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Sidebands in nontunable photoluminescence of Si^+-implanted SiO_2

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Samples of Si^+ implanted in SiO_2, annealed at 1150 °C, have an efficient photoluminescence band centered at 1.55 eV, the latter being independent from the annealing time and consequently on the Si nanocrystals' size. We measured resonantly excited photoluminescence at 1.4 K, which shows two phonon steps, shifted by 56 and 112 meV from the excitation energy, similar to porous silicon; however, with significantly different relative intensities. Based on a quantitative analysis of this measurement, on time-resolved spectroscopy and on comparison with similar measurements of direct semiconductors, we conclude that the existence of phonon replicas *does not* imply that the luminescence originates from quantized levels in Si nanocrystals.
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The luminescence properties of silicon based structures are still of great interest. A major interest exists due to their potential utilization in integrated optoelectronics. Porous silicon (PoSi) is the most studied silicon based luminescing material. The origin of the luminescence is still a matter of controversy. It either originates from quantum size effect or from surface perturbed states recombinations. The Si^+-implanted SiO_2 (ImSi) was developed as an alternative system to PoSi in order to achieve controllable sized nanocrystals of Si with higher mechanical and chemical stability. The manufacturing technology, common for many electronic devices, consists in our case of a Si^+-ion implantation in a dose of about 10^{16} atoms/cm^2 at the energy of 50 keV in a 1000 Å thin SiO_2-layer thermally grown on a *c*-Si [100] wafer, followed by an annealing process at temperatures ranging between 900-1150 °C. The first successful attempt of continuously tunable luminescence from ImSi was achieved by Fischer *et al.*,[1] after annealing the samples at 900 °C for a duration between 3 and 30 min. However, the luminescence was very broad and with low efficiency. A further work, done by Schuster *et al.*,[2] demonstrated that annealing samples at 1150 °C, with a dose of 5×10^{16} atoms/cm^2, led to a photoluminescence (PL) band centered at 800 nm with higher efficiency and a relatively narrow band width (0.26 eV). The efficiency at room temperature is comparable to that of aged PoSi.[2] The annealing duration changes only the intensity of the PL band without shifting its energy. Similar results for ImSi were obtained by Song *et al.*[3] and Iwayama *et al.*[4] Nontunable PL fixed in color at ≈1.6 eV was reported for strongly oxidized PoSi,[5] oxidized gasphase grown nanoparticles[6] and oxidized chemical vapor deposition (CVD) Si layers.[7,8] In the present work we used the resonantly excited PL technique in order to elucidate whether the luminescence in ImSi annealed at 1150 °C, originates from an ideal quantum confinement effect, a surface state or a mixture of them.

Figure 1 represents the nonresonant PL spectra of ImSi samples processed with different annealing times as indicated in the caption and in Ref. 2 recorded at room temperature. One can observe that the 4 min annealed sample has a lower PL-band energy than that for 3 min. This would be in agreement with the quantum-size effect. However, the further annealing up to 30 min does not change the peak position, but only its intensity. A longer annealing time than 40 min produces a shift back to higher energies. The samples were annealed in forming gas, so that no additional oxidation may occur. We expect therefore a constant increasing of the samples' size as the annealing time is longer. Evidences of this increase are presented in Ref. 1 by using high-resolution

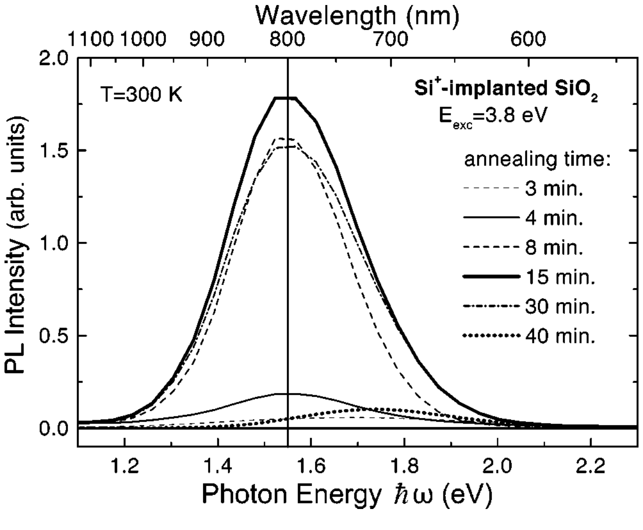

FIG. 1. Nonresonant PL spectra of ImSi samples annealed at different times as shown above.

