Temperature dependence of the resistivity and tunneling magnetoresistance of sputtered FeHf(Si)O cermet films

Temperature dependence of the resistivity and tunneling magnetoresistance of sputtered FeHf(Si)O cermet films

G. J. Strijkers,[a] H. J. M. Swagten, B. Rulkens, R. H. J. N. Bitter, and W. J. M. de Jonge
Department of Physics and COBRA, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

P. J. H. Bloemen
Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

K. M. Schep[b]
Faculty of Applied Physics and DIMES, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

(Received 18 March 1998; accepted for publication 27 May 1998)

We have studied the tunneling resistivity and magnetoresistance of reactive sputter deposited FeHfO and FeHfSiO thin granular films. Maximum magnetoresistance ratios at room temperature of 2% and 3.2% were observed for films with compositions of $Fe_{47}Hf_{10}O_{43}$ and $Fe_{40}Hf_6Si_6O_{48}$, respectively. The magnetoresistance shows a decrease with temperature, which cannot be explained by spin-dependent tunneling only. We propose that spin-flip scattering in the amorphous FeHf(Si)O matrix causes this decrease as function of temperature. A two current model for the tunnel magnetoresistance, taking into account spin-flip scattering, is presented which can describe the observed temperature dependence of the magnetoresistance. © *1998 American Institute of Physics.* [S0021-8979(98)02917-X]

I. INTRODUCTION

Recently there has been a great deal of interest in the magnetoresistance (MR) effect in materials which combine ferromagnetic metals and insulators. The observed MR effect in these materials is often denoted as tunnel magnetoresistance (TMR) or junction magnetoresistance (JMR) because it is ascribed to the spin-dependent tunneling of electrons between two ferromagnetic materials across an insulating barrier.

This TMR effect can be found in layered structures in which a current flows from one ferromagnetic layer (e.g., Co, CoFe) across an insulating layer (often Al_2O_3) to another ferromagnetic layer in a so-called tunnel junction.[1,2] The preparation of these junctions is, however, rather difficult as it requires lithographic techniques or shadow evaporation with the help of masks. TMR can also be observed in a different class of materials, the so-called cermet films. These are composed of metallic magnetic grains embedded in an insulating matrix, in which the probability for electrons to tunnel from one grain to another depends on the relative orientation of the magnetic moments of the grains. Several granular systems have been studied, for example $CoSiO_2$,[3] $FeSiO_2$,[4,5] $CoAl_2O_3$,[6–8] and FeHfO.[9] Among these materials there is particular interest in FeHfO not only for its magnetoresistance but also for its soft magnetic properties.[10–12]

In this article we report on the observed TMR in reactive sputter deposited FeHfO and FeHfSiO thin films. We will focus on the temperature dependence of the TMR and resistivity which has not been studied in great detail so far and this yields additional insight into the mechanisms for spin-dependent conductivity. The unusual temperature dependence of the TMR of our films is in contrast with earlier studies of, for example, $CoAl_2O_3$ (Ref. 8) and $FeSiO_2$ (Ref. 5) and cannot be explained with spin-dependent tunneling only. We propose a model for the temperature dependence of the magnetoresistance in which we have included spin-flip scattering.

II. EXPERIMENT

All films were prepared by rf diode sputtering on a Perkin–Elmer 2400 machine, with a base pressure of about 4×10^{-7} mTorr, at a sputter pressure of 3–4 mTorr from a $Fe_{83}Hf_{17}$ target. The composition of the films was varied by changing the partial O_2 pressure of the Ar/O_2 flow. For the sputtering of the FeHfSiO films 4% of the target was covered with Si pellets. The films are sputtered on glass and the thickness of the FeHfO and FeHfSiO films is 2.1 and 0.7 μm, respectively. The composition of the materials was determined with electron probe microanalysis (EPMA). Details on the microstructure of these films will be published in a separate article.[13] Resistivity and TMR measurements were done in a standard four point contact geometry with current and field in the plane of the films.

