L-to-*X* crossover in the conduction-band minimum of Ge quantum dots

F. A. Reboredo and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 7 April 2000)

Screened-pseudopotential calculations of large ($\lesssim$3000 atoms) surface-passivated Ge quantum dots show that below a critical dot diameter that depends on the passivant, the character of the lowest conduction state changes from an *L*-derived to an *X*-derived state. Thus, in this size regime, Ge dots are Si-like. This explains the absence, in a pseudopotential description, of a crossing between the band gaps of Si and Ge dots as a function of size, predicted earlier in single-valley effective-mass calculations. The predicted $L \to X$ crossing suggests that small Ge dots will have an *X*-like, red shift of the band gap with applied pressure, as opposed to an *L*-like blue shift of large dots.

Although the band gap of bulk Ge (0.76 eV) is smaller than that of bulk Si (1.17 eV), Takagahara and Takeda[1] [Fig. 1(a)] and Hill *et al.*[2] [Fig. 1(b)] predicted that small Ge quantum dots would have a *larger* band gap than Si dots of the same size. This predicted crossing of the optical gap as a function of size raises the promise of easier access to blue light emission using Ge instead of Si dots. In the effective-mass approximation,[1] (EMA) one would indeed expect a crossing of the gap energies of two semiconductors A and B at size *R* if

$$\varepsilon_A^{Bulk} - \varepsilon_B^{Bulk} = \left[\frac{1}{m_e^*(B)} + \frac{1}{m_h^*(B)} - \frac{1}{m_e^*(A)} - \frac{1}{m_h^*(A)} \right] \frac{3\alpha(\pi\hbar)^2}{8R^2}, \quad (1)$$

where ε_A^{Bulk} and ε_B^{Bulk} are the band gaps of semiconductors A and B, while $m_e^*(X)$ and $m_h^*(X)$ are the isotropic effective masses of electrons and holes, respectively, in the material X, and α is a geometric factor that depends on the shape of the dot. Whereas the measured masses of Si and Ge indeed suggest[1] that a crossing exists (at $R \approx 31$ Å), in this size regime the validity of the EMA and Eq. (1) is questionable: The observation of photoluminescence (PL) in dots made of indirect-gap semiconductors implies the presence of some $\mathbf{k}=0$ (Γ like) momentum components in the electronic wave function. But $\mathbf{k}=0$ is quite distant from the momentum corresponding to the indirect conduction-band minimum in these materials (at the *L* and near the *X* points in Ge and Si, respectively). Because the components of the wave function, which are far away from the band edges, are poorly described by the EMA, a more general method that describes the full-zone band structure is required in order to reliably account for the optical properties of such indirect-band-gap dots.

In this paper we report empirical-pseudopotential calculations for Ge dots and compare them with equivalent calculations for Si dots. We find (i) there is no clear crossing in the band-gap energies of Ge and Si dots as a function of size [Fig. 1(c)]. (ii) The reason is that the wave function at the conduction band minimum (CBM) in Ge dots changes from

