Quantum-Size Effects on the Pressure-Induced Direct-to-Indirect Band-Gap Transition in InP Quantum Dots

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We predict that the difference in quantum confinement energies of Γ-like and X-like conduction states in a covalent quantum dot will cause the direct-to-indirect transition to occur at substantially lower pressure than in the bulk material. Furthermore, the first-order transition in the bulk is predicted to become, for certain dot sizes, a second-order transition. Measurements of the “anticrossing gap” could thus be used to obtain unique information on the Γ-X-L interband couplings, predicted here to be surprisingly large (50–100 meV). [S0031-9007(98)06301-7]

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Reduced dimensions usually cause pressure-induced structural phase transitions to occur at elevated pressures relative to the bulk solid. This is the case for the AlAs layers in AlAs/GaAs superlattices [1], for the transition to β-Sn structure in Si nanocrystals [2], and for the wurzite-to-rocksalt structure in CdSe dots [3]. Here, we show that reduced dimensionality causes another type of pressure-induced transition—the electronic direct-to-indirect transition—to occur at reduced pressures relative to the bulk.

Pressure-induced direct (Γ1c) to indirect (X1c) transitions occur in bulk zinc blende semiconductors [4,5] because under pressure, the Γ1c energy goes up while the X1c energy goes down [Figs. 1(a) and 1(b)]. This reflects the fundamentally different charge distribution in these two states [6]: the antibonding Γ1c state has a node along the cation-anion bond, so it is destabilized (moves up in energy) as this bond is shortened, while the X1c state has most of its amplitude in the interstitial volume, where no atoms exist. As a result of the different signs of the Γ1c and X1c deformation potentials, in materials where at zero pressure the energy of the X1c state is not too far above the Γ1c state (GaAs, InP, but not InAs or CdSe), a pressure-induced first-order Γ1c → X1c level crossing [7] occurs before the material is structurally phase transformed.

Reduced dimensionality can alter the energetic separation between the Γ1c-like and X1c-like states even without pressure [Figs. 1(b) and 1(c)]. This results from the fact that quantum confinement raises the energy of Γ1c (with lighter mass) faster than the energy of X1c (with heavier mass) [Figs. 1(b) and 1(c)]. Thus, if the energy of the X1c state is not too far above the Γ1c state in bulk, reduced size alone can cause a direct-to-indirect transition to occur at zero pressure. Detailed calculations [8] without pressure effect predicted this to occur in GaAs films, wires, and dots as size diminishes. Because of the larger (~0.95 eV, measured [9]) Γ1c - X1c separation in bulk InP relative to in bulk GaAs (0.55 eV [10]), no direct-to-indirect transition was predicted to occur in free-standing InP dots at zero pressure [11]. Since, however, quantum confinement in InP dots could reduce the Γ1c - X1c energy separation relative to the bulk, it might take less pressure to transform the dot than to transform the bulk into an indirect band gap [Figs. 1(c)–1(d)]. This hypothesis is examined and verified here. We show that the predicted low-pressure direct-to-indirect transition opens the door to obtaining unique information on the Γ-X-L interband mixings in dots via measurements of their energy levels vs pressure. We predict surprisingly large Γ-X-L couplings in dots (50–100 meV), suggesting that one (effective-mass) or a few (k · p) band models which neglect (or significantly restrict) such interactions may be inadequate for describing such systems.

We construct Γ-symmetric InP quantum dots by including in the model all atoms within a given radius. The dots are either P centered or In centered. All surface dangling bonds are passivated [11] by attaching to them fictitious atoms. The atomic arrays in the interior of the dot are assumed to be bulklike, which is a good approximation for passivated dots [11]. We then solve the single-particle Schrödinger equation

\[
\left\{-\frac{1}{2} \nabla^2 + \sum_{n,\alpha} V_{\alpha}(r - R_n - d_n, \Omega)\right\} \psi_i = \epsilon_{i}(\Omega) \psi_i,
\]

