

Optimizing the giant magnetoresistance of symmetric and bottom spin valves (invited)

W. F. Egelhoff, Jr., P. J. Chen, C. J. Powell, M. D. Stiles, and R. D. McMichael
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

C.-L. Lin,^{a)} J. M. Sivertsen,^{a)} and J. H. Judy^{b)}
Center for Micromagnetics and Information Technology, University of Minnesota, Minneapolis, Minnesota 54455

K. Takano and A. E. Berkowitz
Department of Physics, University of California at San Diego, LaJolla, California 92093

T. C. Anthony and J. A. Brug
Hewlett-Packard Laboratories, 1501 Page Mill Road, Palo Alto, California 94304

We have attempted to optimize the values of the giant magnetoresistance in symmetric spin valves of the type NiO/Co/Cu/Co/Cu/Co/NiO (achieving 23.4%) and in bottom spin valves of the type Co/Cu/Co/NiO (achieving 17.0%), the largest values ever reported for such structures. The key elements in this achievement are improved vacuum conditions and careful attention to the film thicknesses. © 1996 American Institute of Physics. [S0021-8979(96)53408-3]

I. INTRODUCTION

Symmetric¹ (or dual²) spin valves are important in the field of giant magnetoresistance (GMR) because they offer the possibility of achieving large GMR values in magnetic multilayers which exhibit relatively low saturation fields. To put the issues in context, it is helpful to note that GMR values as large as 80% have been achieved in Co/Cu superlattices but at the cost of very large saturation fields, e.g., ~ 1 T, or 10^4 Oe.³ Saturation fields as low as 0.2 mT, or 2 Oe, have been reported for simple spin valves (containing only one Cu film), but the GMR of such structures is only 3%.⁴ Symmetric or dual spin valves represent an intermediate case (with two Cu films). Figure 1 illustrates a symmetric spin valve typical of those investigated in the present work. Also illustrated is one type of simple spin valve, a so-called bottom spin valve,¹ which may be viewed as the lower part of a symmetric spin valve.

The term bottom spin valve refers to the location of the pinning film, here NiO, which is at the bottom of the spin valve. In more conventional spin valves, the pinning film of FeMn is at the top.⁵ The NiO in the structures of Fig. 1 pins the adjacent magnetic films in a different manner than does FeMn. The FeMn acts by providing an exchange bias, whereas the NiO acts by inducing a very large coercivity in the adjacent Co film. In the bottom spin valve, the top Co film is unpinned and free to switch magnetically at relatively low fields. In the symmetric spin valve the top and bottom Co films are pinned and the central Co film is free.

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-film structure) for spin-allowed conduction paths when the Co films are magnetically in a parallel alignment state. However, in the antiparallel alignment state, symmetric spin valves should

exhibit short MFPs just as simple spin valves or superlattices do.

The goal of the present work is to achieve the largest GMR values possible in symmetric spin valves and bottom spin valves. A comparison of the resulting values should help to put on a quantitative basis the magnitude of the advantage that can be gained by the symmetric spin valve concept.

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 the University of Minnesota.⁶ At the National Institute of Standards and Technology, the wafers were cleaved into ~ 1 cm² squares, cleaned ultrasonically, rinsed, dried, and installed in the deposition chamber. The base pressure before depositing a spin valve was typically 2×10^{-8} Torr ($\sim 2 \times 10^{-6}$ Pa) of which $\sim 95\%$ was H₂ and the remainder primarily H₂O (as indicated by a mass spectrometer). The presence of H₂ during deposition has no apparent effect on spin valve properties unless the partial pressure exceeds $\sim 10^{-6}$ Torr. The base pressure is achieved partly by depos-

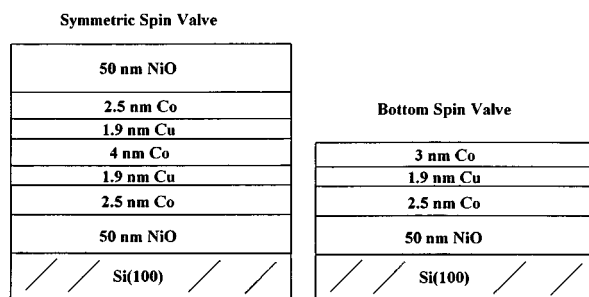


FIG. 1. An illustration of the symmetric spin valve and bottom spin valve structures typical of those investigated in the present work.

