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Structural parameters effect on the electrical and electroluminescence properties of silicon nanocrystals/SiO₂ superlattices

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Abstract
The effect of the oxide barrier thickness (t_SiO₂) reduction and the Si excess ([Si]_{exc}) increase on the electrical and electroluminescence (EL) properties of Si-rich oxynitride (SRON)/SiO₂ superlattices (SLs) is investigated. The active layers of the metal–oxide–semiconductor devices were fabricated by alternated deposition of SRON and SiO₂ layers on top of a Si substrate. The precipitation of the Si excess and thus formation of Si nanocrystals (NCs) within the SRON layers was achieved after an annealing treatment at 1150 °C. A structural characterization revealed a high crystalline quality of the SLs for all devices, and the evaluated NC crystalline size is in agreement with a good deposition and annealing control. We found a dramatic conductivity enhancement when the Si content is increased or the SiO₂ barrier thickness is decreased, due to a larger interaction of the carrier wavefunctions from adjacent layers. EL recombination dynamics were studied, revealing radiative recombination decay times of the order of tens of microseconds. Lower lifetimes were found at higher [Si]_{exc}, attributed to exciton confinement delocalization, whereas intermediate barrier thicknesses present the slowest decay. The electrical-to-light conversion efficiency increases monotonously at thicker barriers and smaller Si contents. We ascribe these effects mainly to free carriers, which enhance carrier transport through the SLs while strongly quenching light emission. Finally, the combination of the different results led us to conclude that t_{SiO₂} ~ 2 nm and [Si]_{exc} from 12 to 15 at% are the ideal structure parameters for a balanced electro-optical response of Si NC-based SLs.

Keywords: silicon nanocrystals, superlattices, electroluminescence, barrier thickness, silicon excess

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

1. Introduction

Huge efforts have been dedicated to adequately control the size of silicon nanocrystals (Si NCs) at nanometer scale, as it allows for band gap engineering thanks to the quantum confinement effect, which provides an enormous potential for light conversion [1, 2] and light emission [3–5] applications. Sandwiching the nanostructures between the proper Si-based matrix material has been demonstrated to produce the desired...
vertical size confinement at dimensions of few nanometers [6]. This can be achieved by means of the superlattice (SL) approach, which consists of the deposition of alternating nanometric silicon-rich and stoichiometric dielectric or semiconductor layers, followed by a high-temperature annealing treatment to induce phase separation within the Si-rich layers and consequent Si excess precipitation and crystallization in the form of Si NCs [6]. In particular, many works have focused on the usage of SiO2 to contain Si NCs and to be used as thin barriers in SiO2/Si NC SLs [7], because it efficiently blocks layer intermixing, and its control and manipulation are well achieved in the microelectronics industry.

The structural and optical properties from Si NCs have been extensively studied in the past, as a function of the nanostructure size and the stoichiometry of the Si-rich layers, with the nanostructures embedded either in bulk matrix [8, 9] or in conveniently arranged ensembles (SL structures) [7, 10, 11]. The assessment of the electrical behavior of NCs is more complex, requiring the deposition of metallic contacts to design a metal–oxide–semiconductor (MOS) device, for instance, which allows for a proper charge injection and extraction. Besides, the insulator matrix material usually states a drawback for carrier conduction, especially in the case of silicon oxide, whose barrier height can be hardly overcome by carriers [12]. After the long-term study on the electrical properties of bulk matrix-embedded NCs [13–15], many recent works have focused on the carrier transport taking place through the quasi-dielectric NC SLs. In these systems, lateral transport studies (i.e. along the Si-rich layers) have revealed a strong conduction dependence on the Si content as predicted by percolation theory, Si NC coalescence leading to a tune of transport mechanism from charge migration and Coulomb-like effects to tunneling [16]. Instead, vertical transport (i.e. across the layers) is commonly ascribed to trap-assisted- or tunnel-like mechanisms, depending on the structure parameters and the fabrication technique [17, 18]. The electroluminescence (EL) properties of this material structure have been investigated and correlated to the vertical size confinement at dimensions of few nanometers [6]. However, the in addition, time-resolved EL measurements allowed studying the carrier recombination dynamics within the SL structures. Finally, the EL emission power efficiency of the SL-based devices allowed determining the ideal SL structural parameters for obtaining a proper balance between carrier conduction and EL.

