CHAPTER 4
GROWTH BEHAVIOUR OF III-V COMPOUND SEMICONDUCTOR NANOPARTICLES

4.1 Introduction

With the current growing interest in nanotechnology and miniature devices, nanoparticles and quasi-1D nanostructures of III-V compound semiconductors have attained great importance. As discussed in Chapter 2, so far much theoretical effort has been devoted to atomic and electronic structure studies of III-V (III: Al, Ga, In; V: N, P, As) compound semiconductor nanoparticles. However, these studies demonstrate that the atomic structure and growth behaviour of these nanoparticles need to be further explored. Also, if we have a clear demonstration of the bonding characteristics of these nanoparticles then it will be of great help to better understand and use them for applications.

As compared to III-V nanoparticles, behaviour of II-VI nanoparticles is well established. For CdSe nanoparticles, a striking observation has been the high abundance of (CdSe)$_n$ for $n=13$, 33 and 34 atomic sizes and almost nothing of any other size (Kasuya et al. (2004)). These findings were understood from first principles calculations and a novel atomic structure of (CdSe)$_{13}$ was obtained in the form of a highly puckered cage-like $sp^3$ bonded zigzag network of alternately connected Cd and Se atoms and a Se atom at the center of a Cd$_{13}$Se$_{12}$ cage, while for (CdSe)$_{33}$ and (CdSe)$_{34}$, $n=28$ BN-like cages filled with a core of (CdSe)$_5$ and (CdSe)$_6$ respectively were obtained. (CdSe)$_6$ was shown to be optimal to fit inside the $n=28$ cage. Thus, in contrast to the empty cage structures of nanoparticles of BN and other III-V semiconductors, stabilization of CdSe nanoparticles was shown to occur via filling of the cages with an internally connected core. Since both the III-V and II-VI compound semiconductors share similar bonding characteristics in bulk, so similarity in the behaviour of atomic structures is also expected in their nanoparticles.

The encouraging and well established results on (CdSe)$_n$ nanoparticles ($n=13$ and 34) motivated us to perform similar empty (2D) and filled (3D) cage structure studies on
III-V semiconductor nanoparticles too. In the present chapter, atomic and electronic structure of (III-V)_n nanoparticles (III: Al, Ga, In; V: N, P, As) for n=12, 13, 28, 32, and 34 atomic sizes has been studied both in common-cation and common-anion modes. The structural transition from empty to filled cages has been indeed observed for III-P and III-As nanoparticles but III-N nanoparticles are exceptional. Among III-N nanoparticles too, behaviour of InN nanoparticles is strikingly different from AlN and GaN nanoparticles, as it also favours filled cage structure. III-N nanoparticles exhibit different bonding characteristics than III-P and III-As nanoparticles. These results will provide a new direction in the understanding of growth behaviour and properties of technologically important III-V nanoparticles. From the optimized geometries, further analysis has been carried out to study the electronic structure and bonding characteristics of nanoparticles.

Details of the computational methodology, results and discussion of the atomic and electronic structures of III-V nanoparticles, and conclusions of the results are given ahead in sections 4.2, 4.3 and 4.4, respectively.

4.2 Computational methodology

The calculations have been carried out using VASP package (Kresse and Furthmuller (1996a, 1996b)) with projector augmented wave (PAW) method [Blochl (1994); Kresse and Joubert (1999)] and generalized gradient approximation (GGA) for the exchange correlation energy (Perdew (1991)). This approach is known to provide good atomic structure of many semiconductor nanoparticles. The valence configuration for cations and anions was taken to be s^2p^1 and s^2p^3, respectively. The cut-off energy (E_{cut}) for the plane wave expansion is set to 400 eV. The nanoparticles are placed within a cubic supercell such that the distance between the outermost atoms in the cluster and the simulation box boundary is at least 15 Å. Such a large box is sufficient to keep the interaction between the nanoparticles and its periodic images to be negligibly small. The convergence criteria for energy and forces were ~0.0001 eV and ~0.005 eV/Å, respectively. Brillouin zone integrations have been performed using only the Γ point.
4.3 Results and discussion

In the following sub-sections, a discussion on the optimized empty and filled cage structures of III-V nanoparticles is presented.

