Oxygen as a surfactant in the growth of giant magnetoresistance spin valves

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We have found a novel method for increasing the giant magnetoresistance (GMR) of Co/Cu spin valves with the use of oxygen. Surprisingly, spin valves with the largest GMR are not produced in the best vacuum. Introducing 5×10^{-9} Torr (7×10^{-7} Pa) into our ultrahigh vacuum deposition chamber during spin-valve growth increases the GMR, decreases the ferromagnetic coupling between magnetic layers, and decreases the sheet resistance of the spin valves. It appears that the oxygen may act as a surfactant during film growth to suppress defects and to create a surface which scatters electrons more specularly. Using this technique, bottom spin valves and symmetric spin valves with GMR values of 19.0% and 24.8%, respectively, have been produced. These are the largest values ever reported for such structures. *© 1997 American Institute of Physics.* [S0021-8979(97)00924-9]

I. INTRODUCTION

A key goal of research in the field of giant magnetoresistance (GMR) is to retain large GMR values while limiting the magnetic saturation field or the switching field to levels compatible with practical applications.[1] In general, his limitation means a switching field below ~5 mT, i.e., 50 Oe.

The largest GMR value ever recorded at room temperature is 110% (for a CoCu superlattice).[2] Unfortunately, the saturation field in this case was rather large (~3 T, i.e., 30 kOe). Nevertheless, the achievement of such large GMR values in superlattices offers the hope that significantly improved GMR values may be achievable in simple (one or two Cu layers) spin valves, which have the advantage that they generally exhibit far lower saturation fields.

In our pursuit of larger GMR values we found recently[3] that improving the base pressure of our magnetron-sputtering deposition system produced larger GMR values. It appeared that the most likely cause was a reduction in the partial pressure of water vapor, $p(H_2O)$. The largest GMR values (over 23% in symmetry spin valves) were obtained at the lowest achievable $p(H_2O)$, $\sim10^{-9}$ Torr ($\sim10^{-7}$ Pa). However, soon after publishing these results[3] two very important facts came to light. First, a further reduction in $p(H_2O)$ to $\sim10^{-10}$ Torr produced sharply lower GMR values (~17% for symmetric spin valves). Second, it became apparent that $p(H_2O)$ was not the direct cause of the differing GMR values. The $p(H_2O)$ was only an indirect indicator to the true cause, which appears to be contamination of the growing film by carbon and oxygen atoms, as seen by x-ray photoelectron spectroscopy (XPS) measurements of the surface after deposition. These atoms are presumed to be knocked off the chamber walls by the magnetron plasma. Apparently when $p(H_2O)$ is high, there is more contamination on the chamber walls.

Ironically, if this contamination is at just the right level and of the right type, it significantly increases the GMR. It appears that oxygen is primarily responsible for the GMR increase by acting as a surfactant during film growth, although all the details are not yet clear. The main purpose of the present article is to explain this complicated and surprising effect and to show how it may be utilized by the deliberate introduction of O_2 during spin valve growth.

II. EXPERIMENT

The NiO substrates used in this work were polycrystalline films ~50 nm thick, deposited on 3 in. Si wafers by reactive magnetron sputtering at the University of California at San Diego and University of Minnesota. At the National Institute of Standards and Technology, the wafers were cleaved into ~1 cm^2 squares, cleaned ultrasonically in a detergent solution, rinsed in distilled water, blown dry, and installed in the deposition chamber.

The metal films were deposited at room temperature (RT) by dc magnetron sputtering in 2 mTorr (0.27 Pa) Ar at a rate of ~0.1 nm/s. For symmetric spin valves, the top NiO layer was deposited by sputtering a Ni target with an 85/15 mixture of Ar/ O_2.

The magnetoresistance (MR) measurements were made at RT using the four-point probe dc mode in a vacuum chamber connected to the deposition chamber.

Some additional experimental details may be found in Refs. 3 and 4.

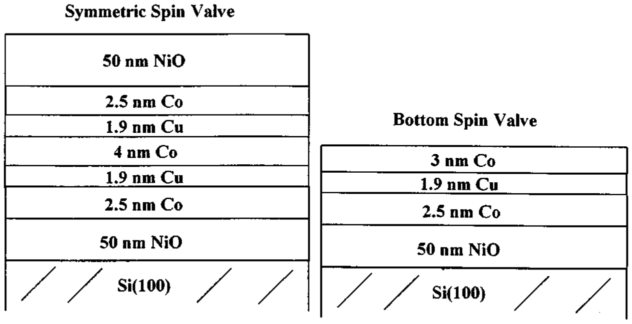

FIG. 1. An illustration of the standard spin valve structures that are the basis for the present investigations. The terms symmetric and bottom refer to the location of the NiO pinning layers.

III. RESULTS AND DISCUSSION

The improved vacuum of the present work was achieved partly by baking the deposition chamber longer and at higher temperatures than before and partly by running the magnetron sputtering guns longer prior to spin valve growth to coat the interior walls of the chamber more effectively with fresh metal films. A base pressure of 5×10^{-10} Torr (7×10^{-8} Pa), of which 90% is H_2, is achievable in this manner. In contrast, the base pressure of an unbaked chamber is $\sim10^{-8}$ Torr ($\sim10^{-6}$ Pa), of which 90% is H_2, after depositing a few spin valve films. Unfortunately, pressure is a poor indicator of the level of cleanliness of the walls of the chamber. However, it is very clear from the present work that the level and type of contamination on the walls have a profound influence on spin valve properties.

The presence of contamination on the surface of a spin valve is directly observable *in situ* by XPS in an adjacent vacuum chamber. Normally, the only contaminants observed are carbon and oxygen, although other species could be present at levels as high as a few percent of a monolayer (ML) and go undetected by XPS. The extent of carbon and oxygen contamination can be estimated on the basis of relative photoelectron cross-sections,[5] measured O 1*s* intensities from NiO, and the photoelectron attenuation lengths in NiO.[6] Under the cleanest possible conditions we find that, immediately after deposition, bottom spin valves exhibit an oxygen intensity equivalent to ~0.1 ML (ML is defined here as 1.6×10^{15} atoms/cm^2) and carbon is not detectable. However, we found that such clean conditions consistently yielded spin valves with lower GMR values than less clean conditions (such as an unbaked chamber) for which we observe ~0.5 ML oxygen and ~0.1 ML carbon by XPS for bottom spin valves. The oxygen seems to be present mostly as adsorbed atoms on the surface, but the observed carbon could be both at the surface and in the bulk. Symmetric spin valves show similar levels of contamination if growth is interrupted for examination by XPS. The typical structures of these types of spin valves are illustrated in Fig. 1.

