Chapter 7

Conclusions
Nanostructures of III-V compound semiconductors such as quantum wells (QWs), quantum wires (QWRs) and quantum dots (QDs), are attracting considerable attention recently because they exhibit novel physical properties and also because of potential applications involving them. In recent years, a number of innovative techniques have been developed to grow or to fabricate and to study experimentally a variety of these semiconductors nanostructures. The optical properties of these systems are especially useful in giving detailed information about their microscopic physics.

The goal of this thesis is to address few of the unsolved problems related to III-V semiconductor nanostructures. We first summarize the main achievements of the research in this thesis, followed by suggestions for some future work related to III-V semiconductor nanostructures.

After introducing the subject in chapter 1, we interpret theoretically the interdiffusion induced changes in the photoluminescence (PL) spectra of annealed In$_x$Ga$_{1-x}$As/GaAs QDs in chapter 2 through suitable quantum mechanical models and concepts. The experimental results of various reports
Conclusions

round the world on the annealing of $\text{In}_x\text{Ga}_{1-x}\text{As/GaAs}$ QDs agree strongly on one particular phenomenon, that is, the initially observed PL spectrum is very broad. After annealing, the PL peak undergoes a strong blueshift and the full width at half maximum (FWHM) decreases very significantly, while there is an increase in the intensity. The change in the PL was thought to be due to relaxation of strain, homogenization of the size distribution of QDs, and reduction of dislocations and defects. These fail to explain the observed strong changes in the PL spectra clearly.

While interpreting this interdiffusion related PL phenomenon, a very important point was overlooked by the research workers in the field. When an $\text{In}_x\text{Ga}_{1-x}\text{As/GaAs}$ single QD emerges from a strained layer crossing the critical thickness, initially a small three dimensional pyramid highly rich in indium is formed on the indium rich strained layer. As the dot grows in size, the nucleus is surrounded by $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers which are progressively depleted of indium and the indium rich bottom strained wetting layer loses its thickness. The dot is then covered with GaAs. It is quite difficult to visualize the band structure of an as grown $\text{In}_x\text{Ga}_{1-x}\text{As/GaAs}$ QD. If we take a close look at the structure from the GaAs substrate in the growth direction, at different vertical sections across the QD, the conduction and valence bands have the nature of asymmetric triangular wells due to the strong gradient of the indium concentration at each section. The width varies at different sections and the depth varies with the variation of indium concentration. On annealing, indium outdiffuses from the central core of the single dot to homogenize the distribution and the triangular wells under consideration, ultimately, after long annealing, leads to rectangular wells. The wells thus obtained have the same depth since the concentrations of indium and gallium have homogenized, only the widths of the rectangular wells vary. The resulting PL arises from the transitions of these wells. Our quantum mechanical computations on the triangular band structures of the as grown QDs reveal that the optical
transitions are spread out over energy, while the transitions in the rectangular wells of the annealed dots bunch up in a small energy space resulting in a blueshifted, narrow, and intensity enhanced PL spectrum. Our theoretical PL results are very similar to experimental observations. Thus the experimental observations are explained. This phenomenon is modified by the superposed effects of redistribution of the QD size, strain relaxation, and reduction of dislocations and defects.

In chapter 3 we show the dependence of the PL of annealed $\text{In}_x\text{Ga}_{1-x}\text{As/GaAs}$ and $\text{In}_x\text{Ga}_{1-x}\text{N/GaN}$ QDs on their shape and dimension. Model quantum mechanical calculations are carried out for pyramidal, truncated pyramidal and lens shaped dots, which are of practical interest. We have stressed on the changes of shapes of the conduction and valence bands and the successive changes in the energy levels due to the variation of the dot shape and size. The asymmetric triangular shaped energy bands of the as grown QDs due to a strong gradient of indium move towards rectangular quantum wells on annealing. The PL spectra change correspondingly, as discussed earlier. The variation of the blueshift with the dot shape and dimension is presented in this chapter. For pyramidal and truncated pyramidal dots, the blueshift increases monotonically with varying aspect ratio. As the dimension of the QDs is typically 5 – 50 nm, in order to keep the complexity within presentable limits, we vary the aspect ratio from 0.5 to 2.0. In case of lens shaped dots, the blueshift increases initially and seems to saturate at larger dot dimensions. The PL spectra of long annealed lens shaped dot structures are found to be sharper than the other structures indicating an improved optical property desirable for optoelectronics application.

