Nature of Luminescent Surface States of Semiconductor Nanocrystallites

G. Allan, C. Delerue, and M. Lannoo
Institut d'Electronique et de Microélectronique du Nord, Département Institut Supérieur d'Electronique du Nord,
41 boulevard Vauban, 59046 Lille Cédex, France
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We present semiempirical tight-binding and *ab initio* local density calculations demonstrating the (meta)stability of self-trapped excitons at the surface of silicon nanocrystallites. These are obtained for dimer bonds passivated, for instance, by hydrogen atoms or by silicon oxide. Light emission from these trapped excitons is predicted in the infrared or in the near visible. We are thus led to the interpretation that part of the luminescence is due to such surface states while optical absorption is characteristic of quantum confinement effects. These conclusions should extend to other semiconductor crystallites.

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Since the discovery of luminescence from porous silicon [1] there has been some debate about the origin of such a phenomenon in an indirect band-gap material. The most natural explanation is quantum confinement [1–3], which seems to be confirmed by the calculated radiative lifetimes [2] and by the existence of phonon structures in the excitation spectrum of the photoluminescence, showing full similarity with bulk crystalline silicon [4]. However, a puzzling problem is the large difference between luminescence energies and calculated band gaps [5]. This would correspond to a huge Stokes shift (~1 eV for a crystalline diameter $d \sim 1.5$ nm [6]), much larger than predicted values (<100 meV [7]). In fact, as shown in [6] optical absorption energy gaps are in agreement with calculated values for crystallites. Only the luminescence energies differ greatly and, for small crystallites, are practically independent of the size [6] while predicted values behave as $d^{-1.47}$ [2]. Such a behavior is more consistent with the eventual existence of deep luminescent centers such as the "surface" states postulated by Koch, Petrova-Koch, and Muschik [8]. The problem with such possible surface states is that nothing is presently known regarding their nature and origin. The aim of this Letter is thus to investigate the possibility of existence of intrinsic localized states which might behave as luminescent systems. We shall demonstrate, from both empirical tight binding and first principle local density calculations, that such states indeed exist under the form of "self-trapped excitons" which are stabilized because of the widening of the gap induced by the confinement. This possibility is not restricted to the case of silicon crystallites but, from general considerations discussed in the following, is likely to be valid for all types of semiconductor crystallites.

To illustrate the physical basis of such self-trapped excitons let us consider an isolated single covalent bond. This one is characterized by a σ bonding state filled with two electrons and an empty σ^* antibonding state. The origin of the binding is the gain in energy resulting from having the two electrons in the lower bonding state. Optical absorption in this system leads to the excitation of one electron in the σ^* state. In such a case there is essentially no binding and the repulsive force between the atoms dominates so that the molecule eventually dissociates. If, on the other hand, the molecule is embedded in an elastic medium then it cannot dissociate but one ends up with a large distance between the constituent atoms and a reduced separation between the σ and σ^* states. The resulting luminescence energy is thus much smaller than the optical absorption energy, corresponding to a Stokes shift of the order of the binding energy, i.e., ~1 eV.

The applicability of this model to a silicon crystallite essentially depends on the possibility of localizing the electron-hole excitation on a particular covalent bond, i.e., of creating a self-trapped exciton. For this one must be able to draw a configuration coordinate diagram like the one shown in Fig. 1 where the configuration

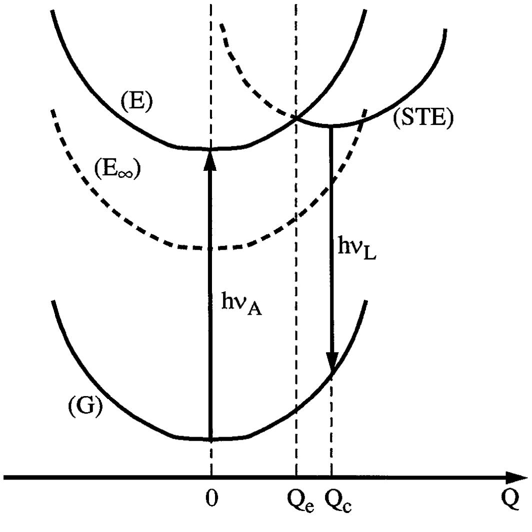

FIG. 1. Schematic configuration coordinate diagram showing the energies of the ground state (G), the normal excitonic state (E), and the self-trapped exciton state (STE). The curve (E_∞) corresponds to a very large crystallite with no blueshift, showing that the STE state might not exist for large crystallites.

