Excitation wavelength-independent sensitized Er$^{3+}$ concentration in as-deposited and low temperature annealed Si-rich SiO$_2$ films

Oleksandr Savchyn,$^{1, a)}$ Ravi M. Todi,$^2$ Kevin R. Coffey,$^{2, 3}$ Luis K. Ono$^3$, Beatriz Roldan Cuenya$^3$ and Pieter G. Kik$^{1, 3}$

$^1$CREOL, the College of Optics and Photonics, University of Central Florida, Orlando, FL 32816 USA
$^2$Advanced Materials Processing and Analysis Center (AMPAC), University of Central Florida, Orlando, FL 32816 USA
$^3$Department of Physics, University of Central Florida, Orlando, FL 32816 USA

Erbium sensitization is observed in as-deposited Er$^{3+}$ doped Si-rich SiO$_2$, ruling out the involvement of Si nanocrystals in the Er$^{3+}$ excitation in these samples. The Er$^{3+}$ absorption cross section in this material is similar within a factor 3 to that of samples annealed at 600$^\circ$C under 355 nm and 532 nm excitation. The density of excitable Er$^{3+}$ ions is shown to be excitation wavelength independent, while the shape of the Er$^{3+}$ excitation spectra is governed by a wavelength-dependent Er$^{3+}$ absorption cross section. These findings enable the use of a broad range of wavelengths for the efficient excitation of this gain medium.

$^a)$ Electronic mail: osavchyn@mail.ucf.edu
Among the different approaches to the realization of a Si laser\textsuperscript{1-5} using the emission from Er\textsuperscript{3+} sensitized in Si-rich SiO\textsubscript{2} (SRSO) received significant attention.\textsuperscript{6} Recently it was shown that luminescence centers (LCs), not Si nanocrystals (NCs), are the dominant Er\textsuperscript{3+} sensitizer in SRSO.\textsuperscript{7,8} The ability to sensitize Er\textsuperscript{3+} without Si NCs has a number of advantages: a higher density of sensitized Er\textsuperscript{3+} ions,\textsuperscript{7} a favorable temperature dependence of the Er\textsuperscript{3+} emission,\textsuperscript{9} and a possible reduction of confined carrier absorption\textsuperscript{10, 11} and scattering.\textsuperscript{12} While the sensitization of Er\textsuperscript{3+} by LC is highly excitation wavelength ($\lambda_{\text{exc}}$) dependent,\textsuperscript{7} it is not clear if this is due to a wavelength-dependent concentration of sensitizers (and thus excitable Er\textsuperscript{3+} ions) or due to a wavelength-dependent cross section of the sensitizers. The former would correspond to excitation via an inhomogeneous distribution of LC related levels in the SRSO bandgap leading to a wavelength-dependent number of possible transitions, while the latter would correspond to excitation through LCs with an intrinsic wavelength-dependent absorption cross section associated with a broad absorption band of each LC. In the present study we demonstrate that the density of sensitized Er\textsuperscript{3+} ions is remarkably constant with changing $\lambda_{\text{exc}}$ while the Er\textsuperscript{3+} effective absorption cross section shows a significant wavelength dependence.

An Er-doped Si-rich SiO\textsubscript{2} film (thickness 110 nm) containing 12 at. % of excess Si and 0.63 at. % of Er was sputter deposited onto a Si wafer (sample temperature $< 40^\circ$C). An as-deposited sample and two samples respectively annealed at 600°C and 1100°C (labelled LTA and HTA) for 100 s in flowing N\textsubscript{2} and subsequently passivated for 30 min. in forming gas (N\textsubscript{2}:H\textsubscript{2}=95\%:5\%) at 500°C were studied. X-ray photoelectron spectroscopy (XPS) measurements were performed on etched to a thickness of 50 ± 8 nm samples using the Al K\textalpha 
 line (1486.6 eV) of an X-ray source. Photoluminescence (PL) spectra (resolution ~ 10 nm) were taken at room temperature using the 351 nm line of a Kr-ion laser (0.7 W/cm\textsuperscript{2}). Excitation spectra were taken using Xe-lamp emission filtered through a monochromator. Time-dependent PL measurements (resolution 80 ns) were done under pulsed excitation using the 355 nm and 532 nm lines of a Nd-doped yttrium aluminum garnet laser (pulse length 5 ns). The laser spot area was determined with an accuracy better than ± 10 %. All spectral PL measurements were done in
the linear regime of PL vs. power and corrected for system response. The absence of pump induced sample damage was verified for the highest pump power used. More information on the experimental techniques can be found in Refs. 7, 13.

