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# Optical gap of silicon crystallites embedded in various wide-band amorphous matrices: role of environment

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## Abstract

Within the framework of the envelope-function approximation the single-particle and the optical gaps of silicon nanocrystals embedded in amorphous  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  dielectric matrices were calculated. We employ the model of an Si quantum dot surrounded by a spherical thin intermediate layer with a radially varying permittivity, separating the nanocrystal and the host dielectric matrix. The latter was modelled by the finite-height potential barriers. It has been shown that both the single-particle and optical gaps of the nanocrystals essentially depend on the surrounding material due to the variation of the band offsets for different matrices, which leads to essential shifts of the size-quantized levels. At the same time, an influence of the polarization fields on the optical gap was found to be weak compared to the variation of the confining potential, because of the mutual cancellation of single- and two-particle polarization contributions, which is known as a 'compensation effect'. As a result, hydrogen-like screened electron-hole Coulomb interactions, in fact, individually contribute to the excitonic correction. It has been revealed that the excitonic corrections have close values for the nanocrystals embedded in all the considered matrices: the dispersion of their values is even considerably less than that of the polarization correction values.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

It is well known that use of indirect bandgap semiconductors in optical applications is awkward because of the small probability of indirect optical transitions that are completely forbidden in bulk materials in the absence of phonons. In connection with this, a lot of research activity in the last 15 years has been concentrated on the optical properties of silicon nanocrystals (quantum dots), with sizes of about several nanometres, in which the electron-hole interband transition becomes allowed even without phonons. Usually, however, Si crystallites are formed in some wide-band dielectric matrices which can influence the properties of the crystallites.

In particular, the matrix has a dielectric constant  $\epsilon_d$  different from that of bulk Si ( $\epsilon_s$ ). The dielectric constant mismatch creates polarization fields which can be treated as fields induced by the electron and hole images. Sometimes, these fields play an important role in the formation of quantum electron states in various low-dimensional structures. For

instance, earlier, the so-called dielectric amplification effect for excitons in quantum wires has been theoretically predicted [1]. In quantum dots, due to the 3D confinement of the carriers, it is possible to expect as well a significant influence of the polarization fields on the electron and hole states, and the optical gap. If so, then different host dielectric matrices could strongly influence the nanocrystal's bandgap.

Besides, the host matrices differ from each other by their forbidden bands. This results in different band offsets from Si for different matrices. Consequently, the carriers turn out to be confined inside the nanocrystal by the potential barriers of different heights, which can appreciably shift the energy levels of the carriers and change the nanocrystal's gap as well.

In this work we examine the influence of the dielectric surroundings, and of the direct electron-hole Coulomb interaction on the optical gap of silicon nanocrystals, taking into account finite band discontinuity at the interface. For this purpose, we shall calculate the single-particle gap defined by the size quantization only, and the optical gap of a

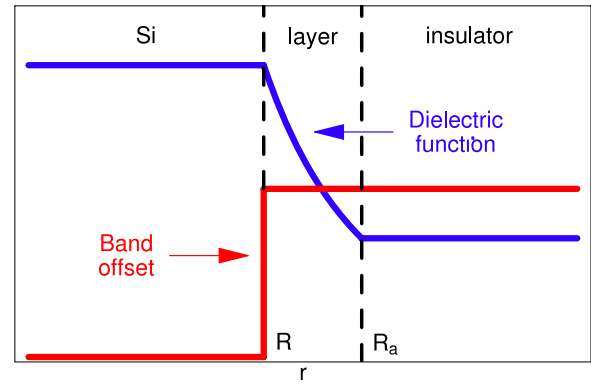
silicon quantum dot placed in various amorphous dielectric matrices with different forbidden bands and different dielectric constants. It is important to emphasize that all these dielectric materials are supposed to be amorphous in order to minimize the contribution of strain fields arising in the interface domain. In what follows, we neglect the effect of strain and consider some typical dielectrics being usually the host matrices for Si crystallites, such as: SiO<sub>2</sub> ( $\epsilon_d = 3.9$  [2, 3]); Si<sub>3</sub>N<sub>4</sub> ( $\epsilon_d = 7$  [3]); Al<sub>2</sub>O<sub>3</sub> ( $\epsilon_d = 10$  [4]) and ZrO<sub>2</sub> ( $\epsilon_d = 25$  [5]).

