

Sensitized erbium emission from silicon-rich nitride/silicon superlattice structures

L. Dal Negro,^{1,a)} R. Li,¹ J. Warga,¹ and S. N. Basu²

¹Department of Electrical and Computer Engineering, Boston University 8 Saint Mary's Street, Boston, Massachusetts 02215-2421, USA

²Department of Manufacturing Engineering, Boston University 15 Saint Mary's Street, Brookline, Massachusetts 02446, USA

(Received 19 February 2008; accepted 16 April 2008; published online 7 May 2008)

Erbium-doped silicon-rich nitride/silicon superlattice structures were fabricated by direct magnetron cosputtering deposition on Si substrates. Rapid thermal annealing resulted in the nucleation of small amorphous Si clusters, which efficiently sensitize 1.54 μm emission via a nanosecond-fast nonresonant energy transfer process, providing an alternative route toward the fabrication of Si-compatible devices based on Er sensitization. © 2008 American Institute of Physics.

[DOI: 10.1063/1.2920435]

Rare-earth doping of Si nanostructures is motivated by the recent discovery of efficient resonant energy transfer between Si nanocrystals (Si-nc) embedded in SiO₂ and erbium (Er) ions.^{1–6} This energy transfer process could provide a valuable approach for the integration of light-emitting devices with the silicon electronic platform.^{2–4} More recently, Er sensitization has been demonstrated in Er-doped Si/SiO₂ multilayered structures.^{7–11} To date, a significant amount of experimental work has been devoted to the understanding and optimization of Er energy sensitization in crystalline^{1–11} and amorphous¹² Si quantum dots in SiO₂ matrices. However, the nucleation of light-emitting Si-nc has also been recently demonstrated in amorphous silicon nitride as well, which offers a more suitable host matrix for the fabrication of electrically pumped light-emitting devices due to its smaller bandgap with respect to SiO₂.^{13,14} Intense visible and near-infrared light emission with nanosecond-fast dynamics and electroluminescence have been demonstrated in Si-nc embedded in amorphous silicon nitride.^{13–20} However, due to the large structural complexity of Si-rich nitride matrices, a comprehensive explanation for the light emission mechanism in nitride-based Si nanostructures is still missing. In fact, quantum-size effects,¹³ defect recombination in amorphous silicon nitride,²¹ and N-related localized exciton transitions at the surface of small Si clusters^{17–20} have been discussed as the possible origin of light emission in Si-rich nitride. Recently, efficient Er emission sensitization has also been reported in amorphous Si clusters embedded in silicon nitride, and it has been shown that small dot sizes are essential to effectively enhance Er emission.^{17,22,23} However, it is presently unknown whether silicon-rich nitride/Si superlattice structures (SRN/Si-SLs) would provide an alternative strategy for efficient Er sensitization under optical and electrical pumping.²⁴

In this letter, we study light emission and Er sensitization via optically excited amorphous Si clusters in Er-doped SRN/Si-SLs (Er:SRN/Si-SLs) fabricated by direct cosputtering and we show that nanosecond-fast transfer times to Er ions can be achieved when amorphous Si clusters are formed inside nanometer-size layers.

Er:SRN/Si-SLs and reference homogeneous Er:SRN samples with 400 nm total thickness were fabricated on Si substrates by radio frequency magnetron cosputtering from Si, Si₃N₄ and metallic Er targets and annealed using a rapid thermal annealing furnace in N₂/H₂ forming gas (5% hydrogen) for 10 min at temperatures ranging between 500 and 1000 °C. The sputtering was performed in a Denton Discovery 18 confocal-target sputtering system, as described elsewhere.²⁰ The atomic concentrations of Si, N, and Er in the deposited films were measured, within 0.5% accuracy, with energy dispersive x-ray (EDX) analysis (Oxford ISIS). Time-resolved photoluminescence (PL) experiments have been performed using a frequency doubled Ti:sapphire laser (Mai Tai HP, Spectra Physics) with 100 fs pulses at 430 nm, using 3.7 $\mu\text{J}/\text{cm}^2$ fluence. The emitted light was dispersed through a double grating spectrometer (Acton Spectra Pro. 2300i) and detected using a single-photon counting streak camera with 10 ps time resolution (Hamamatsu, C4770). Steady-state room temperature PL was excited using the 457 nm line of an Ar pump laser (Spectra Physics, 177-602) and detected using either a photomultiplier tube (Oriel 77348) for the visible range or an InGaAs detector (Oriel 70368) for the 1.54 μm Er emission. All PL spectra have been accurately corrected by the spectral response of the PL setup.

