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Stretched-exponential decay of the luminescence in porous silicon

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An experimental study of the luminescence time decay in porous silicon as a function of temperature, excitation, and observation energies is reported. The decay line shape is well described by a stretched exponential for a variety of experimental conditions. A hierarchy of waiting times for carrier hopping, of intersite distances, and of site energies result from the analysis of our data.

The fundamental issue of the physical mechanism responsible for the photoluminescence (PL) of porous silicon (p-Si) is still unresolved.[1-5] Structural characterization as well as optical data suggest that a key role is played by disorder in the form of (i) a wide distribution of the size of the Si nanocrystals (whose diameter is of the order of some nm) which form the p-Si skeleton (turned by a random arrangement of pillars some 100 nm long), (ii) a random spatial arrangement of the nanocrystals, and (iii) the structure of the nanocrystal surfaces. All the published recombination models make use of the notation of disorder: the quantum-recombination model[1,2] assumes that the luminescence is due to the recombination of localized excitons in undulating quantum wires or dots; the surface-state emission model[3] postulates the formation of localized states due to the random termination of the Si nanocrystals, the luminescence is due to the recombination of electrons or holes localized in these surface states; the amorphous model[4] assumes the formation of an amorphous Si layer on top of the Si nanocrystals where the carriers recombine; in the chemical models, where the luminescence is due to some chemical entity [SiH_x (Ref. 5) or polysilane chains or siloxene groups[6]], their random distribution causes disorder. An experimental confirmation of the role of the disorder lies on the fact that different time-resolved studies reported a nonexponential decay in the luminescence.[4,7-10] The decay is formed by two components:[9] one fast, in the time range of 10^{-9} sec,[10] and the other slow, in the time range of $10^{-6}-10^{-2}$ sec. The slow, nonexponential decay, is adequately modeled by a stretched exponential:[7-9]

$$I(t) = I_0 \exp[-(t/\tau)^{\beta}], \tag{1}$$

where τ is a lifetime and β a dispersion factor. This decay law is often encountered in disordered systems and is considered a consequence of the dispersive diffusion of the photoexcited carriers.[11-13] Carrier diffusion among different spatial regions (sites) can be due to the excitation of carriers from localized to extended states or to hopping among localized states.[11] In the first case, the localized states act as traps and the disorder causes a distribution of release rates and of trap energies; the diffusion arises from a multiple trapping-detrapping (MTD) mechanism. In the MTD scheme, a measure of the dispersion is given by the β parameter in Eq. (1) that provides information about the density of trap states and trap release rates. In an alternative model of diffusion, based on the hopping (H) mechanism, the parameter β depends on the spatial distribution of localized states.[13]

In this paper we address the problem of the diffusion mechanism which causes the stretched exponential behaviors in the p-Si *slow* luminescence decay, by presenting an evaluation of τ and β [Eq. (1)] as a function of different parameters: the sample temperature (T), the excitation energy ($\hbar\omega_{\mathrm{exc}}$), and the observation energy ($\hbar\omega_L$).

The p-Si samples were obtained from p-type silicon wafers, with 3 Ω cm resistivity. The anodization was performed in an ethanoic HF solution (20% HF concentration) and for various current densities and durations. Mainly samples with a porosity of about 70% were investigated. Details regarding the electrochemical cell and the anodization procedure were reported elsewhere.[14] A pulsed dye laser (20-nsec pulse width and 14-Hz repetition rate), pumped by an excimer laser, or a pulsed Ar laser (variable pulse duration down to 0.5 msec) were used as excitation source for the PL. This was analyzed by a double monochromator and detected by a cooled photomultiplier (rise time of 20 nsec) interfaced by standard photon counting techniques to a fast multichannel analyzer. An external reference triggered the excimer laser and the scans of the multichannel analyzer. Using this system a time resolution of 0.4 μsec was achievable. The p-Si samples were placed in a He flux cryostat.

