Hydrogenic impurity levels, dielectric constant, and Coulomb charging effects in silicon crystallites

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The notion and usefulness of the effective dielectric constant in silicon nanocrystallites are analyzed using a self-consistent linear screening calculation of hydrogenic impurities. It is shown that the self-consistent screened potential induced by the defects can be reasonably approximated by the classical electrostatics expression of the Coulomb potential because the impurity energy levels are dominated by the surface polarization effects. The impurity binding energy, the exciton binding energy, and the exchange splitting are estimated taking into account the modified dielectric properties of the crystallites. The consequences of charging effects on carrier injection are discussed and shown to be important.

I. INTRODUCTION

The recent discovery of the luminescent properties of porous silicon[1] has generated intense research, with the hope of realizing silicon optical devices. For this purpose, efficient doping of the material will be necessary. In the effective-mass approximation, it has been shown[2] that the donor binding energy is strongly enhanced in porous silicon. Polarization effects at the interface between a silicon dot and its surrounding medium are also particularly important. But due to the reduced size of the particles, which leads to a large confinement energy (of the order of a few tenths of an eV), the effective-mass approximation can only give the qualitative behavior of the energy levels. We have previously shown that, for a cluster radius R lying between 1 and 4 nm, the energy gap does not follow the R^{-2} law given by the effective-mass approximation, but rather a R^{-n} one with n close to 1.4.[3] Moreover, the conduction-band minimum and the valence-band maximum are degenerate, and this has been generally neglected when applying the effective-mass approximation to porous silicon. Thus one aim of the present work is to calculate the hydrogenic impurity levels in porous silicon without use of this approximation.

In a bulk semiconductor, it is assumed that, at a distance r from the ionized impurity (whose charge is $+e$ for a donor or $-e$ for an acceptor, e being the absolute value of the electronic charge), the bare electrostatic potential $\pm e/r$ induced by the impurity is screened by the bulk macroscopic dielectric constant ε. However, such a quantity can only be defined for a bulk material, and is no more valid in a cluster where one must use the dielectric matrix $\varepsilon(\mathbf{r},\mathbf{r}')$ which relates the potential at site $\mathbf{r}'$ to the charge at site $\mathbf{r}$.[4] Moreover, due to the broadening of the band gap in a cluster, this quantity is no more equal to the bulk value. A simple model[2] and a pseudopotential calculation[5] have recently predicted a reduction of the macroscopic constant for a cluster of nanometer size, but the two calculations differed with respect to the magnitude of this reduction. This is one reason why here we present a complete self-consistent treatment of the hydrogenic impurity. From this, we will try to define an average effective dielectric constant for a semiconductor cluster. This is an essential quantity if one wants to calculate physically important parameters such as the impurity binding energy, exciton binding energy, exciton exchange splittings, carrier self-energy, and Coulomb shift.

In Sec. II, we calculate the electrostatic screening of the potential induced by an impurity at the center of the cluster. We verify that if one takes into account polarization effects due to the difference between the dielectric constants inside (ε_{in}) and outside (ε_{out}) the cluster, the classical expression for the potential remains a good approximation at the condition of redefining ε_{in}. We also find that the impurity binding energy is large and does not depend very much on ε_{in} when $\varepsilon_{in} \gg \varepsilon_{out}$. In Sec. III, we study the variation of the impurity levels as a function of the cluster size. We reconsider the notion of impurity binding energy, since one cannot define a conduction band in an isolated cluster. We show that in any case the carrier wave function is close to the cluster effective-mass solution, which allows us to consider the dielectric screening in the case of the excitons, particle self-energies, and Coulomb charging effects within a simple formulation. In Sec. IV, we examine the validity of the notion of dielectric constant in a semiconductor nanocrystallite.[4] We show that only average values can be defined to estimate some experimentally important quantities like impurity and exciton binding energies, exchange splittings, self-energies, and Coulomb shifts induced by injection of several carriers within a given crystallite.

