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Preparation and characterization of Copper/Nikel nanostructurated multilayers using thermionic vacuum Arc method

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Copper and nickel multilayers were prepared in order to obtain nanostructured giant magnetoresistive (GMR) thin films. In this respect we followed the original method of thermionic vacuum arc (TVA), which uses an external source of electrons for the creation of both metal vapors and metal ions. The low arc currents used in this case allow gentle evaporation of the anode material, which results in high smoothness of the films. The deposition thicknesses were controlled to be of 2.5-10 nm for Cu and 4-10 nm for Ni, using a Cressington quartz balance monitor. Morphology and structure of the prepared films were analyzed using electron microscopy techniques (transmission electron and scanning electron microscopy, energy dispersive X-ray spectroscopy). The thickness of the Cu layer influence on the properties of the prepared film was inferred in correlation with giant magneto-resistive effect.

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1. Introduction

Optical**,** electrical and magnetic properties of a material significantly differ when is analysed in bulk form or in thin films form. This kind of films are the object of an esential research during the last years due to the numerous technological aplications, the most important being spin-electronics.

Magnetoresistance is an effect defined as the change in electrical resistance (R) of a material in response to an externally applied magnetic field. Theoretically, the magnetoresistance is written as: MR=[R(H)-R(0)]/R(0), where R(H) and R(0) are the resistance of the material in the presence of applied magnetic field (H) and in the absence of an external magnetic field, respectively [1].

Giant magnetoresistance (GMR) is a quantum mechanical effect based on spin-scattering phenomena in M/N/M multilayers, where M = magnetic metal (ferromagnetic) and N = non-magnetic metal (antiferromagnetic). Resistance in this kind of structure changes when the magnetic field aligns the magnetisations of succesive ferromagnetic layers and the result is a drop of electrical resistance.

In order to obtain the GMR effect in multilayered nanostructures, magnetic moments of ferromagnetic layers must be oriented in parallel directions in the presence of the external magnetic field and they should have antiparallel orientations in zero – point field. This second situation is achived if we introduce one nonmagnetic layer between two succesive feromagnetic layers. The interlayer exchange coupling is mediated by the mobile electrons in the non-magnetic spacer layer like Cu and is analogous to Ruderman-Kittel-Kausya-Yosida (RKKY) interaction between localized magnetic moments present in a matrix of non-magnetic metal [1]. The interlayer exchange coupling oscillates between two modes: ferromagnetic and antiferromagnetic as a function of the antiferromagnetic spacer layer thickness. For a judicious and suitable value of the antiferromagnetic spacer layer thickness, one can obtain the antiparallel alignment of magnetisations in zero – point field.

2. Experimental

For preparation of GMR nanostructurated multilayers we use an original method, which is an intermediate between Electron Beam Evaporation Method and Electrical Vacuum Arc Discharge Method, known as Thermionic Vacuum Arc (TVA) Discharge Method [2-4]. An electron beam is emitted by an externally heated cathode and then is accelerated by a high anodic voltage. The electron beam hits and evaporates the anode material (Cu or Ni, in our case) as neutral particles and facilitates their deposition on a substrate. If the anode potential is increased up to a certain value, the evaporation rate increases as much as to allow an electrical discharge to be ignited in the evaporated material. Even though the discharge current is as low as a few hundred mA, the electric discharge is maintained [5].

The nanostructurated thin film was obtained inside a vacuum chamber with a minimum pressure of 4×10^{-5} Torr. Successive layers of Cu and Ni were deposited on silicon

substrates using tungsten crucibles, containing Cu and Ni metals, respectively. The deposition thickness was controlled using a Cressington quartz balance monitor.

The experimental data used in the deposition process are noted in the Table 1.

