NMR studies of interlayer boundaries in Co/Cu superlattices

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Abstract. Effects of Cu layer thicknesses and annealing temperature on structural features of Co/Cu superlattices have been studied by nuclear magnetic resonance (NMR), electron microscopy, X-ray diffraction and X-ray reflectometry. Determination of a fraction of perfect boundaries and of Co atoms in interfaces based on NMR studies is demonstrated. Correlation of these parameters with the probability of a single electron scattering event at an interface and magnetoresistance is analyzed.

1. Introduction
Co/Cu superlattices possess giant magnetoresistance which can reach 65 % [1, 2], and their magnetic and magneto-transport properties depend on structural features of layers and interfaces formed under sputtering. Structural studies of multilayers and, particularly, of their interfaces are required to reveal possible correlations between the multilayers structure and their properties.

One of the most effective methods of getting information on the structure and composition of interfaces in nanometer scales is the nuclear magnetic resonance. The main idea in using this method is that the superfine field on the $^{59}$Co nuclei depends on magnetic and structural characteristics of the nearest neighborhood of a nuclear-probe, and its effectiveness was demonstrated in the previous studies [3-5]. Popularity of NMR studies for Co/Cu multilayers is conditioned by high sensitivity of this method and 100 % of $^{59}$Co nuclei in natural cobalt. The NMR investigations of multilayers give information on Co crystal structure (FCC, HCP, stacking faults presence), reveal stressed state in Co layers and get the data on interfaces character.

The main goal of the present study is to demonstrate capabilities of the NMR method for determination of the state of layers and interfaces in Co/Cu superlattices and to analyze correlation of the NMR results and X-ray reflectometry data, as well as the relationship between structural parameters of interfaces and magnetoresistance.

2. Experimental
Specimens for the study were fabricated in the sputtering system Ulvac MPS-4000-C6 by the method of the direct current magnetron sputtering on glass substrates at room temperature. The protective layer was Cr 2 nm thick and the buffer layer was Fe 5 nm thick. Two sets of specimens was prepared, the first one being glass/Fe(5nm)/[Co(1.5nm)/Cu(t_Cu)]10/Cr(2nm), where $t_{Cu} = 0.85, 0.93, 2.28$ and 2.7 nm. The formula of the second was glass/Fe(5nm)/[Co(1.5nm)/Cu(0.9nm)]10/Cr(2nm). These specimens were annealed at 150, 200 and 300°C under the pressure of $P = 10^{-5}$ Pa for 1 h.

The structure was studied in transmission electron microscope Tecnai G-30. X-ray studies were carried out using the program-apparatus complex Philips Empyrean. The low-angle reflectometry investigations were carried out in CrK radiation. The reflectometry data were treated in the program
PANalytical X’Pert Reflectivity. The technique and details of reflectometry patterns treatment are described in [6].

The NMR spectra were taken in the impulse NMR spectrometer at liquid helium temperature (4.2 K) in local magnetic field, the external magnetic field being absent. The NMR spectra on $^{59}$Co nuclei were taken from all the specimens in the frequency range of 80-240 MHz. The pulse duration was 0.5 μs and the time between pulses was 20 μs. The pulse power was kept constant. The frequency step was 1 MHz. The NMR technique is described in more detail in [6-8].

Magnetoresistance was measured at room temperature by a standard technique of four-contact method on direct current in the current flow in layers plane. The magnetoresistance was determined as $MR = (R(H)-R_s)/R_s$, where $R_s$ is the resistance in the magnetic saturation field.

3. Results and discussion

According to the data of TEM studies, all the specimens have nanocrystalline structure, with crystallite sizes in the range of 7-45 nm, most of them being of about 20 nm.

All specimens have the $<111>$ axial texture, with the axis perpendicular to the substrate plane. It is illustrated by figure 1, in which the diffraction pattern of specimen glass/Fe(5nm)/[Co(1.5nm)/Cu(2.28nm)]$_{10}$/Cr(2nm) after sputtering is shown. Only one line corresponding to the $\{111\}$ planes is seen in this diffraction pattern.

![Figure 1. Diffraction pattern of specimen glass/Fe(5nm)/[Co(1.5nm)/Cu(2.28nm)]$_{10}$/Cr (2nm).](image)

The NMR spectra of all specimens are qualitatively similar, only relative intensities of the spectra components being different. Typical NMR spectra are shown in figure 2.

![Figure 2. Spin echo intensities versus frequency for specimens glass/Fe/[Co(1.5nm)/Cu(tCu)]$_{10}$/Cr, where tCu = 0.93 nm (a) and tCu = 2.28 nm (b).](image)
The spectra are well approximated by 7 Gaussians, and the main peaks ($I_0$) correspond to atoms in Co layers. They have the center near 218 MHz, which is very close to that of bulk cobalt [4], and it can be concluded that there are no pronounced micro-strains in Co layers. Since there is no peak at 228 MHz and no high-frequency shoulder of the main peak, one can conclude that the HCP cobalt is absent as well as stacking faults in FCC Co layers.