4.3.1 Atomic structure of III-V nanoparticles

The atomic structures of nanoparticles with \( n = 12, 13, 28, 32, \) and \( 34 \) have been studied in the common-cation (Al, Ga, In) and common-anion (N, P, As) modes. The high symmetry cages of BN for \( n = 12 \) and 28 have served our purpose well to produce filled cage structures of nanoparticles (Kasuya et al. (2004)). The bulk fragments of GaN nanoparticles were also considered and since these lie significantly higher in energy than the lowest energy cage isomers, so they are not discussed here. The energy differences (\( \Delta \)) between empty and filled cage structures of III-V compound semiconductor nanoparticles are given in Table 4.1. The optimized empty cage structures for \((\text{GaN})_n\) nanoparticles with \( n = 12, 13, 28, 32, \) and \( 34 \) are shown in Figure 4.1. It is clear from values given in Table 4.1 that for \((\text{GaN})_n\) with \( n = 13, 32, \) and \( 34 \) filled cage structures lie higher in energy. Similar results have been obtained for nanoparticles of AlN too. For \( n = 12 \), an empty cage is highly stable with cubic symmetry for all III-V compounds and for \((\text{GaN})_{12}\) the structure is shown in Figure 4.1(a). Two bond lengths have been observed in this case. The bonds sharing hexagons are shorter (1.87 Å) and have more \( \text{sp}^2 \) bonding character whereas bonds sharing hexagon with a rhombus are relatively longer (1.95 Å) and have more \( \text{sp}^3 \) bonding character. However, there is a variation in the bond angles in the cages of different III-V compounds. Cages of III-P and III-As nanoparticles are more buckled which may be due to the development of stronger \( \text{sp}^3 \) character as compared to that in \((\text{III-N})_{12}\). This can be clearly seen by comparing Figures 4.1(a) and 4.2 (a,b). The later shows that the \((\text{AlP})_{12}\) and \((\text{InAs})_{12}\) cage structures are more buckled. The \((\text{AlAs})_{12}, (\text{InP})_{12}\) and \((\text{GaAs})_{12}\) cages are also similar to \((\text{AlP})_{12}\) and \((\text{InAs})_{12}\). Similar to \((\text{GaN})_{13}\) and \((\text{AlN})_{13}\), empty cage structures are favoured for \((\text{InN})_{13}\) also and therefore for \( n = 13 \), all III-N’s favour an empty cage structure but the energy difference between the empty and filled cages decreases (Table 4.1) as we go down from AlN to InN.
Figure 4.1: Optimized atomic structures of (GaN)$_n$ empty cages for $n=12$ (a), 13 (b), 28 (c), 32 (d), 34 (f), and the filled cage for (InN)$_{32}$ (e). Dark blue (light gray) balls represent anion (cation) atoms, respectively.
Therefore, a transition to the filled cage structure could occur first in InN nanoparticles with an increase in size (n). On the other hand, for n=13 nanoparticles of phosphides such as (AlP)$_{13}$, (InP)$_{13}$ and arsenides (AlAs)$_{13}$, (GaAs)$_{13}$ filled cage isomers have lowest energy as shown in Figure 4.2(c,d) for (AlP)$_{13}$ and (InAs)$_{13}$. Among phosphides, (GaP)$_{13}$ is an exception as it favours an empty cage structure similar to that of GaN. But, the energy difference between the empty and filled cages is only 0.185 eV (Table 4.1). In the filled cage of n=13, there is one anion inside the cage and the cage is puckered with more sp$^3$ bonding character than in an empty cage as will be discussed further. Also among the (III-V)$_n$ nanoparticles with n=13, filled cages of (AlP)$_{13}$ and (AlAs)$_{13}$ are special as the central P and As ions are well bonded with six Al ions on the cage whereas in other cases the anion drifts towards the wall of the cage and is not optimally bonded.

