

УДК 538.975 + 537.622.4 + 539.143.43

The Study of Co-Cu Heterogeneous Alloy Thin Films by NMR Method

Dmitriy L. Khalyapin*

Siberian Federal University,
Svobodny 79, Krasnoyarsk, 660041,

Russia

Kirensky Institute of Physics, SB RAS,
Akademgorodok 50, Krasnoyarsk, 660036,

Russia

Vadim K. Maltsev

Petr D. Kim

Igor A. Turpanov

Anna Ya. Betenkova

Kirensky Institute of Physics, SB RAS,
Akademgorodok 50, Krasnoyarsk, 660036,

Russia

Received 10.12.2009, received in revised form 10.01.2010, accepted 20.01.2010

In the present work we discuss the structure of magnetic layer in magnetron sputtered Co/Cu multilayers with ultrathin magnetic layers (effective layer thicknesses $d_{Co} \approx 3.5$ and 4.5 \AA) obtained by means of ^{59}Co NMR method. In spite of such a small effective thicknesses of sputtered layers it has been found that the NMR spectra are the superposition of two peaks with central frequencies $f_1 = 190\text{-}196 \text{ MHz}$ and $f_2 = 208\text{-}213 \text{ MHz}$ which obviously correspond to Co-atoms which have 0 and 1 Cu-atom in the nearest-neighbor shell indicating that cobalt preferably forms clusters with large number of atoms involved.

Keywords: nuclear magnetic resonance, Co-Cu heterogeneous alloy, multilayers.

Co/Cu multilayers and granular alloys have been intensively studied since the discovery of the giant magnetoresistance (GMR) effect in this system [1–3]. It was considered that structures based on the Co-Cu system possess sharp Co/Cu interfaces and exhibit good stability because of very small intersolubility of Co and Cu according to the equilibrium phase diagram [4]. However, a great number of experimental studies performed for the last decade on this system have revealed the wide range of structural imperfection, such as different stages of intermixing etc. which mainly determined by the preparation technique used and affects the physical properties of the material, in particular, the value of GMR effect [5]. Even in the multilayers grown by molecular beam epitaxy (MBE) intermixing at the interfaces occurs due to the differences in free energies of the Co and Cu surfaces [6–8]. In the case of multilayers with extremely thin magnetic layers which are the object of researcher's interest for the last years [9–13] due to the large potential of these structures for low-field magnetic sensor applications the processes of intermixing and diffusion could play a major role for magnetic layer formation. For such type of multilayer films the structure of magnetic layers is mainly determined by the method used for the sample preparation.

*dimlh@iph.krasn.ru

© Siberian Federal University. All rights reserved

This fact stimulates the numerous efforts of researchers for understanding the processes occurring upon synthesis of the GMR materials and for working through the technology at any specific task of the material preparation.

In the present study we discuss the results of magnetic layer structure analysis of Cu/Cu multilayers with ultrathin Co layer performed by NMR method. The NMR frequency depends only on the magnetic field on nucleus which in magnetic materials is determined by the electronic structure of the sample under study. The later is influenced by such factors as the presence of foreign atoms in the nearest neighborhood (*n.n.*) of magnetic atom, changing of crystallographic symmetry, crystal lattice tension etc. [14]. Thus, NMR frequency is a very sensitive probe to the sample structure analysis via the analysis of NMR spectra which reflect all the factors mentioned above.

1. Experimental Procedure

The Co/Cu films were deposited onto glass substrates at room temperature by DC sputtering in Ar atmosphere. Two magnetron sources with Co and Cu targets were separated from a vacuum chamber with a substrate holder and from one another by screens. During a sputtering cycle substrates mounted onto revolving holder subsequently passed over windows in the screens placed in front of the magnetrons. Thus, deposition was performed only in immediate proximity to the magnetrons. The amounts of Co or Cu sputtered during one cycle were controlled by changing the size of the corresponding window with a shutter. The basic pressure was 10^{-6} Torr and Ar pressure was 2×10^{-4} Torr. The deposition ratio was $\sim 3.5 \text{ \AA/s}$ for both Co and Cu. A set of samples with the nominal structure $100 \times [\text{Co}(d_{Co})/\text{Cu}(d_{Cu})]$ was obtained with *effective* Co layer thickness $d_{Co} \sim 3.5$ and 4.5 \AA and different Cu layer thickness d_{Cu} .

The structure of the as-deposited samples was characterized with a Θ - 2Θ X-ray diffractometer DRON-4 (Cu $K\alpha$ radiation). Chemical composition was controlled by methods of X-ray fluorescence analysis. The NMR spectra were obtained at room temperature in zero applied field; the sensitivity of NMR spectrometer was in the range of 150–250 MHz.

