Effects of dielectric discontinuity on the ground-state energy of charged Si dots covered with a

SiO_2 layer

Effects of dielectric discontinuity on the ground-state energy of charged Si dots covered with a SiO$_2$ layer

Masao Iwamatsu†, Makoto Fujiwara, Naohisa Happo and Kenju Horii

Department of Computer Engineering, Hiroshima City University, 3-4-1 Ozuka-higashi, Asaminami-ku, Hiroshima 731-31, Japan

Abstract. The one- and two-electron ground-state energies of singly and doubly charged silicon (Si) dots modelled by a sphere covered with a silicon dioxide (SiO$_2$) layer embedded in various dielectric media can be calculated as functions of the sphere size and the thickness of the oxide by extending the work of Allan *et al* and Babić *et al*. The electron-self-polarization, electron–electron and electron-polarization energies are treated by first-order perturbation theory, taking the confined free-electron state as the unperturbed state. By changing the thickness of the oxides or the surrounding dielectric medium, the applied voltage required for the tunnelling of one electron when one electron already exists inside the dot is greatly reduced. We discuss the possible consequence of electron tunnelling in a Si dot and the electroluminescence of porous Si.

1. Introduction

Since the discovery of the visible-light emission from porous silicon (Si) [1], there has been growing interest [2, 3] in the electronic and optical properties of various types of nanoscale Si. There is also a steady interest in electron transport by resonance tunnelling [4] in a double barrier composed of nanoscale Si clusters in an amorphous silicon dioxide (SiO$_2$) matrix [5]. Experimental evidence of strong single-charge effects in the operation of Si nano-crystal memory due to Coulomb blockades and three-dimensional confinement has also appeared in the literature recently [6]. Electroluminescence from various Si nanostructures has also been investigated [2, 7–9].

In the Si nanostructure, it appears that the quantum confinement and charging effect of the Si dot covered with an SiO$_2$ layer embedded in various media plays a dominant role in optical as well as transport properties. In this short report, we will consider the one- and two-electron ground-state energies of a spherical Si dot covered with an SiO$_2$ layer embedded in an infinite medium, similar to that considered in the work of Babić *et al* [10] and Allan *et al* [7], as a guide to fabricating efficient electroluminescent devices and single-electron devices from the silicon nanostructure.

2. Model

The model system that we consider (see figure 1) consists of a dielectric sphere of radius *a* with a dielectric constant ϵ_1 (region I), a surrounding layer with outer radius *b* and inner radius *a* with a dielectric constant ϵ_2 (region II), and an outermost region with a dielectric

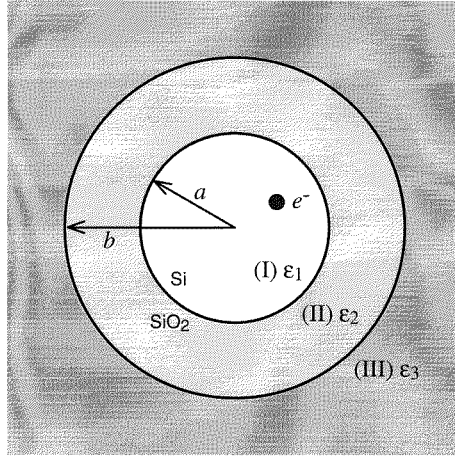† To whom any correspondence should be addressed (e-mail: iwamatsu@ce.hiroshima-cu.ac.jp).

Figure 1. A schematic diagram of a silicon dot covered with silicon dioxide embedded in a dielectric medium. Region I is a silicon dot modelled by a sphere with radius a. Region II is an amorphous silicon dioxide layer, and region III is a surrounding third medium.

constant ϵ_3 (region III). More specifically, we will regard region I as the nanoscale Si cluster (dot), and region II as the oxidized layer, whose existence can be directly [11] and indirectly [12] verified in the light-emitting Si nanostructure, and region III as the surrounding medium. A similar dielectric problem of a spherical semiconductor quantum was considered by Allan *et al* [7] and others [10, 13]. However, they considered a dot directly embedded in an infinite surrounding medium without a finite oxide layer [7, 13] or directly embedded in infinite silicon dioxide (SiO_2) [10].

The electrostatic problem of this system can be studied by the standard textbook method [13, 14]. The electrostatic potential $\phi(\mathbf{r})$ at point $\mathbf{r}$, created by a point charge having q at $\mathbf{s}$ within spherical region I, consists of a direct Coulomb potential as well as an indirect polarization potential ϕ_{pl} created by the image charge

$$\phi(\mathbf{r}) = \frac{q}{4\pi\epsilon_0\epsilon_1|\mathbf{r}-\mathbf{s}|} + \phi_{\mathrm{pl}}(\mathbf{r}) \tag{1}$$

where

$$\phi_{\mathrm{pl}}(\mathbf{r}) = \frac{q}{4\pi\epsilon_0\epsilon_1}\sum_{l=0}^{\infty} A_l r^l s^l P_l(\cos\theta). \tag{2}$$

