Magnetoresistance values exceeding 21% in symmetric spin valves

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We report values of the giant magnetoresistance (GMR) effect exceeding 21% in symmetric spin valves, the highest values ever reported for such structures. The key elements in this achievement are the use of a Co/Cu/Co/Cu/Co multilayer in which the center Co layer is substantially thicker than the outer Co layers and the use of the antiferromagnetic insulator NiO at the top and bottom to pin the adjacent Co layers magnetically. The relative Co layer thicknesses suggest that some specular scattering of conduction electrons may occur at the metal/insulator interfaces and may enhance the GMR. © *1995 American Institute of Physics.*

I. INTRODUCTION

Symmetric[1] (or dual[2]) spin valves are a subject of interest due both to their importance for a fundamental understanding of spin-dependent electron transport and to their importance for device applications.[3] Symmetric spin valves are one of three basic types of magnetic multilayer structures which exhibit the giant magnetoresistance (GMR) effect. The first basic type is the simple spin valve,[4] which consists of two magnetic layers (often Co or $Ni_{80}Fe_{20}$) separated by a nonmagnetic spacer layer (often Cu). The magnetization direction of one magnetic layer in the device is pinned and that of the other is free to rotate so that their alignment may be switched by an external field from parallel to antiparallel. This switching produces a "giant" increase in the resistance as spin-allowed conduction paths become spin forbidden. A second basic type of magnetic multilayer exhibiting the GMR effect is the magnetic/nonmagnetic superlattice.[5,6] These structures depend on an inherent antiferromagnetic alignment of successive magnetic films, and the switching is accomplished by an external field of sufficient strength to induce parallel alignment. The third basic type is the symmetric (or dual) spin valve,[1–3] in which there are three magnetic layers separated by two nonmagnetic layers. The center magnetic layer is free to rotate while the outer two are magnetically pinned.

Simple spin valves have the advantage that the switching field can often be only a few Oersteds (Oe) but suffer from a relatively small GMR, with 13.5% being the highest value reported to date.[1] Superlattices can exhibit room temperature GMR values as large as 65% but generally have the disadvantage of large switching (or saturation) fields.[6] Symmetric spin valves represent an opportunity to achieve the common goal of large GMR at small fields, although to date the largest reported value is 13.3%.[1]

Figure 1 presents an illustration of a typical symmetric spin valve. Symmetric spin valves might be expected to have substantially larger GMR values than simple spin valves because significantly longer electron mean free paths (MFPs) should be possible (perhaps through the entire five-layer structure) for spin-allowed conduction paths in the parallel alignment state. However, in the antiparallel alignment state, symmetric spin valves should exhibit short MFPs just as simple spin valves or superlattices do. These short MFPs in the antiparallel alignment state occur for all GMR structures as an electron leaving one magnetic film and crossing the nonmagnetic spacer layer will tend to scatter as it tries to enter the next magnetic layer because its spin orientation is wrong for that layer. In the parallel alignment state, the same electron will be less likely to scatter since entry into the next magnetic layer is then a spin-allowed conduction path, and such paths increase the MFP. Note here that, although the GMR effect depends on electron paths crossing the layers, the GMR is conventionally measured by a standard four-point probe with net current flow in the plane of the film.

Thus, the large potential advantage of the symmetric spin valve over the simple spin valve lies in the potential increase in MFP due to having a five-layer structure rather than a three-layer structure. (This statement is based on the assumption that the MFPs are terminated by diffuse scattering at the top and bottom of either structure.) The symmetric spin valve should still exhibit a low switching field since the center magnetic layer (the valve) is not magnetically pinned. Therefore, the advantages of both superlattices and simple spin valves may be present without the disadvantages of either.

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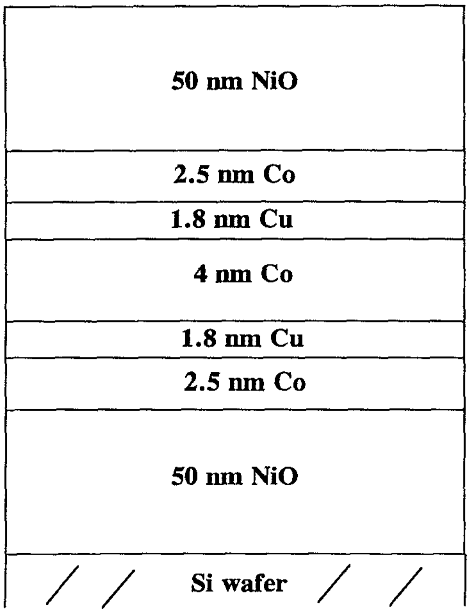

FIG. 1. An illustration of a symmetric spin valve structure typical of those investigated in the present work.

