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Giant Magnetoresistance in Ni-Fe/Co/Al-AlOx/ Co/Ni-Fe/Fe-Mn Ferromagnetic Tunnel Junctions

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To develop candidate magnetic sensors for the future generation of magnetic read heads, we have fabricated Ni-Fe/Co/Al-AlO$_x$/Co/Ni-Fe/Fe-Mn/Ni-Fe ferromagnetic tunnel junctions with oxidized Al barriers. To form the barrier layer, the Al was oxidized in air or in oxygen plasma. These junctions showed changes in tunnel resistance (magneto-resistance ratio) of 10 to 15% upon the application of a magnetic field. Some of the junctions exhibited good thermal stability over 300°C and the magneto-resistance (MR) ratios were increased by annealing. The largest MR ratio after annealing at 300°C for one hour was 24%, which is much larger than that of spin-valve films. The junctions with naturally oxidized barriers and plasma-oxidized barriers had almost the same properties, but the plasma-oxidization process is much faster. Current research indicates that ferromagnetic tunnel junctions have good potential for use in magnetic read heads.

1. Introduction

The capacity of magnetic disk systems is growing year by year with the advance of the information-oriented society, and the areal density of magnetic recording is increasing by 60% every year.1) Currently the highest areal density in commercial HDDs is about 4 Gbit/in^2, but this will surely grow to 10 to 20 Gbit/in^2 in the next few years.

To read recorded information from smaller areas, magnetic heads with higher sensitivities are needed. MR (Magneto Resistive) heads are now in commercial use. The electrical resistance of an MR element can be changed by about 2 to 3% by the application of a magnetic field. This type of head is expected to have the potential for up to 5 Gbit/in^2.

Because of their high sensitivity in low magnetic fields,2),3) spin-valve elements which show a giant magnetoresistive effect of 5 to 7% are strongly expected to be developed as replacements for MR elements. This type of head is thought to have the potential for up to 20 Gbit/in^2.

We are developing ferromagnetic tunnel junctions to supersede spin-valve sensors. It is known that the ferromagnet/insulator/ferromagnet tunnel junction changes its tunnel resistance as the relative angle of magnetization changes.4),5) This effect is theoretically predicted to give MR ratios of 20 to 50%, which are larger than those of spin-valve films.5)

Therefore, ferromagnetic tunnel junctions will be one of the candidates for use as a post-spin-valve head in future magnetic read heads. However, since this effect was first reported, only very small changes in resistivity (below 1%) have been experimentally observed. Since those junctions had large junction areas, for example, 1 mm × 1 mm, they may have included many pinholes and local defects, mainly due to dust. Recently however, large MR ratios of over 10% have been obtained at room temperature.6),7) Furthermore, in terms of applicability to heads, a large MR ratio at low magnetic fields and with low resistivity and good thermal stability are necessary.

We have fabricated ferromagnetic tunnel junctions in which the top ferromagnetic layer is pinned by an Fe-Mn antiferromagnetic layer, as in a spin valve. In this paper, we describe the relationship between the fabrication conditions and the tunnel MR properties.[8)-10)]

2. Experiment

The fabricated layer structures were Ni-Fe [171 Å (Å=0.1 nm)] / Co(33 Å) / Al-AlOx (9 - 21 Å) / Co(33 Å) / Ni-Fe(171 Å) / Fe-Mn(450 Å) / NiFe(86 Å) on 4-inch silicon wafers with 1 µm thermally oxidized surfaces. Thin Co layers with larger polarizations than the Ni-Fe layers[11)] were inserted to increase the MR ratio. The Fe-Mn layer was covered with a thin Ni-Fe layer to avoid oxidization. Each layer was deposited by dc magnetron sputtering (except the Fe-Mn, which was deposited by rf magnetron sputtering) and patterned by metal masks. **Figure 1** shows the schematic diagram of the junction and the layer structure. The junction areas were 0.01 to 0.123 mm^2, and 400 junctions were patterned on a single wafer.

To form the insulating layer, a 9 to 21 Å Al layer was deposited on the Ni-Fe/Co bottom ferromagnetic layer. Then the surface was oxidized by exposure to air or an oxygen plasma. The oxygen plasma was produced by applying rf power. All processes were carefully carried out in a cleanroom to avoid contamination.

