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The additions effect on the microstructure and magnetic properties of [NdFeB/M]×n thin films

H. CHIRIAC, M. GRIGORAS, M. URSE*
National Institute of R&D for Technical Physics Iasi, 47 Mangeron Blvd., 700050 Iasi, Romania

This paper reports some results concerning the influence of the Cu, Nb, and NbCu as additions M and Nb, Ta and NbCu as buffer and capping layers N on the microstructure and magnetic properties of multilayer N/[NdFeB/(M)]·n/N thin films. The materials used as additions were 'mixed' with NdFeB alloy either by stratification as multilayer system or by disposing of the additions on the target's surface and simultaneously by stratification as multilayer system. When the additions were introduced in NdFeB alloy by stratification, the thickness of individual NdFeB layer was held fixed at 180 nm, while the M spacer layer thickness was varied from 3 to 10 nm. The Si/NbCu/[NdFeBNbCu(180nm)/NbCu (3nm)]·3/NbCu and Si/Ta/NdFeBNbCu(540nm)/Ta systems exhibit an enhanced coercivity of about 1510 kA/m and 1580 kA/m, respectively, in comparison with the NdFeB single layer having the same thickness.

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1. Introduction

The thin - film NdFeB permanent magnets have been extensively investigated as promising candidates for actuation components in specific applications for planar magnetic microdevices and micro-electromechanical systems [1]. Optimization of microstructure is the key to improve the hard magnetic of the thin film NdFeB permanent magnets. Refinement of the microstructure in less than 20 nm is essential to obtain high coercivity and high energy product [2]. Many metallic elements can be added to the ternary NdFeB system with the aim of enhancing the magnetic properties. Among them, Cu or/and Nb are known to act in the sense of promoting the formation of nucleation sites and decreasing the grain growth, respectively [3, 4].

This paper reports some results concerning the influence of the Cu, Nb and NbCu additions M and buffer and capping layer N on the microstructure and hard magnetic properties of multilayer N/[NdFeB/(M)]·n/N thin films. The materials used as additions were 'mixed' with NdFeB alloy either by stratification as multilayer system or by disposing of the additions on the target's surface and simultaneously by stratification as multilayer system. When the additions were introduced in NdFeB alloy by stratification, the thickness of individual NdFeB layer was held fixed at 180 nm, while the M spacer layer thickness was varied from 3 to 10 nm. For the all samples the total thickness of the NdFeB layers was of about 540 nm.

2. Experimental details

The NdFeB and M thin films (with M = Nb, Cu, NbCu) were prepared, by sequential deposition from two targets (with 7.5 cm in diameter) mounted on two separate guns, using a conventional R.F. diode sputtering system (Laboratory Sputtering Plant Z-400). For preparation by sputtering of the NdFeB/M films were used elementary targets (Nb and Cu) and composed targets (NdFeB, NdFeBM, NbCu). The NdFeB composed target was made in two variants: a plate of commercial $Nd_{12}Fe_{82}B_6$ alloy with Nd chips on its surface; a plate of commercial $Nd_{12}Fe_{82}B_6$ alloy with Nd, Cu or/and Nb chips on its surface. The NbCu composed target was made of a plate of Nb with the Cu discs disposed on its surface (surfaces ratio Cu/Nb is of 1/3). The [NdFeB-/M]×n films have a total thickness of NdFeB layers of about 540 nm and they deposited at room temperature, on different substrates depending on the intended measurements.

During the deposition process, the thickness of the successive layers were monitorized with a thickness monitor (FTM 6 Film Thickness Monitor) which has a resolution of 0.1 nm.

The crystallographic structure of the [NdFeB/M]×n thin films was investigated using X-ray diffraction analysis. An X-ray diffractometry in a Bragg-Brentano arrangement with a monochromatized Co-Kα radiation was used. For estimation of the grains size the Warren – Averbach method was used [5].

The microstructure of the [NdFeB/M]×n thin films was investigated by transmission electron microscopy (TEM), using molibdenum 'microscope grids' coated with an evaporated carbon (8-10nm) film as substrates. NdFeB(60nm) sample and M(5nm)/NdFeB(60nm)-/M(5nm) samples with a total thickness of about 70 nm were used for TEM analysis.

