INFLUENCE OF ADDITIONS AND EMBEDDING MODE ON THE HARD MAGNETIC PROPERTIES AND THERMAL STABILITY OF ND-FE-B FILMS

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The paper presents the influence of the Mo and Mo-Cu additions on the magnetic properties and thermal stability of Nd-Fe-B films. The influence of the direct embedding of additions by alloying or indirect embedding by stratification on the physical properties of Nd-Fe-B films is also presented. The Nd-Fe-B films with Mo or Mo-Cu additions present an enhanced coercivity in comparison with the Nd-Fe-B single layer having the same thickness due to the formation of MoB precipitates at grain boundaries, which constitutes pinning centres for the domain walls. Moreover, these films present a reduction in the crystallization temperature of 50°C.

Keywords: Multilayered films; Hard magnetic properties; Additions; Crystallization temperature.

1. Introduction

The Nd-Fe-B thin film permanent magnets have been extensively investigated as promising candidates for magnetic microdevices and actuation components [1]. The addition of different metals with high and low melting points to the ternary Nd-Fe-B alloy is an effective method for improvement of the microstructure and hard magnetic properties. Supplementary, lower crystallization temperature for Nd-Fe-B thin film permanent magnets is desired for applications related to the CMOS technologies.

Many metallic elements with high melting point (such as Nb, Mo, Zr, V, Ti, etc.) and low melting point (such as Cu, Al, Ga, In, Sn) can be added to the Nd-Fe-B system with the aim of enhancing the hard magnetic properties and decreasing the crystallization temperature [2-4]. Among them, Cu is known to act in promoting the formation of nucleation sites, and Mo in decreasing the grain growth and crystallization temperature [2,4]. Supplementary, the Mo addition enhances the corrosion resistance [5] and leads to an almost rectangular demagnetization curve.

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In this paper, some comparative results concerning the influence of the Mo and Mo-Cu additions on hard magnetic properties and thermal stability of the single layer Ta/NdFeBMo(540nm)/Ta thin films and multilayered Ta/[NdFeB(*x*)/MoCu(*y*)]×3/Ta thin films are presented. The influence of the direct embedding of additions by alloying or indirect embedding by stratification in the Nd-Fe-B film volume on their hard magnetic properties is also presented.

For all the samples, the total thickness of Nd-Fe-B layer was of about 540 nm. For multilayered films, the thickness, *x*, of Nd-Fe-B layer was varied from 90 to 540 nm and the thickness, *y*, of Mo-Cu spacer layer was increased in increments of 2 nm from 0 to 10 nm. The samples were sandwiched between two Ta layers with the thickness of 20 nm for the buffer layer and 40 nm for the capping layer.

2. Experimental details

Single layer Ta/[NdFeB(Mo,Mo-Cu)/Ta films and multilayer Ta/[NdFeB (x)/MoCu(y)]×n/Ta thin films have been prepared by vacuum deposition on silicium (111) substrates, at room temperature, using r.f. sputtering technique.

The sputtering targets were mounted on separate guns and consisted of a disc of $Nd_{12}Fe_{82}B_6$ alloy with Nd chips and Mo or Mo-Cu on its surface, a disc of Mo with Cu chips on its surface (surfaces ratio Mo/Cu is 85/15), and a disc of Ta for the buffer and capping layers.

The thickness of the individual layers was verified 'ex-situ" by the KLA Tencor Alpha – Step IQ Profilometer. Thus, the thickness of each layer from multilayer film was controlled during vacuum deposition by controlling the sputtering time.

The crystallographic structure was investigated using X-ray diffraction (XRD) analysis. A X-ray diffractometer (Diffractometer D8 Advance) with a monochromatized Cu-Kα radiation was used, in a Bragg-Brentano arrangement. The Warren-Averbach method [6] was used to estimate the crystalline grain sizes (with an error of about 15%).

The composition of the samples was investigated by a Scanning Electron Microscope (SEM) - JEOL JSM 6390 using Energy Dispersive Spectrometry (EDS) technique.

