X-ray absorption spectroscopy study of granular Fe / Si$_3$N$_4$ systems

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Abstract. [Fe (t Fe) / Si$_3$N$_4$ (3 nm)] multilayers were prepared by sequential magnetron sputtering. The Fe layer thickness has been varied for every sample. Magnetic properties show a gradual evolution from a ferromagnetic state for samples with larger metal thickness to a granular behaviour for the samples with the smallest Fe layer thickness. Microstructural features such as average thickness and granularity, as well as the local order around Fe atoms, were studied by x-ray reflectometry and x-ray absorption spectroscopy, respectively. X-ray reflectometry suggests that the formation of discontinuous metal-insulator multilayers is produced at $t_{Fe} \leq 1.3$ nm. Extended x-ray absorption fine structure (EXAFS) analysis shows a reduction of the Fe-Fe coordination shell as the metal layer thickness decreases. Moreover, a new phase emerges, and it is visible at the samples with $t_{Fe} \leq 1.3$ nm. This coordination shell is attributed to the formation of Fe-N bonds likely placed at the interface regions. X-ray absorption near edge spectroscopy (XANES) shows as well the evolution from the metallic spectrum to a combined contribution of 2 phases as the metal layer thickness decreases. XANES calculations performed within the real-space multiple-scattering formalism of two nanometric phases for metal bcc Fe and tetrahedral FeN in zinc-blende structure provide a successful explanation of the XANES spectral evolution. The appearance of a new phase linked to the interface regions obtained by X-ray absorption analysis suggests the granular morphology of samples with $t_{Fe} \leq 1.3$ nm.

1. Introduction

X-ray absorption spectroscopy (XAS) is a very powerful tool to reveal the structural features at the short range order around an absorbing atom. Its strength as a local probe of the structural features is crucial to consider it a useful technique for materials at the nanoscale, thus helping to determine their physical properties. Extended x-ray absorption fine structure (EXAFS) can determine the local order parameters around the absorbing atom, such as coordination number and distance between atoms. Particularly, in nanosystems, considering the enhanced surface-to-volume ratio, and taking advantage of the loss of average coordination number of atoms at the surface, EXAFS has been proved to be a quite useful tool to estimate the average particle dimensions.[1-3] X-ray absorption near-edge structure (XANES), applied to nanostructured materials, probes any modification of the local geometry and the electronic structure, due to finite size or interface effects. The reduction in number of the ejected photoelectron scattering paths due to the progressive loss of near neighbours and

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changes in the electronic structure in surface atoms modifies as well the XANES spectral shape.[4,5] Recent improvements during the last decade in the computation methods of XANES spectra have led to a qualitative improvement of the feasibility of the near-edge spectra analysis.[6,7]

Magnetic nanostructured systems formed by metal nanoparticles embedded in an insulating matrix are nowadays a topic of intense research, due to their enhanced properties respect to their bulk counterparts, and the appearance of new phenomena related to the nanoscale. Such outstanding properties, including enhanced coercivity or tunnel magnetoresistance, are critically determined by the quality of the metal-insulator interface. The formation of new phases in intermediate regions between metal and ceramic and modifications in the local environment around surface atoms can affect dramatically to the properties of such materials. For instance, it has been recently observed through EXAFS and XANES analysis that granular metal-insulator materials can lead to reduction of the magnetization signal in magnetic particles[8,9] or even to the rise up of magnetization in a priori non-magnetic systems,[10,11] due to the formation of an atomic-scale intermediate phase at the metal-insulator interfaces.

In this work we report on the study of the structural and magnetic properties of high quality Fe / Si$_3$N$_4$ magnetic multilayers. These metal / insulator systems are a very promising material for their potential applications in magnetic recording and spintronics. Special attention has been paid in the transition from continuous ferromagnetic samples to magnetic granular systems. A previous microstructural characterization has been achieved by using x-ray techniques. X-ray reflectometry (XRR) has given information about the microstructural features of the layers, such as thickness and roughness. X-ray absorption spectroscopy (XAS) measurements have been performed to determine the local geometry around Fe atoms. The XAS analysis is mainly focussed in the loss of coordination number and the presence of Fe phases with different environment coming form the interface regions. Results of the structural characterization will be linked to the magnetic properties of the films. Special attention will be devoted to the magnetic transition from ferromagnetic multilayers in percolated systems to granular behaviour presented in discontinuous metal-insulator multilayers.

2. Experimental

Fe / Si$_3$N$_4$ multilayered films were prepared by sequential magnetron sputtering. Details of the deposition process are shown elsewhere.[12] Nominal Fe layer thickness has been varied, form 10 to 0.7 nm in order to observe the transition from continuous to discontinuous metal layers. Once the samples have been deposited, they have been subsequently annealed at 700 °C in a vacuum of ~10$^{-6}$ mbar in order to minimize the presence of intermediate FeN phase at the interface regions and between the clusters.

