

STRUCTURE, HARDNESS AND THERMAL STABILITY OF ELECTRODEPOSITED Cu/Ni NANOSTRUCTURED MULTILAYERS

Adam Tokarz, Tadeusz Frączek, Zbigniew Bałaga and Zygmunt Nitkiewicz

Institute of Materials Engineering, Faculty of Materials Processing Technology and Applied Physics,
Częstochowa University of Technology, Al. Armii Krajowej 19, 42-200 Częstochowa, Poland

Received: January 22, 2007

Abstract. Cu/Ni multilayers have been grown by electrodeposition from single solution with potentiostatic control. Several Cu/Ni samples deposited on (001)-oriented Si and polycrystalline copper plates with different sublayer thickness in the range of 1 to 20 nm were investigated. One series of the multilayers with constant bilayer thickness and two other series with constant Cu or Ni sublayer thickness (and varying Ni or Cu sublayer thickness respectively) were electrodeposited on copper substrates. Some Cu/Ni multilayers were annealed in a vacuum furnace at temperature increasing from 150 °C to 450 °C. X-ray diffraction investigations and SEM observations were used to analyse the modulated structure and determine the bilayer thickness of the nanomultilayers. The SEM and XRD investigations confirmed the layered structure of all deposited samples. The multilayered Cu/Ni coatings exhibit the bigger hardness than single Ni and Cu layers when the thickness of the bilayers is approximately a few nanometers. Maximum of the hardness values were measured when the bilayer thickness was around 10 nm and was about 25% bigger than the Ni single layer hardness. Subsequent anneals led to a significant change in the preferential crystallographic orientation, quality of modulation structure, and size of crystallites.

1. INTRODUCTION

In recent years, nanostructured materials like CMA (compositionally modulated alloys) multilayers have become widely studied. These materials with bilayer period thickness less than 100 nm have very interesting properties, which are unattainable in bulk materials. The primary interest is in magneto-electrical properties (GMR effect) [1,2] with the secondary goal of improving the tribological and mechanical properties of the surface [3-6]. Many metallic multilayers have been produced using vacuum techniques (sputtering, MBE) [7,8] but the application of these techniques is limited by their high cost. Recent investigations showed that electrodeposition is very valuable method for obtaining

metallic multilayers [9-11]. In spite of some limitations (like conducting substrates, not all metals can be deposited using aqueous baths) the electrochemical method has been successfully used for preparation of such multilayer-superlattice systems as Ni/Cu [12], NiCo/Cu [13], Co/Cu [14], NiFe/Cu [15], Co/Pt [16].

At present, metallic multilayers are produced by two kinds of electrochemical methods. In both methods, multilayers are grown in a single electrolyte containing ions of metals that form alternate layer. The difference lies in modulating either the plating current or potential during deposition. Because the concentration of ions of the nobler metal is about 100 times lower than the concentration of ions of the less noble metal by changes of the cur-

Corresponding author: Adam Tokarz, e-mail: adam@mim.pcz.czyst.pl

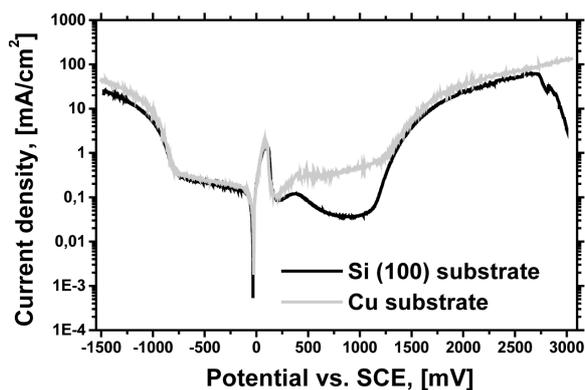


Fig. 1. Voltammograms of a 1.5 mol/l $\text{Ni}(\text{SO}_3\text{NH}_2)_2$, 0.01 mol/l CuSO_4 , 0.5 mol/l H_3BO_3 solution for Cu and Si substrates. Starting potential -1500 mV (vs. SCE). Potentials scan rate = 10 mV/s.

