Theoretical calculations of shallow impurity states in deformed quantum wires with an application to porous silicon

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We present results on the ground-state binding energies for donor (acceptor) impurities in a deformed quantum wire. The impurity effective-mass Schrödinger equation is reduced to a one-dimensional equation with an effective potential containing both the Coulomb interaction and the effects of the wire surface irregularities through the boundary conditions. Studying the ground-state wave functions for different positions of the impurity along the wire axis, we have found that there are wire deformation geometries for which the impurity wave function is localized either on the wire deformation or on the impurity, or even on both. With the wire geometries compatible with the light emission in porous silicon, we show that a distribution of impurities along the wire axis leads to a ladder of energy states spanning an interval of about 0.290 eV.

There is no doubt that the most exciting advances in semiconductor physics of recent years are the low dimensional systems. Among the many, a particular place is occupied by porous semiconductors, namely, porous silicon[1] and gallium arsenide.[2] Porous silicon is certainly the most studied[3] because of its simplicity in preparation and its ability of emitting intense visible light at room temperature. There is a vast consensus on the fact that this emission is originated from those parts of the material composed of nanodimensional structures where quantum confinement plays a central role. It has been demonstrated that the large difference between the light absorption and emission energies can be accounted for in a structural model where quantum confinement occurs in a undulating quantum wire with the formation of states localized along the wire axis.[4]

In this paper we present the results of our theoretical studies on the influence of hydrogenic impurities on the electron localization in a deformed quantum wire. Although our primary interest is on porous silicon, it must be said that the calculation methods we are going to illustrate are very general and can be applied to all those situations where the effects of the nanostructure geometry cannot be neglected.

The deformed wire we have considered for this work is shown in the panel (a) of Fig. 1. The cylindrical quantum wire with radius R_0 has been deformed in such a way that its lateral surface S has the equation

$$\rho = R(z) = R_0[1 + \varepsilon \exp(-2z^2/\Delta z^2)], \tag{1}$$

representing a bulge centered at $z=0$ with an extension Δz, depth εR_0, and an aspect ratio $\delta = \varepsilon R_0/\Delta z$. Within the effective mass approximation, the Schrödinger equation for a donor (acceptor) impurity located on the wire axis z is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_C(\vec{\rho}) - \frac{e^2}{\varkappa\sqrt{\rho^2+(z-z_0)^2}} \right) \Psi(\vec{r}) = E\Psi(\vec{r}), \tag{2}$$

where z_0 is the impurity position, $V_C(\vec{\rho})$ the wire confining potential, and $\varkappa$ the static dielectric constant. For simplicity, we take the potential $V_C(\vec{\rho})$ as diverging on the wire surface, that is, we only consider the hard wall boundary conditions. Given the nanostructure cylindrical symmetry and the fact that we locate the impurity on the wire axis, the lowest energy impurity wave function can be written as

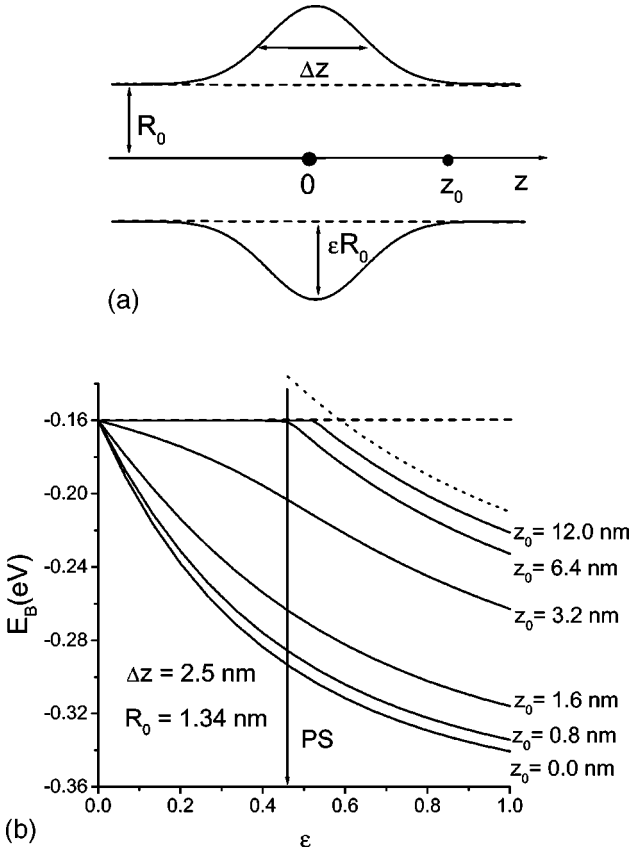

FIG. 1. In panel (b) ground-state binding energy as a function of ε for the deformed cylindrical wire shown in panel (a) and with the impurity located at z_0. The dotted line corresponds to an impurity with $z_0=\infty$ whereas the dashed line corresponds to the case of a straight cylinder ($\epsilon=0$). The material parameters are those of silicon.

