Report on the experiment MA429: XAS on Er-Au doped silixa to single out the sensitizing agent (Au oxidized or Au aggregates) for the Er PL photoluminescence.

We have focused on the EXAFS analysis of silica slides doped by ion implantation with Er and Au atoms (Au fluence = $3 \cdot 10^{14}$ Au^{+}/cm^{2}); some tests were also done on similar samples with higher Au concentration. The aim of the experiment was to investigate if the Au-related structures that are responsible for the enhancement of the Er^{3+} photoluminescence (PL) emission are subnanometric Au clusters or Au atoms that are dispersed into the matrix and oxidized.

In Fig. 1 the EXAFS spectra of some from some of the samples are reported, upon H_2-annealing at different temperatures (up to 800 ºC). Although the spectra are quite noisy, a structural modification of the Au site by increasing the annealing temperature is evident. Correspondingly, in Fig. 2 the Fourier transform of the as-implanted, 100 ºC- and 800ºC-annealed samples are shown: while in the as-implanted and low temperature annealed sample (left) the main visible coordination is a Au-O one (peak at R~1.5 Å), for the 800ºC-heated one (right) the main visible coordination is the Au-Au one (peak at R~2.5 Å), indicating that the most part of Au aggregates into metallic clusters (from the preliminary analysis of the Au-Au distance, the average cluster size in this last case is 0.6 nm, corresponding to a 10-12 atoms cluster). For the as-implanted and 100ºC-heated samples, the presence of a Au-Au coordination is not quantifiable, because of the low signal-to-noise ratio (the intensity of the Au-Au coordination signal, if any, is well comparable with the noise visible in the range R=5-8 Å): from these data, we can roughly estimate that the fraction of Au atoms that aggregate into clusters is less than ~40%, but a more accurate estimation of the 'metallic' fraction is prevented. Similar considerations lead to the conclusion that in the 800ºC-heated sample the residual fraction of Au oxidized is difficult to estimate accurately. This point is quite critical for this experiment, because prevent us to find out if the Au-nanostructures that are responsible for the Er^{3+} PL enhancement are Au clusters or Au-oxidized.

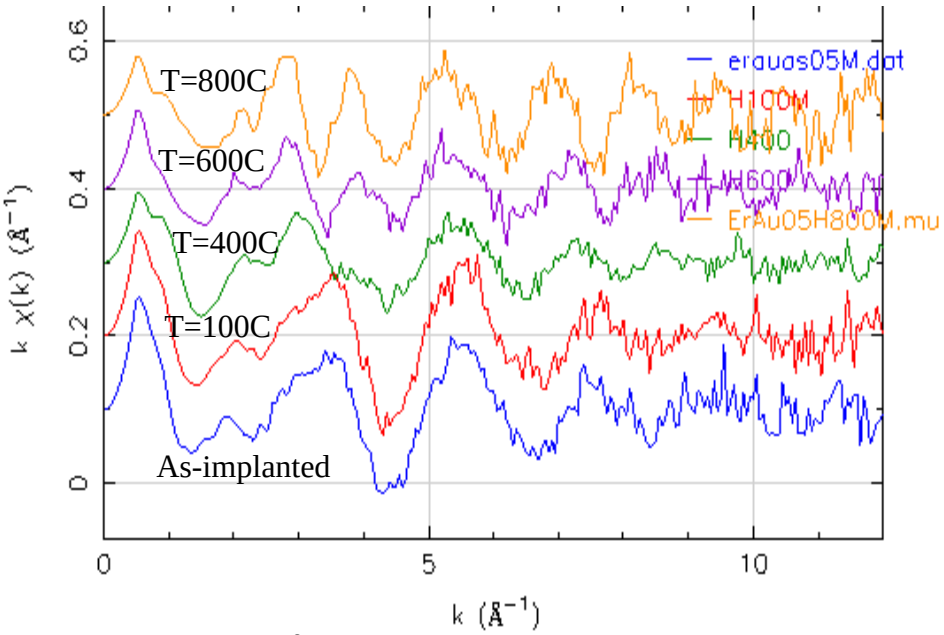

Fig. 1: EXAFS spectra of the Er+Au implanted samples, upon H_2-annealing at different temperatures.

