Enhancement of magnetoresistance by hydrogen ion treatment for current-perpendicular-to-plane giant magnetoresistive films with a current-confined-path nano-oxide layer

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We have enhanced magnetoresistance (MR) for current-perpendicular-to-plane giant-magnetoresistive (CPP-GMR) films with a current-confined-path nano-oxide layer (CCP-NOL). In order to realize higher purity in Cu for CCPs, hydrogen ion treatment (HIT) was applied as the CuO_x reduction process. By applying the HIT process, an MR ratio was increased to 27.4% even in the case of using conventional FeCo magnetic layer, from 13.0% for a reference without the HIT process. Atom probe tomography data confirmed oxygen reduction by the HIT process in the CCP-NOL. The relationship between oxygen counts and MR ratio indicates that further oxygen reduction would realize an MR ratio greater than 50%. © 2010 American Institute of Physics. [doi:10.1063/1.3486117]

Current hard disk drive (HDD) reader head technology utilizes MgO tunneling magnetoresistive (TMR) films owing to their high magnetoresistance (MR) ratio.^{1,2} However, for larger areal density, it is difficult to realize the smaller resistance area product (RA) required for low noise and a high-speed data transfer rate. On the contrary, current-perpendicular-to-plane giant magnetoresistive (CPP-GMR) films have been developed because their RAs are much smaller than those of TMR films. However, it has been difficult to realize a large MR ratio. One approach is to use of Heusler magnetic alloy combined with a metallic spacer layer such as Cu (Ref. 3) and Ag. (Ref. 4). However, a thick seed layer required for the realization of epitaxial film for Heusler alloy cannot be used for narrower gap in HDD read head. Additionally, large spin-transfer-induced noise (STIN) is an issue in the case of using a metallic spacer layer.

On the other hand, CPP-GMR films with a current-confined-path nano-oxide-layer (CCP-NOL) spacer layer can realize MR enhancement,⁵⁻⁷ and STIN is smaller than that for CPP-GMR films with a metallic spacer⁸ without using any thick seed layer. We have reported that the purer CCPs with lower resistivity can realize a higher MR ratio,⁵⁻⁷ and we have confirmed the evidence that the samples having a larger MR ratio have purer CCP than the samples having a smaller MR ratio, which was analyzed by atom probe tomography (APT).⁹ However, although the samples with the better MR ratio had the purer Cu of the CCP-NOL, its value was far from the ideal bulk Cu,¹⁰ which was confirmed both by fitting experimental data to a theoretical model^{5,6} and APT analyses.⁹ The imperfect purity of Cu is considered to be due to the formation process of the CCP-NOL in which the ion-assisted oxidation (IAO) process¹¹ was applied just after the metallic AlCu deposition. The original intention was to leave Cu in the AlCu layer unoxidized as CCPs and to oxidize Al in the AlCu layer to Al_2O_3 as insulator. However, it is reasonable to suppose that Cu in the CCP-NOL was also oxidized unintentionally.

In this report, in order to overcome the unintentional Cu oxidation of the CCP-NOL, we have adopted the hydrogen reduction process. We have applied hydrogen ion treatment (HIT) as the reduction process to reduce the oxides in the CCPs and realized a large MR ratio of 27.4%. In addition to the MR enhancement, the direct evidence of the reduction effect for the CCP-NOL was confirmed by APT analysis.

The CPP-GMR films with a CCP-NOL were made in a dc magnetron sputtering system connected to an ion-beam chamber. The film structure was substrate/Ta(1 nm)/Ru(2 nm)/IrMn(7 nm)/ $\text{Co}_{90}\text{Fe}_{10}$ (4.2 nm)/Ru(0.9 nm)/ $\text{Fe}_{50}\text{Co}_{50}$ (1.8 nm)/Cu(0.25v nm)/ $\text{Fe}_{50}\text{Co}_{50}$ (1.8 nm)/CCP-NOL spacer/ $\text{Co}_{60}\text{Fe}_{40}$ (2 nm)/ $\text{Ni}_{95}\text{Fe}_5$ (3.5 nm)/Capping layer. The CCP-NOL spacer was formed by the sequential steps; a non-magnetic AlCu metal alloy was deposited, transferred to the ion-beam oxidation chamber and then the IAO process was carried out. During the IAO process, Al in the AlCu layer was oxidized to Al_2O_3 , and Cu in the AlCu layer was left unoxidized to form metallic paths (CCPs). This basic formation process was the same as that employed previously⁵ except for using the HIT process as explained below. After the CCP-NOL formation processes, the remaining layers were deposited.

