Electronic structures and optical properties of dilute nitride quantum dots

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Electronic Structures and Optical Properties of Dilute Nitride Quantum Dots

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Abbreviations

BAC	Band-anticrossing
CBO	Conduction Band Offset
CCD	Charge Coupled Device
CE	Continuum Elasticity
DBR	Distributed Bragg Reflector
EEEE	Edge-Excitation and Edge-Emission
ES	Excited State
FIR	Far-Infrared
FWHM	Full Width at Half Maximum
GS	Ground State
HR-SEM	High Resolution Scanning Electron Microscopy
MIR	Mid-Infrared
N	Nitrogen
OTR	Operating Temperature Range
P	Phosphorus
PL	Photoluminescence
QD	Quantum Dot
QW	Quantum Well
VCSEL	Vertical-Cavity Surface-Emitting Laser
VFF	Valence Force Field

Symbols

a_0	Lattice constant
c	Speed of light
$c1$	Ground state of conduction band
$c2$	First excited state of conduction band
e	Electron charge
E_{AE}	Total strain energy
$E_C, E_{HH}, E_{LH}, E_{SO}$	Band edge energies for conduction band, heavy hole, light hole and spin-orbit, respectively
E_f	Quasi-Fermi level
E_g	Band gap
E_N	Nitrogen related energy level
E_p	Matrix element in Kane's theory
ϵ_0	Free space dielectric constant
ϵ_{ij}	Strain component in i-j direction
f_c	Probability to find an electron in a conduction state
f_v	Probability to find a hole in a valence state
$h1$	Ground state of valence band
$h2$	First excited state of valence band
λ	Spin-orbit coefficient
k	Wave vector

L_x, L_y, L_z	Periodicity of unit cell system in x, y, z directions
L, M, N	Luttinger parameters
m_0	Free electron mass
m_c	Electron effective mass
M^{cv}	Optical transitional matrix element
N-CB	Nitrogen-conduction band
n_{eh}	Number of carrier in quantum dot
n_r	Refractive index
n_x, n_y, n_z	Plane wave number in x, y, z directions
p	Momentum operator
Φ	Envelop function
Ψ	Total wavefunction
$\mathbf{r}$	Position vector
R_{in}	Inner radius
R_{out}	Outer radius
Δ_{SO}	Spin-orbit splitting energy
τ	Interband relaxation time
V_{NC}	Coupling strength between conduction band edge and the N band

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Summary

Dilute nitride III-V compounds are potential candidate materials for the next generation of telecommunication optoelectronic device such as laser and photodetector. In this thesis, we have investigated the electronic structure and optical properties of quantum dots (QDs) using eight-band or ten-band **k.p** methods with the strain distribution calculated by the valence force field (VFF) model. Because of QD's novel electrical and optical properties and quantum confinement effects, we simulate and study these QDs for better understanding. The optical gains are calculated using the zero-dimensional optical gain formula taking into consideration inhomogeneous broadening due to QD size fluctuation.

With variations of pyramidal InAs(N) QD size, shape and nitrogen(N) composition, we find that when N composition is higher, the ground state (GS) of conduction band c1 is forced to be lower so that the c1-h1 GS transition energy is less, and the intersubband energy separation c2-c1 is greater so that the higher excited states transition is harder to occur. The incorporated N can facilitate to achieve shorter emission wavelength 1.3 μm or even 1.55 μm , with higher maximum optical gain and less detrimental effect induced by higher excited state transition. If we truncate the full pyramidal shape, the QD height in z -direction is reduced. This truncation changes the strain distribution and increases the confinement in z -direction resulting in greater GS transition energy, greater transition matrix element (TME), less detrimental effect of higher excited transition, higher saturation gain and differential gain.

For pyramidal InAsPN/GaP(N) QDs, with GaP barrier, for smaller InAsPN QDs, the GS transition energy is smaller at a lower phosphorus (P) composition of InAsPN. But for larger InAsPN QDs, the GS transition energy increases as P composition increases due to the increased bandgap. To obtain laser materials with a lattice constant comparable to Si, we incorporated 2% of N into GaP barrier. So the conduction band offset and the quantum confinement are reduced resulting in a smaller transition energy and longer wavelength. Meanwhile the optical gains are less than those without N in the barrier at a low carrier density, but the maximum GS optical gain increases faster and surpass to reach a greater saturation optical gain when the carrier density increases.

From quantum lens to volcano shape and to quantum rings (QRs), the shape effects of $\text{InAs}_{1-x}\text{N}_x/\text{GaAs}$ nanostructures are that the s - s transition energy decreases first, reaching the minimum value at volcano shape, then it increases. Both electron and hole states changes dramatically from disk-like to ring-like. Meanwhile the TME increases first, reaching the maximum value at volcano shape, then decreases, and the energy spacing becomes smaller causing the problem of higher excitation transition more significant. For QR structure, the first two gain peaks may merge together to form a boarder peak due to its small s - p spacing. We recommend volcano structure in which the maximum gain occurs. Our simulation results can help a researcher select the appropriate shape of nanostructures and N composition according to the specific requirements

Chapter 1: Introduction

1.1 Background and motivation

Low dimensional systems such as semiconductor quantum dots (QDs) [1-5] and quantum wires (QWs) [6-7] have promising and technologically useful electrical and optical properties. Due to their unique structural zero-dimensionality and discrete density of states in these systems, electrons and holes are confined in all directions so the energy levels are discrete instead of continuous [3-5]. The studies and research on these systems are very helpful for understanding quantum effects on material properties and to design optoelectronic devices.

Recently, semiconductor QDs grown using Stranski-Krastanov mode have been of great interest [8-10]. Such heterostructures are made by epitaxially depositing the semiconductor onto a substrate of lattice-mismatched material, so the deposited material spontaneously forms an array of three-dimensional nanometer-scaled islands after the heights of the deposited semiconductor reaches the critical thickness, and then these islands are subsequently covered by deposition of the substrate material [11-13]. In this strain-induced method, the presence of strain significantly alters the electronic structure of QDs, and the strain distribution of QDs is subject to QDs dimensions and more complicated than that of QW in which the strain distribution can be assumed to be uniform in simulation. So the electronic structure of QDs is more sensitive to strains which must be handled carefully. Initially

proposed by Keating *et al.* [14], the atomic valence force field (VFF) model describes the strain energy in terms of potentials between actual atoms, and then VFF model was developed by Martin *et al.* [15]. Wang *et al.* [8] and Jiang *et al.* [16] have successfully applied VFF model in QDs simulation.

Due to the delta-like density of states, semiconductor QD lasers in their active region provide superior lasing characteristics compared to quantum-well lasers [17]. The QD lasers are expected to have ultralow threshold currents and temperature insensitive operation [18]. Owing to the advent of the self-assembling growth process of QDs and the subsequent development of their crystal growth technique, the performance of self-assembled QD lasers have steadily improved, and such improved laser performance has enabled more researchers to study various unique properties about the interaction between QD and light [19].

Among vast choices of materials, dilute nitride III-V semiconductors have received greater attention mainly because the techniques of dilute nitride III-V QW lasers are very mature, and the upgrading technology from QW to QD is more convenient and the risk of technical obstacles is relatively lower. Another reason is that the self-assembled III-V QDs have been under intense research both in simulation and in experiment over the last decade [20, 21]. A lot of efforts have been done to expand the emission wavelength towards 1.3 μm that Chen *et al.* [22] and Zhukov *et al.* [23] tried to embed InAs QDs into an InGaAs quantum well or stacking of QDs. After discovery of strong negative band gap bowing effects in dilute nitride semiconductor [24-27], small amount of N atoms are incorporated into

QDs [28-30]. The progress in the fabrication techniques of dilute nitride QD facilitates the realization of the 1.3 μm optical fiber laser, and even to reach 1.55 μm becomes possible [31]. Theoretically, the incorporated N atoms introduce a localized state with energy level E_n in the host material. The repulsion between the conduction band edge and the higher-lying N resonant state causes a splitting of the conduction band, and the fundamental band gap is reduced [32]. This band anticrossing (BAC) model have been successfully applied in theoretical study of the properties of dilute nitride group III-V materials [33-36].

As a result, we are highly motivated to theoretically investigate the properties of dilute nitride group III-V QDs which has greater potential to fabricate advanced GaAs-based optical fiber communication lasers with larger gain and larger output powers than conventional lasers. The electronic structure of QDs can be studied theoretically by the **k.p** method which is firstly introduced by Bardeen [37] and Seitz [38]. The **k.p** method is very useful and effective to be applied to the band edges calculations, and many scientists have applied it to semiconductor QDs [39, 40]. Pryor [41] compared the simulation results of strained InAs/GaAs QDs with four-band, six-band and eight-band, and Wang *et al.* [9] and Pryor [10] examined the effects of island geometry and confined state energies of InAs/GaAs QDs using eight-band **k.p** Hamiltonian. Schliwa *et al.* [42] systemically investigated the impact of size, shape and composition on the electronic properties of In(Ga)As/GaAs QDs. For N-incorporated QDs, Tomić [43] applied ten-band model to study the electronic properties of InGaAsN/GaAs(N) QDs with a base length of 11.3 nm. Experimentally

there is evidence that in many cases the shape of QDs more closely approximated by truncated pyramid (the top of the pyramid is removed) [44, 45], and Lee *et al.* showed that the calculated energies provide the best fit to photoluminescence experiments for truncated pyramids [46].

Besides GaAs-based QD, the dilute nitride III-V materials are also promising to enable mid-infrared (MIR) and far-infrared (FIR) devices such as laser diodes and detectors in many applications such as infrared counter-measures, low-cost medical diagnostics and chemical gas analysis [47]. The InAsPN is still a relatively new and open field with few theoretical reports. The experimental results of Biwa *et al.* [48] and Yonezu *et al.* [49] suggest that InAsPN/GaP(N) QDs may have the advantages of low power consumption due to low threshold current operation, longer wavelength and low cost due to simple growth and fabrication techniques, so our theoretical results can help further deepen the understanding of properties and application of these materials.

1.2 Objectives

As explained in the previous section, there are two major objectives of our projects. One of them is to simulate dilute nitride semiconductor QDs to study their electronic structures with eight-band or ten-band **k.p** methods which include the coupled conduction and valence bands, and orbit-splitting and N bands, and the

strain distribution is calculated using the VFF model. We investigate the energy levels and the GS transition energy after incorporating N into QDs. To determine the GS transition energy is the key point to estimate the emission wavelength whether it can achieve 1.3 μm or 1.55 μm . For InAsN/GaAs pyramidal QDs, the size and the N composition vary to investigate their impacts, and we change its shape from lens to volcano and to ring to observe the shape effect on electronic structures. To compare all these results, we can select size, shape and N composition for different requirements. For InAsPN/GaP(N) QDs, the compositions of P and N in QD can change the electronic structures. The lattice of GaP is close to Si, and we can obtain a barrier material with lattice-matched to Si by incorporating 2% of N into the barrier GaP. For GaPN barrier, the new electronic structure of QD is to be determined. We study and compare the difference in N composition to determine whether GaPN barrier is an appropriate lattice-matched barrier material.

The other objective is to determine the optical properties of InAsN/GaAs and InAsPN/GaP(N) QDs. The optical gains are calculated considering inhomogeneous broadening which is caused by size fluctuation of QDs. By increasing the carrier densities, we investigate the increase of optical gains of pyramids with different size, shape or N compositions. The wavelength emission, optical maximum gain and differential gain are the key properties we are concerned, and we investigate how these factors affect optical properties.

1.3 Major contributions

We systematically simulate the QDs using VFF model to calculate strains which includes the four nearest-neighbor interactions for each atom in the system, and the ten-band **k.p** method and the zero-dimensional optical gain formula are applied to accurately investigate their electronic and optical properties. After analyzing the relations between the factors and properties, theoretically we can decide the specific QDs we need according to the requirement in optoelectronic telecommunication applications.

- 1) The VFF model is applied to alloy structures and system, and we accurately take into count of strain which can significantly affect the band structure in **k.p** method. The strains including 9 components of each atom are considered to investigate the energy levels and wave functions.
- 2) The conventional pyramidal InAs/GaAs QDs are well documented. The simulation shows that InAsN QDs can achieve short wavelength emission closing to desirable 1.3 μ m. Before reaching saturation gain, the optical gain of InAsN QDs is greater than that of InAs QDs.
- 3) Overall performance of truncated pyramidal InAsN QDs is better than the full pyramidal ones. We recommend the truncated pyramidal QDs with its half of top part truncated
- 4) The lens, volcano and ring shaped QDs are simulated thoroughly to study their electronic structure differences and optical gain properties. The volcano shaped QD has better overall advantages due to its longer wavelength emission.

- 5) Incorporation 2% of N into GaP barrier is an effective way to fabricate GaPN barrier lattice-matched to Si, while InAsPN QDs can achieve longer wavelength up to 1.3 μm .

1.4 Organization of the thesis

In this thesis, **Chapter 1** provides an introduction of some background knowledge and the motivation of the thesis, followed by the objectives, and the contributions of the work. In **Chapter 2**, the fundamental knowledge, the basic theory of electronic band structures and the VFF model is described. The theoretical models and optical gain calculation are shown in details. In **Chapter 3**, the results of simulation of pyramidal InAs QDs are discussed, and compared with experimental measurement. In **Chapter 4**, the results of simulation and characterization of pyramidal InAsN QDs are shown, followed by the investigations of truncated pyramidal InAsN QDs in **Chapter 5**. **Chapter 6** shows the study of InAsPN/GaP(N) QDs which are relatively a new topic. In **Chapter 7**, we focus on shape effect on the electronic structure and the optical gain of InAs(N)/GaAs nanostructures: from quantum lens to quantum volcano to quantum ring. The last chapter summarizes the whole thesis, and provides a conclusion based on the results of this work, and projects key thrusts for future research.

Chapter 2: Theoretical models and related calculations

2.1 Basic theory of electronic band structures

2.1.1 The Bloch theorem

For a periodic potential, the electronic band structure and the wave function can be derived from the Hamiltonian, which satisfies the symmetry of the semiconductor crystals. The general theory follows the Bloch theorem [50], and the interest is near the band edges of direct band-gap semiconductors where the wave vector $\mathbf{k}$ deviates by a small amount from a vector $\mathbf{k}_0$, where a local minimum or maximum occurs [51]. The $\mathbf{k}\cdot\mathbf{p}$ method was introduced by Bardeen [37] and Seitz. [38] For an electron in a periodic potential

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}), \quad (2.1)$$

where $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the lattice vectors, and n_1, n_2 and n_3 are integers, the electron wave function satisfies the Schrödinger equation

$$H\Psi(\mathbf{r}) = \left[\frac{-\hbar^2}{2m_0} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = E(\mathbf{k})\Psi(\mathbf{r}), \quad (2.2)$$

where H is the Hamiltonian, Ψ is the total wave function, $\mathbf{r}$ is the position vector, $\hbar$ is

the Planck constant $\hbar$ divided by 2π , m_0 is the free electron mass, and E is the total energy. The Hamiltonian is invariant under translation by the lattice vectors, $r \rightarrow r + R$. If $\psi(r)$ describes an electron moving in the crystal, $\psi(r + R)$ will also be a solution to Equation (2.2). The general solution of the above equation is given by

$$\psi_{nk}(r) = e^{ik \cdot r} \Phi_{mk}(r), \quad (2.3)$$

where
$$\Phi_{mk}(r + R) = \Phi_{mk}(r), \quad (2.4)$$

is a periodic function. This result is the Bloch theorem. Here m refers to the band index and $\mathbf{k}$ refers to the wave vector of the electron [52]. Many approximate methods are applied to solve Eq. (2.2), such as the Augmented Plane Wave, the Green's Function, the Orthogonalized Plane Wave, and the Pseudopotential methods [53].

2.1.2 The $k \cdot p$ method

The $\mathbf{k} \cdot \mathbf{p}$ method is a useful technique for analyzing the band structure near a particular point $\mathbf{k}_0$, especially when it is near an extremum of the band structure. Our interests focus near the direct band gap (Γ valley) between the valence band edge and the conduction band edge, where the energy dispersion for a small $\mathbf{k}$ vector is considered. So the $\mathbf{k} \cdot \mathbf{p}$ method is very suitable and effective to study III-V direct

bandgap semiconductors [54, 55]. Consider the general Schrödinger equation for an electron wave function $\psi_{mk}(r)$ in the m th band with a wave vector $\mathbf{k}$,

$$\left[\frac{p^2}{2m_0} + V(r) \right] \psi_{mk}(r) = E_m(k) \psi_{mk}(r). \quad (2.5)$$

When written in terms of $\Phi_{mk}(r)$, it becomes

$$\left[\frac{p^2}{2m_0} + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p} + V(r) \right] \Phi_{mk}(r) = \left[E_m(k) - \frac{\hbar^2 k^2}{2m_0} \right] \Phi_{mk}(r). \quad (2.6)$$

The above equation can be expanded near a particular point $\mathbf{k}_0$ of interest in the band structure. When $\mathbf{k}_0 = 0$, the above equation is expanded near $E_m(0)$.

$$\left[H_0 + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p} \right] \Phi_{mk}(r) = \left[E_m(k) - \frac{\hbar^2 k^2}{2m_0} \right] \Phi_{mk}(r), \quad (2.7)$$

$$\text{where } H_0 = \frac{p^2}{2m_0} + V(r), \quad H_0 \Phi_{mk}(r) = E_m(0) \Phi_{mk}(r). \quad (2.8)$$

The standard procedure is to find the eigenvalue $E_m(k)$ with the corresponding eigenvector because the Hamiltonian matrix is known. The $\mathbf{k} \cdot \mathbf{p}$ method is further developed by Kane *et al.* [56] to take into account the spin-orbit interaction and by Luttinger *et al.* [57, 58] for degenerate bands.

