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XAFS Studies of the Behaviour of Bi in Co/Cu Multilayers

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The atomic environment of Bi atoms in the Co/Cu multilayered system was studied with X-ray absorption fine structure spectroscopy. Experiments were carried out on a Co(1 nm)/Cu(2 nm) system with 5 and 10 repetitions of Co/Cu evaporated with very low deposition rate in ultrahigh vacuum. A very small amount of Bi (0.06 nm) was deposited on each Cu film in the system. The X-ray absorption fine structure spectra were measured at the BiL_3 edge in the X-ray absorption near-edge structure and extended X-ray absorption fine structure ranges at the Beamline X1 of HASYLAB/DESY synchrotron laboratory in Hamburg. The experimental data showed different local neighbourhood of Bi, depending on the number of Co/Cu bilayer repetitions. The results are discussed in terms of the location and segregation of the Bi atoms as well as its possible oxidation ways.

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1. Introduction

Vapour deposited Co/Cu multilayers with high quality interfaces exhibit significant giant magnetoresistance (GMR) effect [1]. These systems are extensively investigated as a potential reading heads in ultrahigh-density data storage devices. The value of magnetoresistance is mainly affected by the atomic scale structure, i.e. interfacial roughness [2]. Smooth Co/Cu layer interfaces reveal usually larger GMR effect in comparison with rough and mixed interfaces. The bigger roughness is experimentally found to occur predominantly at the Co on Cu interfaces. This results from the surface free energy which is smaller for Cu than for Co. It makes difficulties in obtaining multilayers with optimal GMR value.

One of the solutions to these problems is the addition of surfactants, i.e. low surface energy metals like Bi, to the films. Addition of small amount of surfactant into the Co/Cu multilayered system significantly reduces degree of an interfacial roughness [3]. Smoothing of the interfaces is a result of surfactant segregation to the surface of Co/Cu multilayers. The results showing correlation between structural and magnetic properties of surfactant mediated Co/Cu multilayers were published elsewhere [4, 5]. It is also of great interest to know how surfactant atoms interact with other atoms in the multilayer system, and this can be deduced from the information about the nearest neighbourhood of surfactant atoms obtained with a local probe experimental technique. This paper presents the results obtained by the X-ray absorption fine structure (XAFS) spectroscopy.

2. Experimental details

The sample preparation was done in an ultrahigh-vacuum system at pressures below 10^{-6} Pa. The substrates were Si(100) wafers, covered with native SiO_2 and before the deposition process were ultrasonically cleaned in organic solvents and rinsed in deionised water. [Co(1 nm)/Cu(2 nm)] multilayers with 5 and 10 number of bilayers repetitions have been obtained by sequential thermal evaporation. In addition the surfactant was introduced in a very small amount (0.06 nm), at each interface of the Co/Cu bilayers before Co deposition. The layers were deposited at the room temperature, with rates around 0.6 nm/min for Co and Cu, and 0.06 nm/min for Bi at the working pressure in the range of 10^{-5} Pa. The chemical analysis of the surface was studied *in situ* during the deposition process using Auger electron spectroscopy (AES). AES measurements

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showed additional small amount of the oxygen, however the concentration of oxygen never exceeded 1%. Furthermore, composition of residual gas in the preparation chamber was analysed before and during deposition using quadrupole mass spectrometry (QMS). The measurements showed mainly presence of nitrogen and hydrogen. Small concentration of oxygen was observed too, however partial pressure of oxygen always amounts to approximately 10^{-9} Pa. For all Co/Cu samples prepared in the same experimental conditions the similar concentration of oxygen and other chemical elements was observed. However, for XAFS measurements only two of them were selected due to the limited beamtime.

X-ray absorption spectra were recorded at X1 beamline of the HASYLAB/DESY synchrotron laboratory in Hamburg, Germany. The storage ring was operating at 4.45 GeV positron energy and 140 mA positron current. The beam was monochromatised by a double crystal Si(111) monochromator and the energy resolution $\delta E/E$ was estimated to be about 10^{-4} for all measurements. The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were recorded at the Bi L_3 edge at room temperature using fluorescence detection mode. The XANES spectra were normalised to the high energy part of each spectrum ($\approx$ 200 eV beyond the edge) after the background subtraction. The EXAFS structural analysis was performed using the ARTEMIS program [6], which makes use of theoretical standards from the FEFF6 [7]. The EXAFS spectra $\chi(k)$ were obtained from the experimental data by careful subtraction of the atomic absorption background. The $\chi(k)$ function was Fourier transformed using the Hanning window in the range of k = 1–5 Å^{-1}.

3. Results and discussion

Figure 1 shows the Fourier transforms (FT) of the Bi EXAFS spectra for samples with 5 and 10 repetitions of [CoCuBi] trilayers. The FT for the sample with 5 trilayer repetitions shows a strong peak at $\approx$ 2.5 Å, which is attributed to the Bi–Co or Bi–Cu distance. It is not possible to distinguish between the contribution from Co and Cu due to their very similar atomic radius. In the case of FT for the sample with 10 trilayer repetitions other environment of Bi atoms is observed. The peak at $\approx$ 1.8 Å dominates. It denotes the nearest neighbour Bi–O distance and its position stays in agreement with FT EXAFS spectra for other alloys and compounds [8–10]. The same peak, but with smaller amplitude, is clearly visible also for the [CoCiBi]×5 sample after decomposition of the FT EXAFS signal. The decomposition has been done using two Gaussian functions, which have been fitted to the FT EXAFS signal. Different amplitude of Bi–O peak in both spectra suggests that the amount of oxygen atoms surrounding Bi increases with the number of trilayer repetitions. The next coordination shell is not visible for both samples, especially no Bi–Bi distance corresponding to the metallic Bi is seen.

