Structural and magnetic properties of NdFeB and NdFeB/Fe films with Mo addition

M Urse, M Grigoras, N Lupu and H Chiriac
National Institute of R & D for Technical Physics, 47 Mangeron Blvd.,
700050 Iasi, Romania
E-mail: urse@phys-iasi.ro

Abstract. The influence of the Mo addition on the microstructure and magnetic properties of Nd-Fe-B and Nd-Fe-B/Fe films was studied. The coercivity is a key parameter in the control of technical performances of Nd-Fe-B films. A small amount of about 1 at.% Mo can enhance the coercivity of Nd-Fe-B film by controlling the growth of soft and hard magnetic grains. A coercivity of 22.1 kOe, a remanence ratio, $M_r/M_s$, of 0.83 and a maximum energy product of 8 MGOe were obtained for Ta/[NdFeBMo(1at.%)(540nm)/Ta films annealed at 650°C for 20 minutes due to Mo precipitates formed at the Nd$_2$Fe$_{14}$B phase boundaries which prevent the nucleation and expansion of the magnetic domains. Simultaneous use of Mo as addition and the stratification of Nd-Fe-B-Mo films using Fe as spacer layer are important tools for the improvement of the hard magnetic properties of Nd-Fe-B films. The Ta/[NdFeBMo(1at.%)(180nm)/Fe(1nm)]×3/Ta multilayer film annealed at 620°C exhibits an increase in the coercivity from 12.1 kOe to 22.8 kOe, in the remanence ratio from 0.77 to 0.80, and in the maximum energy product from 4.5 to 7.1 MGOe in comparison with Ta/Nd-Fe-B/Ta film. As compared to Ta/Nd-Fe-B/Ta film, the Ta/[NdFeBMo(1at.%)(180nm)/Fe(1nm)]×3/Ta film presents a decrease in the crystallization temperature of about 30°C.
1. Introduction

The thin-film Nd-Fe-B permanent magnets have been extensively investigated as promising candidates for magnetic microdevices actuation components [1]. Refinement of the Nd-Fe-B films microstructure to less than 40 nm for the hard grains is essential to obtain the high coercivity, $H_c$, and high-energy product, $(BH)_{\text{max}}$. A number of specific factors including sample composition, spacer layer material and annealing temperature can affect the structure of the thin films and its magnetic properties [2]. The addition of different metals with high and low melting points to the ternary Nd-Fe-B alloy is an effective method for microstructure improvement. For thin-film Nd-Fe-B permanent magnets a lower crystallization temperature is desired for applications which integrate such magnets with existing 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 [3]. Among them, Mo is known to act in the sense of preventing the grain growth and decreasing the crystallization temperature [4]. Supplementary, the Mo addition enhances the corrosion resistance [5] and leads to a more rectangular hysteresis loop.

In this paper, we report the influence of the Mo addition on the microstructure and magnetic properties of Nd-Fe-B and Nd-Fe-B/Fe films. For Ta/[Nd-Fe-B-Mo/Fe(t)]×n/Ta films, the thickness (t) of Fe spacer layers was varied from 1 to 3 nm. For all multilayered samples the total thickness of the Nd-Fe-B-Mo layers was maintained at about 540 nm. All the samples were sandwiched by two Ta layers with the thickness of 20 nm for the buffer layer and 40 nm for the capping layer.

2. Experimental details

Ta/Nd-Fe-B/Ta and Ta/[Nd-Fe-B-Mo/Fe]×n/Ta multilayer films have been deposited by r.f. sputtering and electron beam evaporation (i.e. Fe film) on silicium (111) substrates, at room temperature. The sputtering targets were mounted on separate guns and consisted of a disc of Nd$_{12}$Fe$_{82}$B$_6$ alloy with Nd and/or Mo chips on the surface and a disc of Ta for the buffer and capping layers. The thickness of the individual sputtered layers was measured ‘ex-situ’ by the KLA Tencor Alpha – Step IQ Profilometer and ‘in-situ’, during the deposition process, by a quartz-crystal deposition monitor (FTM 6 Film Thickness Monitor) having a resolution of about 0.1 nm.