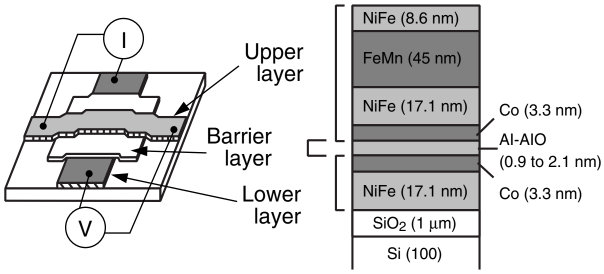

Figure 1
Schematic diagram of junction.

Samples were also subsequently annealed at a pressure of under 1.0 × 10^{-5} torr at 100 to 350°C for one hour with an applied field of about 1 kOe [(1000/4π)A/m] in the same direction as that of the magnetization in the pinned layer.

The four-probe method was used for measuring the resistances, MR properties, and current-voltage characteristics. The magnetic field was applied in the same direction as that of the magnetization in the pinned layer (Co/Ni-Fe top ferromagnetic layers). All measurements were conducted at room temperature.

3. Results and Discussion

3.1 Natural oxidization

3.1.1 Oxidization time of Al layer

Figure 2 shows the dependence of the tunnel resistances of as-deposited 0.01 mm^2 samples on the Al oxidization time. The resistance values are broadly distributed between 0.1 and 3,000 Ω, and show a general tendency to increase with the Al oxidization time.

The junctions with slightly oxidized (< 5 hours) Al barriers are almost short-circuited and do not show any tunnel characteristics. Some junctions exhibit tunnel characteristics with a small resistance (< 1 Ω) and nonlinear I-V characteristics. Some of these junctions exhibit extraordinarily large MR ratios (20 to 180%), which is

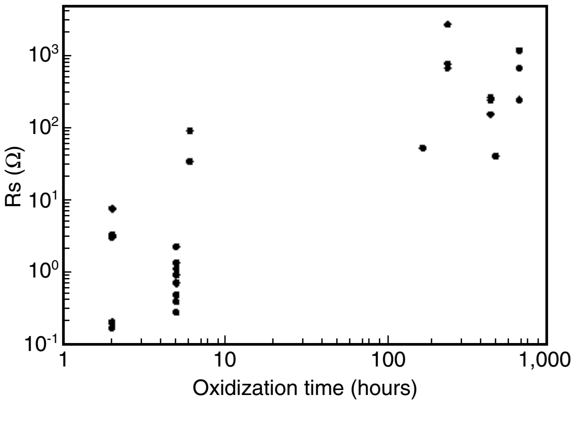

Figure 2
Dependence of tunnel resistance on Al natural-oxidization time.

thought to be due to "geometrically enhanced magnetoresistance".[12] Some samples have different resistances corresponding to different current-flow paths. This is thought to originate from non-uniform tunnel barriers.[8] The measured values of these junctions with low tunnel resistances are thought to be incorrect. The resistance values of these junctions increased or short-circuited over time.

In contrast, almost all of the junctions with well oxidized (> 100 hours) Al barriers have high resistance values (100 to 3,000 Ω) and these values do not change over time. They show nonlinear I-V characteristics that are unique to tunnel junctions and MR ratios of 10 to 15%.

Figure 3(a) shows the R-H curve of a junction that has an Al layer thickness of 17 Å and was exposed to Al oxidization for 241 hours. A spin-valve-like R-H property is clearly observed. A 10% MR ratio was obtained in a low field of 20 Oe. When a large magnetic field is applied, the tunnel resistance is low because the magnetizations of the Ni-Fe/Co bottom layer and Co/Ni-Fe top layer are parallel. On the other hand, the tunnel resistance is high when a low magnetic field which can switch the Ni-Fe/Co bottom layer's magnetization is applied.

Figure 3(b) shows the I-V characteristics of the same junction. According to Simmons' equations,[13] the I-V characteristic obeys the equation $J = \theta(V + \gamma V^3)$, where J and V are the tunnel current density and the applied voltage, respectively, and θ and γ depend on the barrier height, φ, and barrier thickness, s. By fitting to the measured I-V characteristics, φ and s were calculated to be 1.4 eV and 15 Å, respectively. More than 100 hours

