Optical Properties of Low Dimensional Semiconductor Materials

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Abstract

The interaction between light and matter can tell us a great deal of information about the properties of matter through many different spectroscopies that cover a wide range of wavelengths. This dissertation presents a serial study about the optical properties of different semiconductor materials. It is motivated by the fact that semiconductors are extremely important in modern technology and relates to many applications of low-dimensional semiconductor nanostructures in the fields of ultraviolet optoelectronics, multiphoton bio-imaging, and quantum dot detectors and lasers.

Three main types of studies are addressed: (1) The role of doping levels of N and Al atoms in room-temperature photoluminescence of 4H-SiC films for optoelectronic applications; (2) Kinetic Monte Carlo methods combined with probability calculations of the time-dependent Schrödinger equation to study multi-photon absorption and emission of II-VI compound quantum dots (QDs) for bioimaging; (3) Advanced quantum chemistry approaches to study structure and optical properties of InGaAsN and GaAs clusters for laser technology applications.

4H-SiC films were grown on AlN/SiC(100) substrates by a chemical vapour deposition system. Three well-defined room-temperature photoluminescence peaks close to the bandgap energy were observed. By a detailed theoretical analysis of optical transitions in the samples, it was found that the photoluminescence peaks most probably are due to optical transitions between impurity levels and band edges, and the optical transition between the second minimum of the conduction band and the top of the valance band. Special attention has been paid to effects of doping levels of N and Al impurities.

Optical transitions in several II-VI QDs have been studied by a quantum Monte Carlo method. We model the QD energy band structure by a spherical square quantum well and the electrons in the conduction band and holes in the valence band by the effective mass approximation. The probabilities of optical transitions induced by ultrafast and ultraintense laser pulses are calculated from the time-dependent Schrödinger equation. With the inclusion of the nonradiative electron-phonon processes, the calculated absorption and emission spectra are in agreement with experimental results. The dynamic processes and up-conversion luminescence of the QDs, required for many applications such as bio-imaging, are demonstrated.

Quantum chemistry approaches are used to study InGaAsN and GaAs nano systems. Dilute-nitride zincblende In$_x$Ga$_{1-x}$N$_y$As$_{1-y}$ clusters are examined from the energy
point of view with a semi-empirical method, and optimum cluster configurations are identified by which we can extract detailed bonding structures and the effects of In doping. A central insertion scheme has been implemented to study the electronic band structures of GaAs nanocrystals at the first-principles level. The formation of energy bands and quantum confinement effects have been revealed, providing theoretical support for laser design.
Preface

The work presented in this thesis has been carried out at the Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, Stockholm, Sweden.


**Paper IX**  Quantum chemistry study of energy band structures of GaAs nano

**List of papers not included in the thesis**


**Paper XI**  Band structure study of dilute-nitride zincblende In$_x$Ga$_{1-x}$N$_y$As$_{1-y}$, Y. Fu, Y. Luo, J. Jiang, **T.-T Han**, S.-M. Wang, and A. Larsson, Swedish Theoretical Chemistry, May 4-5, 2006, Stockholm, Sweden.
Comments on my contribution to the papers included

- I was responsible for all calculations and writing of papers I, II, III, IV, and VIII.
- I was responsible for discussion and parts of the calculations of papers V, VI, and VII.
- I was responsible for parts of the experiments in paper I.
- I was responsible for discussion and writing of paper IX.
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Contents

1 Introduction 11

2 Basic theory of semiconductors 15
   2.1 Crystal structure of semiconductors 15
   2.2 Energy band structures 16
   2.3 Effective mass approximation 19
   2.4 Density of states and dimensions of materials 20

3 Photoluminescence from 4H-SiC thin films 23
   3.1 Indirect optical transitions 23
   3.2 Overview of SiC materials 28
   3.3 Experiment and results analysis 29

4 Multiphoton quantum dots 33
   4.1 Introduction 33
   4.2 Multiphoton processes 36
   4.3 Kinetic Monte Carlo method 40
   4.4 Optical properties of multiphoton QDs 41

5 Quantum chemistry study of InGaAsN clusters 43
   5.1 Basics of Quantum Chemistry theory 43
   5.2 Structure study by a semi-empirical method 45
   5.3 Quantum Chemistry study of GaAs clusters 46
6 Comments on included papers 49
Chapter 1

Introduction

The complexity for minimum component costs has increased at a rate of roughly a factor of two per year ... Certainly over the short term this rate can be expected to continue, if not to increase. Over the longer term, the rate of increase is a bit more uncertain, although there is no reason to believe it will not remain nearly constant for at least 10 years...I believe that such a large circuit can be built on a single wafer.

Moore’s Law, Gordon E. Moore *Electronics Magazine* April 19, 1965

Information technology has become a most important industry nowadays. The information revolution from the 1980’s changed our life and ways of living a lot. Computers, mobile phones, and other modern electronics have already become a part of our daily life, which are all based on semiconductors (*Chapter 2*). The progress of technology and science has driven the development of semiconductor industry with an amazing speed. Gordon Moore, one of the founders of Intel, predicted empirically in 1965 that the number of transistors on a chip will double about every two years. This prediction has largely been successful even until today. In general, silicon has been used for most commercial semiconductor products. Dozens of other materials have been catching up as well. For example, wide-bandgap semiconductors such as SiC are good candidates for applications of high-temperature, high-speed, and high-power devices [1, 2, 3, 4] (*Chapter 3*), II-VI compound semiconductors have been widely used for growing colloidal nanocrystals for fluorescent applications in biotechnology [6, 7] (*Chapter 4*), and dilute-nitride materials In$_x$Ga$_{1-x}$N$_y$As$_{1-y}$ have a great range of potential applications including long-wavelength semiconductor lasers and
quantum well infrared photodetectors [10, 11, 12, 13] (Chapter 5).

The interaction between light and matter can tell us a great deal of information about the properties of matter through our eyes and through many different spectroscopies covering all the wavelengths we thus far have developed. For semiconductors, the optical properties are directly related to the electron energy band structure. Starting from the study of band structure, we will thus be able to figure out the interaction property between photons and electrons in semiconductors. After knowing the nature of the materials, it is possible to make proper use of them. For instance, the radiative recombination between photon excited electrons in the conduction-band and holes in the valence-band can lead to photon emission, which is a basic physical process of photoluminescence (Chapter 3). Moreover, the multiphoton process, predicted by Goeppert-Mayer [43] in 1931, has already become an important field of optics, which has been recently extended very successfully for bioimaging applications (Chapter 4).

Solid state physics is focused on crystals, which has a periodical structure of atoms. Starting from the Schrödinger equation of quantum mechanics, solid state physics theory describes the band structure and optical transition properties of solid-state semiconductors together with some basic approximations, such as the effective mass approximation, and perturbation theory (Chapter 3).

The increase in the number of devices on a chip accompanies the reduction in size of each unit. Ever since the first transistor became available, there has been a constant trend to make devices smaller and smaller. When the miniaturization of device size approaches the nano scale, the energy band structure becomes quantized. Moreover, ultra-intense and ultra-short lasers are usually used in multiphoton microscopies, so that conventional steady-state perturbation theory is not valid. Solving the time dependent Schrödinger equation non-perturbatively becomes necessary to study the dynamics of multiphoton processes properly (Chapter 4).

On the other hand, well-established theory in quantum chemistry is extremely powerful to study steady-state electronic properties of small systems at the first-principles level. While quantum chemistry can describe very well the fundamental behaviour of matter at the molecular scale, it can, however, in general only deal with systems containing some hundreds of light atoms like C, H, and O because of the poor particle scaling and limited computational capability. An InGaAsN nanoparticle with a diameter of 4 nm contains more than 700 heavy atoms, which is too much for conventional quantum chemistry to deal with without further sophisticated numerical algorithms. With the latest development of high-performance computers
(because of Moore’s Law) and the help of modern numerical algorithms, it is though possible now to apply quantum chemistry to study relatively large semiconductor clusters [68, 69, 70, 71, 72, 73, 74].

The semi-empirical PM3 method is an approach that drastically reduces the computational requirements, and can be used to obtain optimized structures of large systems. An efficient computational method called the central insertion scheme (CIS) has been developed by Jun Jiang and Bin Gao et al. in our laboratory [74, 79]. The method is implemented in conjunction with modern quantum chemical density functional theory (DFT). The CIS method allows to calculate electronic and optical properties of a relatively large-scale system with periodic structures of atoms from an initial central structure. In the last part of this thesis, we will study the cluster of a GaAs system by this CIS method (Chapter 5).

In a brief summary, I have studied the optical properties in various low dimensional semiconductor materials with different methods. Well defined photoluminescence peaks from doped SiC films were observed both theoretically and experimentally. By solving the time-dependent Schrödinger equation, we demonstrated the dynamic multiphoton processes in quantum dots which are useful for many applications such as bio-imaging. Adopting the methods from quantum chemistry, we studied the structural properties of $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$ systems and the electronic band structures of GaAs clusters with a size up to 17 nm. We foresee an impact of the current work on applications in ultraviolet optoelectronics, multiphoton bio-imaging, and quantum dot detectors and lasers.
Chapter 2

Basic theory of semiconductors

*Science is concerned only with observable things and that we can observe an object by letting it interact with some outside influence.*

Paul Adrien Maurice Dirac

Semiconductors are widely used in our daily life. They are essential in modern electrical devices such as personal computers, digital cameras, and mobile phones. The main reason that makes semiconductor materials so important in modern industrial technology are their unique electrical and optical properties. A semiconductor has electrical conductivity in between that of a conductor and an insulator, which can be easily controlled over a wide range. These are essential advantages for such a wide range of applications. The energy band structure of the semiconductor is the origin of these magic physical properties. The energy band structure of electrons in a semiconductor crystal reflects the periodic potential of the crystal. In the following sections of this chapter, we will present a brief description of the crystal structure, the energy band structure, the effective mass approximation, and the density of states of electrons, to describe the motion of electrons in semiconductors and to study their optical and electrical properties.