Figure 1 shows the PL spectra of the as-deposited, LTA and HTA samples taken under continuous wave (cw) excitation at 351 nm. The spectra of as-deposited and LTA samples contain emission bands peaking at ~ 550 nm, 981 nm and 1535 nm corresponding to the emission from the Si-excess-related LCs \(^{14}\) and \(^{15}\) Er\(^{3+}\) transitions \(^{4}I_{11/2} \rightarrow ^{4}I_{15/2}\) and \(^{4}I_{13/2} \rightarrow ^{4}I_{15/2}\) respectively. The spectrum of the HTA sample exhibits emission bands peaking at ~ 780 nm and 1535 nm corresponding to the emission from Si NCs and \(^{3+}\) Er\(^{3+}\) transition \(^{4}I_{13/2} \rightarrow ^{4}I_{15/2}\) respectively. No \(^{3+}\) Er emission was observed in the sample containing a similar Er concentration but no silicon excess under cw and pulsed excitation.

The inset of Fig. 2 shows XPS spectra from the Si-2p core level region of Er-doped SRSO films for an as-deposited sample and samples annealed at 600°C and 1100°C as well as reference data from a Si (100) substrate and a co-sputtered unannealed Er-doped SiO\(_2\) film. The known binding energies (BEs) of Si\(^0\) and Si\(^4+\) are indicated by the vertical lines. The XPS spectrum of the as-deposited film shows a clear Si\(^{4+}\) peak, as well as a small broad shoulder in the BE region where Si\(^3+\), Si\(^{2+}\) and Si\(^+\) species are expected (~100-102 eV).\(^{15}\) The latter is attributed to the presence of excess Si in the film. In the sample annealed at 600°C no Si\(^0\) signal is observed. The sample annealed at 1100°C does exhibit a clear Si\(^0\) peak, indicative of the nucleation and growth of extended Si inclusions. These results conclusively show that no extended Si aggregates are present in the as-deposited sample and the sample annealed at 600°C.

Figure 2 shows the excitation spectra corrected for photon fluence \((I(\lambda_{\text{exc}})/\varphi(\lambda_{\text{exc}}))\), with \(I\) the PL intensity and \(\varphi\) (m\(^2\)) the pump photon fluence) \(^{3+}\) Er PL at 1535 nm in as-deposited, LTA and HTA samples, the LC PL at 850 nm in the as-deposited and LTA samples and the Si NC PL at 850 nm in the HTA sample. The 1535 nm excitation spectra show a gradual increase of the PL intensity for decreasing \(\lambda_{\text{exc}}\). The absence of resonances in the \(^{3+}\) Er excitation spectra and their identical behavior
confirms that the excitation of Er\(^{3+}\) is predominantly indirect and of the same origin in all samples. Furthermore, the similarity between the 1535 nm Er\(^{3+}\) excitation spectra and the 850 nm LC PL of the as-deposited and LTA samples strongly suggests that the sensitization is mediated by the LCs, as was previously proposed.\(^7\) Finaly, the significantly different spectral shape of the Si NC excitation spectrum of the HTA sample demonstrates that Si NCs are not the dominant source of Er\(^{3+}\) excitation in HTA samples.

Figure 3 shows the 1535 nm Er\(^{3+}\) PL intensity at t=80 ns after the pulse as a function of pump photon fluence per pulse \(\phi\) (m\(^{-2}\)) under 355 nm and 532 nm excitation for the as-deposited and LTA samples, shown on the same relative scale. No significant relaxation at 1535 nm could be detected on a time scale shorter than \(\sim 80\) ns, and consequently the signal recorded at \(t = 80\) ns is considered to be representative of the Er\(^{3+}\) PL intensity immediately after the excitation pulse. Data on the HTA sample are not included due to the presence of a fast background signal at 1535 nm unrelated to Er\(^{3+}\). This fast background was also observed in previous work by independent authors.\(^{16,17}\) The exact origin of the background is not known, however its presence only in HTA samples suggests that this component is related to transitions in the Si NC or at the Si NC surface. Figure 3 demonstrates the increase and subsequent saturation of the Er\(^{3+}\) PL at 1535 nm with increasing photon flux. Assuming that no significant Er\(^{3+}\) relaxation takes place during the excitation, the LC-mediated Er\(^{3+}\) excitation efficiency is pump fluence independent, and the Er\(^{3+}\) radiative rate is identical in both the samples, the Er\(^{3+}\) PL intensity immediately after pulsed excitation is given by