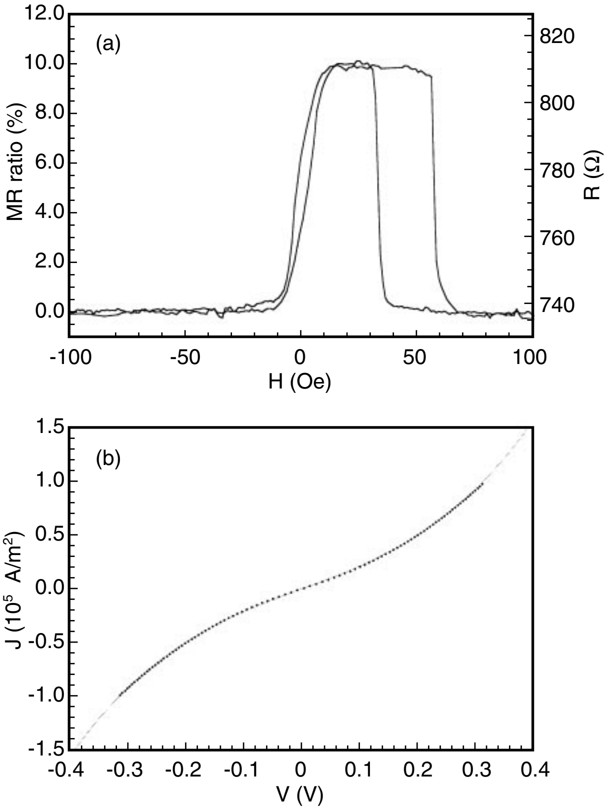

Figure 3
(a) R-H curve of junction having Al layer thickness of 17 Å and Al oxidization time of 241 hours, and (b) its I-V characteristic.

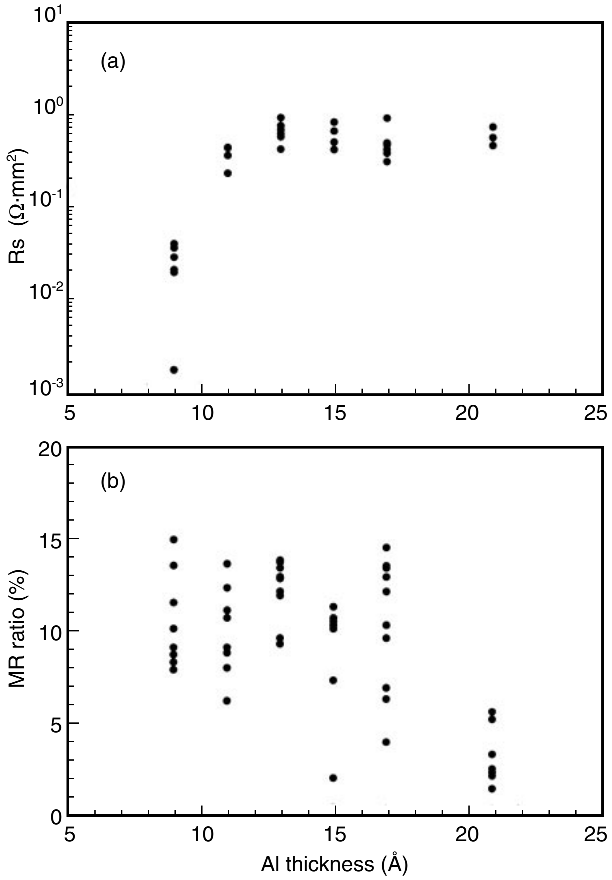

Figure 4
(a) Dependence of tunnel resistivity and (b) MR ratio on Al thickness.

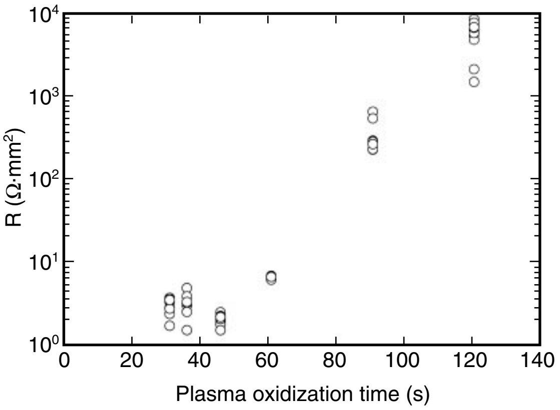

Figure 5
Dependence of tunnel resistivity on plasma oxidization time.