coordinate Q corresponds to the stretching of the covalent bond. For small Q the ground and first excited states are delocalized over the crystallite and show a normal parabolic behavior. However, for Q larger than a critical value Q_c the system localizes the electron-hole pair on one particular single bond, leading to a larger bond length Q_e and a smaller luminescence energy. This self-trapped state can be stable or metastable. An interesting point is that it may exist only for small enough crystallites, in view of the important blueshift as pictured in Fig. 1. Such a self-trapped exciton is likely to be favored at surfaces of crystallites where the elastic response of the environment is likely to be weaker than in the bulk. We have made calculations predicting several distinct situations of self-trapped states (mostly at the surface but also some inside the crystallites) showing that self-trapped excitons are a common rule for small crystallites and that they should provide a sound physical basis for the luminescent surfaces states postulated by Koch, Petrova-Koch, and Muschik [8]. Because the self-trapping mechanism is always the one discussed above, we describe here only two typical results, and we report the description of the others in another publication.

We have used two different techniques for the calculations. The first one is a total energy semiempirical tight binding (TB) technique, which allows the treatment of quite large crystallites (~180 Si atoms). The Hamiltonian includes interactions up to the second neighbors and the total energy is the sum of one-electron energies plus repulsion terms between first and second neighbors. The parameters [9] of the system are fitted on the band structure, the lattice parameter, the elastic constants, and the cohesive energy of bulk silicon. The calculation reproduces the reconstruction of the (2×1) 100 silicon surface. Details can be found in Ref. [9]. The second calculation technique is based on the *ab initio* local density calculation using the DMOL code [10] which has already been applied with success to silicon clusters [11]. For the computation, we have used a double numeric basis set (two atomic orbitals for each occupied orbital in the free atom) together with polarization functions ($3d$ for Si, $2p$ for H) and the spin-density functional of Vosko, Wilk, and Nusair [12]. Because of computational limits, the clusters studied by the local density approximation (LDA) are restricted to a maximum of ~30 Si atoms. This is not a severe restriction since we are interested here in localized surface states. With the two techniques, the total energy is minimized with respect to all the atom positions to get the stable atomic configuration for the ground and first excited states. We take advantage of the symmetry of the studied clusters to work in the irreducible representations of the corresponding point groups. We have studied spherical crystallites centered on a silicon atom with the dangling bonds saturated by hydrogen atoms. When needed, we create one surface dimer just be removing the two closest hydrogen atoms of two second neighbor silicon atoms at the surface (see schematic side views of Fig. 2). We present here results for two crystallites: We start with a crystallite with 29 silicon and 36 saturating hydrogen atoms (diameter = 1.03 nm, TB band gap = 3.4 eV LDA band gap = 3.5 eV) where we show that the TB and LDA techniques predict similar behavior. Then we can use with confidence TB for a much bigger crystallite (123 silicon atoms, 1.67 nm, TB band gap = 2.63 eV [13]).

Before considering possible surface excitonic states, we have minimized the total energy of the excited crystallites starting from the atomic positions corresponding to the ground-state situation. We obtain that the exciton remains delocalized for large enough crystallites [14]. The lattice relaxation is due to the weakening of the Si-Si bonds because an electron has been transferred from a delocalized bondinglike state to an antibondinglike state [7]. For example, we obtain with TB for the 1.67 nm cluster a relaxation energy of 86 meV. This is a substantial Stokes shift, but it cannot explain the much larger value discussed above [5].

