Thin Solid Films 665 (2018) 68–74

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# Layering influence on Nd agglomeration and hard magnetic properties of Mo/NdFeB/Mo thick films

M. Grigoras, F. Borza*, M. Urse, G. Stoian, G. Ababei, N. Lupu, H. Chiriac

*National Institute of Research & Development for Technical Physics, 700050 Iasi, Romania*

ARTICLE INFO

*Keywords:*
Thin films
Thick films
Nd-Fe-B compound
Agglomeration
Hard magnetic properties
Out-of-plane anisotropy
Multilayers

ABSTRACT

The hard magnetic characteristics of the Nd-Fe-B films deteriorate and the c-axis alignment of anisotropic $Nd_2Fe_{14}B$ hard magnetic grains tends to be deviated from the out-of-plane orientation when thickness of the films increases over a critical value. At the same time, a Nd agglomeration effect was found in the Nd-Fe-B layer volume, which is accentuated by the increase in the treatment temperature and is stronger when the Nd content is higher. In order to prevent these drawbacks we have divided the Nd-Fe-B thick films in a number of *n* NdFeB(*x* nm)/Mo(5 nm) bilayers using molybdenum (Mo) film as interlayer. The variable thickness, *x*, of the Nd-Fe-B magnetic layers along with the annealing conditions (temperature and time) influences both the microstructure and the hard magnetic characteristics of Nd-Fe-B thick films. Single-layer and multilayer Nd-Fe-B films of various total thickness ranging between 540 nm and 1620 nm, have been deposited by vacuum r.f. sputtering on a (001) silicon (Si) substrate heated at about 470 °C. The resulted multilayer Nd-Fe-B thick films with a total thickness of about 1620 nm (three times higher than 540 nm thin film), stratified in 9 sequences - NdFeB(180 nm)/Mo(5 nm) bilayers and annealed for 40 min at low temperature (550 °C) exhibit coercive field and remanence of the same order of magnitude with the single-layer anisotropic Nd-Fe-B thin films having the thickness of about 540 nm. At the same time, these multilayer Nd-Fe-B thick films preserve the out-of-plane anisotropic character and present a 26% increased maximum energy product as compared to the single-layer Mo/NdFeB(540)/Mo thin films.

## 1. Introduction

Thick film permanent magnets with out-of-plane texture of $Nd_2Fe_{14}B$ grains have many applications in micro-electromechanical devices, millimeter-sized actuators and magnetic sensors [1]. For these type of applications, the use of Nd-Fe-B thick films with large maximum energy product $(BH)_{max}$ is essential. A large $(BH)_{max.}$ can be obtained in anisotropic Nd-Fe-B magnet when the remanence ($M_r/M_s$ ratio) and coercive field ($H_c$) take high values [2,3]. However, when the thickness of Nd-Fe-B films increases, the coercive field is altered and the c-axis alignment of $Nd_2Fe_{14}B$ hard magnetic grains tends to be deviated from the out-of-plane orientation [4,5]. Therefore, keeping unaltered the hard magnetic characteristics of Nd-Fe-B films when the thickness of the film increases is a challenge.

The improvement of coercive field value for Nd-Fe-B thick films has been achieved by the addition of heavy rare earth (RE) such as Dy, and Tb or by the partition of the magnetic thick film using Tb layer [2,5]. Due to the increasing cost and scarcity of heavy RE elements, the development of other ways to improve the hard magnetic characteristics of Nd-Fe-B thick films was stimulated [3]. Many authors have replaced these expensive heavy RE by increasing the Nd content over the value taken in the stoichiometric composition ($Nd_{12}Fe_{82}B_6$) [2,7,8]. It was reported that the high value of coercive field is due to a very good coverage of $Nd_2Fe_{14}B$ grains by the Nd-rich material favoured by the high Nd content as well as by the extrusion of Nd-rich material through the $Nd_2Fe_{14}B$ grains. After thermal annealing, the Nd was found to diffuse into the Nd-Fe-B layer volume, predominantly towards the capping layer, where bumps are formed [9]. Generally, the coercive field, reduced remanence, and out-of-plane texture of the Nd-Fe-B films can be optimized by a good control of thermal treatments, a suitable stratification of Nd-Fe-B film [10–13], and also by the use of suitable materials for the layers which are adjacent to the Nd-Fe-B magnetic film.