2.1 Crystal structure of semiconductors

Solid state physics is mainly related to crystals and the movements of electrons in crystals. The structure of all crystals can be described in terms of lattice sites, and
of atom located at these lattice sites. Because of the periodicity of crystals, any two lattice sites \( R, R' \) in a crystal are correlated

\[
R' = R + m_1 R_1 + m_3 R_3 + m_3 R_3
\]  

(2.1)

where \( m_1, m_2, m_3 \) are integers, and \( a_1, a_2, \) and \( a_3 \) are three independent primitive vectors.

In the three-dimensional space, there are totally 14 different lattice types, among which face-centered cubic (fcc) is the most common crystal structure of semiconductors. An fcc lattice can be obtained by adding an atom at the centre of each face of a simple cubic lattice, where the simple cubic system consists of one lattice point at each corner of the cube. The fcc crystal structure is shown in Fig. 2.1(a). The primitive vectors are: \( a_1 = a(x_0 + y_0)/2, a_2 = a(z_0 + y_0)/2, a_3 = a(x_0 + z_0)/2, \) where \( a \) is normally referred to as the lattice constant. \( x_0, y_0, \) and \( z_0 \) are the unit vectors along the \( x, y, \) and \( z \) directions.

To study the periodic properties of a crystal, the definition of a reciprocal lattice is introduced as

\[
e^{iG \cdot r} = 1
\]  

(2.2)

where \( r \) characterizes the lattice point in the real space, \( G = n_1 b_1 + n_3 b_3 + n_3 b_3 \) describes the reciprocal space, and \( n_1, n_2, n_3 \) are integers. For a three dimensional lattice, the reciprocal lattice is determined by

\[
b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}, \quad b_2 = 2\pi \frac{a_3 \times a_1}{a_2 \cdot (a_3 \times a_1)}, \quad b_3 = 2\pi \frac{a_1 \times a_2}{a_3 \cdot (a_1 \times a_2)}
\]  

(2.3)

The Wigner-Seitz cell in the reciprocal lattice contains all points which are nearer to one considered lattice point than to any other, which is also denoted as the first Brillouin zone. The first Brillouin zone of an fcc lattice is presented in Fig. 2.1(b) together with labels of high symmetry lines and points.

### 2.2 Energy band structures

Periodic lattice structures create a special situation for the electrons. If one denotes the periodic electronic potential \( V(r) \) of the lattice by

\[
V(r + R) = V(r),
\]  

(2.4)
2.2. ENERGY BAND STRUCTURES

Figure 2.1: (a) Schematic structure of an fcc lattice, $a$ is the lattice constant. (b) The first Brillouin zone of an fcc lattice.

where $R$ is an arbitrary lattice vector, one can write the Schrödinger equation for the electrons in a periodic potential as

$$\left[ -\frac{\hbar^2}{2m_0} \nabla^2 + V(r) \right] \Psi(r) = E\Psi(r) \quad (2.5)$$

where $m_0$ is the mass of the free electron. Because of the periodicity of $V(r)$, the electron wave function has the following form

$$\Psi_{nk}(r) = e^{ikr}u_{nk}(r)$$

$$u_{nk}(r) = u_{nk}(r + R) \quad (2.6)$$

which is the Bloch theorem. Here $k$ is called the electron wave vector and $u_{nk}$ is a periodic function (periodic Bloch function).

It is normally difficult to characterize, both experimentally and theoretically, the band structure in the whole Brillouin zone. Many theoretical methods adopt some assumptions and approximations and have to be calibrated together with the experiments. One method to calculate the band structure is called the linear combination of atomic orbitals (LCAO) method, which is also the basis for the so-called as the tight-binding method [5, 14]. In the tight-binding method, one assumes that the wave functions of the electrons of the crystal atoms are very similar to the ones of the isolated atom in free space, and consider only the interaction between atoms to those of the nearest neighbours. We choose the wave functions of the electrons (orbitals) of 'free' atoms as basis states. Most compound semiconductor materials, have zincblende structures, which is a structure based on an fcc lattice with a
cation-anion pair occupying each lattice site. In the \( sp^3 \)-type tight-binding method of \([5, 14]\), the electron wavefunctions of outer-most shell are described by four atomic orbitals \( s, p_x, p_y, \) and \( p_z \). Each of the atomic orbitals can occur for each of the two sites in the unit cell. Thus the Bloch wavefunction is

\[
\Psi(r) = \sum_m \sum_{j=1}^2 C_{mj}(k) \Psi_{mj}(r - r_j) e^{i k \cdot r} \quad (2.7)
\]

where \( j = 1, 2 \) correspond to the different atoms in the unit cell and \( m \) refers to the 4 different atom orbitals. By solving the secular equation

\[
|\langle \Psi_{m'j'} | H - E | \Psi(k, r) \rangle| = 0 \quad (2.8)
\]

the band structure can be calculated for different values of \( k \), which is normally referred to as the energy dispersion \( E = E(k) \). In general, empirical input parameters are used to evaluate the Hamiltonian matrix. There are many research works in which parameters are modified by comparing with experiments, see e.g., \([5, 14]\) and references therein.

Besides the tight-binding approach, there are other methods. One of the well-known methods was developed by Koringa, Kohn and Rostoker \([15, 16]\) based on the Green’s function technique and muffin-tin potential (KKR Green-function method). Another one is called the pseudopotential method \([8, 9]\), where an empirical pseudopotential is introduced in order to obtain good agreement of electronic band structures with experiments. The pseudopotential method gives surprisingly accurate results with respect to the computation time and resource requirements. Another widely used method is the \( k \cdot p \) theory which was introduced by Kane in 1956 to analyse the energy band structures of III-V compound semiconductors \([17]\).

Fig. 2.2 shows a schematic diagram of the band structure of crystal 4H-SiC. \( \Gamma_{15e} \) is the energy of the valence band top at the centre of the Brillouin zone \([000]\). The conduction band minimum is on the M valleys, while \( \Gamma_{1e} \) is the conduction band energy at the centre of the Brillouin zone \([000]\). The energy values of these points determine whether we have a direct or an indirect band gap. If the minimum of the conduction band lies vertically above the maximum of the valence band in the \( k \) space, it is called a direct bandgap material, otherwise it refers to an indirect bandgap material. In the particular case of this figure under investigation, 4H-SiC is an indirect semiconductor.
2.3 Effective mass approximation

An electron in a lattice is under the influence of the periodic lattice potential. To describe the movement of electrons inside the solid material, we introduce the concept of an effective mass. By the Bloch theorem, a definite Bloch state \( \mathbf{k} \) in a periodic lattice is described by its energy dispersion relationship, \( E = E(\mathbf{k}) \), its crystal momentum \( \hbar \mathbf{k} \), and a group velocity

\[
\mathbf{v} = \frac{1}{\hbar} \frac{dE(\mathbf{k})}{d\mathbf{k}} \tag{2.9}
\]

To describe approximately the electron motion in the crystal, we consider an external force \( \mathbf{F} \) and Newton’s second law of motion that

\[
\mathbf{F} = \frac{d(\hbar \mathbf{k})}{dt} \tag{2.10}
\]

Now we introduce a quantity called “effective mass” such that

\[
\frac{dv_i}{dt} = \sum_j \left( \frac{1}{m^*} \right)_{ij} F_j \tag{2.11}
\]
Since
\[ \frac{dv_i}{dt} = \frac{d}{dt} \left( \frac{1}{\hbar} \frac{\partial E}{\partial k_i} \right) = \sum_j \frac{1}{\hbar} \frac{\partial^2 E}{\partial k_i \partial k_j} \frac{dk_j}{dt} \] (2.12)

where \( i, j = x, y, z \). The effective mass therefore is given
\[ \left( \frac{1}{m^*} \right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j} \] (2.13)

The effective mass can be negative or positive due to different dispersion relations. Notice that the effective mass is in general a tensor, which means that it can depend strongly on the crystal direction.

Many properties of semiconductors can be described by using the effective mass approximation.

### 2.4 Density of states and dimensions of materials

To calculate various optical properties such as the rate of absorption or emission and how electrons and holes distribute within the energy band structure of the solid, we need to know the electron density of states (DOS). In semiconductors, the density of states is a property that quantifies how closely energy levels are packed. It is defined as the number of available states per unit volume per unit energy. In a three dimensional bulk system, the number of states between \( k \) and \( k + dk \) is
\[ dN_{3D} = 2 \left( \frac{L}{2\pi} \right)^3 4\pi k^2 dk \] (2.14)

where we assume that the semiconductor is a cube with side \( L \). By using the dispersion relation \( E(k) = \hbar^2 k^2 / 2m^* \), we can obtain the density of states in terms of energy as
\[ g_{3D}(E) = \frac{dN_{3D}}{dE} = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E} \] (2.15)

For \( E \geq 0 \). For a two-dimensional semiconductor such as a quantum well, in which electrons are confined to a plane, we can get the density of states
\[ g_{2D}(E) = \frac{m}{\pi \hbar^2} \] (2.16)

for \( E \geq 0 \). In one dimension, the density of states becomes
\[ g_{1D}(E) = \frac{1}{\pi} \left( \frac{m}{\hbar^2} \right)^{1/2} \frac{1}{\sqrt{E}} \] (2.17)
2.4. DENSITY OF STATES AND DIMENSIONS OF MATERIALS

Figure 2.3: The relationship between the density of states and the system dimension.

for $E \geq 0$. And finally, for a zero dimensional system, e.g. a quantum dot, the energy states are quantised in all directions, and the density of states consists of only $\delta$ functions.

