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Magnetic and Electrical Properties of the Spin Valve Structures with Amorphous CoNbZr

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A spin valve structure of NiO(40 nm)/Co(2 nm)/Cu(2.6 nm)/Co(x nm)/CoNbZr(y nm)/Ta(5 nm) has been investigated for the application of magnetic random access memory (MRAM). The spin valve structure exhibited very large difference in the coercivities between pinned and free layers, a relatively high GMR ratio, and a low free layer coercivity. The spin valves were prepared by sputtering and were characterized by dc 4-point probe, and VSM. The spin valves with combined free layer exhibited a maximum GMR ratio of 10.4 % with a free layer coercivity of about 82 Oe. The spin valves with a single 10 nm thick a-CoNbZr free layer exhibited a GMR ratio of about 4.3 % with a free layer coercivity of about 12 Oe. The GMR ratio of the spin valves increased by addition of Co between Cu and a-CoNbZr. It has been confirmed that the coercivity of free layer can be decreased by increasing the thickness of a-CoNbZr layer without losing the GMR ratio substantially, which was mainly due to high resistivity of the amorphous "layers".

I. Introduction

Exchange-biased spin valve structures have received increasing attention for possible application in magnetoresistive sensors, most notably in read heads for hard disk (HD), due to their enhanced sensitivity compared with conventional magnetoresistive NiFe materials [1-4]. Another promising application of the spin valves is in the Magnetic Random Access Memory (MRAM) [5-6]. From the viewpoint of application, a spin valve structure with two weakly coupled ferromagnetic layers possessing different coercivities is a hopeful candidate because of its low switching field [7]. It was observed that the magnetization in a hard magnetic layer degraded during repeated switching of soft magnetic layer in a quarternary memory cell [8]. The degradation was mainly caused by rotation of the magnetization of the hard magnetic layer under small-field excitation along a loop articulated by Rayleigh [9]. This degradation problem can be minimized by providing small ferromagnetic coupling strength and large difference in coercivities between the two magnetic layers.

In this paper, an amorphous CoNbZr-based spin valve structure of NiO(40 nm)/Co(2)/Cu(2.6)/Co(x)/CoNbZr(y)/Ta(5) is introduced for the first time for the application of magnetic random access memory (MRAM). NiO and Co films constituted the antiferromagnetic and pinned layers of the spin valve structures, respectively, since Co film on NiO exhibited rather larger coercivity and spin dependent scattering effect than NiFe film [1-4, 10]. Amorphous CoNbZr (a-CoNbZr) met the requirement of low coercivity as well as thermal stability [11-12]. We also inserted thin Co films between Cu and amorphous films to increase GMR ratio since Co gives larger spin dependent scattering at the interface [13]. The magnetic and electrical properties of the spin valves have been investigated as a function of free layer characteristics. A combined layer consisting of Co and a-CoNbZr as well as a single CoNbZr layer was employed as a free layer. The effect of thickness of each free layer on the magnetoresistive properties of the spin valves was mainly investigated.

II. Experimental

Spin valve structures of NiO(40 nm)/Co(2)/Cu(2.6)/Co(x)/CoNbZr(y)/Ta(5), as shown in Fig. 1, were fabricated on either n-type Si (100) or glass substrate in a uniform dc field of around 100 Oe. Glass substrates were used only for the resistivity measurement of each layer. NiO and CoNbZr films were deposited in Ar ambient from NiO and $Co_{88}Nb_8Zr_4$ targets, respectively, by rf-magnetron sputtering at 100 watt and 3.5 mTorr. Cu was prepared by dc-magnetron sputtering at 50 watt and 5 mTorr and the other metal layers by dc-magnetron sputtering at 100 watt and 5 mTorr. A combined layer consisting of

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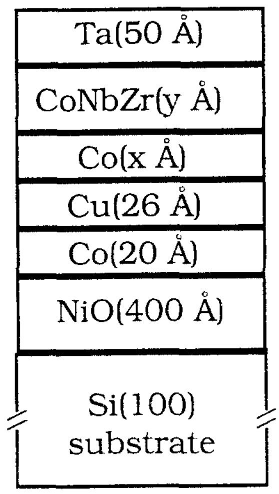

Fig. 1. An illustration of a spin valve structure.