The morphology of the samples was investigated by Transmission Electron Microscopy (TEM) technique using molybdenum 'microscope grids' covered with C films.

The magnetic characteristics of the samples were determined by a vibrating sample magnetometer (Lake Shore VSM 7410) with a maximum magnetic field of about 3.1 T, applied parallel or perpendicular to the film plane.

The as-deposited samples were annealed in a vacuum atmosphere of 4 x 10^{-4} Pa, for different periods of time at temperatures between 500°C and 650°C, to obtain optimum hard magnetic properties.

3. Results and Discussion

Nd-Fe-B targets with different compositions were tested in view obtaining of single layer Ta/NdFeB(540nm)/Ta films with good hard magnetic properties. The composition of the Nd-Fe-B films was adjusted by changing the numbers of Nd chips on the surface of the $Nd_{12}Fe_{82}B_6$ target. For the Nd-Fe-B thin films, the optimum hard magnetic properties were obtained when the following sputtering target composition was used: disc of $Nd_{12}Fe_{82}B_6$ alloy with the diameter of 7.5 cm having on its surface Nd chips with the area of about 4.9 cm^2. The composition of the Ta(20nm)/NdFeB(540nm)/Ta(40nm) thin film annealed at 650°C for 20 min., detrmined by EDS technique is as follows: Fe 69.63 at.%, Nd 15.02 at.%, Ta 9.43 at.%, and B up to 100 at.%.

The influence of the composition of Nd-Fe-B-(Mo or MoCu) films of the thickness, *x*, of the Nd-Fe-B film and thickness, *y*, of the Mo-Cu spacer layers on the hard magnetic properties of the single layer Ta/NdFeB(Mo or MoCu)/Ta films and multilayered Ta/[NdFeB/MoCu]×n/Ta films, respectively, was studied.

Initially, the effect of the content Mo on the magnetic properties of Nd-Fe-B films was studied. The composition of the Nd-Fe-B-Mo films was adjusted by changing the number of Mo or Mo and Cu chips on the surface of the $Nd_{12}Fe_{82}B_6$ target. Table 1 shows the evolution of the saturation magnetization, M_s, coercivity, H_c, and M_r/M_s ratio (where M_r is remanent magnetization) of the Ta(20nm)/NdFeB(Mo,Mo-Cu)(540nm)/Ta(40nm) thin films annealed at two different temperatures, in function of Mo and Mo-Cu contents.

Good hard magnetic characteristics, especially for the maximum energy product, $(BH)_{max.}$, are obtained for Ta/NdFeBMo(1at.% Mo)/Ta films annealed at 650°C for 20 minutes. It can be observed that by adding 1at.% Mo, the coercivity, H_c, reaches a maximum value of about 22.1 kOe for the samples annealed at 650°C, while a supplementary increase in the amount of Mo of up to 1.7at.% leads to a small decrease of coercivity down to 21.5 kOe. An increase in the maximum energy product value with increasing the Mo content from 0.6at.% up to about 1at.% followed by a decrease for a Mo content of 1.7at.% can be observed for both annealing temperatures.

Table 1.

The Mo and Mo-Cu content dependence of the hard magnetic characteristics of Ta/Nd-Fe-B-(Mo, MoCu)(540nm)/Ta thin films annealed at temperatures of 600°C and 650°C, for 20 minutes

Samples (all the thicknesses of layers are in nm)	Saturation magnetization M_s (emu/g)		Coercivity H_c (kOe)		Remanence ratio M_r/M_s		Energy product $(BH)_{max.}$ (MGOe)	
Annealing temperature (°C)	*600*	*650*	*600*	*650*	*600*	*650*	*600*	*650*
Ta/NdFeB(540)/Ta	94.0	97.8	9.60	14.2	0.77	0.66	3.5	5.5
Ta/NdFeBMo(0.6 at.%)(540)/Ta	65.6	75.0	14.9	16.7	0.82	0.78	2.3	5.7
Ta/NdFeBMo(1 at.%)(540)/Ta	58.0	73.6	15.7	22.1	0.84	0.83	5.6	8.0
Ta/NdFeBMo(1.7 at.%)(540)/Ta	40.0	30.7	20.2	21.5	0.84	0.86	2.3	1.5
Ta/NdFeBMo(1at.%) Cu(0.4at.%)(540)/Ta	38.8	41.5	26.0	26.9	0.74	0.73	2.0	2.3

