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# Theory of optical properties of polysilanes: Comparison with porous silicon

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We have studied the electronic structure of $\sigma$-bonded silicon chains containing between 2 and 66 silicon atoms. Stable atomic configurations are obtained by minimization of the total energy. The exciton spectrum is calculated by diagonalization of the full matrix of the Coulomb interaction taking into account the electron-hole exchange interaction. We predict important atomic relaxations that give polaronic effects for free molecules and explain the observed Stokes shifts. We show that the luminescence properties of silicon chains strongly depend on the interactions between the molecules and the medium in which they are embedded. The energy, the size, and the radiative lifetime of excitons are computed and their dependence on the size of the molecules is analyzed. We deduce that chains of silicon atoms are probably not at the origin of the visible luminescence of porous silicon but could explain its fast band in the blue region.

## I. INTRODUCTION

Because of its 1.1-eV indirect band gap, bulk silicon is a poor material for optoelectronic applications. However, very recently, it has been shown that porous silicon can exhibit visible photoluminescence at room temperature.[1,2] These results have stimulated intensive studies based on the effect of quantum confinement on excitons in silicon.[3] In particular, recent theoretical calculations have shown that visible luminescence could be possible from nanostructures of silicon.[4,5] Alternatively, it has been proposed that the luminescence of porous silicon comes from the formation of siloxene.[6] But the luminescence of siloxene is also interpreted in terms of quantum confinement due to oxygen in Si rings or chains.[7] Therefore quantum confinement seems to be a very promising way to produce optoelectronic material from indirect-gap semiconductors. However, it is difficult to control the atomic structure and the number of atoms in nanostructures. For example, the comparison between experimental results for porous silicon and theoretical calculations is not easy. Recently, Kanemitsu *et al.*[8] have studied the optical properties of chains of silicon atoms. The number of Si atoms which lies between 5 and 110 is controlled quite accurately by organic synthesis. In addition, polysilanes have been proposed to be at the origin of the luminescence of porous silicon.[9,10] In particular, recent molecular calculations show that polysilanes connecting nanostructures of silicon could emit light in the visible range.[10] So there is a need to understand the exciton properties of silicon molecules which can be seen as the optimum structures for the confinement and to compare in detail with the luminescence of porous silicon.

In this paper, we present results of calculations of the electronic structure of $\sigma$-bonded linear silicon molecules. We study the excitonic spectrum of the molecules taking into account all the possible one-electron excitations. The exciton binding energy is given with respect to the size of the molecule. We show the importance of the dielectric screening of the solvent in which the molecules are incorporated. We obtain that the atomic relaxations are quite large as confirmed by the experimental Stokes shifts and depend on the interaction between the molecules and their neighborhood. The radiative decay rate is estimated and compared to the lifetime of the luminescence.

## II. CALCULATION

The chains of silicon atoms produced and studied in Ref. 8 have a molecular structure EtO-($\phi$-Si-$CH_3$)$_N$-OEt where $\phi$ and Et represent, respectively, phenyl and ethyl. The important point is that the silicon atoms are $\sigma$ bonded[8,11] and the lowest exciton is attributed to a transition between the valence and conduction bands of delocalized $\sigma$ electrons.[11] Polysilanes can also be produced with other substituents and may present different optical activities because of the influence of these substituents.[12] We will focus our interest only on the excitons in $\sigma$-bonded chains here. The structure of the molecules we have studied are described on Fig. 1. They consist of a linear chain of $\sigma$-bonded silicon with an usual angle between Si bonds of 109°. The dangling $\sigma$ bonds are saturated by hydrogen atoms. We believe that such a structure simulates correctly the $\sigma$ electrons which are involved in the optical transitions. Note that for $N=2$ our molecule corre-

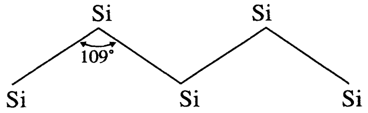

FIG. 1. Atomic configuration of the polysilanes studied in the paper. Only the bonds between the silicon atoms are represented. The silicon dangling bonds are saturated by hydrogen atoms.

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sponds to the disilane $Si_2H_6$.

The electronic levels of Si polymers are computed using a semiempirical tight-binding method. The silicon atoms are described by one $s$ and three $p$ atomic orbitals. To build up the Hamiltonian we use the parameters of Ref. 13 which include the interactions up to the second neighbors. These parameters were fitted to give account of the band structure of the bulk silicon crystal. The $\sigma$ bond which is also the main interaction in the crystal must be well described by this model. The parameters concerning the interactions between Si atoms and the $s$ orbitals of hydrogen atoms are given in Ref. 14. The tight-binding scheme is computationally efficient since it uses a minimal basis for the electronic calculation. It allows us to treat within the same model both the excitonic effects and the atomic relaxations.