Earlier, the single-particle spectra [6–11] as well as the excitonic corrections to the single-particle gap of silicon quantum dots [9–15] have been calculated in the presence of polarization fields. However, previous calculations had some drawbacks. First, in some works, an approximation of infinite potential barriers was used [6, 7, 9, 12, 14, 15], which leads to overestimated values of electron and hole energies. This makes a quantitative comparison of theoretical and experimental results difficult. Second, when solving the electrostatic part of the problem, the step-like model of a dielectric function was usually employed. In this case the self-polarization field creates an infinite impenetrable potential barrier at the interface. Therefore, independently of the band offset values, we have to use the model of infinite potential barrier, leading again to overestimated values of the exciton energy. In the opposite case, if potential barriers for electrons and holes were assumed to be finite, the authors of the mentioned works had to (i) ignore polarization fields and suppose that the single-particle self-polarization and two-particle excitonic polarization corrections cancel each other [11, 13, 14] or (ii) artificially remove the divergence in expressions for the self-polarization fields [10].

An application of the first-principles methods to computing the single-particle energies, self-polarization and excitonic corrections allows one to avoid these troubles. However, *ab initio* methods require lots of time and cannot be really applied to nanocrystals with diameters greater than 2 nm. For this reason, it is so far difficult (or, rather, impossible) to describe correctly with the first-principles methods the screening action of the dielectric environment on the electron and hole states in a nanocrystal. In contrast, various empirical, or semi-empirical, methods such as pseudopotential [16], tight-binding model [17] or envelope-function approximation ( $\mathbf{k} \cdot \mathbf{p}$ -method) allow one to consider polarization fields in a natural manner. We shall further use an approach based on the envelope-function approximation.

In order to avoid unphysical divergences in the self-polarization corrections in the case of finite band offsets at the interface, we shall assume an existence of a narrow transition layer of thickness  $a$  between the nanocrystal and the dielectric matrix. The dielectric function of this layer varies continuously along a radial direction from  $\epsilon_s = 12$  for silicon to  $\epsilon_d$  for the dielectric environment. A similar procedure was used for a model with an isotropic quadratic dispersion law [18]. In contrast to this work, we take into account the anisotropy of the silicon band structure and use some special dependence  $\epsilon(r)$  that makes possible an analytical solution of the electrostatic problem.

In our study we treat the Coulomb interaction as a perturbation with respect to the confining potential. Such



**Figure 1.** Schematic representation of the band structure, and the dielectric function of Si nanocrystal surrounded by a spherical transition layer, and insulating matrix.

an approximation is justified if the nanocrystal radius is less than the exciton Bohr radius. This relationship is valid for sufficiently small quantum dots with diameters about, or less than, 5–6 nm, for which all the calculations have been carried out.

## 2. Electrostatic problem: the model

Let us consider a spherical silicon quantum dot with radius  $R$  and dielectric constant  $\epsilon_s$  embedded in an insulator with dielectric constant  $\epsilon_d$ . We denote potential barriers for electrons and holes at the quantum dot boundary as  $U_e$  and  $U_h$ , respectively, and suppose them to be constant within the transition layer and outside. Neglecting weak exchange interaction, one may write the ground-state wavefunction of the exciton as a product of the electron and hole wavefunctions. Earlier [19, 20], the single-particle electron and hole wavefunctions were found by taking into account the anisotropy of the silicon band structure. In this work, we use the results of our previous calculations [20] where the model of finite potential barriers at the dot interface has been considered.

The key point of our consideration is the position dependence of the dielectric function inside the transition layer. We choose the dependence in the following form:

$$\epsilon(r) = \epsilon_s (r/R)^q \quad (1)$$

with

$$q = \log(\epsilon_d/\epsilon_s)/\log(1 + a/R). \quad (2)$$

We suppose that the thickness  $a$  of the transition layer is much smaller than the dot radius:  $a \ll R$ , hence,  $q \approx R \log(\epsilon_d/\epsilon_s)/a$ .

The dependence  $\epsilon(r)$  given by equation (1) provides a smooth variation of the permittivity value from  $\epsilon_s$  for silicon to  $\epsilon_d$  for the dielectric surroundings, as schematically shown in figure 1. Of course, to a certain extent, such an artificial introduction of the transition layer and position-dependent dielectric function within the layer is not a rigorous procedure which cannot be strictly validated, at least within the framework of the envelope-function approximation. Rigorous

calculations could be performed with first-principles methods but such calculations are very complicated and require lots of computational time and effort. It is clear, however, that some narrow spatial layer, in which structure transition from crystalline Si to amorphous dielectric occurs, really exists around the nanocrystal. At the same time, one can expect an insignificant contribution to the energy spectra from the transition area because of its small thickness. For this reason, it is possible to accept the simplest concept of the local dielectric function  $\varepsilon(r)$  instead of the ‘rigorous procedure’ for the considered system. Then, we have to assign within the layer to  $\varepsilon$  some values being intermediate between  $\varepsilon_s$  and  $\varepsilon_d$ . These values are defined by equation (1).

