Journal of Optoelectronics and Advanced Mateirlas Vol. 7, No. 2, April 2005, p. 853 - 858

MAGNETISM AND MAGNETORESISTANCE IN ELECTRODEPOSITED ($L1_0$) CoPt SUPERLATTICES

V. Georgescu*, M. Daub[a]

Faculty of Physics, Al. I. Cuza University, Iasi, Romania
[a]Max-Planck-Institut für Mikrostrukturphysik, Halle

Over the last few years, the Co/Pt nano-multilayered films have been extensively studied. Owing to their strong perpendicular magnetic anisotropy and their giant magnetoresistance, they are potential materials for high-density magneto-optic recording and for magnetic sensor applications. Our purpose is to perform a comparative investigation of the surface, structural, magnetic and electric properties of ordered ($L1_0$) CoPt alloys grown by electrolysis. The samples were electrodeposited on Pt (100) textured polycrystalline substrates from a bath containing $CoSO_4.H_2O$, K_2PtCl_6 and H_3BO_3 by a potentiostatic technique. Films were characterised using grazing incidence X-ray diffraction, scanning electron microscopy, and magnetoresistance in current-perpendicular-to-plane configuration and torsion magnetometry. Films consist in ordered ($L1_0$) CoPt plane crystallites with diameters in the range of 10 to 50 micrometers. Magnetic behaviour is characterised by an easy axis normal to the film plane concomitantly with an antiferromagnetic coupling of magnetic layers. For specific samples of ordered ($L1_0$) CoPt films, evidence is given regarding an appreciable magnetoresistance effect, of the order 8 – 30% in CPP (current perpendicular to plane) configuration. It can be explained in terms of antiferromagnetic coupling between Co layers.

(Received July 27, 2004; accepted March 23, 2005)

Keywords: Electrodeposition, Thin films, Magnetic properties, Magnetic anisotropy, Magnetic susceptibility

1. Introduction

Co/Pt multilayers and films of Co-Pt alloys system are among the most studied ones in recent years, since they are potential magneto-recording media for blue laser recording and they can produce chemically ordered phases [1-9]. For the study of magnetic anisotropy, Co-Pt is also a well-appropriate system because it displays perpendicular anisotropy. We have reported electrodeposition of the Co/Pt multilayers with periods of (2.5 to 15) nm [10-13]. Their magnetic behaviour could be explained by the formation of various microstructures for different thickness of individual layers. Electrodeposited Co/Pt multilayers represent a particularly complicated case because the fcc, fct, as well as the hcp phase can be formed, depending on the multilayer periodicity. The Co-Pt alloys thin films with a wide range of composition (15 at % Co - 100 at % Co, balance Pt) have been studied also in our early works [14,15]. We prepared Co/Pt multilayers and Co-Pt alloys by electrodeposition, with the purpose to develop this very cheep technique, which is applicable for surfaces of various shapes (wires, large surfaces or micro-surfaces). A good control of the preparation regime of electrodeposited films assures a good quality and the reproducibility of the magnetic and structural properties of the films. In this paper, we report on a comparative investigation of the structural, magnetic and electric transport properties of ordered ($L1_o$) CoPt alloys grown by the same preparation method as in the case of multilayers. CoPt was chosen because we have found that such films exhibit giant magnetoresistance (GMR) effect.

2. Experimental

The procedure of preparation of CoPt films was performed by electroplating from a single

* Corresponding author: vgeor@uaic.ro

electrolyte, to avoid cathode contamination by the contact with external ambient during the two-bath procedure. The method proposed in our previous studies for electrodeposition of Co/Pt multilayers was employed [10-12].