Figure 1(a) shows a transmission electron microscopy (TEM) bright-field image of our SRN/Si superlattice (SRN/Si-SL) structure in cross-section, taken using a JEOL 2010 TEM operated at 200 KV. This sample has been annealed at 700 °C for 10 min and contains 47% Si, as measured by EDX. The average Si and SRN layer thicknesses were measured to be 3.4 and 4.2 nm, respectively. Figure 1(b) shows a high-resolution micrograph of the region marked by a rectangle in Fig. 1(a). Si quantum dots, some of which are marked by arrows, can be seen in the SRN layers. The Si quantum dots appear to be amorphous with an average diameter of ~ 2.5 nm.

In order to better understand the role of the superlattice structure, a reference SRN sample was also fabricated by cosputtering using the same parameters of the SRN/Si-SL structure. Figure 2(a) shows a direct comparison between the normalized room-temperature PL spectra of the homogeneous SRN (circles) and the SRN/Si-SL (squares) samples, both annealed at 700 °C, which was found to maximize the

^{a)} Author to whom correspondence should be addressed. Electronic mail: dalnegro@bu.edu.

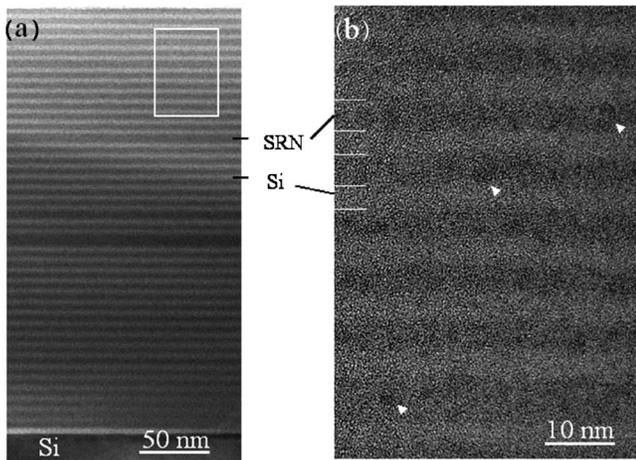


FIG. 1. (a) Bright-field TEM cross-sectional micrograph of a SRN/Si-SL structure. (b) High-resolution image of the rectangular region marked in (a) showing amorphous Si nc in the SRN layers, some of which are marked by arrows.

PL intensity.^{15–18} The PL spectra show comparable peak intensities and normalized lineshapes [Fig. 2(a)], which consist of broad near-infrared bands centered at around 800 nm. Only a negligible spectral shift was observed by varying the annealing temperatures from 400 to 900 °C. The decay dynamics of the emission spectra is strongly nonexponential and generally described by a wavelength-dependent subnanosecond decay (10–200 ps) followed by a slower decay component (1–50 ns), which only weakly depends on wavelength.^{16,18,20} Figure 2(b) displays the wavelength dispersion of the fast decay components (defined by the $1/e$ time constant) for both the samples, which we found to increase at longer wavelengths. Now, we move to the investigation of the 1.54 μm emission sensitization in superlattice structures doped with Er (Er:SRN/Si-SLs). Er sensitization in homogeneous SRN samples has been demonstrated and discussed elsewhere.^{17,20,22,23} Er ions have been incorporated in the superlattice by direct cosputtering from an Er target. It is important to notice that no Er was intentionally deposited (shuttered closed) in the Si layers of the superlattice. EDX analysis, performed on a homogeneous Er:SRN reference sample confirmed a Si concentration of $\approx 47.5\%$, which is almost identical to the Si concentration (47%) of the superlattice samples without Er. Due to the low sensitivity of the EDX technique, we could only estimate an upper limit of $\approx 1\%$ for the total Er concentration in our samples.

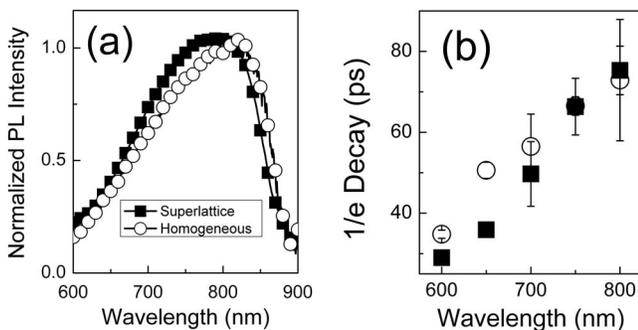


FIG. 2. (a) PL spectra for SRN/Si-SL (squares) and reference homogeneous SRN (circles) samples annealed at 700 °C for 10 min. Both the PL spectra are excited at 457 nm with 5 mW optical power. (b) $1/e$ decay time of SRN/Si-SL (squares) and reference homogeneous SRN (circles) samples measured at different wavelengths.