$$\Psi(\vec{r})=\sum_n \phi_n(\rho,z)f_n(z), \tag{3}$$

where the set of orthogonal and normalized functions

$$\phi_n(\rho,z)=\frac{1}{\sqrt{\pi}|J_1(\chi_n)|R(z)}J_0\left(\chi_n\frac{\rho}{R(z)}\right) \tag{4}$$

satisfies the boundary condition $\phi_n|_S=0$. Here χ_n are the zeros of the Bessel function $J_0(x)$. Inserting $\Psi(\vec{r})$ in Eq. (2) a lengthy calculation leads to the following set of coupled equations for $f_n(z)$

$$\left\{-\frac{\partial^2}{\partial z^2}+\frac{1}{R^2(z)}\left[\chi_{n'}^2+\frac{1}{3}(1+\chi_{n'}^2)R'^2(z)\right]-V_{n'n'}(z)\right\}f_{n'}(z)-\sum_{n\neq n'}W^I_{n'n}(z)f_n(z)=Ef_{n'}(z), \tag{5}$$

where the energy has been scaled with the effective Rydberg $R_y=e^2/2\varkappa a$ with $a=\varkappa\hbar^2/me^2$. The coupling matrix $W^I_{n'n}(z)$ is given by

$$W^I_{n'n}(z)=W_{n'n}(z)+V_{n'n}(z), \tag{6}$$

where

$$V_{n'n}(z)=\frac{4}{J_1(\chi_{n'})J_1(\chi_n)}\int_0^1 xdx\frac{J_0(\chi_{n'}x)J_0(\chi_n x)}{\sqrt{R^2(z)x^2+(z-z_0)^2}}, \tag{7}$$

$$W_{n'n}(z)=-\frac{R'^2(z)}{R^2(z)}\chi_n^2Q_{n'n}-\left(3\frac{R'^2(z)}{R^2(z)}-\frac{R''(z)}{R(z)}\right)S_{n'n}+2\frac{R'(z)}{R(z)}S_{n'n}\frac{\partial}{\partial z}, \tag{8}$$

$$Q_{n'n}=\frac{8\chi_n\chi_{n'}}{(\chi_n^2-\chi_{n'}^2)^2},\quad S_{n'n}=\frac{2\chi_{n'}\chi_n}{\chi_{n'}^2-\chi_n^2}. \tag{9}$$

A complete solution of the set of differential Eqs. (5) is clearly a very complicated task. However, since we are interested in the lowest energy impurity states, we can confine ourselves to the equation for $n'=1$, that is, the impurity states coming from the lowest wire miniband, and search for the conditions under which the coupling terms $W^I_{1n}(z)$ are negligible. Reserving the discussion on this condition for a later paragraph, let us write the diagonal part of Eq. (5) for $n'=1$

$$\left\{-\frac{\partial^2}{\partial z^2}+\frac{1}{R^2(z)}\left[\chi_1^2+\frac{1}{3}(1+\chi_1^2)R'^2(z)\right]-V_{11}(z)\right\}f(z)=Ef(z), \tag{10}$$

where χ_1 is the first root of J_0. This is now a one-dimensional Schrödinger equation for a particle moving in an effective potential comprising two contributions. The first one is given by $V_{11}(z)$ defined in Eq. (7) representing the planar average of the Coulomb interaction. The second one, given by the square parenthesis in Eq. (10), depends on both $R(z)$ and its first derivative. The origin and the role of this last contribution in determining the particle localization along the z direction has been discussed in Ref. 4. For $R(z)$ given by Eq. (1), both the contributions in Eq. (10) are attractive with a weight depending on the bulge geometrical parameters $(R_0,\Delta z,\varepsilon)$ varying which one may have very different electronic configurations.

