Nanostructure of Co/Cu multilayers

H. A. M. de Gronckel, K. Kopinga, and W. J. M. de Jonge
Department of Physics, Eindhoven University of Technology (EUT), 5600 MB Eindhoven, The Netherlands

P. Panissod and J. P. Schillé
Institute Pascal de Chemie et Materiaux Strasbourg, 4 rue Blaise Pascal, 67070 Strasbourg, France

F. J. A. den Broeder
Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands
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The nanostructure and local strain of [111] fcc Co/Cu multilayers are studied by means of nuclear magnetic resonance. The atomic topology of the interface can be deduced from the NMR spectrum and the local strains from the shift in the hyperfine fields. The results show that the Co/Cu interface is a mixed monolayer and that the Co layers, including the interface, have uniform strain inversely proportional to the Co thickness (within experimental error) with the proportionality constant depending on the Cu thickness.

Artificially layered metallic materials have attracted considerable attention during recent years. Interesting—and sometimes spectacular—new magnetic, structural, and transport phenomena have been reported. Among those we mention are dimensionality effects,[1] interlayer couplings,[2] anomalous magnetoresistance,[3] and anisotropy effects.[4]

One of the major problems in this rapidly developing field of research is the characterization of the structural perfection of the multilayered films, which includes the topology (or sharpness) of the interfaces, the lattice parameters, coherency, and strains. At the same time, according to current understanding, these parameters are of vital importance for the physical behavior.[5] For surfaces, detailed information on the topology can be obtained by many experimental techniques. For interfaces and individual layers embedded in the multilayer structure such information is much more difficult to obtain. In principle, however, techniques such as nuclear magnetic resonance (NMR) and Mössbauer spectroscopy provide the possibility to probe the multilayers and the interfaces on a nanoscopic scale.

In this Brief Report we report on NMR measurements in Co/Cu multilayers which probe the actual atomic density within the Co layers for various Co and various Cu layer thicknesses. We will show that a clear distinction can be made between interface and bulk atoms, and how detailed information on the topology of the Co/Cu interface and the strain within the layer can be obtained.

Application of NMR is based on the sensitivity of the hyperfine interaction, $B_{\rm hf}$ to the immediate surrounding of the nucleus. It has been shown that the hyperfine interaction is dominated by the nearest neighbors only.[6,7] The contribution of further shells to $B_{\rm hf}$ is at least 2 orders of magnitude smaller. Basically, it is this fact which makes NMR very suitable as a local probe. Of specific relevance for the present study are the following features.

Replacement of a nearest-neighbor Co ion in a structure by a nonmagnetic ion yields a discrete shift of $B_{\rm hf}$ due to the reduction of the *s*-electron polarization. Quantitative calibration can be obtained by experiments in appropriate diluted alloys. For Co/Cu it has been found that the resonance frequency, as a general rule, decreases with about 18 MHz per replaced Co atom[7] in fcc cobalt. This feature enables one, in principle, to probe the local surrounding of a Co ion and to investigate the topology of the interface on an atomic scale.

$B_{\rm hf}$ depends on the atomic distance as can be deduced from pressure experiments and theoretical calculations.[8] Typical values for Co are $\Delta B_{\rm hf}/B_{\rm hf} = -1.16\Delta V/V$. The shift of a spectrum therefore can be related to the atomic volume or, alternatively, to the strain in the lattice.

$B_{\rm hf}$ depends on the local symmetry. Hence local structures as fcc ($B_{\rm hf}=21.6$ T) or hcp ($B_{\rm hf}\simeq 22.5$ T) can be distinguished.

