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Effects of Impurity Atoms on Sputtered GMR Multilayers

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Abstract—**We have investigated the effects of residual gas impurity atoms on interlayer exchange coupling and giant magnetoresistance (GMR) in Co(9Å)/Cu(9Å) multilayers. Structural analysis was performed by Co^{59} NMR. We deposited sub-monolayer quantities of residual gases at different points in the Co/Cu bilayer; the interfaces, or the middle of the Cu spacers or Co magnetic layers. Impurities at the interface lower the GMR and increase remenant fraction and saturation field. We are able to model these results phenomenologically by adding biquadratic coupling. Impurities in the bulk of the Cu layers lower GMR still further, and such samples are well described by models containing almost 100% biquadratic coupling. We have demonstrated that the transport parameters in our samples are largely unaffected by small quantities of impurities, but that the interlayer coupling is extremely sensitive to them, particularly in the bulk of the Cu spacer layers.**

I. INTRODUCTION

The oscillatory coupling of magnetic multilayers, and the consequential giant magnetoresistance (GMR) is known to be very sensitive to structural defects. We chose to investigate these effects in Co/Cu multilayers as they are a commonly studied system, and exhibit a large GMR [1]. By inserting small amounts of residual gas impurities into the multilayer it is possible to disrupt the structure at specific points, and to probe which parts are most critical to the magnetic and transport properties.

II. SAMPLE PREPARATION & EXPERIMENTAL METHODS

The samples were deposited by DC magnetron sputtering. A Meissner coil was used to remove as much residual H_2O as possible from the vacuum chamber. However on cooling the coil H_2O still accounts for ~20% of the gases present, the remainder being largely N_2. Use of the coil lowers our base pressure by an order of magnitude to $\sim 4\times10^{-8}$ Torr.

The samples were deposited at rates of typically 3-4 Å/s on Si substrates, using 3.0 mTorr of Ar as the sputtering gas. It is possible for us to load fifteen substrates in the chamber for sequential deposition. Samples which are directly compared were grown in a single vacuum cycle, and are thus prepared in as similar conditions as possible. The shuttering of substrates and sources was controlled by computer to give high-precision and repeatability in layer thicknesses. All multilayer samples were of the form {Co(9Å)/Cu(9Å)}×20. Bilayer thicknesses were subsequently confirmed by measurement of Bragg peak positions in low angle X-ray diffraction spectra.

We selectively probed the effect of residual gas atoms at different points in the multilayer structure by pausing growth at that point, and allowing a light coverage of impurities to accumulate before resuming deposition. Exposure was of the order of 0.1 Langmuir, hence coverage is clearly in the sub-monolayer regime. A quadrupole mass spectrometer was used to sample the gases in the chamber immediately prior to and after sample growth. The high pressure of the Ar used as sputtering gas precludes real-time monitoring of background gas levels. The partial pressure of H_2O was the same before and after growth, but considerable levels of N_2 and CO_2 were detected after deposition, the total base pressure rising to $\sim 1.0\times10^{-7}$ Torr. A control sample was also grown with no pauses, this sample will be referred to as a pure sample.

Zero field NMR was performed at 1.5K with a broadband automated spectrometer in order to get information on the bulk and interface short range structure. Magnetoresistance was measured by a four-probe DC technique. Magnetometry was performed using the Magneto-Optic Kerr Effect (MOKE). Both measurements were made at room temperature.

III. NUMERICAL MODELLING

In this section the phenomenological model used to analyse the results will be outlined. We are able to predict remarkably well all the measured properties of our samples using only a few simple principles.

It is possible to determine the preferred state of a magnetic system in a given applied field by minimising the free energy. To model our multilayers we have assumed that the shape anisotropy of each Co layer prevents perpendicular magnetisation. All applied fields are in the plane of the layers, so the only variable for each magnetic layer is θ, the angle between the magnetisation m (1.422×10^{6} $\mathrm{Am^{-1}}$ for Co) of the layer and the applied field H. We write the areal energy density ε of a pair of magnetic layers in the following form:

$$\varepsilon = -\mu_0 mHt(\cos\theta_1 + \cos\theta_2) - J_1\cos\Theta - J_2\cos^2\Theta, \qquad (1)$$

where t is the thickness of the layers. J_1 and J_2 are the bilinear and biquadratic coupling constants respectively, the symbol Θ represents the difference in angle θ_1-θ_2. We have used the sign convention that negative J_1 corresponds to antiferromagnetic coupling, and negative J_2 corresponds to orthogonal coupling. It will be noted that there is no anisotropy term in this expression, we have found no evidence for significant anisotropy in our MOKE measurements, in both the angular independence of the *M-H* loop, and the lack of any noticeable hysteresis. The lack of texture revealed by high angle X-ray

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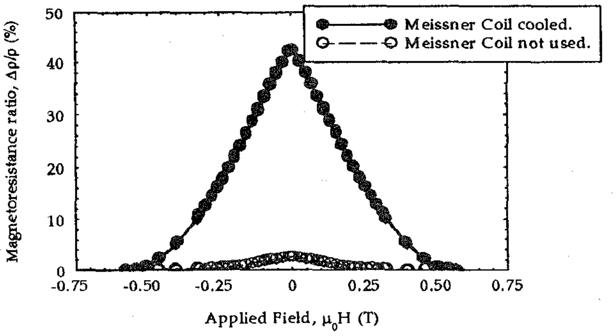

Fig. 1 GMR of Co(9Å)/Cu(9Å) samples grown with (solid circles) and without (open circles) the use of the Meissner coil.

scans also suggests that in-plane anisotropies are likely to be weak.

