CHAPTER 3

GENERAL ROUTE OF SYNTHESIS FOR 1D GaN NANOSTRUCTURES, CHARACTERIZATION, AND GROWTH DYNAMICS

3.1 Introduction:

Several prototype devices have already been realized using GaN and GaN-based alloy III-V compounds. However, large scale applications of 1D GaN nanostructures based devices are limited because of the cost and efforts involved in developing there nanostructures with necessary purity and alignment.

Bulk synthesis of GaN nanostructures mostly involves two typical growth mechanisms, namely, VLS and VS processes. The metal catalyst–assisted growth is widely known as VLS growth. It was initially proposed for the growth of whiskers by Wagner and Ellis. The growth is driven by a catalyst without interfering with the reaction. In most cases, source materials such as liquid Ga are heated in the presence of NH₃ to vaporize the source material at elevated temperature as well as to cause dissociation of NH₃ to take part in nitridation reaction. At a fixed temperature, the vapor phase reactants dissolve in the liquid-phase of metal catalyst. When the liquid metal reaches its solubility limit during the continual addition of reactant species, it starts precipitating into a solid phase. As long as the reactant supply continues, the precipitation is continuous that leads to formation of NW. Transition metals such as Fe, Ni, Co and their oxides are also found to be efficient catalysts for the precipitation of GaN materials from a molten catalyst droplet supersaturated with the metal vapor. Au is a better choice of catalyst for synthesizing GaN nanostructures owing to its high defect formation energy (~4eV) in GaN as compared to Ni substitution (1.2 eV). Hence, product purity is expected to be better while using Au catalyst even though it has poor
solubility for N as compared to other transition metals, like Fe and Ni. However, the radial size distribution of target NWs is strongly influenced by the catalyst particle size. The orientation of the NW can also be controlled via epitaxial growth followed by VLS process.\(^1\) The length of the 1D nanomaterials depends on the reaction time and reactant flux. The choice of catalysts and dopant concentrations also plays a pivotal role. A schematic representation of the VLS based growth process is shown in figure 3.1(a). Catalyst nanoparticulates are often observed in negligible amounts at the tip of the NW [Fig. 3.1(b)].

In contrast with above observations, the VS mechanism relies on direct crystallization of solid from a vapor or via self-catalytic process. VS process excludes inclusion of foreign atoms, which are ubiquitous in the catalytic VLS growth process. In the VLS process, the dominant morphology typically observed is NWs because the liquid catalyst droplet defines nucleation and growth. In contrast, the VS process often results in more varied morphologies, including NWs, NTs, nanotips, NPs, owing to the lack of constraints imposed by the catalyst. In addition, the growth is highly anisotropic in nature despite being relatively simple while compared to VLS process.

![Diagram](image.png)

Fig. 3.1 (a) Schematic representation of the growth of GaN NWs via VLS process; (b) a typical FESEM image of an Au terminated NWs.

However, in all these cases a direct reaction of metallic Ga under flowing NH\(_3\) at a temperature above 900 °C was used for the growth of various GaN nanostructures that follows the reaction:
\[ 2\text{Ga (g)} + 2\text{NH}_3 (g) = 2\text{GaN (s)} + 3\text{H}_2 (g) \]  

(1)

From this perspective, VLS process has been widely exploited in demonstrating controlled growth of 1-D nanostructures. However, the underlying mechanistic concepts involved in the VS growth process for large-scale realization of 1-D GaN nanostructures are still in infancy. In fact, reports on VS grown GaN nanostructures with controlled morphology are limited owing to the difficulties encountered in controlling important growth parameters such as Ga and N flux rates and subsequent switching between the fluxes. Understanding the variation of morphology and crystallographic orientation is very important while building devices out of these highly anisotropic GaN nanostructures.

3.2 Surface Polarity in GaN vs Morphology:

Generally, WZ-GaN contains polar and nonpolar low-index surfaces. When the number ratio between Ga and N of any cleaved surface is 1:1 (i.e. stoichiometric) then, this surface is termed as non-polar. On the other hand, any surface on which the number ratio is out of 1:1 is termed as polar. In principle, the number of polar surfaces available is infinity.\(^8\)

![Fig. 3.2 (a) Atomic geometry of cleaved GaN plane constitutes of polar and non-polar surfaces; (b) Schematic diagram showing the dependence of Ga reactant surface diffusion length on the reaction condition.\(^8\) Under the N-rich condition, the surface diffusion lengths of Ga on polar and non-polar surface are relatively same that results in a small length scale of polar surface, while Ga-rich condition favors a large length scale of polar surface.](image)

However, in case of GaN, only energetically favorable polar surfaces are either Ga- or N-terminated low index surfaces. As shown in figure 3.2(a), \(\{0001\}\) (c-planes) and \(\{10\overline{1}1\}\)
(slanted against the c-axis) are typical polar surfaces that consists of either Ga or N atoms, whereas, \{10\bar{1}0\} and \{\bar{1}2\bar{1}0\} are non-polar surfaces. The difference in growth rates of these aforementioned structurally distinct surfaces has a significant influence on the resulting nanostructure morphology and growth orientation. Interestingly, Polar surfaces in GaN are always favored to be Ga stabilized (one dangling bond per atom in \{0001\} and three in \{000\bar{1}\}) irrespective of the chemical environment (Ga or N-rich), whereas the non-polar surfaces maintain their Ga-N stoichiometry.\textsuperscript{8,9}

These Ga-stabilized polar surfaces play a significant role during growth of GaN nanostructures. As a matter of fact, the Ga adatoms/reactants have a significantly lower diffusion barrier on the polar surface [\(\approx 0.4\,\text{eV along the (0001)}\)] because the adsorbate-surface interaction is dominated by very weak delocalized metallic Ga–Ga bonds owing to the lower melting point of Ga (30 °C).\textsuperscript{8} Notably, it is observed that, in case of GaN thin films grown in [0001] direction, Ga-rich condition results in a broad and smooth polar surface whereas N-rich condition induces formation of roughness or multiple facets that are composed of polar and nonpolar surfaces.\textsuperscript{10} An important consequence is that the effective diffusion length of Ga reactant on the Ga stabilized surface is very sensitive to the chemical environment. If excess N adatoms/reactants are available (N-rich condition), it will frequently interrupt the free surface diffusion of Ga by forming Ga-N covalent bond and reduce the Ga diffusion length. Once the diffusion length becomes shorter than the mean distance between the binding sites, a statistical roughening and formation of facets is expected. Furthermore, in a Ga rich regime, Ga-adatoms are highly mobile and a step flow mode is expected. Consequently, a smoother surface morphology with a lower density of stacking faults is expected.