The Co/Cu multilayers were prepared at the Philips Research Laboratories by *e*-beam evaporation in UHV on oxidized silicon substrates at room temperature. The deposition was started with a base layer of 200 Å Cu, the deposition rate was a few Å/s and the total thickness of the multilayers was about 2000 Å. Chemical analysis was used to check the amount of Co. Values of the layer thicknesses quoted below are accurate to 5%. X-ray diffractometry at high and low scattering angles confirmed the [111] fcc texture and the superlattice modulation. NMR experiments were performed with and without a magnetic field. The in-field spectra were recorded in fields (up to 5 T) applied parallel to the film plane at a temperature of 1.4 K with the incoherent-spin-echo spectrometer at Eindhoven University of Technology. The zero-field spectra were recorded at constant rf field strength with the automated coherent spin-echo spectrometer at the IPCMS. The sensitivity of both in-

stallations amounts to roughly 10^{16} Co spins at 1.4 K.

A typical example of a NMR spectrum is presented in Fig. 1. This figure shows the spin-echo intensity for a 40(12.3 Å Co+42 Å Cu) multilayer versus frequency in zero field. Spectra for different thicknesses of Co (or Cu) are qualitatively similar, but shifted in frequency.

In order to establish the origin of the various parts of the spectrum the following facts should be noted. First, the main line in the spectra in Figs. 1 and 2 appears close to the value of fcc surrounded by bulk Co (217 MHz). The shift of this line with respect to the bulk value is caused by strain in the Co layer, as we will argue in detail later. At the high-frequency side of the fcc line there is practically no intensity, indicating that in our samples the amount of hcp Co is very small. We note in passing that this is in marked contrast with measurements on Co/Pd, Co/Ir, Co/Au,[9] as well as recent x-ray and NMR experiments on some Co/Cu multilayers,[10] where stacking faults and fractions of hcp Co up to 35% were reported. Since the intensity ratio between the main line and the lower frequency part of the spectrum increases systematically with t_{Co} as shown in Fig. 2, the part of the spectrum below the main line is assigned to Co atoms at the interfaces where one or more nearest-neighbor Co atoms are replaced by Cu. This assignment is supported by the observation that the spin-spin relaxation time T_2 for the satellites is typically twice the value measured for the main (bulk) peak, evidencing a different origin of the signals. From the inset of Fig. 2 it appears that the intensity ratio between the main line and the most intense satellite varies as $n_{Co}-2$, indicating unambiguously that the mixed layer is only one layer thick.

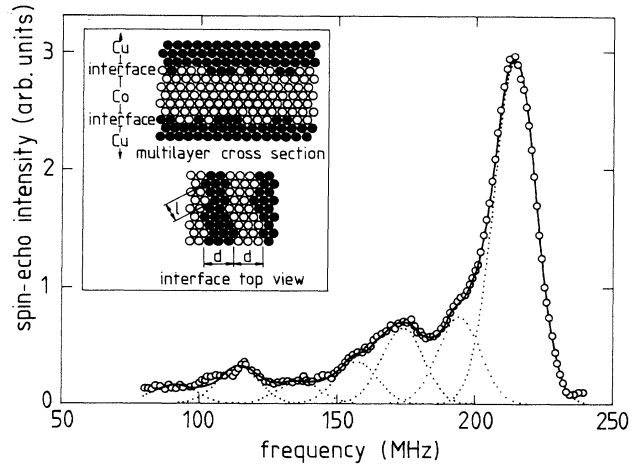

FIG. 1. NMR spin-echo intensity as function of frequency in zero field for a $Co_{12}Cu_{42}$ [111] multilayer as recorded. The solid line represents the result of a fit with seven Gaussians. Each Gaussian (denoted by the dotted lines) corresponds to Co atoms in a specific environment. The dependence of the spin-echo intensity on the square of the frequency has been incorporated in the fitting program. The inset shows a schematic view of a Co/Cu multilayer with atomic step defects in the interface monolayer. Details are discussed in the text.