2. Experimental Data

The analysis of X-ray diffraction spectra revealed the *fcc* crystallographic structure of the samples. The crystal lattice parameters calculated from the XRD patterns had values between those for bulk *fcc* copper and *fcc* cobalt depending on the ratio between Co and Cu in the sample. No texture has been found. Fig. 1 shows the NMR spectra measured on the samples with effective Co layer thickness of 3.5 \AA . The spin-echo signal has been detected only for the effective Cu-layer thicknesses 1.5 and 2 \AA . For the values of d_{Cu} higher than 2 \AA the spin-echo signal was not detected. For the reference the NMR spectrum of pure Co film sputtered at the same conditions as multilayers is presented on the upper graph. The central frequency here is a little bit higher than for bulk *fcc* Co which is about 213 MHz at room temperature. This small shift in frequency could be attributed to the presence of strains or stacking faults. It is easy to see that the spectra of $[3.5 \text{ \AA}_{Co}/1.5 \text{ \AA}_{Cu}]$ and $[3.5 \text{ \AA}_{Co}/2 \text{ \AA}_{Cu}]$ samples are the superposition of two Gaussian peaks with main frequencies 192 and 208 MHz. The spin-spin relaxation times measured at the frequencies marked by arrows are also shown here. The observed spectra are very stable with time indicating the little change of the sample structure with aging (Fig. 2).

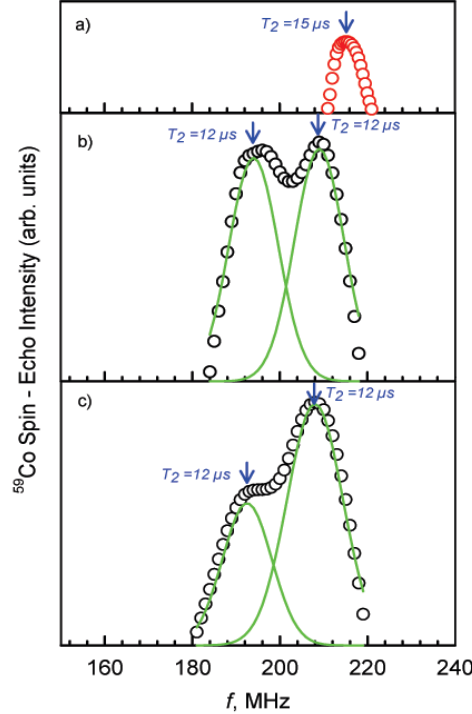


Fig. 1. The NMR spectra observed on the $[3.5\text{\AA}_{Co}/1.5\text{\AA}_{Cu}]$ (b) and $[3.5\text{\AA}_{Co}/2\text{\AA}_{Cu}]$ (c) samples. The upper graph (a) represents the NMR spectrum measured on pure *fcc* Co film sputtered at the same conditions as multilayers

However, the spin-spin relaxation times increase with aging indicating the relaxation processes taking place in the samples.

Fig. 3 shows the NMR spectra for the films with the Co layer thickness of 4.5\AA . This picture is similar to the case of Co layer thickness 3.5\AA , but the main resonance line places closely to the one of bulk cobalt. With increasing in Cu layer thickness the spin-echo signal also disappeared, possibly because of the same reason as for the samples with $d_{Co} \sim 3.5\text{\AA}$. For the $[4.5\text{\AA}_{Co}/6\text{\AA}_{Cu}]$ sample the spin-echo signal was not detected.

3. Discussion

In spite of the fact that MNR resonance peak at the frequency $f=208\text{ MHz}$ observed on the $[3.5\text{\AA}_{Co}/\text{Cu}(d_{Cu})]$ samples is often referred to the amorphous phase or to the Co atoms in *hcp* symmetry which have 1 Cu atom in the nearest-neighbor shell, in our opinion this frequency corresponds to the Co atoms with *fcc* symmetry and with absence of foreign atoms in the *n.n.* shell. Indeed, the frequency shift can arise from the changing of atomic distance and therefore reflects changing of the cell parameter or presence of strains. From the other hand, XRD data confirm only the presence of the *fcc* phase; moreover, the *fcc* phase is preferable for the small