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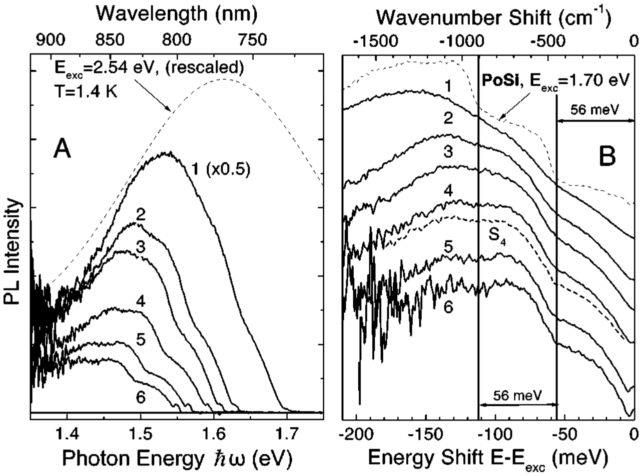

FIG. 2. Full scale (a) and shifted scale $(E-E_{exc})$ (b) representation of the PL spectra of ImSi. The spectra were excited under resonant conditions with the energies: (1) 1.70 eV, (2) 1.63 eV, (3) 1.61 eV, (4) 1.59 eV, (5) 1.57 eV, and (6) 1.55 eV. The simulated PL, S_4 for an excitation at 1.59 eV is presented by thick dashed line (b) and nonresonant PL of ImSi (a) and a resonant PL of PoSi (b) by thin dashed lines.

transmission electron microscopy or in Ref. 9 by using cross sectional TEM.

The resonant excitation PL measurements required an extremely high sensitive technique, in contrary to the case of PoSi. We used a Princeton Image Intensified charge-coupled device (CCD) camera as a detector, coupled with an Acton SpectraPro -300i spectrometer. The light excitation was done by a Ti-Sapphire laser, tunable in the range of 700-800 nm. The excitation power density was 300-500 mW/4 mm^2 ($\simeq$10 W/cm^2). We used a mechanical chopping for both the excitation and PL light in opposite phases and an additional electronic chopping (done by the image intensifier of the CCD), synchronized with the mechanical chopping of the PL. The measurements consisted of 200 accumulations $\times 5$ second integration time. In this way, it was possible to detect a luminescence close to the laser energy, but with 10^{10} times lower intensity.

Resonantly excited PL spectra of the best luminescing ImSi (15-min annealing time) at various excitation energies (indicated in the figure caption), are shown by the solid lines in Fig. 2(a). The nonresonant spectrum at $T=1.4$ K is drawn for comparison by the dashed line. The solid lines in Fig. 2(b) are the resonant spectra, represented in a shifted scale with respect to the excitation energy $(E-E_{exc})$. Figure 2(b) also contains a resonantly excited PL of PoSi (dashed line). Comparison of the ImSi and PoSi spectra indicates that in both cases the spectrum consists of steps separated by 56 meV from the excitation line or from each other, but the relative intensities are substantially different. The position of the phonon steps corresponds to the TO phonon onsets of PoSi. Similar results were obtained by Kanemitsu *et al.*[6] for oxidized Si-nanocrystals obtained from SiH_4. In that case, the PL is centered at 800 nm and exhibit almost no shift as a function of size. The resonant excitation PL presents only one detectable step, as in our case. The quality of the present measurements allows us to make extended quantitative estimations.

