sample thickness of 1 μm, and Co and Cu layer thicknesses of 4 nm. Cross sections of the sample were made by ion polishing (IB-99010CP, JEOL); the cross-sectional samples experienced approximately 120°C heat before the observations due to being mounted on the polisher using hot wax. One of the cross sections was observed using a field-emission scanning electron microscopy (FE-SEM; S-5200, Hitachi). Electron backscatter diffraction (EBSD) measurements on another sample was carried out using another FE-SEM system (ULTRA Plus, Carl Zeiss). The magnetic properties of the sample were measured with a vibrating sample magnetometer (VSM: TM-VSM1550HGC, Tamakawa) at room temperature.

3. Results and Discussion

3.1 Cross-sectional observations

Figure 2 shows an inverse pole figure map from EBSD measurements that indicates an fcc crystal orientation in the direction perpendicular to the substrate. The orientation mapping was incomplete in some areas of the cross section (colored black); nevertheless, Fig. 2 clearly shows that the sample has a polycrystalline structure with columnar grains aligned perpendicular to the substrate. In Fig. 2, the (111) direction appears to be the preferential direction, although it was not universal in this sample. The diameters of the columnar grains were approximately 100 nm or less and their length was several times their diameter. The black colored areas are probably composed of grains that were too small to detect. Most of the crystal grains did not adjoin the substrate. Thus, crystal nucleation likely occurred successively during film growth.

Figure 3 shows FE-SEM images of the sample cross section. Stacked layers with thicknesses of almost 4 nm are evident in Fig. 3(b). The layers are bent regularly on certain boundary lines in the cross section and form a zigzag multilayered structure. The bending angles are relatively obtuse. The intervals between the bending points are below approximately 100 nm and the smallest appears to be 10 nm or less; this value is comparable to the individual layer thickness of 4 nm.

Figures 2 and 3 indicate that a multilayered structure was contained within the crystal grains of the electrodeposited film. Consequently, with both polycrystalline and multilayered structures present, a unique internal structure was formed in the metallic solid.
As we reported earlier, the Co and Cu layers in this sample ought to have grown alternately and epitaxially without misfit dislocations. The observed columnar structure in Figs. 2 and 3 can be regarded as the result of this alternating yet continuous coherent heteroepitaxial crystal growth with the occurrence of random nucleation. The layers were stacked sequentially in the sample, so that each layer in Fig. 3(b) corresponds to the growth surface at a certain moment during electrodeposition, and the growth direction at that moment is perpendicular to the layer. Therefore, some of the boundaries at which the layers are bending in Fig. 3(b) should correspond to the grain boundaries shown in Fig. 2, while others should correspond to edges at which two growth surfaces in a single crystal grain meet during electrodeposition. Figures 2 and 3 indicate that the multilayer electrodeposition conducted in this study generates extreme bending of layers during crystal growth, and yet the order of the alternating Co and Cu layers remains. In addition, the surface morphology should reflect the bending of the final stacked layers.

3.2 VSM measurements

Figure 4 shows hysteresis loops measured by VSM; common magnetic units are used in these graphs (Oe = 10³ / A m⁻¹, emu = 10⁻¹⁵ Am² / kg). The measurements were conducted with the applied magnetic field both in and out of the film plane. The results for Co/Cu multilayers with layer thicknesses of 4 nm are shown in Fig. 4(a). For comparison, two supplemental samples with 500-nm-thick layers were electrodeposited using the same method and were subjected to measurements. Figure 4(b) shows the results for a single 500-nm-thick Co layer, which contains almost the same amount of Co as the sample shown in Fig. 4(a). Figure 4(c) shows the results for a Co/Cu/Co triple layer structure, which contains almost twice the amount of Co as that in the sample shown in Figs. 4(a) and 4(b), and almost the same amount of Cu as that in the sample shown in Fig. 4(a).

The main graphs in Figs. 4(a)–4(c) show hysteresis loops for the in-plane geometry while each inset shows the perpendicular geometry results. Substrate contributions were subtracted from the results. In these VSM measurements, the sample shapes were almost the same but they were different from that of the standard sample used for calibration. Thus, the measured values of the magnetic moment include a certain systematic error caused by the difference in sample shape. The magnetic moment did not saturate for the perpendicular geometry results. Substrate contributions were subtracted from the in-plane geometry results. The coercivity ($H_c$), residual magnetic moment ($m_r$), and saturation magnetic moment ($m_s$) for in-plane geometry are listed in each graph; the magnetic moment when the applied field was $|H| = 2$ kOe was taken as $m_r$. In addition, the estimated mass magnetization of Co ($\sigma_{Co}$) is also shown and its unit is [emu/g].