The decrease of crystallization temperature of Nd-Fe-B thin film permanent magnets is very important for applications. In results presented in Table 1 show that suitable hard magnetic properties are also obtained for Ta/NdFeBMo(1at.% Mo)(540)/Ta annealed at 600°C for 20 minutes.

If Cu is introduced apart from Mo in the volume of the Nd-Fe-B film the main hard magnetic characteristics are altered with the exception of the coercivity, which increases significantly.

At these low Mo or Mo-Cu contents, the compositional control of Nd-Fe-B-(Mo, MoCu) thin films is reduced and therefore it is difficult to obtain homogenous samples with reproducible magnetic and structural properties. To solve this problem, we have prepared and studied Nd-Fe-B thin films stratified with Mo-Cu layers as additions, considering that Cu acts in the sense of promoting the formation of nucleation sites and Mo in the sense of decreasing the grain growth and crystallization temperature [2, 4]. The structure of the multilayered materials, their homogeneity, and reproducibility can be easily controlled during the preparation process by proper arrangement of different layers, proper control of the thickness of the magnetic and non-magnetic layers, and annealing at optimum temperatures.

Initially, Ta/[NdFeB(x)/MoCu(6nm)]×n/Ta multilayer films with different thickness ratios of hard magnetic (Nd-Fe-B) and non-magnetic (Mo-Cu) layers were prepared and studied in order to obtained samples with good and reproducible hard magnetic properties. Figure 1 shows the dependence of the coercivity H_c and M_r/M_s ratio on the thickness (x in nm) of the Nd-Fe-B layers for the Ta/[NdFeB(x)/MoCu(6nm)]×n/Ta multilayer films annealed at 600°C for 20 minutes (n = 6, 3, 2, 0, for x = 90, 180, 270, and 540 nm, respectively).

It can be observed that there is an important increase in the coercivity and M_r/M_s ratio with increasing the thickness of Nd-Fe-B layers up to 180 nm. For thicknesses larger than 180 nm, a gradually decrease in coercivity and M_r/M_s ratio can be observed.

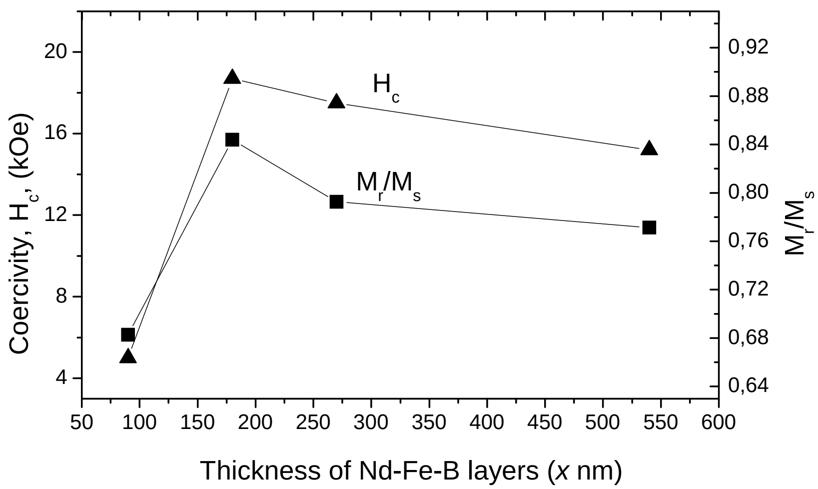

Fig. 1. The dependence of the coercivity, H_c, and M_r/M_s ratio on the thickness (*x*) of the Nd-Fe-B layer for the Ta/[NdFeB(*x*)/MoCu(6nm)]×n/Ta multilayer films annealed at 600°C for 20 minutes

For Ta/[NdFeB(180)/MoCu(*y*)]×3/Ta thin films annealed at 600°C for 20 minutes the composition and thickness, *y*, of Mo-Cu films used as spacer layers were changed in order to optimize their hard magnetic characteristics.

