**INTRODUCTION**

Ion beam processing has been used to synthesize innovative Au nanoparticles (NPs) in silica for applications in telecommunications and nanophotonics [1]. Optical functionalities of ultra-small (i.e., made by few atoms) molecule-like Au NPs, such as their efficient nanoantennas properties for transferring electromagnetic energy to photoemitting systems, like rare earth ions, is the main activity developed by our group using also the National Legnaro Laboratory (LNL) facilities. From the point of view of the optical properties, indeed, such ultra-small nanoclusters are characterized by discrete electronic states and the opening of a HOMO-LUMO gap that exceeds thermal energy already at room temperature, allowing for efficient radiative relaxation and strongly enhancing the luminescence quantum yield [2]. The use of ion implantation as doping technique is strategic for this purpose since it provides a well-controlled way to produce local super-saturation in silica allowing to efficiently control the early stages of nucleation and growth of implanted species by working very close to the critical size of nucleation (i.e., 2–3 Au atoms in silica). Nonetheless, different aspects are involved in the energy-transfer process from ultra-small Au nanoclusters and Er ions and concur in determining its efficiency. Aiming at elucidating some of them, in this work we investigated the interplay between the Au-related room temperature photoluminescence in the visible and near-infrared (NIR) range, and the energy-transfer to Er ions in Er-Au co-implanted silica systems.

**EXPERIMENTAL**

Er-doped silica slides were produced by sequential implantations of Er ions at three energies, 180+100+50 keV, with a total fluence of 7.2 x10^{14} Er+/cm^2 and annealing in nitrogen atmosphere at 800 °C for 1h. Sequential Au implantations were then performed on the Er-doped silica slabs with an analogous triple energy scheme. The implantation energies were 190+110+60 keV and the total Au fluence was 7.2 x10^{15} Au+/cm^2. All the implants were performed with the Low-Energy Ion Implanter facility at LNL-INFN. The Er and Au implantation parameters were chosen to obtain almost flat implantation profiles (about 70 nm thick) and their overlap in the Er-Au co-implanted samples. Both Er and Au implantation fluences were estimated by Rutherford Backscattering Spectrometry (RBS) at AN2000 accelerator, LNL-INFN. After Au implantation, the samples were then heated for 1h in nitrogen atmosphere at temperatures in the range 300-800 °C to induce Au clustering and implantation damage recovery of the silica matrix. In the following the samples will be named according to the [Au]/[Er] concentration ratio ([Au]/[Er] = 10) as Er1Au10. The Er-implanted reference sample (prior to Au implantation) will be referred as Er800.

To determine the Au nanocluster size and its evolution upon annealing, Extended X-ray Absorption Fine Structure (EXAFS) experiments were performed at the Au L3-edge in fluorescence mode at the Italian beamline GILDA of the European Synchrotron Radiation Facility (Grenoble, France). Photoluminescence (PL) measurements were performed at room temperature by pumping the samples with the 488 nm line of a cw Ar laser.

**RESULTS AND DISCUSSION**

In Fig. 1 we reported the room temperature PL spectra of the Er1Au10 samples annealed in nitrogen atmosphere at 300 °C, 550 °C and 700 °C. The measurements have been taken upon resonant Er^{3+} excitation at 488 nm. The PL spectrum of the reference sample Er800 (prior to Au implantations) is also reported as a continuous line. The spectra are vertically shifted to improve the visualization. All the samples exhibit a distinctive PL feature at 1540 nm that is characteristic of the Er^{3+} luminescent emission. The intensity of this band varies as a function of the annealing temperature and its maximum is reached for thermal treatments at 550 °C: in this case the sample exhibits an intense PL peak at 1540 nm, about a factor of two higher with respect to the Er800 reference sample. Concerning the physical origin of such luminescence bands we have shown very recently that they are due to the presence in the Er-Au co-implanted samples of the ultra-small AuN aggregates responsible for the sensitized Er^{3+} luminescence [3]. Structural characterizations performed by EXAFS measurements revealed the formation in the samples of ultra-small Au nanoclusters whose size increases by increasing the annealing temperature, reaching N = 50 atoms for annealing at 800°C. Owing to their ultra-small dimensions such Au nanoclusters have a molecule-like character with an electronic structure characterized by discrete energy levels whose energy separation at room temperature is larger than thermal energy, making radiative transitions competitive with non-radiative phonon transitions competitive with non-radiative phonon...
mediated relaxation processes. On the other hand, no evidence of damage-related luminescence (possibly due to Er and/or Au implantations) is observed in the wavelength range explored, as confirmed by looking at the spectra of the Er800 sample (continuous line) and of the Er1Xe12 sample annealed at 600 °C (white diamonds) reported in Fig. 1 [4].