Co and a-CoNbZr as well as a single CoNbZr layer was prepared as a free layer for the spin valves. Thickness of each layer in the free layer was varied as a parameter. Some samples were annealed at 200 ℃ for 1 hour under vacuum. The pressure of the annealing chamber was kept at 2×10^{-7} Torr during annealing. Crystallographic structures of deposited films were investigated by an X-ray diffractometer (XRD) with Cu K_α radiation. The thickness was measured by the stylus method. Resistivities of Co, Cu, and CoNbZr were estimated by dc 4-point probe with the layered structures of NiO/Co, NiO/Co/Cu, and NiO/Co/Cu/CoNbZr, respectively, prepared on either Si (100) or glass substrates. Magnetoresistance of the samples was measured by dc 4-point probe. Magnetic properties were measured by the vibrating sample magnetometer (VSM).

Ⅲ. Results and Discussion

Fig. 2 (a) shows a typical GMR versus field curve of the designed spin valves of NiO(40 nm)/Co(2)/Cu(2.6)/Co(1.2)/CoNbZr(y)/Ta(5), with combined free layer consisting of Co and CoNbZr layers. The spin valve exhibited a very high GMR ratio of 10.4 % with a free layer coercivity of about 80 Oe. Most of the 2 nm thick Co films on NiO (40 nm) exhibited average coercivities larger than 500 Oe, but the coercivity values had some distribution depending on the surface state of NiO since antiferromagnetic coupling is main origin of the large coercivity. Coercivities of Co films decreased with Co film thickness and increased with NiO film thickness.

M-H curve for the spin valve with the combined free layer [Fig. 2 (b)] exhibited a distinctive two-staged magnetization process. Alphabetical symbols shown in Fig. 2 (b) represent magnetization process corresponding to the identically symbolized stage in GMR-H curve. The gradual increase in GMR ratio of the spin valve with decreasing the absolute value of the applied field [regions a and e] is mainly due to the partial rotation of the local pinned-layer moment in accordance with the local distribution of the pinning field. The free layer is thought to be almost saturated under such a large field. A rapid increase in GMR ratio in the regions b and f is due to rotation of the free layer moment, and the free layer moment is antiparallel to average pinned layer moment in the regions c and g. The regions d and h correspond to the total switching of the pinned layer. The critical field for the switching of pinned layer in the ascending direction (from e to h) is smaller than the descending direction, and the difference is two times as large as the pinning field (hysteresis loop shift) coming from antiferromagnetic exchange coupling between NiO and pinned layers.

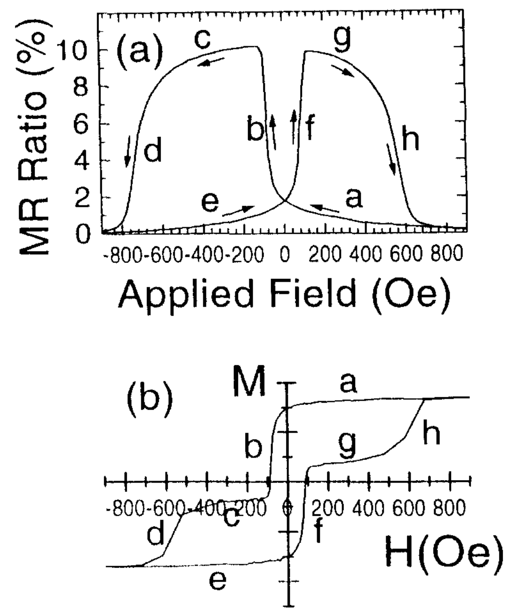

Fig. 2. Hysteresis curves of (a) magnetoresistance and (b) magnetization along easy direction of the spin valve of NiO(40 nm)/Co(2)/Cu(2.6)/Co(1.2)/CoNbZr(3)/Ta(5).

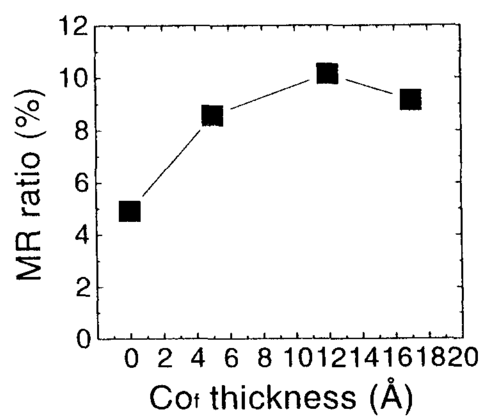

Fig. 3. Effect of Co addition on the GMR property of the spin valve of NiO(40 nm)/Co(2)/Cu(2.6)/Co(x)/CoNbZr(3)/Ta(5).

