



XPS and AES investigations of hard magnetic Nd–Fe–B films

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Abstract

Nd–Fe–B is a promising material system for the preparation of thin films with good hard magnetic properties. One problem of this material class is the sensitivity against oxidation, resulting in a degradation of the magnetic properties. Using XPS depth profiling in combination with peak-shape analysis it is shown that already after several hours oxygen can diffuse deep into the thin laser-deposited films and that Nd is mainly responsible for the oxidation. Local element analysis with AES revealed boron inhomogeneities from droplet formation during laser deposition. These problems can be solved by using a capping Cr layer and an FeB target for thin film preparation, respectively.

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1. Introduction

The development of microelectromechanical systems and magnetic recording devices requires hard magnetic films with both high coercivity and remanence. Promising systems are rare earth magnetic materials such as Nd–Fe–B. Bulk magnets with the Nd₂Fe₁₄B phase have a very good energy density, and in highly textured granular films coercivity fields up to 2 T can be reached [1]. However, problems from an unsatisfying corrosion behavior still occur, which is mainly connected with Nd-rich phases used for

decoupling the Nd₂Fe₁₄B phase magnetically [2,3]. In thin Nd–Fe–B films this is much more evident because of the high surface-to-volume ratio [4,5]. The aim of this paper is to study the corrosion process of thin multiphase Nd–Fe–B films in more detail using ion sputtering depth profiling and electron-spectroscopic methods, such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

2. Experimental details

Film preparation was performed in an ultra-high vacuum pulsed laser deposition system (Lambda Physik LPX305, KrF excimer laser, 248 nm, 25 ns, 5 J/cm², 10 Hz, base pressure 10^{–9} mbar). Deposition

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was done from element targets of Nd, Fe, and B, which allows a variation of film stoichiometry. The exact stoichiometry of the films, however, was not known (quantification of the B content is difficult with standard methods as electron microprobe analysis), and a crude optimization of the magnetic properties was obtained simply by variation of the Nd–Fe–B laser pulse ratios. The Nd–Fe–B films of 50 nm thickness were prepared in a previously optimized way for high coercivity and *c*-axis structure (deposition on a Ta buffer of a nominal thickness of 100 nm on Al₂O₃(0 0 0 1), 560 °C [4]) with a significant surplus of Nd to decouple the grains magnetically. After deposition the films were stored in air and the magnetic properties were measured after different storage periods [5]. In the same time scale XPS depth profiling was done at a PHI 5600 CI instrument under typical measuring conditions (3.5 keV, Ar⁺, sputtering rate about 1 nm/min, 58 eV pass energy). In addition, AES measurements were performed in a PHI 660 system with primary electrons of 10 keV, 100 nA and an energy resolution of $\Delta E/E = 0.6\%$. In the AES

depth profiles the samples were sputtered by 1.5 keV argon ions with an equivalent sputtering rate in SiO₂ of about 3 nm/min.

3. Results and discussion

The degradation of the magnetic properties during storage in air up to several weeks can be summarized as following [5]: the out-of-plane coercivity decreases to about 80% after 1 day, to 60% after 1 week and to 30% after 30 weeks. As degradation affects mostly coercivity whereas magnetization and magnetocrystalline anisotropy are almost unchanged, oxidation is believed to form nucleation sites for domain reversal. Because this degradation could be stopped by the implementation of a Cr capping layer (30 nm), an influence of atmospheric oxygen was expected. XPS depth profiling measurements of a non-protected sample prepared parallel to the sample for magnetization measurements after 2, 24, 168, and 672 h (see

