Atomistic Origin and Pressure Dependence of Band Gap Variation in Semiconductor Nanocrystals

G. Ouyang,* C. Q. Sun, and W. G. Zhu

School of Electrical & Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

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We have investigated band gap variation of semiconductor nanocrystals based on the extension of the bond-order-length-strength (BOLS) correlation mechanism to the pressure domain with the local bond average (LBA) approach. An analytical solution has been developed to connect the band gap energy with the bonding identities by considering the joint effects of size and pressure and the nature of the bond involved, which is consistent with understanding the interdependence of these quantities and their common atomistic origin. It has been clarified that the bond contraction associated with the single bond energy strength originates with size- and pressure-induced change, leading to crystal potential variation. Theoretical results are in agreement with the experimental measurements.

Introduction

In recent years, the high pressure investigations of semiconductor nanostructures such as nanocrystals, nanowires, and nanotubes have become a focus area in condensed matter physics and material science because of their tunable optical properties for applications in optoelectronics, nanostructure lasers, high-density memory, bioengineering, etc. Because the band gap energy of semiconductors plays a fundamental role in electrical and optical properties, it is important and necessary to investigate the band gap change in order to gain a better understanding of their relevant properties. Thus, it is a significant way to understand the modification of band gap energy of semiconductor nanocrystals under the condition of external stimuli such as pressure, temperature, etc.

It is well-known that nanostructures have a significant fraction of atoms associated with the imperfection of the coordination numbers (CNs) at the surface, which induces their properties differently from their bulk counterpart because of size effects. It is reported that band gap energy increases with decreasing size because of surface or interface quantum trapping. Surprisingly, the band gap of Si nanorods, measured using scanning tunneling spectroscopy, has increased from 1.1 to 3.5 eV when the rod diameter is reduced from 7.0 to 1.3 nm, which is associated with a 12% Si—Si bond contraction. The variation in the band gap of semiconductor nanocrystals can be directly related to transformation of the dielectric constant and photo-absorption edges. Furthermore, the alloying effect could be a dominant role in the electronic state and structure transition of alloy quantum dots (QDs) under high pressure. Many attempts have been employed to address the band gaps of semiconductor nanocrystals under different conditions. Theoretically, there have been various calculations used to study band gap energy and relevant properties, including thermodynamics, semiempirical methods, ab initio calculations, etc. There are several conflicting models concerning the mechanisms responsible for band gap expansion. Existing methods include quantum confinement, phonon-assisted free-exciton collision, impurity centers, cluster interaction, oxidation effects, etc.

It would be effective to connect the band gap energy directly to the Hamiltonian that is determined by interatomic binding energy under the stimuli of pressure, temperature, or their combination, which will result in a change in bond length and bond energy. However, among the theoretical methods mentioned, understanding chemical bonding and its effect on band gap energy as well as band gap change under external stimuli remain poorly understood.

Very recently, a local bond average (LBA) approach has been applied to deal with stress (thermal) driven phonon (softening) stiffening in the pressure or temperature domain by relating lattice dynamics of the response of bonding identities to external stimuli such as pressure, temperature, and coordination environment, which has been used successfully in investigations of the surface free energy of nanostructures. In this paper, we establish an analytical model and present an atomistic insight into the size effect of the pressure-induced band gap variable of semiconductor nanocrystals under hydrostatic pressure in terms of the functional dependence on the bonding identities (bond length, bond strength, and bond order) based on the recently developed bond-order-length-strength (BOLS) correlation mechanism using the LBA approach. The developed theoretical methods show that the blue shift of band gap energy is dependent on lattice strain and skin quantum trapping. The pressure enhances the size effect through bond shortening and stiffening.

Principle

In terms of the BOLS sketch and LBA method, the nature and number of bonds remain unchanged unless a phase transition occurs for a given specimen. If we consider the property changes of the specimen under the applied stimulus such as pressure, temperature, electric field, etc., we should explore the response of the strength and the length of all bonds or an average of their representatives. It indicates that if one bond breaks, the remaining bonds among the under-coordinated atoms will shrink spontaneously and become stronger. Thus, the densification of charge and energy will be influenced by external stimuli, together with the perturbation to the Hamiltonian and relevant properties such as core level shift and band gap energy.