The composition of the Mo-Cu films was adjusted by changing the numbers of Cu chips on the surface of the Mo target. Optimal results were obtained for the following sputtering target composition: disc of Mo with the diameter of 7.5 cm having on its surface Cu chips with the area of about 6.6 cm^2. For this sputtering target, the corresponding composition of Mo-Cu film performed by EDS technique is as follows: Mo 86.09 at.%, Cu 13.91 at.%.

Figure 2 shows the dependence of the coercivity and M_r/M_s ratio on the thickness, *y*, of the Mo-Cu layers for Ta/[NdFeB(180nm)/MoCu(*y*)]×3/Ta multilayer films annealed at 600°C for 20 minutes.

It can be observed that the highest value of coercivity and M_r/M_s ratio are simultaneously reached when the thickness of the Mo-Cu layers increases to about 6 nm. A gradual decrease in coercivity and M_r/M_s ratio was noticed when the thickness of Mo-Cu layers is further increased up to 10 nm.

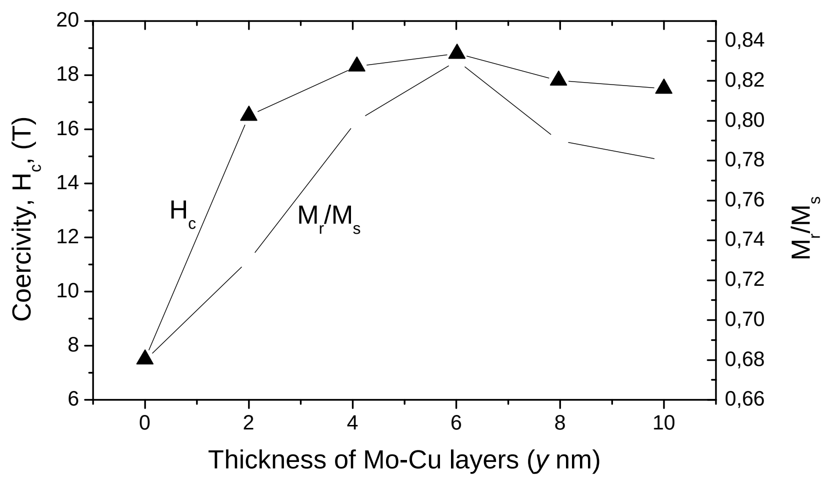

Fig. 2. The dependence of the coercivity and Mr/Ms ratio on the thickness (*y*) of the Mo-Cu layers for Ta/[NdFeB(180nm)/MoCu(*y*)]×3/Ta multilayer films annealed at 600°C for 20 minutes

In order to determine the optimum magnetic parameters after annealing two sets of experiments have been performed: annealing in constant period of time and aneeling in constant temperature. Typical magnetic hysteresis loops for Ta/[NdFeB(180nm)/MoCu(6nm)]×3/Ta multilayer thin films annealed at different temperatures between 580 and 620°C for 20 minutes are shown in Figure 3. It can be observed that the optimum hysteresis parameters are obtained for the samples annealed at temperature of about 600°C for 20 minutes. Considering this optimum temperature/time sequence of annealing, further experiments have been performed by varying the annealing period and keeping the temperature constant.

In Figure 4 the hysteresis loops for Ta/[NdFeB(180nm)/MoCu(6nm)] ×3/Ta thin films annealed at a temperature of 600°C, for different periods of time, are presented. It can be observed that an optimum in the coercivity value is obtained for samples annealed in the same conditions as above, i.e. at 600°C for 20 minutes.

