Growth of giant magnetoresistance spin valves using Pb and Au as surfactants

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We have investigated the use of Pb and Au as surfactants in an attempt to achieve smoother and sharper interfaces in three types of giant magnetoresistance (GMR) spin valve multilayers: symmetric spin valves, bottom spin valves, and top spin valves. The coupling fields are reduced by a factor of 10 for symmetric and bottom spin valves and by a factor of 3 for top spin valves, presumably by suppressing roughness and interdiffusion at the Co/Cu/Co interfaces, when ~1 monolayer of Pb is deposited in the early stages of spin valve growth. The Pb has a strong tendency to float out or segregate to the surface during deposition of the spin valve leaving the GMR largely unaltered. Au is almost as effective as Pb, however the Au tends to be left behind in the spin valve, and the GMR is reduced slightly. Attempts to use Hg as a surfactant were unsuccessful. The coupling field increased, and the GMR decreased sharply. © *1996 American Institute of Physics.* [S0021-8979(96)08321-1]

I. INTRODUCTION

A key goal of research in the field of giant magnetoresistance (GMR) is to retain large GMR values while decreasing the size of the magnetic switching or saturation field required to produce the effect.[1] Technological applications of great economic importance are likely to result if such efforts are successful.

There does not appear to be any fundamental impediment to achieving large GMR at low switching field. If samples could be synthesized at the atomic level with complete control, it should be possible to reduce the contributions to the switching fields considerably. Control of the atomic microstructure should make it possible to reduce contributions to the switching field such as the coercivity, the anisotropy, and the magnetostatic coupling to almost arbitrarily low levels.

The present state of the art is far removed from that goal. Both the largest GMR values ever reported[2] and the lowest switching fields ever reported[3] were for samples fabricated by magnetron sputter deposition, which is a relatively messy technique. The base pressure of the deposition chamber is not in the ultrahigh vacuum range, the energetic electrons, atoms, and ions generated by the plasma introduce contaminants into the chamber by desorbing them from the chamber walls, and samples are polycrystalline.[2–4]

It is ironic that samples prepared by molecular beam epitaxy, a seemingly more ideal technique, has never been shown to approach either the largest GMR values (80% at room temperature has been reported[2]) or the smallest switching field values (0.2 mT, or 2 Oe, has been reported[3]). Perhaps the ideal atomic microstructure is not one of crystalline perfection.

It seems more likely, therefore, that the goal of achieving a large GMR at a low field will be reached through the development of improved techniques for the control of atomic structure during thin-film deposition. One promising avenue for such improvement is the use of surfactant layers to modify film growth.

In the years since it was first suggested and successfully demonstrated[5] that adsorbate layers that float out or segregate to the surface during growth might be used to modify or control epitaxy in a favorable manner, there has been an extraordinarily rapid development of this concept. This development has occurred primarily in the field of semiconductors,[6] but also in metal-on-metal systems.[5,7,8] Among the adsorbed species that have been investigated as surfactants are H, C, N, O, CO, and S,[5] and As, Ag, In, Sn, Sb, Te, Pb, and Bi.[6–8] A variety of favorable effects has been reported for surfactant-assisted growth, but the most common are improvements in the quality of interfaces by making them smoother, more coherent, less prone to interdiffusion, etc. However, so far, only Ref. 1 has considered surfactant-assisted GMR spin-valve growth.

In that earlier paper we reported the results of the use of indium as a surfactant to reduce the coupling field in top spin valves.[1] The work was only a partial success. The coupling field was reduced significantly, but the GMR effect was also reduced significantly. In the present work we report the results of two new surfactants for spin valve systems, lead and gold. An important difference between the earlier work and

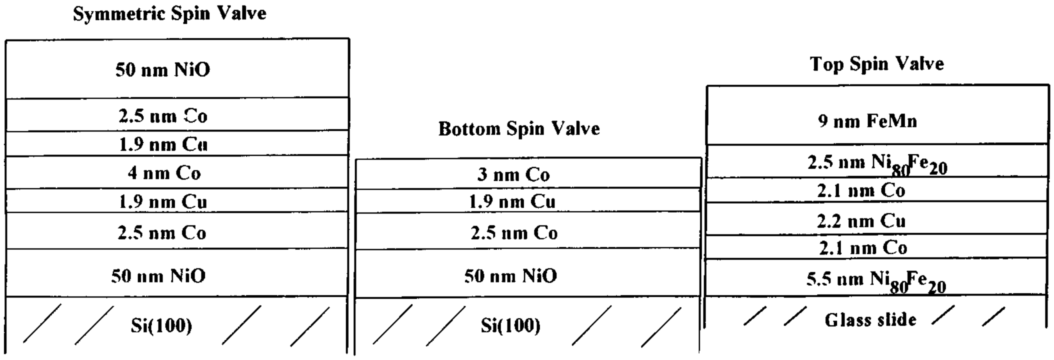

FIG. 1. An illustration of the standard spin-valve structures that are the basis for the present investigations. The terms symmetric, bottom, and top refer to the location of the pinning layers, NiO or FeMn.

the present work is the magnitude of the coupling that the surfactant is intended to reduce. In the earlier work, spin valves that exhibited a small coupling (<1 mT, i.e., <10 Oe) and a small GMR ($<8\%$) were investigated. The present work considers spin valves with larger coupling (>4 mT, i.e., >40 Oe) and larger GMR ($>15\%$), and for these samples much better results have been obtained. Figure 1 illustrates the three basic types of spin valve structures investigated in this work.

