PHYSICAL REVIEW B **78**, 245425 (2008)

Catalytic role of adsorbates in the photoluminescence emission of Si nanocrystals

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(Received 21 July 2008; revised manuscript received 19 November 2008; published 30 December 2008)

Silicon nanocrystals were synthesized and deposited on different substrates. In order to clarify the photoluminescence (PL) emission of these agglomerates, we studied the luminescence spectra of several samples as a function of the exposure to air, oxygen, nitrogen, and rare gases. Measurements at different pressures reveal a strong enhancement of the PL at atmospheric pressure, when the sample is in air. In contrast no significant PL is observed for clean Si quantum dot in rare-gas atmosphere and in air at low pressure. Different behavior is detected in oxygen and in nitrogen as a function of the pressure. These data point out a catalytic role of the surface adsorption adding significant information for clarifying the PL mechanism. A comparison of our results, including the decay-time spectra with data and models of literature, demonstrates the important role of the phonon interaction in the relaxation and decay processes.

DOI: 10.1103/PhysRevB.78.245425 PACS number(s): 78.67.Hc, 78.55.Ap, 78.60.−b

I. INTRODUCTION

The luminescent properties of silicon quantum dots (QD) are very important for optoelectronics as optical gain of the luminescence emission intensity can be achieved in several cases.[1–5] In fact, in the last decade experimental evidence of high photoluminescence (PL) intensity was reported for silicon nanocrystals in somewhat oxidized form with strong similarity with porous silicon.[2] Several mechanisms have been suggested for explaining the origin of the photoluminescence obtained in a variety of experiments[1–7] but the general mechanism is still under a wide debate, including the specific differences between amorphous-Si QDs, crystalline-Si QDs, and porous Si. Often, for explaining the broad PL spectrum obtained, the recombination of localized states was proposed in the presence of silicon suboxide at the interface with the Si QDs.[8,9] In single Si quantum dot,[1] however, narrow peaks were detected that were attributed to excitons interacting with acoustic phonons. For porous silicon several authors conclude that luminescence originates from luminescence centers in SiO_x layers.[2]

In general, various experiments[3,4,7,9–12] confirm the following behavior of Si QDs observed at room temperature in air: (1) wide photoluminescence intensity in the range of wavelength of 400–1000 nm; (2) radiative recombination rate for amorphous-Si QDs comparable to that of porous silicon but higher than for crystalline-Si QDs;[13] (3) blueshifted PL peak with decreasing nanocrystal size;[4] (4) blueshifted spectra for aged samples in porous deposition, as a function of time; (5) high influence of the oxygen contained in the sample during preparation; (6) photoluminescence stretched-exponential decay in the range of several microseconds.

The interpretation of the above results, on the other hand, is under deep investigation and the following intriguing questions are intensely debated: (1) why is there no PL observed for clean Si QDs, whereas PL appears only in the presence of substoichiometric oxides? (2) what is the role of oxygen in the absorption of laser radiation and in the subsequent light emission? (3) how do the electron excitation process and the relative decay evolve, as phonon contribution is concerned? (4) where are these processes localized in **k** space? (5) if the adsorbates at the QD surface are so important, which model can be developed in real and **k** spaces for the behavior of the excited electron before its radiative decay?

From the above considerations it seems very important to have an accurate control not only of the size of the nanocrystals but also of the stoichiometry of its surface. In fact pure Si QDs do not emit any luminescence, whereas stoichiometric silicon dioxide produces PL spectra very different from those of Si QDs in air.

In order to investigate the mechanism governing the PL emission, we observed several samples of crystalline-Si QDs in controlled atmosphere. In fact, we performed PL measurements as a function of the exposure in air atmosphere. Similarly, we performed PL measurements as a function of the pressure in oxygen, nitrogen, and rare gases. Surprisingly, we detected unexpected results in the performed PL measurements as a function of the pressure. Huge enhancement of PL emission was found around atmospheric conditions in air, not in oxygen.

