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Correlation between physical properties of superlattices obtained by means of electrochemical deposition method and ion spraying

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This paper compares structural and magnetic properties of Cu/Ni and Ni/Cu multilayer systems obtained by means of ion sputtering and electrochemical deposition method. The impact of both thickness of Cu and Ni sublayers and a number of bilayers repetition on magnetic properties was also investigated. The purpose of this work was to verify which method for multilayer system deposition enables samples of better structural and magnetic properties to be obtained.

Keywords: multilayer systems, superlattice, ion sputtering, electrochemical deposition.

1. Introduction

Technological advances in production of thin layers have sparked their extensive investigation, particularly due to their potential use in microelectronics. Multilayers with thickness of several nanometers constitute so called *artificial superlattice*. First structures focused on semiconductor superlattices, then multilayer systems started to be produced. Leading-edge vacuum technologies and techniques of epitaxial growth of layer on monocrystalline substrate enable multilayer metallic systems to be produced with unaffected planar structure; these systems are currently termed *superlattices*. Nowadays, investigations of superlattices focus on the testing of their physical properties as well as application to nanotechnology, nanoelectronics and spintronics.

Not all metallic magnetic multilayer systems obtained by means of different methods show the same structural and magnetic properties. In [1], permaloy/Cu multilayer systems with the same sublayer thickness were investigated, however obtained by means of different methods (ion sputtering and evaporation). The authors proved that antiferromagnetic (A-F) coupling and the giant magnetoresistance effect (GMR – *ca*. 22%) appear only in samples obtained by means of ion sputtering. The main reason for the absence of A-F coupling and GMR effect in these systems is an increased roughness over a large area of the interface as compared to multilayers obtained by means of ion sputtering [1]. In the case of electrochemically deposited multilayer Ni/Cu systems [2], GMR effect was barely 1.5%.

X-ray diffraction is numbered among the most important, non-invasive and thus most commonly used methods of investigation of multilayer systems. Knowing the parameters determined on the basis of diffraction spectra allows researchers to come to the conclusions concerning interlayer couplings that occur in multilayer magnetic systems. Therefore, the results of structural investigations comprise essential supplement to magnetic testing and provide information on the quality of the structure of layer growth.

There are two types of periodicity in superlattices: *i*) small – coming from lattice constants that comprise superlattice, *ii*) large – described by superlattice period.

As a result of overlapping of the above-mentioned periodicities, a diffraction image is obtained. Diffraction maxima positions in the diffraction image depend on periodicity of the system (lattice parameters) while their intensity results from the arrangement of atoms within unit cells [3].

The presence of satellite peaks proves periodicity of the investigated structure – superlattice. The position of the peaks is used for determination of the parameters of the multilayer system (superlattice), which are closely related to its physical properties.

Reflectometry in mirror geometry (measurement of an angle of incidence from zero to more than ten degrees), besides information on the value of bilayer period thickness, provides data on the quality of interlayer planes (roughness); its higher values cause disappearance of antiferromagnetic coupling [1].

All imperfections of multilayer structure (*e.g.*, roughness of interlayer boundary between ferromagnetic and non-magnetic layers) have large impact on magnetic properties of multilayer metallic systems.

The aim of the present work was to verify which method for obtaining multilayer systems enables samples of better structural and magnetic properties to be obtained.

2. Materials and methods

The following multilayer systems were tested [4]:

– Cu/Ni with variable thickness of Ni *obtained by means of ion sputtering* [5]. This series encompassed layers with constant thickness of Cu (20 Å) and variable thickness of Ni: 10, 12, 16, 20, 25, 30 and 60 Å;

– Ni/Cu with variable thickness of Cu *obtained by means of potentiostatic electrochemical method* [6]. In this series, Ni layer had a constant thickness of 20 Å while the thickness of Cu layer varied: 9, 12, 18 and 20 Å;

– Cu/Ni and Ni/Cu with variable number of repetition, obtained by means of electrochemical potentiostatic method. The thickness of Cu and Ni layers was constant with 20 Å each while the number of repetitions was 10, 20, 50 and 100 times.

Structural investigation was carried out by means of mirror diffraction while measuring θ–2θ and directions of crystallites orientation (ω angle).

Investigation of magnetic properties of multilayers was carried out by means of vibrating sample magnetometer at room temperature. The measurements were taken with sample surface positioned parallel to the external magnetic field.

3. Results and discussion

Diffractogram spectra of 100×[Cu/Ni] multilayer systems with constant thickness of Cu layer (20 Å) and variable thickness of ferromagnetic layer (10 Å ≤ t_{Ni} ≤ 60 Å) are presented in Fig. 1. The diffractograms were obtained using Cu lamp with the wavelength of λ_{Cu} = 1.540 Å.