^{a)}Dept. of Chemical Engineering and Materials Science.

^{b)}Dept. of Electrical Engineering.

iting 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.

A base pressure of 3×10^{-10} Torr was achieved after baking the chamber overnight at 150°C , but this base pressure was degraded sharply when films were deposited by magnetron sputtering. During magnetron sputtering the walls of the chamber are bombarded by energetic electrons, atoms, and ions which desorb gases from the walls and degrade the vacuum. The best base pressure achievable within an hour after deposition of a symmetric spin valve was typically in the high 10^{-9} Torr region, even in a baked chamber. Thus, with the passage of time and with the deposition of many symmetric spin valves both a baked and an unbaked chamber converge on a base pressure of $\sim 10^{-8}$ Torr. Part of the problem is that some H_2O is formed from H_2 and O_2 during the deposition of the top 50 nm of NiO in a symmetric spin valve. However, even after repeated deposition of bottom spin valves (no NiO deposited) the base pressure was still no better than the low 10^{-9} Torr range.

The magnetoresistance (MR) measurements were made *in situ* at room temperature (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. However, exposure to O_2 did produce significant effects, as discussed below.

It is very important to remove the hydrocarbon contamination (several tenths of a nanometer, which 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 100 eV until the carbon was removed (as judged by *in situ* x-ray photoelectron spectroscopy). 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 RT by dc-magnetron sputtering in 2 mTorr Ar at a rate of ~ 0.1 nm/s. The top NiO film was deposited by sputtering a Ni target with an 85/15 mixture of Ar/ O_2 .

III. RESULTS AND DISCUSSION

A. Symmetric spin valves

In a previous publication,⁷ we presented our initial studies of symmetric spin valves. We found that the largest GMR values occurred in samples with film thickness values typical of those illustrated in Fig. 1. We also reported the dependence of GMR on the thickness of the Co films and on the sample temperature.

Subsequently, the most interesting result we have obtained on symmetric spin valves is the dependence of the GMR on the partial pressure of H_2O in the chamber just prior to deposition of the structure. The results are presented in Fig. 2 and indicate that the largest GMR values are obtained for the lowest H_2O partial pressures. Moreover, we find no indication that the GMR values are saturating at the lowest H_2O partial pressures we can reach.

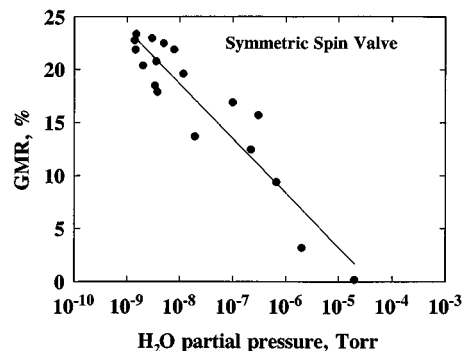


FIG. 2. A plot of the GMR values obtained for symmetric spin valves of the type illustrated in Fig. 1 as a function of the partial pressure of H_2O in the chamber just prior to deposition.