After annealing at 620°C for 20 minutes or at 600°C for 30 minutes, the specific hysteresis loops (Figures 3 and 4) present two shoulders (in the quandrants II and IV), the coercivity slightly decreases and the saturation magnetization slightly increases. These two shoulders are due to the existence of large amount of Fe_2B and Fe_3B crystallites that occur after annealing at temperature of 620°C for 20 min., or after annealing at temperature of 600°C for 30 min.

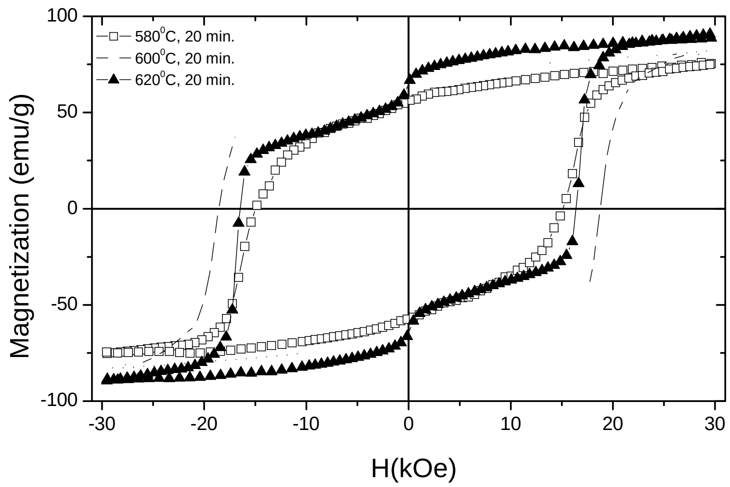

Fig. 3. The magnetic hysteresis loops for Ta/[NdFeB(180nm)/MoCu(6nm)]×3/Ta multilayer thin films annealed at different temperatures between 580 and 620°C, for 20 minutes

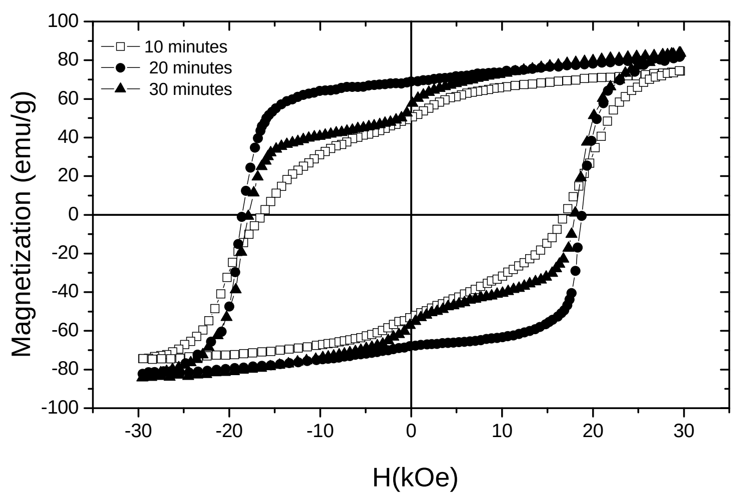

Fig. 4. The hysteresis loops for Ta/[NdFeB(180nm)/MoCu(6nm)]×3/Ta thin films annealed at 600°C, for different periods of time

During the annealing process, the Ta/[NdFeB/MoCu]×n/Ta multilayer thin films are broken and a mixture consisting of hard magnetic and soft magnetic phases is created in different ratios depending on the thicknesses of the constituent layers and on the annealing temperature.

The X-ray diffraction investigation indicates that Ta/[NdFeB/ MoCu]×n/Ta thin films, in as-deposited state and after thermal treatments at temperatures below 500°C, have amorphous structure. At annealing temperatures between 500°C and 580°C, the microstructure of the samples consists of a small number of Fe_2B or Fe_3B dispersed nanograins, which are embedded in the amorphous matrix. Samples annealed at temperatures higher than 580°C exhibit a complex multiphase structure of tens of nanometers.