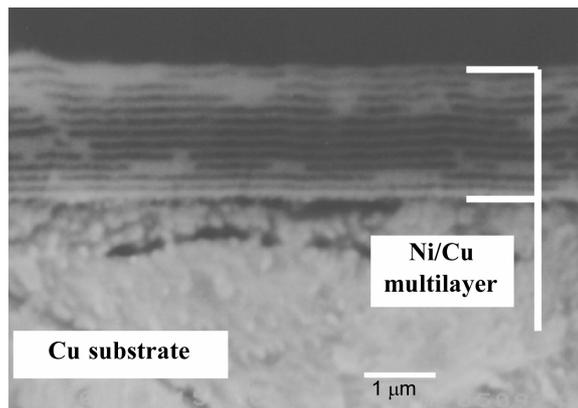


Fig. 2. Typical cross-sectional SEM image of a $12 \times (100 \text{ nm Cu} + 100 \text{ nm Ni})$ multilayered structure grown on a Cu polycrystalline substrate by electrodeposition.

rent or potential alternating layers of two metals are deposited. The first method is more suitable for technological applications, because it needs only two electrodes and the thickness of individual layers is controlled only by time and current density. The other method needs a three-electrode cell (reference electrode has to be added) and the process control is more complicated. During deposition (at suitable potential) the recorded current is integrated, which gives the charge passed between the anode and the cathode.

In this paper, we report on the electrodeposition of Cu/Ni multilayers onto Cu polycrystalline and Si monocrystalline substrates. We show some polarisation investigations of Cu and Si (100) substrates, paying attention to the establishing of proper deposition potentials for the Cu and Ni sublayers. We present the microstructural characterisation of the multilayers by high angle X-ray diffraction (XRD) and scanning electron microscopy (SEM). We show how the structural properties depend on the total thickness of the deposit and different annealing temperatures. Finally we present the influence of bilayer thickness Λ and sublayer (Ni and Cu) thickness on the multilayer hardness.

2. EXPERIMENTAL

Ni/Cu multilayers were electrolytically deposited from a single solution having the composition as follows: 1.5 mol/l $\text{Ni}(\text{SO}_3\text{NH}_2)_2$, 0.01 mol/l CuSO_4 ,

0.5 mol/l H_3BO_3 . The pH of the bath was maintained at 3.5. All solutions were prepared with analytical grade chemical reagents and deionised water ($\rho = 18.2 \text{ M}\Omega\text{cm}$). Single-crystalline n-type silicon (100) oriented wafers (Sb doped) and polycrystalline copper plates were used as substrates. All electrochemical experiments and the deposition processes were carried out in a standard three-electrode electrochemical cell equipped with platinum net as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The polarisation investigations were performed using an AMEL 7050 potentiostat/galvanostat controlled by a microcomputer with Juniorassist software. Multilayers were prepared using a potentiostat AMEL 2053 controlled by microcomputer with our own software. This software allows to keep substrate potentials at prescribed values and to measure the electric current during deposition of Cu or Ni sublayers. Recorded current during electrodeposition of each sublayer was integrated and calculated to its thickness in real time. When the demanded sublayer thickness (for example Ni sublayer) was reached, the system switched deposition potential to another value, suitable for Cu sublayer deposition.

The cross section of metallic multilayers was studied by SEM using a JEOL JSM-5400 microscope. For these investigations samples were cut along the diameter, mechanically polished and directly before SEM observations all cross-section samples were selective etched.

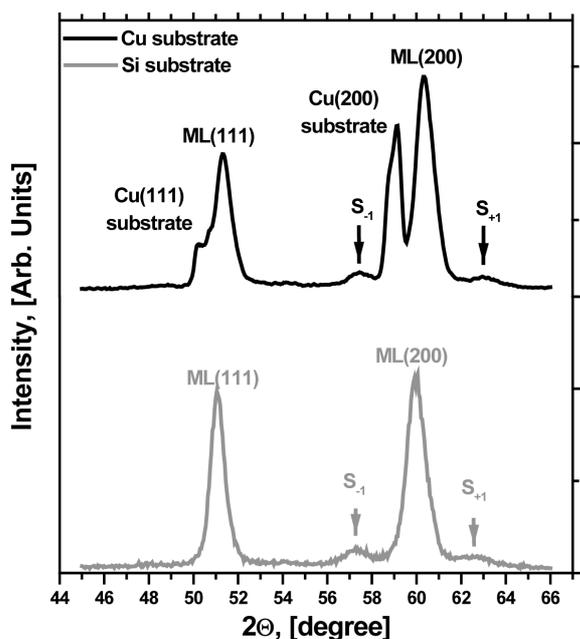


Fig. 3. X-ray diffraction patterns of multilayer 750× (2.1 nm Cu+2.1 nm Ni), grown on Cu and Si(100) substrates by electrodeposition.