It should be emphasized that the H_2O partial pressures just prior to spin valve deposition in Fig. 2 are probably somewhat lower than the partial pressures during spin valve deposition. The presence of the sputtering gas (2 mTorr of Ar) prevents such a measurement during deposition. Nevertheless, during spin valve deposition, the partial pressure of H_2O and other contaminant gases is probably higher than just prior to deposition. This likely increase is due to the desorption of atoms and molecules from walls of the chamber by the impact of the energetic electrons, atoms, and ions produced by the magnetron sputtering process. In general, we find that immediately after the Ar has been pumped out following the deposition of a spin valve, the H_2O partial pressure is higher than just before deposition. (Note here that H_2O pumps away more slowly than Ar due to its tendency to stick to the walls.) This increase is about a factor of 2 for bottom spin valves and about a factor of 5 for symmetric spin valves (deposition of the final NiO film by reactive sputtering apparently synthesizes some H_2O). Therefore, although the values of H_2O partial pressure plotted in Fig. 2 are not the actual pressures during spin valve deposition, they are probably a reasonable indication of the relative H_2O partial pressures during deposition.

The results of Fig. 2 are important because most laboratories make GMR spin valves in deposition systems for which the base partial pressure of H_2O is considerably higher than the best we can achieve. Typically, base pressures are $\sim 10^{-7}$ Torr, and H_2O is the primary component. The implications of Fig. 2 are that lower partial pressures of H_2O in the system should lead to significant increases in the GMR and that efforts to improve base pressures would be worthwhile for most laboratories.

It is possible that H_2O is not the contaminant responsible for the loss of GMR in Fig. 2, but it is the most likely candidate. As discussed in Sec. II, the chamber contains predominantly H_2 at the base pressure. However, the H_2 partial pressure is then typically around $\sim 10^{-8}$ Torr and one must introduce $\sim 10^{-6}$ Torr of H_2 into the chamber during deposition to produce a noticeable reduction of GMR in these samples (i.e., more than the usual $\pm 10\%$ scatter in the data). Another contaminant in the chamber is CO, which typically has a partial pressure a factor of ten lower than that of H_2O ,

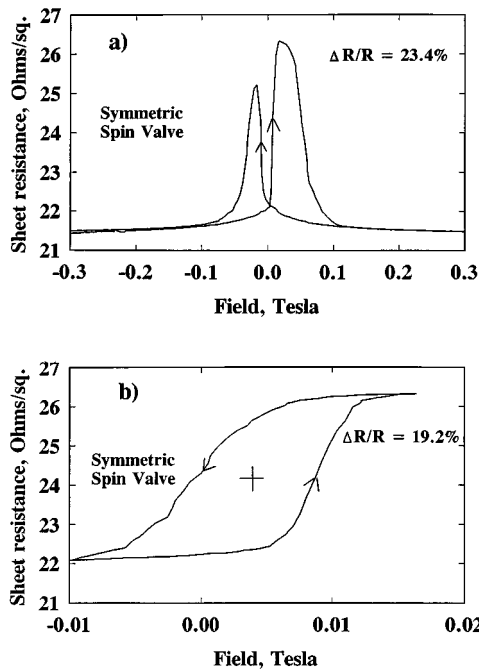


FIG. 3. Magnetoresistance loops for the symmetric spin valve with the largest GMR ($\Delta R/R$) for (a) high fields and (b) low fields, recorded after saturation in a negative field (see arrows). The cross in (b) marks the center of the loop, which is shifted from zero field due to the coupling between the center Co film and the top and bottom Co films. (Note: 0.01 T=100 Oe.)

and could possibly make a contribution to the GMR reduction. The ratio of CO and H₂O partial pressures does not change much because our primary method of varying the H₂O partial pressure is the length of the pumpdown time since the last exposure of the chamber to air. The H₂O partial pressure is also modified by the deposition of spin valves and by the deposition of Ti films, but the ratio of CO and H₂O partial pressures is approximately constant. Other contaminants in the chamber typically have partial pressures at least a factor of five less than CO and are probably unimportant.

The mechanism for the reduction in GMR in Fig. 2 is not known, but one possibility is impurity scattering of conduction electrons by oxygen-atom impurities. The sheet resistance (in a saturation field) of the samples used for the data in Fig. 2 increases from 21.5 Ω /sq. to 28 Ω /sq. as the GMR drops from 23.4% to 3.1%.