Figure 5 shows the X-ray diffraction patterns for two different samples after annealing at specific optimum temperatures as follows: Ta/NdFeB (540nm)/Ta thin film (curve a); multilayer Ta/[NdFeB(180nm)/ MoCu(6nm)]×3/Ta films (curve b) after annealing at 600°C for 20 min.

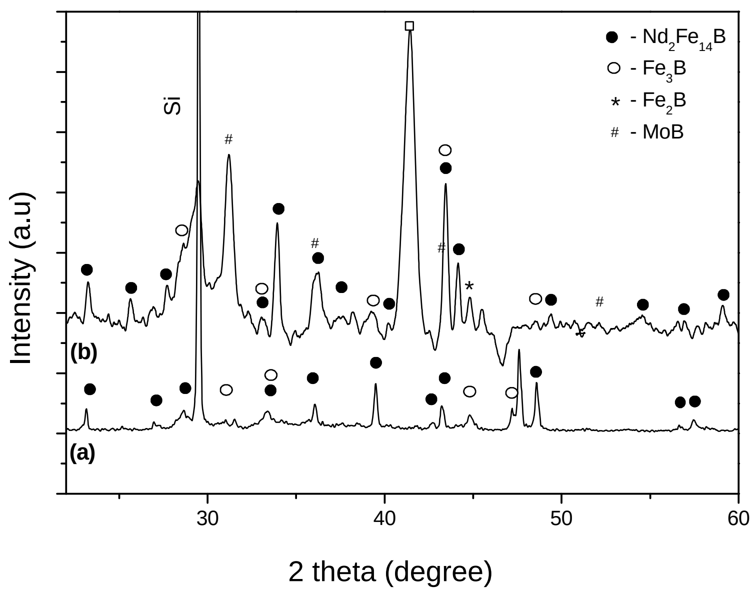

Fig. 5. The X-ray diffraction patterns for: (a) Ta/NdFeB(540nm)/Ta film; (b) multilayer Ta/[NdFeB(180nm)/MoCu(6nm)]×3/Ta film, after annealing at 600°C for 20 minutes

It can be observed that after annealing, the structure of the Ta/[NdFeB(540nm)/Ta thin film consists of nanograins of 2:14:1 hard magnetic phase and Fe_2B soft magnetic phases. The average nanograin size for this sample is in the range of 43-45 nm for the $Nd_2Fe_{14}B$ hard magnetic phase and of about 12 nm for the Fe_2B soft magnetic phase.

The Ta/[NdFeB(180nm)/MoCu(6nm)]×3/Ta multilayer film (curve b) presents a multiphase structure consisting of a mixture of nanograins of 2:14:1

hard magnetic, Fe_3B soft magnetic, and MoB non-magnetic phases. The average grain size is in the range of 30-35 nm for the $Nd_2Fe_{14}B$ hard magnetic phase, 13-14 nm for the Fe_3B soft magnetic phase, and of 18-20 nm for the MoB non-magnetic phase.

The results observed in Table 1 and Figure 2 show that the single layer Ta/NdFeBMo(with 0.6 or 1 at.% Mo)(540)/Ta films and Ta/[NdFeB/MoCu]×3/Ta multilayer films present an enhanced coercivity in comparison with the single layer Ta/NdFeB/Ta films having the same thickness. This is due to the formation of the MoB precipitates at grain boundaries which constitutes pinning centres for the domain walls. This pinning effect can leads to high coercivity of these films.

In order to understand the effect of the Mo-Cu addition on the physical and microstructural properties of the Nd-Fe-B, TEM analyses were performed. Figures 6 a and b show the TEM micrographs of Nd-Fe-B(60nm) film (a), and MoCu(2nm)/NdFeB(60nm)/MoCu(2nm) film (b), annealed at 600°C for 20 min.

