

# Surface-passivation-induced optical changes in Ge quantum dots

F. A. Reboredo\* and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401

-Received 25 September 2000; published 29 May 2001!

One of the most interesting properties of quantum dots is the possibility to tune the band gap as a function of their size. Here we explore the possibility of changing the lifetime of the lowest-energy excited state by altering the surface passivation. We show that a moderately electronegative passivation potential can induce long-lived excitons without appreciable changes to the band gap. In addition, for such passivation the symmetry of the valence-band maximum is  $\mathcal{G}_{8_v}$  ( $t_1$  derived! instead of the more usual  $\mathcal{G}_{8_v}$  ( $t_2$  derived!). This reverses the effect of the exchange interaction on the bright-dark exciton splitting.

DOI: 10.1103/PhysRevB.63.235314

PACS number-s!: 78.67.Hc, 73.21.La, 71.35.-y

## I. INTRODUCTION

The order of the single-particle energy levels of different symmetries in nanostructures controls much of their optical and transport properties. In near-spherical quantum dots made of either diamond-like -Si, Ge! or zinc-blende -InP, InAs! materials, the allowed single-particle orbital symmetries are  $a_1$ ,  $a_2$ ,  $e$ ,  $t_1$ , and  $t_2$ . These orbital symmetries give rise to specific selection rules. These global symmetries can be rationalized, in the context of the envelope-function approximation, as the product of the symmetry of the underlying bulk Bloch function -e.g.,  $G_{15v}$  and  $G_{1c}$ , that transform as  $t_2$  and  $a_1$ , respectively! and the envelope function -e.g.,  $a_1$  and  $t_2$ , that are most  $s$  and  $p$  like respectively!. As shown in Table I, one can distinguish a few cases of orbital symmetries and the resulting excitonic symmetries. For example, the most commonly encountered cases -labeled “case I”! of direct-gap nanostructures -InP, GaAs, CdS! involves a valence band of  $t_2$  symmetry -made of a  $G_{15v}$  Bloch state and an  $a_1$  envelope! and a conduction band of  $a_1$  symmetry -made of an  $G_{1c}$  Bloch state and an  $a_1$  envelope!. The direct product  $t_2 \times a_1$  of the electron and hole symmetries gives the orbital symmetry of the excitonic wave function. In this case the 12-fold degenerate-dipole-allowed  $T_2$ . Consideration of electron-hole exchange<sup>1,2</sup> splits  $T_2$  into singlet  $^1T_2$  and triplet  $^3T_2$ , being, respectively, spin allowed and spin forbidden. In the presence of spin orbit -see below! the ground state  $^3T_2$  is split into a lower fivefold-degenerate *forbidden*  $E+T_1$  multiplet and a higher allowed  $T_2$ . Case II involves a valence band of  $t_1$  symmetry -made again of a  $G_{15v}$  Bloch function but with a  $t_2$  envelope!. If we consider the same  $a_1$ -symmetric conduction band as before, the exciton resulting of the direct product  $t_1 \times a_1 = T_1$  is now spatially forbidden for dipole transitions: Exchange splits it into a singlet  $^1T_1$  and a triplet  $^3T_1$ . In the presence of spin orbit the ground state is fivefold degenerate,  $E+T_2$ , which includes the *dipole-allowed* component  $T_2$ . We see that the question whether the valence-band maximum -VBM! has  $t_2$  or  $t_1$  orbital symmetry -or in other words, if the VBM envelope has a node or not! can decide if the exciton at threshold is orbital allowed, i.e., has a short radiative lifetime or not.

gling bonds are passivated with pseudoatomic potentials located at 1.06 Å from the Ge site, and possessing a single bound state at energy  $E_p$  which will be varied. We consider dots with radii ranging from 10.5 to 24.5 Å, containing 281–3049 Ge atoms, respectively. Single-particle energy levels and wave functions are obtained from the Hamiltonian<sup>10,11</sup>

$$H = -\frac{\hbar^2}{2am} \nabla^2 + \sum_{\mathbf{R}_{Ge}} v_{Ge}(\mathbf{r} - \mathbf{R}_{Ge}) + \sum_{\mathbf{R}_p} v_p^{(h)}(\mathbf{r} - \mathbf{R}_p). \quad -1!$$