II. SELF-CONSISTENT TREATMENT OF THE HYDROGENIC IMPURITY

Let us first consider a hydrogenic impurity at the center of a spherical cluster whose dangling bonds are saturated by hydrogen atoms to avoid spurious states in the gap. Several methods can be used to calculate the electronic structure of silicon clusters. Among them, tight binding has already been applied to determine intrinsic porous silicon energy levels.[3] In tight binding, the solution of the Schrödinger equation is written as a linear

combination of atomic orbitals located on each lattice site. In this basis, the Hamiltonian matrix can be expressed as a function of a certain number of parameters which are fitted to the bulk electronic structure. A good description of the bulk band dispersion energy curves can be obtained within a two-center approximation and a nonorthogonal basis.[6] For a perfect cluster, the energy levels we have obtained with this approximation[3] agree very well with the values given by an empirical pseudopotential calculation.[7]

For simplicity, and to reduce the computation time, here we have considered the case of a donor at the center of a spherical cluster (the case of the acceptor is symmetrical). Taking the center of the cluster as the origin, the potential energy $V(r)$ created by the impurity is the sum of two terms. One is the bare Coulomb potential energy $V_b(r) = -e^2/r$, and the second, $V_p(r)$, is due to the cluster dielectric polarization induced by the total perturbative potential energy. In the tight-binding basis, $V(r)$, $V_b(r)$, and $V_p(r)$ are defined by their matrix elements V_j, V_{bj}, and V_{pj} on each atomic site j. We have

$$V_{bj} = \frac{e^2}{R_j} , \tag{1}$$

except on the impurity site, where we take V_{b0} to be equal to the average of the Coulomb potential energy $-e^2/r$ on the atom. Using the silicon atomic wave functions of Ref. 8, we calculate $V_{b0} = -15.9$ eV.[9] V_j induces modifications of the atomic charges Q_i which, to first order, are related to V_j by the matrix relation

$$Q = \chi V , \tag{2}$$

where χ is the susceptibility matrix. On the other hand, the potential energy V_p is simply related to the charge Q by the Coulomb law

$$V_p = C^{-1}Q . \tag{3}$$

In this linear model (as $V = V_b + V_p$), a self-consistent solution can be easily derived using (2) and (3):

$$V = (I - C^{-1}\chi)^{-1}V_b , \tag{4}$$

where $(I - C^{-1}\chi)$ is just equal to the dielectric matrix corresponding to the tight-binding form of $\varepsilon(\mathbf{r},\mathbf{r}')$. Let us recall that for a cluster $\varepsilon(\mathbf{r},\mathbf{r}')$ is not equal to the bulk semiconductor value. But for very large clusters, Eq. (4) converges to the usual classical approximation for a donor impurity potential energy $V(r) = -e^2/\varepsilon r$, where ε is the bulk semiconductor dielectric constant.

Each matrix element H_{ij} of the Hamiltonian is modified by the total perturbative potential. Using a nonorthogonal basis, a usual approximation is to take this shift to be equal to $S_{ij}(V_i + V_j)/2$ (where S_{ij} is the overlap matrix element between the functions i and j), which is exact in the two limits: $S_{ij} = \delta_{ij}$ (orthogonal basis) and V_j constant, independent of the lattice site. The susceptibility matrix χ (whose matrix elements are defined as $\chi_{ij} = \partial Q_i/\partial V_j$) can be obtained by small variations of the potential around zero. In the same spirit, the matrix elements of the Coulomb matrix C^{-1} in Eq. (3)

are given by

$$C_{ij}^{-1} = -\frac{e}{R_{ij}} \quad \text{for } i \neq j ,$$
$$C_{ii}^{-1} = -U_{at}/e , \tag{5}$$

where R_{ij} is the distance between atoms i and j, and U_{at} is the intra-atomic Coulomb interaction. Using silicon atomic wave functions,[8] we obtain $U_{at} = 10.6$ eV.[9] Testing this tight-binding technique in the case of bulk silicon, we calculate static dielectric constants $\varepsilon(q=0) = 14.1$ and $\varepsilon(q=4\pi/a_0) = 1.86$, where a_0 is the lattice constant. These values are in good agreement with the calculated random-phase-approximation dielectric function of Walter and Cohen,[10] showing that our calculation correctly describes the response to both long-range and short-range perturbations.