2.1.3 Strain effects on band structures

When a crystal is under a uniform deformation, it may preserve the periodic property such that the Bloch theorem may still be applicable. The modulating part of the Bloch function remains periodic, with a period equal to that of the new elementary cell, since the elementary cell is also deformed. Applications of the strained-layer superlattices to long wavelength photodetectors [59] and semiconductor lasers [60] have been proposed and demonstrated, and they can exhibit superior performance compared to conventional ones in many aspects [61]. To demonstrate the strain analysis, we assume the unit vectors $\hat{x}, \hat{y}, \hat{z}$ are basis vectors in the undeformed crystal, and they are related to x', y', z' in the uniformly deformed crystal by [62, 63]

$$\begin{aligned} x' &= (1 + \varepsilon_{xx})\hat{x} + \varepsilon_{xy}\hat{y} + \varepsilon_{xz}\hat{z}, \\ y' &= \varepsilon_{yx}\hat{x} + (1 + \varepsilon_{yy})\hat{y} + \varepsilon_{yz}\hat{z}, \\ z' &= \varepsilon_{zx}\hat{x} + \varepsilon_{zy}\hat{y} + (1 + \varepsilon_{zz})\hat{z}, \end{aligned} \tag{2.9}$$

where ε_{ij} denotes the strain component in the i - j direction. We assume a homogeneous strain and $\varepsilon_{ij} = \varepsilon_{ji}$.

The strain can affect the electronic structure significantly. At the zone centre, $\mathbf{k}=0$, for eight-band method which include the coupled conduction and valence bands, and orbit-splitting, the band-edge energies are shown below [64]

$$\begin{aligned}
E_c(0) &= E_g + a_c(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}), \\
E_{HH}(0) &= -P_\varepsilon - Q_\varepsilon, \\
E_{LH}(0) &= -P_\varepsilon + \frac{1}{2}(Q_\varepsilon - \Delta_{SO} + \sqrt{\Delta_{SO}^2 + 2\Delta_{SO}Q_\varepsilon + 9Q_\varepsilon^2}), \\
E_{SO}(0) &= -P_\varepsilon + \frac{1}{2}(Q_\varepsilon - \Delta_{SO} - \sqrt{\Delta_{SO}^2 + 2\Delta_{SO}Q_\varepsilon + 9Q_\varepsilon^2}), \tag{2.10}
\end{aligned}$$

where $P_\varepsilon = -a_v(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})$, $Q_\varepsilon = -\frac{b}{2}(\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz})$, Δ_{SO} is the spin-orbit split-off energy, a_c is the deformation potential for conduction band, and a_v and b are the deformation potential for the valence band, respectively.

2.2 Valence Force Field (VFF) model

The QDs are surrounded by the substrate material, thus the strain components exist in all direction. This is different from QW system in which we can assume the strains are uniform in QW region, and strain components $\varepsilon_{xx} = \varepsilon_{yy} = \frac{a_{sub} - a_w}{a_w}$, where a_{sub} and a_w are the lattice constants of the substrate and the well materials, respectively, if the growth direction is along z -direction.

The main basic approaches to calculate strains are harmonic continuum elasticity (CE) and atomistic elasticity, and VFF model is based on the atomistic elasticity approach [39]. Pryor *et al.* [65] compare the strain distributions of pyramidal InAs/GaAs QDs using CE model and VFF model, and suggest that the large strains existing between lattice-mismatched III-V semiconductors may be

outside the linearity regime of CE model (e.g., 7% for InAs/GaAs). So we choose the VFF model to calculate the strains in this thesis.

In the VFF model, before relaxation, each atom in the system has its original position $\mathbf{R}_0$. The total strain energy is expressed as a function of atomic positions, as [65]

$$\begin{aligned}
E_{AE} &= \sum_{ij} V_2(R_i - R_j) + \sum_{ijk} V_3(\hat{\theta}_{ijk}) \\
&= \frac{1}{2} \sum_i^N \sum_j^{nn} \frac{3\alpha_{ij}}{8(d_{ij}^0)^2} \left[(R_i - R_j)^2 - (d_{ij}^0)^2 \right]^2 + \\
&\quad \frac{1}{2} \sum_i^N \sum_{j,k>j}^{nn} \frac{3\beta_{i,jk}}{8(d_{ij}^0) \cdot (d_{ik}^0)} \left[(R_j - R_i) \cdot (R_k - R_i) - \cos \theta_0 (d_{ij}^0)^2 \right]^2
\end{aligned} \tag{2.11}$$

where V_2 is a two-body term and V_3 is a three-body function of the bond angle θ_{ijk} , d_{ij}^0 denotes the ideal bond length between atoms i and j , and θ_0 is the ideal bond angle. For the zincblend structure, $\cos \theta_0 = -1/3$. The local-environment-dependent coefficients, α_{ij} and $\beta_{i,jk}$ are fitted to the elastic constants of bulk materials [15].

The relaxed atomic configuration is obtained by conjugate gradient minimization of E_{AE} with respect to the atomic positions. At each minimization step, the atoms are displaced along the conjugate direction $\{\mathbf{h}\}$ by a finite increment λ . E_{AE} is a fourth-order polynomial that depends on only the relative positions $\mathbf{R}_i - \mathbf{R}_j$ of each atom [66]

$$\begin{aligned}
E_{AE}[\{R + \lambda h\}] &= E_{AE}[\{R_i - R_j\}] + \lambda E^{(1)}[\{R_i - R_j\}, \{h_i - h_j\}] + \lambda^2 E^{(2)}[\{R_i - R_j\}, \{h_i - h_j\}] \\
&+ \lambda^3 E^{(3)}[\{R_i - R_j\}, \{h_i - h_j\}] + \lambda^4 E^{(4)}[\{R_i - R_j\}, \{h_i - h_j\}]
\end{aligned} \tag{2.12}$$

The terms, $E^{(1)}$, $E^{(2)}$, $E^{(3)}$, and $E^{(4)}$ are also simple polynomials of $\{\mathbf{R}\}$ and $\{\mathbf{h}\}$. The increment λ minimizing the elastic energy is then obtained by solving exactly

$$\frac{\partial E_{AE}[\{\mathbf{R} + \lambda \mathbf{h}\}]}{\partial \lambda} = E^{(1)} + 2\lambda E^{(2)} + 3\lambda^2 E^{(3)} + 4\lambda^3 E^{(4)} = 0. \quad (2.13)$$

Fig 2.1 Schematics to illustrate how the local strain is calculated. For a cation, three vectors forming a distorted tetrahedron after atomic relaxation are related to the equivalent vectors of an ideal tetrahedron via the strain tensor.

Fig 2.1 shows the positions of the atoms after being relaxed by minimizing E_{AE} , the local strain tensor at a cation site is calculated by considering a tetrahedron formed by four nearest neighbouring anions. The distorted tetrahedron edges, $\mathbf{R}_{12}$, $\mathbf{R}_{23}$ and $\mathbf{R}_{34}$, are related to the ideal tetrahedron edges $\mathbf{R}^0_{12}$, $\mathbf{R}^0_{23}$ and $\mathbf{R}^0_{34}$ via [65]

$$\begin{pmatrix} R_{12,x} & R_{23,x} & R_{34,x} \\ R_{12,y} & R_{23,y} & R_{34,y} \\ R_{12,z} & R_{23,z} & R_{34,z} \end{pmatrix} = \begin{pmatrix} 1 + \varepsilon_{xx} & \varepsilon_{yx} & \varepsilon_{zx} \\ \varepsilon_{xy} & 1 + \varepsilon_{yy} & \varepsilon_{zy} \\ \varepsilon_{xz} & \varepsilon_{yz} & 1 + \varepsilon_{zz} \end{pmatrix} \times \begin{pmatrix} R^0_{12,x} & R^0_{23,x} & R^0_{34,x} \\ R^0_{12,y} & R^0_{23,y} & R^0_{34,y} \\ R^0_{12,z} & R^0_{23,z} & R^0_{34,z} \end{pmatrix}. \quad (2.14)$$

Then the local strain is calculated by a matrix inversion as:

$$\begin{pmatrix} \varepsilon_{xx} & \varepsilon_{yx} & \varepsilon_{zx} \\ \varepsilon_{xy} & \varepsilon_{yy} & \varepsilon_{zy} \\ \varepsilon_{xz} & \varepsilon_{yz} & \varepsilon_{zz} \end{pmatrix} = \begin{pmatrix} R_{12,x} & R_{23,x} & R_{34,x} \\ R_{12,y} & R_{23,y} & R_{34,y} \\ R_{12,z} & R_{23,z} & R_{34,z} \end{pmatrix} \times \begin{pmatrix} R_{12,x}^0 & R_{23,x}^0 & R_{34,x}^0 \\ R_{12,y}^0 & R_{23,y}^0 & R_{34,y}^0 \\ R_{12,z}^0 & R_{23,z}^0 & R_{34,z}^0 \end{pmatrix}^{-1} - I, \quad (2.15)$$

where I is the unit matrix.

In this thesis, the in-house code of VFF model is written with Fortran language. In the first step, we must define the dimensions of the system including QD and substrate materials to be L_x, L_y and L_z that $L_x = x_1 a_{sub}, L_y = y_1 a_{sub}, L_z = z_1 a_{sub}$ where x_1, y_1 and z_1 must be positive integers. Thus the total number of atoms can be easily calculated as $8x_1 y_1 z_1$ (including the atoms at the lower boundary and excluding the atoms at the upper boundary for all 3 directions) We can arrange these atoms according to the required shape and structure, and each atoms has its original co-ordinates making sure that the number of cations is always equal to the number of anions. If small amount of N atoms are incorporated into InAs QD, we replace the As atoms in QD with the N atoms. We try to distribute the N atoms uniformly which is an ideal case in simulation. Once this unit cell system is fixed, we have to be consistent in the band structure calculation with the **k.p** method later. The second step is to let all atoms relax to their new positions so that the total strain energy E_{AE} is a minimum. This step follows Eqs.(2.11)-(2.13), and is crucial because each atom is numbered, after relaxation, each cation (anion) must find its four neighbouring anions (cations) with their new positions. The third step follows Eq.(2.15) to calculate the strain components for each cation. The co-ordinates of all cations are also included, and each cation is identified as In or Ga for InAs(N)/GaAs QD for the convenience of later calculation.

The parameters used in InAsN/GaAs VFF calculation are listed in Table II [65-68].

Table I: Parameters of InAsN and GaAs used in VFF calculation

		Bond distance d_{ij}^0 (Å)	α (10^3 dyne/cm)
In-As		2.623321	35.180
Ga-As		2.447929	41.190
In-N		2.156	79.200
Ga-N		1.949	96.300
	$\beta(10^3$ dyne/cm)		$\beta(10^3$ dyne/cm)
As-In-As	5.48808	In-As-In	5.48808
As-Ga-As	8.93823	Ga-As-Ga	8.93823
N-In-N	7.10000	In-N-In	7.10000
N-Ga-N	14.8000	Ga-N-Ga	14.8000
Ga-N-In	10.9500	N-In-As	6.294040
N-Ga-As	11.869115	Ga-As-In	7.213155

The InAsPN parameters are interpolated from InAs, InP and InN parameters.

The parameters used in VFF calculations are listed in Table II [16, 65-68].

Table II: Parameters of InAsPN and GaPN used in VFF calculation

	Bond distance d_{ij}^0 (Å)	α (10^3 dyne/cm)
In-As	2.623	35.180
In-P	2.542	43.040
In-N	2.154	79.200
Ga-P	2.360	47.320

Ga-N		1.935		96.300	
		$\beta(10^3 \text{ dyne/cm})$			$\beta(10^3 \text{ dyne/cm})$
As-In-As		5.48808	In-As-In		5.48808
P-In-P		6.24080	In-P-In		6.24080
N-In-N		7.10000	In-N-In		7.10000
As-In-P		5.86444	As-In-N		6.29404
P-In-N		6.67040	P-Ga-N		12.62886
P-Ga-P		10.45772	Ga-P-Ga		10.45772
N-Ga-N		14.800	Ga-N-Ga		14.800

2.3 The ten-band k.p method

2.3.1 The eight-band k.p method

For zinc-blende III-V structures, we need include eight functions considering the conduction, the heavy-hole, the light-hole, and the spin-orbit split-off bands with double degeneracy both spin-up and spin-down to be expanded at wave vector $\mathbf{k}$ near the Γ point. The conduction band edges functions are $|S\rangle\uparrow$ and $|S\rangle\downarrow$, and the valence band edges functions are $|X\rangle\uparrow, |Y\rangle\uparrow, |Z\rangle\uparrow, |X\rangle\downarrow, |Y\rangle\downarrow, |Z\rangle\downarrow$. It is more convenient to choose the Bloch function basis [69] as:

$$u_1 = |S\rangle\uparrow \quad (2.16a)$$

$$u_2 = |1, +1\rangle \uparrow = \frac{1}{\sqrt{2}} |X + iY\rangle \uparrow, \quad (2.16b)$$

$$u_3 = |1, 0\rangle \uparrow = |Z\rangle \uparrow, \quad (2.16c)$$

$$u_4 = |1, -1\rangle \uparrow = \frac{1}{\sqrt{2}} |X - iY\rangle \uparrow, \quad (2.16d)$$

$$u_5 = |S\rangle \downarrow, \quad (2.16f)$$

$$u_6 = |1, +1\rangle \downarrow = \frac{1}{\sqrt{2}} |X + iY\rangle \downarrow, \quad (2.16g)$$

$$u_7 = |1, 0\rangle \downarrow = |Z\rangle \downarrow, \quad (2.16h)$$

$$u_8 = |1, -1\rangle \downarrow = \frac{1}{\sqrt{2}} |X - iY\rangle \downarrow. \quad (2.16i)$$

We assume that the dots are three-dimensionally periodically arranged, and the periodicities are L_x , L_y , and L_z . The eight-dimensional electron and hole envelope wave functions for the quantum dots can be expressed as

$$\Phi_m = \{\Phi_m^j\} \quad (j = 1, 2, \dots, 8), \quad (2.17)$$

where
$$\Phi_m^j = \frac{1}{\sqrt{L_x L_y L_z}} \sum_{n_x, n_y, n_z} a_{m, n_x, n_y, n_z}^j \exp[i(k_x x + k_y y + k_z z)], \quad (2.18)$$

where $k_x = k_{x0} + \frac{2\pi}{L_x} \cdot n_x$, $k_y = k_{y0} + \frac{2\pi}{L_y} \cdot n_y$, $k_z = k_{z0} + \frac{2\pi}{L_z} \cdot n_z$, k_{x0} , k_{y0} , k_{z0}

represent the wave vectors of the dot. We set $k_{x0} = k_{y0} = k_{z0} = 0$. And n_x , n_y , n_z are the integers of plane wave numbers, m is the index for energy subbands, and j is the index

for basis. In this thesis, the range of n_x, n_y, n_z are from -3 to 3. The eight-band Hamiltonian is represented as [69]:

$$H_{\text{eight}} = \begin{pmatrix} H_{\text{int}} & 0 \\ 0 & H_{\text{int}} \end{pmatrix} + H_{\text{so}} + V_0, \quad (2.19)$$

where H_{so} is the valence band spin-orbit coupling Hamiltonian (Δ_{so} is the spin-orbit splitting energy), V_0 is the confining potential of the QD (V_0 is zero in the dot and finitely high in the barrier), and H_{int} contains all the k -independent, k -linear and k -quadratic terms. H_{int} can be written as [69]:

$$H_{\text{int}} = \begin{pmatrix} E_g + P_e & \frac{i}{\sqrt{2}} p_0 (k'_x + i k'_y) & i p_0 k'_z & \frac{i}{\sqrt{2}} p_0 (k'_x - i k'_y) \\ -\frac{i}{\sqrt{2}} p_0 (k'_x - i k'_y) & P_1 & S & T \\ -i p_0 k'_z & S^* & P_3 & S \\ -\frac{i}{\sqrt{2}} p_0 (k'_x + i k'_y) & T^* & S^* & P_1 \end{pmatrix}, \quad (2.20)$$

where E_g is the band gap of bulk material, $p_0 = \hbar \sqrt{\frac{E_p}{2m_0}}$, where E_p is the matrix element of Kane's theory, and

$$k'_x = k_x - \varepsilon_{xx} k_x - \varepsilon_{xy} k_y - \varepsilon_{xz} k_z, \quad (2.21a)$$

$$k'_y = k_y - \varepsilon_{xy} k_x - \varepsilon_{yy} k_y - \varepsilon_{yz} k_z, \quad (2.21b)$$

$$k'_z = k_z - \varepsilon_{xz} k_x - \varepsilon_{yz} k_y - \varepsilon_{zz} k_z, \quad (2.21c)$$

$$P_e = \frac{\hbar^2}{2m_0} \gamma_c (k_x^2 + k_y^2 + k_z^2) + a_c (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}), \quad (2.21d)$$

$$P_1 = -\frac{\hbar^2}{2m_0} \left[\frac{L' + M'}{2} (k_x^2 + k_y^2) + M' k_z^2 \right] + \left(a_v + \frac{b}{2} \right) (\varepsilon_{xx} + \varepsilon_{yy}) + (a_v - b) \varepsilon_{zz} , \quad (2.21e)$$

$$P_3 = -\frac{\hbar^2}{2m_0} \left[M' (k_x^2 + k_y^2) + L' k_z^2 \right] + (a_v - b) (\varepsilon_{xx} + \varepsilon_{yy}) + (a_v + 2b) \varepsilon_{zz} , \quad (2.21f)$$

$$S^* = -\frac{\hbar^2}{2m_0} \left[\frac{1}{\sqrt{2}} N' (k_x + i k_y) k_z \right] + \sqrt{6} d (\varepsilon_{xz} + i \varepsilon_{yz}) , \quad (2.21g)$$

$$T^* = -\frac{\hbar^2}{2m_0} \left[\frac{L' - M'}{2} (k_x^2 - k_y^2) + i N' k_x k_y \right] + \frac{3}{2} b (\varepsilon_{xx} - \varepsilon_{yy}) + i 2 \sqrt{3} d \varepsilon_{xy} , \quad (2.21h)$$

where $\varepsilon_{xx}, \varepsilon_{yy}, \dots$ are the strain components, a_c and a_v are the conduction band and the valence band hydrostatic deformation potential of the host material, respectively, and b and d are the shear deformation potentials along [001] and [111] direction of the host material, respectively. And γ_c, L', M', N' are given by

$$\gamma_c = \frac{m_0}{m_c} - \frac{E_p}{3} \left(\frac{2}{E_g} + \frac{1}{E_g + 3\lambda} \right), \quad L' = L - E_p / E_g, \quad M' = M, \quad N' = N - E_p / E_g ,$$

where m_c is the electron effective mass, λ is the spin-orbit coefficient, $\lambda = \Delta_{so}/3$ (Δ_{so} is the spin-orbit splitting energy), and L, M and N are the Luttinger parameters. The origin of energy is the top of valence band of barrier material.

