Report of the experiment 08-01-677: *Gold and erbium local environment in co-doped glasses for optoelectronics*

The x-ray absorption spectra were recorded for a set of Er+Au implanted silica samples (as-implanted and annealed up to T=800ºC) at both Er and Au L_{III}-edges; due to low dopant concentration, they were collected in fluorescence mode (by a 13-element high purity Ge detector), while the spectra of metallic Au and of Er_2O_3 crystalline powder were measured as standard references in transmission mode; all the samples were cooled at liquid nitrogen temperature to reduce the atomic thermal vibrations. Data analysis was carried out by FEFF8-FEFFIT package [ankPRB90,feff8]: for the analysis of the Au-edge (Er-edge) spectrum, the muffin tin potentials for the calculation of the Au-Au and Au-O (Er-O) scattering phase shifts and amplitude were calculated starting from a the structure of an Au or Au_2O_3 cluster (Er_2O_3 cluster); the analysis was based on a multiparameter fit in R-space of the Au-Au and Au-O correlations for the Au-edge spectrum and of the Er-O correlation for the Er-edge one.

Local structure around Au atoms.

The EXAFS spectra collected from the samples are reported in Fig. 1a and compared with the reference spectrum of the metallic Au. For the spectra of the samples annealed at 600 and 800 ºC one oscillation extending at least up to k=12 Å^{-1} is evident, that makes the spectra similar to that one of the Au foil; the sample heated at 400 ºC and the as-implanted samples give spectra similar one to each other, characterized by a low-frequency oscillation dumped in the high-k region. In Fig. 2a the k^3-weighed Fourier transform spectra are shown and compared with the relative fit of the Au-Au and Au-O coordinations: it is evident that the increase of the annealing temperature determines an increase of the peak located at R =2.5-3 Å and, starting from the sample heated at 400 ºC, a decrease of the amplitude of the peak located at R≅2.8 Å. The quantitative analysis showed that this last peak indicates an Au-O correlation, while the other an Au-Au one; the two coordinations are present in all the samples except for the sample heated at 800 ºC, where only the metallic coordination was detected. This last fact indicates that, within the experimental uncertainty, in that sample all the Au atoms are aggregated in clusters and the fraction of Au atoms that remain dispersed into the matrix is negligible. In general, the coordination number N of the metallic shell can be reduced with respect to the bulk one (12 for an fcc structure) both because of the cluster size (i.e. of the fraction of atoms that are on the cluster surface) and because of the fraction f of atoms that are dispersed into the matrix and oxidized. If Nc(D) is the average coordination number expected for atoms that constitute a cluster of diameter D, N=Nc(D)*(1-f). As already noted, for the sample heated at 800 C f=0, and so from the measured coordination number of the metallic shell, one can estimate the average cluster size, that for a fcc structure with the measured interatomic distance is about 1 nm (Nc(1 nm)=6.4) [friZFP93]. It is interesting to notice that for this sample the interatomic distance is about 2% shorter than the corresponding value of the bulk phase: this is consistent with the presence of small Au clusters, that are known to exhibit a contraction of the interatomic distances [marPRB90,balPRB85,dagPRB93]. As a comparison, Au clusters of 1.1 nm deposited on mylar exhibit the same 2% contraction of the Au-Au interatomic distances [balPRB85]. By decreasing the annealing temperature the contraction is larger and larger (up to 5% for the as-implanted sample), indicating that the average size of the aggregates

decreases. This picture is further supported by the lack of significant correlation peaks at distances larger than that one described for the samples heated up to 600 ºC. Correspondingly, the Au coordination number decreases (see Fig. 2b) and an Au-O coordination is present (more evident for the as-implanted and 400 ºC-annealed sample), related to the fraction of Au atoms that are dispersed into the matrix and correlated with O atoms.

Finally, the mean-square relative displacement for the Au-Au shell is larger than the bulk reference one for which we measured $\sigma^2 = (33\pm1) \ 10^{-4} \ \text{Å}^2$.

About the Au-O coordination, the interatomic distance varies from 1.94 Å and 2.02 Å, i.e. in the range of the first Au-O shell in the Au_2O_3 crystal (the first 6 O atoms around Au are located in the range 1.93-2.90 Å). Other considerations will be reported in a dedicated paper.

Table 1. Results of EXAFS analysis: coordination number N, interatomic distance R, and MSRD σ^2 for the Au-O and Au-Au coordination. Metallic Au crystallographic data are reported in brackets for comparison. The annealing temperature labels the samples.

	Au-O			Au-Au		
	N (±0.1)	R (±0.02) (Å)	σ^2 ($\pm30\%$) ($\times10^{-4}\text{Å}^2$)	N (±0.2)	R (±0.01) (Å)	σ^2 ($\pm30\%$) ($\times10^{-4}\text{Å}^2$)
As-implanted	1.1	2.02	51	0.8	2.73	56
400	1.3	1.96	51	1.2	2.74	56
600	0.5	1.94	51	3.7	2.79	75
800	-	-	-	6.7	2.81	75
Au foil				(12)	(2.88)	

