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Impurity scattering from δ-layers in giant magnetoresistance systems

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The properties of the archetypal Co/Cu giant magnetoresistance (GMR) spin-valve structure have been modified by the insertion of very thin (submonolayer) δ-layers of various elements at different points within the Co layers, and at the Co/Cu interface. Different effects are observed depending on the nature of the impurity, its position within the periodic table, and its location within the spin valve. The GMR can be strongly enhanced or suppressed for various specific combinations of these parameters, giving insight into the microscopic mechanisms giving rise to the GMR. In particular, the doping of Fe and Ni into the spin valve close to, but not at the interface, leads to an increase in GMR, as does the introduction of Cu, a nonmagnetic impurity, into the Co layers.

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Ever since the development of the first transistor, solid-state science and technology has sought a proper description of the details of electronic transport in heterostructures. The past few years have seen a remarkably high level of activity in the area of magnetic heterostructures on the nanometer scale, not least in the area of giant magnetoresistance (GMR),[1] observed in ultrathin layered structures featuring transition-metal ferromagnets that can have the relative orientation of their layer moments altered by a magnetic field. The broad physical picture describing GMR is that it arises from spin-dependent scattering, so that parallel or antiparallel magnetic layer moments correspond to aligned or anti-aligned filters for the spin-polarized current. Approaches to the theory based on the Boltzmann formalism[2,3] can give a good phenomenological description of the basic effects. Early quantum pictures used a free-electron-like band, evaluating the Kubo formula for the case of spin-dependent scattering potentials.[4,5] More recent theoretical treatments have emphasized the importance of the electronic structure to the GMR,[6–10] which yield a better quantitative agreement with experiment.

Nevertheless these theories only consider pairs of materials (e.g., Fe/Cr, Co/Cu), limiting the understanding of more complex experimental structures. One area of contention is the microscopic location of the spin-dependent scattering—in the bulk or at the interface of the ferromagnetic layers. It has been attempted to get directly at the microscopic origin of the GMR by deliberately doping with impurities. This was reported for Fe/Cr multilayers using a few different dopants placed at the interface.[11,12] The different impurities have been characterized by the scattering spin asymmetry α, defined as the ratio of spin $\uparrow$ to spin $\downarrow$ scattering from the impurity $\rho_{\downarrow}/\rho_{\uparrow}$,[13–15] an essentially phenomenological parameter—only in the last few years have attempts been made to determine α from electronic band-structure calculations.[16] Similar interfacial doping experiments were reported by Shinjo.[17] Nevertheless these experiments were carried out using AF coupled superlattices, complicating the interpretation, as the AF state is ill defined and is easily degraded by the insertion of the dopants, leading to a loss of GMR merely due to loss of AF alignment.[18] Meanwhile Vouille *et al.* have studied the effects of doping various elements into the magnetic layers as alloys[19]—although this varied the α of the dopants, determining the relative bulk and interface contributions of these scatterers is model dependent.

A noteworthy theoretical treatment of the both the position and spin asymmetry (α) properties of impurities in Co/Cu multilayers has been given by Zahn *et al.*[20] Using the tight-binding Korringa-Kohn-Rostoker technique they were able to calculate the local density of states[21] and hence the effect of the impurity scatterers on the GMR. In this way direct conclusions can be drawn about the relative importance of bulk and interface scattering. However, these ideas have not been tested at all stringently by any of the experiments cited above.

In this paper we wish to address these issues, reporting on experiments in which we have systematically doped archetypal Co/Cu spin valves by the insertion of δ-layers of various elements to localize scattering with a certain value of α. The use of spin valves removes the difficulties in ensuring a proper AF alignment, as we always have a clear distinction between parallel ($\uparrow\uparrow$) and antiparallel ($\uparrow\downarrow$) moment alignments, so we can be certain to have measured the full GMR amplitude, defined as $(\rho_{\uparrow\downarrow}-\rho_{\uparrow\uparrow})/\rho_{\uparrow\uparrow}$. The previous experiments used only a few impurities. We have prepared a much larger set of samples to systematically study the dependence of the GMR on the changes in the electronic structure caused by the introduction of a wide variety of different dopants. In addition our δ-doping technique yields important information on the position dependence of the impurities that cannot be obtained by forming alloys or interfacial layers alone. We have observed long-ranged interactions between several different impurities and the interfacial spin-dependent scattering, over distances up to an order of magnitude greater than those previously reported[22] or predicted.[23]