The piezoelectric effect is not included in our simulation, because Bester *et al.* [70] calculated the piezoelectric tensors of QD from first principles and found surprisingly large nonlinear components, then Zunger *et al.* [71] suggested that if the quadratic piezoelectric tensors are unknown, it is better to neglect piezoelectricity altogether than to simply include the linear term.

The strains ε_{ij} calculated from the VFF model are localized strains. In **k.p** calculation, the strain-related Hamiltonian element can be written as

$$\langle \Phi_m | \varepsilon_{ij} | \Phi_m' \rangle = \text{Re}(\text{strain}) + i \cdot \text{Im}(\text{strain}) \quad (2.22)$$

where Φ_m is the envelop function, ε_{ij} is the strain component and

$$\begin{aligned} \text{Re}(\text{strain}) &= \frac{1}{N} \sum_N \varepsilon_{ij} \cdot \cos \left[(n_{x1} - n_x) \frac{2\pi}{L_x} \cdot x + (n_{y1} - n_y) \frac{2\pi}{L_y} \cdot y + (n_{z1} - n_z) \frac{2\pi}{L_z} \cdot z \right], \\ \text{Im}(\text{strain}) &= \frac{1}{N} \sum_N \varepsilon_{ij} \cdot \sin \left[(n_{x1} - n_x) \frac{2\pi}{L_x} \cdot x + (n_{y1} - n_y) \frac{2\pi}{L_y} \cdot y + (n_{z1} - n_z) \frac{2\pi}{L_z} \cdot z \right] \end{aligned} \quad (2.23)$$

where N is number of cations with nine strain components substituting in the Hamiltonian matrix, and x, y, z are the coordinates of those cations.

H_{so} can be written as [69]:

$$H_{so} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\lambda & 0 & 0 & -\sqrt{2}\lambda & 0 & 0 \\ 0 & 0 & 0 & -2\lambda & 0 & 0 & \sqrt{2}\lambda & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\sqrt{2}\lambda & 0 & 0 & -2\lambda & 0 & 0 \\ 0 & 0 & 0 & \sqrt{2}\lambda & 0 & 0 & -\lambda & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (2.24)$$

The parameters of InAs and GaAs are listed in Table III [72-74].

Table III: Parameters of InAs and GaAs used in the calculation

Material	$a_0(\text{nm})$	$E_g \text{ (eV)}$	$\Delta_{so}(\text{eV})$	$a_c \text{ (eV)}$	$a_v \text{ (eV)}$	$b \text{ (eV)}$	$d \text{ (eV)}$
GaAs	0.56533	1.424	0.341	-7.17	1.16	-1.7	-4.55
InAs	0.60583	0.354	0.38	-5.08	1.0	-1.8	-3.6
Material	L	M	N	$m_c(m_0)$	$E_p(\text{eV})$		
InAs	53.15	2.93	55.74	0.02226	22.2		

The conduction band offset of InAs/GaAs is assumed to be 70% of the band-gap difference [75], so the conduction band (valence band) offset is 749 meV (321 meV). The eight-band Hamiltonian matrix is solved by direct diagonalization using a standard code, the energy levels of conduction and valence bands and the wave functions can be obtained.

In order to identify the electron (e), heavy hole (h), band components in the energy states, from the function basis we choose, we introduce the following probability functions:

$$P_m^e = \sum_{j=1,5} \sum_{n_x n_y n_z} a_{m,n_x,n_y,n_z}^{j*} \cdot a_{m,n_x,n_y,n_z}^j, \quad (2.25a)$$

$$P_m^{hh} = \sum_{j=2,6} \sum_{n_x n_y n_z} a_{m,n_x,n_y,n_z}^{j*} \cdot a_{m,n_x,n_y,n_z}^j, \quad (2.25b)$$

$$\text{and } \sum_{j=1}^8 \sum_{n_x n_y n_z} a_{m,n_x,n_y,n_z}^{j*} \cdot a_{m,n_x,n_y,n_z}^j = 1.$$

M^{cv} is the optical transition matrix element (TME), and the squared optical transition matrix elements measure the momentum of the transition between the hole subbands and the electron subbands [17]. M^{cv} can be represented as:

$$M_i^{cv} = \langle \Psi_{n_v,k} | \hat{p}_i | \Psi_{n_c,k} \rangle, \quad i=x,y,z \quad (2.26)$$

where $\hat{p}_i$ is the momentum operator, and $\Psi_{n_c,k}$ and $\Psi_{n_v,k}$ are the real electron and hole wave functions, respectively. The real wave function is the product of the envelope wave functions in Eq. (2.17) and the Bloch wave functions basis. The final expression for optical TME in the x , y and z directions are:

$$\begin{aligned} M_x^{cv} &= \langle \Psi_{n_v,k} \uparrow | \hat{p}_x | \Psi_{n_c,k} \uparrow \rangle + \langle \Psi_{n_v,k} \downarrow | \hat{p}_x | \Psi_{n_c,k} \downarrow \rangle \\ &= M_x^{cv} = p_0 \sum_{n_x, n_y, n_z} \left[\frac{1}{\sqrt{2}} (a_{v,n_x,n_y,n_z}^2 + a_{v,n_x,n_y,n_z}^4) \cdot a_{c,n_x,n_y,n_z}^{1*} + \frac{1}{\sqrt{2}} (a_{v,n_x,n_y,n_z}^6 + a_{v,n_x,n_y,n_z}^8) \cdot a_{c,n_x,n_y,n_z}^{5*} \right] \\ M_y^{cv} &= \langle \Psi_{n_v,k} \uparrow | \hat{p}_y | \Psi_{n_c,k} \uparrow \rangle + \langle \Psi_{n_v,k} \downarrow | \hat{p}_y | \Psi_{n_c,k} \downarrow \rangle \\ &= M_y^{cv} = p_0 \sum_{n_x, n_y, n_z} \left[\frac{i}{\sqrt{2}} (a_{v,n_x,n_y,n_z}^2 - a_{v,n_x,n_y,n_z}^4) \cdot a_{c,n_x,n_y,n_z}^{1*} + \frac{i}{\sqrt{2}} (a_{v,n_x,n_y,n_z}^6 - a_{v,n_x,n_y,n_z}^8) \cdot a_{c,n_x,n_y,n_z}^{5*} \right] \\ M_z^{cv} &= \langle \Psi_{n_v,k} \uparrow | \hat{p}_z | \Psi_{n_c,k} \uparrow \rangle + \langle \Psi_{n_v,k} \downarrow | \hat{p}_z | \Psi_{n_c,k} \downarrow \rangle \\ &= M_z^{cv} = p_0 \sum_{n_x, n_y, n_z} [a_{v,n_x,n_y,n_z}^3 \cdot a_{c,n_x,n_y,n_z}^{1*} + a_{v,n_x,n_y,n_z}^7 \cdot a_{c,n_x,n_y,n_z}^{5*}] \end{aligned} \quad (2.27)$$

where $p_0 = \langle S | p_x | X \rangle = \langle S | p_y | Y \rangle = \langle S | p_z | Z \rangle$. The transition $S^C \rightarrow X^V, Y^V, Z^V$ is much greater than $X^C, Y^C, Z^C \rightarrow S^V$ which is still included in the calculations. The TME will be further discussed in optical gain calculation.

2.3.2 The BAC model and ten-band $\mathbf{k.p}$ method

The conventional eight-band $\mathbf{k.p}$ method is applied to calculate III-V structure which does not contain any N, but for dilute nitride III-V QD, ten-band $\mathbf{k.p}$ method is applied to include the additional two spin-degenerated N-related resonant bands. Based on the BAC model, the reduction of the band gap is due to the highly localized nature of the perturbation introduced by N atoms [33]. The largest contribution to this reduction is caused by structural relaxation and charge exchange, respectively [33,76].

The ten-band Hamiltonian is represented in the Bloch function basis [77]:

$$u_1 = |S\rangle \uparrow, \quad (2.28a)$$

$$u_2 = |1,+1\rangle \uparrow = \frac{1}{\sqrt{2}} |X + iY\rangle \uparrow, \quad (2.28b)$$

$$u_3 = |1,0\rangle \uparrow = |Z\rangle \uparrow, \quad (2.28c)$$

$$u_4 = |1,-1\rangle \uparrow = \frac{1}{\sqrt{2}} |X - iY\rangle \uparrow, \quad (2.28d)$$

$$u_5 = |S_N\rangle \uparrow, \quad (2.28e)$$

$$u_6 = |S\rangle \downarrow, \quad (2.28f)$$

$$u_7 = |1,+1\rangle \downarrow = \frac{1}{\sqrt{2}} |X + iY\rangle \downarrow, \quad (2.28g)$$

$$u_8 = |1,0\rangle \downarrow = |Z\rangle \downarrow, \quad (2.28h)$$

$$u_9 = |1,-1\rangle \downarrow = \frac{1}{\sqrt{2}} |X - iY\rangle \downarrow, \quad (2.28i)$$

$$u_{10} = |S_N\rangle \downarrow, \quad (2.28j)$$

as

$$H_{\text{ten}} = \begin{pmatrix} H_{\text{int}} & 0 \\ 0 & H_{\text{int}} \end{pmatrix} + H_{\text{so}} + V_0 \quad (2.29)$$

where $|S_N\rangle$ is the basis of the N, and H_{int} contains all the k -independent, k -linear and k -quadratic terms. H_{int} can be written as [77]:

$$H_{\text{int}} = \begin{pmatrix} E_g + P_e & \frac{i}{\sqrt{2}} p_0 (k'_x + ik'_y) & ip_0 k'_z & \frac{i}{\sqrt{2}} p_0 (k'_x - ik'_y) & V_{NC} \sqrt{x} \\ -\frac{i}{\sqrt{2}} p_0 (k'_x - ik'_y) & P_1 & S & T & 0 \\ -ip_0 k'_z & S^* & P_3 & S & 0 \\ -\frac{i}{\sqrt{2}} p_0 (k'_x + ik'_y) & T^* & S^* & P_1 & 0 \\ V_{NC} \sqrt{x} & 0 & 0 & 0 & E_N \end{pmatrix} \quad (2.30)$$

where E_g is the band gap of bulk material, and x is the composition of N incorporated in host material. E_N is the N energy level relative to the valence band maximum of host material, and V_{NC} is the coupling strength between conduction band edge and the N resonant band.

H_{so} can be written as [77]:

$$H_{so} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\lambda & 0 & 0 & 0 & -\sqrt{2}\lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\lambda & 0 & 0 & 0 & \sqrt{2}\lambda & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\sqrt{2}\lambda & 0 & 0 & 0 & -2\lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{2}\lambda & 0 & 0 & 0 & -\lambda & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (2.31)$$

The Hamiltonian matrix is solved by direct diagonalization, and the TME changes accordingly as

$$\begin{aligned} M_x^{cv} &= \langle \Psi_{n_v,k} \uparrow | \hat{p}_x | \Psi_{n_c,k} \uparrow \rangle + \langle \Psi_{n_v,k} \downarrow | \hat{p}_x | \Psi_{n_c,k} \downarrow \rangle \\ &= M_x^{cv} = p_0 \sum_{n_x, n_y, n_z} \left[\frac{1}{\sqrt{2}} (a_{v,n_x,n_y,n_z}^2 + a_{v,n_x,n_y,n_z}^4) \cdot a_{c,n_x,n_y,n_z}^{1*} + \frac{1}{\sqrt{2}} (a_{v,n_x,n_y,n_z}^7 + a_{v,n_x,n_y,n_z}^9) \cdot a_{c,n_x,n_y,n_z}^{6*} \right] \\ M_y^{cv} &= \langle \Psi_{n_v,k} \uparrow | \hat{p}_y | \Psi_{n_c,k} \uparrow \rangle + \langle \Psi_{n_v,k} \downarrow | \hat{p}_y | \Psi_{n_c,k} \downarrow \rangle \\ &= M_y^{cv} = p_0 \sum_{n_x, n_y, n_z} \left[\frac{i}{\sqrt{2}} (a_{v,n_x,n_y,n_z}^2 - a_{v,n_x,n_y,n_z}^4) \cdot a_{c,n_x,n_y,n_z}^{1*} + \frac{i}{\sqrt{2}} (a_{v,n_x,n_y,n_z}^7 - a_{v,n_x,n_y,n_z}^9) \cdot a_{c,n_x,n_y,n_z}^{6*} \right] \\ M_z^{cv} &= \langle \Psi_{n_v,k} \uparrow | \hat{p}_z | \Psi_{n_c,k} \uparrow \rangle + \langle \Psi_{n_v,k} \downarrow | \hat{p}_z | \Psi_{n_c,k} \downarrow \rangle \\ &= M_z^{cv} = p_0 \sum_{n_x, n_y, n_z} [a_{v,n_x,n_y,n_z}^3 \cdot a_{c,n_x,n_y,n_z}^{1*} + a_{v,n_x,n_y,n_z}^8 \cdot a_{c,n_x,n_y,n_z}^{6*}]. \end{aligned} \quad (2.32)$$

2.3.3 The Stark effect

The Stark effect is the shifting and splitting of spectral lines of atoms and molecules due to presence of an external static electric field. The amount of splitting and or shifting is called the Stark splitting or Stark shift. The Stark effect can lead to splitting of degenerate energy levels of nanostructures such as QW and QDs, and it was studied experimentally [78] and theoretically [79,80]. When an electric field F is applied, we need include additional term for the electrical induced potential V_F in Eq.(2.19). For example, if F is along the z direction, then $V_F(z) = \int e \cdot F_z dz$, where e is the electron charge.

2.4 The optical gain calculation

Derived from Fermi's golden rule using perturbation theory, the optical gain spectrum of QD active region is presented as [19]:

$$G(E) = \frac{\pi e^2 \hbar}{m_0^2 \varepsilon_0 n_r c E} \sum_{n_c, n_v} \frac{1}{V} |M^{cv}|^2 [f_c + f_v - 1] \times \frac{1}{\pi} \times B_{cv}(E - E_{cv}) \quad (2.33)$$

where E is the photon energy, e is the electron charge, ε_0 is the free-space dielectric constant, n is the refractive index, c is the speed of light, M^{cv} is the TME calculated

from section 2.3, and E_{cv} is the transition energy. The Fermi-Dirac distributions f_c and f_v are for electrons in the conduction bands and holes in the valence bands, respectively, as

$$f_c = \frac{1}{1 + \exp\left[\left(E_{nc} - E_{fc}\right)/k_B T\right]} , \quad (2.34a)$$

$$f_v = \frac{1}{1 + \exp\left[\left(E_{nv} - E_{fv}\right)/k_B T\right]} , \quad (2.34b)$$

where E_{nc} and E_{nv} are the quantized electron and hole energy levels, respectively. E_{fc} and E_{fv} are the electron and hole quasi-Fermi level, respectively.