Interfaces are thought to play a key role in properties of GMR spin valves. Therefore, it seems very appropriate to investigate whether surfactants used during deposition can improve any of these properties. Some degree of success seems quite likely since there are so many possibilities for the use of surfactants. There are quite a number of elements that could potentially act as surfactants in spin-valve systems. Moreover, the optimum conditions for surfactant-assisted spin-valve growth might well involve deposition of some layers of the spin valve at temperatures other than room temperature, and different surfactants might be appropriate for different layers. A simple estimate of the possible permutations of these parameters indicates that a vast expanse of parameter space awaits exploration.

In general, soft, relatively unreactive metals with a large atomic volume should be the best surfactants. Such metals tend to exhibit rapid surface diffusion and low surface free energies, properties that should favor their smoothing an otherwise rough surface and also favor their floating out to the surface during overlayer deposition. The large atomic volume favors the floating-out process since the incorporation of a large atom in a small lattice costs a great deal of energy in the form of lattice strain.

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 at University of Minnesota.[9] At the National Institute of Standards and Technology (NIST), 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.

It is very important to remove the hydrocarbon contamination (several tenths of a nanometer, that accumulates 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 largest GMR values. Samples were sputtered with a neutralized-beam Ar-ion gun at a beam energy of only 100 eV until the carbon was removed, as judged by *in situ* x-ray photoelectron spectroscopy (XPS). (Ion beam energies 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 (RT) by dc-magnetron sputtering in 2 mTorr 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 base pressure before depositing a spin valve was typically 2×10^{-8} Torr ($\sim2\times10^{-6}$ Pa) of which ~95% was H_2 and the remainder primarily H_2O (as indicated by a mass spectrometer). The presence of H_2 during deposition has no apparent effect on spin-valve properties unless the partial pressure approaches $\sim10^{-6}$ Torr. The 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 (MR) measurements were made *in situ* at RT using the four-point probe dc mode. Several symmetric spin valves were checked *ex situ* in two separate facilities and were found to have the same MR values. The bottom spin valves did not appear to be affected by exposure to background gases during the MR measurements.

III. RESULTS AND DISCUSSION

A. Pb as a surfactant

Pb was shown recently to have surfactant properties in the epitaxial growth of Co on Cu(111) in the work of Camarero *et al.*[8] They found that the presence of a monolayer of Pb preserved the *abcabc* stacking of the face-centered cubic (fcc) lattice as Co was deposited on Cu(111). Without the Pb, numerous stacking faults occurred (e.g., *abab* stacking). This effect is expected to be especially strong on large perfect (111) terraces on which most Co atoms cannot diffuse to a step site and bond there (an effect that also preserves the correct stacking). Nevertheless, the

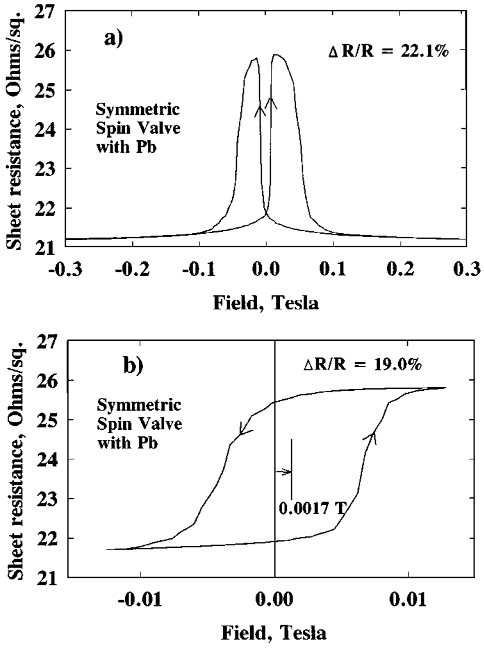

FIG. 2. Magnetoresistance loops for a symmetric spin valve with 0.17 nm of Pb deposited on each Cu layer for (a) high fields and (b) low fields, recorded after saturation in a negative field (see the arrows). A vertical line in (b) marks the center of the loop, which is shifted from zero field due to the coupling between the center Co film and the top and bottom Co films. (Note: 0.01 T=100 Oe.)