Fig.2.3 shows the density of states for a bulk material, a quantum well with infinite barriers, a quantum wire with infinite barriers, and a quantum dot. The relationship between density of states and the system dimension is clearly shown in this figure. The DOS in 3D system is a function of $E^{1/2}$. For a 2D system, the DOS is a step function with steps occurring at the energies of quantized levels. The DOS in a 1D system has an $E^{-1/2}$ relation with energy. For a 0D system, it is a $\delta$ function of $E$ [19].
Chapter 3

Photoluminescence from 4H-SiC thin films

3.1 Indirect optical transitions

As mentioned in Chapter 2, in semiconductor physics a direct bandgap means that the minimum of the conduction band lies directly above the maximum of the valence band in the $k$ space. In contrast, an indirect semiconductor refers to a semiconductor with a bandgap in which the minimum energy in the conduction band is shifted by a $k$ vector relative to the top of the valence band.

Because of the small momentum associated with photons, optical transitions in which both initial and final states are band states are allowed only if the crystal momentum is conserved. Such processes are depicted by vertical lines in the $E(k)$ diagram and are termed vertical transitions. For non-vertical transitions to occur the momentum has to be supplied from other sources including impurities and phonons. Transitions involving a photon state and a phonon or impurity state are termed indirect. Two important examples of indirect radiative transitions are the interband transition from the top of the valence band to a conduction band valley at or near the zone boundary, and intra-valley transitions responsible for free-carrier absorption. Fig. 3.1 shows the optical transition (emission in this case) processes in semiconductors with a direct bandgap and an indirect bandgap. Basic theory about indirect optical transitions can be found in, e.g. [20], whereas here we limit ourselves to describing the rate of phonon-assisted optical transitions.
Figure 3.1: Scheme of optical transition in semiconductor with a (a) direct bandgap and (b) indirect bandgap.

The transition rate from an initial state \( |i \rangle \) to a final state \( |f \rangle \) is given as

\[
w_{f \rightarrow i} = \frac{\Gamma_i / \hbar}{(E_f - E_i)^2 + \Gamma_i^2} \left| \sum_{\alpha} \langle f | H | \alpha \rangle \langle \alpha | H | i \rangle \right|^2
\]

by the second-order perturbation theory, where \( H = H_{h\omega} + H_{ep} \), \( E_i \) and \( E_f \) are the energies of the initial state and final states, respectively, and \( \Gamma \) is the relaxation energy.

One route of the transition is that \( H_{h\omega} \), the optical perturbation, first induces an direct optical transition from the initial state \( |i \rangle \) to an intermediate state \( |\alpha \rangle \), requiring conservation of momentum. The phonon perturbation \( H_{ep} \) completes the transition by taking the system from \( |\alpha \rangle \) to the final state \( |f \rangle \) by contributing the phonon momentum in order to conserve the overall momentum and energy conservation. Alternatively, the first step can be accomplished by the phonon perturbation and the second step by the optical perturbation. Here we do not consider the less possible two-phonon (\( H_{ep} \) active in both steps) or two-photon processes (\( H_{h\omega} \) active in both steps).

Let the initial state be a Bloch state of the valence band \( v \) denoted by \( |v k \rangle \) and the final state be a Bloch state of the conduction band \( c \) denoted by \( |c k' \rangle \). Consider the absorption of a photon of energy \( \hbar \omega \), of a phonon of energy \( \hbar \omega_q \) and crystal
momentum $\hbar \mathbf{q}$. The total energies of the initial and final states are then
\[
E_i = E_{v\mathbf{k}} + \hbar \omega + \hbar \omega_q
\]
\[
E_f = E_{c\mathbf{k}+\mathbf{q}}
\] (3.2)

Here we have already used the relationship of $\mathbf{k}' = \mathbf{k} + \mathbf{q}$ due to the momentum conservation.

If the phonon is absorbed first, the intermediate energy is given by
\[
\begin{align*}
(a) \quad E_\alpha &= E_{v\mathbf{k}+\mathbf{q}} + \hbar \omega \\
(b) \quad E_\alpha &= E_{c\mathbf{k}+\mathbf{q}} + \hbar \omega
\end{align*}
\] (3.3)

When the photon is absorbed first
\[
\begin{align*}
(a) \quad E_\alpha &= E_{c\mathbf{k}} + \hbar \omega_q \\
(b) \quad E_\alpha &= E_{v\mathbf{k}+\mathbf{q}} + \hbar \omega_q
\end{align*}
\] (3.4)

(neglecting the photon momentum). Processes (a) and (b) are mutually distinct only when the initial and final states are in different bands. When this is the case the optical transitions for processes (b) are forbidden since they depend upon a matrix element of the form $\langle v\mathbf{k}|v\mathbf{k} \rangle$ or $\langle c\mathbf{k}+\mathbf{q}|c\mathbf{k}+\mathbf{q} \rangle$, whereas processes (a) entail allowed transitions, therefore we do not need to consider processes (b) further.

The sum $S$ over the intermediate states is therefore
\[
S = \langle \mathbf{k}+\mathbf{q}|H_{\text{h\omega}}|\mathbf{v}\mathbf{k}+\mathbf{q} \rangle \langle \mathbf{v}\mathbf{k}+\mathbf{q}|H_{\text{ep}}|\mathbf{v}\mathbf{k} \rangle \quad + \quad \langle \mathbf{k}+\mathbf{q}|H_{\text{ep}}|\mathbf{c}\mathbf{k} \rangle \langle \mathbf{c}\mathbf{k}|H_{\text{h\omega}}|\mathbf{v}\mathbf{k} \rangle \quad \frac{E_{v\mathbf{k}} + \hbar \omega - E_{c\mathbf{k}} + i\Gamma_i}{E_{v\mathbf{k}} + \hbar \omega_q - E_{v\mathbf{k}+\mathbf{q}} + i\Gamma_i}
\] (3.5)

If $E_{g\mathbf{k}} = E_{c\mathbf{k}} - E_{v\mathbf{k}}$ is the direct energy gap between bands $v$ and $c$ at $\mathbf{k}$ we can use Eq. (3.2) in the first denominator to write the sum thus
\[
S = \langle \mathbf{k}+\mathbf{q}|H_{\text{h\omega}}|\mathbf{v}\mathbf{k}+\mathbf{q} \rangle \langle \mathbf{v}\mathbf{k}+\mathbf{q}|H_{\text{ep}}|\mathbf{v}\mathbf{k} \rangle \quad - \quad \langle \mathbf{k}+\mathbf{q}|H_{\text{ep}}|\mathbf{c}\mathbf{k} \rangle \langle \mathbf{c}\mathbf{k}|H_{\text{h\omega}}|\mathbf{v}\mathbf{k} \rangle \quad \frac{E_{g\mathbf{k}} - \hbar \omega + i\Gamma_i}{E_{g\mathbf{k}+\mathbf{q}} - \hbar \omega + i\Gamma_i}
\] (3.6)

To obtain the total rate associated with the absorption of a photon we must add two further terms to the sum, similar in form to those in Eq. (3.6) which describe the emission of a phonon. If the two terms in Eq. (3.6) are labelled, respectively, $S_{1+}$ and $S_{2+}$, the similar terms associated with phonon emission $S_{1-}$ and $S_{2-}$, the sum over intermediate states is given by $S_{1+} + S_{2+} + S_{1-} + S_{2-}$.

In silicon the optical absorption edge is associated with a transition between the top of the valence band and one of the six $\Delta$ valleys, and in germanium between the top of the valence band and one of the four $L$ valleys in the conduction band.
CHAPTER 3. PHOTOLUMINESCENCE FROM 4H-SIC THIN FILMS

All of them are indirect transitions. The full calculation of the transition rate is rather complicated since it involves eight matrix elements (two for each $S$). Here we only consider a calculation of the partial rate arising from important contributions which we assume to be embodied in the terms $S_{2+}$ and $S_{2-}$, because of their small denominators. Since the cross terms between $S_{2-}$ and $S_{2+}$ do not contribute to the rate, we can write

$$w_{f\rightarrow i} = \frac{\Gamma_i/\hbar}{(E_f - E_i)^2 + \Gamma_i^2} \left( |S_{2+}|^2 + |S_{2-}|^2 \right)$$  \hspace{1cm} (3.7)

$$|S_{2\pm}|^2 = \frac{\langle c\mathbf{k} \pm \mathbf{q}|H_{ep}|c\mathbf{k}\rangle^2 |\langle c\mathbf{k}|H_{ph}|v\mathbf{k}\rangle|^2}{(E_{gk} - \hbar \omega)^2 + \Gamma_i^2}$$  \hspace{1cm} (3.8)

The optical matrix element is identical to that for a direct transition. The square of the phonon matrix element for a given $\mathbf{q}$ has the following general form [20]

$$|\langle c\mathbf{k} \pm \mathbf{q}|H_{ep}|c\mathbf{k}\rangle|^2 = \frac{\hbar}{2N_{cell} M'} C_q^2 I(k, k + q) \frac{N(\omega_q)}{\omega_q} \left[ \frac{N(\omega_q)}{N(\omega_q) + 1} \right]$$  \hspace{1cm} (3.9)

where $N_{cell}$ is the number of unit cells in the periodic crystal, $M'$ is the appropriate mass of the oscillator, e.g., the total mass of the unit cell in the case of acoustic modes, $M_1 + M_2$, or in the case of long-wavelength optical modes the reduced mass of $1/(1/M_1 + 1/M_2)$. Here $M_1$ and $M_2$ are the masses of the two atoms in the unit cell. $N(\omega_q)/V$ is the phonon density

$$\frac{N(\omega_q)}{V} = n(\omega_q) = \frac{1}{e^{(\hbar \omega_q/k_B T)} - 1}$$  \hspace{1cm} (3.10)

In the case of scattering between valley $i$ and $j$ (inter-valley) involving a phonon of frequency $\omega_q$ with an inter-valley deformation potential constant $D_{ij}$

$$\frac{C_q^2 I(k, k + q)}{M'} = \frac{D_{ij}^2}{M_1 + M_2}$$  \hspace{1cm} (3.11)

where $M_1 + M_2$ is the total mass of the unit cell. Thus

$$|\langle c\mathbf{k} \pm \mathbf{q}|H_{ep}|c\mathbf{k}\rangle|^2 = \frac{\hbar D_{ij}^2}{2\rho V \omega_q} \left[ \frac{N(\omega_q)}{N(\omega_q) + 1} \right]$$  \hspace{1cm} (3.12)

where $\rho$ is the mass density, $V$ the volume of the crystal within which the photon, electron and photon waves are normalized. We assume that inter-valley scattering is isotropic and independent of $\mathbf{q}$. 

