Screening in Semiconductor Nanocrystallites and Its Consequences for Porous Silicon

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Consequences of the modified dielectric properties of semiconductor crystallites are explored. The notion and usefulness of an effective dielectric constant are analyzed using a self-consistent linear screening calculation. The binding energy of hydrogenic impurities is defined and calculated, and it is shown why these are always ionized in porous silicon. Self-energy terms associated with the surface polarization charge are discussed in the context of Coulomb charging effects. Their contribution to exciton binding energies is also determined. Consequences of charging effects on carrier injection in porous silicon are finally considered and shown to be important.

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Electrostatic screening in semiconductor quantum dots is expected to be different from its bulk counterpart. In particular, there is doubt of whether or not a macroscopic treatment based on the use of an effective dielectric constant ε is still meaningful. Such a macroscopic formulation combined with effective mass theory was used previously to calculate the binding energies of excitons [1,2] and hydrogenic impurities [2]. The important question there is to know which value, if any, should be given to ε. This was recently addressed in two different calculations, a phenomenological one [2] and a full quantum mechanical one [3] which concluded that confinement should reduce ε but differed with respect to the magnitude of this reduction. However, both of them assumed the notion of ε to remain a valid one and did not check it on the basis of a microscopic self-consistent calculation. Our aim here is to address this important question by performing self-consistent linear screening calculations for quantum sized clusters. We will consider four distinct situations: hydrogenic impurities, particle self-energies, Coulomb charging effects, and finally excitons. The numerical calculations are performed here in the case of silicon clusters, but the conclusions are general. Some consequences for porous silicon are also discussed.

Let us first discuss the hydrogenic impurity case. We start with one single donor within a spherical crystallite of radius R ($= 3a_0^3N/32\pi$, where a_0 is the bulk lattice constant and N is the number of Si atoms). The bare potential energy of the donor electron at a distance r from the nucleus of charge $+e$ is $V_b(r) = -e^2/r$. This will polarize the electron gas of the crystallite and, within linear screening theory, will result in a self-consistently screened potential $V(r)$ which can be written

$$V(\mathbf{r}) = \int \varepsilon^{-1}(\mathbf{r},\mathbf{r}')V_b(\mathbf{r}')d\mathbf{r}'. \quad (1)$$

The problem is to know if there is a local relationship between V and V_b and, if so, whether or not the ratio V/V_b is related to the bulk dielectric constant. A complete answer to the question necessitates a full first order self-consistent calculation. At present this cannot be achieved by *ab initio* methods for the clusters of interest with size in the 2 nm range. We have thus decided to use a semiempirical LCAO (linear combination of atomic orbitals) technique as describe in Ref. [4]. Following Ref. [5], this can be made self-consistent by adding to the original matrix elements charge dependent Coulomb terms. It is reduced to a calculation of potentials, due to point atomic charges, which allows us to cast the final result under a form similar to (1) but in a matrix formulation, whose size is equal to the number of atoms.

We then apply it to spherical crystallites containing one donor. These crystallites are saturated by hydrogen atoms to avoid dangling bonds. Typical results for the impurity at the center are given on Fig. 1, where the ratio V_j/V_{bj} is plotted versus the distance from the center. 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 result can be given a straightforward interpretation in the classical picture, where the crystallite is considered as a continuous medium of dielectric constant $\varepsilon_{\rm in}$ embedded in

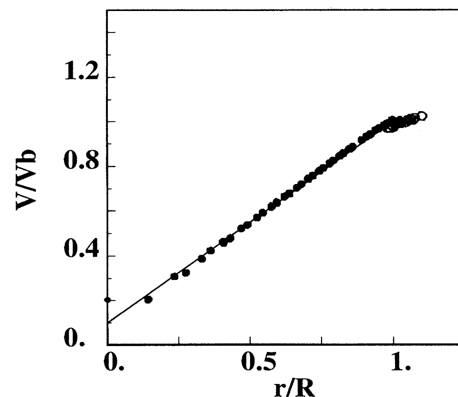

FIG. 1. Ratio of the self-consistent values of the potential to the bare one as a function of the position in a cluster with 915 silicon atoms. The open circles correspond to hydrogen atoms. The straight line corresponds to the classical expression [see text, Eq. (3)].