* Corresponding author: E-mail: gangouy@hunnu.edu.cn.
According to the nearly free-electron approach, the single body Hamiltonian can be written as \(^2\)

\[
\hat{H} = \hat{H}_0 + \hat{H}'
\]

with

\[
\hat{H}_0 = -\frac{\hbar^2 \nabla^2}{2\mu} + V_g(r) + V_c(r + R_c) \text{ and } \hat{H}' = V_c(r + R_c)\Delta
\]

where \(\mu\) is the effective mass of an electron. The \(V_g(r)\) is the intra-atomic trapping potential of an isolated atom and the \(V_c(r)\) is the periodic potential of the crystal. \(R_c\) is the lattice constant. Physically, the band gap energy is from the crystal potential, and the width of the gap is an approximation determined by the first Fourier coefficient of the crystal field in proportion to the mean cohesive energy per bond \((E_b)\), i.e., \(E_g = 2|V_i| \approx (E_b)\), where \(V_i = (\sqrt{N}r)\) \(e^{\mu_ir}dr\). Note that the interatomic potential \(V_c(r)\) forms the key to the band structures with a given set of Bloch wave functions under equilibrium and static states. Any perturbation to the \(V_c(r)\) will modify the entire band structure. In the case of nanosolids under the condition of applied pressure, the perturbation can be divided into two contributions

\[
\Delta = \Delta_D + \Delta_p
\]

where the \(\Delta_D\) denotes the size effect on potential energy, while the \(\Delta_p\) is the pressure-induced energy change.

On the basis of the BOLS correlation mechanism,\(^19\) the size effect on the potential energy \(\Delta_D\) is determined by the change of the crystal potential of the system, i.e.,

\[
\Delta_D = \frac{\Delta V_g(N_i)}{V_g(\infty)} = \sum_{j \neq 3} \gamma_j \left( \frac{E_i}{E_b} - 1 \right) + \delta_D(D)
\]

\[
\gamma_j = \frac{2\hbar c_j}{D}
\]

where \(D\) is the diameter of a spherical dot or rod or across the thickness of a thin plate. \(d\) is the atomic diameter. \(i\) denotes the \(i\)th atomic layer, which may be counted up to three from the outermost atomic layer to the center of the solid as no CNs reduction. \(E_i\) and \(E_b\) are the single bond energies at the surface layer and the bulk, respectively. \(\delta_D(D)\) describes the intercluster interaction, which can be negligible if the particle size is sufficiently large. \(\gamma_j\) represents the surface-to-volume ratio of nanosolids. \(\tau\) is the shape factor of a thin plate \((\tau = 1)\), rod \((\tau = 2)\), and spherical dot \((\tau = 3)\) for any dimensions. Noticeably, the interatomic binding energy at equilibrium atomic separation can be expressed as \(E_i = c_i E_b\). \(c_i\) is the CN dependence of the bond contraction coefficient, extending from the Goldschmidt premise, Feibelman’s considerations, and the associated bond-strength enhancement. The index \(m\) represents the nature of the bond. In general, for metals, \(m = 1\), and for alloys and compounds, \(m\) is around 4.\(^19\)

In addition, the \(\Delta_p\) originates from the external applied pressure. Physically, the external pressure would induce the unit cell distortion energy enhancement. So, in accordance with the previous consideration,\(^23\) the \(\Delta E_p\) (Figure 1, inset) can be expressed as the integral area of \(V_0\Delta S\).

\[
\Delta E_p = -\int_{V_0}^V p(u)du
\]

where \(p\) and \(V_0\) are the external pressure and the volume of the unit cell at zero pressure and zero temperature, respectively.

The cohesive energy of a spherical nanoparticle under the condition of ambient pressure can be deduced as

\[
E_{\text{cohesive}}(D, p) = \sum_{i \geq 3} N_i E_i^s + c_i E_c (N - \sum_{i \geq 3} N_i)
\]

where \(E_c\) and \(E_b\) are the cohesive energy with and without external pressure stimuli, respectively.

Therefore, from the above deductions, we can obtain the size- and pressure-dependent cohesive energy, which is shown as

\[
\frac{\Delta E_{\text{cohesive}}(D, p)}{E_{\text{cohesive}}(\infty, 0)} = \sum_{i \geq 3} \gamma_i \left[ \frac{\Delta E_p}{E_b} - 1 \right] + \frac{\Delta E_p}{\zeta_{ib} E_b} + \sum_{i \geq 3} \gamma_i \Delta E_p^p - \sum_{i \geq 3} \gamma_i \Delta E_p^p
\]

with

\[
\zeta_{ib} = \zeta / z_b
\]

where \(\zeta_i\) and \(z_b\) are the CN of atoms in \(i\)th atomic layer and the bulk, respectively. The third and fourth part in eq 7 refer to the energy discrepancy between the surface layer and core. As a first approximation, we assume the same elastic strain energy deposited in the surface shell and core section. That is