III. RESULTS AND DISCUSSION

Figure 1 shows the MR ratio as a function of the applied field at room temperature of a $Fe_{47}Hf_{10}O_{43}$ film. The MR is measured with current either perpendicular or parallel with respect to the applied field. As can be seen, there is almost no

[a]Author to whom correspondence should be addressed; electronic mail: Strijkers@phys.tue.nl
[b]Present address: Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

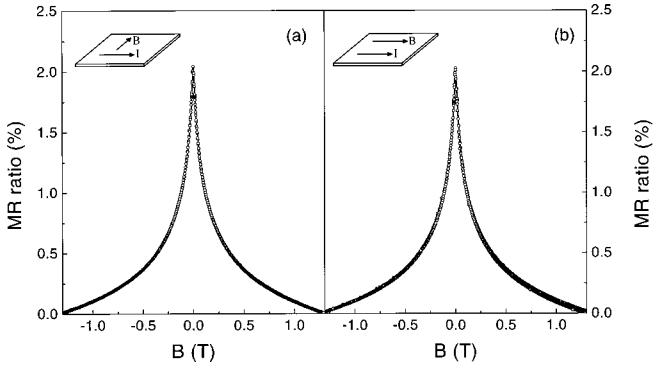

FIG. 1. MR ratio as a function of the applied field at room temperature for $Fe_{47}Hf_{10}O_{43}$ with current perpendicular (a) and parallel (b) with respect to the applied field. The MR ratio is defined as $[\rho-\rho(B=1.3\ \mathrm{T})]/\rho(B=1.3\ \mathrm{T})\times 100\%$.

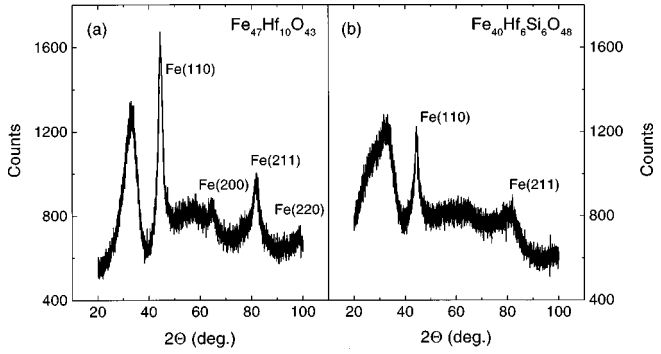

FIG. 3. X-ray diffraction θ-2θ scan with Cu K_α radiation for (a) $Fe_{47}Hf_{10}O_{43}$ and (b) $Fe_{40}Hf_6Si_6O_{48}$. The patterns display clear Fe peaks from the grains, a large amorphous background, and a peak around 30°, which possibly results from a combination of HfO_2, Fe_2O_3, and SiO_2 crystalline phases.

difference between the two geometries, which shows the absence of a significant contribution of an anisotropic MR effect. The MR curves of this film are typical for all of our FeHfO and FeHfSiO cermet materials.

We have prepared a series of FeHfO and FeHfSiO films in which we have varied the partial O_2 pressure during the sputter process. This allows us to fabricate films with different Fe concentrations. Figure 2 shows the Fe concentration dependence of the TMR and the resistivity at room temperature. The resistivity is extremely large and increases strongly with decreasing Fe concentration. This can be understood as follows. For a large Fe concentration a metallic conductance arises because part of the Fe grains are connected. For lower Fe content the percolation concentration will be approached[14–16] and the grains become electrically isolated by an insulating amorphous FeHf(Si)O phase resulting in tunnel-type conductivity with orders of magnitude larger resistivities as compared to metallic iron ($\rho_{Fe}\approx 10\ \mu\Omega$ cm). Note the difference in scale between the resistivity of FeHfO and the FeHfSiO films. For Fe concentrations below 45% for FeHfO and below 40% for FeHfSiO the layers become fully oxidized and insulating. In both cases the TMR at room temperature peaks near the percolation limit where a small barrier between the grains can be expected. The TMR for the FeHfSiO films has a maximum of about 3.2% for the composition $Fe_{40}Hf_6Si_6O_{48}$. For the FeHfO films the maximum TMR of approximately 2% appears at higher Fe concentration for the film with composition $Fe_{47}Hf_{10}O_{43}$.