Finally, the optical transition between a valence band \( |v_k\rangle \) and a conduction band state becomes

\[
\begin{align*}
 w_{f,vk}(\hbar\omega) &= \frac{\langle f|H_{hv}|vk \rangle|^2}{(E_{vk} - \hbar\omega)^2 + \Gamma_k^2} \frac{\hbar D_{ij}^2 N_{\text{val}}}{2\rho V \omega_q} \times \\
 &\left\{ \frac{N(\omega_q)\Gamma_k/\hbar}{(E_f - E_{vk} - \hbar\omega_q - \hbar\omega)^2 + \Gamma_k^2} + \frac{[N(\omega_q) + 1]\Gamma_k/\hbar}{(E_f - E_{vk} + \hbar\omega_q - \hbar\omega)^2 + \Gamma_k^2} \right\} \quad (3.13)
\end{align*}
\]

when the transition takes place between valley \( i \) and \( j \) (inter-valley) involving a phonon of frequency \( \omega_q \) with an inter-valley deformation potential constant \( D_{ij} \). \( N_{\text{val}} \) is the number of equivalent conduction band valleys containing final states. In Eq. (3.13), the first term headed by \( N(\omega_q) \) corresponds to the phonon absorption, while the other term is the phonon emission.

Only one final state is coupled to a given initial state by \( k \) conservation for direct inter-band transitions. For indirect transitions the situation is different. Corresponding to a given initial state \( |v_k\rangle \) there is a spread of final states in the conduction band brought about by phonon scattering, and hence the transition rate is given by

\[
\begin{align*}
 w_{vk}(\hbar\omega) &= \sum_f w_{f,vk}(\hbar\omega) = \frac{\langle f|H_{hv}|vk \rangle|^2}{(E_{vk} - \hbar\omega)^2 + \Gamma_k^2} \frac{\hbar D_{ij}^2 N_{\text{val}}}{2\rho V \omega_q} \\
 &\left\{ N(\omega_q)N_c(E_{vk} + \hbar\omega + \hbar\omega_q) + [N(\omega_q) + 1]N_c(E_{vk} + \hbar\omega - \hbar\omega_q) \right\} \quad (3.14)
\end{align*}
\]

where \( N_c(E) \) is the density of states in a given conduction band valley.

To obtain the total transition rate induced by a given photon energy which determines the photoluminescence intensity, we have to sum over all \( w_{vk}(\hbar\omega) \) which correspond to allowed processes, keeping \( \hbar\omega \) constant. This means summing over all possible initial states from \( E_{vk} = 0 \) to \( E_{k_{\text{max}}} \), where

\[
\begin{align*}
 E_{k_{\text{max}}} &= \hbar\omega - E_g + \hbar\omega_q \quad \text{phonon absorption} \\
 E_{k_{\text{max}}} &= \hbar\omega - E_g - \hbar\omega_q \quad \text{phonon emission} \quad (3.15)
\end{align*}
\]

where \( E_g \) is the indirect band gap between two bands under investigation (between which the optical transitions occur). We multiply \( w_{vk} \) by \( N_v(E_k)dE_k \), where \( N_v(E) \) is the density of states in the valence band. In the case of parabolic bands

\[
\int_0^{E_{k_{\text{max}}}} \sqrt{E_k(E_{k_{\text{max}}} - E_k)} dE_k = \frac{\pi E_{k_{\text{max}}}^2}{8} \quad (3.16)
\]

and hence we obtain

\[
 w(\hbar\omega) = \frac{\langle \epsilon \Gamma|H_{hv}|\epsilon\Gamma \rangle^2 D_{ij}^2 N_{\text{val}}(m^*_c m^*_v)^{3/2}}{(E_{\epsilon\Gamma} - \hbar\omega)^2 8^2 \hbar^6 \rho \omega_q V}
\]
\[
\left\{ N(\omega_q)(\hbar\omega - E_g + \hbar\omega_q)^2 + \left[N(\omega_q) + 1\right](\hbar\omega - E_g - \hbar\omega_q)^2 \right\} \quad (3.17)
\]

where the optical matrix element is approximated by the one at the \(\Gamma\) point.

At room temperature \(N(\omega_q) \gg 1\), so that

\[
w(\hbar\omega) = \frac{|\langle c\Gamma|H_{\text{hh}}|v\Gamma\rangle|^2D_{ij}^2N_{\text{val}}(m^*_e m^*_v)^3/2n(\omega_q)}{(E_g - \hbar\omega)^28\pi^2\hbar^6\rho\omega_q}
\]

\[
\left[ (\hbar\omega - E_g + \hbar\omega_q)^2 + (\hbar\omega - E_g - \hbar\omega_q)^2 \right] \quad (3.18)
\]

Each type of allowed phonons contributes to the rate expressed by the above equation with \(D_{ij}\) and \(\omega_q\) characterizing the mode. Furthermore, indirect inter-band optical transitions differ significantly from direct inter-band transitions in their dependence on photon energy. Near the threshold energy, \(E_{\text{th}} = E_g \pm \hbar\omega_q\) for indirect transitions, while \(E_{\text{th}} = E_g\) for direct transitions, the former varies as \((\hbar\omega - E_{\text{th}})^2\) while the latter varies as \((\hbar\omega - E_{\text{th}})^{1/2}\).

### 3.2 Overview of SiC materials

In this chapter we focus on silicon carbide (SiC). SiC is a wide bandgap semiconductor with band gaps of 3.28 eV (4H) and 3.03 eV (6H), respectively. Due to the outstanding properties including high electron mobility, high breakdown electric-field strength, and high thermal conductivity, SiC has an enormous potential for high-temperature and high-speed-power-device applications, which can work under extreme environments [21, 22]. SiC has also the strong tolerance to radiation damage, making it a good candidate material for defence and aerospace applications. Because of the convenience of combining the well developed Si process technology, SiC-based devices are easier to manufacture compared with other competitors.

Starting from 1893, when the properties of SiC were first described, the research on SiC has received growing attention. Continuous progress in the crystal-growth technology of SiC has resulted in large size wafers. Of the large number of its possible polytypes, 4H- and 6H- SiC have now been commercially produced in a quality considered appropriate for device applications.

Fig.2.2 shows the band structure of 4H-SiC. A band gap of 3.23 eV occurs between the \(\Gamma\) and \(M\) points. Due to its indirect bandgap, SiC has an inevitable disadvantage in optical applications although it has been already used for blue light emitting diodes (LEDs). Most of the photoluminescence (PL) of SiC is observed at very
3.3. EXPERIMENT AND RESULTS ANALYSIS

In our work, 4H-SiC films were grown on AlN/Si(100) substrates using the chemical vapour deposition (CVD) method. In a typical CVD growth process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. In this work, the substrate is Si(100) with a AlN thin film as a buffer layer. AlN was chosen as the buffer layer here because of the small lattice mismatch between AlN and SiC. SiH₄ and C₂H₄ were the reaction precursors, shown in Fig. 3.2(a). The deposition temperature was in the range of 1030-1130°C. The sample cross section structure is schematically shown in Fig. 3.2(b). The AlN layer has a thickness of 200–300 nm [30].

The PL measurements were carried out at room temperature by a 325-nm He-Cd
laser. The excitation power was about 20 mW on the sample surface with a beam diameter of 1 mm. The experimental results are presented in Fig. 3.3, where $P_{\text{C}_2\text{H}_4}$ and $P_{\text{SiH}_4}$ denote the partial pressures of C$_2$H$_2$ and SiH$_4$, respectively. Three PL peaks have been observed which are centred at 3.03, 3.17, and 3.37 eV. When $P_{\text{C}_2\text{H}_4}/P_{\text{SiH}_4}$ is lower than 1.62, room-temperature PL spectra of 4H-SiC films on AlN/Si(100) show two main peaks located around 3.03 and 3.17 eV, which are attributed to the radiative recombinations between 4H-SiC conduction-band minimum and Al acceptor level (whose ionization energy is around 0.20 eV) [31, 32], and between the valence-band top and N donor level (ionization energy is around 0.06 eV) [32, 33], respectively. This strongly indicates that the fabricated films are 4H-SiC. The PL peak at 3.37 eV becomes more prominent when $P_{\text{C}_2\text{H}_4}/P_{\text{SiH}_4}$ is higher than 1.62. This corresponds to the recombination between the secondary minimum in the conduction band and the top of the valance band. Except these peaks near the band gap energy of 4H-SiC, no other clear peaks were observed in the low energy regime.

