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The Behaviour of Surfactants during the Growth of Co/Cu Multilayers

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The $[Co(1\,nm)/Cu(2\,nm)]_N$ multilayers with different numbers of bilayer repetitions ($N = 3$ and 10) were thermally evaporated on Si(100) substrates with a small amount of Bi or Pb deposited only on the first and on the second Cu layer. The chemical composition of the surface after each step of the preparation process was studied by Auger electron spectroscopy. The evolution of the Auger peaks showed the segregation of Bi and Pb surfactants. During the evaporation of the subsequent Co and Cu layers, gradual decrease in the surfactant amount on the surface was observed. No appearance of Co peak on the Cu layer, and Cu peak on the Co layer even for a coverage of a few Å indicates the layer continuity. The interface roughness of the surfactant-mediated Co/Cu layers analyzed by X-ray reflectometry (when surfactant was deposited twice) was similar to the pure Co/Cu samples. However, more repetitions of surfactant, by reduction of interface roughness, improve the layer quality.

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1. Introduction

The cobalt/copper multilayers belong to the systems which have been extensively investigated, mostly due to the discovery of the interlayer exchange coupling [1–3], and giant magnetoresistance effect (GMR) [4]. The GMR is affected by the oscillatory exchange coupling which strongly depends on the structure of the Co/Cu interfaces [5]. Therefore interface modification techniques are of the great interest nowadays.

It is known that Co surface free energy is higher [6] than Cu [7] which may lead to the island growth of Co on Cu. There are several methods of preventing this

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type of growth and improving the interface quality. One of them is an application of a small amount of surfactants (i.e. Bi, Pb, In, Sb) between the adjacent Co and Cu layers. If an adsorbed species or surfactant is present at the surface prior to the deposition of an overlayer, the balance of free energies can be drastically altered, inducing two-dimensional growth of thin films in conditions not favourable for such growth [8]. Low-surface-energy elements are used as surfactants so that they can continuously segregate to the surface during deposition and no impurities are introduced into the growing film. Moreover, they reduce the Ehrlich–Schwoebel barrier or increase the surface activation energy of the deposited material.

In the previous work [9] it was shown that the surfactants, evaporated at each Cu layer of Co/Cu system, segregate to the surface during the deposition process, leading to a reduction of an interface roughnesses. The aim of the present work is to study in details the mechanism of the segregation process as a function of the thickness of Co/Cu layers deposited on top of it, and to analyze the interface quality of the multilayers.

2. Experimental

The $[\mathrm{Co}(1\ \mathrm{nm})/\mathrm{Cu}(2\ \mathrm{nm})]_N$ multilayers (with $N = 3$ and 10 repetitions) were thermally evaporated on Si(100) polished wafers. Before deposition process substrates were cleaned in organic solvents and rinsed in deionized water. The base pressure of the preparation chamber was in the range of 10^{-8} Pa. The layers were deposited at room temperature, with rates around 0.6 nm/min for Co and Cu, and 0.06 nm/min for Bi and Pb. The evaporation rates and layer thicknesses were monitored in situ by the quartz balance. The thickness of Cu layer (2 nm) corresponds to the second antiferromagnetic maximum of the exchange coupling between Co layer through Cu spacer [3]. The thickness of Co layer (1 nm) ensures the continuity of the layers and simplifies magnetic measurements. After the deposition of a first and a second (Co/Cu) bilayer, 0.06 nm of surfactant (Bi or Pb) was evaporated. The surfactants were introduced two times to enhance intensities of Auger peaks.

The chemical analysis of the surface and the segregation process of the surfactants were studied using Auger electron spectroscopy (AES). AES measurements were performed using a spectrometer operating with a beam energy of 3000 eV and a beam current of 40 μA equipped with retarding field analyzer. Two kinds of AES measurements were performed: (1) the spectra were taken after deposition of each 1 nm Co layer, 2 nm Cu layer and surfactants; (2) the spectra were taken during the deposition of third Co/Cu bilayer after each 0.1 nm of the Co and Cu layers on the (Co/Cu/surfactant)$\times$2 surface. The Auger electron spectroscopy was also used to analyse the chemical purity of the surface; small carbon and oxygen peaks were initially visible on the Si(100) surface. However, its intensities diminished after a successive step of evaporation. The multilayer quality was analyzed by X-ray reflectometry (XRR) carried out on an X'Pert PRO (PANalytical) difractometer operated at 40 kV and 30 mA using the Cu K_α radiation ($\lambda = 1.54178$ Å).