The TME M_x^{cv} (M_y^{cv}) corresponds to the transverse electric (TE) mode (polarized in the x or y direction) optical transition, and M_z^{cv} corresponds to the transverse magnetic (TM) mode (polarized in the z direction) optical transition [17]. The average TE mode optical gain is made with their squared absolute values $|M_x^{cv}|^2$ and $|M_y^{cv}|^2$, because both M_x^{cv} and M_y^{cv} correspond to TE mode, and their values are very close to each other. We also assume the TME between the $|S_N\rangle$ state and the valence band state is zero. The squared optical TME for the TE mode is the sum of the major contribution from the electron to heavy hole transition and the minor contribution from the electron to the hybrid state of light hole and spin-orbit split-off hole transition. For the TM mode, the contribution comes from the electron to the hybrid state of light hole and spin-orbit split-off hole transition. In this thesis, the strain in QDs is compressive. Due to deformation potential, the compressive strain

raises the energy level of heavy hole above light hole. So the numerical value of M_x^{cv} (M_y^{cv}) is much greater than M_z^{cv} , and TE mode optical gains are much greater than TM mode. In this thesis, we only focus on TME M_x^{cv} (M_y^{cv}) and TE mode to investigate the optical properties for laser fabrication.

The homogeneous or intrinsic broadening of a Lorentz shape is caused by carrier scattering processes [51], and can be written as [19]

$$B_{cv}(E - E_{cv}) = \frac{\hbar/\tau}{(E - E_{cv})^2 + (\hbar/\tau)^2}, \quad (2.35)$$

where τ is the intraband relaxation time.

In the actual quantum-dot lasers, due to the dot size fluctuation and composition variations [81], we must take into account of inhomogeneous broadening in terms of a convolution integral as [19]:

$$G(E) = \frac{\pi e^2 \hbar}{m_0^2 \epsilon_0 n_r c E} \sum_{n_c, n_v} \frac{1}{V} |M^{cv}|^2 \int_{-\infty}^{\infty} [f_c + f_v - 1] \times \frac{1}{\pi} \times G(E' - E_{cv}) B_{cv}(E - E') dE' \quad (2.36)$$

where the energy fluctuation of dots are represented by $G(E' - E_{cv})$, E_{cv} is the centre of the energy distribution function of each interband transition. We take a Gaussian distribution function as [19]:

$$G(E - E_{cv}) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-(E - E_{cv})^2 / (2\sigma^2)\right]. \quad (2.37)$$

Eq. (2.36) indicates the optical gain at a given energy E is created by collecting the individual contribution of all dots within the homogeneous broadening around the energy. If the homogeneous broadening is a δ function, i.e. $B_{cv}(E)=\delta(E)$, then Eq.(2.36) is reduced as [19]:

$$G(E) = \frac{\pi e^2 \hbar}{m_0^2 \epsilon_0 n_r c E} \sum_{n_c, n_v} \frac{1}{V} |M^{cv}|^2 [f_c + f_v - 1] \times \frac{1}{\pi} \times G(E - E_{cv}) \quad (2.38)$$

The QDs with different energies have no correlation to each other and give optical gain independently since they are spatially isolated from each other [82]. In our calculation, we take the inhomogeneous broadening $\sigma = 20$ meV, because Lorke *et al.* [81] showed that the spectra of InAs QDs with inhomogeneous broadening of 20 meV resemble those observed in experiment by Osborne *et al.* [83], and Sugawara *et al.* [19] also took this value in their simulation and achieved positive results successfully.

The factor $f_c + f_v - 1$ is important in optical gain calculation. According to the Ref. 51, regarding the electron-hole recombination, we have to consider both total upward transition rate $R_{a \rightarrow b}$ and downward transition rate $R_{b \rightarrow a}$ to calculate the optical gain. The factor related to Fermi-Dirac distribution in $R_{a \rightarrow b}$ is $f_a(1-f_b)$, and the factor related to Fermi-Dirac distribution in $R_{b \rightarrow a}$ is $f_b(1-f_a)$. (f_a is the probability to find an electron in a conduction state, and f_b is the probability that a valence state is occupied by an electron) The net upward transition rate $R = R_{a \rightarrow b} - R_{b \rightarrow a}$. After taking out the common factors, the factor related to Fermi-Dirac distribution is $f_a - f_b$. In our calculation, we

define f_c as the same as f_a which is the probability to find an electron in a conduction state, but the definition of f_v is different from f_b . We define f_v as the probability to find a hole in a valence state, so $f_b = 1 - f_v$. Then $f_a - f_b = f_c - (1 - f_v) = f_c + f_v - 1$. Carrier density is an input parameter we substitute in the calculation. When carrier density increases, the number of carriers in QD increases, then it is more likely to find an electron in a conduction state. So the value of $f_c + f_v - 1$ increases as well. When it becomes positive, the optical gain is positive, and the carrier density at this moment is the transparency carrier density.

From the calculated maximum gain, we can deduce the differential gain which is $d(\text{Gain})/d(\text{carrier density})$. Differential gain is an important characteristic of a semiconductor laser, and it measures how faster the optical gain changes correspondingly to the carrier density change. The resonant frequency in a semiconductor laser is proportional to the square root of the differential gain with respect to the carrier density [84], and it is crucial in small signal ac analysis and modulation frequency. The small signal frequency response shows a flat respond at low frequencies, and then rolls off when the frequency increases greater than the resonant frequency. So differential gain is an important factor in modulation bandwidth [85, 86], and we include it in our optical properties.

Linear interpolation method

For InAsPN alloy, we need both InAs and InP parameters to calculate the parameters for ternary compound $\text{InAs}_x\text{P}_{1-x}$ by linear combination or considering bowing effect.

Table IV: Parameters of InAs, InP and GaP used in the calculation [72-74, 87]

Material	InAs	InP	GaP
$a_0(\text{nm})$	0.60583	0.58697	0.54505
$E_g(\text{eV})$	0.354	1.3529	2.7770
$\Delta_{so}(\text{eV})$	0.380	0.108	0.080
$m_c(m_0)$	0.02226	0.07950	
$E_p(\text{eV})$	22.2	20.7	
$a_c(\text{eV})$	-5.08	-6.00	-8.20
$a_v(\text{eV})$	1.00	0.60	1.70
$b(\text{eV})$	-1.8	-2.0	-1.6
$d(\text{eV})$	-3.6	-5.0	-4.6
$E_N(\text{eV})$	1.44	1.79	2.18
$V_{NC}(\text{eV})$	2.0	3.0	3.05
L	53.15	14.6	
M	2.93	2.12	
N	55.74	16.56	
$VBO(\text{eV})$	-0.59	-0.94	-1.27
n_r	3.516	3.327	

The parameters are listed in Table IV. The reference energy for VBO(eV) is the valence band top of InSb. The bowing factors of the bandgap of InAsP at Γ and Δ_{so} are 0.10 and 0.16, respectively.

Chapter 3: Pyramidal InAs/GaAs QDs

3.1 Introduction

In past decade, InAs/GaAs pyramidal QDs grown by using Stranski-Krastanov mode have been under intense research. Theoretically the electronic structure of these quantum dots has been studied by empirical pseudopotential [9] and effective-mass methods [10, 88-90]. In this chapter, we focus on the study of the Stark effect of InAs/GaAs pyramidal QDs, and then calculate the optical gain of a single QD. The effect of electric field along different directions on the electronic structures may be interesting because of the asymmetrical dot shape. The effect of homogeneous or intrinsic broadening of optical gain on lasing spectra in QD lasers has been studied [19].

Recently, Semiconductor lasers have become ubiquitous [5]. The well synthesized InAs/GaAs QDs were widely used in QD lasers, and the optical gain of QD lasers was widely measured and calculated [91-94]. We compared the simulation result with the experimental micro-photoluminescence (μ -PL) result which is from InAs/GaAs QD vertical cavity surface emitting lasers (VCSELs) structure wafer at room temperature. As we know, the features of QD-VCSELs should be dissimilar under different ambient temperature, which is commonly believed to be due to the detuning between the gain spectra and the cavity resonance wavelength. The prediction of QD emission wavelength and width of the emission spectrum at different temperature by the abovementioned model have a realistic significance for

design optimization of QD-VCSELs with a desirable operating temperature range (OTR) and an acceptable temperature-insensitivity.

3.2 Theoretical study and discussion

Fig 3.1 Top view of the schematic diagram square-based full pyramidal QD.

A typical semiconductor QD system consists of an island QD material with narrow bandgap and a barrier material which is surrounding the island QD. For QD in this thesis, we assume that the growing direction is along the direction of positive z direction, and the two-monolayer wetting layer is in the x - y plane.

For pyramidal shape, every surface of the pyramid is a simple crystal plane shown in Fig 3.1. The size of the pyramid is parameterized by the length of the base (b) which is 2 times of the height h . This ratio is set for the simulation for

comparison convenience with previous calculations [9, 39, 95]. The fixed dimension ratio of QD is shown in Fig 3.2. The assumed temperature is $T= 300\text{K}$.

Fig 3.2 Schematic diagram of a square pyramidal dot with side view. The height (L_z) and the width (L_x or L_y) of the unit cell are 3 and 4 times of the height h of QD, respectively.

Size effect on state energies when $F=0$

Fig 3.3 shows electron and hole energy levels of InAs/GaAs pyramidal QDs at $F=0$ as functions of base width (b). The energy reference point is the valence band maximum of GaAs barrier material. The electron energy levels decrease as the base width increases. The band gap of the dot is larger than the bulk InAs due to the quantum confinement and compressive strain. For the smallest size $b = 6.5\text{nm}$, there is only the ground state of electron in the dot, the excited states of electron are higher than the energy levels of wetting layer or GaAs barrier.

Fig 3.3 Electron (a) and hole (b) energy levels of InAs/GaAs pyramidal QD at $F=0$ as functions of base width b .

3.2.1 The Stark effect when electric field F is along z direction

Fig 3.4 shows the electron (a) and hole (b) energy levels of InAs/GaAs QDs with $b = 11.3$ nm as functions of F ($F \parallel z$). The Stark effect is asymmetrical, because the dot shape is asymmetrical along the z direction. When F is along the positive (negative) z direction, the electron levels decrease (increase), the hole levels also decrease (increase). In the presence of electric field, the electron (hole) moves antiparallel (parallel) to field direction, its electric potential decreases, so its energy levels have a decrease (increase, actually moves to the hole ground level). While the

electron levels may have an increase (decrease) under the electric field when the electron moves into a narrower (wider) space due to the increase (decrease) of quantum confinement. When the hole moves into a narrower (wider) space, the hole levels have a decrease (increase). When F is along the positive z direction, the electron moves to wider space, so the electron levels decrease, the hole moves to narrower space, so the hole levels have a decrease due to the increase of quantum confinement and an increase due to the change of electric potential and the former dominates. When F is along the negative z direction, the cases are inverse.

Fig 3.4 Electron (a) and hole (b) levels of InAs/GaAs pyramidal QDs with $b = 11.3$ nm as functions of F ($F \parallel z$).

Fig 3.5 shows the band gap of InAs/GaAs pyramidal QDs with $b = 11.3$ nm as a function of F ($F \parallel z$). When F is along the negative z direction, the band gap decreases as the electric field strength increases, this is the red Stark shift. When F is along the positive z direction, as F increases, the band gap increases as first, and then decreases. When F is not very large, the band gap increases in the presence of F , this is the interesting blue Stark shift in InAs/GaAs pyramidal QDs.

3.2.2 The Stark effect when electric field F is along x direction

Fig 3.5 Band gap of InAs/GaAs pyramidal QDs with $b=11.3$ nm as a function of F ($F \parallel z$).

Figs. 3.4 and 3.5 show that the Stark effect is asymmetrical when the electric field F is along the z direction, because the dot shape is asymmetrical along the z direction. While the dot shape is symmetrical in the x direction, for comparison, we show the energy levels of InAs/GaAs pyramidal QDs with $b = 11.3$ nm as functions of F ($F \parallel x$) in Fig 3.6. We suggest that the Stark effect is symmetrical in this case. The Stark effect in Fig 3.6 can also be explained by the two factors, the quantum confinement and the electric potential mentioned in section 3.2.1.

Fig 3.6 Electron (a) and hole (b) levels of InAs/GaAs pyramidal QDs with $b = 11.3$ nm as functions of F ($F \parallel x$).

3.2.2 Optical properties

Fig 3.7 shows the optical gain spectra at $T = 300\text{K}$ for InAs/GaAs pyramidal QDs with $b = 11.3\text{ nm}$ in the absence of electric field at different numbers of carriers n_{eh} . We see that there is no positive gain when $n_{eh} = 1$. For $b = 11.3\text{ nm}$, the optical gain starts to appear when $n_{eh} = 2$, and increases as n_{eh} increases. The optical gain is highly polarized that the TE mode (polarized in the x direction) optical gain is much larger than the TM mode (polarized in the z direction) optical gain. When $n_{eh} = 2$, there is no positive gain for TM mode, while the gain is sufficiently large for TE mode, so the optical gain is purely polarized. The TM mode optical gain starts to appear when $n_{eh} = 3$.

Fig 3.7 Optical gain spectra at $T = 300\text{K}$ for InAs/GaAs pyramidal QDs with $b = 11.3\text{ nm}$ in the absence of electric field at different numbers of carriers. (a) $n_{eh} = 1, 2$. (b) $n_{eh} = 3, 4$. (c) $n_{eh} = 5, 6$.

Figs 3.8(a) and 3.8(b) show the maximum GS gains at $T = 300\text{K}$ for InAs/GaAs pyramidal QDs with $b = 11.3\text{ nm}$ at $F = 0$ as functions of n_{eh} . The TE mode and TM mode maximum GS gains both increase as n_{eh} increases. The TE mode maximum gain can be as large as $3 \times 10^4\text{ cm}^{-1}$ and is much larger than the TM mode maximum gain. As n_{eh} increases, the maximum gains show saturating trends, the TE mode maximum gain shows saturating trend at smaller n_{eh} than that of the TM mode.

Fig 3.8 Maximum GS gains and differential gains at $T = 300\text{K}$ for InAs/GaAs pyramidal QDs with $b = 11.3\text{ nm}$ at $F = 0$ as functions of n_{eh} . (a) Maximum gain for TE mode. (b) Maximum gain for TM mode. (c) Differential gain for TE mode. (d) Differential gain for TM mode.

Fig 3.8(c) shows the TE mode GS differential gain as a function of n_{eh} which is calculated as the maximum GS gain at $n_{eh}+1$ subtracts the maximum GS gain at n_{eh} ,

and it means the increase of maximum gain by increasing one electron-hole pair. Fig 3.8(d) shows the TM mode differential gain. As n_{eh} increases, the differential gains decrease because the maximum gains show saturating trends, and the differential gains also show saturating trends. The TE mode differential gain shows saturation occurs at smaller n_{eh} than that of the TM mode. The differential gain by increasing one electron-hole pair can be as large as 10^4 cm^{-1} .

3.3 Some comparison with experiments

3.3.1 VCSELs structure and experimental details

InAs QD vertical cavity surface emitting lasers (VCSELs) structure wafer was used for experimental comparison. We employed the edge-excitation and edge-emission (EEEE) μ -PL technique to determine the precise QD luminescence spectra at room temperature within an as-grown QD-VCSEL structure [96]. In this way, the influence of distributed Bragg reflectors (DBRs) in QD-VCSEL structure can be eliminated completely.

The InAs QD-VCSEL epitaxial wafers were prepared by MBE on n+-GaAs substrates. The epitaxial structure consists of QD's active region sandwiched in between top and bottom DBR mirrors. The 17 layers of InAs QDs include five groups QDs and two separated QD sheet layers. Each group of QDs consists of three sheets of QD and was situated around the antinode position of standing wave. The 6

nm-thick QDs are grown directly on GaAs and capped by an 8 nm-thick $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ layer. The surface density of QDs is about $3 \times 10^{10} \text{ cm}^{-2}$. A 5 nm-thick undoped GaAs layer is grown after the InGaAs cap layer, followed by a 5 nm-thick p-doped GaAs layer which p-type modulation doping is expected to improve the hole thermalization and temperature insensitivity of the threshold current in QD lasers. The total 32 nm-thick GaAs spacer layers between QD layers are used for eliminating high strain accumulation in each QD layer which may lead to strain relaxation with the formation of misfit dislocations and degradation in optical properties [97].

Fig 3.9 HR-SEM images of cross section of QD layers in InAs QD-VCSEL epitaxial structure.

The high resolution scanning electron microscopy (HR-SEM) image of cross section of QD layers in InAs QD-VCSEL epitaxial structure is shown in Fig 3.9. The light gray and dark gray layers in the middle (active region) are InAs/InGaAs and GaAs, respectively, and the top and bottom are DBR. The active region is enlarged to show the detailed layers which are consistent with the text description above.

