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Erbium emission in MOS light emitting devices: from energy transfer to direct impact excitation

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Abstract
The electroluminescence (EL) at 1.54 µm of metal–oxide–semiconductor (MOS) devices with Er 3+ ions embedded in the silicon-rich silicon oxide (SRSO) layer has been investigated under different polarization conditions and compared with that of erbium doped SiO 2 layers. EL time-resolved measurements allowed us to distinguish between two different excitation mechanisms responsible for the Er 3+ emission under an alternate pulsed voltage signal (APV). Energy transfer from silicon nanoclusters (Si-ncs) to Er 3+ is clearly observed at low-field APV excitation. We demonstrate that sequential electron and hole injection at the edges of the pulses creates excited states in Si-ncs which upon recombination transfer their energy to Er 3+ ions. On the contrary, direct impact excitation of Er 3+ by hot injected carriers starts at the Fowler–Nordheim injection threshold (above 5 MV cm −1) and dominates for high-field APV excitation.

(Some figures may appear in colour only in the online journal)

1. Introduction

The realization of an efficient and integrated silicon based light emitter is considered as one of the key points if silicon photonics are to achieve monolithic electronic and photonic functional integration in the same chip. In particular, Er 3+ doped materials have been thoroughly studied, as the radiative 4f shell intraband transition provides efficient emission at telecom wavelengths (1.54 µm) [1–3].

Several works have cited the silicon-rich silicon oxide (SRSO) system as the most promising host for Er 3+ ions [4–6]. When an as-deposited SRSO undergoes annealing at high temperature, the excess silicon segregates into a nanophase composed of nanoclusters and/or nanocrystals depending on the annealing conditions. The optimized environment of the erbium ions inside the silicon oxide matrix and the contribution of silicon nanostructures to Er 3+ emission results in an enhancement and a spectral broadening of the effective excitation cross-section at 1.54 µm under optical pumping [6–8].

Nonetheless, under electrical pumping the coupling between silicon nanoclusters or nanocrystals (Si-ncs) and Er 3+ ions is still controversial. Some authors have reported an enhancement of the Er 3+ electroluminescence (EL) in SRSO
at low voltages [9, 10]. Others reported a diminution of the EL signal for increasing Si excess and postulated leakage of currents through Si-ncs paths and/or less energetic injected carriers—in comparison with pure SiO$_2$—as the main reason for decreasing efficiency [11].

The visible/near infrared emission of Si-ncs under different polarization conditions, i.e. a direct current (DC) or alternate pulsed voltage (APV) regime, has been widely studied. In APV conditions, EL at low voltages is greatly enhanced due to the sequential injection of electron and holes into Si-ncs at the edges of the pulses and the following radiative recombination [12, 13]. However, the behavior of Er$^{3+}$ emission under APV excitation has not been studied in detail. If indirect excitation of Er$^{3+}$ ions (through Si-ncs) were to occur efficiently for electrical excitation, APV polarization could bring about significant improvement in the performance of Er$^{3+}$ MOSLEDs (MOS capacitor or transistors acting as light emitting devices).

In this work, we have fabricated Si based MOSLEDs containing Er$^{3+}$ ions embedded in either stoichiometric SiO$_2$ or SRSO layers. We have characterized the electrical and optical response when polarizing MOSLEDs under DC or APV signals. Results show two different EL excitation mechanisms for the coupled system with Si-ncs and Er$^{3+}$: (i) indirect excitation—cold carriers excite Si-ncs by sequential injection and the energy is transferred to Er$^{3+}$; and (ii) direct excitation—Er$^{3+}$ is directly energized by hot energetic carriers through impact excitation. Moreover, we demonstrate the existence of a narrow voltage window, where the Er$^{3+}$ excitation mechanism changes from energy transfer to direct impact excitation. Finally, a fast EL overshoot has been observed at high APV signals, attributed to the emission of highly stressed defects in the host matrix.

