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Si nanoparticle–Er\(^{3+}\) coupling through contact in as-deposited nanostructured films

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The efficient excitation of Er\(^{3+}\) ions through contact with Si nanoparticles (NPs) is demonstrated. A nanostructured doping process has been developed that leads to contact between Si NPs formed in situ and optically-active Er\(^{3+}\) ions embedded in Al\(_2\)O\(_3\). This is achieved by independent and consecutive deposition of the dopants and matrix. The Si NP–Er\(^{3+}\) contact regime enhances the probability of efficient interaction due to the local spatial overlap of the electronic states of the Er\(^{3+}\) and of the Si NP exciton, enabling energy transfer by interband exciton recombinations. This leads to up to 53% of the Er\(^{3+}\) ions being excited in as-deposited films. © 2011 American Institute of Physics. [doi:10.1063/1.3579523]

The codoping of SiO\(_2\) with Er\(^{3+}\) and Si-based sensitizers, mainly Si nanoparticles (NPs), has been studied intensively for more than a decade in order to achieve a gain material suitable for the development of integrated waveguide amplifiers. These studies show that the relatively short range of the Si NP–Er\(^{3+}\) interactions precludes the fabrication of materials with efficient energy transfer. 1 This limitation arises because codoping is usually performed by mixing the Si and Er components such that there is no control over their local relative position and thus their separation. 2,4 This limits the percentage of Er\(^{3+}\) ions that are optically excited, usually to values of a few percent; and only recently has a value of 23% been achieved. 4 This is still far below the excitation fraction of 50% that is considered to be necessary to achieve gain, as has been proposed by recent reports, which suggest different routes to improve the excitation by achieving a longer excitation energy-transfer distance, 5 by using alternative excitation routes such as Si-related luminescent centers, 6,7 or by Er-doping of amorphous silicon-rich oxides. 8 The use of synthesis processes that allow control of the dopant location at the nanoscale is also a promising route. 1–3,5,9

This work proposes an alternative excitation route which allows achieving efficient Dexter-type energy transfer through Si NP–Er\(^{3+}\) contact coupling. In this contact regime the spatial overlap of the electronic states of the Er\(^{3+}\) and the excitons of the Si NPs is maximized and efficient direct Er\(^{3+}\)-excitation is achieved by recombination of the Si NP exciton. 10 This process has rarely been observed as it is negligible for samples in which the Si NP and Er\(^{3+}\) doping is random. 10,11 In addition the results show that through Si NP–Er\(^{3+}\) contact coupling large fractions of Er ions (>50%) can be efficiently excited by Si NPs in films prepared at room temperature and with no post-deposition annealing. Finally, it is shown that the use of amorphous alumina oxide (Al\(_2\)O\(_3\)), rather than SiO\(_2\), as the dopant matrix allows obtaining relevant spectroscopic information on the Si NP–Er\(^{3+}\) interaction.

The nanostructured thin films consist of twenty Si NP–Er\(^{3+}\) doping layers embedded in Al\(_2\)O\(_3\). They have been synthesized by pulsed laser deposition in vacuum (base pressure \(-10^{-6}\) Torr) on silicon and fused-silica substrates held at room temperature. The laser energy density on the targets was below 2 J cm\(^{-2}\) to avoid mixing and resputtering effects. 12 Further details can be found elsewhere. 9,10 The Si NP–Er\(^{3+}\) doping layers are produced by depositing the two dopants independently and sequentially from pure Si and Er targets. The Si NP–Er\(^{3+}\) doping layers were formed using 185 pulses on the Si target and one pulse on the Er target. Deposition of Si on Al\(_2\)O\(_3\) leads to the formation of amorphous Si NPs. 9 The inset (a) in Fig. 1 shows energy-loss filtered transmission electron microscopy (EFTEM) cross-section images formed by selecting the energy window that corresponds to the Si–Si signal (a) and to the Al signal in Al\(_2\)O\(_3\) (b). In both images the lines correspond to the Si NPs

FIG. 1. (Color online) Transmission measurements for the Er-only (dotted line), SE (full line, red online), and ES (dashed line, blue online) films deposited on fused silica substrates. The inset shows EFTEM cross-section images for a Si NP-Er\(^{3+}\) film. The images have been formed by selecting the energy window that corresponds to the Si–Si signal at 16 eV (a) and to that of Al in Al\(_2\)O\(_3\) at 60 eV. In (b) on top of the image intensity profiles are shown. The profiles have been obtained from line traces in the direction parallel to the Si NPs layers either on top of a Si NPs layer (upper profile, red online) or on the Al\(_2\)O\(_3\) area (lower profile, cyan online). In the former case the minima are related to individual Si NPs presence.

