ELECTRON TECHNOLOGY
ISSN 1897-2381
http://www.ite.waw.pl/etij/
Internet Journal

THE DEPENDENCE OF MAGNETIC PROPERTIES ON CRYSTALLOGRAPHIC STRUCTURE OF ELECTROCHEMICALLY DEPOSITED Ni/Cu SUPERLATTICES

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Received November 11, 2003; published December 31, 2003

ABSTRACT

Ni/Cu superlattices have been grown by electrodeposition from a single sulfamate bath (based on $Ni(SO_3NH_2)_2$ and $CuSO_4$) by using the potentiostatic method. Chemical composition of single layers was investigated with SIMS. The Cu layers were almost pure (99.85% Cu) while Ni layers contained 2 ÷ 5% Cu. The lambda period (Λ) and crystallographic structure of the superlattices were established by X-ray investigations. Good quality of the Ni-Cu interface was indicated by the presence of second-order satellite peaks around the main multilayer peak. The changes of crystallographic orientation as a function of the total thickness of the deposit demonstrate also the influence of the preferential crystallographic orientation of the multilayers on the size and nature of the magnetoresistance effect. The giant magnetoresistance effect (GMR) was dominant in samples with strong (111) texture and the anisotropy magnetoresistance (AMR) effect was observed in samples without any preferential crystallographic orientation.

1. Introduction

In recent years the structures composed from alternating layers of ferromagnetic and paramagnetic metals have been intensively studied. The main reason for this interest is based on the giant magnetoresistance effect associated with such metallic multilayers [1]. In most cases the metallic multilayers have been produced using vacuum techniques (sputtering, MBE) [2, 3]. Although those techniques allow high quality structures to be obtained, they are very expensive. Over last ten years electrodeposition has been shown to be a valuable technique for obtaining metallic multilayers. The electrochemical method has been used for preparation of such multilayer-superlattice systems as Ni/Cu [4], NiCo/Cu [5], Co/Cu [6], NiFe/Cu [7], Co/Pt [8]. Although these systems have been the subject of many studies the correlation between conditions of growth (substrates used for deposition, parameters of the electrochemical process) and the obtained structure is not well known. Szczurek et al. [9] show that several different kinds of the substrates can be used for deposition of Ni/Cu superlattices. The crystallographic structure of Ni/Cu superlattices was derived from preferential crystallographic orientation of the substrates. Lenczowski et al. [10] used two kinds of buffer layers evaporated onto Si wafers to modify the structure of Co/Cu multilayers. They obtained (111) and (100) preferential crystallographic orientation for the Au and the Cu buffer layer respectively. Many authors have tried to improve the structure of metallic superlattices by different heat treatments. For example Tosin et al. [11] obtained better-defined Co-Ag interfaces in Co/Ag superlattices using annealing at temperatures of 260 ÷ 360°C.

In this paper we present a study of the structure and properties of Ni/Cu superlattices grown by electrodeposition. The aim of our paper is was to show how the structural and magnetic properties of Ni/Cu multilayers depend on the total thickness of the deposit. The chemical composition of the single layers was checked by the SIMS method.

2. Experimental

A single bath method under controlled potential was used. The deposition was carried out in a typical three-electrode electrochemical setup. We have used the AMEL model 2053 potentiostat with our own

software. Si monocrystalline wafers with (100) orientation were used as substrates for deposition. Prior to electrodeposition a thin layer of Cu (50 nm) was evaporated onto the Si surface as a buffer layer. Only the samples that were used to determine the chemical composition by SIMS were without this buffer layer. Before placing the substrate in the working bath the Cu surface was cleaned in 10 % H_2SO_4 to remove oxides. The multilayers were plated from a solution containing 1.5 mol $Ni(SO_3NH_2)_2$, 0.01 mol $CuSO_4$, 0.5 mol H_3BO_3. The pH was held at 3.5. The process was carried out at room temperature (20°C). All potentials were measured versus a saturated calomel electrode (SCE). Applied deposition potentials of Cu and Ni layers were established by polarization measurements and then checked by SIMS. The structure of the multilayers was determined using XRD. The CIP (current in plane) magnetoresistance measurements were made in a typical four-point configuration in magnetic field in the range of 1.5 T.

3. Results and discussion

The potentials for deposition of Ni and of Cu were chosen from a polarization investigation (Fig. 1).