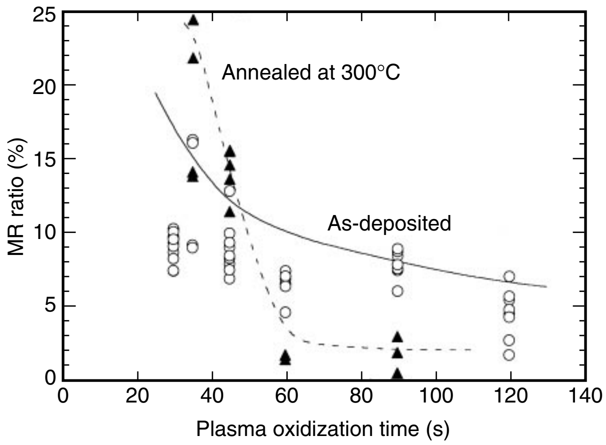

Figure 6
Dependence of MR ratio on plasma oxidization time.

were required to form a good barrier without short-circuiting.

3.1.2 Thickness of Al layer

Figures 4(a) and (b) show the dependence of the tunnel resistivities and MR ratios on the Al thickness of the junctions. The Al layers were oxidized for 450 to 700 hours. Although the tunnel resistivities are almost constant over a thickness of 13 Å, they have a tendency to decrease steeply as the Al thickness is decreased below this value. In contrast, the MR ratios are almost constant from 10 to 15%, except for $d_{\mathrm{Al}} = 21$ Å.

It is theoretically considered that the electron spin is preserved and that this conservation is the origin of the resistance change.[4),5)] In the junctions with a thick barrier, the reduction in the MR ratios may be due to an inhibition of spin-preserved electron tunneling caused by the higher presence of impurities.

For application in heads, the junction should have a low resistivity, and this can be attained by decreasing the thickness of the Al. Because the resistance of the sample with a 9 Å Al thickness and 100 µm × 100 µm size is only 3 Ω, it will exhibit geometrically enhanced MR. We should reduce the junction size to evaluate the tunnel resistance precisely. Also, we should study tunnel junctions with a thinner Al barrier in order to achieve junctions with low resistivities.

3.2 Plasma oxidization

It takes much time to form a good barrier with almost no pinholes by natural oxidization. This process is also affected by humidity and temperature and is not so clean. Plasma oxidization is a promising method of fabricating barriers speedily with greater controllability than natural oxidization. To form the insulating layer, a 13 Å Al layer was first deposited. Then the process gas was introduced to the chamber at a pressure of 0.5 Pa, and rf power was applied for a few seconds to a few minutes at an intensity of 0.01 W/cm^2.

Figure 5 shows the dependence of tunnel resistivity on the plasma oxidization time. The process gas was pure oxygen. The tunnel resistances increased rapidly with the plasma oxidization time. This indicates that as oxidization progresses, the barrier gets thicker. Using this technique, a tunnel resistivity of 10 Ω mm^2 can be obtained in only about one minute, which is much faster than the several hundreds of hours which would be required when only natural oxidization is employed.

MR changes were observed in almost all of the samples. **Figure 6** shows the dependence of the MR ratio on the plasma oxidization time. The MR ratios gradually decreased as the oxidization time was increased. The maximum MR ratio for

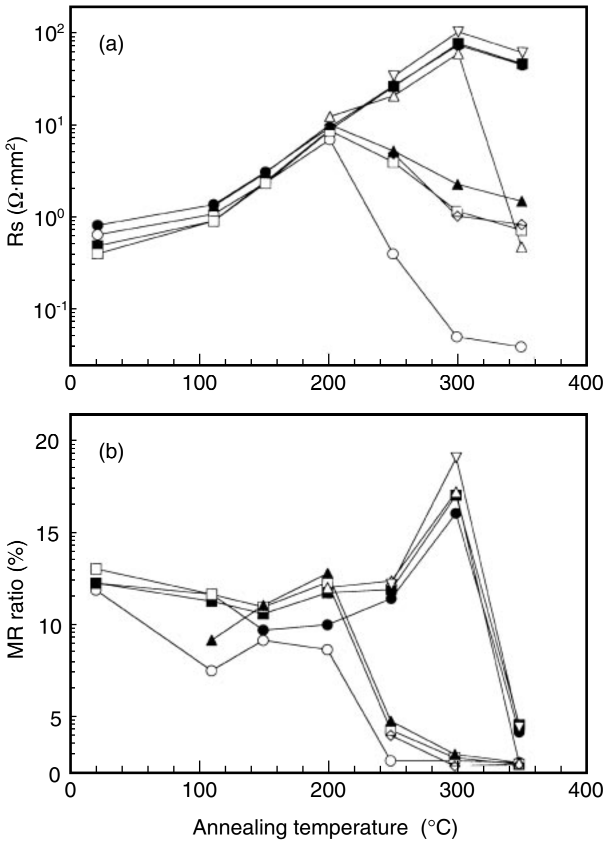

Figure 7
Dependence of tunnel resistivity and MR ratio on annealing temperature.