Under excitation of an electron from the $\sigma$ bondinglike states of the valence band to the $\sigma^*$ antibondinglike states of the conduction band, a lattice relaxation is expected. To estimate the order of magnitude of this relaxation and its dependence on the size of the molecules, one can use a simple model in which only the interactions between $sp^3$ states of nearest neighbors involved in the same bond are included (molecular model). This is developed in Appendix A and describes fairly well the physical origin of the atomic relaxation. We also evaluate the lattice relaxation more accurately. We calculate the total energy of the system with respect to the atomic configuration. For that purpose, we adopt the same prescriptions as in Ref. 15. We write the interatomic matrix elements $\beta_{ij}$ under the form

$$\beta_{ij}=\beta_{ij}^0 \exp[-q(R_{ij}-R_0)] , \tag{1}$$

where $\beta_{ij}^0$ are the interatomic matrix elements for the bulk silicon crystal,[13] $R_{ij}$ is the interatomic distance between two silicon atoms $i$ and $j$, $R_0$ is the interatomic distance in bulk silicon, and $q$ is a constant. It is then possible from (1) to calculate the sum of one-electron energies. To obtain the total energy one adds a repulsive energy between atoms which is short ranged in nature.[15] The repulsive energy between two neighbors $i$ and $j$ is written as

$$C \exp[-p(R_{ij}-R_0)] , \tag{2}$$

where $C$ and $p$ are two constants. Similar procedures applied to many physical situations proved to be very efficient, for example, to describe lattice relaxations at semiconductor surfaces.[16] $C$, $p$, and $q$ are adjusted to fit the cohesive energy, the bulk modulus, and the interatomic distance of the bulk silicon crystal which are known experimentally.[15] We calculate $C=3.032$ eV, $pR_0=5.412$, and $qR_0=2.620$. The total energy for a molecule with $N$ silicon atoms is written as

$$E_{\text{tot}}(\{R_k\})=\sum_i n_i E_i(\{R_k\}) + \frac{C}{2}\sum_{i,j}\exp[-p(R_{ij}-R_0)] , \tag{3}$$

where $E_i(\{R_k\})$ are the one-electron energies which are function of the atomic positions $\{R_k\}_{k=1,n}$ through Eq. (1) and $n_i$ are the occupation numbers ($n_i=0,1,2$). The repulsive energy in Eq. (3) is restricted to the first and second neighbors $i$ and $j$. For each electronic configuration—fundamental or excited—the equilibrium interatomic distances are computed by minimization of the total energy of Eq. (3).

The last step of our calculation consists of the description of the excitonic effects in the molecules. Let us call $\psi_i^c$ and $\psi_j^v$ the one-electron conduction- and valence-band states. The ground state of the molecules corresponds to filled valence states and empty conduction states. After excitation of one electron from a valence state $\psi_j^v$ to a conduction state $\psi_i^c$, the system is characterized by a Slater determinant which we note $|ci,vj\rangle$. Because the optical transitions do not change the total spin, only singlet states are taken into consideration. For one-electron excitations, singlet states are $|ci,vj\rangle+|\overline{ci},\overline{vj}\rangle/\sqrt{2}$, where the bars indicate states with spin down (no bars for states with spin up). Then we write the wave function of the exciton $\Psi_{\text{exc}}$ as a linear combination of one-electron excitations

$$\Psi_{\text{exc}}=\sum_{i,j}\alpha_{i,j}\frac{|ci,vj\rangle+|\overline{ci},\overline{vj}\rangle}{\sqrt{2}} , \tag{4}$$

where $\alpha_{i,j}$ are the variational parameters. The wave function of Eq. (4) means that we have neglected the interaction with configurations corresponding to excitations of more than one electron. The total Hamiltonian $H$ of the system can be expressed in terms of the one-electron Hamiltonian $H_0$ and of the screened Coulomb interactions between electrons $e^2/\varepsilon r_{\mu,\nu}$ where $\varepsilon$ describes the dielectric screening in the molecule

$$H=H_0-\sum_{\mu,\nu}\frac{e^2}{\varepsilon r_{\mu,\nu}} . \tag{5}$$

Substituting Eq. (4) into the Schrödinger equation $H\Psi_{\text{exc}}=E_{\text{exc}}\Psi_{\text{exc}}$, multiplying on the left by $\langle ci',vj'| + \langle\overline{ci'},\overline{vj'}|/\sqrt{2}$, and making use of the fact that $\psi_i^c$ and $\psi_j^v$ are eigenstates of $H_0$ for, respectively, the energies $E_i^c$ and $E_j^v$, we obtain

$$(E_i^c-E_j^v-E_{\text{exc}})\alpha_{ij}+\sum_{i',j'}\alpha_{i',j'}(2\langle ci,ci'|H_{ee}|vj,vj'\rangle-\langle ci,vj|H_{ee}|ci',vj'\rangle)=0 , \tag{6}$$

where, for example, the Coulomb terms are equal to (similar definition for the exchange term)

$$\langle ci,vj|H_{ee}|ci',vj'\rangle=\left\langle \Psi_i^c(r_e)\Psi_j^v(r_h)\,\middle|\,\frac{e^2}{\varepsilon|r_e-r_h|}\,\middle|\,\Psi_{i'}^c(r_e)\Psi_{j'}^v(r_h)\right\rangle . \tag{7}$$

