Absorption Mechanisms of Silicon Nanocrystals in Cosputtered Silicon-Rich–Silicon Oxide Films

A. Podhorodecki,[a,z] J. Misiewicz,[a] F. Gourbilleau,[b] and R. Rizk[b]

[a]*Institute of Physics, Wroclaw University of Technology, 50-370 Wroclaw, Poland*
[b]*Laboratory of Interface Structure and Thin Layer Functionality (SIFCOM), UMR CNRS 6176, 14050 Caen Cedex, France*

Optical properties of silicon-rich–silicon oxide (SRSO) films have been investigated by emission and absorption spectroscopies in the broad spectral range. The impact of the different hydrogen partial pressure of the sputtering method on the absorption properties of SRSO films has been described and commented on. For all samples, a strong and complex emission band, centered at ~ 1.6 eV, has been observed. It has been shown that the most dominant absorption transition, centered at ~ 4.0 eV, is related to the direct absorption in Si nanocrystals and depends on their size. Moreover, no evidence of a quasidirect absorption band was identified.
© 2008 The Electrochemical Society. [DOI: 10.1149/1.2828207] All rights reserved.

Recently, a significant effort has been focused on the formation and characterization of Si nanocrystals (Si-nc), which can play a key role as an emission source (electroluminescent diodes and lasers) for silicon-based optoelectronic applications, even considering the fact that silicon is an indirect material with low emission efficiency. This is because of the spatial confinement of excitons in small enough silicon nanoparticles, which leads to the delocalization of the wave vector **k** in reciprocal lattice and may then break the **k** selection rules, enhancing the probability of the indirect optical transition.[1,2] Moreover, it has been already shown by many authors that indirect transition (or quasidirect) will strongly depend on the size of nanocrystals and shift to higher energies due to the quantum confinement for small enough nanocrystals.

Properties of the direct optical transitions in Si-nc have not been extensively investigated thus far, experimentally. The issues related to their dependence on nanocrystal size and their importance in the absorption mechanism are still open questions.

Lack of an answer to this questions is one reason why the commercial requirements for most of the existing devices are still not completely satisfied. It is mostly because many significant problems are unresolved thus far, such as the controversy concerning the Stokes shift between the absorption gap and the photoluminescence peak,[3] the size dependence of the oscillator strengths;[4] the specific influence of quantum confinement, defect-related, or Si/SiO$_2$ interfacial states on photoluminescence;[5,6] and the direct or indirect nature of the transition between discrete or continuous energy levels.[7,8]

The lack of information that could help answer all these open questions is mostly because most of the studies have concerned the behavior of the emission spectra, whereas only a few studies[9-15] have addressed the experimental investigations of the optical absorption processes in such a complex system.

Moreover, most of the existing absorption data have been obtained from transmission-type experiments, whose interpretation could be questionable in the case of such a complex system and could lead to some overinterpretation, as previously argued, for example, by Elliman et al.[16] The reason for this lies with both the scattering and interference effects and the complexity of the system, which should be considered in the framework of the effective medium theory. Additionally, the density of states in the case of the three-dimensional confinement has a δ-like shape, whereas the approximation applied thus far to the absorption edge is based on the Tauc model, which deals with the bulklike density of states. This explains the controversial character of the values and conclusions obtained for the absorption edge for Si-nc.

This work deals with the investigations of the absorption and emission properties of the silicon-rich–silicon oxide (SRSO) films obtained by reactive magnetron sputtering with different hydrogen partial pressures. Two absorption-type experiments have been used to investigate the nature of the dominant absorption mechanism: transmittance together with reflectance and total photoluminescence excitation (PLE) spectroscopies, where the integrated PL spectra have been collected as a function of the excitation wavelength and compared to the PL results.

The SRSO layers, with a nominal thickness of 500 nm used for this study, were deposited onto quartz substrates. The Si excess was monitored through the variation of the hydrogen rate r_H [$r_H = P_{H_2}/(P_{Ar} + P_{H_2})$] from 10 to 50%. The films were deposited without any intentional heating of the substrates and with a power density of 0.75 W/cm^2. All samples were subsequently annealed at 1100°C during 1 h under N$_2$ flux in order to favor the precipitation of Si excess and to induce the phase separation between Si and SiO$_2$.[17]

PL spectra were obtained using the 488 nm excitation wavelength of Ar$^+$ continuous wave laser. For PLE measurements, a 450 W Xe arc lamp connected to a 0.18 m Jobin Yvon monochromator was used as an excitation source. More details can be found elsewhere.[18] The width of the excitation line was less than ~ 8 nm, and the excitation power was on the order of 0.1 W/cm^2. In both the PL and PLE cases, the signal was detected by using an Ocean Optics HR4000 spectrometer.

