EXAFS and XANES study of selective oxidation of FeCoZr nanoalloy

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Granular nanocomposite metal-insulator films containing soft ferromagnetic FeCo-based nanogranules are very promising in development of advanced micro-electronic (spintronic) devices for high-frequency applications. The important feature of such granular films is spin-dependent tunneling between metallic nanogranules within percolation regime leading to the negative tunneling magnetoresistance phenomena of a relatively high magnitude. Such an effect has very promising technological applications, i.e. in magnetic recording media and magnetic sensors. It is experimentally proven that physical properties of granular films, apart from chemical composition of nanogranules and matrix, are particularly related to a possible surface oxidation and state of the interface between nanogranules and matrix. The aim of this work is the investigation of the local arrangement of Fe, Co and Zr atoms and study of their oxidation dynamics in Fe₄₅Co₄₅Zr₁₀ nanoalloys deposited by ion-beam sputtering in oxygen-containing atmosphere to obtain metal core-oxide shell nanostructures.

The films were deposited by dc ion sputtering, using 2 keV argon ion gun, at 0.28 nm/s, to a thickness 1–6 μm onto Al and glass–ceramic substrates. Oxygen pressure (P_{O2}) in the chamber in the case of reactive deposition was 4.3 and 9.8 mPa. Sputtering targets were composed of Fe₄₅Co₄₅Zr₁₀ alloy plates covered with strips of CaF₂. In this way, by changing the coverage area, the metal/insulator ratio in the deposited films is modified [1]. Composition of (FeCoZr)ₓ(CaF₂)₁₀₀-x films varies in the range of 27 ≤ x ≤ 74 at.%. XANES and EXAFS measurements were performed at the beamline C of the synchrotron laboratory Hasylab/DESY (Hamburg) using transmission and fluorescence detection [2]. Linearly polarized X-ray radiation from bending magnet was monochromatized with a pair of flat Si (111) and (311) single crystals for Co & Fe K-edges and Zr K-edge, respectively. The absorption profiles were detected probing total fluorescence yield by means of passivated implanted planar Si (PIPS) diode. Analysis of the spectra was performed using the IFEFFIT package [3].

Figure 1: XANES spectra and EXAFS Fourier transforms, χ(R) at the Fe K-edge of (FeCoZr)₇₃(CaF₂)₂₇ films deposited in atmospheres with different oxygen pressure P_{O2}.
EXAFS data of non-oxidized films reveal two types of local ordering. The first one is highly disordered state of Fe and Co local environment in films with x of 28-46 at.%, which is evidenced from the negligible contribution of the second and farther shells to the EXAFS spectra (fig.1). The second one is well ordered arrangement of atoms in subsequent coordination shells of Fe and Co, which confirms a good crystallinity of nanocomposites with x of 58-67 at.%. The latter finding is in agreement with X-ray diffraction data. Bcc structure of metallic alloy (determined by comparing with corresponding references) is typical for these films.

Deposition at low oxygen pressure ($P_{O2} = 4.3$ mPa) leads to a partial oxidation of Fe and very low degree of Co oxidation. This conclusion is drawn from the position of spectral line of the first coordination shell for Fe (see fig.1) and Co edges in the Fourier transformed EXAFS spectra. This can be explained by a higher iron-oxygen affinity as compared with that of cobalt-oxygen. Interestingly, more advanced oxidation of Fe and Co was detected for the film containing 33 at.% of FeCoZr (see fig.2). The effect can be explained by small particle sizes and low amount of metallic fraction at such a small concentration, which make oxidation more effective. Application of higher oxygen pressure ($P_{O2} = 9.8$ mPa) during deposition results in full oxidation both iron (see fig.1) and cobalt, irrespective of film composition.

Analysis of Zr K-edge spectra of the FeCoZr-CaF$_2$ nanocomposites evidences non-metallic Zr state even in films deposited in oxygen-free atmosphere. This could be attributed to the reaction between Zr and F or O that originates from very strong affinity of Zr to these elements (the highest one from Fe, Co and Zr). Non-metallic Zr state, in turn, means that it is more likely localized at the interface between matrix and metallic particles and not incorporated into FeCo-based bcc structure of nanogranules.

![Figure 2: XANES spectra at Fe and Co K edges for (FeCoZr)$_n$(CaF$_2$)$_{100-n}$ films with different compositions deposited at $P_{O2} = 4.3$ mPa.](image)

Thus, the results of the study of FeCoZr-CaF$_2$ films reveal a general tendency of increasing Fe and Co oxidation degree with increasing oxygen pressure at the deposition. High oxygen pressure ($P_{O2} = 9.8$ mPa) is sufficient for full oxidation of particles, whereas lower oxygen pressure ($P_{O2} = 4.3$ mPa) leads to their partial oxidation with possible formation of “metallic core – oxide shell” structure of particles. A thorough oxidation is characteristic for samples with lower x of 30-40 at.%. 

References