Electroluminescence of single silicon nanocrystals

Jan Valenta,[a] Nenad Lalic,[b] and Jan Linnros
Department of Microelectronics and Information Technology, Royal Institute of Technology, Electrum 229, 164 21 Kista-Stockholm, Sweden

(Received 19 September 2003; accepted 6 January 2004)

We report on measurements of room-temperature electroluminescence from single silicon nanocrystals. The electrically driven emission reveals typical characteristics of single-nanocrystal luminescence: the peak wavelength variations, narrowing of spectral bands, a high degree of linear polarization, and intensity fluctuations (blinking) observed on a scale of minutes. From the count rate statistics of individual nanocrystals, we conclude that the yield of radiative emission is as high as 19%. These findings may open a route to highly efficient all-silicon light emitters. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1655705]

Semiconductor quantum dots (QDs) are becoming important building blocks in nanoelectronics and photonics. The confinement of carriers within the QD provides efficient shielding from nearby defects and also stronger oscillator strength, resulting in an increased rate of radiative decay. Although optical excitation of carriers in a QD is relatively straightforward, electrical excitation is more difficult. This is because the confining barrier acts against carrier injection requiring transport by tunneling or, alternatively, from a higher bandgap material.

In silicon, extensive research on nanostructures has been partly motivated by the potential fabrication of Si light-emitting devices (LEDs) by methods compatible with the present microelectronic technology. Many different LED systems containing Si nanocrystals (Si-NCs) were prepared and investigated[1] from the point of view of technology and device characterization. Only a few reports have been published[2] describing the application of advanced microspectroscopy techniques to study electroluminescence (EL) of Si-NCs. Such techniques are currently used to measure photoluminescence (PL) and EL spectra of single QDs of III-V and II-VI semiconductors.[3] However, for Si-NCs, the single QD spectroscopy encounters two major difficulties: the low emission rate (long radiation lifetime resulting from the indirect transition) and the complicated preparation of diluted and well-defined systems of Si-NCs. The group of Buratto[4] reported studies of PL from single porous Si grains with exceptionally high quantum efficiency (QE)$>$80% for some grains.[5] Recently, our group performed single-dot PL spectroscopy of individual Si-NCs fabricated using electron-beam lithography.[6] We confirmed a high value of QE ($\leqslant$35%) and demonstrated PL intermittence and polarization.

In this letter, we present micro-EL studies of Si-NC LEDs using sensitive imaging spectroscopy. We interpret luminescence of bright spots in the LED structure as efficient EL emission from single or a few Si-NCs. Our results prove that a small fraction of Si-NCs in our structure can be efficiently excited by passing current up to the limit of the emission rate imposed by the (long) excited state lifetime.

EL structures [Fig. 1(a)] were prepared according to the following procedure.[7] Thermal oxide layers (12 nm thick) were grown on p-type (100) Si wafers (20 Ω m) and subsequently covered by an amorphous Si layer (210 nm). A dose of 1×10^{17} cm^{-2} of $^{28}Si^{+}$ ions was then implanted at 150 keV. Si-NCs were grown from the excess Si in SiO_2 by annealing at 1100 °C in N_2 for 1 h. A 160-nm-thick poly-Si layer highly doped with phosphorus was deposited on top. The circular shape of the diodes was defined by the reactive ion etching.

EL and PL images and spectra were collected using an imaging spectrometer connected to a microscope. The light

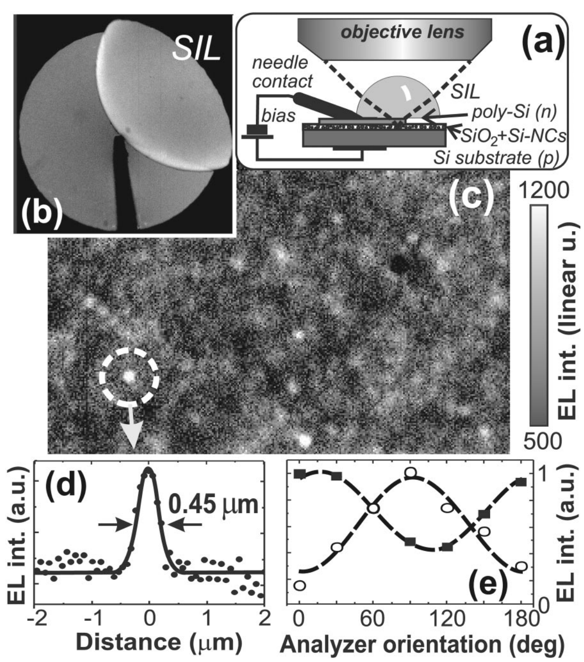

FIG. 1. (a) Sketch of the sample structure and collection optics. (b) EL image of the whole-area LED structure with a SIL placed on it (diameter of the contact and the SIL is 2 mm). (c) EL image of a small part (area 34 $\times21$ μm^2) of a diode under a forward bias of 10 V. (d) Detail of the EL profile of one emitting spot (indicated by a circle). (e) Polarization-sensitive detection of EL from two single spots (10 V, 0.68 mA). The EL signal is plotted versus the analyzer orientation. Experimental points are fitted with a squared sinusoid.

