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Ultrafast photoluminescence dynamics of nitride-passivated silicon nanocrystals using the variable stripe length technique

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The ultrafast photoluminescence dynamics of nitride-passivated silicon nanocrystals is investigated using the variable stripe length geometry with 200 femtosecond pump pulses. We find that the luminescence lifetimes are in the nanosecond range throughout the entire spectral range. However, no evidence for optical gain is observed even when the pump fluence is in excess of 40 mJ/cm^2. A comparison with similarly prepared, oxide-passivated silicon nanocrystals suggests that oxide passivation plays an important role in providing optical gain from silicon nanocrystals. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2803071]

Realization of optical gain and lasing in a silicon-compatible material is regarded as a key step for the development of silicon photonics. While gain has been reported using different approaches,[1–3] these do not rely on carrier injection involving silicon. Gain from nanocrystalline silicon (nc-Si) was first reported in 2000 following photocarrier injection.[4] Since then, this approach has attracted of lot of interest due to its simplicity, the prospect for electrical carrier injection, and the physical significance of overcoming the inherent limitation of the indirect bandgap of bulk Si through nanoscale engineering.

To date, the origin and exact mechanism of the optical gain from nc-Si have not been established. There is a general consensus that when optical gain is observed, a set of similar results is nearly always observed independent of the preparation methods (e.g., reactive ion deposition,[5] magnetron sputtering,[6] plasma enhanced chemical vapor deposition,[7] porous silicon grains embedded in sol-gel derived SiO_2 matrix,[8] or heavily oxidized porous silicon[9]). First, there exists a fast, nanosecond-range component that is blueshifted compared to the omnipresent "slow," microsecond-range nc-Si luminescence peak in the near infrared region. Second, optical gain is observed only within the fast component, within nanoseconds of an excitation pulse, while the slow component always shows optical loss.

We note, however, that most of the research on optical gain from nc-Si relied on oxide-passivated nc-Si. As the optical properties of nc-Si are very sensitive to surface passivation,[10] it is not clear whether the fast component that is associated with optical gain is intrinsic to nc-Si or is due to specific defects related to the oxide passivation. In this paper, we report on the ultrafast photoluminescence dynamics of nc-Si passivated by silicon nitride measured using the variable stripe length (VSL) geometry. Silicon nitride was used as the matrix because it is widely used in the complementary metal-oxide semiconductor industry.[11] Furthermore, there have been recent reports that the luminescence lifetime from nitride-passivated nc-Si is in the nanosecond-range,[12,13] comparable to the fast component in the oxide-passivated nc-Si luminescence that is associated with optical gain. Finally, since silicon nitride has a much smaller bandgap than silicon dioxide, electrical current injection is expected to be easier, leading to more efficient electroluminescence. The VSL geometry was used in order to directly and quantitatively search for the presence of optical gain. We find that the luminescence from nitride-passivated nc-Si is comparable to the fast component in the oxide-passivated nc-Si luminescence. However, we do not observe any optical gain in the VSL geometry for all luminescence wavelengths and pump powers. A comparison with the luminescence from comparable, oxide-passivated nc-Si suggests that the optical gain is not intrinsic to nc-Si but depends critically on the passivating oxide matrix.

Nitride-passivated nc-Si thin films were grown *in situ* on a Si wafer covered with a 15 μm thick thermal oxide layer by plasma enhanced chemical vapor deposition using SiH_4 and N_2 as source gases. The film thickness was about 150 nm, and the flow rates of SiH_4 and N_2 were adjusted to control the size of the silicon nanocrystals. A more detailed description of the deposition process can be found in Ref. 14. High resolution transmission electron microscopy study confirms the existence of silicon nanocrystals in the silicon nitride film.[14] Two samples with average nanocrystal sizes of 4.6 and 3.1 nm, showing red (800 nm) and green (550 nm) luminescences, respectively, were studied. The silicon content in the two samples is 59% and 41%, respectively. The nanocrystal density is estimated to be around 2×10^{18} cm^{-3}. The refractive index of the sample with red luminescence is 1.98 and that of the sample with green luminescence is 1.80. For comparison, an oxide-passivated nc-Si thin film was also fabricated by depositing an amorphous silicon-rich oxide

