Auger and Coulomb Charging Effects in Semiconductor Nanocrystallites

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Theoretical and experimental results are presented providing evidence for fast Auger recombination in silicon nanocrystallites. Calculations give nonradiative lifetimes in the 1 ns range. Luminescence experiments on porous silicon exhibit a saturation at high excitation power. The Auger effect gives a natural explanation for this saturation as well as for the recently observed quenching of the photoluminescence and voltage tunable electroluminescence. In this last case the importance of Coulomb charging effects is shown to be at the origin of the linewidth. The consequences of such fast Auger recombination for the optical efficiency of indirect band-gap semiconductor nanocrystallites are discussed.

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There have been many recent efforts to obtain efficient optical devices from indirect band-gap semiconductors based on rare-earth doping, SiGe alloys, or superlattices and nanoconfinement. Up to now, these techniques have not succeeded in giving materials as efficient as direct band-gap semiconductors. In silicon nanocrystallites, for example, although the confinement partially breaks the k vector selection rule and allows direct radiative transitions even without phonon assistance, the calculated radiative lifetime remains long ($>10\ \mu$s) for crystallites containing more than ~20 Si atoms [1] as confirmed experimentally [2]. Under such conditions nonradiative recombination processes play an important role. In this Letter we want to emphasize the role of the Auger effect which is one of the most efficient channels for electron-hole (eh) recombination in bulk silicon. We first present results of tight binding calculations showing that it remains as efficient even in very confined systems with a lifetime in the nanosecond range. We then discuss new photoluminescence (PL) experiments performed on porous silicon samples exhibiting a saturation at high excitation power which is explained quite naturally by the Auger effect. The voltage quenching of the PL [3] and the voltage tunable electroluminescence (EL) [4] of porous silicon are also reconsidered on this basis. We show that, in addition, the Coulomb charging explains the experimental width of the EL spectra.

We consider spherical silicon crystallites of radius R whose surface is passivated by hydrogen atoms [1]. Let us assume that there is one eh pair in a crystallite plus one additional carrier—electron or hole—introduced by injection or another excitation. In the Auger process, the eh pair recombines nonradiatively transferring its energy to the third carrier. In bulk silicon, the Auger probability per unit time and volume is equal to $Apn^2 + Bnp^2$, where p and n are, respectively, the hole and electron concentrations. A and B are not known accurately; values have been reported between 10^{-30} and 10^{-32} cm^6/s [5,6]. Let us first extrapolate these data to nanocrystallites taking the concentrations n and p to correspond to one carrier confined in a spherical volume $4\pi R^3/3$. We see in Fig. 1 that such extrapolated Auger lifetimes τ lie between 0.1 and 100 ns for crystallite radius $R < 2.5$ nm, which is several orders of magnitude faster than the

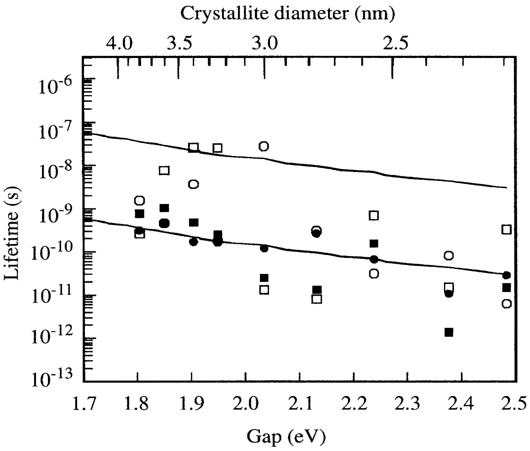

FIG. 1. Auger recombination time vs energy gap for spherical silicon crystallites. The squares (circles) represent the results from the direct calculation for the Auger process with two electrons and one hole (two holes and one electron). Empty symbols correspond to a level broadening induced by the electron-lattice coupling and full symbols to a level broadening of ~0.1 eV (see text). The two continuous curves represent upper and lower bounds of an extrapolation from the bulk values.

radiative lifetime. The recombination should thus occur by the Auger process instead of light emission.