P_l is the Legendre polynomial and θ is the angle between $\mathbf{r}$ and $\mathbf{s}$. The first term is the direct Coulomb and the last term is the indirect polarization potential whose coefficient A_l is given by

$$A_l = \frac{(l+1)}{a^{2l+1}} \frac{a^{2l+1}(\epsilon_2-\epsilon_3)(\epsilon_1+l(\epsilon_1+\epsilon_2)) + b^{2l+1}(\epsilon_1-\epsilon_2)(\epsilon_3+l(\epsilon_2+\epsilon_3))}{M_l} \tag{3}$$

with the denominator M_l given by

$$M_l = a^{2l+1}(\epsilon_1-\epsilon_2)(\epsilon_2-\epsilon_3)l(l+1) + b^{2l+1}(\epsilon_2+l(\epsilon_1+\epsilon_2))(\epsilon_3+l(\epsilon_2+\epsilon_3)). \tag{4}$$

We note that $b \to a$ or $\epsilon_2 = \epsilon_3$ gives the well documented result [10, 13]

$$A_l \to \frac{(l+1)}{a^{2l+1}} \frac{\epsilon_1-\epsilon_3}{\epsilon_3+l(\epsilon_1+\epsilon_3)} \tag{5}$$

for the dot covered by an infinite medium with the dielectric constant ϵ_3.

Although they are irrelevant to the present discussion, we will present the expressions for the electrostatic potential for regions II and III outside this sphere for the sake of completeness. The potential ϕ_2 in the layer region II is given by

$$\phi_2(r) = \frac{q}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \left(C_l r^l + \frac{D_l}{r^{l+1}} \right) s^l P_l(\cos\theta) \tag{6}$$

where

$$C_l = (\epsilon_2 - \epsilon_3)(l+1)(2l+1)/M_l \tag{7}$$

and

$$D_l = (2l+1)(\epsilon_3 + l(\epsilon_2 + \epsilon_3))b^{2l+1}/M_l. \tag{8}$$

Similarly, the potential ϕ_3 of the outermost region III is given by

$$\phi_3(r) = \frac{q}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \frac{F_l}{r^{l+1}} s^l P_l(\cos\theta) \tag{9}$$

where

$$F_l = (2l+1)^2 \epsilon_2 b^{2l+1}/M_l \tag{10}$$

and the denominator M_l is given by equation (4).

When we put one electron having the charge q into this Si dot, the electron creates a polarization potential ϕ_p given by the second term of (1). This electron then interacts with the polarization potential it has created itself, known as the self-polarization energy. This energy becomes

$$V_s(r) = \frac{q^2}{8\pi\epsilon_0\epsilon_1} \sum_{l=0}^{\infty} A_l r^{2l}. \tag{11}$$

The factor $1/8\pi\epsilon_0\epsilon_1$ comes from the self-energy correction $1/2$ and the factor $1/4\pi\epsilon_0\epsilon_1$ of equation (2).

When there are two electrons at r_1 and r_2 in the dot, there are altogether four electrostatic energies, listed below.

(i) The two self-polarization energies $V_s(r_1)$ and $V_s(r_2)$ for each electron.
(ii) The direct Coulomb energy between the two electrons

$$V_c(r_1, r_2) = \frac{q^2}{4\pi\epsilon_0\epsilon_1|r_1 - r_2|}. \tag{12}$$

(iii) The polarization energy, which is the energy of interaction between the electron and the image charge created by another electron, given by

$$V_p(r_1, r_2) = \frac{q^2}{4\pi\epsilon_0\epsilon_1} \sum_{l=0}^{\infty} A_l r_1^l r_2^l \tag{13}$$

where the coefficient A_l is given by (3).

3. Ground-state energy

Next the ground-state energies are calculated using the perturbation theory by regarding the above electrostatic energies as perturbations. It is implicitly assumed that the size of the dot is of the order of a nanometre, and that the kinetic energy is dominant in relation to the total energy [10]. Therefore we are going to look at the *strong-confinement regime* [15].

The Hamiltonian for the one-electron case is given by

$$H = -\frac{\hbar^2}{2m_e^*}\nabla^2 + V(\boldsymbol{r}) + V_s(\boldsymbol{r}) \tag{14}$$

where m_e^* is the effective mass of the conduction electron in the Si dot, $V(\boldsymbol{r})$ is the infinite barrier potential for the electron, which confines the electron within this Si sphere with radius a. $V_s(\boldsymbol{r})$ is the self-polarization energy (11).

It is well recognized that the effective-mass equation and the infinite barrier potential cannot give a quantitative account of the energy levels in a dot [16]. However, since our main purpose in this report is to find the qualitative effect of the finite oxide layer on the ground-state energy level, we will use this effective-mass model to make the formulation as simple as possible. A simple inclusion of the finite barrier potential [13, 16, 17], for example, will improve our results quantitatively.