Before discussing of the results we have obtained from Eq. (10), we must return to the conditions under which the terms $W^I_{1n}(z)$ are negligible. It is clear from Eq. (6) that the weight of the off-diagonal terms depends on the wire bulge geometry. There are, of course, geometries where this weight is significant and others where the contributions coming from Eq. (6) are negligible. We are going to show that the latter is the case for porous silicon. In order to get a precise assessment of this point we have developed a perturbation expansion for the corrections to the ground state energy and wave functions calculated from Eq. (10). In the perturbation scheme the eigenstates $|f_{n'\alpha}\rangle$ of the diagonal part of Eq. (5) are considered as unperturbed states with energies $E_{n'\alpha}$. The matrix elements $W^I_{n'n}(z)$ are considered as the perturbation. For the sake of brevity we report only the second order correction to the total energy $E=E_{10}$ of the unperturbed ground state $|f_{10}\rangle$ resulting from Eq. (10)

$$\Delta E^{(2)}=\sum_{k\neq 1}\sum_{\alpha}\frac{(W^I_{1k})_{0\alpha}(W^I_{k1})_{\alpha 0}}{E_{10}-E_{k\alpha}}, \tag{11}$$

where $(W^I_{kl})_{\alpha\beta}\equiv\langle f_{k\alpha}|W^I_{kl}|f_{l\beta}\rangle$. In practical calculations we can break out the sum on k in Eq. (11) when the energy differences $E_{10}-E_{k\alpha}$ become very large. On this basis, we can consider the two diagonal terms in Eq. (5) with $n'=1,2$ corresponding to the first two zeros of $J_0(x)$. Separating the contributions coming from the discrete part of the unperturbed spectrum from those of the continuum, Eq. (11) reads

$$\Delta E^{(2)}=\sum_j\frac{|\langle f_{10}|W^I_{12}|f_{2j}\rangle|^2}{E_{10}-E_{2j}}+\int_{E_{2C}}^{\infty}g(E)\frac{\langle f_{10}|W^I_{12}|f_{2E}\rangle|^2}{E_{10}-E}dE, \tag{12}$$

where E_{2C} is the continuum bottom edge with $n'=2$, $|f_{2E}\rangle$ is the corresponding eigenfunction with eigenvalue E, and $g(E)$ is the density of states.

We have found that both $W_{1n}(z)$ and the Coulomb potential off-diagonal matrix elements $V_{1n}(z)$ defined in Eq. (7) are negligible if the bulge dimensions are such that $\varepsilon<1$, $R_0/\Delta z<1$. Moreover, the electron wave function extension in the z direction must be larger than the wire radius R_0. The wire and bulge geometries we are going to consider all satisfy the above restrictions. As an example, using silicon parameters, our numerical calculations have shown that for $\Delta z=1.5$ nm, $\varepsilon=0.51$, $R_0=1.03$ nm with the impurity in $z_0=9.0$ nm the ground state total energy we have is $E_{10}=415$ meV with $\Delta E^{(2)}=2$ meV. Moving the impurity at

$z_0 = 0.0$ nm we have $E_{10} = 206$ meV and $\Delta E^{(2)} = 19$ meV. Considering that these are among the largest corrections we have found, we can safely conclude that Eq. (10) is a good approximation.

Although the calculation methods and approximations presented in this work are applicable to many semiconductor nanostructures, we have considered, in some detail, the case of light emitting porous silicon, for which the restricted class of deformed wire geometries [see panel (a) of Fig. 1] compatible with the measured photoluminescence peak energies, has been determined.[4] With reference to the case of donors and using a spherical average for the bulk silicon conduction effective mass, we have solved the differential Eq. (10) numerically with an ordinary midpoint shooting method and defined the electron binding energy as $E_B = E - \hbar^2 \chi_1^2 / 2mR_0^2$. The Coulomb interaction in Eq. (2) is screened by a dimension dependent dielectric constant $\varkappa$ which we have chosen as that given by Ref. 5. In panel (b) of Fig. 1 we show the binding energy as a function of ε for a wire with radius $R_0 = 1.34$ nm deformed with a bulge having $\Delta z = 2.5$ nm and with several values of the impurity position z_0 [see panel (a) of Fig. 1]. The dotted line corresponds to the case without impurity (the electron is localized on the bulge), whereas the straight dashed line is the impurity binding energy in a undeformed wire ($\varepsilon = 0$) which agrees with the results of Refs. 6 and 7. The arrow pointing at $\varepsilon = 0.46$ corresponds to an average porous silicon nanostructure with light emission peak at about 1.7 eV.[4] When the impurity is inside the wire bulge, the electron is tightly bound to the impurity. For $\varepsilon = 0.46$ we have found a binding energy of about 290 meV. When $z_0 \gg \Delta z/2$, the impurity is far away from the wire bulge and it is possible to define a ε_{cr} such that when $\varepsilon = \varepsilon_{cr}$, the binding energy starts to deviate from the value corresponding to a straight wire. If $\varepsilon < \varepsilon_{cr}$ the electron is always localized on the impurity, whereas for $\varepsilon > \varepsilon_{cr}$ the electron can be localized within the wire bulge even if the impurity is far away from it. This effect is testified to by the fact that all the curves tend asymptotically to the binding energy of an electron localized within the bulge without the impurity (dotted line). Panel (b) of Fig. 1 also shows that upon moving the impurity from $z_0 < \Delta z/2$ to $z_0 \gg \Delta z/2$ the binding energy curves span the region contained by the curve with $z_0 = 0$, the dashed line and the dotted line.