Table 1. Experimental data used in the deposition process

Layer number	Material	Anodic voltage (V)	$I_{filament}$ (A)	I_{anode} (mA)	Layer thickness (nm)
I	Cu	1.07	40	92	10
	Ni	2.4	40	44	9,7
II	Cu	9.0	40	90	4,2
	Ni	2.3	40	140	10
III	Cu	9.0	40	80	2,5
	Ni	2.5	40	100	4

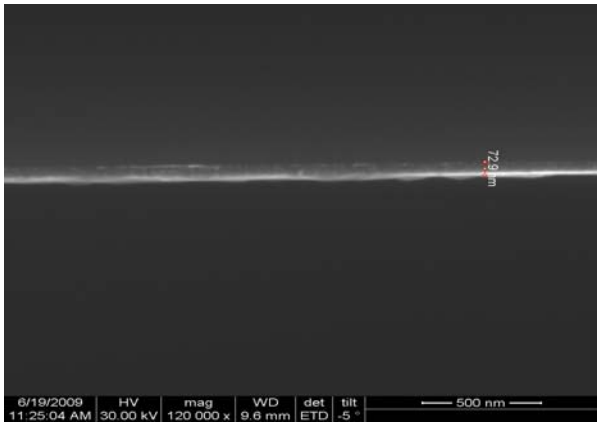
3. Results and discussion

The thin film morphology and structure were first analyzed using scanning electron microscopy techniques.

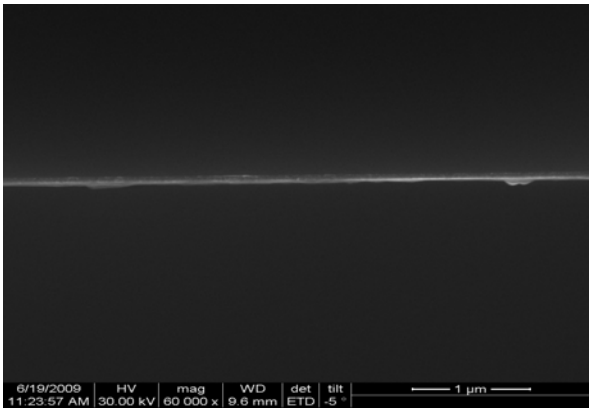
The sample was examined in cross section, by cutting with diamond on the uncover surface and then it was maintained in liquid nitrogen. SEM analysis intends to establish the quality of the deposition and the thickness of the thin film.

The microstructural aspect of the film in cross-section is revealed in Figure 1a,b (images obtained with secondary electrons - SEI) and Fig. 1c (image obtained with retroscattered electrons - BSED). In figure 1b, at a 60,000x magnitude, it is observed a cross section of the film (the horizontal bright line). A superior magnitude, 120,000x (Fig. 1c), reveals the uniform aspect of the film which has the thickness of 72.8 nm. A more careful examination of this image points out a columnar feature of the deposition. The image created by the back-scattered electrons makes a connection between the image contrast and the atomic number of the sample element. Therefore, Fig. 1c evidences the existence of some chemical elements with a big atomic number, such as Cu and Ni, within film (accordind to the bright line of the image) and the presence of chemical element with low atomic number, such as Si in the silicon substrate wich corresponds to the dark contrast from the superior half of the image.

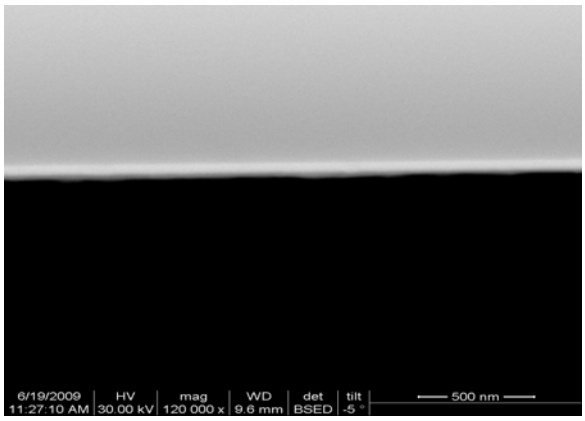
Fig. 2a exhibits a section of the sample and the aspect of the film surface. Image was obtained at oblique incidence of the electronic beam related to the sample. A detail of this image is presented in Fig. 2b, where it can be observed very clear, in the section, the columnar character of the deposition and, at the surface, a homogeneous appearance of this kind of deposition (small undulations similarly with "hillocks").