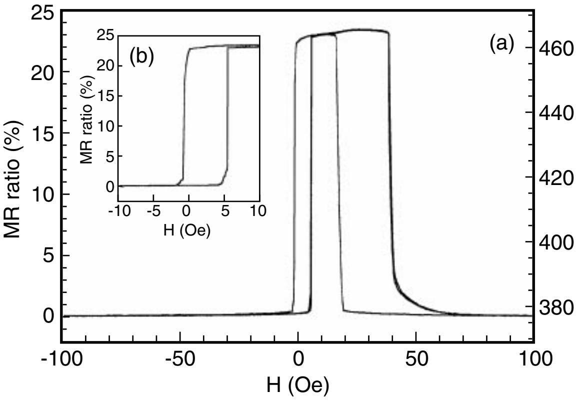

Figure 8
R-H curve of junction having Al layer thickness of 13 Å after annealing at 300°C for one hour.

an as-deposited junction was 16% and was achieved by plasma oxidizing for 35 seconds, which is a much shorter time than the corresponding time for natural oxidization. We believe that barriers with almost no pinholes can be formed by plasma oxidization.

3.3 Annealing effects

3.3.1 Natural oxidization

Figures 7(a) and (b) show how the tunnel resistivities and MR ratios of several samples changed as the samples were taken to increasingly higher annealing temperatures. The Al thickness was fixed at 15 Å and was naturally oxidized. As can be seen, the tunnel resistivities increased up to a certain temperature and then decreased. There are two kinds of tendencies. One tendency is a decrease in tunnel resistivity above 200°C, and the other is a decrease above 300°C. The MR ratios also show the same two tendencies. The decreases in MR ratio probably correspond to the decreases in tunnel resistivity. The mechanism of the increase in tunnel resistance and MR ratio is not simple, but we did obtain some useful information by XRD and XPS which indicated that the movement of oxygen atoms plays an important role in the annealing effect.[14]

Annealing at 350°C reduced the tunnel resistances in all of the junctions, and we think that at this temperature the structure of the sandwich is short-circuited. Some junctions exhibit thermal stability at above 300°C, which is better than what can be achieved with spin-valve films.

Figures 8(a) and (b) show the R-H curve of a junction with a 13 Å thick Al layer after annealing at 300°C for 1 hour. The Al layer was naturally oxidized for 576 hours. A spin-valve-like R-H property can clearly be observed. A 24% MR ratio was obtained for Hc = 3.2 Oe.

According to a simple model,[5] the MR ratio is described by:

$$\Delta R/R_p = (R_{\uparrow\downarrow}-R_{\uparrow\uparrow})/R_{\uparrow\uparrow} = 2P_{F1}P_{F2}/(1-P_{F1}P_{F2}),$$

where P_{F1} and P_{F2} are the spin polarizations of each metal beside the barrier layer. As $P_{F1} = P_{F2} = P_{Co} = 0.35$[12] in our junctions, $\Delta R/R_p$ is calculated to be 28%. The MR ratio of 24% we ob-

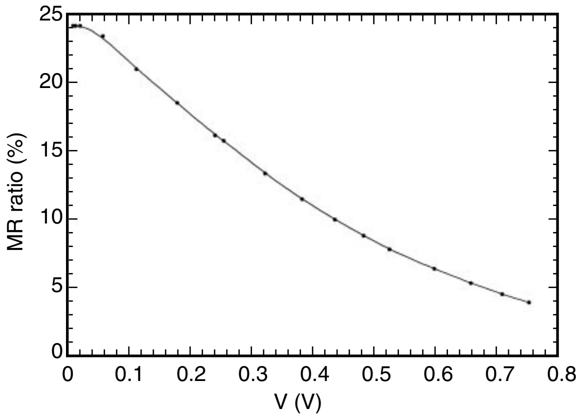

Figure 9
Dependence of MR ratio on applied voltage.