Local structure around Er atoms.
The EXAFS spectra collected from the samples are reported in Fig. 1 and compared with the reference spectrum of the Er_2O_3. In all the spectra from the samples only one main oscillation is evident, that corresponds to the peak located at about R = 1.5 Å in the Fourier transform modulus, reported in the Fig. 2. The quantitative EXAFS analysis has found that the first shell of atoms around Er is composed of O atoms in all the analyzed samples. Moreover, the absence of significant correlation signal beyond the first shell indicates a disordered environment around Er. The EXAFS analysis is still in progress, anyway some considerations can be made. Preliminary results indicate that the Er-O distance of the Er1000 sample (Er-implanted silica annealed at 1000C) is (2.28±0.02) Å, comparable with the corresponding distance in the Er_2O_3 standard reference (where the average value is 2.27 Å), while for all the other samples is lower, as already reported in previous EXAFS analysis of Er-implanted silica systems [OptMat2004]. The fact that the Er-O distance is lower than the corresponding value for the Er-oxide could likely indicate that in these samples no extended Er-oxide phases are present, as also suggested by the absence of long-range order correlations.
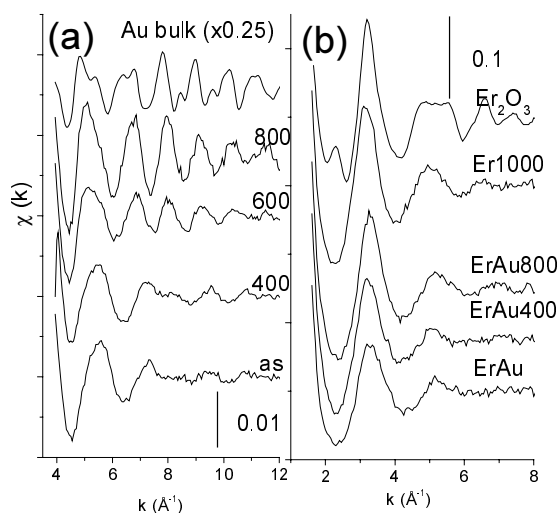
Fig. 1. (a) EXAFS spectra recorded at the Au L_{III}-edge of the samples, compared with the spectrum of metallic Au. (b) EXAFS spectra recorded at the Er L_{III}-edge of the samples, compared with the spectrum of Er_2O_3 crystalline powder.
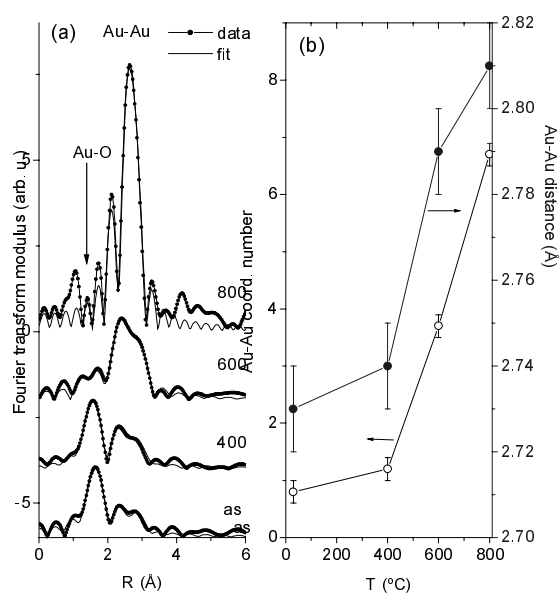

Fig. 2. (a) Amplitude of k^3-weighted Fourier transform of the EXAFS spectra of the samples (markers) and relative fits (solid line) of the Au-O and Au-Au coordination. The transformation range is k = 4-14 Å^{-1} for the sample annealed at 800 ºC and k=4-11 Å^{-1} for all the others. (b) EXAFS results on the coordination number and interatomic distance for the Au shell as a function of the annealing temperature.
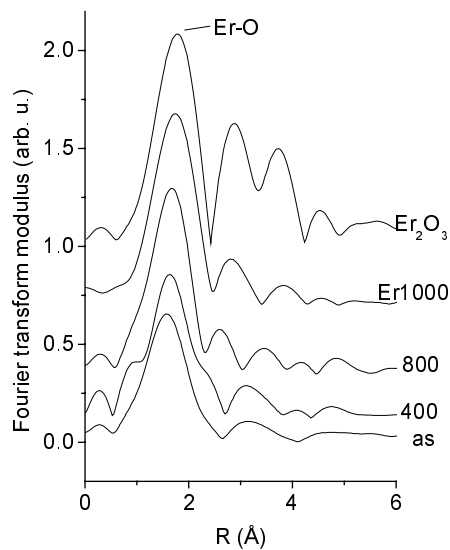
Fig. 3. Amplitude of k^2-weighted Fourier transform of the Er-EXAFS spectra of the samples, compared to the corresponding signal of the Er_2O_3 reference; the Er-O coordination shell is labelled; the transformation range is $k = 2\text{-}7.5$ Å^{-1}.

References

[GILDA] F. D'Acapito, et al., ESRF Newsletter **30**, 42 1998.

[HRDY] J. Hrdy', Rev. Sci. Instrum., **65**, 2147 (1994).

[ankPRB90] A. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, Phys. Rev. B **56**, 7565 (1990).

[feff8] A. Ankudinov, B. Ravel, J. J. Rehr and M. Newville, *FEFFIT manual within the FEFF project*, (University of Washington, Seattle, USA, 1992-1999).

[rehRMP00] J. J. Rehr and R. C. Albers, Rev. Mod. Phys. **72**, 621 (2000).

[friZFP93] C. G. Fritche and R. E. Benfield, Z. Phys. D **26**, S 15 (1993).

[marPRB90] M. A. Marcus, M. P. Andrews, J. Zegenhagen, A. S. Bommannavar, P. Montano, Phys. Rev. B **42**, 3312 (1990).

[balPRB85]A. Balerna, E. Bernieri, P. Picozzi, A. Reale, S. Santucci, E. Burattini and S. Mobilio, Phys. Rev. **B 31** 5058, (1985).

[dagPRB93] G. D'Agostino, A. Pinto, and S. Mobilio, Phys. Rev. B. **48**, 14447 (1993).

[OptMat2004]C. Maurizio, F. D'Acapito, F. Priolo, G. Franzò, F. Iacona, E. Borsella, S. Padovani, P. Mazzoldi, *Optical materials*, 27 (2004) 900-903]