Figure 1 presents some typical PL decays at different temperatures. The room-temperature steady-state luminescence spectrum of this sample is shown in the inset. The full lines through the experimental data are least square fits with stretched exponentials. This procedure yields a good fitting of the data and reliable τ and β parameters can be extracted in such a way. Errors of about 10% on τ and of 0.05 on β can be estimated. In Fig. 2 the temperature dependence of β and τ is reported. The measured β vs T relations show a linear increase at low T and a saturation at high T (see the linear fits reported in Fig. 2 as continous lines or see Fig. 3). τ increases strongly as the T decreases (see Figs. 1 and 2). In the inset of Fig. 2, τ and β vs $\hbar\omega_{\mathrm{exc}}$ are reported. Within the experimental errors, no dependence has been observed, at least for the few points we have investigated.

In discussing these behaviors, our basic assumptions are the following: (i) in p-Si, due to the different nanocrystal sizes and surfaces, the quantum confined levels associated with each nanocrystal are spread in energy leading to the formation of a band of localized states; and (ii) the slow luminescence decay is due to recombi-

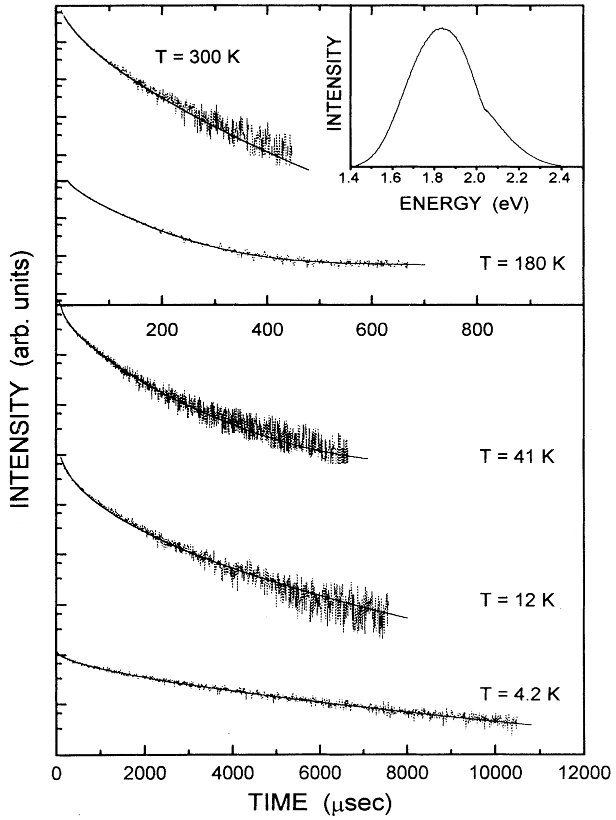

FIG. 1. Time decay of the luminescence for different temperatures indicated on the plots. The experimental curves (dotted lines) and the fitted stretched exponentials (full lines) are reported. The excitation energy was 2.541 eV and the observation energy 1.860 eV. Note the time scale change in the upper panels. The inset shows the room-temperature steady-state luminescence spectrum of this sample. The feature at about 2 eV is an experimental artifact.

