Analysis of Co/Cu multilayers by SNMS reverse depth profiling


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Abstract

The overall quality of multilayer thin films prepared by electrodeposition could strongly be influenced by the surface and interface roughness. The roughness, however, may increase with the number of layers. For that very reason the reliable analysis of the first few layers is essential. However, in depth profiling methods based on sputtering techniques the first layer is always found at the bottom of the sputter crater. Since the depth resolution might decrease during sputtering, the analysis of the first few layers is often very difficult. In order to circumvent this problem, we performed SNMS depth profiling in the direction from the substrate. We prepared thin film samples in two ways. First, Co/Cu multilayer stacks were electrodeposited on Si/Cr/Cu substrates and SNMS depth profiling was carried out from the direction of the topmost layer. Secondly, electrodeposited Co/Cu multilayer stacks were coated with a few microns thick Ni layer and detached from the Si substrate in order to study the film structure from the side of the substrate. Using this latter method, which we denote as “reverse depth profiling”, we were able to analyze the first and, probably, the most even layers of the thin film structure with high resolution.

1. Introduction

Magnetic/non-magnetic multilayers with a bilayer thickness of a few nanometers have been widely investigated since they show the giant magnetoresistance (GMR) effect [1,2]. Nanostructured magnetic multilayers can be prepared by a variety of thin film deposition techniques, such as magnetron sputtering, evaporation or molecular beam epitaxy (MBE). Among these, electrodeposition is considered to be one of the simplest techniques for the deposition of nanoscale metallic multilayers [3,4]. However, in contrast to physical vapour deposition techniques, which require high vacuum systems, electrodeposition takes place in a reactive environment, which means that the surface composition of the sample may change after deposition. The overall quality of layered structures (consisting of 3 or more different materials) or multilayers can strongly be determined by the first few layers. In most cases the quality of the interfaces changes with the increase in the number of layers. There are many methods to improve the quality of the layers (e.g. ion bombardment, optimization of the substrate temperature) but it is quite difficult to employ them during electrodeposition. For that reason it is very important to obtain reliable information about the quality of the layered structure for samples prepared by electrodeposition.

Depth profiling is a powerful tool for the analysis of thin film multilayer structures. Among the variety of depth profiling methods, Secondary Neutral Mass Spectrometry (SNMS) is a suitable technique for precise determination of the depth distribution of the constituents in thin film materials [5]. In particular, quantifiability is one of the major merits of SNMS, in contrast to other sputter depth profiling methods, where preferential sputtering makes quantitative analysis more difficult.

In previous work [6] we reported on the successful application of SNMS for characterization of electrodeposited CoCu/Cu and CoNiCu/Cu multilayers by measuring the composition gradient along the growth direction of the thin films. We found that the depth resolution decreased significantly with increasing crater depth.

In order to clarify the origin of this significant decrease, we investigated the possible source of the low depth resolution. In SNMS depth profiling using low ion energy for sputtering, two phenomena can cause low depth resolution: bad quality of the crater profile [7], and high surface and interface roughness. The first assumption that the low depth resolution was caused by inappropriate crater profile can easily be excluded because the crater profile of all the studied samples was almost ideal. As an example, in Fig. 1 we show a crater profile measured on one of the samples discussed in Ref. [6]. In spite of the good crater shape even at
300 nm depth, the depth resolution was very low (see Fig. 2 in Ref. [6]). We suppose that this is due to the inhomogeneity in the composition of the layers arising from the sample preparation method and surface roughness. The aim of our work is to show a method by which the first few layers of an electrodeposited multilayer stack can be analyzed with high resolution.

2. Sample preparation and measurements

“Reverse depth profiling” simply means that the layer structure of a multilayer stack is studied from the direction of the substrate. In order to examine the applicability of reverse depth profiling to the aforementioned problem, we performed measurements on samples of two kinds. First, Co/Cu multilayer stacks were electrodeposited on Si/Cr/Cu substrates and SNMS depth profiling was carried out from the direction of the topmost layer. Secondly, electrodeposited Co/Cu multilayer stacks were coated with a few microns thick Ni layer which made it possible to remove the self-supporting deposit with the evaporated Cr/Cu layer from the Si substrate and to study the film structure from the direction of the substrate. Using this latter method, we were able to analyze the first and, probably, the most even layers of the thin film structure.