The crystallographic structure of electrochemically deposited Cu/Ni multilayers was investigated by XRD using a Seifert 3000 T/T diffractometer with a Co K_{α} radiation source ($\lambda = 0.1788965$ nm). All diffractograms were mathematically computed and fitted in order to precisely establish position of diffraction peaks and other parameters (FWHM, maximum peak intensity) using DHN-PDF software. Cross-sections of multilayers were examined with a Joel JSM-5400 scanning electron microscope.

Hardness of the electrodeposited multilayers was measured using a Futuretech FM7 microhardness tester with a Knoop indenter and 10 g load. All measured deposits (multilayers) had the same thickness (about 3 μm), which allowed comparative measuring.

3. RESULTS

In order to establish the right deposition potentials of single nickel (E_{Ni}) and copper (E_{Cu}) layers a voltametric study was made. Fig. 1 shows the polarisation data for the starting potential -1500 mV to the anodic limit 3000 mV collected on both tested substrates. For the cathodic region two

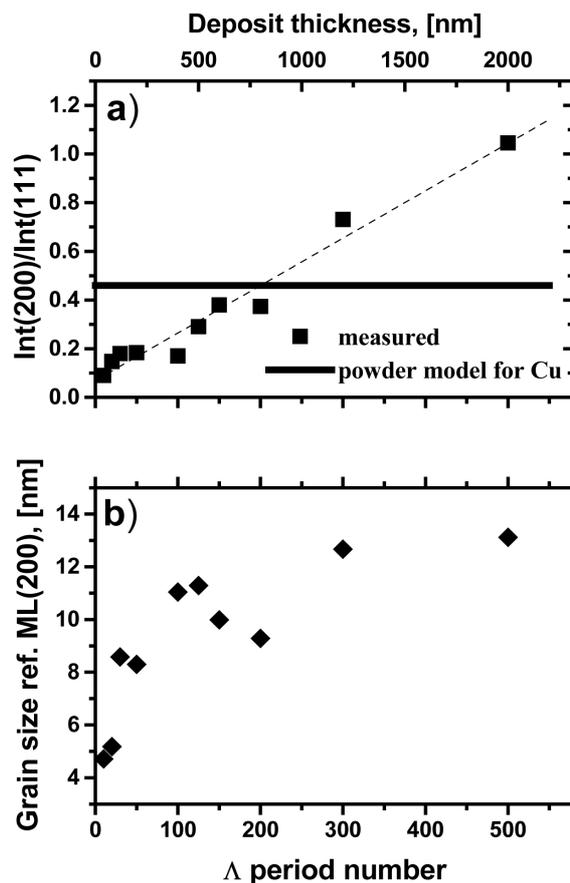


Fig. 4. Preferential crystallographic orientation a) and grain size b) versus Δ period number (deposit thickness).

ranges of current densities were observed. In the first range from the cathodic limit to circa -800 mV current densities possess high values and rich nickel layers were grown, above this potential only copper was deposited. Polarisation investigations show that Cu substrate is more active than Si for electrodeposition (higher current densities were recorded for Cu substrate), which leads to differences in the deposition rate. Based on the polarisation experiments appropriate values of potentials for Cu and Ni sublayers were selected. All multilayers were prepared at $E_{\text{Ni}} = -1300$ mV and $E_{\text{Cu}} = -500$ mV potential values for Ni and Cu sublayer respectively.

