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Specular and diffuse X-ray reflectivity study of surfactant mediated Co/Cu multilayers*

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The application of X-ray techniques for studies of the interface structure of Co/Cu multilayers has been presented with a pre-deposited ultrathin film of Bi and Pb. The [Co(1 nm)/Cu(2 nm)] multilayers were thermally evaporated at very low deposition rates with a small amount of Bi and Pb surfactant (about 0.2 ML) introduced at each Cu layer. The structure of Co/Cu multilayers with added surfactant has been studied using low-angle specular and nonspecular X-ray reflectivity. In all studied specimens, the off-specular reflectivity replicates some of the features of specular reflectivity. The presence in diffuse spectra of a Bragg peak due to coherent scattering, as well as visible finite thickness clearly indicates a high degree of conformality and interface roughness replication in the surfactant mediated Co/Cu multilayers. X-ray reflectivity as well as X-ray diffuse scattering measurements showed a distinct variation in the structure of the multilayers with introduction of surfactant which leads to well-ordered periodic structures with small roughness.

Key words: *surfactant; surface segregation; Co/Cu multilayers; Auger electron spectroscopy; X-ray reflection; bismuth; lead*

1. Introduction

The discovery of the giant magnetoresistive (GMR) effect in magnetic multilayers which contain alternate layers of a magnetic element and a non-magnetic element as the basic building blocks offers a route to small bit size random access memories. In applications for magnetic storage devices, Co/Cu multilayers [1] form one of the most promising materials because of a very large GMR effect even at room temperature [2]. However, a wide variation of results for Co/Cu multilayers has been observed, due to the fact that the magnetic transition metals tend to agglomerate over the noble metals

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because the surface free energy of Cu is significantly lower [3] than that of Co [4]. As a result, Co agglomerates rather than wets the Cu surface. It is also known that, in addition, noble atoms segregate out onto the transition metal surface, giving rise to intermixing across the interface. This results in multilayers with rough, diffuse, and intermixed interfaces which influence the magnetotransport properties. The strength of the antiferromagnetic coupling between the layers depends on the spacer thickness and can be disrupted by significant interface roughness. Therefore, smooth layer morphology is required for many modern electronic devices, and one promising approach that has been pursued to obtain heterostructures with atomically sharp interfaces is through the use of surface modifiers known as surfactants [5, 6]. Using this approach, 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 2-dimensional growth of thin films in conditions not favourable for such growth. 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. The surfactant-mediated growth technique provides a good way to fabricate the films with desired, atomically smooth interfaces. It was originally introduced in semiconductor superlattice growth good results were also obtained, however, in polycrystalline spin valve and multilayers deposition [7–9]. In this paper, we present the application of X-ray technique for investigation of the effect of a pre-deposited Bi and Pb surfactants on the interface structure of Co/Cu multilayers.

2. Experimental

Sample preparation and characterization were done in an ultrahigh-vacuum system at pressures about 10^{-8} Pa. Si(100) wafers, covered with native SiO_2, were ultrasonically cleaned in organic solvents and rinsed in deionized water. Co/Cu multilayers with 10 repetitions of [Co/Cu/surfactant] trilayers have been obtained by sequential thermal evaporation of Co, Cu and Bi or Pb surfactant at the rates between 0.05 and 0.5 ML/min, and the thicknesses of Co (1 nm) and Cu (2 nm) correspond to the second maximum of the oscillating thickness dependence of magnetoresistance. The surfactants were introduced in very small amounts, about 0.2 ML, at each interface of the Co/Cu bilayers before Co deposition. Our earlier results [10] showed that addition of surfactant at each Co/Cu bilayer has better effect on the quality of the interface structure than for the case of its repetition at every second bilayer. Reference samples with the same number of Co/Cu bilayer repetitions were deposited without the introduction of surfactants. During deposition, the sample was kept at room temperature. Chemical composition of successive Co and Cu layers was monitored during growth after deposition of the individual elements by the Auger electron spectroscopy (AES). Low energy electron diffraction (LEED) measurements, performed simultaneously, did not show any distinct features associated with an ordered structure, indicating the polycrystalline structure of the samples. After deposition, the sample structure was investigated *ex-situ* by X-ray reflectometry (XRR) performed with a Philips X'Pert MRD Pro diffractometer. CuK_α radiation operated at 40 kV and 30 mA was converted to a parallel beam by an incident beam optics with 0.03125° divergence slit and a diffracted beam parallel plate collimator with equatorial acceptance of 0.18°. The 0.04 rad. Soller slits were used on both, incident and diffracted beams. A programmable beam attenuator was used to reduce radiation intensity by a specific factor at small angles.The axial width of the incident beam was restricted by incident beam mask to 5 mm for all measurements.