The magnetic characteristics of the samples were determined at room temperature using a SQUID magnetometer in a maximum applied magnetic field of 5600 kA/m.

The structural analysis and magnetic measurements were made on as-deposited and thermally treated samples. The as - deposited N/[NdFeB-/M]·n/N films were subsequently annealed, in vacuum of 4 x 10^{-4} Pa, for different periods of time (5 ÷ 30 min.), at temperatures between 400 ^{o}C and 750 ^{o}C.

3. Results and discussion

The materials used as additions were introduced in NdFeB alloy in two modes: 1. by stratification corresponding to the structure Si/N(20nm)/[NdFeB(180nm)/M]·n/N(20nm); 2. by disposing of the additions M on the target's surface, to obtain the structure Si/N(20nm) /[NdFeBM]·n/N(20nm). For these structures the materials N = Nb, Ta and NbCu were used as buffer and capping layers.

At the beginning, the multilayer [NdFeB/M]·n and N(20nm)/[NdFeB/M]·n/N(20nm) films were studied, and then the comparative results about N(20nm)/[NdFeBM]·n/N(20nm) will be presented.

The effect of the composition and thickness of the M spacer layers on the magnetic properties of the NdFeB/M thin films was studied. The different variants of NdFeB and M composed targets were tested in order to obtain good magnetic properties for the [NdFeB/M]·n thin films. The optimal hard magnetic properties were obtained for a structure of the composed targets as follows: a disc of commercial $Nd_{12}Fe_{82}B_6$ alloy with the diameter of 7.5 cm having on its surface the Nd chips with the area of about 5 cm^2; a disc of Nb with the diameter of 7.5 cm (the target surface is of 44.16 cm^2) having on its surface the Cu chips with the area of about 14.72 cm^2.

In [NdFeB(180nm)/M]·3 systems, the Cu, Nb and NbCu films were used as spacer layer M. For these samples the magnetic measurements and microstructure analysis were used to study the effect of the additions. In Table 1 the main magnetic properties of [NdFeB(180nm)/M(5nm)]·3 films, annealed at 650^{o}C, for different period of time, are shown.

Table 1. The magnetic properties of [NdFeB(180nm)/M(5nm)]·3 annealed at 650^{o}C for different periods of time.

Samples	Saturation magnetization M_s (Am^2/kg)	Coercive force H_c (kA/m)				
	Annealing time (min.)	Annealing time (min.)				
	10	20	30	10	20	30
[NdFeB(180nm)/Cu(5nm)]·3	76	80	85	670	856	723
[NdFeB(180nm)/Nb(5nm)]·3	73	78	80	537	630	580
[NdFeB(180nm)/NbCu(5nm)]·3	74	79	82	1002	1150	988

One can see that for all the samples annealed at 650^{o}C, for different periods of time, the optimal magnetic properties are obtained for an annealing time of 20 min., and the better results were obtained for NdFeB(180nm)/NbCu(5nm)]·3 film.

For the understanding of the additions effect on the physical and microstructural properties of the NdFeB, the TEM analyses were performed. The figures 1 (a) – (d) show the TEM micrographs of NdFeB(60nm), Cu(5nm)/NdFeB(60nm)/Cu(5nm), Nb(5nm)/NdFeB(60nm)/Nb(5nm) and NbCu(5nm)/ NdFeB(60nm)/NbCu(5nm) thin films annealed at 650^{o}C for 20 min.

The TEM micrographs of NdFeB, Cu/NdFeB/Cu, Nb/NdFeB/Nb films (Fig. 1-(a)-(c)) reveal a grain structure with irregular shapes. The average grain size of the NdFeB film is of about 50 nm, while those of the Cu/NdFeB/Cu film is of about 30 nm. The average grain size of the Nb/NdFeB/Nb film (about 60 nm) is larger than that of the NdFeB film. The TEM micrograph of NbCu/NdFeB/NbCu film (Fig.1d) reveals a fine nanocrystalline structure with approximately spherical grains and the average grain size of about 25 nm. It should be observed that simultaneous adding of Cu and Nb in the Cu/Nb ratio of 1/3 to the NdFeB film is effective to reduce the grain size of NdFeB.