If we regard the self-polarization energy as a perturbation, then the wavefunction $\psi_0(\boldsymbol{r})$ for the ground state is given by [15]

$$\psi_0(\boldsymbol{r}) = \sqrt{\frac{\pi}{2a^3}} j_0(\pi r/a) \tag{15}$$

where j_0 is the spherical Bessel function, and the unperturbed ground-state energy E_0 is given by

$$E_0 = \frac{\hbar^2}{2m_e^*}\left(\frac{\pi}{a}\right)^2. \tag{16}$$

We use the effective mass of Si, $m_e^* = 0.26m_e$, where m_e is the electron mass, derived from $1/m_e^* = (1/3)(1/m_l^* + 2/m_t^*)$ with $m_l^* = 0.916m_e$ and $m_t^* = 0.19m_e$ are the longitudinal and the transverse effective masses of the conduction electron. Then we find

$$E_0 = \frac{1.446}{(a \text{ (nm)})^2} \text{ eV} \tag{17}$$

where the energy is given in eV and the radius a in nanometres.

The first-order perturbation energy $E_s = \langle \phi_0(\boldsymbol{r})|V_s(\boldsymbol{r})|\psi_0(\boldsymbol{r})\rangle$ of the self-polarization energy V_s is given by

$$E_s = \frac{q^2}{8\pi\epsilon_0\epsilon_1 a} S_s \tag{18}$$

where S_s is a function of the ratio b/a as well as of the three dielectric constants ϵ_1, ϵ_2 and ϵ_3, and is given by the series

$$S_s = 2\pi^2 \sum_{l=0}^{\infty} a^{2l+1} A_l \int_0^1 j_0^2(\pi x)x^{2l+2}\,\mathrm{d}x$$

$$= 2\pi^2 \sum_{l=0}^{\infty} \frac{(l+1)[(\epsilon_2 - \epsilon_3)(\epsilon_1 + l(\epsilon_{1,2})) + (b/a)^{2l+1}(\epsilon_1 - \epsilon_2)(\epsilon_3 + l(\epsilon_{2,3}))]}{(\epsilon_1 - \epsilon_2)(\epsilon_2 - \epsilon_3)l(l+1) + (b/a)^{2l+1}(\epsilon_2 + l(\epsilon_{1,2}))(\epsilon_3 + l(\epsilon_{2,3}))}$$

$$\times \int_0^1 j_0^2(\pi x)x^{2l+2}\,\mathrm{d}x \tag{19}$$

where, in this expression *only*, we have replaced $\epsilon_1 + \epsilon_2$ by $\epsilon_{1,2}$, and $\epsilon_2 + \epsilon_3$ by $\epsilon_{2,3}$, to assist with the layout.

This series should be numerically evaluated [10], and the final result has the form

$$E_{\mathrm{s}} = \frac{\eta_{\mathrm{s}}}{(a \text{ (nm)})} \text{ eV.} \tag{20}$$

So far we have not considered the size dependence of the Si sphere's dielectric constant. Several recent theoretical works [18–20], have shown that the size dependence of the dielectric constant is significant. In this work, we will include the radius dependence of the Si sphere's dielectric constant, for which we employ the interpolation formula proposed by Lannoo *et al* [20, 7]:

$$\epsilon_1 - 1 = \frac{11.4 - 1}{1 + (0.92/a)^{1.18}} \tag{21}$$

where the sphere radius a is given in nm. The dielectric constant becomes a function of the dot radius and is reduced from the value 11.4 of the bulk Si as the dot grows smaller, as the energy gap opens up due to the quantum confinement of the free carrier [18–20]. For example, the dielectric constant of a Si dot with radius $a = 1$ (nm) becomes $\epsilon_1 = 6.456$, which is about 50% of the bulk dielectric constant. The parameter η_{s} in (20) is not a constant but a function of the radius a.
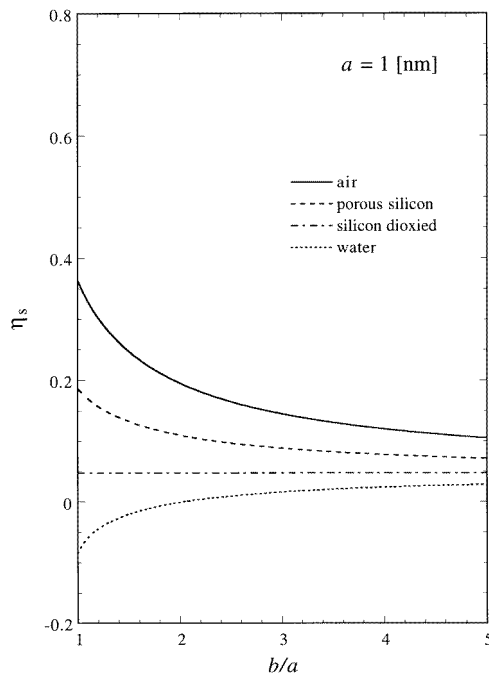

Figure 2. The coefficient η_{s} of the self-polarization energy as a function of the ratio b/a of the oxide thickness $b - a$ to the dot radius a. The dot radius is $a = 1$ (nm). Note that it is negative when $\epsilon_3 > \epsilon_1$ and b/a is less than ∼2.