2. Sample fabrication and experimental setup

Two series of MOS devices were fabricated using standard complementary metal–oxide–semiconductor (CMOS) techniques, where the oxide layer has been replaced either by a SRSO or by a dry thermal silicon oxide with the same Er$^{3+}$ implantation. In the following, all the devices with a SRSO layer will be labeled as ‘device 1’, while those containing a thermal silicon oxide will be labeled as ‘device 2’.

Concerning device 1 a 50 nm thick substoichiometric SiO$_x$ ($x < 2$) film was deposited on a low resistivity p-type Si substrate by low pressure chemical vapor deposition (LPCVD). The nominal value of silicon excess in the matrix was 12%, allowing Si-nc formation after annealing at 900 $^\circ$C for 1 h. The same annealing treatment was applied to grow the thermal oxide in device 2.

After the annealing treatment, both films were implanted with Er$^{3+}$ ions with a dose of $10^{15}$ at cm$^{-2}$ at 20 keV of energy. Finally, post-implantation annealing was performed in order to activate Er$^{3+}$ ions and cure the matrix from the implantation. Further details concerning Er$^{3+}$ implantation profiles, photoluminescence (PL), x-ray photoelectron spectroscopy (XPS) and surface ion mass spectrometry (SIMS) measurements can be found in [14].

In addition, 100 nm thick poly-crystalline silicon with an n-type doped layer ($1 \times 10^{20}$ at cm$^{-3}$) was deposited on top and used as an optically semi-transparent gate electrode. 100 $\times$ 100 $\mu$m$^2$ aluminum pads were photolithographically defined on the devices to facilitate electrical polarization and light extraction. The emission area is composed of a square of area 0.09 mm$^2$. The cross-section of the devices can be observed in the inset of figure 1(a).

A semiconductor device analyzer (Agilent B1500A) and a probe station (Cascade Microtech Summit 1100) were used for current–voltage ($I–V$) measurements. APV excitation under a square voltage signal at low frequencies was performed replacing the semiconductor device analyzer by a pulse generator (Agilent 8114A).

EL signals were analyzed by an Acton 2300i grating spectrometer and detected by a cryogenically cooled PI spec-10-100B/LN charge-coupled device or a photomultiplier tube (H10330-25). A digital oscilloscope was finally used for data collection with a temporal resolution of 1 $\mu$s.

The micro-photoluminescence ($\mu$PL) measurements were performed in a standard $\mu$PL setup in a 45° configu-
ration. The PL signal of the samples was studied by using two different lines of an argon laser (488 and 476 nm) as a pump source. The 488 nm line is resonant with the \(^{4}I_{15/2} \rightarrow ^{4}I_{15/2}\) transition of the Er\(^{3+}\) ions, while the 476 nm line is non-resonant with an Er\(^{3+}\) transition and only excites the Si-ncs, which have slightly higher excitation cross-section at this wavelength than at 488 nm.

The shape of the pumping spot on the sample is ellipsoidal, with an area of \(6 \times 10^{-5}\) mm\(^2\), which is small enough to ensure the excitation of a single device.

A short working distance objective was used to collect the PL emission and to focus it in a monochromator with focal length of 750 mm and a spectral resolution of 0.03 nm, coupled to the same photomultiplier tube described above.

3. Results and discussion

3.1. Electro-optical characterization

The electrical excitation in DC was done under accumulation conditions, i.e. applying negative voltages over the gate electrode with the substrate grounded (see figure 1(b)). This configuration is more convenient as it provides the majority of carriers from both the gate electrode (electrons) and from the substrate (holes). Quasi-static \(I(V)\) characteristics of devices at room temperature are shown in figure 1 (20 mV s\(^{-1}\)). A difference of 17 V between the SRSO layer (device 1) and the pure SiO\(_2\) (device 2) is observed in the threshold voltage for conduction (\(V_{TH}\)), defined arbitrarily as the voltage required to obtain 1 nA of gate current. It is worth noting that a homogeneity study was performed on each wafer obtaining around 95% of reproducibility in the electro-optical characteristics.