Equations (6) and (7) are equivalent to the calculation of the singlet states of an electron and a hole with a screened Coulomb interaction of the form $-e^2/\varepsilon|r_e-r_h|$ taking into account all the possible electron-hole excitations. Equation (6) supposes that the origin of the energy corresponds to the molecule in its ground state so that $E_{\text{exc}}$ are the excitation energies. We use for $E_i^c$ and $E_j^v$ the one-electron energies of the tight-binding calculation described above. To evaluate the Coulomb and exchange terms in Eq. (6), we expand the one-electron wave functions in terms of the atomic orbitals of the tight-binding basis. We have a sum of terms such as

$$V_{a,b}^{a',b'}=\left\langle \varphi_a(r_e)\varphi_b(r_h)\left|\frac{e^2}{\varepsilon|r_e-r_h|}\right|\varphi_{a'}(r_e)\varphi_{b'}(r_h)\right\rangle , \tag{8}$$

where $\varphi_a$, $\varphi_b$, $\varphi_{a'}$, $\varphi_{b'}$ are atomic orbitals. As in tight binding we neglect the overlaps and we get

$$V_{a,b}^{a',b'}=\delta_{a,a'}\delta_{b,b'}\int\frac{|\varphi_a(r_e)|^2|\varphi_b(r_h)|^2e^2}{\varepsilon|r_e-r_h|}d^3r_e d^3r_h . \tag{9}$$

As the atomic orbitals are by definition strongly localized on the atoms, we approximate $|r_e-r_h|$ by its value at the centered positions $R_a$ and $R_b$ of the atoms with respective wave functions $\varphi_a$ and $\varphi_b$. We finally obtain a simple expression

$$V_{a,b}^{a',b'}=\delta_{a,a'}\delta_{b,b'}\frac{e^2}{\varepsilon|R_a-R_b|} . \tag{10}$$

A problem occurs in Eq. (10) which is no longer valid when $R_a$ and $R_b$ are equal. In that case, the term $V_{a,b}^{a',b'}$ is the Coulomb energy between two electrons on the same atom which we call $U$. For the free silicon atom, $U$ is of the order of 10 eV but for the molecule it must be screened by an important factor which must be of the order of the dielectric constant. In bulk silicon, for example, $U$ can be estimated at about 1.75 eV from the exchange splitting of the Ga isoelectronic donor.[17] As in the molecule the screening is not the same as in bulk silicon, we have decided to scale the value $U$ with respect to the dielectric constant of the molecule $\varepsilon$. We simply write

$$U=1.75\times\frac{\varepsilon_0}{\varepsilon}eV , \tag{11}$$

where $\varepsilon_0$ is the dielectric constant of bulk silicon ($=12$). Therefore, the expression of the Coulomb matrix elements is very simple. This allows us to take into account all the possible electron-hole excitations in the expansion of the exciton wave function $\Psi_{\text{exc}}$ in Eq. (4). We have checked that a large number of excitations are necessary to converge the calculation when the size of the molecule becomes important. For a molecule with $N$ silicon atoms, to form the basis of Eq. (4), we have considered $N^2$ excitations, i.e., the $N$ lowest states in the conduction band and the $N$ highest valence states which per symmetry give a nonzero contribution. Finally, note that even with simple expressions due to our tight-binding technique, the computation is time and memory consuming. For $N=66$ it requires several hours of supercomputer time.

## III. RESULTS AND DISCUSSION

We calculate the energies of the lowest exciton for optical absorption and luminescence. The difference between the two—the Stokes shift—is due to atomic relaxation. In effect, for the absorption, the energy of the transition is the energy of the exciton calculated for the atomic configuration of the fundamental state, i.e., with all the electrons in the valence band. For the luminescence, it is the energy of the exciton for the relaxed atomic configuration of the excited state, i.e., with one electron in the conduction band. As expected (Appendix A), we calculate a very strong electron lattice coupling. For the free molecules that we study here, we obtain polaronic effects. The electron-hole pair becomes localized in its own potential created by the lattice relaxation. This effect is so efficient that we predict that the free molecules tend to split into two parts, the relaxation being localized on the bonds at the center of the molecule. After this relaxation, the energy of the excited state is only $\sim 0.2$ eV higher than the energy of the ground state (in agreement with recent results of Ref. 10). The exciton is localized on the stretched—nearly dangling—bond states. This result means that polysilanes must be easily dissociated by excitation with light. Photodissociation of polysilanes is confirmed by many experimental works.[18] However, there are many experimental studies in which the polymers do not dissociate after optical excitation. Actually, the polysilanes are often in solvents or are prepared to form solid thin films. Therefore, when the molecules relax after excitation, it is reasonable to believe that there is an interaction between the molecules and the medium (solvent, other molecules). It is very difficult to estimate this interaction because it depends on many unknown parameters. For example, the exact nature of the radicals must be of importance. Therefore, we have simulated the influence of the medium imposing an additional force between pairs of neighbor silicon atoms. So, we add to the total energy of Eq. (3) the following energy:

$$\frac{k}{2}\sum_{i,j}\left[\frac{R_{ij}-R_{ij}^{\text{eq}}}{R_{ij}^{\text{eq}}}\right]^2 , \tag{12}$$

where $k$ is an elastic constant and $R_{ij}^{\text{eq}}$ is the calculated equilibrium distance between atoms $i$ and $j$ for the molecule in its ground state. The summation in Eq. (12) is restricted to first-neighbor silicon atoms $i$ and $j$. Note that as written in Eq. (12), the exciton energy for the optical absorption does not depend on the constant $k$ because we suppose that the interaction only occurs during the relaxation of the molecule, therefore only in its excited state.