Next we present the temperature dependence of the resistivity and the TMR ratio of the FeHfO and FeHfSiO films. We will focus on the films around maximum TMR because they are believed to have an optimal grain size and separation between the grains with respect to the observation of spin-dependent tunneling. X-ray diffraction with Cu K_α radiation for these films, presented in Fig. 3, display clear Fe peaks from the grains, a large amorphous background, and a peak around 30° of which the origin is not clear, but possibly this is a combination of HfO_2, Fe_2O_3, and SiO_2 crystalline phases. The temperature dependence of the resistivity of several FeHfO and FeHfSiO films, around maximum TMR, is presented in Fig. 4, plotted as $\log\rho$ vs $T^{-1/2}$. This proportionality should represent a thermally activated tunneling current flowing from grain to grain through an insulating matrix as calculated by Sheng *et al.*,[14–16] viz. ρ

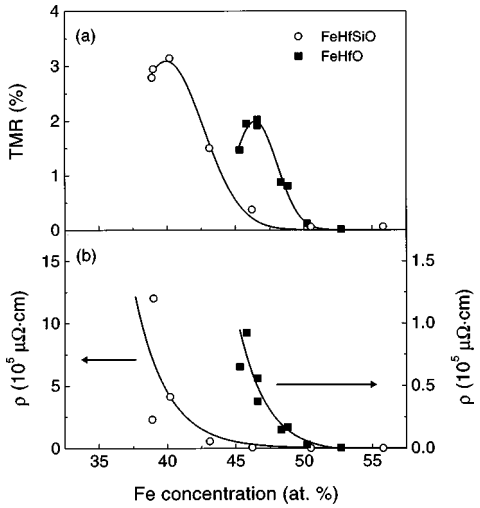

FIG. 2. (a) TMR and (b) resistivity ρ at room temperature as a function of the Fe concentration for FeHfO and FeHfSiO. The solid lines are guides for the eye only.

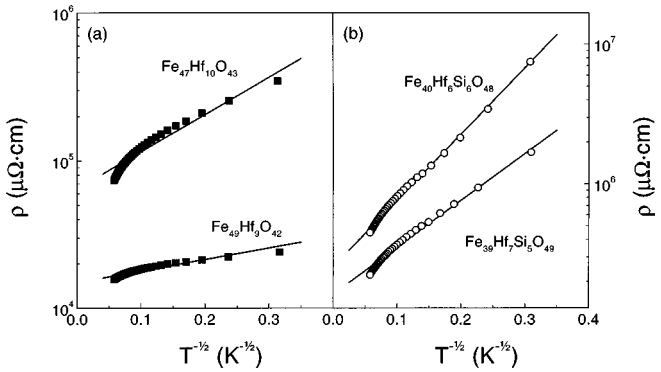

FIG. 4. Temperature dependence of the resistivity, $\log\rho$ vs $T^{-1/2}$, for several (a) FeHfO and (b) FeHfSiO films with compositions around maximum TMR. The solid lines are fits to the experimental data according to $\rho\propto\exp 2\sqrt{(C/k_BT)}$, which represents a thermally activated tunneling current flowing from grain to grain through an insulating matrix.

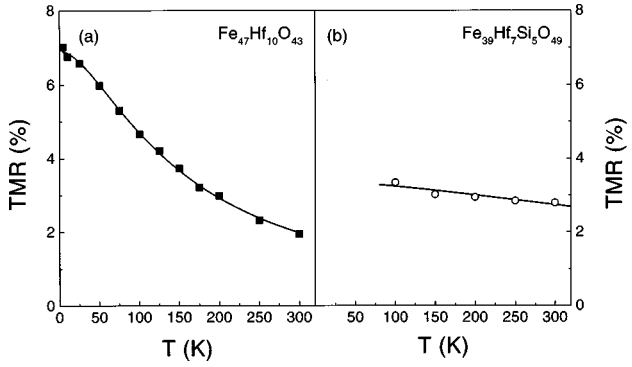

FIG. 5. Temperature dependence of the TMR for (a) $Fe_{47}Hf_{10}O_{43}$ and (b) $Fe_{39}Hf_7Si_5O_{49}$. The solid lines are fits to the experimental data with the proposed resistor model for TMR in granular alloys, which includes spin-flip scattering.