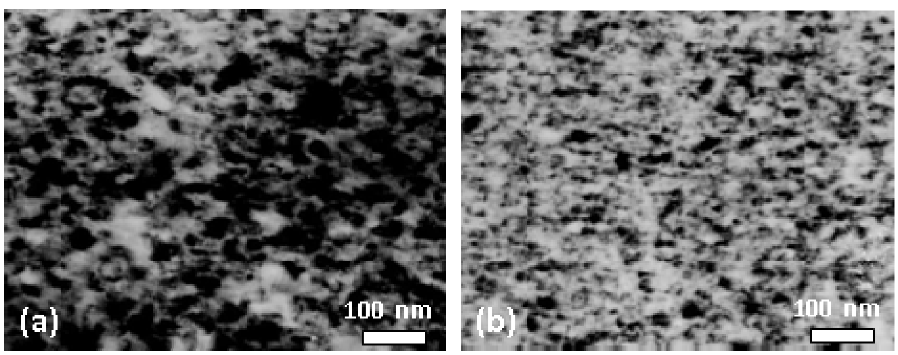

Fig. 6. TEM micrographs of Nd-Fe-B(60nm) film (a) and MoCu(2nm)/NdFeB(60nm)/MoCu(2nm) film (b), annealed at 600°C for 20 minutes

The TEM micrograph of Nd-Fe-B film (Figure 6 a) reveals a grain structure with irregular shapes. The average grain size of the Nd-Fe-B film is of about 50 nm. The TEM micrograph of MoCu/NdFeB/MoCu film (Figure 6 b) reveals a fine nanocrystalline structure with fine and almost spherical grains with an average size of up to about 35 nm.

The results presented in Figures 5 and 6 reveal that the presence of Mo and Mo-Cu addition in the Nd-Fe-B volume refine the grain size of soft and hard magnetic phases.

In Figure 7, the hysteresis loops for Ta/[NdFeB(540nm)/Ta film annealed at 650°C for 20 min., optimal annealing temperature for this film (Table 1), and

Ta/[NdFeBNbCu(180nm)/MoCu(6nm)]×3/Ta thin film annealed at 600°C for 20 min are presented.

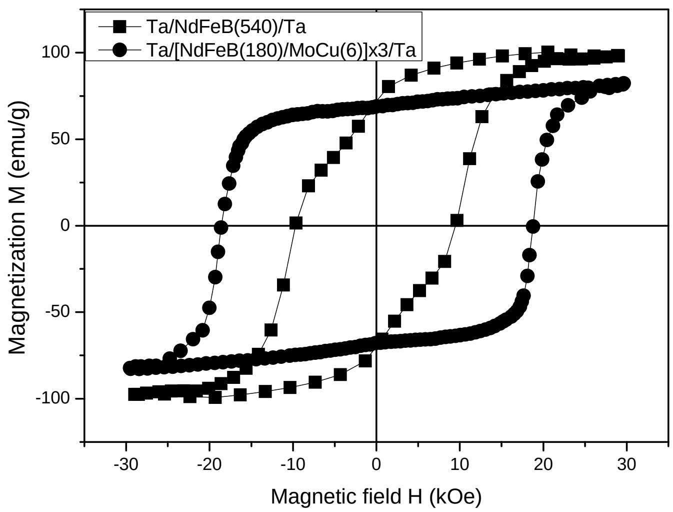

Fig. 7. The hysteresis loops for Ta/[NdFeB(540nm)/Ta film annealed at 650°C for 20 min. and Ta/[NdFeB(180nm)/MoCu(6nm)]×3/Ta film annealed at 600°C for 20 min.

It can be observed that the stratification effect, using Mo-Cu film as spacer layer, has an important influence on the aspect of the hysteresis loop of the Ta/[NdFeBNbCu(180nm)/MoCu(6nm)]×3/Ta thin film, which presents an almost rectangular shape in comparison with the hysteresis loop of the Ta/[NdFeB (540nm)/Ta thin film.