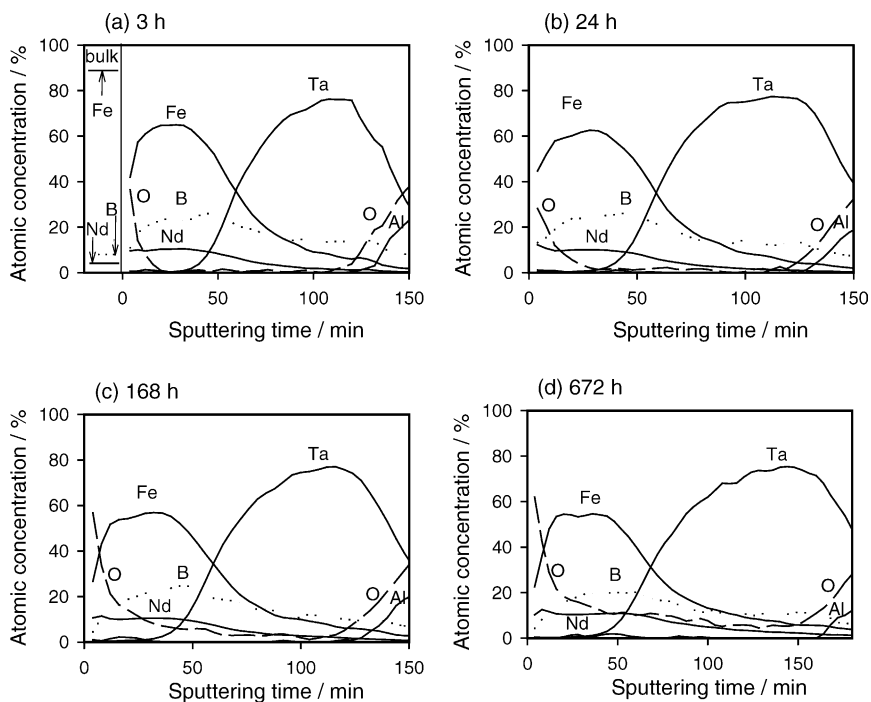


Fig. 1. XPS sputtering depth profiles for 50 nm thick NdFeB films on Ta/Al₂O₃ samples after (a) 2 h, (b) 24 h, (c) 168 h and (d) 672 h storage on air. In (a) is additionally shown the composition measured at an Nd₂Fe₁₄B single crystal measured under the same sputtering conditions. A surplus of Nd (solid line) and still much more of B (dotted line) is visible when the single crystal and film concentration values are compared. The oxygen content increases with the storage time (dashed line).

Fig. 1 with concentration values calculated using standard single elemental sensitivity factors from the PHI-MULTIPAK software) demonstrate that the oxygen content is clearly increased with time and that a diffusion of O into the films is found. For the Nd photoelectron spectra (here Nd 3d) also changes of the peak-shape can be observed. The Fe and B peaks remain fixed at the pure element positions during the depth profile measurements, only at the outermost surface some shifts occurred. No sharp separation between the Nd–Fe–B layer and the Ta-buffer is observed. This is not necessarily connected with interdiffusion, as these granular films exhibit a significant roughness.

To analyze relations between the concentration of the several elements and typical peak-shape changes, factor analysis (implemented in a self-written software package [6]) was used as this method proved to be very helpful for a variety of material classes [6–10]. This method is based on a principal component analysis (PCA). At first, it delivers the number of relevant spectra, which are necessary to describe the measured data satisfactorily. In a second step, the mathematical abstract spectra have to be transformed into realistic spectral shapes, appropriate for the chemical situation in the samples. Afterwards, the corresponding portions of these spectra (usually still named (principal) “components” because originally coming from the PCA), which describe the original depth profile data can be concluded. Results for the Nd–Fe–B films using this method are shown in Fig. 2. Data analysis included both the Nd 3d and O 1s peaks and the data of all four depth profiles in one calculation. This allows us to study typical peak-form and intensity changes in all samples simultaneously. With this one can clearly distinguish between two typical spectral features (see Fig. 2(b)) in the Nd–Fe–B films: metallic Nd (sharp Nd peak and no oxygen, solid line) and an Nd-oxide component (double peak for Nd and high oxygen intensity, dashed line) which shows different depth distributions (see Fig. 2(a)) in the four samples. The complex shape of the Nd component is not typical of metal oxides where mostly a shifted (with respect to the metallic peak) but sharp peak is found (for Nd₂O₃ at about 982 eV [11]). As no reference data for the shape of the Nd oxide peak in Nd–Fe–B are available, the oxide layer from natural oxidation on air of a sample deposited from pure metallic Nd was investigated. After removing the contamination layer