However, the transfer of the Auger coefficients A, B from bulk to nanocrystallite semiconductors is questionable. In crystallites, the energy quantization (level spacing ~ 10 meV) makes it impossible to find a state for the third carrier with the excitation energy exactly matching the exciton energy. Consequently, the Auger effect is possible only if one takes into account the broadening of the electronic levels which can come, for example, from the coupling with neighboring crystallites through a silicon oxide barrier or a silicon bridge ("undulating wires" [7]) or from the electron lattice coupling. We have taken this effect into account by replacing the Auger final state by a Gaussian density of states. For undulating wires the barrier between crystallites is small, the broadening is important, and we have adjusted the width of the Gaussian to get a continuous density of excited states (~ 0.1 eV is enough). For pure electron-lattice coupling we have used previously calculated values of the Franck Condon shift d_{FC}, i.e., the relaxation energy of the crystallite following electron-hole excitation, estimated between 14 and 1 meV for diameters between 2 and 4 nm [8]. In that case the use of a Gaussian is completely justified [9], and its width is directly proportional to d_{FC}. The probability of Auger recombination ($= 1/\tau$) is calculated with the Fermi rule [5]

$$\frac{1}{\tau} \sim \frac{2\pi}{h} \sum_{f} \left| \langle \Psi_i \left| \frac{e^2}{\varepsilon r} \right| \Psi_f \rangle \right|^2 \rho(E_f - E_i), \qquad (1)$$

where Ψ_i and Ψ_f are, respectively, the initial and final states of energy E_i and E_f and ρ is the density of final states discussed above. For the initial state Ψ_i, we take the Slater determinant corresponding to two electrons in the lowest conduction state and one hole in the highest valence state (eeh process). For the final states, we explore all the possible Slater determinants corresponding to filled valence states and one excited electron in the conduction band. The use of Slater determinants is justified because in such confined systems the electron and hole wave functions remain almost uncorrelated [8]. For the same reason, one can show that the results can be easily extrapolated to the case of higher excitation or injection conditions just be rescaling ($1/\tau \propto pn^2$ or np^2). In the case of a hhe Auger process, the situation is formally symmetric. The Slater determinants are built from the one-electron spin orbitals obtained from a tight binding calculation [8]. The matrix elements of the screened Coulomb potential in Eq. (1) are calculated as in Ref. [8]. Other details on the calculation will be given elsewhere [10]. The calculated eeh Auger lifetimes plotted in Fig. 1 and are mostly in the range 0.1 to 1 ns, with similar values for the hhe process. The scattering is relatively large because the eh energy can be more or less close to the possible excitation energies of the third carrier. These results are close to the previous simple estimation (Fig. 1) because the broadening induced by the electron-phonon coupling is sufficiently large to smooth the effect of the quantization. We have verified that additional sources of broadening do not change drastically the Auger lifetime. The good agreement with the extrapolated bulk values for small gaps gives confidence into our results. We recall that Fig. 1 gives an upper limit for the lifetime which must strongly decrease at higher excitation with more than three carriers in a crystallite ($1/\tau \propto pn^2$ or np^2).

We now discuss the implications of the Auger effect by reconsidering already published experiments and by presenting new ones on the time-resolved PL or porous silicon. For the latter, different lightly doped p-type samples with different porosity (from 65% to 80%), as-formed or anodic oxidized, fresh or 2 yr old, with thickness varying from 0.1 to 40 μm, are studied. We use a N_2 laser (337 nm) with a pulse width of 3 ns and a repetition rate of 20 Hz in order to avoid thermal effects. The temporal resolution of the analysis chain is ~ 5 ns. The laser beam is unfocused (area ~ 0.7 cm^2) or slightly focused (area ~ 0.2 cm^2) when higher excitation densities are required. The maximum beam energy is of order 125 μJ/pulse and all the measurements are made at room temperature. Photoacoustic measurements are used to estimate the absorbed light in the samples [11]. Time evolutions of the PL typically show two components [12]: (i) a fast one with a lifetime smaller than 20 ns associated with a defect either in the oxide or at the interface with silicon [13] and (ii) a slow one which is often attributed to recombination in confined silicon structures [2,12]. Typical results are plotted in Fig. 2. The intensity of the fast component and the photoacoustic signal vary linearly with the excitation intensity showing that the absorbed light is proportional to the incident one. In contrast, the intensity of the slow component saturates