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**Figure 1.** (a) Dependence of the single bond strength on \(\xi\) of CdSe in bulk. The solid line represents the theoretical results, while the dashed line are from the experimental data.\(^{39}\) (b) Pressure dependence on bond length. The inset is the schematic illustration of the energy storage \((\Delta E_p)\) induced by external compressive stress that causes bond energy elevation. The necessary calculating parameters are listed as \(B_0 = 53.3\ GPa\), \(B'_0 = 4\ GPa\), and \(V_0 = 112.2\ \text{Å}^3\).
\[ \frac{\Delta E_{\text{cohesive}}(D, p)}{E_{\text{cohesive}}(\infty, 0)} = \sum_{i=3}^{N_s} \gamma_i \left[ z_i c_i^{m-1} - 1 \right] + \frac{\Delta E^p}{z_b E(0)} \quad (8) \]

Considering the average single bond energy is equal to cohesive energy per bond, we obtain the size- and pressure-dependent band gap by

\[ \frac{\Delta E_g(D, p)}{E_g(\infty, 0)} = \Delta_D + \Delta_p = \frac{z_b}{z} \left[ \sum_{i=3}^{N_s} \gamma_i \left[ z_i c_i^{m-1} - 1 \right] + \frac{\Delta E^p}{z_b E(0)} \right] + \frac{z_b}{z} - 1 \quad (9) \]

where \( z \) means the average CNs.

It is interesting to note that the CN of atoms of nanoparticles, especially surface atoms, plays a significant role in physical and chemical properties.\(^{24,25}\) Assuming a nanoparticle containing \( N \) atoms with a core--shell configuration, we can define the average CNs in terms of its imperfection in the surface layer as

\[ z = \left( 1 - \gamma_i \right) z_b + \gamma_i \frac{N_c}{N} \quad (10) \]

where \( N_c \) and \( N_s \) are the number of interior (core) atoms and surface atoms, and \( z \) and \( z_b \) are the CNs of the lattice and surface layer, respectively. Clearly, the total number of atoms in the nanoparticles is the summation of contributions from the core and shell. Also, the average CN varies with the dimension because of the change in curvature.\(^{25}\) We can further assume \( z \) is equal for all of the core atoms the bulk value. However, it is noteworthy that \( z \) cannot be considered the same because of differences in the CNs for the surface layer. Sun et al. suggested that the CNs of the outermost three atomic layers of the nanosolids are empirically expressed as 4, 6, and 12, respectively.\(^{27}\) Accordingly, in terms of the relation \( N = N_c + N_s \), we have

\[ z = (1 - \gamma_i) z_b + \gamma_i \frac{N_c}{N} \quad (11) \]

where \( \bar{z} \) is the average CNs of the surface layer.

**Results and Discussion**

It is well-known that the wide band gap semiconductor CdSe nanocrystals has been attracting increasing attention for potential applications such as micro- and nano-optoelectronics.\(^{26}\) A number of studies on the electronic and optical properties of CdSe nanostructures and bulk under applied stimuli such as external pressure have been reported.\(^{27,28}\) Thus, we take the CdSe nanocrystals as an example for performing validity. From eq 4, we calculated the pressure-induced additional energy within a unit cell. The inset in Figure 1a shows the distortion energy dependence on the \( \xi \). Clearly, the distortion energy increases nonlinearly with pressure. It is concluded that the initial unit cell in the lattice would be compressed with pressure, and the value of \( \xi \) becomes smaller. Accordingly, the binding energy per atom would become larger when the applied pressure increases. Notably, the experimental measurements are consistent with the theoretical predictions.