In Fig. 1 we show the variation of V/V_b for a cluster with 705 silicon atoms (and a size close to 3 nm). Similar results have been obtained for smaller or larger clusters. The results for the Si atoms within the cluster are seen to scatter around a straight line ending on the point $V/V_b = 1$ when $r = R$. This behavior can be understood by comparing to the expression of the potential deduced from classical electrostatics for a spherical crystallite. Indeed, using the Gauss theorem, one can calculate the classical potential energy V_c induced by the donor impurity, taking into account the difference of the dielectric constants in the silicon cluster (ε_{in}) and in the surrounding medium (ε_{out}):

$$V_c(r) = -\frac{e^2}{\varepsilon_{out}r} , \quad r > R , \tag{6}$$

$$V_c(r) = -e^2\left[\frac{1}{\varepsilon_{in}r} - \frac{1}{R}\left[\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right]\right] , \quad r < R . \tag{7}$$

The second term in the bracket of Eq. (7) is due to the polarization effects or image charge distribution at the interface between the cluster and the surrounding medium. In the case of the isolated cluster we have studied above, ε_{out} is equal to unity. We see in Fig. 1 that V/V_b [where
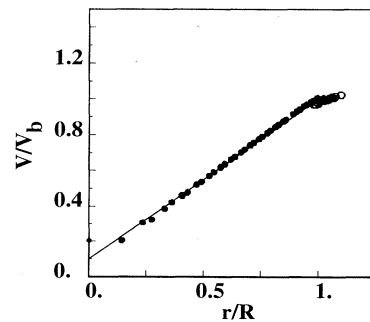

FIG. 1. Ratio of the self-consistent values of the potential to the bare one as a function of the position in a cluster with 705 Si atoms. The open circles for $r > R$ corresond to hydrogen atoms. The straight line corresponds to the classical expression (see text).

V is the self-consistent solution given by (3)] on the silicon atoms is close to the classical expression $V_c/V_b = (1/\varepsilon_{in}) + (r/R)[(1/\varepsilon_{out}) - (1/\varepsilon_{in})]$. Small deviations are due to charge oscillations near the surface of the cluster. However, even if these deviations are small, Fig. 1 shows that an effective dielectric constant ε_{in} cannot be determined precisely, since the intercept of the straight line at $r = 0$ is subject to some uncertainty. We shall reconsider this important problem in Sec. IV. When the impurity is not located at the center of the cluster, the potential energy can also be calculated.[11] If the position vector of the impurity is $\mathbf{r'}$, the potential energy at position $\mathbf{r}$ is

$$V_c(\mathbf{r}) = -\left[\frac{e^2}{\varepsilon_{in}|\mathbf{r}-\mathbf{r'}|}\right] - V_{in}(\mathbf{r},\mathbf{r'}), \qquad (8)$$

where

$$V_{in}(\mathbf{r},\mathbf{r'}) = e^2 \sum_{n=0}^{\infty} \frac{(\varepsilon_{in}-\varepsilon_{out})(n+1)r^n r'^n P_n(\cos\theta)}{\varepsilon_{in}[\varepsilon_{out}+n(\varepsilon_{in}+\varepsilon_{out})]R^{2n+1}}, \qquad (9)$$

where θ is the angle between the two vectors, and P_n the nth Legendre polynomial. The $n = 0$ term in the sum is just equal to the polarization term in expression (7).

III. IMPURITY BINDING ENERGY AND COULOMB EFFECTS IN CRYSTALLITES

The defect binding energy $E_B(R)$ cannot be calculated as the energy difference between the hydrogenic levels and the continuum, as the continuum does not exist in a cluster which has a discrete energy spectrum. Let us then ionize the hydrogenic impurity by taking the electron (or hole) from the defect cluster into a cluster free of impurity but with the same size and located far away from the first one. In this way, Coulomb interactions between the cluster electrons and the impurity extra electron (or hole) are the same before and after impurity ionization, and do not contribute to the binding energy. The electron and the impurity nucleus self-energies due to the difference of the dielectric constants are also identical before and after the impurity ionization. Thus in such an ideal case, the binding energy is simply the energy difference between the levels of a cluster with and without an impurity. As regards the ionization energy, the situation differs from the bulk where this is equal to the binding energy, since the conduction states form a continuum. In crystallites this is not true, since the low-lying conduction states form a discrete spectrum. Ionization in a perfect crystallite occurs in principle via the continuum of states above the potential barrier which exists at the surface, with an ionization energy $I_0(R)$. For the doped crystallite the ionization energy simply becomes $I_0(R) + E_B(R)$. For an on-center impurity and ε_{out} equal to unity, one can see in Fig. 2 that the donor (or acceptor) binding energy is quite large. It varies from ~ 1 eV for a cluster diameter close to 3 nm to ~ 4 eV when the diameter is close to 1 nm. Such an energy range is characteristic of deep levels, and one cannot expect impurity ionization even at high temperature. How-
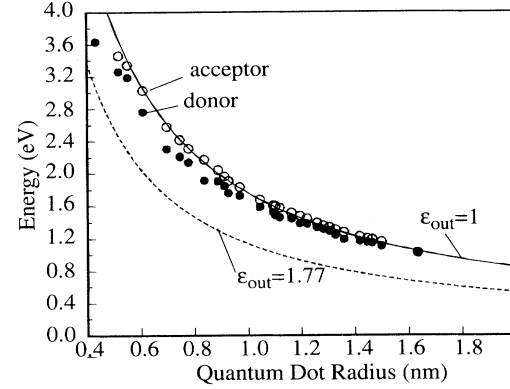