We showed the η_{s} as functions of the thickness of the oxides represented by the ratio b/a in figure 2, when the dielectric constants of the surrounding medium are $\epsilon_3 = 1$ (air), $\epsilon_3 = 1.77$ (porous silicon with a porosity of 74% [7, 21]), $\epsilon_3 = 4$ (silicon dioxide), and

$\epsilon_3 = 80$ (water). We considered a Si dot with the dot radius $a = 1$ (nm) and the dielectric constant $\epsilon_1 = 6.456$ calculated from (21).

We note that the sign of η_s depends on that of the effective image charge, which becomes positive for an electron when the dielectric constant ϵ_3 of the surrounding medium is higher than that of the Si sphere ϵ_1, and the thickness of the oxide is thin. In such a case, the increase in the electronic energy level due to quantum confinement weakens, and the injection of the electron should occur at a lower threshold voltage. The change in sign of η_s occurs when $b/a \sim 2$; therefore this image-charge effect which weakens the strong-confinement effect on the kinetic energy is effective when the thickness of the oxide is less than about 50% of the radius of the dots. In table 1, we show the numerical value of η_s for $b/a = 1.0$ (without oxide), $b/a = 1.1$ (thin oxide), $b/a = 2.0$ (thick oxide) and $b/a = 5$ (very thick oxide) when the dot radius $a = 1$ (nm) and the dielectric constant $\epsilon_1 = 6.456$, and the dot is embedded in various media.

Table 1. Numerical values of η_s for a Si dot covered with SiO_2 embedded in various media with different levels of oxidization b/a when the dot radius $a = 1$ (nm) and $\epsilon_1 = 6.456$. Note that when $b/a \to \infty$, the dot is embedded in bulk SiO_2 and $\eta_s \to 0.047$ [5], while when $b/a = 1.0$, the dot is embedded in the third medium with the dielectric constant ϵ_3 and, in particular, η_s becomes negative when $\epsilon_3 > \epsilon_1$.

	$b/a = 1.0$	$b/a = 1.1$	$b/a = 2.0$	$b/a = 5.0$
Air ($\epsilon_3 = 1$)	0.364	0.329	0.195	0.105
Porous silicon ($\epsilon_3 = 1.77$)	0.186	0.169	0.110	0.072
Silicon dioxide ($\epsilon_3 = 4$)	0.047	0.047	0.047	0.047
Silicon ($\epsilon_3 = 11.4$)	−0.037	−0.023	0.014	0.034
Water ($\epsilon_3 = 80$)	−0.084	−0.059	−0.001	0.029
Metals ($\epsilon_3 = \infty$)	−0.093	−0.066	−0.004	0.028

The dependence on the size a (in nm) of the one-electron ground-state energy is given by

$$E_{\text{tot}}^{(1)} = E_0 + E_s = \frac{1.446}{a^2} + \frac{\eta_s}{a} \tag{22}$$

in eV. We have to recall that η_s is also a function of a. Naturally, when the oxide is thin, the effect of this oxide is small, and the behaviour of the energy level is close to that of the Si dots directly embedded in the medium with the dielectric constant ϵ_3.

The two-electron Hamiltonian is given by

$$H = -\frac{\hbar^2}{2m_e^*}(\nabla_1^2 + \nabla_2^2) + V(\boldsymbol{r}_1) + V(\boldsymbol{r}_2) + V_s(\boldsymbol{r}_1) + V_s(\boldsymbol{r}_2) + V_c(\boldsymbol{r}_1, \boldsymbol{r}_2) + V_p(\boldsymbol{r}_1, \boldsymbol{r}_2). \tag{23}$$

Now the four electrostatic energies V_s (two cases), V_c and V_p are the perturbations.

The self-polarization energy is given by (20), and the first-order perturbation energy $E_c = \langle \psi_0(\boldsymbol{r}_1)\psi_0(\boldsymbol{r}_2)|V_c(\boldsymbol{r}_1, \boldsymbol{r}_2)|\psi_0(\boldsymbol{r}_1)\psi_0(\boldsymbol{r}_1)\rangle$ of the direct Coulomb energy (12) was calculated in [10], and is given by