Our measurements clarify: (i) the excitation and deexcitation correlations including the localization of the *e-h* couples and their energetics (energy bands, relaxation, and

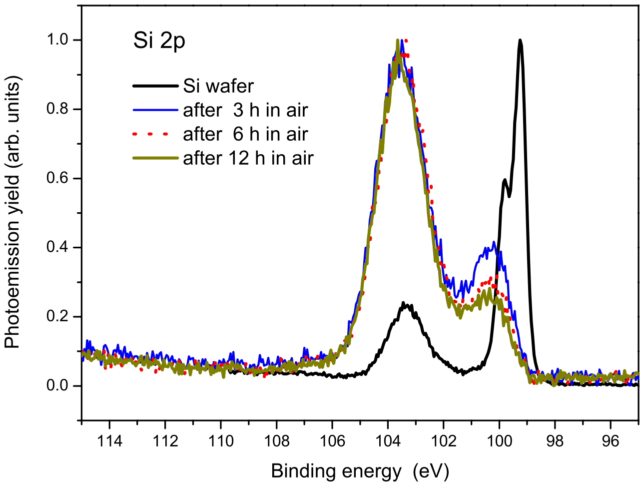

FIG. 1. (Color online) Photoemission Si 2p spectrum of our typical QD sample after exposure in air for a few hours. The well visible main stoichiometric oxide peak, the substoichiometric oxide features at lower binding energy, and the reference Si wafer spectrum with the splitted Si 2p peak.

decay); (ii) the dependence of the spectral features on the nanocrystal size and the reasons for the energy shift; (iii) finally and most importantly, the role of the oxygen and of adsorbates on the surface and/or interface of the Si QDs.

II. EXPERIMENT

We prepared our silicon quantum dots using the apparatus described in detail in Ref. 14. A beam of helium, inseminated with silicon vapors, produced clean silicon nanocrystals, expanding in supersonic configuration in a vacuum chamber at a pressure of 10^{-9} Torr. Being synthesized in high vacuum, the clean Si agglomerates were deposited *in situ*, with size in the range of 2–12 nm, on highly oriented pyrolitic graphite (HOPG), quartz, and crystalline Si with native oxide substrates. Several QD layers were accumulated on these substrates having ascertained that the nanocrystals maintain their individual configuration. Passivation of the surface dangling bonds could also be obtained by the presence of a low oxygen exposure during cluster evaporation. However, as explained in the following, we are interested in investigating the behavior of the dangling bonds of our clusters. For this reason we avoided any thermal treatment so as to maintain a dynamical situation under a controlled gas exposure, and/or an aging of the samples in air. In these conditions, of course, the effective size of the Si nanocrystals is determined by the central core of the clusters since their surface in air can progressively transform in Si (sub)oxide. This effect in turn produces a shell of oxide of increasing thickness at the expense of the crystalline core getting smaller and smaller. This is the aging effect. The size distribution of the nanocrystals therefore is changing but we know that the quantum confinement is practically due to the smallest sizes (smaller than 5 nm).[14,15]

This morphology was checked by x-ray photoemission investigation (see Fig. 1) and Raman spectroscopy.[14] In Fig. 1 the surface modification of the clusters is clearly visible with the growth of suboxide components and of SiO_2 peak at higher binding energy. In fact, the figure shows at about 4 eV higher binding energy with respect to the clean Si 2$p_{3/2}$, the main silicon dioxide peak, and at about 1 eV, the onset of broad substoichiometric oxides. Many samples were investigated by photoluminescence experiments operating in air, rare-gas, oxygen, and nitrogen atmospheres from about 10^{-5} mbar up to atmospheric pressure.

Room-temperature PL measurements were performed by pumping with the 488 nm line of Ar^+ laser. The laser power was 10 mW over a circular area of about 0.1 mm in diameter. The laser beam was chopped by an acousto-optic modulator. The PL signal was analyzed by a single grating monochromator and it was detected by a photomultiplier tube. Spectra were recorded with a lock-in amplifier synchronized to the acousto-optic modulator. All spectra have been corrected for the detector response. PL lifetime measurements were performed using the signal from the modulator as a trigger. The overall time resolution of the system is about 30 ns.