3. Results and discussion

In the chemical analysis of the samples low energy Auger transitions were chosen to ensure strong surface sensitivity. The Auger MNN lines of Co (57 eV) and Cu (66 eV) with the NOO lines of Bi (105 eV) or Pb (97 eV) were analyzed. They correspond to the effective mean penetration depth of 0.47 nm and 0.45 nm for Co and Cu, and 0.57 nm and 0.55 nm for Bi and Pb, respectively [10]. In Fig. 1a AES spectra taken after deposition of the first and the second Co/Cu/Bi layers, and the topmost (tenth) Co and Cu layer are presented. The similar graph for Pb-mediated multilayer is shown in Fig. 1b. No appearance of the Co peak after deposition of 2 nm of Cu and similarly, no appearance of the Cu peak after deposition of 1 nm of Co were observed, and this indicates that both layers are continuous considering the mean penetration depth of the electrons. In the insets at magnified scale, the Bi (105 eV) and Pb (97 eV) peaks, measured after the first and the second repetition of 0.06 nm surfactant are shown. It is seen that even after the first repetition of a very small amount of surfactant, peaks coming from Bi and Pb are clearly visible on the Co/Cu surface and their intensity increases after the second repetition of surfactant. After deposition of eight bilayers of Co/Cu, peaks coming from the surfactants are still to be seen, which means that both surfactants segregate to the surface.

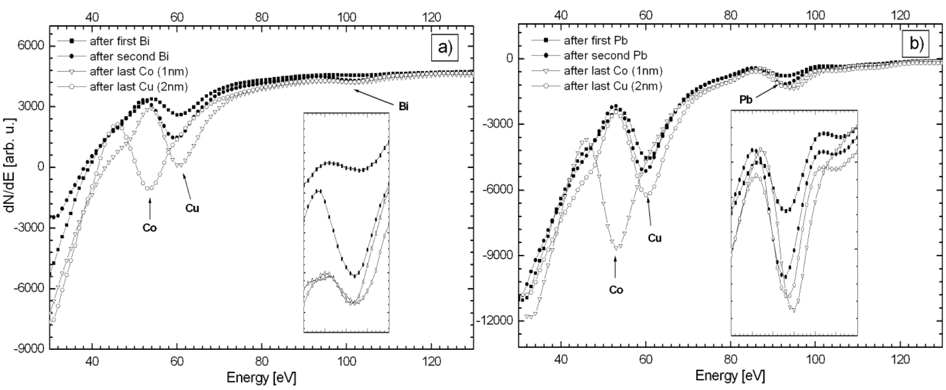

Fig. 1. The AES spectra taken after deposition of the first and the second repetition of (Co/Cu/surfactant) and the topmost (tenth) Co and Cu layer. In the insets at magnified scale, the Bi (105 eV) and Pb (97 eV) peaks were shown.

The Auger peak intensity of Bi (105 eV) and Pb (97 eV) as a function of the deposited Co/Cu layer thickness are presented in Fig. 2. This parameter was chosen for analysis because of ambiguities of the matrix correction factor values and of not sufficient information about elemental sensitivity factors. As observed previously, the surfactants are visible on the surface of the Co/Cu multilayers even for coverage of eight (Co/Cu) bilayers. The amount of surfactant gradually drops after subsequent deposition of cobalt and copper layers which indicates that during the segregation process surfactant atoms partially remain in the whole sample. Taking into account the mean penetration depth of the electrons [10] and the results from [11], the AES signal coming from substrate layer should decrease exponentially with the adsorbate layer thickness and should totally disappear after coverage of approximately one Co/Cu bilayer. The significantly different behaviour of Bi and Pb (Fig. 2) from the described above, confirm the previously mentioned segregation process.

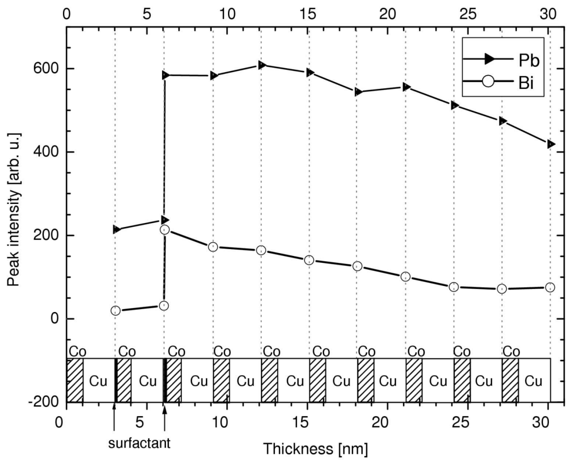

Fig. 2. The surfactant peak intensities as a function of Co/Cu multilayers thicknesses. The lines are drawn to guide the eye. At the bottom of the graph the scheme of the sample is drawn.