being *L* character in the large size regime to being *X* character in the small size regime. Consequently, (iii) small quantum dots of Si and Ge have similar gaps and wave functions, because in both materials the CBM is derived from the minima near *X*. (iv) We predict that this change might be observed experimentally in Ge dots under pressure by noting a redshift (i.e., X_{1c}-like) of the PL with pressure for small dots, but a blueshift (i.e., L_{1c}-like) in larger dots. (v) The CBM of Ge dots mixes in more Γ character than in Si, so in
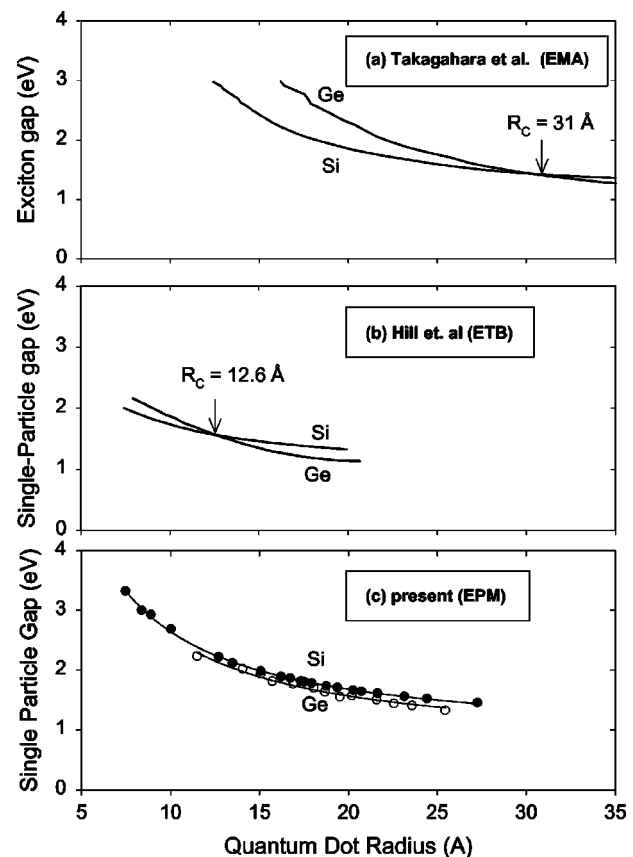

FIG. 1. Theoretical predicion for the gaps of Ge and Si dots as a function of size. (a) Takagahara and Takeda (Ref. 1) EMA calculations. (b) Hill *et al.* (Ref. 2) empirical tight binding calculation (ETB). (c) Present empirical pseudopotential calculations (EPM).

the absence of symmetry-induced selection rules, the PL efficiencies would be larger in the Ge case. Finally (vi), we find that the dependence $\varepsilon_g \sim R^{-\gamma}$ of the band gap on size is changed when band crossings exist.

We consider approximately spherical Ge crystallites centered around a Ge atom. The dots thus have T_d point-group symmetry. All Ge atoms are assumed to be located at their ideal bulk positions. The surface atoms with three dangling bonds are removed, while those with one or two dangling bonds are passivated with pseudohydrogen atoms. The passivated dots are then surrounded by a vacuum and placed in a large supercell that is repeated periodically. We calculate the electronic structure of this artificial periodic structure via ordinary "band structure" methods applied to the supercell, where the Hamiltonian, including spin-orbit, is given by[3]

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \sum_{\mathbf{R}_{Ge}} v_{Ge}(\mathbf{r}-\mathbf{R}_{Ge}) + \sum_{\mathbf{R}_P} v_P(\mathbf{r}-\mathbf{R}_P), \quad (2)$$

where m is the free electron mass while v_{Ge} and v_P are the screened-atomic-empirical pseudopotentials of Ge and the passivant. Here, v_{Ge} was fitted to the measured bulk gaps at L, near X, and at Γ, the anisotropic electron effective masses at the L and Γ points, the spin-orbit splitting, the hole masses at the Γ point, and the energies of the remaining high-symmetry points of bulk band structure. The pseudopotential v_P of the passivating v_P was fitted to remove gap states within 1.5 eV of the band edges[4] arising from the Ge dangling bonds on (111) and (100) surfaces. We thus assume that the dots are perfectly passivated and that the band-edge wave functions are confined in the bulk regions of the dots. We do not consider here the case incomplete passivation that would produce surface states due to dangling bonds. The passivation shell is characterized by its highest occupied level (HOE) E_{HOE}. In the present study, $E_{HOE} = E_{VBM} - 5.2$ eV, i.e., we assume a rather ionic passivant.