The samples were deposited by dc magnetron sputtering in a computer controlled custom vacuum system with a base pressure of 2×10^{-8} Torr. The substrates were pieces cut from a (001) Si wafer, the working gas was 3.0 mTorr of Ar, and typical deposition rates were $\sim$3 Å s^{-1}. The substrates are heat sunk during deposition so that the temperature does not rise by more than a few °C above ambient. Magnetore-

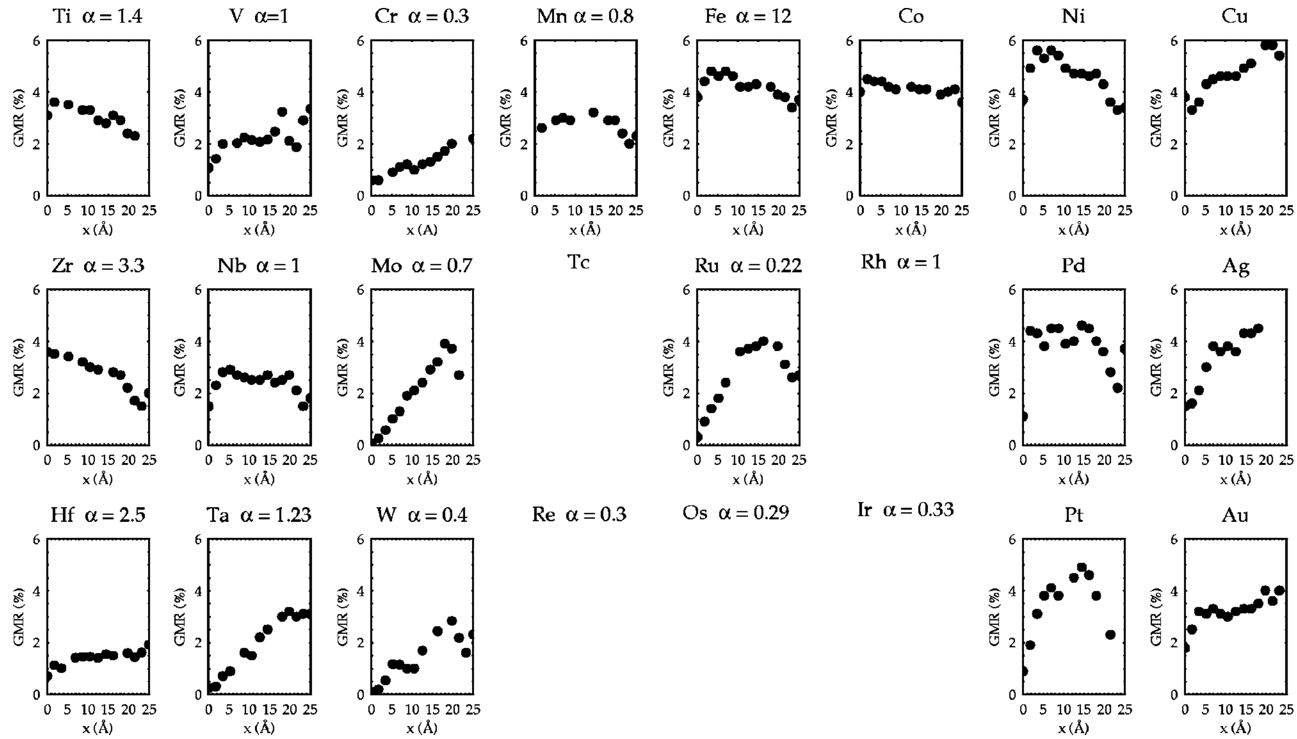

FIG. 1. Position dependence of the giant magnetoresistance for various transition metal impurities in the Co layer of the spin valves. At the top of each panel any available α data from Ref. 13 are given for comparison. The graph width represents the Co layer thickness. As x increases in each graph we move from the Co/Cu interface to the outermost surface of the Co layers.

sistance was measured by a standard dc four-probe method, at room temperature. The sample structure comprises those elements found in a typical spin valve—two Co layers separated by Cu, with an FeMn pinning layer. The impurity δ-layer is inserted into the Co at different points so that the overall structure is as follows: Si substrate / Ta(50) / Co(25-x) / X / Co(x) / Cu(30) / Co(x) / X / Co(25-x) / FeMn(80) / Ta(25); all thicknesses are given in Å. Since both the Ta and FeMn have resistivities of much greater than 100 $\mu\Omega$cm, we should expect most of the in-plane conduction to take place in the GMR active Co/Cu/Co sandwich. In all cases the amount of impurity corresponds to a few tenths of a monolayer—we used standard conditions of 0.5 s deposition using a power density of 1 W/cm^2. In some cases the introduction of the δ-layer close to the Co/FeMn interface reduced the exchange bias to the point where the $\uparrow\downarrow$ state cannot be accessed; such data points have been omitted from all the figures that we present.

