phys. stat. sol. (c) **3**, No. 11, 3832–3835 (2006) / **DOI** 10.1002/pssc.200671553

Pressure-induced optoelectronic properties of InP nanocrystals: Tight-binding approach

J. G. Díaz *[1,2], **W. Jaskólski**[1], **M. Zieliński**[1], and **G. W. Bryant**[2]

[1] Instytut Fizyki UMK, Grudziądzka 5, 87-100 Toruń, Poland
[2] National Institute of Standards and Technology, Gaithersburg, MD 20899-8423, USA

Received 1 May 2006, revised 14 June 2006, accepted 18 July 2006

PACS 73.22.–f, 78.67.Bf

An empirical tight-binding theory is used to investigate pressure effects on the electronic and optical properties of InP nanocrystals. For bulk InP, our model predicts the $\Gamma - X$ crossing of the conduction band minima at exactly the same lattice contraction as measured in the experiment. For small InP nanocrystals, the model correctly predicts the pressure dependence of the fundamental energy gap and luminescence intensity.

External hydrostatic pressure can significantly change the physical properties of semiconductor crystals. As pointed out in Refs. [1, 2], the modification of the electronic and optical properties of bulk zinc-blende semiconductors is a direct consequence of a strong dependence of the character of the valence (VB) and conduction (CB) band-edge states on a reduction of the lattice constant. For low and moderate pressures, this dependence manifests mainly as a modification of the fundamental energy gap. At higher pressures the growing energy of the antibonding CB-edge may exceed the decreasing energy of the bonding-like X-edge leading to the $\Gamma - X$ crossover observed e.g., for GaAs at $\approx$4 GPa [3] and InP at $\approx$10 GPa [1]. At even higher pressures, bulk crystals undergo structural phase transitions, for example from zinc-blende to rock-salt at $\approx$11 GPa in case of InP [4], or complex sequences of several phase transitions in case of Si, Ge and InAs [5, 6].

In quantum confined systems with reduced dimensionality (quantum wells, wires, superlattices and quantum dots), the bulk band structure transforms into a series of discrete subbands, minibands or energy levels. The discrete states arising from different bulk-band valleys behave in different ways and can undergo state-mixing [7] with changing system size. This size-dependence can substantially alter optoelectronic properties, as, for example, happens for porous silicon [8]. For InP nanocrystals, the reduced dimensionality reduces the energy separation between the Γ-like and X-like states [2] even when no pressure is applied [9, 10]. Low-dimensional structures can therefore undergo direct-to-indirect gap transitions and strong modifications of optoelectronic properties at reduced pressures compared to the bulk systems. In contrast, a large number of surface atoms and the absence of internal defects in small nanocrystals can push structural phase transitions in such systems to elevated pressures [11].

A $\Gamma - X$ crossover at reduced pressure in InP nanocrystals was first predicted in Ref. [2] based on pseudopotential calculations and then confirmed by calculations performed using a Wannier functions approach [12]. The predictions of Ref. [12] did not fully agree with the experiment. Therefore, we have studied the pressure-induced $\Gamma - X$ crossover in spherical InP nanocrystals within an empirical tight-binding (TB) theory [13]. In our TB approach each atom is described by 10 outer valence orbitals in a $sp^3s^*d^5$ model. Only coupling of on-site and nearest neighbor orbitals is included. Empirical parameters of Ref. [15] are

---

[*] Corresponding author: e-mail: jdiaz@nist.gov

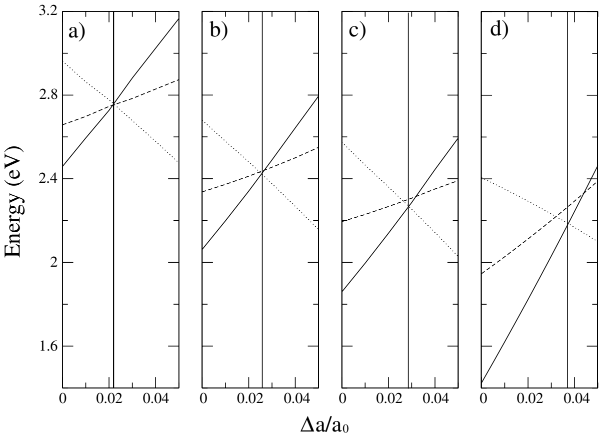

Fig. 1 Energies of the lowest Γ- (solid lines), L- (dashed lines) and X- (dotted lines) derived states versus lattice contraction for InP nanocrystals of radii: (a) $2a$, (b) $3a$, (c) $4a$, and (d) the bulk. Vertical lines mark the pressure at which the $\Gamma - X$ crossover occurs.

employed. We passivate surface dangling bonds to exclude nonphysical states trapped at the nanocrystal surface. The passivation is modeled by shifting the energy of these bonds high above the conduction band edge so they do not modify states near the band gap. In our recent studies of the optical properties of GaAs [13], CdSe [14] and strained multishell quantum dots, we showed that the inclusion of d orbitals into a minimal TB basis set is necessary for a successful description of the electronic states and optical properties of small nanocrystals.