Given these experimental results we are now in the position to explore the interface spectrum more quantitatively. Since the spectrum originates from Co atoms with one or more Cu atoms in their nearest-neighbor shell, it should consist of a number of absorption lines shifted with respect to the bulk fcc line by approximately 18 MHz per substituted Cu atom as deduced from experiments in diluted alloys quoted above. Although the lines are rather broad, the discernible peaks near the bulk line seem, at first glance, to be shifted by the amount. We therefore fitted the intensity of the spectrum by separate Gaussian lines. The solid line in Fig. 1 shows that the structure of the spectrum is well fitted by seven approximately equally spaced Gaussians (denoted by the dotted lines). All parameters in the fit were free except for the linewidth, which was constrained to have the same value for all lines. We stress that the fit was insensitive to changes in the starting parameters and always converged to the same positions and intensities for the lines. Attempts to reduce the number of lines gave evident misfit, whereas attempts to introduce more than seven lines re-

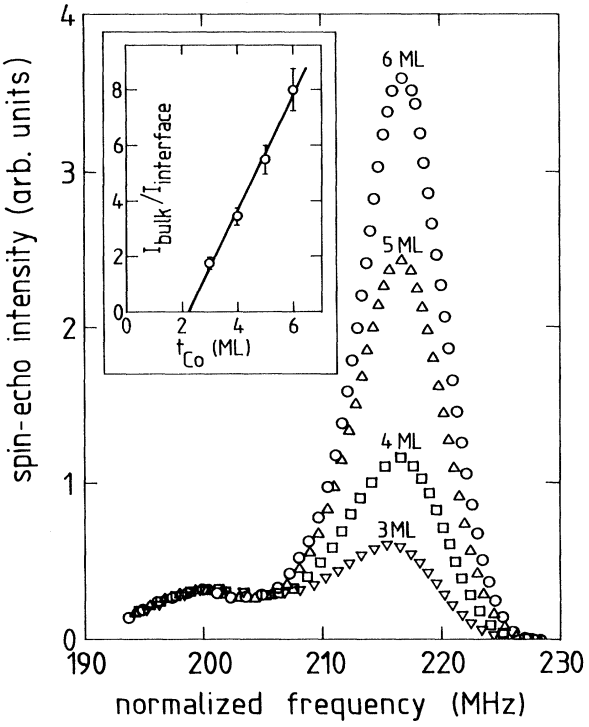

FIG. 2. In-field spectra (corrected for enhancement) of Co_xCu_{21} multilayers showing the systematic increase in intensity ratio between the main line and the most intense satellite as function of the Co thickness t_{Co} (expressed in monolayers). For easy comparison the spectra have been normalized to the first satellite (in intensity as well as in frequency). The decrease in linewidth with respect to the zero-field spectra is due to the homogenization of the magnetization. The inset shows the ratio of intensity of bulk to interface as function of Co thickness.

sulted in a merging of the supplementary lines into one of the seven within less than 1 MHz. We are thus very confident that the reconstructed spectrum with seven lines represents the actual hyperfine field distribution to a fair degree of correctness.

The average spacing between the lines is found to be 19 MHz with a scatter of 3 MHz. This value is very close to the reported shift of 18 MHz per substituted Cu quoted above.[7] The various lines can thus be assigned to Co nuclei having 12 Co neighbors ("bulk" atoms) and nuclei having 11 to 6 Co neighbors ("interface atoms").

For a perfectly flat interface one would expect a bulk line (12 Co neighbors) and one single interface line (9 Co neighbors for [111] oriented growth). This is apparently not the case. From the appreciable relative intensity of the first satellites below the main line, representing Co atoms with one or two Cu nearest neighbors, one can already conclude that the interface layer is rather thoroughly mixed and contains a large number of atomic steps.

In order to substantiate this conclusion, we have compared the experimental intensity of the satellite spectrum with a complete random distribution as well as a more structured model. The latter model, schematically shown in the inset of Fig. 1, contains monatomic steps with an average width equal to the average distance d between them. To comply with the symmetry an average length l of the straight sections of the step is also introduced (see Fig. 1). The relative occurrence of various neighborhoods in the two tentative models determines the intensity. A surprising agreement (within 10%) between the step model (with d and l in the order of two atomic distances) and the experimental data was obtained. These values for d and l show that indeed in the interface monolayer atomic steps are quite numerous. However, it must be stressed that the observed distribution of neighborhoods clearly differs from the limiting case of the random distribution of 50% Co and 50% Cu in a flat but diffused interface layer. This means that in the mixed interface layer the Co atoms prefer to be surrounded by Co and the Cu atoms by Cu, which is not unlikely.