\[
I_{Er}(\phi) \propto N_{Er}^* = N_{Er} (1 - e^{-\sigma_{Er} \phi})
\]  

with \(N_{Er}^*\) the density of excited Er\(^{3+}\) ions, \(N_{Er}\) the density of sensitized Er\(^{3+}\) ions, and \(\sigma_{Er}\) the total effective Er\(^{3+}\) absorption cross section. Note that due to the multilevel nature of the Er\(^{3+}\) excitation\(^{13,18}\) the value of \(\sigma_{Er}\) represents the sum of the absorption cross sections of all sensitized Er\(^{3+}\) levels due to the fact that the observed saturation results from ground state depletion. The solid lines in Fig. 3
represent fits to the measured data using Eq. (1), and show good agreement for both $\lambda_{\text{exc}}$ and for both samples.

Table I lists the obtained values of $\sigma_{\text{Er}}$ and $N_{\text{Er}}$ based on the fits in Fig. 3. The value of $\sigma_{\text{Er}}$ at 355 nm in the LTA sample is in agreement with that found previously from cw measurements. For both 355 nm and 532 nm excitation the difference in cross section between the as-deposited and the LTA sample is found to be less than a factor $\sim 3$. The fact that similar values of the $\sigma_{\text{Er}}$ are observed in as-deposited, LTA and HTA samples, combined with the similar Er$^{3+}$ excitation spectra in these samples (Fig. 2) provides further evidence that the indirect excitation of Er$^{3+}$ in as-deposited SRSO is the same as in LTA samples and the sample containing Si NCs (HTA).

While the fits in Fig. 3 do not provide absolute values for $N_{\text{Er}}$, the relative magnitudes of $N_{\text{Er}}$ can be compared. We find that $N_{\text{Er}}^{\text{LTA}}/N_{\text{Er}}^{\text{as-dep}} \approx 1.4$ for both 355 nm and 532 nm excitation. Apparently the 600°C anneal of the LTA sample only slightly increases the density of indirectly excitable Er$^{3+}$ ions. This in turn suggests that the density of Si-excess-related sensitizers present in as-deposited samples is not strongly affected by a low-temperature anneal.

Using the values in Table I the origin of the wavelength dependent excitation spectra in Fig. 2 can be determined. At low power, the excitation spectrum is given by

$$I_{\text{Er}}(\lambda_{\text{exc}})/\varphi(\lambda_{\text{exc}}) \propto \sigma_{\text{Er}}(\lambda_{\text{exc}}) \times N_{\text{Er}}(\lambda_{\text{exc}})$$

(2)

Note that this relation leaves open the possibility of a wavelength-dependent number of sensitized Er$^{3+}$ ions. Fig. 2 shows that $I_{\text{Er}}(\lambda_{\text{exc}})/\varphi(\lambda_{\text{exc}})$ increases by a factor $\sim 20$ and $\sim 32$ for as-deposited and LTA samples respectively as $\lambda_{\text{exc}}$ decreases from 532 nm to 355 nm. By comparison, in this same wavelength range the term $\sigma_{\text{Er}}(\lambda_{\text{exc}})\times N_{\text{Er}}(\lambda_{\text{exc}})$ obtained from pulsed measurements increases by a factor $\sim 15$ and $\sim 32$ for the as deposited and LTA sample respectively. The good correspondence between these values indicates that we may directly compare the excitation spectra in Fig. 2 with the values in Table 1 obtained under pulsed excitation. We find that the $N_{\text{Er}}$ is approximately independent of $\lambda_{\text{exc}}$ (Table I). It is therefore concluded that the rapid increase in Er$^{3+}$ PL with decreasing $\lambda_{\text{exc}}$ is due predominantly to an
increase of $\sigma_{Er}$ and thus of the LC absorption cross section, assuming a fixed number of LCs per Er$^{3+}$ ion.