The resonant PL spectral line shape was simulated by a mathematical description, utilized under different forms but *equivalent* in several other cases, such as in the explanation of the fluorescence line narrowing of CdSe[10] (based on the displaced harmonic oscillator model) or in the luminescence of PoSi.[11,12] This description considers the intensity of the photoluminescence $PL(E_{det})$ as a sum of contributions (convolution) of every subset of particles, with energy gaps between ε and $\varepsilon+d\varepsilon$, ε ranging from detection energy E_{det} to excitation energy E_{exc}. Each subset contains a number of particles proportional to a distribution function $D(\varepsilon)$. The emission of one particle is proportional to the number of absorbed photons with the energy $E_{exc}>\varepsilon$, $A(E_{exc}-\varepsilon)$ multiplied by the number of emitted photons at the energy $E_{det}<\varepsilon$ for each absorbed photon, $F(\varepsilon-E_{det})$. Then, at low temperatures, where anti-Stokes components are negligible, the photoluminescence line shape is given by Eq. (1):

$$\mathrm{PL}(E_{det})=\int_{E_{det}}^{E_{exc}} D(\varepsilon)A(E_{exc}-\varepsilon)F(\varepsilon-E_{det})d\varepsilon. \quad (1)$$

Empedocles[13] and several others showed that the fluorescence of a single particle is extremely sharp, accompanied by additional sharp phonon replicas. Therefore, $F(\varepsilon-E_{det})$ can be suitably simulated either by $\delta(E)$ functions or by sharp gaussians. In our simulations, we considered only TO phonons with the energy of $E_p=56$ meV and a Stokes shift (singlet - triplet splitting) Δ of 1 - 3 meV. The distribution function $D(\varepsilon)$ was taken as the gaussian fit of the nonresonant PL at 1.4 K, assuming that the oscillator strength is constant over the range of investigation. The physical coupling process is different for quantum dots of direct and indirect semiconductors. The generated or recombined exciton couples with the ionic lattice dipole, creating a LO phonon in the first case. In the second case the generation or recombination process requires the conservation of momentum and hence, the creation of a (most probable) TO phonon. However, we can speak in both cases about a coupling parameter S (called Huang-Rhys parameter for coupling with polar lattices) and a shift of E_p for each additional phonon replica. Therefore, the single-dot absorption and fluorescence functions can be expressed as sums of several such replicas (here for compatibility, $n_{max}=1$).

$$A(E_{exc}-\varepsilon)=\sum_{n=0}^{1}\frac{S^n}{n!}A_n(E_{exc}-\varepsilon-nE_p) \quad (2)$$

$$F(\varepsilon-E_{det})=\sum_{n=0}^{1}\frac{S^n}{n!}\delta(\varepsilon-\Delta-E_{det}-nE_p). \quad (3)$$

The experiments show that for a direct semiconductor there is always a *lower* probability of phonon-coupled transitions than direct transitions, leading to $S<1$. Furthermore, the experimental absorption functions A_n appear to be of quasi-δ-shape,[10,14] corresponding to sharp levels instead of bands, as predicted by the theory of zero-dimensional systems (see also our calculations in Fig. 3(a) on CdSe). On the other hand, for indirect semiconductors, we expect a *higher* probability of phonon-assisted transitions. In PoSi indeed, $S>1$. In addition, the shape of the experimentally deter-