2. Experimental details

Alternating SRON and SiO2 SLs were deposited on B-doped (100)-Si substrates (base resistivity of 1–20 Ω cm) via plasma-enhanced chemical-vapor deposition, with a total number of five bilayers. In all samples, the SL thicknesses, \( t_{SRON} \), was held constant at 3.5 nm, observed in a previous work to be close to the optimum EL performance [20]. The fabricated samples are summarized in table 1. In a first set of samples, labeled as ‘B’ in the table, the SiO2 barrier thickness \( t_{SiO2} \) was varied from 1 to 3 nm (leading to a total thickness from 22.5 to 30.5 nm, respectively), whereas the stoichiometry of the Si-rich layers (SiONx) was fixed at \( x=0.93 \), which corresponds to a local Si excess \((|Si|_{exc})\) of 17 at% within the SRON layer. A second set of samples, labeled ‘E’ in the table, was aimed at the study of the Si excess effect on the EL properties. It consisted of five bilayers with a constant \( t_{SiO2} = 1 \) nm (the optimum achievable thickness for efficient electron conduction in these SL systems [18]), whereas the stoichiometry of the SiOx layers ranged between \( x=0.64 \) and 1.1, which is translated into \(|Si|_{exc} \) from 27 to 12 at%, respectively. A 22.5 nm bulk SRON sample was also deposited for the sake of comparison to the SL structure, with a global Si excess of 17 at%. All samples underwent an annealing treatment at 1150 °C for 1 h in N2, in order to promote phase separation and achieve the precipitation and crystallization of Si NCs. In addition, the samples were hydrogen passivated in a pure H2 ambient at 500 °C for 1 h. To analyze the electrical and electro-optical properties of the SLs, MOS-like capacitor devices were fabricated by means of photolithographic patterning of sputtered 70 nm thick ITO layer on top, as well as full-area Al on the bottom (see figure 1). The employed top-electrode circular area was \( \sim 2 \times 10^{-3} \) cm2. Further information on the material deposition and the device processing has been reported in previous works [7, 18, 20].

The structural quality of the Si NC/SiO2 SLs was monitored by Raman scattering, exciting the devices with the 325 nm line of a He–Cd continuous laser and collecting the resulting Raman spectra (via a 40× near-UV objective) with a Horiba Jobin-Yvon LabRam spectrometer (0.5 cm−1 resolution) coupled to a high-sensitive CCD. The laser beam was precisely focalized on the SL structure to get rid of the Si substrate Raman contribution. The electrical characterization was carried out in dark conditions and at room temperature by means of an Agilent B1500 semiconductor device analyzer, placing the devices in a Cascade Microtech Summit 11000
Table 1. Summary of the superlattice characteristics corresponding to the devices fabricated for the present study. Set labeled ‘B’ states for the barrier thickness study, whereas label ‘E’ refers to the Si excess (within SRON layer) study. Please note that devices B1.0 and E17 are indeed the same.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$t_{SRON}$ (nm)</th>
<th>$t_{SiO2}$ (nm)</th>
<th>$[Si]_{exc}$ (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1.0</td>
<td>3.5</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>B1.5</td>
<td>3.5</td>
<td>1.5</td>
<td>17</td>
</tr>
<tr>
<td>B2.0</td>
<td>3.5</td>
<td>2</td>
<td>17</td>
</tr>
<tr>
<td>B2.5</td>
<td>3.5</td>
<td>2.5</td>
<td>17</td>
</tr>
<tr>
<td>B3.0</td>
<td>3.5</td>
<td>3</td>
<td>17</td>
</tr>
<tr>
<td>E12</td>
<td>3.5</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>E15</td>
<td>3.5</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>E17</td>
<td>3.5</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>E19</td>
<td>3.5</td>
<td>1</td>
<td>19</td>
</tr>
<tr>
<td>E27</td>
<td>3.5</td>
<td>1</td>
<td>27</td>
</tr>
<tr>
<td>Bulk</td>
<td>22.5</td>
<td>—</td>
<td>17</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Structural investigation of the NC SLs

Prior to the device characterization, the structural quality of the Si NC/SiO$_2$ SLs was inspected by means of Raman spectroscopy. The resulting Raman spectra acquired for the different sets of devices are displayed in figures 2(a) and (b). The spectra exhibit three main features: (i) a sharp peak around 517 cm$^{-1}$ corresponding to the crystalline Si TO-LO mode, (ii) a broad shoulder growing at lower frequencies than the crystalline peak, coming from the amorphous Si phases present within the SL, and (iii) an overall background ascribed to disorder-activated SiO$_2$ or acoustic amorphous Si modes [10, 11].

