1.1 General introduction

III-V compound semiconductors are composed of one element from group 13 and the other from group 15 of the periodic table such as GaN, InP, AlAs etc. There exist ternary (comprising of three elements) and quaternary (comprising of four elements) alloys of III-V compound semiconductors as well, such as InGaN and AlGaInP respectively. Bulk compound semiconductors can have different crystal structures but two most commonly exhibited types are zinc-blende and wurtzite. The unit cells of these two crystal structures are shown in Figure 1.1. Zinc-blende crystal structure has two fcc lattices, one occupied by the elements of group 13 while other occupied by the elements of group 15 as shown in Figure 1.1(a). On the other hand, wurtzite is a hexagonal crystal structure with alternating atoms of elements of group 13 and 15 that follow an ABAB… alternating layer arrangement, Figure 1.1(b).

![Unit cells of two common crystal structures exhibited by bulk III-V compound semiconductors: (a) zinc-blende and (b) wurtzite. Yellow (gray) balls represent III (V) atoms, respectively.](image)

Research on these binary compounds has led to seven Nobel prizes in physics so far. They have changed our life enormously during the past 50 years, and are promising materials for device applications which are active at wavelength regions spanning from red
and well into the ultra-violet. Recently, the NASA 'Earth at Night' satellite images have shown another potential market for them, as the light necessary for human civilization will soon be derived from compound semiconductor based chips. Some promising applications of these materials include optical fiber communication, CD and DVD players, cell phones, home and office lights, power amplifiers at microwave frequencies, laser diodes, light-emitting diodes, solar cells etc.

1.2 III-V compound semiconductor nanostructures

The world of nanostructures starts below 1 µm and ends at about 1 nm. However, this is not a strict limit but mostly all dimensions of nanostructures lie within this range. They are a new phase of matter, which are intermediate between molecules and bulk with dimensions of the order of $10^{-7}$ cm. Based upon technological demand, the study of atomic and electronic structure of III-V semiconductor nanostructures is an active area of research now days as electronic industries are developing miniature devices of the order of few nanometers.

![Diagram of research areas related to III-V compound semiconductor nanostructures.](image)

**Figure 1.2:** Research areas related to III-V compound semiconductor nanostructures.

They have revolutionized the world of optoelectronics industry by increasing device efficiency and at the same time decreasing their physical dimensions. These further can act as building blocks to design materials with desirable characteristics. Research on III-V
nanostructures is also related to many other important areas as shown in Figure 1.2 in the form of a flow chart. Thus, understanding and attaining an atomic level control of III-V semiconductors have technological implications.

1.2.1 Importance of nanoscale

The semiconductors at nanoscale can have completely different physical and chemical properties than their bulk counterparts although both are having the same constituents. At nanoscale, properties of a material are more interesting because of the following two factors which are dominant at this level:

1. **Quantum size effect**: The excitation of a semiconductor leads to the generation of an electron and a hole. This electron and hole can combine to form a bound electron-hole pair, also referred to as an exciton. The exciton has a certain size, known as the Bohr exciton radius and for most semiconductors the Bohr radius is of the order of a few nanometers. When the size of nanoparticles approaches the size of Bohr exciton radius, quantum confinement effects become very important. The conduction and valence bands split into discrete levels and the band gap increases with decreasing particle size, leading to a blue shift in the absorption and emission spectrum. Nanoparticles that show these phenomena are often called quantum dots because they show quantum confinement.

2. **Increase in surface area to volume ratio**: With the reduction in size, the percentage of surface atoms becomes larger. Also, the surface atoms have lower co-ordination as compared to inner atoms and are more easily mobilized. It enhances the chemical reactivity of a material at the nanoscale significantly as they can make use of their bonding possibilities with other atoms and molecules.

After observation of size-quantization effect in semiconductors, efforts are going on to study size-dependent properties of these materials [Khanna et al. (2002); Rossetti et al. (1983); Byrappa et al. (2008)]. While going from nano to bulk scale, it is interesting to analyze the evolution of different properties in a material. Also, the structure exhibited at bulk could be remarkably different than the structure at nanoscale. Broadly, nanostructures can be divided into following three distinct classes:

- **Two-dimensional nanostructures**: Thin films of the order of nanometers, which are generally deposited on a bulk material, fall in this category. The electrons are confined
in a direction perpendicular to the film only and in the other two dimensions electrons behave as in a bulk material.

