

PAPER

Modeling on the size dependent properties of InP quantum dots: a hybrid functional study

To cite this article: Eunseog Cho *et al* 2013 *Nanotechnology* **24** 215201

View the [article online](#) for updates and enhancements.

You may also like

- [Selective epitaxy of semiconductor nanopyrramids for nanophotonics](#)
P J Poole, D Dalacu, J Lefebvre et al.
- [Perspective—Synthesis and Light-Emitting Diode Applications of High Efficiency Indium Phosphide Core/Shell Quantum Dots using Tris\(Dimethylamino\) Phosphine](#)
Tianyu Lin, Tongtong Xuan and Rong-Jun Xie
- [Single-photon emission from InAsP quantum dots embedded in density-controlled InP nanowires](#)
Shougo Yanase, Hirotaka Sasakura, Shinjiro Hara et al.



*Benefit from connecting
with your community*

ECS Membership = Connection

ECS membership connects you to the electrochemical community:

- Facilitate your research and discovery through ECS meetings which convene scientists from around the world;
- Access professional support through your lifetime career;
- Open up mentorship opportunities across the stages of your career;
- Build relationships that nurture partnership, teamwork—and success!

Join ECS!

Visit electrochem.org/join



Modeling on the size dependent properties of InP quantum dots: a hybrid functional study

Eunseog Cho, Hyosook Jang, Junho Lee and Eunjoo Jang

Advanced Material Research Center, Samsung Advanced Institute of Technology (SAIT), Samsung Electronics Co., Mt.14-1, Nongseo-Dong, Giheung-Gu, Yongin-Si, Gyeonggi-Do, 449-712, Korea

E-mail: ejjang12@samsung.com


Received 25 November 2012, in final form 1 April 2013

Published 25 April 2013

Online at stacks.iop.org/Nano/24/215201

Abstract

Theoretical calculations based on density functional theory were performed to provide better understanding of the size dependent electronic properties of InP quantum dots (QDs). Using a hybrid functional approach, we suggest a reliable analytical equation to describe the change of energy band gap as a function of size. Synthesizing colloidal InP QDs with 2–4 nm diameter and measuring their optical properties was also carried out. It was found that the theoretical band gaps showed a linear dependence on the inverse size of QDs and gave energy band gaps almost identical to the experimental values.

 Online supplementary data available from stacks.iop.org/Nano/24/215201/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

One of the most fascinating phenomena in semiconductor quantum dots (QDs) is their optical properties which depend on size changes [1]. This size tunability is due to the quantum confinement effect (QCE) that occurs when the physical dimensions of the semiconductor are comparable to or smaller than the exciton wavelength. Recently, because of their light emission, which spans the entire visible range by controlling the magnitude of QCE, increasing attention has been paid to InP QDs as an environmentally benign candidate to replace the most studied cadmium selenide (CdSe) [2, 3]. In order to design proper QD structures such as core/shell, core/multi-shell, and alloy structures [4–6] for potential applications, it is necessary to predict the magnitude of the QCE and the corresponding actual InP size. However, to the best of our knowledge, there is still a lack of accurate information on the variation of band gap of InP QDs derived by the QCE.

It is well known that effective mass approximation (EMA), performed by adopting a particle-in-a-box (PIB) model, shows the confinements in spherical dots proportional to $1/d^2$ (where d = diameter) [7]. So, the band gap (E_g) of

a semiconductor QD is simply expressed according to the following analytical equation [8],

$$E_g = E_{g,\text{bulk}} + C/d^\alpha \quad (1)$$

where $E_{g,\text{bulk}}$ is the bulk band gap, C is a proportional constant, and α is a real number. Since the band gap of bulk InP can be definitely measured, determining the parameters C and α is crucial to complete the analytical equation that clearly represents the size dependent features of InP QDs. For the PIB model, the interface potential between the QD and ligand (or matrix) is assumed to be a hard wall, but the real potential of QD is not the rigid wall owing to the charge transfer at the interfaces. Our previous calculation for CdSe QDs based on the EMA using a modified Kohn–Sham equation showed that the interface potential with the finite rigid wall led to overestimated energy band gaps compared to the experimental values [9]. Therefore, the simplified assumptions in the EMA are subject to limitations when attempting to predict QCE in a real situation. Actually, according to a recent experiment, the optical properties of InP/ZnS core/shell QDs do not follow the dependence on $1/d^2$ but rather depend approximately inversely linearly on the dot size ($\sim 1/d$) [10]. However, the actual QCE of InP QDs is different from that of