The main results of our calculation are summarized in Fig. 2. The predicted energies of the lowest transitions in luminescence and optical absorption are plotted versus the number $N$ of silicon atoms. The two lowest curves correspond to the luminescence (continuous line: $k=40$ eV; dashed line: $k=20$ eV), and the highest to the absorption. In comparison, we have reproduced the experimental results of Ref. 8 giving the absorption and

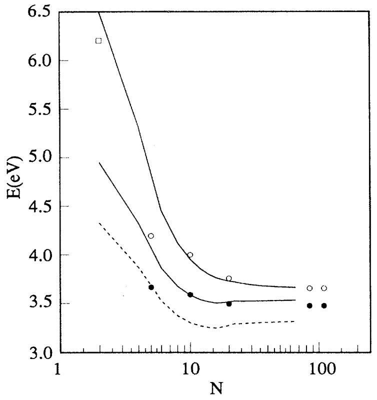

FIG. 2. Calculated exciton energies with respect to the number $N$ of silicon atoms in the molecule. The two lowest curves correspond to the predicted energy in luminescence (continuous line: $k=40$ eV; dashed line: $k=20$ eV) and the highest to the absorption (continuous line). The circles represent the experimental exciton energies of Ref. 8 (empty circles: absorption; full circles: luminescence). The empty square at $N=2$ is the lowest excitation energy of disilane (6.2 eV) (Ref. 8).

luminescence peak energies as a function of the number of Si atoms in chains. As discussed later, all the calculations are done with $\varepsilon=7.4$ which gives the best fit between theory and experiments for the optical-absorption energies. The agreement between these energies for optical absorption is quite good over the whole range of $N$. Small discrepancies maybe due to the fact that our molecules are not exactly the real molecules. Also note that the experimental width of the absorption and luminescence peaks is large, about 0.4 eV.[8] For $N=2$ (disilane) our calculated exciton energy for optical absorption is in reasonable agreement with the experimental value (6.2 eV, represented by a square in Fig. 2). As discussed above, the calculated energies for the luminescence are strongly dependent on the elastic constant $k$. A value $k=40$ eV gives a reasonable agreement with experiments for the luminescence (Fig. 2). Note that the equivalent elastic constant $k$ for the stretching mode of vibration of a bond in bulk silicon is estimated at about 26 eV.[19] This shows that the interaction between the molecules and their surrounding medium must be large to explain the luminescence energies. This effect is possibly due to the substituents which are big molecules (phenyl, methyl, ethyl) which restrict the motion of the silicon atoms. The Stokes shift is quite well predicted by theory. Note that in the case of delocalized excitons (no polaronic effects), the Stokes shift should decrease as $\sim 1/N$ (see Appendix A) and the theory could not explain the amplitude of observed Stokes shift for large $N$ ($N\sim 70$). Therefore, we believe that the experimental results provide good support for the existence of polaronic effects in polysilanes.

We have not yet discussed the important and complex problem of the dielectric constant $\varepsilon$ in the molecules. The static dielectric constant in bulk silicon is equal to 12. But it is obvious that the dielectric screening in a linear molecule must be much less important than in bulk crystal. We have estimated with several models the amplitude of $\varepsilon$ (see Appendix B). We have found in all cases that $\varepsilon$ is quite close to unity. Using this value and Eq. (10), we would obtain exciton energies in disagreement with the experimental results of Ref. 8. Therefore, there must be another "source of dielectric screening" than the intrinsic screening in the molecule. Other sources of screening may be the substituents (phenyl, methyl, ethyl) and the solvent. The Si-backbone polymers of Ref. 8 are solved in tetrahydrofuran (THF) whose static dielectric constant is equal to 7.39 at 300 K. Interestingly, we have seen that a value of about 7.4 for the dielectric constant gives the best fit to the experimental optical-absorption peak energies. Therefore it is clear that the Coulomb interaction between the hole and the electron is mainly screened by the solvent. This conclusion is important because it means that the measured exciton energy depends on the solvent used—more precisely on its dielectric constant.

In Fig. 3, we plot the calculated exciton energy in luminescence (after relaxation) for a molecule with 20 silicon atoms with respect to the elastic constant $k$. For high values of $k$ ($k>50$ eV), the energy tends to saturate at the exciton energy of the unrelaxed molecule which corresponds to the optical absorption. In that case, the interaction with the medium is strong and the molecule cannot relax after excitation. For decreasing values of $k$, the exciton energy decreases because the relaxation is easier. For small $k$, it saturates and tends to 0.2 eV which is the value obtained for $k=0$ eV and which corresponds to a nearly dissociated molecule. Therefore, all the energies between $\sim 3.6$ and 0.2 eV are *a priori* possible for the luminescence of polysilanes depending on the surrounding medium.

In Fig. 4, we have reported the exciton binding energy corresponding to the exciton energy minus the one-electron band-gap energy. As expected, the binding energy increases when the size of the molecules decreases due to the "confinement of the Coulomb interaction." We have verified that, for big molecules, the contribution of the exchange terms in the exciton binding energy is small

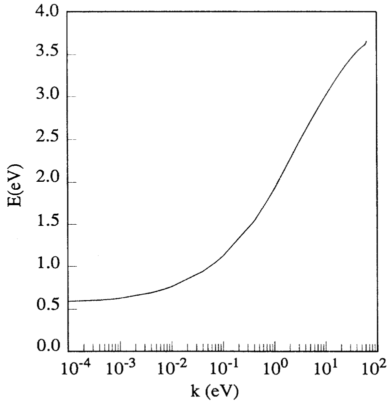

FIG. 3. Dependence of the calculated luminescence energy with the elastic constant $k$ which describes the interaction between the molecules and their surrounding medium. The calculation is done for a molecule with 20 silicon atoms.