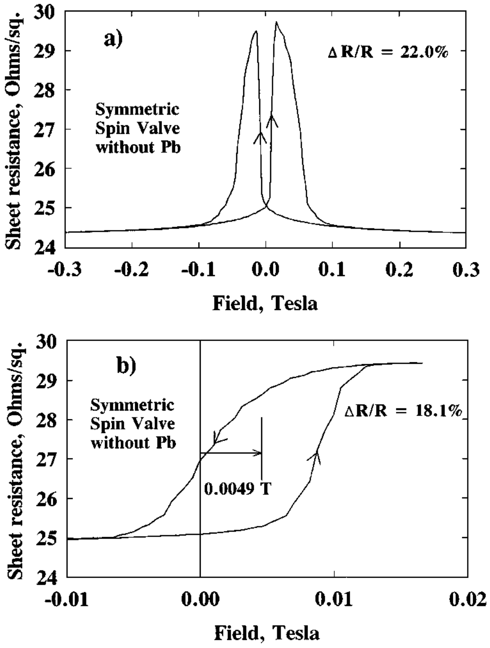

FIG. 3. Magnetoresistance loops for a symmetric spin valve without any Pb for (a) high fields and (b) low fields, recorded after saturation in a negative field (see the arrows). A vertical line in (b) marks the center of the loop, which is shifted from zero field due to the coupling between the center Co film and the top and bottom Co films. (Note: 0.01 T=100 Oe.)

effect may not be particularly important in our fine-grained polycrystalline films, which probably contain relative few (111)-oriented grains and small ones at that. However, the occurrence of surfactant properties for Pb in the Co/Cu(111) system suggests that favorable effects, even if different in detail, might still occur in polycrystalline Co/Cu systems.

In a series of preliminary experiments, we investigated the deposition of Pb at different stages of spin-valve growth. We found that, to have any positive effect, the Pb must be deposited before the deposition of a Co layer on a Cu layer. The most effective treatment was found to be the deposition of Pb on the Cu just prior to deposition of Co. For symmetric spin valves, a Pb film was deposited on each Cu layer. (This procedure gives slightly better results than using a Pb film only on the first Cu layer.)

The basic effect of Pb as a surfactant in spin valves is illustrated in Figs. 2 and 3. They present the magnetoresistance loops for symmetric spin valves, of the type illustrated in Fig. 1, with (Fig. 2) and without (Fig. 3) the use of Pb as a surfactant. For the data of Fig. 3, a 0.15-nm-thick Pb film was deposited on top of each Cu layer.

In each case, both the high-field [Figs. 2(a) and 3(a)] and low-field [Figs. 2(b) and 3(b)] loops are presented. The shape of the high-field loops is easily explained. The top and bottom Co layers are pinned by the adjacent NiO so that they exhibit large coercivities (~0.05 T or 500 Oe), and the center Co layer has a small coercivity (~0.005 T or 50 Oe). The magnetization is parallel for all three Co layers at high field. As the field is reduced and crosses zero, the center Co layer switches from parallel to antiparallel. This switching produces a sudden increase in resistance near the center of the high-field loop (see the arrows). As the field continues to increase, the pinned layers switch parallel to the center layer around 0.05 T, and the resistance drops. This general shape of GMR loop is common in simple spin valves that employ magnetic layers of differing coercivity.[10] In the low-field loop, the top and bottom Co layers remain pinned, and only the center (or valve) Co layer is switched.

The most striking difference between the two cases is that the coupling is about a factor of 3 smaller when Pb is used. The coupling is defined as the shift from zero field observed for the center of the low-field loop. For both cases, the shift is to positive field, which means that there is, in effect, a ferromagnetic coupling between the center Co layer and the other two Co layers.

The dependence of the coupling strength on Pb thickness is illustrated in Fig. 4. The coupling can be reduced almost to

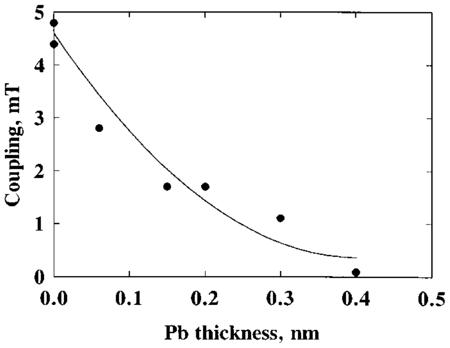

FIG. 4. A plot of the coupling strength in mT (1 mT=10 Oe) as a function of the thickness of Pb deposited on each Cu layer for symmetric spin valves. The solid line is a polynomial fit to the data. (Note that 1 ML Pb≈0.28 nm.)