Another possible contribution to the drop in GMR is a weakening observed in the strength of the pinning of the top Co film by the top NiO. This weakness indicates that the magnetization of the top and center Co films are never completely antiparallel.

Figure 3 presents the high-field and low-field GMR loops for the sample with a GMR of 23.4%, the largest value we achieved. The shape of the high-field loop in the Fig. 3(a) is explained by the top and bottom Co films being pinned by the adjacent NiO so that they exhibit large coercivities. The center Co film 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 (see arrows). The general shape of this loop is typical for simple spin valves which employ magnetic films of differing coercivity.⁸

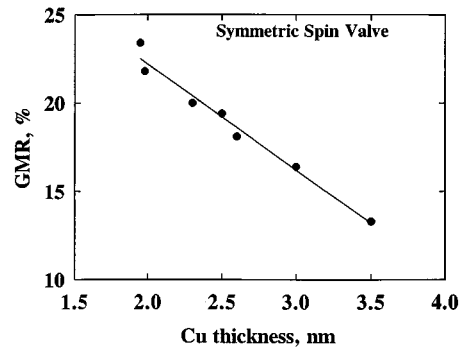


FIG. 4. A plot of the GMR vs the thickness of the Cu films for symmetric spin valves of the type illustrated in Fig. 1.

In the low-field loop in Fig. 3(b), little change occurs in the magnetization of the top and bottom Co, and only the center Co film is switched. Note that the high-field loop exhibits a weak tail extending out beyond 0.1 T (1000 Oe) so that the GMR of the low-field loop is only 19.2%. 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.

Figure 4 shows the strong dependence of the GMR on the thickness of the Cu films (the dependence on the Co film thicknesses was published in Ref. 7). The steep increase in GMR with decreasing Cu thickness is a strong motivation to investigate novel methods of deposition that will permit the use of thinner Cu films in these structures. The impediment to thinner Cu films is that the ferromagnetic coupling of the center Co film to the top and bottom Co films rises very sharply for Cu thickness less than about 1.8 nm so that complete antiparallel alignment cannot be attained and the GMR drops. This coupling is attributable partly to magnetostatic “orange peel” coupling caused by interfacial roughness,⁹ and partly to the well-known oscillatory exchange coupling.¹⁰ In recent work, we have investigated the correlation between the surface roughness during spin valve deposition, as observed by *in situ* scanning tunneling microscopy, and the coupling strength.¹¹ Although that work was primarily based on glass and aluminum oxide substrates, a brief examination of spin valves deposited on NiO substrates found general similarities in grain size (~ 10 nm) and roughness (0.5–0.9 nm).¹¹

We are presently investigating various approaches to reducing the ferromagnetic coupling, including deposition at low substrate temperatures to suppress interdiffusion at the Co/Cu interfaces and the use of surfactants such as In, Pb, and Au to smooth the Co and Cu surfaces during deposition. These studies will be the subject of future publications.

The thermal degradation of our spin valves by prolonged annealing at 250 $^{\circ}$ C is the subject of other publications. See Ref. 12.

B. Bottom spin valves

Bottom spin valves do not appear to have any important performance advantages over symmetric spin valves. Nevertheless, it was useful to investigate their properties since some interesting insights have emerged.

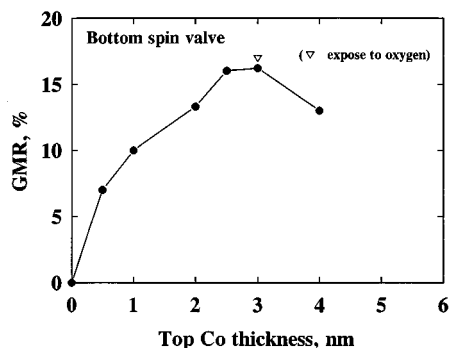


FIG. 5. A plot of the GMR (in vacuum) vs the top Co film thickness for bottom spin valves of the type illustrated in Fig. 1 (the bottom Co film thickness is 2.5 nm). The effect of exposing the 3 nm Co sample to $\sim 10^{-2}$ Torr s of O_2 is also plotted.