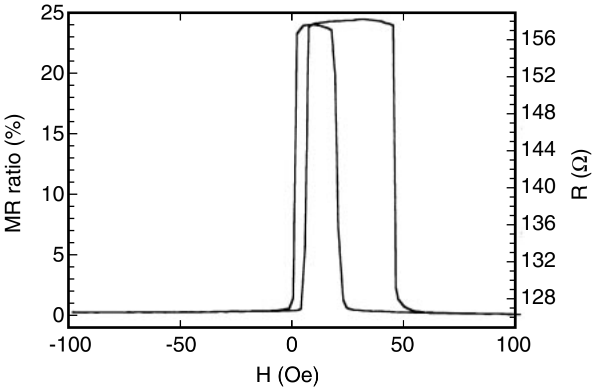

Figure 10
MR curve of junction whose barrier layer was oxidized for 35 seconds in oxygen plasma after annealing at 300°C for one hour.

served agrees well with the calculated value.

Figure 8(b) shows the minor loop of the junction. We find a loop shift of 2.1 Oe, which seems to come from the ferromagnetic interaction, but its origin is unclear.

Using Simmons' equations,[15] the barrier height and thickness were calculated to be 2.64 eV and 12.6 Å, respectively, after fitting to the measured I-V characteristics. According to Slonczewski,[15] the effective spin polarization depends on the barrier height. In our samples, the increase in MR ratio might be due to the increase in the barrier height.

Figure 9 shows the dependence of the MR ratio on the applied voltage. The MR ratio decreases as the voltage is increased. This finding is similar to findings reported elsewhere[8] and is not yet understood, but this decrease in MR ratio is very important. We need a large resistance change at a practical bias voltage and need to reduce the applied voltage dependence of the MR ratio.

3.3.2 Plasma oxidization

The MR ratios after annealing at 300°C for one hour are shown in Figure 6. The MR ratios of junctions with oxidization times of under 60 seconds were increased by annealing, as was the case for the samples with naturally oxidized barriers. However, in the samples whose barriers were oxidized for over 60 seconds, annealing decreased the MR ratio. This is assumed to occur due to the following mechanism. In samples with oxidization times of under 60 seconds, the Al layer is gradually oxidized from the surface, and the bottom of the layer still remains unoxidized. In these samples, oxygen atoms at the Co surface move into the Al layer by annealing, and the polarization of electrons at the interface of Co and Al increases. In samples that were oxidized for more than 60 seconds, however, the entire Al layer and the inside of the Co layer become oxidized. In these samples, the oxygen atoms at the Co surface move into the Co layer and reduce the polarization of electrons in the Co layer, thereby disturbing the spin-preserved tunneling.

Figure 10 shows the MR curve of a junction that was annealed at 300°C for one hour and had its barrier layer oxidized for 35 seconds in oxygen plasma. A spin-valve-like MR property can clearly be observed. The MR ratio of this sample is 24%, and its properties are almost the same as those of junctions whose Al barriers were subjected to a prolonged natural oxidization after annealing at 300°C.

Although we expected to obtain junctions which have constant, high MR ratios with better reproducibility by oxidizing in a closed chamber, the present data still indicate large spreads of resistances and MR ratios. These large spreads are thought to be caused by the exposure to air which occurred when the mask was changed or by the roughness of the bottom layer.

4. Summary

We have fabricated ferromagnetic tunnel junctions with spin-valve-like layer configurations by magnetron sputtering and metal mask patterning. The oxidized Al barrier layers were formed by exposure to air or to oxygen plasma. Junctions with appropriately oxidized Al barriers exhibited a resistance change of 10 to 15%, and some of these samples exhibited a further increase in resistance change after annealing at 250 to 300°C. Some junctions exhibit thermal stability at above 300°C, which is much higher than the maximum stable temperature of the junctions of spin-valve films.

The Ni-Fe(171 Å)/Co(33 Å)/Al-AlO_x(13 Å)/Co(33 Å)/Ni-Fe(171 Å)/Fe-Mn(450 Å)/Ni-Fe(86 Å) junction shows a 24% spin-valve-like MR change for Hc = 3.2 Oe after annealing at 300°C for one hour.

These results demonstrate that ferromagnetic tunnel junctions have good potential for use as post-spin-valve magnetic read head sensors.

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