A. The role of background gases

In response to the very surprising result that the cleanest conditions yielded reduced GMR, we attempted to clarify the role of contaminants by achieving the cleanest possible conditions and then deliberately introducing gases such as H_2, CO, CH_4, N_2, H_2O, and O_2 into the chamber during spin valve growth.

A preview of our interpretation of the results may be helpful to the reader at this point. Dissociation of gas phase molecules by the sputtering plasma is not an important source of sample contamination under typical deposition conditions. However, energetic electrons, ions, and atoms from the plasma knock contaminants off the walls of the chamber and some of these adsorb on the growing sample surface. This contamination can be beneficial in some cases, and it appears that a particular coverage of oxygen on the surface during growth leads to improved properties for the spin valves.

1. Methane and nitrogen

Since CH_4 and N_2 do not react directly with Co or Cu surfaces but must first be dissociated by the magnetron plasma, their introduction during growth provided an excellent test of how efficiently the plasma dissociates molecules. For either gas, the partial pressure had to be increased to $\sim1\times10^{-5}$ Torr ($\sim10^{-3}$ Pa) to produce a measurable decrease in GMR. This decrease correlated with the appearance of carbon (for the case of CH_4) and nitrogen (in the case of N_2) in XPS data of the spin valve surface. Since electron-induced dissociation cross-sections do not vary greatly among the common gases,[7] these results suggest that the magnetron plasma is not particularly efficient in dissociating the gases found in deposition chambers. Thus, we may draw the conclusion that under vacuum conditions commonly found in magnetron-sputtering deposition (e.g., base pressures $<10^{-7}$ Torr or $<10^{-5}$ Pa) contamination of the growing samples by the dissociation of background gases by the magnetron plasma is not important.

2. Water vapor

Deeper insight into what is occurring is provided by the case of H_2O. Like CH_4 and N_2, H_2O does not react very readily directly with Co or Cu surfaces.[8] The available evidence suggests that at room temperature in a vacuum chamber H_2O does not adsorb at all on Co or Cu surfaces consisting of the low-index crystal planes although a slight tendency to dissociate into adsorbed OH and H species may occur on high-index planes (atomically rough).[8] However, in spite of this low reactivity, the introduction of only 10^{-7} Torr (10^{-5} Pa) H_2O during growth produces a factor-of-two reduction in GMR.[3] Since neither dissociation by the plasma nor direct reaction with the surface are the mechanism, what appears to happen is that the H_2O adsorbs on and saturates the walls of the chamber (H_2O is well known for dissociating into OH and H on the iron oxide walls of vacuum systems[8]), and the energetic impact of atoms, ions, and electrons (produced by the magnetron plasma) on the chamber walls liberates dissociated fragments of H_2O, and some of these adsorb on the growing spin valve.

This conclusion that the walls are primarily responsible for the contamination should not be surprising since the chamber walls have the potential to hold far more H_2O than is present in the gas phase. Note that 1 ML corresponds to $\sim 10^{15}$ molecules/cm^2, whereas 10^{-7} Torr corresponds to only 3×10^9 molecules/cm ^{3}, so that a typical vacuum chamber at 10^{-7} Torr (10^{-5} Pa) might contain $\sim 10^{15}$ molecules in the gas phase and $\sim 10^{20}$ molecules adsorbed on the walls. Therefore, energetic atoms, ions, and electrons emitted by the magnetron plasma should be far more likely to impact an HO molecule on the walls than an H_2O molecule in the gas phase.

This effect of enhanced concentration of molecules on the chamber walls does not occur for CH_4 and N_2 because they are chemically much more inert and have little, if any, tendency to adsorb on the chamber walls.

3. Hydrogen

Molecular hydrogen readily adsorbs on Co but not on Cu (at 300 K). If the H_2 partial pressure is less than $\sim 10^{-5}$ Torr ($\sim 10^{-3}$ Pa), adsorbed hydrogen atoms on Co (and the growing Co surface must be saturated with hydrogen atoms whenever the H_2 partial pressure is $> \sim 10^{-7}$ Torr or $\sim 10^{-5}$ Pa) have no significant effect on spin valve growth. Based on earlier studies,[9] it seems very likely that the adsorbed hydrogen atoms are not extensively incorporated in the growing film (except possibly at grain boundaries), but instead, and because they are highly mobile, they float out to the surface.

A different effect is found for partial pressures of H_2 around 10^{-5} Torr (10^{-3} Pa). At such pressures, the effect of H_2 is very similar to that of oxygen (and indeed XPS confirms an increased coverage of oxygen on the spin valve surface). The most plausible interpretation is that the hydrogen atoms and ions produced in the plasma must be reacting at the walls of the chamber to liberate oxygen atoms or oxygen-containing molecular fragments which then adsorb on the growing spin valve and behave in a manner much like the adsorbed oxygen resulting from the presence of O_2.

4. Carbon monoxide

Carbon monoxide also readily adsorbs on Co (but not on Cu) at 300 K. It is not clear how much dissociation of CO occurs on Co, but some may occur. In any case, no reduction in GMR was observed for partial pressures of CO, deliberately introduced during spin valve growth, below 10^{-6} Torr (10^{-4} Pa). Only at 10^{-5} Torr (10^{-3} Pa) did a substantial reduction in GMR occur. Perhaps the Co does not dissociate on the surface, and merely floats out on an otherwise unperturbed growing film. In any case, it appears that the background pressure of CO in typical deposition chambers is much too small to impair the properties of GMR spin valves.