As a first example let us consider the simple case of Si-H surface bonds. We find that it is always possible to trap an exciton when these are sufficiently stretched. Then the minimum of energy corresponds to the broken bond, i.e., to hydrogen desorption. In the same spirit, one can get SiH_3 desorption by breaking the Si-Si backbond in a process similar to polysilanes [15].

A second interesting situation is obtained when stretching the Si-Si bond of a surface dimer. Then the stable situation for the excited state corresponds to the surface Si atoms almost returned to their original lattice sites (Fig. 2). The electron and the hole are localized on the weakly interacting Si dangling bonds (second nearest neighbors),

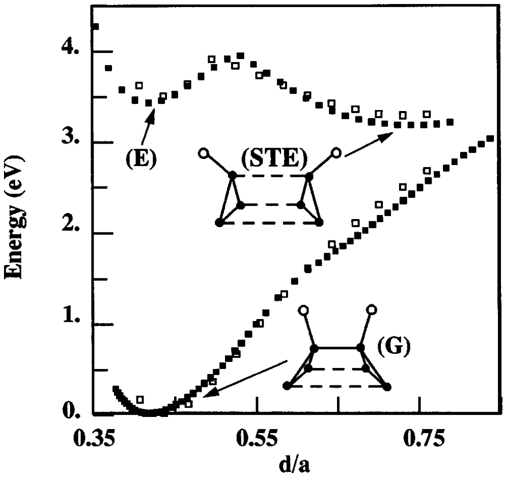

FIG. 2. Total energy (full symbols: tight binding; empty symbols: LDA) of a spherical crystallite with 29 silicon atoms in the ground state and in the excitonic state as a function of the dimer interatomic distance d ($a = 0.54$ nm). The arrows indicate the energy minima. Schematic side views of the cluster surface dimer in the ground state (G) and in the self-trapped state (STE) are also shown (○ = hydrogen, ● = silicon).

which form bonding and antibonding states whose gap is equal to 0.72 eV in the TB calculation for the 1.03 nm crystallite (29 Si atoms). These results are totally confirmed by the LDA calculation with a gap of 0.80 eV. Because the delocalized excited state (E in Fig. 1) is not stable for the 1.03 nm crystallite [14], we calculate the configuration coordinate diagram by interpolating the atomic positions between the configurations of the ground state (G) and of the self-trapped state (STE), and by calculating the energies of the fundamental and first excited states for these fixed positions. The result (Fig. 2) fully corresponds to the general schematic picture of Fig. 1. As expected for a localized state, the STE band gap only slightly depends on the crystallite size: We obtain 0.52 eV for the 1.67 nm crystallite. For this crystallite, the configuration coordinate diagram (Fig. 3) is obtained by calculating the total energies of the fundamental and first excited states with respect to the dimer interatomic distance *d*, the cluster—except the dimer bond—being fully relaxed in each case. We see from this diagram that the STE becomes metastable in a larger crystallite because the E state has decreased in energy following the crystallite band gap. We also plot in Fig. 3 the radiative lifetime in the excited state (calculated following Ref. [2]). In the E state, the lifetime is long because of the indirect nature of the silicon band gap [2]. Increasing the dimer bond length, the lifetime first decreases because the localization of the exciton on one bond relaxes the selection rules. Finally, the lifetime increases because the optical matrix element between the two silicon atoms of the dimer decreases with the bond length. From this, we conclude that the light emission is possible in the STE state. Interestingly, at high temperature, the recombination could be at some intermediate coordinate *Q* with a smaller lifetime and a larger emission energy.