We will now focus on the dependence of the spectra on the Co thickness (t_{Co}). NMR spectra have been recorded by field sweeps for multilayer samples with $t_{Cu}=21$ and 42 Å and t_{Co} from 6 to 40 Å. The positions of the main line are plotted in Fig. 3(a) as ΔB_{hf} against $1/t_{Co}$. The hyperfine field B_{hf} was obtained from the resonance field B_0 and the frequency f by the relation $f=\gamma(B_{hf}-B_0)$, where $\gamma=10.054$ MHz/T is the ^{59}Co nuclear gyromagnetic ratio. The "bulk" value $B_{hf}=21.54$ T observed for a 1000-Å-thick Co layer is used as reference value. It is

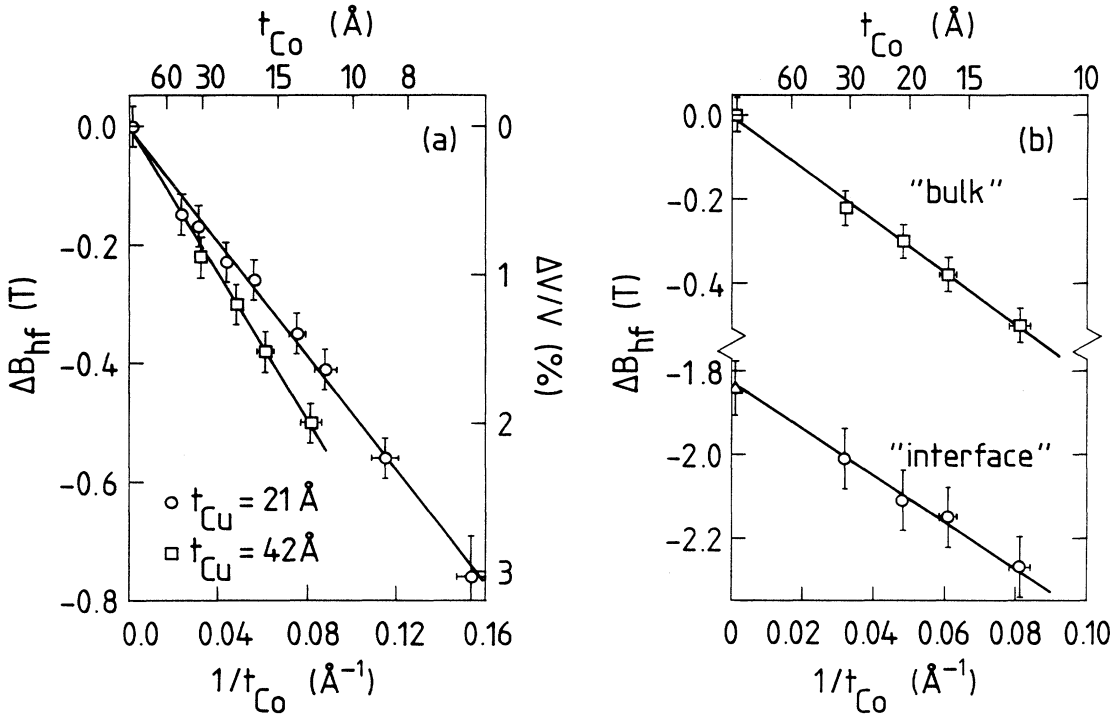

FIG. 3. (a) Hyperfine field B_{hf} derived from in-field spectra as a function of Co thickness $1/t_{Co}$ for [111] Co/Cu multilayers with a Cu thickness of 21 and 42 Å. The solid lines represent least-squares fits of a straight line to the data. (b) Hyperfine field B_{hf} derived from in-field spectra as function of inverse Co thickness $1/t_{Co}$ for [111] Co/Cu multilayers with a Cu thickness of 42 Å. The squares represent the hyperfine field of Co atoms with 12 Co atoms as nearest neighbor ("bulk" atoms). The triangle (data taken from Ref. 9) and circles represent the hyperfine field of Co atoms with 11 Co nearest neighbors and 1 Cu nearest neighbor (atoms at the interface).