In the larger size range, a symmetric cubic cage is obtained for (GaN)$_{28}$ which is similar to (BN)$_{28}$ as shown in Figure 4.1(c). In this case, the bonds sharing hexagons are 1.87, 1.90, and 1.92 Å long while the length of the bonds sharing hexagon and rhombus is 1.93 Å. This is in contrast to the bond length of 1.97 Å in bulk GaN and therefore there is a significant contraction in the bond lengths of GaN nanoparticles. For the filled cage isomer of n=32, first the n=28 cage was optimized and then an n=4 cubical unit (core) was embedded in it in different ways. The optimized filled cage structures for (AlP)$_{32}$, (GaAs)$_{32}$ and (GaP)$_{32}$ are shown in Figure 4.2 (e, f & g respectively). Our results suggest that the best way to fill the cage is by embedding a squashed cube inside the cage in such an orientation that the filled atoms make correct bonds with the atoms on the cage i.e. anion binds with cation and vice versa. The energy differences ($\Delta$) between the empty and filled cage isomers are given in Table 4.1 for different compounds. It can be seen that the tendency to have a filled cage structure for n=32 becomes much stronger as compared to n=13 case with a large decrease in $\Delta$. Most importantly, among III-N’s, (InN)$_{32}$ filled cage is lower in energy than the empty cage isomer (Figure 4.1(e)) although AlN and GaN still favour empty cage structures. Furthermore, among III-P nanoparticles, (GaP)$_{32}$ shows a transition
to a filled cage structure while (AlP)$_{32}$ continues to favour a filled cage as in the case of (AlP)$_{13}$. These results show that already at around n=32 size, there is a preference to have 3D filled cage structure even for a nitride.

Figure 4.2: Optimized atomic structures of some selected III-V compound semiconductor nanoparticles: (a) (AlP)$_{12}$ empty cage, (b) (InAs)$_{12}$ empty cage, (c) (AlP)$_{13}$ filled cage, (d) (InAs)$_{13}$ filled cage, (e) (AlP)$_{32}$ filled cage, (f) (GaAs)$_{32}$ filled cage, (g) (GaP)$_{32}$ filled cage,
(h) \((\text{AlP})_{34}\) filled cage and (i) \((\text{InAs})_{34}\) filled cage. Dark (light) balls represent anion (cation) atoms, respectively.

In the case of In and Al compounds that favour a filled cage structure for \(n=32\), there is a remarkable change in the optimized structure. As we filled a cubical unit inside the 28 atom empty cage, one bond of the cube inside the cage opened up after optimization and transformed two adjacent rhombi into a hexagonal ring making bonds with atoms on the surface of the cage. This structural change somewhat distorts the symmetry of the cage in contrast to \(n=32\) filled cages of GaP and GaAs that are highly symmetric and do not undergo this kind of structural change. Furthermore, except for AlN and GaN, all other systems favour filled cage isomers for \(n=32\) and even for AlN and GaN the energy difference between the empty and filled cage isomers decreases as we go from \(n=13\) to 32 size (see Table 4.1).

For \(n=34\), the atomic structure of \((\text{CdSe})_{34}\) has been followed which is obtained by filling \(n=28\) cage with a \((\text{CdSe})_{6}\) molecule and further empty and filled cage isomers of III-V nanoparticles have been studied. The filled cage structures for \((\text{AlP})_{34}\) and \((\text{InAs})_{34}\) are shown in Figure 4.2 (h & i). All the III-P and III-As semiconductor nanoparticles favour filled cage structures for this size similar to the case of \(n=32\) size, except III-N’s which still favour empty cage structures at this size too. InN in exception to \(n=32\) size, favours an empty cage structure at \(n=34\) size however, the difference in energy between empty and filled cage structures is not much as shown in Table 4.1. A sharp increase in the energy difference between empty and filled cages for \(n=34\) in the cases of AlN and GaN indicates that 3D structures of AlN and GaN nanoparticles with \(sp^3\) bonding are unlikely around these sizes but filled cages with less number of atoms inside may exist for somewhat larger nanoparticles (see Table 4.1).