The microstructures of the samples were characterized using both the X-ray diffraction (XRD) in grazing incidence with Cu $K\alpha$ radiation, and scanning electron microscopy. The alloy compositions were determined by energy-dispersive X-rays analysis (EDAX). The magnetic properties of the films were studied at room temperature using a torque magnetometer in fields up to 300 $kA.m^{-1}$. The DC magnetoresistance measurements were performed applying the current perpendicular to the plane of the film (CPP configuration) and the external magnetic field applied perpendicular to the film plane, by using a two-terminal platinum pressure contacts. A digital multimeter HM 8112-2 type was used for resistance measurements. Field dependence of the magnetoresistance (MR) was defined as

$$MR(H) = 100\left[R(H) - R(H_s)\right] / R(H_s), \quad (1)$$

where H_S denotes the saturation magnetic field. $H = 0$ in the above equation defines the GMR value.

3. Results and discussions

We will describe firstly in brief the technique of sample preparation. Cobalt and platinum ions were introduced in a single bath. The composition of the metal electrodeposited from a solution containing Co and Pt ions may be controlled by varying deposition parameters such as the substrate potential, the current density and pulse duration in pulsed electrodeposition [11 - 14]. One way to achieve a large composition modulation for a superlattice, is to switch between a deposition potential only sufficiently negative to reduce the more noble metal (Pt) and a deposition potential sufficiently negative to reduce both metals. This gives an alloy consisting of alternating layers of pure Pt and a Co-Pt alloy. The concentration of Pt in the Co-Pt alloy may be kept low by keeping the concentration of Pt in the electrolyte very low [11]. The plating potential was alternated for controlled duration between a value of -0.15 V (*versus* saturated calomel electrode, *SCE*, as reference electrode) corresponding to the reduction potential of the Pt ions and a more negative potential (-1.8 V, *versus SCE*). The bath composition was: 0.66 $g.l^{-1}$ K_2PtCl_6, 40.0 $g.l^{-1}$ $CoSO_4.7H_2O$ and 40.0 $g.l^{-1}$ H_3BO_3. The working parameters were: pH = 4.0, bath temperature was (30 ± 0.5) ^oC, without stirring the solution. Platinum foils (100)-textured or (100)-textured polycrystalline copper foils covered with a 50 nm buffer layer of platinum were used as substrates. A top layer of 20 nm Pt was electrodeposited on each sample in a view to obtain the reproducibility of magnetoresistance measurements. A jig of inert plastic was used to hold the sample and restrict deposition to a circular surface (10 mm in diameter) on the cathode. The anode was a cobalt foil with the same area as those of the cathode. This technique allows obtaining Co/Pt multilayers with controlled thickness of the Co or Pt layers by controlling the pulse duration [10, 13].

We prepared a series of samples with the electrolysis parameters chosen as to obtain about CoPt equiatomic alloy composition. Three samples (labelled I, II, and III) were selected for magnetic characterisation and analysis in this paper, taking into account their mean composition (expressed as a media between the composition in the central part and the peripheral part of a sample). These samples contain: sample (I) (50.850 %) Co, (49.150 %) Pt, sample (II) (46.780 %) Co, (53.220 %) Pt and sample (III) (54.170 %) Co, (45.830 %) Pt. The film thicknesses are of 300 nm, 160 nm and 157 nm, respectively. Thus, the three samples have a composition in a domain range close to ordered phase (L10) CoPt.

It is known that the Co-Pt phase diagram of bulk alloys displays at high temperatures a disordered fcc solid solution over the whole composition range, and at room temperatures two fcc ($L1_2$) ordered phases around the composition $CoPt_3$ and Co_3Pt and one tetragonal ($L1_0$) ordered phase around the equiatomic composition CoPt. The microstructure of Co/Pt nano-multilayers critically depends on the thickness of the Co and Pt layers, the period and the total number of periods included in multilayers [6]. In our previous studies [11,12] we have found that multilayers with low period $\lambda = (t_{Co} + t_{Pt}) < 2.5$ nm are formed by insular grains of ordered phases ($L1_o$) CoPt or ($L1_2$) $CoPt_3$, depending on the t_{Co}/ t_{Pt} ratio. The multilayers with $\Lambda > 2.5$ nm consist in amorphous Pt layers stacked with polycrystalline hcp Co layers. This paper will be concerned to films containing ordered ($L1_o$) CoPt phase.