5. Carbon

While not usually thought of as a background gas in vacuum chambers, carbon is very important because hydrocarbons adsorbed on the walls of the chamber have a tendency to be knocked off by the energetic electrons, atoms, and ions emitted by the magnetron discharge. Hydrocarbon fragments are very reactive and very likely dissociate on the surface of a growing spin valve. We attempted to mimic this effect by the deliberate introduction of atomic carbon during spin valve growth by co-deposition using a carbon target in one of the magnetron guns.

We found that carbon reduces the GMR of spin valves severely. Even a few atomic percent carbon (based on sputtering rates) incorporated in a spin valve reduces the GMR by more than half. This effect appears to correlate with the fact that carbon bonds very strongly to the growing surface and has little tendency to float out to the surface of the growing film. This tendency of carbon to incorporate in growing films has been noted earlier.[9]

The incorporation of carbon also tends to reduce the coercivity of the unpinned Co film and increase the resistivity of the spin valve. This coercivity reduction suggests that carbon reduces the grain size in the film. The coercivity is lowered by the presence of a few atomic percent of carbon, typically from 5 mT (1=10 Oe) to 3 mT. A reduction in grain size will often reduce coercivity,[10] and carbon would be expected to reduce grain size because it is well known for reducing the diffusion rate of the metal atoms on metal surfaces.[11]

Furthermore, the resistivity of the spin valve increases by ~40% upon incorporation of even 1 at.% carbon (e.g., from 25 to 35 $\mu\Omega$ cm for a symmetric spin valve), and this increase is too large to be accounted for by impurity scattering by carbon. Impurities typically only contribute $\sim 1\times 10^{-6}$ Ω cm/at. %[12] too small to explain our data. This result also suggests that carbon contamination leads to smaller grain size since diffuse scattering at the grain boundaries is more likely to be responsible for most of the increase in resistivity.

6. Oxygen

The discovery of the importance of oxygen in spin valve growth was made during our earlier work on the use of Pb as a surfactant to reduce the ferromagnetic coupling (H_f) between Co layers across the Cu spacer layer in spin valves.[13] This magnetic coupling is generally believed[1] to have two sources, one a magnetostatic effect due to nonflat interfaces often called orange-peak coupling and the other an electronic coupling mediated by exchange which oscillates from ferromagnetic and antiferromagnetic as a function of Cu spacer layer thickness. As a consequence of the oscillatory effect H_f can have negative values (antiferromagnetic).

We found by XPS that under conditions which yielded surfaces contaminated by 0.5 ML or more of oxygen atoms, the use of Pb did not reduce the coupling, and indeed under these conditions H_f was already low as if Pb had been used. These results suggested that oxygen was acting as a surfactant during growth to improve the structure of the spin valves and led to the investigations reported here.

Our initial approach was to use oxygen in much the same manner as Pb. Spin valve growth was interrupted after the deposition of the Cu film and the surface exposed to $\sim 10^{-4}$ Torr·s (10^{-2} Ps·s)O_2 to achieve an oxygen atom coverage of ~0.6 ML, after which growth of the sample was completed. The oxygen produced dramatic effects, as may be seen by comparing Figs. 2(b) and 2(c) for bottom spin valves. The reduction in coupling at a Cu thickness of 2 nm

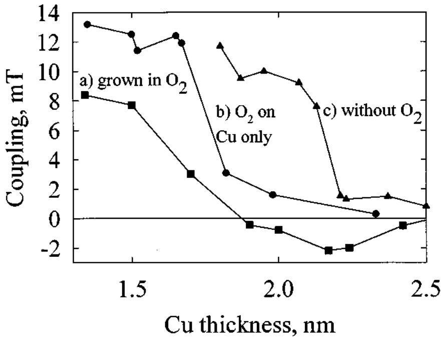

FIG. 2. The value of the coupling field (H_f) for bottom spin valves deposited (a) in 5×10^{-9} Torr O$_2$, (b) with the top of the Cu film exposed to O$_2$, and (c) without the use of O$_2$. (Note: 1 mT=10 Oe).

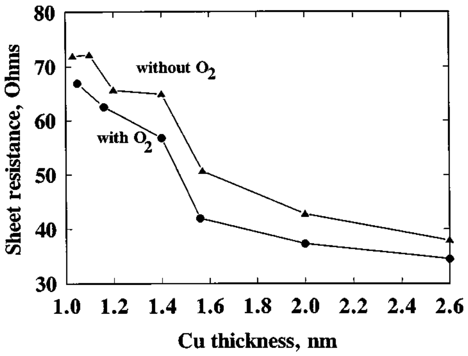

FIG. 3. The sheet resistance of bottom spin valves with and without exposing the Cu surface to oxygen as a function of Cu thickness.

was very similar to our results for the use of 1 ML Pb. However, the effect is not as simple as a mere reduction in H_f. As Figs. 2(b) and 2(c) demonstrate, the use of oxygen appears to shift the plot of H_f vs Cu thickness by ~0.4 nm. The steep drop apparent in Figs. 2(b) and 2(c) as a function of Cu thickness appears to be due to the oscillatory exchange coupling effect, which is well known for producing such a drop at approximately this Cu thickness, particularly for Cu/Co superlattices.[1] None of the samples in this series actually exhibited antiferromagnetic coupling. It may well be that the orange-peal coupling makes a ferromagnetic contribution which is too strong for the oscillatory effect to overcome. Evidence for this interpretation, to be discussed below, is found in the data of Fig. 2(a) for samples grown in 5×10^{-9} Torr (7×10^{-7} Pa) O$_2$ for which the negative values of the coupling, an indication of the oscillatory effect, are observed. It appears likely that growth in oxygen tends to suppress the orange-peal effect.

The most likely consequence of the use of covering the Cu film with 0.6 ML of oxygen, as in Fig. 2(b), is the suppression of interdiffusion at the Cu/Co interface when Co is deposited on the oxygen-covered Cu surface. This effect is well known in single crystal studies of epitaxial growth in systems similar to these.[9,14]

The cause of the shift of 0.4 nm corresponds to ~2 ML, is not clear, but it is plausible that the phase of the oscillations will change in the presence of interdiffusion. However, a concurrent change in the maximum strength of coupling would also have been expected but is not apparent in the data. Thus, the origin of the shift remains unresolved.