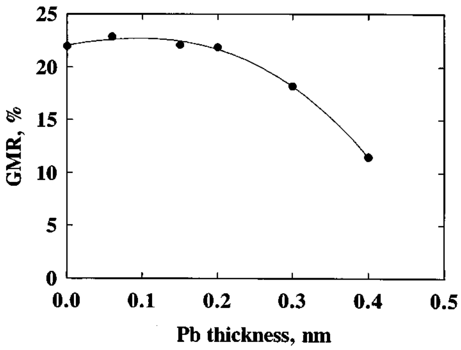

FIG. 5. A plot of the GMR as a function of Pb thickness for symmetric spin valves. The solid line is a polynomial fit to the data.

zero by the deposition of enough Pb. However, there is a trade off. Too much Pb reduces the GMR of the sample. Figure 5 illustrates this effect. There is a significant loss of GMR when enough Pb is used to reduce the coupling to near zero. Nevertheless, for 0.2 nm Pb, there is no apparent loss of GMR but there is a substantial reduction in the coupling. Such an effect should be very useful in producing spin valves with improved performance.

The coupling has two likely sources, orange-peel coupling and oscillatory exchange coupling. The former is a topological magnetostatic effect that results from roughness in the Co and Cu layers.[11] This coupling is ferromagnetic if the roughness is conformal, as is generally expected in multilayers such as these.[11] The latter possible source is an effect that oscillates as a function of Cu thickness between ferromagnetic and antiferromagnetic.[12] A Cu thickness of 1.9 nm is near a crossover but slightly on the ferromagnetic side. Note here that the cross-over thicknesses in the Co/Cu system are often slightly different for spin valves and superlattices (cf. Refs. 12 and 13).

Both types of coupling appear to be present in symmetric spin valves and bottom spin valves of the type illustrated in Fig. 1. If the Cu thickness is less than 1.9 nm, the strength of the ferromagnetic coupling increases sharply (~0.005 T per 0.1 nm). This slope is much too steep to be due to orange-peel coupling but is consistent with the oscillatory effect.[14] When the Cu thickness is slightly larger than 1.9 nm, antiferromagnetic coupling would be expected if the oscillatory effect dominates. In fact, the expected antiferromagnetic coupling is difficult to obtain unless special measures, such as deposition at cryogenic temperatures, are employed.[15] This result suggests that orange-peel coupling is present and is usually large enough to overcome any oscillatory antiferromagnetic coupling that may occur. Therefore, it seems clear that both types of coupling are present in our symmetric and bottom spin-valve samples (but only orange-peel coupling is apparent in the top spin valves; see below).

In principle, the question of which type of coupling is being influenced by Pb could be addressed by investigating the effect of Pb on the antiferromagnetic coupling at Cu thicknesses slightly larger than 1.9 nm. However, since we find that the antiferromagnetic state is difficult to achieve reproducibly, such studies must be postponed.

It is easy to suggest models to explain how the two types of coupling would be reduced by a surfactant. In the case of orange-peel coupling, the reduction would most plausibly be produced by smoother surfaces during film growth. In our scanning tunneling microscopy (STM) studies of spin valves, we have found that the dominant type of roughness is grain boundary valleys.[16] A lessening of the depth of grain boundary valleys would produce smaller orange-peel coupling. Such an effect would be quite plausible since a common characteristic of a surfactant is the reduction in interfacial tension.

Another possible mechanism for the suppression of orange-peel coupling would be a reduction in the extent of conformal roughness. The surfactant might produce such an effect if it interrupted the pseudomorphic growth that tends to occur within columnar grains in the Co/Cu/Co system. We presently have studies underway using transmission electron microscopy that should resolve the issue of which mechanisms are at work.

In the case of oscillatory exchange coupling, the reduction would most plausibly be attributed to a suppression of interdiffusion when Co is deposited on Cu. Such interdiffusion is well known in single-crystal Co/Cu systems.[17] The driving force is the lower surface free energy of Cu, which tends to promote surface segregation of Cu during the deposition of Co. The Cu gradually gets left behind in the first few atomic layers of Co so that an alloy is left at the Co/Cu interface. Such Cu segregation may be expected to reduce the effective thickness of the Cu. In our case, this thinning of the Cu would mean that the samples are moving up the steep slope, mentioned earlier, of the oscillatory coupling versus Cu thickness. Since this slope is ~0.005 T (50 Oe) per 0.1 nm Cu, a small amount of Cu segregation can produce a large coupling. However, if Pb acts as a surfactant to suppress this Cu segregation, the effective Cu thickness would be greater and the coupling substantially reduced. A suppression of the Cu segregation would be expected for a surfactant such as Pb since Pb would lower the surface free energy and eliminate the driving force for Cu segregation.

At present, we cannot prove that either of these two surfactant mechanisms is responsible for the dramatic reduction in the coupling due to Pb. However, it would seem likely that at least one of them is operative, and it may be that both are. We have STM and transmission electron microscopy (TEM) investigations underway at present that may clarify the situation.

A common characteristic of a surfactant is that it is mobile. In the case of thin film growth, it is of particular interest to determine whether the surfactant is sufficiently mobile to float out or segregate to the growing surface. It would be easy to imagine the disruptive effects of Pb if large amounts of it were incorporated in the spin valve. We have used XPS to investigate the tendency of Pb to float out or segregate to the surface during deposition.