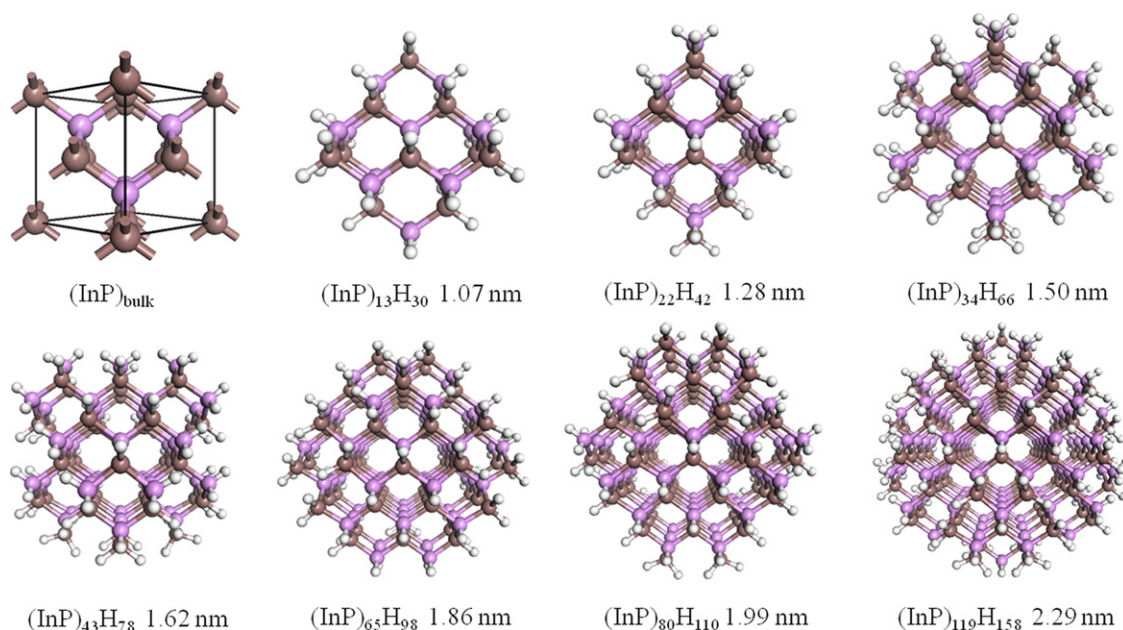


Figure 1. Relaxed structures of InP bulk and $(\text{InP})_n\text{H}_m$ QDs. Chemical formula and sizes of the QDs are represented under the structures. In, P, and fictitious H atoms are shown as brown, pink, and white colored spheres, respectively.

core/shell QDs because the optical and structural properties are significantly altered by the interaction at the core/shell interface. In order to obtain reliable experimental data on QCE, the synthesized InP QDs should be mono-disperse over a wide range of size and their exact sizes should be precisely measured. However, it is still challenging to prepare perfectly homogeneous InP QDs and to precisely assign the size of colloidal QDs, especially those with less than 2 nm diameter, by electron microscopic characterizations. Therefore, it is of importance to study a theoretical model based on density functional theory (DFT) that can predict more reliably the size dependent electronic properties of InP QDs.