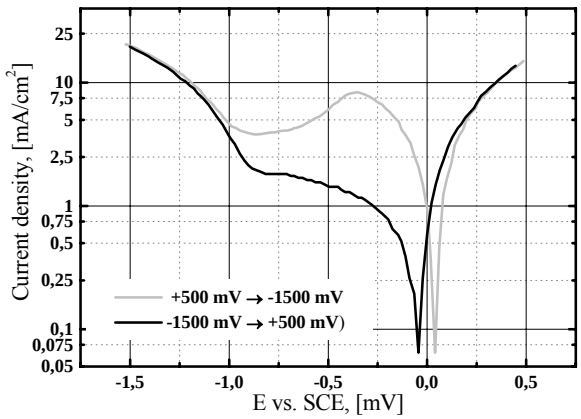

Fig. 1. Cyclic voltammogram of Cu electrode recorded in solution containing 1.5 mol/l $Ni(SO_3NH_2)_2$, 0.01 mol/l $CuSO_4$, 0.5 mol/l H_3BO_3; pH=3.5. The scan rate is 10 mV/s

In the –200 mV to –900 mV range only Cu ions were reduced. The values of the cathodic current were limited by the rate of diffusion of the Cu^{2+} ions to the working electrode surface. Typical current densities were about 1 mA/cm^2. At potentials of above –900 mV the reduction of Ni^{2+} ions started. In practice deposition potentials of –500 mV and –1300 mV were applied for Cu and Ni layers, respectively. Using these two potentials a composition of 200 nm Ni and 200 nm Cu was deposited. The SIMS depth profile of this bilayer structure is shown in Fig. 2. The layer deposited at –500 mV was composed of almost pure cooper (~ 99.7 % Cu) whereas the layer deposited at –1300 mV was mainly composed of nickel with 2÷5 % of Cu contamination. The existence of a characteristic Cu-rich layer near the Si surface is visible (peak of increasing of Cu content in Ni-rich layer marked with *1* in Fig. 2).

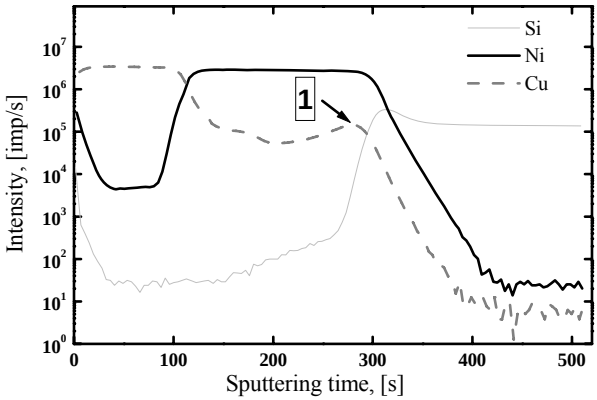

Fig. 2. SIMS depth profile of structure Si (100) + 200 nm Ni + 200 nm Cu. The layers of Cu and Ni were deposited at –500 mV and –1300 mV, respectively (vs. S.C.E).

This is because copper is a more noble metal and a sufficient quantity of Cu^{2+} ions is near the cathode. Further deposition of Cu is determined by ionic transport of Cu species to the cathode and its quantity in the Ni-rich layer decreases, Roy and Landolt [12] obtained similar results confirmed by Auger analysis. The SIMS investigations confirmed that –500 mV and –1300 mV were satisfactory conditions for deposition single Cu and Ni layers respectively.

High-angle X-ray diffraction was used to determine the crystalline properties of both the multilayers and the substrates (Si + 50 nm Cu). In the structure containing evaporated Cu layers the (111), (200), (220), (311) diffraction peaks are apparent. The strongest peaks derive from (111) planes. The simple criterion of the texture extent was established as a ratio of the intensity derived from (200) planes to intensity from (111) planes. For a powder model this ratio should be amount to 0.46 and for Cu buffer layer this ratio was 0.12. A similar method was used to determine preferential crystallographic orientation of the multilayers. The results from Fig. 3 show that in the multilayers about the total thickness 0 ÷750 nm is dominated by the (111) crystallographic orientation derived from the substrate structure but samples with larger thickness are dominated by the (100) orientation.

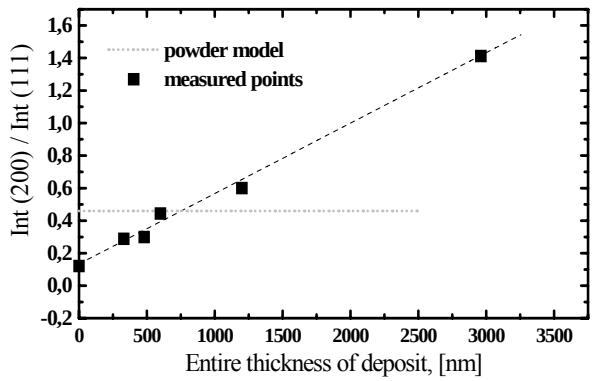

Fig. 3. The dependence of preferential crystallographic orientation on the total thickness of the deposit.

