Abstract

As early as 10 years after the discovery of the giant magnetoresistance (GMR) the magnetic/non-magnetic multilayers found their first application in the read-out units of magnetic recording media, and the hard disk drives with GMR-based sensors since gained a dominating market share. In spite of the large number of works published on nanoscale multilayers, data on the depth profile of electrodeposited multilayers samples are very scarce. This work deals with the depth profile analysis of electrodeposited CoNiCu/Cu and Co/Cu multilayers films. Commercial Cu sheet and a Cr/Cu layer evaporated onto Si (1 1 1) surface were used as substrates with high and low roughness, respectively. The Secondary Neutral Mass Spectrometry (SNMS) depth profile analysis clearly revealed the layered structure of the samples. The resolution of the individual layers varied with the initial roughness of the substrate. The SNMS spectra showed that the oxygen incorporation into the layers is insignificant. When both Ni and Co are present in the magnetic layer, the composition of the samples is influenced by both the anomalous codeposition properties of the iron-group elements and the mass transport of the corresponding ions in the electrolyte. This observation draws the attention to the possible inhomogeneity of the magnetic layers in electrodeposited samples.

1. Introduction

Nanoscale multilayers have been in the focus of research since the discovery of the giant magnetoresistance (GMR) effect in this family of nanostructures. The first observation of GMR on sputtered magnetic/non-magnetic multilayers was followed by the detection of the same effect in electrodeposited Co–Ni–Cu/Cu multilayers within half a decade [1]. Co–Ni–Cu/Cu multilayers were electrodeposited by using various deposition systems and electrolyte compositions [e.g. 2,3]. The possible application of these structures as magnetic field sensors has been the main driving force of the research of electrodeposited nanoscale multilayers.

Electrodeposition has long been considered as an inexpensive alternative of the high-vacuum methods to produce multilayers with GMR, although the GMR effect observed for electrodeposited multilayers is usually inferior to multilayers produced by physical methods. Electrochemistry appears to be an exclusive technology to produce multilayered nanowires by using porous templates. In spite of the large number of papers about the multilayers themselves, data on the depth profile of electrodeposited multilayer samples are very scarce. The most common method for depth profile analysis of electrodeposited coatings is XPS. To the best knowledge of the authors, this is the first attempt to apply Secondary Neutral Mass Spectrometry (SNMS) for this purpose.

It has long been known that the simultaneous electrodeposition of the iron-group metals takes place in the so-called anomalous manner [4]. The diagnostic criterion of the anomalous codeposition is that the metallic component of lower standard potential (the Co in the case of Ni/Co) can be discharged together with the more noble one (Ni) at potentials where the less noble component (Co) alone cannot be deposited onto a substrate composed of the parent metal; moreover, the less noble metal (Co) is
deposited preferentially. Abundant up-to-date literature data can be found on the anomalous codeposition of Co and Ni [e.g. 5,6], and various theoretical approaches have also been published on the possible origin of the phenomenon.

In spite of the long history of research on both electrodeposited multilayers and anomalous codeposition, systematic studies on the impact of the anomalous codeposition on multilayer composition appeared only quite recently [7,8]. Both experimental results and theoretical simulations of the deposition process revealed that the composition of the alloyed layers substantially changes during the initial stage of the layer deposition. This composition variation may persist over several nanometers. The composition change along the growth direction is due to the depletion of the ions of the preferentially deposited less noble metal in the electrolyte close to the cathode surface as a result of the fairly high current density.

The aim of this work was to investigate the capability of the SNMS method to observe layer structure in electrodeposited Co–Cu/Cu samples and to determine the composition gradient along the growth direction of electrodeposited Co–Ni–Cu/Cu multilayers films by SNMS.

2. Experimental

Samples were electrodeposited using the single bath method. Commercial Cu sheets and an Cr/Cu layer evaporated onto Si (1 1 1) surface were used as substrates with high and low roughness, respectively. When using the Cu foil as a substrate, a thin Pd layer was deposited as a marker to distinguish the substrate from electrodeposited Cu layers. In the case of the Si wafer, the Cr layers provides sufficient adherence, while the Cu layer is necessary for both increasing electric conductivity and creating the growth conditions of the fcc lattice of the deposit.

Analytical grade chemicals and double distilled water were used for the preparation of all electrolytes. A tubular cell of 60 ml internal volume was used in all experiments. A fully computer-controlled EF453 type combined potentiostat/galvanostat (Elektroflex, Hungary) was used as a current source. The magnetic layer was produced with a fixed current, while the non-magnetic Cu layer was deposited under potentiostatic conditions [9]. The potential during the deposition of Cu was optimized by the method suggested in [10], and all Cu layers were deposited at −585 mV. This ensures that the actual layer thicknesses are equal to nominal ones.