The X-ray diffraction spectra in grazing incidence for the sample labelled (I) are shown in Figs. 1 and 2(a). The spectra in fig. 2(a) are performed in the large angles region for grazing incidence angles of 5^o (A) and 8^o (B). It is evident from the patterns that the sample exhibit ordered structure of type ($L1_0$)

CoPt. The diffraction lines in Fig. 1 are identified by their Miller indices and theirs calculated interplanar spacing. For brevity of notation, the peaks in fig. 1 are labelled by numbers from *1* to *22*. The structures lines of fct CoPt alloy are the following: *4* - (111), *5* - (200), *6* - (002), *11* - (311), *12* - (222), *15* - (400), *16* - (004), *18* - (331) - (133), *19* - (420), *20* - (024), and for Pt substrate *3*- (111), *5* - (200), *8* - (220), *10* - (311). The following peaks are attributed to ordered ($L1_0$) CoPt phase: *2* - (110), *9* - (221), *13* - (203), *14* - (312), *17* - (401), (223), *21* - (421), and *22* - (332). There are also small peaks at the left-hand side of the main peak (111) and (200) and of the right side of (200) peak; we denoted them as *1*, *2*, and *7*, respectively.

The investigated sample shows CoPt (111) and CoPt (200) peaks that are consistent with an $L1_0$ phase with a plane spacing for the 100 plane of $d_{100} = 0.372$ nm.

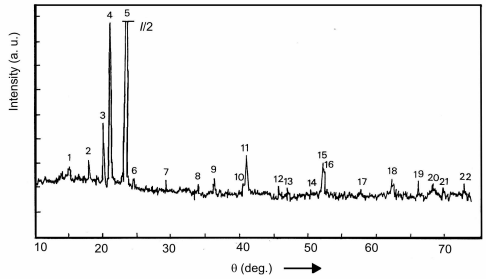
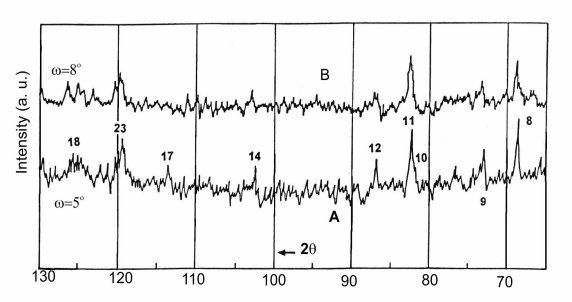
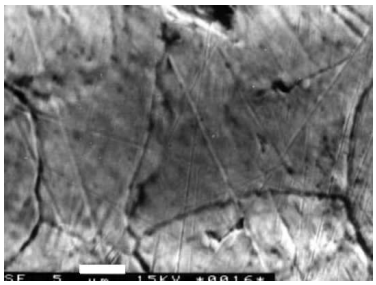


Fig. 1. X-ray diffraction pattern in Cu $K\alpha$ radiation and grazing incidence of the sample containing (50.850 %) Co, balance Pt, electrodeposited onto Pt (100) textured substrate. The structures lines of fct CoPt alloy are labelled as follows: *4* - (111), *5* - (200), *6* - (002), *11* - (311), *12* - (222), *15* - (400), *16* - (004), *18* - (331) - (133), *19* - (420), *20* - (024), and for Pt substrate *3*- (111), *5* - (200), *8* - (220), *10* - (311). The following peaks were attributed to ordered ($L1_0$) CoPt phase: *2* - (110), *9* - (221), *13* - (203), *14* - (312), *17* - (401), (223), *21* - (421), and *22* - (332). The small peaks neighbour to the main peaks (111), (200) and to the (200) peak; were denoted as *1*, *2*, and *7*, respectively.