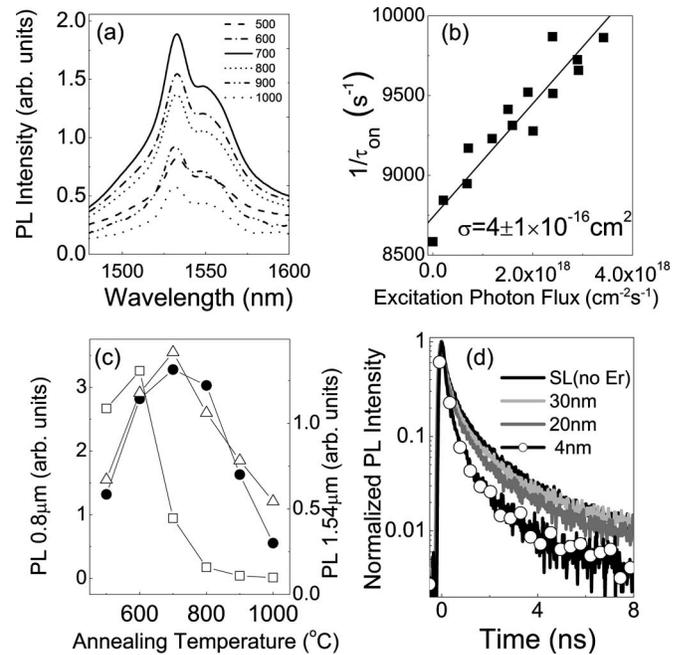


FIG. 3. (a) Typical PL spectra of Er:SRN/Si-SLs samples annealed at different temperatures for 10 min. The PL has been excited at 457 nm with 5 mW. (b) Reciprocal of the rise time of the PL at 1540 nm excited at 457 nm with different excitation photon fluxes. (c) PL peak intensity at 800 nm from SRN (circles) and Er:SRN/Si-SLs (squares), and PL peak intensity at 1540 nm from Er:SRN/Si-SLs (triangles) annealed at temperatures from 500 to 1000 °C. (d) PL decay curves measured at 800 nm under identical pumping conditions for SRN/Si-SL and Er:SRN/Si-SLs samples with different layer thicknesses, as written in the legend.

Figure 3(a) shows the PL spectra of Er:SRN/Si-SL structures, excited under nonresonant (457 nm) optical pumping and directly demonstrates that Er can be efficiently sensitized over a large temperature range by small amorphous Si clusters embedded in the superlattice structure. We notice from Fig. 3(a) that the optimum Er emission is again obtained at 700 °C, which is the temperature that maximizes the near-infrared emission of the superlattice (at 800 nm) in the absence of Er ions. For this optimum temperature, we measured the Er effective excitation cross section in the Er:SRN/Si-SL. This parameter can be measured directly in the weak pumping regime by the linear dependence of the Er PL rise-time versus the pumping photon flux [Fig. 3(b)]. The linear fit to the experimental data yields a cross section value of $\sigma_{\text{exc}} = (4 \pm 1) \times 10^{-16} \text{ cm}^2$, which is almost an order of magnitude larger than the values recently measured for sputtered Er:SRN homogeneous samples²⁰ and comparable to the values of cross sections reported in the literature for Er:SiO_x systems.^{3,24,25} However, different from the Er:SiO_x systems, the PL lifetime of Si clusters in SRN/Si-SLs is almost three orders of magnitudes shorter, resulting in a smaller steady-state excited population under comparable excitation conditions and cluster densities, which we estimate to be of the order of 10^{18} cm^{-3} in our SRN samples.²⁰ This fact has strong implications for the maximum transfer efficiency achievable in Er:SRN/Si-SLs. In fact, the steady-state effective Er excitation cross section σ_{eff} in the low pumping regime,²⁰ $\sigma_{\text{eff}} \propto \tau N_v \gamma$ is directly proportional to the Si clusters' excited state decay time τ (N_v is the cluster's volume density, γ is a spatially averaged coupling rate). Therefore, the experimental observation of comparable σ_{eff} for SiO_x-based systems and Er:SRN/Si-SLs implies a signifi-

cantly larger γ in Er:SRN/Si-SLs. We can conjecture that the strong localization of excitons at the surface of nitrogen-passivated Si-clusters predicted by first-principle calculations^{17–21} plays an important role in enhancing the coupling rate to Er ions, which have been found to be preferentially located in close proximity to the Si-nc's surfaces.^{26,27}