III. RESULTS

We obtained the following results. For fresh as-prepared samples in vacuum, the PL yield was negligible up to the atmospheric pressure. Only at ambient pressure, in air, did the PL show a remarkable sharp increase. This effect was reversible, i.e., the PL intensity was rapidly decreasing as a function of decreasing pressure, maintaining however a base PL dependent on the air exposure.

In Fig. 2(a) we display PL spectra in air from low pressure up to $p=p_0$ (ambient pressure). The spectrum shows a behavior typical of Si nanocrystals[10] in air with a peak around 725 nm, characteristic of a size distribution around 2–5 nm as confirmed for these samples by our Raman measurements.[14] In the figure the significant growth of the yield is visible as the pressure increases, demonstrating the influence of the adsorption of foreign molecules from the ambient gases. We emphasize that the behavior shown in Fig. 2(a) was reversibly reproduced several times. It is obvious to suspect oxygen, nitrogen, and/or water as possible saturation agents for surface dangling bonds. Therefore, we repeated the same measurements in oxygen, nitrogen, and, as reference, rare-gas atmospheres.

In Fig. 2(b) we report the behavior of PL yield in oxygen atmosphere at various pressures. Here, not only do we not observe any increase in the yield but in contrast a decrease in the emission yield is clearly visible. This confirms that oxygen cannot be responsible for any adsorption state. In fact, it gives rise only to stable chemisorbed (sub)oxide species which however need a long time to get stabilized at room temperature.

In Fig. 2(c) the data obtained in nitrogen atmosphere are also reported. Here, as expected, the trend is similar to that observed in air.

In Fig. 3 the PL intensity dependence as a function of pressure is displayed for aged samples. We observe that such intensity strongly increases at $p=p_0$, in air, and N_2, whereas at low pressure the yield is age dependent, being quite negligible for as-prepared Si nanocrystals.