(a)

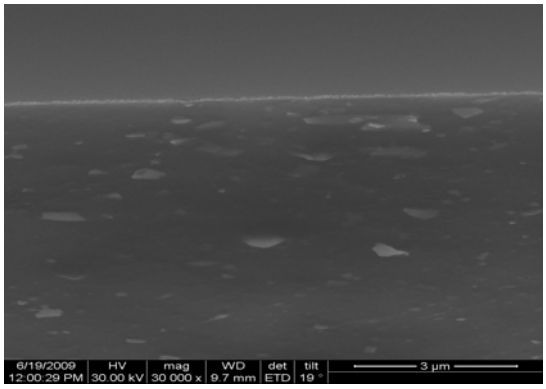


(b)

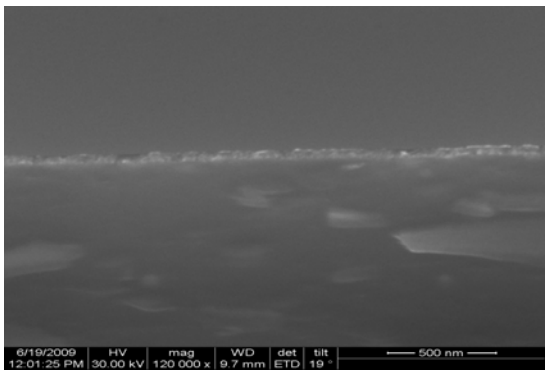


(c)

Fig. 1. Cross section through CuNi film on the silicon substrate at different magnitudes: (a) 60,000×; (b) 120,000×; (c) 120,000×.



(a)



(b)

Fig. 2. The surface of the film at oblique incidence of the electronic beam related to the sample at different magnitudes: (a) 30,000×; (b) 120,000×.

Fig. 3 shows the distribution of Si, Ni, Cu (through a cross section of the sample) by the distribution of SiK_{α}, NiK_{α}, CuK_{α} characteristic X-ray inside the microarea, which is presented in the superior side of the left corner. The inferior side of Fig. 3 reproduces the X-ray dispersive spectrum (EDAX) corresponding to the examined microarea.

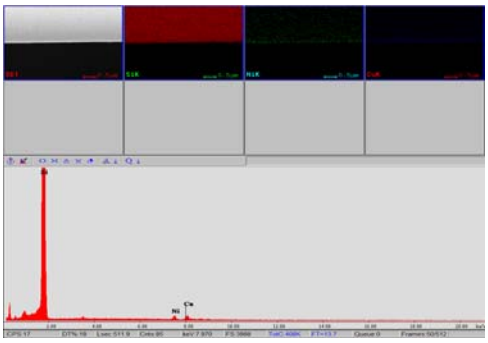


Fig. 3. Secundary electrons image and associated images of the distribution (in the surface) of relative intensity of SiK_{α}, NiK_{α}, CuK_{α} characteristic X-ray through the cross section of the film.

Characteristic X-ray images of distribution are processed in Fig. 4, where it can be better observed (through the relative density of the coloured points) the concentration of the chemical elements Cu and Ni.

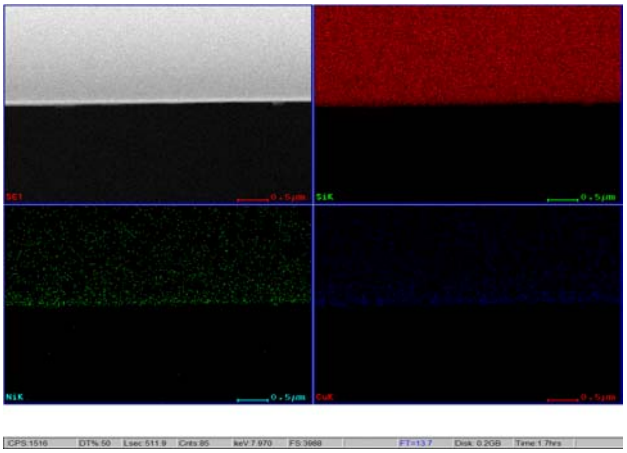


Fig. 4. The distribution map of the SiK_{α}, NiK_{α}, Cu K_{α} characteristic X - ray in the microarea section situated in the left superior corner.