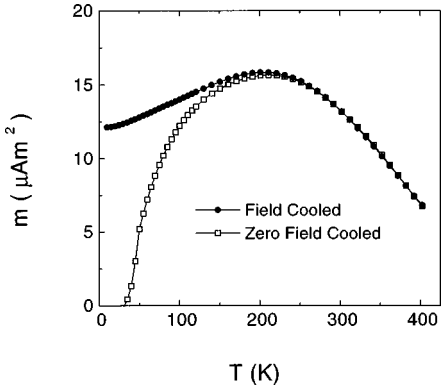

FIG. 6. Field-cooled and zero-field-cooled magnetic moment as a function of temperature of $Fe_{47}Hf_{10}O_{43}$.

$\propto \exp 2\sqrt{(C/k_BT)}$, with activation energy $C=(2m\phi/\hbar^2)^{1/2}sE_c$ (where m is the electron mass, ϕ the effective barrier height, s the separation between the grains, and E_c the charging energy). The solid lines are fits to our experimental data of $\rho \propto \exp 2\sqrt{(C/k_BT)}$. As can be seen, the fits for FeHfSiO are rather good ($C=2.6\times10^{-3}$ eV for $Fe_{40}Hf_6Si_6O_{48}$). On the contrary, for FeHfO there is a strong deviation between calculation and experimentally observed data ($C=0.7\times10^{-3}$ eV for $Fe_{47}Hf_{10}O_{43}$). Recently[5] a similar deviation was observed for $FeSiO_2$ and this was attributed to a leak conductivity which flows through interconnected grains. As we will show later on, this seems not to be applicable to our films since a leak conductivity leads to zero TMR at low temperature when all of the current is shunted through the interconnected grains. We also have to realize that $\rho \propto \exp 2\sqrt{(C/k_BT)}$ was derived for $C>k_BT$, a condition not satisfied in our films and therefore a deviation from this proportionality may be expected at higher temperatures. The magnitude C is to a great extent determined by the average separation between the grains s and the effective barrier height ϕ. Since the values of C obtained from our data are on the order of 10^{-3} eV, which is one to two orders smaller as compared to, for example, $CoAl_2O_3$ (Ref. 7) and $NiSiO_2$,[16] this suggests that the individual grains are only poorly separated by the amorphous matrix.

In Fig. 5 the temperature dependence of the TMR ratio is presented. The TMR ratio of $Fe_{47}Hf_{10}O_{43}$ increases strongly with decreasing temperature from about 2% at room temperature to about 7% at 4.2 K, in contrast to the TMR ratio of $Fe_{39}Hf_7Si_5O_{49}$ which increases only slightly. Inoue *et al.*[17] have shown that the magnetoresistance for ferromagnetic metallic clusters in an insulating matrix is equal to P^2 for small values of P, with $P=(N_\uparrow-N_\downarrow)/(N_\uparrow+N_\downarrow)$ the spin polarization in the ferromagnetic material. Here, $N_{\uparrow,\downarrow}$ is the density of states at the Fermi level with spin-up and spin-down, respectively. Within this model the magnetoresistance is independent of temperature, more or less consistent with the TMR ratio for $Fe_{39}Hf_7Si_5O_{49}$, but in contrast with the data for $Fe_{47}Hf_{10}O_{43}$.