Evidently, the potential barrier at the interface should behave similarly. It is logical to assume a gradual rise of the barrier height within the transition layer from zero to  $U_{e,h}$  as  $r$  increases from  $R$  to  $R_a = R + a$ . However, such a model of the band offset would essentially impede our calculations with no real corrections to the computed energies, as was, in fact, estimated by Bolcatto and Proetto [18]. Therefore, we accept the step-like model for the band offset, supposing the ‘step’ to be at  $r = R$  as shown in figure 1.

As was just pointed out, the transition layer is expected to be weakly contributing to the energy-gap corrections because of the small thickness. Therefore, an explicit form of  $\varepsilon(r)$  is not so important, and we can choose any smooth monotonic dependence for the dielectric function. The chosen form of  $\varepsilon(r)$  (equation (1)) is caused only by convenience, because only a power law allows one to solve the electrostatic problem exactly.

Indeed, within the intermediate layer, when finding the electrostatic potential induced by the point charge situated, for example, inside the nanocrystal, we have to solve the Laplace equation  $\text{div}[\varepsilon(r)\nabla\varphi] = 0$ . Drawing the  $z$  axis through the point charge, we can expand the potential as follows:  $\varphi(r, \theta) = \sum_{\ell} \varphi_{\ell}(r) P_{\ell}(\cos \theta)$ . Functions  $\varphi_{\ell}(r)$  obey the equation

$$\frac{d^2\varphi_{\ell}}{dr^2} + \left( \frac{1}{\varepsilon} \frac{d\varepsilon}{dr} + \frac{2}{r} \right) \frac{d\varphi_{\ell}}{dr} - \frac{\ell(\ell+1)}{r^2} \varphi_{\ell} = 0. \quad (3)$$

It is seen that equation (3) transforms into the standard Euler equation if  $\varepsilon^{-1}d\varepsilon/dr = q/r$  with some arbitrary parameter  $q$ . In other words, the dielectric function inside the layer is of the following form:  $\varepsilon(r) = Cr^q$ . Both  $C$  and  $q$  are found from the boundary conditions  $\varepsilon(R) = \varepsilon_s$  and  $\varepsilon(R_a) = \varepsilon_d$ , which lead to equations (1) and (2). As a result, the solution of equation (3) is given by  $\varphi_{\ell}(r) = A_{\ell}r^{\alpha} + B_{\ell}r^{-\beta}$ , where  $(\alpha \beta) = (-+) (1+q)/2 + \sqrt{(1+q)^2/4 + \ell(\ell+1)}$ . Constants  $A_{\ell}$  and  $B_{\ell}$  can be found, as usual, from the boundary conditions for the electrostatic potential.

The solution of the electrostatic problem allows us to obtain the total potential energy of the electron–hole pair in the system. The Coulomb potential energy consists of two parts. The first part, usually called the self-polarization potential energy  $V_{sp}(r)$ , corresponds to the interaction between each carrier and its own image. The second part represents the electron–hole interaction, in which both the screened direct Coulomb interaction and interaction of each carrier with an image of another carrier are taken into account.

After some algebra, we obtain analytical expressions for the electron potential energy in the self-polarization field:

$$\begin{aligned} V_{sp}(r < R) &= \frac{e^2q}{2(q+1)} \left( \frac{1}{\varepsilon_d R_a} - \frac{1}{\varepsilon_s R} \right) + \frac{e^2q}{2R\varepsilon_s} \\ &\times \sum_{l=1}^{\infty} \frac{(l+1)(1 - (R_a/R)^{\alpha+\beta})(r/R)^{2l}}{(\alpha-l)(l+1-\beta) + (l+1+\alpha)(l+\beta)(R_a/R)^{\alpha+\beta}}, \\ V_{sp}(R < r < R_a) &\approx \frac{e^2q}{8\varepsilon(r)r} \left( \frac{R}{r} \log \left( 1 - \left( \frac{R}{r} \right)^2 \right) \right. \\ &\quad \left. - \frac{r}{R_a} \log \left( 1 - \left( \frac{r}{R_a} \right)^2 \right) \right), \\ V_{sp}(r > R_a) &= -\frac{e^2q}{2R_a\varepsilon_d} \\ &\times \sum_{l=1}^{\infty} \frac{l(1 - (R_a/R)^{\alpha+\beta})(r/R)^{2l}}{(\alpha-l)(l+1-\beta) + (l+1+\alpha)(l+\beta)(R_a/R)^{\alpha+\beta}}. \end{aligned} \quad (4)$$

If the electron is situated inside the transition layer, the explicit expression for the self-polarization potential is too cumbersome. This is why we keep in  $V_{sp}(R < r < R_a)$  only the main terms giving logarithmic divergence. Note that outside the layer the self-polarization potential energy also logarithmically diverges at  $r \rightarrow R - 0$ , and  $r \rightarrow R_a + 0$ . Such potential barriers, however, permit electron tunnelling in contrast to the model of the step-like dielectric function. As a result, the self-polarization corrections to the single-particle energies and exciton binding energy turn out to be finite. Therefore, the use of the model with finite potential barriers becomes possible. Expressions for the self-polarization potential energy of holes are the same.