With the indirect optical transition theory discussed in this chapter, we can reproduce the PL spectra as shown in Fig. 3.4. In the theoretical calculations we have associated the electron states at the conduction band bottom with the impurity
3.3. EXPERIMENT AND RESULTS ANALYSIS

\[ N_D = 8.0 \times 10^{15} \text{ cm}^{-3} \]
\[ N_A = 2.5 \times 10^{14} \]

(a)

\[ N_D = 5.0 \times 10^{16} \]
\[ N_A = 1.0 \times 10^{15} \]

(b)

\[ N_D = 1.0 \times 10^{15} \]
\[ N_A = 5.0 \times 10^{14} \]

(c)

\[ N_D = 1.0 \times 10^{16} \]
\[ N_A = 2.0 \times 10^{15} \]

(d)

Figure 3.4: Theoretical room-temperature PL spectra of doped 4H-SiC films. Solid lines: \( \Gamma = 50 \text{ meV} \); dotted lines: \( \Gamma = 10 \text{ meV} \). The photocarrier density is set to be \( N_{\text{ph}} = 10^{16} \text{ cm}^{-3} \).

states so that the transition from the conduction band bottom to the top of the valance band is hardly observable. A weak peak near 2.95 eV appears when the impurity concentration becomes high and/or \( \Gamma \) is small, which corresponds to a radiative recombination between the N donor level and the Al acceptor level.

We further studied the influence of the photocarrier density and doping levels on the shape of the PL spectrum. Combined with experimental data, the analysis allows us to study the doping level directly from the PL spectra.

Our approach thus makes it possible to determine the doping level of doped SiC by simple optical PL measurements. Furthermore, we expect a deep impact of the current work on optoelectronic applications of SiC. The optical transitions from its wide band gap makes SiC a good candidate for ultraviolet-band devices. Particularly, SiC based devices can work under the conditions of high power, high frequency and high temperature because of the unique carrier transport, mechanical and thermal properties.
Chapter 4

Multiphoton quantum dots

4.1 Introduction

Quantum dots (QDs) are semiconductor nano sized particles, which confine the motion of electrons in the conduction band, of holes in the valence band, or of excitons (bound pairs of conduction band electrons and valence band holes) in all three spatial directions. Small QDs, such as colloidal semiconductor nanocrystals, can be as small as 2 to 10 nm, corresponding to 10 to 50 atoms in diameter and containing 100 to 100,000 atoms within the QD volume. Due to the strong confinement effect, the energy band structure of QDs is discrete. By controlling the size and shape of QDs, one can easily adjust the band gap; the larger the size, the longer the wavelength of the light absorbed and emitted. Due to their high quantum yield, QDs are ideal for many photonic applications. They have been developed for use in diode lasers and amplifiers [35, 36, 37, 38, 39, 40, 41]. Moreover QDs are highly fluorescent with excellent photochemical stability, extreme brightness, and broad excitation spectral range, which make them suitable for multiphoton bio-imaging applications where intense electromagnetic fields induce multiphoton absorption and emission in the QDs [42]. Many applications in biotechnology are already available now in the laboratory. An example is given by Fig. 4.1 which shows multi-coated CdS/Cd_{0.5}Zn_{0.5}S/ZnS CdSe QDs in arthritis cells.

Starting from the prediction of Goeppert-Mayer [43], physicists and chemists have extensively studied multi-photon absorption and emission. In 1961, Franken and his colleagues demonstrated the phenomenon for the first time by producing light with a wavelength of 347 nm using a laser excitation of 694 nm from a quartz sample [44]. After that, multiphoton technology (nonlinear optics) has been rapidly developed
into one of the most important fields of photonics. The multiphoton process has largely been treated theoretically by steady-state perturbation approaches [45, 46]. However, in modern applications of ultra-fast and ultra-intense lasers, the peak power of the ultra-short laser pulse can be as high as 30 GW/cm$^2$ [47], and the steady-state perturbation theory is not valid under such circumstances. In our work, we solve the time-dependent Schrödinger equation non-perturbatively in order to study the dynamic properties of multiphoton optical processes in semiconductor QDs.

The energy band structure of bulk semiconductor materials is almost continuous. In nano-size particles, the bands are split into sublevels because of the quantum confinement (see section 2.4). We consider an one-electron Hamiltonian in the form

$$H_c = -\frac{\hbar^2 \nabla^2}{2m^*_c} + V_c(r)$$

(4.1)

for conduction-band electrons in a QD, where $m^*_c$ is the effective mass of the electron. The QD is defined by a square potential well.

$$V_c(r) = \begin{cases} E_c & r \leq a \\ E_c + \Delta_c & r > a \end{cases}$$

(4.2)

where $a$ is the radius of the QD. $E_c$ is the conduction band edge and $\Delta_c$ is the band offset between the QD and the surrounding medium. Referring to vacuum, $\Delta_c = \chi$, which is the electron affinity of the material surface. Similar expressions can be written down for valence band holes.
Because of the rotational invariance, the eigenfunctions of the Schrödinger equation

\[ \left[ -\frac{\hbar^2}{2m^*} \nabla^2 + V_c(r) \right] \psi(r) = E \psi(r) \]  

(4.3)

can be expressed in the form

\[ \psi_{\ell m}(r, \theta, \phi) = R_{\ell}(r) Y_{\ell m}(\theta, \phi) \]  

(4.4)

from which we get the radial Schrödinger equation

\[ \frac{d^2 R_{\ell}(r)}{dr^2} + \frac{2}{r} \frac{dR_{\ell}(r)}{dr} - \frac{\ell(\ell + 1)}{r^2} R_{\ell}(r) + \frac{2m^*}{\hbar^2} \left[ E - V(r) \right] R_{\ell}(r) = 0 \]  

(4.5)

while \( Y_{\ell,-m}(\theta, \phi) = (-1)^m Y_{\ell m}^*(\theta, \phi) \) are the angular momentum eigen functions.

After introducing the function \( u_{\ell}(r) = rR_{\ell}(r) \), we get

\[ \frac{d^2 u_{\ell}(r)}{dr^2} + \frac{2m^*}{\hbar^2} \left[ E - V(r) - \frac{l(l + 1)\hbar^2}{2m^*r^2} \right] u_{\ell}(r) = 0 \]  

(4.6)

We consider the potential well in the form of \( V(r) = -\Delta_c \) when \( r \leq a \) and \( V(r) = 0 \) when \( r > a \). We write \( q^2 = 2m^*(E + \Delta_c)/\hbar^2 \) and \( k^2 = 2m^*E/\hbar^2 \). For continuum solutions \( E > 0 \), the solution for \( r \leq a \) is

\[ R_{\ell}(r) = A_{\ell j}(q r) \]  

(4.7)

while the solution for \( r > a \) is

\[ R_{\ell}(r) = B_{\ell j}(k r) + C_{\ell n}(k r) \]  

(4.8)

For bound states \( E \leq 0 \), the solution for \( r \leq a \) must be regular

\[ R_{\ell}(r) = A_{\ell j}(q r) \]  

(4.9)

and the solution for \( r > a \) must be

\[ R_{\ell}(r) = B_{\ell h}(i \alpha r) \]  

(4.10)

where \( \alpha^2 = -2m^*E/\hbar^2 \).

The boundary conditions require that the two solutions and the derivatives match at \( r = a \)

\[ q \frac{d j_{\ell}(\rho)}{d \rho} \bigg|_{\rho=q a} = i \alpha \frac{d h_{\ell}(\rho)}{d \rho} \bigg|_{\rho=ia a} \]  

(4.11)

Fig. 4.2 shows the energy states in the conduction band of a CdS QD having a radius of 3.7 nm. For a given angular momentum integer \( l \), there is a \((2l + 1)\)-fold degeneracy. There are as much 416 confined sublevels in the conduction-band and 609 confined in the valence-band sublevels even for a QD of such a small size.
Figure 4.2: (a) Confined energy states in a CdS QD having a radius of \( a = 3.7 \) nm. (b) Density of confined states.

## 4.2 Multiphoton processes

Denoting \( \mathbf{A} \) as the vector potential of the electromagnetic field, the Hamiltonian describing an electron in this field is

\[
H = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m_0} - e\phi + V(\mathbf{r})
\]

(4.12)

where \( \mathbf{p} \) is the electron momentum, \( \phi \) is the scalar potential of the electromagnetic field. Explicitly, the above Hamiltonian is

\[
H = \frac{\mathbf{p}^2}{2m_0} + \frac{e\mathbf{A} \cdot \mathbf{p}}{2m_0} + \frac{e\mathbf{p} \cdot \mathbf{A}}{2m_0} + \frac{e^2\mathbf{A}^2}{2m_0} + V(\mathbf{r})
\]

(4.13)

and we consider the following ratios

\[
\left| \frac{e\mathbf{A} \cdot \mathbf{p}}{\mathbf{p}^2} \right| \approx \left| \frac{e^2\mathbf{A}^2}{e\mathbf{A} \cdot \mathbf{p}} \right| \approx \frac{e\mathbf{A}}{\mathbf{p}}
\]

(4.14)

Since (see, for example, [20, 49])

\[
\langle A^2 \rangle = \frac{\hbar n_\omega}{2\epsilon\omega}
\]

(4.15)
where \( h \omega \) is the photon energy and \( n_{\hbar \omega} \) is the photon density. Notice that \( \langle A^2 \rangle \) is proportional to the optical power so that \( eA/p \) is still very small when the optical power is increased to a relatively high level. Therefore, the electron energy term containing \( A^2 \) in Eq. (4.13) is very small as compared with the term linear in \( A \). However, the term containing \( A^2 \) in Eq. (4.13) causes two-photon transitions between states of opposite parity when going beyond the dipole approximation. It can be neglected as compared with the term linear in \( A \). In our work, we re-write the first-order perturbation in \( A^2 \) as

\[
\frac{eA^2}{2m_0} e^{2i(q \cdot r - \omega t)}
\]

where the \( q \) is the optical wave vector. For an optical wavelength of 681 nm (\( \hbar \omega = 1.82 \text{ eV} \)), the above perturbation is basically constant within the volume of a QD, it thus does not induce optical transitions between conduction-band and valence-band states. The total Hamiltonian of the electron in the electromagnetic field is thus [49, 55]

\[
H(r, t) = H_0(r) + \frac{e}{m_0} A \cdot p
\]

where \( H_0 \) is the Hamiltonian of the electron in the unperturbed quantum dot. In obtaining the \( H \) expression we have specified the gauge so that \( \nabla \cdot A = 0 \) and \( \phi = 0 \). Under these circumstances \( p \cdot A = A \cdot p \). In the case that there is only one electron in the system \( H_0 = H_n \), where \( H_n \) is the one-electron Hamiltonian of Eq. (4.1). By denoting \( A = Aa \), where \( a \) the polarization unit vector of the optical field, \( A(t) \) is given by [50]

\[
A(t) = \begin{cases} 0 & t < 0 \\
\frac{\hbar}{2m_e \Omega} \left[ b^+ e^{i(\omega t + q \cdot r)} + b e^{-i(\omega t + q \cdot r)} \right] & t \geq 0
\end{cases}
\]

where \( b^+ \) and \( b \) are creation and annihilation operators of the photon field, \( \Omega \) is the normalization space volume. Here \( t = 0 \) is the time at which the optical field is switched on. For the optical transitions of QDs, the wavelength of the radiation is in the order of 700 nm, which is much larger than the geometric size of the QD so that one can set \( e^{i q \cdot r} = 1 \) in the dipole approximation.