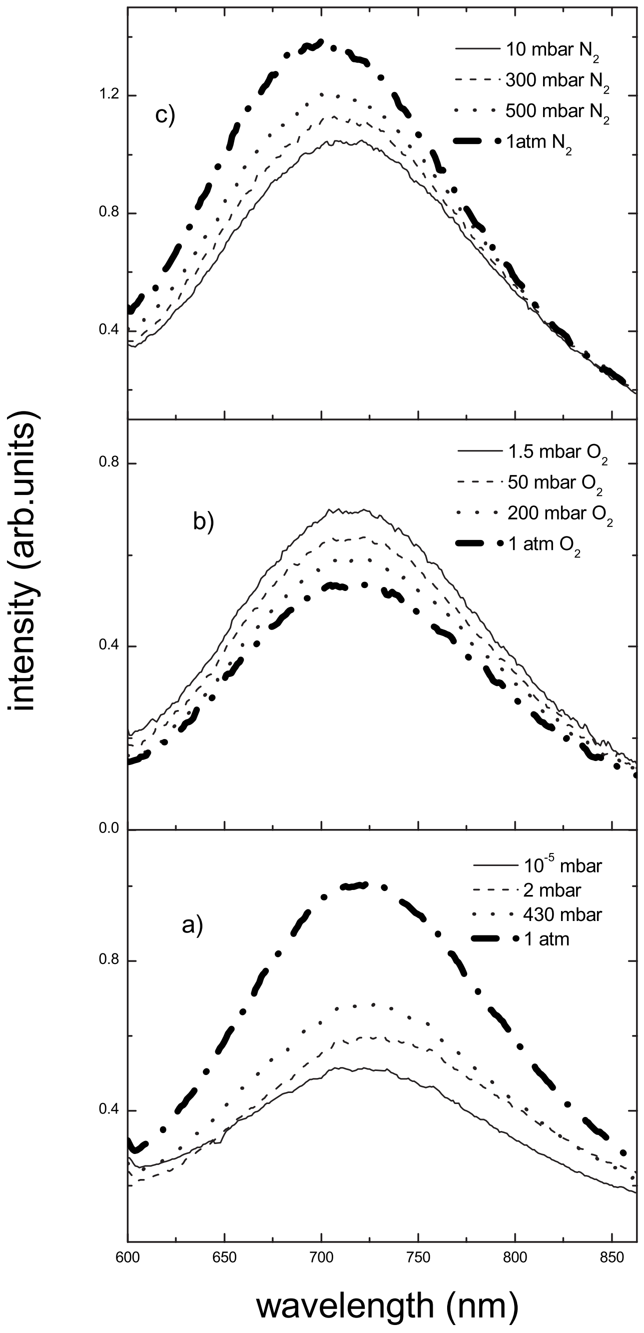

FIG. 2. PL spectra in (a) air, (b) oxygen, and (c) nitrogen.

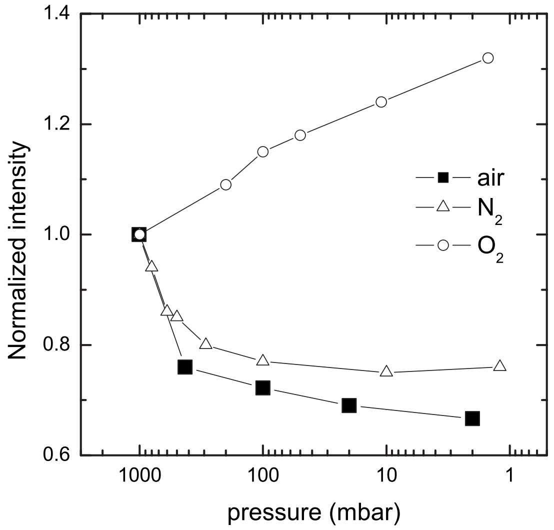

FIG. 3. PL intensity as a function of pressure in air, nitrogen, and oxygen atmosphere. Not reported in the figure are the very low intensity obtained for clean QD in a wide pressure range. Lines are a guide to the eye.

The comparison of the curves of Fig. 2 indicates a high contribution to PL coming from weak bonded adsorbates in pure nitrogen.[16] In pure oxygen the trend is opposite because of the slow chemisorption of this gas, and because of impurity passivation. In air, in fact, we do not find a behavior intermediate between the O_2 and N_2 curves but a somewhat stronger dependence from pressure since the oxygen gas produces the quenching of some adsorbates with a partial passivation of luminescence centers.

In the following these results will be explained in the light of the peculiar morphology of our Si nanocrystals. These important data compelled us to verify also the influence of a long store in air and/or oxygen. A spectrum similar to those of Fig. 2(a) was obtained by aged samples stored few months in air. Actually, the broad PL spectrum presents a higher intensity and a small blueshift. This confirms the slow oxidation causing a progressive reduction in the size of the crystalline-Si core surrounded by a layer of Si suboxides.[10]

In fact, our sample configuration consists of Si nanocrystals, when, in the as-prepared sample, agglomerates are synthesized in a porous deposition with a dynamical cluster population and size dispersion due to the aging in controlled atmosphere. Of course, the sample extracted out of the high-vacuum preparation chamber allows the covering of each cluster by a thin suboxide shell. The longer the storing time in air the thicker the surface layer of oxide gets, favoring the development of stoichiometric SiO_2. In Fig. 4 the blueshift of the PL peak is reported as a function of the age. This confirms the slow progressive reduction in the crystalline-Si