In Fig. 3(c) we show the annealing temperature dependence of the PL intensity at 1.54 μm (triangles) and 800 nm (squares) for Er:SRN/Si-SL samples. In addition, we show the 800 nm Si-clusters emission from reference (same Si concentration) superlattice structures (SRN/Si-SLs) without Er (circles). It is clear that a direct correlation exists between the 800 nm emission of SRN/Si-SLs and the 1.54 μm sensitized emission of Er:SRN/Si-SL samples annealed at different temperatures (triangles and circles). In addition, Fig. 3(c) shows that the 800 nm PL of the Er:SRN/Si-SL samples is significantly quenched (squares) due to efficient energy transfer to Er. Moreover, the strongest quenching occurs in the temperature range of 700–800 °C, which maximizes both the Er emission of Er:SRN/Si-SLs and the 800 nm emission of the same structure without Er. Therefore, it could be assumed that energy transfer in silicon nitride superlattices simply occurs via direct radiative energy transfer where photons emitted from Si clusters are directly absorbed by Er ions. However, according to this picture, the PL lifetime of the Si clusters should not be affected by Er ions, if present in small concentrations. Therefore, information on the de-excitation dynamics of Si clusters coupled to Er ions is important in order to understand the nature of the energy transfer mechanism in Er:SRN/Si-SLs. For this reason, we have directly measured the effect of Er incorporation on the PL decay dynamics of Si clusters by comparing the PL emission peak (800 nm) for SRN/Si-SL and Er:SRN/Si-SL samples with different thicknesses ranging between ~ 4 and 30 nm, all annealed at 700 °C. EDX analysis confirmed that no significant perturbation of the donor SRN stoichiometry was induced by the small fraction ($<1\%$) of incorporated Er ions. However, our time-resolved data shown in Fig. 3(d) demonstrate that for Er-doped superlattices, the 800 nm PL lifetime can be significantly affected by the presence of Er, depending on the thickness of the Er:SRN layers. In particular we found that for the thinnest superlattice structures, the long PL decay component τ_1 (~ 1.5 ns) in the presence of Er ions (solid line) is approximately a factor of 2 shorter than the PL decay component (τ_2) of the reference structure (SRN/Si-SL, open dots) without Er. At the same time, no PL lifetime changes have been observed for the same samples without Er as a function of the layer thicknesses. Therefore, at low Er concentrations ($<1\%$), we found that the energy transfer mechanism strongly affects the Si-clusters emission dynamics in ~ 4 nm thin layers Er:SRN/Si-SLs. As a result, the nature of the transfer process cannot be related to direct photon exchange (radiative transfer), but it relies on a non-radiative process, which can be controlled by the layer's thickness. By measuring the shortening of the Si clusters PL lifetime due to Er incorporation, we can simply estimate the maximum transfer rate of the system as $w_{tr} = 1/\tau_1 - 1/\tau_2$, which is compatible with a transfer time of ~ 3 ns and a maximum transfer efficiency $\eta_{tr} = 1 - \tau_1/\tau_2 \approx 50\%$ for the Er:SRN/Si-SLs with ~ 4 nm SRN layers.

In conclusion, we have fabricated SRN/Si-Ls and showed that ~ 4 nm thin layers superlattice structures annealed at 700 °C result in the nucleation of small (~ 2.5 nm) amorphous Si clusters, which can efficiently excite Er ions via a nanosecond-fast non-resonant energy transfer with an effective Er excitation cross sections of $\sim 10^{-16}$ cm². These results demonstrate the potential of Er:SRN/Si-SLs for the fabrication of efficient light-emitting devices based on Er sensitization.

This work was supported by the U.S. Air Force MURI program on “Electrically-Pumped Silicon-Based Lasers for Chip-Scale Nanophotonic Systems” supervised by Dr. Ger-not Pomrenke.