The potential energy of the electron–hole interaction has no non-integrable peculiarities even if  $\varepsilon(r)$  is the step-like function. Therefore, the presence of the intermediate layer has no principal mean for the excitonic correction in contrast to the self-polarization shift. Nevertheless, when calculating the excitonic correction to the optical gap, we employ the model with an intermediate layer. Explicit expressions for the potential energy of the electron–hole interaction are very cumbersome; therefore, we do not adduce them here. Note only that this expression can be written as the sum  $V_{eh} = V_{eh}^{(c)} + V_{eh}^{(p)}$ , where  $V_{eh}^{(c)}$  represents the direct screened Coulomb interaction, while the second term,  $V_{eh}^{(p)}$ , stands for the interaction of one carrier with the image of another carrier, i.e. the polarization electron–hole interaction.

It is worth noting that taking into account the macroscopic polarization fields induced by the charge images is similar to the introduction of some effective dielectric function  $\varepsilon_{eff}(r)$  of the whole nanocrystal [21] (do not confuse this with  $\varepsilon(r)$  in the transition layer). The distinguishing feature of  $\varepsilon_{eff}(r)$  is that its value varies over the nanocrystal, and at the nanocrystal interface it coincides, in fact, with  $\varepsilon_d$  [21–26]. Thus, inside the nanocrystal, the effective dielectric function differs from the static bulk silicon permittivity  $\varepsilon_s$ . The origin of the existing difference between  $\varepsilon_{eff}(r)$  and  $\varepsilon_s$  is caused precisely by the polarization charges which screen the external electric field in addition to the screening effect of Si valence electrons.

**Table 1.** Band offsets from Si for electrons ( $U_e$ ) and holes ( $U_h$ ), and dielectric constants ( $\epsilon_d$ ) for: SiO<sub>2</sub> [3], Si<sub>3</sub>N<sub>4</sub> [3, 32] ( $\epsilon_d$ , and band offsets, respectively), Al<sub>2</sub>O<sub>3</sub> [4, 32] and ZrO<sub>2</sub> [2, 5].

Material	$U_e$ (eV)	$U_h$ (eV)	$\epsilon_d$
SiO <sub>2</sub>	3.2	4.5	3.9
Si <sub>3</sub> N <sub>4</sub>	2.4	1.7	7
Al <sub>2</sub> O <sub>3</sub>	2.8	4.8	10
ZrO <sub>2</sub>	1.4	2.4	25

The screening action of the polarization charges is completely described by the interaction of the electron, and the hole with their own images and with the image of the carrier of the opposite type, which is included in our consideration.

### 3. Results and discussion

Solving the Schrödinger equation for the electron and hole single-particle energies and wavefunctions, one can compute the nanocrystal's optical gap  $\Delta$  represented as the sum of two parts:  $\Delta = \Delta_0 + \delta$ . The first of these is the single-particle gap  $\Delta_0$  defined exclusively by the quantum confinement effect without self-polarization and excitonic corrections. In turn,  $\Delta_0$  is the sum of the bulk silicon bandgap  $\epsilon_g = 1.17$  eV and the single-particle energies of the electron and the hole counted from the corresponding band edges of the bulk Si. The second part,  $\delta$ , stands for the correction to  $\Delta_0$  caused by the polarization fields and the direct Coulomb electron-hole interaction. Correspondingly, the total correction  $\delta$  consists of two parts: polarization correction,  $\delta_p$ , and Coulomb correction,  $\delta_c$ .

To the first order of perturbation theory, the polarization correction  $\delta_p$  equals the matrix element of the total 'polarization' potential energy:

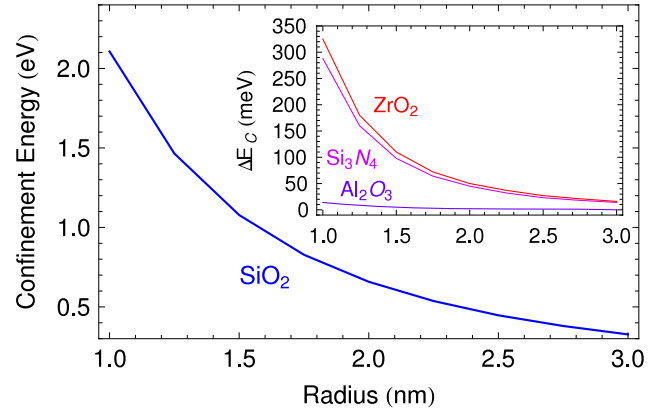
$$\delta_p = \langle \psi_e | V_{sp} | \psi_e \rangle + \langle \psi_h | V_{sp} | \psi_h \rangle + \langle \psi_e \psi_h | V_{eh}^{(p)} | \psi_e \psi_h \rangle. \quad (5)$$