A notable feature of the experiment is the use of hydrogen reduction by the HIT process for the CCP-NOL after the IAO process. The purpose of the HIT process after the IAO process is to reduce CuO_x in the CCP-NOL to Cu by hydrogen reduction, where CuO_x is CuO or Cu_2O . It is known that CuO or Cu_2O oxides can be reduced to metallic Cu by using hydrogen molecules, as shown in the following equations:¹²⁻¹⁴

The hydrogen reduction has been studied for the interconnect application for semiconductor devices. In general, reduction efficiency depends on the temperature during the process; CuO_x cannot be reduced easily below room

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FIG. 1. (Color online) MR ratio dependence on RA for CPP-GMR films with a CCP-NOL. Black circle and blue square denote MR ratio for film I (without HIT) and film II (with HIT), respectively. Solid lines are guides for the eye. Insets are schematic images of the CCP-NOL with and without HIT.

temperature.^{12–14} However, the heating during the HIT process is disadvantageous from the viewpoint of production throughput. In order to promote the reduction process even at room temperature, we have adopted the HIT process to break H_2 molecule to the hydrogen ion H^+ . H_2 gas was introduced into a plasma source with Ar gas, where Ar was used for plasma excitation, and H_2 gas was separated into the hydrogen ions H^+ by Ar plasma. The surface of CCP-NOL was then exposed to the hydrogen ion H^+ . The Ar plasma was excited by rf 300 W, and the H_2 flow and time were set at 50 SCCM and 60 s, respectively. The other experimental conditions are described in the literature.^{5–7}

In order to confirm the hydrogen reduction, we carried out x-ray photoelectron spectroscopy (XPS) analysis for uniform Cu film intentionally oxidized. In this experiment, it was confirmed that CuO_x was completely reduced to Cu by HIT process. Since the complete hydrogen reduction from CuO_x to Cu was confirmed by the HIT process, we applied the HIT process to the CPP-GMR films with a CCP-NOL. Film I was the reference sample without the HIT process, and film II was advanced samples with the HIT process just after the IAO process. Figure 1 shows the MR ratio dependence on RA for films I and II. While the reference sample of film I showed an MR ratio of 13.0% at an RA of $0.9 \Omega \mu m^2$, application of the HIT process just after the IAO process greatly increased the MR ratio, to 20.0% at an RA of $0.9 \Omega \mu m^2$, clearly indicating that the MR enhancement effect was realized by the adoption of the HIT process. This MR enhancement effect was also observed in a wide range of RA, indicating that the MR enhancement effect by HIT is universally independent of RA. Since we have already confirmed the hydrogen reduction effect by the HIT process for the model samples, the MR enhancement is considered to be due to the realization of purer Cu of the CCPs by the HIT process.

In order to confirm reduction status of CCPs, XPS does not have sufficient spatial resolution. Compare to this, APT by using local electrode^{15,16} is appropriate for the detection of CuO_x in atomic orders, and the use of pre-sharpened substrates enables us to obtain quick feedback.¹⁷ By using this method, we have detected atomic information for the analysis of the CPP-GMR films with a CCP-NOL.¹⁸ We performed the same analysis in order to detect reduction effect.

FIG. 2. (Color online) APT images for CCP-NOLs for film I (without HIT) and film II (with HIT). The taken data was 10 nm in the direction of the page in order to include whole of NOL with curvature. The region inside the white circle is the observed field. Grey dot indicates CuO molecule and yellow region indicates CCP with Cu of over 60 at. %.

The observation was carried out by using voltage mode of LEAP3000 at a temperature of 106 K in a vacuum pressure less than a 9.0×10^{-11} Torr. Figures 2(a) and 2(b) show the APT analysis data of film I and II, respectively. For the APT analysis, only the capping layer was changed from the samples for MR ratio and RA measurement, and a thick capping layer was used, namely, 10 nm of NiFe. In Fig. 2, the gray dots denote CuO molecules and the yellow region denotes the CCP with Cu concentration of over 60 at. %. Comparison of Fig. 2(a) with Fig. 2(b) clearly revealed that the extent of CuO molecules in the CCP region was decreased by applying the HIT process. Thus, we have obtained evidence that oxide was reduced by the HIT process. Additionally, we confirmed that the samples with a lower concentration of CuO showed a higher MR ratio, which coincides with our original intention in using the HIT process. This relationship between MR ratio and the extent of oxides agrees well with the model proposed in our previous works.^{5–7} Hydrogen reduction from CuO_x to Cu in this experiment is considered to occur owing to the use of ion plasma H^+ , which is necessary for efficient reduction. More importantly, it is reasonable to assume that the difference of the Cu thickness is the main reason for the difference. The CuO_x thickness in this experiment was only 2–3 nm, but it is several hundreds of nm in the interconnect application for semiconductor devices. The activation energy of hydrogen diffusion in Cu was reported to be 18.6 kJ/mol, which is ten times smaller than that of oxygen diffusion, 168 kJ/mol.¹⁹ It is considered that H^+ ions easily penetrate 2–3 nm Cu, because even oxygen atoms penetrate several nm of Cu. The difference in thickness of CCP and interconnect application should make it easier for H^+ ions to penetrate the whole CuO_x in CCP, which results in H_2O evaporation from the surface of the CuO_x layer in our experiment.