where

\[
\psi_i(r) = \sum_{n,\alpha} C_{i,n,\alpha} \phi_{n,\alpha}(r)
\]

\[
\epsilon_{i}(\Omega) = \frac{\hbar^2}{2m^*} \Omega^2 + \sum_{n,\alpha} V_{\alpha}(r - R_n - d_n, \Omega)
\]

\[
C_{i,n,\alpha} = \langle \phi_{n,\alpha}(r) | \psi_i(r) \rangle
\]

\[
\phi_{n,\alpha}(r) = \frac{1}{\sqrt{V}} \sum_{\mathbf{G}} \phi_{\mathbf{G}}(r) e^{i \mathbf{G} \cdot \mathbf{R}_n}
\]

\[
\phi_{\mathbf{G}}(r) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{k}} e^{i \mathbf{k} \cdot \mathbf{r}} C_{\mathbf{k},\alpha} \phi_{\mathbf{k},\alpha}(r)
\]

\[
\mathbf{G} = \mathbf{k} - \mathbf{F} \Omega
\]

\[
\mathbf{F} = \mathbf{R}_n - \mathbf{R}_m
\]

\[
\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2
\]

\[
\phi_{\mathbf{k},\alpha}(r) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{r}} e^{i \mathbf{k} \cdot \mathbf{r}} \phi_{\mathbf{r},\alpha}(r)
\]

\[
\phi_{\mathbf{r},\alpha}(r) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{k}} e^{i \mathbf{k} \cdot \mathbf{r}} C_{\mathbf{k},\alpha} \phi_{\mathbf{k},\alpha}(r)
\]

\[
\epsilon_{\mathbf{k},\alpha} = \frac{\hbar^2}{2m^*} \mathbf{k}^2 + \sum_{\mathbf{G}} V_{\alpha}(r - R_n - d_n, \Omega) e^{i \mathbf{G} \cdot \mathbf{R}_n}
\]

\[
\epsilon_{\mathbf{k},\alpha}(\Omega) = \frac{\hbar^2}{2m^*} \mathbf{k}^2 + \sum_{\mathbf{G}} V_{\alpha}(r - R_n - d_n, \Omega) e^{i \mathbf{G} \cdot \mathbf{R}_n}
\]

\[
\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2
\]

\[
\phi_{\mathbf{k},\alpha}(r) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{r}} e^{i \mathbf{k} \cdot \mathbf{r}} \phi_{\mathbf{r},\alpha}(r)
\]

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\epsilon_{\mathbf{k},\alpha}(\Omega) = \frac{\hbar^2}{2m^*} \mathbf{k}^2 + \sum_{\mathbf{G}} V_{\alpha}(r - R_n - d_n, \Omega) e^{i \mathbf{G} \cdot \mathbf{R}_n}
\]

FIG. 1. Schematic illustration of the relative energy positions of Γ1c, X1c, and L1c states of InP, showing how the Γ-X separation changes due to quantum size effect and pressure.
as a function of volume $\Omega$. Here, $\nu_\alpha(r)$ is the screened, strain-dependent nonlocal pseudopotential of atom type $\alpha$ (e.g., In, P, or passivant) fitted [11] to the measured bulk band structure and effective masses, and to the calculated [via local density approximation (LDA)] deformation potentials and charge densities. Using our pseudopotentials the calculated absolute InP deformation potentials are $-1.39$, $-7.73$, +0.88, and $-3.38$ eV for $\Gamma_{15s}$, $\Gamma_{1c}$, $X_{1c}$, and $L_{1c}$, respectively, while the ab initio LAPW (linearized augmented plane wave) values [12] are $-1.00$, $-6.26$, +0.65, $-3.30$ eV, respectively. The measured [13,14] relative $\Gamma_{1c}$-$\Gamma_{15s}$ and $X_{1c}$-$\Gamma_{15s}$ deformation potentials are $-6.40$ and +2.20 eV, respectively, compared with our calculated values $-6.34$ and +2.27 eV, respectively. To solve Eq. (1) we expand $\{|\psi_i\}$ in plane waves, and evaluate the matrix elements in this basis numerically. We diagonalize directly the Hamiltonian using the linear-size-scaling folded spectrum method [15]. We consider two experimentally accessible [2,3] dot sizes with diameters of 20.2 and 34.8 Å (175 and 891 atoms, respectively). Precisely the same method (i.e., pseudopotentials and basis set) is used to calculate the bulk band structure of InP, except that zinc blende periodic boundary conditions are applied.