There are several possible explanations why a temperature dependent TMR may still be observed in these materials. First of all, a reduction of the polarization P at higher temperatures leads to a decrease of the TMR.[18] However, we expect this to be a small effect because of the high Curie temperature of Fe. Moreover an almost temperature independent TMR was already observed for $FeSiO_2$.[5] Second, the temperature dependence of the TMR might be related to a change in magnetization behavior of the grains at low temperature. It is known that a superparamagnetic behavior of the magnetic grains in these material leads to a $1/T^2$ dependence of the TMR.[17] Therefore we have measured the field-cooled and zero-field-cooled magnetic moment of $Fe_{47}Hf_{10}O_{43}$ as a function of temperature as shown in Fig. 6. A wide peak in the zero-field-cooled measurement indicates a large spread in grain sizes, with a blocking temperature between 200 and 300 K. Superparamagnetic behavior is limited to temperatures above the blocking temperature, which is well above the regime where the strongest temperature dependence of the TMR is observed. Moreover, Fig. 7 shows four magnetization loops measured at $T=10$, 75, 150, and 300 K of $Fe_{47}Hf_{10}O_{43}$ with the applied field in the plane of the layers. For all temperatures the magnetization loops are similar in shape and seem to behave like a ferromagnetic layer, with out of plane loops (not shown) that saturate at $H=M_s$. For the interpretation of the magnetoresistance data it is important to mention that the magnetization in plane is well saturated at 1.3 T, the maximum field applied in the transport measurements, which ensures a good parallel align-

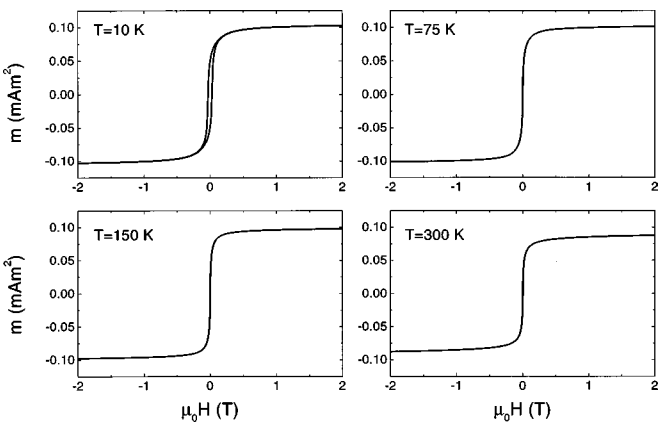

FIG. 7. Magnetization loops with the applied field in plane at various temperatures of $Fe_{47}Hf_{10}O_{43}$.

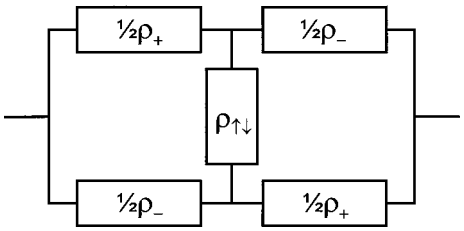

FIG. 8. Resistor scheme, which describes the resistivity in our granular materials including spin-flip scattering.

ment of the grains at all temperatures. On the other hand the remanent magnetization is close to zero which guarantees a high degree of antiparallel alignment of the grains at zero field. It should be noted that the saturation magnetization decreases slightly with increasing temperature which may indicate a small fraction of paramagnetic grains.

It is clear from the foregoing analysis that there is no dramatic change in magnetization behavior which can account for the large decrease of TMR at higher temperatures, and we believe another mechanism plays a role, causing the temperature dependence of the magnetoresistance. We propose that the strong decrease of TMR at higher temperatures is due to spin-flip scattering which is caused, for example, by magnetic impurities or iron-rich phases in the matrix. Recently, the effect of barrier impurities in ferromagnetic tunnel junctions was investigated and it was shown that these impurities can severely reduce the TMR as a result of spin-flip scattering.[19] The impact of spin-flip scattering will be analyzed via a simple model calculation. Fert *et al.*[20,21] described the temperature dependent resistance in ferromagnetic materials diluted with transition metal ions and used the resistor scheme as illustrated in Fig. 8 to account for the resistivity including spin-flip scattering. The resistance of such a circuit is given by

$$\rho = \frac{\rho_+\rho_- + \rho_{\uparrow\downarrow}(\rho_+ + \rho_-)}{\rho_+ + \rho_- + 4\rho_{\uparrow\downarrow}}, \tag{2}$$

where ρ_+ and ρ_- denote the resistivities of the up and down electrons, respectively, and where $\rho_{\uparrow\downarrow}$ is the spin-mixing resistivity. We apply this model directly to our granular system. The resistivities ρ_+ and ρ_- now consist of the sum of the part of the grains with magnetization ''up'' and magnetization ''down,'' respectively:

$$\begin{aligned} \rho_+ &= \frac{N}{M}\,\rho_\uparrow + \left(1 - \frac{N}{M}\right)\rho_\downarrow, \\ \rho_- &= \frac{N}{M}\,\rho_\downarrow + \left(1 - \frac{N}{M}\right)\rho_\uparrow. \end{aligned} \tag{3}$$