If the use of oxygen in this manner is indeed suppressing interdiffusion, it might be expected that the films would exhibit a lower resistivity since randomly intermixed alloys generally have quite high resistivities. Figure 3 indicates just this effect. The sheet resistance of our spin valves is systematically lower when oxygen is used.

It may seem surprising that the deliberate adsorption of an impurity such as oxygen on the very sensitive interior of a spin valve could decrease the resistivity. It might have been thought that the resistivity would increase since impurities tend to scatter conduction electrons diffusely. However, the crucial fact here is that oxygen is highly mobile and has a strong tendency to float out to the surface during subsequent metal deposition.[9]

There is one important point to emphasize about adsorbates that float out to the surface during film deposition. The extent to which they float out correlates approximately with the strength of their bond to the surface.[9] Adsorbates such as carbon, which bond very strongly to the surface, have little mobility and little tendency to float out to the surface during deposition, while those which bond relatively weakly, such as hydrogen atoms, are highly mobile and float out to the surface very efficiently.[9] Oxygen is an intermediate case. In the present work, it will float out to the extent that, if 0.6 ML of oxygen is present on a Co surface (polycrystalline), approximately 2 nm of additional Co must be deposited to reduce the oxygen coverage to 0.3 ML. Since oxygen atoms are quite mobile on Co surfaces, it is likely that the oxygen which does not float out is trapped in grain boundaries. The lattice strain associated with oxygen as a substitutional impurity inside a grain makes it unlikely that oxygen atoms simply get buried as substitutional impurities to any large extent.

Additional evidence against oxygen atoms as substitutional impurities comes from the reduction in resistivity observed for spin valves deposited in the presence of 5×10^{-9} Torr (7×10^{-7} Pa) O$_2$. The sheet resistance is consistently 10%–20% lower than for spin valves deposited in the cleanest possible conditions. Substitutional oxygen impurities would almost certainly increase the resistivity. Since grain boundaries probably already have a strong tendency to scatter electrons diffusely, the addition of oxygen atoms to grain boundaries may make little difference.

Perhaps the most important result of the present investigations has been the discovery that the best spin valves are produced by deposition in a continuous background of 5×10^{-9} Torr (7×10^{-7} Pa) O$_2$. Figures 4 and 5 illustrate the results for symmetric spin valves deposited, respectively, in the cleanest possible conditions and in the cleanest possible conditions with the addition of 5×10^{-9} Torr O$_2$. Unfortunately, it is difficult to quantify the cleanest possible conditions since the base pressure appears to be only an indirect measure of what gets knocked off the chamber walls by the magnetron plasma. Perhaps the best measure is the

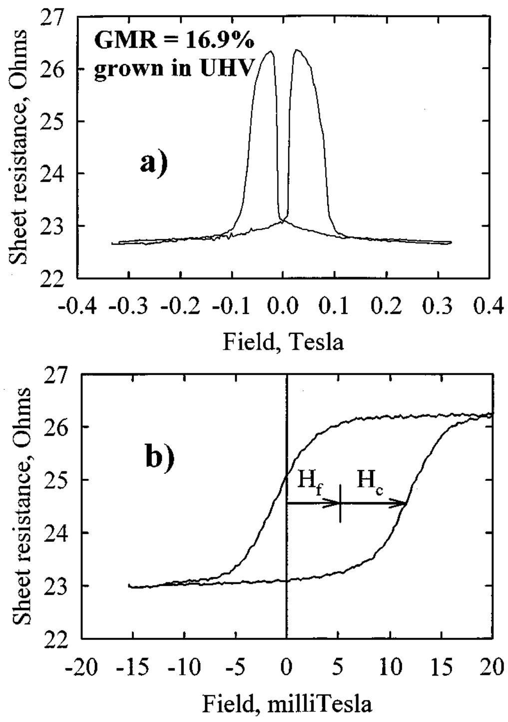

FIG. 4. Magnetoresistance loops for a symmetric spin valve grown in the cleanest conditions achievable for (a) high fields and (b) low fields, recorded after saturation in a negative field. A vertical line in (b) marks the center of the loop, which is shifted from zero field due to the coupling (H_f) between Co films. In this sample H_f=5.2 mT (52 Oe) and H_c=6.4 mT (64 Oe).

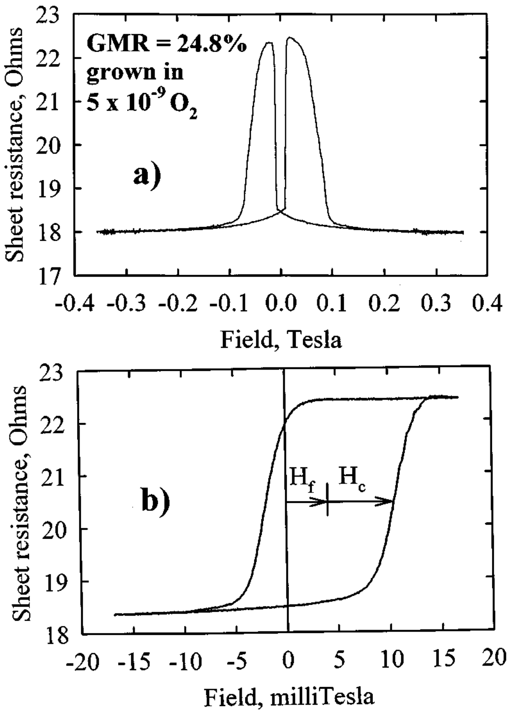

FIG. 5. Magnetoresistance loops for a symmetric spin valve grown in the cleanest conditions achievable but with 5×10^{-9} Torr (7×10^{-7} Pa) O_2 present for (a) high fields and (b) low fields, recorded after saturation in a negative field. A vertical line in (b) marks the center of the loop, which is shifted from zero field due to the coupling (H_f) between Co films. In this sample H_f=4.1 mT (41 Oe) and H_c=6.2 mT (62 Oe).

contamination observed by XPS on the spin valve surface, as discussed above.