Variation of the GMR ratio with different Co thickness in the combined free layer is shown in Fig. 3. The GMR ratio increased and became a maximum with a slight indication of decrease with increasing Co thickness in the combined free layer. The increase in MR ratio is due to larger spin dependent scattering effect of Co layer at the interface [13]. The MR ratio increases with increasing Co thickness until electron shunting effect through Co film becomes dominant.

To achieve a lower coercivity of the free layer, we investigated the effect of the free layer thickness on the GMR properties of the spin valves. Coercivity of the free layer is mainly determined by local magnetic anisotropy of free layer, which is governed by intrinsic magnetic property, ferromagnetic and antiferromagnetic exchange coupling between pinned and free layer, and interfacial topographic effect. Amorphous film has a smaller coercivity than Co. A 10 nm thick CoNbZr film deposited on glass at the same condition as for the spin valves had a coercivity of about 3 Oe, whereas a Co film of the same thickness had a coercivity of 17 Oe along the easy direction. Furthermore, the effect of ferromagnetic and antiferromagnetic exchange coupling, and interfacial topographic effect on the coercivity are larger for the thinner free layer. Therefore, it is expected that increase in amorphous film thickness could reduce the coercivity of the free layer.

Fig. 4 shows changes in GMR-H curve with different thickness of CoNbZr layers in the spin valves having a single CoNbZr film as a free layer. Figs. 4 (a) and 4 (b) have 3 nm and 10 nm CoNbZr films for the free layer, respectively. The GMR ratio decreased a little, but coercivity of the free layer decreased dramatically with increasing thickness of the amorphous film. Figs. 5 (a) and 5 (b) show the minor GMR loops corresponding to the samples shown in Figs. 4 (a) and 4 (b), respectively, which were measured along the pinned direction after saturation of the pinned layer along the pinned direction. These minor loops also clearly show that the coercivity decreases with increasing amorphous film thickness. The measured coercivities were about 85 Oe [Fig. 5 (a)] and 12 Oe [Fig. 5 (b)], respectively.

This trend was also observed in the spin valves with a combined free layer. Figs. 6 and 7 are the major and minor

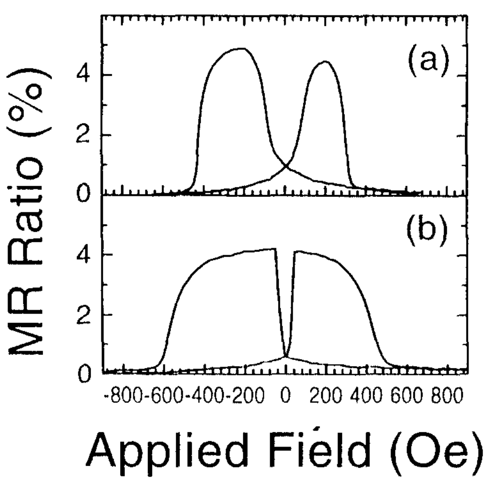

Fig. 4. Hysteresis curves of magnetoresistance of NiO(40 nm)/Co (2)/Cu(2.6)/free layer/Ta(5) with different free layers: (a) CoNbZr (3), and (b) CoNbZr(10).

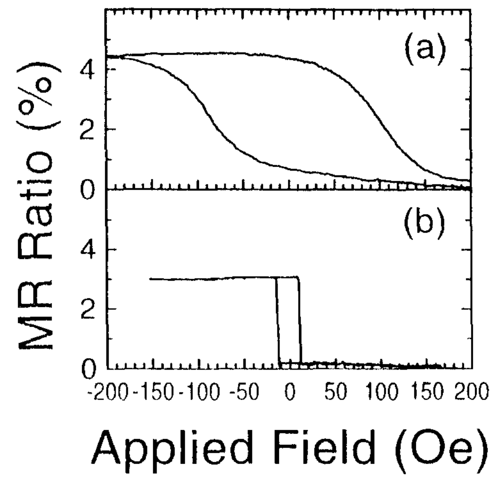

Fig. 5. Minor hysteresis curves of magnetoresistance of NiO(40 nm)/Co(2)/Cu(2.6)/free layer/Ta(5) with different free layers: (a) CoNbZr(3), and (b) CoNbZr(10). These curves were obtained along pinned direction after saturation of pinned layer along pinned direction.

