

## Thermally activated deterioration processes in Co/Cu GMR multilayers

M. Hecker, D. Tietjen, D. Elefant, and C. M. Schneider<sup>a)</sup>

*Institute of Solid State and Materials Research Dresden, Dresden 01171, Germany*

An Qiu, N. Cramer, R. E. Camley, and Z. Celinski

*University of Colorado, Colorado Springs, Colorado 80918*

The magnitude of the giant magnetoresistance (GMR) observed in multilayers is known to change irreversibly at elevated temperatures. To improve the thermal stability of devices, a fundamental understanding of the GMR and its correlation to the temperature-induced structural and morphological changes in a given system is mandatory. We therefore investigated the structural and magnetic properties of sputtered Co/Cu multilayers in the pre- and postannealed states (temperature regime for annealing up to 750 °C) by *in situ* x-ray diffraction, transport measurements, ferromagnetic resonance (FMR), and magneto-optical Kerr effect (MOKE). We were able to identify a sequence of distinct structural changes each of which sets in above a characteristic critical temperature. These critical temperatures depend strongly on the thickness of the individual layers. The structural alterations observed range from interfacial sharpening through texture reorientations up to the formation of a granular state, and are associated with distinct in/decreases of the GMR signal. Using FMR and MOKE we determined in-plane magnetic anisotropies and interlayer coupling for as-grown and annealed samples. © 2001 American Institute of Physics.

[DOI: 10.1063/1.1359223]

Multilayer systems composed of alternating ferromagnetic and nonmagnetic films are of great fundamental and technological importance due to their particular magnetic and transport properties, such as interlayer coupling and giant magnetoresistance (GMR). Specific material combinations such as Co/Cu or Ni<sub>81</sub>Fe<sub>19</sub>/Cu have been found to show large GMR effects<sup>1-3</sup> and are therefore also utilized in spin-valve systems for magnetic sensor applications.<sup>4</sup> Together with the application comes the question to what extent these layered systems survive at elevated temperatures. Several thermally activated microscopic processes (interdiffusion, grain boundary diffusion, grain growth, etc.) are likely to destroy the interface quality or the layered structure itself and may thus irreversibly impair GMR properties and device operation. Knowing the individual deterioration mechanism and its effect on the GMR is a first step towards tailoring thermally stable GMR film systems for operation at elevated temperatures.

In order to elucidate the situation in the popular Co/Cu system, we studied the properties of Co/Cu multilayers during a postgrowth annealing procedure as a function of temperature. The aim of this work was to correlate the structure and morphology of the multilayers after annealing with their transport and magnetic properties. Our films, grown on thermally oxidized (100) Si substrates, were prepared by dc magnetron sputtering in an Ar atmosphere of 0.6 Pa. The nominal layer sequence of the films consisted of 30x[Co (2.2 nm)+Cu (2.1 nm)]+Co (2.2 nm), corresponding to the second antiferromagnetic coupling maximum.

All samples were annealed for 1 h in vacuum (10<sup>-6</sup> mbar) up to different temperatures  $T_{an}$  in the range

between 100 and 740 °C. After the annealing procedure structural, transport, and magnetic properties were measured with a variety of techniques at room temperature. The x-ray diffraction experiments employed a Philips-XPert diffractometer with Cu  $K\alpha$  radiation, a Eulerian cradle and thin-film equipment. The transport properties were measured by a standard four-point probe system. The ratio  $(R_{max} - R_{sat})/R_{sat}$  served as a measure of the GMR, with  $R_{max}$  and  $R_{sat}$  being maximum and saturation resistance at high external magnetic fields in CIP geometry, respectively. The magnetic properties were determined using ferromagnetic resonance (10 and 24 GHz) and the magneto-optical Kerr effect (MOKE).

In previous high contrast reflectometry experiments with synchrotron radiation, which dealt with annealing up to 300 °C, we found only minor modifications in the film stack.<sup>5</sup> Our new measurements of the Co/Cu system using Cu  $K\alpha$  radiation (Fig. 1) show a surprising stability of the

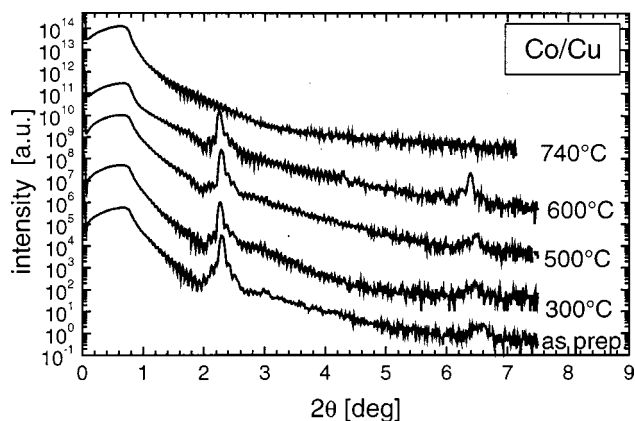


FIG. 1. X-ray reflectometry measurements of the Co/Cu multilayers.