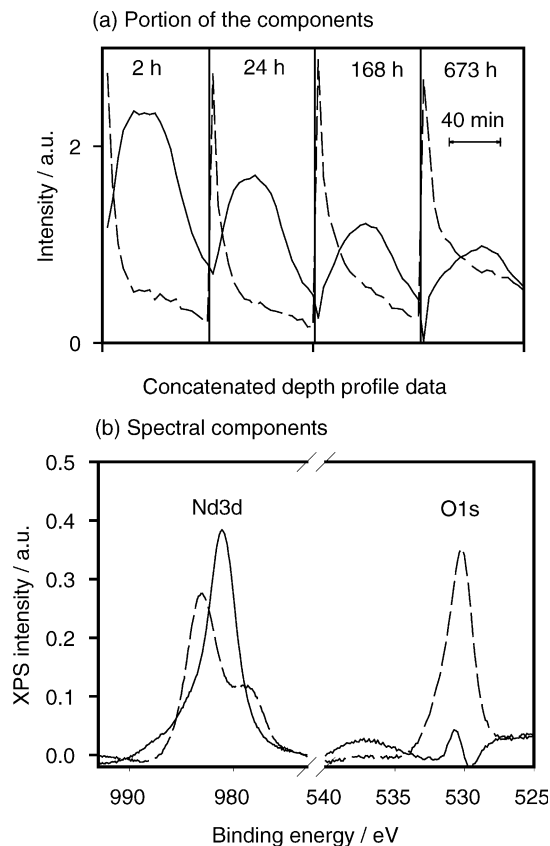


Fig. 2. Factor analysis results for the Nd 3d and O 1s spectral windows from the depth profiles presented in Fig. 1. The four data sets of the four Nd and O depth profiles were concatenated for comparison. Two typical spectral shapes are found in the samples (b) which have different depth distributions (a). The metallic component (solid line) decreases in the samples with the storage time, whereas the oxide component (dashed line) increases.

by ion sputtering (Ar⁺, 1.5 keV, about 1 nm removal) a similar peak-shape for the Nd 3d peak and also exactly the same O 1s peak position are observed as found from factor analysis in the films. The double peak therefore is obviously the effect of the formation of a defect Nd oxide during the sputtering process, which modifies the chemical neighborhood with respect to the oxide state. Similar peak-shape variations of the Nd 3d peak are also found in more complex oxide materials containing additional elements [12,13].

The depth profiles of the metallic Nd and oxide Nd components are plotted in Fig. 2(a). The oxide component decreases for each sample with sputtering

time as expected when oxidation of the film begins at the uncovered surface. The general amount of the oxide component increases with larger storage time in air, whereas the metallic Nd component decreases. For the other elements (Fe, B) no correlations can be observed by factor analysis. Even for the longest time metallic Nd is present, and XRD and magnetic measurements suggest that this Nd is bound within the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase [5]. Thus one can conclude that firstly the intermetallic Nd-rich phase oxidizes.

Nevertheless these Nd–Fe–B films do not exhibit the $\text{Nd}_2\text{Fe}_{14}\text{B}$ stoichiometry (see Fig. 1). A comparison with measurements on an $\text{Nd}_2\text{Fe}_{14}\text{B}$ single crystal under the same sputtering conditions (concentration values of the sputter-cleaned single crystal are given in Fig. 1(a), left) shows that a higher Nd concentration is found in the films, which is in agreement with the Nd surplus intended from preparation. Also an excess in B is observed within the Nd–Fe–B films, and even the B depth distribution extends into the Ta interlayer and the substrate. By AES measurements local inhomogeneities were found in the films (see Fig. 3) which are spherical droplets of different size often found in laser-deposited films [14]. Element maps show that boron is enriched in these regions. Local AES depth profiles recorded in such inhomogeneities and in undisturbed film regions (see Fig. 4) confirm that the droplets consist mostly of B. Even in the undisturbed areas a B surplus in comparison with $\text{Nd}_2\text{Fe}_{14}\text{B}$ material (tested