These reasonings are applied to understand the observed morphological variations in our GaN nanostructures. In this regards, various CVD process parameters like incoming
Ga/N flux rate and incubation time were varied for the optimization of particular GaN nanostructure synthesis such as NW, NT, nanotips and NPs.

3.3 Vapor-Liquid-Solid Growth: GaN Nanowires

3.3.1 Synthesis of GaN Nanowires:

In all the GaN nanostructure synthesis processes used in the present work, Ga was employed source and NH$_3$ as a reactant gas in a thermal CVD system. In detail, molten Ga (~0.5 mg) is placed on the up-stream of a high pure ceramic crucible, and at the same time, different substrates (for NWs and NTs) coated with 2-10 nm of Au are kept at a distance of 3-8 cm away from the Ga source. The substrates are often placed in both vertical and horizontal directions. The source and the substrates loaded in the ceramic crucible and kept at the centre of the quartz tube within a horizontal tube furnace (detailed in the experimental section). The system is pre-evacuated at a temperature of 300-400 °C down to a base pressure of one mbar [Fig. 3.3(a)]. Then, the temperature of the furnace is gradually increased at a rate of 10-50 °C/min from 400 °C to the reaction temperature of 800-1000 °C, and kept for 10 to 300 min under a constant flow of 10 sccm of NH$_3$. In all these cases, growth occurs at atmospheric

![Fig. 3.3 (a) Temperature profile with respect to the growth time and partial pressure inside the chamber; (b) shows the different temperature ramping rate employed for the growth of NWs with varying morphology.](image)

Fig. 3.3 (a) Temperature profile with respect to the growth time and partial pressure inside the chamber; (b) shows the different temperature ramping rate employed for the growth of NWs with varying morphology.
pressure. After the reaction gets over, the furnace is cooled down to room temperature and the resulting nanostructures are collected for further study. Typical temperature profile with respect to the base pressure and growth time in the CVD [Figs. 3.3(a,b)] system employed for growth of GaN NWs with varying morphology. Different NWs morphologies, namely, cylindrical, hexagonal, triangular, and square types could be realized by precisely controlling the ramping rate of temperature [Fig. 3.3(b)] from 400 to 900 °C and accurate inclusion of NH₃ gas flow. The optimum growth parameters used are as follows:

- Temperature of Substrate = 900 °C
- Base Pressure = 1 mbar
- Deposition pressure = 1000 mbar
- NH₃ Flow rate: 10 sccm
- Distance between substrate and source = 30 mm

3.3.2 Morphological and Structural Variation:

In an effort to optimize the growth morphology for a particular set of NW, several CVD parameters were considered. Apart from the aforementioned optimized CVD parameters, variation of incubation time was carried out, which in turn depended on the ramping rate of temperature between 400 to 900 °C, as a most decisive parameter. It is found that faster ramping rate [Region I, Fig. 3.3(b)] increases the roughness as well as causes diameter oscillation along the length of the NWs [Figs. 3.4(a-c)], whereas slow ramping rate [Region II and III, Fig. 3.3(b)] gives rise to relatively smooth and controlled NWs [Figs. 3.4(d-f)]. During the faster ramping rate, it is observed that an amorphous layer is formed initially in the base region of the NWs and further growth occurs over this layer irrespective of the growth duration. Figures 3.5(a,b) show a cross sectional view of NWs grown on Si substrate for 180 min and 30 min, respectively. In both of these samples, an amorphous layer of thickness ~ 0.5 to 2 µm is observed. It may be arising due to over supplied of Ga vapor species during the nucleation stage. On the other hand, samples grown with a slow ramping
Fig. 3.4 FESEM micrographs of GaN NWs grown in (a-c) faster and (d-f) relatively slow ramping rate of temperature in the CVD system; Faster temperature ramping rate randomizes the growth whereas slow ramping rate gives smooth and well defined geometry of NWs.

Fig. 3.5 Cross-sectional FESEM images of NWs grown under faster temperature ramping rate for (a) 180 min and (b) 30 min growth condition; (b) slow ramping rate of 30 min. rate (more than 20 min) possess smooth and well defined geometry [Figs. 3.5(c)]. Notably, these NWs grow presumably over the Si substrate directed by the metal catalyst while maintaining a specific geometry.

Apart from the above optimized conditions used for the growth of well-directed NWs, it is noticed that catalyst particle size also influences the diameter of the resulting NWs.
Fig. 3.6 TEM images of GaN NWs with catalyst particle (a) compared with NW diameter, (b) bigger than NW diameter, and (c) for a long NW with small catalyst particle compared to NW diameter.

Bigger catalyst particles compared to the NW diameter induces severe secondary effects such as diameter oscillation and roughness. Figure 3.6(a) shows an optimally sized catalyst particle in order to obtain NW of a regular size and atomically smooth sidewalls. Tapering and diameter modulation are observed when catalyst particle size exceeds the size of NW diameter [Fig. 3.6(b)]. In contrast, the smaller catalyst particles are able to maintain uniform cross-section of the NW over several micrometers in length without tapering [Fig. 3.6(c)]. Together, choosing a small catalyst particle (3 nm Au film) and slower ramping rate (20 to 35 min), it is possible to obtain wide control over NWs growth with particular geometry.