2. Methodology

The first-principles calculations for InP QDs were carried out by means of a pseudo-potential plane wave method using the Vienna *ab initio* simulation Package (VASP). The energy cutoff was selected to be 270 eV and atomic positions were fully relaxed until the Hellmann–Feynman force on each atom was smaller than $0.02 \text{ eV } \text{\AA}^{-1}$. To improve the accuracy of the calculation, the following things were considered: first, the generalized gradient approximation (GGA) or local density approximation (LDA) methods are known to produce lower band gaps compared to the experimental ones. Our test calculation for bulk InP with the GGA method implemented by Perdew, Burke, and Ernzerhof (PBE) also gave only 0.59 eV band gap, which is much less than the experimental value of 1.41 eV at 70 K [11]. In order to correct this seriously underestimated energy band gap, we adopted the hybrid functional approach proposed by Heyd–Scuseria–Ernzerhof (HSE06) and obtained InP bulk gap of 1.401 eV. Second, since QDs have a large surface-to-volume ratio, properly passivating the surface atoms is significantly important when

attempting to obtain well-defined band gaps. An improper surface passivation can mislead into quite unreasonable geometries or give rise to undesirable band edge or midgap states that could distort the electronic structures. For group IV QDs like Si, hydrogen atoms are generally used as appropriate passivating agents due to the integer charge of their surface dangling bonds [12]. For nongroup IV QDs like InP, however, fictitious hydrogen atoms with fractional charges are required to saturate their surface dangling bonds [13]. For InP bulk structure, each In atom is surrounded by four P atoms, and the formal valence of In atom is three and P atom is five. So, $0.75e$ of each In atom and $1.25e$ of each P atom combine to form an In–P covalent bond. In the present calculation, fictitious hydrogen atoms with charges of $0.75e$ and $1.25e$ were chosen to saturate the P and In atoms exposed on the QD surface respectively. Seven $(\text{InP})_n\text{H}_m$ stoichiometric clusters, $(n, m) = (13, 30), (22, 42), (34, 66), (43, 78), (65, 98), (80, 110),$ and $(119, 158)$, were selected by cutting out the bulk zinc blende (ZB) structure. The diameter of QD was calculated using $d = a(3N/4\pi)^{1/3}$ with the assumption of spherical shape, where a is the calculated lattice constant of bulk InP (5.964 \AA) after structure relaxation and N is the total number of In and P atoms in the QDs.

3. Results

Figure 1 shows the relaxed InP bulk and QD structures arranged in order of increasing size. The In–P bond lengths ($2.580\text{--}2.584 \text{ \AA}$) of the interior atoms in the QDs are identical to that of the InP bulk structure (2.583 \AA), and surface atoms have about 1% reduced In–P bond lengths of $2.550\text{--}2.559 \text{ \AA}$. For all QDs, the ZB bulk geometry remains almost intact, even after the structure relaxation. Figure 2(a) shows formation energy (E_f) and surface energy (σ) according to the QD sizes

defined as,

$$E_f = \frac{E_{\text{total}}(\text{QD}) - n(\mu_{\text{In}} + \mu_{\text{P}}) - m\mu_{\text{H}}}{N} - E_{f,\text{bulk}} \quad (2)$$

$$\sigma = \frac{E_{\text{total}}(\text{QD}) - (n/4) E_{\text{bulk,unit}} - m\mu_{\text{H}}}{A} \quad (3)$$

where $E_{\text{total}}(\text{QD})$ is the total energy of QD, $E_{f,\text{bulk}}$ is the bulk formation energy, $E_{\text{bulk,unit}}$ is the bulk energy per unit-cell, and A is the surface area of QD, and μ_{In} and μ_{P} are the chemical potentials of In and P, which were calculated from the energies of bulk In metal and white solid P, respectively. It should be noted that the chemical potential of the fictitious hydrogen (μ_{H}) differs from that of general atomic hydrogen, and moreover, μ_{H} depends on the facets where the fictitious hydrogen binds. This facet dependent μ_{H} and calculation details are disclosed in supplementary data (SD available at stacks.iop.org/Nano/24/215201/mmedia). In figure 2(a), both formation and surface energies decrease as the size of QD increases. This shows that the surface stability dominantly affects the overall stability since QDs are composed of a large number of surface atoms. But, while the surface energy decreases monotonically with increasing size, the formation energy fluctuates to some extent. For example, the E_f at a diameter of 1.62 nm is relatively high and the E_f at 1.86 nm is quite low compared with nearby energies. Such different behaviors between the E_f and the σ at several particular sizes suggest that, in addition to the surface energy, some other factors such as specific number of atoms or size can also play extra roles, raising or lowering the total energy of InP QDs. Furthermore, the noticeably low E_f at the specific size opens up the possibility that there may exist magic-sized InP clusters characterized with high stability, like the $(\text{CdSe})_{33}$ structure [14], although magic-sized InP has not been experimentally reported yet.