A possible additional important factor for both symmetric and simple spin valves is that the MFP in the parallel alignment state should be lengthened still further if the electron can reflect specularly when it reaches the top or bottom of the metallic structure. In general, the more the MFP increases when spin-allowed conduction paths are turned on by parallel alignment, the greater will be the GMR. In the event of perfect specular reflection at the top and bottom of a spin valve, the electron paths would mimic those in a superlattice and a very high GMR should be possible.

With these ideas in mind, both simple spin valves and symmetric spin valves have been investigated with the aims of gaining a better understanding of both while optimizing the latter. The work on simple spin valves will be published separately since, surprisingly, it has little bearing on the results on symmetric spin valves.

II. EXPERIMENT

The NiO substrates used in this work were polycrystalline films ~50 nm thick, deposited on 3″ Si wafers by reactive magnetron sputtering at the University of California at San Diego and University of Minnesota.[7–9] At the National Institute of Standards and Technology, the wafers were cleaved into $\sim 1\ \mathrm{cm}^2$ squares, cleaned ultrasonically, rinsed, dried, and installed in the deposition chamber. The base pressure before depositing a spin valve was typically 1×10^{-8} Torr ($\sim 10^{-6}$ Pa) of which ~95% was H_2 and the remainder largely H_2O. The presence of H_2 during deposition has no apparent effect on spin valve properties unless the partial pressure exceeds $\sim 10^{-6}$ Torr. The low base pressure is achieved partly by depositing a ~1.5 nm Ti film on the inside of the deposition chamber from a centrally mounted Ti filament just prior to deposition of each spin valve.

The magnetoresistance measurements were made *in situ* using the four-point probe dc mode. Several films were checked *ex situ* in two separate facilities and were found to have the same values of magnetoresistance. The multiplicative conversion factor from four-point resistance to sheet resistance is of the order of 4, but depends on the dimensions of the individual sample.

It is very important to remove the hydrocarbon contamination (several tenths of a mm of which is accumulated on the NiO from exposure to the laboratory air) prior to the deposition of each spin valve in order to achieve strong pinning and the highest GMR values. Samples were Ar sputtered with a neutralized-beam ion gun at a beam voltage of 100 eV until the carbon was removed (as judged by *in situ* x-ray photoelectron spectroscopy). Beam voltages of several hundred eV gave reduced pinning and GMR values, probably due to damage of the NiO surface. The metal films were deposited at room temperature by dc-magnetron sputtering in 2 mTorr Ar at a rate of ~0.1 nm/s. The top NiO layer was deposited by sputtering a Ni target with an 85/15 mixture of Ar/O_2.

III. RESULTS AND DISCUSSION

A. General results

The largest values of GMR obtained for symmetric spin valves in this work were for structures of 50 nm NiO/2.5 nm Co/1.8 nm Cu/3.0–4.5 nm Co/1.8 nm Cu/2.5 nm Co/50 nm NiO. Figure 2 presents the high-field and low-field GMR loops for a typical sample which exhibits a maximum GMR of 21.5% (the highest we have achieved is 23.4%). The shape of the high-field loop in Fig. 2(a) is explained by the top and bottom Co layers being pinned by the adjacent NiO so that they exhibit large coercivities. The center Co layer has a small coercivity and switches from parallel to antiparallel to produce the increase in resistance found in the center of the high-field loop. This general shape of loop has been seen before in a type of simple spin valve which employed magnetic layers of differing coercivity.[10]

In the low-field loop in Fig. 2(b), little change occurs in the top and bottom Co, only the center Co layer is switched. Note that the high-field loop exhibits a weak tail extending out beyond 80 mT (800 Oe) so that the GMR of the low-field loop is only 18.2%. The weak tail is likely due to some grains in the polycrystalline NiO strongly pinning small patches of Co in random directions so that a large field is required for complete parallel alignment. We tried a variety of modifications to eliminate this weak tail. Field annealing, among other ideas, failed completely to eliminate the tail. One idea which worked was to deposit the symmetric spin valve on an epitaxial film of NiO on MgO(110). This procedure flattened out the tail completely, but the center Co layer then exhibited a coercivity of 37.5 mT (375 Oe), which is unacceptable for most device applications. The cause of the large coercivity is likely to be spatially extended defects in these epitaxial films (such as misfit dislocations in the NiO giving rise to misfit dislocations in the symmetric spin valve due to the lattice mismatches among these materials). Extended defects such as these may be expected to impede domain wall motion. The mean grain size in our symmetric