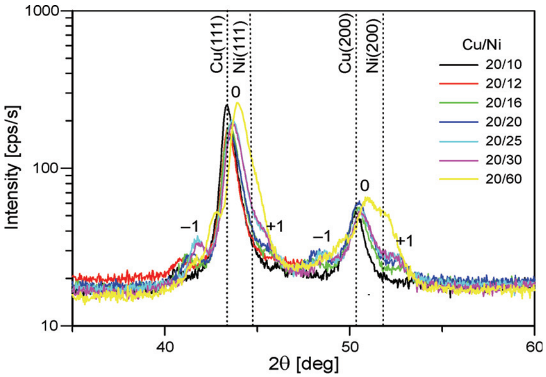

Fig. 1. Diffractograms of Cu/Ni multilayers with constant thickness of Cu (20 Å) and variable thickness of Ni (10 Å ≤ t_{Ni} ≤ 60 Å). Dashed lines indicate tabular peak positions for solid Cu and Ni materials.

The diffraction images also show superlattice peaks of +1, 0, –1 order from (111) and (200) surfaces and vertical dashed lines which indicate positions of the peaks that correspond to *fcc* (111), (200) Cu and Ni cubic structure lattice planes. Zero peaks in the superlattice are located between two theoretical values, for *fcc* (111) and (200) planes, respectively. Accurate determination of the position of zero peak is the basis for determination of the ratio of the thickness values in each layer in a multilayer system. It is remarkable that an increase in Ni thickness causes that diffraction peaks maxima from (111) and (200) surfaces move towards tabular value for pure Ni.

The system with reverse order of 100×[Ni/Cu] superlattice layer deposition with constant thickness of Ni layer of 20 Å and variable thickness of non-magnetic Cu interlayer (9 Å ≤ t_{Ni} ≤ 20 Å) is presented in Fig. 2.

Satellite peaks are clearly visible only for Cu(20 Å)/Ni(20 Å) sample. In all the remaining samples peaks are not developed, which is likely due to a large difference between Bragg intensity in zero peak and in the first order peaks.

In the case of diffraction image analysis for multilayer systems it should be remembered that if the lattice constants in sublayers incorporated in multilayers have similar values, satellite peaks are less visible than for sublayers with more varied values. In our case, Cu and Ni comprise the elements which are located next to each

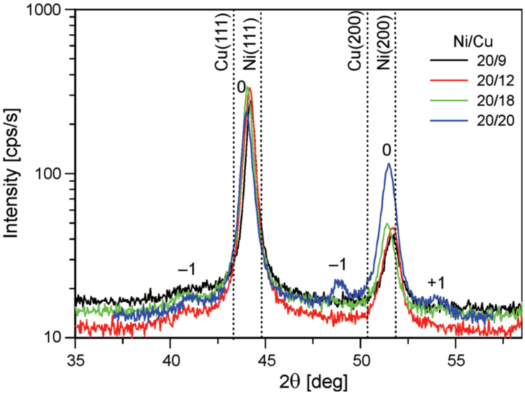

Fig. 2. Diffraction image of 100×[Cu(t)/Ni(20 Å)] multilayer systems in initial state, where t = 9, 12, 18, 20 Å. Dashed lines show peak positions for solid material of Cu and Ni.

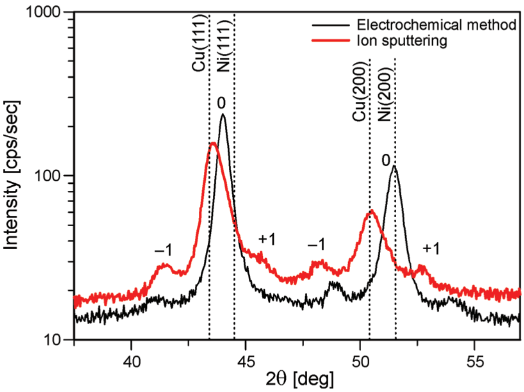

Fig. 3. Comparison of diffractograms for 100×[Cu(20 Å)/Ni(20 Å)] systems obtained by electrochemical deposition and ion sputtering.

other in the periodic table of elements; both their lattice constants and plane distances are very similar. Due to that, the intensity of satellite peaks is very low as compared with zero peak.

After X-ray analysis for these multilayer systems obtained by means of different methods (Fig. 3) one can perceive a shift of zero peaks in electrochemical sample from lattice planes (111) and (200) towards larger 2θ angles and their larger intensity as compared to the peaks in samples after ion sputtering. The shift of zero peaks is probably caused by stress that results from the deposition technology.