[a]Permanent address: Dept. of Chemical Physics & Optics, Charles University, Prague, Czechia; electronic mail: jan.valenta@mff.cuni.cz
[b]Present address: Zarlink Semiconductor AB, P.O. Box 520, 175 26 Järfälla, Sweden.

0003-6951/2004/84(9)/1459/3/$22.00

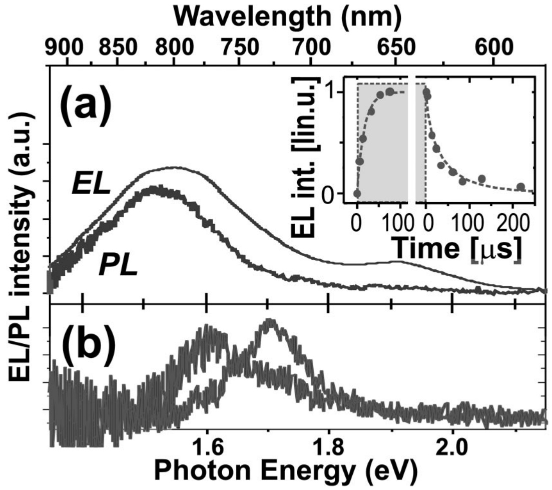

FIG. 2. (a) The overall EL spectrum compared with a PL spectrum. The inset shows the EL signal rise and decay under a pulsed bias of 8 V. (b) EL from two different brightly emitting spots (14 V).

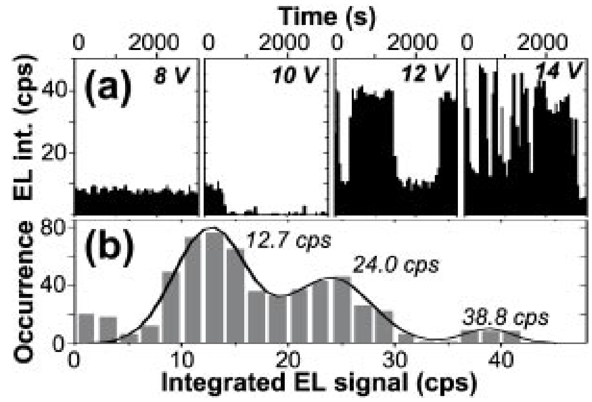

FIG. 3. (a) Fluctuations of the EL signal from a single bright spot: Integrated EL intensity measured in 50 consecutive 1 min acquisitions under biases of 8, 10, 12, and 14 V plotted vs time (for the same spot). (b) Histogram representing the occurrence of certain EL signal rates in 50 observations on 12 single spots (in total, 600 values). The line is a fit of three Gaussians, which peak positions are indicated.

from the sample was collected by a microscope objective (100×/0.73), imaged onto the entrance slit of the spectrometer and detected by a liquid-nitrogen-cooled CCD camera. For time-resolved detection, we used a gated image intensifier placed on the CCD. PL was excited by the frequency-doubled output (532 nm) of a Nd:YAG laser (pulse duration of 3 ns). All spectra were corrected for spectral sensitivity of the detection system. For some measurements a solid-immersion lens (SIL) was placed on the top of a diode in order to increase both the numerical aperture of signal collection and the spatial resolution of images. Our SIL is made of the BK7 glass ($n\sim1.517$).[8] Tests confirmed an increase of magnification and image resolution by a factor of 1.5 and the collection efficiency by a factor of about 2.

The fabricated structures show EL under forward bias with an onset voltage of ~5 V. The $J-V$ characteristics[7] show a rectification factor of about 10 and the shape of curves indicate that the main transport mechanism is tunnel or field emission. The EL is excited most probably by impact excitation of electron–hole (e–h) pairs in Si-NCs.