Here, single-particle wavefunctions  $\psi_e$  and  $\psi_h$  describe the electron and hole ground states, respectively. The Coulomb shift  $\delta_c$  is defined to first order as

$$\delta_c = \langle \psi_e \psi_h | V_{eh}^{(c)} | \psi_e \psi_h \rangle. \quad (6)$$

Thus, the total bandgap correction has the form:  $\delta = \delta_p + \delta_c$ .

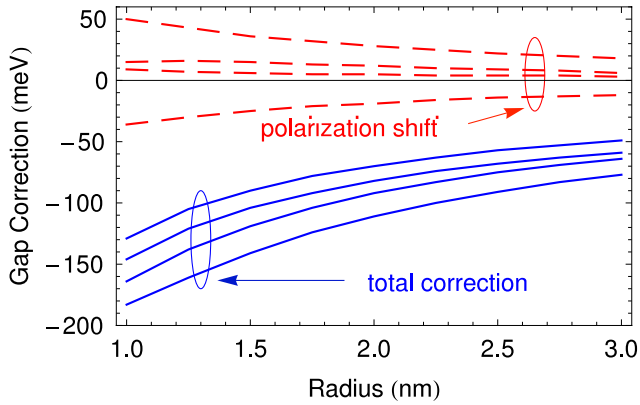
When computing the single-particle wavefunctions, we assume the  $\mathbf{k} \cdot \mathbf{p}$  Hamiltonian operator outside the nanocrystal to be the same as that employed inside [19, 20]. Strictly speaking, such an assumption is, of course, incorrect. Nevertheless, we have to apply some macroscopic procedure, like the  $\mathbf{k} \cdot \mathbf{p}$  method, for the amorphous surroundings in order to retain a unified approach for the description of the electronic states in the system. This treatment is, in part, justified by the weak penetration of the wavefunctions into the outer region which causes only a small contribution to the optical gap and its corrections. As a result, we characterize the outer material, including the transition layer, by the potential barriers  $U_e$  and  $U_h$  for the electrons and the holes, respectively. This is the only way which distinguishes between the dielectric matrix and the nanocrystal within the framework of our model.



**Figure 2.** Size dependence of the confinement energy  $E_C$  of a non-interacting electron-hole pair in silicon nanocrystal embedded in an SiO<sub>2</sub> matrix. Inset shows the differences of the confinement energies for nanocrystals embedded in SiO<sub>2</sub> and in other matrices indicated in the inset.

As has been already mentioned above, in the present paper, we examine, in particular, the effect of a host dielectric matrix on the optical gap of silicon nanocrystals embedded in this matrix. We consider several amorphous matrices, in which photoluminescence of nanocrystalline silicon was observed: SiO<sub>2</sub> (see, e.g., [27]); Si<sub>3</sub>N<sub>4</sub> [28], Al<sub>2</sub>O<sub>3</sub> [29, 30] and ZrO<sub>2</sub> [31]. An external dielectric can influence the bandgap of Si nanocrystals via two 'mechanisms', as was pointed out above. First, the confining potential leads to the size quantization of the electron and hole energies in the nanocrystal. These energies, in common with the bandgap of the bulk Si, define the single-particle gap  $\Delta_0$ . Second, the difference in dielectric constants of the host matrix and the nanocrystal induces the polarization charges at the interface and, consequently, the polarization fields which correct the nanocrystal bandgap. Because of different values of band offsets, as well as of dielectric constants for different matrices (see table 1), it is possible to expect some quantitative, and even qualitative, features in the formation of the optical gap of Si nanocrystals surrounded by different oxides or nitrides.