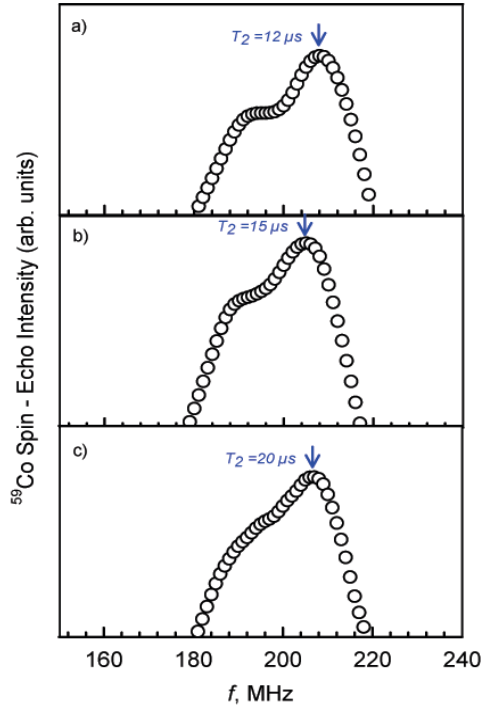


Fig. 2. The evolution of NMR spectrum, obtained from the $[3.5\text{\AA}_{Co}/2\text{\AA}_{Cu}]$ sample, with time. The spectra were measured on as-deposited sample (a), 1.5 months after deposition (b) and 2 years after deposition (c)

Co clusters and thin films [15]. The frequency of 192 MHz in this case is due to the presence of 1 Cu-atom in the nearest-neighborhood. The typical value of the hyperfine field change for Co is $\frac{\Delta B_{hf}}{B_{hf}} = -1.16 \frac{\Delta V}{V}$ (for isotropic pressure) as it was deduced from pressure experiments and theoretical calculations [16–18]. Here $\Delta V/V$ is a relative change of volume. It is easy to see that homogeneous expansion of Co lattice cell to the size of Cu cell leads to the frequency shift $\Delta f \approx 0.5$ MHz. The more pronounced change in the resonance frequency is evidently originated from the strains due to interface effects and possible intermixing with Cu. In experiments with Co/Cu multilayers the shift of resonance line was observed reaching $\Delta f \approx 8$ MHz when the thickness of Co layer was reduced from 100 to 6 Å [18]. This shift is also forced by the increasing role of interface and near-the-interface atoms, *id est* by the increasing influence of interface regions on the total magnetic layer properties.

Taking into account the reasoning mentioned above the NMR spectrum shown on Fig.1(b) can be interpreted as a homogeneous Co-Cu alloy with Cu concentration of ~ 3.7 at.%. This alloy is the main magnetic phase of the sample, and the sample structure can be presented as the *fcc* Co-Cu alloy of ~ 3.7 at.% Cu with encapsulated areas of pure Cu or Co-Cu alloy with low Co-concentration. The absence of NMR signal from the interface Co atoms can be connected with the small fraction of them among the total number of Co atoms or with the drastic decrease of the spin-spin relaxation time for these atoms. The NMR spectrum of $[3.5\text{\AA}_{Co}/2\text{\AA}_{Cu}]$ sample is very similar to the one of $[3.5\text{\AA}_{Co}/1.5\text{\AA}_{Cu}]$ sample; the only difference is the slight increasing

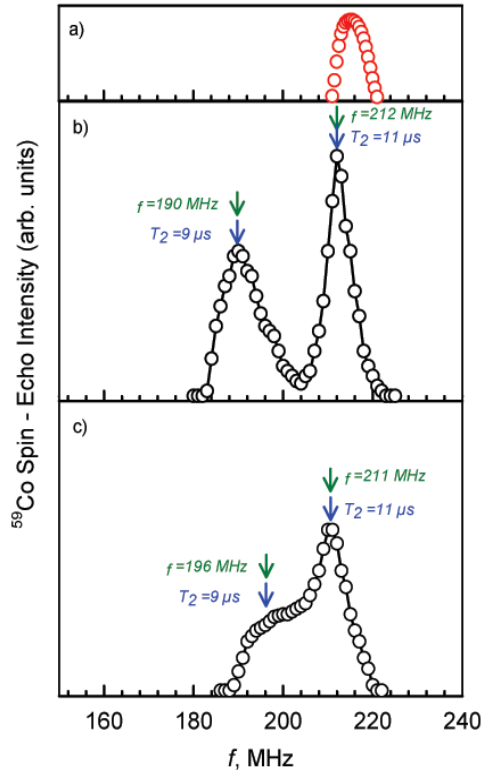


Fig. 3. The NMR spectra observed on the $[4.5\text{\AA}_{Co}/1.5\text{\AA}_{Cu}]$ (b) and $[4.5\text{\AA}_{Co}/3\text{\AA}_{Cu}]$ (c) samples. The upper graph (a) represents the NMR spectrum measured on pure *fcc* Co film sputtered at the same conditions as multilayers

of the ratio between the atoms which have no foreign atoms in the *n.n.* shell and which have one. One can suppose that for the $[3.5\text{\AA}_{Co}/2\text{\AA}_{Cu}]$ sample the separation of Co-rich regions starts and Cu begins to form more spread areas with larger number of atoms involved; it leads to the decrease of the influence of Cu on magnetic phase properties.