3.3.2.1 Hexagonal GaN Nanowires:

Figure 3.7(a) shows lattice resolved TEM image corresponding to the perfectly hexagonal GaN NW. A smaller catalyst particle of ~10 nm is observed at the tip of the NW as revealed by the FESEM images [as shown in the inset as well as in Fig. 3.4(f)]. The near-perfect lattice fringes with an inter-planar spacing of 2.76 Å, corresponds to (10\text{1}0) non-polar plane of WZ- GaN. The growth of NW is subtended along the c-axis.
smooth surface termination with very small roughness amplitude extending up to 2-3 atomic layers is observed. The corresponding SAED pattern further demonstrates that the NWs are single crystalline in character, which can be indexed to [0001] zone axis of the WZ-GaN. The clear electron diffraction data reveal that the NW is crystalline and ideally possesses neither extended defects like dislocations nor stacking faults.

### 3.3.2.2 Triangular GaN Nanowires

Figure 3.8(a) shows an HRTEM image of a triangular NW with Au metal catalyst at the tip. These NWs are obtained in 1 h growth condition with temperature ramping rate of 25 min and keeping the substrate in a vertical position that is 30 mm away from the Ga source. While resolving the lattice image during the HRTEM analysis, only one face could be seen at a time and other inclined face becomes more obscure. This confirms that the NWs are of triangular type [Fig. 3.8(a)]. One of the exposed faces is composed of (0001) plane and the NW is subtended along [1$ar{1}$00] direction. The NW grown in this direction are enclosed with(1$ar{1}$20), ($ar{1}$120) and (0001) side planes. Figure 3.8(b) is the fast Fourier transformed (FFT) image corresponding to the dotted square region from the figure 3.8(a). It reveals that...
the tip region is composed of two distinct phases which are mostly belongs to WZ-GaN with zone axes along [0001] and the encircled region corresponds to cubic Au phase. The inverse Fourier transformed (IFT) image reveals that well crystalline WZ-GaN phase is formed only beneath the Au droplet [Fig. 3.8(c) and inset], whereas the tip region is mostly dominated by cubic Au phase [Fig. 3.8(d) and inset]. The lattice spacing belonging to the catalyst droplet at the tip can be indexed to (200) plane of cubic Au. This infers that only Ga precipitates on the Au droplet and subsequent nitridation occurs around the neck region forming GaN phase because N$_2$ has poor solubility in Au. This result is consistent with the reported arguments made by many research groups towards elucidation of the underlying VLS mechanism of NW growth process.\textsuperscript{7}
3.3.2.3 Wurtzite/Zinc-blende Biphase Homostructure in Triangular GaN Nanowires:

A unique WZ and zinc-blende homostructure of GaN was formed in a typical case of triangular NW. The HRTEM image of a triangular NW with alternating strips parallel to the NW longitudinal direction is shown in the figure 3.9 (a) and in the inset. It indicates a sharp transition of ~1-3 atomic layers between phases. An interplanar spacing of 2.68 Å is

Fig. 3.9 (a) HRTEM image of a biphase GaN NW; inset shows the TEM image of a triangular shaped NW (upper right), and (bottom right) showing a schematic representation along with the growth direction of the NW; (b) SAED pattern from the biphase region showing the presence of WZ and zinc-blende (noted as ZB) phase of GaN; (d) IFT lattice imaging corresponding to the zinc-blende phase of GaN.
measured from the base region, which has been assigned to the d-spacing of $(10\overline{1}0)$ planes of WZ-GaN. The observed value is less than that of the bulk lattice spacing ($2.76 \text{ Å}$). However, this is assigned as c-plane keeping in mind that these planes are inclined to the electron beam position during TEM measurements and hence a reduction of the bulk value is expected.

SAED patterns are used to substantiate the presence of biphasic structure inside the NW, as shown in figure 3.9(b). The diffraction pattern is composed of both WZ ([$0001$] zone axes) and zinc-blende ([110] zone axes) phase of GaN. It was further confirmed with FFT and IFT in the same area where SAED is taken. The IFT lattice images corresponding to the zinc-blende phase is shown in figure 3.9(c). By indexing appropriate diffraction spots it is concluded that the growth direction of the NW is in the $[\overline{1} \overline{0}0]$ direction of the WZ phase, and in the $[110]$ of zinc-blende phase. On the other hand it is found that triangular NW is grown along the $[1\overline{2}10]$ direction [Fig. 3.10(a)] exhibiting a large number of stacking faults [Figs. 3.10(a,b)] on the basal plane similar to that reported in the literature.\textsuperscript{11} The formation of such structure may arise as a result of any small fluctuation in growth parameters or from strain accumulation and relaxation during growth process.\textsuperscript{11,12}

![Fig. 3.10 (a) HRTEM image of a triangular NW grown along $[\overline{1}\overline{2}10]$ direction of WZ-GaN phase; Inset showing the SAED pattern index to $[\overline{1}\overline{1}00]$ zone axis; (b) a typical IFT lattice image of transition region which clearly showing the presence of stacking faults on the surface.](image-url)
3.3.2.4 Square Shaped GaN Nanowires:

Figure 3.11(a) shows a HRTEM image of a square shaped NW with perfect lattice fringes. The corresponding FESEM image [Fig. 3.11(b)] clearly illustrates the presence of distinct edges of these NWs which are grown over 1 h duration with 35 min of temperature ramping rate where the substrate was kept in a vertical position 30 mm away from the Ga source. The observed bright patches over the NW surface emerge from Au nanoparticles deposited for the purpose of SEM analysis. Fig. 3.11(c) shows the SAED pattern corresponding to the figure 3.11(a), which can be indexed to [0001] zone axis of WZ-GaN. By indexing this diffraction pattern, it is found that these square shaped NWs are grown along [1120] direction and these are enclosed with {0001} and {1100} side faces. These

![HRTEM and FESEM images](image)

Fig 3.11 (a) HRTEM image of a square shaped GaN NW grown along [1120] direction and enclosed with {0001} and {1100} side faces; (b) Typical cross-sectional FESEM images of the vertically aligned square shaped GaN NW, Inset-images are from different set of sample with Au nanoparticle at the tip; (c) SAED pattern of a NW, corresponding to the HRTEM image, indexed to [0001] zone axis of WZ-GaN phase.
NWs grow on the Si(100) substrate via VLS method and vertically aligned with aspect ratio reaching around ~350 [Fig. 3.5(c)]. In addition, stacking faults or dislocation lines are also not observed in this growth condition used for square shaped NWs. Such materials are ideal candidates for NW based optoelectronics.