X-ray absorption spectroscopy measurements at Fe K-edge energies were achieved at the Spanish CRG beamline (SpLine-BM25A) at the ESRF. The electron beam energy of the storage ring was 6 GeV and the average current was around 200 mA. Data were collected in the fluorescence yield mode within the standard 90° set-up. The incoming beam was monitored by a N$_2$ filled ionization chamber, and the Fe K$_\alpha$ fluorescence line was detected using a one element Si(Li) detector (from e2v Instruments). Several spectra were taken in order to obtain a good statistic. EXAFS analysis was performed with the VIPER fitting software, developed by K. Klementiev.[13] The Fourier transforms were obtained from the EXAFS signal using a Hanning window between 3.5 and 12 Å$^{-1}$, and the filtered EXAFS signals result from Fourier transform of the first coordination shells, using another Hanning window between 0.8 and 2.6 Å. Amplitude and phase functions of the coordination spheres were calculated with the FEFF8 code (version 8.4), developed by J. Rehr.[6]

XANES calculations at the Fe K-edge have been achieved using the real-space multiple-scattering formalism of the FEFF8 code. Atomic potentials were approximated by a set of spherically muffin-tin potential, using the Mattheiss prescription,[14] and following the Norman rule for the determination of the atomic radii. Self-consistency to produce ab-initio calculations of the electronic structure is achieved with a cluster size of around 4 Å. A default value of 15 % of overlapping has been imposed to simulate the XANES spectra of the Fe phases. Several energy-dependent exchange correlation
potentials were checked, and the self-energy Hedin-Lundqvist model results to give the best spectrum simulation. Real-space multiple scattering calculations have been performed within the core-hole final-state approximation.

Finally, magnetization loops at room temperature for the series of samples were measured in a SQUID magnetometer (MPMS-5, from Quantum Design).

3. Results and discussion

Figure 1 shows the x-ray reflectivity data from a selection of samples. The actual Fe layer thickness obtained from the analysis is illustrated in the figure. The average roughness for all samples is about 8 Å. The disappearance of the Kiessig fringes is due to the larger total thickness of the samples with smaller Fe layer thickness, in order to preserve the total amount of iron in the samples. It should be remarked the decrease in intensity and increasing broadening of the Bragg peaks for the samples with smaller Fe thickness, probably due to the transition to discontinuous Fe layers for such films, consistent with the relationship between the thickness and the estimated roughness.

![Figure 1. X-ray reflectivity of selected Fe/Si$_3$N$_4$ multilayers.](image)

Figure 2 represent the extended x-ray absorption fine structure (EXAFS) signals (figure 2a), and their corresponding Fourier transforms (FT, see figure 2b) of a set of samples. The corresponding spectra filtered to the first two coordination shells are also shown in Fig. 2a. Results from the analysis of a Fe foil spectrum are used as reference, as well as to determine the inelastic loss factor, $S_0^2$. From the EXAFS analysis, a reduction in the coordination number around iron is observed, resulting in a decrease of the intensity of the first FT peak associated to Fe-Fe coordination, as well as a decrease in the amplitude of the EXAFS signal. This reduction is subtle in the multilayers with larger Fe thickness, but it is appreciable in the loss of neighbours from the first coordination shells in the samples with thinner Fe layers, as obtained from the analysis. This reduction in the number of first and second neighbours, affecting also to all the coordination shells, is typical of nanosystems, due to finite size effects. Estimated values of the structural parameters, obtained from fitting the EXAFS signal, are shown in table 1.

Furthermore, as the decrease of the Fe layer thickness enhances the contribution of the Fe atoms at the interface to the total EXAFS signal, in the samples with the thinnest Fe layers another peak, corresponding to a bond at around 1.9 Å, becomes visible. This peak appears in the two samples with thinnest Fe layers ($t_{Fe} \leq 1.3$ nm). We associate this peak to Fe-N coordination at the interface, and accounting for the Fe-N distance, we can consider a tetrahedral geometry similar to zinc-blende symmetry.[15] The environment of Fe atoms at the interface is different than that of the core, due to a possible diffusion of N inside the Fe layer. This effect becomes more important in such thin layers. From the number of neighbours obtained from the fitting, we consider an appropriate geometrical model to estimate the average dimensions of the clusters,[1,16] directly linked to this parameter,
idealized for spherical clusters. We can then determine that the average size of the particles for the 
t_{\text{Fe}} = 0.7 \text{ nm} gives an average particle diameter around 7 \text{ Å}, in agreement with the nominal thickness, though an underestimation of the average dimension, due to the lack of accuracy in the model for treating big particles,[3] and possible overestimation of the loss of coordination number of atoms in the surface, cannot be ruled out.