We denote the wave function of the total system composed of electrons and photons as

\[
\Psi(r, t) = \sum_j C_j(t) \psi_j(r) u_j \exp(-iE_j t/\hbar) |N_{\hbar \omega}
\]

where \( |N_{\hbar \omega}\rangle \) describes the photon field with \( N_{\hbar \omega} \) as the number of photons at energy \( \hbar \omega \) (\( n_{\hbar \omega} = N_{\hbar \omega}/\Omega \)).

\[
H_0(r) \psi_j(r) = E_j \psi_j(r)
\]
describes the unperturbed electron system (again notice that \( H_0 \) is the Hamiltonian describing electrons in the QD). As before, \( u_j \) is the lattice-periodic Bloch function. For conduction-band electrons it is denoted as \( u_c \) and for valence-band holes, it is \( u_v \). It is easy to obtain the following equation for the wave function coefficient

\[
\frac{i\hbar}{m_0} \frac{dC_j(t)}{dt} = e \frac{\hbar}{2\omega\epsilon \Omega} \sum_i \langle \psi_j(r)u_j | \mathbf{a} \cdot \mathbf{p} | \psi_i(r)u_i \rangle C_i(t) \\
\times \left\{ \sqrt{N_{\hbar\omega}} \exp \left[ \frac{i(E_j - E_i - \hbar\omega)t}{\hbar} \right] + \sqrt{N_{\hbar\omega} + 1} \exp \left[ \frac{i(E_j - E_i + \hbar\omega)t}{\hbar} \right] \right\} (4.21)
\]

by inserting Eq. (4.19) into the time-dependent Schrödinger equation. The term headed by \( \sqrt{N_{\hbar\omega}} \) corresponds to the photon absorption, while the one with \( \sqrt{N_{\hbar\omega} + 1} \) is the photon emission.

When the optical power of the external light source is rather high so that \( N_{\hbar\omega} \gg 1 \), \( N_{\hbar\omega} \approx N_{\hbar\omega} + 1 \). In this case, Eq. (4.21) becomes

\[
\frac{i\hbar}{m_0\omega} \sqrt{\frac{2S}{c}} \sum_i \langle \psi_j(r)u_j | \mathbf{a} \cdot \mathbf{p} | \psi_i(r)u_i \rangle C_i(t) G (4.22)
\]

where

\[
G = \frac{\hbar}{i(E_j - E_i - \hbar\omega)} \exp \left[ \frac{i(E_j - E_i - \hbar\omega)t}{\hbar} \right] \left[ \exp \left[ \frac{i(E_j - E_i + \hbar\omega)\Delta t}{\hbar} \right] - 1 \right]
\]

by utilizing Eq. (4.24) and by integrating Eq. (4.21) from \( t \) to \( t + \delta t \). \( S \) is denoted as the time-averaged amplitude of the Poynting vector representing the optical power of an electromagnetic field

\[
S = n_{\hbar\omega} c \hbar \omega \quad (4.24)
\]

c is the speed of light. Fig. 4.3 shows the temporal variation and photon-energy dependence of \( |G|^2 \), where we set \( t = 0 \). Since \( E_j - E_i \) is set as 2.5 eV here, the excitations with a photon energy below 2.5 eV result multiphoton processes. We can clearly see a broad multiphoton induced region from this figure.

The optical matrix element of transitions from the ground valence-band state to a conduction-band state is

\[
\langle \psi_j u_v | \mathbf{a} \cdot \mathbf{p} | \psi_i u_i \rangle = \mathbf{a} \cdot \mathbf{p} \langle \psi_j | \psi_i \rangle \\
= \mathbf{a} \cdot \mathbf{p} c \int_0^\infty r^2 dr \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi R_{ij}^*(r) Y_{l_m}(\theta, \phi) R_{il}(r) Y_{l_m}(\theta, \phi)
\]
4.2. MULTIPHOTON PROCESSES

Figure 4.3: $|G|^2$ with the variations of photon energy and $\Delta t$. $E_j - E_i$ is set as 2.5 eV, $t = 0$.

$$
G^2 = a \cdot p_{cv} \delta_{l_l} \delta_{m_i m_i} \int_0^{\infty} r^2 dr R^*_{l_j}(r) R_{l_i}(r) \tag{4.25}
$$

The optical transition is characterized by $E_p = p_{cv}^2 / 2m_0$, where $p_{cv} = \langle u_c | \hbar \nabla | u_v \rangle$. Because the spherical harmonics of the valence-band ground state is $Y_{00}$, the non-zero interband optical transitions are limited to $l = m = 0$. For this case, the bound states ($E_{j0} \leq 0$) in the conduction band are

$$
\Psi_{j0} = \begin{cases} 
A_{j0} \frac{\sin(q_{j0}r)}{q_{j0}r} & |r| < a \\
B_{j0} e^{-\alpha_{j0}r} & |r| \geq a
\end{cases} \tag{4.26}
$$

where $E_{j0} = -\hbar^2 \alpha_{j0}^2 / 2m^*_c$. The interband optical matrix element is expressed as

$$
a \cdot p_{cv} \int_0^{\infty} \Psi_{j0}^* \Psi_v r^2 dr = a \cdot p_{cv} A_{j0} \frac{\pi \sqrt{2a} \sin(q_{j0}a)}{q_{j0}^2 a^2 - \pi^2} \tag{4.27}
$$

For a transition between two states within the same conduction band, referred as an intraband transition, the optical matrix element is

$$
\langle \psi_j u_c | a \cdot p | \psi_i u_v \rangle = \langle \Psi_j | a \cdot p | \Psi_i \rangle = m_0 a \cdot \langle \Psi_j | \frac{dr}{dt} | \Psi_i \rangle
$$
\[ \begin{align*}
\psi_j &\cdot (\nabla \cdot \mathbf{r}) \langle \psi_j | [H_0, \mathbf{r}] | \psi_i \rangle \\
\rho &\cdot \mathbf{r} \langle \psi_j | [H_0, \mathbf{r}] | \psi_i \rangle
\end{align*} \]

\[ \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} d\Phi d\theta d\Phi
\int_0^\infty r^2 dr \sin \theta \psi_j^* \mathbf{R} \mathbf{l}_j \mathbf{Y} (\theta, \Phi)
\mathbf{a} \cdot \mathbf{p} \mathbf{R} \mathbf{l}_j \mathbf{Y} (\theta, \Phi)
\]

Here \( \mathbf{r} = \mathbf{r_0} \), where \( \mathbf{r_0} \) is the unit vector, \( \mathbf{a} = a_x \mathbf{x_0} + a_y \mathbf{y_0} + a_z \mathbf{z_0} \), and \( \mathbf{x_0}, \mathbf{y_0} \) and \( \mathbf{z_0} \) are unit vectors along \( x-, y-, z- \) directions, respectively,

\[ \begin{align*}
\mathbf{a} \cdot \mathbf{r}_0 &= a_x \sin \theta \cos \phi + a_y \sin \theta \sin \phi + a_z \cos \phi \\
&= \sqrt{\frac{4\pi}{3}} \left( -a_x + i a_y \sqrt{2} \right) Y_{11} + a_z Y_{10} + a_x + i a_y \sqrt{2} Y_{11}
\end{align*} \]

so that the angular integral can be analytically evaluated by using the addition theorem for spherical harmonics

\[ Y_{l_1 m_1} (\theta, \phi) Y_{l_2 m_2} (\theta, \phi) = \sum_{l=|l_1-l_2|}^{l_1+l_2} C(l, m_1 + m_2 | l_1 m_1; l_2 m_2) Y_{l, m_1+m_2} (\theta, \phi) \]

The above Clebsch-Gordan coefficients \( C(lm | l_1 m_1; l_2 m_2) \) can be obtained from analytical expressions [56, 57]. We introduce a positive \( \gamma \) to account phenomenologically for the relaxation of the system by following [51, 52]. On the other hand, the non-radiative phonon-electron scattering processes for electrons in high-energy states is believed to be a major source of optical dephasing and damping in semiconductor QDs [53]. The phonon-electron interaction normally does not allow one to incorporate both incoherent relaxation phenomena and dephasing due to fluctuations of the environment. In our work the probability for an electron relaxing from state \( k \) to state \( q \) by emitting a phonon at a time duration of \( \Delta t \) is expressed as [54, 48]

\[ P_{pk}(t) = \frac{\pi(D_t K)^2 (n_p + 1)}{\rho \Omega \omega_p} \times \delta[E_q - E_k + \hbar \omega_p] \Delta t \]

where \( D_t K \) is the optical deformation potential, \( \rho \) is the mass density of the QD material. Supscript “p” stands for phonon-electron interaction. \( \hbar \omega_p \) is the optical phonon energy. \( n_p = 1/(e^\hbar \omega_p/k_B T - 1) \) denotes the phonon population.