We treat the effects of pressure by assuming that external pressure leads to a simple scaling of the bond lengths. A power-law scaling is used to modify the off-site TB parameters, V_{lm}, due to the changed bond lengths: $V_{lm} = V_{lm}^0 \left(\frac{d_{ij}^0}{d_{ij}}\right)^{\kappa_{lm}}$, where d_{ij} is the bond length between the nearest-neighbors i and j, and the superscript 0 corresponds to the unstrained values. The exponent κ_{lm} is determined by fitting the InP volume deformation potentials under hydrostatic pressure to their experimental values and takes different values for different off-site parameters [15]. The effect of pressure can be measured in terms of the contraction of the lattice constant contraction a, $\Delta a/a_0$, where a_0 is the bulk lattice constant at zero applied pressure. The compression can be related to the pressure, p, via the Murnaghan's equation [16]: $p = \left(\frac{B_0}{B_0'}\right)\left[\left(\frac{a_0}{a}\right)^{3B_0'} - 1\right]$, where B_0 is the bulk modulus ($B_0 = 76 \pm 4$ GPa [4]) and B_0' is its derivative with respect to pressure ($B_0' = 4 \pm 0.2$ GPa [4]).

Figure 1 shows the variation of the Γ, X and L bulk CB energies versus lattice compression. The variation of quantum confined states originating from the corresponding bulk band valleys, for nanocrystals of radii $2a$, $3a$ and $4a$ are also shown. The most striking result is that we predict the bulk $\Gamma - X$ crossing at exactly the same lattice contraction, $\Delta a/a_0 = 0.037$ as measured in experiment [1]. When only a single κ exponent is used to scale all of the off-site tight-binding parameters, the TB model yields $\Delta a/a_0 = 0.044$. Pseudopotential calculations [2] also yield a higher $\Delta a/a_0$ equal to 0.0414, that differs by more than 10% from the experimental result. All of these methods predict that the direct-to-indirect transition should occur at reduced pressures relative to the bulk. It is worthwhile to note that when the nanocrystal size decreases, the pressures where the Γ-, X- and L-derived states cross converge to a single value. Thus, for the smallest nanocrystal of radius $R = 2a$, the TB model predicts a single pressure (corresponding to lattice contraction 0.022) at which the ground CB state becomes totally mixed.

This characteristic pressure dependence of the ground CB state energy determines how the effective band-gap varies with pressure. This band-gap variation is shown in Fig. 2 (top). The gap varies linearly, but with very different slopes for small and large lattice contractions, respectively, below and above the crossover. A simple extrapolation of these two linear dependences (for each nanocrystal size) yields *kinks*

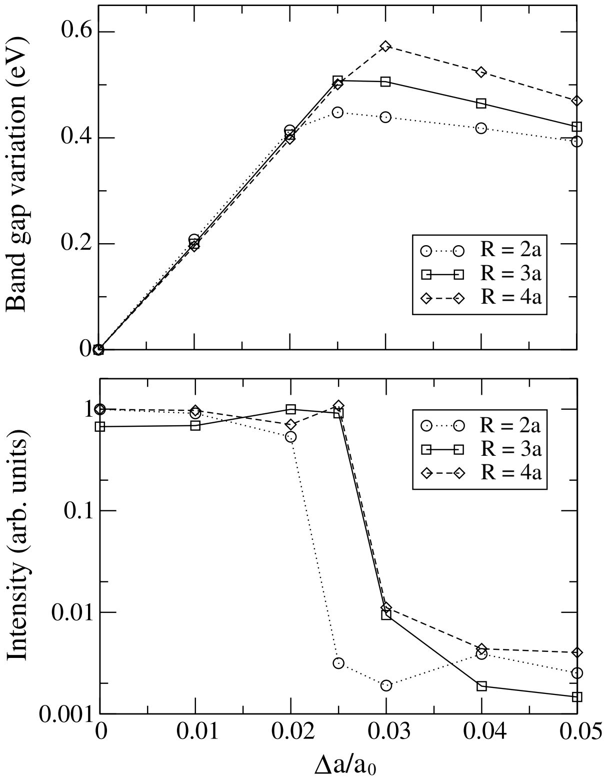

Fig. 2 Top: band gap variation versus lattice contraction for three nanocrystal radii R (in lattice constants). Bottom: intensity of the ground state transition.