Figure 2(b) presents the energy band gaps obtained by modeling and the experiment. By fitting the modeling gaps to equation (1) using the calculated $E_{g,\text{bulk}}$ (1.401 eV), we determined the parameters $C = 3.493$ eV nm and $\alpha = 1.172$ that complete the analytical equation that represents the band gap energy as a function of size. Interestingly, the obtained $\alpha = 1.172$ shows that the band gap of InP QD linearly depends on the inverse size, which is a huge difference from the value ($\alpha = 2$) derived by EMA based on the PIB model, and rather shows a similarity with the results of the InP/ZnS core/shell experiments. The wide disparity with the EMA proves that the charge transfer at the QD–ligand interface considerably affects the QCE for actual InP QDs. In addition, our parameters present better prediction to the experimental values than the previous ones, $C = 3.90$ eV nm and $\alpha = 1.10$ for InP QDs [15], which were obtained by the charge patching method based on the LDA approach; the band gaps obtained by the charge patching method gave ~ 0.2 eV larger than our data obtained by the hybrid functional method and 0.3 eV larger than the experimental values. The GaN QDs [16] calculated by DFT-GGA led to a smaller value of C ($C = 3.179$ eV nm) and a larger value of α ($\alpha = 1.452$) than each value of InP QDs, which indicates that the QCE of InP QD more sensitively depends on the size than does

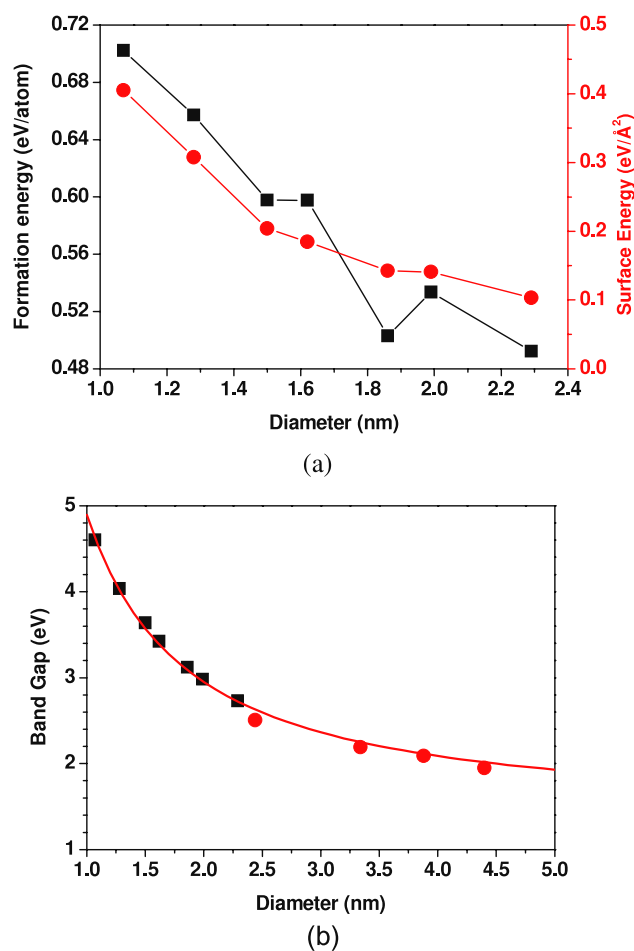


Figure 2. (a) Formation energies (black squares) and surface energies (red circles) according to the QD sizes. The black and red lines are for guidance only. (b) Band gap energies based on the modeling (black squares) and the experiment (red circles) depending on the QD sizes. The red line is obtained by fitting the black squares and follows the analytical expression of $1.401 + 3.493/d^{1.172}$.

the QCE of GaN QDs. In order to confirm the validity of the calculated energy band gaps, colloidal InP QDs were synthesized according to the following procedure. 0.2 mmol of indium acetate, 0.6 mmol of palmitic acid, and 10 ml of octadecene were mixed together and degassed for 1 h at 120 °C under vacuum. Then, the temperature was increased to 280 °C and 0.1 mmol of tris(trimethylsilyl)phosphine was rapidly injected into the solution. To obtain various sized QDs, the reaction time was controlled in a manner similar to that in the previous literature [17]. Experimental band gaps of the InP QDs with different sizes were assigned by the first absorption peak wavelengths of the UV–vis absorption spectra, and the sizes were measured directly from the transmission electron microscopy (TEM) or scanning transmission electron microscopy (STEM) images. The UV–vis absorption spectra, TEM and STEM images, and measurement methods are also disclosed in SD.