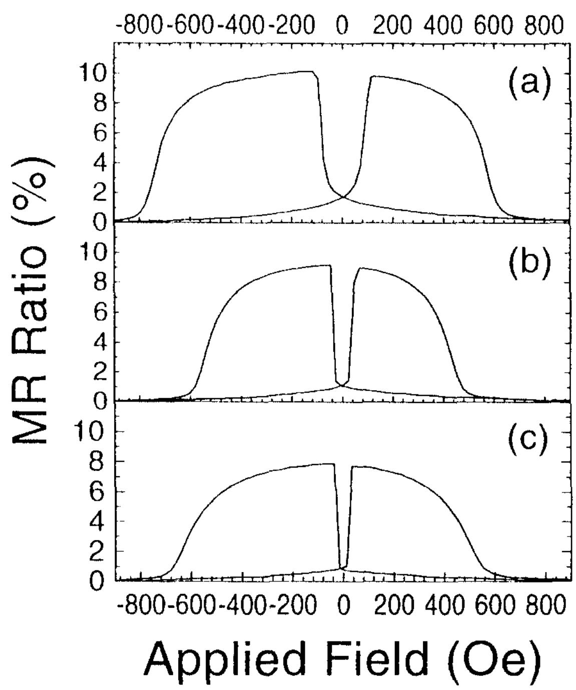

Fig. 6. Hysteresis curves of magnetoresistance of NiO(40 nm) /Co(2)/Cu(2.6)/free layer/Ta(5) with different free layers: (a) Co(1.2)/CoNbZr(3), (b) Co(1.2)/CoNbZr(10), and (c) Co(1.2) /CoNbZr(20).

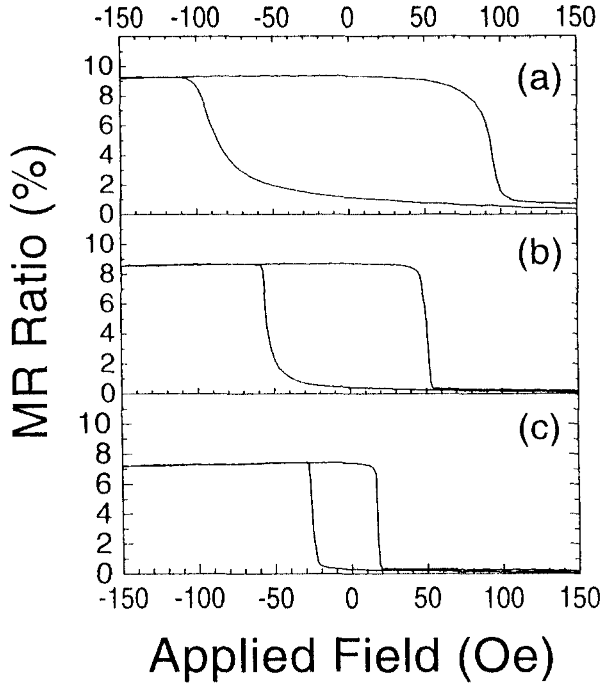

Fig. 7. Minor hysteresis curves of magnetoresistance of NiO(40 nm)/Co(2)/Cu(2.6)/free layer/Ta(5) with different free layers: (a) Co(1.2)/CoNbZr(3), (b) Co(1.2)/CoNbZr(10), and (c) Co(1.2)/CoNbZr(20). These curves were obtained along pinned direction after saturation of pinned layer along pinned direction.

GMR loops of the spin valves with a combined free layer, respectively. Figs. 6 (a), 6 (b), and 6 (c) are for the samples with Co(1.2 nm)/CoNbZr(3), Co(1.2)/CoNbZr(10), and Co(1.2)/CoNbZr(20) for the free layers, respectively. The minor loops were measured along the pinned direction after saturation of the pinned layer along the pinned direction. The GMR ratio decreased a little with increasing thickness of the amorphous film, but the coercivity of free layer decreased substantially. Measured coercivities were about 82 Oe [Fig. 7 (a)], 52 Oe [Fig. 7 (b)], and 22 Oe [Fig. 7 (c)], respectively. Most of the spin valves exhibited a weak ferromagnetic coupling strength of about 3 Oe between the pinned and free layers.

Figs. 8 (a) and 8 (b) show major and minor M-H loops of the annealed spin valve with the combined free layer, respectively, which correspond to Fig. 6 (c). The spin valves were annealed at 200 ℃ for 1 hour under vacuum. The pressure of the annealing chamber was kept at 2×10^{-7} Torr during annealing. The major loop was measured along the easy direction. The minor loops were measured along the easy and hard directions after saturation of the pinned layer along the easy direction. According to our annealing experiment [14], any significant changes in the physical properties of the spin valve were not observed up to annealing temperature of 300 ℃.