Indeed, the observations from both device sets are tightly related to the structural formation of Si NCs within the SLs, of great importance to understand the electrical and EL properties of the system. From the Raman spectra, it was possible to extract information on the crystallized fraction of Si within the devices. For this, the SiO$_2$ Raman contribution was subtracted. The spectra were then fitted using a phonon confinement model for the crystalline peak and taking into account the shoulder related to the optical phonons contribution from amorphous Si. An average crystalline size of 3.6 nm was obtained for all samples, with a size dispersion of ±0.3 nm. Afterwards, the crystalline fraction ($f_c$) was retrieved establishing a proportion between the crystalline ($I_c$) and amorphous ($I_a$) integrated areas as $f_c = [1 - \gamma \cdot (I_a/I_c)]^{-1}$, where $\gamma$ is the crystalline-to-amorphous Si Raman scattering cross-section, evaluated in a reference sample with the same crystalline size excited at 532 and 325 nm. An exhaustive description of the crystalline size and crystalline fraction estimation method is found in [10]. The final results on $f_c$ are summarized in figure 2(c) for both sets of devices, all displaying a very high crystalline quality. It should be mentioned that, although the Si substrate signal has been carefully avoided, some signal might be still superposing the Si NCs contribution, inducing a systematic overestimation of $f_c$ in all devices; nevertheless, the trends, and therefore the consequent discussion, are reliable. On one hand, and as predicted by the spectra similitude in the barrier thickness device set, the crystalline fraction remains almost constant when increasing $t_{SiO2}$; therefore, we expect a similar NC structure in all devices. On the other hand, the Si excess increase does induce a reduction of the crystalline fraction. Despite larger Si content implies a higher crystalline signal, and thus a higher
presence of crystalline Si domains, the amorphous Si counterpart is also enhanced, resulting in an increasing amorphous Si phase within the SL. In addition, the fact that the crystalline signal increases but not the NC crystalline size indicates a larger number of NCs, which is in agreement with reported in-plane TEM images on similar NC-based samples showing higher density of NCs at higher Si contents [9].

3.2. Electrical and EL characterization

To determine the electrical properties of the devices under study, intensity versus voltage sweeps were carried out under accumulation regime (V < 0 applied to the gate) at room temperature, employing a constant ramp rate of 50 mV s\(^{-1}\). The results are summarized in figure 3, where the current density (J) versus voltage (V) curves are plotted (both in absolute value), to take into account the device area. The curves corresponding to some devices exhibit two different behaviors; a slowly varying current density is observed at low voltages, whereas it notoriously increases at medium-high voltage range. The former effect, attributed to a capacitor-related displacement current, suggests that charge is being trapped within the material in this regime. Instead, high voltages provide a conduction zone, associated to a Poole–Frenkel (bulk-limited) mechanism through NC allowed energy levels, demonstrated in a previous work on similar structures to be the dominant transport mechanism [20].

To analyze in more detail the effect of the barrier thickness and Si excess variation on the electrical properties of the SL systems, figure 3(a) shows the J(V) curves for different \(t_{\text{SiO}_2}\), with a constant Si excess in the SRON layers (17 at%), whereas figure 3(b) displays the curves for a different Si-rich layer stoichiometry, being \(t_{\text{SiO}_2} = 1\) nm. The most general feature we can draw from the curves, when decreasing the oxide barrier thickness and increasing the Si excess, is a clear and progressive increase of the current density within the conduction regime, as previously reported [18], indicating a better carrier flux. In addition, the bulk-limited conduction regime starts at lower voltages in increasingly conductive devices, which implies a lower charge trapping within the capacitor structure.