In order to discuss this tendency more quantitatively, we extracted the ion counts for several different samples with and without the HIT process. Figure 3 shows the MR dependence on oxide concentration in the CCP-NOL extracted from the APT analysis. The oxide concentration was normalized by the value of film I (reference sample without HIT). A normalized oxide concentration of less than 1 indicates the reduction in oxides in the CCP-NOL. It was obvious that the oxides were reduced by the HIT process as visually shown in Fig. 3, which should result in the increase in the MR ratio. Additionally, this tendency is on the same linear line in the logarithmic scale of a normalized oxide concentration. The XPS analysis indicated that CuO_x can be reduced to metallic

FIG. 3. (Color online) MR ratio dependence on oxide counts in CCP-NOL derived from 3DAP analysis. Black circle and blue square denote MR ratio without the HIT process and with the HIT process, respectively. Broken line is a guide for the eye.

Cu completely by the HIT process, which means that we can realize the normalized oxide concentration of zero. For instance, even in the case of realization of the normalized oxide concentration of 0.15, the extrapolated MR ratio is estimated to be 50%.

It should be noted that a large MR ratio was obtained without using any special magnetic material with large spin polarization such as Heusler magnetic alloy. We only used conventional 3d transition FeCo magnetic alloy, which has a high Curie temperature and is known to be a proven material for reader head applications. Using a CCP-NOL spacer layer formed by the HIT process, we can enhance the MR ratio even in the case of using a conventional FeCo magnetic layer. If Heusler magnetic alloy becomes more suitable for practical application, such as the realization of thinner magnetic thickness or on thinner seed layer, it is reasonable to expect that a larger MR ratio than that indicated in Fig. 3 would be realized by using a CCP-NOL made by the HIT process.

Based on this prediction, the HIT process was further optimized. The CuO_x in the model sample of film C was completely reduced to Cu but CuO_x in the CCPs of film II was not completely reduced. The difference between film C and film II is the existence of Al_2O_3 surrounding the CCPs. In the case of film II, it is expected that Al_2O_3 is reduced slightly by the HIT process and oxygen diffuses from Al_2O_3 to CCPs. In order to restrain reduction in Al_2O_3 , we have optimized several conditions. One of the improvements was the change in hydrogen gas flow from 50 to 10 SCCM. The CPP-GMR films with a CCP-NOL with improved HIT process were film III. As a result, MR ratios of 27.4% and 25.0% were achieved at RAs of $2.9 \Omega \mu\text{m}^2$ and $0.5 \Omega \mu\text{m}^2$, respectively, as shown in Fig. 4. The solid line in Fig. 4 is fitted to a modified Valet-Fert model for the CCP-NOL.⁵ By calculating RA and the MR ratio while changing the CCP resistivity ρ_{CCP} , it was determined that the HIT process has decreased the CCP resistivity ρ_{CCP} from 55 to $35 \mu\Omega \text{cm}$.

The MR dependence on RA for further lower resistivity was estimated by the same calculation as the above fitting and as shown in Fig. 4. The value of $1.5 \mu\Omega \text{cm}$ is the resistivity of the bulk Cu.¹⁰ The calculated result indicated that an MR ratio of over 50% at an RA of $0.4 \Omega \mu\text{m}^2$ would be obtained by complete reduction from CuO_x to Cu in the CCPs.

FIG. 4. (Color online) MR ratio dependence on RA. Black dot and blue square are the same data as those in Fig. 2. Red diamond denotes an MR ratio of CPP-GMR films with a CCP-NOL formed by the improved HIT process. Solid lines are the results fitted using the modified Valet-Fert model while changing the CCP resistivity, ρ_{CCP} . Broken line is an MR ratio calculated by the same fitting with the CCP resistivity ρ_{CCP} reduced to 20, 10, and $1.5 \mu\Omega \text{cm}$.

In conclusion, we have realized a large MR ratio of 27.4% by adopting the HIT process after the oxidation process even in the case of using conventional FeCo magnetic alloys for the magnetic layers of the CPP-GMR films. The MR enhancement is due to the CuO_x reduction in the CCP-NOL. The evidence of the CuO_x reduction was confirmed by APT analysis. The relationship between MR ratio and oxide concentration in the CCP-NOL obtained by APT showed that further reduction from CuO_x to Cu would enable realization of an even higher MR ratio, namely, an MR ratio greater than 50%.

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