Here M is the total number of grains and N is the number of grains with magnetization up, $\rho_\uparrow$ and $\rho_\downarrow$ are the resistivities for the majority and minority spin electrons with respect to the local magnetization, respectively. The resistivity of Eq. (2) can now be expressed in terms of the relative magnetization $m = (2N\text{-}M)/M$, as

$$\rho(m) = \frac{1}{4}(\rho_\uparrow + \rho_\downarrow) - \frac{1}{4}\,m^2\,\frac{(\rho_\uparrow - \rho_\downarrow)^2}{\rho_\uparrow + \rho_\downarrow + 4\rho_{\uparrow\downarrow}}. \tag{4}$$

Equation (4) can be transformed to a similar equation for the resistivity as derived by Inoue *et al.*[17] with $\rho_\uparrow$, $\rho_\downarrow \propto \exp 2\sqrt{(C/k_BT)}$, yielding:

$$\rho(m) = \rho_0(1 - P^2m^2F)\exp(2\sqrt{C/k_BT}), \tag{5}$$

with ρ_0 constant and F representing the spin-flip scattering term given by

$$F = \frac{1}{1 + \dfrac{\rho_{\uparrow\downarrow}}{\rho_0}\exp(-2\sqrt{C/k_BT})}, \tag{6}$$

and P the polarization of the ferromagnetic material [in this model given by $(\rho_\uparrow - \rho_\downarrow)/(\rho_\uparrow + \rho_\downarrow)$]. We use Eqs. (5) and (6) to describe our data of the TMR ratio, which is defined as

$$\mathrm{TMR} = 100\% \cdot \frac{\rho(m=0) - \rho(m=1)}{\rho(m=1)}. \tag{7}$$

The spin-mixing rate at finite temperature has been modeled by Fert *et al.*[21,22] and evaluated as $\rho_{\uparrow\downarrow} = \rho^*_{\uparrow\downarrow}T^n$ ($n=2$ in case of electron-magnon scattering). The solid lines in Fig. 5 show that this model can describe the temperature dependence of the TMR ratio very well with $P=0.26$, $\rho^*_{\uparrow\downarrow} = 138\ \mu\Omega\ \mathrm{cm\,K}^{-n}$, with $n=1.3$ for FeHfO, and $P=0.18$, $\rho^*_{\uparrow\downarrow} = 38\ \mu\Omega\ \mathrm{cm\,K}^{-n}$, with $n=1.3$ for FeHfSiO (ρ_0 and C are the same as for the resistivity measurements). The magnitude of $\rho^*_{\uparrow\downarrow}$ and n are determined by the details of the spin-flip scattering mechanism, of which we don't know the exact origin. The spin polarization P is for both systems lower than the polarization of iron $P_{\mathrm{Fe}}=0.4$ as reported by Meservey *et al.*,[23] determined from $Al/Al_2O_3/Fe$ junctions at low temperatures. We should not be surprised by this, since our calculations are inspired by the models of Julliere[1] and Inoue *et al.*,[17] in which the TMR is determined solely by the spin polarization of the ferromagnetic material. However, it is theoretically argued[24] that the barrier material and the interface matching between barrier and magnetic material may determine the TMR effect as well, although no conclusive experimental data are available yet to verify this. Additionally, we have to realize that our granular films are far from an ideal system of pure Fe grains in an isolating $Hf(Si)O_2$ matrix and therefore negative effects on the magnitude of the polarization can be expected from, for example, intermixing of Fe and Hf and oxidation of Fe. Further experimental study is necessary to determine the exact composition of the grains and the matrix and this may also reveal why spin mixing is much more prominent in FeHfO than in FeHfSiO.