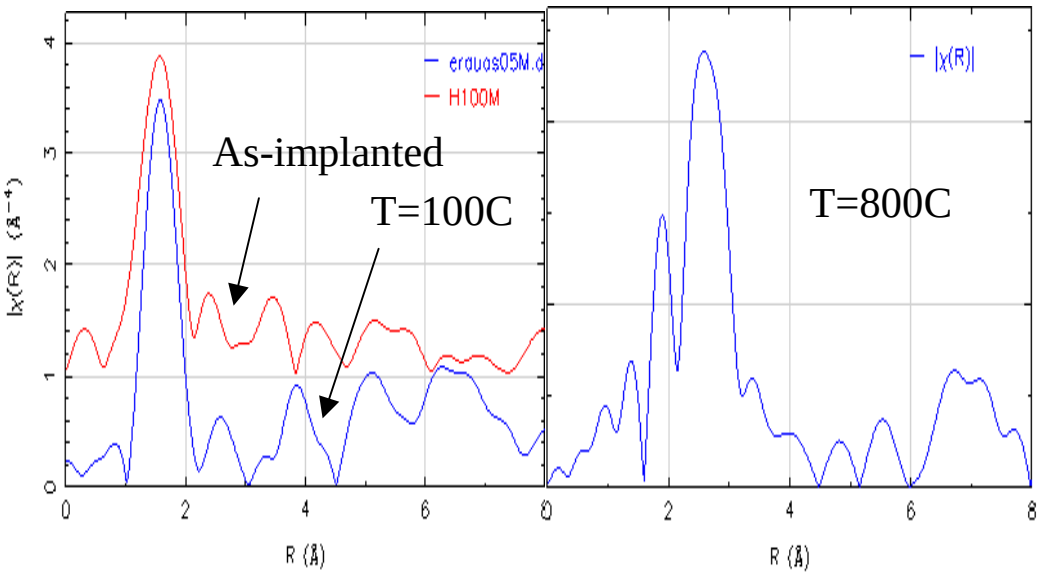

Fig. 2: Fourier transform moduli of some of the EXAFS spectra in Fig. 1.

Apart from the normal beamtime employed for the alignment, part of the beamtime was employed to optimize the data collection. The instability of the software for the fluorescence collection resulted in some time lost (1-2 shifts). These are the different configurations tested and the comments on the results obtained.

a) Traditional fluorescence detection:

- k-scan (normal EXAFS scan): we had evidence for some distortion in the spectra (see for example Fig. 3 left).
- Fast scan (continuous scan of the insertion device and monochromator): it worked better, few low-frequency distortions in the spectra, that almost do not affect the data analysis (see Fig. 3 right), apart from few cases.

b) Fluorescence detection by a 13-element Ge detector, coupled with a bent Laue crystal and suitable slits to filter out the elastic peak and select mainly the Au fluorescence line. During the experiment this set-up did not work, probably because of the large beam spot size. During an IHR test (16-bunches), where the beam spot size was reduced to few tens of μm, this setup worked properly. Nevertheless, in that case the signal to noise ratio was too poor to obtain quantitative reliable results.

To better measure by EXAFS these kind of samples, with the advice of the beamline staff, two ways are enlightened: i) to use a bent Laue crystal, a full x-ray beam and, with respect to the test made, a longer integration time (at least 12h per sample) or ii) to use a crystal analyzer coupled with a detector to record only the Au fluorescence line (likely a part of).

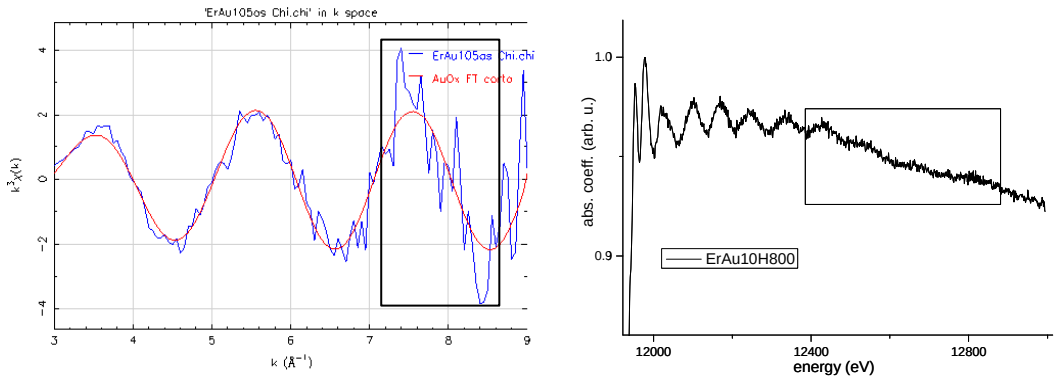

Fig.3. Artifacts in the EXAFS spectrum, indicated by boxes, of the as-implanted (left) sample and in one high-dose implanted sample (right). In the left panel, the best-fit curve (Au-O coordination) is shown in red.