![Figure 3](image3.png)

**Figure 3.** (Color online) Cross-sectional FE-SEM images of Co/Cu multilayers. (a) Entire cross-section of electrodeposited sample. The film surface was covered with contaminants, probably formed during preparation of the cross section. (b) Enlarged part of film cross section. A zigzag multilayered structure is observed and the layer thickness is very close to the target value.

![Figure 4](image4.png)

**Figure 4.** Magnetic hysteresis loops measured by VSM. The main figures are for the $H ||$ plane and the inset figures are for the $H \perp$ plane geometry. (a) Co/Cu multilayers with individual layer thicknesses of 4 nm and a total thickness of 1 µm. (b) 500-nm-thick Co film, for comparison. (c) Co/Cu/Co three-layer film with individual layer thicknesses of 500 nm, for comparison. Each sample was electrodeposited on an approximately $5 \times 10$ mm² area on a rolled brass substrate. Coercivity ($H_c$), residual magnetic moment ($m_r$), and saturation magnetic moment ($m_s$) at $H ||$ geometry are shown in the figure: the units are the same as in the graph. Estimated mass magnetization of Co ($\sigma_{Co}$) is also shown and its unit is [emu/g].
estimated mass magnetization of Co ($\sigma_{\text{Co}}$) is listed; $\sigma_{\text{Co}}$ is $m_s$ divided by the target mass of the electrodeposited Co in each sample. In this calculation, both the current efficiency and purity of the Co layer are assumed to be 100%.

The coercivity in Fig. 4(c) is close to that in Fig. 4(b). The presence of the 500-nm-thick Cu layer between the 500-nm-thick Co layers did not have a strong effect on the coercivity. However, the coercivity in Fig. 4(a) is almost five times that in Fig. 4(b). Thus, this result indicates that the multilayer electrodeposition with 4-nm-thick layers in this study causes an increase in coercivity. On the other hand, the values of $\sigma_{\text{Co}}$ are very similar in Figs. 4(b) and 4(c), and they are not very different from that in Fig. 4(a). This implies that the saturated magnetic moment depends heavily on the Co content in each sample. The difference in $\sigma_{\text{Co}}$ between Figs. 4(a) and 4(b), which is approximately 8%, is not evidence of a thickness dependence of the magnetic moment of the Co layer. This probably reflects the variation in current efficiency or purity of the Co layer, and we are now investigating this aspect minutely and carefully. The ratio $m_s/m_b$ was approximately 80–86% in Figs. 4(a)–4(c) and there was little difference among samples.

3.3 Mechanism of coercivity increase

In this study, it was revealed that the electrodeposited Co/Cu multilayered structure is maintained with extreme layer wrinkling and this also increases the coercivity. This coercivity increase is likely related to the ferromagnetic coupling between Co layers. Néel proposed a model for topological coupling between two magnetic layers separated by an undulating nonmagnetic layer. This model is generally called “orange-peel” coupling. Figure 5 shows schematic diagrams of the topological coupling. It is caused by magnetic field leakage arising from the rough surface of the magnetic layer and the leaked field rearranges the moment of the next magnetic layer. The orange-peel ferromagnetic coupling energy is given by

$$J_c = \frac{\pi^2 M^2 h^2}{\sqrt{2}} \exp \left( -\frac{2\pi \sqrt{2d}}{\lambda} \right)$$

(1)

where $M$ is the magnetization of the magnetic layers, $h$ and $\lambda$ are the amplitude and wavelength of the undulation, respectively, and $d$ is the thickness of the nonmagnetic layer. Some studies have used this formula to interpret the influence of slight defects in the multilayered structure on its magnetization behavior and have succeeded in approximate interpretations.15,16,17