- **One-dimensional nanostructures**: Nanowires and nanotubes are 1D nanostructures with diameter in nanometer range and length in micrometer range. Along the structure, electrons are free to move while they are confined in the transverse directions.

- **Zero-dimensional nanostructures**: Nanoparticles, nanoclusters, colloids, nanocrystals and fullerenes are all zero-dimensional nanostructures. The electrons are confined in them in all directions.

   In the present thesis, our discussion will be mainly focused on nanoparticles i.e. zero-dimensional nanostructures of III-V (III: Al, Ga, In; V: N, P, As) compound semiconductors. A discussion on the bonding characteristics of ultra-thin layers and infinite surfaces of III-N compound semiconductors is also included, in order to correlate their bonding characteristics with nanoparticles.

### 1.2.2 III-V compound semiconductor nanoparticles

After the discovery of $C_{60}$ by Kroto *et al.*, carbon fullerenes altogether opened up new research fields which are of importance to nanoscience and nanotechnology, as they exhibit unique physical and chemical properties (Kroto *et al.* (1985)). Since then, many research groups have put their efforts both at theoretical and experimental levels to achieve non-carbon fullerenes such as endohedral Si fullerenes (Yoo *et al.* (2004)), transition metal doped Si$_n$ cages (Hiura *et al.* (2001)), different metals doped Si cages (Kumar and Kawazoe (2001)), BN fullerenes [Terauchi *et al.* (1997); Stephan *et al.* (1998); Golberg *et al.* (1998); Hirano *et al.* (2000)], “golden fullerene” of Au [Gu *et al.* (2004); Johansson *et al.* (2004)] etc. Besides these, fullerene-like cage structures of II-VI compound semiconductor nanoparticles have been also extensively investigated. One such II-VI semiconductor is ZnO. Nanoparticles of ZnO were reported long back in 1985 (Koch *et al.* (1985)), and recently, laser ablation experiments revealed the magic cage-like structures of these nanoparticles for the atomic sizes, n=34, 60 and 78 (Dmytruk *et al.* (2009)). First principles calculations also supported these predictions. Another important II-VI semiconductor is CdSe. Experimentally, highly stable (CdSe)$_{13}$, (CdSe)$_{33}$ and (CdSe)$_{34}$ nanoparticles were grown, and further their atomic and electronic structure was understood from first
principles calculations [Kasuya et al. (2004); Botti and Marques (2007)]. Similar results have been also reported for ZnSe nanoparticles (Nanavati et al. (2009)).

Theoretical studies on small III-V semiconductor nanoparticles also predicted empty fullerene-like cage structures for these systems [Costales et al. (2002, 2003, 2006); Tozzini et al. (2000); Zhao et al. (2006)], which consist of six- and four-membered rings (as shown in Figure 1.3) in contrast to six- and five-membered ring structures of carbon fullerenes. Besides fullerene-like cage structures, cages with interior atoms (Costales et al. (2005)), two shell structures (Zope and Dunlap (2005)), double-bubble cage structures (Shevlin et al. (2008)) or bulk fragments (Brena and Ojamae (2008)) have been also predicted in some cases for larger atomic size III-V semiconductor nanoparticles, which however do not show bulk behaviour.

![Figure 1.3: (GaN)$_{32}$ empty cage, (GaAs)$_{32}$ filled cage and (InN)$_{34}$ empty cage. All these cage structures consist of six- and four-membered rings. Dark (light) balls represent anion (cation) atoms, respectively.](image)

Experimentally also, several research groups have reported the formation of III-V nanoparticles using different methodologies such as solvo thermal method, nitrogen plasma annealing method, microwave plasma enhanced method, ball milling method, DC-arc plasma method, reactive gas condensation method etc. Generally, experiments produced III-V nanoparticles in the size range 5-100 nm [Kabra et al. (2003); Shimada et al. (2010); Ogi et al. (2009); Shimada et al. (2006); Iskandar et al. (2006); Schwenger et al. (2003); Sun and Li (2004); Kuo et al. (2009); Lin and Huang (2009); Mann et al. (2008); Ploch et al. (2009); Schwenger et al. (2004); Cingarapu et al. (2011); Baker et al. (2006); Lan et al. (2011)].
Some experimental studies also reported the stability of non-stoichiometric AlP and GaP nanoparticles \cite{Taylor et al. (1998); Gomez et al. (2001)]. However, the stoichiometry and intensities of clusters generally depend on the laser power being used for laser ablation experiments as well as on the angle at which laser light is incident. So, our focus of discussion in this work is mainly on stoichiometric nanoparticles.