If we look at the binding energy per atom trends, it increases for each compound with an increase in size (Table 4.1). It is expected as each system is slowing emerging towards its bulk structure. Among III-N’s, \((\text{InN})_{32}\) filled cage is having higher binding
energy per atom as filled isomer is lower in energy for this, rest of the systems have higher binding energy per atom of empty cage isomers. In III-P and III-As semiconductor nanoparticles, \( (\text{AlP})_{13}, (\text{AlP})_{32}, (\text{GaP})_{32}, (\text{AlAs})_{32}, (\text{AlAs})_{34} \) and \( (\text{InAs})_{34} \) filled cage structures have significantly higher binding energy per atom than their respective empty cage structures.

| Atomic Structures | MN | | | MP | | | | MAs | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | B. E. (eV) | Gap (eV) | Δ (eV) | B. E. (eV) | Gap (eV) | Δ (eV) | B. E. (eV) | Gap (eV) | Δ (eV) |
| | 4.686 | 0.657 | 3.680 | 2.279 | | | 1.413 | 1.928 | 1.928 |
| 32 empty & filled cage | 5.119 | 1.454 | -0.551 | 3.705 | 2.375 | 3.562 | 3.370 | 3.428 | 2.438 |
| | 5.112 | 1.360 | 3.760 | 1.421 | | | 1.991 | 1.206 | 1.206 |
| 34 empty & filled cage | 5.134 | 0.425 | 0.275 | 2.821 | 1.294 | 2.364 | 2.654 | 0.964 | 2.399 |
| | 5.032 | 0.591 | 2.858 | 1.219 | | | 0.964 | 1.347 | 1.347 |
| | 3.901 | 1.547 | -6.947 | 3.176 | 1.810 | 0.265 | 2.924 | 2.943 | 1.287 |
| | 3.799 | 0.701 | 3.180 | 1.212 | | | 1.079 | 1.275 | 1.275 |
| 34 empty & filled cage | 3.143 | 0.490 | -0.092 | 2.823 | 1.359 | 2.235 | 2.636 | 0.898 | 4.082 |
| | 3.142 | 0.125 | 2.856 | 0.928 | | | 0.898 | 0.883 | 0.883 |

**Table 4.1:** Binding energy per atom (B.E.), HOMO-LUMO gap, and the difference in energies (Δ) of empty and filled cages of (III-V)\(_n\) compound semiconductor nanoparticles. M stands for Al, Ga, and In for each of the three rows of \( n=13, 32, \) and 34 atomic structures, respectively.
The bonding characteristics and electronic structure of empty and filled cage structures of (III-V)_n nanoparticles for atomic structures with n=13, 32, and 34 have also been compared by keeping the anion fixed and changing the cation and then by keeping the cation fixed and changing the anion in the next section, as we go down in the periodic table from Al to In and N to As.

4.3.2 Bonding characteristics of III-V nanoparticles

To understand the bonding characteristics of III-V compound semiconductor nanoparticles, the variation in some of the bond angles for n=13 filled cage isomer in common-cation and common-anion mode has been plotted in Figure 4.3. It can be seen that in common-cation mode, the nitrides show significantly different bond angles compared with phosphides and arsenides. This is more so for AlN nanoparticles. Hence, the bonding behaviour of nitrides is different than in phosphides and arsenides. The variation in bond angles in the later two cases is small. Further, comparing the trends in phosphides and arsenides in common-anion mode, it is clear that (AlP)_{13} and (AlAs)_{13} nanoparticles behave differently than the corresponding gallium and indium nanoparticles whereas the variation among nitrides is much smaller. The nitride cage structures are less puckered as compared to cage structures in their respective counterparts of phosphides and arsenides.

The empty cage structures of III-N with n=12, 13, 32 and 34 show significant sp^2 bonding with less puckering (see Figure 4.1). However, for all III-P and III-As nanoparticles, empty cages become more puckered and develop more significant sp^3 bonding. That is why filled cages become more favourable in these cases as shown in Figure 4.2. The difference in the bonding features can also be clearly seen in Figure 4.3, where the atomic structures are shown in the same orientation for different III-V compounds and the changes in the bond angles are evident. In the filled cage isomers of III-P and III-As nanoparticles, there is sp^3 bonding with suitable cation and anion combinations on the core and the cage and this leads to strongly puckered cages with anion lying at the outermost position on the surface. AlN and GaN nanoparticles do not favour
sp³ bonding however, for (InN)₃₄ empty and filled cages are nearly degenerate though for (InN)₃₂, the filled cage is lower in energy than the empty cage.