By numerically minimising the energy density as H is varied, we traced out the magnetisation and magnetoresistance loops, according to these expressions:

$$M/M_s \propto (\cos\theta_1 + \cos\theta_2), \quad \Delta R/R \propto \cos(\theta_1 - \theta_2). \qquad (2)$$

Finally in order to transfer the model from a trilayer to a multilayer, one notes that all the magnetic layers in the larger structure are coupled to two others (apart from the ones at the ends of the stack, negligible for enough bilayers). We have taken this into consideration when presenting numerical data.

IV. RESULTS AND DISCUSSION

GMR loops for samples grown with and without the use of the Meissner coil are shown in Fig. 1. The relative magnitudes of the magnetoresistance are what would be expected from the relative remnant fractions measured by MOKE, in accord with our simple model. The saturated resistivities of the two samples are too similar to explain the difference in $\Delta R/R$. The importance of a clean vacuum to large GMR is immediately evident. Our experience over the growth of large numbers of multilayer samples has been that H_2O is particularly damaging, in accord with others [2].

NMR spectra for the two samples are shown in Fig. 2. There are no differences in the spectra indicating that the interfaces have the same short range morphology in both samples. The main peaks indicate that the bulk Co is fcc-like, whilst the extended low frequency part of the spectra indicates that both samples have intermixed interfaces. The slight difference in the height of the main peaks indicates that there are Co thickness fluctuations of only about 6% from sample to sample. First analyses show that the amount of intermixing at the interfaces is about 1.5 full Co atomic planes suggesting that the interfaces are of quite good quality. (A perfectly flat interface would contain 1 atomic plane.) However it was not possible to reproduce the shape of the NMR spectra with a step interface model, nor with a simple diffuse interface model[3]. To simulate the NMR spectra we had to assume that the Co layers are composed of clustered Co atoms separated by a random CoCu alloy containing about 60% of Co. The height of the clusters is about 6 atomic planes and the surface area occupied by clustered Co atoms follows this sequence : 12%, 83%, 92%, 92%, 83%, 12%. This model has already been used in [4]. This particular structure of the Co layers (in particular the reduced magnetisation in the alloyed part) may play an important role in the magnetotransport behaviour of those samples.

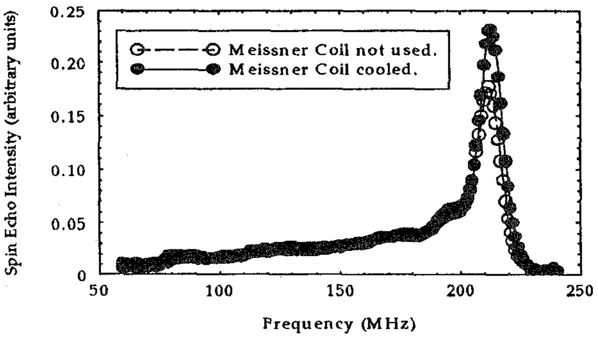

Fig. 2 NMR Spectra for Co(9Å)/Cu(9Å) samples grown with and without (solid & open circles) the use of the Meissner coil.

Further detailed analysis of such a pair of samples has been undertaken using synchrotron X-ray diffraction. No measurable differences were detected. The rms conformal roughness was 1.0Å, with a total rms roughness of 1.4Å. This represents an unusually high degree of correlation for sputtered samples. Full details of this work will be published elsewhere [5].

The GMR results of the selective probing experiments are shown in Fig. 3. The observed GMR ratio correlates with the remenance, with the exception of the sample with the impurities in the middle of the Co layer. We will discuss the other samples and then touch on this point briefly below. All the samples had similar values of saturated resistivity, 20±2μΩcm.

The pure sample can be seen to have a remenance of almost zero from the MOKE data (Fig. 4(a))- hence this sample should posses the largest possible GMR for a given set of transport parameters. In the fits to the data all magnetoresistance changes are expressed as fractions of this value ($\Delta R/R$ = 47%). Since the curves have symmetry and exhibit no hysteresis we show only one half of the MR loop, and one quadrant of the magnetometry data, although both forward and backward sweeps are shown in all panels of Fig. 4. The model does not predict the high field tail of the magnetoresistance well as it does

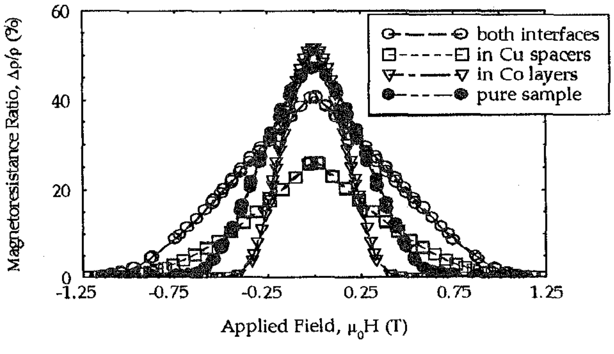

Fig. 3 GMR of Co(9Å)/Cu(9Å) samples doped in different places in the stack, and the result for the pure sample.