For all samples, a comparative analysis of thermal stability characterized by the losses in coercivity, H_c, and in the remanent magnetization M_r, measured at room temperature (25°C) before (H_{cB}, M_{rB}) and after (H_{cA}, M_{rA}) the samples have been exposed at high temperatures (i.e. 350°C) has been performed. The losses in H_c (L_{Hc}) and M_r (L_{Mr}) were calculated using following equations [7]:

$$L_{H_c} = \frac{H_{cB}(25^o C) - H_{cA}(25^o C)}{H_{cB}(25^o C)} \times 100\%$$

$$L_{Mr} = \frac{M_{rB}(25^o C) - M_{rA}(25^o C)}{M_{rB}(25^o C)} \times 100\%$$

Table 2 presents the losses in H_c and M_r for the addition-free Nd-Fe-B film and Nd-Fe-B films with Mo and Mo-Cu additions. It can be observed that Ta/NdFeB(540nm)/Ta thin film has very low losses in M_r and high losses in H_c. The Ta/NdFeBMo(1at.% Mo)(540nm)/Ta thin film has very low losses in H_c and relatively low losses in M_r. As compared to Nd-Fe-B and NdFeBMo(1at.% Mo) films, the MoCu - containing samples present large values of the losses in H_c, especially in the case of samples containing Mo-Cu embedded in the volume of Nd-Fe-B film.

Table 2

Losses in H_c and M_r of addition-free Nd-Fe-B film and Nd-Fe-B films with Mo and Mo-Cu additions

Samples (all the thicknesses of layers are in nm)	L_{Hc} (%)	L_{Mr} (%)
Ta/NdFeB(540)/Ta	- 5.35	- 0.76
Ta/NdFeBMo(1at.%)(540)/Ta	- 0.31	- 0.46
Ta/NdFeBMo(1at.%)Cu(0.4%)(540)/Ta	- 2.45	- 38.64
Ta/[NdFeB(180)/MoCu(6)]×3/Ta	- 4.31	- 11.84

Analyzing the data in Table 2, it can be observed that the Ta/NdFeBMo(1at.%Mo)(540)/Ta films and the multilayer Ta/[NdFeB(180nm)/MoCu(6nm)]×3/Ta thin films annealed at 600°C for 20 minutes present the most suitable hard magnetic properties for practical applications as thin film permanent magnets.

4. Conclusions

Results on the influence of the Mo and Mo-Cu additions, their embedding mode, and of the thickness of magnetic and non-magnetic layers (for multilayer systems) on the hard magnetic properties of Nd-Fe-B thin films are presented. The Mo addition was found to refine the grain size of soft and hard magnetic phases. Optimal values of maximum energy product have been obtained for a Mo content of about 0.6 at.% after annealing at 600°C for 20 min. and for a Mo content of about 1at.% after annealing at 650°C for 20 min. The stratification of the Nd-Fe-B layer by using Mo-Cu (Mo/Cu ratio of about 85/15) film as spacer layer is effective in reducing the size of the $Nd_2Fe_{14}B$ grains and in improving the homogeneity and reproducibility of Nd-Fe-B samples. For Ta/[NdFeB(180nm)/MoCu(6nm)]×3/Ta thin films, by increasing the annealing temperature from 580 to 600°C, the coercive field increases from 14.8 kOe to 18.6 kOe and the remanence ratio, M_r/M_s, increase from 0.76 to 0.83. For samples annealed around 600°C for 20 min., the $Nd_2Fe_{14}B$ hard magnetic grains reach an optimum size of about 35 nm and also some secondary phases appear. The single layer

Ta/NdFeBMo(with 0.6 at.% or 1 at.% Mo)(540)/Ta films and Ta/[NdFeB(180)/MoCu(6)]×3/Ta multilayer films present an enhanced coercivity in comparison with the Ta/NdFeB(540)/Ta single layer having the same thickness. This is due to the formation of the MoB precipitates at grain boundaries, which constitutes pinning centres for the domain walls. Moreover, as compared to single layer Ta/NdFeB(540)/Ta films which has an optimum crystallization temperature of 650°C, the multilayer [NdFeB(180)/MoCu(6)]×3/Ta thin films present a reduction in the crystallization temperature of about 50°C. This sample also presents an almost rectangular demagnetization curve.

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R E F E R E N C E S

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