We expand the wave functions $\psi(\mathbf{r})$ in a plane wave basis set and diagonalize the Hamiltonian of Eq. (2) using the folded spectrum method.[3] The symmetry of the wave functions was obtained using the method explained in Ref. 5. In order to obtain information on the reciprocal-space representation of the dot wave function, we expanded them[6] in terms of the Bloch wave functions of bulk Ge:

$$\psi_i^{dot}(\mathbf{r}) = \sum_{n\mathbf{k}} C_{n\mathbf{k}}^{(i)}[e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}^{bulk}(\mathbf{r})], \quad (3)$$

where $u_{n\mathbf{k}}^{bulk}$ is the Bloch part of the bulk wave function, and $C_{n\mathbf{k}}^{(i)}$ is the projection of the $\psi_i^{dot}(\mathbf{r})$ on the bulk state $n\mathbf{k}$. The contribution to the dot state $\psi_i^{dot}(\mathbf{r})$ from the conduction-band-bulk-Bloch states within the momentum shell $k \rightarrow k + \Delta k$ is defined as

$$\rho_{CB}(\mathbf{k}) \simeq \Delta k^3 \sum_{n\mathbf{k}} \theta[\epsilon_{nk}^{bulk} - 1/2(\epsilon_{CBM}^{bulk} + \epsilon_{VBM}^{bulk})]|C_{n\mathbf{k}}^{(i)}|^2, \quad (4)$$

where ϵ_{nk}^{bulk} is the dispersion of the bulk-band n at wave vector $\mathbf{k}$ and $\theta(x)$ is the Heaviside function.

The indirect band gap of bulk Si is 1.17 eV while that of Ge is only 0.76, so the band gap of large ($R \rightarrow \infty$) Ge dots is expected to be smaller than for Si dots. When the size of the dots is reduced, quantum confinement effects shift both the

conduction-band-edge and the valence-band-edge energies. In effective-mass theory, the shift is in inverse proportion to the respective effective masses, so the Ge gap is expected to increase more quickly than the Si gap as R is reduced. In our pseudopotential approach we indeed find [see in Fig. 1(c)] that the blue shift of Ge dots at $R \approx 25$ Å is $\varepsilon_{Ge}^{QD} - \varepsilon_{Ge}^{Bulk} \approx 0.57$ eV, which is larger than in the Si case, $\varepsilon_{Si}^{QD} - \varepsilon_{Si}^{Bulk} \approx 0.38$ eV. However, both shifts are smaller than those predicted by the EMA,[1] (~ 0.94 eV Ge and ~ 0.42 in Si) [Fig. 1(a)]. Furthermore, in sharp contrast to the expectations based on the EMA, Fig. 1(c) shows that as the size of the dot is further reduced, the gap of Ge dots becomes similar to that of Si. This means that, although at first the gap increases more quickly in Ge dots, at some special size the dependence of the Ge gap changes to a Si-like behavior. We can explain this non-EMA effect by inspecting the structure of the wave function in reciprocal space:

L-to-X crossover. The L point in the Brillouin zone of bulk Ge is degenerate with fourfold equivalent valleys in the (111) directions. Thus, in a large quantum dot, the L minima will give rise to four energy levels (eight including spin). However, because the finite size of the dot breaks the translational symmetry, these eight levels are no longer degenerate in the dot. In fact, in absence of spin-orbit coupling,[7] the eight bulk states at the L point would give rise in a T_d-symmetric dot to six states with t_2 orbital symmetry and two states with a_1 orbital symmetry with a total of eight levels. When spin-orbit is included, the sixfold t_2 states split into a twofold γ_7 state and a fourfold γ_8 state, while the a_1 orbital is a twofold state with γ_6 symmetry. The calculated symmetry projections for the largest dot studied ($R = 24.5$ Å) confirm these conclusions: We find that the first eight electron levels are in a multiplet,[8] have symmetries γ_7, γ_8, and γ_6 and degeneracies 2, 4, and 2, respectively. In Fig. 2 we show the character $\rho_{CB}(\mathbf{k})$ of some wave functions in a Ge dot. We represent $\rho_{CB}(\mathbf{k})$ of Eq. (4) by solid circles centered at point $\mathbf{k}$ with a diameter proportional to $\sqrt[3]{\rho_{CB}(\mathbf{k})}$ projected in the (001) plane. The inset shows the corresponding projected positions of the L and X points. As expected from the above consideration for such a large dot, the first eight electron states are derived primarily from the L state [see Fig. 2(a)].