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another medium of dielectric constant ε_{out}. Then, taking the center of the cluster as origin, the potential energy of an electron at point $\mathbf{r}$ due to the charge $+e$ at point $\mathbf{r}'$ can be obtained from simple electrostatics as the sum of direct interaction $-e^2/(\varepsilon_{\text{in}}|\mathbf{r} - \mathbf{r}'|)$ and a corrective term [1,6],

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

where θ is the angle between $\mathbf{r}$ and $\mathbf{r}'$. $V_{\text{in}}(\mathbf{r},\mathbf{r}')$ is due to the surface polarization charge density which we shall call the "image" charge density by analogy with planar situations. The calculation of Fig. 1 corresponds to the centered impurity, where the potential energy simplifies to

$$V(r) = -e^2\left[\frac{1}{\varepsilon_{\text{in}}^r} + \frac{1}{R}\left(\frac{1}{\varepsilon_{\text{out}}} - \frac{1}{\varepsilon_{\text{in}}}\right)\right]. \tag{3}$$

When $\varepsilon_{\text{out}} = 1$ we get $V/V_b = 1$ at the surface as found in the numerical calculation. The dispersion of the calculated points around the straight line [Eq. (3)] in Fig. 1 shows that the effective dielectric constant ε_{in} (i) can only be defined as an average property and (ii) cannot be determined precisely, since the intercept of the straight line at $r = 0$ is subject to some uncertainty.

We now consider the donor binding energy E_B which we define as the difference between the lowest conduction states of the same crystallite with one excess electron, without and with the donor impurity. The computed values are plotted in Fig. 2 which shows that E_B can take fairly large values, in agreement with the conclusions of Ref. [2]. A fairly accurate expression is found in first order perturbation theory by calculating the average potential from expression (3) with the wave function $\sin kr/r$ of effective mass theory. This gives

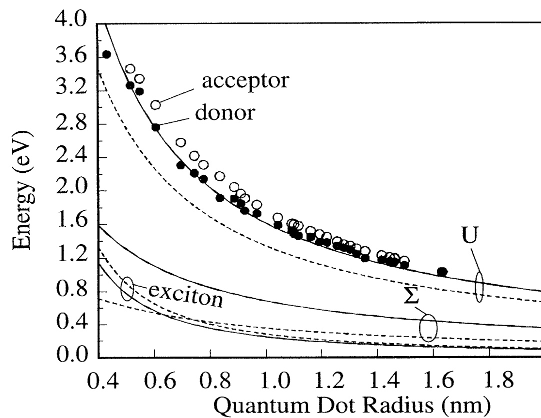

FIG. 2. Energy levels of hydrogenic impurities (●, donor; ○, acceptor) obtained with the self-consistent calculation ($\varepsilon_{\text{out}} = 1$), self-energy $\Sigma(R)$, Coulomb energy $U(R)$, and exciton binding energy $E_{\text{BX}}(R)$ as a function of the particle radius R (continuous lines for $\varepsilon_{\text{out}} = 1$, dashed lines for $\varepsilon_{\text{out}} = 1.77$ (porous silicon [9]).

$$E_B(R) = \left(\frac{1}{\varepsilon_{\text{out}}} + \frac{1.44}{\varepsilon_{\text{in}}}\right)\frac{e^2}{R}. \tag{4}$$

An interesting point to notice is that this result remains practically unchanged when the impurity is moved away from the center. This is drastically different from what is obtained in quantum wells. In the bulk the binding energy is equal to the ionization energy, since the conduction band states form a continuum. This is no more true in crystallites, since these states now form a discrete spectrum. In a perfect crystallite ionization will occur 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 $I_0(R) + E_B(R)$. It is thus strongly enhanced for small crystallites so that the donor electron should remain trapped. For porous silicon this is in contradiction with EPR measurements concluding that hydrogenic impurities are always ionized but also that the corresponding carriers are not found as free carriers [7]. To provide an explanation for this discrepancy we consider the following reaction: The initial situation consists of a neutral donor and a neutral dangling bond in two different crystallites, the final one resulting from the electron transfer between the donor and the dangling bond defect. Taking the bottom of the bulk conduction band as the origin of energies, the energy of the extra electron in the initial situation is $\Delta E_c - E_B(R)$, where ΔE_c is the blueshift of the crystallite containing the donor. In the final situation it become $\varepsilon_{db} - e^2/(\varepsilon_{\text{out}}d)$, where ε_{db} is the binding energy of the dangling bond state and $-e^2/(\varepsilon_{\text{out}}d)$ comes from the electrostatic attraction by the ionized donor in the other crystallite at distance d. The total difference in energy between the final and initial states becomes

$$\Delta E = -(\Delta E_c + \varepsilon_{db}) + E_B(R) - e^2/(\varepsilon_{\text{out}}d). \tag{5}$$