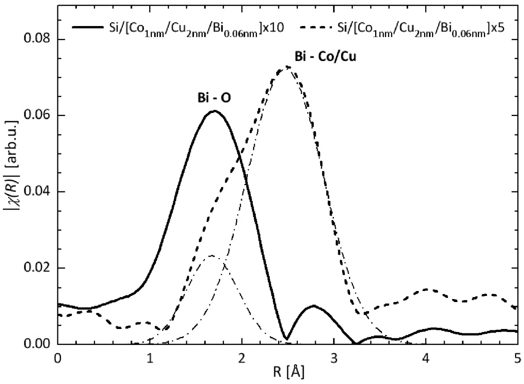

Fig. 1. Fourier transforms of the EXAFS spectra for [CoCuBi]×5 (dashed line) and [CoCuBi]×10 (solid line). The curve for [CoCuBi]×5 has been fitted to two Gaussian functions (thin dash-and-dotted lines).

Figure 2 shows the Bi L_3-edge XANES spectra of the [CoCuBi]×5 and [CoCuBi]×10 samples. The shape of both edges is similar, however as can be seen in Fig. 2, the absorption edge for the [CoCuBi]×10 sample appears at the energy by 1.8 eV more than the absorption edge energy of the [CoCuBi]×5 sample. It can indicate that the oxidation state of the surfactant depends on the number of deposited trilayers and increases with the number of trilayers repetitions. On the other hand, the shift of Bi absorption edge can be caused also by a modification of the kind of surrounding around the surfactant atoms. Both interpretations are in a good agreement with the EXAFS results, but the second is more comprehensible.

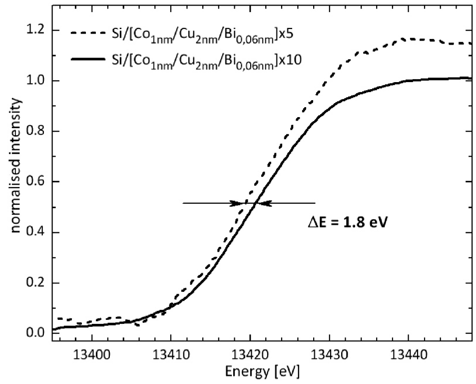

Fig. 2. Normalised Bi L_3-edge XANES spectra for [CoCuBi]×5 (dashed line) and [CoCuBi]×5 (solid line). Shift of the edge position is clearly visible.

Origin of the oxygen atoms in the close vicinity of Bi can be explained in terms of three possible ways of bismuth oxidation:

1. Oxidation with residual gas in the preparation chamber. Bi atoms, evaporated from the crucible, could capture residual O atoms remaining in vacuum chamber, but according to the QMS measure-

ments concentration of oxygen was very small during the deposition process and it seems the least probable way of Bi oxidation.

2. Oxidation of the sample surface after removing the sample from the preparation chamber after the deposition. The oxygen atoms from atmosphere can react with the bismuth atoms on the sample surface, however it is not possible to oxidise in such way Bi inside the system. On the other hand, some papers [11, 12] report that bismuth can attach the oxygen atoms effectively only in temperature above 700 K. In our case the samples were kept always at room temperature, so we suspect air cannot be the only source of oxygen in the vicinity of Bi.

3. Diffusion of the oxygen atoms from substrate or from slight contamination of deposited materials. We assume that there is a possibility of oxygen diffusion from the substrate covered with native SiO_2 to the first Bi layer and next to the whole multilayer system. In such scenario the bismuth atoms act as local traps for oxygen and segregate with them to the sample surface. This concept stays in agreement with different character of FT EXAFS spectra for 5 and 10 repetitions of [CoCiBi] trilayers. In case of larger number of trilayers, the diffusion length of bismuth is longer causing the increase in probability of oxygen attachment. Origin of oxygen from slight contamination of deposited materials is also possible, but the least probable. During the deposition process the materials of very high purity were used and additionally each material was annealed before sample preparation at high temperature in vacuum chamber in order to eliminate adsorbed gases.

It should be mentioned that AES, as an integral technique, showed small oxygen content in the whole sample surface, whereas EXAFS, as a local technique, indicated significant oxygen occurrence in the vicinity of Bi atoms. Assuming homogeneous and random distribution of oxygen in the sample and taking into account the small Bi concentration (not exceeding a few %), we should not have obtained such strong Bi–O peak in FT EXAFS spectrum. It suggests that oxygen atoms tend to locate near Bi more willingly than near Co and Cu. It can be explained by means of the Allred–Rochow electronegativity scale [13]. According to this scale, Bi is less electronegative than Co and Cu. It causes that the difference in the Allred–Rochow electronegativity between oxygen and bismuth is the largest, so location of the oxygen atoms in the vicinity of Bi is energetically favourable. It suggests that Bi atoms trap the oxygen atoms in the Co/Cu system during the segregation process.

4. Conclusions

The Bi behaviour and the atomic environment of Bi atoms in surfactant mediated Co/Cu system were analysed with the X-ray absorption spectroscopy. In the EXAFS spectra two contributions to the measured signal, coming both from O as well as from Co/Cu atoms in the close vicinity of Bi, were seen. No Bi–Bi environments corresponding to the metallic Bi were found, which indicates that the Bi atoms do not form clusters. Origin of oxygen atoms in the samples is unclear and next studies are needed, but it is likely that oxygen is introduced into the sample during the deposition process. Moreover, it was proved that the local environment of the surfactant atoms depends on the number of deposited [CoCuBi] trilayers. The contribution coming from the O atoms is larger for [CoCuBi] multilayers with 10 repetitions of trilayer. It is clearly seen both in the EXAFS and the XANES spectra. It suggests that Bi acts as a local trap of O during its segregation to the sample surface.

Acknowledgments

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