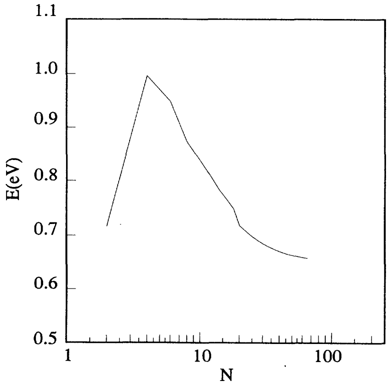

FIG. 4. Calculated exciton binding energy in absorption as a function of the number $N$ of silicon atoms in the chain.

compared to the Coulomb terms. For small molecules ($N<6$), the exciton binding energy tends to decrease because the contribution of the exchange terms in the binding energy quickly become important and tend to compensate the Coulomb terms. Finally, we can note that the exciton binding energy is always very large, of a few tenths of eV. This is two orders of magnitude larger than in bulk silicon and is, of course, attributed to quantum confinement. It also means that the size of the exciton is strongly reduced compared to the bulk one. In Fig. 5, we have reported the calculated average distance between the electron and the hole which we define as $\langle \Psi_{\text{exc}}(r_e,r_h)||r_e-r_h||\Psi_{\text{exc}}(r_e,r_h)\rangle$. For $N>30$, this expectation value $\langle |r_e-r_h|\rangle$ saturates at about $a_0 \approx 6.0$ Å meaning that the exciton is no longer influenced by the confinement. The size of the molecule for $N=30$ is about 57 Å which means that the saturation occurs when the size of the one-dimensional chain is at least nine times the effective Bohr radius $a_0$. In bulk silicon crystal the ratio is about 2.7.[20] This difference can be explained using the effective-mass theory which can be applied to the one-dimensional chain. In that case, this is equivalent to the problem of the one-dimensional hydrogen atom with truncated Coulomb potential.[21] Then it is shown that, although the wave function has an exponential behavior at long distances, the wave function is more complex at small distances. Therefore the behavior with the confinement must be different than in the three-dimensional case.

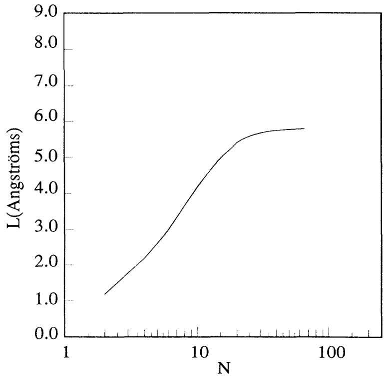

FIG. 5. Expectation value $\langle |r_e-r_h|\rangle$ for the exciton in absorption as a function of the number $N$ of silicon atoms in the chain.

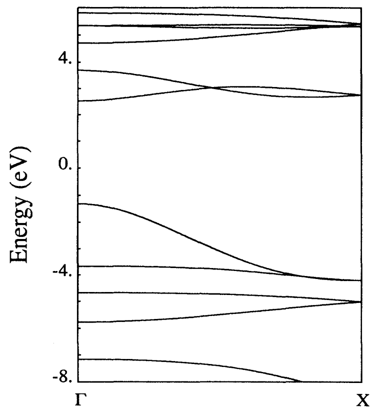

FIG. 6. Band structure of an infinite chain of silicon atoms. States below 0 eV are occupied, those above are empty.

Finally, it is interesting to have a look at the optical properties. We have first calculated the electronic band structure for the infinite one-dimensional chain of silicon atoms (Fig. 6). We obtain that the band gap is direct and the lowest band-gap transition is dipole allowed by symmetry. Therefore, the absorption and emission of photons are allowed without phonon coupling. Second, we have estimated the radiative recombination time using the procedure described in Ref. 4, taking into account the exciton wave function. The calculated time $\tau$ is plotted in Fig. 7 and compared to the experimental lifetime of photoluminescence of Ref. 8 (black dots in Fig. 7). The calculated time is quite independent of the size of the

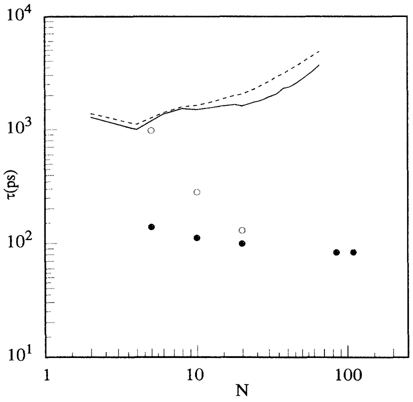

FIG. 7. Calculated radiative lifetime (in picoseconds) of the luminescence for chains of $N$ silicon atoms (continuous line: $k=40$ eV; dashed line: $k=20$ eV). Black dots: experimental lifetime of the luminescence (Ref. 8). Open dots: radiative decay time of the luminescence estimated from experiments (Ref. 8).

molecule. This is due to the fact that the band gap of the one-dimensional chain is direct. This is in contrast with the case of silicon quantum crystallites where the lifetime sharply decreases with the size because the band gap of bulk silicon is indirect.[4] The experimental time is ~30 times smaller but is also independent of the size. This discrepancy is not too serious in view of the uncertainties in the calculation (for example, the formula of the radiative recombination time $\tau$ involves the refractive index $n$ which is unknown here and we arbitrarily took the same value as for the bulk silicon[4]). Anyway, the factor 30 means that other nonradiative recombination mechanisms probably occur. The authors of Ref. 8 also tried to estimate the radiative decay time of photoluminescence from experimental results (open dots in Fig. 7). In that case, we are unable to explain the amplitude of the dependence of this decay time on the size of the molecules for $N<20$. But we believe that the way to estimate experimentally this radiative decay time needs to be refined and that other recombination processes must be studied.