The fabrication procedures include a few steps. Firstly, the mesas were formed by lithography and wet-etching, then oxide apertures were formed by wet oxidation in the mesas. After depositing SiN_x dielectric film and opening contact windows on the top of the mesas, p-type contact electrode was deposited, and the n-type contact metal was deposited onto the bottom side of the wafer after substrate thinning. Because we applied the EEEE μ -PL technique to investigate QD luminescence spectra, we focus only on the active region. The μ -PL measurements were carried out at room temperature (RT). An argon laser with a wavelength of 514 nm was used for excitation. The excitation beam was focused onto a spot with a diameter of several microns on the cross section of QD layers which is shown in Fig 3.9 with the as-grown QD-VCSEL sample stand on edge for this EEEE μ -PL measurement. The emission spectra in PL measurements collected through the same microscope objective was detected by InGaAs array detectors for spectral analysis or dispersed into a charge coupled device (CCD) camera for imaging. The detailed measurement setup can be found in Ref. 96.

3.3.2 Simulation model

The simulation is consistent with the structures shown in Fig. 3.9 that the $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ capped InAs/GaAs lens-shaped QD. We assume that the lens axis is along the direction of positive z direction, and the two-monolayer wetting layer is in the x - y plane. The radius of the base is about 10.2 nm, and the height is about 6.2 nm. Above the wetting layer, there is $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ capping layer with thickness of 7.9 nm. This capping layer alleviates the strain between the mismatched InAs/GaAs, and material quality can be improved. The schematic diagram of QDs structure is shown in Fig 3.10. The detailed ten-band Hamiltonian and theoretical model can be found in Chapter 2.

Fig 3.10 Schematic cross-sectional structure of active region for simulation.

Strain distribution and analysis Fig 3.11 shows the strain ($\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$) distribution in y-z plane in the middle of x axis at $T = 300\text{K}$. The red colour denotes positive value, and blue colour denotes negative value. We can observe that InAs QD region is most compressive (negative), and GaAs barrier is positive. The capping layer is between QD and barrier, and it is less compressive than QD. This side view of QD is consistent with Fig 3.10. Above the wetting layer, $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ layer reduces the strain-mismatch between InAs QD and GaAs barriers. In the VFF model and **k.p** method calculations, this capping layer was handled particularly in such a way that the atoms in the capping layer are considered as one material virtually whose properties and parameters are calculated by linear interpolation.

Fig 3.11 The strain distribution in y-z plane in the middle of x axis at $T = 300\text{K}$.

Temperature dependent transition energy

From the simulated results, Fig

3.12 shows the GS of conduction band c1 and the GS of valence band h1 from $T = 200\text{K}$ to $T = 400\text{K}$. The reference energy level is the valence band maximum of barrier for all the temperatures. When temperature increases, both c1 and h1 decrease, and c1 decreases faster, so the GS c1-h1 transition energy decreases. At $T = 300\text{K}$, the GS transition energy is about 983.82 meV which corresponds to the wavelength of 1261.4 nm .

Fig 3.12 The ground states of electron and hole for different temperatures. The reference energy level is always the valence band maximum of barrier for all the temperatures.

3.3.3 Comparison

From μ -PL spectrum of QD layers, distinct GS and excited state (ES) transition peaks can be seen in Fig 3.13. The QD GS transition peak is about 1262 nm. Because the QD is under compressive strain in which the TE mode (polarized in x or y direction) is much greater than the TM mode (polarized in z direction). In the simulation, we only show TE mode in the PL and gain calculations. We can calculate the spontaneous emission rate theoretically, and compare with the experimental PL intensity result also in Fig 3.13. It shows at 300K the transition energies of simulation result agree well with experimental results. We can suggest this nanostructure model is suitable for the simulation of optical properties of InAs/GaAs QDs in the VCSELs structure.

Fig 3.13 The comparison between experimental PL intensity and simulated spontaneous emission rate at $T = 300\text{K}$.

Accordingly, the temperature-dependent spontaneous emissions of QDs are calculated. Fig 3.14 shows simulated spontaneous emission spectra of QDs from 200K to 400K. We find that the QD GS transition energy decreases from 1004 meV to 963 meV corresponding to emission peak wavelength increase from 1235 nm to 1288 nm with temperature from 250K to 350K. The average red shift rate of the QD GS transition peak is about 0.53 nm/K from 200 Kto 400K. In VCSELs, the gain spectrum shifts distinctly more rapidly than the cavity modes. The corresponding gain peak is approximately considered to shift ~50 nm between 250K and 350K. In consideration of the full width at half maximum (FWHM) of emission spectra of 50—60 nm in Fig 3.14, the detuning between gain spectra and the cavity resonance wavelength can be accepted within a wide range even if the shift of cavity resonance range in the same direction is small (less than 0.1 nm/K) with the temperature from 250K to 350K. The selective cavity mode position from DBRs cavity structure and the adequate QD gain from epitaxy growth (because higher temperatures result in lower gains (as shown in Fig 3.14) and higher optical losses) will be important to achieve the desirable lasers which can work well over a wide range of temperatures without temperature controller. Consequently, optimized design for QD-VCSELs with a wide OTR can be made according to the red shift rate of the QD GS transition peak as well as shape and FWHM of emission spectra simulated on the present nanostructure model.

Fig 3.14 Simulated spontaneous emission spectra at different temperature ranging from 200K to 400K.

3.4 Summary

The electronic structure, Stark effect, and optical gain of InAs/GaAs pyramidal quantum dot were investigated in the framework of effective-mass envelope function theory using the strain distribution calculated by the VFF model. The effect of electric field along different directions on the electronic structure was studied thoroughly. When $F \parallel x$, the Stark effect is symmetrical as the dot is symmetrical in this direction. When $F \parallel z$, the Stark effect is asymmetrical due to the asymmetrical shape of the dot along z direction. When F is along the positive (negative) z direction,

the electron and hole levels both decrease (increase) as F increases. It is interesting to find that the band gap is increased by the electric field when F is not very large and is along the positive z direction. This is the blue Stark shift in InAs/GaAs pyramidal QD. The Stark effect of QD is affected by two factors, quantum confinement and electric potential. The optical gain of single InAs/GaAs pyramidal QD is calculated using the zero-dimensional optical gain formula. We find that the TE mode optical gain is much greater than the TM mode optical gain. The peak photon energy of the TM mode is higher than that of the TE mode. The maximum gain (differential gain) increases (decreases) as n_{eh} increases. InAs/GaAs QD lasers are suitable for optical application with photon wavelengths at around $1\mu\text{m}$.

For InAs/GaAs QDs in a VCSEL structure, the simulation result is in good agreement with the experimental $\mu\text{-PL}$ result at room temperature. The spontaneous emission spectra of QDs from 200K to 400K are subsequently simulated by our nanostructure model. A decrease of 41 meV of QD ground state transition energy from 250 K to 350 K and FWHM of emission spectra of 50—60 nm can be predicted. From the simulation results, optimized design rules can be achieved for QD-VCSELs with a wide OTR. Furthermore, QD material gain and differential gain dependence on carrier density at 300 K are calculated and presented, which has potential significance for the predicting modulation characteristics QD-VCSELs or ultrashort pulse generation of QD-VECSELs.

Chapter 4: Pyramidal InAs_{1-x}N_x/GaAs QDs

4.1 Introduction

For dilute nitride III-V QDs, the N was added during the QDs growth in the Stranski-Krastanov mode [98,99]. During the process of growth, active N species were created in radio-frequency plasma source from ultrapure N₂ gas, and incorporated in InAs QDs [28]. The presence of N significantly changes the electronic structure of QD states, resulting in a very promising low threshold current density. The potential applications of such QD systems include high performance lasers and single-electron devices

In this chapter, we apply the ten-band **k.p** method which includes the coupled conduction and valence bands, and orbit-splitting and N bands to study the electronic structure and optical gain saturation of pyramidal InAsN/GaAs QDs. As strain is a significant factor, we calculate the strain using the VFF model. We take into account the inhomogeneous broadening for the optical gain spectrum. The inhomogeneous broadening of the quantized energies is due to size fluctuation of the QDs. Then we present the comparison of optical gain among N-incorporated and N-free QDs and the effect of QDs size and carrier density on the optical gain.

The size of QDs and the N compositions are varied to investigate the size effect and N composition influence on their electronic structure and optical properties. The QDs consist the ones with height x of 14, 18, 22 and 23 lattice constants (their actual lengths are 7.91 nm, 10.2 nm, 12.4 nm and 13.0 nm, respectively, and we call these

structures as h14, h18, h22 and h23 for convenience).

4.2 The strain distribution in $\text{InAs}_{1-x}\text{N}_x/\text{GaAs}$ QD

The lattice-mismatch induced strain distribution is considered and calculated by the VFF model. The VFF model is a microscopic theory which considers both bond stretching and bond bending in the calculation.

Fig 4.1 The top view and side view of N distribution in QD and wetting layer. The blue dots represent N atoms.

When N atoms substitute the As atoms, the lattice constant of InN is smaller than that of GaAs, the compressive strain in QDs decreases. In order to consider this

variation, in our simulation, we distribute N atoms uniformly in QD (including wetting layer) that every layer of QD has equal density of N atoms shown in Fig 4.1. Fig 4.1(a) shows in the x - y plane, N atoms are distributed uniformly, and Fig 4.1(b) shows the side-view of atoms distribution in QD and wetting layer. At the location of In with neighbouring N atom, the compressive strain is less than that of In with all As neighbouring atoms. The strain distributions for h18 sized QD with 1% N atoms are shown on Fig 4.2 and Fig 4.3. Fig 4.2 shows the strain distribution profiles in 2D graphs. The strain is the sum of $\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$. As x and y directions are symmetrical, we show the strain in x and z directions in Fig 4.2(a) and Fig 4.2(b), respectively. Fig 4.2 (a) shows that the centre part is QD region, and the strain is compressive (negative strain value), and the strain in the side region is very small. This is consistent with the structures shown in Fig. 3.2. Inside the InAsN QD region, at the location of In with neighbouring N atom, the compressive strain has smaller amplitude than that of In without neighbouring N atom. So the strain is less compressive showing uprising small peaks. Fig 4.2(b) shows the strains along z direction that the strain values are all taken from the atoms in the centre of the base. The middle part represents InAsN QD region, and the strain is very compressive. The most compressive location is the pyramid apex which is surrounded by GaAs barrier, and compressed showing a dip. The strain in the interface is very dramatic, and it agrees with the structures shown in Figs. 3.2 and 4.1.

Fig 4.2 The 2D strain distribution in the unit cell for h18 sized QD with 1% of N in two dimensions (a) along x direction (x and y are symmetrical) (b) along z direction.

Fig 4.3 The 3D strain distribution in the unit cell for h18 sized QD with 1% of N (a) in x-y plane and (b) in x-z plane.

Fig 4.3 shows the strain distribution profiles in 3D graphs with 2 different view angles on the x-y and x-z planes, respectively. Fig 4.3(a) shows the x-y plane in the middle of the total height L_z , so the wetting layer is not included in that plane. In the

centre (QD region) N atoms are mixed inside QD, and small peaks appear at the location of N. It shows the compressive strain at N atom is smaller than its surrounding As atoms. The rest is barrier region which has very small strains almost 0. Fig 4.3(b) shows the x - z plane in the middle of total y dimension. It shows the compressive strain inside QD is greater than the compressive strains induced from N locations in QD and wetting layer. Compared to the N-free QD, this decrease of compressive strain inside QD can affect our calculation of energy band significantly.

4.3 Electronic structures of InAsN/GaAs QD

For QDs with different size and N compositions, we can solve the ten-band Hamiltonian shown in Section 2.3.2 to obtain the conduction and valence bands energy levels and their wave functions which can be used to calculate TME and optical gains in following sections. We can tabulate these results and analyse the effect of size and N composition for the electronic structures and optical properties.

4.3.1 The size effect and N influence on c1-h1 transition energy

We are more interested in the GS transition from c1-h1. From the obtained energy levels, we can plot Fig 4.4 showing the GS transition energies from c1 to h1 as a function of QDs height for different N compositions. When the size increases,

the valence-band energies decrease slightly, but the conduction band energies decrease more rapidly. The reduction of effective c1-h1 transition energy is contributed by the reduction of conduction band energy level. Another important factor is the strain which can modify the band structure via the deformation potentials [100]. The decrease of the conduction band is almost directly proportional to the N composition. It implies the more incorporated N atoms, the stronger repulsion interaction between N resonant band and conduction band in QDs. Without incorporating N atoms, h18, h22 and h23 sized QDs can achieve 1.30 μ m wavelength (corresponding to the transition energies of 954 meV), but h14 sized QDs cannot, so we can incorporate about 0.60% N atoms into them to achieve 1.30 μ m wavelength. To achieve the wavelength of 1.55 μ m (corresponding to the transition energies of 800 meV), we can incorporate 2.7% or 2.5% N atoms into h22 and h23 sized QDs, respectively.

Fig 4.4 The GS transition energies from c1 to h1 as a function of QDs height for different N compositions.

4.3.2 The size effect and N influence on c1-h1 TME

Fig 4.5(a) shows the TME of c1-h1 as a function of QD size for different N compositions. The presence of N increases the confinement of the QD electron wave functions compared to equivalent N -free structures [101]. At the same time, the strong N -conduction band (N -CB) mixing reduces the QD optical TME at the band edge, as a significant part of the electron ground state belongs to the $|s_N\rangle$ character [26]. Because our QDs are assumed to grow along the [001] direction, and we do not include piezoelectric effects in our simulation. That may be the reason for the slight

difference between our results and Ref.98. As size increases, for N-incorporated QDs, the electron wave function confinement decreases, but the N-CB mixing decreases resulting reducing the $|s_N\rangle$ character in electron ground state too. Both effects occurs at the same time, hence the optimal TME occurs at different size for different N composition depending on which effect can dominate the other. Fig 4.5(a) shows the QDs with 1% N reaches its optimal value at smaller size than 2%, and the QDs with 3% N have not reached their optimal value yet. Fig 4.5(b) shows the TME of c1-h1 decreases as N composition increases due to the increasing stronger N-CB mixing [98], and for smaller QDs, this decrease is faster. Because c1 energy level is closer to N resonant level for smaller QD, the N-CB mixing is also stronger. So when N increases, the repulsion interaction increases more significantly.

Fig 4.5 The TME of c1-h1 as (a) a function of height of QDs for different N composition, and (b) a function of N composition for different QDs size.

4.4 Optical properties of InAsN/GaAs QD

4.4.1 The factor of $(f_c + f_v - 1)/E$ for different size and N composition

Fig 4.6 shows the $(f_c + f_v - 1)/E$ is a function of carrier density for h18 sized QDs. E is the c1-h1 transition energy. For h18, E is 944.3 meV, 889.9 meV, 844.7 meV and 816.6 meV for N composition 0, 1%, 2% and 3%, respectively. As $(f_c + f_v - 1)/E$ is a factor in our gain calculation in Eq.(2.38), we write it in this form for comparison purpose. Fig 4.6 shows that for different carrier density, the QDs with higher N composition have greater value of $(f_c + f_v - 1)/E$. It suggests that f_c and f_v have greater values for higher N, because when more N is incorporated, the c1 energy level is

repulsed to be lower, then the electrons are easier to occupy GS, so the probability to find an electron in c1 increases. This applies to QDs with other size too.

Fig 4.6 For h18 sized QDs, $(f_c + f_v - 1)/E$ as a function of carrier density. E is the c1-h1 transition energy. For different N composition, E is different.

4.4.2 Optical gain spectra and maximum gain

Fig 4.7 shows the optical gain spectrum for different low N compositions. We take the QD with h18 sized QD as an example. As TM mode is much smaller than TE mode, and TM mode is not our focus, Fig 4.7 only shows TE mode and neglect TM mode. For the same N composition, when carrier density increases from $2.0 \times 10^{18} \text{ cm}^{-3}$ to $8.0 \times 10^{18} \text{ cm}^{-3}$, more and more carriers occupy the higher energy levels, and the first peak (the maximum gain for our concern) denoted as c1-h1 transition increases, and the c2-h2 and c3-h3 excited states optical gain appears. The excited states transitions are undesirable. The difference between c2-h2 and c3-h3

Fig 4.7 Optical gain vs. photon energy for h18 QD with different carrier densities D (1) $2 \times 10^{18} \text{cm}^{-3}$; (2) $4 \times 10^{18} \text{cm}^{-3}$; (3) $6 \times 10^{18} \text{cm}^{-3}$; and (4) $8 \times 10^{18} \text{cm}^{-3}$, and different N compositions (a) 0.01, (b) 0.02, (c) 0.03.

transition energies is so small that their optical gains merge to form a broader peak. When N composition increases, the gain spectrum peak shifts to lower energy (longer wavelength), mainly due to the bandgap decrease. It makes the emission of longer wavelength possible. These trends apply to QDs with other size too.

In Fig.4.8, we fix the N composition at 1% and carrier density at $6 \times 10^{18} \text{ cm}^{-3}$, then plot the graph of optical gain for different sized QDs. As the size increases from h14 to h23, the c1-h1 transition energy decreases which agrees with Fig 3.4. At this N composition and carrier density, h14 has only c1-h1 positive gain and h18 has both c1-h1, c2-h2 and c3-h3 peaks, but for h22 and h23, their c4-h4 optical gain even appears. It agrees with the fact that for larger QDs, the energy separation between c1-c2 and h1-h2 are smaller, so the excited states transition can easily happen and increase faster. At 1% N composition and the carrier density $6 \times 10^{18} \text{ cm}^{-3}$, h14 has the greatest optical gain.