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: c.m.schneider@ifw-dresden.de

layer sequence up to 600 °C. This stability manifests itself in the persistence of the Kiessig fringes and Bragg peaks indicative of the multilayer stacking. Only after annealing up to 740 °C is the multilayer structure effectively destroyed, which can be inferred from the disappearance of the Bragg peaks. Still the Kiessig fringes persist, indicating a film of well-defined thickness. Not only does the layer stacking remain stable, but the interfaces in the Co/Cu multilayer also turn out to be “sharp” to  $T_{\text{an}}=600$  °C. The reflectometry curves at  $T_{\text{an}}=600$  °C are best described by sharp interfaces with a mean interface roughness parameter of 0.5 nm. Apparently, there is no significant intermixing taking place up to this temperature, which is compatible with the immiscibility of Co and Cu deduced from the bulk phase diagram. Additional wide-angle diffraction experiments (not shown here) are incompatible with simple intermixing even after annealing up to  $T_{\text{an}}=740$  °C, but rather suggest a transition into a granular CoCu system. Although the first signs of multilayer breakup already appear in the wide-angle diffraction patterns after annealing at 500 °C (see below), this effect may be partially compensated for by interface sharpening in the remaining multilayer volume and is thus detected by the reflectometry measurements only at higher temperatures. The transition into the granular state takes place probably via grain boundary diffusion, as has been concluded from investigations of Co/Cu multilayers with a rather thick (4 nm) Cu interlayer.<sup>6</sup>

The diffraction peaks in the wide-angle region show several changes due to structural alterations appearing with increasing annealing temperatures. For  $T_{\text{an}}>220$  °C, Co/Cu multilayers show a decrease in the diffraction peak widths, indicating the onset of grain growth and a reduction of the defect density in the layers. The lower limits for the grain size  $D_{\text{vert}}$  in the direction vertical to the layer sequence can be estimated from the peak widths. In the as-deposited state, values of about 20 nm result for  $D_{\text{vert}}$ , and after the 500 °C thermal treatment  $D_{\text{vert}}$  increased to about 40 nm. Since these values are lower limits and neglect other reasons for broadening such as interface roughness or thickness fluctuations, it seems reasonable that a considerable fraction of the crystallites has grown through the complete layer stack above 400 °C.

In the as-prepared state, the multilayers show a broad  $\langle 111 \rangle$  fiber texture with a full width at half maximum (FWHM) <sub>$\psi$</sub>  of 17° (cf. Ref. 5). Up to an annealing temperature of 300 °C the ratio of crystallites with  $\{100\}$  and  $\{111\}$  planes parallel to the surface is about 0.1. However, this ratio increases to about 100 after annealing at 400 °C, and after reaching 500 °C, the  $\{111\}$  crystallite fraction has almost completely disappeared. Strong layer strains, in particular coherency strains, were concluded to be the driving force for this transition.<sup>7</sup> A second essential change in the layer structure is the transformation from a multilayer to a granular structure. The first signs of this transformation can be found in the wide-angle measurement after annealing at 500 °C, which show slightly enlarged intensities at the positions of pure face-centered-cubic (fcc) Co and Cu reflections. At about 650 °C, these peaks begin to dominate the multilayer

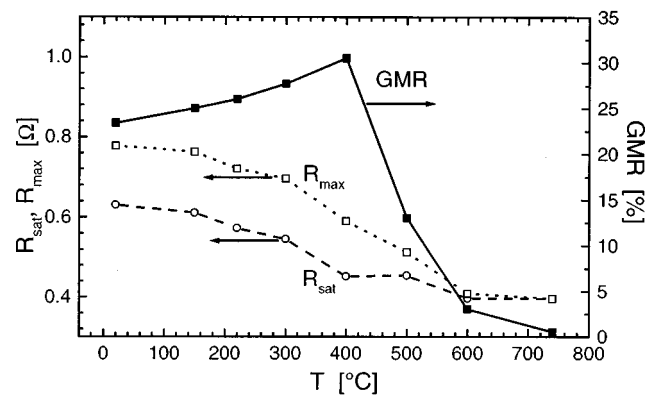


FIG. 2. Electrical resistance and GMR as a function of temperature.

peaks<sup>5</sup> and after reaching 740 °C the multilayer peaks have disappeared.