Co/Cu multilayers were electrochemically deposited by the twopulse plating method from the following electrolyte: 0.8 mol/l CoSO₄, 0.015 mol/l CuSO₄, 0.2 mol/l H₃BO₃ and 0.2 mol/l (NH₄)₂SO₄. Electrodeposition was performed in a tubular electrochemical cell, where the cathode was placed at the bottom in horizontal position. A detailed cross-sectional view of the electrochemical cell and the electrode arrangement is contained in Ref. [8]. Si (111) wafers with a thin buffer layer of Cr (20 nm thick) and a seed layer of Cu (20 nm thick), both deposited by vacuum evaporation at room temperature, were used as substrates. While the Cr layer assured sufficient adherence to the Si wafer during deposition, the Cu layer served as a seed layer for the first electrodeposited Cu layer. The multilayer stacks were deposited in the G/P mode [9], i.e. the magnetic Co layer was produced with a high constant current of ~60 mA/cm² (galvanostatic or G mode), and the non-magnetic Cu layer was deposited at low cathodic potential (potentiostatic or P mode), at ~600 mV vs. a saturated calomel reference electrode. After preparation of the required thin film structure the electrolyte was changed to a Watts type Ni plating electrolyte and the Co/Cu multilayer was coated with a 3 μm thick Ni layer whose mechanical toughness made it possible to remove the whole metallic thin film from the Si wafer. The disadvantage of this method was that the boundary between the Co/Cu multilayer and the Ni coating was a bit smeared out due to corrosion caused by the electrolyte used for the deposition of the Ni supporting layer.

After sample preparation, the Si wafer (0.26 mm thick) was broken at its centre and the film was simply pulled off from it. In the present experiment we performed measurements on a number of samples with nominal compositions of Si/Cr(20 nm)/Cu(20 nm)/[Co(5 nm)/Cu(4 nm)] × 7, but in this paper we present the results measured on two of them. One was pulled off from the substrate with the help of the thick Ni layer (sample “A”), the other multilayer sample was not coated with Ni and remained on the Si wafer (sample “B”).

The depth profile analysis of the samples was performed by SNMS in Direct Bombardment Mode (type INA-X, SPECS GmbH, Berlin), as described in a previous paper [10]. In order to achieve high depth resolution, 350 eV Ar⁺ ions were used for sputtering. The erosion area was confined to a circle of 2 mm in diameter by means of a Ta mask. The lateral homogeneity of the ion bombardment was examined by the measurement of the sputter crater with a profilometer (Ambios Technology, 1 nm depth resolution) after each run.

![Fig. 1. A crater profile in an electrodeposited multilayer stack created by 350 eV Ar⁺ ion bombardment (Ref. [6], sample “B”)](image1)

![Fig. 2. Intensities of the Cu, Co and Cr signals as a function of depth for both multilayer samples. For the sake of clarity, the elements of the wafer and the support (i.e. Si and Ni, respectively) are not shown, although we detected them during sputtering. The arrows indicate the sputtering direction.](image2)
3. Results and discussion

The surfaces of the sample “A” and the Si wafer were checked by an optical microscope. We found that although the detachment of the film from the Si wafer occurred at the interface between the Si wafer and the Cr layer, the surface of the Cr film was not smooth and some Cr moieties remained on the Si crystal. Since this effect caused an extra surface roughness which would have decreased the depth resolution due to the intermixing of the emission of various layers, we performed our measurements on the plain areas of the sample.

Fig. 2 shows the depth profiles of sample “A” and sample “B”. The relative signal variation is much higher for sample “A”, i.e. when sputtering was started at the Cr layer. The increased layer resolution is also accompanied with lower noise. The depth profile obtained in the reverse sputtering direction resolves the layer structure in the vicinity of the Si wafer much better than the conventional depth profile analysis for the other sample. The higher depth resolution due to the reverse sputtering was observed on each sample we investigated. Thus, on a statistical basis one can conclude that reverse depth profiling yields better results for the layers of an electrodedeposited multilayer stack. We are aware that the best comparison between the two depth profiling methods would have been performed on the same sample, but unfortunately the small volume of our electrochemical cell precluded preparation of samples with large enough dimensions. Also, the pull-off procedure of the samples works better the smaller the sample surface area.

We think that in our SNMS experiments the depth resolution was predominantly determined by the surface roughness. Other effects of ion bombardment, e.g. knock-on-effects and atomic mixing, were significantly diminished by the low energy of bombarding Ar\(^+\) ions. The surface roughness was analyzed by both surface profilometry and Atomic Force Microscope (AFM). (The detailed results of the AFM measurements will be published in a separate paper [11].) We found that the height distribution of surfaces can be perfectly fitted by a Gaussian-function, and that the full width at half maximum (FWHM) value of the Gaussian-function which characterizes the surface roughness was increasing during sputtering. At a hundred nm sputtering depth, the FWHM could increase from an initial value of 2 nm to 8 nm which is higher than the thicknesses of the single layers. In our experiments we also observed dependence of surface roughness on sample thickness.

4. Conclusion

We demonstrated by our measurements that SNMS is a very useful method for analyzing multilayer samples produced by electrochemical deposition. Applying reverse order sputtering for depth profile analysis, the layer structure of electrochemically deposited Co/Cu multilayers can be studied with higher resolution than using the conventional depth profile analysis where the sputtering is started at the final sample surface. The results can bear important information on the electrochemical layer growth processes at the nanometer scale especially at the beginning of the deposition. It is necessary to emphasize that this method is applicable only for layers, where the pull-off technique works.

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References