The X-ray dispersive spectrum (Figure 5) obtained using a very tight electronic beam focused on the sample shows the presence of Cu and Ni across the section of the film (Si and O result from the film substrate).

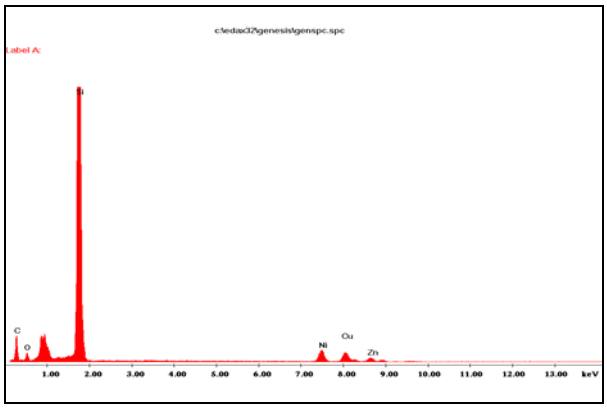
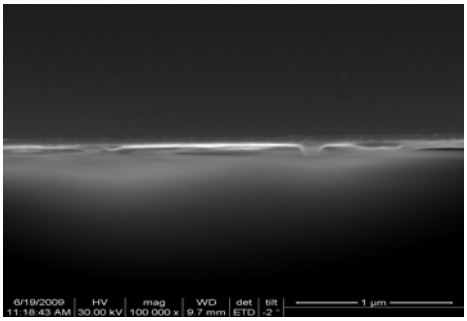
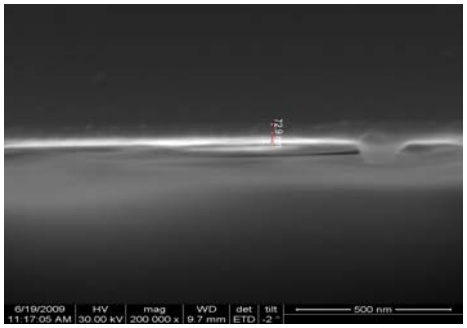


Fig. 5. The X - ray dispersive spectrum.

Fig. 6 a, b shows another microarea of the sample. These images confirm the uniformity, the thickness (72.9 nm) and the columnar aspect of the film.



(a)



(b)

Fig. 6. Images of another microarea of the thin film at different magnitudes: (a) 100,000x*; (b)* 200,000x.

To acquire more information about the structural properties of the CuNi deposition, there were used the following techniques: BF-TEM (Bright Field Transmission Electron Microscopy), SAED (Selected Area Electron Difraction) and HR-TEM (High Resolution Transmission Electron Microscopy).

Fig. 7 offers a general view of the CuNi film. On the edge of the film one can observe the nanoparticle originating from the silver paste used to realize the electric contacs for further experiments.

Fig. 7. TEM image of CuNi film.

Figs. 8 and 9 present details of the film edge and the dimension measurements of the nanoparticles.

Fig.8. Detail of the film edge at 1,050,000x *magnitude.*

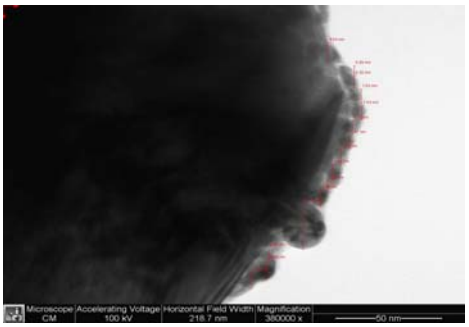


Fig. 9. Detail of the film edge and marked nanoparticles for dimension measurements.

There is a difference between the nanoparticles size, which can be observed in both images, because the Ag paste was not uniformly distributed. As the result of this study, we found four nanoparticles indicated in Fig. 8 with diameters estimated to be around 20 nm value. Fig. 9 shows one nanoparticle, which has approximately 20 nm in diameter and a series of nanoparticles with diameters estimated to be around 10 nm value.

The SAED and HR-TEM images are used to determine crystalline structure of the sample. The electron diffraction pattern obtained for the CuNi/Ag film is shown in Fig. 10.