3.3.3 Steady State Growth of Nanowires:

It is believed that the catalyst mediated VLS mechanism is very stable with the alloy droplets which generally do not get consumed even when the reaction conditions change. However, recent experiments differ, which suggest that even under cleanest growth conditions, VLS mechanism may not produce long, thin, uniform, single-crystal NWs of high purity (Fig. 3.12). The electrical, hydrodynamic, thermodynamic, and surface tension related properties have strong influence on NW growth. Furthermore, parameters accruing from mesoscopic effects like nanoparticle seeds, charge distribution in catalyst droplets, electronegativity difference between catalyst droplet and reactive NW vapor species, growth

![Diagram of NW growth](image)

Figs. 3.12 (a-e) Schematic representation and the corresponding observed NWs (indicated by arrow) grown by VLS mechanism with metal catalyst at the tip.
temperature, and chamber pressure also play an important role in VLS based growth processes. Indepth analysis on various issues illustrate that the VLS process may generate NWs of various shapes and sizes with slight fluctuations in any intriguing parameters (Fig. 3.12). Most of the NWs exhibit metal droplets at the tip region in varying sizes that dictates the resulting morphology as well. The different shapes and morphologies of NWs observed include; 1) cylindrical [NW of uniform diameter with catalyst droplet of equal size; Fig. 3.12(a)], 2) conical at the tip [uniform morphology up to a certain extent but narrow down around the tip region with catalyst droplets of smaller size; Fig. 3.12(b)], 3) needle shape [the NW is gradually thinned as it grows, and is pointed at the droplet edge; Fig. 3.12(c)], 4) tapered NWs [the catalyst droplet is much bigger than the NW diameter; Fig. 3.12(d)] and 5) diameter modulated NWs [Fig. 3.12(e)]. Keeping all this in mind, it is found that the variation in NW morphologies with growth condition is in close agreement with the simple steady state model propounded by Kuo et al. It explains that the NW with a smaller catalyst droplet is ideal for obtaining regulatory growth than an NW with a larger size catalyst droplet. It is assumed that Ga is activated through the catalyst and the reaction takes place only at the AuGa/GaN interface, and, NH₃ does not dissolve into the catalyst, as shown in figure 3.13.

![Fig. 3.13 Schematic representation showing steady state growth of NWs with (a) a smaller catalyst droplet and (b) a larger catalyst droplet; Assuming that Ga is activated through the catalyst and the reaction takes place only at the AuGa/GaN interface.](image-url)
When the radius of catalyst particle \( r_{Au} \) is smaller than the radius of the NW \( r_{NW} \), as illustrated in figure 3.1(a), the conditions: \(^7\)

\[
R_{in} = \alpha \cdot r_{Au}^2 \\
R_{GaN} = \beta \cdot r_{NW}^2
\]

where \( R_{in} \) and \( R_{GaN} \) are incoming flux rates for Ga and formation rate of GaN, respectively; \( \alpha \) and \( \beta \) are rate constants, would be applicable. Under these conditions, the growth of NW always converges to a certain critical radius meaning thereby that it does not depend much on the mean fluctuation of \( R_{in} \) [Figs 3.13(a) and Figs. 3.4(d-e)]. Whereas for \( r_{NW} < r_{Au} \), as shown in figure 3.13(b), the growth rate of GaN becomes \(^7\)

\[
R_{GaN} = \delta \cdot r_{NW}
\]

where \( \delta \) is rate constant. The diffusion of N takes place only in the circumferential region between Au and GaN. Here, the growth of the NW is likely to become unstable beyond a critical point. This situation often leads to occurrence of diameter oscillation and tapering in NWs [Fig. 3.13(d) and Figs. 3.4(a-c)].

This study finds that increase in diameter of the droplet with a time of tapered NWs results primarily from the gradual incorporation of oversupplied NW species into the catalyst mediated droplet. It also finds that optimum compositions of the droplet constituents are crucial for VLS NW growth. In general, smaller the size of the catalyst particle lower is the probability of formation of disorder and defects in the resulting NWs grown through VLS process.

### 3.3.4 Optical Properties:

The detailed studies of optical phonons and types of native defects present in the as-grown GaN samples are essential for their further uses as light emitters and detectors. In this
regard, optoelectronic properties of NWs are studied using Raman and Photoluminescence spectroscopy.