The crystallographic structure was investigated using X-ray diffraction (XRD) analysis. A X-ray diffractometer (Diffractometer D8 Advance) with a monochromatized Cu-K$_\alpha$ 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 ±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 molibdenum ‘microscope grids’.

The magnetic characteristics of the samples were determined by a vibrating sample magnetometer (Lake Shore VSM 7410) with a maximum magnetic field of about 31 kOe applied parallel with the film plane. The as–deposited samples were annealed in 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

Different compositions of Nd-Fe-B target were tested in view of obtaining the Ta/NdFeB(540nm)/Ta thin 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. The optimum hard magnetic properties of Nd-Fe-B thin films were obtained when the following configuration of sputtering target 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 a total area of about 4.9 cm$^2$ and B chips with the a total area of about 5.3 cm$^2$. The composition of Ta(40nm)/Nd-Fe-B(540nm)/Ta(20nm) film obtained by EDS technique is as follows: Fe 69.63 at.%, Nd 15.02 at.%, Ta 9.43 at.% B up to 100 at.%.
Different Mo contents were tested in order to obtained samples with good hard magnetic properties. Table 1 shows the evolution of the main magnetic characteristics of Ta(20nm)/Nd-Fe-B-Mo(540nm)/Ta(40nm) films annealed at two different temperatures as function of Mo content.

**Table 1.** The Mo content dependence of the magnetic characteristics of Ta/Nd-Fe-B-Mo(540nm)/Ta thin films annealed for 20 minutes at 620°C and 650°C.

| Samples/ (all the thicknesses in nm) | Saturation magnetization $M_s$ (emu/g) | Coercivity $H_c$ (kOe) | Remanence ratio $M_r/M_s$ | Energy product $(BH)_{max}$ (MGOe) |
|-------------------------------------|--------------------------------------|------------------------|--------------------------|----------------------------------|
| NdFeB(540)                          | 94.0                                 | 70.1                   | 62.0                     | 50.0                             |
| NdFeBMo(0.6 at.%)(540)              | 97.8                                 | 75.0                   | 73.6                     | 55.0                             |
| NdFeBMo(1 at. %)(540)               | 121                                  | 19.1                   | 16.9                     | 22.4                             |
| NdFeBMo(1.7 at. %)(540)             | 14.2                                 | 16.7                   | 21.1                     | 22.1                             |

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

In Figure 1 the typical magnetic hysteresis loops for Ta/(NdFeB)$_{1-x}$Mo$_x$(540nm)/Ta thin films annealed at temperatures of 650°C for 20 minutes are presented.

**Figure 1.** Typical magnetic hysteresis loops for Ta/(NdFeB)$_{1-x}$Mo$_x$(540nm)/Ta thin films annealed for 20 minutes at 650°C.

It can be observed that in samples with a small Mo content (i.e. about 0.6 at.%), annealed at 650°C for 20 minutes, the soft and hard magnetic phases coexist. This fact is confirmed by two small shoulders in the II and IV quadrants. By increasing the Mo content over 0.6 at.%, the soft phase (i.e. Fe$_2$B, Fe$_3$B) amount is reduced and a good control on Nd$_2$Fe$_{14}$B grain growth is obtained. For samples with a Mo content higher than 0.6 at.%, the saturation magnetization decreases and the coercivity increases due to the domain wall pinning effect as a result of the Mo-based precipitated fine grains at the Nd$_2$Fe$_{14}$B boundaries. The optimum magnetic characteristics are obtained for Nd-Fe-B films with a Mo content of about 1 at. %.
The X-ray diffraction investigations indicate that Ta/NdFeB/Ta and Ta/[NdFeBMo/Ta thin films, in as–deposited state and after thermal treatments at temperatures below 500°C, have amorphous structure. For samples annealed at temperatures between 500°C and 560°C, the microstructure of the samples consists of a small number of Fe$_2$B or Fe$_3$B nanograins embedded in an amorphous matrix. Figure 2 shows the XRD patterns for Ta/NdFeB(540nm)/Ta film (curve a) and Ta/NdFeBMo(1at.%)(540)/Ta film (curve b), after annealing for 20 minutes at 650°C.