As shown in [8] this equation still holds true within the same crystallite with $d = R$. With ε_{out} equal to 1.77 measured for a porous layer with a porosity of 74% [9], typical values for $R = 1.5$ nm are $\Delta E_i = 0.33$ eV [10], $\varepsilon_{db} = 0.3$ eV, and $E_B(R_i) = 0.72$ eV [Eq. (4)] so that ΔE is negative when $d < 9.3$ nm. Because of the high density of dangling bonds in porous silicon [7], this means that donor states should remain ionized, their electron being trapped at defects like dangling bonds since the previous reasoning remains valid for all deep defects.

The following interesting question concerns the self-energy of particles and Coulomb charging effects. Until now the level structure of crystallites has been obtained from semiempirical calculations which implicitly contain the same self-energy corrections (due to exchange and correlation) as in the bulk. In crystallites we thus need to determine corrections brought by the finite size of the system. We do this within an electrostatic formulation which corresponds to the "static Coulomb hole approximation" of GW theory [11]. This is not very good for the bulk but here we determine in this way only the change in self-energy due to

the image charge distribution on the surface, which should be more reasonable. Let us then put an extra electron in the lowest conduction state ψ_c. The image contribution Σ to its self-energy is $\frac{1}{2}\langle\psi_c|V_{\rm in}(\mathbf{r},\mathbf{r})|\psi_c\rangle$ with $V_{\rm in}$ given by Eq. (2) with opposite sign. Taking again $\psi_c \propto \sin kr/r$, which provides an excellent approximation, we get

$$\Sigma = \frac{1}{2}\left(\frac{1}{\varepsilon_{\rm out}} - \frac{1}{\varepsilon_{\rm in}}\right)\frac{e^2}{R} + \delta\Sigma, \quad (6)$$

where the first term comes from $n = 0$ in (2) and $\delta\Sigma$ is the corrective term due to the remaining sum. This one simplifies greatly when $\varepsilon_{\rm in} + \varepsilon_{\rm out} \gg 1$ in which case one gets

$$\delta\Sigma = 0.47\frac{e^2}{\varepsilon_{\rm in}R}\left(\frac{\varepsilon_{\rm in} - \varepsilon_{\rm out}}{\varepsilon_{\rm out} + \varepsilon_{\rm in}}\right), \quad (7)$$

which is usually small but not negligible. This gives the shift in energy of the extra electron in the lowest conduction band state which represents the experimentally important quantity (Fig. 3). The injection of a second electron leads to an additional upwards shift given by the average repulsion with the other electron and its "image charge" (Fig. 3). With an electron distribution close to $\sin kr/r$ this shift is given by

$$U(R) = \left(\frac{1}{\varepsilon_{\rm out}} + \frac{0.79}{\varepsilon_{\rm in}}\right)\frac{e^2}{R}. \quad (8)$$

Under injection of n electrons (n small) the lowest filled conduction states will thus exhibit a shift approximately equal to $\Sigma + nU$ (Fig. 3). Finally, the situation for holes is completely symmetrical.

We now consider the same corrections applied to exciton states. To get the proper value for the exciton binding energy $E_{\rm BX}$ we must add the contribution of the direct electron-hole interaction $-e^2/\varepsilon_{\rm in}r_{\rm eh}$ and the different image terms: self-energies of the electron and of the hole [both given by (6)] plus the interaction of one particle with the image charge distribution of the other. The latter one is equal to $(1/\varepsilon_{\rm in} - 1/\varepsilon_{\rm out})e^2/R$, and obviously almost exactly compensates the sum of the two self-energies so that image contribution to the exciton binding energy reduces to the constant term $-2\delta\Sigma$. With a carrier distribution close to $\sin kr/r$, we have

$$E_{\rm BX}(R) = 1.79e^2/\varepsilon_{\rm in}R - 2\delta\Sigma. \quad (9)$$

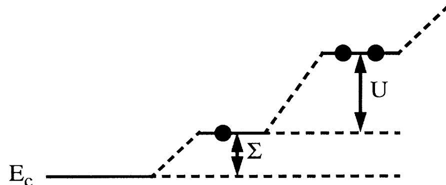

FIG. 3. Shift of the lowest conduction level due to the injection of one electron (Σ) or two electrons ($\Sigma + U$). The situation for holes is symmetrical.