Figure 6 illustrates a typical set of XPS data. In this case, a Pb film 0.28 nm thick (on average) was deposited on the first Cu layer, and the decline in the intensity of the Pb 4*f* peaks was monitored during deposition of the Co, Cu, Co, NiO overlayers. This decline with increasing overlayer thick-

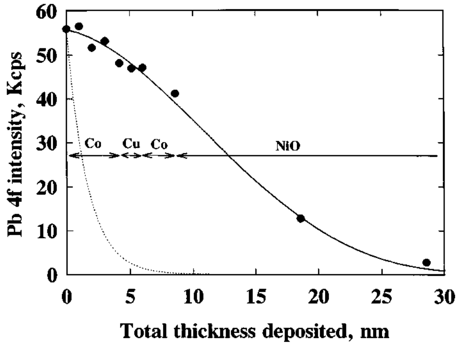

FIG. 6. A plot of the Pb 4f x-ray photoelectron intensity for 0.28 nm Pb deposited on the first Cu layer of a symmetric spin valve as a function of the thickness of subsequently deposited layers of Co, Cu, Co, Ni, and NiO. The solid line is a polynomial fit to the data. The dotted line is the decrease in intensity predicted on the basis of photoelectron escape depths if there were no surface segregation of Pb.

ness is due to the incomplete segregation of Pb, i.e., it gradually gets left behind, with most of it trapped in the NiO. Normally, a second Pb film would be deposited on the second Cu layer of a symmetric spin valve, but in the present example only one Pb film was used (for simplicity). For Pb, a thickness of 0.286 nm corresponds to a close-packed (111) monolayer.

The dotted curve in Fig. 6 indicates a decline in the Pb 4f intensity that would be expected on the basis of photoelectron inelastic mean free paths if no Pb surface segregation occurred.[18] A comparison of the dotted curve with the data suggests that roughly 0.75 monolayer (ML) of the Pb remains at the surface after the last Co layer is deposited. The thermodynamic driving forces for this segregation are the larger atomic volume of Pb which strains the Cu lattice upon incorporation and the lower surface free energy of Pb. The mechanism of surface segregation is likely to involve surface diffusion of Pb atoms. The rate of diffusion of Cu adatoms at room temperature on Cu surfaces is very high.[19] Since Pb is a softer metal than Cu, it should experience an even higher rate of diffusion. In this active environment, deposited Co atoms will make their way through the (Pb) to the Cu, with which they are well lattice matched, and will bond there. The Pb film, which is very poorly lattice matched to the substrate, must be very disordered and may even be a near-liquidlike overlayer.

It should be noted that, while 4–5 mT (40–50 Oe) is the normal value we obtain for the coupling, there have been occasional periods when we obtained larger values, such as 8–9 mT (80–90 Oe). The reason for this increase is not clear, however these increases do come in groups, with consistently large coupling values for perhaps 10–20 samples before the coupling returns to normal. One possible explanation would be that a layer of trace impurities sometimes occurs in a Co magnetron source, and the impurity adversely affects film growth until continued use of the source sputters through the impurity layer. We use the term ''trace impurities'' here because we have been unable to detect any such impurities with XPS, which is sensitive to many (though not all) elements at the ~1% level. The only exception to this is that XPS always shows that there is some adsorbed carbon and oxygen on our spin valves at each stage of growth. The oxygen coverage is typically a few tenths of a monolayer and the carbon one-tenth. These species seem to come from the background gases that are present during magnetron sputtering. In the near future, we plan to investigate possible interference between these adsorbed species and the metallic surfactant layers.

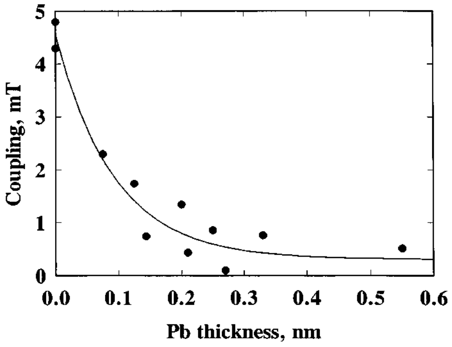

FIG. 7. A plot of the coupling strength in mT (1 mT=10 Oe) as a function of the thickness of Pb deposited on the Cu layer for bottom spin valves. The solid line is a polynomial fit to the data. (Note that 1 ML Pb≈0.28 nm.)

While we cannot be sure of the cause of the anomalously large coupling, we have had an opportunity to test the effectiveness of Pb in reducing it. Although the large values did not persist long enough for an extensive study, we did establish that 0.25 nm of Pb deposited on the first Cu film in symmetric spin valves lowered the coupling from 8–9 mT (80–90 Oe) to 0.7 mT (7 Oe), and the result was reproducible.