Under the cleanest conditions we can achieve, the GMR values we obtain for symmetric spin valves and bottom spin valves are generally about 17% and 14%, respectively. The largest values we achieved *before* experimenting with the deliberate introduction of O_2 were 23.4% for symmetric spin valves and 16% for bottom spin valves. However, in both cases, these record-setting values were achieved in an unbaked deposition chamber (base pressure $\sim10^{-8}$ Torr or $\sim10^{-6}$ Pa), and it now appears that some of the oxygen impurities knocked off the walls adsorbed on the growing spin valves and improved their properties.

The introduction of 5×10^{-9} Torr of O_2 during growth has allowed us to reach new record-setting values of the GMR for both symmetric and bottom spin valves. For symmetric spin valves, we have achieved 24.8% (as illustrated in Fig. 5) and for bottom spin valves we have achieved 18%.

The effect of oxygen is very similar for spin valves based on pure $Ni_{80}Fe_{20}$ rather than on pure Co. The largest GMR again results from an O_2 pressure of 5×10^{-9} Torr (7×10^{-7} Pa). However, the GMR is always much smaller when $Ni_{80}Fe_{20}$ replaced Co. In bottom spin valves, 6.5% was the largest GMR we achieved using pure $Ni_{80}Fe_{20}$ for both magnetic layers and 8.7% when one layer was pure $Ni_{80}Fe_{20}$ and the other pure Co.

The beneficial effect of O_2 exists in a rather narrow window around 5×10^{-9} Torr. Figure 6 illustrates this point for bottom spin valves. When the O_2 pressure is increased to only 1×10^{-8} Torr (1.3×10^{-6} Pa), all GMR gain due to O_2 is lost. At O_2 pressures higher than this, the fall-off in GMR is rapid (e.g., 5% GMR at 5×10^{-8} Torr O_2).

The arrows and triangles in Fig. 6 illustrate a very interesting and important point about bottom spin valves. The results demonstrate the drop in GMR which occurs when 2 ML Ta is deposited on the surface. We found in earlier work that an important requirement for achieving the highest possible GMR in spin valves is having surfaces that reflect conduction electrons specularly.[15] The deposition of 2 ML Ta was found to be an ideal method for suppressing specular scattering due to the extensive interdiffusion of Ta at the

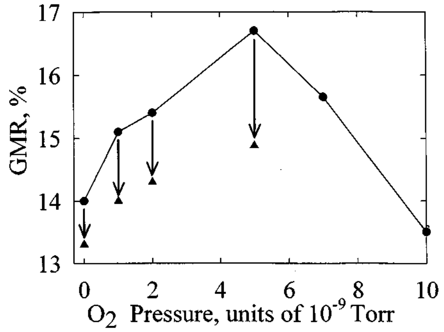

FIG. 6. A plot of the GMR of bottom spin valves as a function of the pressure of O_2 in which they are grown (solid circles). The arrows indicate the drop in GMR which occurs when 2 ML Ta is deposited to suppress the specular scattering at the surface (solid triangles). Note that 1×10^{-9} Torr equals 1.3×10^{-7} Pa.

surface. The increasing length of the arrows with increasing pressure indicates that growth in the presence of oxygen increases the extent of specular scattering. For pressures above 5×10^{-9} Torr (7×10^{-7} Pa) O_2, the degree of specular scattering falls rapidly, and the data point at 1×10^{-8} Torr actually showed a very slight increase in GMR upon Ta deposition.

The increase in specular electron scattering at the surface of spin valves deposited in 5×10^{-9} Torr (7×10^{-7} Pa)O_2 suggests that the surface of these films must be smoother or more well ordered that those deposited without O_2 present. The explanation for this effect is probably that oxygen acts to lower the so-called Schwoebel barrier for metal atoms to descend to a lower terrace. This effect is well established as a mechanism by which a surfactant can give a more layer-by-layer growth mode and thus a flatter surface.[16]

An additional insight may be derived from the triangles in Fig. 6. The triangles exhibit an increasing GMR with increasing O_2 pressure during growth. However, for the triangles specular scattering was suppressed by the deposition of Ta. Thus, an additional effect seems to be increasing the GMR. The most likely explanation is that oxygen on the growing surface is suppressing the interdiffusion at the interfaces, as discussed above.

The data of Fig. 2(a) provide additional support for the idea that growth in oxygen reduces structural imperfections in the films. The oscillatory coupling is clearly observed in Fig. 2(a). In general, oscillatory coupling is degraded by structural imperfections.[1] It is often not observed at all for simple (one Cu film) spin valves.[1] Superlattices, which exhibit a higher degree of crystalline order than simple spin valves (especially, larger grain size), more commonly exhibit oscillatory coupling than simple spin valves. Therefore, the observation of negative (antiferromagnetic) coupling values in Fig. 2(a) suggest a lower level of defects when the spin valves are grown in oxygen.

One surprising result that is not yet understood about the use of 5×10^{-9} Torr (7×10^{-7} Pa) O_2 is that, for the best GMR it must be used continuously during spin valve growth. It is especially important for the early and middle stages of growth. It is less important near the end of the deposition of the last Co layer, but still the best results come from continuous use. (In contrast, adsorbing oxygen only on the Cu surface, as in Figs. 2 and 3, did nothing to improve the GMR.) It seems that specular surfaces and sharp interfaces are only part of the story. Something in the early stages of nucleation and growth must also be involved. Perhaps adsorbed oxygen suppresses the tendency of Co to bead-up on the NiO substrate, to which it bonds weakly, by lowering the surface free energy. Improved wetting of the NiO by Co might increase grain size and thereby lengthen electron mean free paths.

If the deposition of Ta suppresses specular scattering, an increase in resistivity would be expected. Just such an effect is observed, and Fig. 7 presents the data. The lower right corner presents the data on samples for which oxygen was used (at various pressures) to increase the GMR. Decreases in GMR always correlate with increases in resistance. In Fig. 7, ''ΔGMR'' is an absolute difference (e.g., 14%–16% $=-2\%$), whilc ''resistance change'' is a relative increase in sheet resistance (e.g., 35 Ω/□ to 38.5 Ω/□ is a 10% increase). These data in the lower right corner of Fig. 7 are not surprising results.

