Effect of the annealing atmosphere on the Au site in Er+Au implanted silica

C. Maurizio[*,a], G. Perotto[b], E. Trave[c], G. Pellegrini[b], G. Mattei[b], P. Mazzoldi[b]

[a]INFM-CNR, OGG-European Synchrotron Radiation Facility, GILDA-CRG B.P. 220, F-38043 Grenoble, France
[b]Dipartimento di Fisica, Università di Padova, Via Marzolo 8, 35131 Padova, Italy
[c]Dipartimento di Chimica Fisica, Università Ca' Foscari, Dorsoduro 2137, 30123 Venezia, Italy

Abstract

The Au site in Er+Au-implanted silica has been investigated by x-ray absorption spectroscopy, after annealing at 600 °C in either neutral (N_2) or reducing ($H_2(4\%):N_2(95\%)$) atmosphere. High resolution x-ray fluorescence spectra collected near the Au L_{III}-edge indicate the presence of oxidized Au atoms in the N_2-annealed sample. Correspondingly, the EXAFS analysis shows a weak Au-O coordination only for the sample annealed in neutral atmosphere. For both cases, the EXAFS results evidence the presence of sub-nanometer metallic Au clusters: the cluster size, always below 1 nm, is smaller for the sample annealed in reducing atmosphere. The Au clusters embedded in the Er-doped layer promote a strong enhancement of the Er photoluminescence emission at 1.5 μm.

Key words: Ion implantation, x-ray absorption spectroscopy, EXAFS, XANES, rare-earth photoluminescence, Er and metal-doped glasses

1. Introduction

Er-doped silica-based materials have been widely and deeply investigated during the last decade because of their promising application in optoelectronics. An effective route to increase the small cross section of the Er^{3+} ions

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[*]Corresponding author
Email address: maurizio@esrf.fr (C. Maurizio)

1.5 μm emission is the co-doping of the Er-doped silica with other species that can absorb the light from the pump source and partially transfer it to the Er ions, that then de-excite radiatively [1, 2, 3, 4]. In this framework, it has been recently demonstrated that Au clusters embedded in Er-doped silica can act as efficient sensitizers for Er ions [5, 6]. In this case, an enhancement of the Er emission has been observed in presence of large Au clusters, i.e. likely triggered by the strong fields induced by the surface plasmon resonance [6], but also in presence of only sub-nanometer clusters, that efficiently transfer the energy to the Er ions [5]. In the range of size below the nanometer, where the number of atoms per cluster is small (typically less than 50), the Au electronic band structure is expected to depend on the cluster size; correspondingly, the energy transfer process from the Au clusters to the Er ions could also depend on the Au cluster size, since it is suggested to be triggered by the Au $5d$ to $6sp$ interband transitions [5]. To this respect, the control of the Au nucleation process and of the first steps of the cluster growth is very desirable; nevertheless, the clustering process involves the nucleation of clusters of critical size, i.e. formed of few atoms, whose detection is challenging. About this point, x-ray absorption spectroscopy is an elective tool to investigate this heterogeneous nucleation, being able to detect Au-Au coordination independently from any long-range order considerations [7], as well as to reveal the fraction of Au atoms dispersed in the matrix and that constitute a reservoir for the cluster nucleation and growth process. Moreover, it has been recently demonstrated that the use of high resolution x-ray fluorescence detection for the x-ray absorption near edge structure (XANES) analysis allows to evidence much better the x-ray absorption features close to the photoelectric absorption edge from a core state, [8] that are strongly dependent from the oxidation state: these data can efficiently complement those obtainable from the extended part of the x-ray absorption spectrum (EXAFS, Extended X-ray Absorption Fine Structure), that give information on the structure of the local site of Au atoms. By the combined use of the two techniques a complete view of the Au site at the sub-nanometer scale can be obtained.

In this paper we have investigated the Au cluster formation in Er+Au sequentially implanted silica, after annealing in inert or reducing atmosphere. It is shown how the annealing atmosphere determine the dispersed Au fraction and the cluster size at the sub-nanometric scale; in both cases, it is demonstrated that the Au clusters enhance the Er 1.5 μm photoluminescence emission.

2. Experimental and data analysis

Pure silica slides were doped with Er and Au ions by sequential ion implantation: for each ion species a series of three implants at different energies was performed, obtain an almost flat concentration depth profile; moreover, the implantation energies for the two ion species were chosen to maximize the overlap of the two concentration depth profiles. After the implantation of the Er ions, with total fluence of 7×10^{14} Er$^+$/cm^2, the Er-implanted slides were then heated for 1 h in N$_2$ atmosphere at T=900°C to activate the Er luminescence. Then, after the triple Au$^+$ implants, with a total fluence of 7×10^{15} Au$^+$/cm^2, the co-doped silica slides were heated at T = 600 °C for 1 h in reducing (5% H$_2$:95% N$_2$) or neutral (N$_2$) atmosphere: the annealing temperature was chosen to maximize of the Er 1.5μm photoluminescence emission [5].