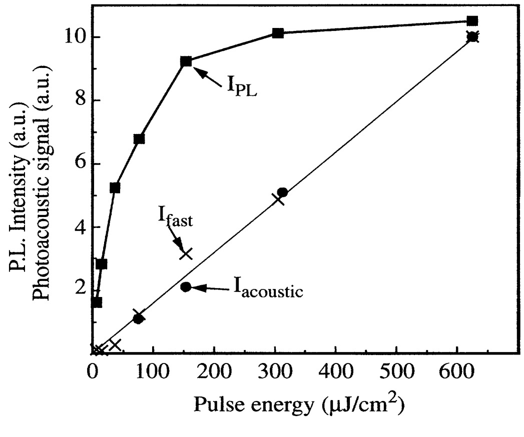

FIG. 2. Comparison of the PL intensity [for the slow (■) and fast (×) components] and the photoacoustic signal (●) as a function of the excitation intensity for 1 μm 65% anodic oxidized sample. The lines are only guides for the eye.

at high flux. Heating effects can be ruled out to explain the saturation: (i) the luminescence lifetime, which is known to be strongly temperature dependent [2], remains constant, and (ii) a simple calculation of the temperature increase ΔT in the extreme case where all the light would be transferred into heat gives $\Delta T = 15$ K which is not sufficient to induce a noticeable quenching of the PL.

The Auger effect gives a simple and natural explanation of this saturation. Let us assume that the "slow band" comes from the radiative recombination in luminescent (L) crystallites, i.e., those without efficient nonradiative recombination centers. As long as the excitation intensity remains weak, there is only one eh pair per L crystallite and the luminescence follows linearly the excitation power. At higher flux, when two eh pairs are created in the same crystallite, the first one quickly recombines nonradiatively by the Auger effect. The absorption coefficient at 337 nm being between 10^4 and 9×10^4 cm^{-1} [14], we suppose that the excitation light is entirely absorbed in a thickness of 1 μm. With $\sim 10^{18}$ crystallites/cm^3, we estimate that the saturation occurs when the number of absorbed photons per crystallite is of the order of 1, strongly supporting our interpretation. As for bulk silicon, the experimental determination of the Auger coefficients is not straightforward but the estimations are coherent with our calculated values. Limited by the time resolution of our experimental system, we can just deduce that the experimental Auger lifetime is faster than ~ 1 ns. This is confirmed by recent ultrafast PL experiments showing that the Auger lifetimes certainly are in the subnanosecond range [15] (the number of photons per crystallite is not estimated).

In the same spirit, let us consider the voltage quenching of the PL [3]. In these experiments, the PL is observed on n-type porous silicon samples cathodically polarized in an aqueous solution of sulfuric acid. The measured spectra are very close to those taken "in air" for a polarization between 0 and -1 V, but they are narrowed and blueshifted at increasing potential leading to a complete quenching of the emitted light at -1.5 eV [3]. Actually, the blueshift is due only to the fact that the red part (low energy part) of the spectrum is quenched first and the energy cutoff depends linearly on the potential. Let us consider crystallites of radius R characterized by a blueshift of the conduction band $\Delta E_c(R)$. We can define the ionization level $\varepsilon_R(1/0)$ for the filling of the lowest conduction state by one electron [9]. It corresponds to the bottom of the conduction band of the bulk silicon when R tends to infinity (see Fig. 3). We also define an electron injection level $\varepsilon_F(V)$ (the effective Fermi Level) in porous silicon which depends linearly on the applied voltage [16]. All the crystallites with $\varepsilon_R(1/0)$ lower than $\varepsilon_F(V)$ have at least one electron injected in the conduction band. When excited, they are nonluminescent because of the fast Auger recombination mediated by the injected electron. They are the larger crystallites characterized by a small $\Delta E_c(R)$ (Fig. 3). Therefore, the PL from the crystallites with a small band gap ("red part") is quenched by the Auger effect.