Three types of scans in coplanar geometry were recorded: specular θ–2θ (Q_z) reflectivity scans, transverse ω rocking scans in which only the transverse component of the scattering vector varies, and offset scans, with the reciprocal space direction parallel to a θ–2θ scan, but offset by some amount in Q_z.

3. Results and discussion

X-ray reflectivity spectra of $[Co/Cu/surfactant]_{10}$ multilayers are shown in Fig. 1. The spectra of $[Co/Cu/surfactant]_{10}$ multilayers with Bi and Pb demonstrate well-defined Kiessig fringes, a similar fall-off of intensity with increasing angle, and well-resolved Bragg peak indicating that the bilayer thickness is conserved through the whole sample. The spectrum of a Co/Cu multilayer without surfactant shows that both finite-size peaks as well as superlattice reflections have smaller amplitude. Low angle specular X-ray reflectivity is sensitive only to the vertical structure of the multilayers averaged over horizontal dimensions of sample surface, and can provide information about the thicknesses, electronic densities of layers and the roughnesses characterized by the standard deviation of the height fluctuations of the interfaces [see for example [11]]. The increase in surface and interface roughness gives a lower reflectivity and smearing and broadening of the fringes. The detailed analysis of experimental data was done with simulation program REFLECTIVITY of Panalytical which applies the Parratt formalism for reflectivity [12]. The software allows the fitting of thickness t, rms roughness σ_{rms} and density d for groups or individual adjacent layers. Since a reliable refinement of multilayer system requires the minimum number of variable layer parameters, the best result was obtained by modeling the sample as the sum of the following contributions with common parameters for each group: the first Co/Cu bilayer close to substrate surface $(Co/Cu)_1$, followed by 8 repetitions of Co/Cu bilayers $(Co/Cu)_8$ and finally the Co/Cu-surfactant alloy bilayer, as observed in Auger spectra [13], or Co/Cu bilayer in case of multilayers prepared without surfactant. A good agreement was found between nominal and estimated Co and Cu thicknesses. The densities of Co and Cu films differed by no more than 10% from bulk density values. The fitted interface roughnesses for each component of this model are shown in Fig. 2. It is seen that the multilayer with surfactants had roughness of the order of 1–2 ML, but the multilayer without them had much larger roughness and strongly mixed interfaces, the result confirmed by a very small Bragg peak.

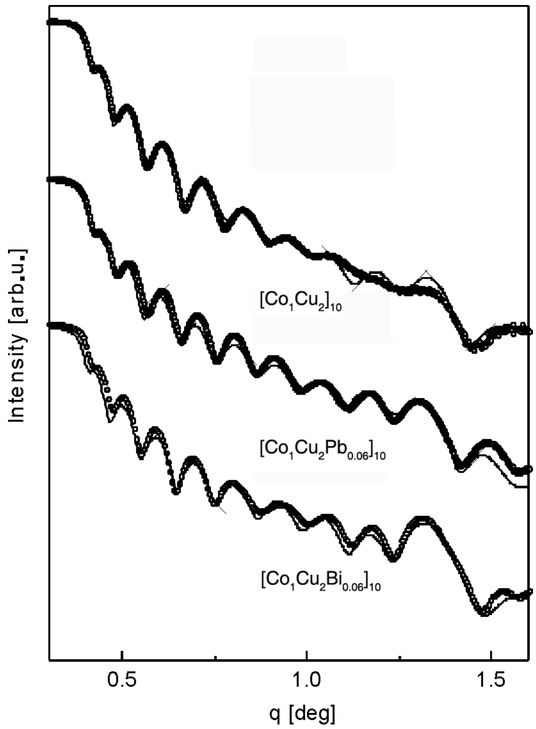

Fig. 1. Low-angle X-ray reflectivity data for $[CoCuBi]_{10}$ and $[CoCuPb]_{10}$ multilayers in comparison with $[CoCu]_{10}$. Theoretical fits to the specular reflectivity data are also shown (continuous lines)