$$E_c = \frac{2.57}{\epsilon_1 a \ \text{(nm)}} \ \text{eV}. \tag{24}$$

Only the $l = 0$ component survives [10, 22] in the first-order perturbation energy $E_p = \langle \psi_0(\boldsymbol{r}_1)\psi_0(\boldsymbol{r}_2)|V_p(\boldsymbol{r}_1, \boldsymbol{r}_2)|\psi_0(\boldsymbol{r}_1)\psi_0(\boldsymbol{r}_1)\rangle$ of the polarization potential (13), and the
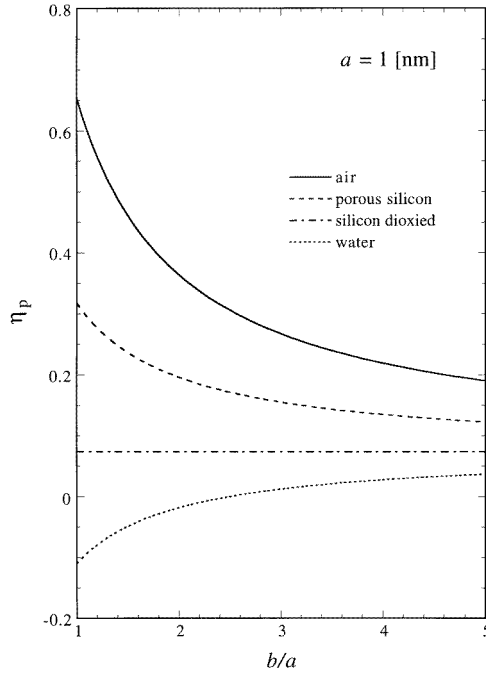
Figure 3. The coefficient η_p of the polarization energy as a function of the ratio b/a of the oxide thickness to the dot radius. The dot radius is $a = 1$ (nm). Note that it is negative when $\epsilon_3 > \epsilon_1$ and b/a is less than ~ 2.

result is written as

$$E_p = \frac{\eta_p}{a} \tag{25}$$

where the coefficient η_p is given by an analytic formula:

$$\eta_p = \frac{q^2}{4\pi\epsilon_0\epsilon_1} \frac{a(\epsilon_2 - \epsilon_3)\epsilon_1 + b(\epsilon_1 - \epsilon_2)\epsilon_3}{b\epsilon_2\epsilon_3}. \tag{26}$$

We showed the η_p as functions of the thickness of the oxides represented by the ratio b/a in figure 3, where the energy E_p is given in eV, and the radius a is in nm. Again, we considered a Si dot with the dot radius $a = 1$ (nm) as in table 1. As in the case of η_s, because of the reversal of the sign of the image charge, the sign of η_p, and hence the sign of the potential V_p, becomes negative when $\epsilon_3 > \epsilon_1$ and the thickness of the oxide layer is low. In table 2, we showed the numerical values of η_p for various oxide thickness for a Si dot with $a = 1$ (nm).

Then, the total energy of the two-electron system is given by

$$E_{\text{tot}}^{(2)} = 2E_{\text{tot}}^{(1)} + E_c + E_p = \frac{2.892}{a^2} + \frac{2.57/\epsilon_1 + 2\eta_s + \eta_p}{a} \tag{27}$$

where the energy is given in eV and the radius a in nm, and the difference ΔE_{tot} between the two-electron and one-electron ground-state energies is given by