The possible reasons for why the spin-echo signal has not been detected in the case of effective Cu-layer thicknesses more than 2\AA could be following:

i) A more homogeneous Co-Cu alloy forms where at least four Cu atoms in the nearest-neighbor shell are presented leading to the shift of NMR spectra into the low frequency region beyond to the sensitivity of NMR spectrometer;

ii) The magnetically hard phase forms. The increasing of magnetic anisotropy leads to decreasing of enhancement factor and NMR signal intensity drop drastically. In this case the actuating signal amplitude and pulse duration used in the experiment are not sufficient for excitation of spin-echo signal;

iii) The spin-spin relaxation time decreases drastically with d_{Cu} increasing.

The first two reasons were confirmed by a more detailed investigation of the structure and properties of the samples with effective Cu -layer thicknesses more than 2\AA which will be published separately. It has been shown that the magnetically hard phase is associated with nano-

sized Co grains where surface anisotropy plays a main role in total anisotropy increasing. In the other worlds, with increasing of Cu-layer thickness the sample structure changes qualitatively: the separation of Co-areas leads to formation of high-anisotropy Co clusters and intermixing increases leading to the low-concentration Co-Cu solution formation.

As it was mentioned above, the small change of NMR spectra with aging indicates the good stability of the sample structure, or, at least the good stability of main magnetic phase (Fig. 2). However, increasing of the spin-spin relaxation time indicates the sample became more ordered.

The NMR spectra of the films with $d_{Co} \sim 4.5 \text{ \AA}$ have the main resonance line at the position almost equivalent the same of the bulk cobalt. But for the $[4.5\text{\AA}_{Co}/1.5\text{\AA}_{Cu}]$ sample the shift of the resonance maximum corresponded to atoms with 1 Cu-atoms in the *n.n.* shell in the low-frequency region is more pronounced then for $[3.5\text{\AA}_{Co}/Cu(d_{Cu})]$ samples. Probably these atoms are localized in areas near the Co/Cu interface which in case of small amount of Cu (small Cu-grains in the Co-matrix) can produce more intensive stress on the crystal lattice. With increasing of d_{Cu} ($[4.5\text{\AA}_{Co}/3\text{\AA}_{Cu}]$ sample) the NMR spectrum becomes similar to the ones for $[3.5\text{\AA}_{Co}/Cu(d_{Cu})]$ samples, indicating the ratio between total amount of the Co and Cu atoms is the most important parameter which influences the structure of the Co/Cu films with ultrathin layers (small amounts of Co- and Cu-atoms sputtered during the deposition cycle).

4. Conclusions

Investigation of Co/Cu multilayers with ultrathin magnetic layers ($d_{Co} \sim 3.5$ and 4.5 \AA) by NMR method shows that cobalt is just slightly intermixes with copper, but influence of copper gives rise to the increasing number of the structure defects like strains etc. and to the visible shift of resonance lines into the low-frequency region. We found that Co forms large grains instead of layers and the chemical composition of these grains is Co-Cu alloy with Cu concentration of about 3.7 at.%. Increasing of d_{Cu} leads to pronounced changes in the samples structure and their magnetic characteristics following the decreasing of spin-echo signal intensity beyond the sensitivity of the NMR spectrometer used.

References

- [1] 1. S.S.P. Parkin, R. Bhargava, K.P. Roche, Oscillatory magnetic exchange coupling through thin copper layers, *Phys. Rev. Lett.*, **66**(1991), 2152–2155.
- [2] A.E. Berkowitz, J.R. Mitchell, M.J. Carey, A.P. Young, S. Zhang, F.E. Spada, F.T. Parker, A. Hutten, G. Thomas, Giant magnetoresistance in heterogeneous Cu-Co alloys, *Phys. Rev. Lett.*, **68**(1992), 3745–3748.
- [3] J.Q. Xiao, J.S. Jiang, C.L. Chien, Giant magnetoresistance in nonmultilayer magnetic systems, *Phys. Rev. Lett.*, **68**(1992), 3749–3752.
- [4] T. Nishizawa, K. Ishida, The Co-Cu System, *Bull. Alloy Phase Diagrams*, **5**(1984), 161–165.
- [5] E.Y. Tsybal, D.G. Pettifor, Perspectives of Giant Magnetoresistance, *Solid State Physics*, **56**(2001), 113–239.