This set of data was the most dramatic example of the successful use of a surfactant that we have found. Equally remarkable is that during this episode we found that the use of 0.5 nm of In as a surfactant produced an almost identical result. This reduction in the coupling by more than a factor of 10 for In stands in contrast to the factor of 2 reduction in the coupling reported for 0.5 nm In in top spin valves in Ref. 1. While we have a limited set of data for comparison, it is worth noting that the larger the coupling the greater the effectiveness of a surfactant.

A further lesson from this episode came from XPS data on the incorporation of Pb in the spin valve. The drop in Pb 4f intensity with overlayer thickness was approximately twice as fast as the data presented in Fig. 4. This result may be important because the initial coupling of 8–9 mT (80–90 Oe) was approximately twice as large as that in Fig. 2. It would seem that a larger quantity of Pb is consumed in the act of suppressing the larger coupling. Perhaps the Pb is being incorporated in the grain boundaries to reduce the interfacial tension acting on the grain boundary valleys. If so, a smoother surface (shallower grain boundary valleys) would be expected,[20] and this effect would reduce orange-peel coupling. The most plausible interpretation of the larger consumption of Pb would be that the grain size is smaller. A smaller grain size would mean larger grain boundary area (hence greater Pb consumption) and a greater density of

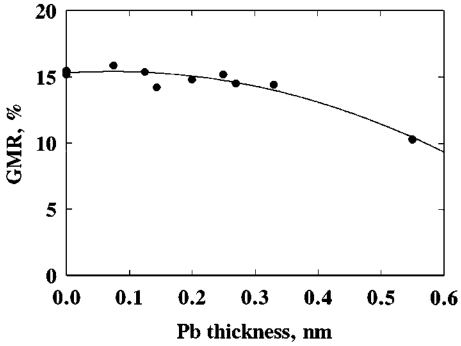

FIG. 8. A plot of the GMR as a function of Pb thickness for bottom spin valves. The solid line is a polynomial fit to the data.

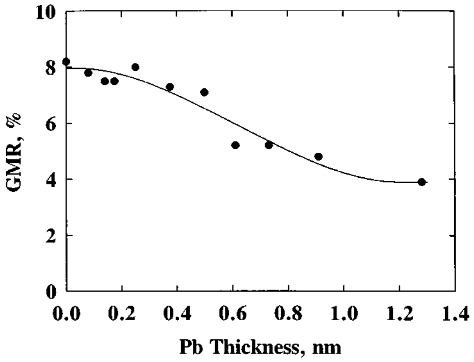

FIG. 10. A plot of the GMR as a function of Pb thickness for top spin valves. The solid line is a polynomial fit to the data.

grain boundary valleys (hence larger coupling). *In situ* STM studies presently underway may provide some insight into these issues in our future publications.

In bottom spin valves of the type illustrated in Fig. 1, the surfactant effect of Pb is very similar to that in symmetric spin valves. Figures 7 and 8 present the data. The coupling is very effectively suppressed by the deposition of ~1 ML Pb on the Cu layer. The decrease in GMR with Pb thickness is somewhat less than for symmetric spin valves. The decrease in GMR is barely noticeable for ~1 ML Pb.

In top spin valves of the type illustrated in Fig. 1 the surfactant effect of Pb is much less pronounced than in the cases discussed above. In this respect, the results are reminiscent of the results we obtained earlier using In as a surfactant in top spin valves.[1] The coupling is not large to begin with, and the surfactant reduces it by only a factor of 3 rather than a factor of 10. Figures 9 and 10 present the data.

It is not clear why the results for top spin valves are so different from those for the two previous types of spin valves. However, there are some clues. For top spin valves slightly thicker Cu layers must be used to observe a GMR effect than in the two previous cases. Top spin valves are less tolerant of large coupling because FeMn provides weaker pinning than NiO. The thinnest practical Cu layer for a top spin valve of this type is ~2.2 nm.[15] One result of the thicker Cu is that the samples are well removed from the steep slope, as mentioned earlier, in the coupling versus Cu thickness relationship. Therefore, the smaller surfactant effect could be attributed to a less steep slope (if the surfactant operates by suppressing Co/Cu interdiffusion and its consequent thinning of the Cu layer). However, it could also be true that there is no oscillatory coupling present in this case, and the surfactant operates by smoothing the surfaces to reduce the orange-peel coupling. Perhaps our STM studies will clarify this point in the future.

It is somewhat disappointing that, while Pb can reduce the coupling, apparently by improving the quality of the Co/Cu/Co interfaces, it does not increase the GMR concurrently. It could easily be expected that this might occur because the interfaces are generally thought to play a key role in producing the GMR effect. Perhaps the coupling is much more sensitive to the quality of the interfaces than is the GMR, and the improvement in the quality of the interfaces by Pb is evident in the coupling but not in the GMR.

B. Au as a surfactant

Gold provides an interesting contrast to Pb as a surfactant. Figures 11–13 present the data on Au as a surfactant in symmetric spin valves of the type illustrated in Fig. 1. As was the case with Pb, the indicated thicknesses of Au were deposited on each Cu layer in the symmetric spin valves (for Figs. 11 and 12).