obvious that in the multilayers B_{hf} is shifted from the bulk value by an amount ΔB_{hf} depending on both t_{Co} and t_{Cu}. Using the relation $\Delta B_{hf}/B_{hf} = -1.16\Delta V/V$ quoted above[8] (which is actually derived for isotropic pressure) the observed change in B_{hf} can be related to changes in atomic volume or, alternatively, strain. This implies that the data in Fig. 3 indicate that the strain in the Co layers as probed by the bulk atoms seems to be inversely proportional to t_{Co} from 6 Å up to bulk. The magnitude, however, clearly depends on t_{Cu}. For the interface atoms the same analysis can be performed to probe the strain at the interface. This provides us with the unique opportunity to probe the *variation of strain in the whole Co layer.* Figure 3(b) reveals that, within experimental accuracy, the relative shift $\Delta B_{hf}/B_{hf}$ of the hyperfine field of the "interface" atoms is equal to the relative shift of the "bulk" atoms. This strongly indicates that the atomic distances within the Co layers are equal on a microscopic scale, including the interface.

Currently, the strain and coherency in multilayered systems are often described in terms of the dislocation model.[11] In this elastic model the strain is caused by the misfit between the layers. For thin layers, coherent behavior is predicted, with a Co layer strain given by

$$\epsilon_{Co} = m/(1+qt_{Co}/t_{Cu}) , \quad (1)$$

where m is the lattice mismatch and q is the ratio between the elastic moduli of Co and Cu. Above a critical layer thickness t_{crit} the strain relaxes through the creation of dislocations at the interface. This results in incoherency and in that regime the strain will be inversely proportional to t_{Co} and independent of t_{Cu}. According to the results of recent x-ray investigations on Co/Cu superlattices,[10] a coherent behavior should be present for layers up to 40 Å and hence Eq. (1) should apply. The present microscopic experiments, however, do not support such a coherent behavior, since a satisfactory description of the data plotted in Fig. 3(a) by Eq. (1) is only possible for $q > 100$, which is completely unphysical. On the other hand, an incoherent structure is at variance with the observed dependence on t_{Cu}. Hence one is inclined to conclude that the dislocation model does not describe the observed effects, and that the origin of the strain may not solely be due to the mismatch between the constituents. Alternatively, the strain effects might be of electron origin, as, for instance, incorporated in the model of Huberman and Grimsditch,[12,13] which involves a coherent structure and reproduces the $1/t_{Co}$ behavior of the strain. We believe, however, that pertinent conclusions require comparable data on other multilayered structures, which obviously, are not yet available.

We would like to conclude with some comments. The present analysis is based on strain and neighbor effects. In general, nonuniform magnetization due to layers near the interface with an enhanced or reduced moment might also influence B_{hf}. Systematic magnetization measurements, however, yielded a constant magnetization per Co atom for the present range of t_{Co}, indicating the absence of such phenomena in this case.[14] Nevertheless, the existence of such layers would not yield a shift of B_{hf} in the bulk atoms, in contrast to what is observed in the present study.

A final comment concerns the magnetoresistance. Recently large magnetoresistance was reported in sputtered Co/Cu multilayers.[15] The present UHV deposited multilayers did not display this effect. One might conjecture that the roughness of the interface (as scattering source) is of decisive importance. A comparison using the present analysis between sputtered and UHV deposited layers will therefore be undertaken.

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