The theoretical modeling equation gives band gaps that are slightly larger but almost identical to the experimental values; the largest difference in band gap is just 0.124 eV ($\sim 5\%$ of modeling gap) at a diameter of 2.44 nm (table 1).

Table 1. Diameters (D) determined by TEM or STEM images, experimental band gaps (E_g (Exp)) based on the first absorption peak wavelengths of UV–vis absorption spectra, calculated band gaps (E_g (DFT)), and Coulomb attraction energies (E_{Coul}) in eV.

D (nm)	E_g (Exp)	E_g (DFT)	E_{Coul}
2.44 ± 0.31	2.505	2.629	0.149
3.34 ± 0.25	2.191	2.251	0.101
3.88 ± 0.31	2.091	2.114	0.087
4.40 ± 0.28	1.950	2.016	0.058

However, it should be noted that the calculated energy band gaps were acquired by the ground state energy calculation at 0 K; however, the experimental energy band gaps were measured under ambient conditions. Moreover, the experimental UV–vis absorption spectra intrinsically involve the effect of exciton binding, but this effect was not reflected in our calculation. For a close comparison, we examined how much those two factors affected the calculated band gaps. First, semiconductors generally have reduced band gaps at higher temperature; this can be expressed using the empirical Varshni relation [18],

$$E_g(T) = E_{g0} - \alpha \frac{T^2}{T + \beta} \quad (4)$$

where E_{g0} is the band gap at 0 K, and the parameters α and β are taken as $363 \mu\text{eV K}^{-1}$ and 162 K, respectively from the InP bulk data [19]. Considering the temperature effect, the band gaps obtained from the modeling are reduced by about 0.06 eV at 298 K. Second, if the exciton binding effects are incorporated in the modeling, the calculated band gaps should be reduced by Coulomb attraction energy (E_{Coul}) between electron and hole carriers. The accurate electron–hole Coulomb interaction energy cannot be calculated with conventional DFT theory with the hybrid functional method because the energy basically involves many body effects. Thus, in our study, the Coulomb attraction was estimated in the framework of first-order perturbation theory combined with the EMA [9] that we previously developed; the calculated energies for InP QDs are given in table 1. The Coulomb energies for QDs with diameters of 1.50 nm and 1.99 nm are 0.254 eV and 0.182 eV, respectively; these values constantly diminish with increasing size, and become only 0.058 eV for the QD with a diameter of 4.40 nm. We fitted the band gaps corrected with exciton binding effects to equation (1) and obtained the modified parameters $\alpha = 1.210$ and $C = 3.227 \text{ eV nm}$. In the experimental size regime, these new parameters reduced the band gaps by 0.1 eV compared to the values given by the hybrid functional method without the correction of Coulomb energy (figure S2 available at stacks.iop.org/Nano/24/215201/mmedia). If we consider both the temperature effect and the exciton binding energy, the calculated band gaps should be lowered by 0.118–0.209 eV, resulting in modeling gaps slightly smaller than the experimental ones; however, the largest difference was only 0.085 eV ($\sim 3\%$ of modeling gap). Therefore, even after the incorporation of both effects, the theoretical data still give almost the same band gaps as did the experiment.