Figures 4a and b present diffraction patterns for samples containing 400 × (2 nm Cu + 5.3 nm Ni) and 100 (2 nm Cu + 4 nm Ni), respectively around the main multilayer peak (200).

The presence of the satellite peaks $S_{\pm i}$ confirms periodical structure of the superlattices. The second-order satellite peaks indicate good quality of the Cu-Ni interface. The second order peaks are not very stronger as noise, but its place is exactly there where ought to appear after calculating from the position of the first. Such behaviour seems to be more reliable as a measure of period thickness. The structure from Fig. 4a with total thickness of ~2.9 μm had strong (200) texture while the structure of the sample from Fig. 4b with thickness of ~0.6 μm was dominated by (111) preferential crystallographic orientation.

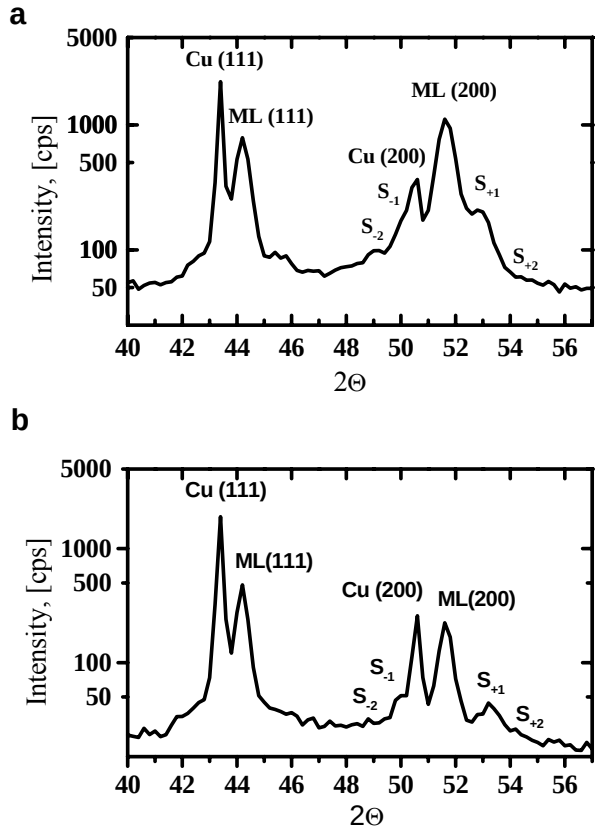

Fig. 4. X-ray patterns for 400 × (2 nm Cu + 5.3 nm Ni) (a) and 100 (2 nm Cu + 4 nm Ni) samples (b).

The MR was measured for (0.6 ÷ 3.8 nm Cu + 4 nm Ni) superlattices with 50 and 100 bilayers. The MR in 50 × Λ samples was dominated by the GMR effect, probably due to the presence of the preferential crystallographic orientation (111). The resistance of the structures decreased both in magnetic field perpendicular (Fig. 5a) and parallel (Fig. 5b) to the transit of current in the samples, which confirmed the presence of the GMR effect. Completely different behaviour observed for samples with 100 × Λ. In magnetic field perpendicular to the current the magnetoresistance had positive values (Fig. 6a), while for magnetic field parallel to the current (Fig. 6b) the MR values were negative. The samples with 100 bilayers were in range where no preferential crystallographic orientation was observed. This was probably the reason for observation of the typical magnetoresistance anisotropy.