For transmittance and reflectance measurements, a tungsten halogen lamp was used as a source of the transmitted light. A GaAs photomultiplier and InGaAs pin photodiode combined to a Triax 550 Jobin Yvon monochromator was used as a detection system.

In our previous works,[19,20] detailed structural investigations (atomic force microscopy, X-ray diffraction, high-resolution electron microscopy, dark field, Raman, Rutherford backscattering, and secondary-ion mass spectrometry) of SRSO films codoped with Er^{3+} ions have been reported for the films fabricated in the same conditions. The main conclusions of these investigations are as follows: (*i*) the Si excess seems almost constant for all r_H rates, (*ii*) the increase in r_H decreases the disorder in the sample. Additionally, samples obtained at different r_H rates can be characterized as follows: (*i*) $r_H = 10\%$, more crystallized Si-nc with sizes $\geqslant 3$ nm, and (*ii*) $r_H = 50\%$, smaller ($\leqslant 2$ nm) and higher density of mostly amorphous Si nanograins, induced by increased number of nucleation sites.

Figure 1 shows the effect of hydrogen rate on the PL spectra of SRSO films. It can be clearly seen that (*i*) the PL peak position (and shape) do not change with the changes of r_H, and (*ii*) the emission signal from all samples has a rather complex structure. The complex nature of the emission bands is probably due to the sample geometry
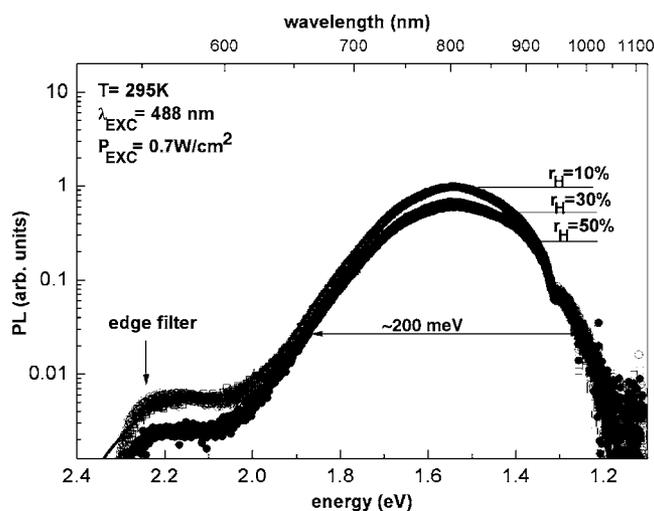
[z] E-mail: artur.p.podhorodecki@pwr.wroc.pl

Figure 1. Photoluminescence spectra measured for SRSO films obtained at different hydrogen rate (r_H).

Figure 3. Normalized PL yield vs excitation wavelength measured for SRSO films obtained at different hydrogen partial pressure and PL spectrum obtained for $r_H = 50\%$ (right axis).

inducing the interference effect, which has been discussed previously in other works.[9,21]

The lack of the PL shift with r_H variation indicates that the emission could not be unambiguously attributed to the quantum confinement effect. It may, however, be related to (*i*) some defects or interfacial states or (*ii*) Si-nc size/shape distribution that is large enough to cover this effect.

Figure 2 shows the absorption spectra obtained for all samples at room temperature from reflectance (R) and transmittance (T) spectra by using the following well-known formula[22]

$$\alpha = -\frac{1}{d}\ln\left(\frac{T}{(1-R)^2}\right) \qquad [1]$$

By considering the SRSO films as an effective medium, we analyzed the optical absorption edge by using the following Tauc relation[23]