(a)



(b)

Fig. 2. (a) Large angles XRD patterns in Cu $K\alpha$ radiation and grazing incidence (A – 5^o, B – 8^o) of the sample (I). The peaks are marked as follows: *8* - (220), *9* - (221), *10* - (311), *11* - (311), *12* - (222), *14* - (312), *17* - (401), (223), *18* - (331) - (133), and *23* - (303), (411). Fig. 2. (b). Scanning electron microscopy images of the same film (I). The marker bar shown in the image has a dimension of 5 μm.

In Fig. 2(b) we show a typical SEM image of the sample labelled (I). The film contains polygonal grains with diameters of 10 - 50 microns composed of (L10) CoPt ordered alloys. The growth mechanism seems to be a quasi-layer-by-layer growth, as it was found also for Co/Pt multilayers prepared by other low-energy processing (vacuum evaporation deposition, or RF, and DC magnetron sputtering deposition) [6]. To give an explanation, we remember that the Co-Pt binary system of alloys is a completely miscible system. The Co-Pt atom pairs are more stable than Pt-Pt and Co-Co pairs because of its negative mixture heat ($\Delta H = -11$ kJ/g). Therefore, for the Co/Pt binary system, the formation of ordered phases in the deposit is favoured. The electrodeposition at room temperature is a low-energy process and the adatoms do not have sufficient energy to move at the surface and produce disorder in the film. The interface between cathode and electrolyte and the electric double-layer at the interface have an important influence on the formation of such favourable energetic ions pairs and on the growing of the

new phases in deposit. As consequence, the film grows in a partially ordered state, without any subsequent thermal annealing.

Magnetic properties of the samples were investigated by means of torque magnetometry, at room temperature. Figs. 3 and 4 show the static torque curves performed for clockwise and anticlockwise rotation of the magnetic field, for the samples II and III, respectively. The film plane was oriented perpendicular to the field-rotation plane, e. g. the torque was measured around an arbitrary axis parallel to the film plane, starting from the plane of the film ($\theta = 0$). The applied magnetic field was of 9.55 kA m^{-1} (in Figs. 3a and 4a), of 28.65 kA m^{-1} (in Figs. 3b and 4b), and 95.5 kA m^{-1} (in Figs. 3c and 4c).

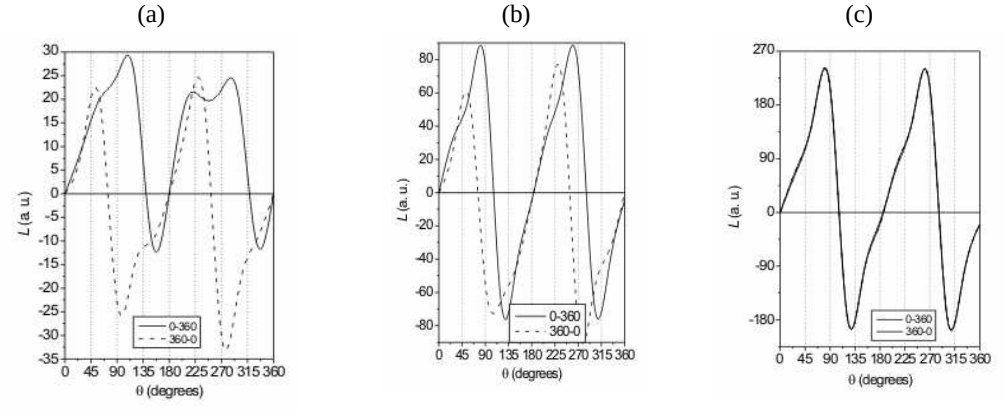


Fig. 3. Torsion magnetometry curves for the sample II with ferromagnetic interlayer coupling, measured for the fields: (a) 9.55 kA/m, (b) 28.65 kA/m and (c) 95.5 kA/m.

