Materials

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Structural changes of Fe precipitates in annealed Fe-Al_2O_3 films

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We report on the structural changes of Fe-Al_2O_3 films deposited - both co-evaporated and multilayered samples - at room temperature and subsequently annealed at 400°C during 5h. Our results suggest that the Fe precipitates in Al_2O_3 matrix are forming disordered nanoparticles. The discontinuous multilayers presents rather small evolution under annealing whilst the co-evaporated films evolves from an ill ordered to a much better ordered bcc-structure. All samples present a similar super-paramagnetic behavior.

Keywords: Granular metals, multilayers, magnetoresistance. XAS, Fe-Al_2O_3

1. Introduction

Granular metals are composite materials that consist of finely dispersed mixtures of immiscible metals and insulators. The interest for applications of these materials comes from several areas such as microelectronics (as cermets resistors), magnetic core materials, selective solar energy absorbers and more recently as tunnelling magnetoresistive sensors (Sankar et al., 1997), (Shelp et al., 1997). These materials can be prepared by co-evaporation or co-sputtering of immiscible metals and insulators or by post-annealing of deposited discontinuous multilayers (Dieny et al., 1998). By reducing the volume fraction of the metal to the percolation limit, the structure breaks up into isolated metal grains embedded in a dielectric continuum. There is a close relation between all physical properties and the nano-structure of the granular metals. Varying the nano-structure parameters their physical properties can be greatly altered and tailored. We report on the structural changes of Fe/Al_2O_3 films deposited at room temperature and subsequently annealed at 400°C during 5 hours. All samples studied presented super-paramagnetic behavior.

2. Materials and methods

The samples were prepared at room temperature by evaporation of Fe and Al_2O_3 in a dual e-beam system at a base pressure lower than 1×10^{-8} mbar. The rate of deposition, as well as the thickness, was monitored by a computer controlled quartz balance. Two kinds of samples were prepared: a co-evaporated sample, corresponding to 1000 Å of granular metal deposited on 1000 Å of SiO_2 buffer grown on a Si(111) substrate, and a multilayer sample, corresponding to discontinuous multilayer of $[\mathrm{Fe}(10Å)/Al_2O_3(25Å)]_{20}$ deposited on an oxidized Si(111) substrate. Both samples were within the percolation threshold with an overall composition of 52% of Fe, confirmed by Rutherford Backscattering Spectroscopy. As deposited samples were subsequently annealed at 400°C during 5 hours under vacuum better than 1×10^{-7} mbar.

X-ray diffraction analyses were performed in a θ-2θ Bragg-Brentano geometry. Magnetization measurements were obtained using an Alternated Gradient Field Magnetometer. XAS experiments at the Fe K edge were performed at room temperature in total electron yield (TEY) on XAS beam line at LNLS (Tolentino et al., 1998). XANES data were analysed by extracting a base line and normalising the data at 7240 eV. The EXAFS spectra were analysed using Winxas program (Ressler, 1997) and following standard recommendations of the International XAFS committee. The Fourier Transform (FT) of the EXAFS signal were obtained from 4 to 12 $Å^{-1}$ using a Bessel window with a coefficient of 4. Fitting results were obtained by using experimental phase and amplitude functions deduced from standard Co metal.

3. Results and discussion

A broad peak ($\Delta\theta\approx2.6°$) due to Fe(110) reflection was observed in the XRD data for co-evaporated Fe-Al_2O_3 sample. No evidence of Al_2O_3 reflections was observed, indicating that the sample was formed by Fe nanoparticles embedded in the amorphous Al_2O_3 matrix. In fact, all samples presented the same broad peak, characteristic of a truncated periodic structure, suggesting that even the Fe layers are discontinuous and that the particle size does not change very much after thermal treatment. A simple analysis, for the co-deposited samples, using a Scherrer formula gives Fe clusters with a mean diameter of 35 Å, which would correspond, in a close packed structure, to clusters with around 1920 atoms. This result may be an overestimation of the particle size. XRD is not sensitive to smaller clusters because it is necessary at least a few atomic plans to produce a diffraction peak. From the super-paramagnetic behaviour of co-evaporated Fe-Al_2O_3 samples, observed through magnetization measurements, and a fitting using the Langevin function weighted by a log-normal distribution of moments, mean particle sizes of 18 Å and 24 Å were obtained for the as-deposited and treated samples, respectively.