The previous annealing experiments on similar Co/Cu multilayers up to 200 °C revealed a slight increase of the GMR signal, which is interpreted as a “curing” effect associated with interface demixing. If no other mechanisms are involved, this process should become even more pronounced at high temperatures (or prolonged annealing times). This is exactly what we find in the resistivity measurements (Fig. 2). The corresponding GMR signal is initially 24% and increases up to a maximum of 30% after annealing at 400 °C. At the same time, the values of both the saturation resistance and the maximum resistance at zero field decrease monotonically (Fig. 2). In particular, the latter finding is a strong argument against intermixing or alloying in the multilayer because these processes would just lead to an increase of the resistivity, as observed in the NiFe/Cu system.<sup>8,9</sup> We note that the decrease in  $R_{\text{sat}}$  and  $R_{\text{max}}$  well above 200 °C may also partially be due to grain growth.

The trend in the behavior of  $R_{\text{sat}}$  and  $R_{\text{max}}$  continues even up to 600 °C and seems to reach a saturation at the highest annealing temperature of 740 °C. This is fully in line with the demixing behavior concluded from the x-ray reflectometry data. The GMR signal, however, starts to decrease after annealing in excess of 400 °C. At 500 °C, a GMR value of only 13% remains and a further reduction occurs down to below 1% after annealing up to 740 °C (Fig. 2). On the basis of the above arguments, interfacial mixing can be excluded as the microscopic mechanism for this breakdown. In other words, the disappearance of the GMR cannot be associated with a major change in the spin-dependent transport processes due to modified interfaces. Other processes with a magnetic or structural origin must be held responsible for this behavior. Therefore, further investigations of the magnetic properties by means of ferromagnetic resonance (FMR) and MOKE were carried out to clarify this point.

The MOKE results clearly prove the antiferromagnetic coupling in the Co/Cu multilayers. As shown in Fig. 3, the multilayer loop is initially slanted, indicating antiferromagnetic coupling (of  $J_1 = -0.015$  erg/cm<sup>2</sup>) which, however, is weak in the second antiferromagnetic coupling maximum. The loops were analyzed with two different numerical simu-

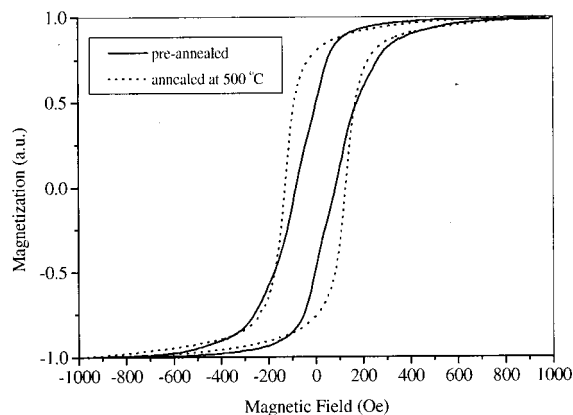


FIG. 3. MOKE measurements of the hysteresis loops.

lations: energy minimization and a discrete-time solution of the Landau–Lifshitz equation of motion. The multilayer hysteresis loops show a larger coercive field compared with that of a single Co layer. Between annealing steps of successively higher temperatures, two clear trends were observed. First, the coercivity remains near 85 Oe up to anneals of 200 °C, then increases somewhat linearly up to 130 Oe (corresponding to an anneal of 420 °C). After an anneal at 500 °C, the coercivity remained near 130 Oe. Second, the slant of the loop changed. For anneals up to 200 °C, the slant remained essentially unchanged. After an anneal of 260 °C, there was an increase of the loop slant. For successive anneals, the slanting decreased rapidly. The loop from the final anneal at 500 °C, shown in Fig. 3, shows little slant, indicating ferromagnetic coupling or no coupling. The latter finding provides an initial explanation for the strong decrease of the GMR signal. If the antiferromagnetic coupling breaks down, the system can no longer switch between an antiparallel (ground state) and parallel aligned state (applied field). It will assume, rather, noncollinear alignment or more or less parallel alignment of the individual magnetic layers, resulting in a reduced or almost vanishing GMR.