Regarding the SiO\(_2\) barrier study, when reducing the barrier thickness of the SL stack, the current density gradually increases, which is about several orders of magnitude larger than the single layer sample (device labeled as ‘Bulk’). In fact, the progressively lower distance from adjacent Si NCs layers (i.e. \(t_{\text{SiO}_2}\) is reduced) results in an increasing interaction of the carrier wavefunctions that leads to a current increase. It is also remarkable that similar J(V) curves were obtained for

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Figure 2. Raman spectra corresponding to the devices of the (a) barrier thickness (constant [Si]\(_{\text{exc}}\) = 17 at%) and (b) Si excess (fixed \(t_{\text{SiO}_2} = 1\) nm) sets. (c) Evaluated crystalline fraction from the spectra displayed in (a) and (b), taking into account the formalism described in [10]. The error bars account for a 2% fitting uncertainty of the Raman spectra.

Figure 3. Current density versus applied voltage, both in absolute value, corresponding to devices containing the SL structure under study: (a) different \(t_{\text{SiO}_2}\) at a fixed Si excess of 17 at% and (b) different Si excess at a constant \(t_{\text{SiO}_2} = 1\) nm. The corresponding curve for the bulk SRON layer (global Si excess of 17 at%) is displayed in both graphs.
SiO$_2$ barrier thicknesses of $t_{\text{SiO}_2} = 1.5$ to 1 nm, which suggests a very similar wavefunctions overlapping from adjacent layers for very short distances. In addition, the charge trapping region decreases when reducing $t_{\text{SiO}_2}$, which is directly associated to the decrease of the total thickness of the capacitor-like structure. Finally, and comparing our SL devices with the reference one with a single SiO$_2$ active layer, we observed that the bulk device exhibits a slightly larger conduction than the device containing SLs with $t_{\text{SiO}_2} = 3$ nm, which is an indication that the inter-NC distance in bulk is lower than 3 nm.

The Si excess effect on the device electrical properties is also relevant. On one hand, the high-field conduction is found to dramatically increase at higher $[\text{Si}]_{\text{exc}}$, indicating that the presence of larger amounts of precipitated Si notably favors the conductivity of the SL structure. On the other hand, the capacitor displacement current region clearly decreases until disappearing at larger Si excess. Taking into account that no variation exists of the total capacitor dimensions in this set of samples, this observation suggests that the increase of Si content in the SL reduces charge trapping. EL investigation is required in order to determine how this Si excess is affecting the charge transport of the material under study, considering its distribution throughout the SRON layer. In addition, monitoring the time evolution of the EL emission can provide valuable information about the recombination dynamics.

We spectrally analyzed the EL emission from the devices under study. Figure 4 displays the normalized acquired spectra for each structure corresponding to both device sets, the SiO$_2$ barrier thickness (figure 4(a)) and Si excess (figure 4(b)) dependences. The bulk sample was also analyzed for the sake of comparison to the SL structure results, which presents two well-defined features: a Gaussian-like emission beyond 800 nm and a low-intensity broad band centered around 550 nm. Whereas the former emission is related to the radiative recombination of the excitons formed within the Si quantum dots, the latter is typically attributed to electronic relaxation in oxide-related defects [3, 21]. When observing the spectra provided by the SLs, the absolute EL intensity corresponding to the defects band remains unchanged, while there is an increase of the excitonic recombination emission. In addition, the overall EL emitted by the single layer device is notably lower than its SL counterparts (about two orders of magnitude). The fact that the relative intensity of the recombination emission with respect to the defects-related one is strongly enhanced in the SL structure indicates that the vertical ordered arrangement of NCs (the emitting centers), which modifies transport, strongly affects the EL excitation efficiencies. Therefore, these results evidence the high quality of the fabricated SL structures. It should be noted that almost identical recombination-related peak position is observed for the device containing a bulk SRON layer and the SL-based ones (corresponding to the barrier thickness study and intermediate Si excesses), which is in accordance to the 3.5 nm NC size reported for bulk SRON in [22].

A more in-depth analysis can be performed on the EL emission coming from the SL-based devices, the figure revealing valuable information regarding its dependence on the structural parameters under study. Samples with different barrier thickness and constant Si excess exhibit an almost identical emission lineshape centered at $\sim 830$ nm (see figure 4(a)), with a small intensity variation from sample to sample. On the other hand, devices with different Si excess concentration display an emission peak that shifts to longer wavelengths ($\sim 60$ nm between the most opposite stoichiometries), a lineshape broadening and a huge intensity reduction when increasing the Si amount (see figure 4(b)).