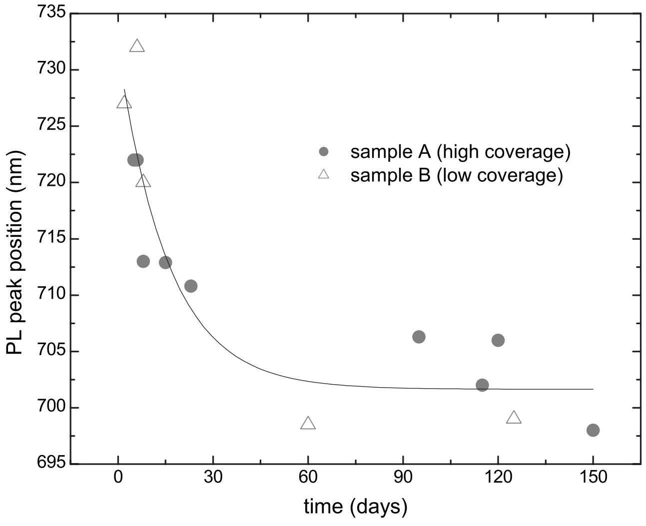

FIG. 4. Aging shift of the PL peak. The line is only a guide to the eye.

core because of the growth of silicon oxide. We note the sample with low coverage appears somewhat faster in reducing its size, shifting more than the sample with high coverage. This is expected because a low coverage implies a higher permeability of the few layers deposited on the substrate.

We note that Si quantum dots in crystalline phase do not show any PL emission whenever their surface is not covered by a suboxide layer. The same results were verified in rare-gas (argon and xenon) atmosphere at several pressures. In contrast aged samples do show a typical PL emission since the nanocrystals are now covered by a layer of substoichiometric SiO_x oxides.[10]

Therefore, aged samples at different pressure in air were also checked. They show a net increase in PL emission as that shown in Fig. 2(a) for fresh samples. The reversibility of such effect demonstrates the great catalytic influence of surface adsorbates on the nanocrystal PL emission. These adsorbates in fact can easily penetrate in our porous samples, filling the intercluster empty space and establishing weak bonding on the cluster surface. In order to discriminate the nature and species of adsorbate, further investigation was added repeating, as already mentioned, these measurements as a function of pressure with pure oxygen and pure nitrogen for fresh and aged samples.

The results indicate that a dramatic influence of the adsorbates is much stronger for fresher samples (i.e., samples that are not oxidized enough). These adsorbate states amplify the PL spectrum at room pressure, whereas a pumping down washes out the enhancement. It is obvious to attribute such effect to saturation of the dangling bonds by nitrogen and/or other impurities (water, H, CO, etc.), establishing weak adsorption states which can be easily eliminated at low pressure.

The previous measurements are supported by the decay time of the emitted radiation. This decay time was checked for our samples at fixed PL energy. The correspondent values were taken not only at the peak of the PL curve but also at lower and higher energies. In Fig. 5, the decay curves are reported together with their best fits. A single exponential curve does not represent a good fit. In fact, as reported in the literature, these curves were usually fitted by a stretched-exponential function such as $I=I_0\exp(-t/\tau)^{\beta}$, where τ is the PL lifetime and $0\leq\beta\leq 1$ is the dispersion factor.[3,10,11] Decay time in the order of 1–50 μs demonstrates the prevalent role of direct processes (see Ref. 10) in radiative decay.

For the curves reported in Fig. 5, we obtain the following parameters: λ=700 nm (1.77 eV): $\tau=4.63$ μs and $\beta=0.45$ (fresh sample); λ=633 nm (1.95 eV): $\tau=16.1$ μs and $\beta=0.60$ (aged sample); λ=683 nm (1.81 eV): $\tau=29.5$ μs and $\beta=0.69$ (aged sample); λ=733 nm (1.69 eV): $\tau=41.9$ μs and $\beta=0.69$ (aged sample).

IV. DISCUSSION

The PL behavior as a function of pressure now requires a detailed discussion. We propose the following scenario, distinguishing three steps: namely, radiation absorption with *e-h* production, relaxation, and radiative emission. Pure nanocrystals (as-prepared samples) or aged samples (nanocrystals surrounded by thin SiO_x and SiO_2 layers) absorb the laser radiation since their gap for size confined in the nanometer range is around 1.5–2.0 eV,[16,17] smaller than the radiation energy of the laser (2.5 eV).