To estimate $\Sigma(R)$, $U(R)$, $E_{\rm BX}(R)$ numerically, the problem is still to know what value of $\varepsilon_{\rm in}$ should be used. Wang and Zunger [3] treated this problem by computing the quantity $1 + 4\pi\chi$, where χ is the quantum polarizability of the whole sphere. In the bulk this procedure is exact provided one neglects local field effects which introduces an error of order 10% to 20%. Assuming this to hold true in crystallites the procedure of calculating $1 + 4\pi\chi$ might be justified if the following conditions are met: (i) one can define macroscopic quantities as averages over unit cells and treat them as continuous variables, and (ii) the local ratio between the macroscopic polarization and field is constant and equal to χ. We have seen in Fig. 1 that this seems more or less verified despite substantial scatter around the average value. From that point of view, $1 + 4\pi\chi$ represents one particular way of calculating an average $\varepsilon_{\rm in}$. To get some feeling about the accuracy of such an averaging procedure we have estimated $\varepsilon_{\rm in}$ using three different approaches: (i) a fit of the self-consistent donor potential of Fig. 1 by Eq. (3), (ii) the classical donor potential (3) is used in the LCAO calculation, and $\varepsilon_{\rm in}$ is adjusted to fit the self-consistent donor binding energy (Fig. 2), and (iii) a least-square minimization of $V/\varepsilon_{\rm in} - V_b$ in a case corresponding to a bound exciton with the electron confined on the central atom and the hole in the highest valence state. Figure 4 shows that there are substantial differences between the three results mostly for small crystallite radii due to the different ways of computing the spatial average of $\varepsilon^{-1}(\mathbf{r},\mathbf{r}')$. Our results lie between those of Refs. [2] and [3], and their average value

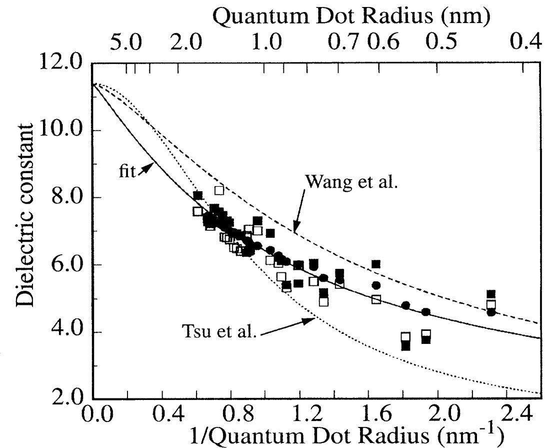

FIG. 4. Plot of the calculated $\varepsilon_{\rm in}$ obtained by the fit of the donor potential (■) and of the self-consistent donor binding energy (□) with classical laws and by a least-square minimization of $V/\varepsilon_{\rm in} - V_b$ in a case corresponding to a bound exciton (●). The continuous line is a fit of these values ($\tilde{\varepsilon}_{\rm in} = 1 + (11.4 - 1)/[1 + (0.92/R)^{1.18}]$). The dashed curve corresponds to $\tilde{\varepsilon}_s$ of Ref. [3] and the dotted line to the generalized Penn model of Ref. [2].

can be well approximated by $\tilde{\varepsilon}_{\text{in}} - 1 = (11.4 - 1)/[1 + (0.92/R)^{1.18}]$ with R in nanometer units [2]. Figure 2 gives $\Sigma(R)$, $U(R)$, and $E_{\text{BX}}(R)$ computed with $\tilde{\varepsilon}_{\text{in}}$ for $\varepsilon_{\text{out}} = 1$ and $\varepsilon_{\text{out}} = 1.77$ (porous silicon). The values of U are so large that the injection of more than one electron—or hole—in silicon nanocrystallites in porous silicon must be very difficult if not impossible. However, when $\varepsilon_{\text{out}} \rightarrow \infty$ corresponding to the experimental case where porous silicon samples are in aqueous electrolyte ($\varepsilon_{\text{out}} \approx 80$), U reduces to ~ 0.15 eV so that the injection of two carriers becomes easier [12]. This could explain the different transport properties of porous silicon in "air" and in electrolyte.

In summary, we have computed the linear self-consistent response of semiconductor nanocrystallites in various physical situations and compared the results to the macroscopic description. We have considered hydrogenic impurities and Coulomb charging effects and evaluated the importance of the so-called image corrections as well as the justification of the use of a macroscopic formulation with an average dielectric constant. Consequences on the properties of porous silicon have been discussed.

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