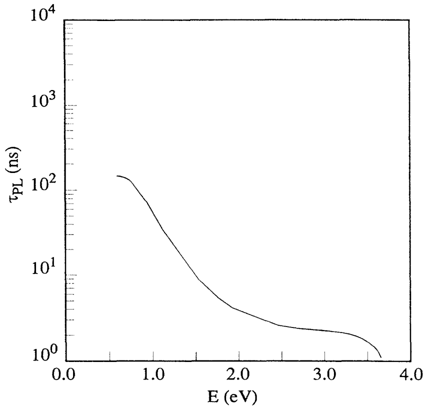

FIG. 8. Dependence of the calculated radiative recombination time with respect to the calculated luminescence energy of a polysilane with $N=20$ silicon atoms. The variation in the luminescence energy is made by varying the elastic constant $k$ (see Fig. 3).

## IV. COMPARISON WITH THE VISIBLE BAND OF POROUS SILICON

Polysilanes have been proposed as a possible interpretation of the visible luminescence of porous silicon.[9,10] In particular, in Ref. 10, it has been shown from calculations that polysilanes pinned at the both ends and bridging two Si clusters could efficiently emit light in the visible range. The energy of the light could greatly vary depending on the ends which act as geometrical constraints. From our calculations, we totally confirm this view, the elastic constant $k$ being connected to these geometrical constraints. Anyway, contrary to Ref. 10, we do not conclude that the polysilanes could explain the visible luminescence of porous silicon. The reason comes from the comparison of the radiative recombination times in polysilanes and porous silicon. In porous silicon, the experimental decay time of the visible luminescence is always between 10 $\mu$s and 1 ms.[3] It means that the radiative lifetime is always longer than 10 $\mu$s. This is much longer than calculated and experimental lifetimes in polysilanes (Fig. 7) which are in the nanosecond range. To confirm this important conclusion, we have calculated the radiative recombination time in a polysilane with $N=20$ silicon atoms varying the elastic constant $k$ (the following conclusions do not change for a molecule with a different number of silicon atoms $N$). We plot in Fig. 8 these times with respect to the calculated luminescence energies. We see that for photon energies between 1.4 and 2.2 eV which correspond to the emission band of porous silicon, the recombination time is always between 1 and 10 ns. This is three orders of magnitude faster than the lifetime of luminescence of porous silicon. The long lifetime of porous silicon is more compatible with the hypothesis of quantum confinement in reasonably large silicon crystallites (diameter $>10$ Å) for which we have predicted long radiative recombination times.[4] Therefore we conclude that polysilanes are good candidates for the interpretation of the visible luminescence of porous silicon.

## V. BLUE BAND OF POROUS SILICON

Recently, a photoluminescence band of porous silicon has been reported in the 1.8–2.8-eV energy range ("blue band") which is characterized by a fast lifetime of ~30 ns.[17] From the above discussion, we conclude that polysilanes could explain this fast luminescence with a high photon energy. More generally, linear chains of silicon atoms embedded in a material with large band gap ($\gg 3.6$ eV) could be at the origin of the observed blue luminescence. The material with large band gap is here simulated by hydrogen atoms. As treatments like a rapid thermal oxidation[22] or a boiling water technique[23] seems to increase the emission of the blue components, linear chains of silicon atoms in $SiO_2$ (or $SiO_x$) are possible explanations (the simplest case is a Si-Si bond). As discussed before, the energy of the emitted light should be dependent on the atomic relaxation in the excited state which itself depends on the elastic constraints imposed by the medium. This strong electron-phonon coupling should give a broadened emission peak, as observed.

The fast optical properties of linear chains of silicon atoms are due to the fact that the infinite chain has a direct band gap and that the optical transitions have a similar oscillator strength to that of a single Si-Si bond. In previous papers, we have shown that this is not the case in silicon crystallites or quantum wires[4] where the optical matrix elements quickly decrease with the size of the nanostructure. We calculate that radiative recombination times in the nanosecond range are only possible for crystallites or wires with diameters lower than ~10 Å (maximum of ~20 silicon atoms for a crystallite). But we obtain that the band gap of such nanostructures is large ($>3.5$ eV). Of course, this corresponds to isolated crystallites or wires which have a larger band gap than the same structures in a material with finite band gap such as $SiO_2$. Anyway, an emission in a 1.8–2.8-eV range could be only possible with a large relaxation energy which itself is only possible in very small two- or three-dimensional structures ($<10$ atoms) or in one-dimensional structures such as polysilanes (polaronic effects).

## VI. CONCLUSION

In conclusion, we have performed a complete calculation of the excitons in linear chains of silicon atoms. The one-electron spectrum, the excitonic effects, and the atomic relaxation have been included. We show that the dielectric screening of the electron-hole interaction in the exciton and the atomic relaxation are mainly controlled by the nature of the solvent in which are the molecules. We predict polaronic effects which would lead to a photodissociation of the free molecules. Calculations of the radiative lifetimes of excitons in polysilanes show that these cannot be at the origin of the visible luminescence of porous silicon but could be responsible for its fast band in the blue part of the spectrum.