Actually, considering that the origin of this emission is tightly related to the quantum confinement of carriers within the nanostructures [23], the structural parameters effect on the
variation of the EL peak position and broadness can be indirectly related to the NC formation and size control. In particular, the invariance of the peak position when reducing the oxide barrier thickness (see figure 4(a)) indicates that the morphology of the nanocluster remains unchanged, which is supported by the almost constant NC crystalline size determined by Raman. In other words, the different barrier thicknesses are acting well avoiding outdiffusion of Si excess into the barrier layer and, therefore, they do not alter the NC size control. Regarding the Si excess increase (see figure 4(b)), the peak redshift and broadening suggests that the quantum confinement within NCs is being progressively lost at larger \([\text{Si}]_{\text{exc}}\). This latter fact could be associated to the precipitation of larger nanoaggregates and/or a shorter inter-NC distance. Since 1 nm barriers have shown to preserve the vertical SL structure [11], the increase in Si content could induce the in-plane presence of either larger NCs or a higher density of nanostructures [9]. Actually, the Raman analysis described in section 3.1 provides consistence to the hypothesis of a larger number of NCs while preserving the mean NC crystalline size, which induces a shorter inter-NC distance and possibly causes Si coalescence. In fact, Si NC lateral coalescence at high Si content (above the percolation threshold) was reported in [16] in similar SL systems, producing the carrier wavefunction delocalization within the nanostructures and subsequent coupling of the electronic states. Due to the shorter inter-NC distance supported by the structural characterization, this effect might also take place in our devices, resulting in the relaxation of the quantum confinement effect, as observed in the past in III–V semiconductor quantum wells [24–26]. As well, this wavefunction coupling hypothesis is in agreement with the electrical characterization results, larger Si excesses considerably improving the system conductivity as observed in figure 3(b).

The EL peak intensity evolution under the different structural conditions was also monitored, whose results are summarized in figure 4(c). In the figure, a clear decrease of EL intensity is observed at larger Si excesses, whereas for a constant Si excess it exhibits a maximum at intermediate oxide barrier thicknesses \((t_{\text{SiO}_2} \approx 2 \text{ nm})\). In the case of higher \([\text{Si}]_{\text{exc}}\), the larger amorphous Si phase suggested by the structural characterization results in a higher presence of defects and other non-radiative recombination centers that quenches the overall EL intensity. As well, the higher density of Si NCs at higher Si content is translated into a shorter inter-NC distance, which also takes place at thinner oxide barriers, producing the delocalization of the carrier wavefunctions, the consequent radiative recombination diminution and therefore an EL emission decrease. A different mechanism takes place at thicker SiO\(_2\) barriers, probably ascribed to the higher degree of NC isolation (in the SL growth direction), impeding the NC interaction and thus the effective exciton formation within the nanostructures. Further investigation is needed towards the understanding of this latter effect, which, as well as the EL intensity effect on the overall device efficiency, will be discussed in the following sections.

### 3.3. Carrier recombination dynamics

To complement the information provided by the electrical and EL characterization, the carrier recombination dynamics corresponding to the different SL structures was also investigated by means of time-resolved EL measurements. For this, a square-pulse between 0 and \(-8 \text{ V}\) (with a duty cycle of 25%) was applied to all devices, the resulting integrated EL signal being monitored by a high-sensitive oscilloscope. As an example, figures 5(a)–(c) depict the applied pulse and the resulting current intensity and integrated EL intensity for the sample with \(t_{\text{SiO}_2} = 1 \text{ nm}\) and \([\text{Si}]_{\text{exc}} = 17 \text{ at}\%\) (named B1.0 and E17 in table 1). When the negative voltage is applied, electron injection takes place within the device, as shown by the negative (i.e. under accumulation) current intensity circulating through it. Consequently, EL rapidly increases (in a time scale of some microseconds for all samples) until the stationary emission is reached (labeled as dc level in the figure). The EL remains constant for the rest of the voltage pulse until the excitation drops to zero, which produces a sudden emission increase (labeled as EL overshoot in the figure). Afterwards, the emission decrease (EL decay in the figure) takes place, attaining complete decay at a time that strongly depends on the sample under study. This general behavior was also observed in all devices. In particular, figure 5(d) displays the integrated EL signal dynamics corresponding to the devices with different Si excess. In order to focus the dynamics study on both the overshoot and the EL decay, we normalized all signals to their dc level.