Fig. 2. (a) k-weighted filtered EXAFS signals and (b) Fourier transforms of the EXAFS signal of the Fe/Si$_3$N$_4$ series, and their corresponding fittings.

Table 1. Structural parameters obtained by the EXAFS analysis of the Fe/Si$_3$N$_4$ samples. Inelastic factor, $S_0^2$, has been estimated as 0.83.
Figure 3 shows the x-ray absorption near edge spectra (XANES) of the multilayers. A Fe foil reference spectrum has been added for comparison. Results show that the samples with largest Fe layers reproduce the XANES features of the metallic Fe. However, as the Fe layer decreases, subtle differences appear in the spectra. For the two samples with smaller Fe thickness, a slight increase in intensity in the deep at around 7140 eV and a subtle reduction of the broad shoulder centred at 7180 eV is observed. Since such evolution appear for the samples with the thinnest Fe layers, this can be interpreted as an enhanced contribution of the interface Fe atoms, which may present another different local environment. These results are consistent with the EXAFS analysis. The pure metallic component is still the main contribution, but increasing signatures from other local geometries can be detected in the near-edge region for the samples with $t_{\text{Fe}} \leq 1.3$ nm. XANES computations have been performed to interpret the evolution of the near-edge spectra with decreasing metallic layer thickness and a linear combination of the calculated spectra has been represented in order to compare with the granular samples. To account for the loss of coordination number in the nanometric scale and the subsequent reduction of the scattering paths, real-space multiple-scattering calculations have been performed using a cluster of about 4 Å for both the metallic and the nitride phase. Results show that the formation of new features with decreasing Fe layer thickness and the attenuation of others, like for instance the plateau at around 7160 eV, typical of metal bcc-Fe, can be explained by the presence of a secondary FeN phase.

Figure 3. XANES spectra of Fe/Si$_3$N$_4$ multilayers and XANES calculations for nanometric metal Fe (core) and tetrahedral FeN (interface).

Figure 4. Magnetization loops at room temperature of the Fe/Si$_3$N$_4$ multilayers.

Figure 4 shows the magnetization loops at room temperature of three representative samples, with nominal Fe layer thickness of 2.5, 1.3 and 0.7 nm. The sample with the largest Fe layer thickness presents a pure ferromagnetic character, as corresponds to continuous metal layers, being remanence values next to the saturation magnetization. However, as the nominal Fe thickness decreases, a paramagnetic component contribution appears, resulting in a reduction of the remanence and a decrease of magnetization with temperature. This decrease of the magnetization is due to the enhanced contribution of a FeN phase with zinc-blende structure, which is non-magnetic.[15] Furthermore, the sample with $t_{\text{Fe}}=1.3$ nm, which is just below the percolation threshold, seems to present exchange coupling between the Fe clusters, likely supported by interactions with ultrasmall superparamagnetic Fe particles. Finally, the sample with $t_{\text{Fe}}=0.7$ nm presents a remarkable superparamagnetic behaviour, with zero values for coercivity and remanence, though dipolar interactions between the metallic particles cannot be ruled out. This enhanced superparamagnetism is strongly influenced by the discontinuous morphology of the Fe layers, as it was predicted by the structural characterization performed by x-ray techniques.
4. Conclusions
Granular magnetic Fe/Si₃N₄ multilayers have been characterized by x-ray techniques to determine their structure and understand the evolution or their magnetic properties. Several series of samples have been prepared by sequential magnetron sputtering and subsequent annealing, modifying the metallic layer thickness in each sample. X-ray absorption analysis reveals a remarkable reduction of Fe-Fe neighbours, and an increasing contribution different from the pure metallic Fe, attributed to Fe-N coordination, in samples with \( t_{Fe} \leq 1.3 \) nm and increasing as the Fe layer thickness decreases.

From these results, we can deduce that the existence of FeN contribution seems to correspond to an intermediate phase at the metal-insulator interface. This intermediate phase associated to the surface regions of the Fe particles appearing in samples with \( t_{Fe} \leq 1.3 \) nm, together with the noticeable reduction of Fe-Fe coordination number, and supported by x-ray reflectometry results, suggest that such samples present a granular morphology formed by metallic Fe clusters embedded in a ceramic matrix, corresponding to discontinuous metal-insulator multilayers. Magnetic features confirm the granular behaviour of these samples. An enhanced contribution of a superparamagnetic behaviour in the multilayers with \( t_{Fe} \leq 1.3 \) nm has been observed in the magnetization loops, in full agreement with the conclusions obtained from the x-ray reflectometry and x-ray absorption spectroscopy analysis.

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