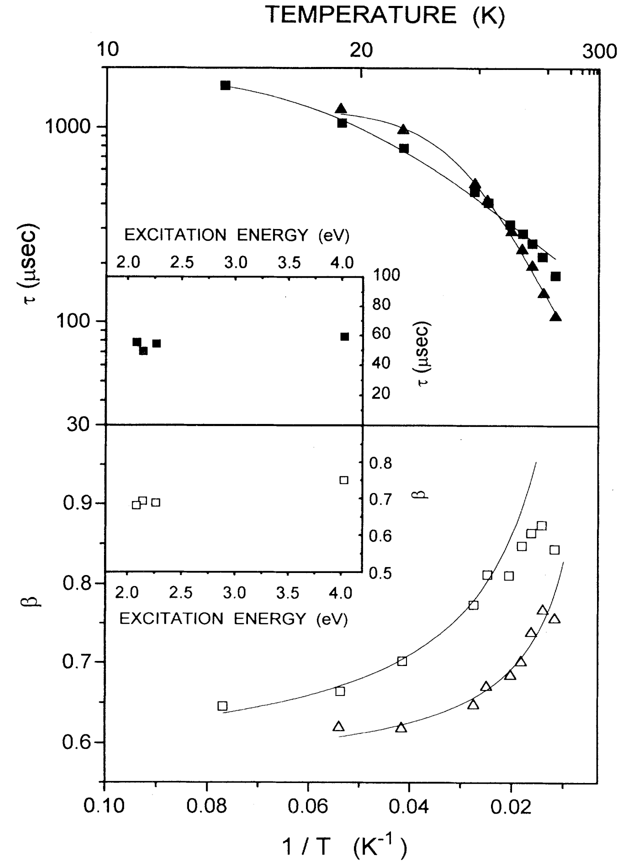

FIG. 2. Temperature dependence of the τ (upper panel) and β (lower panel) parameters obtained through a least square fit of luminescence decay data. Two different observation energies are reported: squares, 1.612 eV; triangles, 1.860 eV. The lines through the τ data are least square fits with Eq. (2), while the lines through the β data are linear fits. The excitation energy was 2.541 eV. The inset shows the excitation energy dependence of τ (upper panel) and β (lower panel). The temperature was 300 K. The observation energy was 1.488 eV.

nations of electron-hole pairs (or excitons) which come from different spatial regions. The fast luminescence decay is possibly due to recombinations of electron-hole pairs generated within the same spatial region as suggested in Ref. 10. The relaxation rate of the electrons and holes photoexcited at an energy $\hbar\omega_{\rm exc}$ is not a relevant rate in the recombination process. τ and β are independent on $\hbar\omega_{\rm exc}$ (see the inset of Fig. 2).[4] To recombine radiatively an electron and a hole need to be on a same site. Hence the recombination dynamics is influenced by the encounter probability, i.e., by the electron and hole diffusion.[7] The on-site recombination yields a radiative lifetime $\tau_{\rm rad}$ which has to be compared to the capture time (MTD mechanism) or the hopping time (H mechanism) typical of the intersite diffusion. All these times concur in determining τ in Eq. (1). By the term "hopping" time we mean the waiting time for hopping in a random environment.[13] Its value depends on both the intersite distance and the site energy. The β exponent in Eq. (1) is independent of the on-site recombination dynamics and is determined only by the dispersive motion.[13] Indeed, in absence of disorder, the electron diffusion will not modify the decay line shape, at most it will change the decay constant τ. In the presence of dispersive motion, e.g., MTD mechanism, the carriers are temporarily frozen into the traps. The late arrival of some electrons (holes) at the sites where holes (electrons) are present provides the long-time recombinations which modify the decay law yielding a stretched exponential. In this scheme we are not able to assert whether the diffusion is ambipolar or unipolar and whether the recombining pair has formed an exciton or not. However, it has been recently reported by resonantly excited luminescence that the recombination is excitonic in nature.[1,15]

Theory predicts for β a temperature independence for the H mechanism and a linear increase with T when the MTD mechanism dominates.[11,13,16] The slope of the β increase is related to the width of the trap energy band.[11] The measured behavior (Figs. 2 and 3) is hardly explained by a single MTD or H mechanism. In particular, if the saturation of β at high T is an indication of a very

