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

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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 $L \rightarrow X$ 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

$$\epsilon_A^{Bulk} - \epsilon_B^{Bulk} = \frac{1}{m_e^*(B)} + \frac{1}{m_h^*(B)} - \frac{1}{m_e^*(A)} - \frac{1}{m_h^*(A)} \frac{3(\hbar)^2}{8R^2}, \quad (1)$$

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 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 (~respectively!. Because the comp
whichXcharac-ter in the small size regime. (ii
tum dots of Si and Ge have similar gaps and w
because in both materials the CBM is deri
minima near *X*. (iv) We predict that this cha
observed experimentally in Ge dots under press
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

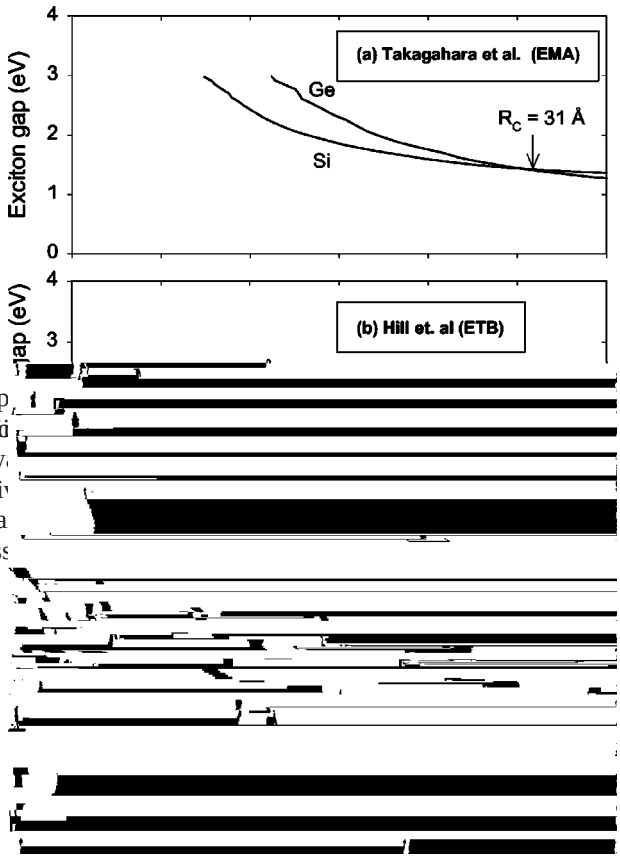

FIG. 1. Theoretical predicion for the gaps of Ge and Si dots as a function of size. (a) Takagahara and Takeda (Ref. 1) EMA calculations. (b) Hill *et al.* (Ref. 2) empirical tight binding calculation (ETB). (c) Present empirical pseudopotential calculations (EPM).

the absence of symmetry-induced selection rules, the PL efficiencies would be larger in the Ge case. Finally (vi), we find that the dependence $\prime_g \sim R^{-}$ 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, $E_{\mathrm{HOE}}=E_{VBM}-5.2$

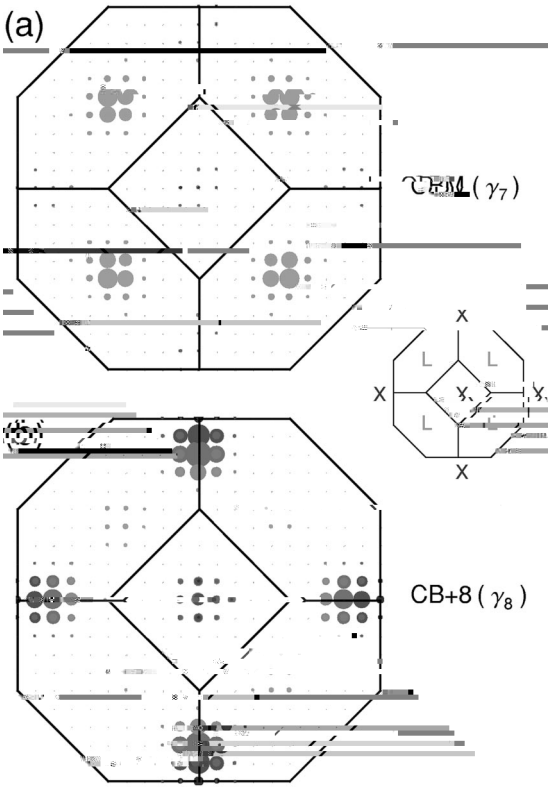

FIG. 2. Brillouin zone projection [see Eq. (4)] of the conduction-band wave functions for different energies. The size of the points shows the weight of the wave function $\psi_{CB}(\mathbf{k})$ on a particular $\mathbf{k}$ point which is projected in the (001) plane. The inset shows the position of 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.

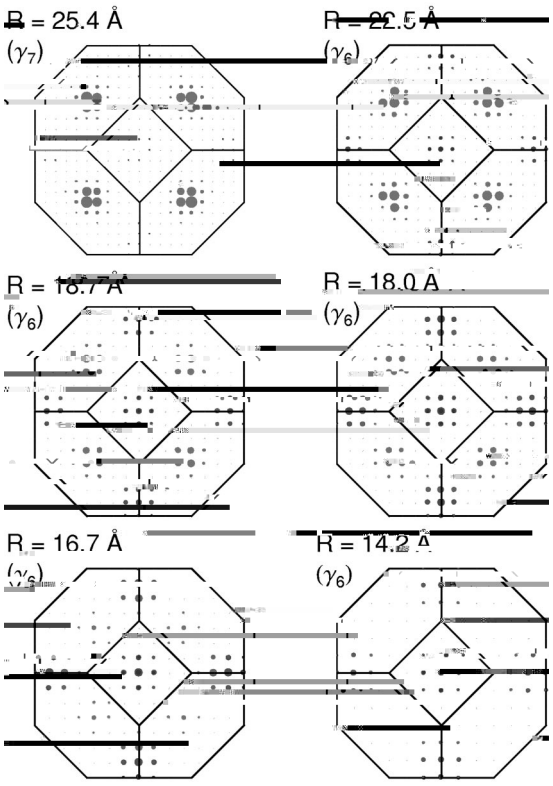

FIG. 3. Brillouin zone projection of the CBM wave functions as a function of size. Same conventions as in Fig. 2

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 $E_{\mathrm{gap}}^{Bulk}+AR^{-}$. 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 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 $E_{\mathrm{Ge}}^{Bulk}+A/R$ is not appropriate to fit the Ge band gap data (in particular in the crossover region), because the parameters A, , and E_{Ge}^{Bulk} must change as a function of size. For example, for small dots one should use E_{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 $R\approx 11$ Å, the Γ component in Ge dots is four orders of magnitude larger than in Si dots. Therefore, provided that symmetry-derived selection

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