IV. CONCLUSIONS

In summary we have measured the TMR and the resistivity of reactive sputtered FeHfO and FeHfSiO cermet films. Maximum magnetoresistance ratios of 2% and 3.2% at room temperature are observed for films with the composition $Fe_{47}Hf_{10}O_{43}$ and $Fe_{40}Hf_6Si_6O_{48}$, respectively. The resistivity and magnetoresistance show an unusual temperature dependence which cannot be explained by spin-dependent tunneling only. We propose that spin-flip scattering in the amorphous FeHf(Si)O matrix causes a decrease of the TMR as a function of temperature.

ACKNOWLEDGMENTS

The authors would like to thank J. J. P. A. W. Noijen and G. W. M. Baselmans for technical assistance and H. J. M. Heijligers for EPMA measurements. The research of G. J. Strijkers was supported by the Foundation for Fundamental Research on Matter (FOM). This work was supported in part by the European Community ESPRIT Long Term Research Project No. 20 027, ''Novel Magnetic Nanodevices of artificially layered Materials (NM).'' [2]

[1] M. Juliere, Phys. Lett. **54A**, 225 (1975).
[2] J. S. Moodera, L. S. Kinder, T. M. Wong, and R. Merservey, Phys. Rev. Lett. **74**, 3273 (1995).
[3] A. Milner, A. Gerber, B. Groisman, M. Karpovsky, and A. Gladkikh, Phys. Rev. Lett. **76**, 475 (1996).
[4] S. Honda, T. Okada, and M. Nawate, J. Magn. Magn. Mater. **165**, 153 (1997).
[5] S. Honda, T. Okada, M. Nawate, and M. Tokumoto, Phys. Rev. B **56**, 14566 (1997).
[6] S. Mitani, H. Fujimori, and S. Ohnuma, J. Magn. Magn. Mater. **165**, 141 (1997).
[7] H. Fujimori, S. Mitani, and S. Ohnuma, J. Magn. Magn. Mater. **156**, 311 (1996).
[8] H. Fujimori, S. Mitani, and S. Ohnuma, Mater. Sci. Eng., B **31**, 219 (1995).
[9] Y. Hayakawa, N. Hasegawa, A. Makino, S. Mitani, and H. Fujimori, J. Magn. Magn. Mater. **154**, 175 (1996).
[10] A. Makino and Y. Hayakawa, Mater. Sci. Eng., A **181/182**, 1020 (1994).
[11] P. J. H. Bloemen and B. Rulkens (to be published).
[12] J. Huijbregtse, F. Roozeboom, J. Sietsma, J. Donkers, T. Kuiper, and E. van Riet, J. Appl. Phys. **83**, 1569 (1998).
[13] G. J. Strijkers, H. J. M. Swagten, and W. J. M. de Jonge, Presented at the 3rd MML Conference, Vancouver, BC, Canada, June 14–19, 1998.
[14] J. S. Helman and B. Abeles, Phys. Rev. Lett. **21**, 1429 (1976).
[15] B. Abeles, H. L. Pinch, and J. I. Gittleman, Phys. Rev. Lett. **35**, 247 (1975).
[16] P. Sheng, B. Abeles, and Y. Arie, Phys. Rev. Lett. **31**, 44 (1973).
[17] J. Inoue and S. Maekawa, Phys. Rev. B **53**, R11 927 (1996).
[18] J. S. Moodera, J. Nowak, and R. J. M. van de Veerdonk, Phys. Rev. Lett. **80**, 2941 (1998).
[19] R. Jansen and J. S. Moodera, J. Appl. Phys. **83**, 6682 (1998).
[20] A. Fert and I. A. Cambell, J. Phys. F **6**, 849 (1976).
[21] I. A. Cambell and A. Fert, *Ferromagnetic Materials*, edited by E. P. Wolfarth (North–Holland, Amsterdam, 1982), Vol. 3.
[22] A. Fert, J. Phys. C **2**, 1784 (1969).
[23] R. Meservey and P. M. Tedrow, Phys. Rep. **238**, 173 (1994).
[24] J. C. Slonczewski, Phys. Rev. B **39**, 6995 (1989).