FIG. 2. Binding energies of the hydrogenic impurities ($\bullet$, donor; $\circ$, acceptor) obtained with the self-consistent calculation for $\varepsilon_{out} = 1$ and with a first-order perturbation formula [Eq. (10)] [continuous line for $\varepsilon_{out} = 1$, dashed line for $\varepsilon_{out} = 1.77$, corresponding to porous silicon (Ref. 17)].

ever, we have recently shown that the hydrogenic states can remain ionized because their carriers are trapped at deep defects.[4] This could explain why the hydrogenic impurities are not seen by electron paramagnetic resonance (EPR) in highly porous silicon, where, for example, the density of dangling-bond deep defects is large.[12]

Similar results are obtained when the impurity is not at the center of the crystallite. Injecting the classical potential energy (8) into the tight-binding calculation, we found that the donor or acceptor energy levels do not depend very much on the impurity location (Fig. 3) when $\varepsilon_{in} \gg \varepsilon_{out}$. This is quite different from the infinite quantum-well case, where the binding energy of an impurity at the edge of the well is reduced to 25% of the value of the on-center impurity. This difference is reduced for a finite quantum well, but remains non-negligible.[13]

The large binding energy and its independence from the impurity location can be easily explained. In a first-
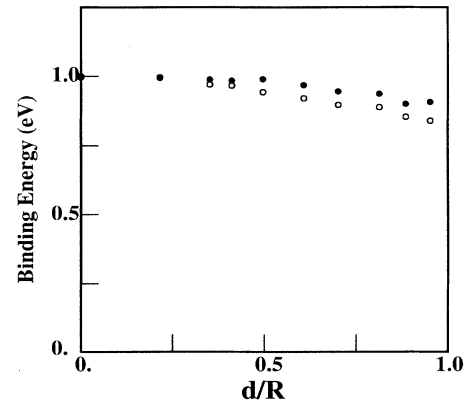

FIG. 3. Variation of the binding energies of the hydrogenic impurities ($\bullet$, donor; $\circ$, acceptor) obtained with the self-consistent calculation for $\varepsilon_{out} = 1.77$ corresponding to porous silicon (Ref. 17).

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order perturbation theory, the impurity eigenstate is equal to the lowest eigenfunction of the cluster without impurity $\Psi_0(r)$. This is not a bad approximation if we compare the lowest eigenstate of the conduction band in a cluster free from impurity [Fig. 4(a)], with the donor eigenstate [Fig. 4(b)] of an on-center impurity. This is due to the strong confinement: the cluster radius is much smaller than the Bohr hydrogenic impurity radius in bulk silicon. The confinement also imposes a solution which is equal to zero on the cluster surface. As the impurity potential only mixes states with the same symmetry which are higher in energy, the impurity state is close to the cluster effective-mass solution which is equal to the zeroth spherical Bessel function $j_0(\pi r/R) \sim \sin(\pi r/R)/r$. Even when the impurity is close to the interface, and when the impurity potential can mix the degenerate states at the bottom of the conduction band, the modification of the donor state is not very important [Fig. 4(c)]. The binding energy is, within first-order perturbation theory, equal to the energy shift due to the electrostatic potential $E_B(R) = \langle \Psi_0(r)|V(\mathbf{r})|\Psi_{(r)}\rangle$. For an on-center impurity, using Eq. (7), we obtain