We also briefly comment on the behavior of the coercive field. One possible explanation for the increased coercive field is the presence of randomly oriented grains with corresponding random orientation of the crystalline anisotropy. We have found in our numerical simulations that random orientation of a fourfold anisotropy (anisotropy fields on the order of 280 Oe) does indeed lead to an increase in coercivity consistent with the experiments. Furthermore, we find that this increase in coercivity does not influence the slant of the hysteresis curve and thus our previous analysis of the coupling between films is unaffected.

Ferromagnetic resonance measurements on both the Co/Cu multilayer and the Co single film show in-plane uniaxial anisotropy of about 20 Oe. This uniaxial anisotropy is growth induced. After annealing at 100 °C, there is a slight increase in anisotropy to about 30 Oe. With higher temperature anneal steps, the anisotropy monotonically de-

creases and is essentially eliminated after annealing at 500 °C. The effective magnetization,  $4\pi M_{\text{eff}}$ , is nearly constant (15.1 kG) for annealing up to 250 °C. For higher annealing temperatures the effective magnetization changes irregularly within 1.5 kG of the initial value. Note that in the analysis of the FMR data we did not include the presence of any random anisotropy fields. The inclusion of these fields would reduce  $4\pi M_{\text{eff}}$  by about 3 kG.

The 24 and 10 GHz FMR measurements of the Co/Cu multilayers confirm the MOKE results. The FMR spectra show both acoustic and optical modes. For annealing temperatures up to 350 °C the optical mode resonance occurs at field values above those for the acoustic mode. This clearly indicates the antiferromagnetic coupling in these structures in accordance with the GMR and MOKE data. The amplitude of the optical mode increases with the annealing temperatures while the separation between acoustic and optical modes remains the same—700 Oe at 24 GHz. The dynamical calculations determined the strength of the exchange coupling to  $-0.014 \text{ erg/cm}^2$ . In contrast, for the samples annealed at 420 and 500 °C the FMR measurements of Co/Cu structures showed two optical modes, one below and a second above the resonance position of the acoustic mode. This indicates the presence of both antiferromagnetic and ferromagnetic coupling in our structures; that is, some of the adjacent layers are coupled antiparallel while other are coupled parallel. Furthermore, the linewidth of these optical modes is significantly larger than that for the acoustic mode and this suggests that we have a whole spectrum of coupling strengths.

In conclusion, our x-ray studies reveal that the interfaces in sputtered Co/Cu multilayers remain sharp and stable during annealing up to 600 °C. At higher annealing temperatures we find a reduction of the antiferromagnetic coupling and (from the position of the optical mode in FMR) the onset of ferromagnetic coupling, which explains the deterioration of the GMR signal for samples annealed above 400 °C.

The authors acknowledge financial support from DAAD (315/PPP), the NSF (INT-9815225 and DMR-9970789), and the SFB 422.

<sup>1</sup>S. S. P. Parkin, Z. G. Li, and D. J. Smith, *Appl. Phys. Lett.* **58**, 2710 (1991).

<sup>2</sup>G. Reiss, L. van Loyen, T. Lucinski, D. Elefant, H. Brueckl, N. Mattern, R. Rennekamp, and W. Ernst, *J. Magn. Magn. Mater.* **187**, 281 (1998).

<sup>3</sup>For a compilation of data on metallic magnetic multilayers, see, for example, I. K. Schuller, S. Kim, and C. Leighton, *J. Magn. Magn. Mater.* **200**, 571 (1999).

<sup>4</sup>See, for example, K. Y. Kim and J. E. Evetts, *J. Magn. Magn. Mater.* **198–199**, 92 (1999).

<sup>5</sup>M. Hecker, L. van Loyen, D. Tietjen, N. Schell, and C. M. Schneider, *Mater. Sci. Forum* (submitted).

<sup>6</sup>K. Rätzke, M. J. Hall, D. B. Jardine, W. C. Shih, R. E. Somekh, and A. L. Greer, *J. Magn. Magn. Mater.* **204**, 61 (1999).

<sup>7</sup>M. Hecker, W. Pitschke, D. Tietjen, and C. M. Schneider, *Thin Solid Films* (submitted).

<sup>8</sup>L. van Loyen, D. Elefant, D. Tietjen, M. Hecker, J. Thomas, and C. M. Schneider, *J. Appl. Phys.* **87**, 4852 (2000).

<sup>9</sup>W. Brückner, S. Baunack, M. Hecker, J.-I. Mönch, L. van Loyen, and C. M. Schneider, *Appl. Phys. Lett.* **77**, 358 (2000).