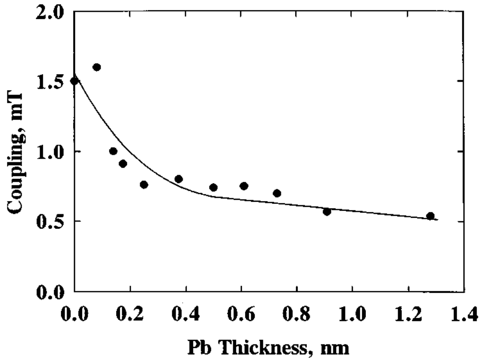

FIG. 9. A plot of the coupling strength in mT (1 mT=10 Oe) as a function of the thickness of Pb deposited on the Cu layer for top spin valves. The solid line is a polynomial fit to the data.

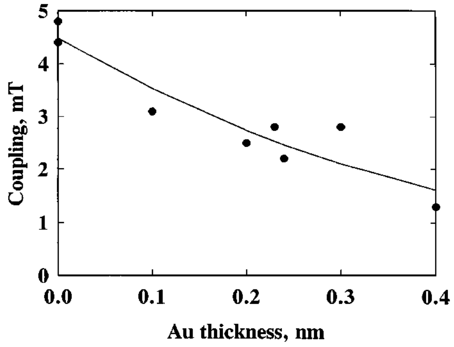

FIG. 11. A plot of the coupling strength in mT (1 mT=10 Oe) as a function of thickness of Au deposited on each Cu layer for symmetric spin valves. The solid line is a polynomial fit to the data.

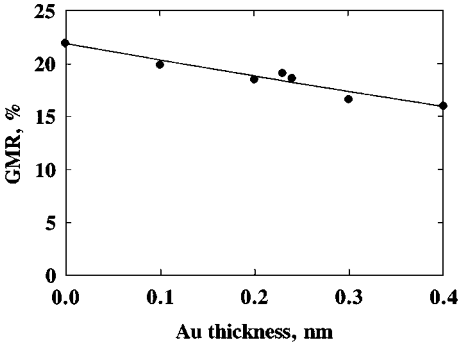

FIG. 12. A plot of the GMR as a function of Au thickness for symmetric spin valves. The solid line is a polynomial fit to the data.

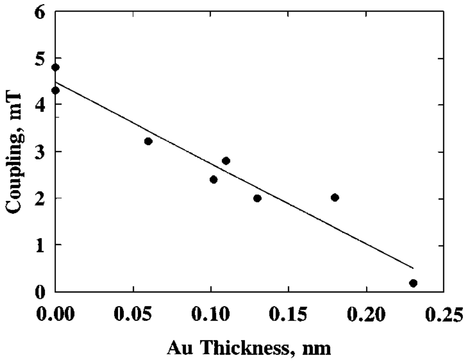

FIG. 14. A plot of the coupling strength in mT (1 mT=10 Oe) as a function of the thickness of Au deposited on the Cu layer for bottom spin valves. The solid line is a polynomial fit to the data.

Figure 11 demonstrates that the coupling is indeed suppressed by Au deposition on the Cu layer, although not quite as well as by Pb (cf. Fig. 4). Figure 12 demonstrates that the reduction in GMR due to Au is rather small, as was the case with Pb (cf. Fig. 5). However, the XPS results of Fig. 13 reveal a major difference for Au. It has very little tendency to float out or segregate to the surface when subsequent metal layers are deposited. Note that in Fig. 13 the Au was deposited only on the first Cu layer so that the results are directly comparable to the Pb results (cf. Fig. 6). As in Fig. 6, the dotted line is the attenuation expected if no segregation occurs. Given the uncertainty of inelastic mean free paths and their relation to attenuation lengths, the difference between the dotted line and the data in Fig. 13 is so small that it may be that almost no segregation of Au is occurring.

Figures 14–16 present the data for Au as a surfactant in bottom spin valves. Figure 14 demonstrates that the Au is very effective in suppressing the coupling. It is interesting that this suppression is much more effective than it was for symmetric spin valves (cf. Fig. 11). It is not clear why Au behaves so differently in the two types of spin valves. The behavior of Au seems more complicated than that of Pb, perhaps because of the lack of segregation. Figure 15 demonstrates that the reduction in GMR due to Au is rather small, as was also the case with symmetric spin valves (cf. Fig. 12).

Even without segregation Au could still suppress either of the effects discussed above as possible causes of the coupling. The orange-peel coupling could be suppressed if the Au tends to diffuse to the grain boundary valleys and fill them. The Au could also reduce the oscillatory coupling if, as discussed above, the interdiffusion at the Co/Cu interface is suppressed.