In our previous work [13,14] we have reported preliminary results to demonstrate that the afore mentioned magnetic characteristics of Nd-Fe-B thin films can be improved by using thin Mo layers as buffer layer, interlayer and capping layer, since it was found that the Mo layer is a useful tool to promote the growth of the $Nd_2Fe_{14}B$ phase with out-of-plane orientation [15,16], to protect the Nd-Fe-B film from oxidation originating from a substrate reaction, to improve the adhesion to Si, to

* Corresponding author.
*E-mail address:* fborza@phys-iasi.ro (F. Borza).

https://doi.org/10.1016/j.tsf.2018.09.008
Received 13 December 2017; Received in revised form 5 September 2018; Accepted 5 September 2018
Available online 07 September 2018
0040-6090/ 

prevent the interdiffusion at the interface regions, as well as to decrease the crystallization temperature of the $Nd_2Fe_{14}B$ hard magnetic compound [12,13,17].

In order to (i) preserve the hard magnetic characteristics of the Nd-Fe-B films while the thickness of the film increases from thin to thick, (ii) to ensure a more uniform distribution of Nd in the whole volume of the Nd-Fe-B thick film as well as (iii) to avoid the bumps formation at the surface of the film due to Nd diffusion, we present a systematic study of Nd-Fe-B thick layers partitioned into convenient thinner layers using Mo films as interlayers, concurrently with the application of an appropriate heat treatment. The influence of the thickness, *x*, of the magnetic Nd-Fe-B component layers, as well as of the annealing temperature and time on the microstructure and hard magnetic characteristics of anisotropic multi-layered Nd-Fe-B thick films is investigated.

## 2. Experimental details

Standard vacuum deposition r.f. and d.c. sputtering techniques were used to prepare Nd-Fe-B thin and thick films in single-layer and multilayer variant on commercially available (001) silicon (Si) wafers precutted into 5 × 5 mm chips. Mo films were deposited by d.c. sputtering, while Nd-Fe-B films were deposited by r.f. sputtering. The base pressure in the vacuum chamber was close to $8 \times 10^{-6}$ Pa. The argon pressure was kept at 0.7 Pa during sputtering deposition. The Si substrates were cleaned in vacuum for 30 min by r.f. sputtering before deposition.

The steps for the preparation by vacuum depositions of the Nd-Fe-B thin and thick films, in single-layer and multilayer variant, were as follows: (i) a Mo film with a thickness of about 40 nm, used as buffer layer, was deposited on the Si substrate which was kept at room temperature (RT) during deposition; (ii) a simple Nd-Fe-B film -for single-layer variant, or alternating Nd-Fe-B/Mo bilayers (*n* times) - for multilayer variant, were deposited on the *Si substrate/Mo buffer layer* ensemble heated at 470 °C (optimum deposition temperature established in our previous work [13]); (iii) the *Si substrate/Mo buffer/NdFeB film - for single-layer or (NdFeB/Mo)xn - for multilayer variant* ensemble was cooled down to RT, and then a Mo film with a thickness of about 20 nm, used as capping layer, was deposited.

The thickness of Mo film used as interlayer for multilayer variant was 5 nm (which was found to be the optimum interlayer thickness [13]).

For all studied samples, the thicknesses of the component layers (buffer and capping layers, interlayer, and Nd-Fe-B magnetic layer) are given in nanometers (nm).

The as-deposited samples have been annealed in high vacuum ($2 \times 10^{-5}$ Pa) at different temperatures ($T_{ann.}$) between 500 and 650 °C for 20 and 40 min.

A quartz-crystal deposition monitor (FTM 6 Film Thickness Monitor) with a resolution of about 0.1 nm was used 'in-situ' during the deposition processes in order to establish the deposition rate of each material (Nd-Fe-B and Mo). At the end of each deposition stage, the thicknesse of the single-layer film or the total thickness of multi-layered films have been further measured 'ex-situ' using a KLA Tencor Alpha - Step IQ Profilometer.

In order to determine the density of Nd-Fe-B film, two witness samples of 540 nm and 1620 nm have been deposited on identical precutted cips. The weight of Nd-Fe-B samples has been determined using a Mettler Toledo microbalance - Model UMX5 Comparator.

