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Reply to the comment on ‘Monte Carlo simulations of the recombination dynamics in porous silicon’

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Abstract. The role of diffusion of charge carriers in radiative recombination processes for porous silicon is discussed. The conducting porous material is modelled on a lattice in which each occupied site represents an Si crystal of nanometre size. To describe the recombination dynamics of particles and holes, two extreme situations are considered: one in which the electron and the hole diffuse as a single entity (exciton-like motion) and a second one in which they diffuse independently of each other (two-species motion). In both cases the recombination is excitonic and takes place on a single site. The present results are compared with other theoretical approaches, originally developed for describing photoluminescence in hydrogenated amorphous silicon (a-Si:H).

It is well known that hydrogenated amorphous forms of silicon show efficient photoluminescence in a wide range of temperatures [1]. A theory of geminate recombination of the electron and the hole, which takes both diffusion and tunnelling effects into account, yields results in satisfactory agreement with experiments [2, 3].

More recently, it has been observed that also porous forms of Si display remarkable photoluminescence properties [4]. Despite the extensive attention devoted to these materials in recent years, the actual mechanism responsible for the recombination process in porous Si is still a matter of controversy. Time resolved experiments show seemingly different behaviours of the photoluminescence decay, $L(t)$. For a wide range of porosities (50–90%), temperatures (2–300 K) and emission energies (1.4–2.4 eV), a stretched exponential form

$$L(t) \sim \exp[-(t/\tau)^\beta] \quad (1)$$

with (a porosity and temperature dependent) exponent $\beta < 1$, reproduces the experimental results quite accurately in the relevant range of time scales [5]. At room temperature and for higher emission energies, evidence has been found for a power-law decay at long time scales [6], i.e.

$$L(t) \sim t^{-\alpha} \quad (2)$$

with α consistent with the value 3/2 predicted theoretically for a-Si:H [2, 3].

In an attempt to elucidate the mechanism behind such intriguing behaviour of $L(t)$, we have recently introduced a simple lattice model for porous Si and studied it by means of Monte Carlo simulations [7]. In the lattice, each occupied site represents an Si nanocrystal

and hopping of carriers between nearest-neighbour occupied sites is allowed. The pores are represented by the unoccupied sites, and the porosity is given by the ratio between the latter and the occupied ones.

To describe the hopping process, we consider for simplicity two limiting situations. In the first case, the Coulomb attraction between the electron and the hole is sufficiently strong that both carriers diffuse in the disordered structure as a single entity. The recombination dynamics of such an ‘exciton-like’ particle leads to the stretched exponential behaviour, (1). In the second case, the electron and the hole are no longer bound by their Coulomb interaction and can perform jumps independently of each other (‘uncorrelated electron–hole pair’). For simplicity we neglect tunnelling recombination from different sites, so that the pair can recombine radiatively only when both carriers are located on the same site. In this case, we find power-law decay for $L(t)$ at long times, (2), in a qualitatively similar way to that observed in porous Si at high emission energy [6] and in a-Si:H [2, 3]. In general, the exponent α we find turns out to be systematically smaller than $3/2$, but seems to tend to this value at higher temperatures. Indeed, the value $3/2$ is consistent with our numerical data for $T = 300$ K at long times (see e.g. figure 16 in [7]).

In the light of these results, we argue that the photoluminescence decay in porous Si is determined by the nature of the diffusing entity (either as an exciton-like particle or as an uncorrelated electron–hole pair), and its time decay may be more complex than that observed in a-Si:H, contrarily to what is claimed in [6] and [8]. Our simple model is able to encompass the two limiting cases observed in the experiments, (1) and (2), suggesting that in porous Si a quite rich behaviour of $L(t)$ may indeed be expected. Motivated by a recent criticism [8], we wish to discuss our results further in this work.

To this end, it is useful to draw attention to the standard theoretical approach for describing geminate recombination in hydrogenated amorphous Si [2, 3]. This theory is based on a modified diffusion equation describing the diffusive motion of the electron relative to the hole, so that the relevant spatial variable in the problem is the distance r between the carriers. In this case, the quantity of interest is the probability density, $P(r, t)$, that the carriers are separated by a distance r at time t , if they were separated by a distance r_0 at time $t = 0$. Taking tunnelling recombination processes and driving Coulomb forces into account, $P(r, t)$ satisfies the following differential equation (see e.g. [2]),

$$\frac{\partial P(r, t)}{\partial t} = D_p \left(\nabla^2 P(r, t) + \frac{r_c}{r^2} \frac{\partial P(r, t)}{\partial r} \right) - v_0 f(r) P(r, t) \quad (3)$$

where D_p is the total diffusion constant of the pair, $r_c = q^2/(\epsilon K_B T)$ is the Onsager radius, q is the elementary charge and ϵ the dielectric constant, v_0 is the tunnelling transition rate and $f(r)$ is usually taken as a simple exponential with a characteristic tunnelling length r_0 , i.e. $f(r) = \exp(-2r/r_0)$. Asymptotically, $P(r, t) \sim t^{-3/2}$ [2, 3].

The diffusion process described by (3) is equivalent to a standard random walk of a single particle (characterized by a diffusion constant D_p) in the presence of a driving (bias) field towards an annihilation centre at $r = 0$, where the second component of the pair is located. Since the successive jumps of the equivalent random walker are not correlated to the previous ones (i.e. they do not depend on the history of the process (Markov process)), (3) describes the motion of what we refer to as an uncorrelated electron–hole pair, which closely corresponds to our definition above.

In addition, (3) assumes that diffusion takes place in a homogeneous medium characterized by a macroscopic diffusion constant D_p , where the structural disorder of the medium has been averaged out. It is clear, then, that it cannot be expected to hold true for strongly heterogeneous materials such as porous Si in general. This is the reason why

we proposed to study instead a microscopic model in which the local and structural disorder of the material is considered explicitly in the dynamics of the charge carriers.

In general, it is necessary to evaluate to what extent the geometry of the conducting paths determines the nature of the diffusing entity. For porous Si, considered for instance as an ensemble of quantum dots (as in our model), the strong spatial heterogeneities in the system may actually play a more important role than the structural disorder in a-Si:H does. It is then possible that for porous Si at low emission energies (corresponding to large Si nanoparticles), the electron and the hole remain bound together by their Coulomb interaction, inside a single dot and after hopping to one nearest-neighbour dot of comparable size. In contrast, for high emission energies (corresponding to small Si particles) the pair may break up more easily by thermally activated hopping to a neighbour dot, leading to our uncorrelated electron-hole pair.

As a final remark, there is a bulk of experimental data on porous Si, such as transmission electron microscopy images clearly demonstrating the occurrence of crystalline nanostructures, x-ray excited optical luminescence experiments providing evidence for the crystalline nature of the emitting centres, the temperature dependence of the emission intensity showing a maximum at about 200 K (in contrast to the one in a-Si:H which decreases monotonically as the temperature is raised), the vibronic structure of the resonantly excited luminescence etc [9], all indicating a quite different behaviour of the luminescence than in amorphous Si.

Further theoretical and experimental work would be desirable in order to confirm or modify the present picture for the recombination dynamics in porous Si.

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