![Figure 2. The X-ray diffraction patterns for Ta/NdFeB(540nm)/Ta film (curve a) and Ta/NdFeBMo(1at.%)(540)/Ta film (curve b), after annealing at 650°C for 20 minutes.](image)

All the samples annealed at temperatures higher than 580°C exhibit a complex multiphase structure of tens of nanometers: Ta/[NdFeB(540nm)/Ta film annealed at 650°C, for 20 minutes (curve a), shows nanograins of Nd$_2$Fe$_{14}$B hard magnetic phase and Fe$_2$B soft magnetic phase. The average grain size is in the range of 43-45 nm for the Nd$_2$Fe$_{14}$B hard magnetic phase and of about 12 nm for the Fe$_2$B soft magnetic phase; Ta/NdFeBMo(1at.%)(540nm)/Ta multilayer film (curve b) presents a multiphase structure consisting of a mixture of nanograins of hard magnetic Nd$_2$Fe$_{14}$B, soft magnetic Fe$_2$B and non-magnetic MoB, phases. The average grain size for Ta/NdFeBMo(1at.%)(540nm)/Ta multilayer film is in the range of 30-35 nm for the hard magnetic Nd$_2$Fe$_{14}$B phase, of 13-14 nm for the soft magnetic Fe$_3$B phase and of 18-20 nm for the non-magnetic MoB phase.

TEM analyses were performed in order to understand the effect of the Mo addition on the physical and microstructural properties of the Nd-Fe-B. Figure 6 (a, b) shows the TEM micrographs of NdFeB(60nm) and NdFeBMo(1at.%)(60nm) films annealed at 650°C for 20 min.

The TEM micrograph of Nd-Fe-B film (figure 3a) 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 NdFeBMo(1at.%)(60nm) film (figure 3b) reveals a fine nanocrystalline structure with fine and almost spherical grains having an average size of about 35 nm.

From the analysis of the structural and morphological data it results that the Nd-Fe-B samples with a Mo content of about 1 at.% present a uniform distribution of grains with an average size of about 35 nm. As compared to Nd-Fe-B films, the NdFeBMo(≥1 at.%)(60nm) films (see the Table 1) exhibit higher values of the coercive field due to the domain wall pinning effect within the intergranular region.

The coercivity is one of the key factors controlling the properties of nanocomposite materials. For multilayer [NdFeBMo(Fe)x]n samples, the soft Fe grains act as nuclei for the formation of magnetic domains during the magnetization reversal. The dependence of the magnetic characteristics on the thickness (t) of Fe layers for Ta/[Nd-Fe-B-Mo(1at.%)/Fe(t)]xn/Ta films annealed at different temperatures between 600°C and 650°C, for 20 minutes is presented in Table 2.
Optimum hard magnetic characteristics, especially for maximum energy product, are obtained for Ta/[NdFeBMo(1at.%)(180nm)/Fe(1nm)]x3/Ta thin films annealed for 20 minutes at 620°C. From the analysis of the thermal treatment data presented in Table 2, it can be observed that the use of Fe film as spacer layer with a thickness of about 1nm takes down the optimal crystallization temperature of Ta/[NdFeBMo(1at.%)(180nm)/Fe(1nm)]x3/Ta films with about 30°C.

Figure 3. TEM micrographs of NdFeB(60nm) and NdFeBMo(1at.%)(60nm) films annealed at 650°C for 20 minutes.