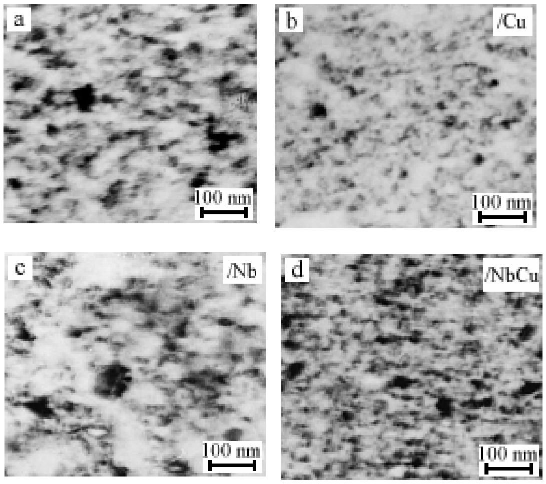

Fig. 1. TEM micrographs of NdFeB (a), Cu/NdFeB/Cu (b), Nb/NdFeB/Nb (c) and NbCu/NdFeB/NbCu (d) thin films, annealed at 650^{o}C for 20 min.

As-deposited NdFeB and [NdFeB(180nm)/NbCu]·3 samples were annealed, in vacuum, for different periods of time, at temperatures between 400^{o}C and 750^{o}C. The X-ray diffraction patterns show that the NdFeB and [NdFeB/NbCu]·n samples, in as-deposited state and after thermal treatment at temperatures below 550°C, have an amorphous structure. After annealing at temperatures over 550°C, the NdFeB and [NdFeB/NbCu]·n thin films undergo a transition from amorphous to crystalline structure and the main diffraction peaks are identified as corresponding to $Nd_2Fe_{14}B$ tetragonal phase. For annealing temperatures around 650°C, the grains reach an average size of about 30 nm and some Nb- and Cu- secondary phases appear. In Figs. 2 (a) and (b) are presented the X-ray diffraction patterns of NdFeB(540nm) film (Fig.2a) and [NdFeB(180nm)/NbCu(5nm)]·3 film (Fig. 2b), in as - deposited state and after annealing at 650°C, for 20 min.

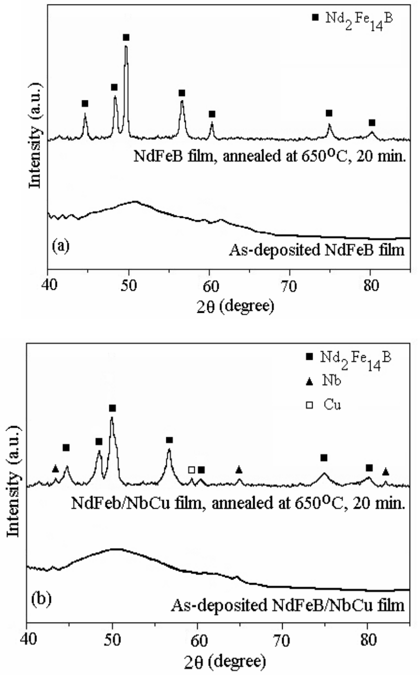

Fig. 2. X-ray diffraction patterns of NdFeB(540nm) film (a) and [NdFeB(180nm)/NbCu(5nm)]·3 film (b), in as - deposited state and after annealing at 650°C, for 20 min.

The average grain sizes obtained from X-ray diffraction data, are of about 55 nm for NdFeB(540nm) film and of about 30 nm for [NdFeB(180nm)/NbCu(5nm)]·3 film and these big values, as compared with the data performed from TEM analyses, are due to the more thickness of NdFeB layer of about 540 nm.

Several buffer layers such as Nb, Ta and NbCu have been used between the NdFeB and silicium substrates to improve the NdFeB thin films magnetic properties. In same time, several capping layers have been used to outside protect the NdFeB films. The buffer and capping layers protect the NdFeB alloy from oxidation by the oxigen in oxide form on silicium substrates and the oxigen traces from vacuum atmosphere, both during the film deposition and its annealing.