$$\Delta E_{\text{tot}} = E_{\text{tot}}^{(2)} - E_{\text{tot}}^{(1)} = \frac{1.446}{a^2} + \frac{2.57/\epsilon_1 + \eta_s + \eta_p}{a}. \tag{28}$$
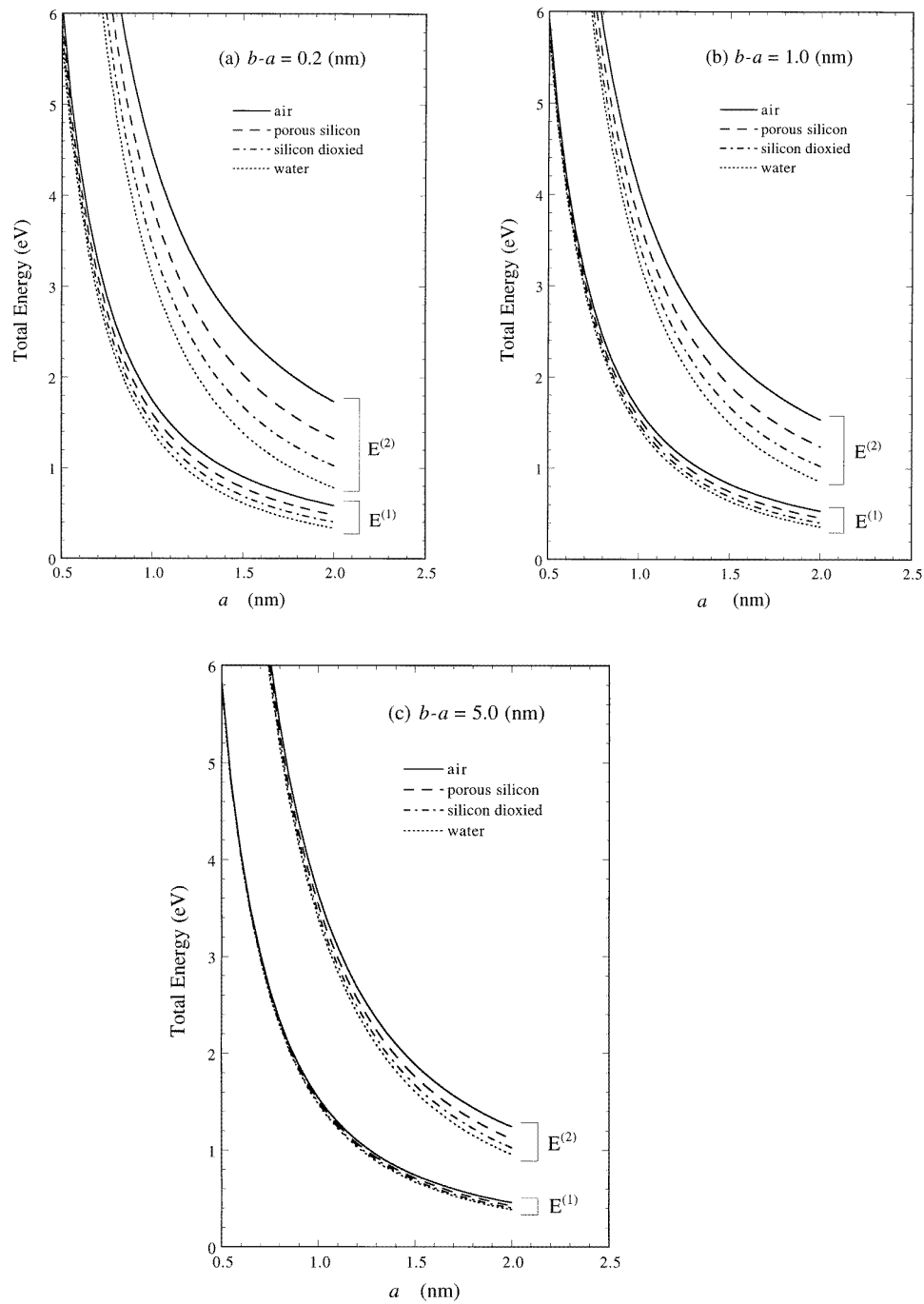
Figure 4. The one-electron ground-state energy $E_{\text{tot}}^{(1)}$ and two-electron ground-state energy $E_{\text{tot}}^{(2)}$ as functions of the dot radius a for various oxide thicknesses $b - a$: (a) thin oxide, $b - a = 0.2$ (nm); (b) thick oxide, $b - a = 1.0$ (nm); and (c) very thick oxide, $b - a = 5.0$ (nm).
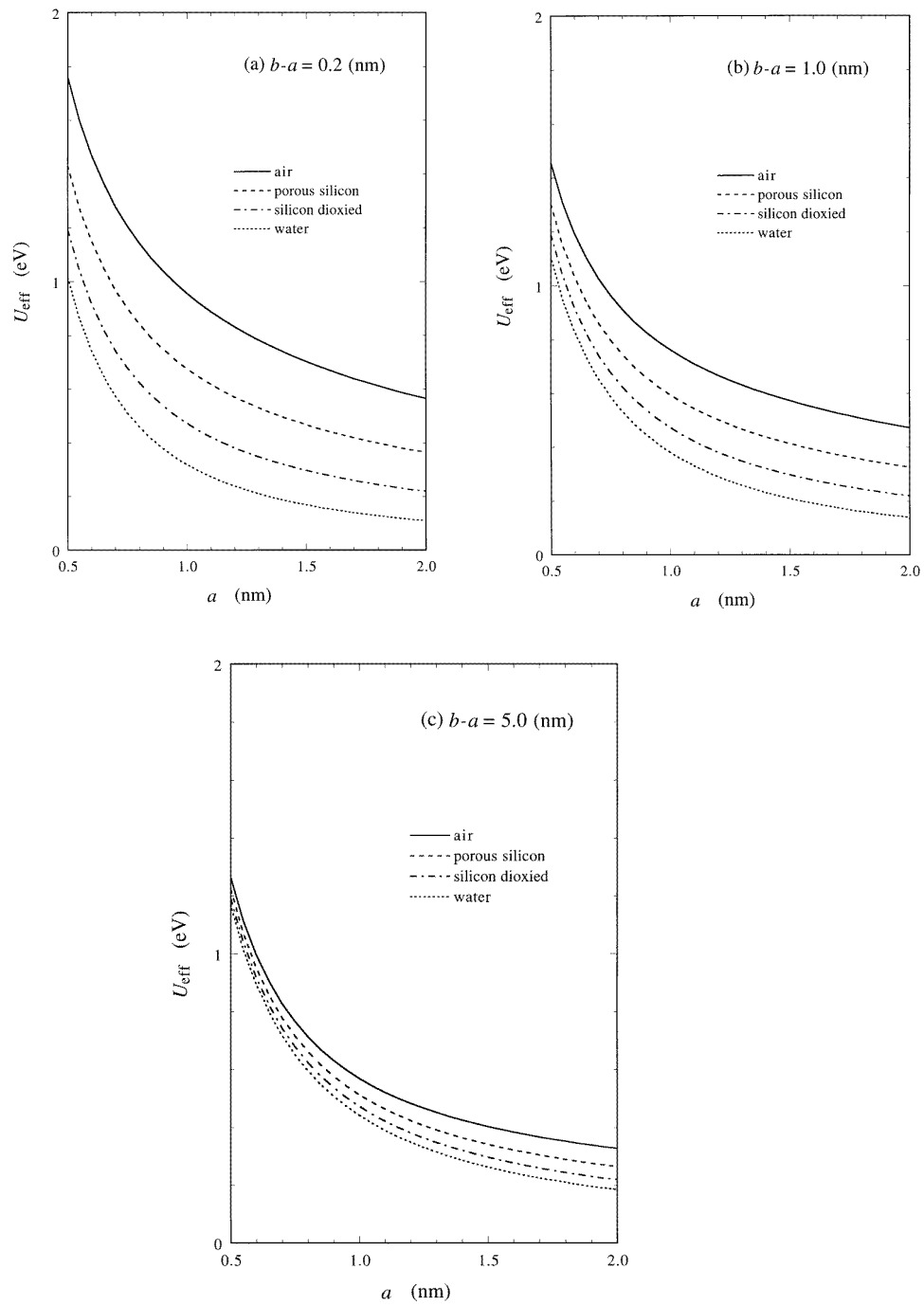
Figure 5. The effective electron–electron interaction energy U_{eff} as a function of the dot radius a for various oxide thicknesses: (a) thin oxide, $b - a = 0.2$ (nm); (b) thick oxide, $b - a = 1.0$ (nm); and (c) very thick oxide, $b - a = 5.0$ (nm).