So far, experimental research on III-V semiconductor nanoparticles is aimed at achieving uniform, mono-dispersed nanoparticles with reduced particle sizes, and further to use them for various possible applications. But these studies somehow lack information on correct bonding characteristics of these nanoparticles, which is actually important to know both from synthesis and applications point of view. As discussed above, often theoretical studies of III-V nanoparticles report empty cage structures for (GaN)$_n$ and other III-V compound semiconductors up to a size of $n \sim 100$ atoms similar to BN. However, none of these compounds exhibit layered structure in bulk as exhibited by BN. If empty cage structures of III-V nanoparticles are true then it raises an interesting question i.e. up to what size these nanoparticles will continue to favour empty cage structures. As slowly with an increase in size, nanoparticles are emerging towards their bulk structure so it is certain that around some atomic size a transition from two-dimensional (2D) to three-dimensional (3D) structures will happen. However, the answer to this question is still not clear. A transition from 2D to 3D structures will also affect the quantum confinement and in turn various size dependent properties of III-V nanoparticles. So, it will be interesting to monitor the change in atomic and electronic structures of these nanoparticles with an increase in their size. In III-V nanoparticles too, one would expect change in their bonding characteristics in going from top to the bottom in a column in the periodic table (i.e. from AlN to InN, and similarly for other III-P and III-As nanoparticles) because of the different orbitals involved.

Further, the cage structures in nanoparticles would have large surface area due to their small size and all the atoms being on the surface of cage. So, one can expect similar bonding tendencies on the surfaces of nanoparticles and their infinite surfaces except for the role of curvature and the absence of interior atoms in nanoparticles.
1.2.3 Infinite surfaces and ultra-thin layers of III-V compound semiconductors

In order to understand the bonding characteristics, a correlation study between nanoparticles and their infinite surfaces would be of great help. The bonding characteristics at infinite surfaces of III-V semiconductors can give a clue of the correct bonding behaviour on the surface of their cage structures. Also, as compared to nanoparticles of III-V semiconductors their infinite surfaces are very well studied both experimentally and theoretically [Jaffe et al. (1996); Ye et al. (2008); Grossner et al. (1998); Alves et al. (1991)]. Infinite surfaces of III-N compound semiconductors have been generally reported to stabilize into less buckled structures as compared to III-P and III-As infinite surfaces. The magnitude of buckling in III-P and III-As surfaces is two to three orders more than buckling in III-N surfaces. A recent study on honeycomb monolayer structure of III-V semiconductors has also shown that III-N’s i.e. AlN, GaN and InN have planar stable structures similar to graphene, and III-P’s and III-As’s relax to buckled stable structures (Sahin et al. (2009)). Few layers of III-N compound semiconductors have also been reported to persistently have planar graphene-like structures [Freeman et al. (2006); Song et al. (2008); Wu et al. (2011)]. These studies are an indicative of the different bonding characteristics in III-N’s than III-P’s and III-As’s. They also rule out the possibility of empty cage structures in III-P and III-As nanoparticles. Also, empty cage structures in nanoparticles and further planar behaviour of few ultra-thin layers as well as infinite surfaces of III-N’s indicate the stability of empty cage structures in these semiconductors for somewhat larger atomic sizes. However, at what size they will start having bulk structure is an open question.

In nanoparticles, numbers of atoms are few as compared to their bulk counterparts, and the bonding characteristics as well as other physical and chemical properties are dependent on the arrangement of atoms in them. So, the atomic arrangement acts like a tuner in the hands of a researcher to tune the properties of nanomaterials for applications of choice. However, atomic structure prediction at nanoscale is very tedious job as discussed in the next section.