The rest peaks originate with almost regular intervals of 17-18 MHz from the main peak, which is close to the data of [4, 5, 9], according to which the resonance frequency of Co/Cu superlattices is, as a rule, decreased by 16-19 MHz per every substituted atom of cobalt in FCC Co. Thus, the $I_1$, $I_2$, $I_3$, $I_4$, $I_5$, and $I_6$ peaks correspond to the 1, 2, 3, 4, 5 and 6 atoms of Cu in the Co atom neighborhood. These peaks correspond to cobalt atoms in interfaces.

According to [5], when there is the <111> texture in Co/Cu superlattices, the $I_3$ peak corresponds to an ideally flat boundary. In case of superlattices obtained by molecular-beam epitaxy, in some of them there were only two peaks in the spectra, namely, $I_0$ formed by Co nuclei localized in layers and $I_3$ formed by the nuclei in interfaces [3, 10].

Another situation is observed in case of superlattices fabricated by magnetron sputtering, for which the best result is obtained for the spectra approximation by 7 Gaussians [4, 11].

In some studies attempts were undertaken to get information on the interface structure based on the NMR spectra analysis [4, 5, 12]. In these attempts different models of interfaces were used, and calculated spectrum was fitted an experimental one by varying parameters characterizing the interface structure in the corresponding model. It is surely a promising approach, but its realization requires a very high quality of spectra. Besides, it seems impossible to simulate the real interface structure only based on the NMR data.

In our previous studies [6, 11, 13] and in the present paper another approach is used. We were not aimed to get detailed information on the interface structure, but determined only two parameters characterizing the interfaces state. The first of them is the fraction of Co atoms in interfaces, namely,

$$\sum_{i=1}^{6} I_i / \sum_{i=0}^{6} I_i$$

This parameter characterizes the width of interlayer boundaries. The second is the fraction of perfect boundaries

$$I_3 / \sum_{i=1}^{6} I_i$$

The values of these parameters determined from the NMR spectra for a series of specimens with formula glass/Fe/[Co(1.5nm)/Cu($t_{Cu}$)]10/Cr are given in Table 1 along with the roughness determined based on the X-ray reflectometry studies.

| $t_{Cu}$, nm | $\sum_{i=1}^{6} I_i / \sum_{i=0}^{6} I_i$ | $I_3 / \sum_{i=1}^{6} I_i$ | roughness, nm |
|--------------|-----------------------------------|-------------------------|---------------|
| 0.85         | 0.45 ± 0.04                       | 0.24 ± 0.02             | 0.37 ± 0.04   |
| 0.93         | 0.38 ± 0.04                       | 0.25 ± 0.02             | 0.44 ± 0.04   |
| 2.28         | 0.40 ± 0.04                       | 0.19 ± 0.02             | 0.56 ± 0.09   |
| 2.70         | 0.40 ± 0.04                       | 0.17 ± 0.02             | 0.70 ± 0.11   |

It is seen that with the increasing thickness of Cu layers the fraction of Co atoms in interfaces practically does not change, i.e. the width of interlayer boundaries is the same, but the fraction of perfect interlayer boundaries decreases. The latter is obviously due to the increasing defectiveness of layers with the longer time of sputtering. It should be also noted that the decreasing fraction of perfect
boundaries correlates with increasing roughness of interfaces determined from reflectometry investigations.

Glass//Fe(5nm)/[Co(1.5nm)/Cu(0.9nm)]_{10}/Cr(2nm) specimens annealed at different temperatures were studied to reveal the effect of the annealing temperature on the state of interlayer boundaries and the influence of the latter on magnetoresistance. In Co/Cu superlattices under study the maximal magnetoresistance after sputtering is $\Delta R/R_s = 34\%$. When the annealing temperature is increased from 150°C to 300°C, the magnetoresistance decreases from 29 to 15 % respectively (see Table 2).

Table 2. Magnetoresistance and probability of a single electron scattering event dependently on the annealing temperature for specimens glass//Fe(5nm)/[Co(1.5nm)/Cu(0.9nm)]_{10}/Cr(2nm).

| $T$, °C | MR, % | $P$ |
|---------|-------|-----|
| as-sputtered | 34    | 0.14 |
| 150     | 29    | 0.21 |
| 200     | 26    | 0.27 |
| 300     | 15    | 0.69 |

Parameters characterizing the fraction of perfect interfaces, the fraction of Co atoms in interfaces and the roughness of interlayer boundaries depending on the annealing temperature for specimens glass//Fe(5nm)/[Co(1.5nm)/Cu(0.9nm)]_{10}/Cr(2nm) are given in Table 3. With the increasing annealing temperature the fraction of Co atoms in interfaces increases from 0.38 in the as-sputtered state to 0.49 after the annealing at 300°C, and the fraction of perfect boundaries decreases. As in the previous case, the decrease of the perfect boundaries fraction correlates with interface roughness determined from the reflectometry.