XANES spectra at the Fe K edge for Fe-Al_2O_3 granular and multilayered films (fig.1) present many features similar to bulk Fe-bcc XANES spectrum. The main evolution, when comparing all samples (from treated to as-deposited), is the smearing out of all spectral features. It is interesting to note that in the case of multilayers the as-deposited and treated samples are very similar, whilst in the case of co-evaporated samples the as-deposited presents much more smeared features than the treated one. The Fe K edge EXAFS signals (fig. 2) and Fourier Transforms (fig. 3) in comparison with the pattern of Fe standard metal leads to the same conclusions as the XANES data. The amplitudes of the EXAFS oscillations, and the corresponding Fourier transforms, are significantly reduced in all samples but many of the bcc spectral features are preserved. Thermal treatment induces a better definition on EXAFS oscillations, being much more effective on the co-evaporated sample. Indeed, only the FT of the as-deposited co-evaporated sample does not display higher order shells, indicating an ill-ordered structure within Fe particles. All results discussed above could come from two origins, i) reduced particle size within the amorphous matrix or ii) a large degree of disorder, even in the large particles.

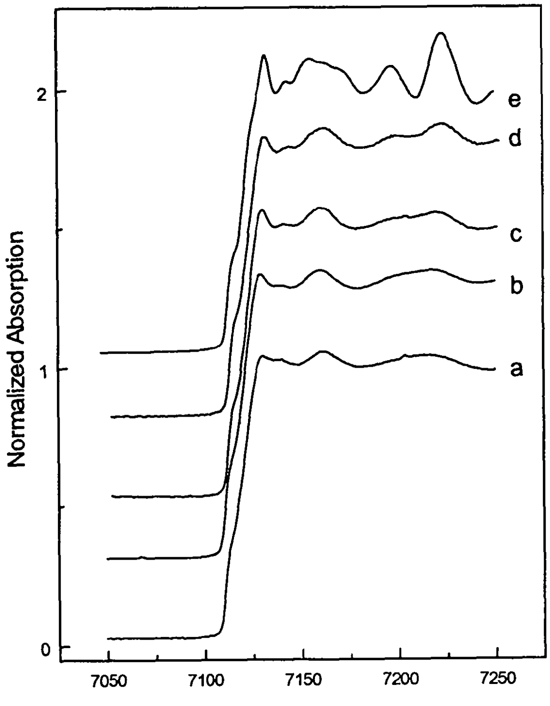

Figure 1
Fe K-edge XANES signal for the Fe-Al_2O_3 : a) co-evaporated as deposited, b) multilayer as-deposited, c) multilayer 400°C/5h, d) co-evaporated 400°C/5h and e) Fe-metal.

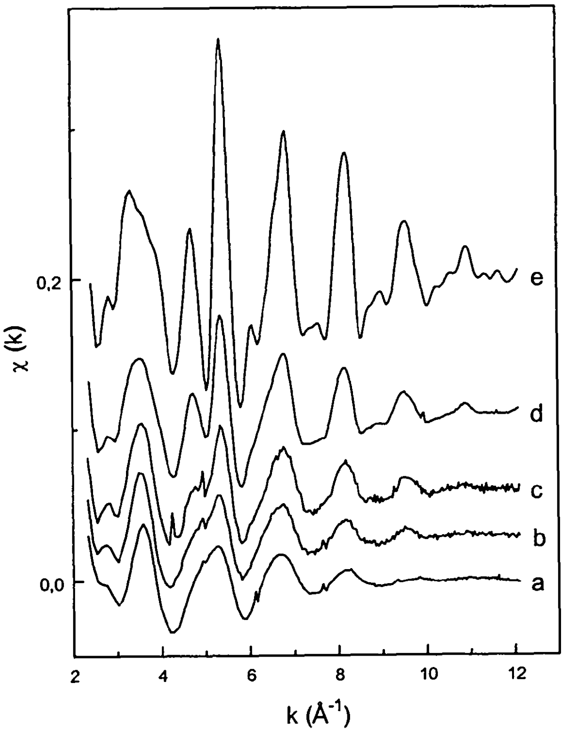

Figure 2
Fe K-edge EXAFS signal for the Fe-Al_2O_3 : a) co-evaporated as deposited, b) multilayer as-deposited, c) multilayer 400°C/5h, d) co-evaporated 400°C/5h and e) Fe-metal.