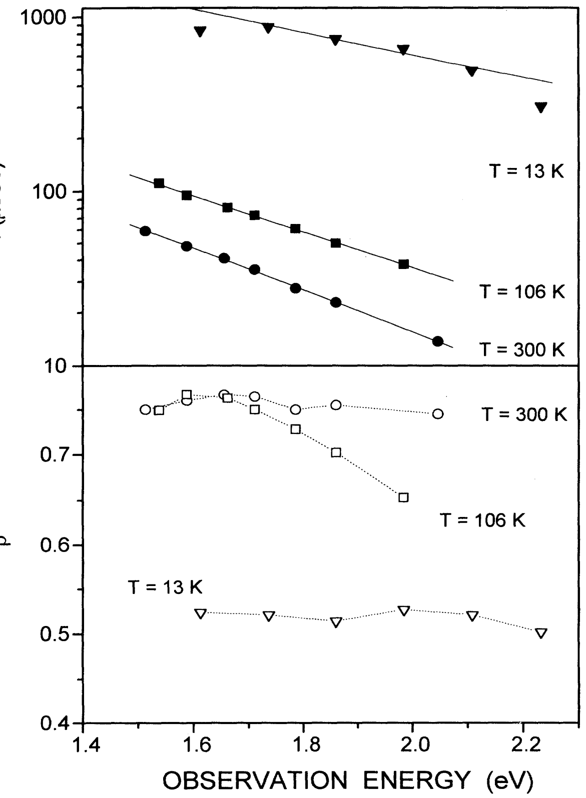

FIG. 3. Observation energy dependence of the τ (upper panel) and β (lower panel) parameters obtained through a least square fit of luminescence decay data and for three temperatures as indicated. The straight lines through the τ data are least square fits with an exponential, while the dotted lines through the β values are only guides for the eyes. The excitation energy was 4.026 eV. Note that the different values for β with respect to those reported in Fig. 2 are due to the use of a different sample.

efficient detrapping one would expect values of β very near to one, i.e., a dynamics typical of extended states. Indeed no simple exponential decay has been reported, even for $T > 300$ K.[2] In p-Si, there are both a dispersion in site energies, which arises from the various nanocrystal sizes, and a dispersion in the intersite distances which is caused by the random arrangement of the nanocrystals in space. In this case a so-called trap-controlled hopping diffusion mechanism acts.[12,17] Let us consider two sets of sites: one labeled h with a concentration N_h and the other labeled r with a concentration N_r. Different energy levels (higher energies for the h sites) are associated with the two sets with a different energy spacing among them, Δ_h for the h sites and Δ_r for the r sites, where $\Delta_h \ll \Delta_r$. Diffusion through the h sites and from the h to the r sites is possible by hopping, while the low density of the r sites renders highly improbable direct tunneling among them. The carriers "trapped" into these r sites should reach the high-energy h sites to diffuse. The r sites behave similarly as temporary traps. Hence the following simplified scheme is possible, where two kinds of states are assumed: localized states (h sites) where carriers can move through hopping and, at lower energies, trap states (r sites) where carriers are trapped. If the concentration of traps is lower than that of hopping sites and the mean release time from traps is longer than the hopping time among sites, the trapping limits the carrier diffusion. To diffuse one carrier needs to be released from the traps and to reach the band of localized states from which it can hop away. Instead, if the hopping time is longer than the release time, the hopping limits the carrier diffusion. This model explains the trend observed in β at low temperatures, where trapping dominates. The slope of the β increase yields for Δ_r a value of $\lesssim 0.04$ eV, with smaller values for low $\hbar\omega_L$. These numbers are very similar to those found for amorphous hydrogenated Si.[16] At higher temperatures, the release rate from the traps becomes faster than the hopping rates among different sites. In this temperature range the diffusion is limited by hopping and β is independent of the temperature. In this case β is related to the geometrical structure of the site network. Following the model of Refs. 18 and 13, the room-temperature values of β shown in Fig. 3 would suggest a fractal structure of p-Si with a spectral (fracton) dimension $\tilde{d} \simeq 1.52$. This aspect of the work should deserve a more careful investigation in the future.