In order to apply Formula (1) to interpret the Co/Cu multilayers, the layer undulation amplitude should be lower than some upper limit, because the orange-peel coupling is based on the assumption that a pair of magnetic layers has in-plane uniaxial anisotropy. For Co/Cu multilayers, $h$ is not only the undulation amplitude of the nonmagnetic Cu layers but also that of the magnetic Co layers. Thus, if $h$ is larger than the thickness of the Co layers, the undulation is not the roughness of the Cu layer surface any longer and this means that the Co layers are bending. Figure 5(b) shows a schematic diagram of such a case with a zigzag multilayered structure, such as that observed in this study. In this experiment, the undulation amplitude of the layers was considerably larger than the thickness of the layers as shown in Fig. 3(b). In this case, a Co layer should be regarded as assembled flat Co plates, like a patchwork, with the Co plates forming various angles at each joint. In Fig. 5(b), the hatched area corresponds to a cross section of the Co plate. When a Co layer is magnetized, the magnetic moments of the Co plates in the layer should be arrayed to minimize the angle of each vector with respect to that of the Co layer, as shown in Fig. 5(b). The magnetic moment of a Co layer is the summation of those of the Co plates in the layer. In this case, the principal direction of a leaked field at any given point can roughly be regarded as being parallel to the summed magnetic moments of the neighboring Co plates in the Co layer, because the leaked field is a tributary of the magnetic flux through the outside of the Co layer and the magnetic moment in the Co layer corresponds to its main stream. If the direction of the leaked field is near the in-plane direction of a Co plate that is influenced by the leaked field from the next Co layer, the leaked field would cause significant ferromagnetic coupling between the Co plate and the Co layer which is the source of the leaked field. This geometrical condition should be realized if the Co plates are connecting at sufficiently obtuse angles. The sample in this study appears to mostly have this qualification for ferromagnetic coupling, as shown in Fig. 3(b). Therefore, the increased coercivity in this experiment can be considered to be the result of topological coupling between the Co layers, similar to the orange-peel coupling. Thus, Formula (1) should provide a rough interpretation of the results of this experiment.

On the assumption that $M$ is constant, Formula (1) indicates that $J_c$ is proportional to the product of $h^2/\lambda$ (former factor) and approximately $e^{-2d/\lambda}$ (latter factor). The former factor is related to the undulation amplitude $h$ and the latter factor is related to the layer thickness $d$. In the case of zigzag multilayers, the former factor probably needs some correction to reduce its value, because too large an $h$ value in comparison to $\lambda$ and $d$ becomes an impediment to the ferromagnetic topological coupling. Moreover, in this experiment, $\lambda$ is probably limited to below the diameter of the crystal grain. Therefore, the value of the former factor might have some upper limit in this case. On the other hand, the latter factor is close to 1 when $\lambda > 9d$ but it is close to 0 when $\lambda < 9d$; therefore topological coupling becomes obvious when the thickness of the nonmagnetic layer $d$ is sufficiently small in comparison with the undulation wavelength of the layer $\lambda$.

In some areas of Fig. 3(b), $\lambda$ was very small and comparable with $d$, so that the topological coupling should be small in such areas. If the ferromagnetic order is disturbed in such an area, this will result in a significant decrease in $m_s/m_b$, because such areas appear to not be very small in Fig. 3(b). However, the value of $m_s/m_b$ in Fig. 4(a) is almost the same as in Figs. 4(b) and 4(c). Thus, the topological coupling ought not to be the only cause of the ferromagnetism seen in Fig. 4(a). It is likely that the ferromagnetic order in a Co layer remains and maintains a spontaneous magnetization of the Co layer, which would give rise to the chain-like structure shown in Fig. 5(b).
Therefore, the observed increased coercivity in this study can be considered to be caused by partial topological coupling among the Co layers, which are single-domain and have in-plane magnetic anisotropy.

In addition, the present research revealed that this electrodeposition technique provides a method to synthesize at least three types of films with different magnetic properties from a single electrolyte. The first is relatively hard, the second is relatively soft, and the third is nonmagnetic; the third corresponds to the Cu interlayer shown in Fig. 4(b). Therefore, it is probable that the single-bath method will be useful to develop novel magnetic films as a surface finishing process.

4. Conclusions

In summary, it was revealed that an electrodeposited Co/Cu multilayered structure is maintained with extreme layer wrinkling. When Co/Cu multilayers were electrodeposited on a rolled brass substrate with a target layer thickness of 4 nm, the structure was composed of columnar crystal grains standing vertically on the substrate, and each crystal grain had a Co/Cu multilayered structure. This internal structure was observed as a zigzag multilayered structure in cross section. The saturation magnetization and residual magnetization of Co in this sample were not very different from those for a single thick Co layer, whereas the coercivity was significantly increased. These results suggest that single-bath multilayer electrodeposition is effective for controlling the magnetic properties of electrodeposited films on ordinary metal surfaces.

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References