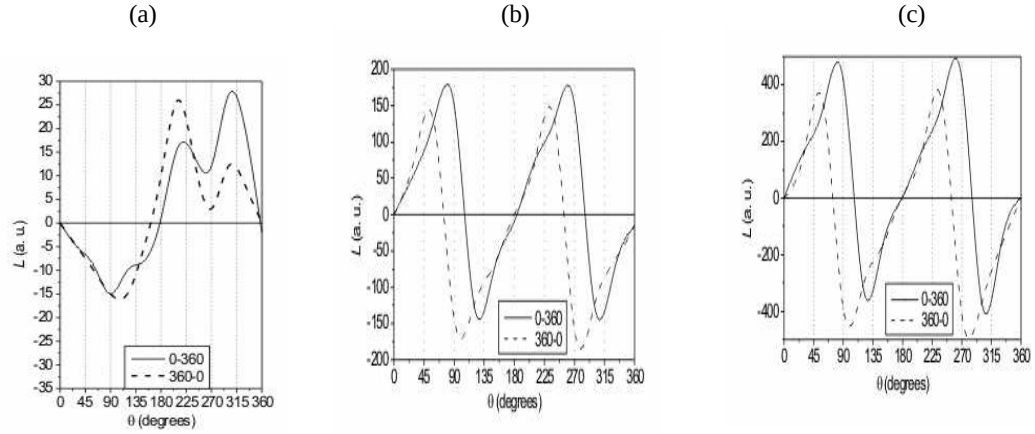


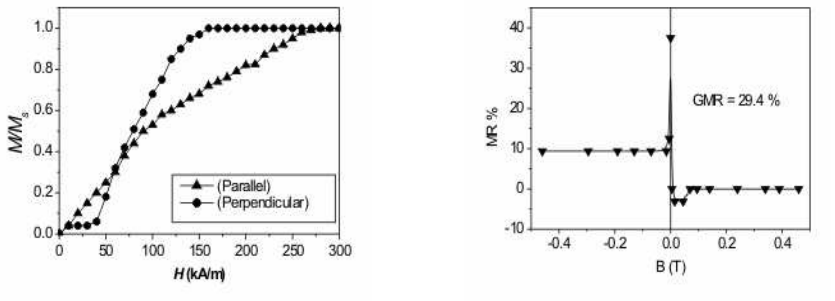
Fig. 4. Torsion magnetometry curves for the sample (III) with antiferromagnetic interlayer coupling, measured for the fields: (a) 9.55 kA/m, (b) 28.65 kA/m and (c) 95.5 kA/m.

As the applied field increases, the torque curves become asymmetric, i. e. the rotational loss appears and it is measurable from the area enclosed by clockwise and anticlockwise curves. For fields exceeding the anisotropy field, the torque curves become symmetric and reversible in fig 3(c) and irreversible in Fig. 4(c), and the torque is proportional to $\sin 2\theta$. This behaviour could be ascribed to the ferromagnetic type interlayer coupling for the sample II, and antiferromagnetic type interlayer coupling for the sample III, respectively. The experimental torque curves exhibit mainly a twofold symmetry with a positive slope at $\theta = 0^o$ and a negative slope around $\theta = 90^o$. This indicates that the easy magnetisation direction is perpendicular ($\theta = 90^o$) to the film plane. There is an exception for the torque curve in fig. 4(a). The proportionality between the torque L and $\sin\theta$ which occurs at relatively low fields for the sample III could be accounted for the presence of antiferromagnetic type coupling between Co layers in ($L1_0$) CoPt superlattices [16].

In previous studies [10] we have determined the effective anisotropy energy (K_{eff}) for a series of Co/Pt multilayers with the same Pt layer thickness of 1 nm, as a function on the thickness of Co layer (t_{Co}). The interface anisotropy energy (K_{int}) and the volume anisotropy (K_v) were calculated by fitting experimental data with the phenomenological equation

$$K_{eff} = -\mu_o \frac{M_s^2}{2} + K_{mc} + K_{me} + 2K_{\text{int}}(t_{Co})^{-1} \quad (2)$$