SEM investigations confirm the periodical formation of obtained multilayers for the sample Cu + 12×(100 nm Cu + 100 nm Ni) (Fig. 2). However these investigations are limited by resolution of the

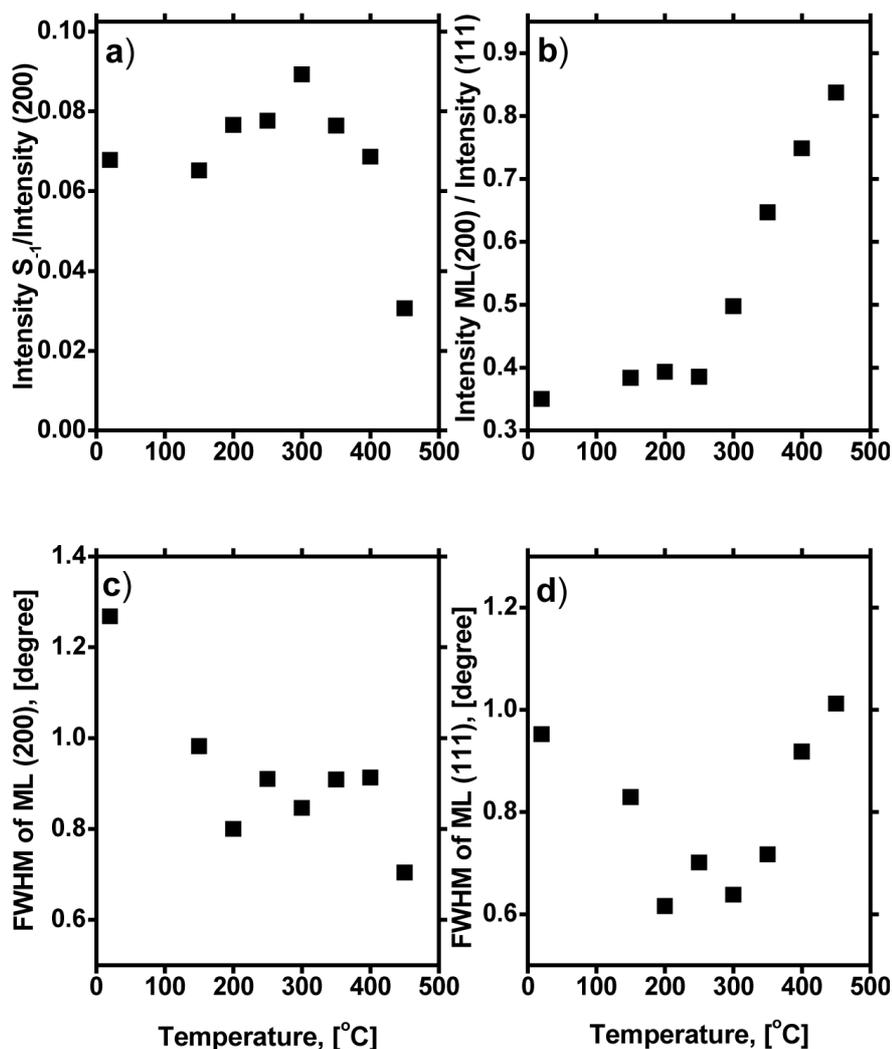


Fig. 5. XRD analysis results: intensity of S_{-1} satellite peak to intensity ML(200) main multilayer peak ratio a), changes in preferential crystallographic orientation b), FWHM values measured for (111) and (200) multilayer peaks c)-d) versus annealing temperature of $200 \times (2.1 \text{ nm Cu} + 2.1 \text{ nm Ni})$ multilayer films.

scanning electron microscope, satisfactory quality of SEM images was possible when the thickness of the single Ni or Cu layer exceeds 50 nm. Based on SEM investigations high efficiency of the deposition process can be stated because the deposited thickness measured by SEM was similar to that predicted from deposition charge. The visible areas where single Cu or Ni layers seem to be not continuous are caused by some difficulties in etching during sample preparation.