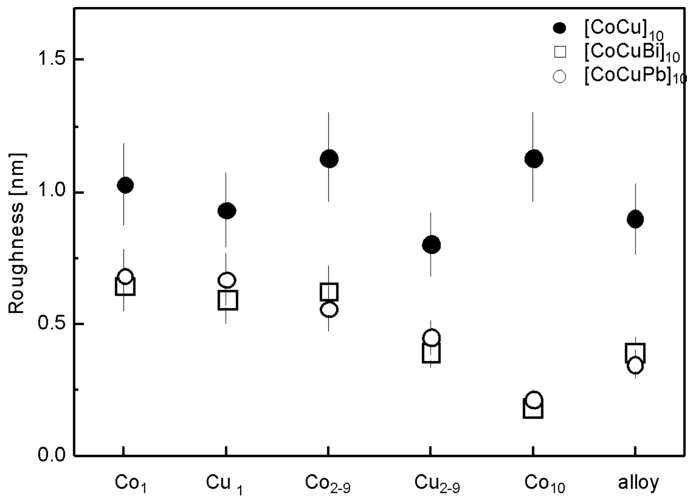

Fig. 2. The rms roughness σ_{rms} for $[Co/Cu]_{10}$ multilayers, with and without surfactant in function of film position in the multilayer system according to the model described in text

The specular XRR curves give no information on how roughness is correlated. Determination of the degree of roughness correlation requires looking at the diffuse scattering. Scans made in the slightly offset Q_z direction show the diffuse scattering resulting from correlated interfaces. For fully uncorrelated interfaces, the diffuse scattering along the Q_z direction is featureless and much lower in intensity than the specular scattering. For fully correlated interfacial roughness, the diffuse scattering is an exponentially modulated copy of the specular scattering. The replication of finite thickness oscillations in the offset scans and the diffuse scattering in the vicinity of the superlattice Bragg peaks with essentially the same shape as in specular scans is indicative of the increased layer to layer correlation of the roughness of the films.

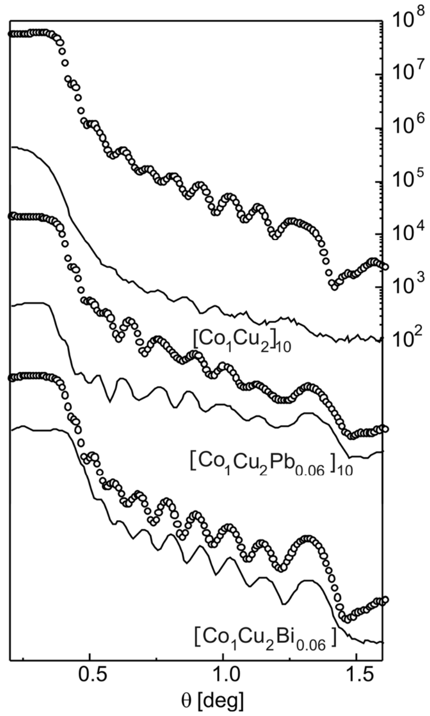

Fig. 3. The X-ray specular reflectivity and off-specular reflectivity scans (lines) of $[Co/Cu]_{10}$ multilayers prepared with and without surfactants. All spectra are drawn in the same logarithmic scale. For the clarity of the figure the scale is only marked for the top two lines

Specular and offset (offset angle $\Delta\varpi = 0.1°$) scans of Co/Cu multilayers shown in Fig. 3 exhibit the replication of the features from specular to diffuse for Co/Cu multilayers prepared with Pb and In, however, reference Co/Cu system without surfactant shows no replication. The presence of Bragg peak due to coherent scattering, as well as visible finite thickness clearly indicates a high degree of conformality and interface roughness replication in the surfactant mediated Co/Cu multilayers.

