Surface-passivation-induced optical changes in Ge quantum dots

F. A. Reboredo* and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401
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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 g_{8_v} (t_1 derived! instead of the more usual g_{8v} (t_2 derived!. This reverses the effect of the exchange interaction on the bright-dark exciton splitting.

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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[1,2] 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* $\mathrm{E}+\mathrm{T}_1$ 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, $\mathrm{E}+\mathrm{T}_2$, 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[10,11]

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

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[11] of Ge and the passivant atom, respectively. We represent the Ge pseudopotential in reciprocal space, using the functional form

$$v_{Ge} = a_1(q^2 - a_2)/(a_3 e^{a_4 q^2} - 1) + b v_{Ge}^{SO}, \tag{2}$$

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.[12] 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 $a = 1.190\,264\,5$ [Eq. (1)] and $a_1 = 0.584\,954$, $a_2 = 2.344\,131$, $a_3 = 3.244\,96$, $a_4 = 0.649\,70$, and $b = 0.213\,137$ 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

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

with $b_1 = -0.1770$, $c_1 = 0.1534$, $b_2 = 0.029\,82$, $c_2 = 0.085\,228$, $b_3 = -0.010\,24$, $c_3 = 0.630\,689$, $b_4 = -0.1035$, and $c_4 = 0.3409$ in atomic units.[13] Here h is scanned to alter the passivation. For $h = -1$ we find that the passivant has a single bound state[14] with $E_p = -18$ eV $= E_V - 12.9$ eV, while for $h = 1$ 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 $g_{8v}(t_2)$ and the $g_{8v}(t_1)$ states can occur if $De@g_{8v}(t_2),h\#$ is different from $De@g_{8v}(t_1),h\#$ as a function of h. As can be seen in Fig. 1~a! the $g_{8v}(t_2)$ 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 $g_{8v}(t_1)$ 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 $g_{8v}(t_2$

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 $+0.8$, $\Delta E_{VBM}(R)$ and $\Delta E_{CBM}(R)$ change by 11% and 14%, respectively. The gap $E_g = \Delta E_{VBM}(R) + \Delta E_{CBM}(R) + E_g$ remains almost constant ~within 3%! because both the conduction and valence bands are dragged down by the passivation. However, the $\Delta E_{VBM}(R)/\Delta E_{CBM}(R)$ ratio changes by as much as 30% due to surface passivation.

VI. OPTICAL CONSEQUENCES

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

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

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