The fact that the density of indirectly excitable Er$^{3+}$ ions does not change with the $\lambda_{exc}$ rules out the possibility that the shape of the LC excitation spectrum is related to a varying density of LC levels in the SRSSO gap. Instead, we must conclude that the LCs exhibit an increasing optical cross section as the excitation wavelength is decreased and exhibit a broad absorption band that extends at least from 2.3 eV to 3.5 eV. The fact that all LCs exhibit a similar absorption spectrum while a broad PL spectrum is observed seems to suggest that significant relaxation of the LCs can occur after excitation, leading to homogenous broadening. The absence of resonant features in the LC PL spectra around Er$^{3+}$ transitions seems to indicate that the LC mediated Er$^{3+}$ excitation is non-resonant, however further research is needed to determine the details of the energy transfer mechanism.

In summary, indirect excitation of Er$^{3+}$ in as-deposited Si-rich SiO$_2$ has been demonstrated. The observation of similar values of the Er$^{3+}$ effective absorption cross section and similar excitation spectra in as-deposited samples and samples annealed at 600°C and 1100°C shows that the excitation mechanism is largely independent of annealing treatment. The increase of the Er$^{3+}$ emission intensity at 1535 nm with decreasing excitation wavelength is demonstrated to be predominantly due to an increase of the Er$^{3+}$ effective absorption cross section rather than due to an increase of the density of sensitized Er$^{3+}$ ions. The demonstrated excitation wavelength independent density of indirectly excited Er$^{3+}$ ions implies that similar gain could be achieved in amplifiers and lasers based on this material using a broad range of pump wavelengths.

**Acknowledgement**

This work was supported by the National Science Foundation CAREER No. ECCS-0644228.
References

Table 1. Values of $\sigma_{Er}$ and $N_{Er}$ under pulsed 355 nm and 532 nm excitation for as-deposited and LTA samples.

<table>
<thead>
<tr>
<th>Parameter \ Sample</th>
<th>As deposited</th>
<th>LTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{Er}(355 \ nm)$, ($10^{-16}$ cm$^2$)</td>
<td>2.09±0.22</td>
<td>6.14±0.63</td>
</tr>
<tr>
<td>$N_{Er}(355 \ nm)$, (arb. units)</td>
<td>0.70±0.07</td>
<td>1.00±0.10</td>
</tr>
<tr>
<td>$\sigma_{Er}(532 \ nm)$, ($10^{-16}$ cm$^2$)</td>
<td>0.164±0.018</td>
<td>0.237±0.025</td>
</tr>
<tr>
<td>$N_{Er}(532 \ nm)$, (arb. units)</td>
<td>0.58±0.07</td>
<td>0.82±0.09</td>
</tr>
</tbody>
</table>
List of figure captions

Figure 1. (Color online) PL spectra of Er-doped SRSO of as-deposited, LTA and HTA samples under cw excitation at 351 nm.

Figure 2. (Color online) Excitation spectra of Er$^{3+}$ emission at 1535 nm (as-deposited, LTA and HTA samples), LC emission at 850 nm (LTA sample) and Si NCs emission at 850 nm (HTA sample). The corresponding scaling factors are included. Inset: XPS spectra of as-deposited and annealed (600°C and 1100°C) Er-doped SRSO, a Si (100) substrate and a sputtered Er:SiO$_2$ film.

Figure 3. (Color online) The dependence of the relative density of excited Er$^{3+}$ ions $N_{Er^*}$ in LTA (squares) and as-deposited (circles) Er-doped SRSO on pump flux under (a) 355 nm and (b) 532 nm pulsed excitation. The solid lines represent fits to the data.
(a) $\lambda_{\text{exc}} = 355 \text{ nm}$

- $\sigma_{\text{LTA Er 355 nm}} = 6.14 \times 10^{-16} \text{ cm}^2$
- $\sigma_{\text{as-dep Er 355 nm}} = 2.09 \times 10^{-16} \text{ cm}^2$

(b) $\lambda_{\text{exc}} = 532 \text{ nm}$

- $\sigma_{\text{LTA Er 532 nm}} = 0.24 \times 10^{-16} \text{ cm}^2$
- $\sigma_{\text{as-dep Er 532 nm}} = 0.16 \times 10^{-16} \text{ cm}^2$