Size dependence of the confinement energy  $E_C = \Delta_0 - \epsilon_g$  of the non-interacting electron-hole pair in Si nanocrystals placed in SiO<sub>2</sub> is presented in figure 2. The dependence is approximately described by the law:  $E_C \sim R^{-b}$ ; with  $b$  varying from 1.67 to 1.9 as  $R$  increases from 1 to 3 nm. The inset shows  $\Delta E_C = E_C^{\text{SiO}_2} - E_C^X$  as a function of the dot radius, where  $X$  stands for the surrounding matrix: Si<sub>3</sub>N<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub>. One can see that, when the surrounding matrix is SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, the confinement energies almost coincide since  $\Delta E_C = E_C^{\text{SiO}_2} - E_C^{\text{Al}_2\text{O}_3}$  remains small enough at any  $R$ .  $\Delta E_C$  for Si<sub>3</sub>N<sub>4</sub>, and ZrO<sub>2</sub> are not so small, but remain very close, i.e. the confinement energies in these cases have close values as well. This is obviously due to the close values of the band offsets (potential barriers for the carriers) at the interfaces Si/SiO<sub>2</sub> or Si/Al<sub>2</sub>O<sub>3</sub>, as well as at the Si/Si<sub>3</sub>N<sub>4</sub> or Si/ZrO<sub>2</sub> interfaces. At the same time, significant difference in the bandgaps (and, correspondingly, in the band offsets) of SiO<sub>2</sub> (8.9 eV) or Al<sub>2</sub>O<sub>3</sub> (8.8 eV), and Si<sub>3</sub>N<sub>4</sub> (5.3 eV) or



**Figure 3.** Total and polarization corrections to the single-particle gap of Si nanocrystals as functions of the nanocrystal radius at the transition layer thickness  $a = 0.2$  nm. The surrounding matrix is (from top to bottom): SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>.

ZrO<sub>2</sub> (5 eV) provides a considerable (of the order of tens of a per cent) shift of the confinement energy. Note also that the parameter  $b$  for the case of the ZrO<sub>2</sub> matrix varies from 1.5 to 1.8 as  $R$  increases from 1 to 3 nm. We can thus conclude that the bandgap width of the surrounding dielectric is an essential factor affecting both single-particle and optical gaps of a silicon nanocrystal.

Corrections to the single-particle gap  $\Delta_0$  caused by both the polarization fields and the direct screened electron–hole Coulomb interaction at  $a = 0.2$  nm are shown in figure 3 for all the dielectric matrices mentioned above. We have depicted in the figure the total correction  $\delta$  and, separately, the polarization correction  $\delta_p$ . It is worth noting that the total correction is of the same order of magnitude as the difference in the confinement energies (or in the single-particle gaps)  $\Delta E_C$  for nanocrystals embedded in matrices with strongly different bandgaps. In contrast, the polarization correction turns out to be sufficiently small compared to  $\delta$ , and especially compared to  $\Delta E_C$ . Consequently, the polarization fields do not contribute substantially to the optical gap of Si crystallites.

This is a consequence of the compensation effect. Separately, the single-particle (the first two terms on the right-hand side of equation (5)) and the two-particle (the third term on the right-hand side of equation (5)) polarization corrections are large enough. For the SiO<sub>2</sub> matrix, their values equal 270 meV and  $-220$  meV, respectively, for the nanocrystal with  $R = 1$  nm. However, because of their opposite signs these terms considerably compensate each other. As a result, the total polarization shift is relatively small.

Earlier, the compensation effect in Si crystallites has been discussed within the framework of the empirical pseudopotential [16] and the tight-binding [17] calculations. It was found that the single-particle self-polarization correction and the two-particle polarization correction almost cancel each other. Admittedly, Delerue *et al* [17] have found the compensation to be incomplete. It was presumably due to the inclusion of the direct screened Coulomb interaction into the two-particle compensating contribution. According to our estimations, the Coulomb shift is less than 0.15–0.2 eV for

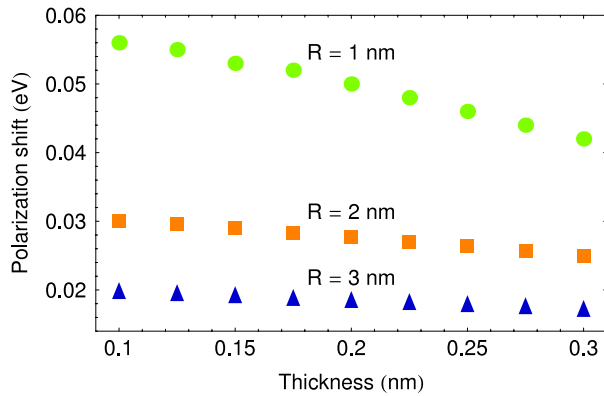
1 nm radius nanocrystals. This magnitude agrees well with the uncompensated part of the total gap correction that was obtained by Delerue *et al* [17].