3.3.4.1 Raman Scattering Study:

The phonon dispersion of hexagonal WZ-GaN has a close relation to that of zinc-blende GaN (cubic) phase. In the hexagonal structure, the primitive cell contains four atoms (two Ga-N pairs) while it contains only two atoms in the cubic phase (one Ga-N pair). Therefore, the number of phonon branches in the WZ structure is doubled than that of zinc-blende phase. Furthermore, as shown schematically in figure 3.14, the phonon dispersion along $\Gamma \rightarrow A$ [0001] direction in the WZ structure can be constructed by simply folding the phonon dispersion of the cubic structure along $\Gamma \rightarrow L$ [111] direction in half with respect to the $A$ point. The Brillouin zone of the zinc-blende extends twice longer than that of WZ owing to

![Fig. 3.14](image_url)

(a) Schematic representation of the phonon dispersion in wurtzite and zinc-blende structure [with permission, Ref. 14]; Phonon branches along [111] in the zinc-blende structure is folded to approximate those of wurtzite structure along [0001] (b) Optical phonon modes in the wurtzite structures; (c) Schematic representation of surface phonon and bulk phonons.
the difference in the length of unit cells along the direction. In addition, in WZ structure, some phonon branches are split due to the electrostatic field created by the polar character of the phonons. From the group theory analysis, WZ structure has eight sets of phonon normal modes at the $\Gamma$ point, $2A_l + 2E_l + 2B_l + 2E_2$. These modes are classified into Raman ($2A_l + 2E_l + 2E_2$), silent ($2B_l$), and infrared active ($A_l + E_l$). Although the GaN is noncentrosymmetric, the $A_l$ and $E_l$ modes are further split into LO (longitudinal optical) and TO (transverse optical) components. The atomic displacement schemes of these optical modes are depicted in figures 3.14(b,c).

The typical Raman spectrum of GaN NWs samples using Ar$^+$ ion (514.5 nm) laser excitation source is shown figure 3.15. The peaks at 533, 560, 569, 725 cm$^{-1}$ agree with the phonon vibration frequencies of $A_1$(TO), $E_1$(TO), $E_2$ (high), $A_1$(LO), respectively, of the crystalline WZ-GaN.$^2$ The frequencies and assignments of the phonon modes corresponding to figure 3.15 are listed in Table 3.1. Within the experimental error, our results are agreed well with those of reported value for GaN bulk.$^{14,15}$ In polar semiconductor NWs, peaks in the Raman spectra are usually identified with the TO and LO phonon modes at zero wave vector ($q = 0$), because the wavelengths of light used as an excitation source were a small

![Raman spectrum](image)

Fig. 3.15 Room-temperature Raman-scattering spectrum of GaN NWs showing the experimentally observed data and the Lorentzian fits for the individual peaks.
fraction of the Brillouin zone. The frequencies of these peaks are similar to that reported for the bulk. However, the long-range nature of the electromagnetic fields associated with the phonons has also derived from the “shape effect” for polar semiconducting NWs. The result of shape effect can induce new optic modes whose frequency may differ by 2-10 cm\(^{-1}\) from that of the \(q = 0\) optic mode.\(^2\) Influence on the intensity of LO mode in the presence of surface plasmon resonance of Au nanocluster is insignificant because the amount of Au in the catalyst droplet at the tip of the NW is very small.

Table 3.1 Raman modes in the bulk and various GaN nanostructures reported in this study at 300 K, and the corresponding phonon lifetime (for NWs) and symmetry assignments; ZB refer to the zone-boundary phonon. The Raman spectra of GaN nanotip, nanoparticles, and nanotubes are discussed subsequently.

<table>
<thead>
<tr>
<th>Bulk GaN (Ref. 14,15)</th>
<th>GaN Nanowire</th>
<th>GaN Nanotip</th>
<th>GaN Nanoparticles</th>
<th>GaN Nanotube</th>
<th>(\tau = (2\pi\tau)^{-1}) ps [Bulk ~1-10 ps]</th>
<th>Symmetry Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>254</td>
<td>253</td>
<td>265</td>
<td>252</td>
<td>0.32</td>
<td>ZB</td>
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<tr>
<td>-</td>
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<td>421</td>
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<td>0.9</td>
<td>ZB</td>
</tr>
<tr>
<td>533</td>
<td>533</td>
<td>535</td>
<td>535</td>
<td>541</td>
<td>0.28</td>
<td>(A_1(\text{TO}))</td>
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<tr>
<td>561</td>
<td>560</td>
<td></td>
<td></td>
<td></td>
<td>0.15</td>
<td>(E_2(\text{TO}))</td>
</tr>
<tr>
<td>569-570</td>
<td>569</td>
<td>567</td>
<td>569</td>
<td>571</td>
<td>0.36</td>
<td>(E_2(\text{high}))</td>
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<tr>
<td>735</td>
<td>725</td>
<td>726</td>
<td>732</td>
<td>732</td>
<td>0.35</td>
<td>(A_1(\text{LO}))</td>
</tr>
<tr>
<td></td>
<td>652</td>
<td>634</td>
<td>609</td>
<td>624</td>
<td>0.13</td>
<td>(\text{SO}(A_1))</td>
</tr>
<tr>
<td></td>
<td>691</td>
<td>693</td>
<td>702</td>
<td>692</td>
<td>0.24</td>
<td>(\text{SO}(E_1))</td>
</tr>
</tbody>
</table>

The observed phonon peaks for the GaN NWs broaden substantially. The line width (FWHM) of these phonon peaks can be correlated with the phonon lifetime as \((2\pi\tau)^{-1}\). The FWHM increases roughly by a factor of 2 to 5, as compared to that for the bulk. The lifetime of optical phonons in these NWs is calculated and found to be a fraction of picoseconds (Table 3.1). This shorter lifetime in NWs than that of the bulk (1-10 ps) is due to the increased anharmonic interaction of the optical phonons in the former, resulting the possibility of the decay into acoustic branches.\(^2\)
Four additional modes are also observed at ~ 254, 421, and 652, and 691 cm\(^{-1}\), all of which are not allowed by the \( C_{4v} \) space group in first-order Raman scattering at the zone center. Possible mechanisms that could bring about these features are discussed as follows. In the reduced dimension for nanostructured materials, the relaxation of the \( q=0 \) selection rule due to the effect of finite crystallite size not only broadens the Raman-allowed modes, but also causes new modes to appear that correspond to \( q \neq 0 \) phonons. Two extra peaks seen at ~254 and 421 cm\(^{-1}\) in GaN NWs could possibly be attributed to the zone boundary (ZB) phonons.\(^{16}\) It is worth mentioning that the 254 and 421 cm\(^{-1}\) features are consistently observed for all types of GaN NWs samples. Raman bands around 652 and 691 cm\(^{-1}\) may be identified with SO modes, as the larger surface-to-volume ratio along with surface corrugation and roughness inducing instability in surface potential (SP) along the diameter of the NW. The instability in SP may activate the SO phonon in the Raman scattering. This phenomenon were also reported extensively for II-VI, and other group III-nitrides.\(^{17}\) In all these cases the broken translational symmetry of surface wave vector, induced by the surface disorder, cause the surface to absorb the phonon momentum in units of \( q=2\pi/\lambda \), where \( \lambda \) is the length of the surface modulation. In case of a perfect surface, the SO modes cannot be observed optically due to momentum conservation constraints. However, optical detection of the surface modes is possible only if a source of wave vector is supplied through strong Fourier components of the surface potential.\(^{17,2}\)