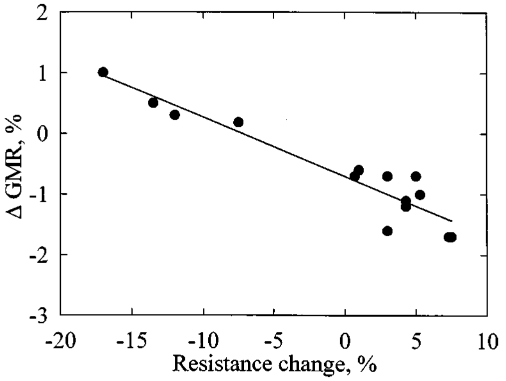

FIG. 7. A plot of the change in GMR as a function of the change in resistance of bottom spin valves (grown in various pressures of O_2) when 2 ML Ta is deposited.

The data in the upper left corner of Fig. 7 are perhaps more interesting. These data correspond to samples in which the oxygen pressure during growth was too large and the GMR was thereby reduced. For such samples, the deposition of Ta increased the GMR. It seems likely that excessive pressures of oxygen leave the top Co surface partially oxidized and the Ta acts as a reducing agent taking oxygen away from Co and, in a sense, repairing the surface. This interpretation is plausible since the heat of oxidation is much larger for Ta than for Co.

As a final note on growth of bottom spin valves in oxygen, Fig. 8 presents the sheet resistance as a function of O_2 pressure during growth. As in Fig. 6, it is clear that the beneficial effects of O_2 lie in a rather narrow window of O_2 pressure.

B. Effects of post-deposition processing of spin valves

In an earlier paper,[4] we reported that after optimizing the layer thicknesses of a bottom spin valve and obtaining a GMR of 16%, an increase to 17% could be obtained by exposing the surface to $\sim10^{-2}$ Torr s ($\sim$1 Pa s) of O_2. This treatment produces about 0.3–0.4 nm of CoO at the surface

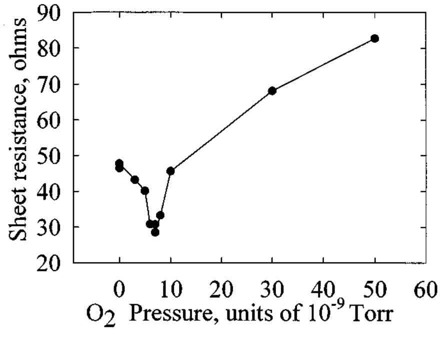

FIG. 8. A plot of the sheet resistance of bottom spin valves as a function of the pressure of O_2 in which they are grown. Note that 1×10^{-9} Torr equals $1.3\times'10^{-7}$ Pa.

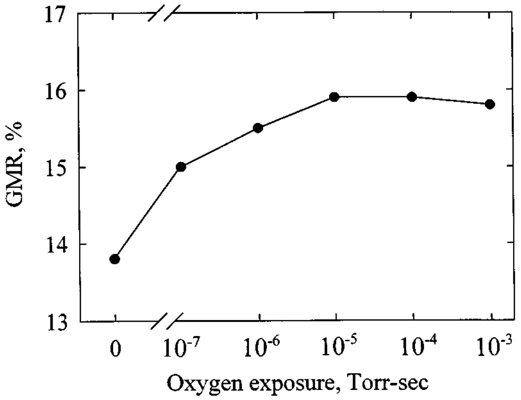

FIG. 9. A plot of the GMR of a bottom spin valve as a function of the exposure to O_2 after deposition. Note that 1×10^{-7} Torr·s equals 1.3×10^{-5} Pa·s.

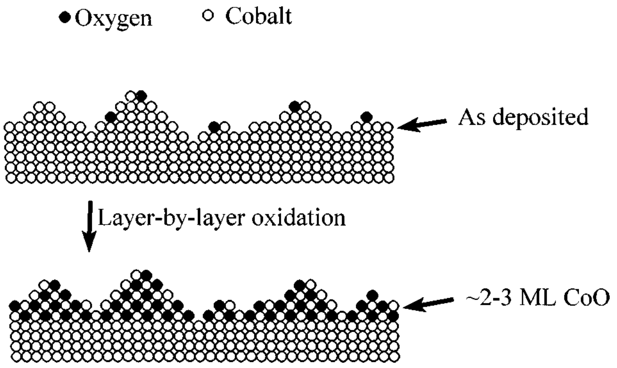

FIG. 10. A proposed model for the surface oxidation process that may explain data of Fig. 9.

(~2 ML). We suggested that the increase of 1% (absolute) in GMR might be explained if the extent of specular electron scattering at the Co/CoO interface is larger than at the Co/vacuum interface. Specular electron scattering is favored by a smooth, well-ordered, and atomically sharp interface. If the Co/vacuum interface is somewhat rough and the high points oxidize more readily than the low points (due to attack from the sides), one could easily imaging the Co/CoO interface to be very smooth and sharp.

In more recent work on bottom spin valves, we have established that an increase of about 1%–2% in GMR (absolute, i.e., ΔGMR) upon exposure to O_2 is quite reproducible even for spin valves deposited in 5×10^{-9} Torr (7×10^{-7} Pa) O_2. This is particularly true for those spin valves which do not exhibit a particularly large GMR as deposited. Figure 9 presents an example of this. This particular spin valve happened to have a GMR of only 13.8% as deposited (even though it was grown in 5×10^{-9} Torr O_2.) Upon exposure to O_2 the GMR increases 2% (absolute). Spin valves which have the highest GMR, as deposited, tend to show smaller increases, but even for the best samples there is almost always some increase in GMR upon O_2 exposure.

The reason for this effect is not clear. It appears that sometimes, for unknown reasons, growth in 5×10^{-9} Torr O_2 is not particularly effective, resulting in an imperfect surface, and subsequent exposure to O_2 can somehow repair the deficiency. Figure 10 presents one suggestion for what might be occurring. If the surface—as deposited—is not very smooth, it is likely that the oxidation of the surface will begin at high points or protrusions and progress downwards (protrusions should oxidize more readily). Many surfaces oxidize very quickly to a depth of a few ML, after which the oxidation slows down dramatically. The suggestion of Fig. 10 is that oxidizing the high points leaves a metal/insulator interface (CoO/Co) that is more flat than the Co/vacuum interface, and this effect may increase specular electron scattering. The process (suggested in Fig. 10) may be termed layer-by-layer oxidation.