When the bilayer thickness (Λ) does not exceed 10 nm XRD method is the most suitable for determining layered structure of the deposits. Presented in Fig. 3 X-ray diffractograms obtained for Cu/Ni

multilayer samples grown on both Cu and Si substrates confirm a well-defined periodic structure of the multilayers. Multilayer reflections are clearly visible, which allows determining the bilayer thickness (Λ period) and structural properties of the multilayers such as preferential crystallographic orientation and crystallite grain size. A series of $(2.1 \text{ nm Cu} + 2.1 \text{ nm Ni})_x$ multilayer films with various number of Λ period repeats X was deposited for investigations of the preferential crystallographic orientation. The simple criterion of the texture extent was established as a ratio of the intensity derived from (200) planes to intensity from (111) planes. This ratio for copper and nickel (powder

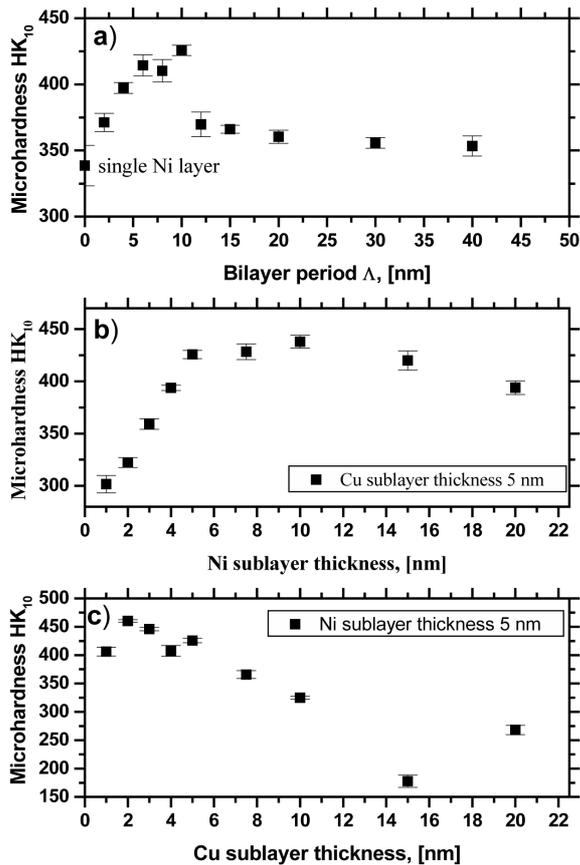


Fig. 6. Hardness of Cu/Ni electrodeposited multilayers versus bilayer period a), Ni sublayer thickness b), and Cu sublayer thickness c).

models) should amount to 0.46 and 0.42 respectively. For our multilayers changes in preferential crystallographic orientation for the range of X from 10 to 500 was observed (Fig. 4a). This suggests that deposits with relatively low thickness (below ca. $0.9 \mu\text{m}$) exhibit a (111) texture while with increasing multilayer thickness the (200) oriented grains predominate. Similar behaviour in different stages of Cu/Ni multilayers deposition (nucleation and growth of crystallites) based on TEM results was presented by Wang *et al.* [17]. Along with the increasing of preferential orientations of the grains in [200] direction the grain size of crystallites increase as can be seen in Fig. 4b. This figure shows the grain size of crystallites measured with Scherrer method (where the crystallite size depends on the full width at half-maximum of the diffraction line).

The size of crystallites changes in the range of 5 nm to 12 nm for multilayers with $X = 10$ and $X = 500$, respectively.

Samples with bilayer period $\Lambda = 4.2$ nm (Si substrate, 200 bilayer repeats) were annealed for 1 hour at 150, 200, 250, 300, 350, 400, and 450 °C, in order to investigate the thermal stability of the Cu/Ni multilayers. Fig. 5 depicts the changes in structural properties based on analysis of the X-ray diffractograms obtained for deposits after annealing at temperatures mentioned above. Changes of the intensity derived from $S_{\pm 1}$ peak versus intensity from ML (200) peak (presented in Fig. 5a) suggest that well-defined multilayers seem to be preserved upon annealing at 300 °C, while annealing above this temperature leads to degradation of the periodic structure. Annealing also causes changes in the preferential crystallographic orientations (Fig. 5b) and grain size (Figs. 5c and 5d).

Fig. 6 shows the hardness as a function of the bilayer period (Fig. 6a), thickness of the Ni sublayer (Fig. 6b) and thickness of the Cu sublayer (Fig. 6c). The hardness of the Cu/Ni multilayer films shows strong dependence on the period Λ as well as on the thickness of each kind of sublayer.