Table 2. The dependence of the magnetic characteristics on the thickness of Fe layers for Ta/[Nd-Fe-B-Mo(1at.%)/Fe(t)]xn/Ta films annealed for 20 minutes at different temperatures between 600°C and 650°C.

| Samples / (all the thicknesses in nm) | Coercivity $H_c$ (kOe) | Remanence ratio $M_r/M_s$ | Energy product $(BH)_{max}$ (MGOe) |
|-------------------------------------|------------------------|--------------------------|----------------------------------|
|                                     | Annealing temperature (°C) | Annealing temperature (°C) | Annealing temperature (°C)       |
| NdFeB Mo(540)                       | 15.7                   | 16.9                     | 22.1                             |
|                                     | 600                    | 620                      | 650                              |
| [NdFeBMo(180)/Fe(1)]x3              | 20.9                   | 22.8                     | 24.8                             |
|                                     | 600                    | 620                      | 650                              |
| [NdFeBMo(180)/Fe(2)]x3              | 20.4                   | 26.7                     | 25.5                             |
|                                     | 600                    | 620                      | 650                              |
| [NdFeBMo(180)/Fe(3)]x3              | 23.9                   | 24.5                     | 14.7                             |
|                                     | 600                    | 620                      | 650                              |
|                                     | 3.7                    | 5.8                      | 8.0                              |
|                                     | 6.4                    | 7.1                      | 2.8                              |
|                                     | 2.7                    | 1.1                      | 2.0                              |
|                                     | 2.6                    | 3.1                      | 1.2                              |

In Figure 4, the magnetic hysteresis loops for Ta/[NdFeBMo(1at.%)(540nm)/Ta single layer and Ta/[NdFeBMo(1at.%)(180nm)/Fe(t)]x3/Ta multilayer films with different thickness, t, of Fe spacer layer, annealed for 20 minutes at 620°C, are presented.

Figure 4. The magnetic hysteresis loops for Ta/[NdFeBMo(1at.%)(180nm)/Fe(t)]x3/Ta thin films with different thickness, t, of the Fe spacer layer, annealed for 20 minutes at 620°C.
The optimal magnetic properties are obtained for Ta/[NdFeBMo(1at.%) (180nm)/Fe(1nm)]×3/Ta film with a thickness of the Fe spacer layer of about 1 nm. It is clear that the Ta/[NdFeBMo(1at.%) (180nm)/Fe(1nm)]×3/Ta film with a Mo content of 1 at.% and multilayered with a Fe thinner soft magnetic layer may be available for the formation of nanostructure more favourable for exchange coupling between the soft and hard phases.

4. Conclusions

The influence of the Mo addition on the structural and magnetic properties of Nd-Fe-B-Mo and [NdFeBMo/Fe]×n thin films has been investigated. The Mo addition refines the grain size of soft and hard magnetic phases. The optimum magnetic properties such as, coercivity $H_c = 22.1$ kOe, remanence ratio $M_r/M_s = 0.83$ and maximum energy product $(BH)_{max} = 8$ MGOe are obtained for Ta/NdFeBMo (1at.%) (540nm)/Ta films annealed at 650°C for 20 minutes.

Simultaneous utilization of Mo as addition and Fe film as spacer layer is important for the enhancement of the hard magnetic characteristics of Nd-Fe-B films. As compared to Ta/NdFeB(540nm)/Ta single layer annealed at 620°C, the Ta/[NdFeBMo(1at.%) (180nm)/Fe (1nm)]×3/Ta multilayer film annealed at 620°C exhibits an increase in the coercivity from 12.1 kOe to 22.8 kOe, in the remanence ratio from 0.77 to 0.80, and in the maximum energy product from 4.5 to 7.1 MGOe. The Ta/[NdFeBMo(1at.%) (180nm)/Fe(1nm)]×3/Ta multilayer films exhibit a decrease in the crystallization temperature of about 30°C in comparison with Ta/NdFeBMo(1at.%) (540nm)/Ta thin film.

By analyzing the presented results it can be seen that the Ta/[NdFeBMo(1at.%) (180nm)/Fe(1nm)]×3/Ta multilayer films are interesting as actuation elements for magnetic microdevices.

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