The sum of the first three terms represents the volume anisotropy K_v which contains: the shape anisotropy, magneto-crystalline anisotropy (K_{mc}) and magneto-elastic anisotropy (K_{me}). We obtained for volume anisotropy $K_v \sim 4\times10^4$ J m^{-3} and the interface anisotropy of $K_{int}=1\times10^{-4}$J m^{-2} in the case of (L10) CoPt superlaticces. For these samples, magneto-crystalline anisotropy, magneto-elastic anisotropy (resulting from the deformation of the crystalline cfc lattice in tcf one) and interface anisotropy surpass the shape anisotropy, and $K_{eff}>0$; that means out of plane effective anisotropy. The compositional order enhances the magnitude of magneto-crystalline anisotropy energy by comparison with disordered samples.



(a) (b)

Fig. 5. (*a*) Magnetization curves measured in fields parallel to (circle) and perpendicular (triangle) to the film plane for the sample labelled (III). (*b*) Magnetoresistance (CPP configuration) versus magnetic induction *B* at room temperature for the sample III.

Torque measurement is a sensitive tool for the detection of out of plane magnetisation. Another experimental method is the measurement of magnetisation curves in plane, and perpendicular to the plane of the film. Fig. 5(a) shows an example for the magnetisation curves of the sample labelled III (starting from the demagnetised state of the sample, only till positive saturation). The *M(H)* curves in the perpendicular direction (circles) and in plane (triangles) are quite different. It is obvious from the curves that the sample magnetises easier perpendicular to the film plane for fields larger than 50 kA/m and in the film plane for lower fields. This observation is in good accordance with the torsion anisotropy curves shown in fig. 4(a) for the same film. For the sample III, the *M(H)* curve in the perpendicular direction has a plateau in the domain of low fields; it could be considered as a consequence of the antiferromagnetic interactions in film. For the sample labelled I the magnetisation curves have the same behaviour as for the sample III. Instead, the sample II shows that the easy axis of magnetisation is perpendicular to the film plane for every field domain.

It is possible to explain this behaviour by analogy with the data concerning the magnetic structure of bulk samples of ($L1_0$) CoPt alloys [16]. In an $L1_0$-type ordered film the stacking sequence along the [001] easy direction of magnetisation consists of alternate pure Pt and Co planes, while along the hard axes [100] and [010] all the planes have equiatomic composition. Therefore, all nearest-neighbour CoPt pairs are oriented out of the (001) CoPt film plane. The existence of strong perpendicular magnetic anisotropy stems from the hybridisation between Co atoms of large magnetic moment and Pt atoms of strong spin-orbit coupling, preferentially along the surface normal. As a function of the composition and the local order parameter, there are two possible arrangements for magnetic structure. We suppose that Co layers are ferromagnetically coupled for the samples with some Co in excess (as in the sample II). The coexistence of antiferromagnetic coupling for some Co-Co pairs and ferromagnetic for others Co-Pt or Co-Co pairs are supposed for the samples I and III.

The magnetotransport properties of the samples were measured at room temperature. Fig. 5(b) shows the field dependence of the CPP magnetoresistance for the sample III. The CPP MR ratio is ranged between 5% and about 30% for our samples, with the similar kind of field dependence. The samples exhibit Hall effect that can be observed from different values of MR for different sense of magnetic field. In particular, the lowest resistivity corresponds to the parallel configuration. We have found that in the case of Co/Pt multilayer systems, which show an antiferromagnetic coupling between subsequent Co layers there are the largest magnetoresistance effects. In multilayers, the GMR effect can occur only

when the external magnetic field drives a transition from the antiparallel (or canted) to the parallel arrangement of the magnetization vectors in neighboring ferromagnetic layers [17, 18]. The antiparallel ordering of the magnetization vectors is obtained thanks to the interlayer exchange coupling. The dispersion of anisotropy and the local variations in the structure and the order parameter of crystalline grains generate the dispersion of data on GMR between various samples and various experiments. The interface roughness and the presence of pinholes influence on the interlayer exchange coupling and on the GMR measurements. These effects depend on the polarization processes acting on the spin of conduction electrons, as well as on the magnetic configuration of the system. The GMR effect in multilayers is very sensitive to changes in the layer thickness. The magnetic coupling as well as GMR in (L10) CoPt samples will strongly depend on the roughness of the interfaces and other structural imperfections such as local discontinuities of layers.