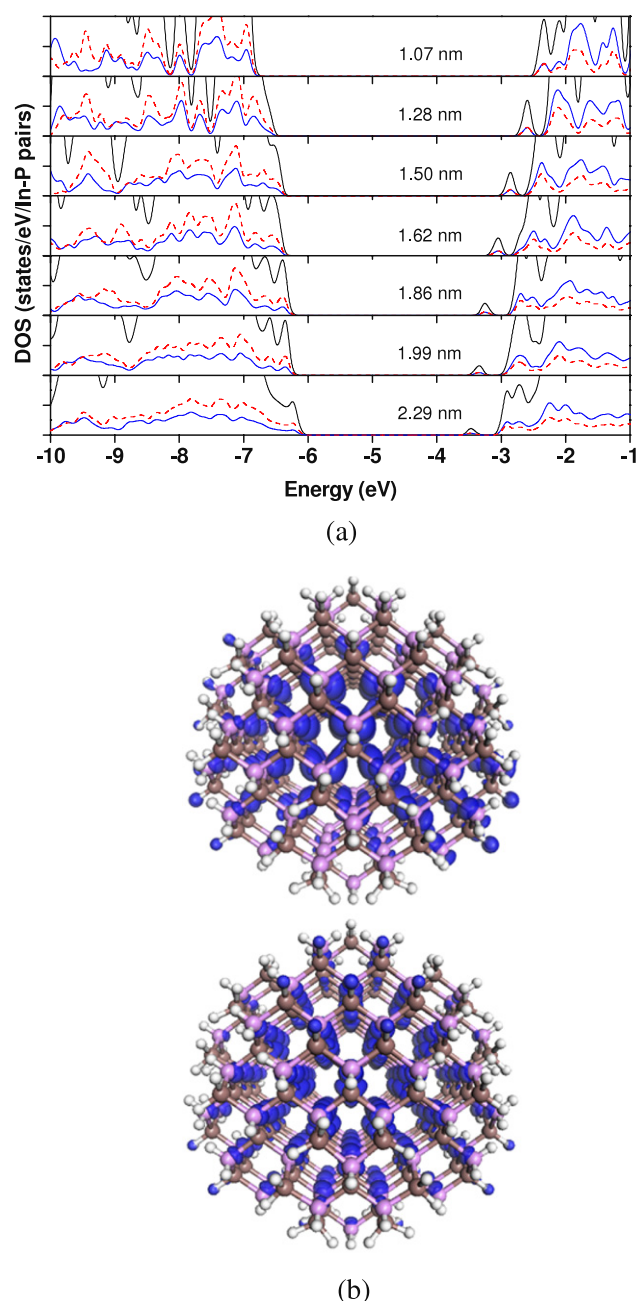


Figure 3. (a) Total density of states (black solid lines) and atom-projected density of states for In atoms (blue solid lines) and for P atoms (red dashed lines) per In–P pairs are plotted relative to the vacuum energy (0 eV) as a function of QD size. (b) Spatial density distributions of HOMO (upper) and LUMO (lower) levels of $(\text{InP})_{119}\text{H}_{158}$ QD with a diameter of 2.29 nm.

Figure 3(a) shows the total density of states (TDOS) and atom-projected density of states (PDOS) with respect to vacuum energy (0 eV). In order to assign the vacuum level, local potentials were averaged over the radial direction of the QDs and the stationary potential energy was set to the vacuum energy. As the size increases, the corresponding band gap clearly diminished. When the diameter of QD increases from 1.07 to 2.29 nm, the highest occupied molecular orbital (HOMO) level goes up as much as 0.73 eV, but the lowest unoccupied molecular orbital (LUMO) level declines as much

as 1.14 eV. The fact that LUMO varies more significantly than HOMO indicates that the electrons are more strongly confined than the hole carriers when the size is reduced. The PDOS shows that the P atoms are dominant near the HOMO, whereas the LUMO is controlled by both In and P atoms, although In atoms prevail in the upper region of the LUMO. Since atomic P is more electronegative than atomic In, the 3p-orbital level of atomic P is located below the 5s-orbital level of atomic In. Thus, it is reasonably understood that the HOMO is mainly occupied by the 3p-orbital level of P atoms and the LUMO is dominated by the 5s-orbital level of In atoms through the bonding/anti-bonding orbital interactions in the process of building QDs. However, for the LUMO, an empty 4s-orbital of atomic P, whose energy level is higher than the 3p-orbital level of the same atom, is concerned with generating the LUMO as an almost equally mixed level with the 5s-orbital of atomic In. Figure 3(b) shows the spatial density distributions of the HOMO and the LUMO states of the representative (InP)₁₁₉H₁₅₈ dot with a diameter of 2.29 nm. It can be clearly seen that the spatial density of the HOMO mainly resides in the P atoms, representing the p-orbital character oriented to the [1 1 1] direction, while the LUMO is composed of s-orbitals of both In and P atoms. Moreover, most of both the HOMO and LUMO spatial densities are accumulated in the interior regions, unlike the case of GaN QD, which has an extended HOMO density to the surface [16]. Therefore, the band gaps for InP QDs, directly affected by both HOMO and LUMO states, could loosely depend on the ligand species binding to the surface or to the shell passivation.