Table 2. Numerical values of η_{p} for a Si dot covered with SiO_2 embedded in various media with different levels of oxidization b/a when the dot radius $a = 1$ (nm) and $\epsilon_1 = 6.456$. Note that when $b/a \to \infty$, the dot is embedded in bulk SiO_2 and $\eta_{\mathrm{p}} = 0.074$ [8], while when $b/a = 1$, the dot is embedded in the third medium with the dielectric constant ϵ_3.

	$b/a = 1.0$	$b/a = 1.1$	$b/a = 2.0$	$b/a = 5.0$
Air ($\epsilon_3 = 1$)	0.655	0.602	0.364	0.190
Porous silicon ($\epsilon_3 = 1.77$)	0.318	0.295	0.196	0.122
Silicon dioxide ($\epsilon_3 = 4$)	0.074	0.074	0.074	0.074
Silicon ($\epsilon_3 = 11.4$)	-0.052	-0.041	0.011	0.049
Water ($\epsilon_3 = 80$)	-0.110	-0.094	-0.018	0.037
Metals ($\epsilon_3 = \infty$)	-0.120	-0.102	-0.023	0.035

The effective electron–electron interaction energy U_{eff} [7] is given by

$$U_{\mathrm{eff}} = E_{\mathrm{tot}}^{(2)} - 2E_{\mathrm{tot}}^{(1)} = \frac{2.57/\epsilon_1 + \eta_{\mathrm{p}}}{a} \tag{29}$$

which corresponds to the difference between the ionization energy and the electron affinity of the atoms [4]. Note that, in the above formulae, η_{s} and η_{p} both depend on the dot radius. We show the size dependence of the one- and the two-electron ground-state energies in figure 4 and that of the effective electron–electron interaction energy U_{eff} in figure 5 for a thin oxide layer (a), for a thick oxide layer (b) and for a very thick oxide layer (c) as functions of the sphere radius a. As would be expected, when the oxide is thin and the dielectric constant of the surrounding medium ϵ_3 is higher than that of the dot ϵ_1, the induced image charge of the electron is positive, and the η_{p} becomes negative. Therefore, when $\epsilon_3 > \epsilon_1$, the charging effect or the Coulomb blockade represented by the effective electron–electron interaction U_{eff} is less pronounced.

4. Discussion

In this short note, we have calculated the one- and two-electron ground-state energies of a Si dot covered with a SiO_2 layer embedded in a dielectric medium. It is important to note that all of the electrostatic terms have been included. Our results for the two-electron ground state clearly indicate the importance of the self-polarization and polarization energies, which are comparable in magnitude to the direct Coulomb interaction energy. A similar conclusion had already been reached by Babić *et al* [10] for a Si dot covered with an infinite SiO_2 layer and by Allan *et al* [7] for a Si dot covered with an infinite porous Si layer. Because these polarization potentials are determined by the effective image charge, the sign of the potential can be tuned by changing the sign of the effective image charge. This effective charge can be made either positive or negative by changing the thickness of the oxide as well as the surrounding medium in our three-component model.

A comparison of the one- and two-electron ground-state energies in figure 4 shows the charging effect and the Coulomb blockade, demonstrating that the injection of more than one electron needs extra energy of the order of a few tenths of an eV to a few eV. Therefore, the theories regarding the transport properties of porous silicon and various silicon dots must take into account this charging effect. In this case, however, the charging effect comes not only from the classical electrostatic energies, but also from the quantum confinement effect of the kinetic energies. Therefore, the effective capacitance of the Si dot should be smaller than that of its classical counterpart [5]. This charging effect has been observed in

the conductance peak of the Si nano-crystal double barrier [5] and in the discrete change of the threshold voltage in the Si nano-crystal memory [6].