The GMR loops of bottom spin valves generally have a very similar appearance to those of symmetric spin valves, e.g., Fig. 3. The principal difference is that the GMR is significantly smaller for bottom spin valves. Minor differences are often noted in the coercivity and coupling exhibited by the unpinned Co film, and they are generally slightly smaller for the bottom spin valves.

Figure 5 presents the dependence of the GMR on the thickness of the top Co film. The GMR is a maximum for a Co thickness of about 2.5–3.0 nm of Co. The results here are quite different from those for the center Co film of a symmetric spin valve (see Ref. 7), where the GMR exhibited a maximum for a center Co film thickness of about 3.0–5.0 nm of Co. One possible explanation for the bottom spin valve requiring less Co in the unpinned or “valve” film would be that some conduction electrons reflect specularly at the Co/vacuum interface. Note that specular reflection at this interface would increase the effective thickness of the Co.¹³

Also of interest in Fig. 5 is the effect of exposure to O_2 . We have consistently found that when the thickness of the top Co is close to its optimum value, a small additional increase in GMR can always be obtained by exposure of the sample to O_2 . It was found by x-ray photoelectron spectroscopy that the top two or three atomic layers of Co are readily oxidized, but as the surface oxidizes it becomes passivated, and O_2 exposures larger than $\sim 10^{-2}$ Torr s have little additional effect. The mechanism for the increase in GMR is not known, but one possibility is that an increase occurs in the amount of specular scattering (i.e., Co/CoO interface might scatter a larger fraction of the incident electrons specularly than does the Co/vacuum interface). Note here that specular scattering (as opposed to diffuse scattering) has the effect of allowing an electron to travel farther (in the direction of the current).

The GMR of 17.0% found after the exposure to O_2 (Fig. 5) is the largest value ever reported for a simple (one Cu film) spin valve. However, a disadvantage of this treatment is that the coercivity of the unpinned Co film increases from 3.5 to 5.4 mT (35 to 54 Oe).

This increase in coercivity represents the initial stage of the pinning process that occurs when a NiO film is deposited

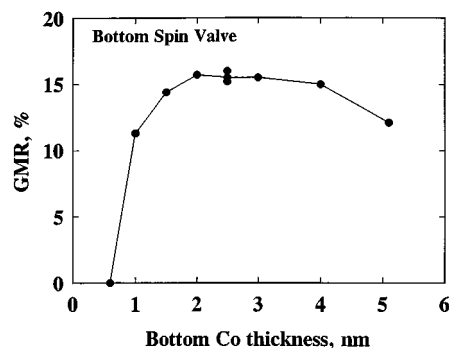


FIG. 6. A plot of the GMR (in vacuum) vs the bottom Co thickness for bottom spin valves of the type illustrated in Fig. 1 (the top Co film thickness was 3 nm).

on Co (as in a symmetric spin valve). The NiO film is deposited after 2 mTorr of an 85/15 Ar/ O_2 mixture is introduced into the chamber and the Ni magnetron gun is turned on. Two or three atomic layers of Co will oxidize under these conditions before any NiO is deposited. Thus, CoO is actually in contact with the top Co film in a symmetric spin valve. We have attempted to increase the pinning of the top Co film in symmetric spin valves by depositing a few atomic layers of Ni on the Co prior to NiO deposition to prevent formation of the CoO, but so far no increases in the pinning have been achieved. The rationale for these attempts was that NiO has a much higher Néel temperature than CoO.

The maximum GMR without the use of O_2 is 16.2% (in Fig. 5). This value should be compared with the maximum GMR of 23.4% achieved for symmetric spin valves. The increase from 16.2% to 23.4% appears to be representative of the degree of improvement that can be expected in going from a simple spin valve to a symmetric spin valve.

