Interatomic coupling of Au molecular clusters and Er\(^{3+}\) ions in ion implanted silica

T Cesca\(^1\), B. Kalinic\(^1\), C. Maurizio\(^1\), C. Scian\(^1\), G. Battaglin\(^2\), P. Mazzoldi\(^1\), G. Mattei\(^1\)

\(^1\) Physics and Astronomy Department and CNISM, University of Padova, Padova, Italy.
\(^2\) Department of Molecular Sciences and Nanosystems, Ca’ Foscari University of Venice, Venice, Italy.

INTRODUCTION

Due to the sharp room temperature radiative emission at \(\lambda_{\text{em}}=1.54\ \mu\text{m}\), which matches the window of minimum loss in silica optical fibers, the Er\(^{3+}\) ion is the optical dopant of choice for many optoelectronic applications [1]. Unfortunately the long lifetime of characteristic transition \(4I_{13/2} \rightarrow 4I_{15/2}\) of Er ions embedded in a glassy matrix is one of the major limitation in the realization of photonic and optoelectronic devices based on Er-doped materials, because the long permanence of the ion in the excited state makes it prone to non-radiative decay processes such as energy migration, cooperative up-conversion and concentration quenching [2]. Moreover, strong limitations are also related to the small cross-section for Er excitation, which is typically of the order of \(10^{-21} - 10^{-19}\ \text{cm}^2\), depending on the matrix. The interaction with sensitizing species to enhance the Er pumping efficiency represents a possible solution to this problem. To this aim, in the present work we studied the Er-related luminescence properties of Er–Au co-doped silica samples obtained by ion implantation at different fluences. To investigate in detail the interaction among Au sensitizers and Er ions the relative concentration of the two species in the samples was varied over more than 1 order of magnitude. This, coupled with proper annealing conditions, allowed a fine tuning of the Au cluster sizes in the subnanometer range. By systematic photoluminescence characterizations performed for both resonant and out-of-resonance Er excitation conditions we developed a phenomenological model through which the relevant photophysical aspects of the energy-transfer mechanism are unveiled.

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 \(6.7 \times 10^{14}\ \text{Er}^+/\text{cm}^2\) 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 designed to have a \([\text{Au}]/[\text{Er}]\) ratio spanning the range 0.5-10. All the implants were performed with a Danfysik 1090 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 \([\text{Au}]/[\text{Er}]\) concentration ratio (\([\text{Au}]/[\text{Er}] = 1\) as Er1Au1. 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 L\(_3\)-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

The Au implantation fluence has a remarkable effect on the temperature evolution of the PL emission, in particular on the peak position (peak temperature) and the maximum intensity. Figure 1 shows the PL peak intensity (a) and the peak temperature (b) as a function of the \([\text{Au}]/[\text{Er}]\) concentration ratio. The open circles and the half-filled dot represent the results obtained from three different series of Er–Au coimplanted samples in which Er was implanted at a lower total fluence. Following the adopted notation these series can be indicated as Er0.7Au1, Er0.7Au5, and Er0.4Au1, respectively. The Au fluences are the same as for the Er1Au1 and Er1Au5 samples. These data can be treated consistently with those of all the other sample series, thus suggesting that the mechanisms to be considered are indeed dependent on the relative concentration of Au sensitizers and Er ions. As shown in Figure 1a, the evolution of the peak intensity as a function of the relative Au concentration with respect to Er is not monotonic but exhibits a maximum when the Au concentration equals the Er one (\([\text{Au}]/[\text{Er}] = 1\)). On the contrary, the peak temperature (Figure 1b) is characterized by a monotonic decrease with increasing \([\text{Au}]/[\text{Er}]\) ratio. The dashed line is a polynomial fit of the data. This behavior can be understood by taking into account that the Au implantation process followed by thermal treatments is expected to induce the growth of Au clusters with an average size which is smaller for lower Au fluences. The increase of the peak temperature for decreasing \([\text{Au}]/[\text{Er}]\) concentration ratios is related to the growth of the Au NCs in the optimal size range for the Er sensitization (10–20
atoms, as obtained by EXAFS analysis) that occurs at increasing annealing temperatures for decreasing Au concentrations.

Fig. 1: PL peak intensity (a), PL peak temperature (b) and effective cross-section (c) as a function of the [Au]/[Er] concentration ratio of the different sample series. The red dots indicate the series of samples implanted with Er at a concentration of $9.6 \times 10^{19}$ Er$^+/cm^3$ ([Er] = 1). The open circles are the data of the sample series Er0.7Au1 and Er0.7Au5, while the half-filled dot corresponds to the Er0.4Au1 series.

Moreover, by comparing the PL emission results measured from samples containing the same amount of gold but implanted with Er at different fluences (open circles and half-filled dot), it emerges that an increase of the maximum PL emitted intensity can be obtained when higher Er concentrations are incorporated in the samples. To highlight this effect we have reported in the inset of Figure 1a the PL intensity as a function of the Er concentration for the samples with the same Au concentration of about $1 \times 10^{20}$ Au$^+/cm^3$ ([Au] = 1 in the adopted units). The graph shows a linear trend up to the Er concentration of $9.6 \times 10^{19}$ Er$^+/cm^3$ ([Er] = 1). It is worth noting that this value corresponds to half of the reported limit for Er concentration quenching in silica. For this reason, to rule out possible Er–Er cooperative effects which could mask or hinder the AuN–Er interaction we limited the maximum Er concentration investigated to this value and explored the effect of the Er concentration on the PL emission intensity by reducing it down to [Er] = 0.7 and [Er] = 0.4. In the hypothesis that the Au cluster configuration is the same and defining an interaction volume around the AuN clusters for the AuN–Er coupling, the observed linear trend of the PL emission versus Er concentration is consistent with the corresponding increase of the number of active Er ions in this volume. Nonetheless, it is important to point out that the data in Figure 1b show that the annealing temperature at which the maximum PL emission occurs varies as a function of the [Au]/[Er] concentration ratio, thus suggesting that the Er concentration has indeed an effect also on the Au cluster nucleation.