**Figure 4.3:** Bond angle trends in filled cage structures of (III-V)₁₃ compound semiconductor nanoparticles in common-cation and common-anion modes. Different
colors show the variation of different bond angles. Each line in a graph shows the variation of a particular bond angle for the three systems.

A comparison of the energies of \( n=32 \) and \( 34 \) filled cages for AlP and AlAs shows that \( n=34 \) filled cage is slightly more favourable than \( n=32 \) and therefore the transition to 3D structure is more dramatic for Al-V nanoparticles. However for InP, \( n=32 \) filled cage is slightly more favourable than \( n=34 \) case but for InAs, \( n=34 \) filled cage is significantly more favourable than \( n=32 \). Therefore, nanoparticles of InP and InAs behave slightly different. In general, we find that for some compounds \( \text{28+4} \) filled cage is more favourable while for some others \( \text{28+6} \) filled cage is more favourable. Therefore, the bonding character is found to be material specific. Some compounds favour sp\(^3\) well bonded structures and some do not. As all or a large fraction of atoms in these nanoparticles lie on the surface, it is of interest to correlate their bonding nature with that on surfaces of III-V compound semiconductors.

Recently, stability of a hexagonal monolayer of III-V compounds, similar to graphene, has been studied and it has been shown that a planar structure is stable for III-N’s while for other compounds with Al, Ga, In and P, As and Sb, the honeycomb structure develops low buckling of hexagons (Sahin et al. (2009)). Therefore, these calculations also reveal that N plays a special role in the stability of sp\(^2\) bonded structure of these compounds. This tendency of double or triple bond formation is specific to first row elements (B, C, N, and O) as the core consists of 1s shell only and no p-orbitals. In phosphides and arsenides, \( \pi \) bonding is weakened due to an increase in the bond length that reduces the overlap of \( p_z \) orbitals and hence the structures tend to develop sp\(^3\) bonding with puckering. Infinite surfaces of III-N’s also exhibit different behaviour compared with surfaces of other III-V compounds.

In III-N, the bonding is more ionic due to strong electronegativity of N. The ionicity values of 0.794, 0.781 and 0.853 have been reported for AlN, GaN, and InN, respectively (Garcia and Cohen (1993)) and these are remarkably higher than the value 0.316-0.506 for phosphides and arsenides of bulk III-V compound semiconductors. A large charge-transfer
from cation to anion leads to stronger Coulomb attraction between surface cations and anions in nitrides. Also, there is re-hybridization such that a part of the electron charge associated with the occupied lone pair orbital on the anion is found in the surface bond region making those bonds shorter and stronger. As a result, the cations with three valence electrons have a tendency to form planar configuration on the surface (Grossner et al. (1998)) and the buckling amplitudes in nitrides become smaller by a factor of 2-3 than in other III-V compounds with P, As, and Sb atoms on the surface top layer [Alves et al. (1991); Sabisch et al. (1995)]. Similar peculiar behaviour of III-N surfaces has also been observed in their nanoparticles. However, on a surface the top layer atoms are interacting with the underlying bulk layers while in cage structures, atoms on the surface of a cage do not interact with any interior atom. So, the above said facts and the tendency to form sp$^2$ bonding are likely to be even more pronounced in nanoparticles. On the other hand, the curvature in nanoparticles cage structures would create stronger local sp$^3$ bonding. Therefore nanoparticles of nitrides have mixed sp$^2$-sp$^3$ bonding.

4.3.3 Electronic structure of III-V nanoparticles

The HOMO-LUMO gap of empty and 3D filled cages of nanoparticles of III-V compound semiconductors have been calculated and are given in Table 4.1. The HOMO-LUMO gaps for different nanoparticles are shown below in Figure 4.4. As we move from Al to Ga, and further to In in common-anion mode, the HOMO-LUMO gap generally decreases for nitrides, phosphides, and arsenides. However, there are exceptions for n=32 filled cage of GaP and GaAs. For (GaP)$_{32}$, the HOMO-LUMO gap is higher than its value for (AlP)$_{32}$ while for (AlAs)$_{32}$ the HOMO-LUMO gap is smaller than the value for (GaAs)$_{32}$ and (InAs)$_{32}$. Therefore, n=32 filled cage structures of GaP and GaAs show exceptional stability with symmetry, optimal filling, and large HOMO-LUMO gap among these systems. In the common-cation mode, as we go down from nitrides to phosphides of Ga, the HOMO-LUMO gap increases and then decreases as we move towards arsenides for n=13 and 32 but for n=34, the HOMO-LUMO gap decreases monotonically from nitrides to phosphides and arsenides.
Figure 4.4: HOMO-LUMO gap and binding energy per atom for different (III-V)$_n$ nanoparticles studied, n=13, 32 and 34. Note that x axis is not to scale.