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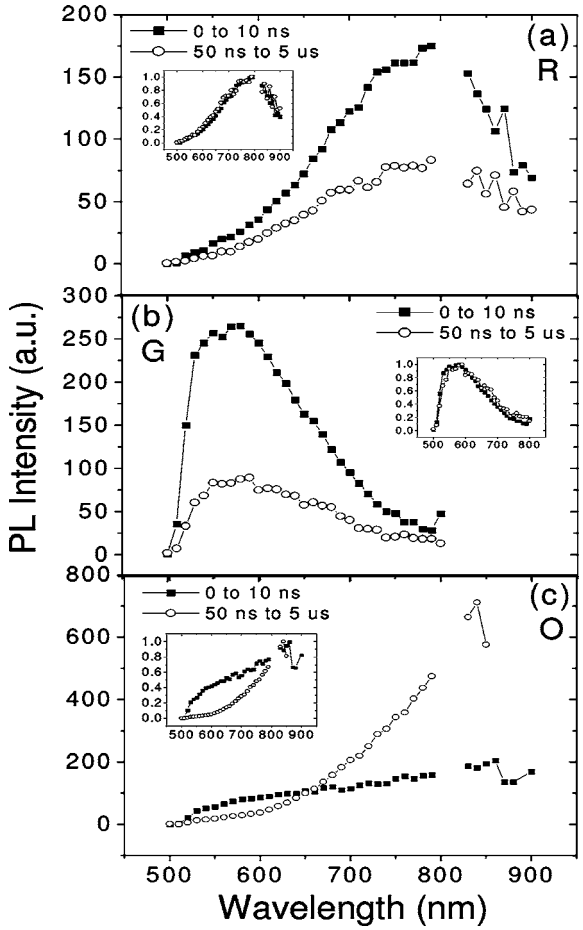

FIG. 1. (a) Fast (solid squares) and slow (empty circles) PL spectra of sample R. (b) Fast (solid squares) and slow (empty circles) PL spectra of sample G. (c) Fast (solid squares) and slow (empty circles) PL spectra of sample O. The insets show the normalized PL spectra.

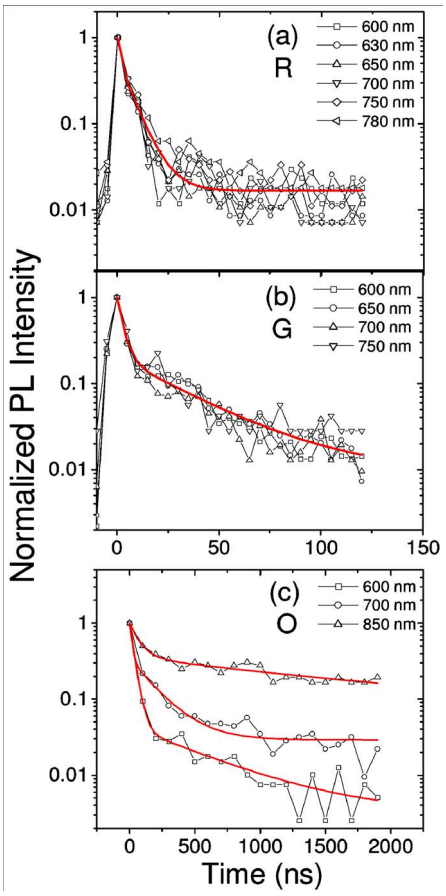

FIG. 2. (Color online) (a) Normalized PL decay traces at different wavelengths for sample R. (b) Normalized PL decay traces at different wavelengths for sample G. (c) Normalized PL decay traces at different wavelengths for sample O. The solid lines are fits achieved with double exponential functions.

film on a quartz wafer using plasma enhanced chemical vapor deposition followed by a 1 h, 1100 °C anneal in flowing Ar environment to precipitate the nc-Si. The silicon content in this sample is about 40% and the average nanocrystal size is 3 nm. The nanocrystal density is estimated to be around 7×10^{18} cm^{-3}. Henceforth, these three samples will be referred to as samples R (red), G (green), and O (oxide), respectively.

Time-resolved and spectrally resolved VSL measurements were performed using a frequency doubled amplified Ti-sapphire system[6] with ultrashort laser pulses (~200 fs, 1 kHz, and 405 nm) focused at normal incidence into a 50 μm$\times$1 mm spot. The pump fluence was varied between 4 and 40 mJ/cm^2. As both nitride and oxide-passivated nc-Si thin films form natural waveguides, the guided signal was collected from the sample edge using a microscope objective and analyzed by a scanning monochromator equipped with a photomultiplier tube and a gated photon counter. Since the VSL method is susceptible to measurement artifacts,[15] we aligned the microscope objective to the waveguiding mode by first coupling in an external laser light into the film and collecting the guided signal. Afterwards, shifted-excitation-spot measurements were used to confirm the correct optical alignment and the suppression of artifacts.[15,16]