Fig 4.8 TE mode optical gain for different sized QD with 1% of N versus photon energy for the same carrier density of $D=6 \times 10^{18} \text{ cm}^{-3}$

The c1-h1 maximum gain varies with carrier density for different N compositions. In Fig 4.9, for each size of QDs, we plot the graph of maximum optical gain of c1-h1 transition against carrier density for four different N compositions. Fig 4.9(a) and 4.9(b) shows that for smaller QDs, it reaches its saturation gain at very high carrier density. For h14 sized QDs in Fig 4.9(a), when carrier density increases, the optical gain is higher for N-incorporated QDs, it shows the factor of $(f_c+f_v-1)/E$ still dominate over TME which is decreasing for increasing N. But for h18 sized QDs in Fig 4.9(b), at larger carrier density, the optical gain of N-free QDs surpass that with N, it shows the effect of factor $(f_c+f_v-1)/E$ is gradually balanced and overwhelmed by the TME. In Fig 4.6, we can observe that at carrier density $2 \times 10^{18} \text{cm}^{-3}$, the $(f_c+f_v-1)/E$ for $N=3\%$ QDs is about 2.4 times of that value for N-free QDs. When carrier density increases to $8 \times 10^{18} \text{cm}^{-3}$, the $(f_c+f_v-1)/E$ for $N=3\%$ QDs is about only 1.2 times of that value for N-free QDs. It shows the percentage weight of factor $(f_c+f_v-1)/E$ decreases in the gain calculation. Fig 4.9(c) and 4.9(d) shows that for larger QDs, it can reach its saturation optical gain in a lower carrier density than smaller QDs, and for different N composition, its saturation gain are almost the same, but smaller than the saturation gain of N-free QD. It suggests that the factor of $(f_c+f_v-1)/E$ can dominate over the factor of TME at smaller carrier density for larger QDs, and the difference of saturation gain between N-incorporated QDs is small.

Fig 4.9 Maximum optical gain of c1-h1 transition versus carrier density for different N compositions and sizes (a)h14, (b)h18,(c)h22,(d)h23.

4.4.3 Differential maximum gain

In a semiconductor laser, we are also interested in the differential gain which is $dGain/dn$ with respect to carrier density. Fig 4.10 shows the differential gain for different sized QDs with different N composition. As QDs size increases from h14 to h23, the differential gain drops tremendously, so the QD size should not be too large in order to achieve high resonant frequency. Fig 4.10(a) shows for smaller QDs,

differential gain is not so different at low carrier density, but differential gains drop faster for the QDs with N, resulting the QDs without N has obvious larger differential gain at high carrier density. Fig 4.10 (b), Fig 4.10(c) and Fig 4.10(d) shows for larger QDs, differential gain is obvious greater for non-nitrogen QDs at low carrier density, but at high carrier density, the differential gains are all very low. When we judge the performance of various QD, we should consider its wavelength, initial optical gain, saturation optical gain and differential gain.

Fig 4.10 The differential maximum gain of c1-h1 transition for different N compositions and size (a) h14, (b) h18, (c) h22, and (d) h23 versus carrier density.

4.5 Summary

The electronic structures of InAsN/GaAs QDs are investigated using the ten-band **k.p** method with consideration of strains and inhomogeneous broadening effect of optical gain due to the size fluctuation of QDs. When more N is incorporated in the QDs, the repulsion between the resonant energy level of N atom and c1 increases and c1 is forced to be lower making the reduction of c1-h1 transition energy. So the long-wavelength emission becomes possible, even 1.55 μm . At the same time, the intersubband energy is greater, so higher excited states combination transition is harder to occur. To achieve desired lasers, the tradeoff between wavelengths, transparency carrier density and saturation optical gain must be considered. For the same QD size, when N composition is higher, it can have longer wavelength, higher maximum optical gain and less detrimental effect induced by higher excited states transition. However our simulation is in ideal condition, in real experiment, the higher N composition may cause more N-related defects. The extra N atoms may become non-radiative recombination centres. So depending on the specific application requirements, we should select the N composition and QDs size accordingly.

Chapter 5: Truncated Pyramidal $\text{InAs}_{1-x}\text{N}_x/\text{GaAs}$ QDs

5.1 Introduction and structure

Fig 5.1 Schematic diagram showing square-based truncated pyramidal QD.

We have applied the ten-band **k.p** method in Chapter 4 to calculate the electronic structure and optical gain of the full pyramidal InAsN/GaAs QDs which has greater potential to fabricate advanced GaAs-based optical fiber communication lasers. However experimentally there is evidence that in many cases the QDs more closely approximate to truncated pyramid [44, 45], and the calculated energies provide the best fit to photoluminescence experiments for truncated pyramids [46].

So in this chapter, we apply the ten-band **k.p** method to investigate the QDs in

which the top of the pyramid-shape is truncated (shown in Fig 5.1), and the height of the truncated pyramidal QDs varies. As strain is still a significant factor, we calculate the strain with the VFF model. The effective height of QDs and the N compositions are varied to investigate the truncation effect and N influence on their electronic structure and optical properties. The base length b of QDs is 24 or 36 lattice constants (their actual base lengths are 136 Å and 204 Å, respectively), and the effective height h is a variable. (For convenience we call these structures $b24$ based or $b36$ based QDs).

5.2 The strain distribution in truncated pyramidal InAs_{1-x}N_x/GaAs QDs

When the top part of pyramid is truncated, the strain distribution on the structure changes dramatically, so the electronic structure is affected significantly. First of all, we should re-analyse the strain distribution. Fig 5.2(a) shows the hydrostatic strain (absolute value) increases when the effective height increases. The flatter QD has more uniform strain distribution. Fig 5.2(b) shows similar trend as Fig 5.2(a), and the compressive strain is smaller than Fig 5.2(a) due to the incorporated N atoms which are smaller than As atoms. In Fig 5.2(b) for some truncations ($b18h9$ and $b18h12$), the dip represents the location of pyramidal apex, and it shows the interface

between InAs QD and GaAs barrier material. The strains at the interface can be very large due to the compressive force from surrounding barrier to the apex.

Fig 5.2 The hydrostatic strain in the centre of x - y plane along the z direction for $b36$ based QD with different heights in which (a) no N and (b) 2% of N is incorporated.

To analyze the effect of strain on hole levels, we have to look at the strain on

different component individually. For *b36* based QD without N, when the height h increases, Fig 5.3(a) shows the compressive strain in x component decreases, and Fig 5.3(b) shows the tensile strain in z component decreases (The strain components affect the hole levels as shown in Eq.(2.10) in Section 2.1.3). So when the heights keep increasing, the strains make the hole levels increase. The same trends are shown in Fig 5.3(c) and 5.3(d) for *b36* based QD with 2% of N.,

Fig 5.3 The strain distribution in the centre of x - y plane along the z direction for *b36* based QD with different heights in which (a) strain component x without N, (b) strain component z without N, (c) strain component x for 2% of N incorporated and (d) strain component z for 2% of N incorporated.

5.3 Electronic structures of truncated pyramidal InAsN/GaAs QDs

Fig 5.4 For *b36* based QDs, the energy levels of c1, c2, h1 and h2 versus QDs height for (a) no N and (b) 2% of N incorporated.

By solving the ten-band Hamiltonian shown in Section 2.3.2, we can obtain the conduction and valence bands energy levels and their wave functions for truncated pyramidal QDs with different effective height and N composition. Fig 5.4 shows the electron and hole energy levels of *b*36 based QDs of different height for N free and 2% of N. As the heights increase, the electron energy decreases and the hole energy increases, because the strain distribution is changed when top part is truncated, and the confinement is reduced in *z* direction. Fig 5.5 shows the transition energy from c1 to h1 as a function of QDs height for N-free and 2% of N QDs. As height increases, this transition energy decreases, and it shows the truncation can affect the N-incorporated QDs more significantly. If one third of the top part of the pyramid QD is truncated, the increase of the transition energy is not much, but this truncation can increase the quantum confinement which can bring more advantages than full pyramidal QDs.

Fig 5.5 The GS transition energies from c1 to h1 as a function of QDs effective height for N-free and 2% of N incorporated.

TME is calculated by Eq.(2.32) in Section 2.3.3. Fig 5.6 shows the TME of c1-h1 as a function of height for *b36* QDs without N and with 2% of N incorporated. When the effective height decreases, the strong confinement in *z* direction makes the overlapping of electron and hole more effectively resulting in increase in the TME for both with or without N. The change is the fastest when half of the top part is truncated. And when the quarter of the top part is truncated, the TME has no significant change. It shows the apex of pyramid has less effect on the confinement, and the electron-hole interaction occurs unlikely near the apex of QD.

Fig 5.6 The TME of c1-h1 as a function of height for *b36* based QDs without N and with 2% of N incorporated.

5.4 Optical properties of truncated InAsN/GaAs QDs

Figure 5.7 shows for b36 based QDs, $(f_c + f_v - 1)/E$ is a function of carrier density for different truncated heights for QD (a) without N and (b) 2% of N incorporated. E is the c1-h1 transition energy. It shows if the top part truncated is not very big, the factor $(f_c + f_v - 1)/E$ is close even they have different value of E . The significant difference only occurs when more than half of the top part is truncated. These trends are true for both with and without N.

Figure 5.8 shows the optical gain of b36 based QDs with 2% of N for different carrier densities and for different heights. As the heights increase, the first peak denoting the c1-h1 transition shifts to lower energy (implying longer wavelength). It agrees with the transition energy shown in Fig 5.5. The second peak denotes higher excited states transition which is undesirable. For flatter QDs (smaller height, more truncation), the c2-h2 and c3-h3 peak exceeds the c1-h1 peak at larger carrier density. It shows the problem of higher excited states transition is alleviated for flatter QDs, because due to the increased confinement, the energy differences between c2-c1 and h1-h2 are larger for flatter QDs. The increased carriers are more difficult to be promoted to higher energy states.

Fig 5.7 For *b36* based QDs, $(f_c + f_v - 1)/E$ is a function of carrier density for different heights for QDs (a) without N and (b) 2% of N incorporated. E is the c1-h1 transition energy. For different heights and N composition, E is different.

Fig 5.8 Optical gain versus photon energy for *b*36 based QDs with 2% of N and with different carrier densities D (1) $2 \times 10^{18} \text{ cm}^{-3}$, (2) $4 \times 10^{18} \text{ cm}^{-3}$, (3) $6 \times 10^{18} \text{ cm}^{-3}$, and (4) $8 \times 10^{18} \text{ cm}^{-3}$, and different heights (a) $h_{4.5}$, (b) h_9 , (c) $h_{13.5}$ and (d) h_{18} .

Fig 5.9 Maximum optical gain of c1-h1 transition versus carrier density for different heights (a)without N for h4.5, h6 and h9, (b)without N for h12, h13.5 and h18,(c)2% of N incorporated for h4.5, h6 and h9, (d)2% of N incorporated for h12, h13.5 and h18.

Fig 5.9 shows the maximum optical gain of c1-h1 transition as a function of carrier density for different heights for both with and without N. At low carrier density, the flatter QDs have lower optical gain due to its low value of $(f_c+f_v-1)/E$ despite they have much larger value of TME. When carrier density increases, the factor $(f_c+f_v-1)/E$ of flatter QDs increases faster and the factor of TME become more important to affect the optical gain. So the optical gain of flatter QDs can finally reach a greater saturation gain. These trends are true for both with and without N. We are also interested in the differential gain, because the resonant frequency in a semiconductor laser is proportional to the square root of the differential gain with respect to the carrier density.

Fig 5.10 shows the differential maximum gain of c1-h1 transition as a function of carrier density for different heights and for both with and without N. The differential gain is decreasing for increased carrier density, and the flatter QDs (smaller height and more truncation) have relatively higher differential gain. When we judge the performance of QD with various truncations, we should consider its wavelength, initial optical gain, saturation optical gain and differential gain.

Fig 5.10 The differential maximum gain of c1-h1 transition versus carrier density for different heights (a) without N for h4.5, h6 and h9 (b) without N for h12, h13.5 and h18, (c) 2% of N incorporated for h4.5, h6 and h9 (d) 2% of N incorporated for h12, h13.5 and h18.

5.5 Summary

The electronic structures of truncated pyramidal InAs(N)/GaAs QDs are investigated using a ten-band **k.p** method with consideration of the strains calculated by VFF model and inhomogeneous broadening effect of optical gain. When more top part of the squared-based pyramid QD is truncated, the height is smaller, and truncated QD is flatter. This truncation changes the strain distribution and the confinement in the z direction inside the system. The flatter QD have larger c1-h1 transition energy, greater TME, less detrimental effect of higher excited transition, higher saturation gain and differential gain. To achieve desired lasers, the tradeoff between those properties must be considered. From our simulation figures, we suggest the square-based QDs with its half of top part truncated have better overall performance. Because for that truncated QDs, its c1-h1 transition energy is only about 27.9 (or 23.4) meV higher than the complete pyramidal InAsN (or InAs) QDs, and this energy increase is only about 3.3 % (or 2.5%) of its original transition energy, but its TME is increased by 30% resulting in obviously significant increase in GS saturation optical gain and differential gain. So our suggested truncated shaped QD can provide guidance for the QDs grown in the experiment in which proper growing conditions can be controlled to achieve desirable-shaped QD.

Chapter 6: Pyramidal InAsPN/GaP(N) QDs

6.1 Introduction

The investigation of novel mid-infrared (MIR) and far-infrared (FIR) semiconductor materials for devices such as laser diodes and detectors had received increasing interest for many applications, such as infrared countermeasures, optical communications, low-cost medical diagnostics and chemical gas analysis [102]. The dilute nitride III-V materials are promising to enable MIR and FIR devices, because theoretically, incorporation of nitrogen reduces the energy gap and increases the electron effective mass in the conduction band [43]. GaAsPN/GaP lattice-matched structures have been successfully realized by metalorganic vapor phase epitaxy [48]. The lattice of the barrier GaP is very close to the lattice of Si. GaAsPN/GaPN quantum well structures lattice-matched to Si substrate have been done to combine optics and electronics in a single chip [49]. However, our simulation results showed that due to the large bandgap of GaAsPN, it is extremely difficult to achieve the emission wavelength at 1.3 μm . The bandgap of InAsPN is much smaller than that of GaAsPN, so we discuss in details InAsPN/GaP(N) lattice-mismatched QDs.

The InAsPN parameters are interpolated from InAs, InP and InN parameters. The barrier materials are GaP or $\text{GaP}_{0.98}\text{N}_{0.02}$, and the other alloy parameters are calculated by linear interpolation. The compositions of P and N are varied to investigate their influence on the electronic structure and optical properties. The

shape and the structure of QDs are the same as in Chapter 3. There are 4 different sizes of QDs which have the heights of 10, 14, 18 and 23 lattice constants (their actual lengths are about 5.45 nm, 7.63 nm, 9.81 nm and 12.54 nm), respectively. We call these structures h10, h14, h18 and h23 for convenience.

6.2 Electronic structures of InAsPN/GaP(N) QD

Pyramdial InAsPN/GaP(N) QD is under compressive strain, so its strain distribution is similar to those in Chapter 4 and 5. After substituting the strains and parameters in the Hamiltonians, and solving the Hamiltonians, we can tabulate the calculated energy levels in Fig 6.1 which shows the GS transition energies c1-h1 as a function of P composition in QDs for h10, h18 and h23 sized QDs.

6.2.1 The effects of N and P compositions on GS transition energy

The N compositions in the QDs are 3% or 5%. When the P composition increases, the bandgap of QD alloy increases because the bandgap of InP is much greater than that of InAs, and the repulsion between the conduction band and the N resonant energy band is stronger, and the strain in the QDs is less compressive. The overall strained band alignment is that for greater P composition, the conduction band offset is less. Fig 6.1 shows that for h10, the minimum value of c1-h1 transition

energy is not at $P=0$, because for smaller sized QD the c1 energy level is very high due to the quantum confinement effect. However, for larger sized QD (h18 or h23), due to less quantum confinement effect, the c1 energy level is closer to the band edge, so the c1-h1 transition energy of larger QDs increases as P composition increases. Fig 6.1 also shows for greater N composition, the transition energy is less for the same P composition due to the greater repulsion between conduction band and N resonant band resulting in a lower c1 energy level.

Fig 6.1 The c1-h1 transition energy of h10, h18 and h23 sized InAsPN QDs with GaP barrier versus P composition in QDs. The N compositions in QD are 3% and 5%.

6.2.2 The effects of N and P compositions on GS TME

Fig 6.2 The TME of c1-h1 as a function of P composition in QDs for h10, h18 and h23 sized InAsPN QDs with GaP barrier. The N compositions in QD are 3% and 5%.

Fig 6.2 shows the TME of c1-h1 as a function of P composition in QDs for h10, h18 and h23 InAsPN QDs with GaP barrier. The N compositions in QDs are 3% and 5%. Fig 6.2 agrees with Fig 6.1 that the case with smaller transition energy has greater TME, because the electron and hole wave functions are better confined in the QD region. The overlapping of electron and hole functions is more effective, resulting in greater TME. Fig 6.2 also shows that for the case with 3% N, the TME is lower than those with 5% N. For higher N composition, though the N-CB mixing is stronger causing a significant part of the electron ground state belong to the $|s_N\rangle$

character [43], the conduction band is lower and electrons are better confined in the QD region, and the electron-hole overlapping is more effective, so the confinement factor dominates the N-CB mixing factor.