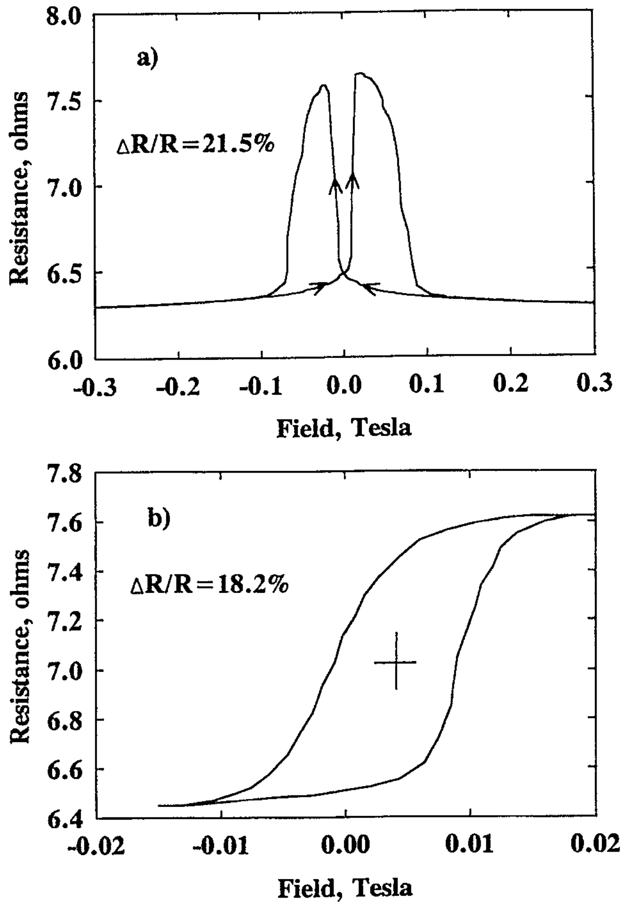

FIG. 2. Magnetoresistance loops for a typical symmetric spin valve for (a) high fields and (b) low fields, recorded after saturation in a negative field (see arrows). The four-wire resistance values may be converted (approximately) into sheet resistance by multiplying by a factor of ~4.

spin valves is ~7 nm, as observed with an *in situ* scanning tunneling microscope. This small grain size presumably allows a low coercivity since no single defect has a spatially extended influence.

The low-field loop in Fig. 2(b) exhibits a coercivity of 5 mT (50 Oe) and a positive (i.e., ferromagnetic) coupling field (a shift of the loop center away from zero) of 4.3 mT (43 Oe). These relatively low values together with the relatively large GMR should make such structures attractive for sensor applications when the dynamic range is ~5 mT (50 Oe), which is about the upper limit in the case of hard-disk read heads. Attempts to reduce these values further by use of a 4 nm film of $Ni_{80}Fe_{20}$ instead of 4 nm Co in the center were not promising. The coercivity and coupling were typically reduced by more than half, but the GMR dropped to ~13%. In contrast, preliminary results indicate that placing a single monolayer of $Ni_{80}Fe_{20}$ in the center of the 4 nm Co film reduces the coercivity by about a fourth and coupling by about half while the GMR remains above 20%. Some variation on this "doping" idea may be a more promising avenue for improvements. However, it should be emphasized that most compositional variations on the standard structure of Fig. 1 (e.g., those just described) exhibit surprising and complex behavior which defies a simple explanation. Clearly, much remains to be learned about these structures.

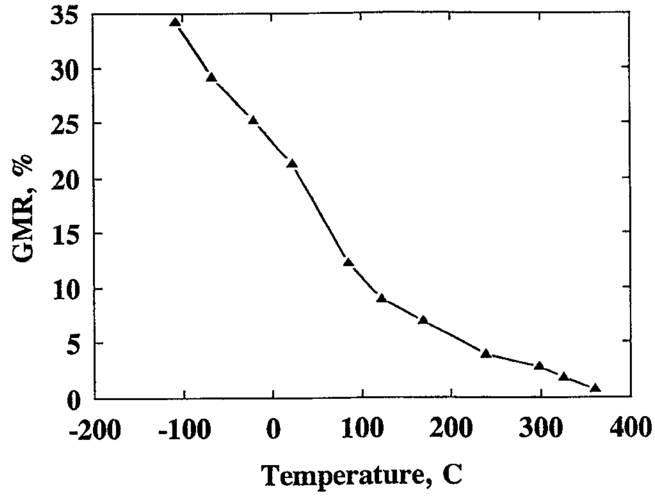

FIG. 3. The temperature dependence of the GMR for a typical symmetric spin valve. After making measurements above ~300 °C, the decline in the GMR is not reversible upon cooling.