Moreover, by comparing the PL emission results measured from samples containing the same amount of gold but implanted with Er at different fluences (open circles and half-filled dot), it emerges that an increase of the maximum PL emitted intensity can be obtained when higher Er concentrations are incorporated in the samples. To highlight this effect we have reported in the inset of Figure 1a the PL intensity as a function of the Er concentration for the samples with the same Au concentration of about $1 \times 10^{20}$ Au$^+/cm^3$ ([Au] = 1 in the adopted units). The graph shows a linear trend up to the Er concentration of $9.6 \times 10^{19}$ Er$^+/cm^3$ ([Er] = 1). It is worth noting that this value corresponds to half of the reported limit for Er concentration quenching in silica. For this reason, to rule out possible Er–Er cooperative effects which could mask or hinder the AuN–Er interaction we limited the maximum Er concentration investigated to this value and explored the effect of the Er concentration on the PL emission intensity by reducing it down to [Er] = 0.7 and [Er] = 0.4. In the hypothesis that the Au cluster configuration is the same and defining an interaction volume around the AuN clusters for the AuN–Er coupling, the observed linear trend of the PL emission versus Er concentration is consistent with the corresponding increase of the number of active Er ions in this volume. Nonetheless, it is important to point out that the data in Figure 1b show that the annealing temperature at which the maximum PL emission occurs varies as a function of the [Au]/[Er] concentration ratio, thus suggesting that the Er concentration has indeed an effect also on the Au cluster nucleation.

Moreover, by comparing the PL emission results measured from samples containing the same amount of gold but implanted with Er at different fluences (open circles and half-filled dot), it emerges that an increase of the maximum PL emitted intensity can be obtained when higher Er concentrations are incorporated in the samples. To highlight this effect we have reported in the inset of Figure 1a the PL intensity as a function of the Er concentration for the samples with the same Au concentration of about $1 \times 10^{20}$ Au$^+/cm^3$ ([Au] = 1 in the adopted units). The graph shows a linear trend up to the Er concentration of $9.6 \times 10^{19}$ Er$^+/cm^3$ ([Er] = 1). It is worth noting that this value corresponds to half of the reported limit for Er concentration quenching in silica. For this reason, to rule out possible Er–Er cooperative effects which could mask or hinder the AuN–Er interaction we limited the maximum Er concentration investigated to this value and explored the effect of the Er concentration on the PL emission intensity by reducing it down to [Er] = 0.7 and [Er] = 0.4. In the hypothesis that the Au cluster configuration is the same and defining an interaction volume around the AuN clusters for the AuN–Er coupling, the observed linear trend of the PL emission versus Er concentration is consistent with the corresponding increase of the number of active Er ions in this volume. Nonetheless, it is important to point out that the data in Figure 1b show that the annealing temperature at which the maximum PL emission occurs varies as a function of the [Au]/[Er] concentration ratio, thus suggesting that the Er concentration has indeed an effect also on the Au cluster nucleation.

A primary parameter that characterizes the energy-transfer process from AuN nanoclusters to Er ions is the effective cross-section for Er sensitization $\sigma_{\text{eff}}$. Measuring the Er$^{3+}$ luminescent emission at 1540 nm as a function of the photon flux with out-of-resonance excitation (at 476.5 nm), we estimated the effective cross-sections for all the “best-performing” samples (Figure 1c): the trend of $\sigma_{\text{eff}}$ as a function of the [Au]/[Er] concentration ratio is not monotonic: a maximum (of the order of $8 \times 10^{-18}$ cm$^2$) is obtained for a concentration ratio [Au]/[Er] of about 5. It is worth noting that the corresponding parameter measured in the Er reference sample is $4.4 \times 10^{-21}$ cm$^2$, i.e., three orders of magnitude less [3]. For all the investigated samples the estimated sensitized fractions are very small, below 1%. This means that in spite of the measured very high sensitization cross-sections (see Figure 1c), the number of Er ions that can be indirectly excited through the energy transfer from the AuN nanoclusters is indeed much limited. Assuming a random distribution of Er ions and Au clusters a quantitative estimation of the interaction radius $R_{\text{int}}$ (i.e., the radius of the spherical volume containing the Er sensitized fraction) has been obtained as in the range 0.4−0.8 nm. This demonstrates that the energy-transfer process from the AuN nanoclusters to the Er$^{3+}$ ions is indeed a short-range coupling mechanism occurring at interatomic distances.

CONCLUSIONS

The effect of AuN molecular clusters as sensitizing agents of the Er$^{3+}$ luminescence in Er–Au coimplanted silica has been elucidated. In particular, the investigation of systems in which the [Au]/[Er] concentration ratio was spanned over more than 1 order of magnitude revealed that the sensitization mechanism is characterized by a large effective cross-section, more than 3 orders of magnitude larger than the intrinsic cross-section for Er emission. Moreover, we found that the energy-transfer is a short-range coupling occurring at interatomic distances in the range 0.4−0.8 nm. Nonetheless, in spite of the very large cross-section of the process, it was also demonstrated that...
only a limited fraction of the Er ions can be indirectly excited by energy transfer from the AuN nanoclusters and that better performances can be achieved by increasing the Er concentration.