These results seem entirely plausible in terms of the differences between Pb and Au. Gold is not quite as large an atom as Pb, so the lattice strain upon incorporation should provide a smaller driving force for floating out or segregation. Gold has a surface free energy slightly less than that of Cu, so it might be expected to suppress the segregation of Cu when Co is deposited. However, it might not do so as effectively as Pb, which has a much lower surface free energy than Cu.[21] As far as smoothing the surfaces to reduce the orange-peel coupling, Au should be quite mobile on Cu at room temperature, and it should thus be able to diffuse to the grain boundary valleys and fill them if such an effect is thermodynamically favored. We hope to clarify this matter with STM in the future.

A final point of interesting concerning Au is shown in Fig. 16. The coercivity of the unpinned or top Co layer in-

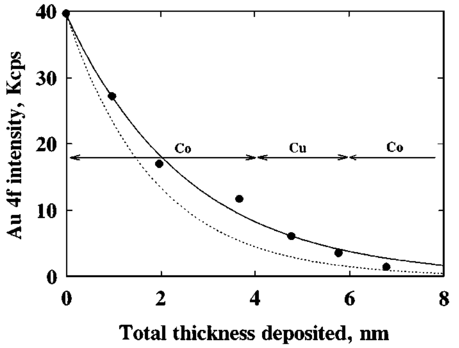

FIG. 13. A plot of the Au $4f$ x-ray photoelectron intensity for 0.17 nm Pb deposited on the first Cu layer of a symmetric spin valve as a function of the thickness of subsequently deposited layers of Co, Cu, and Co. The solid line is a polynomial fit to the data. The dotted line is the decrease in intensity on the basis of photoelectron inelastic mean free paths predicted if there were no surface segregation of Au.

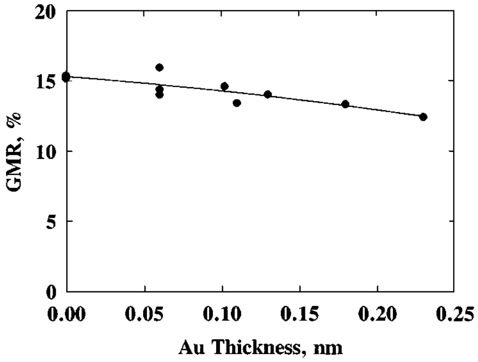

FIG. 15. A plot of the GMR as a function of Au thickness for bottom spin valves. The solid line is a polynomial fit to the data.

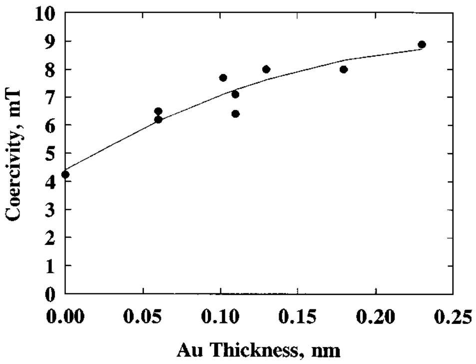

FIG. 16. A plot of the coercivity of the top Co layer as a function of Au thickness for bottom spin valves. The solid line is a polynomial fit to the data.

creases with the thickness of Au deposited on the Cu layer. This effect was not seen for Pb and may be a result of the lack of segregation by the Au. The lattice match between Au and Co is a poor one, and if patches of Au occur after deposition (such as at grain boundary valleys), the Co may be expected to experience locally high strains. Since Co is quite magnetostrictive, a spatially varying anisotropy should result, and this would be expected to cause an increase in the coercivity, as observed.

C. Hg as a surfactant

During the course of this work we made a brief investigation of the use of Hg as a surfactant. The results were not encouraging. The spin-valve properties deteriorate from the outset as the exposure to Hg is increased. Even for coverages of Hg that are just detectable by XPS the coupling begins to increase and the GMR begins to decrease. For Hg coverages estimated (using XPS) to be on the order of a monolayer the coupling exceeds 10 mT (100 Oe) and the GMR is below 5% for bottom spin valves. The reasons behind the failure of Hg are not apparent.

IV. CONCLUSIONS

The major conclusions of this work are the following:

(1) Lead is very effective as a surfactant in GMR spin-valve systems to reduce the ferromagnetic coupling (by as much as a factor of 10) between magnetic layers with very little loss of GMR.

(2) Lead is most effective when deposited on a Cu layer before the deposition of a Co layer.

(3) A Pb thickness of ~1 ML is sufficient to approach maximum effectiveness. Larger thicknesses produce little additional reduction in coupling and lead to a decrease in GMR.

(4) The Pb has a strong tendency to float out or segregate to the surface as subsequent layers are deposited.

(5) It appears likely that Pb has two effects, suppression of the interdiffusion at the Co/Cu interfaces and a smoothing of the interfacial roughness.

(6) Gold also tends to suppress the coupling with little reduction in GMR, but it appears to act in a different manner than Pb, since it does not float out or segregate to the surface of subsequently deposited layers.

(7) Gold requires slightly thicker films than Pb for the same effectiveness and leads to an undesirable increase in coercivity.

(8) Mercury does not appear to be useful as a surfactant in spin valves.

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