B. Temperature dependence

Potentially even larger GMR values may be close at hand from structures such as those studied here. Figure 3 presents the temperature dependence of the GMR of a typical sample. The decrease in GMR with increasing temperature is unusually steep for a GMR structure.[11] The corresponding loops show that with increasing temperature the coercivity of the top and bottom Co layers decreases markedly. [The contributions of the top and bottom Co layers are not separately resolved in Fig. 2(a) but below room temperature they are.] Since the coercivity of the top Co layer is somewhat smaller than that of the bottom Co layer, it is likely that the decrease in GMR occurs because, with increasing temperature, some overlap occurs between the loops of the top and center Co layers. This situation would mean that the center Co layer is never completely antiparallel to the top Co layer (except well below room temperature where the loops do not overlap). Clearly, it would be desirable to increase the coercivity of the top Co layer at and above room temperature.

We made many modifications to the basic film structure and to the deposition process to try to increase the coercivity of the top Co layer but none succeeded. If we had succeeded and a more typical temperature dependence had been achieved of the GMR (e.g., like that of Ref. 6), then the 34% GMR which we found at −108 °C should have produced ~27% GMR at room temperature. Further work on this point would clearly be worthwhile.

Pinning of the top Co layer can be achieved by the use of 10 mm FeMn instead of NiO; however the current shunted by the conducting FeMn (and a likely reduction in any specular scattering) limit the GMR to 18% in the high-field loop. A further disadvantage of FeMn (for device applications) is its tendency to oxidize (a disadvantage not found in NiO).

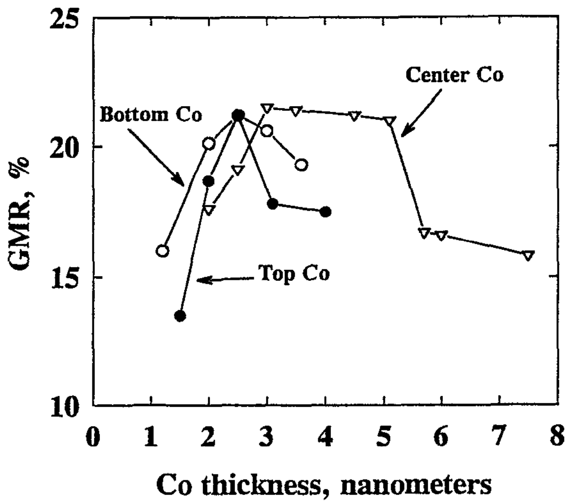

FIG. 4. The dependence of GMR on the Co layer thicknesses. The plotted thicknesses represent deviations from the standard values of 2.5 nm Co/1.8 nm Cu/4.5 nm Co/1.8 nm Cu/2.5 nm Co.

The data of Fig. 3 are reversible for brief heating (~1 min) up to about 300 °C. Above that temperature, irreversible loss of GMR occurs. For example, after the 360 °C data of Fig. 3 were taken, the sample exhibited a GMR of 10% at room temperature. We found that other spin valve structures, which contained $Ni_{80}Fe_{20}$, showed severe losses of GMR after heating to only 225 °C. Thus, a key to survivability at high annealing temperature seems to be avoidance of $Ni_{80}Fe_{20}$.

C. Dependence on Co thicknesses

The dependence of the GMR in the symmetric spin valve structures on the thicknesses of the Co layers is very interesting. Figure 4 shows variations of the GMR as the thickness of each Co layer was varied systematically from the standard values of 2.5 nm Co/1.8 nm Cu/4.5 nm Co/1.8 nm Cu/2.5 nm Co. The GMR peaks sharply when the thicknesses of both the top and bottom Co layers are 2.5 nm. In contrast, the GMR has a broad maximum when the center Co thickness is 3–5 nm. The shape of the GMR loops for the samples on which Fig. 4 is based are all rather similar, suggesting that the degree of antiferromagnetic alignment at the resistance maxima is not what is being optimized in Fig. 4. Instead, it seems the distance the electrons travel through Co is being optimized.