It is thus clear that Si-ncs are responsible for an increased conductivity in the SRSO with respect to pure SiO\(_2\). By a detailed fitting procedure, it has been determined that the dominant conduction is injection limited and proceeds for both SRSO and SiO\(_2\) (after a threshold voltage) by Fowler–Nordheim (FN) tunnel injection of hot electrons coming from the gate electrode [15]:

\[
J = \frac{q^{2}E^{2}}{8\pi\hbar\phi_{b}} \exp \left( -\frac{4\sqrt{2m_{\text{ox}}^{\ast}(q\phi_{b})^{3}}}{3\hbar qE} \right)
\]

where \(m_{\text{ox}}^{\ast}\) is the effective mass of electrons in the conduction band, \(E\) is the electric field applied, \(\phi_{b}\) is the potential barrier height, \(q\) is the single electron charge and \(\hbar(h)\) is the (reduced) Planck’s constant.

The agreement with the FN conduction law suggests that a homogeneity study was performed on each wafer as taken by various authors [18, 20].

A thorough study of the evolution of the EL at 1.54 \(\mu m\) as a function of the applied DC voltage is reported in figure 2. The voltages were swept from low to just below the breakdown voltage, integrating the whole EL spectrum at each voltage value (see inset of figure 2). However, care should be taken with the highest electric fields applied (above 7 MV cm\(^{-1}\) for device 1 and 10 MV cm\(^{-1}\) for device 2), as Si bulk emission at 1.1 \(\mu m\) has been observed in the spectra leading to a tail until the 1.5 \(\mu m\) region. In this regime, the active layer is not thick enough to cool down the highly energetic electrons from the gate, which pass through the layer and impact the silicon bulk directly. Furthermore, at these high electric fields the devices are partially broken due to the high electric stress, providing (i) higher leakage currents for a given voltage, (ii) lower EL values for a given current, and (iii) poor device reliability. As a consequence, the depletion of the EL\((V)\) characteristic at high voltages cannot be considered as a complete saturation of the optically active Er\(^{3+}\) ions, but as a diminution of the electro-optical properties of the devices.

Therefore, the optimum working conditions were established below these maximum fields. Additionally, the threshold voltage for the EL (\(V_{EL-TH}\)) can be extracted from figure 2, determining a minimum voltage for light emission of 25 V in device 1 (5 MV cm\(^{-1}\)) and 41 V (8 MV cm\(^{-1}\)) for device 2. These values are very similar to the threshold voltage for conduction and allow extracting a minimum gate current to observe EL of around 1 nA. From those results, the power efficiency was found to be very similar in both devices with values around 0.01%, pointing out that the emission properties at 1.54 \(\mu m\) are not enhanced by the presence of Si-ncs, although the conductivity across the active layer is improved.

In order to study the dynamics of our system in the infrared region, time-resolved EL measurements centered at
rate equations for a nearly two-level system \cite{21, 22}:

\[ \text{Er} \]

\[ \tau_{\text{rise}} = 1 \text{ ms} \]

\[ \tau_{\text{decay}} = 1.2 \text{ ms} \]

Figure 3. (a) EL(t) at 1.54 \( \mu \text{m} \) of device 1 with the exponential fits of the decay and rise times. (b) A negative square voltage (from 0 to \(-30 \text{ V}) was used for the excitation. (c) Effective excitation cross-section fit at 1.54 \( \mu \text{m} \) for the \( \text{Er}^{3+}: \text{SRSO} \) sample (solid line, black circles) and for the \( \text{Er}^{3+}: \text{SiO}_2 \) system (dashed line, red triangles). Error bars are smaller than the experimental points shown.