In our scheme, the electron-hole recombinations in the localized states (h sites) give the p-Si visible emission band. It has been demonstrated that this emission displays features typical of localized exciton recombination in an indirect gap semiconductor.[1] This has been also confirmed in recent fluorescence line narrowing experiments.[8]

The τ parameter results from the interplay between hopping, trapping processes, and the radiative recombinations. The hopping and trapping rates are almost independent of T. The radiative lifetime has a temperature dependence given by the exchange splitting of the exciton in singlet and triplet states:[1]

$$\tau_{\rm rad} = \tau_T \frac{1 + 3\exp(-\Delta_{\rm exc}/kT)}{1 + 3\tau_T/\tau_S \exp(-\Delta_{\rm exc}/kT)}, \tag{2}$$

where $\Delta_{\rm exc}$ is the triplet-singlet energy splitting, τ_T and τ_S the triplet and singlet lifetime, respectively, and kT the thermal energy. For low temperatures, as shown in Fig. 2, τ has a strong temperature dependence which is given essentially by $\tau_{\rm rad}$. In fact, the data of Fig. 2, for $4 < T < 100$ K, are very well fitted by assuming $\tau \simeq \tau_{\rm rad}$ with singlet and triplet lifetimes in the range of μsec and msec, respectively, and $\Delta_{\rm exc} \approx 10$ meV depending on $\hbar\omega_L$. These values are consistent with other published data.[1,2] For higher temperatures, $\tau_{\rm rad}$ becomes comparable or even shorter than the hopping time. In this case τ in the stretched exponential decay represents the hopping time.

The proposed recombination scheme is also able to interpret the β data of Fig. 3 where at low and high temperature β is essentially independent of $\hbar\omega_L$ because of a dominance of the MTD or H mechanisms, respectively. At 100 K, an intermediate situation occurs. For low $\hbar\omega_L$, the release from the trap is so efficient that the carrier diffusion is limited by hopping only, and the β value is similar to the room-temperature value. At high $\hbar\omega_L$ the release rate is low and the carrier diffusion is limited by the release from the trap states. Consequently the β value is lower than the room-temperature value. This figure also explains the $\hbar\omega_L$ dependence of Δ_r discussed above: for high $\hbar\omega_L$ one sees the large Δ_r.

In Fig. 3, it an exponential dependence of τ on $\hbar\omega_L$ is observed: $\tau = \tau_0 \exp(-\gamma\hbar\omega_L)$ with $\gamma \approx (1.1 \pm 0.1)$ eV^{-1} (lines). γ decreases weakly as T decreases. A similar behavior has been observed for room temperature in Ref. 2 and explained as carrier tunneling out of the Si nanocrystals. In our scheme, the $\hbar\omega_L$ dependence in τ is due to the energy dependence of τ_{rad}, i.e., of Δ_{exc},[1,2] and of the hopping time. The energy distribution of the localized states yields an observation energy dependence of the hopping rate. A very similar modeling as that derived in Ref. 2 is suitable in this case. As a result, it is possible to show that γ is related to the mean nanocrystal size. We found γ values slightly smaller than those reported in Ref. 2 which suggests a smaller mean size of the nanocrystals in our samples.

In conclusion, we have presented an experimental study and an interpretative scheme of the luminescence decay in *p*-Si. The time constant characteristic of the stretched exponential decay is due to the combined effect of the radiative lifetime (low temperature) and of the hopping rate (high temperature), while the dispersion (β) results from the dispersive electron and hole motion due to the disorder. The dispersive motion is strongly influenced by the random distribution of the site energies and intersite spacing. From the experimental data a scheme is inferred where both hopping and detrapping processes are relevant. The relative importance of the two processes is temperature and sample dependent. A still open problem is the microscopic identification of the localized states. It is tempting to identify the so-called h states with disorder-induced localized states associated with the low-dimensional quantum confined states in the nanocrystals (dots or wires) of various sizes[1,2] and the "trap" r states to the unpassivated surface state on each nanocrystal,[3] e.g., dangling bonds. However, this issue is beyond the aim of this paper and will be addressed in a forthcoming paper where more experimental data will be also presented. We hope that this work will stimulate a theoretical modeling of the luminescence decay.

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