$$E_B(R) = \left[\frac{1}{\varepsilon_{out}} + \frac{1.44}{\varepsilon_{in}} \right] \frac{e^2}{R} \qquad (10)$$
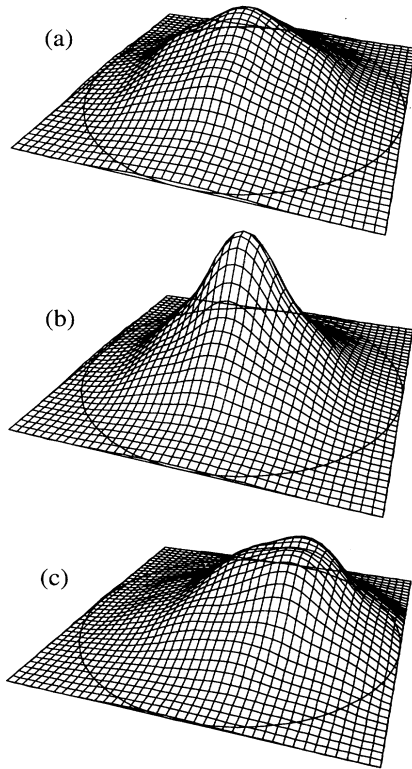

FIG. 4. Lowest eigenstate of the conduction band in a cluster (a) without an impurity, (b) with an on-center impurity, and (c) with an off-center impurity shifted to the right of the figure. $|\Psi_0(r)|^2$ has been plotted in a plane passing through the center of the cluster, and in case (c) through the impurity. The circle indicates the limit of the cluster.

if $E_B(R)$ and R are given in atomic units. Due to the relative values of the static dielectric constants, one can see that the main contribution to $E_B(R)$ comes from the ε_{out} term when $\varepsilon_{out} \ll \varepsilon_{in}$. When we move the impurity toward the cluster, due to the symmetry of $\Psi_0(r)$, only the $n=0$ term of the sum in (9) makes a nonzero contribution to the binding energy. This contribution due to polarization does not depend on the impurity location. When one moves the impurity, there is only a slight reduction of the contribution due to the first term in (8), but as we saw above this is not the main contribution to the binding energy. Then the binding energy does not vary very much with the impurity position. Other states of the cluster with an impurity are also shifted by the impurity Coulomb potential, but as we saw above, the main contribution comes from the polarization term, and this shift will be almost constant, and we do not expect any strong modification of the luminescence spectrum for doped crystallite. Finally, from Eq. (10) we see that the impurity binding energy is considerably reduced when the crystallite is embedded in a medium with a high dielectric constant.

Another interesting problem concerns the particle self-energies and the Coulomb charging effects when injecting electrons or holes into a crystallite. In fact, the tight-binding technique already includes in an empirical way the electron self-energy corresponding to bulk silicon, but here we want to estimate its change induced by the confinement. Let us call $\Sigma(R)$ this change for one electron in the lowest conduction state of the crystallite of radius R. The situation for the energy levels is summarized in Fig. 5. Starting from the bottom of the bulk conduction band $E_c(\infty)$, one-electron calculations like the tight-binding calculation[3] predict a shift of the lowest state to higher energy for crystallites because of the confinement. This latter is further shifted by the quantity $\Sigma(R)$ which includes changes in the many-electron effects (exchange and correlation). Only the final level represents an important physical quantity in the case of the injection of an electron into a semiconductor crystallite. Adding another electron to the crystallite, the level is again shifted to higher energy by a quantity $U(R)$, which represents the effective Coulomb repulsion in the crystallite. Under injection of a small number n of electrons (n smaller than the spin-valley degeneracy of the lowest one-electron level), the lowest filled conduction
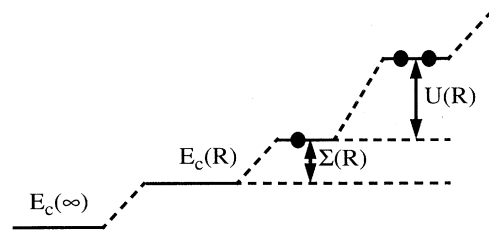

FIG. 5. Shift of the lowest conduction level $E_{BX}(R)$ of a crystallite of radius R due to the injection of one electron [$\Sigma(R)$] or two electrons [$\Sigma(R)+U(R)$]. $E_{BX}(\infty)$ is the bottom of the conduction band for the bulk silicon. The situation for the holes is symmetrical.

states will thus exhibit a shift approximately equal to $\Sigma(R) + nU(R)$ (Fig. 5). In the case of the injection of a large number of electrons, one has to take into account both the discrete character of the one-electron spectrum due to the confinement, and its shift due to the Coulomb charging.[14] Finally the situation for holes is completely symmetrical.