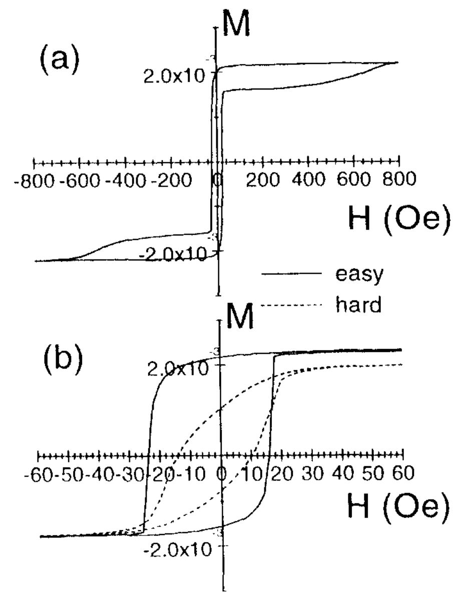

Fig. 8. (a) Major and (b)minor hysteresis curves of magnetization of NiO(40 nm)/Co(2)/Cu(2.6)/ Co(1.2)/CoNbZr(20)/Ta(5) spin valve, which was annealed at 200 ℃ and 2×10^{-7} Torr.

The major M-H loop [Fig. 8 (a)] exhibited a clear two-staged magnetization hysteresis curve. The minor M-H loop along easy direction [Fig. 8 (b)] showed that the combined free layer has a coercivity of 19.5 Oe and that the ferromagnetic coupling strength between the pinned and free layer is 3.5 Oe. These results are similar to what we obtained from minor GMR loop [Fig. 7 (c)]. The saturation magnetization of the minor loop along the easy direction at negative field regions is smaller than that at positive field regions by the amount of saturation magnetization of pinned layer.

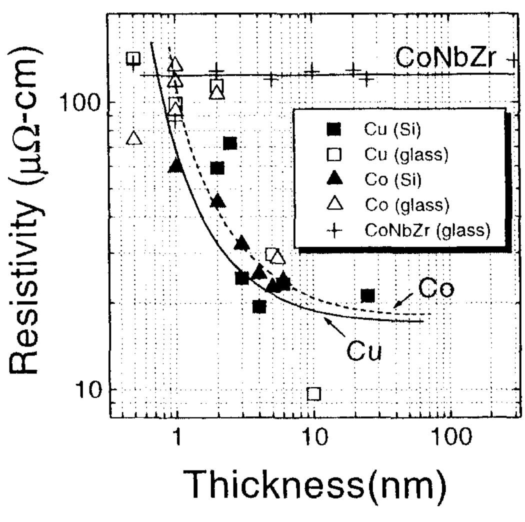

Fig. 9. Thickness dependence of resistivities of each metal layer in the spin valve structures of NiO(40 nm)/Co/Cu/CoNbZr/Ta(5). The closed symbols are for the samples prepared on Si(100), and the open symbols and cross are for the samples on glass substrate.

The reason why we did not lose the GMR ratio substantially appears to be small shunt effect through the amorphous layer due to its high resistivity even though we increased the thickness of amorphous layer to achieve a lower free layer coercivity. Fig. 9 shows measured resistivities of each metal layer in the spin valve structure as a function of thickness. The resistivities of Co and Cu layers were larger than 50 $\mu\Omega$-cm with relatively large scattering at the thickness lower than 2 nm and decreased with increasing thickness, while those of amorphous CoNbZr layer were around 125 $\mu\Omega$-cm and did not exhibit significant changes. The large scattering in the resistivities of Co and Cu layers may imply that the films are not continuous at the film thickness around 2 nm. From the resistivity measurement, it is believed that most of the electrons pass through Cu layer and there will be very small shun effect through the thick CoNbZr layer in the spin valves of NiO(40 nm)/Co(2)/Cu(2.6)/Co(1.2)/CoNbZr(20)/Ta(5).

Ⅳ. Conclusion

A spin valve structure with a-CoNbZr films for free layer has been investigated for the application of magnetic random access memory (MRAM). The spin valves with a combined free layer consisting of a-CoNbZr and Co exhibited a maximum GMR ratio of 10.4 % with a free layer coercivity of about 82 Oe. The spin valves with a single 10 nm thick a-CoNbZr free layer exhibited a GMR ratio of about 4.3 % with a free layer coercivity of about 12 Oe. GMR ratio of the spin valve increased by addition of Co between Cu and a-CoNbZr. The coercivity of free layer decreased by increasing the thickness of a-CoNbZr layer without losing the GMR ratio substantially, which was mainly due to high resistivity of the amorphous films.

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