Fig. 1: Room temperature PL spectra (excited at 488 nm) of the Er-Au co-implanted silica samples (Er1Au10) annealed in nitrogen atmosphere at the indicated temperatures. For comparison the PL spectrum of the reference sample Er800 and the Er1Xe12 sample annealed in nitrogen atmosphere at 600 °C are also shown. The spectra are vertically shifted of an arbitrary amount to improve the visualization.

In order to highlight the correlation between the AuN – related luminescence and the Er emission we have compared in Fig. 2 the room temperature PL spectrum of the Er1Au10 sample annealed at 550 °C with the spectra of analogous Er-Au co-implanted samples in which Au has been implanted at lower fluences corresponding to [Au]/[Er] concentration ratios of [Au]/[Er] = 5 (Er1Au5) and [Au]/[Er] = 1 (Er1Au1). These two samples have been annealed in nitrogen atmosphere at 620 °C and 720 °C, respectively. To improve the visualization of all the spectral features, different vertical scales have been used for wavelengths shorter (left-hand scale) and longer (right-hand scale) than 1400 nm, as indicated by the vertical dashed line at 1400 nm in the figure. We have found that the annealing temperature necessary to get the maximum Er emission shifts towards higher values for decreasing Au fluence. For each sample series in Fig.2, therefore, the chosen temperatures represent the thermal treatment conditions to get the maximum Er3+ luminescence at 1540 nm. The dashed gray arrows in the figure highlight the anti-correlated trend exhibited by the PL emission at 1540 nm and at 980 nm: the progressive increase of the Er3+ luminescence at 1540 nm is related to the corresponding decrease of the AuN related component at 980 nm and thus this may represent a channel for the transfer of energy from the ultra-small AuN nanoclusters acting as sensitizers and the Er3+ ions, giving rise to the enhancement of the Er3+ emission.

![Fig. 2: Comparison between room temperature PL spectra of the Er1Au10 sample annealed at 550 °C (black squares), the Er1Au5 sample annealed at 620 °C (black continuous line) and the Er1Au1 sample annealed at 720 °C (white dots). The samples have been thermally treated in nitrogen atmosphere. The annealing temperatures represent the thermal treatment conditions to get the maximum Er3+ PL emission at 1540 nm.](image)

**CONCLUSIONS**

In summary, the room temperature photoluminescence properties of Er-Au co-implanted silica samples have been characterized in the wavelength range 600-1700 nm as a function of the annealing temperature under Er3+ resonant excitation at 488 nm by a cw Ar laser. Besides the characteristic Er3+ PL emission at 1540 nm, the spectra revealed the occurrence of three main luminescence bands at about 750 nm, 980 nm and 1150 nm related to the formation in the samples of ultra-small Au aggregates with less than 50 atoms (AuN luminescence). The relative intensity of these bands depends on the annealing temperature and an anti-correlated behavior has been shown between the Er3+ luminescence at 1540 nm and the 980 nm AuN - related component that, being resonant with the Er3+ absorption transition 4I15/2 → 4I11/2 at 980 nm, may represent a possible path for the energy-transfer from AuN nanoclusters to Er3+ ions giving rise to the Er3+ sensitized emission.