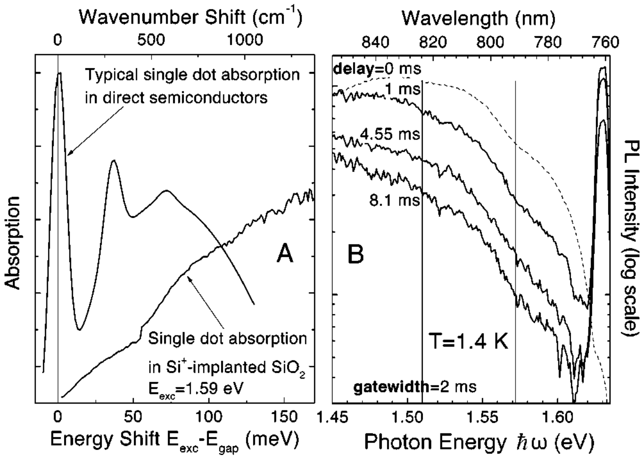

FIG. 3. The calculated single dot absorption curve of a direct semiconductor and of ImSi (a). The time resolved, resonantly excited PL of ImSi with laser energy at 1.63 eV (b). The dashed line is the steady state PL.

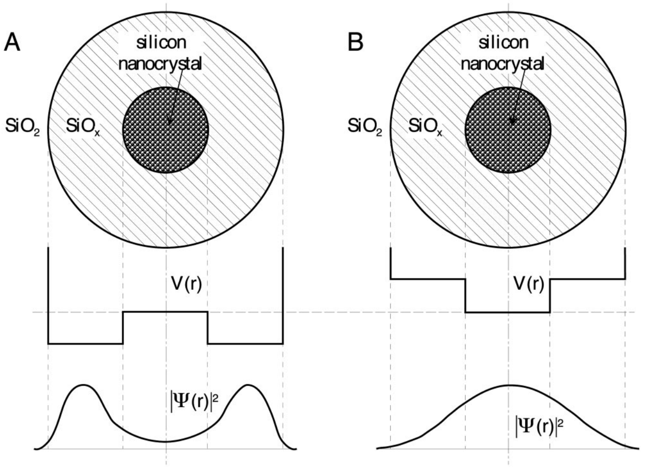

FIG. 4. The exciton localization around a Si nanoparticle in our model (a) and in the quantum confinement model (b). The potential $V(r)$ indicates the spatially change of energy gap.

mined absorption function (Refs. 11 and 12) deviates strongly from a δ function. We calculated the absorption function $A(E_{exc}-\varepsilon)$ from our measurements deconvoluting the Eq. (1), with the help of fast Fourier transform, denoted here by $\mathcal{F}$. Hence,

$$A(E_{exc}-\varepsilon)=\frac{1}{D(\varepsilon)}\,\mathcal{F}^{-1}\left\{\frac{\mathcal{F}[PL(E_{det})]}{\mathcal{F}[F(\varepsilon-E_{det})]}\right\}. \tag{4}$$

The simulation of our measurements gives, for the considered PoSi, a coefficient $S\simeq 1.8$ and for ImSi $S=0.18-0.22$. One calculated single dot absorption curve (A_4 for $E_{exc}=1.59$ eV) is presented in Fig. 3(a). All other calculated absorption curves look similar. The shape (except of the step at 56 meV) resembles the $\sqrt{E-E_g}$ law for *direct bulk* semiconductors. The contrast between the absorption curve of a single-dot direct semiconductor and that of ImSi (A_4) is shown in Fig. 3(a). The latter absorption curve and Eq. (1) enabled us to simulate the PL curve 4 labeled S_4 in Fig. 2(b).

An additional test on the optical properties of ImSi consisted of the time resolved resonantly excited PL, shown in Fig. 3(b). A similar measurement was also done for PoSi. In both cases, all the phonon features decay at the same rate and in the same multiexponential way. Thus, we conclude that the zero phonon and the two distinct TO shoulders all belong to the same luminescence event. This conclusion contradicts the hypothesis of Rosenbauer *et al.*[15] that two distinct luminescent materials may coexist in Si nanoparticles and hence, it supports the excitonic hypothesis of the luminescence. The nonexponential decay was explained by Calcott[12] to originate from a set of particles with the same energy gap but different shapes and hence different exponential decays.

The following discussion will put in balance the pro and contra arguments concerning the quantum confinement effect, i.e., the formation of quantum-size levels (QSL's) in silicon nanocrystals and the exciton energy determined by these levels.