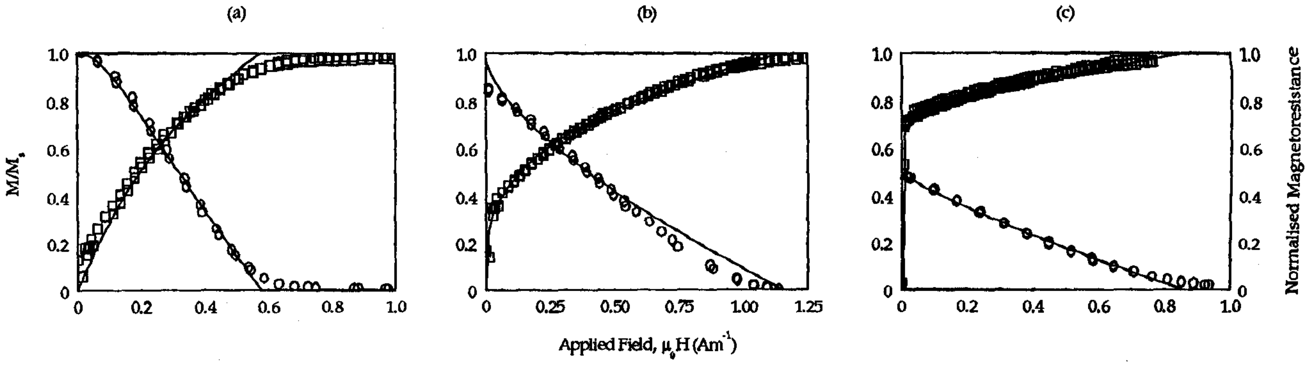

Fig. 4 MOKE (squares) and GMR (circles) room temperature data with fits from the model (solid lines). (a) Pure sample, (b) Impurities at placed at Co/Cu interfaces, (c) Impurities in Cu spacers.

not take into account small effects such as the ordinary magnetoresistance. The values of the coupling constants used in modelling the pure sample were $J_1 = -0.14$ mJm^{-2}, and $J_2 = -0.02$ mJm^{-2}.

Interface results (shown in Fig. 4(b)) are modelled with $J_1 = -0.18$mJm^{-2} and $J_2 = -0.09$mJm^{-2}. Here we have a larger biquadratic term. Fig. 4(c) presents the results for the sample where the impurities are in the middle of the spacers. Here there is considerable remenance, indicating poor antiferromagnetic alignment in zero field. A purely biquadratically coupled sample would have a remenant fraction of $\sqrt{2}/2$, and would display a GMR of half that of a perfectly antiferromagnetic sample. These values are very nearly what we measure, and we are able to calculate the solid line shown using the following numerical values: $J_1 = +0.01$ mJm^{-2}, and $J_2 = -0.15$ mJm^{-2}.

When the impurities were placed in the middle of each Co layer, a reduction in saturation field and a small rise in GMR ratio were observed. One might speculate that the impurities had caused the formation of magnetically dead regions inside the Co, reducing the average value of m, in turn reducing H_s. It is possible that the small but repeatable rise in GMR ratio is due to impurity atoms causing additional spin-dependent scattering, as they are embedded in a ferromagnetic matrix.

The same experiment has also been undertaken using spin-valve structures of the form Co/Cu/Co/FeMn. The FeMn layer exchange-biases the adjacent Co layer so that it is fully saturated in zero field[6]. The antiparallel alignment of magnetic layers required for GMR is now independent of interlayer coupling. The GMR ratio $\Delta R/R$ of all these samples was found to be in the range 5.8±0.2%, whether or not the sample contained impurity gas atoms, or their whereabouts in the structure. This demonstrates further that the large changes in GMR ratio seen in the multilayer samples are due entirely to changes in the nature of the interlayer coupling.

V. CONCLUSIONS

We have found that it is possible to dramatically reduce the GMR in Co/Cu multilayers with only small amounts of residual gas impurities introduced into the structure. We have shown that the electron transport parameters of the multilayers are minimally affected, and that the changes in GMR are driven by changes in the nature of the interlayer coupling.

A control sample deposited without the deliberate introduction of impurity species exhibited almost zero remenance, and was well described by a model with a large antiferromagnetic bilinear coupling term. When the impurities were placed in the centre of each spacer layer the GMR ratio was roughly halved. Good fits to the data could be achieved using a model where we supposed that coupling was overwhelmingly biquadratic in character. This was a much larger effect than when impurities were placed at the interfaces in the multilayer. We have shown that whatever the nature of this effect, the system is much less susceptible to residual gas damage at the interfaces than in the bulk of the spacers which must be good quality continuous copper to achieve the zero remenance necessary for a large giant magnetoresistance.

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