In order to understand the SO band quantitatively in our NWs, theoretical calculation was performed considering the cylindrical geometry of GaN NWs. The dispersion relation \( \omega_{SO}(q) \) for an infinite long cylindrical wire, in the limit where the phonon wave vector \( q >> \omega/c \), can be written as\(^{18}\)

\[
\omega_{SO}^2 = \omega_{TO}^2 \frac{\varepsilon_0 - \rho_{nx}\varepsilon_m}{\varepsilon_\infty - \rho_{nx}\varepsilon_m} 
\]

(3.4)
where $\omega_{TO}$ is the frequency of the TO phonon, $\varepsilon_0$ and $\varepsilon_\infty$ are the static and high frequency dielectric constant of the material, and $\varepsilon_m$ is the dielectric constant of the medium. $\rho_{nx}$ is given by

$$
\rho_{nx} = \frac{K_1(x)I_0(x)}{I_1(x)K_0(x)}
$$

(3.5)

Where $I_j$ and $K_j$ are the modified Bessel functions and $x = qr$ ($r$ being radius of the nanostructure). From the Lyddane-Sachet-Teller relation, $\omega_{LO}^2/\omega_{TO}^2 = \varepsilon_0/\varepsilon_\infty$, the LO-TO splitting of $E_1$ mode gives a static dielectric constant of $\varepsilon_0 = 10.2$ using $\varepsilon_\infty = 5.8$. The SO phonons associated with $A_1$(TO) at 533 cm$^{-1}$ and $E_1$(TO) at 560 cm$^{-1}$ are calculated for GaN by taking the $qr$ value of 1.07, which yields SO phonon frequencies ($\omega_{SO}$) pertaining to $A_1$ (654 cm$^{-1}$) and $E_1$ (688 cm$^{-1}$) characters [Fig. 3.15]. Hence, the observed peaks around 652 and 691 cm$^{-1}$ may be assigned to SO modes in GaN.

![Figure 3.16](image)

Fig. 3.16 (a) Calculated SO phonon frequencies as a function of qr, full curve: SO($E_1$), dashed curve: SO($A_1$), horizontal lines are the LO and TO frequencies of $E_1$ and $A_1$ modes, Vertical dotted line is marked for qr=1.07; (b) Morphological study at high resolution for the GaN nanowire with arrows showing the modulation of the surface in the range of 150-300 nm.

The magnitude of surface roughness determines the SO peak intensity owing to the breakdown of the translational symmetry of the SP. The wavelength $\lambda = 2\pi/q$ (qr=1.07; $r$
~250) corresponding to the perturbation of surface potential can be estimated as ~ 1500 nm for the GaN nanostructures (using the dispersion relations in Fig. 3.16(a) and for typical nanostructure of diameter of ~300 nm). Surface roughness with a modulation of ~150-300 nm is observed [indicated by the arrows in Fig. 3.16(b)] with any integral multiple equivalent to the $\lambda$ (10x150 nm=5x300 nm=1500 nm) will be sufficient to initiate the breakdown of translational symmetry for the contribution of SP toward SO modes. This makes the intensity of the surface mode comparable to that of the other phonons. This surface modulation or self-oscillating nature of the NW cross section, stemming via VLS mechanism, is related to growth conditions such as temperature, impurities, and supersaturation. Moreover, the appearance of SO modes in the phonon spectra should be a general indicator of the presence of a corrugated surface along the wire cross section.

### 3.3.4.2 Photoluminescence Study:

Typical Low temperature micro-PL spectra of NWs grown under optimized condition (grown for 1 h) show strong emission in the region of photon energy 3.1 - 3.5 eV [Fig. 3.17(a)]. The PL emission line at 80 K is dominated by a strong peak at 3.394 eV which has been assigned to the near band-edge-emission (NBE) line of WZ-GaN.$^{3,19,20}$ As the temperature increases, its intensity gradually decreases, due to the thermal dissociation of carriers. It is interesting to note that the NBE is the only dominating emission process in the as-grown NWs even at 300 K. The NBE is blue shifted by 20 meV while decreasing the temperature from 300 to 80 K. In addition, the intensity of NBE at 80 K is increased by ~ 95% to that observed at 300 K. It is observed that as temperature decrease from 300 to 80 K, an additional shoulder appears at 3.43 eV and on the lower-lying side of NBE. The peak at 3.43 eV corresponds to the recombination of exciton bound to neutral donors ($I_2$).$^{20}$ The additional peaks observed at 3.31, 3.28 eV and 3.19 eV have been assigned to zero phonon line and their phonon replica of the free-to-bound (FB) emission, respectively.$^{20}$ The broad
full-width-half-maximum (FWHM) of the PL spectra probably reflects to the wide size distribution of GaN NWs as well as to the small crystallite sizes.