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## APPENDIX A: ATOMIC RELAXATIONS IN POLYSILANES MOLECULES

We want to describe here a molecular model which allows one to understand the physical origin of the lattice relaxation in molecules in a very simple way. We consider a linear chain of $N$ silicon atoms bound by $\sigma$ interactions. In the simplest tight-binding description, we can describe the molecule by a set of $N-1$ pairs of paired $sp^3$ orbitals involved in $\sigma$ bonds (the others are saturated by hydrogen atoms). We call $\beta_0$ the $\sigma$ interaction between two $sp^3$ orbitals at equilibrium distance $R_0$ (we take $\beta_0>0$). The electronic structure of the polysilanes consists of $N-1$ degenerate bonding states with energy $-\beta_0$ and $N-1$ degenerate antibonding states with energy $\beta_0$. Therefore, the total energy of the molecule in its fundamental state is

$$E=-2(N-1)\beta_0+(N-1)E_{R0} , \tag{A1}$$

where $E_{R0}$ is the repulsion energy between two Si atoms at equilibrium distance (see Sec. II). Here, for simplicity, we only take into account the interactions between first-neighbor atoms. Using the prescriptions described previously, the coupling parameter $\beta$ and the repulsion energy $E_R$ depends on the interatomic distance $R$ such as, respectively, $e^{-qR}$ and $e^{-pR}$ ($\beta$ and $E_R$, are respectively, equal to $\beta_0$ and $E_{R0}$ at equilibrium distance in the fundamental state). At equilibrium, the condition of minimization of energy requires that

$$2q\beta_0=pE_{R0} . \tag{A2}$$

If one electron is excited from the valence band to the conduction band and if we assume that the exciton is uniformly localized the molecule, the total energy becomes

$$E'=-2(N-2)\beta+(N-1)E_R . \tag{A3}$$

Minimizing with respect to the interatomic distance $R$ and using the Eq. (A2), one gets the energy $E'_{\text{eq}}$ at equilibrium

$$E'_{\text{eq}}=-2\beta_0\left[1-\frac{q}{p}\right]\frac{(N-2)^{p/p-q}}{(N-1)^{q/p-q}} . \tag{A4}$$

The Stokes shift $\Delta E$ is defined as the difference between the total energy ($E'_0$) of the excited system at the interatomic distance $R_0$ and the total energy [$E'_{\text{eq}}$, Eq. (A4)] of the excited system at its equilibrium interatomic distance

$$\Delta E=E'_0-E'_{\text{eq}} . \tag{A5}$$

The total energy at $R_0$ is

$$E'_0=-2(N-2)\beta_0+(N-1)E_{R0} . \tag{A6}$$

Using the previous equations and in the limit where $N\gg 1$, one obtains

$$\Delta E=\beta_0\frac{q}{p-q}\frac{1}{(N-1)} . \tag{A7}$$

The conclusion is that the Stokes shift must decrease as $1/N$ for large molecules. This is clearly not the case in the experimental results of Ref. 8 (see Fig. 2). The dependence in $1/N$ is due to the hypothesis that the exciton is uniformly delocalized in the molecule. This hypothesis is not confirmed by our more complete calculation which predicts a strong localization of the exciton. In the extreme limit, we can suppose that the exciton is localized on only one bond. In that case, in the simple molecular model, there is one electron on the bonding state of energy $-\beta$ and one on the antibonding state of energy $\beta$. Therefore, the electronic energy on the bond is equal to zero and the total energy of the bond is equal to the repulsive energy. Then the minimum of the total energy is obtained for the minimum of the repulsive energy, i.e., for silicon atoms at infinite distance. This corresponds to a dissociated molecule. In that case, the Stokes shift is given by

$$\Delta E=E_{R0}=\frac{2q}{p}\beta_0 . \tag{A8}$$

This Stokes shift is independent on $N$ and is larger than the one obtained in the limit of a delocalization exciton [Eq. (A7)]. Therefore, this model explains well the results of the complete calculation.

## APPENDIX B: SCREENING OF THE ELECTRON-HOLE INTERACTION

Here we want to investigate the screening of the electron-hole interaction for a covalent chain embedded in a dielectric. For this we simplify somewhat the situation by considering a strictly linear chain in which the atoms are bonded via $\sigma$ bonds (corresponding to filled bonding states and empty antibonding states). In a first step we determine the contributions of these covalent bonds and assume the dielectric to be vacuum.