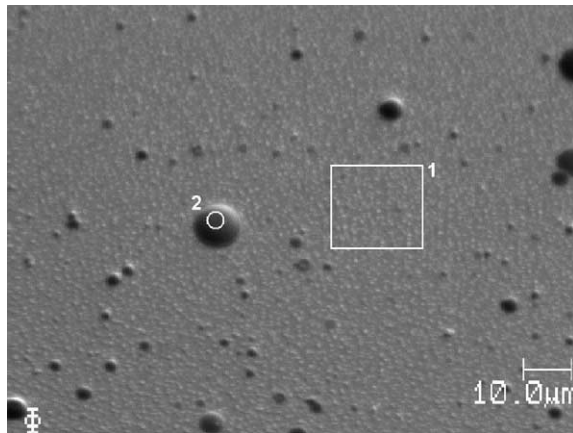


Fig. 3. The secondary electron image taken in the AES instrument shows irregularities with the spherical shape looking like droplets. The measuring areas for the AES depth profile (see Fig. 4 at an undisturbed surface region (1) and a droplet (2) are marked).

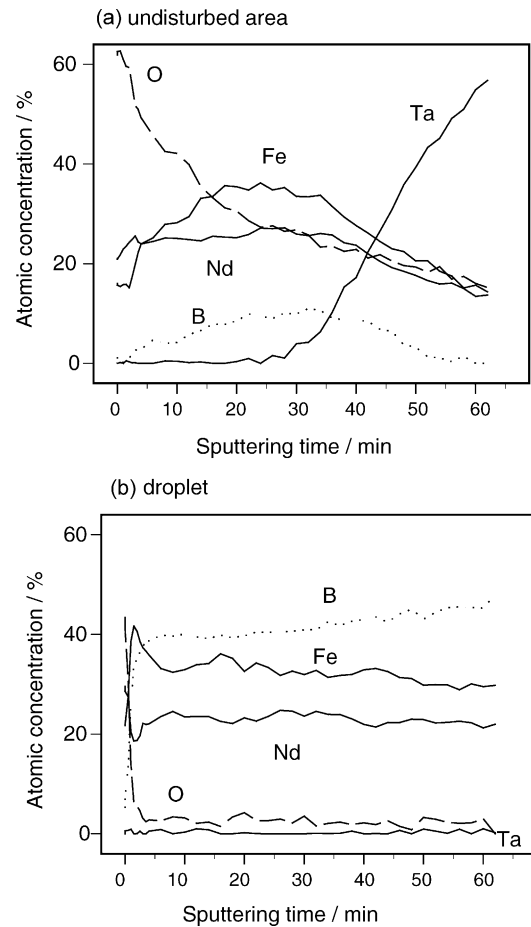


Fig. 4. Comparison of local AES depth profiles measured in an undisturbed region (a) and a droplet region (b) (see Fig. 3 of the Nd–Fe–B film. In the droplet region mainly B is found, which explains the B surplus measured with XPS (see Fig. 1)).

with reference measurements at the single crystal) is found, which points to smaller B droplets which cannot be separated in the AES measurements also in those regions. Because pure boron additionally has a lower sputtering rate than Nd–Fe–B, the observed overestimation is much more evident than expected. Some of the droplets are relatively thick, as can be concluded from their morphology shown in Fig. 3 and from a comparison of the time scales in Fig. 4(a) and (b). Therefore the B signal is measured in the XPS depth profiles up to the substrate level (Fig. 1). The free boron has, however, no negative influence on the magnetic and oxidation properties of the films. Nevertheless, using a dense intermetallic FeB target

instead of a pure B one this droplet formation could be avoided nearly completely.

4. Conclusions

Uncovered hard magnetic Nd–Fe–B films are very sensitive to oxidation in air. XPS depth profiles show that already after several hours oxygen can diffuse deep into the films. Peak-shape analyses of the XP spectra by means of factor analysis demonstrate clearly that the oxidation is mainly connected with the most reactive component (Nd). The existence of an Nd-rich intergranular phase, necessary for magnetic decoupling, accelerates the oxidation process as known from bulk material. The oxidation of the thin films can be prevented effectively by the use of a thin Cr capping layer. AES measurements point to a relative high amount of boron-rich droplets, which does not influence the magnetic properties, but pretends a wrong B behavior in the lateral integrating XPS depth profiles. The droplet formation is now minimized using a FeB target for the film preparation.

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