Structural changes have been noted in similar experiments: the use of submonolayer amounts of impurities as surfactants[24,25] can change the resistivity as they alter growth modes while floating out of the film on the growth front. We have tested for such effects and not found them: there is little change in the observed GMR if we restrict ourselves to a δ-layer in only one or other Co layer. Since the δ-layer is being moved, in sequential samples, in opposite directions through the stack in these two cases the effects cannot be due to changes due to its floating out, as surfactant effects can only occur in layers deposited after the δ-layer.

Other structural effects might affect the GMR by changing, e.g., the grain size or the interfacial roughness. Separate Co/Cu multilayer samples with such δ-layers in the Co have been thoroughly characterized by synchrotron x-ray diffraction and reflectometry.[26] No significant or systematic variations in crystallography, grain size, or interfacial roughness or grading were found for Cr, Ta, Pd, or Cu dopants, a representative sample of those we investigate in the present work. Moreover, no systematic or significant variation in the sheet resistance of the samples was found, so that the overall scattering is largely unaffected by the presence of the δ-layers, only the spin-dependent scattering leading to GMR is affected.

In Fig. 1 the GMR is plotted against the position of the dopant δ-layer for a variety of elements from the central part of the transition metal block. Firstly the reader should note that the graph for Co is quite flat at $\sim$4.5%, and this can be regarded as the control experiment—a δ-layer of Co was inserted into both Co layers. This modest value is due to the thinness of the Co layers compared to those used in device applications.[27] It is immediately evident that it is not possible to increase the GMR of a Co/Cu structure by putting *any* other impurity at the interface, previously thought to be that part of the structure most susceptible to changes in chemical species.[22]

On the other hand, certain impurities will increase the GMR when placed *within* the Co, contrary to commonly held views about the pre-eminence of the interfaces for GMR. The neighboring plots for Ni and Fe show a similar behavior: both curves show a pronounced rise in GMR when the δ-layer is placed just behind, but not at, the interface. The effect is larger for Ni—almost 50% higher. One possible interpretation is that the δ-layer forms a second highly effective spin-filter just behind the first filter of the Co/Cu interface. Although no value is reported in Ref. 13 for Ni, the value of $\alpha_{\mathrm{Fe}}=12$ given for Fe in Co leads one to suppose that the value of α_{Ni} must also be $\gg 1$, and likely to be even higher still than the value for Fe.

The effects of Cu impurities are also of particular interest. When close to the interface there is little effect, or a small suppression, due presumably to the artificial creation of a more interdiffused, alloyed interfacial layer. However, once the Cu is deep inside the layer we see an enhanced GMR, somewhat unexpected in the light of the fact that these are nonmagnetic impurities. An obvious comparison here is with the large bulk spin anisotropy in the resistivity of Ni layers doped with Cu observed by Vouille *et al.*[19]

Within the group of noble metals, the GMR is lower for Ag impurities than for Cu, and lower still for Au. The behavior is consistent with greater spin-orbit scattering—the heavier elements flip spins more readily, mixing the spin current channels. A comparison with, for example, Pd and Pt is consistent; the GMR recovers more rapidly as Pd is moved away from the Co/Cu interface. Both these elements, with strong Stoner susceptibility enhancements in the bulk, are readily polarized by the Co matrix, leading to little loss in GMR.

On the other hand the graphs for Cr, Mo, Ru, Ta, and W all show that the insertion of the δ-layer at the interface almost totally suppresses the GMR. As the impurity is moved back into the Co the GMR rises in a roughly linear fashion. For Ru and Ta the GMR appears to plateau when the dopant is ~ 10 and 20 Å from the interface, respectively. This is exactly the behavior expected given the importance attached to interfacial scattering, but the length scale is greater than that of only ~ 2.5 Å previously reported when Co δ-layers were inserted into NiFe,[22] suggesting that the lengthscales involved in discussions of interfacial or bulk scattering must be highly material system dependent. For all of these materials but Ta, the reported α value is <1. The value of $\alpha_{\mathrm{Ta}}=1.23$ appears to be an overestimate.