6.2.3 The effects of incorporating N into GaP barrier

The lattice constant of GaP is 0.54505 nm, very close to that of Si which is 0.5431 nm. To grow materials with lattice constant comparable to that of Si substrate is an interesting topic for research, and some experiments have tried to incorporate nitrogen atoms into GaP barrier [49]. We have incorporated 2% N into GaP to shorten the lattice constant to 0.5431 nm, and investigate the effect of incorporating N into barrier. Fig 6.3 shows the c1-h1 transition energy of InAsPN with 5% P and 5% N as a function of the height of QD for both GaP and $\text{GaP}_{0.98}\text{N}_{0.02}$ barriers. When the size increases, the transition energies decrease due to less quantum confinement effect, and the QDs with N in barrier have smaller transition energy than QDs without N in the barriers. A possible reason is that the N resonant band is lower than the conduction band of barrier, and it reduces the conduction band offset, resulting in less quantum confinement. We aim to achieve 1.3 μm wavelength (corresponding to 954 meV transition energy), and it can almost be achieved by incorporating 2% nitrogen into the GaP barrier for h26 sized InAsPN QD with P=5% and N=5%.

Fig 6.3 The c1-h1 transition energy of InAsPN QDs with 5% P and 5% N versus QDs height for both GaP and GaP_{0.98}N_{0.02} barriers.

Fig 6.4 The TME of c1-h1 of InAsPN QDs with 5% P and 5% N versus the height of QD for both GaP and GaP_{0.98}N_{0.02} barriers.

Fig. 6.4 shows the TME of c1-h1 of InAsPN with 5% P and 5% N as a function of QDs height for both GaP and GaP_{0.98}N_{0.02} barriers. Due to the reduced conduction band offset after incorporating N into the barriers, the electrons are less confined in the QD region, causing less overlapping of electron-hole wave functions. Therefore the TME of QDs with N in barrier is less than those without N in the barrier. When the size increases, for both cases the TME increases due to the smaller transition energy, in agreement with Fig 6.3.

6.3 Optical gain of InAsPN/GaP(N) QDs

Fig 6.5 Maximum optical gain of c1-h1 transition of h26 sized InAsPN QDs with 5% P and 5% N versus the carrier densities for both GaP and GaP_{0.98}N_{0.02} barriers.

With calculated energy levels and TME for various cases, we can investigate the optical properties of InAsPN QDs with 1.3 μm wavelength which can be used to fabricate high quality laser and other optoelectronic devices. Fig 6.5 shows that the maximum GS gain of h26 sized InAsPN QDs with 5% P and 5% N is a function of carrier density for both GaP and $\text{GaP}_{0.98}\text{N}_{0.02}$ barriers. When carrier density is low, the optical gain for the barrier with N is greater because its TME is greater shown in Fig 6.4, so the TME is the dominant factor at this moment. After the carrier density increases until the maximum gain reaches saturation, the optical gain of the case with $\text{GaP}_{0.98}\text{N}_{0.02}$ barrier exceeds the case with GaP barrier, and its saturation gain is greater. Possible reason is that for the case with $\text{GaP}_{0.98}\text{N}_{0.02}$ barrier, the transition energy E is smaller shown in Fig 6.4, and the barrier lattice is shorter resulting in a smaller volume V of QD. The parameters E and V are the factors being divided in the optical gain calculation formula. So the significance of the factors of E and V increases when they reach saturation, and balance off the TME factor. The magnitude of the saturation gain is not so great.

6.4 Summary

The electronic structures of InAsPN/GaP(N) QDs are investigated using a ten-band **k.p** method with consideration of the strains calculated by the VFF model and the inhomogeneous broadening effect. When the barrier is GaP, for smaller sized InAsPN QDs, the minimum transition energy may occur at lower P composition due

to the huge conduction band offset and quantum effect. But for larger sized QDs, the transition energy increases as P composition increases because the bandgap of alloy QDs increases significantly, and c_1 is close to band-edge at this time. When the N composition increases, the transition energy decreases due to the stronger repulsion between conduction band and N resonant band, and the TME is more affected by the transition energy rather than N-CB mixing. When the transition energy is small, the electrons are better confined in QD region, and the electron-hole wave functions are overlapped more effectively. To obtain Si-comparable laser materials, we doped 2% N into GaP barrier. We find that in $\text{GaP}_{0.98}\text{N}_{0.02}$ barrier, the conduction band offset is reduced, due to the quantum effect; the conduction band is lower, resulting in a smaller transition energy and longer wavelength. We can achieve 1.3 μm , and at the same time, the TME is reduced due to the reduced conduction band offset. For the case with $\text{GaP}_{0.98}\text{N}_{0.02}$ barrier, the peak gain is less than those with GaP barrier at low carrier density, but it increases faster when carrier density increases, and finally it can surpass and reach a greater saturation optical gain. This shows doping N into GaP barrier is an effective way to achieve desirable wavelength and optical gain.

Chapter 7: Shape effects InAsN/GaAs nanostructures: from a quantum lens to a quantum ring

7.1 Introduction and structures

Recently the growing of self-assembled ring-like dots has been invented by using different technologies controlling the variety of shapes and sizes [103,104]. The QDs have discrete energy levels due to 3D confinement effects, and have attracted great attention due to their interesting magnetic properties such as the Aharonov-Bohm effect [105, 106]. In various semiconductor systems, InAs/GaAs QDs are fabricated successfully [107], and have potential applications in electronics, optics and quantum cryptography [108, 109]. The electronic structures and optical transitions of self-assembled InAs/GaAs QDs have been investigated by using an atomistic pseudopotential method [110], and the strain profiles and single-particle energy levels have been studied with respect to the inner radius of QDs [111].

InAsN/GaAs QDs can provide longer wavelength emission and other better characteristics than InAs/GaAs QDs. Therefore, they have greater potential to fabricate advanced GaAs-based optical fiber communication lasers which are capable of large gain and large output power. In Chapter 4, we have discussed pyramidal InAsN QDs. In this chapter, we apply the ten-band **k.p** method to study

shape effect by varying the shape from lens shape to volcano, then to ring shape with emphasis on its physical and optical properties.

A single nanostructure is an InAsN island grown over a thin InAsN wetting layer and capped with a GaAs layer. The z axis is chosen along the growth direction and the x - y plane is at the interface between the wetting and the cap layers. The island is a piece of a solid torus, whose revolution axis is the z axis, cut by a plane perpendicular to the axis. To understand the cross section of the solid, let us consider a disk of radius r and center $(R_0, h-r)$ on the y - z plane, where $R_0 \geq 0$ and $0 < h \leq r$. The solid is generated by the part of the disk that is above the y axis. In this way, the base of the island is on the x - y plane and the height of the island is h . Moreover, the disk meets the y axis for $R_{in} \leq y \leq R_{out}$, with $R_{in} = R_0 - \sqrt{2 \times r \cdot h - h^2}$ and $R_{out} = R_0 + \sqrt{2 \times r \cdot h - h^2}$. These are called as the inner and outer radii of the nanostructure (see Fig 7.1). In the present work, we fix the values of h and R_{out} , and calculate the electronic structures as a function of R_{in} . It is worth noticing that $R_0 = (R_{in} + R_{out})/2$ and $r = h/2 + (R_{out} - R_{in})^2/(8h)$. Hence, according to the conditions $R_0 \geq 0$ and $h \leq r$, we must consider $-R_{out} \leq R_{in} \leq R_{out} - 2h$ and $h \leq R_{out}$. Hence, as R_{in} increases, the nanostructure evolves from a lens-shaped dot, at $R_{in} = -R_{out}$, to a half-torus shaped quantum ring, at $R_{in} = R_{out} - 2h$. For intermediate negative values of R_{in} , the nanostructure resembles a volcano. In the numerical calculations, we fix $R_{out} = 10.2$ nm and take the height as either $h = 3.4$ nm or $h = 1.7$ nm. Therefore, R_{in} varies from -10.2 nm to 3.4 nm for $h = 3.4$ nm or 6.8 nm for $h = 1.7$ nm, respectively.

Fig 7.1 Schematic diagram of cross-sections of the QDs for (a) $R_{in} < 0$ and (b) $R_{in} > 0$. R_{in} and R_{out} are the inner radius and outer radius of the nanostructures, respectively. The height h is fixed at 3.4 nm or 1.7 nm.

The ratio of the structure is fixed and shown in Fig 7.2. The width of the unit cell L_x and L_y are 40.8 nm, and the height L_z is 30.6 nm. The volume excluding the wetting layer is calculated by the formula

$$V = \left[\left(\sin^{-1} \frac{R_{cl}}{R_{sp}} \right) \times R_{sp}^2 - R_{cl} \times (h_1 + Z_1) \right] \times 2\pi R_{cl} + \pi h_1 (R_{sp}^2 + R_{cl}^2 - \frac{h_1^2}{3} - h_1 Z_1 - Z_1^2) +$$

$$\pi R_{cl} R_{sp}^2 \left[\frac{\sin(2 \sin^{-1}(\frac{h_1 + Z_1}{R_{sp}}))}{2} + \sin^{-1}(\frac{h_1 + Z_1}{R_{sp}}) - \frac{\sin(2 \sin^{-1}(\frac{Z_1}{R_{sp}}))}{2} - \sin^{-1}(\frac{Z_1}{R_{sp}}) \right] \quad , (7.1)$$

where $(R_{cl}, -Z_1)$ is the coordinates of the centre of the circle in the x - z plane, $R_{cl} = (R_{in} + R_{out})/2$, $Z_1 = -[4h^2 - (R_{out} - R_{in})^2]/(8h)$, and R_{sp} is the radius of the circle, $R_{sp} = [4h^2 + (R_{out} - R_{in})^2]/(8h)$, and h_1 is the height when $x=0$, $h_1 = \sqrt{R_{sp}^2 - R_{cl}^2} - Z_1$. For lens-shape, $h_1=h$, and for quantum ring shape, $h_1=0$.

Fig 7.2 The ratio of the structure is fixed, and the height L_z and width L_x (L_y) of the unit cell are 3 and 4 times of R_{out} , respectively.

The detailed ten-band Hamiltonian and optical gain formulae are in Chapter 2.

The optical matrix parameter E_p is 18.00 eV [112]. The plane wave numbers used are from -5 to 5.

7.2 Electronic structures of InAsN nanostructures.

7.2.1 N distribution and strain profile

Fig 7.3 The 2D and 3D views of lens-shaped QD, quantum volcano and quantum ring for which (a) $R_{in} = -10.2$ nm, (b) $R_{in} = -1.7$ nm, and (c) $R_{in} = 2.3$ nm, respectively. The height h is fixed at 3.4 nm. The red-coloured atoms in 2D (3D) view are N atoms and the N composition is about 2%.

When the N atoms substitute the As atoms, the compressive strains in the structure decrease. We distribute N atoms uniformly (including the wetting layer) such that every layer of atoms has equal density of N. Fig 7.3 shows the 2D and 3D structures of lens-shaped QD, quantum volcano and quantum ring, respectively.

Fig 7.4 The hydrostatic strain distribution in the QDs with 2% of N for R_{in} (a)-10.2 nm, (b)-1.7 nm, and (c)2.3 nm for different views (i) y-z plane with x coordinate being 0, and (ii) x-y plane with z coordinate being -3.4 nm.

Their height h is fixed at 3.4 nm. The red coloured atoms in 2D (3D) view are N atoms and the N content is about 2%.

Fig 7.4 shows the strain distribution for different values of inner radius in the y - z and x - y plane, respectively. In the InAsN region, the hydrostatic strain ($\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$) is negative, and at the location of N, this compressive strain is less than that in As atom. So we see many tiny light blue peaks (less strain) among the dark blue region (InAsN region). Compared to the N-free case, this decrease of strain inside InAsN may affect the calculated electronic structure significantly.

7.2.2 Charge density for different conduction and valence band states

When we solve the ten-band Hamiltonian in Section 2.3, the wave functions of conduction and valence band states are available. The charge density equals the wave-function square, including the spin-up and spin-down components. We can choose sufficient points with coordinates and charge density, then use MATLAB to plot Fig 7.5 which shows the top view of the charge density of (a) conduction-band and (b) valence-band states in the nanostructures with 2% of N, height $h = 3.4$ nm, outer radius $R_{out} = 10.2$ nm, and inner radius $R_{in} = -10.2, -1.7$ and 2.3 nm, respectively. The iso-surfaces equal 0.7 of the maximum charge density for both conduction-band and valence-band states. (The cases with the mark * show the iso-surfaces of 0.92). The states E1 to E5 denote the first five electron states, and H1 to H5 denotes the first five hole states. The s state orbital has one peak at the centre,

	$R_{in} = -10.2$ nm Lens-shaped QD	$R_{in} = -1.7$ nm Quantum volcano	$R_{in}=2.3$ nm Quantum ring
	(a) Electron		
E1
E2
E3
E4
E5

	(b) Hole		
H1
H2
H3
H4
H5

Fig 7.5 The top view of the charge density of the (a) conduction-band and (b) valence-band states in the nanostructures. The charge density equals the wave-function square, including the spin-up and spin-down components. We show the charge density in nanostructures with 2% of N, height $h = 3.4$ nm, $R_{out} = 10.2$ nm, and $R_{in} = -10.2, -1.7$ and 2.3 nm. The iso-surfaces equal 0.7 of the maximum charge density for conduction-band and valence-band states, respectively. (The cases with the mark * show the iso-surfaces of 0.92).

and the p state orbitals have 2 peaks along $[1\ 1\ 0]$ or $[1\ -1\ 0]$ directions, and d state orbitals have 4 peaks. The s state is very sensitive to R_{in} , because it feels strong confinement potential from the inner circle of the ring with the increasing of R_{in} [111]. And the s state changes dramatically from disk-like at $R_{in}<0$ (the maximum at the centre) to ring-like (hollow at the centre) at $R_{in}>0$. This phenomenon was shown in Ref. 111, but only for electron. In present simulation results, both electron and hole states have shown this phenomenon which is more reasonable.

7.2.3 Band structures and comparison

Fig 7.6 The energy levels of confined (a) conduction-band and (b) valence-band states for the height of 1.7 nm with 2% of N. (The $p1$ and $p2$ electron levels essentially coincide).

From the identification of conduction-band and valence-band states in Fig 7.5, we can plot the energy levels for different R_{in} for different structures in Figs 7.6-7.8. Firstly, we compare two InAsN cases with heights $h = 1.7$ nm and 3.4 nm in Figs. 7.6 and 7.7, respectively. When the height decreases, the nanostructure is flatter with better confinement in z -direction. Due to the quantum confinement effect, the electron energy levels increase and the hole energy levels decrease resulting in greater transition energy.

Fig 7.7 The energy levels of confined (a) conduction-band and (b) valence-band states for the height of 3.4 nm with 2% of N incorporated.

Secondly, we investigate the electronic structures of InAs and InAsN nanostructures with $h = 3.4$ nm and 2% of N. Figs 7.7 and 7.8 show that when the value of R_{in} increases, the electron energy levels decrease and then increase, but the hole energy levels increase and then decrease, because the confinement of volcano shape is not as strong as lens-shape and quantum ring shape. The minimum of $1s$ state for electron and the maximum of $1s$ state for hole both occur at smaller values of R_{in} than those for the p and d states, because the s state is more sensitive to the change of R_{in} . This trend was shown in Ref. 111 for InAs nanostructures.

Fig 7.8 The energy levels of confined (a) conduction-band and (b) valence-band states for the height of 3.4 nm without N.

We observe that in Fig 7.7 for quantum ring shape, the p state of valence band can be higher than the $1s$ state, because the $1s$ state starts decreasing at smaller value of R_{in} , at that value of R_{in} , the p state still increases. Unlike the conduction band in which the s - p energy difference is large, for the valence band, the s - p energy difference is relatively small, so the p state may be higher than the $1s$ state when R_{in} keeps increasing and the structure becomes a quantum ring.

7.2.4 The s - s transition energy and TME

Fig 7.9 (a) The s - s transition energy versus inner radius for different height and N compositions and (b) the s - s TME.

We are more interested in the interband transition between the s states which is the main transition for lasing. Fig 7.9 shows when the value of R_{in} increases, the s - s transition energy decrease first, then increase, reaching the minimum (maximum) value at about $R_{in} = -1.7$ nm, but the s - s TME increase first, then decrease, reaching the maximum value at about $R_{in} = -1.7$ nm too. For the structures with $h = 3.4$ nm, the transition energies with N are smaller due to the repulsion interaction between electron $1s$ state and N resonant state, and it also has smaller s - s TME. Although the presence of N increases the confinement of the electron wave functions compared to equivalent N-free structures, at the same time, the strong N-CB mixing reduces the optical TME at the band edge, as a significant part of the electron ground state belongs to the $|s_N\rangle$ character [43]. For the two structures with 2% of N and different heights, Fig 7.9 shows the structures with smaller height have greater s - s transition energy due to the greater quantum confinement effect in z direction, but its s - s TME is the smallest. The possible reason is that for $h=1.7$ nm, the transition energy is too great that the wave function is much closer to the band-edge of barrier material so that the wave functions cannot be well-confined in the QD region so the wavefunction overlapping of electron and hole is not as effective as the case with $h=3.4$ nm.