The depth profiles of the samples were recorded using SNMS (INA-X, Specs GmbH, Berlin) in the Direct Bombardment Mode. An inductively coupled low-pressure radio frequency Ar discharge was used to provide sample bombardment and post ionization. The samples were bombarded with Ar⁺ ions extracted from the plasma with the use of high-frequency negative bias on the sample. The residual gas ions were discriminated by energy dispersive ion optics. The bombarding energy was 500 eV in the case of Co/Cu samples and 350 eV in the case of CoNiCu/Cu samples. The elemental composition was determined using relative sensitivity factors of the constituents [11]. The sputtering time was converted to a scale proportional to depth by taking into account sputtering yield changes during profiling and also changes in the layers density [12]. The depth scale was fixed by accepting the nominal thickness of the samples.

3. Results and discussion

The first set of samples (A and B, see Table 1) was prepared on commercial Cu sheets. First, a Pd marker layer of 30 nm was deposited onto the substrate. This was followed by the change of the electrolyte, then the multilayer structure consisting of pure Cu and Co–Cu layers was produced by the modulation of the electrochemical parameters. The Cu content of the magnetic Co layer was 4–12 at%. Depth profiles of samples A and B are shown in Figs. 1 and 2, respectively. As it can be seen, in the case of sample A the individual layers are well resolved, however, deterioration of the depth resolution can be seen from the decreasing amplitude of the layer peaks. In contrast, the depth profile of sample B shows that after removing the topmost \{Cu(45)/Co(65)/Cu(25)/Co(25)/Cu(10)/Co(10)/Cu(20 nm)\}...
Cu\((10)/\text{Co}(10)/\text{Cu}(20\,\text{nm})\) layers the structure is mixed and the individual layers are not clearly resolved, although the eroded depth is not higher than in the case of sample A. The reason for this can be the more complex structure, hence the more complex preparation.

In order to avoid the possible effect of substrate-surface quality on the depth resolution, further samples (C and D, see Table 1) were created using \(\text{Si}(1\,1\,1)\) surface as substrate. In this case, the \(\text{Si}(1\,1\,1)\) surface was first coated with an evaporated \(\text{Cr}(5)/\text{Cu}(20\,\text{nm})\) underlayer, then multilayer samples with Co–Ni–Cu magnetic layers were prepared. The typical Cu concentration of the magnetic Co–Ni–Cu layer was below 2 at\%. The depth profiles of these structures are shown in Figs. 3 and 4. In the case of sample C the depth profile of the magnetic layer shows an inhomogeneity of the constituents, which can be accounted for the anomalous codeposition of Ni and Co and the mass transport of these ions in the electrolyte. This concentration gradient within the magnetic layer is usually neglected, although as it can be seen the concentration change along the growth direction is significant even at the beginning of the layer (closer to the substrate).

In case of sample D the individual layers are clearly resolved and the deterioration of the depth resolution is lower than in the case of sample A (similar samples), as it is visible from the smaller decrease of the amplitudes of the Cu layers. We must note that the difference in the depth resolution in the case of samples A and D is smaller than what could be expected. In this case the concentration profile of the magnetic layers are similar to the profile of sample C, but we must note that at the solution side of the magnetic layers a sudden increase in Ni concentration, with a corresponding decrease in the Co concentration occurs. This phenomenon requires further investigation.

4. Summary

Depth profile analysis of electrodeposited magnetic/non-magnetic layered structures was carried out with various total deposit thickness, sublayer thicknesses, composition and substrates roughness. It was shown that the resolution decreases significantly when the total sample thickness increases from 120 to 500 nm (cf. samples C and D). When the total deposit thickness is high and the sublayer thicknesses are below 30 nm, the individual layers cannot be resolved, but an average composition is observed instead (sample B). Although the depth resolution of samples deposited on commercial Cu sheet was somewhat lower than of the samples deposited on Si wafer, the difference is less pronounced than what could be expected. Additionally the SNMS depth profile analysis revealed a significant concentration gradient in the magnetic layers even in the beginning of the layers. This draws attention on the concentration inhomogeneity in the magnetic layers which could influence GMR properties. While the composition gradient in the Co–Ni–Cu layers is clearly revealed, the magnetic layers in the Co–Cu/Cu multilayers appear to
be homogeneous along the growth direction within the resolution limit of the SNMS method.

Acknowledgments

This work was supported by the Hungarian Scientific Research Fund (OTKA, Grant K-60821).

References