### 4.3 Kinetic Monte Carlo method

We apply the kinetic Monte Carlo (MC) scheme to incorporate system-state transition probabilities obtained from the above equations in order to simulate the dynamic multiphoton process. The general framework of such a kinetic Monte Carlo
4.4 Optical properties of multiphoton QDs

In our work, CdSe QDs were prepared using chemical synthesis methods described in the literature [62, 63]. Different CdSe nanocrystals were obtained after different reaction times. Then a typical (successive ion layer adsorption and reaction) [64] synthesis was performed to grow an epitaxial shell on the CdSe nanocrystals. The reaction temperature was 280°C in this case. The final product has a multi-coated shell-core structure of CdS/Cd_{0.5}Zn_{0.5}S/ZnS-CdSe. UV-Vis spectroscopy was performed and scanned over the spectral range 300-900 nm in a PGENERAL UV TU-1901 spectrophotometer. Single-photon photoluminescence spectroscopy was carried out on a fluorescence spectrometer (Cary Eclipse, VARIAN, USA), and the multi-photon excited fluorescence spectra were obtained by using a femtosecond laser (76 Hz, 130 fs, 800 nm). All the optical measurements were performed at room temperature. Excited by a “multiphoton laser”, whose photon energy is below the QD band gap, an assembly of the QDs shows an emission peak around the band gap in the optical emission spectrum, which results in a non-strict multiphoton excitation condition. The experimental absorption and multiphoton emission spectra have been reproduced with our theoretical study of the spherical CdS QDs and multi-coated CdS/Cd_{0.5}Zn_{0.5}S/ZnS CdSe QDs Fig.4.4 here presents the absorption and emission spectra of multi-coated CdS/Cd_{0.5}Zn_{0.5}S/ZnS CdSe QDs.

Our work relates to the fact that the field of nanotechnology holds great promise for the diagnosis and treatment of human disease. Semiconductor QDs are highly fluorescent, which have captivated the interest of the biomedical community as the ultimate tags for cellular imaging. With multi-photon technology, we can use near-infrared excitation to obtain visible light for imaging. Thus, multi-photon QDs
have been chosen now for bio-imaging applications. Although the success in the laboratory, it remains a long way to clinical translation [65]. One of the most important problems is the possible toxicity of the QDs. Intensive research works are ongoing to find safe and dissoluble coatings for the QDs. Moreover, recent research has reached considerable success in using QDs to label fixed cells and tissues. But only limited progress has been made with QD probes for tracking living cells [66]. Further work is needed for applying modern detective technology and efficient methods for delivering QDs in living environments.
Chapter 5

Quantum chemistry study of InGaAsN clusters

5.1 Basics of Quantum Chemistry theory

Following the fast development of silicon technology, the electronic components become smaller and smaller. As an example, a commercial chip-maker has recently reported the shrinking of a typical length of a typical device structure from 65 nm to 45/32 nm [67]. By Moore’s law, we can expect the typical length in semiconductor industry will reach the region of only a few nanometers before 2012. The miniaturization is now beginning to approach length scales so small that quantum confinement effects can no longer be ignored.

A great number of researchers in this field adopt solid-state-physics based approaches. In this chapter, we will use quantum chemistry methods to study the structures and optical properties of semiconductor clusters, as quantum chemistry provides us a possible way to study nano size semiconductors with first-principles theory to directly describe the interactions among atoms or electrons. Quantum chemistry has been proven to be very useful when describing the geometrical structure of molecular systems and predicting spectra for various processes. With the help of high performance computers, it has recently become possible to simulate and predict the properties of large molecular systems containing more than 1,000 atoms. Such technology has been applied to study structural and electronic properties of II-VI semiconductor clusters [68, 69], III-V compounds [70, 71], as well as carbon nanoparticles [72, 73, 74].
One of the fundamental approximations used in quantum chemistry is the Born-Oppenheimer approximation. Because nuclei are much heavier than electrons, the kinetic energy of the nuclei is much smaller than the electrons. The repulsion between the nuclei can be treated as constants, as this approximation, the nuclear positions are considered to be fixed. Based on the Born-Oppenheimer approximation, the Hartree-Fock (HF) method turns the multi-electron molecular Schrödinger equation into a set of one-electron Schrödinger equations together with the following approximation: (1) Non relativistic operators. (2) Linear combination of a finite number of basis functions is used to describe the variational solution. (3) Electron correlation is neglected. (4) The total wavefunction $\Psi^{HF}$ of the system containing $n$ electrons is then represented by a single Slater determinant composed by one-electron wavefunctions $\psi_k(r_k)$

\[
\Psi^{HF} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_N(r_1) \\ \psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_n) & \psi_2(r_n) & \cdots & \psi_N(r_n) \end{vmatrix}
\]  

(5.1)

The HF approximation is also called the self consistent field (SCF) approximation, since the solution of the HF equations is an iterative self-consistent procedure.

The Hohenberg-Kohn theorems are the basic ideas of density functional theory (DFT) [59], which contain two parts: (1) The ground state energy of a system is a unique functional of the electronic density. (2) Given the ground state density as the variable, minimising the system energy would lead to the ground state energy. The common implementation of modern DFT is through the Kohn-Sham method. In the Kohn-Sham formulation of DFT, the many-body problem (the problem of interacting electrons caused by a static external potential) becomes a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the potential due to the interactions between the electrons, e.g., the exchange and the correlation. In the Kohn-sham equations, the charge density is $\rho(r) = \sum_i |\psi_i(r)|^2$, and the exchange and correlation energy is defined as

\[
E_{xc}[\rho] = F_{HK} - T_s[\rho] - J_s[\rho]
\]

(5.2)

where $T_s$ is the kinetic energy of the electron gas with a density of $\rho$ and $J_s$ is the electron kinetic energy. Thus, the density functional of the system is

\[
E[\rho] = T[\rho] + \int V_{ext}(r)\rho(r)dr + V_c[\rho] + E_{xc}[\rho]
\]

(5.3)
A hybrid method in DFT means that a percentage of the exact exchange contribution from the HF method is included. For an example, the most used hybrid method is B3LYP [60, 61].

\[
E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0(E_{x}^{HF} - E_{x}^{LDA}) + a_x(E_{x}^{GGA} - E_{x}^{LDA}) + a_c(E_{c}^{GGA} - E_{c}^{LDA})
\]

(5.4)

where \(a_0 = 0.20\), \(a_x = 0.72\), and \(a_c = 0.81\) are empirical parameters. \(E_{x}^{GGA}\) and \(E_{c}^{GGA}\) are the generalized gradient approximation. \(E_{c}^{LDA}\) refers to the local density approximation.

### 5.2 Structure study by a semi-empirical method

To reduce the heavy computational requirement, one often applies semi-empirical methods that usually only consider the valence electrons explicitly, while the core electrons are accounted for by reducing the nuclear charge or introducing functions to model the combined repulsion of the nuclei and core electrons. Furthermore, a size reduced basis set for the valence electrons is normally applied. A common assumption in semi-empirical methods is also the zero differential overlap approximation. In this approximation, all the products of basis functions are neglected based on the same electron coordinates when located on different atoms. The most common way to improve the accuracy of the semi-empirical methods is to modify the parameters according to results from experimental studies. For different semi-empirical methods, different parameters are used based on the various experiments. Different integrals are neglected in various methods, motivated by the type of application mode.

In our work, we first apply the semi-empirical quantum chemistry method called the parameterized model number 3 (PM3) [75, 76, 77] by using the SPARTAN program [78] to study the dilute-nitride zincblende In\(_x\)Ga\(_{1-x}\)N\(_y\)As\(_{1-y}\) cluster system. Semi-empirical parameter values are used in the PM3 calculations to neglect differential diatomic overlap integrals. The geometry optimization and total energy calculation are performed by SPARTAN in the following way: Starting from an initial geometry, calculate (a) the kinetic energy of system, (b) the potential energy including the electrostatic repulsions among nuclei and among electrons and the electrostatic attractions among nuclei and electrons, in order to obtain the total energy for this geometry. By modifying the bond lengths and bond angles (geometry optimization) step by step and calculating the total energy for each modification, SPARTAN will eventually find and output the optimized geometry from the convergence of the total energy.
5.3 Quantum Chemistry study of GaAs clusters

In general, one nano-size semiconductor cluster contains around 1,000 heavy atoms, which is too large for standard quantum chemistry methods. To calculate the electronic structures of a large system, an efficient computational method called central insertion scheme (CIS) has been developed by Jun Jiang and Bin Gao et al. in our department [74, 79] in conjunction with modern quantum chemical density functional theory. Starting from an initial structure whose Hamiltonian can be obtained by a traditional DFT calculation, the CIS method elongates the system by adding identical units in the middle of the system continuously to construct the Hamiltonian of a large system. To use the CIS method, there are two basic conditions. First, the central part of a sufficiently accurate initial structure should have converged with respect to electronic structure and charge density. The second one is to assume that the long range interaction between subsystems is negligible.

The CIS procedure can be described simply with the following one-dimensional example. We consider a system that consists of a periodic structure including \( n \)
5.3. QUANTUM CHEMISTRY STUDY OF GAAS CLUSTERS

Figure 5.2: Scheme of GaAs clusters.

uniform units $U_1, U_2, \ldots, U_n$ with two end parts, $L$ and $R$. The wave functions are expanded in terms of a basis by a linear combination of atomic orbitals (LCAO): $|\Psi\rangle = \sum_i c_i \psi_i$. A $(n + 2) \times (n + 2)$ Hamiltonian of the elongated system $LUR$ is defined by $H_{i,j} = \langle \psi_i | H | \psi_j \rangle$, where $i$ and $j$ run over $L, U_1, U_2, \ldots, U_n$, and $R$. The Hamiltonian matrix of an elongated system of $L U_1 U_2 \ldots U_n$ can be obtained by the way schematically shown in Figure 5.1. We start from two initial Hamiltonian matrices. One end part of each matrix is set to zero. By putting the two systems together with one unit mismatched, we construct a $(n + 3) \times (n + 3)$ matrix for the newly elongated system. The matrix elements of the overlap part can be computed through the following relationship $U_{i,j} = \alpha U_{i,j}^L + (1 - \alpha)U_{i,j}^B$. The choice of weighting factor $\alpha$ depends on the system under investigation.