$$(\alpha\hbar\omega) = A(\hbar\omega - E_g)^m \qquad [2]$$

where E_g is the bandgap corresponding to a particular transition occurring in the film, A is a constant, and the exponent m characterizes the nature of the band transition. $m = 1/2$ and $3/2$ correspond to
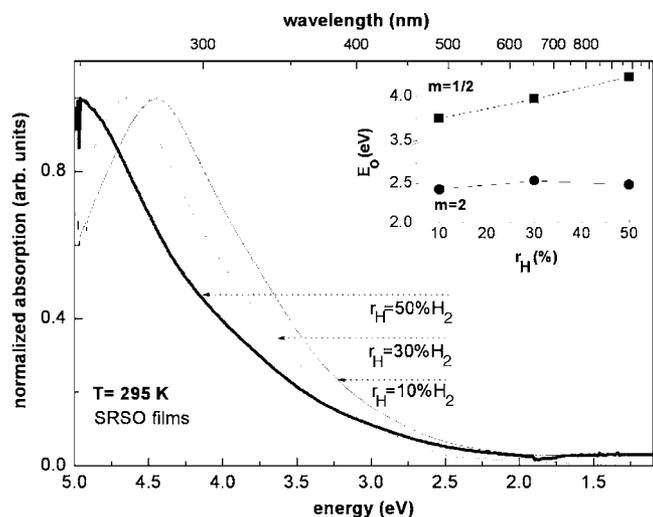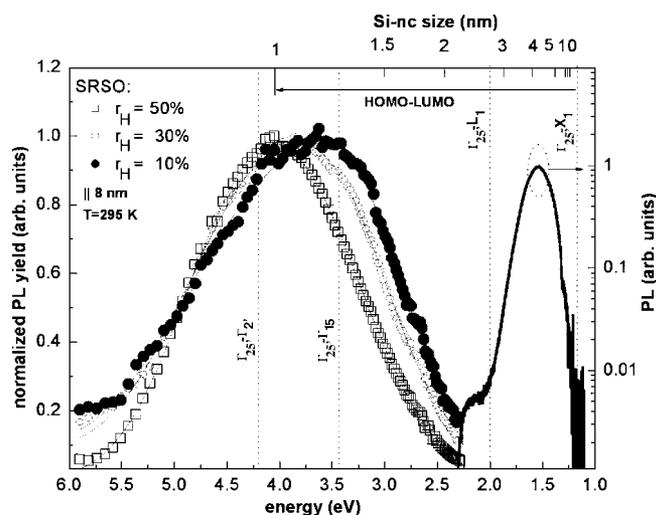

Figure 2. Normalized absorption coefficient determined for SRSO films obtained at different r_H. Inset: Absorption edge values obtained for different parameter m, form the Tauc equation.

allowed and forbidden direct transitions, respectively, whereas $m = 2$ and 3 correspond to allowed and forbidden indirect transitions, respectively.[24,25]

The analysis of the spectra shown in Fig. 2 allows the following remarks: (*i*) all spectra reveal a long absorption tail between 1.1 and ~3.5 eV, reflecting the amorphous nature of the optical absorption or the phonon-assisted transitions or broad size/shape distribution and (*ii*) the absorption signal shows a rapid increase with the photon energy (for $m = 1/2$) at around 3.7, 3.9, and 4.2 eV for r_H equal to 10, 30, and 50%, respectively. The threshold values are close to the optical direct transitions in bulk silicon, which take place at 3.4 and 4.2 eV for ($\Gamma_{25'}-\Gamma_{15}$) and ($\Gamma_{25'}-\Gamma_{2'}$) transitions, respectively.

Moreover, an evident blueshift of the absorption edge can be observed in Fig. 2 when r_H increases. This can be due to (*i*) decrease of nanocrystals size, if the edge is dominated by the nanocrystals optical properties, and/or (*ii*) the changes of the optical properties of the SRSO film treated as an effective medium.

It has been shown theoretically,[26] as well as experimentally,[27] that the absorption coefficient of a small Si-nc is generally shifted with respect to that of the bulk Si, which is characterized by ($\Gamma_{25'}-X_1$), ($\Gamma_{25'}-L_1$), ($\Gamma_{25'}-\Gamma_{15}$), and ($\Gamma_{25'}-\Gamma_{2'}$) absorption transitions at 1.16, 2.0, 3.4, and 4.2 eV, respectively.[28] Wilcoxon and Samara[9] have observed the blueshift in the absorption spectra for Si-nc obtained by inverse micelles from 4.2 to ~4.6 eV and ~5.4 eV. Also Rani et al.[12] have presented the absorption results for nanocrystals prepared by the off-axis pulsed laser deposition technique on different substrates with diameter decreasing from 4 to 0.8 nm. Their absorption edge was estimated at 3.59 or 4.2 eV, depending on the substrate nature.