To calculate $\Sigma(R)$ and $U(R)$, we use an electrostatic formulation. Actually we only determine the change in self-energy $\Sigma(R)$ due to the image charge distribution on the surface when an electron is added to the lowest $\Psi_0(r)$. This contribution to the self-energy is $\frac{1}{2}\langle\Psi_0|V_{in}(r,r)|\Psi_0\rangle$, where V_{in} is given in Eq. (9). Using $\Psi_0(r) \sim \sin(\pi r/R)/r$, we obtain

$$\Sigma(R) = \frac{1}{2}\left[\frac{1}{\varepsilon_{out}} - \frac{1}{\varepsilon_{in}}\right]\frac{e^2}{R} + \delta\Sigma(R), \tag{11}$$

where the first term comes from $n = 0$ in (9), and $\delta\Sigma(R)$ is the corrective term due to the remaining sum. This one simplifies greatly when $\varepsilon_{in} + \varepsilon_{out} \gg \varepsilon_{out}$, in which case one obtains

$$\delta\Sigma(R) = 0.47\frac{e^2}{\varepsilon_{in}R}\left[\frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{out} + \varepsilon_{in}}\right], \tag{12}$$

which is usually small but not negligible. The coefficient 0.47 in Eq. (12) is obtained numerically. The effective Coulomb repulsion $U(R)$ is a sum of two terms. The first one is given by the average repulsion with the other electron,[15]

$$e^2\int\frac{\Psi_0(r)^2\Psi_0(r')^2}{\varepsilon_{in}|r-r'|}dr\,dr' = 1.79\frac{e^2}{\varepsilon_{in}R}, \tag{13}$$

and the second one by the average repulsion with the image charge of the other electron,

$$\int\Psi_0(r)^2V_{in}(r,r')\Psi_0(r')^2dr\,dr' = \left[\frac{1}{\varepsilon_{out}} - \frac{1}{\varepsilon_{in}}\right]\frac{e^2}{R}. \tag{14}$$

In Eq. (14), only the term $n = 0$ of (9) makes a nonzero contribution to the integral. Summing (13) and (14), we obtain

$$U(R) = \left[\frac{1}{\varepsilon_{out}} + \frac{0.79}{\varepsilon_{in}}\right]\frac{e^2}{R}. \tag{15}$$

Similarly, the same corrections apply to exciton states. To calculate the exciton binding energy $E_{BX}(R)$, four Coulomb interactions have to be considered: the direct one between the electron and the hole, given by the negative of (13); the interaction between one carrier and the image charge of the second one, given by the negative of (14); and the self-energies of the electron and the hole both given by (11). We verify that term (14) exactly cancels the first term of the self-energies (11), and we obtain

$$E_{BX}(R) = 1.79e^2/\varepsilon_{in}R - 2\delta\Sigma(R). \tag{16}$$

IV. DIELECTRIC CONSTANT AND NUMERICAL ESTIMATIONS

We now come to numerical estimations of the different quantities defined above. We consider two situations: crystallites isolated in vacuum ($\varepsilon_{out} = 1$) and crystallites in an average surrounding medium typical of porous silicon. Macroscopic porous silicon static dielectric constant measurements vary as a function of porosity. The results can be well reproduced by a Bruggeman effective-medium approximation.[16] This interpolates between the bulk silicon dielectric constant and the vacuum one.[16] We choose the surrounding medium dielectric constant ε_{out} equal to 1.77, which has been measured for a porous layer with a porosity of 74%.[17]