The constant EL emission observed in figure 5(c) within the dc level is in agreement with the constant current injection through the SLs (figure 5(b)), being the electron–hole generation (and thus recombination) rate kept fixed. When the pulsed excitation is switched off, a positive overshoot in current occurs that can be attributed to the extraction of trapped charge towards the opposite electrodes once the electric field disappears, also supported by the fast current intensity overshoot in figure 5(b). This frame can explain the EL overshoot observed at this point, thus ascribed to the created electron–hole pairs by accumulated charge within the device, which almost instantly recombine. In addition, the presence of free carriers in our system may also originate recombination centers that add to the already mentioned discharge carriers. The capacitor-related origin of the overshoot is corroborated by the different signal level in figure 5(d), where the peak intensity notably decreases with the Si excess (it even disappears beyond \([\text{Si}]_{\text{exc}} = 19 \text{ at}\%\)), the SLs becoming increasingly conductive. This, in turn, is in accordance to the lower charge-trapped region found at larger Si contents (see figure 3(b)). The preceding EL decay, on the contrary, is not ascribed to capacitative effects. Evidence of this is given by the fast (almost instantaneous) decay from the current intensity overshoot in figure 5(b) in comparison to the slower decay in EL displayed by the same device in figure 5(c). In addition, the EL decay is different for each device (see figure 5(d)), which reveals a SL structure-dependent characteristic decay time before the emission is totally quenched. To numerically analyze this effect, we fitted
a two-exponential decay function to the obtained decay curves:

\[ I_{EL}(t) \propto I_{EL,0} \cdot \left( e^{-t/\tau_1} + e^{-t/\tau_f} \right), \]

where \( I_{EL,0} \) is a pre-exponential factor. The fit results show that the EL emission decay obeys two well-differentiated time scales: a fast one (\( \tau_1 \)), in the order of tens of \( \mu s \) (in agreement with many reported works [27–29]), which is typically associated to the excitonic recombination within NCs; and a slow one (\( \tau_f \)), of several hundreds of \( \mu s \), which may be ascribed to the emission of larger NCs in the distribution. The origin of the slow lifetime may be related to cross-talk energy transfer between nanostructures, which makes this effect independent from the spectral EL distribution, as proved by the similar lifetime values irrespective of the SL structural conditions. On the contrary, the NC-related fast decay time presents a strong dependence on the SL characteristics (i.e. \( t_{SO2} \) and \([Si]_{exc}\)); therefore, it is the latter recombination time which will be studied in the following lines, whose results are plotted in figure 5(e) for both device sets. For the sake of comparing our EL decay time results with typical NC lifetimes reported in the literature [30, 31], we also fitted a stretched exponential function to our experimental curves, resulting in almost identical values than the NC-related fast decay time. This supports the good election of a two-exponential decay to fit our data, and confirms \( \tau_1 \) as the clue value to discuss the recombination properties of our NC-based SLs.

The results from the fast EL decay time analysis are summarized in figure 5(e). As can be seen, a clear decrease in \( \tau_1 \) occurs when the Si amount increases, whereas an optimum decay time is found for intermediate SiO\(_2\) barrier thicknesses. Both behaviors perfectly scale with the EL peak intensity trends mentioned in the previous section (see figure 4(c)), which allows for establishing a direct relation between the excitonic recombination lifetime and the amount of excited emitting centers. In the case of the Si content increase, one could initially ascribe longer EL decay times to a higher crystalline degree of the nanostructures (thus increasing the radiative recombination probability [32]); nevertheless, the lower crystalline fraction at higher Si content determined by Raman (see figure 2(c)) discards this hypothesis, and a \( \tau_f \) decrease is instead observed in figure 5(e). As previously discussed, higher \([Si]_{exc}\) causes an in-plane larger NC density, which allows associating this exciton lifetime reduction with a loss of quantum confinement of the carriers within the NCs, provided that lower inter-NC distances are found. The consequence is a loss the exciton stability (due to the wave-function delocalization), which strongly reduces \( \tau_1 \). In addition, the presence of higher \([Si]_{exc}\) induces the presence of larger amorphous Si regions (see section 3.1) that increase the probability of non-radiative recombination, thus reducing the overall (and observed) radiative lifetime and quenching the global EL emission.