(down turns) for the same lattice contractions where the band-crossings shown in Fig. 1 occur. As in experiment (Fig. 5 of Ref. [12]), the change in the gap with pressure is larger and the kink is sharper for larger nanocrystals. The main difference from the experimental data is that the experimental kinks appear at slightly higher pressures and seem to be less dependent on the nanocrystal size. In Fig. 2 (bottom), we present the calculated intensity of the ground-state electron-hole transition versus lattice contraction for the three nanocrystal sizes considered here. Our calculations agree well with the experimental data presented in Fig. 4 of Ref. [12]. The transition rate starts to drop at a lattice contraction ≈0.024, almost independent

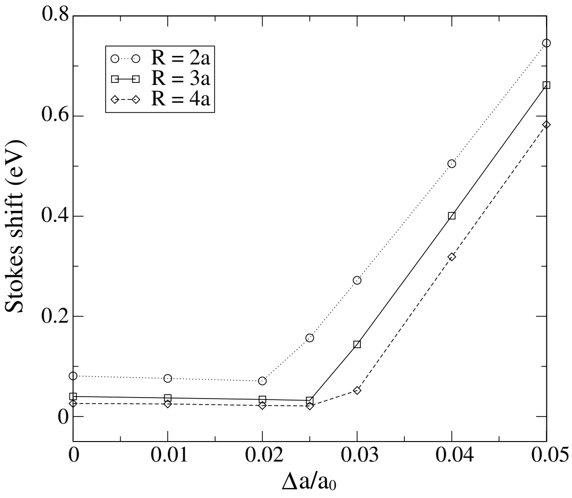

Fig. 3 Stokes shift (eV) versus lattice contraction for three nanocrystal radii R (in lattice constants).

of the nanocrystal size [17]. As in the experiment, the transition intensity decreases by three orders of magnitude when $\Delta a/a_0$ increases from ≈0.02 to 0.04.

For unpressured InP nanocrystals, the ground electron state has S-type symmetry, while the ground hole state has P-type symmetry. This gives rise to a ground transition that is active in emission but dark or barely visible in the absorption spectra. In contrast, the transition involving the hole $S-$ symmetry level and the ground electron state exhibits a considerably larger (4 orders of magnitude) oscillator strength. The energy difference between the lowest absorbing and emitting states defines the Stokes shift. The Stokes shifts calculated for three different nanocrystal sizes are shown in Fig. 3. For lattice contractions below the crossing points (see Fig. 1), the Stokes shift corresponds to the energy difference between the ground hole state (of P symmetry) and the lowest hole state of S symmetry. Therefore, in this interval the Stokes shifts changes little with pressure. When $\Delta a/a_0$ exceeds the crossing point, the calculated Stokes shifts increase linearly with the increasing lattice contraction. This increase occurs because the energy of the lowest Γ-derived state increases rapidly, while the lowest indirect-gap transitions (involving $X-$ and $L-$ point derived electron states) have negligible oscillator strengths [13]. The linear dependence of Stokes shift on the lattice contraction (above the crossing point), could then be exploited as a measure of the pressure applied.

In summary, we have applied tight-binding theory to study pressure-induced direct-to-indirect transitions in bulk InP and small InP nanocrystals. Our TB model correctly predicts the pressure at which the $\Gamma - X$ transition occurs in the bulk. For small nanocrystals, the model yields a pressure dependence of the effective energy gap and luminescence intensity of the ground transition similar to the observed pressure effects. Some discrepancies observed between the experiment and theory are probably due to neglected relaxation and surface reconstruction of the nanocrystal lattice under pressure.

Acknowledgements This work was performed under the sponsorship of the U.S. Department of Commerce, NIST, and was also supported by Polish Projects: 1P03B15129, 3T1104326 and PZB-MIN-008/P03/2003.

References

[1] S. Ernst, A. R. Goni, K. Syassen, and M. Cardona, Phys. Rev. B **53**, 1287 (1996).
[2] H. Fu and A. Zunger, Phys. Rev. Lett. **80**, 5397 (1998).
[3] A. R. Goni, K. Strössner, K. Syassen, and M. Cardona, Phys. Rev. B **36**, 1581 (1987).
[4] C. S. Menoni and I. L. Spain, Phys. Rev. B **35**, 7520 (1987).
[5] Y. K. Vohra et al., Phys. Rev. Lett. **56**, 1944 (1986).
[6] Y. K. Vohra, S. T. Weir, and A. L. Ruoff, Phys. Rev. B **31**, 7344 (1985).
[7] G. H. Li et al., Phys. Rev. B **50**, 18420 (1994).
[8] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1991).
[9] In quantum confined GaAs systems size reduction can even transform the direct band-gap semiconductor to an indirect gap system [10].
[10] A. Franceschetti and A. Zunger, Phys. Rev. B **52**, 14664 (1995).
[11] S. H. Tolbert et al., Phys. Rev. Lett. **76**, 4384 (1996).
[12] Ch.-J. Lee et al., J. Chem. Phys. **113**, 2016 (2000).
[13] J. G. Díaz and G. W. Bryant, Phys. Rev. B **73**, 075329 (2006).
[14] J. G. Díaz and G. W. Bryant, submitted.
[15] J.-M. Jancu, R. Scholz, F. Beltram, and F. Bassani, Phys. Rev. B **57**, 6493 (1998).
[16] F. D. Murnaghan, Proc. Natl. Acad. Sci. USA **30**, 244 (1944).
[17] The calculated intensities for $\Delta a/a_0 < 0.02$ are almost independent of $\Delta a/a_0$, while the experimental intensities increase by one order of magnitude.