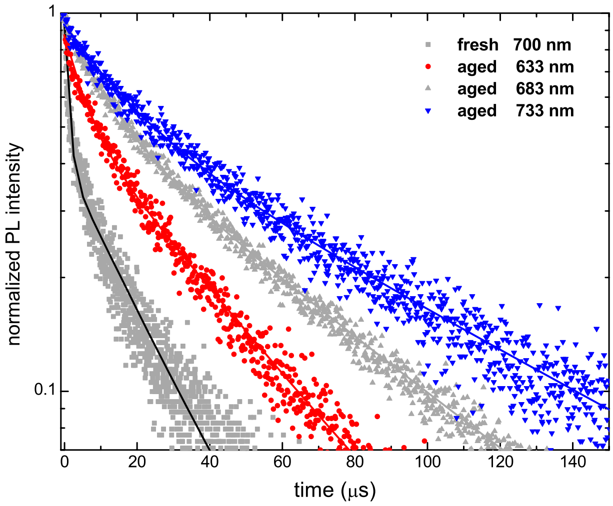

FIG. 5. (Color online) Decay spectra of fresh and aged samples for different wavelengths. The fitting lines are stretched-exponential curves (see text for the parameters).

Couples of *e-h* are therefore produced in the Si QD covered by the suboxide layer, with high kinetic energy. This is obviously due to the excitation laser energy which exceeds the energy gap of the silicon nanocrystals but not those of the silicon (sub)oxides (8.7 eV for SiO_2). We verified in our case, as shown in Fig. 1 for the Si 2*p* core-level binding energy, the presence of crystalline Si together with its suboxides and, of course, of SiO_2. The substoichiometric oxides, of course, have dangling bonds which can act as impurity or adsorbate capture centers. Similarly, the defects and surface impurities have dangling bonds which can modify the relaxation channels, favoring radiative or nonradiative processes.[11] The PL yield does depend in fact on that fraction of the absorbed radiation which decays radiatively, whereas the remaining part undergoes nonradiative processes, according to a well established expression

$$1/\tau = 1/\tau_{\text{rad}} + 1/\tau_{\text{nr}},$$

where τ is the total PL lifetime, and τ_{rad} and τ_{nr} are, respectively, the radiative and nonradiative decay times.[11] Of course, also the above fraction of the absorbed radiation with a radiative decay undergoes relaxation processes since the PL spectrum covers an energy range lower than the excitation energy.

Actually, after the absorption, the energy exceeding the *e-h* binding energy implies a wide electron mobility and an escape probability from the nanoagglomerate is extremely high. The electron is therefore delocalized, and can be easily trapped if it undergoes a fast relaxation and a subsequent capture in a dangling bond. A similar process happens for the hole. This explains why the Si suboxides play an important role together with defects, interface, and surface impurities.

They act with their unsaturated bonds as capture centers for the electrons rapidly relaxing in their movement within the surrounding oxide layer.

Therefore, the relaxed electrons, filling the empty states of the surrounding layer of the Si QD, can radiatively decay into the hole states of the QD, giving rise to the PL spectrum. In this spectrum extending from 400 to 900 nm and beyond, several contributions are present, mainly direct[10] electron-hole transitions in a wide energy range. Indirect transitions are less probable, as shown in investigations, as a function of the temperature.[10]

It is clear now why PL can be enhanced by the presence of adsorbates. They act on the surface of the QD with weak hybrid bonds (H, OH, N, CO, etc), somewhat extending the capture centers in the surface layer and establishing possible interface connections between the clusters. Similar effects were observed[16] for samples containing Si nanocrystals annealed in N_2 or O_2. Also these results point out the crucial role of the surface bonds in stabilized samples. Our experiment, however, observing dynamical surface modifications, makes more evident the adsorbate influence and the difference between weak bonds (easily desorbing ad atoms) with respect to strong bonds (e.g., chemisorbed oxygen and oxide formation, which is very slow at ambient temperature).