The blueshift and the similar shapes of the absorption edges and the closeness of their energy thresholds to those in the spectrum for direct transitions of bulk Si suggests that we are dealing with the direct character of transitions in Si-nc with the evidence of a strong quantum confinement effect reflected in the blushift of the absorption edge. However, the quasidirect transition in the range between 1.1 and 1.9 eV, expected in this case, was not possible to detect.

Having in mind difficulties related with the absorption data obtained from the transmission spectra, discussed in the introduction, and to shed more light on the above reported data, we have performed total photoluminescence excitation (TPLE) measurements aimed at obtaining the integrated PL signal vs the excitation energy, as shown in Fig. 3. For the sample obtained at $r_H = 10\%$ (crystallized Si-nc with the diameter of ~3 nm) a strong absorption peak centered at ~3.6 eV can be observed. For the other two samples

($r_H = 30, 50\%$), broad peaks centered at around 3.9 and 4.0 eV, respectively, have been observed, whose positions are blueshifted in comparison to the spectrum obtained for the sample obtained at $r_H = 10\%$. Similar peaks between 3 and 4 eV have also been reported for PLE spectra recorded on porous silicon.[26,27] Such an absorption peak is also predicted through the imaginary part of the dielectric constant obtained by a theoretical study for Si quantum dots.[29]

The top axis of Fig. 3 marks the changes of energy of the first dipole-allowed transition, which coincides with the highest occupied state (HOMO)-lowest unoccupied state (LUMO) gap, defined as the difference between the LUMO and the HOMO energy, while the dashed vertical lines indicate the energy of the optical absorption in bulk silicon. The correlation between the energy and the nanocrystalline size has been obtained on the basis of the recent results of Niquet et al.[30] As shown in Fig. 3, the lowest absorption edge for Si-nc of sizes of ~ 3 nm ($r_H = 10\%$) should appear at ~ 2 eV, whereas its appears at 3.6 eV.

In the case of small amorphous nanocrystals (~ 1 to 2 nm), strong absorption bands centered between 3.0 and 4.5 eV have also been observed for both $r_H = 30$ and 50%. In this case, the interpretation is more complicated because these absorption bands appear at the energy positions similar to the lowest HOMO-LUMO energy absorption edges of Si-nc, as predicted theoretically (2.5–4.0 eV absorption edges for sizes of 2–1 nm).[29] However, based on obtained results, it has been suggested that, also in this case, the absorption properties are dominated by the direct transition in Si-nc.

The absence of the lowest energetically absorption transition in PLE spectrum for all samples may be due to much lower probability of the quasidirect electronic transition than for the direct one, even if the nanocrystals reach the size of ~ 1 to 3 nm, where the selection rules for **k** are partially lifted.

Thus, in our case, the absorption bands centered at ~ 3.5 to 4.0 eV can be related to the absorption to higher, direct in nature, electronic states of Si-nc, because it is too far from the theoretical predictions for the Si-nc ground state and too far from the edge of silica matrix.[31] The lack of discrete nature of this band and its large broadening is probably due to size/shape distribution of nanocrystals, and their interaction with the matrix. Also because of the large shift and Gaussian-like spectral shape of PLE similar to the PL spectra, the absorption band could be attributed to a Franck–Condon shift due to the strong electron-phonon coupling[32] and mixing of the wave functions of the conduction levels. This gives a possibility of relaxation to the lowest HOMO-LUMO level or surface states and then radiative recombination at ~ 1.6 eV.

The absorption properties of SRSO films obtained at different hydrogen pressures, reflected in the different sizes and crystalline phases of formed Si nanocrystals have been investigated by using absorption, TPLE, and luminescence measurements. Experimental results describing the absorption and emission properties of Si-nc have been shown.

It has been found that for all samples the most intense absorption transition is due to the direct absorption of Si-nc at ~ 4.0 eV, which depends on the nanocrystal size. The changes of r_H from 10 to 50% shifts the absorption edge by ~ 500 meV from 3.7 to 4.2 eV, in the case of PLE and absorption results. It was found that the general emission properties reflected by the shape and the peak positions generally do not depend on size and the crystalline phase of the Si clusters.

The differences in the absorption spectra and their dependence on the nanocrystal size and the similarities in the emission properties for all samples suggest that the emission is related to the surface of the clusters rather than to the quantum confinement within the nanoclusters.