In the simplest model one might expect that the GMR would optimize for Co layers of the same thickness, corresponding to a compromise between two opposing influences. One influence, which favors thicker Co, is the discrimination of spin-allowed electron conduction from spin-forbidden conduction. (Gurney *et al.*,[12] report MFP values in Co of 5.5 nm for spin-up electrons and ≤0.6 nm for spin-down electrons.) The other influence, which favors thinner Co, is the shunting or dilution effect of current that travels within a given Co layer.

Perhaps the simplest explanation for the optimum thickness of the center Co layer being greater than that for the top and bottom layers would be that some specular scattering occurs at the Co/NiO interfaces. Although the concept of specular scattering at surfaces and interfaces has a long[13–17] and controversial[17] history, such scattering does occur in some[18,19] systems. If specular scattering occurred for all electrons in our symmetric spin valves, a simple model would predict that the top and bottom Co should be half as thick as the center layer so that their *effective* thicknesses would be the same as that of the center layer. Since the optimum thickness of the center Co layer in Fig. 4 is somewhat less than twice that of the top and bottom Co layers, it is possible that only some fraction of the electrons scatter specularly. However, it should be emphasized that Fig. 4 is not proof of specular scattering; it is only suggestive. Furthermore, no simple explanation is apparent for the differing widths of the three plots in Fig. 4. Clearly, some additional factors not yet identified are involved here. Nevertheless, if specular scattering does occur in our samples it should certainly contribute to increased MFPs of the spin-allowed paths and thereby increase the GMR.

The drop in GMR in Fig. 4 around 5.5 nm for the center Co layer correlates with a marked increase in the roughness observed by STM. When the deposition is terminated after the deposition of the center Co layer, average local roughnesses (from the local maximum in the center of a grain to the average minimum in the adjacent valleys) of 0.7 and 1.3 nm were found for center Co thicknesses of 4.5 and 6.5 nm, respectively. A possible explanation for this near doubling of the roughness is that a structural transformation (such as the onset of misfit dislocations) occurs at a center Co thickness of around 5.5 nm. Another possible explanation might be an fcc-to-hcp transition, but we have no additional structural information to confirm either of these ideas.

D. Dependence on Cu thicknesses

The dependence of the GMR on Cu thickness is quite different from that of Co and much like the results reported in Ref. 1. The GMR is at a maximum for 1.8 nm of Cu. Below a Cu thickness of 1.7 nm, the GMR falls abruptly to zero. Above 1.8 nm the GMR declines gradually. The behavior below 1.8 nm thickness of Cu occurs because the coupling field rises extremely steeply (values over 10 mT or 100 Oe are found at 1.7 nm), and this leads to a drop in the GMR as the loops overlap.

In a narrow Cu thickness range around 1.9 nm, the coupling field reverses sign and is as much as 2 mT (20 Oe) antiferromagnetic with respect to the top and bottom Co layers. (The magnitude of the coupling is the offset of the center of the low field from zero field. See Fig. 1(b). The sign of the coupling is determined by the direction of the offset with ferromagnetic meaning that the center Co layer experiences an effective field tending to align it parallel to the top and bottom Co layers.) For Cu thicknesses from ~2 to ~2.5 nm, the coupling field is ferromagnetic and drops from ~2 mT (20 Oe) to below 1 mT (10 Oe). A field of 1 mT (10 Oe) corresponds to an energy of 5×10^{-3} erg/cm^2. These results suggest that this coupling (between the center Co layer and the other two Co layers) is partly a result of the well-known oscillatory effect,[6] due to quantum well states in the Cu and partly a result of topological,[20] magnetostatic coupling due to Co/Cu interfacial roughness. Our STM results indicate that this roughness (gentle undulations) has a mean value of ~0.7 nm, which is consistent with ferromagnetic coupling fields on the order of ~0.5–2 mT (5–20 Oe).[20] Therefore, both of the two effects just mentioned probably contribute to the coupling.

IV. CONCLUSIONS

In conclusion, we have developed a symmetric spin valve structure which exhibits an unusually large GMR. The coercivity and the coupling fields are not prohibitively large for device applications. The avoidance of $Ni_{80}Fe_{20}$ in this structure improves its survivability during annealing at ~300 °C. The Co thickness dependence of the GMR suggests that specular scattering of electrons at the Co/NiO interfaces is a possibility.

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