The dependence of the GMR on the thickness of the bottom Co film, shown in Fig. 6, is quite different from that of the top Co film (in Fig. 5). Perhaps the most surprising result is that a mere 1 nm of Co gives a respectable 11.3% GMR. This result is surprising because conductivity measurements indicate that 1 nm Co is near the percolation threshold, and a very patchy film is likely.

Figure 7 presents the coercivity of the bottom (pinned) Co film as a function of its thickness. If the pinning is purely due to the underlying NiO, i.e., if there is no contribution from the Co itself, a $1/t$ dependence would be expected as thicker Co provides a larger lever arm, as it were, to rotate the magnetization. The solid line in Fig. 7 is a $1/t$ extrapolation from the largest Co thickness backwards to smaller values. The fit is quite good down to 2 nm. Below 2 nm it appears that a different effect is occurring. The coercivity appears to be dropping sharply, as illustrated by the dashed line. This drop is presumably associated with the Co film becoming discontinuous.

Figure 8 presents the dependence of the coercivity and the coupling of the top Co film on its thickness. The scatter in the data prevents identification of the functional dependence but the coupling decreases roughly as $1/t$ (the solid

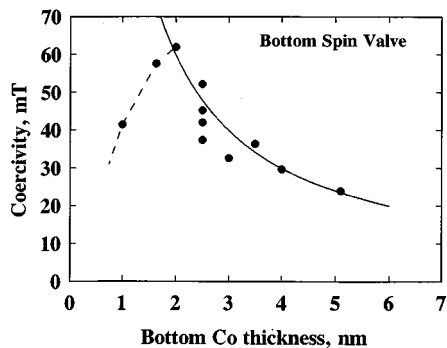


FIG. 7. A plot of the coercivity of the bottom Co film vs its thickness for bottom spin valves. See the text for explanations of the solid and dashed curves. (Note: 10 mT=100 Oe.)

curve), and the coercivity increases roughly linearly (the dashed curve) with Co thickness. From all points of view, the bottom spin valve properties are clearly optimized with a top Co thickness of 2.5–3 nm.

IV. CONCLUSIONS

The major conclusions of this work may be summarized as follows:

- (1) The GMR of symmetric spin valves increases strongly as the partial pressure of H₂O in the chamber prior to film deposition decreases.
- (2) The GMR increase in symmetric spin valves shows no sign of saturating at the lowest H₂O partial pressures obtainable in the present work, $\sim 10^{-9}$ Torr.
- (3) The largest GMR value obtained for a symmetric spin valve in this work is 23.4% at RT.
- (4) The largest GMR value obtained for a bottom spin valve is 17.0% at RT.
- (5) There are some indications that specular scattering of conduction electrons may occur at Co/vacuum and Co/CoO interfaces and may increase the GMR slightly.

ACKNOWLEDGMENTS

This work has been supported in part (W.F.E. and R.D.McM.) by the NIST Advanced Technology Program and in part (A.E.B.) by NSF Program No. DMR-9400439.

¹T. C. Anthony, J. A. Brug, and S. Zhang, IEEE Trans. Magn. **30**, 3819 (1994).

²P. M. Baumgart, B. Dieny, B. A. Gurney, J.-P. Nozieres, V. S. Speriosu,

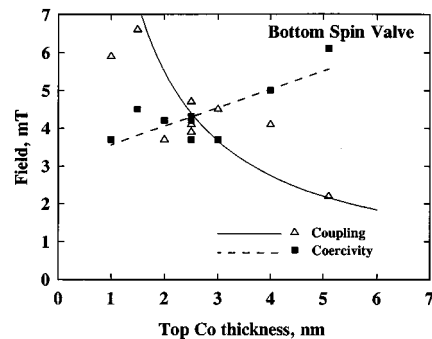


FIG. 8. A plot of the coercivity and the coupling of the top Co film vs its thickness for bottom spin valves. See the text for explanations of the solid and dashed curves. (Note: 1 mT=10 Oe.)