High resolution XANES spectra were collected at the ID26 beamline [9] of the European Synchrotron Radiation Facility (ESRF, Grenoble - F); the energy of the x-ray beam from an undulator source was selected by a couple of (111) Si crystals; the L$_{\alpha1}$ emission from Au atoms was collected using a Rowland circle crystal spectrometer equipped with three Ge crystals; the energy resolution of the collecting apparatus was about 1 eV, to be compared to the core hole width of the Au L$_{III}$ level that is 5.41 eV [10]. The samples were cooled at 20 K to limit thermal vibrations and to avoid the radiation damage; to this respect, we observed that at low temperature the Au white line intensity was stable even after more than 10 hours of exposure to the 12 keV x-ray beam, indicating that the typical phenomenon of chemical reduction induced by the x-ray can in this way be prevented; nevertheless, on a bending magnet beamline of the same synchrotron, where the flux is smaller and spread over a larger area, we observed no radiation damage at all in the 80–300 K range of temperature.

The EXAFS experiment was performed at the Italian bending magnet beamline GILDA [11] of the European Synchrotron Radiation Facility (Grenoble-France) at the Au L$_3$-edge. The monochromator was equipped with a couple of (311) Si crystals and the harmonic rejection was achieved by a couple of Pd-coated mirrors, working at an incidence angle of 3 mrad. Due to low Au concentration, the x-ray absorption spectra were measured in fluorescence mode with a 13-element high-purity Ge detector; the samples where cooled at 80 K to limit thermal vibrations. The EXAFS spectrum of a Au foil was also measured in transmission mode at the same temperature as stan-

dard reference. The analysis of the EXAFS spectra was performed by the FEFF8-FEFFIT 2.98 package [12, 13]. The value of the S_0^2 parameter in the standard EXAFS formula was determined by the EXAFS analysis of the Au metallic foil. The Au-Au (Au-O) backscattering phase and amplitude were calculated from an Au metal (Au_2O_3) cluster, providing also to extend the calculation for different Au–Au interatomic distances down to 2.70 Å. The Au-Au first shell coordination (and the Au-O one, where present) was fitted by a multiparameter single scattering fit into the R-space. To reduce the number of the fitting parameters, the value of the edge energy as well as the Debye-Waller factor were kept the same for the two spectra: this procedure did not alter significantly the fit results.

The optical emission characterization was realized through photoluminescence (PL) spectroscopy at room temperature, using the 488 nm line of a mechanically chopped Ar multilines laser as excitation source operating at a power of 6mW, with a beam spot of 1 mm diameter. The PL signal was analyzed by a single grating monochromator and detected by a near-infrared photomultiplier tube cooled by liquid nitrogen.

3. Results and discussion

The high resolution XANES spectra for the two samples are reported in Figure 1; in the inset two spectra from metallic Au are shown, one collected in total fluorescence detection mode and the other by the high resolution apparatus. The spectra from metallic Au show how the features close to the photoelectric L_{III}-edge are much better resolved by the Rowland circle crystal spectrometer; the differences between the two spectra in the XANES region are practically absent in the EXAFS part, where the oscillation frequency is smaller and the photoelectron kinetic energy higher. The Au-edge XANES spectra of the two Er+Au-implanted silica layers are similar one to each other: both exhibit a white line at about 11920 eV and three other broader peaks (at about 11935, 11950 and 11970 eV) that are present as well in the spectrum of metallic Au, with enhanced intensity. The white line shows that the d states are not completely filled, indicating that at least part of the Au atoms are oxidized; in particular it is evident that the average filling of the d states is lower in the sample annealed in N_2 atmosphere (the white line intensity is lower), and this is the signature of a higher average oxidation state for the Au atoms. It is worth noting that, with respect to the