The previous results and the proposed explanations are in close agreement with the following three step model.

(i) Excitation. The excitation laser light with energy of 2.53 eV can produce a high rate of *e*-*h* couples in the interior of the Si QDs having a smaller energy gap (but higher than the bulk silicon and increasing with reduced cluster size). However, as demonstrated by infrared spectra in Ref. 14, the suboxides surrounding the QDs do have dangling bonds, impurity levels, and interface states which represent a variety of sites available for excitation and/or de-excitation processes.

(ii) Relaxation. The *e*-*h* couples, as already emphasized, undergo various scattering processes owed to their high kinetic energy. The inelastic processes produce a rapid transfer of the couples on the lowest energy levels of the QDs that are much more localized and eventually form excitons with a low binding energy inside the QDs.

(iii) Decay. The final states are therefore formed by weakly interacting excitons (*e*-*h* couples) confined mainly in the QDs where they decay radiatively by direct processes within the entire Brillouin Zone, i.e., with a wide $\mathbf{k}$ and energy spectrum.

In the literature, most of the recent PL studies were performed with annealed samples, i.e., with stabilized structures where the luminescent nanocrystals are frozen within a SiO_2 matrix. The question arises whether the substoichiometric oxides enhance the PL efficiency. We observe that in any case the matrices surrounding the nanocrystals have a high concentration of defects and dangling bonds, both in the suboxide layer at the interface and in the dioxide matrix usually in amorphous phase.[8] Note the fact that the present measurements demonstrate the importance and the role of *surface* bonds, which strongly participate in the PL emission. We argue therefore that the mechanism governing the decay should be phonon assisted because only a vibrational long-range behavior can connect the internal nanocrystal with the surface. This implies that the interaction with phonons, via relaxation channels, can be responsible for energy losses before the radiative decay. This mechanism is similar to that proposed by Sa'ar and co-workers in Refs. 18 and 19. These authors performed PL studies for several Si nanocrystal sizes and found a correlation with Si-O-Si vibrational energy. Their model suggests a polarization field coupled to the quantized states of the nanodots. The vibrational modes can influence slow nonradiative relaxation rates enhancing the PL efficiency.[19] Our results could agree with the previous model assuming, in the amorphous oxide layer of our samples, vibrational spectra connecting Si dots, suboxide interface, and oxide surface.[20]

A final comment concerns the values of the stretched-exponential decay. We compare the values obtained for the curves reported in Fig. 5. Whereas the β parameter is related to the cluster configuration, being roughly independent of the emitted photon energy,[11] the decay time results much longer for aged samples, i.e., when a thicker dioxide layer is established. This demonstrates that electrons need a shorter time to reach the final state when the decay can take place in a reduced suboxide layer. Note also that the radiative decay time depends on the density of electron and hole states, the size of the QD,[19] and the phonon contribution. In fact, the radiative decay time increases for longer wavelengths, as prescribed by the uncertainty principle, whereas the relaxation time, depending on the electron (hole) mobility and on the electron (hole) mean-free path, can be expected to be correlated with the particle energy. Here, we assume that for fresh samples the radiative decay time is smaller than for aged samples because of strong differences in nonradiative processes, and because of the stronger localization of the decaying couples. This in fact implies a wider uncertainty in the wave vector. In addition, the quasicontinuum states in the valence and conduction bands of bulk silicon become now a well separated ensemble. This implies decay times smaller for smaller wavelengths.

In conclusion, we discussed our measurements of PL as a function of the pressure for the important class of silicon nanocrystals. The present paper demonstrates (i) the importance of surface bonds for the PL emission, (ii) the nonlocality of the process, (iii) the absence of PL for native nanocrystals, and (iv) the fundamental role of phonons in the radiative decay. The preparation of the QD and the specific behavior in gas atmosphere permitted the clarification of the catalytic role of the adsorbates, indicating also the mechanism of radiative decay upon laser excitation. A crucial role seems to be due to the phonons, in agreement with a recent model by Sa'ar and co-workers (Refs. 18 and 19).