A Vibrating Sample Magnetometer (Lake Shore 7410 VSM) with a maximum magnetic field of 2460 kA/m was used for magnetic characterization. The demagnetization factor was not taken into consideration in the measurements. The crystallographic structure was investigated using X-ray diffraction (XRD) analysis. A Bruker D8 Advance X-ray diffractometer with a monochromatized Cu-Kα radiation was used, in a Bragg-Brentano arrangement. The Warren-Averbach method [18] was used to estimate the mean crystalline grain sizes (with an error of ~15%). The morphology, elemental mapping, and microstructure of the samples were analyzed using a Scanning Electron Microscope (SEM - Carl Zeiss Neon 40 EsB CrossBeam - acceleration voltage 0.1–30 kV; resolution 1.1 ÷ 2.5 nm at voltages between 20 kV and 1 kV) and a High Resolution Transmission Electron Microscope (LIBRA 200 Cs-TEM - accelerating voltage: 40 to 200 kV) equipped with an Energy Dispersive X-ray spectroscope (EDX). For cross-sectional TEM and STEM imaging, TEM lamellas were prepared by lift-out method using a Focused Ion Beam system (Carl Zeiss NEON 40 EsB CrossBeam) equipped with micromanipulator and Gas Injection System (GIS). The ion column is working with Ga ions accelerated at 30 kV. The following FIB currents were used: 5 and 2 nA for milling of the thick lamella and rough polishing; 500 pA during lift-out process; 20, 10 and 5 pA for final polishing of the lamella to electron trasparency.

## 3. Results and discussion

The Nd-Fe-B samples deposited on substrates maintained during deposition at room temperature have composition close to 2-14-1 compound, namely $Nd_{12.3}Fe_{81.5}B_{6.2}$.

Both TEM and STEM images show columnar (out-of-plane oriented) $Nd_2Fe_{14}B$ grains, especially for the multilayer structure where the size of the grains is limited by the thickness of Nd-Fe-B component layers (Fig. 1b). The formation of ripples can be observed in the Mo capping layer, this fact being more pronounced for the single-layer Mo(40)/NdFeB(540)/Mo(20) thin films (Fig. 1a). However, what it is important here is that the physical integrity of the Mo capping layer and of the Mo interlayers from the multilayer Mo(40)/[NdFeB(540)/Mo(5)]x3/Mo(20) structure are intact and the interfaces are almost smooth (Fig. 1b) even after heat treatment at 550 °C.

The surface morphology of single-layer and multilayer samples was analyzed by SEM microscopy. Fig. 2(a and b) show the SEM secondary electron plan-view images of annealed single-layer Mo(40)/NdFeB (540)/Mo(20) and multilayer Mo(40)/[NdFeB(180)/Mo(5)]x3/Mo(20) thin films.

It can be observed that the surface of the of the single-layer Mo(40)/

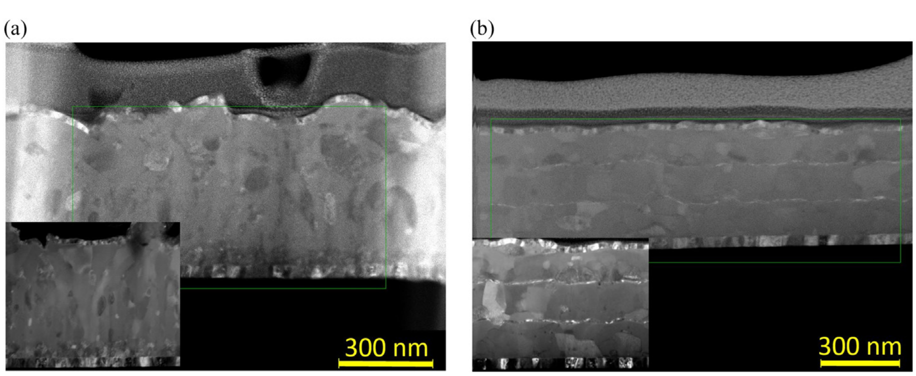


**Fig. 1.** (a and b) presents comparatively the cross-section TEM and STEM (inset) images of single-layer Mo(40)/NdFeB(540)/Mo(20) and multilayer Mo (40)/[NdFeB(180)/Mo(5)]x3/Mo(20) thin films deposited at about 470 °C on heated substrates and subsequently annealed for 20 min. at 550 °C.
(a). TEM and STEM (*inset*) images of the cross section of the single-layer Mo/NdFeB(540)/Mo film (operating voltage 200 kV)
(b). TEM and STEM (*inset*) images of of the cross section of the multilayer Mo/[NdFeB(180)/Mo(5)] x3/Mo film (operating voltage 200 kV)