1.54 \( \mu \text{m} \) were carried out. The time evolution of the EL signal at negative square voltages is reported in figure 3(a) for the \( \text{Er}^{3+}: \text{SRSO} \) sample. The signal can be modeled by using the rate equations for a nearly two-level system \cite{21, 22}:

\[ \frac{dN_2}{dt} = \sigma j e (N_{\text{total}} - N_2) - \frac{N_2}{\tau_{\text{decay}}}, \]

\[ \tau_{\text{rise}} = \frac{1}{\frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{non-rad}}}} \]

where \( \sigma \) is the effective excitation cross-section, \( j \) is the incident current density, \( e \) is the single electron charge, \( \tau_{\text{decay}} \) is the total lifetime \([\text{radiative (}\tau_{\text{rad}}\text{) and non-radiative (}\tau_{\text{non-rad}}\text{)}]\) and \( N_{\text{total}} \) and \( N_2 \) are the total implanted and the excited \( \text{Er}^{3+} \) ions in the first energy level, respectively. When the electric excitation is turned on, the EL intensity behaves as:

\[ \text{EL}_{\text{on}}(t) = \text{EL}_0 \left[ 1 - \exp \left( -\left( \frac{\sigma j e}{\tau_{\text{rise}}} + \frac{1}{\tau_{\text{decay}}} \right) t \right) \right]. \]

With \( \text{EL}_0 \) the electroluminescence in the steady state, the rise time will hence follow the equation:

\[ \frac{1}{\tau_{\text{rise}}} = \frac{1}{\tau_{\text{decay}}} + \frac{j \sigma}{e} \]

and the expression for the turn-off of EL:

\[ \text{EL}_{\text{off}}(t) = \text{EL}_0 \exp \left( -\frac{t}{\tau_{\text{decay}}} \right). \]

Therefore, using equations (4) and (6) to determine the time constants \( (\tau_{\text{rise}} \text{ and } \tau_{\text{decay}}) \), the effective excitation cross-section at 1.54 \( \mu \text{m} \) was extracted. Figure 3(a) shows the fits of the EL signal under a square APV signal from 0 to \(-30 \text{ V at 50 Hz (figure 3(b)) with a rise time of 1 ms and a decay time of 1.2 ms [22]. An effective} \]

\[ \sigma = (5.6 \pm 1) \times 10^{-14} \text{ cm}^2 \]

and determined for the \( \text{Er}^{3+}: \text{SRSO} \) sample, and \( \sigma = (5.8 \pm 1) \times 10^{-14} \text{ cm}^2 \) for the \( \text{Er}^{3+} \) doped SiO\textsubscript{2} layer, with a given current density ranging from 1 \( \mu \text{A cm}^{-2} \) to 5 mA cm\textsuperscript{-2} (figure 3(c)). Then, the resemblance between both values becomes conclusive proof of the direct excitation of \( \text{Er}^{3+} \) ions under DC polarization at high voltages, even when Si-ncs are present in the matrix. Notice that the effective excitation cross-sections presented in the present work are the highest ever reported \cite{23, 24}. The understanding of these values needs further investigation.

3.2. Symmetric alternate pulsed polarization for energy transfer activation

The transient EL signal was also studied in our devices when polarizing under symmetric square voltage signals (i.e. equal negative and positive voltages relative to zero) at frequencies ranging from 25 Hz up to 1 kHz, which corresponds with the typical lifetime of \( \text{Er}^{3+} \) ions \((1 \text{ ms})\). Figure 4 shows the EL at 1.54 \( \mu \text{m} \) for a square voltage switched from \(-20 \) to 20 V at 25 Hz, below the EL threshold voltage in DC. The first thing to point out is that, contrary to the DC case, EL is observed at 1.54 \( \mu \text{m} \) at this low applied voltage, as shown by the EL transients that appear at each voltage switch (by fixing the monochromator at 1.54 \( \mu \text{m} \); see figure 4(c)). Decay times were fitted for both peaks, obtaining values of 1.5 ms (figure 4(a)) and 1.8 ms, respectively (figure 4(b)). Those values are very close to the decay lifetimes measured in figures 3(a) and (b) under a negative APV excitation. Moreover, very fast rise times were observed in the EL when the voltage is switched, showing up the characteristic time \( (\tau = RC) \) of the setup \((\text{about 1 } \mu \text{s})\).