The problem is to determine what the value of ε_{in} has to be used, since we saw in Sec. II that only an average value can defined. However, the value obtained depends on the average procedure, as discussed in Ref. 4. Figure 6 shows effective dielectric constants ε_{in} obtained by three different averaging procedures: (i) a fit of the self-consistent donor potential of Fig. 1 by Eq. (7); (ii) the classical donor potential energy (7) is used in the lowest-combination of atomic orbitals (LCAO) calculation, and ε_{in} is adjusted to fit the self-consistent donor binding energy (Fig. 2); and (iii) a least-squares minimization of $V/\varepsilon_{in} - V_b$ in a case corresponding to a bound exciton with the electron confined on the central atom and the hole in the highest valence state. We see that the scattering of the results is large, especially for small crystallites. This means that a general definition of the effective dielectric constant in semiconductor nanocrystallites is not possible, and an accurate theory of, for example, excitons or hydrogenic impurities requires a complete self-consistent calculation. However, the trend of a decrease
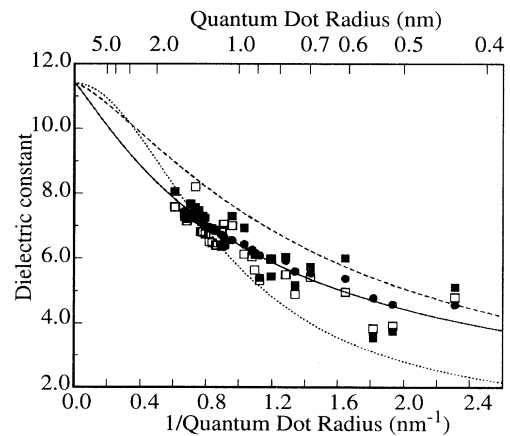

FIG. 6. Plot of the calculated ε_{in} obtained by the fit of the donor potential (■), and of the self-consistent donor binding energy (□) with classical laws and by a least-squares minimization of $V/\varepsilon_{in} - V_b$ in a case corresponding to a bound excition (●). The continuous line is a fit of these values ($\varepsilon_{in} = 1 + (11.4 - 1)/[1 + (0.92/R)^{1.18}]$). The dashed curve corresponds to $\bar{\varepsilon}_s$ of Ref. 5, and the dotted line to the generalized Penn model of Ref. 2.

of the dielectric constant for a small cluster radius is confirmed.[2] Our results lie between those of Refs. 2 and 5. A least squares fit of our data (Fig. 6) is given by

$$\varepsilon_{in} - 1 = (11.4 - 1)/[1 + (0.92/R)^{1.18}] , \qquad (17)$$

with R in nanometer units. In the following, we will use this formula for ε_{in} in the numerical evaluations. In Fig. 2 we see that the donor (or acceptor) binding energy obtained by the self-consistent calculation is well approximated by Eq. (10) because in fact it depends mainly on the value of ε_{out}. In porous silicon, the binding energy is smaller but remains substantial.[2] Figure 7 presents the results for $\Sigma(R)$, $U(R)$, and $E_{BX}(R)$. We see that the charging effects both for crystallites in vacuum or in porous silicon are in the eV range. In these conditions the injection of more than one electron or hole in a crystallite is very difficult. Therefore the theories of transport properties in porous silicon must take into account the charging effects. Comparing the situation of crystallites in vacuum and in porous silicon, one sees that Coulomb effects depend strongly on the dielectric constant of the surrounding medium. Interestingly, when $\varepsilon_{out} \to \infty$, corresponding to the experimental case where porous silicon samples are in aqueous electrolyte ($\varepsilon_{out} \approx 80$), U reduces to ~ 0.15 eV, so that the injection of two carriers becomes easier. As shown in a separate paper,[18] this value, in addition to the Auger effect, can explain the selectivity in energy of the voltage tunable electroluminescence. It can also exist at the origin of the difference in conductivities between porous silicon in air and in aqueous solution.[19] Finally, we must mention that the dielectric screening of delocalized states—in wires, for example—can be quite different from the one of the localized states investigated here.[19]