We now apply the CIS method to the study of spherical GaAs nano clusters in the diamond structure, which is terminated by hydrogen atoms. The initial structure is a 6-shells GaAs cluster, with a diameter of 2.3 nm. The original Gaussian calculation was performed at the first principle level of DFT B3LYP. The Ga and As atom were described with LANL2DZ pseudopotentials and basis set, which means 8 basis functions were used for each Ga or As atom. Following the CIS method, we can construct larger cluster systems with the initial structure (as shown in Fig. 5.2), as well as the Hamiltonian. The largest system under investigation so far is a 38-shell GaAs cluster with about 17 nm in diameter, consisting of 21127 As atoms, 22116 Ga atoms, and 171983 out shell electrons. There are in total about 350,000 basis functions involved.
Figure 5.3: Band gap of GaAs cluster as a function of the cluster size.

The bandgap $E_g$ is given by $E_{LUMO} - E_{HOMO}$. The size dependent energy gap of the GaAs clusters are shown in Fig. 5.3. For comparison, experimental results (labelled with hollow stars) [82, 83, 84] and results from previous reported theoretical methods are also plotted in this figure. The dash line is obtained from the empirical equation mentioned in [85]. We can also model the cluster energy band structure by a spherical square quantum well and the electrons in the conduction band and holes in the valence band by the effective mass approximation. The relevant calculation results are shown in Fig. 5.3 as circles. It is shown that our method gives better agreement when the cluster size is small. For a semiconductor cluster sufficiently small (containing a few monolayers), its properties have some molecular-like character. It has been known that the effective mass approximation is not suitable for small size QDs in connection with $\mathbf{k} \cdot \mathbf{p}$ theory are[86].

The CIS method for large size semiconductor nanoparticles paves a new way to investigate the properties of low dimensional materials. Following the work above, it is possible to study the dilute system of $\text{GaAs}_{1-x}\text{N}_x$ simply by replacing the initial structure with a N-doped GaAs cluster. By changing the number of N atoms in the initial structure, understanding about the effects of N incorporation will be expected, which would have a deep impact on many applications such as design of laser and quantum well infrared detectors based on semiconductor dilute systems.
Chapter 6

Comments on included papers

• Paper 1: *Room-temperature photoluminescence of doped 4H-SiC film grown on AlN/Si(100)*

In this work, we have grown 4H-SiC films on AlN/SiC(100) substrates by CVD. Three strong room-temperature photoluminescence (PL) peaks close to the bandgap energy were observed. The PL spectrum consists of three major emission peaks at 3.03, 3.17 and 3.37 eV. By a detailed theoretical analysis of optical transitions in the samples, it has been concluded that the PL peaks are most probably due to radiative recombinations between the 4H-SiC conduction-band minimum and the Al acceptor level (ionization energy is around 0.20 eV), and between the valence-band top and the N donor level (ionization energy is around 0.06 eV), and between the secondary minimum in the conduction band and the top of the valance band, respectively.

• Paper 2: *Radiative emission from multiphoton-excited semiconductor quantum dots*

This paper describes the dynamic processes of multiphoton optical transitions in semiconductor quantum dots. By calculating the transition probability from the time-dependent Schrödinger equation nonperturbatively and simulating the stimulated photon emission, the stimulated absorption, and the spontaneous photon emission using a kinetic Monte Carlo scheme, the spontaneous photon emission spectrum has been obtained for both the one-photon and multiphoton excitations. The one-photon excitation spectrum shows a sharp emission peak located at the averaged energy band gap of the QD assembly, while the emission peak due to the two-photon excitation is blue shifted and broadened as compared with the one-photon excitation.
• Paper 3: *Dynamic photon emission from multiphoton-excited semiconductor quantum dots*

In order to reduce the counts of high-energy photons in the emission spectra obtained in the previous study of Paper 2, nonradiative phonon-scattering processes have been included in the calculations of the total optical transition probabilities. Assisted by a two-photon excitation by a continuous wave laser, an assembly of the QDs shows an emission peak around the band gap in the optical emission spectrum, while an ultra fast pulsed laser, whose photon energy is below the QD band gap, also induces a similar narrow but weaker emission peak, which results in a non-strict multiphoton excitation condition for many potential applications including biophotonics. The spectrum of continuous-wave excitation shows a sharp emission peak around the band gap of the QDs. Application of the theoretical study to the spherical CdS/Cd$_{0.5}$Zn$_{0.5}$S/ZnS-multicoated CdSe QD has reproduced the experimental absorption and multi-photon emission spectra.

• Paper 4: *Optical properties of multi-coated CdSe/CdS/ZnS quantum dots for multiphoton applications*

To combine the advantages of different shell materials for bio-applications, CdSe-core CdS/Cd$_{0.5}$Zn$_{0.5}$S/ZnS multishell quantum dots (QDs) were synthesized by using the successive ion layer adsorption and reaction (SILAR) method. The optical properties have been studied by experimental characterization. Based on probability calculations of the time-dependent Schrödinger equation, Monte Carlo method was used to simulate and analyze the absorption spectra and spontaneous emission spectra of multi-excited QDs. The coating effect on PL-peak position is also studied to explain the blue-shift caused by the Zn diffusion in the multishell QDs.

• Paper 5: *Multi-photon excitation of quantum dots by ultra-short and ultra-intense laser pulses*

This paper describes the multiphoton processes in semiconductor quantum dots by solving the time-dependent Schrödinger equation unperturbatively. It is found that experimentally observed strong multiphoton excitations can be reproduced when optical transitions among all confined states in the QD and an additional few hundred extended states in the barrier are taken into account.

• Paper 6: *Dynamic analysis of multiple-photon optical processes in semiconductor quantum dots*
A detailed description of multiphoton processes in semiconductor quantum dots studied in Paper 5 is presented in this work. By solving nonperturbatively the time-dependent Schrödinger equation, it has been shown that the large number of energy states densely compacted in both the conduction and valence bands of the QD greatly enhances the inter-band and intra-band optical couplings induced by multiple photons from ultra-fast and ultra-intense lasers. The multiphoton absorption processes are further enhanced by many energy relaxation processes in commonly used semiconductors, which are generally represented by the relaxation energy in the order of tens of meVs.

• Paper 7: Design of semiconductor CdSe-core ZnS/CdS-multishell quantum dots for multiphoton applications
In this paper, we have studied II-VI semiconductor CdSe core ZnS/CdS multishell quantum dots for multiphoton applications. It is demonstrated that due to the large number of energy states densely compacted in both the conduction and valence bands of the QDs, strong interband and intraband optical couplings are induced by the multiphoton excitation. The experimental and theoretical results of one-photon and multi-photon excited fluorescence support that II-VI-based core-multishell CdSe QDs are very useful for multiphoton applications.

• Paper 8: Structural analysis of dilute-nitride zincblende $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$ cluster by a semi-empirical quantum chemistry study
A semi-empirical quantum chemistry method is used in this work to study the total energy of a series of dilute-nitride zincblende $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$ cluster configurations. It has been concluded that the substitutional N incorporation is favoured over interstitial N incorporation. When two N atoms enter into the system they either stay very close to each other or they are completely dissociated. However, an increase of the In mole fraction reduces the impact of N incorporation on the total cluster energy. An interstitial N atom prefers an In-rich environment for all In mole fractions while this is true for the substitutional N atom only when the In mole fraction is smaller than 0.25. Moreover, the dissociation of N–N pairs is found to be dependent on the local environment (In-rich or In-free) along the dissociation trajectory.

• Paper 9: Quantum chemistry study of electronic band structures of GaAs quantum dots
After proper structural constructions of large clusters, we continue to study the electronic states of them by the central insertion scheme, a large-size quantum
chemistry treatment. The largest clusters studied in this work is a hydrogen
terminated GaAs clusters having a size of 16.9 nm in diameter, and it contains
21127 As atoms, 22116 Ga atoms, and 171983 outmost H atoms. Optical ab-
sorption spectra have also been calculated. It has been shown that the real
HOMO and LUMO are localized within the inner shells, and size-dependent
quantum confinement effect shows good agreement with experimental results.

The thesis covers theoretical studies of multi-dimensional materials of ground-IV
(SiC thin film), III-V (dilute nitrite GaInAs and GaAs clusters) and II-VI semi-
conductors (CdSe quantum dots), their optical properties (photoluminescence and
multiphoton optics) and electronic-energy-band-structure properties (formation of
clusters and energy band edges). Solid-state perturbation theory is adopted to deal
with photoluminescence spectra of SiC thin films, a time-dependent quantum treat-
ment is developed for ultrafast and ultra-intense nonlinear multiphoton processes in
QDs, and quantum chemistry theory is applied for nanoscale systems. This work
has now put us at a position where we aim to step into design and development
of multi-dimensional semiconductor materials in corporation with experimental ac-
tivities, and conduct various applications including high-temperature, high-speed
and high-power SiC devices, colloidal-QD-based nanophotonics, dilute-nitride-based
telecommunication lasers, as well as short-wavelength lasers for dense optical stor-
age applications. We will also try to combine the theoretical methods into a generic
framework in order to expand the research and development into other types of
nanostructure.
Bibliography


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