	Experiment title: Metal nanocluster formation in silica glass films by rf co-sputtering technique: an EXAFS study	**Experiment number**: 08-01-205
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Report:

The aim of this experiment was to determinate the local order around the metallic species forming cluster in silica glass films, the sample are prepared by rf-sputtering deposition. Sputtering deposition technique is particularly suitable for co-depositing the matrix together with more than one dopant element. The deposition of the samples was performed by means of a radio frequency sputtering apparatus. The residual pressure, before deposition, was about 2×10^{-7} mbar. The substrates used in each deposition run were silica slabs (25×75 mm^2 size). The sputtering was carried out for 3 hours with an ultra pure Ar gas at a pressure of 7×10^{-3} mbar; the applied rf power was 150 W with a reflected power of 18 W. The deposition was carried out by putting on the target disk of silica (100 mm diameter) some pieces of the different couples of metals (Au-Cu, Au-Ag, Cu-Ag). After the deposition, the samples were heat-treated in air for 1 hour at 250 ¡C in order to remove defects. X-ray absorption spectroscopy was performed at Cu and Ag K-edges, and at Au L_{III}-edge in order to determinate the local order around the dopant species; due to the sample dilution X-ray fluorescence yield detection was used. Data analysis was performed by Fourier filtering and multiparameter fit of first coordination shell in R-space; theoretical scattering amplitudes and phases were generated using the FEFF8 code in the hypothesis of fcc solid solution of binary alloy of AuAg, CuAg and AuCu for the respective samples. Figure 1 shows the moduli of Fourier transform at the three edges for the samples together with the ones from pure Au, Cu and Ag foils measured in transmission mode. For all samples, the

samples, a refinement of the fitting procedure was performed, considering a non Gaussian distribution of interatomic distances; it was necessary to introduce the third cumulant C_3 since the Gaussian model lead to unphysical low values of bond lengths. In particularly in the case of AuAg systems, since lattice parameters of metallic Au and Ag are the same within 1/100 , diffraction techniques are not suitable to evidence Au:Ag alloy, because of the peak broadening peculiar of such small clusters; on the contrary, EXAFS spectroscopy can easily distinguish the two species from the different backscattering amplitude functions. In conclusion, in all the systems EXAFS analysis evidences the presence of alloy nanoclusters and, in particular, the formation of thermodynamically unfavorable mixtures in the case of CuAg systems.

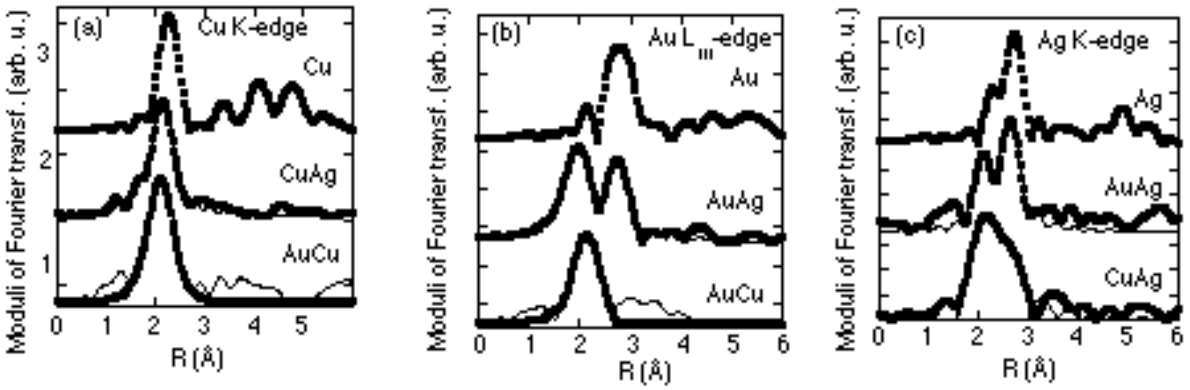

Fig.1. Moduli of Fourier transform of EXAFS spectra (dots: experimental, solid line: fit), compared with the respective standard spectrum at (a): Cu K-edge, (b): Au L_{III}-edge, (c): Ag K-edge.

sample	edge	couple	R ( )	N	σ^2 (10^{-3} ^{2})	C_3 (10^{-4} ^{3})
Cu bulk	K		2.5561	12	4	-
Au bulk	L_{III}		2.8837	12	4	-
Ag bulk	K		2.8894	12	4	-
AuCu	Cu K	Cu-Cu	2.54–0.02	0.8–0.4	5–3	-
		Cu-Au	2.64–0.02	4–1	15–1	-
	Au L_{III}	Au-Cu	2.64–0.02	5.7–0.9	15–1	-
CuAg	Cu K	Cu-Cu	2.51–0.04	9–3	16–4	11–10
		Cu-Ag	2.70–0.04	1.5–0.5	4–2	11–4
	Ag K	Ag-Cu	2.70–0.04	2.0–0.6	4–2	11–4
		Ag-Ag	2.87–0.14	3–5	17–19	-
AuAg	Au L_{III}	Au-Au	2.74–0.04	6–2	12–3	18–7
		Au-Ag	2.93–0.13	1.4–0.4	10–9	75–6
	Ag K	Ag-Au	2.93–0.13	2–3	10–9	41–19
		Ag-Ag	2.81–0.10	3–2	11–3	-

Table I. Results of the EXAFS analysis: first shell distance, coordination number, Debye-Waller factor and third cumulant values are shown.

Publications

S. Padovani, F. D'Acapito, E. Cattaruzza, F. Gonella, A. De Lorenzi, P. Mazzoldi, G. Mattei, C. Maurizio, M. Ferrari, M. Montagna, S. Ronchin and C. Tosello, "Metal nanocluster formation in silica films prepared by rf-sputtering: an experimental study", Eur. Phys. Jour. B, in press.