8.1 Summary

As a preliminary step towards developing an understanding of the growth behaviour of III-V (III: Al, Ga, In; V: N, P, As) compound semiconductor nanoparticles, the present thesis investigated the empty and filled cage structures of (III-V)$_n$ nanoparticles for the atomic sizes, $n=12, 13, 32$ and $34$. The phase transitions in nanoparticles of III-N’s as well as few other binary compounds such as MgS, ZnO, CdSe and AgI from four-fold to six-fold co-ordination at zero pressure, bonding characteristics of III-N ultra-thin layers, and an important application of nanoparticles i.e. Eu and Eu:Si co-doping in (GaN)$_n$, $n=12, 13$ and $32$ atomic size nanoparticles have been also studied. For these studies, we employed ab-initio methods based on density functional theory within pseudopotential approximation using VASP package. For investigating the bonding characteristics of III-N ultra-thin layers, use of VASP as well as FHI-aims computer packages has been made. The conclusions drawn from these studies can be summarized as follows:

1. The growth behaviour of (III-V)$_n$ nanoparticles has been analyzed for selective sizes of $n$ up to 34. It was observed that in the small size range (AlP)$_{13}$ and (AlAs)$_{13}$, and in the intermediate size range (GaP)$_{32}$ and (GaAs)$_{32}$ nanoparticles are magic. All of these nanoparticles have filled cage structures. The behaviour of III-V nanoparticles is different from II-VI compound semiconductor nanoparticles such as CdSe. In CdSe, (CdSe)$_{13}$ and (CdSe)$_{34}$ nanoparticles were found to be magic. It indicates that the magic nature is material specific and the bonding characteristics also play an important role. (AlN)$_n$ and (GaN)$_n$ nanoparticles favour empty cage structures at least up to the size $n=34$ and they may continue to favour these for some larger sizes due to stronger sp$^2$ bonding. However, for (InN)$_{32}$, nanoparticles a filled cage isomer becomes lower in energy. Hence, in contrast to previous studies, a transition to filled cage structure in III-nitrides has been found.

2. As InN nanoparticles stand out to be different among III-N nanoparticles, so the growth mode of these nanoparticles has been investigated in more detail further. InN has wurtzite structure in bulk, however, we found using first principles
calculations that (InN)$_{32}$ nanoparticles favour a rock salt crystal structure at zero pressure though in bulk this structure has been exhibited by InN under 12.1 GPa pressure. So, this finding has even ruled out our earlier prediction of a favourable filled cage structure for (InN)$_{32}$ nanoparticles too. On the other hand, (AlN)$_{32}$ and (GaN)$_{32}$ nanoparticles do not undergo such structural transition, and continue to favour empty cage structures. Nanoparticles of few other compounds such as MgS, AgI, ZnO and CdSe were also studied, which also do not favour four-fold to six-fold co-ordination transition at zero pressure. The cation/anion radius ratio as well as charge asymmetry factor ‘g’ support this phase transition in (InN)$_{32}$. For (InN)$_n$ nanoparticles, growth behaviour in rock salt structure mode has been also investigated for the atomic sizes, $n=4, 8, 16, 60$ and $64$. These studies suggested that around $n=60$ atomic size, the rock salt structure will transform to other structures as the bulk structure is wurtzite.

3. The bonding characteristics of III-N ultra-thin bi-layers (a layer of III and a layer of N atoms) have been also investigated. These layers have been found to stabilize into graphitic-like planar structures. Schematic studies have been performed on these starting from a single bi-layer and continuing up to the number of bi-layers at which they exhibit transition from graphitic-like planar to bulk wurtzite structures. With increasing number of bi-layers, intra-layer bond distances decrease and inter-layer separations increase. The binding energy of a layer is almost 90% and for two and more bi-layers, the contribution from van der Waals is significant, though for monolayer it is small. In AlN, the graphitic-like phase is present up to twenty four bi-layers. However, in GaN and InN, it is stable up to five and ten bi-layers respectively. The transition behaviour of III-N's has been correlated to their ionicity values. Higher is the ionicity of a compound, more is the strength of dipole in it and so it needs larger number of bi-layers to stabilize it and hence for the transition.

4. Eu and Eu:Si co-doping in (GaN)$_n$, $n=12, 13$ and $32$ nanoparticles, an important application of GaN as light emitter, has been studied. Eu doping in GaN nanoparticles is more favourable as compared to its doping in wurtzite GaN. The reason could be the availability of large surface area in nanoparticles at which strain is easier to relieve than in bulk. Eu-N bond is longer than Ga-N, and Eu generally
favours sp³ bonding site (rhombus) that has longer Ga-N bond lengths. Si co-doping facilitates Eu doping even more with large energy gain due to the compensation of strain from an over-sized and an under-sized dopant. These doped nanoparticles could form an important route to develop new luminescent materials. The transition from empty to filled cage has not been observed in GaN nanoparticles even after Eu and Eu:Si co-doping due to a strong preference for sp² bonding in these nanoparticles, and this preference is strengthened in nanoparticles due to shorter Ga-N bonds in them as compared to wurtzite GaN.

8.2 Future scope

As a future plan, the present study on growth behaviour of nanoparticles will be extended to larger nanoparticles of the atomic sizes of few hundred atoms. For AlN and GaN nanoparticles, it is not certain that up to what atomic size they will continue to favour empty cage structures, and when the transition to bulk behaviour can be expected in these semiconductor nanoparticles. So, further investigations will continue in an attempt to find suitable answers to these questions.