4. CONCLUSIONS

It was possible to produce Cu/Ni multilayers in a wide range of sublayer thickness by electrodeposition on Si (100) and polycrystalline Cu substrates. The electrochemical studies allow selecting the proper potential suitable for alternating deposition of Ni and Cu sublayers. SEM investigations confirmed the periodical structure for multilayers with the bilayer period Λ above 100 nm. Below 10 nm bilayer period the XRD experiments confirm the existence of a multilayer structure for both substrates. XRD results reveal the existence of an initial preferential growth of the Cu/Ni multilayers along the (111) direction and reorientation of the main growing direction towards (200) observed for the thicker deposits. The changes in the preferential orientation of the crystallites are connected with an increase in their size. Annealing of the Cu/Ni multilayers led to changes in quality of multilayer structure, preferential crystallographic orientation and grain sizes. Hardness values of Cu/Ni multilayers showing dependence on the bilayer period Λ as well as the Ni and Cu sublayer thickness. The Cu/Ni multilayers in most cases show the enhancement of hardness compared to single Ni layers deposited at the same conditions.

ACKNOWLEDGEMENT

This work has been supported by Polish Ministry of Education and Science Grant No. 3 T08A 078 27.

REFERENCES

- [1] M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich and J. Chazelas // *Phys. Rev. Lett.* **61** (1988) 2472.
- [2] K. Ludwig, J. Hauch, R. Mattheis, K.U. Barholz and G. Rieger // *Sens. Actuators A* **106** (2003) 15.
- [3] X. Zhang, A. Misra, H. Wang, T.D. Shen, M. Nastasi, T. E. Mitchell, J.P. Hirth, R.G. Hoagland and J.D. Embury // *Acta Mater.* **52** (2004) 995.
- [4] P.M. Anderson, J.F. Bingert, A. Misra and J.P. Hirth // *Acta Mater.* **51** (2003) 6059.
- [5] Z.J. Liu, A. Vyas, Y.H. Lu and Y.G. Shen // *Thin Solid Films* **479** (2005) 31.
- [6] A.S.M.A. Haseeb, J.P. Celis and J.R. Roos // *Thin Solid Films* **444** (2003) 199.
- [7] M. Onishi, R. Ishihara, A. Kida, M. Doi, H. Asano and M. Matsui // *J. Magn. Magn. Mater.* **272–276** (2004) E1413.
- [8] D.A.R. Barkhouse, A. Bonakdarpour, M. Fleischauer, T.D. Hatchard and J.R. Dahn // *J. Magn. Magn. Mater.* **261** (2003) 399.
- [9] W. Schwarzacher, O.I. Kasyutich, P.R. Evans, M.G. Darbyshire, Ge Yi, V.M. Fedosyuk, F. Rousseaux, E. Cambil and D. Decanini // *J. Magn. Magn. Mater.* **198-199** (1999) 185.
- [10] J.M.D. Coey and G. Hinds // *J. Alloys Compd.* **326** (2001) 238.
- [11] D. Landolt and A. Marlot // *Surface and Coatings Technology* **169** (2003) 8.
- [12] G. Nabiyouni and W. Schwarzacher // *J. Cryst. Growth* **275** (2005) E1259.
- [13] E. Gomez, S. Pane and E. Valles // *Electrochim. Acta* **51** (2005) 146.
- [14] T. Cziraki, M. Koteles, L. Peter, Z. Kupay, J. Padar, L. Pogany, I. Bakonyi, M. Uhlemann, M. Herrich, B. Arnold, J. Thomas, H.D. Bauer and K. Wetzig // *Thin Solid Films* **433** (2003) 237.
- [15] E. Chassaing // *J. Electrochem. Soc.* **144** (1997) L328.
- [16] V. Georgescu and M. Georgescu // *Surface Science* **507-510** (2002) 507.
- [17] L. Wang, P. Fricoteaux, K. Yu-Zhang, M. Troyon, P. Bonhomme, J. Douglade and A. Metrot // *Thin Solid Films* **261** (1995) 160.