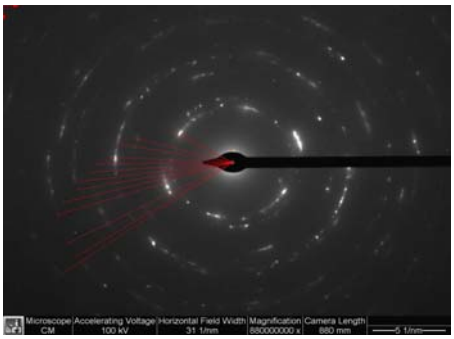


Fig. 10. The electron diffraction pattern obtained for the CuNi/Ag film.

The diffraction data resulted from measurements of the first diffraction rings, provide information about this thin

film structure and they are registered in Table 2, where L is electron wavelength (as a function of the accelerating voltage of the electronic beam), d_{hkl} is the distance between two successive crystalline planes and *h, k, l* are the Miller indices.

Table 2. The diffraction data resulted by measurements of the first diffraction rings

L(nm^{-1})	d_{hkl}(nm)	hkl
4.1742	0.2395	Ag(111)/Ni_{Hex}(100)
4.8341	0.2068	Ag(200)/Cu(111)/ Ni_{Cub}(111)/ Ni_{Hex}(101)
6.8107	0.1468	Ag(220)/ Ni_{Hex}(102)
8.0694	0.1239	Ag(113)/Cu(220)/ Ni_{Hex}(103)
8.4517	0.1183	Ag(222)/Ni_{Hex}(200)
9.2990	0.1075	Cu(113)/ Ni_{Hex}(201)
9.7081	0.1030	Ni_{Hex}(004)

In the diffraction pattern there are visible spots, therefore we came to the conclusion that in interior of the film there exists large crystallites too. The proof is provided in Fig. 11, where the image of a very thin area of the studied sample is shown.

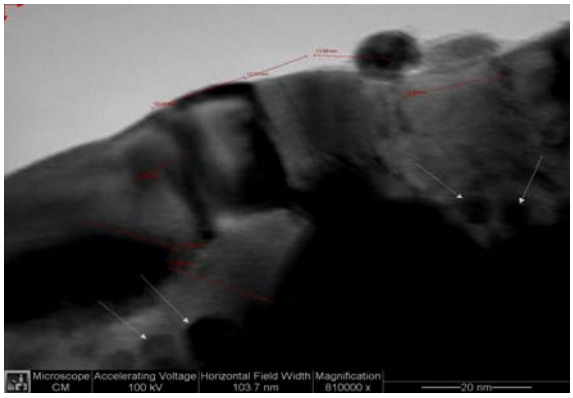


Fig.11. The TEM image of the CuNi film. On this view are marked crystallites (red lines), their dimensions and Ag nanoparticles (white narrows).

The dimension of crystallites is estimated to be approximately 12 nm. This value was used as base for the simulation of the electron diffraction pattern.

4. Conclusions

As a result of CuNi thin film investigations, by scanning electron microscopy techniques, it can be emphasized the columnar character of the metallic film growth and the accentuated homogeneity of the deposition on silicon substrate. EDAX spectra confirm the existence of chemical elements, Cu and Ni. The presence of Zn in obtained spectrums can be explained by electronic beam scattering on the support, which the sample was set inside electron microscope. It is not possible to emphasize the multilayer character of the film, probably because of the interdiffusion between layers or because the limited resolution of the study method.

The CuNi thin film, which was analyzed by transmission electron microscopy techniques, contains Ag nanoparticles that result from deposited contacts in order to continue the experiment in studing the magnetics properties of the film. The nanoparticles distribution is not uniforme on the sample surface. The film has a policrystalline structure, the crystallites dimension is estimated to be around 12 nm value. Electron diffraction pattern confirms the presence of Cu, Ni and Ag. The indexing of the diffraction pattern is a difficult procedure, taking acount of the nearest values of the Cu and Ni constants matrix and the nanoparticles dimensions, thus we are able to say that interplanar distances of Ag can be superposed over those of Cu and Ni.

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