- and D. R. Wilhoit, U. S. Patent 5,287,238; Feb. 15, 1994.
- ³H. Kano, K. Kagawa, A. Suzuki, A. Okabe, K. Hayashi, and K. Aso, Appl. Phys. Lett. **63**, 2839 (1993).
- ⁴Th. G. S. M. Rijks, W. Folkerts, J. C. S. Kools, W. J. M. de Jonge, and R. Coehoorn, in Colloquium Digest, 14th Int. Coll. on Mag. Films and Surf., Dusseldorf, 1994, p. 29.
- ⁵V. S. Speriosu, B. Dieny, P. Humbert, B. A. Gurney, and H. Lefakis, Phys. Rev. B **44**, 5358 (1991); B. Dieny, V. S. Speriosu, S. S. P. Parkin, B. A. Gurney, D. R. Wilhoit, and D. Mauri, *ibid.* **43**, 1297 (1991); C. Meny, J. P. Jay, P. Panissod, P. Humbert, V. S. Speriosu, H. Lefakis, J. P. Nozieres, and B. A. Gurney, Mater. Res. Soc. Symp. Proc. **313**, 289 (1993); B. Dieny, J. Magn. Mater. **136**, 335 (1994).
- ⁶M. J. Carey, F. E. Spada, A. E. Berkowitz, W. Cao, and G. Thomas, J. Mater. Res. **6**, 2680 (1991); M. J. Carey and A. E. Berkowitz, Appl. Phys. Lett. **60**, 3060 (1992); M. J. Carey and A. E. Berkowitz, J. Appl. Phys. **73**, 6892 (1993).
- ⁷W. F. Egelhoff, Jr., T. Ha, R. D. K. Misra, Y. Kadmon, J. Nir, C. J. Powell, M. D. Stiles, R. D. McMichael, C.-L. Lin, J. M. Sivertsen, J. H. Judy, K. Takano, A. E. Berkowitz, T. C. Anthony, and J. A. Brug, J. Appl. Phys. **78**, 273 (1995).
- ⁸A. Chaiken, P. Lubitz, J. J. Krebs, G. A. Prinz, and M. Z. Harford, J. Appl. Phys. **70**, 5864 (1991).
- ⁹L. Néel, Comp. Rend. Acad. Sci. (France) **255**, 1545 (1962); **255**, 1676 (1962).
- ¹⁰S. S. P. Parkin, R. Bhadra, and K. P. Roche, Phys. Rev. Lett. **66**, 2152 (1991).
- ¹¹R. D. K. Misra, T. Ha, Y. Kadmon, C. J. Powell, M. D. Stiles, R. D. McMichael, and W. F. Egelhoff, Jr., Mater. Res. Soc. Symp. Proc. **384**, 373 (1995).
- ¹²R. D. McMichael, W. F. Egelhoff, Jr., and M. Ha, Mater. Res. Soc. Symp. Proc. **384**, 397 (1995); R. D. McMichael, W. F. Egelhoff, Jr., and L. H. Bennett, IEEE Trans. Magn. **31**, 3930 (1995).
- ¹³K. Fuchs, Proc. Camb. Philos. Soc. **34**, 100 (1938); E. H. Sondheimer, Adv. Phys. **1**, 1 (1952); A. E. Ennos, Brit. J. Appl. Phys. **8**, 113 (1957); N. S. P. Lucas, Appl. Phys. Lett. **4**, 73 (1964); J. P. Chauvineau and C. Pariset, Surf. Sci. **36**, 155 (1973); J. R. Sambles, K. C. Elsom, and D. J. Jarvis, Philos. Trans. R. Soc. A **304**, 365 (1982); J. R. Shambles, Thin Solid Films **106**, 321 (1983); M. Jałochowski and E. Bauer, Phys. Rev. B **37**, 8627 (1988); M. Jałochowski and E. Bauer, Phys. Rev. B **38**, 5272 (1988).