Here  $m$  is the bare electron mass,  $a$  is a small adjustment on the electron mass intended to improve the fit, and  $v_{Ge}$  and  $v_p^{(h)}$  are the atomic local empirical pseudopotentials<sup>11</sup> of Ge and the passivant atom, respectively. We represent the Ge pseudopotential in reciprocal space, using the functional form

$$v_{Ge} = a_1 - q^2 - a_2! - a_3 e^{a_4 q^2} - 1! + b v_{Ge}^{SO}, \quad -2!$$

where  $q$  is the reciprocal-lattice wave vector,  $b$  is a coefficient adjusted to obtain the spin-orbit splittings, and  $v_{Ge}^{SO}$  is the spin-orbit interaction matrix.<sup>12</sup> The coefficients of Eq. -2! were fitted at a plane-wave cutoff of 5 Ry to obtain the bulk band structure at high symmetry points, the effective masses at the band extrema, and the spin-orbit splittings. The fitting procedure gives  $a = 1.1902645$  @Eq. -1!# and  $a_1 = 0.584954$ ,  $a_2 = 2.344131$ ,  $a_3 = 3.24496$ ,  $a_4 = 0.64970$ , and  $b = 0.213137$  in atomic units.

The passivation pseudopotential  $v_p^{(h)}$  is designed to remove all states from the gap due to dangling bonds -within 1.5 eV of the band edges!, and at the same time to model the behavior of the dot with different generic chemical passivations via different  $E_p$  values. We use

$$v_p^{(h)}(\mathbf{r}) = \frac{-1 + \hbar!}{2} \sum_{i=1}^3 b_i e^{-c_i q^2} + \frac{-1 - \hbar!}{2} b_4 e^{-c_4 q^2},$$

with  $b_1 = -0.1770$ ,  $c_1 = 0.1534$ ,  $b_2 = 0.02982$ ,  $c_2 = 0.085228$ ,  $b_3 = -0.01024$ ,  $c_3 = 0.630689$ ,  $b_4 = -0.1035$ , and  $c_4 = 0.3409$  in atomic units.<sup>13</sup> Here  $\hbar$  is scanned to alter the passivation. For  $\hbar = -1$  we find that the passivant has a single bound state<sup>14</sup> with  $E_p = -18$  eV  $= E_V - 12.9$  eV, while for  $\hbar = 1$  we have  $E_p = -1.5$  eV  $= E_V + 3.6$  eV where  $E_V$  is the VBM of bulk Ge. In all cases

the gap is free of surface states and the wave function of the

potential and the size of the dot are fixed, a crossing between  $\mathcal{G}_{8v}(t_2)$  and the  $\mathcal{G}_{8v}(t_1)$  states can occur if  $D\mathcal{E}(\mathcal{G}_{8v}(t_2), \hbar)$  is different from  $D\mathcal{E}(\mathcal{G}_{8v}(t_1), \hbar)$  as a function of  $\hbar$ . As can be seen in Fig. 1-a) the  $\mathcal{G}_{8v}(t_2)$  state has an  $a_1(s)$  envelope function for  $E_p = E_V + 0.8$  eV, while for  $E_p = E_V - 12.9$  eV (Fig. 1-b) the  $\mathcal{G}_{8v}(t_1)$  VBM has a  $t_2(p)$  envelope. Because the  $s$ -like envelope function has the lowest angular momentum, within m[!M 6.985 ws5

states can travel longer distances into the vacuum barrier, and have a larger amplitude at the passivant positions than  $g_{8v}(t_1)$  states. This implies in Eq. 4 that  $a@g_{8v}(t_2) \# > a@g_{8v}(t_1) \#$ . Assuming that  $F@E_p(h) \#$  is the same for  $g_{8v}(t_2)$  and  $g_{8v}(t_1)$

## VI. OPTICAL CONSEQUENCES

We next discuss the implications of the change from a  $g_{8v}(t_2)$  VBM to a  $g_{8v}(t_1)$

lieved that both conduction- and valence-band shifts are due only to quantum confinement. However, though the amplitude of the wave-function square is four orders of magnitude smaller at the surface passivation atom than at the center of the dot, the integrated effect of all surface atoms can produce a measurable affect. For example, when  $E_p - E_V$  changes from  $-6$  eV to  $+0.8$ ,  $DE_{VBM}(R)$  and  $DE_{CBM}(R)$  change by 11% and 14%, respectively. The gap  $E_g = DE_{VBM}(R) + DE_{CBM}(R) + E_g$  remains almost constant -within 3%! because both the conduction and valence bands are dragged down by the passivation. However, the  $DE_{VBM}(R)/DE_{CBM}(R)$  ratio changes by as much as 30% due to surface passivation.