- ¹M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, and K. Yamamoto, *Appl. Phys. Lett.* **71**, 1198 (1997).
- ²G. Franzò, V. Vinciguerra, and F. Priolo, *Appl. Phys. A: Mater. Sci. Process.* **69**, 3 (1999).
- ³D. Pacifici, G. Franzò, F. Priolo, F. Iacona, and L. Dal Negro, *Phys. Rev. B* **67**, 245301 (2003).
- ⁴M. Fujii, K. Imakita, K. Watanabe, and S. Hayashi, *J. Appl. Phys.* **95**, 272 (2004).
- ⁵A. Polman and F. C. J. M. van Veggel, *J. Opt. Soc. Am. B* **21**, 871 (2004).
- ⁶K. Imakita, M. Fujii, and S. Hayashi, *Phys. Rev. B* **71**, 193301 (2005).
- ⁷L. Tsybeskov, K. D. Hirschman, S. P. Duttagupta, M. Zacharias, P. M. Fauchet, J. P. McCaffrey, and D. J. Lockwood, *Appl. Phys. Lett.* **72**, 43 (1998).
- ⁸J. H. Shin, W. Lee, and H. Han, *Appl. Phys. Lett.* **74**, 1573 (1999).
- ⁹G. F. Grom, D. J. Lockwood, J. P. McCaffrey, H. J. Lebbe, P. M. Fauchet, B. White, J. Diener, D. Kovalev, F. Koch, and L. Tsybeskov, *Nature (London)* **407**, 358 (2000).
- ¹⁰M. Zacharias, J. Heitmann, R. Scholtz, U. Kahler, M. Schmidt, and J. Blasing, *Appl. Phys. Lett.* **80**, 661 (2002).
- ¹¹V. U. Timoshenko, M. G. Lisachenko, O. A. Shalygina, B. V. Kamenev, D. M. Zhigunov, S. A. Teterukov, P. K. Kashkarov, J. Heitmann, M. Schmidt, and M. Zacharias, *J. Appl. Phys.* **96**, 2254 (2004).
- ¹²G. Franzò, S. Boninelli, D. Pacifici, F. Priolo, F. Iacona, and C. Bongiorno, *Appl. Phys. Lett.* **82**, 3871 (2003).
- ¹³N. M. Park, C. J. Choi, T. Y. Seong, and S. J. Park, *Phys. Rev. Lett.* **86**, 1355 (2001).
- ¹⁴T. Y. Kim, N. M. Park, K. H. Kim, G. Y. Sung, Y. W. Ok, T. Y. Seong, and C. J. Choi, *Appl. Phys. Lett.* **85**, 5355 (2004).
- ¹⁵K. S. Cho, N. M. Park, T. Y. Kim, K. H. Kim, G. Y. Sung, and J. H. Shin, *Appl. Phys. Lett.* **86**, 071909 (2005).
- ¹⁶L. Dal Negro, J. H. Yi, J. Michel, L. C. Kimerling, T.-W. F. Chang, V. Sukhovatkin, and E. H. Sargent, *Appl. Phys. Lett.* **88**, 233109 (2006).
- ¹⁷L. Dal Negro, J. H. Yi, J. Michel, L. C. Kimerling, S. Hamel, A. Williamson, and G. Galli, *IEEE J. Sel. Top. Quantum Electron.* **12**, 1628 (2006).
- ¹⁸L. Dal Negro, J. H. Yi, L. C. Kimerling, S. Hamel, A. Williamson, and G. Galli, *Appl. Phys. Lett.* **88**, 183103 (2006).
- ¹⁹L. Dal Negro, S. Hamel, N. Zaitseva, J. H. Yi, A. Williamson, M. Stolfi, J. Michel, G. Galli, and L. C. Kimerling, *IEEE J. Sel. Top. Quantum Electron.* **12**, 1151 (2006).
- ²⁰L. Dal Negro, R. Li, J. Wurga, S. Yerci, S. Basu, H. Hamel, and G. Galli, in *Silicon Nanophotonics: Basic Principles, Present Status and Perspectives*, edited by L. Khriachtchev (World Scientific, June 30, 2008).
- ²¹S. V. Deshpande, E. Gulari, S. W. Brown, and S. C. Rand, *J. Appl. Phys.* **77**, 6534 (1995).
- ²²N. M. Park, T. Kim, K. Kim, G. Sung, B. Kim, S. Park, K. Cho, J. H. Shin, J. Lee, and M. Nastasi, *J. Electrochem. Soc.* **152**, 445 (2005).
- ²³N. M. Park, T. Kim, S. Kim, G. Sung, B. Kim, K. Cho, J. H. Shin, B. Kim, S. Park, J. Lee, and M. Nastasi, *Thin Solid Films* **475**, 231 (2005).
- ²⁴F. Priolo, G. Franzò, D. Pacifici, V. Vinciguerra, F. Iacona, and A. Irrera, *J. Appl. Phys.* **89**, 264 (2001).
- ²⁵A. J. Kenyon, M. Wojdak, I. Ahmad, W. H. Loh, and C. J. Oton, *Phys. Rev. B* **77**, 035318 (2008).
- ²⁶S. Y. Seo and J. H. Shin, *Appl. Phys. Lett.* **78**, 2709 (2001).
- ²⁷J. H. Jhe, J. H. Shin, K. J. Kim, and D. W. Moon, *Appl. Phys. Lett.* **82**, 4489 (2003).