The EL intensity is very stable and visible by a naked eye as a homogeneous glow for the best diodes. EL images taken with high magnification [Fig. 1(c)], however, reveal that the emission is not homogeneous. It is composed of a quasihomogeneous background emission on which a number of brighter spots may be resolved. Almost all spots are of the same size corresponding to the diffraction limit of the imaging optics. Polarization sensitive detection of EL from single spots was performed using a linear polarization filter (analyzer) inside the microscope. This allows checking the projection of the emitting dipole in a plane parallel to the sample surface. While the background is unpolarized, EL from single bright spots has a high degree of linear polarization and the polarization angle varies from dot to dot, as indicated in Fig. 1(e) for two bright spots.

The overall EL spectrum (from 1 mm^2 of sample surface) is compared with the PL spectrum (excited through the top contact) in Fig. 2(a). The EL spectrum consists of two emission bands. The narrower short-wavelength peak is increasing with implantation dose and can be attributed to emission from oxide defects.[9] The main wide band around 800 nm is most probably due to e–h recombination in Si-NCs. In the PL spectrum, this band is somewhat narrower and comparable with the typical PL of similar samples made by Si^+-ion implantation of SiO_2.[10]

The decay of both PL and EL is long (tens of μs) and nonexponential (well described by a stretch-exponential curve).[7] The inset in Fig. 2(a) shows the rise and decay of the EL signal (under 8 V pulsed bias), which reveals values of the rise time τ_{on} and the decay time τ to be 17 and 50 μs, respectively. The EL excitation cross section can be estimated using the equation $\sigma=(\tau_{on}^{-1}-\tau^{-1})P^{-1}$, where P is the averaged current flow through the diode 1.8×10^{18} electrons/s/cm^2. We obtain cross section $\sigma=2\times10^{-14}$ cm^2, which agrees well with the value found by Irrera *et al.*[11] (4.7×10^{-14} cm^{-2}) and must be interpreted as a lower limit since leakage paths, not contributing to EL, would increase P.

The spectra of the brightest single EL spots can be measured by imaging spectrometry. For each spot, we observe spectra of various intensity, width, and peak position. In Fig. 2(b), we plot such EL spectra of two single spots at a bias of 14 V. The acquisition time was 30 min in order to obtain reasonable signal to noise ratio. Clearly, the single-spot spectra are narrower than the ensemble spectrum. A peak width of 125 meV was measured for the Si nanostructure. It is comparable to that of PL spectra of individual Si-NCs,[6] but is broader than those observed in the PL of direct bandgap semiconductor QDs at room temperature.[12] This seems to be a consequence of the indirect bandgap nature of Si-NCs involving emission or absorption of phonons and we note that even at low temperatures, a wide spectrum is predicted.[13]

Fluctuations of the integrated EL signal from single shining spots were studied by repeated 1 min acquisitions of EL images. Figure 3(a) shows four sequences of 50 measurements, each of the EL signal from one single bright spot under a bias increasing from 8 to 14 V. An intermittence of the EL emission (on-off blinking) is observed for a majority of the spots. Figure 3(a) clearly illustrates a shortening of the on-off period with increasing bias and also a tendency of the EL signal to switch between a few distinct levels. This fact is clearly visualized by constructing a histogram of the integrated EL signals emitted by 12 bright spots at 12 V [50 observations for each, meaning a total of 600 values, Fig. 3(b)]. The histogram reveals three distinct maxima at signal levels of 12.7, 24.0, and 38.8 counts per second (cps). We conclude that one, two, or three Si-NCs may be active in each of the 12 observed spots and that the intermittence observed in Fig. 3(a) results from the turning on/off of individual NCs.

In discussing our experiments we argue that we observe EL from single Si-NCs stimulated by electrical excitation with high efficiency. The evidence for single-dot EL emission may be summarized by the following observations.

(i) *Spectral shape of EL spectrum*. At low bias, the EL band has a full width at half-maximum as narrow as 125 meV, the same bandwidth was found in PL spectra of single Si-NCs. In addition, the peak position varies from dot to dot as expected for QDs subjected to size dispersion.

(ii) *Linear polarization of EL from single spots*. In general, the EL polarization dependence does not reach zero for any angle and can be fitted by the function $I_{EL}^{norm}(\Theta)=[1-K\cos^2(\Theta)]$. This fact suggests that the transition dipole is not unidirectional (bright axis), but degenerated—distributed isotropically in a plane. Such a system is characterized by a unidirectional dark axis normal to the transition dipole plane.[14] The orientation of the dark axis can be deduced from the EL polarization dependence: the angle Θ gives the orientation of the dark axis projected on the sample plane, while the polarization contrast K is equal to $\cos^2(\Phi)$, where Φ is the angle between the dark axis and the sample plane.