Note that the polarization shift and the compensation efficiency strongly depends on the host matrix as seen in figure 3. In particular, the total polarization correction can change its sign when the dielectric constant of the matrix becomes greater than that of silicon. In this case a negative polarization shift adds to the negative Coulomb shift  $\delta_c$  and increases the total correction  $\delta$ . For this reason,  $\delta$  for Si crystallites surrounded by a ZrO<sub>2</sub> matrix is maximal over all the considered cases. In fact, this is a direct consequence of the polarization fields' dependence on  $\epsilon_s - \epsilon_d$ . The polarization shift becomes considerably smaller if the dielectric constants of silicon and the surrounding matrix are close. For instance, for Si<sub>3</sub>N<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> matrices,  $\delta_p$  does not exceed 16 and 10 meV, respectively. Such small values are due to not only the compensation effect but also the weakness of both the single- and two-particle polarization corrections. For instance, in the case of the Al<sub>2</sub>O<sub>3</sub> matrix the magnitudes of the single- and two-particle polarization corrections do not exceed 30 meV and 21 meV, respectively. For SiO<sub>2</sub> or ZrO<sub>2</sub> surroundings, the polarization correction becomes considerably greater than that for Si<sub>3</sub>N<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> but, nevertheless, appreciably less than  $\delta$  and  $\Delta E_C$ .

Thus, in any case, the total polarization correction remains small compared to  $\delta_c$ . We have found the Coulomb shift  $\delta_c$  to be insensitive to the dielectric constant of the surrounding matrix, because the wavefunctions of the carriers weakly penetrate outside the nanocrystal. Therefore, the main contribution to  $\delta_c$  comes from the direct Coulomb electron–hole interaction when the carriers are situated within the quantum dot. In this case, the Coulomb interaction is  $\epsilon_s$  times weakened by the valence electrons of silicon, and does not depend, in fact, on  $\epsilon_d$ . The difference in  $\delta_c$  values is mainly due to the different band offsets but not to the different  $\epsilon_d$ . At  $R = 1$  nm,  $\delta_c$  has the values  $-0.18$  eV for SiO<sub>2</sub>,  $-0.16$  eV for Si<sub>3</sub>N<sub>4</sub>,  $-0.17$  eV for Al<sub>2</sub>O<sub>3</sub>, and  $-0.15$  eV for ZrO<sub>2</sub>. Absolute values of  $\delta_c$  reduce as  $R$  increases. At  $R = 3$  nm,  $\delta_c \approx -66$  meV, independent of the dielectric environment.

The total correction  $\delta$  is of the same order of magnitude as  $\Delta E_C$ . For the surrounding matrices considered in the present paper, we obtain the total correction equal to  $-0.13$  eV for SiO<sub>2</sub>,  $-0.15$  eV for Si<sub>3</sub>N<sub>4</sub>,  $-0.16$  eV for Al<sub>2</sub>O<sub>3</sub>, and  $-0.18$  eV for ZrO<sub>2</sub> at  $R = 1$  nm. As the nanocrystal radius increases, the magnitude of the total correction gradually drops and becomes approximately two times less at  $R = 3$  nm.

Previous calculations carried out for silicon nanocrystals embedded in an infinitely wide bandgap material [12, 14, 15] gave the total correction close to  $-0.25$  eV [12],  $-0.4$  eV [14] and  $-0.3$  eV [15] for 1 nm radius nanocrystal, with the correction decreasing approximately as  $R^{-1}$  with increasing size. Ferreira and Proetto [13] accepted the barrier heights equal to the electron affinity of the corresponding bulk material for electrons, and infinity for holes. They found an exciton correction of the order of  $-0.2$  eV for a 1 nm radius dot. As the nanocrystal size increases, the magnitude of this correction decreased as  $R^{-0.7}$ . However, the authors (as

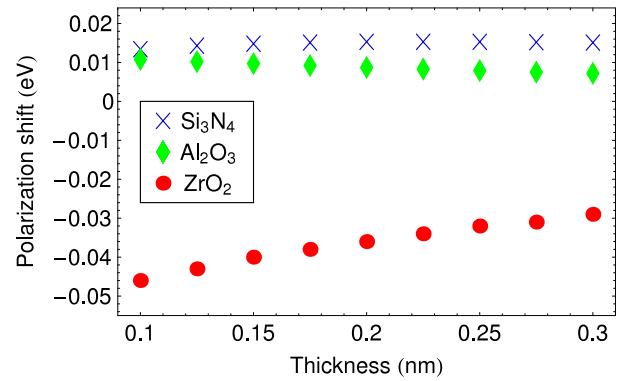


**Figure 4.** Polarization correction as a function of the transition layer thickness for the system  $\text{SiO}_2\text{:nc-Si}$  at three different nanocrystal radii indicated in the figure.

well as the authors of some other works [12, 14]) treated the potential energy of an electron–hole pair in a nanocrystal similar to bulk silicon as  $V = -e^2/\epsilon_s r_{eh}$ , without taking into account any polarization fields. The interaction with the polarization fields has been taken into account by Moskalenko and Yassievich [15] who supposed silicon nanocrystals to be embedded in an  $\text{SiO}_2$  matrix with  $\epsilon_d = 4$ . As one can see, the values of the total shift  $\delta$  obtained in the present work are somewhat less than those calculated earlier [12–15]. It is clear, however, that the main reason for this discrepancy lies in the approximation of infinite barriers that was used, in fact, in all the cited works, which strongly enhances the correction’s magnitude.