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layers. Image (a) confirms the presence of Si-rich areas with Si–Si bonding shown with light contrast. In image (b) the dark features correspond to absence of Al$_2$O$_3$, i.e., to a local increase in the Si concentration. On top of one of the Si NPs layers an intensity profile is shown to evidence that the layers are discontinuous and thus formed by individual Si NPs. From this image the estimated average NP size is $4 \pm 1$ nm.

In order to study the Si NP–Er$^{3+}$ interaction, two doping configurations—SE and ES—have been prepared. For the SE films Si NPs are formed first and Er is deposited subsequently on top leading to the following sequence: Al$_2$O$_3$/Si NPs/Er$^{3+}$/Al$_2$O$_3$. For the ES films the Er is deposited first and the Si NPs are formed on top leading to a sequence as follows: Al$_2$O$_3$/Er$^{3+}$/Si NPs/Al$_2$O$_3$. For both configurations the dopants are deposited immediately after each other with no intermediate Al$_2$O$_3$ layer, thus forming a two-dimensional single Si NP–Er$^{3+}$ doping layer. For reference an Al$_2$O$_3$ film doped only with Er$^{3+}$ (Er-only) was prepared. The films have not been annealed after deposition, therefore the Si NPs remain amorphous and the original film structure is not modified by diffusion processes.$^{12,14,15}$

Figure 1 shows the transmission spectra measured for the SE, ES, and Er-only films deposited on fused silica substrates. The oscillations observed in all spectra are due to the light interference between the film surface and the film–substrate interface. The Er-only film shows a negligible absorption from the visible to the infrared. In contrast the SE and ES films show a clear absorption edge in the near UV–visible region due to the presence of the Si NPs. The absorbing shape, but with a narrower FWHM of 44 nm and a maximum shifted to 1533 nm [see inset (c) of Fig. 2]. The different features in the PL spectra of the Er-only doped film compared to the SE and ES films are a signature of a different local environment for the Er$^{3+}$. A comparison of our spectra with those reported in the literature show that the spectrum for the Er-only film is consistent with an Al$_2$O$_3$ environment, whereas the spectra for the SE and ES films are consistent with a SiO$_2$ rich environment.$^{17}$ Since the Si NP–Er doping layers are embedded in Al$_2$O$_3$ these results indicate that the emitting Er$^{3+}$ ions are most probably located on the surface of the Si NPs where Si–O bonds are formed between Si from the Si NPs and O from the Al$_2$O$_3$.

Figure 2 shows the PL excitation (PLE) spectrum for the films. The Er-only film shows weak emission and only at the wavelengths that are resonant with the Er$^{3+}$ energy levels (488.0 and 514.5 nm). The PLE spectra for the SE and ES films show significant emission in the whole spectral range, which decreases as a function of the wavelength proving that there is efficient Er$^{3+}$ excitation through Si NPs. The SE and ES films show a significant enhancement of the absolute PL intensity at 488.0 nm with respect to the Er-only film that strongly depends on the doping configuration. The PL intensity enhancement is a factor 16 for the SE films and a factor of 36 for the ES films. Nevertheless the similar behavior of the PLE spectra for the SE and ES films suggests a similar Si NP–Er$^{3+}$ interaction mechanism for both films, in agreement with the very similar overall shape of the absorption and PL intensity spectra.

Figure 3(b) shows that the PL decay times for the SE and ES films are the same within the system resolution with a characteristic $\tau$ of 180±6 $\mu$s. This is consistent with both films having a similar Er$^{3+}$ environment leading to the same de-excitation processes. Under steady state excitation at a given pump flux the PL intensity ($I_{PL}$) is directly proportional to the fraction of excited Er$^{3+}$ ($f_{Exc}$), the total concentration of Er$^{3+}$($N_{Er}$), the effective absorption cross section ($\sigma_{eff}$) and the measured PL decay time ($\tau$) according to the expression:

$$I_{PL} \propto f_{Exc} \cdot N_{Er} \cdot \sigma_{eff} \cdot \frac{\tau}{\tau_{rad}},$$