4. Conclusions

Theoretical calculations using the DFT framework have been carried out to elucidate the electronic properties of InP QDs. The hybrid functional approach was successful for the correction of underestimated band gaps, and the surface atoms of QDs were well-passivated with fictitious hydrogen atoms with fractional charges. Both the interior and surface atoms of the InP QDs were found to maintain the ZB bulk geometry even after structure relaxation. It was also found that the energy band gaps of InP QDs with different sizes follow the relation $E_g = 1.401 + 3.493/d^{1.172}$, which showed a large difference from the prediction by the EMA based on the PIB

model. Synthesizing colloidal InP QDs with various sizes and measuring their optical properties and sizes were also carried out. The modeling gaps were found to be almost identical to the results obtained from the actual measurements, which were scrutinized by considering the temperature effect and the exciton binding energy. The PDOS, TDOS plots and spatial density distributions clearly demonstrate that the LUMO level, dominated by s-orbitals of both In and P atoms, was more subject to change than the HOMO level, which is composed of mainly p-orbitals of P atoms as the size of InP QDs changed.

References

- [1] Zhang Z J 2009 *Optical Properties and Spectroscopy of Nanomaterials* (Singapore: World Scientific)
- [2] Cros-Gagneux A, Delpech F, Nayral C, Cornejo A, Coppel Y and Chaudret B 2010 *J. Am. Chem. Soc.* **132** 18147
- [3] Akopian N, Patriarche G, Liu L, Harmand J and Zwiller V 2010 *Nano Lett.* **10** 1198
- [4] Li L R and Reiss P 2008 *J. Am. Chem. Soc.* **130** 11588
- [5] Kim S et al 2012 *J. Am. Chem. Soc.* **134** 3804
- [6] Kim K, Lee H, Ahn J and Jeong S 2012 *Appl. Phys. Lett.* **101** 073107
- [7] Dong A, Yu H, Wang F and Buhro E W 2008 *J. Am. Chem. Soc.* **130** 5954
- [8] Nanda K K, Kruis E F and Fissan H 2001 *Nano Lett.* **1** 605
Brus E L 1984 *J. Chem. Phys.* **80** 4403
- [9] Cho E, Jang H, Jun S, Kang H A, Chung J G and Jang E 2012 *J. Phys. Chem. C* **116** 11792
- [10] Narayanaswamy A, Feiner F L, Meijerink A and van der Zaag J P 2009 *ACS Nano* **9** 2539
- [11] Ma H, Jin Z, Wang L and Ma G 2011 *J. Appl. Phys.* **109** 23105
- [12] Nishida M 2005 *J. Appl. Phys.* **98** 23705
- [13] Huang X, Lindgren E and Chelikowsky R J 2005 *Phys. Rev. B* **71** 165328
- [14] Ben D M, Havenith A R, Broer R and Stener M 2011 *J. Phys. Chem. C* **115** 16782
- [15] Wang L-W and Li J 2004 *Phys. Rev. B* **69** 153302
- [16] Carter J D, Puckeridge M, Delley B and Stampfl C 2009 *Nanotechnology* **20** 425401
- [17] Battaglia D and Peng X 2002 *Nano Lett.* **2** 1027
- [18] Valerini D, Creti A, Lomascolo M, Manna L, Cingolani R and Anni M 2005 *Phys. Rev. B* **71** 235409
- [19] Katz A 1992 *Indium Phosphide and Related Materials* (Boston, MA: Artech House Publishers)
Sze S 1981 *Physics of Semiconductor Devices* 2nd edn (New York: Wiley)