Let us finally discuss the sensitivity of the investigated system to the transition layer thickness. For this purpose we have depicted the total polarization correction  $\delta_p$  as a function of  $a$ . The dependence  $\delta_p(a)$  for the system  $\text{SiO}_2\text{:nc-Si}$  at three different values of the nanocrystal radii, and within reasonable range of the layer thickness, is shown in figure 4. One can see that the polarization correction increases as the crystallite radius decreases but sufficiently slowly varies with changing the layer thickness. A similar smooth behaviour of  $\delta_p(a)$  is observed for the other dielectric matrices (see figure 5). Absolute values of  $\delta_p(a)$  for these three matrices are less than the one obtained for the system  $\text{SiO}_2\text{:nc-Si}$  at the same nanocrystal radii. This is naturally explained by the greater relative difference in the dielectric constants for the  $\text{Si/SiO}_2$  interface. The weak dependence on the layer thickness argues in favour of the fact that concrete parameters of the layer have no fundamental significance. The presence of the layer is rather important because of the removal of the artificial divergence in the self-polarization potential energy, which leads, in turn, to overestimated values of both the nanocrystal gap and its correction.

The Coulomb correction  $\delta_c$  is, in fact, independent of the transition layer thickness. For example, for 1 nm radius nanocrystals in  $\text{SiO}_2$ ,  $\delta_c$  remains constant and equal to  $-0.18$  eV at  $0 < a < 3$  nm. As was already pointed out, the values of  $\delta_c$  for the same nanocrystals embedded in all the other matrices are as follows:  $-0.16$  eV for  $\text{Si}_3\text{N}_4$ ,  $-0.17$  eV for  $\text{Al}_2\text{O}_3$ , and  $-0.15$  eV for  $\text{ZrO}_2$ . These values also remain



**Figure 5.** Polarization correction as a function of the transition layer thickness at  $R = 1$  nm for three different surroundings shown in the figure.

constant within the range considered here ( $0 < a < 3$  nm) of layer thicknesses. Thus, it is indeed possible to conclude that the Coulomb shift is not sensitive to the presence of the transition layer, as was already mentioned earlier.

#### 4. Conclusion

Summarizing our consideration, one can formulate some basic statements reflecting the essence of the investigation performed.

First of all, it has been shown that the influence of the host matrix on the single-particle and optical gaps of silicon nanocrystals is mainly due to a quantum confinement. Franceschetti and Zunger [16] have already pointed out a determinative role of the confining potential in the formation of the exciton spectrum in a silicon quantum dot. They found the single-particle and optical gaps to be only slightly different because of the relatively small contribution of the direct Coulomb interaction to the optical gap. However, they did not examine the effect of different insulating matrices on the nanocrystal’s energy spectrum. We have found that the dispersion of the gap values can be large enough for different surrounding materials. Varying the matrix and, consequently, the band offsets, it is possible to attain essential shifts of the energy levels of electrons and holes in a nanocrystal, which results in an essential change of the nanocrystal’s gap or, similarly, of the confinement energy. In contrast, polarization fields weakly affect the optical gap for all the matrices considered. Their contribution to the gap correction is 1–2 orders of magnitude less than the dispersion of the gap values for different matrices. One may conclude that, in contrast to the quantum wires [1], in silicon quantum dots the polarization shift  $\delta_p$  of the exciton energy is sufficiently small.

As was shown, the polarization correction, being always small, weakly depends on the transition layer thickness. Nevertheless, the role of the layer is very important. Its presence allows one to consider a realistic model of a quantum dot with finite potential barriers, which provides us with real values of the bandgap corrections.

One more factor substantively influencing the optical gap of Si nanocrystals is the direct screened Coulomb electron–

hole interaction always reducing the gap. The Coulomb correction  $\delta_c$  turns out to be much more than the polarization correction, and comparable with some typical values of  $\Delta E_C$ . Moreover, for nanocrystals with radii about, or more than, 2 nm, the Coulomb shift becomes even greater than maximal  $\Delta E_C$  equal to  $E_C^{\text{SiO}_2} - E_C^{\text{ZrO}_2}$ . Thus, the direct Coulomb interaction becomes a determinative factor influencing the optical gap corrections for 2–3 nm radius nanocrystals.

Note at last that the optical gap decrease caused by the direct Coulomb and polarization fields in silicon nanocrystals is considerably less than the basic optical gap  $\Delta_0$  and confinement energy  $E_C$ , both defined by a size quantization. This justifies an application of the perturbation theory in our calculations.

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