Analysing of tabular values of lattice constants and interplanar spacing for Ni and Cu allows an assumption to be made that an increase in the thickness of ferromagnetic layer or non-magnetic interlayer causes a shift in the mean values of Cu/Ni or Ni/Cu interplanar spacing (both for peaks from (111) and (200) planes).

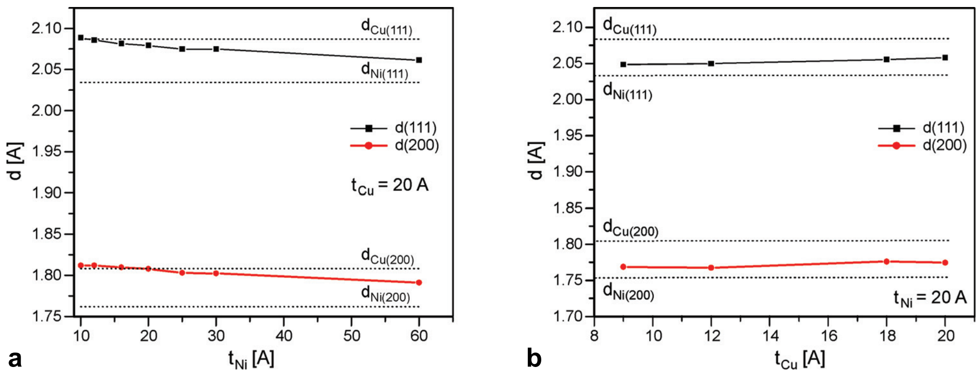

Fig. 4. Dependence of interplanar distances on Ni layer thickness (**a**) and Cu layer thickness (**b**) in Cu/Ni and Ni/Cu systems.

Figure 4 presents a dependence of interplanar spacing on ferromagnetic layer thickness in Cu/Ni systems (Fig. 4**a**) and on the thickness of non-magnetic interlayer in multilayer Ni/Cu system (Fig. 4**b**).

As results from Fig. 4**a**, the rise in Ni layer thickness causes that the mean values of Cu/Ni interplanar spacing, both for peaks coming from (111) and (200) planes, decrease as they approach tabular value for Ni. Such tendencies are the result of increasing thickness of Ni layer, for which the value of lattice constant is lower than for Cu.

However, an increase in Cu thickness (Fig. 4**b**) impacts on insignificant rise in the value of interplanar spacing for (111) and (200) peaks. This tendency is caused by an increase in the thickness of the material being a component of the multilayer with higher value of lattice constant.

Since X-ray reflectometry methods ($I = f(2\theta)$) allow for accuracy of measurements of component layer thickness in the systems investigated as well as measurements of roughness in the upper and lower layer or interlayer areas [7], reflectometry curves for Cu/Ni and Ni/Cu multilayers are presented in Fig. 5.

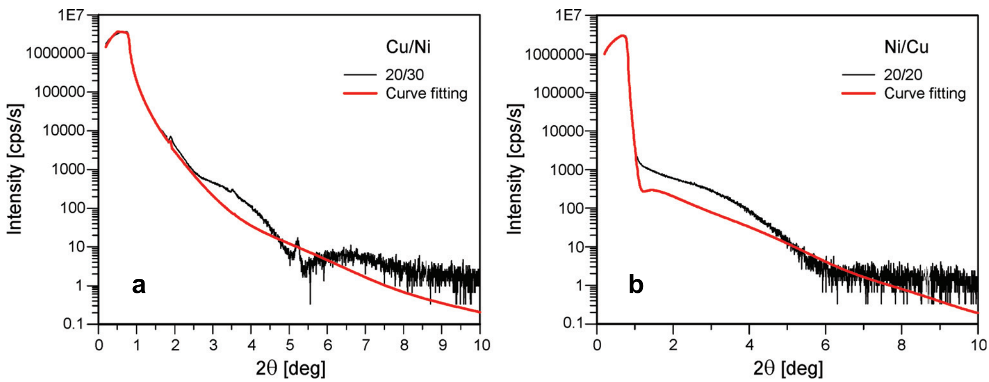

Fig. 5. Reflectometry curves of Cu/Ni (**a**) and Ni/Cu (**b**) multilayers with adjustment curves [5].