(1) Pro arguments, in general, for silicon based materials: (a) The photoluminescence occurs at higher energy than the E_{gap} of bulk Si. (b) Phonon replicas appear at higher energy than the E_{gap} of bulk Si. These mean that the excitons are at least partially located in the Si-nanocrystal *and* the phonon coupling is allowed at their energy. (c) Polarization memory[16] or optically induced polarization memory[17] observed in PoSi, reveal that the shape of excitons is determined by the shape of the nanoparticles, proving that the localization of excitons coincides more or less with the size of the nanoparticle. (d) Tunability as a function of nanoparticle size, for the case when it exists, strengthen the existence of quantum size levels.

(2) Contra arguments for ImSi: (a) The absence of tunability as a function of size. (b) The ability to observe a resonantly excited PL *does not* exclude the possibility that the luminescence shown in Fig. 2 is associated with defect states (in the core or on the surface). If the density of states of the defect sites are high enough, it will lead to a sufficient photoexcitation. (c) The absence of discrete levels in terms of molecular orbitals (MO), that are observed as a peak in the absorption around the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO)-(LUMO) transition, like in direct semiconductors [Fig. 3(a)]. Some direct semiconductors also show QSL's in PL excitation. Distribution of the density of states in an indirect semiconductor nanocrystal such as Si is of course different. From our point of view, the wave function of an electron at the minimum of the conduction band, with **k** vector close to X point, will always satisfy the boundary conditions because the Bloch-wavelength is almost equal to the lattice constant and any nanocrystal has an integer number lattice constants. Therefore, the minimum in the conduction band of bulk Si should remain at the LUMO level, even if the six-times valley degeneration is lifted. Only the HOMO level should be lower than the top of the valence band. We expect, therefore, from QSL's in Si at least one sharp onset in the single-dot absorption curve. (d) The phonon-assisted transitions have, in contrary to PoSi, a smaller probability than the direct transitions ($S=0.18<1<1.8$). Several experimental evidences[12,18] demonstrated that the lower is the PL energy, the smaller is the probability of direct (non-momentum-conserved) transition. It was argued that the bigger is the size of the nanocrystal (lower energy), the smaller is the influence of the surface,

which is responsible for the direct transitions. The case of ImSi does not belong to this category. Kanemitsu showed, against latter argument, that not only the size (i.e., the surface to volume ratio), but also the nature of the surface (hydrogen or oxygen terminated) changes the probability of the transitions without momentum conservation.[19]

It was suggested by Kovalev[18] that the Si-nanocrystals are surrounded by an amorphous nonstoichiometric compound SiO_x, $(x<1)$ with lower energy gap than that of SiO_2. The exciton is extended beyond the Si-nanocrystal and its size and energy is partially determined by the energy gap and thickness of this shell like in Fig. 4(b). However, there should be in this case at least a small correlation between the Si-nanocrystals' size and PL-energy. On the other hand, there are many groups supporting the surface state model.[7,8,15,20–24] Gole *et al.*[24] presented a long list of silanone-based silicon oxihydrates, which have luminescence in the same spectral range (red). Prokes[22] attributed a nonbridging oxygen hole center in a SiO_2 matrix also to the red luminescence or Veprˇek *et al.*[7,8] related the OH centers to the same luminescence.

Based on above observations, we suggest the luminescence model drawn in Fig. 4(a). We suppose that the surrounding shell [marked by lower potential $V(r)$ in Fig. 4(a) as in 4(b)], labeled again by SiO_x, is red luminescing and has a quasicontinuum number of states. The Si-nanocrystals have to be small enough to have quantized levels at a larger energetic distance than the observed PL. The wave function of the shell excitons penetrates partially in the Si-core fitting the lattice periodicity, thus leading to weak coupling with phonons. This may explain the existence of the phonon replicas; however the quantized levels *do not* influence the exciton energy.

We conclude that the observed phonon sidebands are a result of coupling surface excitons with the core Si nanocrystal.

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