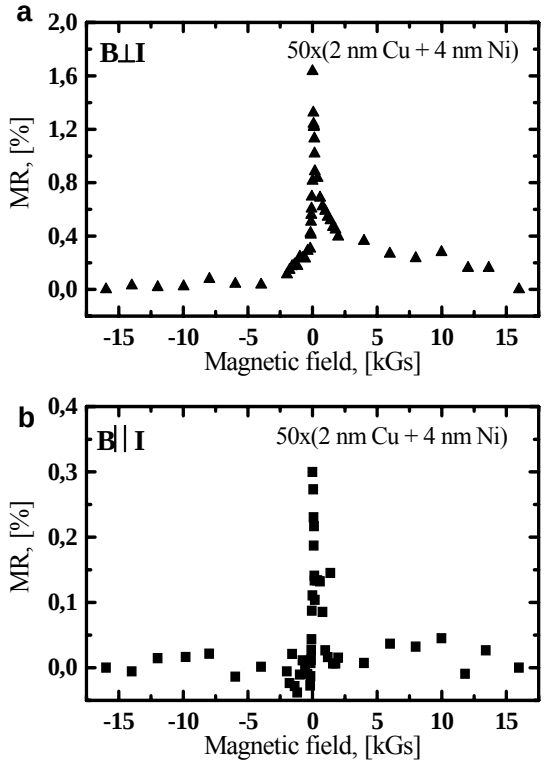

Fig. 5. The percentage magnetoresistance (MR) changes for (111) oriented 50 × (2 nm Cu + 4 nm Ni) multilayer; a) magnetic field perpendicular to the flowing current; b) magnetic field parallel to the flowing current.

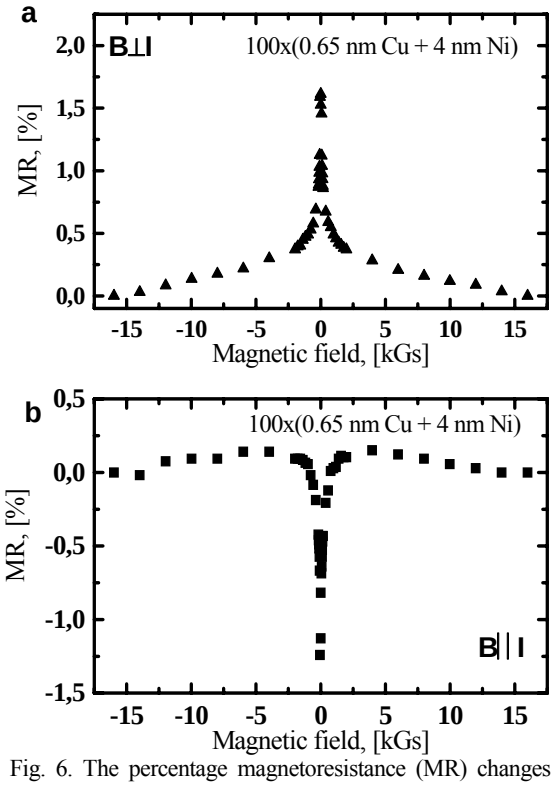

Fig. 6. The percentage magnetoresistance (MR) changes for 100 × (0.65 nm Cu + 4 nm Ni) multilayer without any preferential crystallographic orientation; a) magnetic field perpendicular to the flowing current; b) magnetic field parallel to the flowing current.

The maximum achieved magnetoresistance value was for a sample composed from 50 bilayers (2.1 nm Cu +8 nm Ni) (Fig. 7).

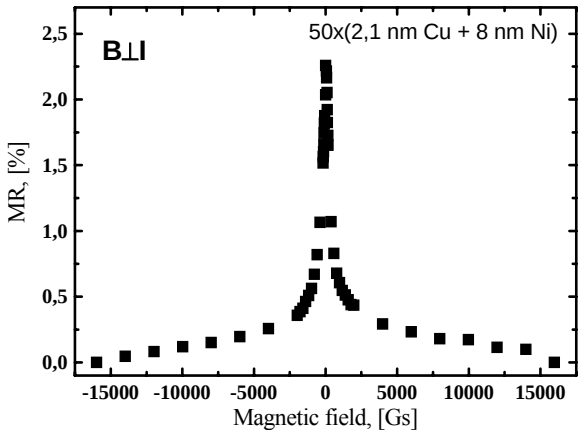

Fig. 7. The percentage magnetoresistance (MR) changes for a (200) oriented 50 × (2.1 nm Cu + 8 nm Ni) multilayer; magnetic field perpendicular to the flowing current.

This sample was very strong (200) textured. It seems that the number of bilayers (total thickness) have a great influence on structural and magnetic properties of the metallic superlattices.

4. Conclusion

In this work the structural and magnetoelectrical properties of the Ni/Cu superlattices have been presented. Typical values of magnetoresistance for Ni/Cu system were achieved. The dependence of the magnetoelectrical properties on the microstructure of the superlattices is shown. Preferential crystallographic orientation of the structures was determined using X-ray diffraction. Only (111)-oriented structures exhibited the GMR effect. The structures without any preferential crystallographic orientation exhibited the AMR effect.

Acknowledgements

The authors wish to thank A. Barcz, and T. Przesławski for carrying out SIMS and galvanomagnetic measurements. This work was financially supported by the State Committee for Scientific Research (grants no. 7 T08C 034 13 and 7 T08C 030 16).

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