Quantum-size-induced electronic transitions in quantum dots: Indirect band-gap GaAs

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We discuss the physical origin of the previously predicted quantum-size-induced electronic transitions in

to observe the direct/indirect transition in GaAs dots. Díaz and Bryant[8] recently reported nearest-neighbor tight-binding calculations of spherical GaAs nanocrystals ranging in radius from 1 to 7 nm. They found that for dot sizes below 1.25 nm in radius, the band gap is indirect in reciprocal space, with the CBM primarily originating from the effective mass approximation. One can then calculate the critical radius R_c at which two levels α and β cross. In the single-band EMA the coupling matrix element $V_{\alpha,\beta}$ is assumed to vanish, so the levels α and β may only *cross* (as opposed to *anticross*) as a function of size. The single-band EMA approach raises the question of which effective mass should be used to describe $\varepsilon_\alpha(R)$ when α has an anisotropic effective mass, as in the case of the X and L valleys in the fcc Brillouin zone. There are three popular definitions of "effective mass" for a valley with longitudinal mass m_l and transversal mass m_t: (a) use the largest component of a given valley, (b) use the reciprocal weighted average $m^*_{\text{cond}} = 3/(1/m_l + 2/m_t)$, and (c) use the density of state mass $m^*_{\text{DOS}} = \sqrt[3]{m_l m_t^2}$. Figure 2(a) shows that if one uses the largest mass $m_l^*(X_{1c}) = 1.30$ and $m_l^*(L_{1c}) = 2.18$ then one finds a Γ-L crossing at $R = 3.4$ nm and a Γ-X crossing at R

lowest-energy confined electron states, with a_1 symmetry, of freestanding spherical GaAs dots as a function of dot size.

GaAs dot of radius $R=4.0$ nm embedded in an $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloy of varying Al concentration ($x=0.3$, 0.6, and 1.0, see Fig. 8), and (ii) a spherical GaAs dot of variable radius R (with $4<R<5$ nm) embedded in pure AlAs (Fig. 9). The results are as follows:

(i) We find that the VBM and the CBM wave functions of a $R=4.0$ nm GaAs dot embedded in $\mathrm{Al}_{0.3}\mathrm{Ga}_{0.7}\mathrm{As}$ [Fig. 8(a)] are located on the GaAs quantum dot and derive from the Γ point (Fig. 10). The band gap is direct both in real space and reciprocal space. As the Al concentration in the matrix increases [Figs. 8(b) and 8(c)], the potential barrier experienced by the Γ-derived CBM of the quantum dot increases, because the Γ_{1c} level of the alloy moves up in energy. At the same time, the X_{1c} level of the alloy moves down in energy, because the Al concentration increases. We find that the band gap of the $\mathrm{GaAs}/\mathrm{Al}_{0.6}\mathrm{Ga}_{0.4}\mathrm{As}$ system is still direct [Fig. 8(b)], but the band gap of the GaAs/AlAs system is indirect both in real space and in reciprocal space [Fig. 8(c)]. The CBM wave functions of the $R=4.0$ nm GaAs dot for different Al concentrations of the alloy ($x=0.3$, 0.6, and 1.0) clearly demonstrate the direct/indirect transition in real space (Fig. 10).

(ii) As the size of a GaAs dot embedded in pure AlAs increases from 4.0 to 5.0 nm (Fig. 9), the quantum confinement decreases, whereas the electronic levels of the alloy remain the same. As a result, the CBM changes its real-space localization from the alloy back to the quantum dot (see Figs. 9 and 10), and its reciprocal-space character from X-like to Γ-like. Figure 10 depicts the CBM wave functions of GaAs dots of radius $R=4.0$ and 4.5 nm embedded in AlAs, clearly showing the real-space electronic transition.

V. EXPERIMENTAL SITUATION FOR TESTING OUR PREDICTIONS

Our prediction of a direct-to-indirect transition for freestanding GaAs spherical nanocrystals of radius $R\sim1.6$ nm calls for experimental investigation. It appears, however, that good quality (well-passivated) freestanding GaAs nanocrystals are difficult to make. Indeed, colloidal synthesis that was very successful for CdSe (e.g., Ref. 3) has hardly been successful for GaAs. The first colloidal GaAs nanocrystals were fabricated by Olshavsky *et al.*[24] Nozik and his colleagues[25–27] systematically measured the optical spectrum of colloidal GaAs nanocrystals. After separating the nanocrystals by a series of ultrafiltrations with pore size of 700, 100, and 15 Å, they found that there was no absorption peak for the 15 Å filtrate while there was a clear peak for 700 and 100 Å filtrates. This can be due to the low concentration of nanocrystals in this colloid or to the transition becoming indirect. Malik *et al.*[28] recently fabricated GaAs nanocrystals from GaCl_3 and $\mathrm{As(NMe}_2)_3$ in 4-ethylpydidine[28] with TEM measured size from 1 to 3 nm in radius. For small GaAs nanocrystals, they observed two absorption peaks that we tentatively assign to the partially allowed Γ-to-X transitions (see Fig. 4

pulsed laser ablation method was used to synthesize spheriundergoes a simultaneous reciprocal-space (type i) and real-space (type ii) direct/indirect transition when the radius of the dot becomes smaller than a critical value R_c that depends on the alloy composition. For example, the CBM of a $R=4.0$ nm GaAs dot embedded in AlAs is localized in the AlAs matrix, and derives from the X_{1c} states of the alloy. The CBM becomes dot-localized and Γ-derived when the size of the dot increases above 5.0 nm, or alternatively when the Al concentration in the matrix decreases below $x=0.6$. Our results determine the conditions that must be satisfied to achieve a direct band gap, and thus strong photoluminescence, in GaAs nanostructures.

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[1] R. Turton, *The Quantum Dot* (Oxford University, New York, 1996).

[2] L. Bányai and S. W. Koch, *Semiconductor Quantum Dots* (World Scientific, Singapore, 1993).

[3] V. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale, H. J. Eisler, and M. G. Bawendi, Science **290**, 314 (2000).

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