References

1. T. Takagahara and K. Takeda, *Phys. Rev. B*, **46**, 15578 (1992).
2. F. Trani, G. Cantele, D. Ninno, and G. Iadonisi, *Phys. Rev. B*, **72**, 075423 (2005).
3. D. J. Lockwood, *Solid State Commun.*, **92**, 101 (1994).
4. I. Vasiliev, S. Öğüt, and J. R. Chelikowsky, *Phys. Rev. Lett.*, **86**, 1813 (2001).
5. F. A. Reboredo, A. Franceschetti, and A. Zunger, *Phys. Rev. B*, **61**, 13073 (2000).
6. M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, *Phys. Rev. Lett.*, **82**, 197 (1999).
7. J. D. Holmes, K. J. Ziegler, R. C. Doty, L. E. Pell, K. P. Johnston, and B. A. Korgel, *J. Am. Chem. Soc.*, **123**, 3743 (2001).
8. M. Rosenbauer, S. Finkbeiner, E. Bustarret, J. Weber, and M. Stutzmann, *Phys. Rev. B*, **51**, 10539 (1995).
9. J. P. Wilcoxon and G. A. Samara, *Appl. Phys. Lett.*, **74**, 3164 (1999).
10. S. M. Orbons, M. G. Spooner, and R. G. Elliman, *J. Appl. Phys.*, **96**, 4650 (2004).
11. Z. Ma, X. Liao, G. Kong, and J. Chu, *Appl. Phys. Lett.*, **75**, 1857 (1999).
12. J. R. Rani, V. P. Mahadevan Pillai, R. S. Ajimsha, M. K. Jayaraj, and R. S. Jayasree, *J. Appl. Phys.*, **100**, 014302 (2006).
13. Y. Kanemitsu, *Phys. Rev. B*, **53**, 13515 (1996).
14. L. Ding, T. P. Chen, Y. Liu, C. Y. Ng, and S. Fung, *Phys. Rev. B*, **72**, 125419 (2005).
15. L. Khriachtchev, *Appl. Phys. Lett.*, **81**, 1357 (2002).
16. R. G. Elliman, M. J. Lederer, and B. Luther-Davies, *Appl. Phys. Lett.*, **80**, 1325 (2002).
17. F. Gourbilleau, X. Portier, C. Ternon, P. Voivenel, R. Madelon, and R. Rizk, *Appl. Phys. Lett.*, **78**, 3058 (2001).
18. A. Podhorodecki, M. Nyk, R. Kudrawiec, J. Misiewicz, and W. Strek, *Electrochem. Solid-State Lett.*, **10**, H88 (2007).
19. F. Gourbilleau, C. Dufour, M. Levalois, J. Vicens, and R. Rizk, *J. Appl. Phys.*, **94**, 3869 (2003).
20. F. Gourbilleau, M. Levalois, C. Dufour, J. Vicens, and R. Rizk, *J. Appl. Phys.*, **95**, 3717 (2004).
21. R. Ferre, B. Garrido, P. Pellegrino, M. Perálvarez, C. García, J. A. Moreno, J. Carreras, and J. R. Morante, *J. Appl. Phys.*, **98**, 084319 (2005).
22. J. I. Pankove, *Optical Processes in Semiconductors*, Dover, New York (1975).
23. J. Tauc, *Optical Properties of Solids*, F. Abeles, Editor, North Holland, Amsterdam (1969).
24. A. Goswami, *Thin Film Fundamentals*, New Age International, New Delhi (1996).
25. S. Y. Ren and J. D. Dow, *Phys. Rev. B*, **45**, 6492 (1992).
26. M. V. Ramakrishna and R. A. J. Friesner, *Chem. Phys.*, **96**, 873 (1996).
27. J. A. Moreno, B. Garrido, P. Pellegrini, C. Garcia, J. Arbiol, J. R. Morante, P. Marie, F. Gourbilleau, and R. Rizk, *J. Appl. Phys.*, **98**, 013523 (2005).
28. P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors, Physics and Materials Properties*, Springer, New York (1996).
29. F. Huaxiang, Y. Ling, and X. Xide, *Phys. Rev. B*, **48**, 10978 (1993).
30. Y. M. Niquet, C. Delerue, G. Allan, and M. Lannoo, *Phys. Rev. B*, **62**, 5109 (2000).
31. S. M. Iftiquar, *J. Phys. D*, **31**, 1630 (1980).
32. J. L. Gole, F. P. Dudel, D. Grantier, and D. A. Dixon, *Phys. Rev. B*, **56**, 2137 (1997).