The idea behind Fig. 10 might seem rather speculative were it not for a very interesting effect we discovered recently. Figure 11 presents an example of the data. Upon exposure to O_2 the coupling (H_f) in bottom spin valves increases. This effect would seem very odd in the context of the usual picture of magnetostatic or orange-peel coupling in which undulations in the spin valve lead to ferromagnetic coupling between Co layers across the Cu. Figure 12(a) illustrates this concept. In the usual picture, growth produces conformal roughness (as is usually observed in transmission electron microscopy of spin valves[17]), and magnetic poles on the Co produce a magnetostatic coupling that is ferromagnetic in sense.

In this standard picture, there is no reason to expect that any surface treatment would affect the coupling since the undulating Co/Cu/Co interfaces are buried well below the surface and presumably are static. Figure 12(b), however, provides a new wrinkle. If conformal roughness is maintained to the surface, magnetic poles will exist on the Co outer surface and, significantly, these poles will couple antiferromagnetically to the lower Co film. Therefore, it seems likely that the net coupling observed experimentally involves a partial cancellation of the dominant ferromagnetic coupling in these systems.

The connection between the antiferromagnetic component of Fig. 12(b) and the model suggested in Fig. 10 is that together they provide an explanation for the otherwise very surprising data of Fig. 11. By oxidizing the Co protrusions at

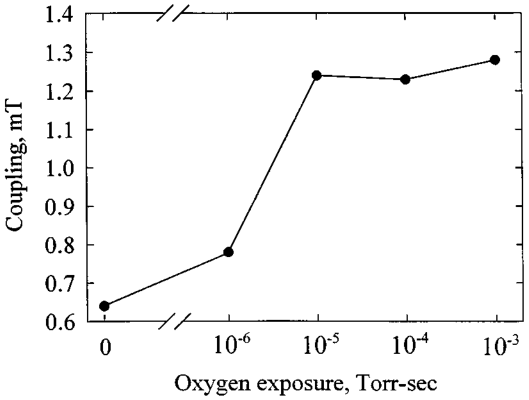

FIG. 11. A plot of the coupling field (H_f) of a bottom spin valve as a function of exposure to O_2 after deposition. Note that 1×10^{-6} Torr·s equals 1.3×10^{-4} Pa·s.

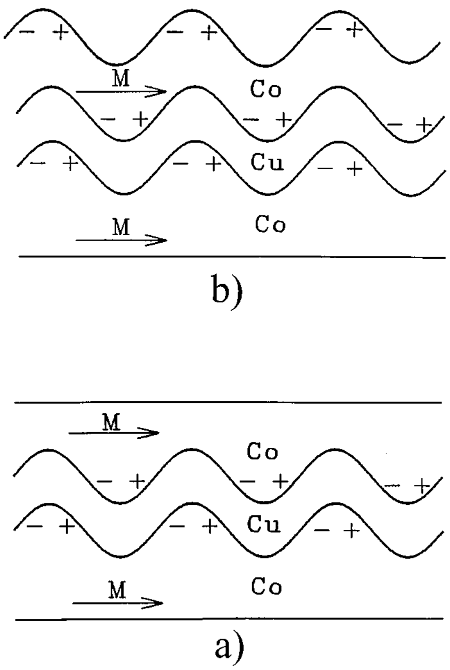

FIG. 12. An illustration of the conventional picture of magnetostatic coupling due to conformal roughness in (a), and how that picture may be modified to explain the data in Fig. 11 in (b).

the surface and rendering them nonmagnetic the antiferromagnetic contribution is suppressed and the net coupling becomes more ferromagnetic.

The increases observed in coupling upon O_2 exposure are too large to be explained by the reduction in the total magnetization of the top Co film. This magnetization acts like a lever arm and should be inversely proportional to the observed magnetostatic coupling. However, the data of Fig. 11, which shows a doubling of the coupling, is typical. We know from XPS that only the top $\sim$2 ML of the Co is oxidized. Therefore, we are not observing a simple lever-arm effect.

One additional note about the roughness of these films may be of interest. The sinusoidal undulations illustrated in Fig. 12 are an oversimplification. We have investigated a variety of spin valves using an *in situ* scanning tunneling microscope.[18] We find that there are two basic types of roughness, an atomic scale roughness (like Fig. 10 but less pronounced) which is almost certainly not conformal through the spin valve and a larger scale roughness (the grain size) which is very likely conformal. The larger scale roughness consists of grains 5–15 nm in diameter separated by $\sim$0.5-nm-deep grooves or valleys at the grain boundaries. The sides of these valleys are the apparent site of the magnetic poles responsible for the coupling.

C. Capping layers

It is common practice with bottom spin valves to deposit a protecting or capping layer before exposing the spin valve to air. The capping layer most widely used seems to be a Ta film 5 nm thick. Based on our experience, this is a poor choice. Not only does the Ta suppress the specular scattering but, as a conductor, it shunts current diluting the GMR effect. In our experience a bottom spin valve that exhibits, for example, 15% GMR will only exhibit 11% after the deposition of 5 nm of Ta. Accordingly, we have investigated a variety of alternative capping layers.

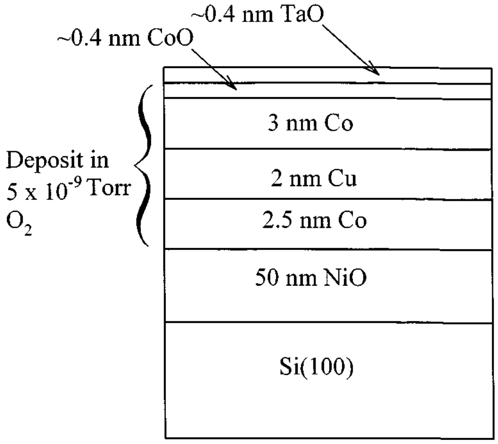

FIG. 13. An illustration of a capping layer which provides excellent protection from exposure to air and which acutally increases the GMR.