Let us then assume that we apply a bare perturbative potential $V_b$ to this system. We make use of a tight-binding approximation where $V_b$ is characterized by its diagonal terms $(V_b)_j$ on each atom $j$. This perturbation induces a change $\delta n_i$ in electron population of atom $i$ which itself creates a potential $\delta V$ characterized by its diagonal terms $\delta V_j$. The relation between $\delta V$ and $\delta n$ is linear

$$\delta V_j = \sum_j \gamma_{ji} \delta n_i \ , \tag{B1}$$

where the interatomic terms $\gamma_{ji}$ are close to $e^2/R_{ij}$ ($R_{ij}$ being the interatomic distance) and $\gamma_{ii}$ is the intraatomic Coulomb interaction $U$. The $\delta n_i$'s are, in turn, functions of the total perturbative potential $V = V_b + \delta V$. As usual we linearize this dependence and write

$$\delta n_i = -\sum_j \chi_{ij} V_j \tag{B2}$$

where $\chi$ is the susceptibility matrix. If we treat the $\sigma$ bonds in a simple molecular bonding-antibonding picture, this relation simplifies to

$$\delta n_i = -\chi[(V_i - V_{i+1}) + (V_i - V_{i-1})] \ , \tag{B3}$$

where $i+1$ and $i-1$ are the nearest neighbors of atom $i$ in the chain and $\chi$ is the bond susceptibility. To express $V$ in terms of $V_b$ we use the translational periodicity and define the Fourier transformation

$$\begin{aligned} V_q &= \frac{1}{N} \sum_j V_j e^{-iqja} \ , \\ V_j &= \sum_q V_q e^{iqja} \ , \end{aligned} \tag{B4}$$

where $a$ is the nearest-neighbor distance. From this and (B1) to (B3) we get

$$V_q = \frac{(V_b)_q}{1 + 4\chi\gamma_q \left[ \sin\left[ \frac{qa}{2} \right] \right]^2} \ , \tag{B5}$$

where

$$\gamma_q = \sum_j \gamma_{0j} e^{iqja} \ . \tag{B6}$$

The denominator in (B5) represents the tight-binding $q$-dependent dielectric constant of the chain. To proceed further, it is interesting to get a more detailed expression of $\gamma_q$. In tight binding we have

$$\gamma_{0j} = \int |\phi(\mathbf{r})^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\phi(\mathbf{r}' - j\mathbf{a})|^2 d\mathbf{r}\, d\mathbf{r}' \ , \tag{B7}$$

where $|\phi(\mathbf{r})|^2$ is a spherically averaged atomic orbital. We can take the three-dimensional (3D) Fourier transform of all quantities in (B7) and reexpress $\gamma_{0j}$ as

$$\gamma_{0j} = 4\pi V \sum_{\mathbf{q}} \frac{|\chi_{\mathbf{q}}|^2}{|\mathbf{q}|^2} e^{-iqja} \tag{B8}$$

where $V$ is the volume of the box in which $\mathbf{q}$ is quantized, $\mathbf{q}$ is the 3D wave vector and $\chi_{\mathbf{q}}$ the Fourier transform of $|\phi(\mathbf{r})|^2$. We call $\mathbf{q}_\perp$ the projection of $\mathbf{q}$ in the plane perpendicular to the chain and $q$ its component along the chain. With this, injecting (B8) into (B6) we get

$$\gamma_q = 4\pi V N \sum_{\mathbf{q}_\perp, K} \frac{|\chi_{\mathbf{q}_\perp, q+K}|^2}{q_\perp^2 + (q+K)^2} \ , \tag{B9}$$

where $N$ is the number of atoms in the chain, and the $K$ are the reciprocal-lattice vectors of the chain, i.e., multiples of $2\pi/a$.

It is clear that $|\chi_{\mathbf{q}}|^2$ is localized in reciprocal space. With the actual extension of the atomic orbitals the terms $K \neq 0$ give a much smaller contribution and we neglect them compared to the $K=0$ term. Furthermore, we use for $|\chi_{\mathbf{q}}|^2$ a model form which is constant for $|\mathbf{q}| < B$ and zero for $|\mathbf{q}| > B$. This allows one to reduce (B9) to the simple form

$$\gamma_q = \frac{1}{a} \ln \left[ \frac{B^2}{q^2} \right] \ . \tag{B10}$$

We can now inject this expression of $\gamma_q$ in (B5) to get the final form of the screened potential. If we now assume that $V_b$ is due to an excess electron localized at site 0, we can invert (B5) to get the screened potential at site $j$

$$V_j = \frac{1}{2\pi} \int_{-\pi/a}^{\pi/a} \frac{\ln\left[ \frac{\beta^2}{q^2} \right] e^{iqja}}{1 + \frac{4\chi}{a} \ln\left[ \frac{B^2}{q^2} \right] \left[ \sin\left[ \frac{qa}{2} \right] \right]^2} dq \ . \tag{B11}$$

To obtain this we have replaced the sum over $q$ by an integral. The denominator in the integrand of (B11) represents $\varepsilon(q)$, the $q$-dependent dielectric constant. Its general properties are quite interesting. Logically, the extension of the atomic orbitals is such that the cutoff $B$ is of order $\pi/a$, i.e., the Brillouin-zone limit. This means that $\varepsilon(q)$ tends to 1 when $q \to 0$ but also when $q = \pi/a$ and has thus a maximum within the Brillouin zone. The fact that $\varepsilon(0) = 1$ means that there is no long-range screening due to polarization of the linear chain. In practice, we have injected reasonable values of $\chi$ and $a$ [which would lead to $\varepsilon(0) = 10$ in bulk silicon using a similar model] and found that this screening mechanism does not reduce effectively the electron-hole interaction with respect to its bare value. This, in turn, leads to a much too large exciton binding energy. This means that there must be a screening of another origin. We have thus looked for the dielectric constant of the solvent which, in our case, turns out to be 7.39. As discussed in the text, this value leads a predicted binding energy completely consistent with experiment. One consequence of this finding is that other solvents with different $\varepsilon$ should lead to different exciton binding energies. This would be very interesting to test experimentally.

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