Table 3. Fraction of Co atoms in interfaces, fraction of perfect interlayer boundaries and interface roughness in glass//Fe(5nm)/[Co(1.5nm)/Cu(0.9nm)]_{10}/Cr(2nm) specimens annealed at different temperatures.

| $T$, °C | $\sum I_{ij}/\sum I_i$ | $I_i/\sum I_i$ | roughness, nm |
|---------|-------------------------|----------------|---------------|
| as-sputtered | 0.38 ± 0.04 | 0.18 ± 0.02 | 0.42 ± 0.04 |
| 150     | 0.44 ± 0.04 | 0.11 ± 0.01 | 0.64 ± 0.09 |
| 200     | 0.46 ± 0.05 | 0.08 ± 0.01 | 0.61 ± 0.09 |
| 300     | 0.49 ± 0.05 | 0.07 ± 0.01 | 0.75 ± 0.11 |

Thus, according to the results obtained the fraction of areas of perfect mating of interlayer boundaries decreases, and the fraction of Co atoms in interfaces, i.e., their width, and the roughness of boundaries increase with the increasing annealing temperature. These factors result in the magnetoresistance decrease with the increasing annealing temperature.

These data can be used for an estimation of probability of a single electron scattering event at an interface. The rate of relaxation of an electron impulse inside the Co layer is determined as a value reciprocal to the relaxation time $\tau$. It can be assumed that the effective rate of relaxation of an electron impulse intersecting a Co layer and its two boundaries is determined as a sum of the relaxation rate inside the layer $\tau^{-1}$ and double relaxation rate at an interface. The rate of impulse relaxation at an interface is $PV_F/L$, where $P$ is the probability of a single scattering event, $V_F$ is the rate of Fermi electrons and $L$ is the Co layer thickness. The relaxation time $\tau$ can be estimated using the simplest Drude-Lorentz formula relating specific electrical resistance of a metal $\rho$ to the electron relaxation time $\tau$. Neglecting
for the simplicity the difference in probabilities of interface scattering for electrons with different spin directions, one obtains the following formula connecting the superlattice magnetoresistance $MR$ with the probability of interface scattering $P$

$$MR = MR_0 \frac{1}{1 + \frac{2mV_F}{\rho L N e^2} P}$$  \hspace{1cm} \text{(3)}$$

Here $MR_0$ is magnetoresistance of a specimen with negligibly small interface electron scattering, $m$, $e$ and $N$ are mass, charge and concentration of conductivity electrons, and $\rho$ is the specific resistance of Co. The values of conductivity electron concentration, Fermi electrons rate and specific resistance were taken from [14-17] as $N = 1.7 \times 10^{29}$ m$^{-3}$, $V_F = 7 \times 10^5$ m/sec, $\rho = 5.8 \times 10^{-8}$ ohm·m. The $MR_0$ was taken equal to 48 %. It is the maximal magnetoresistance for such superlattices with high-perfect interfaces obtained in [2]. The values of probability of a single electron scattering event at an interface are given in Table 2.

Figure 3 illustrates correlation between the fraction of perfect interfaces and of Co atoms in interlayer boundaries and the probability of electron scattering at interfaces. The increase of Co atoms fraction in interlayer boundaries with the increase of annealing temperature indicates the boundaries smearing, and the decrease of the fraction of high-perfect boundaries corresponds to the increase of roughness. Both factors result in the increase of the probability of a single electron scattering event and obviously cause the decrease of magnetoresistance with the increasing annealing temperature.

![Graph](image)

**Figure. 3.** Probability of a single electron scattering event at an interface versus the fraction of perfect boundaries (a) and the fraction of Co atoms in interfaces (b).

4. Summary

Structural characteristics of two types of specimens, glass/Fe(5nm)/[Co(1.5nm)/Cu(t$_{Cu}$)/Cr(2nm)]$_{10}$/Cr(2nm) ($t_{Cu}$ = 0.85, 0.93, 2.28 and 2.70 nm) and glass/Fe(5nm)/[Co(1.5nm)/Cu(0.9nm)]$_{10}$/Cr(2nm) annealed at 150-300°C have been studied by NMR, TEM, X-ray diffraction and X-ray reflectometry.

It is demonstrated that based on the NMR studies one can determine parameters characterizing the fraction of perfect boundaries and of Co atoms in interfaces.

The fraction of perfect boundaries correlates with the roughness of interfaces determined from reflectometry studies.

With the increasing annealing temperature the magnetoresistance decreases due to the change of the state of interfaces, namely, the fraction of perfect interfaces decreases and the number of Co atoms participating in the formation of interlayer boundaries increases.

Probability of a single electron scattering event at an interface has been estimated. It is demonstrated that the probability of a single electron scattering event at an interface increases and, consequently, the magnetoresistance decreases with the increase of interlayer boundary widths due to the increase of the
fraction of Co atoms participating in the formation of these boundaries and with the increasing roughness which is testified by the decrease of the fraction of perfect boundaries.

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