However, Figure 1b shows the pressure-induced ratio of the bond length \( d(p)/d_0 \) for CdSe nanocrystals. Clearly, the bond length becomes shorter with external pressure. To date, many experimental measurements demonstrate the relationship between pressure and the volume of the unit cell, which is directly related to bond length.\(^{29,30}\) Surprisingly, it is also depicted by the Birch–Murnaghan isothermal equation of state.\(^{31}\) Moreover, on the basis of the effective viewpoint of the CNs, the bond nature can also influence

the single bond strength, which is revealed by the size-dependent cohesive energy of the nanocrystals.\(^{32}\)

Figure 2 shows the size effect on the band gap energy of CdSe nanocrystals. Evidently, the band gap energy increases as the size decreases. Therefore, it is concluded that the surface effect with a core--shell configuration of nanocrystals plays a crucial role on physical quantities. The theoretical predictions are consistent with other results.\(^{33–38}\) Similarly, the quantum confinement, extending over the Coulomb interaction of an electron–hole pair of \( R \) separation with a correlation energy \( E_k \) being the Rydberg energy, reveals the same properties.\(^{39}\) Zaknoon et al.\(^{13}\) recently revealed the relationship between the single-particle gap and QD diameter of Si, confirming by scanning tunneling spectroscopy measurements that it can be fit with the equation, \( E_k = 1.136 + 9.75D^{-2} \). Also, Kim et al.\(^{40}\) demonstrated the blue shift of the photoluminescence (PL) of Si QDs with decreasing size.

Furthermore, considering the pressure effect, the compressive energy per atom would lead to the bond strength arising in the system. From eqs 9 and 11, Figure 3 shows the relationship between the band gap expansion and pressure-induced volume reduction of a unit cell of CdSe nanocrystals at 3.5 and 2.4 nm. More importantly, the effect of external pressure could induce band gap expansion, which is well in agreement with the related experimental results.\(^{10}\) In these studies, Zhao et al.\(^{10}\) have studied the PL behaviors of CdSe QDs and CdZnSe and have found that the band gap energy increases almost linearly with pressure.
Li et al. demonstrated that the pressure coefficient is 27 meV GPa$^{-1}$ for CdSe nanocrystals with a radius of 2.4 nm. Actually, the size for nanosolids can be influenced by applied pressure. It is expressed as $D = D_0/[(pB'/B^2 + 1)^{1/3}]$, where $D_0$ is the zero-pressure diameter of nanosolids, $B$ is the bulk modulus, and $B'$ is its pressure derivative.\textsuperscript{10,42} Clearly, the diameter of the nanosolids is in inverse proportion to the pressure. In essence, the dimensions of nanosolids can be modified by pressure, which induces a variation of bond length as well as a bond strength change. Moreover, high pressure can lead to more closely packed structures compared with those at initial situations at zero pressure.\textsuperscript{43} Thus, shorter bond length results in reinforcing covalency and indicates a way to alter the electronic state of semiconductor nanocrystals.

Generally, the phenomena of blue shift in PL in experimental observations have testified the effect of pressure and size. In accordance with above considerations, shortened bond lengths and alternatively charged ions enhance the crystal field and hence band gap energy expansion. It is consequences of the binding energy that can be enhanced by either surface bond contraction or additional compression. More surprisingly, these factors can strengthen each other on the electronic structures and relevant properties of nanosolids. The band gap energy depends on the crystal or a sum of the binding energies over the entire solid. The binding energy, or interatomic potential, depends on the atomic distance and charge quantity of the atoms. Thus, the energy gained by pressure and nanosized effect can tune the band gap energy of semiconductor materials. It implies that it is possible to discover new sources for light emission with a desired wavelength by controlling the physical size or external stimuli.

In addition, many other factors such as the effect of surface oxidation, surface relaxations, and different surface terminations would play a role in band gap modification.\textsuperscript{44,45} Recently, Nolan et al. clarified the band gap variation for silicon nanowires, resulting from the use of different species for surface terminations, and revealed that band gap energies can be tailored not only by the diameter, but also by choice of surface terminations.\textsuperscript{44} Surface terminations such as -OH and -NH$_2$ would lead to a hybridization effect for small silicon nanowires (∼1 nm) that competes with quantum confinement. Likewise, the strain of nanostructures would be a more significant role for band gap variation.

**Conclusion**

In summary, the physical mechanism of the pressure-dependent blue shift of band gap energy of semiconductor nanocrystals has been addressed based on the BOLS correlation mechanism and LBA approach. The nanosized effect and external pressure can lead to bond compression and crystal potential enhancement. Good agreement has been realized with the experimentally measured $p$-dependent band gap energy of CdSe, which means the method we have developed could reveal a better understanding of its atomic origin and physical mechanism. Importantly, the theoretical model develops the essential evidence to connect the macroscopically measurable quantities to the atomic bonding identities and the response of these bond identities to pressure change. Thus, these theoretical studies indicate that the LBA approach and BOLS correlation mechanism are applicable to general high pressure research.

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**References and Notes**


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