Transverse ω rocking scans provide information on the lateral length scale or in-plane correlation length of the film. The rocking curves measured at the Q_z position of the multilayer Bragg peaks are dependent on the sum of the correlated and uncorrelated roughness. Outside the Bragg peaks only the uncorrelated roughness is observed.

Consequently, measuring the diffuse scattering on and off Bragg peaks allows us to distinguish the correlated and uncorrelated roughness. If the roughness is highly correlated, there will be a different curvature of Q_x scans on and off the Bragg position.

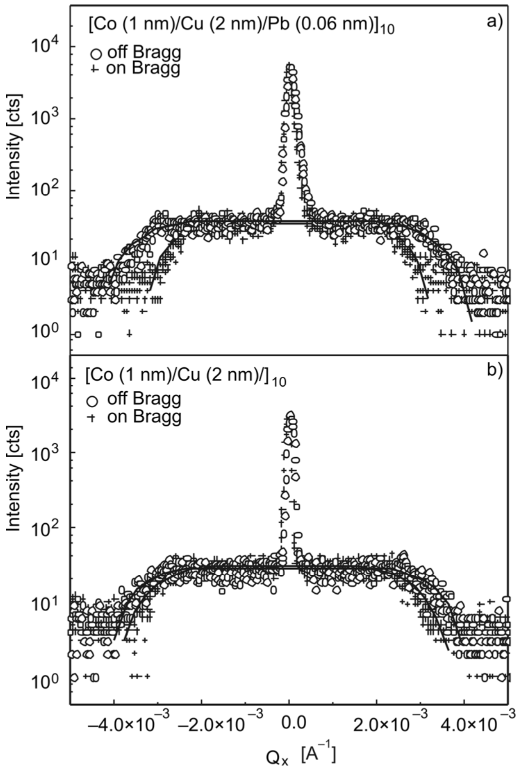

Fig. 4. X-ray rocking scans of $[Co/Cu]_{10}$ multilayer (a) with Pb surfactant compared with $[Co/Cu]_{10}$ multilayer reference sample (b). The spectra are plotted for the scattering angle corresponding to the first Bragg peak (cross symbols) and for the preceding intensity maximum (circles), determined from specular spectra in Fig. 1

Examples of rocking scans taken on and off the Bragg peak position for Co/Cu multilayers with and without surfactant, consisting of narrow resolution-limited specular and broad diffuse components, together with simple approximation [14] of the spectra curvature are shown in Fig. 4. Again we observed that for the Co/Cu multilayers grown with surfactant, the curvature is different on and off the Bragg peak positions, confirming an enhanced degree of correlation, whereas for the reference Co/Cu system curvature is essentially the same. The correlated vertical roughness σ_c was estimated from the ratio of the integrated specular and diffuse components [15] and it is equal 0.3 and 0.45 nm for reference Co/Cu and surfactant assisted Co/Cu multilayers, respectively. However, the precise determination of correlated and uncorrelated roughness as well as the lateral correlation length requires more experimental work, and careful examination of spectra taking into account the effect of instrumental resolution, which is of particular importance in the analysis of the diffuse scattering. The distorted wave Born approximation (DWBA) including different aspects of instrument broadening can be used for detailed analysis of diffuse scattering spectra and this work will be performed in the future.

4. Conclusions

The evolution of roughness and roughness correlation in polycrystalline Co/Cu multilayers grown with assistance of Bi and Pb surfactants has been studied using combined X-ray scattering techniques. X-ray reflectivity and X-ray diffuse scattering spectra show a distinct variation in the structure of the multilayer interface under the influence of surfactant. The structure of Co/Cu multilayers with Bi and Pb deposited at the bilayer interface demonstrated that use of surfactants in growth processes smoothes the interfaces between Co and Cu, and increases the layer-to-layer correlation, leading to the creation of flatter interfaces and films with homogeneous thicknesses. In contrast, the roughness of pure Co/Cu multilayer interfaces is significantly larger, and the periodicity of the bilayer stack is not well conserved. The conformal nature of the roughness in surfactant assisted Co/Cu multilayers was confirmed by the presence of coherent scattering in the diffuse spectra. A careful analysis of data with DBWA will also bring the value of lateral correlation length which can be very useful for determination of energy barrier relations on the surface.

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