Figures 1(a)–1(c) show the photoluminescence (PL) spectra of samples R, G, and O, respectively. The fast (solid square) and slow (empty circle) edge PLs were recorded by gating the photon counter from 0 to 10 ns and from 50 ns to 5 μs after excitation, respectively. The insets show the normalized PL spectra. In the case of samples R and G, we find that the intensity of the fast PL is more than twice that of the slow PL. Furthermore, the two normalized spectra are identical. In the case of sample O, however, we observe that the fast and slow PL spectra are completely different. A

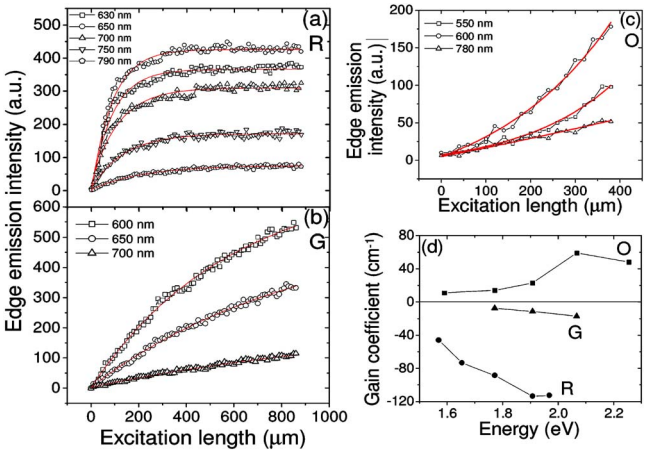

FIG. 3. (Color online) (a) VSL data for sample R taken from 630 to 790 nm. The solid lines are fitting curves using the one dimensional amplifier model. (b) VSL data for sample G taken from 600 to 700 nm. (c) VSL data for sample O taken at 550–700 nm. (d) Optical loss/gain coefficients obtained from the fitting curves vs photon energy. All the measurements were taken with a 40 mJ/cm^2 pump fluence. The time gate was set to detect only the fast component (from 0 to 10 ns).

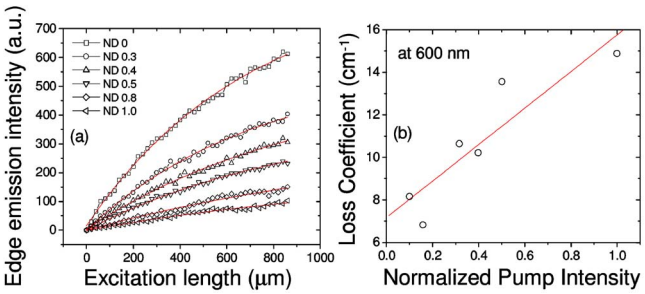

FIG. 4. (Color online) (a) Sample G: VSL data taken at 600 nm with different pump fluences, 40 mJ/cm^2 (square), 20 mJ/cm^2 (circle), 16 mJ/cm^2 (up triangle), 13 mJ/cm^2 (down triangle), 6 mJ/cm^2 (diamond), and 4 mJ/cm^2 (left triangle). (b) Optical loss coefficient vs normalized pump intensity.

broad PL peak in the near IR dominates the slow PL spectrum, and a blueshifted PL component dominates the fast PL spectrum—in agreement with previous reports on oxide-passivated nc-Si PL.[6]

Figures 2(a)–2(c) show the normalized decay curves of samples R, G, and O at various emission wavelengths. In the case of samples R and G, we observe a fast decay with a time constant of about 1 ns at all wavelengths. A fast decay in the luminescence intensity is also observed from sample O but only at shorter wavelengths. In the red spectral region, a significant fraction of the luminescence decays on a microsecond time scale, consistent with the PL spectra, shown in Fig. 1, and with published results on nc-Si passivated with oxide.[17] We note that the PL intensity of the R and G samples is comparable to that of the fast emission component from the O sample. This suggests that the fast emission from R and G samples is due to radiative recombination in nitride-passivated nc-Si and not to a decrease of the intensity of a slow PL component caused by fast nonradiative recombination. This conclusion agrees with a recent theoretical investigation that has suggested that nitride-passivated nc-Si have radiative lifetimes in the nanosecond range.[12,13]

It has been established that optical gain in oxide-passivated nc-Si is associated with a fast, blueshifted component of the luminescence.[6] Since in nitride-passivated nc-Si all the luminescence is fast, this material may be ideal for obtaining strong optical gain. However, this is not the case. Figure 3 shows VSL measurements of the fast PL component at different wavelengths as a function of excitation length for the three samples. The signal with nitride-passivated films shows a sublinear increase with increasing pumping length throughout the entire spectral region (600–800 nm), indicating optical losses. This is in contrast to VSL measurements of sample O, which shows a superlinear increase with increasing pumping length, indicating optical gain, in the same spectral region where samples R and G show optical loss. We need to point out here that optical gain is only observed with the fast component of sample O, while the slow component experiences optical loss (data not shown here). Figure 3(d) show the spectral dependence of the loss/gain coefficient. In samples R and G, losses increase with photon energy, whereas in sample O, gain appears to peak beyond 2 eV.