- [6] U. Bovensiepen, P. Pouloupoulos, W. Platow, M. Farle, K. Baberschke, Sudden jump of the Curie temperature at the coalescence of Co islands on Cu(0 0 1), *JMMM*, **192**(1999), 386–390.
- [7] J. de la Figuera, J.E. Prieto, G. Kostka, S. Muller, C. Ocal, R. Miranda, K. Heinz, Crystallography and morphology of the early stages of the growth of Co/Cu(111) by LEED and STM, *Surf. Sci.*, **349**(1996), 139–145.
- [8] M.Ø. Pedersen, I.A. Bönicke, E. Lægsgaard, I. Stensgaard, A. Ruban, J.K. Nørskov, F. Besenbacher, Growth of Co on Cu(111): subsurface growth of trilayer Co islands, *Surf. Sci.*, **387**(1997), 86–101.
- [9] T.L. Hylton, K.R. Coffey, M.A. Parker, J.K. Howard, Giant Magnetoresistance at Low Fields in Discontinuous NiFe-Ag Multilayer Thin Films, *Science*, **261**(1993), 1021–1024.
- [10] M. Angelakeris, P. Pouloupoulos, O. Valassiades, N.K. Flevaris, D. Niarchos, A. Nassiopoulou, GMR study leading to sensor fabrication on the Ag-Co system, *Sens. Act. A*, **91**(2001), 180–183.
- [11] F. Spizzo, E. Angeli, D. Bisero, P. Vavassori, F. Ronconi, Fragmentation of cobalt layers in Co/Cu multilayers monitored by magnetic and magnetoresistive measurements, *Appl. Phys. Lett.*, **79**(2001), 3293.
- [12] J. Balogh, M. Csontos, D. Kaptas, G. Mihaly, Enhanced granular magnetoresistance due to ferromagnetic layers, *Solid State Comm.*, **126**(2003), 427–429.
- [13] V.K. Sankaranarayanan, O Prakash, S.T. Lakshmikumar, Investigation of Co/Ag Discontinuous Multilayers Prepared by UHV Electron Beam Evaporation, *J. Surface Sci. Technol.*, **22**(2006), 15–23.
- [14] A.P. Guimaraes, Magnetism and Magnetic Resonance in Solids, Chichester, Wiley & Sons, 1998.
- [15] O. Kitakami, H. Sato, Y. Shimada, F. Sato, M. Tanaka, Size effect on the crystal phase of cobalt fine particles, *Phys. Rev. B*, **56**(1997), 13849–13854.
- [16] D.H. Anderson, G.A. Samara, Pressure Dependence of the ^{59}Co Nuclear Magnetic Resonance in Hexagonal Cobalt, *J. Appl. Phys.*, **35**(1964), 3043–3044.
- [17] J.F. Janak, Calculated hyperfine fields and their pressure derivatives in Fe, Co, and Ni, *Phys. Rev. B*, **20**(1979), 2206–2208.
- [18] H.A.M. de Gronckel, K. Kopinga, W.J.M. de Jonge, P. Panissod, J.P. Schillé, F.J.A. den Broeder, Nanostructure of Co/Cu multilayers, *Phys. Rev. B*, **44**(1991), 9100–9103.

Исследование тонких пленок неоднородных сплавов Co-Cu методами ЯМР

Дмитрий Л. Халяпин
Вадим К. Мальцев
Петр Д. Ким
Игорь А. Турпанов
Анна Я. Бетенькова

В данной работе обсуждаются результаты, полученные при исследовании структуры магнитных слоев в мультислойных пленках Co/Cu со сверхтонкими магнитными слоями, приготовленных методом магнетронного ионно-плазменного распыления, методом ЯМР на ядрах ^{59}Co (эффективная толщина слоя Co составляла $d_{\text{Co}} \approx 3.5$ и 4.5 \AA). Несмотря на столь малые значения эффективной толщины слоев, было обнаружено, что спектры ЯМР представляли собой суперпозицию двух пиков с центральными частотами $f_1 = 190 - 196 \text{ МГц}$ и $f_2 = 208 - 213 \text{ МГц}$, которые, очевидно, соответствовали атомам кобальта, имеющим 0 и 1 атом меди в ближайшем окружении. Данный факт указывает на то, что кобальт главным образом организуется в крупные кластеры, включающие большое число атомов.

Ключевые слова: ядерный магнитный резонанс, неоднородные сплавы Co-Cu, мультислойные пленки.