The spatial separation between the ionized impurity and the electron may have interesting consequences on the electrical conductivity. In the case of the particular porous silicon nanostructure we are analyzing ($\varepsilon = 0.46$) this separation between the donor and its electron does not occur. However, there exists, as we shall see, a range of Δz values, compatible with porous silicon, for which moving the impurity away from the wire deformation, the electron remains localized on the bulge. To better illustrate this effect, we have calculated the normalized modulus square wave functions for several values of the impurity-bulge distance z_0. In Fig. 2 we show the results of these calculations for $\Delta z = 2.5$ nm, $\varepsilon = 0.46$, and $R_0 = 1.34$ nm [panels (a) and (b)] and for $\Delta z = 1.5$ nm, $\varepsilon = 0.51$, and $R_0 = 1.03$ nm [panels (c) and (d)]. In the second case the light emission is at about 2.2 eV. The arrows indicate the impurity position z_0. In panel (a) a condition is realized for which the wave function is shared between the bulge at $z = 0$ nm and the impurity at $z_0 = 6.4$ nm. Moving the impurity further away from the bulge, the wave function localizes on the impurity, as shown in panel (b). Reducing the bulge z extension Δz to 1.5 nm, the wave function first localizes on both the bulge and the impurity as shown in panel (c) and then it remains localized on the bulge on moving the impurity away. The results shown in Fig. 2 are indicative of an intrinsic richness in the wave function distribution between the impurity and the wire bulge.

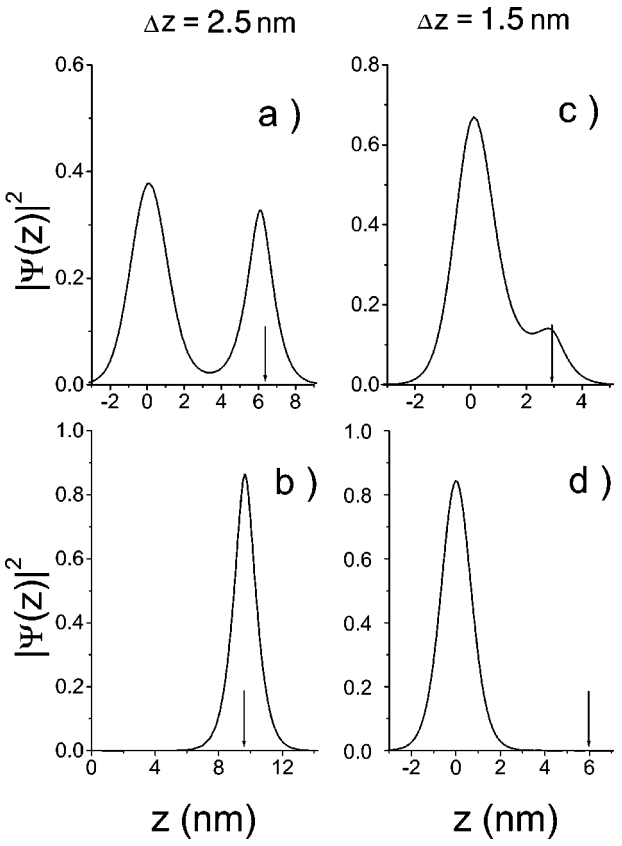

FIG. 2. Ground-state wave functions for two bulge geometries and for different impurity positions. In each panel the impurity position is indicated by an arrow. The wave function is localized on both the impurity and the bulge in (a) and (c), localized only on the the impurity in (b), localized only on the bulge in (d).