(iii) *Blinking behavior*. The non-Poissonian distribution of count rates suggests a nonclassical character of the emitting species. In addition, we observe blinking on a few-minute time scale as observed in many direct bandgap QDs and for individual molecules (often on a much shorter time scale). Indeed, we would not have been able to observe blinking on a faster time scale due to the low count rates we obtain. However, we argue that faster blinking would result in a smearing of the distinct levels observed in Fig. 3 and, thus, we conclude that blinking in the present system is characterized mainly by a time scale of minutes.

In order to discuss the QE of the EL process, we have to know the total extraction efficiency of light emitted inside the diode structure. For simplicity we consider an isotropic emitter inside bulk Si (i.e., dipole orientation and polarization effects are neglected) and obtain an extraction efficiency of 1.8% (with application of the SIL). The efficiency of the detection system is approximately 19%, which gives all together a total detection efficiency $D=0.0034$ counts/emitted photon. The QE η is derived from saturated EL signal[5] $N_{sat}=D\eta/\tau$ (where excited state lifetime $\tau=50\ \mu s$). For $N_{sat}=13$ cps, we get $\eta=0.19$. An alternative calculation from the nonsaturated EL signal using the equation[6] $N=D\eta\sigma P$ gives the value $\eta=0.08$. We have to note, that these values of η must be taken as estimations as we used for their derivation approximate values: ensemble measurements of τ_{on}, τ, σ, and an averaged value of P (most probably the actual values for a single Si-NC vary from dot to dot).

Finally, we note that the values just derived for the QE agree well with the values we found for PL from single Si-NC[6] (up to 35%). The small reduction in QE for EL may be of a generic origin as the conductive or tunneling paths necessary for current conduction would also provide an escape path for carriers. This would result in a slightly shorter EL lifetime due to this nonradiative de-excitation channel (actually, we observe about 2 times shorter EL decay time compared to PL, see Fig. 2 and Ref. 10).

In conclusion, we demonstrated measurements of EL spectra from single Si-NCs in a thin SiO_2 layer. The QE of the best emitting Si-NCs is slightly lower than the values found for PL of single Si-NC,[5,6] while all other characteristics of EL and PL are surprisingly similar. This means that the excitation of luminescence of Si-NC by flowing current (impact excitation) could be as efficient as photoexcitation. This finding could, in principle, lead to highly efficient Si-based LEDs when the structure is optimized; that is, the fraction of efficiently emitting Si-NCs should be substantially increased and the losses by leakage current reduced.

This work was partially supported by the KTH faculty, the Royal Swedish Academy of Sciences, and by the Grant Agency of the Czech Republic (Project No. 202/03/0789).

[1] See, e.g., N. Lalic and J. Linnros, J. Appl. Phys. **80**, 5971 (1996).
[2] K. Ito, S. Ohyama, Y. Uehara, and S. Ushioda, Appl. Phys. Lett. **67**, 2536 (1995).
[3] A. Gustafsson, M. E. Pistol, L. Montelius, and L. Samuelson, J. Appl. Phys. **84**, 1715 (1998).
[4] M. D. Mason, G. M. Credo, K. D. Weston, and S. K. Buratto, Phys. Rev. Lett. **80**, 5405 (1998).
[5] G. M. Credo, M. D. Mason, and S. K. Buratto, Appl. Phys. Lett. **74**, 1978 (1999).
[6] J. Valenta, R. Juhasz, and J. Linnros, Appl. Phys. Lett. **80**, 1070 (2002).
[7] N. Lalic and J. Linnros, J. Lumin. **80**, 263 (1999).
[8] M. Baba, T. Sasaki, M. Yoshita, and H. Akiyama, J. Appl. Phys. **85**, 6923 (1999).
[9] J. Yuan and D. Haneman, J. Appl. Phys. **86**, 2358 (1999).
[10] J. Linnros, N. Lalic, A. Galeckas, and V. Grivickas., J. Appl. Phys. **86**, 6128 (1999).
[11] A. Irrera, D. Pacifici, M. Miritello, G. Franzo, F. Priolo, F. Iacona, D. Sanfilippo, G. Di Stefano, and P. G. Fallica., Appl. Phys. Lett. **81**, 1866 (2002).
[12] U. Banin, M. Bruchez, A. P. Alivisatos, T. Ha, S. Weiss, and D. S. Chemla, J. Chem. Phys. **110**, 1195 (1999).
[13] C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B **64**, 193402 (2001).
[14] S. A. Empedocles, R. Neuhauser, and M. G. Bawendi, Nature (London) **399**, 126 (1999).