1.3 Structure diversity at nanoscale

The study of nanomaterials whether they are in the form of nanoparticles, nanotubes, nanocrystals or ultra-thin films, imposes a great challenge to predict their exact
structure. Maddox once mentioned this in one of his celebrated News and Views article in Nature (Maddox (1988)): “One of the continuing scandals in the physical sciences is that it remains impossible to predict the structures of even the simplest crystalline solids from knowledge of their composition”. Prediction of nanostructures has been one of the important directions in cluster science (Woodley and Catlow (2008)), because both size and structure at nanoscale play an important role in determining their physical and chemical properties. As number of atoms in nanoparticles are few, so there could be many possibilities to have diverse shapes of atomic structures. One more interesting aspect is that these structures are different than exhibited by their bulk counterparts. However, this is not a strict rule and there also exist some exceptional materials which over rule this behaviour. PbS is one such example. \((\text{PbS})_{32}\) is the smallest size cubic crystal that can be replicated in three dimensions to get its bulk structure. So, \((\text{PbS})_{32}\) is a ‘Magic Baby Crystal’ as both the bulk and nanocrystals have the same crystal structure (Kiran et al. (2012)).

At bulk scale, pressure induced phase transitions from one crystal structure to another has been reported very often. III-N (AlN, GaN and InN) compound semiconductors transform from wurtzite to rock salt crystal structure under applied pressure. A schematic representation of this structural phase transition is given in Figure 1.4. The magnitude of applied pressure is however different depending upon the individual constituents as well as the ionicity of these binary semiconductors. Under pressure, these semiconductors could not sustain the strain and transform into rock salt crystal structure (Sowa (2001)). Experimental studies on nanoparticles also reported such phase transitions in them under pressure [Tolbert et al. (1996); Tolbert and Alivisatos (1995)].

![Figure 1.4](image)

**Figure 1.4**: A schematic representation of the structural phase transition from wurtzite to rock salt crystal structure in bulk III-N’s under high pressure.
In contrast to bulk III-N’s, nanoparticles of III-N semiconductors have an in-built pressure in their atomic structures as the mean bond distances in them are generally shorter as compared to bulk bond distances, and also they have large surface area which gives rise to surface tension. Both these factors act as a compression of the bulk structure. So, an interesting aspect will be to investigate that whether the structural transformations which were observed in bulk under pressure could be realized in their nanoparticles without applying any pressure. In bulk, structural transitions in III-N’s and some other binary compounds have been satisfactorily explained by Garcia and Cohen based on the charge asymmetry value ‘g’ (Garcia and Cohen (1993)). Among III-N’s, InN nanoparticles seems to be a suitable case for observing phase transition without applying pressure, as the value of ‘g’ in InN (0.853) is closest to NaCl (0.958), which is a well known ionic material having rock salt structure in bulk.

If such phase transitions could happen in nanoparticles at zero pressure, then it will be a very important and unusual behaviour. It will indicate that they can even have such structure at nanoscale which their bulk counterparts can have under high pressure only. Also, further it will be interesting to investigate the growth mode of such semiconductor nanoparticles to know how long they will continue to favour such behaviour. It will be having implications from applications point of view also, as nanoparticles are generally capped, so capping with different ligands can even further strain the nanoparticles.

1.4 Applications of III-V nanoparticles

III-V semiconductor nanoparticles have been considered as the central building blocks of many optoelectronic devices [Nakamura (1998); Steckl and Zavada (1999); Nakamura (2000)]. However, our main emphasis in the present thesis is on rare earth ions doping in III-V nanoparticles, which is important for optical fiber telecommunications, solid state lasers, light-emitting diodes and biological applications [Colvin et al. (1994); Bouzigues et al. (2011); Steckl et al. (2002); O’Donnell and Hourahine (2006); Dahal et al. (2009); Hirosaki et al. (2007); Steckl et al. (2001); Heikenfeld and Steckl (2002)].

1.4.1 Rare earth (Eu) doping in GaN

Two decades ago, it was discovered that rare earth (RE) doped semiconductors are an important class of materials in the optoelectronics world, which could open up a way to
design efficient light emitters. Since then great efforts have been made by the researchers to achieve light emitting devices based upon a number of hosts and RE atoms combinations. In the beginning, small optical gap semiconductors were of interest to build these devices, but when implemented in experiments it was realized that they lead to thermal quenching of the photoluminescence. After this, interest has been raised in the wide band gap semiconductors. GaN is a material of choice for RE doping as it is having direct wide band gap (3.4 eV). This particular GaN:Eu doping combination exhibits optoelectronic properties of GaN and unique features of luminescence of Eu ions. This system can emit from infrared to blue light region with high brightness, long life, good mono color, and low quenching effect. Eu doping is particularly important for displays and solid state lighting.