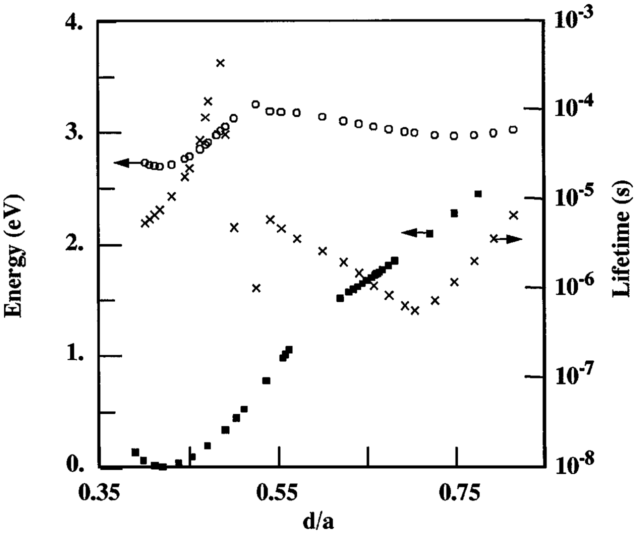

FIG. 3. Energy of a spherical crystallite with 123 silicon atoms (diameter = 1.67 nm) in the ground state (■) and in the excitonic state (○) as a function of the dimer interatomic distance *d* (*a* = 0.54 nm). Crosses are the radiative lifetimes of the excitonic state.

Dimers are also expected at the Si-SiO$_2$ interface. We have studied using LDA (reliable TB parameters are not available for Si-SiO$_2$) a cluster with an interface configuration expected for Si(001)-SiO$_2$ [16] (details will be published elsewhere). Again we obtain that the exciton can be trapped on the dimer. Because of the constraints due to the oxide, the dimer cannot relax as easily as in the case of the hydrogenated surface: We calculate the Si-Si dimer distance to be 3.24 Å in the self-trapped state and an optical gap of 1.51 eV.

One can make some general statements about the conditions favoring the existence of such self-trapped states for a given bond: (i) The elastic response of the environment should be as weak as possible. This is best realized near surfaces. (ii) The size of the crystallite should be as small as possible, favoring a large blueshift and the stabilization of locally distorted excited states. (iii) The capture of the exciton should allow the release of local stresses. This is the case of the Si-Si dimer where the stresses correspond to the bending of the backbonds in the normal state. Such self-trapped states are likely to be metastable in most cases. The question then arises if and how they can be excited. One answer is provided by the well-documented example of the *EL*2 defect in GaAlAs, which can be optically excited with a long lifetime [17]. Here, extrapolation of the energy curve of the self-trapped state in Fig. 4 suggests that a vertical transition energy of ~3.5 to ~5.0 eV would be necessary to excite it directly from the ground state. Once in the metastable state there is also the possibility that the system returns to the normal excited state by thermal excitation over the barrier. This process should thus be in competition with direct radiative recombination from the self-trapped state.

One can question the reliability of the previous predictions especially in view of correlation effects. This is a very difficult problem for the current crystallites of interest with ~2 nm size. However, an interesting point to mention is that for our Si$_{29}$H$_{36}$ cluster we were in the fortunate case where the self-trapped state and the ground state are of different symmetries (C_s point group) and thus are automatically orthogonal. This means that for the LDA calculation the density functional principle can be applied to this excited state, which is just calculated as the ground state of a different representation. This is the best situation one can hope for. As regards TB it is not possible to draw any firm conclusion since correlation effects are incorporated in an implicit empirical way. The convincing evidence there comes from the extremely good agreement with LDA in Fig. 2.

In conclusion, we have shown, from total energy calculations, the existence of self-trapped excitons at some surface bonds of silicon crystallites. These give a luminescence energy almost independent of size and explain the huge Stokes shift observed for small crystallites. In fact the luminescence could originate both from STE states and from the direct transition between the conduction and valence states. This could explain the observation of the phonon structures in the excitation spectrum of the photoluminescence under resonant conditions [4] in which it is not possible to excite directly the metastable self-trapped surface states. Finally, such self-trapped excitons are not specific to silicon crystallites but should also manifest themselves in crystallites obtained from other semiconductors.

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[13] The band gap calculated in Ref. [2] for the same crystallite with 123 silicon atoms is equal to 3.25 eV. We obtain here a smaller value because the present TB parametrization does not give a bulk silicon band structure as good as in Ref. [2] where a nonorthogonal basis was used.

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