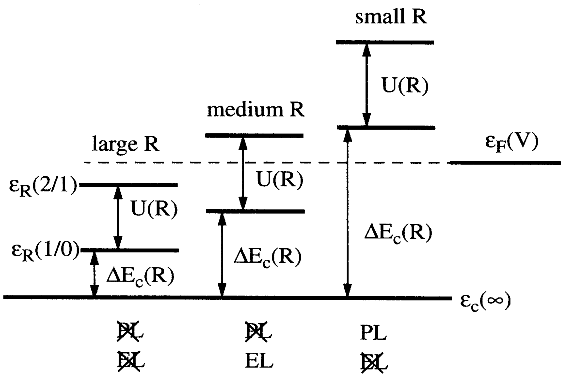

FIG. 3. Ionization levels in crystallites of different sizes R corresponding to the filling of the lowest conduction state by one electron $\varepsilon_R(1/0)$ or by two electrons $\varepsilon_R(2/1)$. By definition, the difference between $\varepsilon_R(1/0)$ and the minimum of the conduction band of the bulk crystal $\varepsilon_c(\infty)$ is $\Delta E_c(R)$, which is due to the confinement. In each case, the possibility of PL and EL is indicated.

The Auger effect, in addition to Coulomb charging effects, also explains the peculiar spectral width ($\sim$ 0.25 eV) of the EL of n-type porous silicon cathodically polarized in a persulfate aqueous solution [4]. In this problem, only the selectivity in the electron injection has to be considered because the holes provided by the solvated species have a broad energy distribution (~ 1 eV) far inside the valence band [4,17]. This is confirmed by the fact that the same EL features can be obtained when the hole source is changed (e.g., H_2O_2) [18]. Under injection, because of the charging effects, the energy of the lowest conduction band level depends on its population [19,20]. If we define $\varepsilon_R(2/1)$ as the ionization level for the filling by a second electron, the difference $U(R) = \varepsilon_R(2/1) - \varepsilon_R(1/0)$ is the average Coulomb electron-electron interaction energy [20]. For a crystallite in an aqueous medium characterized by a large dielectric constant ($\varepsilon_{out} \approx 80$), $U(R)$ is in the 0.1 eV range [$U(R) = 0.11$ eV for $R = 1.5$ nm [20]]. Because of the Auger process only the crystallites with only one electron can give luminescence when a hole is injected, meaning that for a given polarization V [i.e., $\varepsilon_F(V)$], the EL is possible only in crystallites for which $\varepsilon_F(V)$ lies between $\varepsilon_R(1/0)$ and $\varepsilon_R(2/1)$. In that case, we see in Fig. 3 that $\Delta E_c(R)$ must be restricted to an energy window defined by $U(R)$. As from Ref. [1] we know that $\Delta E_g(R) \approx 2.5 \Delta E_c(R)$, we obtain that the width of the EL spectrum is approximately equal to $2.5 U(R) \approx$ 0.27 eV in excellent agreement with experiments [4]. In a detailed publication [10], we show that this can be put on a rigorous but simple basis using the electron statistics corresponding to the energy diagrams of Fig. 3. The

EL spectrum, proportional to the number of crystallites with only one injected electron, explains the shape of the observed spectrum with a width of ~0.25 eV.

An interesting consequence of the interpretation based on the combination of a selective injection and the Auger effect is that the same ionization level $\varepsilon_R(1/0)$ plays a role both in the PL and the EL experiments. At a given polarization, we see in Fig. 3 that a crystallite giving EL (PL) must be inefficient in PL (EL). This conclusion has just been confirmed by simultaneous PL and EL experiments on porous silicon samples polarized in an aqueous solution showing that for any polarization the high energy edge of the EL spectrum always corresponds exactly to the low energy edge of the PL [21]. This is a clear demonstration that the injection of one electron necessary for the EL leads to a quenching of the PL in a crystallite.

The previous interpretations thus give a unified and simple explanation of three distinct experiments mixing electrical and optical properties. Their conclusions can be generalized to nanocrystallites of other semiconductors with indirect band gap: (i) radiative lifetimes are several orders of magnitude larger than Auger lifetimes, which means that the Auger effect kills the luminescence at high optical excitation or at high injection conditions; (ii) the Auger effect can give promising fast nonlinear optical properties; (iii) Coulomb charging effects control the injection of carriers.

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