In the case of WZ/zinc-blende biphase homostructure in triangular GaN NWs, however, peculiar PL spectra are observed [Fig. 3.17(b)]. Two broad peaks at 3.51 and 3.27-3.3 eV are dominated in the room temperature PL spectrum. Interestingly, the relative
intensity of the two leading peaks increases simultaneously while decreasing the temperature from 300 K to 80 K. The peak at 3.51 eV corresponds to $I_2$ line of WZ-GaN, which is blue shifted by ~70 meV. On the other hand, zinc-blende GaN phase usually shows near-band-edge emissions at 3.27–3.30 eV at low temperatures.\textsuperscript{21,22} Therefore, the peak around 3.27-3.3 eV is assigned to the NBE emission of cubic GaN. It is in good agreement with the observed HRTEM results [Fig. 3.9], which indicates the existence of cubic GaN layers in the hexagonal GaN NW matrix. In contrary, a donor-acceptor pair (DAP) emission often appears at 3.28 eV in the low temperature PL spectra of WZ-GaN.\textsuperscript{3} However, the uniform increase in the intensity of relevant bands does not support DAP as the origin of the observed 3.27-3.3 eV peaks.\textsuperscript{22} In fact, the very thin zinc-blende layers embedded in the WZ matrix may be regarded as stacking faults in which electrons can be confined in zinc-blende layers that further attract holes via Coulomb interactions to form excitons.\textsuperscript{22} All these process are responsible for the observed blue shift of $I_2$ line as well the broadening of all the relevant emission bands. The schematic representation of the various emission processes in the WZ-GaN and the WZ/zinc-blende biphase homostructure of GaN NWs are shown in figures 3.17(c) and (d), respectively.

3.4 Vapor-Solid (VS) Growth: GaN Nanotips and GaN Nanoparticles

VS process excludes inclusion of foreign atoms, which are ubiquitous in the catalytic VLS process. In this context, efforts are being made worldwide to grow uniformly distributed 1-D GaN nanostructures in a self catalyzed process via molecular beam epitaxy using a template approach along with controlling the Ga and N flux rates.\textsuperscript{23-26} It is based on the fact that large anisotropy with respect to Ga and N adatom diffusion along the polar and non-polar surfaces leads to formation of 1D NWs and NRs. However, the underlying mechanistic concept involved in uniaxial self-catalyzed growth of 1D GaN nanostructures is still in
infancy. As a matter of fact, reports on self-catalyzed CVD grown GaN nanostructures with controlled morphology are limited owing to the difficulties encountered in controlling important parameters such as Ga and N flux rates and subsequent switching between the fluxes. Growth modes significantly influence the properties of resulting nanostructures, which include shape, size, and crystal structure. Apart from NWs, there are considerable interests in exploring various other forms of GaN nanostructures. Here, an effort has been made to cast light on the evolutionary stages of the nucleation mediated morphology of nanotips, NPs and NTs.

Wide band gap nitride based nanotips with low work function are known to be hard and chemically stable. These qualities make it potentially useful for applications in the field emission devices and scanning near field optical microscopy. Until now, electron beam or focused-ion-beam (FIB) lithography and dry etching techniques, employing SiO₂ nanomask and subsequent reactive ion etching, are widely used for large area growth of aligned nanotips. The processes are limited to specific substrates only. Syntheses of well-aligned GaN nanotips in self-catalytic process have raised sufficient scientific excitement.

3.4.1 Materials and Methodology:

Nanotips and NPs, were synthesized employing same CVD reactor used for the growth of NW. The only difference employed here is the choice of substrate without catalyst. In this case, the Alumina boat itself act as substrate for the growth of nanotips and NPs by playing with the incubation time alone in the optimum growth conditions used for NW growth. For the growth of ultra-long nanotips, a slow temperature ramping rate of ~15 °C per min was maintained, whereas a faster rate of ~ 40 °C per min was maintained for the growth of NPs. In both the cases, 10 sccm of NH₃ was bleeding after the temperature reached around 850 °C, and the growth was carried out at atmospheric pressure. Reaction times and temperatures were varied from 1-3 h to obtain substantial amounts of nanotips/NPs. After the
reaction was over, large quantity of nanotips/NPs were collected from the alumina boat around the source material. The reaction parameters, namely, growth rate, temperature, growth time, and NH$_3$ partial pressure were varied independently to identify the growth mechanism of nanotips. Growth temperature dependent evolution of NPs morphology was studied by varying growth temperature between 880-950 °C. Moreover, the optimized values for the growth of nanotips/NPs were found only at the temperature of 900 °C and NH$_3$ flow rate of 10 sccm.

3.4.2 Characterization

3.4.2.1 Morphological and Structural Properties:

The high-yield, free standing nanotips grow over a large area around the Ga source kept inside alumina boat as substrate [Figs. 3.18(a,b) for 1 h and (c) for 3 h]. The magnified optical micrograph of 1 h grown nanotips is shown in figures 3.18(d). Figure 3.18(e) shows typical FESEM images of a 3 h grown single nanotip and a magnified image of the base region.

Fig. 3.18 (a) Large scale growth of nanotips over an area of 10 mm; (b) a set of nanotips grown in 1 hour and (c) in 3 h; (d) Magnified optical microscopic image of nanotips grown for 1 h, FESEM image (d) of a 3 h grown nanotips; inset shows the broken part of the tip region; (f) the transition of the Ga-rich base region of the N-rich smooth conical region.
region that depicts smooth transition from columnar to conical morphology [Fig 3.18(f)]. Most of the conical nanotips are solid and homogeneous [inset of Fig. 3.18(e)]. The samples grown over 1 h duration possess a base diameter of ~20 µm, tip diameter having a value less than 200 nm and lengths extending up to hundreds of micrometers. The aspect ratio (length/base diameter) is of the order of 20 which is one order of magnitude less than the

![Image](image_url)

**Fig. 3.19** Optical microscopy images of the formation of (a) Ga droplet by annealing Ga nodule in 10 min; Nucleation of GaN by self agglomeration followed by growth of nanotips after (b) 20 min, (c) 30 min, (d) 60 min, (e) 90 min and (f) 180 min. The nanotip grown above 1 h possesses sharp tip type morphology.

sample grown over 3 h duration. At the same time, the base diameter of 1 h grown nanotips is nearly half that of 3 h grown nanotips. Nanotips are grown with varying time to observe the evolution of the tip structure over a period of 10 to 180 min [Fig. 3.19(a-f)]. The formation of Ga droplet of size ~5-20 µm from the Ga nodule and further growth of nanotips are shown with increasing growth period.