The density of states for empty cages of (GaN)$_n$, n=12, 13, 32, and 34 as well as for (InAs)$_{12}$ and selected filled cage structures such as (AlP)$_{13}$, (GaP)$_{32}$, and (InAs)$_{34}$ have been shown in Figure 4.5. The spectrum of (InAs)$_{12}$ is narrower than that of (GaN)$_{12}$ and the former also has a smaller HOMO-LUMO gap. The partial densities of states of N for GaN nanoparticles show higher contribution from N p-states in the valence band as compared to the partial densities of states in other III-V compounds. This is due to a higher charge-transfer to N atoms in III-N’s. Also among phosphides, (AlP)$_{13}$ and (GaP)$_{13}$, show more
significant contribution from p-states of P as well as contribution from cation states due to covalent bonding. In both these cases the HOMO-LUMO gap is the largest.

Figure 4.5: Gaussian broadened total (red curve) and partial (blue curve for anion and green curve for cation) densities of states for some selected III-V nanoparticles. Vertical broken line shows the HOMO.
4.3.4 III-V compound semiconductor “Magic” nanoparticles

Based upon above discussed results, it was analyzed that among large size nanoparticles (n=32 & 34), the transition from an empty to a filled cage in GaP nanoparticles in going from the size n=13 to 32 is remarkable as it can be seen from the energy differences (Δ) given in Table 4.1. In fact, the filled cage of $(\text{GaP})_{32}$ (Figure 4.2(g)) has the highest binding energy (BE) per atom as well as the largest HOMO-LUMO gap (Figure 4.3), and a similar tendency has been observed for $(\text{GaAs})_{32}$ nanoparticles. For small size nanoparticles (n=12 and 13), magic behaviour has been observed in $(\text{AlP})_{13}$ and $(\text{AlAs})_{13}$ semiconductor nanoparticles. For n=13 size, both have large HOMO-LUMO gaps and binding energy per atom. Hence, we conclude that among III-V nanoparticles $(\text{AlP})_{13}$, $(\text{AlAs})_{13}$, $(\text{GaP})_{32}$ and $(\text{GaAs})_{32}$ show magic behaviour. This is in contrast to nanoparticles of II-VI compounds such as CdSe for which n=34 filled cage is magic with an optimally bonded $(\text{CdSe})_{6}$ molecule inside the $(\text{CdSe})_{28}$ cage.

4.4 Conclusions

In conclusion, we have presented results of ab-initio calculations on the growth behaviour of III-V nanoparticles for selective sizes of n up to 34. These results show that in the small size range $(\text{AlP})_{13}$ and $(\text{AlAs})_{13}$ are magic. However, in the intermediate size range $(\text{GaP})_{32}$ and $(\text{GaAs})_{32}$ are magic. All of them have filled cage structures that have been explored for the first time for III-V nanoparticles. The magic behaviour of III-V nanoparticles is different from the one reported for the nanoparticles of II-VI compounds such as CdSe. While $(\text{AlP})_{13}$ is magic similar to $(\text{CdSe})_{13}$, our finding of $(\text{GaP})_{32}$ to be magic compared with $(\text{CdSe})_{34}$ shows that the magic nature is material specific and the bonding characteristics plays an important role. The reason for the preference of empty cage structures for nanoparticles of nitrides has been discussed. Our results show such cages for GaN and AlN nanoparticles with sizes of at least up to around 34 and they may continue to be so even for some larger sizes due to stronger sp$^2$ bonding while for $(\text{InN})_{32}$, a filled cage isomer becomes lower in energy. Therefore, as compared to previous studies, we find that in some cases a transition to 3D structure in III-N’s occurs.