The \( t_{SO2} \) variation case must be treated separately, as the peak-like behavior observed for both lifetime and EL intensity necessarily has to combine different effects that compete at the different barrier thickness ranges. For thinner barriers, and bearing in mind that all measurements were performed under the same voltage pulse polarization (i.e. higher current densities circulate through the lower-barrier SLs, see figure 3(a)), free carriers may play an important role in charge time dynamics. This may induce fast processes such as Auger electron emission or other non-radiative processes associated to the heating of the SL by free carriers, reducing the global radiative lifetime of the system. In the opposite case, i.e. for thicker barriers, the higher stress generated by the larger SiO\(_2\) presence surrounding the NCs [11, 33] may give rise to an instability of the confined excitons, thus reducing the recombination time. The optimum conditions when both
effects are minimized, namely, a lower presence of free carriers and low enough matrix stress, are reached at \( t_{\text{SiO2}} = 2 \text{ nm} \). Both hypotheses are plausible in the frame where the NC interaction does not cause a loss of exciton confinement within the NCs (the nanostructure morphology is not varied [33]), which is corroborated by identical Raman spectra (see figure 2(a)) and the constant EL peak position in the spectra shown in figure 4(a). Other competing effects may take place regarding the barrier thickness modification that are related to the NC excitation, which requires a further analysis on the correlation between charge injection within the SLs and the luminescence yielded by the structures, as will be treated in the following section.

3.4. Structural parameters effect on the electro-optical conversion

Up to now, the electrical, EL and recombination dynamics properties of the Si NC/SiO2 SLs have been separately analyzed, as a function of the SL structural parameters variation. To understand the electrical excitation and resulting luminescence coming from these active layers, we quantified the light emission efficiency by measuring the integrated intensity per unit area emitted by the devices. Out of these results, the EL optical power \( (P_{\text{opt}}) \) was calculated, considering the total amount of light collected by the system microscope in a way as discussed in [34]. Consequently, the emission power efficiency \( (\eta_{\text{PE}}) \) from the devices could be determined, defined as the ratio between the optical emission output and the electrical excitation input:

\[
\eta_{\text{PE}}(\%) = \frac{P_{\text{opt}}}{I \times V} \times 100.
\]

Prior to an in-depth analysis on the device EL power efficiency, we should describe the transport and EL excitation frame within our SL structures. As it was reported in [20], the electrical and EL experimental observation on these structures suggested a relation between the Poole–Frenkel-type transport and the NC excitation. In particular, it was hypothesized that some electrons traveling through allowed high-energy NC-confined states promote to the effective SL conduction band, where they are accelerated by means of the electric field. If the energy of these electrons is higher than the threshold for impact ionization to occur, then the creation of an electron–hole pair is possible within the NC after direct electron energy transfer. Finally, the consequent electron–hole recombination yields a photon with the nanostructure bandgap energy. To study the device behavior within the regime where these phenomena take place, the power efficiency of the devices must be evaluated at a similar conduction regime (see figure 3). Considering this point we have chosen the maximum \( \eta_{\text{PE}} \), provided that the corresponding current injection and applied voltage satisfied these considerations for all devices. The obtained power efficiencies in this way are summarized in figure 6, with values that span from \( 10^{-3} \) to \( 10^{-5}\% \), lower than other results in literature on similar samples [17, 19]. In these former works, tunnel injection of carriers dominates charge transport, which results into more efficient impact ionization than in our devices (dominated by bulk-limited transport mechanisms). In this sense, a possible approach to improve EL emission efficiency in our SL-based devices would be the incorporation of a (20- or 30-nm thick) SiO2 carrier-accelerating layer on top of the SL stack, by means of which injected carriers are accelerated (i.e. they acquire a higher kinetic energy), tunneling becomes dominant and higher emission efficiencies are achieved [34]. However, it is the aim of this work to determine the structural parameters that lead to the optimum SL-based device performance, which will be discussed in the following in terms of the involved physical processes within the SL.