The next group of twelve states are 50 meV higher in energy. These states are not derived from L state, instead they are derived from the six degenerate valleys near the X point in the Brillouin zone, similar to those found in the lowest conduction band of Si dots.[5] For brevity, we will refer to them as the X states or X-derived states, although the minima in the bulk conduction band are not at the X points but near X. One example of these X-derived states (CB+8 with γ_8 symmetry) is shown in Fig. 2(b). Note that a single-valley description of the conduction band[1] would have completely ignored the existence of the energetically close X-derived states.

For $R = 24.5$ Å, Ge dots already show important $L-X$ mixings in the conduction band minimum [small dots near X regions in 2 (a)], so one might suspect an $L \rightarrow X$ crossing to occur if the size of the dot is reduced. This is shown in Fig. 3, demonstrating that as the size of the dot is reduced, the character of the wave function of the lowest electronic state changes from being essentially L derived in large dots, to
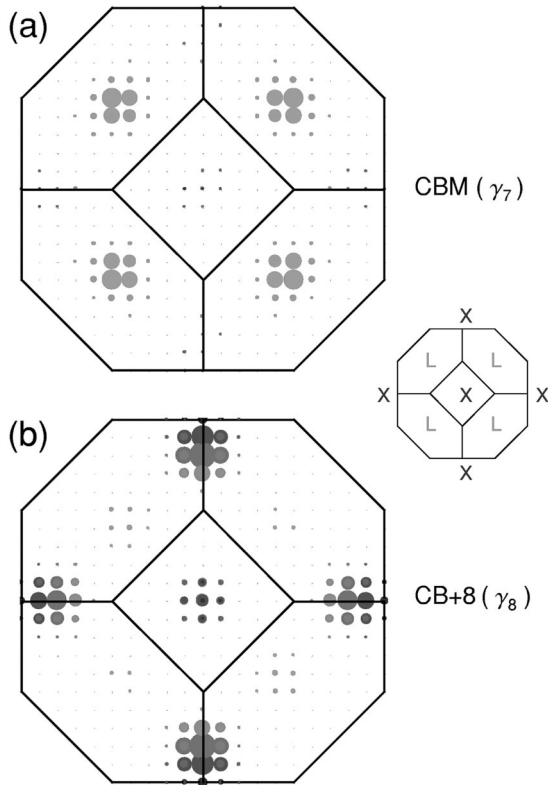
FIG. 2. Brillouin zone projection [see Eq. (4)] of the conduction-band wave functions for different energies. The size of the points shows the weight of the wave function $\rho_{CB}(\mathbf{k})$ on a particular $\mathbf{k}$ point which is projected in the (001) plane. The inset shows the position of the L and X points after being projected in the (001) plane. Case (a) corresponds to the CBM (an L derived state) while case (b) to CB+8 which is X derived.

FIG. 3. Brillouin zone projection of the CBM wave functions as a function of size. Same conventions as in Fig. 2

being essentially X derived in small dots. The particular size where the X-to-L crossing occurs depends on the surface passivation potential E_{HOE}. Deep passivation potentials (E_{HOE} far lower than VBM) shift the crossing to smaller sizes while shallower passivation shift it to larger sizes. Similar crossings in the character of the CBM wave functions were already found in GaAs quantum dots where the CBM changes from Γ to X as a function of size.[9]

The single-band EMA prediction of crossings between the gaps of Si and Ge dots[1] can be reinterpreted as a crossing between the L and X valleys of the conduction band of Ge itself. The conduction-band structure of Ge near X is indeed very similar to the one of Si near X both in the value of the masses and in the band gap, implying that Ge dots have a ''hidden Silicon personality.'' Therefore, even in the frame of the EMA, one would expect to find a critical size R for Ge dots where states derived from the minima near X become lower in energy than those derived from the L points. Because the Ge effective masses in the conduction-band minima near X and at L are both highly anisotropic, similar crossings from L to X can occur as a function of shape alone.