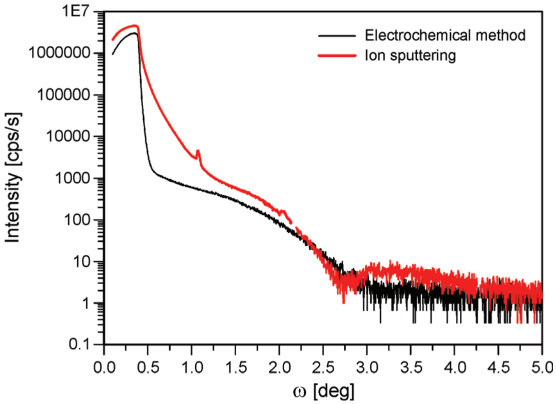

Fig. 6. Reflectometric measurements of 100×[Cu(20 Å)/Ni(20 Å)] systems obtained by means of electrochemical deposition and ion sputtering.

As results from the comparison of the curves presented in Figs. 5**a** and 5**b**, multilayer systems obtained by means of ion sputtering (Fig. 5**a**) are characterized by lower roughness (smaller drop in oscillation curve) as compared to multilayers obtained by means of potentiostatic electrochemical deposition (Fig. 5**b**).

The results of reflectometric measurements also confirm better quality of the structure in multilayers deposited by means of ion sputtering. This is clearly obvious from the lower value of surface roughness and the presence of Bragg peaks coming from interference on periodical structure of Cu/Ni. The value of roughness for the samples after electrochemical deposition is even four times higher while presence of Bragg peaks was not observed (Fig. 6).

During investigation of the physical properties of superlattice some measurements of direction of crystallite orientation (ω angle) have also been taken. After analysis of the intensity and width values for the peak obtained, one can draw conclusions about the degree of texturization in crystallites of a particular direction. The diffraction peak characterized by small FWHM proves sublayers in multilayer clearly texturized in a particular direction.

However, in the layers with poorer texture, FWHM width for the peak analyzed is larger. The results of measurements of directions of crystallite orientation, obtained at a constant 2θ angle, for which a reflex from (111) and (200) plane family can be observed, are presented in Fig. 7 (Cu/Ni) and Fig. 8 (Ni/Cu).

As can be seen from the comparison of the curves presented in Fig. 7, peaks coming from (111) lattice planes are characterized by a lower width and considerably higher intensity as compared to (200) peaks. One can conclude here that a dominating orientation in all the Cu/Ni multilayers under investigation is (111) orientation.

Since the peak from (200) planes is bifurcated, the texture in [200] direction is worse than in [111] direction. This proves the fact that the planes are not parallel to the substrate material (sample surface) in this direction and non-parallel planes predominate.

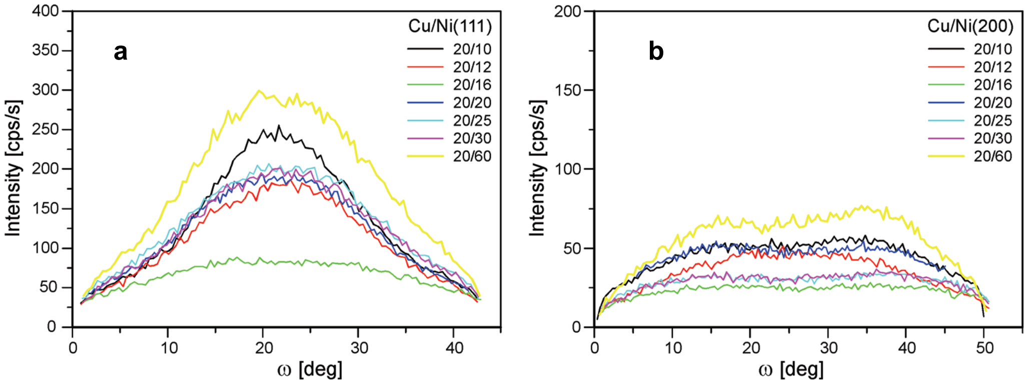

Fig. 7. Measurement of directions of crystallite orientation in the superlattice peak coming from (111) (**a**) and (200) (**b**) planes in Cu/Ni system [5].

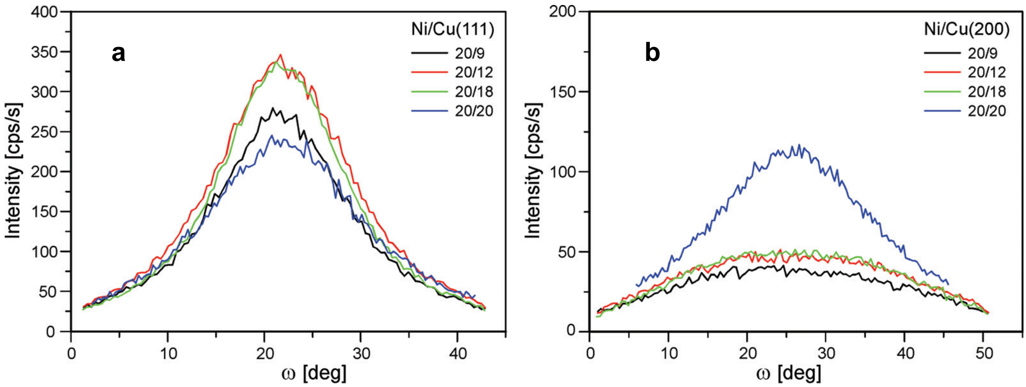

Fig. 8. Measurement of directions of crystallite orientation in superlattice coming from (111) (**a**) and (200) (**b**) planes in Ni/Cu system [5].