4. Conclusions

The growth by electrodeposition of ($L1_0$) CoPt films with perpendicular magnetic anisotropy was investigated. The electrodeposition was performed in a single bath containing $CoSO_4.7H_2O$ and K_2PtCl_6 using a pulsed deposition technique. The films contain polygonal grains with diameters of 10 - 50 microns composed of (L10) CoPt ordered alloys, as it was found by XRD patterns in grazing incidence and SEM images. Comparisons are drawn between the field dependencies of the torque curves, magnetisation and magnetoresistance. In the case of ($L1_0$) CoPt superlattices, which show an antiferromagnetic coupling between subsequent Co layers (deduced from the analysis of torsion curves) there are large magnetoresistance effects.

The electrodeposition under precise control of the bath parameters is a potential method for fabrication of ($L1_0$) CoPt superlattices with a satisfactory degree of homogeneity and very interesting properties (perpendicular anisotropy and large CPP magnetoresistance).

Part of this research was supported by the Project #593/2004 granted by Romanian Ministry of Education and Research. Authors would like to thank V. Mazur and B. Pushcashu for collaboration in XRD and SEM experiments.

References

[1] H. J. G. Draaisma, F. J. A. den Broeder, W. J. M. de Jouge, J. Magn. Magn. Mater. **66,** 351 (1987).
[2] L. Smardz, B. Szymanski, R. Gontarz, P. Stefanski and J. Barnas, J. Magn. Magn. Mater. **120**, 239 (1993).
[3] F. J. A. den Broeder, W. Hoving and P. J. H. Bloemen, J. Magn. Magn. Mater. **93**, 562 (1991).
[4] Z. G. Li, P. F. Carcia, J. Appl. Phys. **71**, 842 (1992).
[5] W. B. Zeper, F. J. A. M. Greidanus, P. F. Carcia, IEEE Transactions on Magn. **25,** 3764 (1989).
[6] J. Wu, Y. Pan, L. Chen, Y. Zhang, R. Wu, Ch. Xie and A. Wang, Surface and Coatings Technology **176**, 357 (2004).
[7] W. Schwarzacher, D.S. Lashmore, IEEE Trans. Magn. **32**, 3133 (1996).
[8] Y. Jyoko, S. Kashiwabara, Y. Hayashi, J. Magn. Magn. Mater. **165**, 280(1997).
[9] H. van der Berg, J. Wecker and H. Schewe, Current Topics in Magnet. Res. **1**, 235 (1994).
[10] V. Georgescu, M. Georgescu, Surface Science **507-510**, 507 (2002).
[11] V. Georgescu, V. Mazur, O. Cheloglu, J. Magn. Magn. Mater. **156**, 27 (1996).
[12] V. Georgescu, V. Mazur, B. Pushcashu, Mat. Sci. Eng. **B68**, 131(2000).
[13] V. Georgescu, J. Optoelectron. Adv. Mater. **4**(2), 271 (2002).
[14] V. Tutovan, V. Georgescu, Thin Solid Films **61,** 133 (1979).
[15] V. Georgescu and V. Tutovan, Thin Solid Films **75,** L15 (1981).
[16] A. Oles, F. Kajzar, M. Kucab, W. Sikora, Magnetic Structures determined by Neutron Diffraction, Panstwowe Wydawnictwo Naukowe, Warszawa (1976).
[17] S. S. Parkin, N. More, K. P. Roche, Phys. Rev. Lett. **64**, 2304. (1990).
[18] M. N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau , F. Petroff, P. Etienne, G. Creuzet, A. Friederich, J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).