The data for Mn, V, and Nb also look similar. These elements have α values reported $\simeq 1$, and we see that the dependence on the position of the dopant layer is quite weak. The GMR is suppressed wherever the δ-layer is placed. There is little or no suppression of the GMR when the elements Ti or Zr, both with $\alpha>1$, are introduced into the interfacial region of the Co layer. The effects of Hf are anomalous in this regard, possibly either $\alpha_{\mathrm{Hf}}=2.5$ is an overestimate, or the high nuclear charge of Hf leads to a large spin-orbit scattering term. This is to be compared with the results found for Ta.

It is also of interest to pose the question regarding the effects of impurities in the Cu spacer layer. The reader's attention is drawn to Fig. 2, where the GMR of the spin valves with Co(Cu) impurities in the Cu(Co) layer(s) is presented. The data for the Cu impurities (solid symbols) is taken from Fig. 1. As we have seen, the GMR rises as the Cu moves back into the Co after a small suppression close to the interface. On the other hand, Co impurities in the Cu spacer strongly reduce the GMR with only a weak position dependence unless they are close to the interface. We should expect that Co atoms or clusters isolated in the Cu should behave (super)paramagnetically, leading to spin-independent scattering when averaging over time or position in the film, as in practical measurements. The decay length of ~ 10 Å is therefore a direct measure of the range of significant exchange interactions for the Co impurities in Cu. Further experiments with other impurities in the spacer layer are all consistent with the same general picture: a position independent suppression of the GMR due to a shortening of the mean-free path in the crucial spacer layer, unless the impurity is within two or three atomic sites of the interfacial region, where the impurity can begin to affect nature of the interfacial scattering.

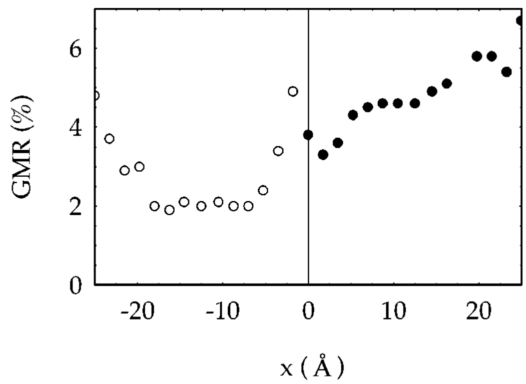

FIG. 2. Dependence of the GMR on the position of Co impurities in Cu (open symbols) or Cu impurities in Co (solid symbols). $x=0$ corresponds to the position of the Cu/Co interface.

We find that the experimental results are at odds with the published theoretical predictions of Zahn *et al.*[20] in the following important ways: impurities with $\alpha<1$ suppress the GMR, usually to a great extent when at the interface, and still have a considerable effect when several lattice constants away from the interface; impurities with $\alpha>1$ sometimes do provide an enhancement of the GMR, but it is only to be found when they are a few Å behind the Co/Cu interface; and impurities in the spacer layer have a dramatic effect by lowering the GMR. There are two omissions in the theory of Zahn *et al.*, which may lead to inaccurate predictions: a lack of interband transitions, found to have an important effect on conductivity calculations when realistic levels of disorder are included;[9] and vertex corrections are required for an accurate description of impurity scattering.[28]

The results of more sophisticated calculations by Binder *et al.*,[29] are qualitatively much more in accord with the observations that we report here. Self-consistently calculated impurity potentials were used, as well as a more correct description of the microscopic transport processes including state-dependent relaxation times and proper account taken of the scattering-in term. In particular, the predictions of the change in GMR when moving the δ-layers of specific materials from the interface in to the bulk of the Co show remarkable similarities with the observations and the sign of this change exhibits strong correlations with the sign of the exchange interaction calculated between the local moment of the impurity ion and the Co matrix.

The comprehensive nature of the data set allows some general conclusions to be drawn—there are consistent trends in the data for impurity δ dopants with $\alpha<1$, $\simeq 1$, and >1. Of course we are comparing our data to published values ofr α that are themselves rather uncertain, and so anomalies such as the case of Ta are to be expected. The position dependence of the scattering that leads to the GMR has been shown to be remarkably rich, and has important implications for what is meant when bulk or interface scattering is discussed. The α value for the δ-layer appears to be a function of x, as the electronic environment around the impurities will depend in the distance to the Co/Cu interface. Finally, there are two striking results, deserving of theoretical explanation: the significant increase in GMR caused by the insertion of $3d$ ferromagnet dopants *behind* the Co/Cu interface; and the marked increase in GMR when a nonmagnetic impurity, Cu, is embedded deep in the bulk of the Co. As well as suggesting possible routes to optimizing GMR materials for devices, any theory found to be capable of reproducing all these effects must contain the correct physics of GMR at a deep level.

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