The presence of these two peaks has already been reported in the visible region by other authors when working
in APV excitation conditions with undoped Si-ncs based devices [25], and was ascribed to the sequential injection of holes and electrons into Si-ncs. Also, the difference in intensity between these two peaks can be explained considering that holes have tunneling back times longer than electrons, increasing the probability of creating an exciton at the positive semi-cycle (electrons tunneling towards Si-ncs). Therefore, the observed temporal behavior of the infrared EL (smaller rise time) suggests the influence of Si-ncs on the emission under this polarization, and more concretely their function as sensitizers for Er$^{3+}$ ions. Moreover, time-resolved measurements were also performed in the visible range under the same polarization conditions, showing two EL peaks similar to the ones reported in figure 4(c) (not shown).

More in-depth evidence of the indirect excitation of the Er$^{3+}$ ions for this excitation scheme comes from the comparison, in device 1, of the EL rise time under both negative (empty squares) and symmetrical (empty circles) square pulse voltage signals (see figure 5). Starting from the assumption that the energy transfer from Si-ncs to Er$^{3+}$ ions is known to be a very fast process [26], we report a difference of at least 200 $\mu$s in the temporal EL response depending on the polarization scheme (see the inset to figure 5). In addition, looking at the rise times, we observe a factor of $\sim$1000 between them, which suggest very different excitation cross-sections (also a factor of 1000) if equation (5) is assumed. Consequently, a correlation between the slower rise time (empty squares) and the direct excitation of Er$^{3+}$ ions, and the faster rise time (empty circles) with the energy transfer between Si-ncs to Er$^{3+}$ ions was inferred.

Visible and infrared spectra were acquired under different electric polarization conditions in order to correlate the emission of Si-ncs and Er$^{3+}$ ions. Figure 6 shows the visible spectra of the EL under both DC and APV excitation on device 1. As can be observed, different radiative transitions belonging to the excited state levels of Er$^{3+}$ ions are detected when a DC voltage is applied. Note that the same line shape was always observed whatever the voltage (from −25 to −45 V). In particular, the most energetic peaks appear at low voltages, preserving a linear ratio between the EL of each peak and the current applied, evincing a direct excitation of Er$^{3+}$ by means of hot carriers injected into the active layer [27].
On the contrary, under a symmetrical square wave voltage excitation (empty circles of figure 6), no \( \text{Er}^{3+} \) related peaks appear in the studied frequency range (25 Hz–1 kHz) and only a broad emission attributed to Si-ncs is observed. Furthermore, lower voltages are required to obtain luminescence in this regime, with a threshold voltage of \( \pm 15 \text{ V} \). Such a value lies 10 V below the minimum DC threshold voltage observed in figure 2.

The latest results provide evidence of different excitation mechanisms depending on the polarization applied in a single device. In particular, we are able to observe: (i) direct impact excitation of \( \text{Er}^{3+} \) ions under a DC regime and (ii) energy transfer from Si-ncs to \( \text{Er}^{3+} \) ions under symmetric square excitation. At this point it is important to state that the applied APV excitation plays a principal role in the energy transfer: for values below the DC threshold (\(< 25 \text{ V}\) ), carriers do not have enough energy to excite Si-ncs or \( \text{Er}^{3+} \) ions directly, although exciton formation is allowed inside nanocrystals by sequential injection, resulting in the energy transfer to \( \text{Er}^{3+} \) ions. On the contrary, when the symmetric APV regime reaches higher values than the threshold voltage in DC (\(> 25 \text{ V}\) ), a large number of carriers are able to excite \( \text{Er}^{3+} \) (and also Si-ncs) by direct impact, screening almost completely the contribution of the energy transfer to the EL at 1.54 \( \mu \text{m} \).