7.3 Optical gain

When the value of R_{in} increases from -10.2 nm to positive, the shapes of nanostructures change from lens-shape to a full ring structure which has two semicircles in cross-sections. Because volume is important in the calculation of optical gain, Fig 7.10 shows when the value of R_{in} increases, the volume of the structure excluding the wetting layer increases, and then decreases for both heights. The maximum volume is at about $R_{in} = 1$ nm (0 nm) for $h = 3.4$ nm ($h = 1.7$ nm).

Fig 7.10 The volume of quantum rings with heights 3.4 nm and 1.7 nm versus inner radius.

The QD is under compressive strain. Due to deformation potential, the compressive strain raises the energy level of heavy hole above light hole. So the numerical values of TE mode are much greater than TM mode, and we focus on TE mode to investigate the optical properties for laser fabrication. In Fig 7.11, we only show TE mode optical gain spectrum and neglect TM mode at $R_{in} = -10.2$ nm, -1.7 nm and 2.3 nm respectively. Due to the volume difference shown in Fig 7.10, the structure with smaller height needs higher carrier density to emit photons. For the height of 3.4 nm, we consider for values of the carrier densities are (1) $4 \times 10^{18} \text{ cm}^{-3}$, (2) $6 \times 10^{18} \text{ cm}^{-3}$, (3) $8 \times 10^{18} \text{ cm}^{-3}$, (4) $10 \times 10^{18} \text{ cm}^{-3}$. Correspondingly, for the height of 1.7 nm, the values of the carrier densities are (1) $10 \times 10^{18} \text{ cm}^{-3}$, (2) $12 \times 10^{18} \text{ cm}^{-3}$, (3) $14 \times 10^{18} \text{ cm}^{-3}$, (4) $16 \times 10^{18} \text{ cm}^{-3}$. Fig 7.11 shows the optical gain increases as carrier density increases for all cases, and when R_{in} is near $-R_{out}$ (lens-shape QD case), the higher excited states transition is not significant. When the value of R_{in} increases to less negative (quantum volcano case), the problem of higher states transition becomes obvious in the sense that the second gain peak may exceed the first peak. If R_{in} increases further to positive (quantum ring), the first two peaks merge together to form a broader peak (so we did not indicate the peaks separately), because the s - p spacing for both conduction and valence bands becomes smaller.

Fig 7.11 The optical gain spectrum for nanostructures at R_{in} (a)-10.2 nm, (b)-1.7 nm and (c)2.3 nm, respectively. For height of 3.4 nm, the carrier densities D are (1) $4 \times 10^{18} \text{ cm}^{-3}$, (2) $6 \times 10^{18} \text{ cm}^{-3}$, (3) $8 \times 10^{18} \text{ cm}^{-3}$, (4) $10 \times 10^{18} \text{ cm}^{-3}$. For height of 1.7 nm, the carrier densities D are (1) $10 \times 10^{18} \text{ cm}^{-3}$, (2) $12 \times 10^{18} \text{ cm}^{-3}$, (3) $14 \times 10^{18} \text{ cm}^{-3}$, (4) $16 \times 10^{18} \text{ cm}^{-3}$.

Fig 7.12 The factor of $f_c + f_v - 1$ vs. inner radius for (a) 0% of N, $h = 3.4$ nm, (b) 2% of N, $h = 3.4$ nm and (c) 2% of N, $h = 1.7$ nm. The carrier densities are the same as those in Fig 7.11.

Fig 7.12 shows the factor of f_c+f_v-1 vs. inner radius for (a) 0% of N, $h = 3.4$ nm, (b) 2% of N, $h = 3.4$ nm and (c) 2% of N, $h = 1.7$ nm. The carrier densities are the same as those in Fig 7.11. The factor (f_c+f_v-1) is involved in the calculation of the optical gain and gives the probability of net transition for the emission of a photon. When R_{in} increases, for all structures, the factor (f_c+f_v-1) increases, and then decreases after $R_{in} > -1.7$ nm. We suggest that there are two possible factors affecting the value of f_c+f_v-1 . One factor is the energy level of the $1s$ state. The injected electrons are more likely to occupy the $1s$ state at lower energy level. In Figs 7.6-7.8, the lowest energy levels are at about $R_{in} = -1.7$ nm. So the maximum value of f_c+f_v-1 may occur at this value of R_{in} . The other factor is the $s-p$ energy spacing. The injected electrons are more likely to be promoted to higher excited states in the structure with smaller $s-p$ energy spacing. In Figs 7.6-7.8, the $s-p$ energy spacing decreases when R_{in} increases especially for holes. So we see an obvious decrease in the value of f_c+f_v-1 after $R_{in} > 0$ nm. For the two structures with $h = 3.4$ nm, the one with 2% of N has greater value of f_c+f_v-1 for the same carrier density. This result is consistent with our previous results in Chapter 4.

Fig 7.13 shows the maximum gain vs. inner radius for (a) 0% of N, $h = 3.4$ nm, (b) 2% of N, $h = 3.4$ nm and (c) 2% of N, $h = 1.7$ nm. The carrier densities are the same as those in Fig 7.11. The transition matrix element, the volume of QD and the factor f_c+f_v-1 have certain effect on maximum optical gain. For low carrier density, when R_{in} increases, the maximum optical gain increases to a maximum value in the range of R_{in} from -5 nm to -1 nm, and then decreases. After analyzing Figs 7.9, 7.10 and

Fig 7.13 Maximum gain vs. inner radius for (a) 0% of N, $h = 3.4 \text{ nm}$, (b) 2% of N, $h = 3.4 \text{ nm}$ and (c) 2% of N, $h = 1.7 \text{ nm}$. The carrier densities are the same as those in Fig 7.11.

7.12, we suggest that at low carrier density, the factor (f_c+f_v-1) has the greatest importance over the other two factors. With $h = 3.4$ nm, the structure with 2% of N has the greater optical gain despite its smaller TME, because its value of f_c+f_v-1 is greater than that of the structure without N. It compensates the decrease of TME. Because the carrier densities are different for these two structures, it is difficult to really compare them, but qualitatively we can observe the structure with greater height has more steady optical gain meaning R_{in} has less influence on optical gain.

When carrier densities are high, more injected carriers are promoted to higher excited states. When the value of R_{in} increases, the maximum gain decreases slightly, but when the value of R_{in} increases further to positive, the merge of the first two peaks can cause a sudden increase in maximum gain. This phenomenon is especially obvious for the structure with 2% of N and $h = 3.4$ nm.

7.4 Summary

Shape effects are that when the value of R_{in} increases, the nanostructure changes shape from lens shape to volcano shape at $R_{in} < 0$, then a quantum ring at $R_{in} > 0$, the s - s transition energy decreases first, reaching the minimum value at about $R_{in} = -1.7$ nm which shows a quantum volcano shape, then the s - s transition energy increases. Both electron and hole states changes dramatically from disk-like at $R_{in} < 0$ to ring-like at $R_{in} > 0$. For the same R_{in} , the structures with N (greater height) have smaller transition energy due to the N -CB repulsion (reduced quantum confinement effect). When the value of R_{in} increases, the TME increases first, reaching the maximum value at about $R_{in} = -1.7$ nm, then decreases, and the energy spacing becomes smaller. Then the problem of higher excitation transition becomes significant. To reduce this detrimental effect, we analyze the optical gain at lower carrier density and suggest that for quantum ring structure, the first two gain peaks may merge together to form a boarder peak due to its small s - p spacing. We recommend the structure with R_{in} in the range of -3 nm to -1 nm in which the maximum gain occurs. The shape is similar in Fig 7.1(a). The structures with nitrogen have greater optical gain due to its overwhelming greater value of factor $f_c + f_v - 1$. For the structures with greater height, the variation of the value of R_{in} has less influence on the change of maximum optical gain. Our simulation results can help researcher select the appropriate shape of nanostructures to design the laser with better performance.

Chapter 8: Conclusion and recommendations

8.1 Conclusion

Firstly, the electronic structures and optical gain of InAs/GaAs pyramidal QDs were investigated in the framework of effective-mass envelope function theory using the strain distribution calculated by the VFF model. The effect of electric field along different directions on the electronic structure is studied thoroughly. The Stark effect of QDs is complicated due to the involving of two factors, the quantum confinement and the electric potential. Then for the InAs/GaAs QDs in VCSEL structure, the simulation result is in good agreement with the experimental μ -PL result at room temperature. The spontaneous emission spectra of QDs from 200K to 400K are subsequently simulated by our nanostructure model. A decrease of 41 meV of QD GS transition energy from 250K to 350K and FWHM of emission spectra of 50–60 nm can be predicted. From the simulation results, optimized design rules can be achieved for QD-VCSELs with a wide OTR.

Secondly, the electronic structures of InAsN/GaAs pyramidal QDs are investigated using the ten-band **k.p** method with consideration of strains calculated by VFF model and inhomogeneous broadening effect of optical gain due to the QDs size fluctuation. When more N atoms are incorporated in QD, the repulsion between the N resonant energy level and c1 increases, and c1 is forced to be lower so that the c1-h1 transition energy is reduced. So the long-wavelength emission becomes

possible, even 1.55 μm . At the same time, the energy separation between c2-c1 is enlarged, which makes higher excited states combination transition harder to occur. For different size of QDs, the strain effect and confinement can significantly affect the energy levels especially conduction band and the optical properties accordingly. To achieve desired lasers, the trade-off between wavelengths, transparency carrier density and saturation optical gain must be considered. For the same size QD, when N composition is higher, it can have longer wavelength, higher maximum optical gain and less detrimental effect induced by higher excited state transition.

For truncated pyramidal InAsN/GaAs QDs, if the effective height is smaller, the truncated QD is flatter. The truncation changes the strain distribution and the confinement in the z direction inside the system. The flatter QDs have greater c1-h1 transition energy, greater TME, less detrimental effect of higher excited transition, higher saturation gain and differential gain. We suggest the shape with its half of top part truncated for its better overall performance. Because for that shape, its c1-h1 transition energy is only about 27.9 (or 23.4) meV higher than the complete pyramidal InAsN (or InAs) QDs, and the GS state transition energy increase is only about 3.3 % (or 2.5%) of its original transition energy, but its TME increases by 30% resulting in significant increase in saturation optical gain and differential gain. So the recommended truncated shaped QD can provide guidance for the QDs grown in the experiment in which proper growth conditions can be controlled to achieve desirable-shaped QD.

Then the electronic structures of InAsPN/GaP(N) QDs are investigated using the

ten-band **k.p** method with consideration of the strains calculated by the VFF method. When the barrier is GaP, for smaller sized InAsPN QDs, the minimum transition energy may occur at lower P composition due to the huge conduction band offset and quantum effect. But for larger sized QDs, the transition energy increases as P composition increases because the bandgap of alloy QDs increases significantly, and c_1 is close to band-edge at this time. When the N composition increases, the transition energy decreases due to the stronger repulsion between conduction band and N resonant band, and the TME is more affected by the transition energy rather than N-CB mixing. When the transition energy is small, the electrons are better confined in QD region, and the electron-hole wave functions are overlapped more effectively. To obtain Si-comparable laser materials, we incorporated 2% of N into GaP barrier. We find that in $\text{GaP}_{0.98}\text{N}_{0.02}$ barrier, the conduction band offset is reduced, due to the quantum effect; the conduction band is lower, resulting in a smaller transition energy and longer wavelength. We can achieve 1.3 μm , and at the same time, the TME is reduced due to the reduced conduction band offset. For the case with $\text{GaP}_{0.98}\text{N}_{0.02}$ barrier, the GS maximum optical gain is less than those with GaP barrier at low carrier density, but it increases faster when carrier density increases, and finally it can surpass and reach a greater value of saturation optical gain. This shows incorporating N into GaP barrier is an effective way to achieve desirable wavelength and optical gain. Comparatively, the optical gains of InAsPN/GaP(N) are smaller than that of InAsN/GaAs QDs. Although InAsPN QDs have better confinement, the strained conduction band is much closer to the N

resonant band so that the interaction between the conduction band and N is stronger and more N component is inside the c1 energy state. The N component does not involve in the optical transition. So the TME and optical gains of InAsPN QDs is much smaller than that of InAsN QD.

Finally, from lens shape to volcano to ring, shape effects are that when the value of R_{in} increases, the nanostructure changes shape from lens shape to volcano shape at $R_{in} < 0$, then a quantum ring at $R_{in} > 0$, the s - s transition energy decreases first, reaching the minimum value at about $R_{in} = -1.7$ nm which shows a quantum volcano shape, then the s - s transition energy increases. Both electron and hole states changes dramatically from disk-like at $R_{in} < 0$ to ring-like at $R_{in} > 0$. For the same R_{in} , the structures with N have smaller transition energy due to the N-CB repulsion. When the value of R_{in} increases, the TME increases first, reaching the maximum value at about $R_{in} = -1.7$ nm, then decreases, and the energy spacing becomes smaller. Then the problem of higher excitation transition becomes significant. To reduce this detrimental effect, we analyze the optical gain at lower carrier density and suggest that for quantum ring structure, the first two gain peaks may merge together to form a boarder peak due to its small s - p spacing. We recommend the structure with R_{in} in the range of -3 nm to -1 nm in which the maximum gain occurs. The shape is similar in Fig 7.1(a). The structures with nitrogen have greater optical gain due to its overwhelming greater value of factor $f_c + f_v - 1$. For the structures with greater height, the variation of the value of R_{in} has less influence on the change of maximum optical gain. Our simulation results can help researcher select the appropriate shape of

nanostructures to design the laser with better performance.

8.2 Future work

To deepen the understanding of dilute nitride QDs, the following research work could be done in the future. Instead of only focusing on interband transitions, we can investigate the intersubband transitions of dilute nitride QDs. Since infrared detector is important in many applications such as medicine, defense, computer etc., the requirement of small transition energy can be satisfied by intersubband transition as the manufacturing of small bandgap materials is very difficult. For dilute nitride QDs, $c1$ energy level can be controlled by adjusting N composition, so the $c2-c1$ intersubband transition can be tuned in certain extent. Another advantage is that the manufacturing technique and process of III-V QDs are very mature and sophisticated; the infrared detector can be integrated with other device if the intersubband transition can be implemented successfully. So the potential of dilute nitride QDs intersubband transition is huge in infrared photodetector and other optoelectronic devices. Another future topic is group IV element QDs, because they are compatible with silicon technology and their optical properties can be applied by using different growth patterns. By controlling the compositions, these alloys have a wide tunability of band gap, indicating a huge potential for optoelectronic applications such as laser

diodes and photodetectors. In this thesis, all systems are under compressive strain, we are interested to study Ge/GeSiSn system in which the tensile strain exist, and may change the indirect bandgap to direct bandgap. These tensile QDs are very interesting, and we can do more theoretical research work to study their properties and potential application in optoelectronics.

Author's Publications

Journal Paper

1. **J. Chen**, W. J. Fan, Q. Xu, X. W. Zhang, J. W. Luo, S. S. Li and J. B. Xia, “Electronic structure and optical gain saturation of $\text{InAs}_{1-x}\text{N}_x/\text{GaAs}$ quantum dots” *Journal of Applied Physics*, **105**, 123705 (2009).

2. **J. Chen**, W. J. Fan, Q. Xu, X. W. Zhang, S. S. Li and J. B. Xia, “Electronic structure and optical gain of truncated $\text{InAs}_{1-x}\text{N}_x/\text{GaAs}$ quantum dots” *Superlattices and Microstructures*, **46**, 498-506 (2009).

3. **J. Chen**, W. J. Fan, Q. Xu, and X. W. Zhang, “Electronic structure and optical gain of $\text{InAsSbN}/\text{InAs}$ quantum dots ” *Computational Materials Science*, Issue 1, Pages S10-S14 (2010).

4. **J. Chen**, W. J. Fan, Q. Xu, and X. W. Zhang, “Electronic structure and optical gain of $\text{InAsPN}/\text{GaP(N)}$ quantum dots ” *Superlattices and Microstructures*, Volume **49**, Issue 1, Pages 1-8 (2011).

5. **J. Chen**, W. J. Fan, Y. Ding, Q. Xu, X. W. Zhang, D. W. Xu, S. F. Yoon, and D. H. Zhang, “Nanostructure model and optical properties of InAs/GaAs quantum dot in

vertical cavity surface emitting lasers” Opto-Electronics Review, Volume 19, Number 4, Pages 449-453 (2011).

6. **J. Chen**, W. J. Fan, Q. Xu, X. W. Zhang, S. S. Li and J. B. Xia, “Shape effects on the electronic structure and the optical gain of InAs(N)/GaAs nanostructures: from a quantum lens to a quantum ring” submitted and accepted by Superlattice and Microstructures.

Conference Paper

1. X. W. Zhang, Q. Xu, **J. Chen**, W. J. Fan, J. W. Luo, S. S. L and J. B. Xia, “Electronic structure and optical gain of InAs/GaAs pyramid quantum dots,” International Conference on Materials for Advanced Technologies, Singapore, July 2009.

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