Figure 4 shows the dependence of optical loss in sample G with increasing pump fluence. We find that at 600 nm, the optical loss increases with increasing pump fluences, indicating that a substantial part of the optical loss was due to photoinjected carrier absorption. At very low pump fluences, the optical loss approaches 7 cm^{-1} in this sample, reflecting propagation losses in the waveguide.

Our results show that nitride passivation of nc-Si does not lead to optical gain despite a fast luminescence decay in the nanosecond range and the possibility of tuning the peak luminescence in the blue. In fact, the overall luminescence dynamics, including the stronger optical loss for the R sample and increasing optical loss at higher energies, is consistent with what is expected of an indirect gap semiconductor and argues against the possibility of achieving optical gain from nitride-passivated nc-Si. Thus, taken together, the data suggest that optical gain from nc-Si is not likely to be intrinsic to nc-Si alone but instead requires the additional presence of oxide passivation. It is not clear what role does the oxide passivation play in providing the blueshifted, fast luminescence component. It may be a surface defect that is analogous to the well-known Si═O bond that leads to redshift of nc-Si PL peak,[10] or it could be a defect in the oxide matrix itself caused by the presence of nc-Si.

In conclusion, time-resolved photoluminescence and VSL measurements were performed on nitride-passivated silicon nanocrystals of different sizes. We observe fast luminescence characteristics at short wavelengths, conditions that are associated with optical gain in oxide-passivated silicon nanocrystals. However, we obtain only optical losses, which suggest that the presence of oxide is critical for achieving optical gain in silicon nanocrystals.

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[1] O. Boyraz and B. Jalali, Opt. Express **12**, 5269 (2004).
[2] H. Rong, R. Jones, A. Liu, O. Cohen, D. Hak, A. Fang, and M. Paniccia, Nature (London) **433**, 725 (2005).
[3] A. Polman, B. Min, J. Kalkman, T. J. Kippenberg, and K. J. Vahala, Appl. Phys. Lett. **84**, 1037 (2004).
[4] L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzò, and F. Priolo, Nature (London) **408**, 440 (2000).
[5] L. Khriachtchev, M. Rasanen, S. Novikov, and J. Sinkknen, Appl. Phys. Lett. **79**, 1249 (2001).
[6] J. Ruan, P. M. Fauchet, L. Dal Negro, M. Cazzanelli, and L. Pavesi, Appl. Phys. Lett. **83**, 5479 (2003).
[7] L. Dal Negro, M. Cazzanelli, L. Pavesi, S. Ossicini, D. Pacifici, G. Franzò, F. Priolo, and F. Iacona, Appl. Phys. Lett. **82**, 4636 (2003).
[8] K. Luterová, K. Dohnalová, V. Svrcek, I. Pelant, J.-P. Likforman, O. Crégut, P. Gilliot, and B. Hönerlage, Appl. Phys. Lett. **84**, 3280 (2004).
[9] M. Cazzanelli, D. Kovalev, L. Dal Negro, Z. Gaburro, and L. Pavesi, Phys. Rev. Lett. **93**, 207402 (2004).
[10] M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, Phys. Rev. Lett. **82**, 197 (1999).
[11] R. Chau, M. Doczy, B. Doyle, S. Datta, G. Dewey, J. Kavalieros, B. Jin, M. Metz, A. Majumdar, and M. Radosavljevic, Proceedings of the Seventh International Conference on Solid-State and Integrated Circuits Technology (ICSICT), Beijing, China, October 2004 (unpublished), pp. 26–30.
[12] L. Dal Negro, J. H. Yi, L. C. Kimerling, S. Hamel, A. Williamson, and G. Galli, Appl. Phys. Lett. **88**, 183103 (2006).
[13] L. 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).
[14] T.-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).
[15] J. Valenta, I. Pelant, and J. Linnros, Appl. Phys. Lett. **81**, 1396 (2002).
[16] L. Dal Negro, P. Bettotti, M. Cazzanelli, D. Pacifici, and L. Pavesi, Opt. Commun. **229**, 337 (2004).
[17] L. Tsybeskov, Ju. V. Vandyshev, and P. M. Fauchet, Phys. Rev. B **49**, 7821 (1994).