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[1] I. Sychugov, R. Juhasz, J. Valenta, and J. Linnros, Phys. Rev. Lett. **94**, 087405 (2005).

[2] G. G. Qin, H. Z. Song, B. R. Zhang, J. Lin, J. Q. Duan, and G. Q. Yao, Phys. Rev. B **54**, 2548 (1996).

[3] F. Trojanek, K. Neudert, P. Malý, K. Dohnalová, and I. Pelant, J. Appl. Phys. **99**, 116108 (2006).

[4] M. Zacharias, J. Heitmann, R. Scholz, U. Kahler, M. Schmidt, and J. Bläsing, Appl. Phys. Lett. **80**, 661 (2002).

[5] S. Boninelli, F. Iacona, G. Franzó, C. Bongiorno, C. Spinella, and F. Priolo, J. Phys.: Condens. Matter **19**, 225003 (2007); L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzó, and F. Priolo, Nature (London) **408**, 440 (2000).

[6] Y. Honda, M. Takei, H. Ohno, S. Shida, and K. Goda, J. Lumin. **113**, 279 (2005).

[7] J. Wan, M. Han, J. Zhou, and G. Wang, Phys. Lett. A **280**, 357 (2001).

[8] N. Daldosso *et al.*, Phys. Rev. B **68**, 085327 (2003).

[9] O. Jambois, H. Rinnert, X. Devaux, and M. Vergnat, J. Appl. Phys. **100**, 123504 (2006); O. Guillois, N. Herlin-Boime, C. Reynaud, G. Ledoux, and F. Huisken, *ibid.* **95**, 3677 (2004).

[10] G. Ledoux, O. Guillois, D. Porterat, C. Reynaud, F. Huisken, B. Kohn, and V. Paillard, Phys. Rev. B **62**, 15942 (2000); Xiaoming Wen, Lap Van Dao, and Peter Hannaford, J. Phys. D: Appl. Phys. **40**, 3573 (2007).

[11] M. Dovrat, Y. Goshen, J. Jedrzejewski, I. Balberg, and A. Sa'ar, Phys. Rev. B **69**, 155311 (2004).

[12] A. Podhorodecki, G. Zatryb, J. Misiewicz, J. Wojcik, and P. Mascher, J. Appl. Phys. **102**, 043104 (2007).

[13] K. Nishio, J. Koga, T. Yamaguchi, and F. Yonezawa, Phys. Rev. B **67**, 195304 (2003).

[14] G. Faraci, S. Gibilisco, P. Russo, A. R. Pennisi, G. Compagnini, S. Battiato, R. Puglisi, and S. La Rosa, Eur. Phys. J. B **46**, 457 (2005).

[15] G. Faraci, S. Gibilisco, P. Russo, A. R. Pennisi, and S. La Rosa, Phys. Rev. B **73**, 033307 (2006).

[16] L. Dal Negro, S. Hamel, N. Zeitseva, J. Hyung Yi, A. Williamson, M. Stolfi, J. Michel, G. Galli, and L. C. Kimerling, IEEE J. Sel. Top. Quantum Electron. **12**, 1151 (2006).

[17] G. Allan, C. Delerue, and M. Lannoo, Phys. Rev. Lett. **78**, 3161 (1997).

[18] A. Sa'ar, Y. Reichman, M. Dovrat, D. Krapf, J. Jedrzejewski, and I. Balberg, Nano Lett. **5**, 2443 (2005).

[19] A. Sa'ar, M. Dovrat, J. Jedrzejewski, and I. Balberg, Physica E (Amsterdam) **38**, 122 (2007).

[20] A. R. Chowdhuri, D. U. Jin, J. Rosado, and C. G. Takoudis, Phys. Rev. B **67**, 245305 (2003).