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sample annealed in reducing atmosphere, the higher average oxidation state of Au in the N_2-annealed sample could be due to a higher fraction of oxidized atoms and/or to a higher oxidation state of the same fraction of dispersed Au atoms. We did not note any energy shift of the edge position, neither between the two samples, nor with respect of the Au metal spectrum. In addition to the oxidized fraction, the three other features in the XANES spectra mentioned above indicate the presence of metallic Au, likely in form of clusters. The EXAFS spectra of the two samples are shown in Figure 2 and compared with the one of metallic Au. With respect to this one, the spectra from the two samples exhibit the same main oscillating signal, but less intense and with slightly lower frequency; this suggest the presence of nanostructured metallic Au in the implanted layers, with a shorter Au-Au coordination distance with respect to the bulk. The quantitative EXAFS analysis confirms this observation. In Figure 3 the k^3-weighted Fourier transform moduli of the two spectra are shown, together with the corresponding fit; the main peak evident for both samples is due to a Au-Au metallic coordination; the possible signal from a Au-O coordination is located in the range R=1–2 Å. While for the sample annealed in inert atmosphere both Au-Au and Au-O coordination have been evidenced and fitted, for the H_2:N_2-annealed sample the Au-O signal did not contribute significantly to the fit and was accordingly neglected, in agreement with the considerations made on the XANES spectra. The results of the EXAFS analysis are reported in Table 1, where they are compared to the crystallographic data of metallic Au and Au_2O_3. For both the samples the Au-Au coordination distance is significantly lower than in the bulk phase, indicating the presence of small metal clusters. The comparison of the interatomic distance with literature data suggests that the clusters are on the average composed of about 10 Au atoms for the sample annealed in H_2:N_2 and of about 25 atoms for the sample annealed in N_2 [14]. This indicates that in both cases the cluster size is less than 1 nm. Finally, considering that in the sample annealed in N_2 part of Au atoms remain dispersed and that at the same time the clusters are larger, we can conclude that the cluster numerical density in this sample is lower with respect to the H_2:N_2-annealed one. The last consideration is about the Au-O distance in the N_2-annealed sample, that is in the same range of the one in crystalline Au_2O_3.

Overall these results enlighten the chemical effect of the annealing atmosphere on the Au clusterization process. In particular, the annealing in neutral or reducing atmosphere promotes the breaking of the Au-O bond and the

Au cluster aggregation; the reducing atmosphere is expected in particular to favor the chemical reduction of the Au ions. In our case, with respect to the neutral annealing, the chemical effect of the H_2:N_2 annealing is twofold: (i) it promotes a stronger chemical reduction of the Au ions dispersed into the matrix and (ii) it induces the formation of a higher density of smaller Au clusters, likely triggered by the diffusion of the reduced Au atoms.

In Figure 4 the 1.5 μm photoluminescence (PL) spectra upon excitation at 488 nm are reported for the two samples: the spectra are normalized to the maximum of the 1.5 μm PL emission of an Er-implanted silica sample after annealing at 900 °C. It is clear that the presence of Au strongly enhances the Er PL emission, in agreement with previous experiments [5]. Among the different factors that control the PL properties of these composite systems and in particular the energy transfer between Au clusters and Er ions, one is likely the Au cluster size, since for aggregates in the sub-nanometer range of size, i.e. involving only few atoms, the Au electronic energy levels are expected to be strongly dependent on the cluster size and shape. Moreover, the cluster density also likely plays a role in driving the optical properties, being the parameter that control the cluster–Er distance. Finally, it has to be taken into account that the Er site can in principle be differently modified by specific heating treatments in selected atmosphere; actually, preliminary x-ray absorption spectroscopy analysis performed at the Er L_{III}-edge indicates a chemical reduction of the Er ions upon annealing in H_2:N_2[15]: this should also be taken into account when discussing the optical properties of these composite materials. A systematic investigation to relate the Au and Er structure at the sub-nanoscale with the optical properties is in progress.

4. Conclusions

The Au site in Er+Au sequentially implanted silica slides has been investigated by the x-ray absorption spectroscopy. The analysis focussed on two samples annealed in neutral or reducing atmospheres at the same temperature (600 °C), chosen to optimize the Er 1.5 μm PL emission. High-resolution XANES analysis revealed that upon annealing in neutral atmosphere part of Au atoms are oxidized, likely dispersed into the matrix. From EXAFS and high-resolution XANES analyses, it comes out that the annealing in H_2:N_2 promotes the practically complete reduction of the Au atoms that aggregates in small clusters, formed of about 20 atoms; at variance to that the cluster size upon annealing in neutral atmosphere is larger (about 25-atoms

cluster), indicating a lower cluster density in the implanted layer. The PL spectra testify that the Er PL emission is strongly enhanced by the Au presence, i.e. that an energy transfer process occurs from the sub-nanometric Au clusters to the Er ions. The structural results show that specific annealing treatments can be successfully employed to tune the very early stages of the Au clusterization process.

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Table 1: EXAFS results for the Au L_{III}-edge analysis of the Er+Au-implanted silica slides: N is the coordination number, R the interatomic distance (Au-Au or Au-O) and σ^2 the Debye Waller factor. The crystallographic values for metallic Au and Au_2O_3 are also reported.