In chapter 4 we investigate the optical absorption spectra of realistic semiconductor QD systems with a nonuniform size distribution described by a Gaussian function. QDs have been previously analyzed with the help of infinite
potential barriers; realistic semiconductor QDs having finite potential barriers have not been widely discussed or analyzed. In this work, we approximate the QD as a quantum box (QB) with finite potential barriers, which may be helpful for a proper analysis of the optical properties of realistic semiconductor QD systems. We find that the absorption spectra of different realistic III-V compound semiconductor QDs depend strongly on the dot size distribution described by the parameter $\xi$, the ratio of the standard deviation of the dot size to the average dot size of the system. Starting from the basic normalized wave function of a three-dimensional rectangular infinite well and the confinement energies of the electron and hole for a finite well, we model the resonance energy and the optical absorption spectra of a realistic cubic dot of finite potential barrier at the boundaries. In the realm of an ideal cubic QD system, our formulation reduces to the already existing formulas for infinite potential barrier. We also formulate suitable expression for the difference in the linewidths of the $n^2$ absorption peak of the ideal and realistic dots. It could be inferred from our formulation that the linewidth is proportional to the size deviation $\xi$ and approaches zero when $\xi \to 0$. Also, the linewidth is larger for higher transition energy levels. Next, the following investigations are carried out:

(i) Absorption spectra of the lowest transition of $\text{In}_{0.7}\text{Ga}_{0.3}\text{N}/\text{GaN}$ QD system corresponding to both real and ideal dots for relative standard deviation $\xi = 0.02, 0.05, 0.10$ and $0.20$ are found out.

(ii) Absorption spectra of the lowest four transitions of $\text{In}_{0.7}\text{Ga}_{0.3}\text{N}/\text{GaN}$ and $\text{In}_{0.66}\text{Ga}_{0.33}\text{As}/\text{GaAs}$ QD system corresponding to both real and ideal dots are evaluated.

(iii) Variation of the energy difference of the absorption peak of the ideal and realistic dots with average dot size was studied. The results of
computations are presented for both In$_{0.7}$Ga$_{0.3}$N/GaN and In$_{0.66}$Ga$_{0.33}$As/GaAs QD systems for the two lowest transitions.

(iv) Variation of the linewidth of realistic QD systems on the average dot size for $\xi = 0.02$ and 0.05 are investigated. The results of computations are presented for both In$_{0.7}$Ga$_{0.3}$N/GaN and In$_{0.66}$Ga$_{0.33}$As/GaAs realistic QD systems for the lowest transition.

(v) Difference in the linewidth, $W_{\text{reduction}}$, of the $n^2$ absorption peak of ideal and realistic In$_{0.7}$Ga$_{0.3}$N/GaN and In$_{0.66}$Ga$_{0.33}$As/GaAs QD systems are also computed for $\xi=0.02$ and $\xi=0.05$.

A comparative study of the ideal and realistic dots is carried out in this chapter. We observe that for realistic dots there is a red shift of the absorption peaks and there is a decrease in the linewidth as compared to the ideal QD system for the same size deviation. The photon energies corresponding to the Gaussian absorption peaks depend on the band gap of the semiconductor material and the confinement energies of the conduction and the valance bands. For realistic dots having finite potential barrier, the confinement energies are less as compared to ideal dots having infinite potential barriers. As a result, the absorption peaks suffer from a red shift. The variation of the energy of the subbands with change in the size of the dots is much more pronounced in the case of infinite wells as compared to finite wells. Hence larger deviation in the absorption energies for a particular $\xi$ is expected in the case of infinite wells and hence the absorption spectra become broader. Moreover in a narrow finite well less number of levels will be available for transitions which will make the spectrum further narrow. This chapter gives an in depth understanding of the nature of absorption in realistic QDs in correlation with the dot size distribution.
In chapter 5 we reestimate the band offsets of In$_x$Ga$_{1-x}$N/GaN QWs. There were several experimental reports [38-40] for the band offsets of In$_x$Ga$_{1-x}$N/GaN QWs. These experimental results did not seem to comply with theoretical calculations. This led to a reestimation of band offset.