Figure 2 shows the energies of the bulk InP $\Gamma_{1c}$ and $X_{1c}$ conduction states vs lattice constant $a$, exhibiting a crossing at $a = 5.5852$ Å; the deformation relative to the LDA calculated zero-pressure lattice constant (at which our pseudopotential is generated) is $\Delta a/a = 0.0414$. The measured [5] bulk $\Delta a/a = 0.0370$ corresponding to a transition pressure [5] of 112 kbar is within 10% (Table I [5,16]).

Figure 3 shows the energies of three lowest conduction states of P-centered InP dots vs lattice constant near the critical transition point. We see that unlike the bulk, where the $\Gamma \rightarrow X$ transition is first order (i.e., level crossing), the transition of the lowest conduction state in dots can be, depending on size, either first order (i.e., level crossing) or second order (i.e., level anticrossing). Table I shows the values of the deformations needed

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Bulk InP</th>
<th>P-centered InP dots</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{eq}$ (expt.)</td>
<td>5.8658*</td>
<td>...</td>
</tr>
<tr>
<td>$a_{eq}$ (calc.)</td>
<td>5.8265</td>
<td>...</td>
</tr>
<tr>
<td>$a_{1-c}$ (expt.)</td>
<td>5.6489b</td>
<td>...</td>
</tr>
<tr>
<td>$a_{1-c}$ (calc.)</td>
<td>5.5852</td>
<td>5.6862(C)</td>
</tr>
<tr>
<td>$\Delta a/a$ (expt.)</td>
<td>0.0370</td>
<td>0.0244(C)</td>
</tr>
<tr>
<td>$\Delta a/a$ (calc.)</td>
<td>0.0414</td>
<td>0.0245(AC)</td>
</tr>
</tbody>
</table>

*Ref. [16], bRef. [5]. cThe transition which occurs at lower pressure.

to obtain the direct-to-indirect transition in quantum dots: for the $D = 34.8$ Å dot, the critical deformation is predicted to be reduced to $\sim 60\%$ of the bulk value. Experimental testings of this prediction of quantum-size induced reduction in the critical pressure are needed.

The reduction of the critical pressure in dots is caused mostly by the reduction of zero-pressure $X_{1c}$-$\Gamma_{1c}$ energy separation in dot relative to in bulk. To estimate this effect we note that at zero pressure ($\Omega = \Omega_{eq}$) and for $D = 34.8$ Å dot, our calculated confinement energies $\Delta \epsilon_{\gamma}(\Omega) = \epsilon_{\gamma}^{\text{dot}}(\Omega) - \epsilon_{\gamma}^{\text{bulk}}(\Omega)$ for the lowest $\gamma = X_{1c}$-like ($\gamma = \Gamma_{1c}$-like) conduction states are 0.31 (0.58) eV.

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FIG. 2. Variations of the $\Gamma_{1c}$ and $X_{1c}$ band energies with lattice compression in bulk InP near the critical point.

FIG. 3. Variations of the three lowest conduction states $\Gamma_{1c}(\Gamma_{1c})$, $\Gamma_{1c}(X_{1c})$, and $\Gamma_{1c}(X_{1c})$ in P-centered InP dots with lattice compression near the critical point: (a) $D = 20.2$ Å dot; (b) $D = 34.8$ Å dot.