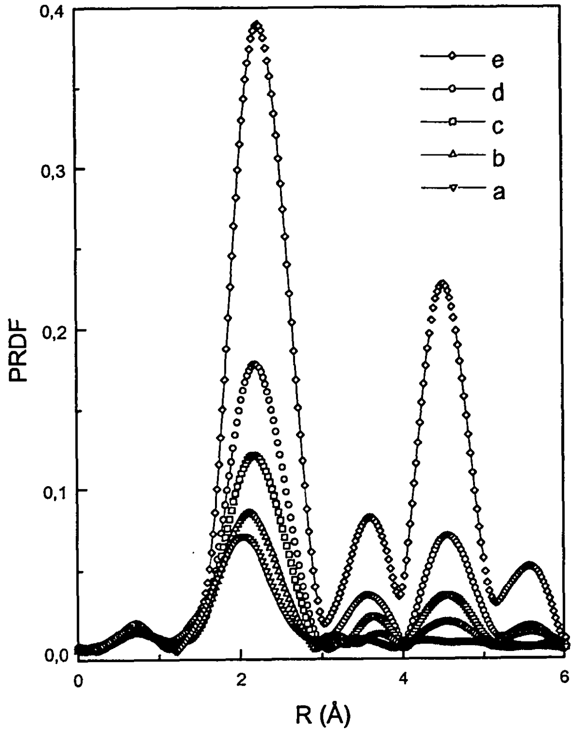

Figure 3
k^3-weighted Fourier Transform of the Fe K-edge EXAFS signal for the Fe-Al_2O_3 : a) co-evaporated as deposited, b) multilayer as-deposited, c) multilayer 400°C/5h, d) co-evaporated 400°C/5h and e) Fe-metal.

Quantitative results were obtained by fitting the first peak of the Fourier Transforms. Fe metal has a bcc structure for which the contributions to the Fourier Transform due to the first and second-neighbour shells cannot be separated (8 at 2.48 Å and 6 at 2.86 Å). Following the procedures adopted by (Traverse et. al., 1994) and (Pizzini et al., 1992), phase shifts and amplitudes extracted from Co metal were used in the analysis for all samples. These phase shifts when used to simulate the spectrum of bulk bcc Fe, gave a first neighbour distance of 2.48±0.02 Å and a second distance of 2.86±0.02 Å, S_0^2 was equal to 1. The inclusion of a second shell was always necessary even in the case of as-deposited samples, which have a large first peak on the Fourier Transform. The obtained parameters are summarised in Table I. Debye-Waller factor represent a relative disorder compared to the standard. For as-deposited samples the relatively high values of the Debye-Waller factor observed indicate the presence of a large static disorder. The coordination numbers and distances remain the same (within error bars) close to the bulk value for the first shell of all samples. In the case of co-evaporated samples the thermal annealing induces a reduction on the static disorder. For multilayers, the Debye-Waller factor remains the same. However, with exception of the annealed multilayer, this reduction is within our experimental error and cannot be estimated.

The values obtained for the second shell of as-deposited samples are more difficult to analyse due to the strong correlation existent between coordination number and Debye-Waller factor. For the annealed samples, where lower Debye-Waller factors are found, there is a reduction on the coordination number. The contraction observed for the second distance remains in the experimental uncertainty. In fact, a reduction of almost 10 % in the

Table 1

Fitting results for the first peak of Fourier Transforms. The fit quality (χ^2) was in the range of 0.5-1. All parameters where allowed to float during the fit.

Samples	N_1	R (Å)	$\Delta\sigma_1^2(10^{-3}Å^2)$	N_2	R (Å)	$\Delta\sigma_2^2(10^{-3}Å^2)$
Fe metal	8	2.48	-1.8±1	6	2.86	-3.2±2
Co-evaporated as-dep	8±0.7	2.45±0.02	9.6±1	6±2	2.65±0.22	27.5±3
Co-evaporated 400 °C	8±0.7	2.48±0.02	3.5±1	4.4±2	2.82±0.03	2.8±2
Multilayer as-dep	8±0.7	2.47±0.02	7.6±1	4.7±2	2.74±0.1	17.7±3
Multilayer 400 °C	8±0.6	2.47±0.03	7.7±1	2.6±2	2.81±0.05	0.3±3

coordination numbers for clusters around 30 Å in diameter would be expected (Di Cicco et al., 1994). The reduction of coordination number comes from surface to volume ratio that is large for small clusters. For multilayers the plate-like clusters have a surface to volume ratio greater than the almost spherical clusters of co-evaporated samples. This should explain why the reduction of coordination number is more evident for the annealed multilayer than for annealed co-evaporated samples.

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