For the multilayerd Si/N(20nm)/[NdFeB/M]·n/N(20nm) structure the best results were obtained when the NbCu with a thickness of about 20 nm is used as buffer and capping layers.

In Table 2 the comparative results concerning the hard magnetic properties NbCu(20nm) /[NdFeB(180nm)/NbCu(tnm)]·3/NbCu(20nm) multilayer films with different thickness (t) of NbCu spacer layer, after annealing under vacuum at temperature of 650°C, for 20 min, are shown. One can see that the better magnetic properties were obtained for annealed NbCu(20nm)/[NdFeB(180nm) /NbCu(tnm)]·3/NbCu(20nm) film having the thickness of the NbCu spacer layer of about 3 nm.

As compared with annealed NbCu(20nm)/NdFeB(540nm)/NbCu(20nm) film, for NbCu(20nm) /NdFeB(180nm)/NbCu(3nm)]·3/NbCu(20nm) film one can notice that after annealing at 650°C, for 20 min., the coercive field H_c reached the value of about 1510 kA/m, possible due to the domain wall pinning effect, the saturation magnetization M_s of about 67.5 Am^2/kg due to enhancing of the crystalline structure of the $Nd_2Fe_{14}B$ crystalline grains and the remanence ratio M_r/M_s of 0.80 as a consequence of the "clean" grain boundaries [6].

Table 2. The magnetic properties of the NbCu(20nm)/NdFeB(540nm)/NbCu(20nm) and NbCu(20nm)/[NdFeB(180nm) /NbCu(tnm)]x3/NbCu(20nm) films with different thickness for spacer layer.

Sample / (with the thickness of the layers in nm)	Saturation magnetizationM_s (Am^2/kg)	Coercive force H_c (kA/m)	M_r/M_s
NbCu(20)/NdFeB(540)/NbCu(20)	98	955	0.60
NbCu(20)/[NdFeB(180)/NbCu(3)]·3/NbCu(20)	67.5	1510	0.80
NbCu(20)/[NdFeB(180)/NbCu(5)]·3/NbCu(20)	65	1353	0.50
NbCu(20)/[NdFeB(180)/NbCu(6)]·3/NbCu(20)	56	959	0.45
NbCu(20)/[NdFeB(180)/NbCu(10)]·3/NbCu(20)	44	923	0.44

Because the microstructure for NbCu(5nm)/$Nd_{12}Fe_{82}B_6$(60nm)/NbCu(5nm) film which is presented in Fig. 1d, shows that the crystalline grains is not very good formed, and the statification procedure for preparation of the NbCu(20)/[NdFeB(180)/NbCu(3)]·3/NbCu(20) structure is difficult, further the materials used as additions M such as Nb and Cu were added at NdFeB alloy by their disposing on the NdFeB target's surface (Nb 6.7% Nb and Cu 2.1% from total NdFeB target surface), in view to obtain the structure Si/N(20nm)/[NdFeBM(540nm)/N(20nm), with M = NbCu.

In Table 3 the comparative results concerning the hard magnetic properties of N(20nm)/[NdFeBNbCu(540nm)/N(20nm) films annealed under vacuum at 650°C, for 20 min, and with different materials N as buffer and capping layers, are shown.

Table 3. The hard magnetic properties of N(20nm)/[NdFeBNbCu(540nm)/N(20nm) films annealed at 650 ^oC, for 20 min, with different N materials as buffer and capping layers.

Sample	Saturation magnetizationM_s (Am^2/kg)	Coercive force H_c (kA/m)	M_r/M_s
Nb(20nm)/NdFeBNbCu(540nm)/Nb(20nm)	68	883	0.72
Ta(20nm)/NdFeBNbCu(540nm)/Ta(20nm)	58	1580	0.80
NbCu(20nm)/NdFeBNbCu(540nm)/NbCu(20nm)	70	1468	0.84

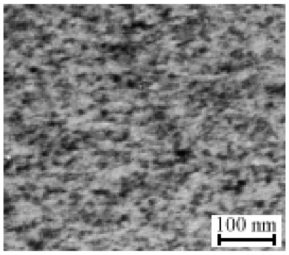

Fig. 3. TEM micrograph of NbCu/NdFeBNbCu/NbCu film annealed at 650 ^oC.