Figure 3-II! shows the case of a  $g_{8v}(t_1)$  VBM, appropriate to dots with electronegative passivation ( $E_p \lesssim E_V$ )

—

- Leung, S. Pokrant, and K. B. Whaley, *ibid.* **57**, 12 291 -1998!.
- <sup>3</sup>G. B. Grigoryan, E. M. Kazaryan, Al. L. Efros, and T. V. Yazeva, *Zh. Éksp. Teor. Fiz.* **32**, 1772 -1990! ©Sov. Phys. Solid State **32**, 1031 -1990!.
- <sup>4</sup>Al. L. Efros and A. V. Rodina, *Solid State Commun.* **72**, 645 -1984!.
- <sup>5</sup>The spin orbit is negligible compared to the quantum confinement energy of the VBM.
- <sup>6</sup>B. Delley and E. F. Steigmeier, *Phys. Rev. B* **47**, 1397 -1993!.
- <sup>7</sup>S. Y. Ren, *Phys. Rev. B* **55**, 4665 -1997!; *Solid State Commun.* **102**, 479 -1997!.
- <sup>8</sup>F. A. Reboredo, A. Franceschetti, and A. Zunger, *Phys. Rev. B* **61**, 13 073 -2000!.
- <sup>9</sup>T. van Buuren, L. N. Dinh, L. L. Chase, W. J. Siekhaus, and L. J. Terminello, *Phys. Rev. Lett.* **80**, 3803 -1998!.
- <sup>10</sup>F. A. Reboredo and A. Zunger, *Phys. Rev. B* **62**, R2275 -2000!.
- <sup>11</sup>L. W. Wang and A. Zunger, in *Semiconductor Nanostructures*, edited by P. V. Kamat and D. Meisel -Elsevier, New York, 1996!, -Vol. 103!.
- <sup>12</sup>L. W. Wang and A. Zunger, *Phys. Rev. B* **51**, 13 798 -1995!.
- <sup>13</sup>Because of the energy cutoff in the kinetic energy of the plane-wave expansion, the real-space potential felt by the electrons is not a closed formula. Accordingly, it is better to characterize the passivation potentials with respect to its bond state.
- <sup>14</sup>The binding energies of  $v_p^h(q)$  are calculated by placing an isolated passivating atom in the supercell.
- <sup>15</sup>G. F. Koster, in *Solid State Physics*, edited by F. Seitz and D. Turnbull -Academic Press, New York, 1957!, Vol. 5, p. 173.
- <sup>16</sup>C. Cohen-Tannoudji, B. Diu, and F. Laloë, in *Quantum Mechanics* -Wiley, New York, 1977!, Vol. II, p. 984.
- <sup>17</sup>A. Franceschetti, H. Fu, L. W. Wang, and A. Zunger, *Phys. Rev. B* **60**, 1819 -1999!.
- <sup>18</sup>The spin-orbit coupling splits  $t_2$  states into  $t_2 \times g_6 = g_{8v}(t_2) + g_{6v}(t_2)$ ,  $t_1$  states into  $t_1 \times g_6 = g_{8v}(t_1) + g_7(t_1)$ , and  $e$  states into  $e \times g_6 = g_{8v}(e)$ . Because  $g_{8v}(t_2)$ ,  $g_{8v}(t_1)$ , and  $g_{8v}(e)$  have the same symmetry, they can be mixed by the spin-orbit interaction.
- <sup>19</sup>J. B. Xia and K. W. Cheah, *Phys. Rev. B* **59**, 14 876 -1999!.
- <sup>20</sup>Y. M. Niquet, G. Allan, C. Delerue, and M. Lannoo, *Appl. Phys. Lett.* **77**, 1182 -2000!.
- <sup>21</sup>The  $g_{6c}(a_1)$  symmetry is very frequent in the  $L$ -to- $X$  crossover region where the  $L$ - $X$  mixing lowers the energy of the  $g_{6c}(a_1)$  CBM states.