TABLE I. Calculated and measured lattice constants $a_{eq}$ (in Å) and relative deformations $\Delta a/a = (a_{eq} - a)/a_{eq}$ for direct-to-indirect transitions in bulk and in spherical quantum dots of InP. Wherever there are two rows in the table, the first row gives the values for level-crossing (C) transition, while the second row gives the values for level anticrossing (AC).
Thus, the $X_{1c}$-$\Gamma_{1c}$ energy difference is reduced in this dot by 0.27 eV relative to the bulk value.

Interestingly, (i) the confinement energies $\Delta_{\epsilon_{c}}(\Omega)$ are nearly pressure independent. They are 0.28 (0.60) eV at the transition volume $\Omega = 0.93\Omega_{\text{eq}}$, and 0.31 (0.58) eV at $\Omega_{\text{eq}}$ for the $X_{1c}$ ($\Gamma_{1c}$) state of the $D = 34.8$ Å dot. This suggests that the reduced size affects the dot’s wave function macroscopically (i.e., by altering the envelope part), while the pressure affects the wave function microscopically (by changing the periodic Bloch part). The fact that the confinement energies are close for the zero-pressure dot and for the compressed dot, provides one way to obtain the quantum size effect on those states at Brillouin-zone edge, which proved to be difficult under ambient pressure [17]. (ii) The $X_{1c}$ confinement energy obtained in our direct diagonalization approach [Eq. (1)] is surprisingly larger than what was expected from effective-mass approximation (EMA): using the calculated effective masses [11] $m_{s}^{*}(\Gamma_{1c}) = 0.095$, $m_{s}^{*}(X_{1c}) = 2.04$, the EMA gives 0.06 (1.31) eV for the confinement energy of $X_{1c}$-like ($\Gamma_{1c}$-like) conduction state. Thus, the EMA predicts that the $\Gamma \to X$ transition will already occur at zero pressure for this $D = 34.8$ Å dot. Actually, we find that an accurate description of the whole lowest bulk conduction band (not just near $\Gamma$ and $X$ as in the EMA) is needed to predict the correct $\Gamma-X$ energy separation (thus the critical pressure) in dots. (iii) Our calculations further show that the reduction of $\Gamma-X$ energy separation relative to the bulk value is not a simple monotonic function of dot size (the reduction is 0.15, 0.27, and 0.00 eV for $D = 20.2$, 34.8, and $\infty$ Å dots, respectively). (iv) One interesting issue regarding InP dots is the envelope-function symmetry of the top valence state. We find that the envelope is $s$-like both at zero pressure and near the transition pressure. This is consistent with point (i) that the pressure does not change the property due to envelope difference.

To understand the level crossings and anticrossings evident in Fig. 3 we consider the symmetries of the states of the bulk and the dots (Table II). In the diamondlike bulk band structure, the lowest $X$ conduction state is twofold degenerate (neglecting spin), while in zinc-blende band structure, it is broken into two singly degenerate states $X_{1c}$ and $X_{3c}$. In both cases, there are three equivalent $X$ valleys. In zinc blende, if the origin of the coordinate system is placed at the anion site [18], the lowest $X$ conduction state (e.g., in InP or GaP) is found [19] to be $X_{1c}$ ($s$ symmetry at the anion, $p$ symmetry at the cation), while the next lowest $X$ conduction state (about 0.4 eV higher in bulk InP) is $X_{3c}$ ($s$ symmetry at the cation, $p$ symmetry at the anion). When the anion is perturbed (e.g., P-centered dots), the new states (marked with an overbar) relate to the parent zinc-blende states (shown in parentheses) as indicated in Table II: $X_{1c}$-derived states yield the $\Gamma_{1c} \bar{\Gamma}_{1c} \bar{\Gamma}_{1c}$ states (singly and doubly degenerate, respectively), while $X_{3c}$-derived states yield the $\Gamma_{1c} \bar{\Gamma}_{1c}$ states (triply degenerate). The original zinc-blende $\Gamma_{1c}$ state retains its $\Gamma_{1c}$ symmetry. For the cation site perturbation (e.g., In-centered dots), the roles of $X_{1c}$ and $X_{3c}$ are exchanged (Table II). Now, states of the same symmetry must repel each other (anticross) in response to a symmetry-preserving perturbation. This is the case for $\Gamma_{1c}, \Gamma'_{1c}$ and $\Gamma_{1c}, \Gamma'_{1c}$. In contrast, states with different symmetries can cross. This is the case for $\Gamma_{1c}, \Gamma_{1c}$ and $\Gamma_{1c}, \Gamma_{1c}$. The symmetry considerations explain the behavior seen in Fig. 3. Figure 3(b) and Table I show that in the larger dot (34.8 Å), crossing occurs first, at $\Delta a/a = 0.0241$, while anticrossing occurs at a slightly larger deformation $\Delta a/a = 0.0245$. The order of these events can change with size [see Fig. 3(a)].