Our primary goals in developing an improved capping layer were to preserve the specular scattering at the top Co surface and to avoid thick Ta films. After numerous attempts, we found what appears to be an excellent recipe for a nearly ideal capping layer for bottom spin valves. It consists of exposing the top Co layer to $\sim 10^{-4}$ Torr·s ($\sim 10^{-2}$ Pa·s) of O_2 to produce $\sim$0.4 nm CoO, depositing $\sim$0.4 nm Ta, and exposing the sample to air to oxidize the Ta. The resulting structure is illustrated in Fig. 13. A remarkable aspect of this particular capping layer is that it produces a further increase in GMR and a further small drop in resistance, suggesting a further increase in specular scattering. Figure 14 presents the GMR data. The GMR of 19% is the largest value ever reported for a spin valve with a single Cu layer.

It is important to note here that the 0.4 nm Ta appears to be playing some role as a catalyst to improve the surface further when the sample is exposed to air. Without the Ta or with significantly thicker Ta, no way could be found to achieve 19% GMR. Figure 15 presents data on the increase in GMR produced by the above recipe as a function of Ta thickness. The ΔGMR values are the GMR after exposure to air minus the GMR as deposited in 5×10^{-9} Torr (7×10^{-7} Pa) O_2 but before exposure to the $\sim 10^{-4}$ Torr s ($\sim 10^{-2}$ Pa s) of O_2. Some samples showed a ΔGMR of almost +2%.

Another important aspect of this capping layer is its stability. After a month in air the GMR was remeasured and found to be still 19%. It seems surprising that such a thin capping layer can provide such good protection.

D. General remarks

Unfortunately, we cannot quantify the degree of specular scattering in any of these samples. However, it does appear likely that the procedure of depositing Ta on a metal surface is very effective in suppressing the specular scattering. Vari-

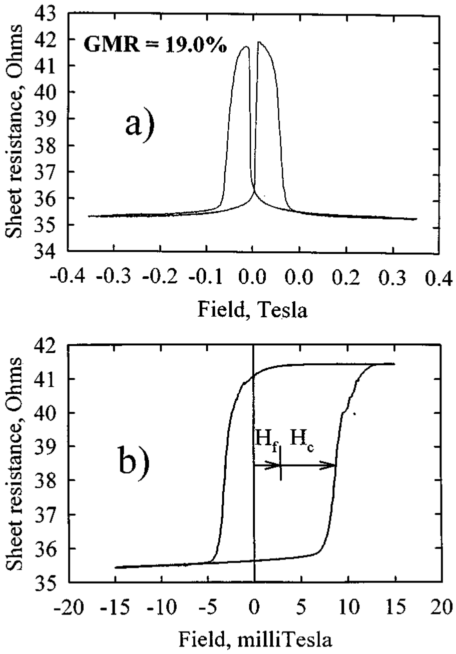

FIG. 14. Magnetoresistance loops for a bottom spin valve of the type illustrated in Fig. 13 for (a) high fields and (b) low fields, recorded after saturation in a negative field. A vertical line in (b) marks the center of the loop, which is shifted from zero field due to the coupling (H_f) between Co films. In this sample, $H_f = 2.7$ mT (27 Oe) and $H_c = 5.9$ mT (59 Oe).

ous other materials, which we expected would suppress the specular scattering, were investigated in the course of this work and our earlier work.[15] These materials were chosen on the basis of our expectation that they would disorder the surface extensively. They included carbon, silicon and, in the case of Au surfaces, $Ni_{80}Fe_{20}$. All materials were found to produce similar results, suggesting that they all succeeded in suppressing specular scattering almost completely.

Increasing specular scattering appears to be one of the best hopes for increasing the GMR in simple spin valves.[19,20] In principle, if both top and bottom surfaces of a simple spin valve scattered electrons specularly the GMR could be as large as that found in the best Co/Cu superlattices ($110\%^2$), if all other characteristics were the same. Unfortunately, all other characteristics will generally not be the same. In particular, the grain size is significantly larger in the best superlattices than in the best simple spin valves. Diffuse scattering of electrons at the grain boundaries will limit the potential of specular scattering for increasing the GMR in such samples; however the limits remain to be explored. Further studies of specular scattering, particularly from a surface science perspective, would seem to be very timely at present and have excellent prospects for discoveries of great practical significance.

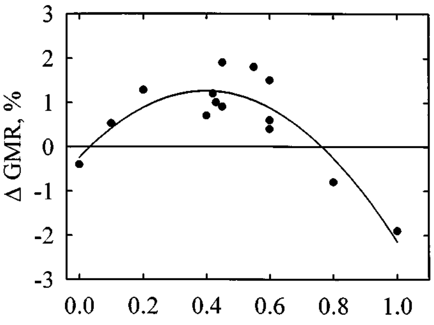

FIG. 15. A plot of ΔGMR as a function of thickness of deposited Ta for bottom spin valves capped as illustrated in Fig. 13. The solid curve is a polynomial fit to the data.

IV. SUMMARY

The major conclusions of this work may be summarized as follows. The cleanest possible deposition conditions do not produce spin valves with the largest GMR. The largest GMR values obtained to date have been achieved by growing the spin valves in 5×10^{-9} Torr O_2. Values of 19.0% and 24.8% have been achieved for bottom spin valves and symmetric spin valves, respectively. These are the largest values ever reported for such structures. Oxygen appears to act as a surfactant during growth, suppressing intermixing at the Co/Cu interface and increasing the extent of specular electron scattering at the top Co surface in bottom spin valves. Background gases typically found in deposition chambers are not, directly, a major cause of small GMR values. Contamination knocked off the chamber walls by energetic electrons, atoms, and ions from magnetron sputter guns appears to be a major contributor to small GMR values. Post-deposition oxidation of the surface of bottom spin valves can increase the extent of specular scattering and increase the GMR in most cases. The deposition of Ta on the surface of bottom spin valves suppresses the specular scattering and, as a consequence, reduces the GMR and increases the resistance of the samples. Pure Ta is a very poor choice of capping layers for bottom spin valves because it reduces the GMR both by suppressing specular scattering and by shunting current. A capping of 0.4 nm Ta, oxidized by exposure to air, not only protects the spin valve from air but also increased the GMR, apparently by increasing the extent of specular scattering.

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