It is, in our opinion, of interest to study the impurity behavior upon changing the bulge geometries among those that we have demonstrated to be compatible with both the light absorption and emission in porous silicon.[4] The results of these calculations are shown in Fig. 3 where the relations between the geometrical parameters are $R_0 = 5.704 + 0.307\Delta z$ and $\delta = 0.497 - 0.010\Delta z$ (lengths in angstroms).[4] This figure contains the electron binding energy in a bulge without the impurity (indicated as ''bulge only''), the impurity binding energy in a straight wire (indicated as ''impurity only''), and the impurity binding energy in a wire with a bulge for $z_0 = 12.0$ nm (dashed line), $z_0 = 3.2$ nm (dotted line), and $z_0 = 0.0$ nm (dash-dotted line). It is interesting to observe that the curve corresponding to $z_0 = 12.0$ nm (dashed line) differs from the curve of the impurity in a straight wire (marked impurity only) only in the interval 1.2 nm $< \Delta z <$ 2.25 nm where the binding energy of an

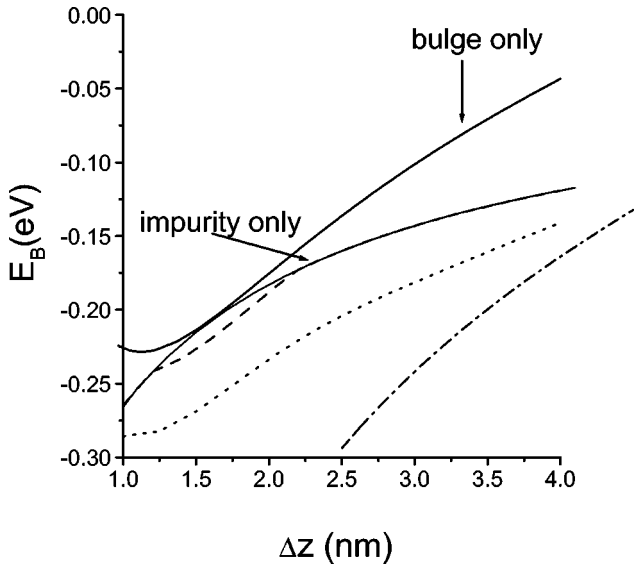

FIG. 3. Donor ground-state binding energy as a function of the bulge extension Δz using the geometrical parameters of Ref. 4. The full lines are the electron localization energy without the impurity and the impurity binding energy without wire deformation. The dashed, dotted, and dash-dotted lines have been calculated with the impurity at $z_0=12.0$ nm, $z_0=3.2$ nm, and $z_0=0.0$ nm, respectively.

electron in a bulge and that of an impurity in a straight wire are very near. In the central part of this Δz interval the electron is localized on the bulge rather than on the impurity [see panel (d) of Fig. 2]. The amplitude of the Δz interval in which the electron remains localized on the bulge rather than on the impurity depends on its position z_0. On increasing z_0, the interval tends to shrink. The effect we have presented gives an ionization mechanism for donors in porous silicon where an electron is moved from the impurity to the wire bulge. This mechanism is alternative to the one proposed in Ref. 8 where an electron is moved from the impurity to surface defect. It is worth mentioning that a preliminary study of the entire energy spectra has shown the existence of geometrical configurations where the ground state wave function is localized on the bulge whereas the first excited state with zero angular momentum is localized on the impurity.

In a recent paper[9] surface photovoltage spectroscopy measurements on freestanding porous silicon films have been reported. All the films considered have bandtails about 0.3 eV wide with an optical band gap of about 2.0 eV. The authors' conclusion is that the origin of the strong photoluminescence is in the optical transition from conduction bandtail to valence bandtail. Our theory on the electronic structure of a deformed wire[4] and on the role of impurities presented in this paper leads us to the same conclusion. The bandtail states are formed by localized states induced by both the wire deformations and the shallow impurities. One of the samples considered in Ref. 9 had an emission peak at 1.7 eV which, on the basis of our theory,[4] should correspond to an average wire bulge with $\Delta z=2.5$ nm, $R_0=1.34$ nm, and $\varepsilon=0.46$. The arrow in the panel (b) of Fig. 1 indicates that for this geometry the combination of bulge states and a distribution of noninteracting impurities along the wire axis covers an energy interval of about 290 meV, in nice agreement with the measured 300 meV bandtail width of Ref. 9.

In conclusion, we have shown that the ground state wave function of a donor (acceptor) impurity in a deformed quantum wire may be either localized on the deformation or on the impurity, according to the deformation geometry. Moreover, there are geometries where the wave function is shared between the wire bulge and the impurities and others where the electron is localized on the wire bulge rather than on the impurity. Finally, the electron binding energies interval for impurities distributed along the wire are in agreement with the bandtail width measured for porous silicon.

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