The “anticrossing gap” (the smallest energy difference between repelling curves in Fig. 3) measures the effective $\Gamma-X$ coupling (i.e., $2V_{\Gamma X}$). We find $2V_{\Gamma X} = 0$ for

<table>
<thead>
<tr>
<th>Bulk states</th>
<th>Anion-centered</th>
<th>Cation-centered</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{1c}$</td>
<td>$\Gamma_{1c}(\Gamma_{1c})$</td>
<td>$\Gamma_{1c}(\Gamma_{1c})$</td>
</tr>
<tr>
<td>$X_{1c}$</td>
<td>$\Gamma_{1c}(X_{1c}) + \Gamma_{1c}(X_{1c})$</td>
<td>$\Gamma_{1c}(X_{1c})$</td>
</tr>
<tr>
<td>$X_{3c}$</td>
<td>$\Gamma_{1c}(X_{3c})$</td>
<td>$\Gamma_{1c}(X_{3c}) + \Gamma_{1c}(X_{3c})$</td>
</tr>
<tr>
<td>$L_{1c}$</td>
<td>$\Gamma_{1c}(L_{1c}) + \Gamma_{1c}(L_{1c})$</td>
<td>$\Gamma_{1c}(L_{1c}) + \Gamma_{1c}(L_{1c})$</td>
</tr>
<tr>
<td>$\Gamma_{1c}$</td>
<td>$\Gamma_{1c}(\Gamma_{1c})$</td>
<td>$\Gamma_{1c}(\Gamma_{1c})$</td>
</tr>
</tbody>
</table>

FIG. 4. Spectral decomposition of the lowest conduction wave functions of the following P-centered dots onto those bulk states with wave vector $k$ in the plane passing $\Gamma, L, K$, $U, X$ points of zinc blende Brillouin zone: (a) $D = 20.2$ Å dot at the anticrossing transition; (b) $D = 34.8$ Å dot before the transition; (c) $D = 34.8$ Å dot after the transition. The larger the sphere size, the larger the contribution from this bulk state.
In summary, we study the interplay between quantum size and pressure effects in InP dots. We find that the quantum confinement energy is nearly independent of the pressure. We predict the $\Gamma \rightarrow X$ transitions in InP dots to occur at finite pressure (unlike GaAs [8]), but significantly below the bulk value. The unexpectedly large confinement energy for an $X$-like state is important in describing the $\Gamma$-$X$ transition. Such $\Gamma$-$X$ transitions can be used to reveal the extent of interband coupling in dots. We predict $\Gamma$-$X$ coupling of 34.2 (3.3) meV and $L$-$X$ coupling of 71.6 (10.2) meV for $D = 20.2$ Å ($D = 34.8$ Å) dots.

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[11] H. Fu and A. Zunger, Phys. Rev. B 56, 1496 (1997); 55, 1642 (1997). These papers describe the zero strain case. For the strain case, the atomic potentials are $V = V_{eq}(1 + \beta s/a_{eq})$ with $\beta = 1.125$ (1.072) for In (P) atom.