The electronic configuration of Eu is $5s^25p^64f^{7}6s^2$, 4f orbital in it is half filled and 5s and 5p orbitals are completely filled. The luminescence arises from transitions within 4f shell, so absorption and emission of Eu ions is not much affected by the environment. It means that the emission and absorption spectra of Eu ion will be similar for a variety of different hosts. However, symmetry of the host will make a difference. 4f-4f transitions are forbidden in the free Eu ion. However, if environment of Eu ion lacks inversion symmetry then the crystal field surrounding the RE ion in a host could produce mixed states. Due to the effective shielding of 4f shell because of the outer 5s and 5p shells, crystal field also has no effect on the energy of the levels of Eu. As is well known, energy levels are denoted as $^{2s+1}L_J$, where S is the spin multiplicity, L is the orbital angular momentum and J is the total angular momentum. The nature of transitions in Eu ion varies from pure magnetic dipole transition to pure electric dipole transition and the mixture of the two. Main emission of this ion occurs from $^5D_0$ to $^7F_J$ ($J = 0, 6$) levels. The $^5D_0$ to $^7F_1$ transition is pure magnetic dipole, which is practically independent of the symmetry of the surrounding. $^7F_{0,3,5}$ transitions are forbidden both in magnetic and electric dipole schemes. Transitions to the $^7F_{2,4,6}$ are pure electric dipole transitions and are strongly dependent on the symmetry of the environment.

Ga sites in GaN have $C_{3v}$ symmetry, which are non-centrosymmetric. Doping of Eu at Ga (+3) site in GaN leads to a large outward relaxation around Eu. So, intra 4f transitions become allowed in Eu doped GaN due to the hybridization of the states with the host and also due to lack of symmetry. However, recent ab-inito calculations on Eu doping
in wurtzite GaN have revealed that due to large size mismatch between Ga and Eu ions, the lattice is strained and doping costs 1.84 eV energy (Cruz et al. (2012)). Also, Eu doping in GaN is not energetically favourable. In the past few years, extensive efforts are in progress among scientific community to increase the luminescence as well as enhance the stability of RE doped semiconductors. Recently, an answer to this problem has been found by the researchers. It has been demonstrated both experimentally as well as theoretically that by doping a suitable co-dopant such as Si both the goals i.e. an increase in luminescence and enhancement in stability can be achieved [Wang et al. (2009); Cruz et al. (2012)]. Mg is also another suitable choice of co-dopant with Eu [Takagi et al. (2011); Lee et al. (2012); Sekiguchi et al. (2013)]. Si is tetravalent as it has electronic configuration: 1s²2s²2p⁶3s² 3p², so it behaves as an intrinsic donor in GaN:Eu doped semiconductor. It reduces the symmetry around Eu atom and enhances intra 4f level transitions in it.

Eu doping in GaN nanoparticles could be even more interesting as the well known quantum confinement effect plays an important role at nanoscale and strongly influences the emission efficiency. Further, it will also be of interest to observe the behaviour of nanoparticles after introducing a co-dopant (such as Si) with Eu in them. However, such studies in literature are few. Some experimental studies exist on Eu doping in GaN nanoparticles (Pan et al. (2012)) but so far theoretical literature lacks such studies.

1.5 Organization of the thesis

The rest of the thesis has been organized into the following chapters:

- In Chapter 2, review of literature on III-V compound semiconductor nanostructures has been given.
- In Chapter 3, the theoretical formulations and the computational methods which are required to carry out first principles calculations reported in the present work are discussed.
- In Chapter 4, the growth behaviour and bonding characteristics of (III-V)ₙ (III: Al, Ga, In; V: N, P, As; n=12, 13, 32, and 34) nanoparticles have been discussed.
- In Chapter 5, the structural phase transitions in nanoparticles of (III-N)₃₂ (III: Al, Ga, In) as well as in few other binary compounds (CdSe, MgS, ZnO, and AgI)₃₂ from four-fold to six-fold co-ordination at zero pressure have been discussed.
• In Chapter 6, the bonding characteristics and a possible transition from graphitic-like to bulk structure in (III-N) (III: Al, Ga, In) ultra-thin layers have been discussed.

• In Chapter 7, an important application of \((\text{GaN})_n\), \(n=32\) size nanoparticles i.e. RE (Eu, Eu:Si) doping in GaN nanoparticles, both within GGA and GGA+U formalisms, has been discussed.

• In Chapter 8, a summary of the work presented in this thesis, and a possible extension of this work in future has been discussed.