In Table 3 one can see that the Ta(20nm)/NdFeBNbCu(540nm) /Ta(20nm) film presents an enhanced coercivity as compared to the NbCu(20nm)/NdFeBNbCu(540nm)/NbCu(20nm) and Nb(20nm)/NdFeB NbCu(540nm)/Nb(20nm) thin films, but then the saturation magnetization M_s is lower.

In Fig. 3 the TEM micrograph of the NbCu(5nm)/NdFeBNbCu (60nm)/NbCu(5nm) thin film annealed at 650^{o}C, for 20 min., is shown. As compared with the micrograph of the NbCu(5nm)/NdFeB(60nm) /NbCu(5nm) thin film - Fig. 1d., the TEM micrograph of the NbCu(5nm)/ NdFeBNbCu(60nm)/NbCu(5nm) film reveals a fine crystalline structure formed of the rather defined grains and relative uniform distributed.

The average grain size of the NbCu(5nm)/NdFeBNbCu(60nm) /NbCu(5nm) thin film is of about 20 nm, while those of the NbCu(5nm)/NdFeB(60nm)/NbCu(5nm) film is of about 25 nm.

4. Conclusions

We have prepared by vacuum sputtering the NdFeB, N/[NdFeB/M]·n/N and N/[NdFeBM/N thin films with M = Cu, Nb and NbCu as additions and N = Nb, Ta and NbCu as buffer and capping layers and the nanocrystallization process in NdFeB amorphous alloy alloyed with Cu and Nb have bee studied by TEM and magnetic measurements. The hard magnetic properties and microstructure of the multilayer [NdFeB/M]·n thin films strongly depend on the additions content and annealing temperature. The addition of NbCu (with Cu/Nb ratio of 1/3) to the commercial $Nd_{12}Fe_{82}B_6$ alloy shows beneficial effect on microstructure and hard magnetic properties. Other effects as the stratification of NdFeB material and used of NbCu and Ta as buffer and capping layers lead to the enhancing of the microstructure and hard magnetic properties of NdFeB. Samples with the largest coercivity (about 1500 kA/m) have $Nd_2Fe_{14}B$ grain size in the range 20 nm - 30 nm. The Si/NbCu/[NdFeBNbCu(180nm)/NbCu(3nm)]·3/NbCu and Si/Ta/NdFeBNbCu(540nm)/Ta thin films annealed under vacuum at 650^{o}C for 20 min., exhibit an enhanced coercivity of about 1510 kA/m and 1580 kA/m, respectively, in comparison with the NdFeB single layer having the same thickness. Although these two materials have approximate same values for the coercivity and energy product, the simplicity of the preparation procedure for Si/Ta/NdFeBNbCu(540nm)/Ta film recommend this material for to be used as thin - film permanent magnet for different specific applications.

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References

[1] T. Okumoto, K.Yamasawa, X.Liu, M. Matsumoto, A.Morisako, IEEE Trans. Magn .**41**, 3139 (2005).
[2] D. H. Ping, Y. Q. Wu, H. Kanekiyo, S. Hirosawa, K.Hono, Proceedings of the 16th International Workshop on Rare-Earth Magnets and their Applications, September 10-13, Sendai, Japan, 2000.
[3] H. Jiang, J. Evans, M. J. O'Shea, Jianhua Du, J.M.M.M **224**, 233 (2001).
[4] M. Müller, N. Mattern, J.M.M.M.**136**, 79 (1994).
[5] H. P. Klug, L. E. Alexander, in: X ray Diffraction Procedures for Polycristalline and Amorphous Materials, Wiley, New York, (1974).
[6] G. Hadjipanayis, W.Gang, J.Appl.Phys. B4, 1998, pp. 5559

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[*] Corresponding author: urse@phys-iasi.ro