The graphs shown in figure 6 exhibit a clear decrease in the power efficiency when increasing the Si excess, whereas it increases at thicker oxide barrier layers. The competition between the terms involved in equation (2), i.e. the electrical power input and the EL yielded by the SLs, can be used to explain the different observed behaviors. Regarding the \( [\text{Si}]_{\text{exc}} \) dependence (figure 6(b)), \( \eta_{\text{PE}} \) continuously decreases at larger Si content. Mathematically, it can be immediately shown that, as the EL intensity drops and the current density
is enhanced at higher Si excess (see section 3.2), the ratio in equation (2) is translated into a dramatic decrease in power efficiency. As commented in previous sections, at higher Si content we find a higher carrier density, and we as well expect the precipitation of a larger number of nanostructures, which results in the inter-NC distance reduction. On one hand, the consequence of a higher carrier density may give rise to the presence of free carriers that are efficiently extracted without contributing to impact ionization, i.e. not producing EL. On the other hand, inter-NC proximity may give rise to non-radiative paths because of in-plane NC–NC coupling. Both effects contribute to the overall EL emission quenching at higher Si excesses.

The case concerning the SiO₂ barrier thickness variation is simpler. Again, the higher NC–NC coupling (now in the SL growth direction) taking place at thinner barrier layers can explain the observed power efficiency decrease, as non-radiative processes are strengthened. In addition, under the conditions where the maximum ηPE was evaluated, thicker barriers require a larger voltage (and thus electric field) that increases the kinetic energy of electrons due to their acceleration within the conduction band, which makes the NCs excitation more probable. These effects result in a more efficient NC excitation at larger t_{SiO₂}.

Finally, from the point of view of the SLs potential applications in the optoelectronics field, the power efficiency together with the total emission helped us determining the best structural parameters for the fabrication of efficient light emitters. It was observed that, although thin layers present excellent carrier transport, their electrical-to-light conversion efficiency is limited. In addition, the Si excess increase (involving in-plane morphologic changes in the SLs) dramatically reduces the device efficiency, evidencing higher electrical conduction at the expense of a drastic EL emission drop. In fact, since it is the overall system emission the interesting parameter for optoelectronic applications, a figure of merit can be defined that weights the optical output power yielded by the devices with their conversion efficiency, ηPE×P_{opt} (see figure 6(b)). This procedure demonstrates that intermediate barrier thicknesses (2–2.5 nm) and low Si content (12–15 at%) are the optimum SL structural parameters for light emission purposes.

4. Conclusions

We have reported on the electrical and EL properties of devices containing Si NCs/SiO₂ SLs as active material, in terms of the oxide barrier thickness and the Si excess contained in the pre-annealed SRON layers. The crystalline quality of the SLs was retrieved by Raman scattering, from which the crystalline NC size was evaluated for all devices, presenting a constant value of 3.6 nm, with a size dispersion of ±0.3 nm. The electrical conduction was found to strongly improve when reducing t_{SiO₂} and increasing [Si]_{exc} attributed, respectively, to lower inter-NC distance and higher in-plane nanostructure density. The lateral inter-NC proximity increase at larger Si contents was found to give rise to a loss of quantum confinement, originating an EL spectra redshift, whereas no morphological variations appeared when employing different t_{SiO₂}, as supported by almost identical Raman spectra. The study on the carrier recombination dynamics within the SL-based devices revealed lifetimes of tens of μs associated to typical NC-based structures. The lifetime was found to decrease at higher [Si]_{exc} due to excitation delocalization induced by proximity between nanostructures, whereas a maximum value was observed at intermediate oxide barriers, where a balance between non-radiative processes and the matrix stress is reached. Finally, the EL power efficiency yielded by the devices was calculated, evidencing a clear dependence of the emitted optical power with the impact ionization-based excitation. Again, the EL quenching induced by carrier wavefunction delocalization and non-radiative processes originated by high current densities, might explain the increase in conversion efficiency observed at thicker oxide barriers and lower Si contents. In conclusion, although the overall power efficiencies do not surpass the barrier of 10⁻³%, we have shown how the SL structural parameters modify the electrical and EL properties of these NC-based devices. Furthermore, we succeeded in determining the optimum parameters for light emission, namely, t_{SiO₂} = 2–2.5 nm and low [Si]_{exc} 12–15 at%, which will vary depending on the optoelectronic application they are meant to.

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