The absence of lattice matched substrates and miscibility problems of InN and GaN make the growth of In$_x$Ga$_{1-x}$N a very difficult task. It often leads to wide composition fluctuations and phase separations in the alloy. The high compositional fluctuation of indium and the wide variation of the thickness of QWs have been observed because of alloy disorder, miscibility problems and clustering of indium. These make the measurement of band offset of the In$_x$Ga$_{1-x}$N/GaN heterostructures a very complicated and difficult problem. Several electrical and optical measurements of band offsets are well established. The measurement has been carried out by various groups of research workers. The band offset ratio, $\Delta E_C : \Delta E_V$ has been estimated to be 83:17, 68:32 from theoretical calculations, 62:38 by PL measurements, 30:70 by X-ray photoemission spectroscopy, 38:62 by optical pumping. This unusual large range of estimated band offsets makes it amply clear that the measurement is complicated and needs deeper understanding. In this chapter 5 we present new estimates of the band offsets for In$_x$Ga$_{1-x}$N/GaN heterostructures and QWs by fitting two sets of reported experimental PL results. In one such experimental report, the peak of the PL spectra of In$_x$Ga$_{1-x}$N/GaN QWs on annealing and interdiffusion, primarily shifts towards lower energies followed by a shift towards higher energies. This strange phenomenon could be explained through quantum mechanical calculations using Fick's law of interdiffusion, a suitable bowing parameter and a band offset for the best fit. In another report, the different interband transition energies of the optical pump spectra were obtained by strong optical pumping of a In$_x$Ga$_{1-x}$N/GaN QW on sapphire. We calculate theoretically these transition energies with the same parameters varying the band offset for the
best fit. From the sets of best agreements between experiment and theory, a new set of band offsets are determined to be $\Delta E_C : \Delta E_V = 55 : 45$.

Finally, in chapter 6 we suggest the prominence of higher order transitions ($e_2 - h_4$) in the PL spectra of the $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ QWs. The PL peak energy of $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ QWs on annealing, initially move towards lower energies. On further annealing at higher temperatures the peaks shift towards higher energies. This is a rather unusual phenomenon which is not observed in other annealed III-V QWs. We show through appropriate quantum mechanical computations that the experimental observations can totally tally only if the higher order transitions, namely the $e_2 - h_4$ transitions are considered to be predominant in the PL spectra. In the typical PL from III-V QWs, when carriers are excited to higher sub-bands they eventually relax to the lowest sub-bands, from which they recombine to emit the corresponding spectrum. Recombination from higher sub-bands may be attributed to the existence of a strong piezoelectric field across the QW due to which the wave functions and carriers are separated spatially and transitions from higher sub-bands seem to become more probable. This explains the strange observations of the PL spectra from annealed $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ QWs.

### 7.1 Suggestions for some future work

We conclude this thesis with few suggestions for future work in the field of III-V semiconductor nanostructures. As stated earlier, in chapter 2 we have interpreted the interdiffusion induced changes in the PL spectra of annealed $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QDs. As an extension of this work we showed the dependence of the PL of annealed $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ and $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ QDs on their shape and dimension. In our studies, we considered the indium concentration of the central core of the dot to be 0.8 or 0.6. Further
investigations can be done by considering different indium concentrations of the central core. In case of In$_x$Ga$_{1-x}$N/GaN QDs, the effect of different important parameters such as effective mass, bowing parameter, etc. on the PL spectra of annealed QDs can be further studied. Moreover, the phenomenon described in chapter 2 can be investigated for other III-V semiconductor QDs such as AlGaN/GaN and others.

In chapter 4, we have investigated the optical absorption spectra of realistic semiconductor QD systems with a non-uniform size distribution described by a Gaussian function. Further studies on the absorption spectra of III-V realistic QD systems can be done for different important parameters such as band offset ratio, effective mass, bowing parameter and so on. In our investigations, we considered the QW profile to finite rectangular. Due to interdiffusion of the third group elements, say for example indium and gallium in case of In$_x$Ga$_{1-x}$N/GaN QDs, the QW profile may be changed to parabolic or Gaussian. The effect of these QW profile, due to interdiffusion, on the absorption spectra of III-V realistic QD systems can be further investigated. The dependence of the optical spectra of realistic semiconductor QD systems on temperature can also be studied.

In recent years semiconductor QD systems in the form of stacked QDs (SQDs) have been extensively studied because they hold great promise for many technological applications. III-V QD systems and/or SQDs have been utilized in the latest photovoltaic devices and solar cells (SC). Generally III-V semiconductor SQDs are grown by Stranski-Krastanow mode. The stacked configuration could be, in general, accompanied by size inhomogeneity. The effect of the non-uniform size distribution on the optical properties of SQDs and SC may be investigated in future.