However, as results from measurements of crystallite orientation for Ni/Cu system (Fig. 8), rise in Cu layer thickness causes visible lower intensity and growing width of the peak for (111) planes. Hence the conclusion about poorer texturization of the layers in [111] direction as the thickness of Cu layer rises. However, due to the loss of dominating orientation [111], strongest texture in [200] direction can be observed as the thicknesses of the layers rise. This means that for 20 Å thickness of Cu layer in Ni/Cu system the peak is characterized by a considerable rise in intensity and smaller width.

The results of investigation of directions of crystallite orientation, both for the samples after ion sputtering and electrochemical deposition revealed that orientation in [111] direction dominates.

Magnetic properties of Cu/Ni and Ni/Cu multilayers were characterized through analysis of the shape of magnetic hysteresis loop. The shape indicated magnetic coupling and antiferromagnetic fraction parameter was determined.

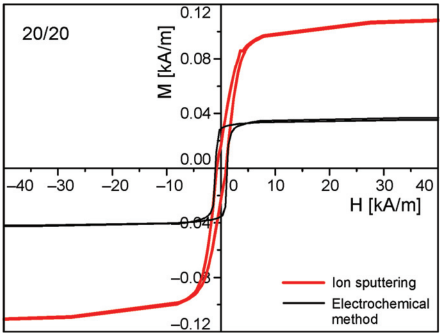

Fig. 9. Magnetic hysteresis curves for 100×[Cu(20 Å)/Ni(20 Å)] multilayers obtained by means of electrochemical deposition and ion sputtering.

Examples of magnetic hysteresis loops from the samples with the same thickness of cuprum and nickel, obtained by different methods, demonstrate dissimilar shape of hysteresis curve, different values of saturation magnetization, magnetic remanence and saturation field, however, similar coercivity values (*ca*. 1.4 kA/m). They also indicate existence of magnetic A-F and F-F exchange coupling, depending on Ni layer thickness (for the samples obtained by means of ion sputtering) or its absence (for the samples obtained by means of electrochemical deposition). In the case of structural properties, the results of magnetic investigation for Cu/Ni samples with variable Cu and Ni sublayer thicknesses (Fig. 9) also proved better quality for ion sputtering samples (existence of A-F and F-F depending on Ni thickness) in comparison to electrochemical deposition samples. Absence of antiferromagnetic coupling in the case of the samples after electrochemical deposition is basically caused by a considerably higher value of roughness.

4. Conclusions

The investigations presented focused on multilayer magnetic Cu/Ni and Ni/Cu systems deposited by means of ion sputtering in vacuum and electrochemical deposition. The factors being investigated included structural properties (by means of X-ray diffraction), surface and interface topology, roughness (X-ray reflectometry) and magnetic properties.

The results of the investigation allow us to draw the following conclusions:

1. Multilayers obtained by means of ion sputtering are characterized by better quality of periodical superlattice structure in comparison with the samples after electrochemical deposition, which manifests itself, in the case of ion sputtering samples, in:

– higher intensity of satellite peaks; FWHM widths in the superlattice are similar;
– lower (*ca*. 4 times) interlayer roughness;
– presence of Bragg peaks (up to 2nd order) in reflectometric measurements;
– domination of crystallographic [111] over [200] orientation.

2. Antiferromagnetic exchange coupling depends on the thickness of ferromagnetic layer (t_{Ni} = 14, 15 and 16 Å).

3. No antiferromagnetic coupling (A-F I and A-F II) was observed for particular thicknesses of non-magnetic Cu layer in Ni/Cu systems obtained by means of electrochemical deposition, probably due to non-periodical growth of the layers and increased roughness in upper, lower and interface layers.

The results obtained within the work proved that existence of antiferromagnetic exchange coupling in Ni/Cu system depends on the quality of manufacturing the artificial superlattice structure. In order to obtain such a coupling, vacuum technologies of thin layer deposition should be employed since they provide smoother surface, as compared to electrochemical deposition methods.

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