The exciton binding energy $E_{BX}(R)$ lies between 0.15 and 1.4 eV for crystallites with a radius between 0.4 and 2 nm. This must be taken into account when comparing experimental luminescence energies with calculated band
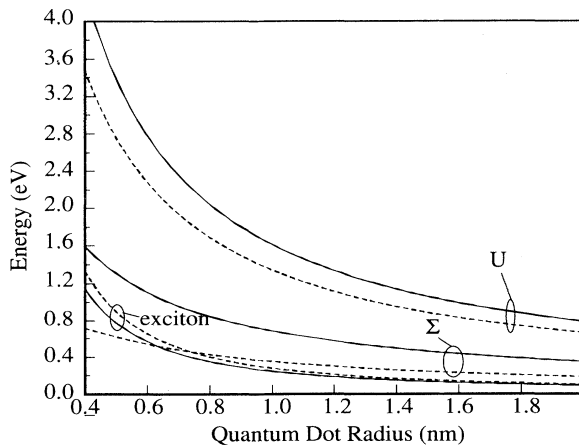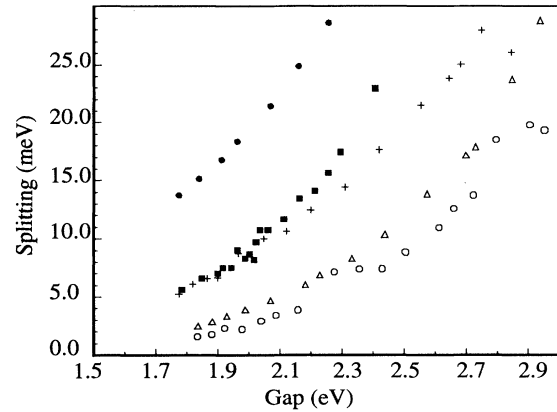

FIG. 8. Splitting between the two lowest calculated excitonic levels in several crystallites with respect to their excitonic bandgap. Crystallites have complex shapes but with a longer axis in the 100 (open circles), 110 (open triangles), and 111 directions (+). Black squares are the first onsets measured by selectivity excited photoluminescence, and black dots are the energy splittings derived from the fit of the temperature dependence of the luminescence lifetime (Ref. 21).

gaps. It does not depend too much on ε_{out}, as one can see in Eq. (16) because $\delta\Sigma(R)$ is small compared to the direct electron-hole interaction. The physical reason is that in the case of an exciton, the cluster remains globally neutral regarding from the outside.

Figure 8 shows the exchange splittings calculated for excitons in nanocrystallites.[20] This splitting which corresponds to the difference in energy between the singlet and triplet levels of the exciton is proposed to be at the origin of the temperature dependence of the luminescence lifetime in porous silicon.[21] In a previous paper, we showed that the triplet-singlet model is valid only for strongly asymmetric crystallites,[20] and that the exciton exchange splitting is greatly enhanced in nanocrystallites compared to the bulk silicon,[21] the predicted values being much smaller than the experimental ones. The discrepancy can be explained by a Stokes shift induced by the exciton lattice coupling.[20] However, the calculations were done using the bulk dielectric constant. As a reduction of the dielectric constant enhances the exchange splitting, it is interesting to include this effect in the calculation. In view of the complexity of the problem, we have followed a simple and natural prescription: considering that the effective dielectric constant is mainly related to the band gap of the cluster,[2] for an asymmetric crystallite of a given band gap we use the effective dielectric constant of Eq. (17) corresponding to a spherical cluster with the same band gap. The relation between the band gap and the cluster radius is given in Ref. 3. Details about the calculation of the exchange splitting are given in Ref. 20. Figure 8 shows that the exchange splittings calculated for various crystallite orientations are on average smaller than the experimental data,[21] in agreement with our previous analyses.[20] We conclude that, even if we include the modified dielectric properties of the crystallites, we

FIG. 7. Self-energy $\Sigma(R)$, Coulomb energy $U(R)$, and exciton binding energy $E_{BX}(R)$ as a function of the particle radius R [continuous lines for $\varepsilon_{out} = 1$, dashed lines for $\varepsilon_{out} = 1.77$ corresponding to porous silicon (Ref. 17)].

cannot explain the observed shifts by the exchange splitting alone, and that a good candidate to explain the discrepancy is the electron-lattice coupling.[20]

In conclusion, we have calculated the hydrogenic impurity levels in silicon crystallites using a self-consistent linear screening calculation. The binding energy is quite large, and can be obtained with a good accuracy by first-order perturbation theory. Such a large value comes from polarization effects due to the difference of dielectric constants inside and outside the silicon clusters. The impurity levels do not depend very much on the impurity position in the cluster when $\varepsilon_{in} \gg \varepsilon_{out}$. A general definition of the dielectric constant in a semiconductor nanocrystallite cannot be found. However, we confirm that the average value of the dielectric constant decreases for a small cluster radius. We have also calculated the exciton binding energies, the carrier self-energies, and the Coulomb charging energies, taking into account the modified dielectric properties of the crystallites. We have shown that charging effects must have dramatic effects on the transport properties of porous silicon.

ACKNOWLEDGMENTS

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