Interestingly, when $\epsilon_3 \rightarrow \infty$, corresponding to an experimental situation where the Si nano-crystal is in an aqueous electrolyte ($\epsilon_3 \simeq 80$) [7] or covered by a metallic electrode ($\epsilon_3 \rightarrow \infty$), as in the case of a porous silicon electroluminescence (EL) measurement, this charging effect is reduced as long as the oxide is thin ($b/a < 2$). The voltage-tunable EL observed for cathodically polarized n-type porous Si in an electrolyte by Bsiesy *et al* [9] indicates that this tunability is related to the size and efficiency distribution of the Si dot associated with an electrically induced resonant carrier injection. Therefore, the applied voltage allows for a selective excitation of specific sizes of dot. The observed range $\sim$1 eV of the peak energy correlates to the observed energy range of the one-electron ground-state energy of dots of a reasonable size [11], as shown in figure 4.

Delerue *et al* [23] has further argued that when there are two electrons in the Si dots, both the photoluminescence (PL) and the EL are quenched by the fast Auger recombination process. As the voltage is increased, the Fermi level scans the one-electron ground-state energies $E_{\mathrm{tot}}^{(1)}$ of dots of successively smaller size; then the first switching on of the EL occurs as a result of the resonant injection of the first electron. As the voltage is further increased and the Fermi level scans across the energies $E_{\mathrm{tot}}^{(1)} + U_{\mathrm{eff}}$, the EL is switched off by Auger quenching as a result of the injection of the second electron. Therefore, the effective electron–electron interaction energy U_{eff} (see figure 5) determines the observed voltage window and the narrow linewidth [9] of the EL spectrum. Although this phenomenon had been observed only for n-type porous Si, the same EL has recently been reported from p-type porous Si [24], caused by illumination. In this case, the free carrier (electron) in the p-type Si substrate is generated by photon absorption.

This charging effect in porous Si has also been noted in the air by Linnros *et al* [8]. They have found that the exhaustion and degradation occur in the porous Si EL diodes operated in ambient air when the total charge injected into the porous layer is of the same order as the number of dots available. They have suggested that the exhaustion is due to the silicon dots being filled with either one electron or one hole. Therefore, the Coulomb blockade inhibits further current transport through the porous layer.

In conclusion, from our simple model calculation, it appears that by changing the thickness of the surface-oxidized layer and the dielectric constant of the surrounding medium, it is possible to tune both the various voltage windows appearing during electron transport in the Si nanostructure and the PL and EL seen from porous Si.

Acknowledgments

References

[1] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046
[2] Collins R T, Fauchet P M and Tischler M A 1997 *Phys. Today* **50** 24
[3] Kanemitsu Y 1995 *Phys. Rep.* **263** 1
[4] Kastner M A 1993 *Phys. Today* **46** 24
[5] Tsu R 1993 *Physica* B **189** 235
[6] Tiwari S, Rana F, Chan K, Shi L and Hanafi H 1996 *Appl. Phys. Lett.* **69** 1232
[7] Allan G, Delerue C, Lannoo M and Martin E 1995 *Phys. Rev.* B **52** 11 982

[8] Linnros J, Lalic N, Knápek P, Luterová K, Kočka J, Fejfar A and Pelant I 1996 *Appl. Phys. Lett.* **69** 833

[9] Bsiesy A, Muller F, Ligeon M, Gaspard F, Hérino R, Romestain R and Vial J C 1994 *Appl. Phys. Lett.* **65** 3371

[10] Babić D, Tsu R and Green R F 1992 *Phys. Rev.* B **45** 14 150

[11] Kanemitsu Y, Ogawa T, Shiraishi K and Takeda K 1993 *Phys. Rev.* B **48** 4883

[12] Vial J C, Bsiesy A, Gaspard F, Hérino R, Ligeon M, Muller F, Romestain R and Macfarlane R M 1992 *Phys. Rev.* B **45** 14 171

[13] Brus L E 1983 *J. Chem. Phys.* **79** 5566

[14] Böttcher J F 1973 *Theory of Electric Polarization* 2nd edn, vol 1 (Amsterdam: Elsevier)

[15] Bányai L and Koch S W 1993 *Semiconductor Quantum Dots* (Singapore: World Scientific)

[16] Delley B and Steigmeier E F 1995 *Appl. Phys. Lett.* **67** 2370

[17] Fishman G, Mihalcescu I and Romestain R 1993 *Phys. Rev.* B **48** 1464

[18] Tsu R and Babić D 1994 *Appl. Phys. Lett.* **64** 1806

[19] Wang L W and Zunger A 1994 *Phys. Rev. Lett.* **73** 1039

[20] Lannoo M, Delerue C and Allan G 1995 *Phys. Rev. Lett.* **74** 3415

[21] Sagnes I, Halimaoui A, Vincent G and Badoz P A 1993 *Appl. Phys. Lett.* **62** 1155

[22] Brus L E 1984 *J. Chem. Phys.* **80** 4403

[23] Delerue C, Lannoo M, Allan G, Martin E, Mihalcescu I, Vial J C, Romestain R, Muller F and Bsiesy A 1995 *Phys. Rev. Lett.* **75** 2228

[24] Peter L M and Wielgosz 1996 *Appl. Phys. Lett.* **69** 806