Because the CBM wave function in Ge dots becomes X-like at small sizes, the band gap of Ge dots is similar to that of Si dots [Fig. 1 (c)]. This explains the absence crossings in the band gaps of Ge and Si dots for small sizes in our pseudopotential calculation.

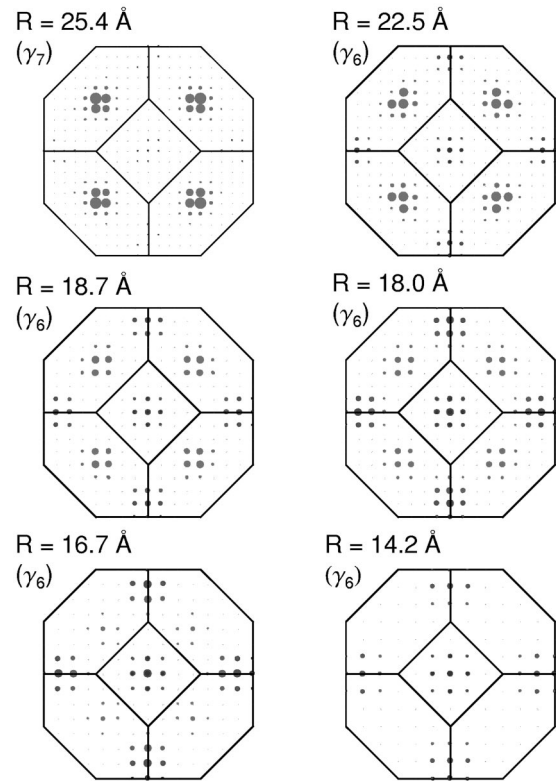**The size-scaling of the band gap**. In quantum dots made

of semiconductors such as InP, Si, or CdSe, where the second-conduction-band minima is energetically far above the lowest-conduction-band minima (e.g., in Si Γ-$X=2.38$ eV, $L-X=1.17$ eV), we have found a size dependence of the band gap of the form $\varepsilon_{\text{gap}}^{Bulk}+AR^{-\gamma}$. Palummo *et al.*[10] have recently reported tight-binding calculations for Ge quantum dots finding size dependences of the gap of the form same with γ as low as 0.8. However, in Ge, where the L, Γ, and X conduction-band extrema all lie in a narrow energy window of 0.4 eV, we find that there are crossings of different minima as a function of the size or shape of the dot. Therefore, a single dependence $\varepsilon_{\text{Ge}}^{Bulk}+A/R^{\gamma}$ is not appropriate to fit the Ge band gap data (in particular in the crossover region), because the parameters A, γ, and $\varepsilon_{\text{Ge}}^{Bulk}$ must change as a function of size. For example, for small dots one should use $\varepsilon_{\text{Ge}}^{Bulk}$ corresponding to the $X-\Gamma$ gap and not the $L-\Gamma$ gap as in large dots.

Expected PL intensities. In dots made of indirect-gap-bulk solids, the emission intensities depend on the extent of Γ-like mixing into the lowest conduction-band state of the dot. Though in bulk Ge the Γ conduction-band minimum is only 0.14 eV higher in energy than the L states, the mass at Γ ($m_{e\Gamma}^{*}=0.038\ m_e$) is lighter than at the minima at L and near the X points. Therefore, the states derived mainly from Γ remain above the CBM for all dot sizes. However, because in the bulk the Γ minimum is much closer in energy to the CBM Ge (0.14 eV) than Si (2.38 eV), in quantum dots the Γ components of the wave functions are much larger in Ge than in Si. For example, in a dot with $R\approx11$ Å, the Γ component in Ge dots is four orders of magnitude larger than in Si dots. Therefore, provided that symmetry-derived selection
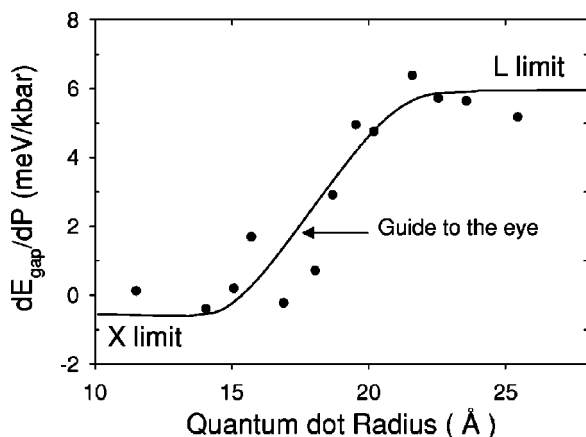
FIG. 4. Calculated pressure dependence of the band gap of Ge dots as a function of size.