In order to further support our interpretation, we did time-resolved measurements under APV excitation around the EL threshold voltage on device 1 (figure 2). Figure 7 shows the transition between the two different EL excitation mechanisms at 1.54 \( \mu \text{m} \), depending on the APV signal applied. As observed, a small shoulder starts to appear on the EL(t) signal at \( \pm 25 \text{ V} \) and it is reinforced as the voltage values become larger, suggesting the appearance of a contribution to the excitation due to direct impact. Such a shoulder completely screens the contribution of the indirect excitation at higher voltages, because (i) the \( \text{Er}^{3+} \) ions excited by transfer are located in a region close to the Si substrate only and (ii) the amount of \( \text{Er}^{3+} \) ions coupled to Si-ncs is only a fraction of those which can be excited directly. Note finally that the transition voltage range (i.e. from energy transfer to impact ionization) is very narrow, about 2 V after the first signs of the EL shoulder.

### 3.3. Fast EL component

In addition to the \( \text{Er}^{3+} \) ions’ EL dynamics at 1.54 \( \mu \text{m} \) discussed above, at larger voltages sharp EL overshoots have been observed, characterized with much smaller decay time (in the order of few \( \mu \text{s} \)). They could be observed either in samples with or without Si-ncs, as shown in figures 7(b)–(d) for device 1 and figure 8 for device 2. In order to discard the influence of Si-nc, we have studied this feature on device 2. As the device requires larger voltages, we had to reduce duty cycle to 10% in order to overcome the power limitation of our setup. This allowed us to observe just one EL transient of typically 4 \( \mu \text{s} \) of decay time, as can be seen in figure 8. Moreover, the same behavior was observed at 1300 nm, which is well away from any \( \text{Er}^{3+} \) related contribution, and also in the visible part of the spectrum (not shown). This fast component has already been observed by other authors [26, 28] when carrying out PL measurements in SRSO layers with and without \( \text{Er}^{3+} \) ions, obtaining very fast decay times (typically of nanoseconds). Nevertheless, the nature of this emission is not clear yet. Some authors [28, 29] suggest an effect of recombination of defective centers either in the silica matrix or at the interface with the Si-nc, or an intraband recombination mechanism [26]. Others attribute this fast emission to Auger processes related to transitions of confined electrons or holes between the space-quantized levels of Si-ncs [30]. In our case, it is clear that it is not provided by any \( \text{Er}^{3+} \) related transitions since it does not show its characteristic spectral features. Furthermore, this fast contribution is also appreciable in pure silica layers with \( \text{Er}^{3+} \) ions, suggesting that it may not be related to Si-ncs but to defects on the silica matrix.

In order to better understand the origin of the fast component, \( \mu \text{PL} \) measurements were carried out. Active device area was pumped at two different wavelengths, one resonant with an \( \text{Er}^{3+} \) transition (488 nm), and the other...
Figure 8. EL(t) at 1.54 µm under a square symmetric voltage signal for device 2. The inset (a) shows the EL decay fit of the sharp EL overshoot.

4. Conclusions

In summary, we have studied the electroluminescence properties in near infrared of silicon based LEDs containing silicon-rich silicon oxide layers doped with Er³⁺ ions under different polarization schemes. Time-resolved EL measurements allowed us to show the presence of two different mechanisms of Er³⁺ excitation under electrical pumping. Under DC excitation, Fowler–Nordheim injection and visible transition on the Er³⁺ spectra suggest that direct impact of Er³⁺ is the main mechanism. Under an alternative pulsed excitation, there is a window of voltages where transfer to Er³⁺ ions is clearly demonstrated, through the creation of exciton in the Si-nc by sequential injection of electrons and holes. Under this regime, a much smaller rise time is observed. This is a promising result, as this lead to a much larger absorption cross-section which can be used in an optimized material to obtain a much larger efficiency of pumping.

Finally, a fast EL overshoot observed in Er³⁺:SRSO and Er³⁺:SiO₂ devices at high alternately pulsed voltages was ascribed to the emission of defects in the host silica matrix, and correlated with the background emission in µPL measurements.

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