where $\tau_{rad}$ is the radiative lifetime. From Eq. (1) the observed difference in the PL intensity values for the SE and ES films.
has to be related to different values of the product $f_{\text{Exc}} \cdot \sigma_{\text{eff}}$. The value of $f_{\text{Exc}}$ for the SE and ES films can be directly estimated from the excitation and de-excitation rate equations under steady state conditions. As described above, the PL decay times shown in Fig. 3(b) indicate that the decay time ($\tau$) is the same for both films. In contrast the rise lifetime ($\tau_{\text{rise}}$) values are different for the SE and ES films being $82 \pm 6$ $\mu$s and $142 \pm 6$ $\mu$s, respectively. Assuming a two level system the excitation rate is defined as $R_{\text{Exc}} = 1/\tau_{\text{rise}} - 1/\tau$, where $\tau_{\text{rise}}$ and $\tau$ are the rise and decay lifetimes. Using this equation, the excitation rate for the SE and ES films can be seen to be faster than for the ES films. Then $f_{\text{Exc}}$ is then given by the expression (2)

$$f_{\text{Exc}} = \frac{1}{1 + R_{\text{Exc}} \tau}.$$  

The value of $f_{\text{Exc}}$ is as high as 53% for the SE film and 23% for the ES film, which are among the largest ever reported. This proves the high efficiency of the excitation process in our as-deposited films. Of further note is the fact that there is a large increase in $f_{\text{Exc}}$, by a factor 53%, which occurs when the order of the dopant distribution is changed. This shows that the overlap of the Si NPs and Er distribution is different for the two configurations, with greater interaction for the SE films.

The question is still whether $\sigma_{\text{eff}}$ is also the same for both doping configurations. For the Si NP-Er$^{3+}$ system $\sigma_{\text{eff}}$ is given by $\sigma_{\text{eff}} = \sigma_{a} \cdot \eta_{\text{ET}}$ where $\sigma_{a}$ is the absorption cross-section of the Si NPs and $\eta_{\text{ET}}$ is the energy transfer efficiency to the Er. From Fig. 1 $\sigma_{a}$ is the same for SE and ES films. Therefore from Eq. (1) the ratio of the PL intensities for the SE and ES films can be written as:

$$\frac{I_{\text{PL}}(\text{SE})}{I_{\text{PL}}(\text{ES})} = \frac{\eta_{\text{ET}}(\text{SE})}{\eta_{\text{ET}}(\text{ES})} \cdot \frac{f_{\text{Exc}}(\text{SE})}{f_{\text{Exc}}(\text{ES})},$$  

where the fact that $\tau$ is the same for both films [from Fig. 3(b)] has been included. From this equation it follows that $\eta_{\text{ET}}$ is the same for both configurations, since from Fig. 3(a) the PL intensity ratio at 488.0 nm is 2.25, and from the calculations of Eq. (3) the ratio of the fraction of excited Er ions is 2.3. This result confirms that the main difference between the ES and SE films is the value of $f_{\text{Exc}}$.

The discussion above shows that for both films the main energy transfer mechanism is the same. This is in agreement with Fig. 2, which shows that the emitting Er$^{3+}$ ions are located in a SiO$_2$-rich environment therefore suggesting that the dominant excitation process has a contact character. The location of the active Er$^{3+}$ on the surface of the Si NPs is consistent with the different geometrical conditions found upon deposition for the ES and SE films. In the insets (a) and (b) of Fig. 2 the schematics of the Si NP and Er dopant distribution show that there is a larger Si NP surface exposed for contact with Er$^{3+}$ when it is deposited after the Si NP formation (SE film) than when it is deposited before the Si NP formation (ES film). In the former case there is a large probability of Er$^{3+}$ being directly deposited on the Si NPs surface. This can account for the increment of 53% for $f_{\text{Exc}}$ in the SE compared to the ES films. Since our results show that only Er$^{3+}$ in contact with a Si NP is emitting thus it is possible that the energy transfer occurs by direct Er excitation through interband exciton recombination in the Si NP.

Izzedin et al. have shown that this mechanism is the most efficient, being up to five orders of magnitude more efficient that dipole-dipole energy transfer. The probability of such contact coupling is low in the usual three-dimensional randomly doped samples. In this work, due to the maximized Si NP–Er$^{3+}$ coupling achieved through contact, the conditions needed to observe efficient energy transfer through exciton interband recombination are met.

In conclusion efficient Er$^{3+}$ excitation through Si NPs has been achieved for nanostructured Si NP-Er$^{3+}$ co-doped Al$_2$O$_3$ films prepared in a single step process at room temperature. The sensitized emitting Er ions are in contact with the Si NPs, since the PL spectra are consistent with a SiO$_2$-rich environment in spite of the Al$_2$O$_3$ embedding matrix. The fraction of excited Er$^{3+}$ is maximized when the Er is deposited directly on the Si NPs, and reaches values as high as 53%. The energy transfer is mainly through the highly efficient interband exciton recombination mechanism. The design of films with coupling through contact opens a new route to build efficient light-emitting devices in codoped systems.

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