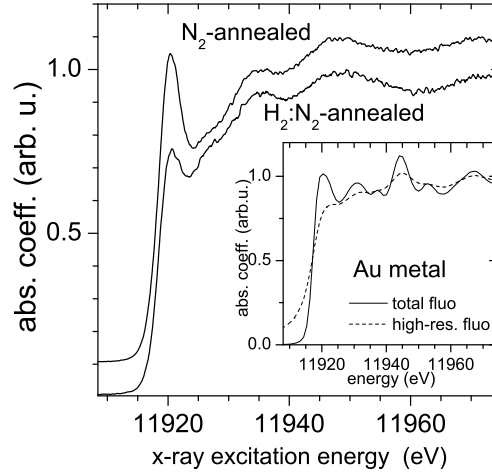| sample name		N	R (Å)	σ^2 $(\times 10^{-4} \text{Å}^2)$
N_2-ann.	O	0.3±0.1	2.06±0.04	18±5
	Au	3.1±1.0	2.77±0.01	77±15
H_2:N_2-ann.	Au	4.2±0.4	2.73±0.02	77±15
Au	Au	12	2.8838	
Au_2O_3	O	4	1.93–2.07	
	Au	1;1	2.81–2.90	

Figure 1: High-resolution Au L_{III}-edge XANES spectra of the Er+Au-doped silica slides; in the inset the XANES spectra of metallic Au, measured in standard fluorescence detection mode (dashed line) and with high-resolution x-ray fluorescence detection (solid line) are compared.
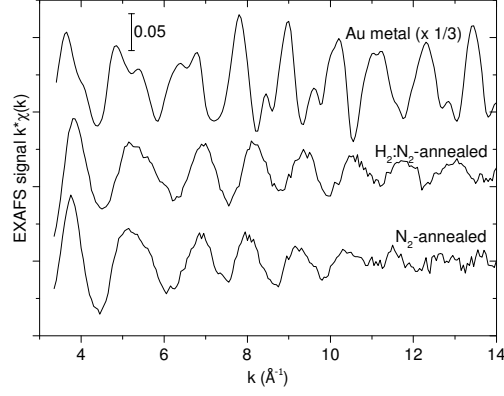
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Figure 2: EXAFS spectra recorded at Au L_{III}-edge of the Er+Au implanted silica samples, after annealing in H_2:N_2 or N_2 atmosphere, compared to the spectrum of metalic Au.
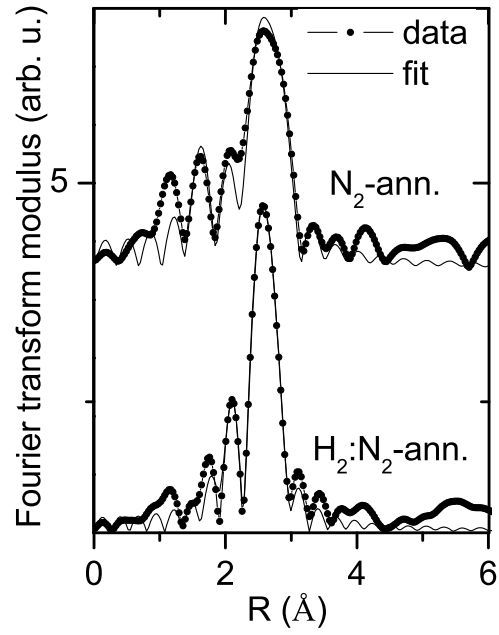

Figure 3: (a) k^3-weighted Fourier transform moduli (markers) and relative fits (solid line) for the H_2:N_2- and N_2-annealed Er+Au implanted SiO_2: the transformation range is $k = 4$-12 (4-15.5) Å^{-1} for the N_2-annealed (H_2:N_2-annealed) sample.
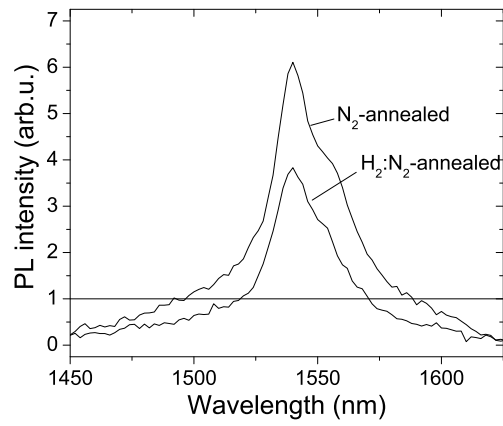
Figure 4: PL emission spectra around 1.5 μm for the Er+Au implanted silica upon annealing at T=600 °Cin reducing or oxidizing atmosphere. The PL intensity is normalized to the maximum emission intensity of a Er-implanted silica slide, i.e. in the same Er implantation conditions of the two samples, but without the subsequent Au implantation and annealing; this maximum value is indicated by the horizontal line.