rules are absent and that the surface is perfectly passivated, radiative electron-hole recombination times are expected to be much shorter in Ge dots than in Si dots.

Pressure dependence of the band gaps. In bulk Ge the pressure dependence of the L and X and Γ conduction-band edges are 5.8, -0.7, and 14.6 meV/kbar, respectively.[11] Because in Ge dots the CBM wave function changes from L-like to X-like as a function of size, one would expect a qualitative change in the pressure coefficients as a function of size. Our calculated values of the pressure coefficients of the band gap Ge dots are given in Fig. 4 showing a direct correlation with the change on the character of the CBM as a function of size (see Fig. 3): we predict that the band gap of large dots behaves under pressure like the bulk $\Gamma_v - L_c$ gap, having a positive pressure coefficient, while the band gap of small dots behaves like the bulk $\Gamma_v - X_c$ gap, having a slightly negative pressure coefficient.[12] The measurement of the pressure dependence would be a direct test of the predicted L-to-X crossing in the structure of conduction-band-minimum wave function of Ge dots.

In summary, Ge quantum dots present states which are derived from different minima of the bulk conduction band and lie very close in energy. Because the quantum-confinement shift as a function of size is different for each minima, the conduction-band structure changes from being L-derived in large dots to being X-derived in small dots. Because the deformation potentials of the X and L states are different, we predict that the change of the wave-function structure of dots as a function of size could be measured as changes in the pressure dependence of the gap of Ge quantum dots. Since the wave function corresponding to the conduction-band minimum of small Ge dots is Si-like, the band gaps of Ge and Si dots do not cross as a function of the dot size.

[1] T. Takagahara and K. Takeda, Phys. Rev. B **53**, R4205 (1996).

[2] N. A. Hill, S. Pokrant, and A. J. Hill, J. Phys. Chem. B **103**, 3156 (1999).

[3] L. W. Wang and A. Zunger, in *Semiconductor Nanostructures*, Vol. 103, edited by P. V. Kamat and D. Meisel (Elsevier Science B.V., New York, 1996).

[4] M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. B **54**, 13 759 (1996).

[5] F. A. Reboredo, A A. Franceschetti, and A. Zunger, Phys. Rev. B **61**, 13 073 (2000).

[6] H. Fu and A. Zunger, Phys. Rev. B **57**, R15 064 (1998).

[7] S. Y. Ren, Phys. Rev. B **55**, 4665 (1997); Solid State Commun. **102**, 479 (1997).

[8] The energy splittings in the L-derived multiplet in large ($R \approx 25$ Å) Ge dots are smaller than 1 meV.

[9] A. Franceschetti and A. Zunger, Appl. Phys. Lett. **68**, 3455 (1996).

[10] M. Palummo, G. Onda, and R. Del Sole, Phys. Status Solidi A **175**, 23 (1999).

[11] S.-H. Wei and A. Zunger, Phys. Rev. B **60**, 5404 (1999).

[12] The "noise" of the points is due to the fact that in our atomistic description the dots are not perfectly spherical. As the size of the dot is reduced the atoms near the (100) and (111) directions are not removed continuously but in a discrete way which affect in a different way the X and L derived states.