The detailed analysis of the segregation process is shown here only for Bi-mediated multilayers, because of the similar behavior of both surfactants. In Fig. 3a the Auger peak intensities of Bi and Co, and Cu layers taken with 0.1 nm step during the preparation of third Co/Cu bilayer together with Bi peak intensity taken before third Co/Cu bilayer is shown. As a reference, the results for Co/Cu layers without surfactant are presented in Fig. 3b. The Bi peak intensity decreases during the Co deposition and Cu deposition in the same way, so the Bi segregation through Co and Cu layer does not differ. Co peak intensity in Bi-mediated sample reaches saturation at 0.5 nm indicating the closing of the layer, while in the reference sample (Fig. 3b) a continuous layer appears after about 0.7 nm. It may suggest that the Co layers in the surfactant-mediated multilayers are smoother than in the reference sample, which indicates the change of the tendency of Co to 3D growth. The detailed analysis of the underlayer peaks is difficult due to the small peak intensities, however some results concerning overlayers are presented. During the cobalt preparation, the decrease in copper peak intensity was observed and after deposition of 0.2 nm of Co, the peak coming from the copper was at the spectra noise level. The similar situation was observed for the cobalt peak registered during the copper evaporation, the cobalt peak vanished after deposition of 0.3 nm copper layer. In the reference sample, total covering of the Co and Cu layers was observed for the same thicknesses as in the surfactant-mediated samples.

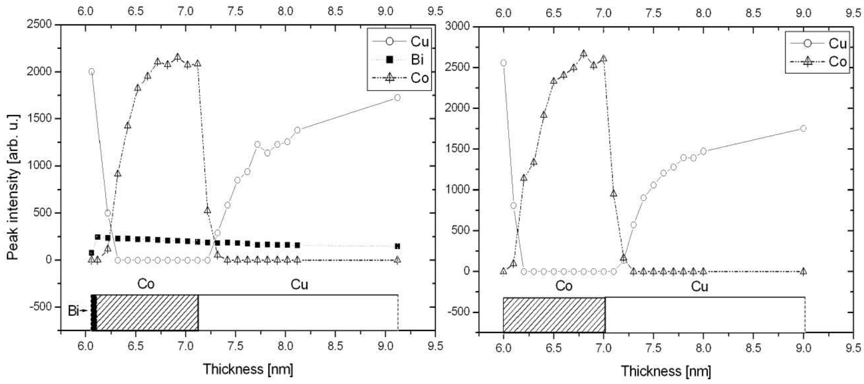

Fig. 3. The peak intensities obtained from the AES spectra taken during the deposition of the third Co/Cu bilayer after each 0.1 nm of the Co and Cu layers. At the bottom of the graph the scheme of the sample is drawn.

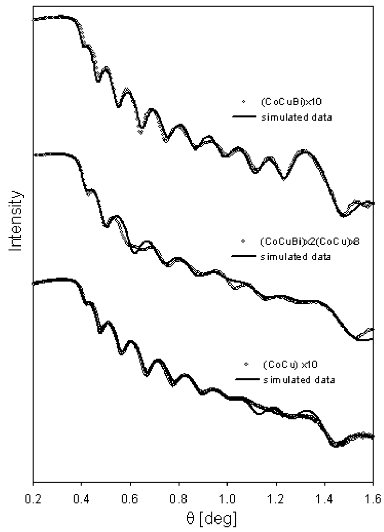

Fig. 4. X-ray reflectometry spectra for $[CoCuBi]_{10}$ and $[CoCuBi]_2[CoCu]_8$ multilayers in comparison with $[CoCu]_{10}$. Theoretical fits to the reflectivity data are also shown (continuous lines).

The structure of multilayers and interface roughnesses were observed using XRR measurements. It is known from the previous studies concerning (Co/Cu/surfactant)×10 multilayers [9] that the application of surfactant causes the smoothing of the layers in comparison with the reference sample, and additionally the interface roughness is smaller when Bi is used. In Fig. 4 the reference sample and two Bi-mediated samples with 2 and 10 surfactant repetitions are presented. It is seen that the application of two repetitions of Bi has a very small influence on the sample structure. The intensity of the Kiesig fringes in Bi-mediated sample is smaller than in the reference multilayers. In both samples the Bragg peak is not well resolved. The same situation was observed for Pb surfactant. It means that the two repetitions of surfactant does not bring any positive effect on the interface quality, although smoothening of the third Co layer was observed by AES. This is caused by the fact that XRR gives average information about the interface structure. The efficiency of the surfactant is clearly visible in the spectrum measured for Co/Cu multilayers with 10 repetitions of Bi surfactant, where the pronounced Kiesig fringes and Bragg peak are seen. The above-mentioned features proved the high quality of the multilayer structure and small interface roughness below 1 nm.

4. Conclusions

The surfactant behaviour in Co/Cu system and the structure of surfactant-mediated multilayers were analyzed. It was proved that the 1 nm Co layers and the 2 nm Cu layers are continuous. The segregation of Bi and Pb surfactant to the surface was observed through eight repetitions of Co/Cu bilayers. The segregation process through the Co and Cu layer does not differ. A detailed analysis of the AES peak intensities suggests that the Co layers in surfactant-mediated multilayers are smoother than in the sample without surfactant. A high quality of the multilayer structure and a small interface roughness, below 1 nm, were observed only for 10 repetitions of surfactant. The results showing the correlation between structural, magnetic, and magnetotransport properties of surfactant-mediated Co/Cu multilayers will be published elsewhere.

Acknowledgments

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