Morphological features for GaN NPs are shown in figures 3.20(a-c). The FESEM image [Fig. 3.20(a)] of the sample grown at 900 °C and the corresponding TEM image [Fig.
3.20(b)] show that the as-grown samples have platelet type surface morphology with average particle size of ~ 50 nm and thickness less than 15 nm whereas the sample grown at 950 °C mostly exhibit elongated morphology. All the samples are crystalline in nature.

![Fig. 3.20](image_url) (a) FESEM image of the NPs grown at 900°C, the corresponding TEM image of NPs grown at (b) 900 °C and (c) 950 °C.

From EDX analysis, along the longitudinal direction of nanotip, it is found that the Ga/N ratio decreases from 4.8 to 0.64 in atomic percentage (data not shown).³ It indicates that the growth that occurs in the Ga rich condition eventually ends up with N rich condition. HRTEM image along the basal plane shows that the surface is relatively smooth and consists of lattice fringes [Fig. 3.21(a)]. The near-perfect lattice spacing, with an inter-planar spacing of 2.598 Å, corresponds to (0002) plane of WZ-GaN. Growth occurs along [0001] direction with relatively smooth surface termination having a minimal amount of extended defects like dislocations and stacking faults along the surface. However, two distinct interfaces are observed around the tip region of the nanotips [Figs. 3.21(b,c)]. It is found that the surface layer is consisting of mostly (10\̅0) non-polar, and few polar (10\̅1) planes. These planes are presumably grown over (0002) polar surface belonging to WZ-GaN phase. The transition from polar to non-polar surface results in accumulating large amounts of stacking faults at the interface [inset of Fig. 3.21(c)]. The Formation of these stacking faults may have been favored by the N rich condition.¹⁰ The lattice images became obscured towards the core region as the thickness increases. Figure 3.22(a) shows the typical lattice images of NPs.
Fig. 3.21 HRTEM image of a single nanotips around (a) base region, (b) tip region and (c) high resolution image of the transition region between polar (0001) and non-polar (10\bar{1}0) surface, around the tip region of the nanotips. Inset in (c) shows the magnified region of the transition region with large stacking faults.

Fig. 3.22 (a) HRTEM image of the NPs grown at 900 °C, (b) SAED pattern of single NPs obtained along the WZ <\bar{1}2\bar{1}0> zone axis.

grown at 900 °C. Inter-planar spacing of 2.76 Å corresponds to the (10\bar{1}0) polar surface of WZ-GaN. The corresponding SAED pattern is taken from a NP [Fig. 3.22(b)] which is indexed to <\bar{1}2\bar{1}0> zone axis of the WZ-GaN.
3.4.2.2 Raman Scattering Study:

Typical micro-Raman spectrum [Fig. 3.23(a)] for nanotip shows mode frequencies around 535, 567 and 726 cm\(^{-1}\). Raman spectrum for NPs shows [Fig. 3.23(b)] modes around 533, 569 and 732 cm\(^{-1}\). All these peaks correspond to \(A_1\) (TO), \(E_2\) (high) and \(A_1\) (LO) phonon modes of WZ-GaN phase.\(^2\) All the spectra exhibit strong \(E_2\) (high) mode. A relatively smaller line width of 8 cm\(^{-1}\) of the nanotips than that of NPs (11.9 cm\(^{-1}\)) proves the superior crystalline quality of nanotips. Broad line width of NPs may arise due to the small grain size. LO modes are blue shifted to 9 cm\(^{-1}\) (line width ~ 17 cm\(^{-1}\)) and 3 cm\(^{-1}\) (line width ~18 cm\(^{-1}\)) for nanotips and NPs, respectively. Additional peaks at 253-265 cm\(^{-1}\), 421 cm\(^{-1}\) are primarily attributed to ZB phonons arising from the finite size effect. The peaks at 96, 609 and 702 cm\(^{-1}\)
in NPs may be related to acoustic phonon overtones. The broad peaks around 634 and 693 cm$^{-1}$ in NTs are surface disorder induced SO modes.\textsuperscript{2}

### 3.4.2.3 Stress Analysis:

Typical phonon modes along the lateral cross-section are shown in figure 3.24(a). Similar phonon spectra, as recorded in the surface region of nanotips [Fig. 3.23(a)], are observed around the shell region. However, a blue shift of 18 cm$^{-1}$ for the $E_2$(High) mode is estimated at the core region of the nanotips. It shows the presence of a compressive strain developed along the core direction during the radial growth. The relation between the frequency shift $\Delta \omega$ (cm$^{-1}$) of $E_2$ (high) mode and biaxial stress $\sigma$(GPa) is estimated to be $\Delta \omega=(4.2\pm0.3)\sigma$.\textsuperscript{30} Thus, the compressive stress developed inside the nanotip core is nearly equal to 4.29 GPa. Furthermore, the alternation of LO mode from $A_1$ to $E_1$ symmetry in the

![Fig. 3.24](image-url)

Fig. 3.24 (a) Typical Raman spectra along the diameter of a GaN nanotip at three different locations, surface, middle and core region; Cross-sectional Raman area mapping of a nanotip (b) along the diameter and (c) intensity distribution at 569 cm$^{-1}$; (d) differential stress mapping image corresponding to peak intensity observed at 569 cm$^{-1}$ and the shifted peak at 587 cm$^{-1}$. 
core region may be of geometric origin. The asymmetric behavior of optical phonons along the lateral cross section [Fig. 3.24(b)] of the nanotips is further analyzed by 3D mapping over an area of 20×20 μm. The map of the intense band of GaN phase with 568 cm\(^{-1}\), \(E_2\) (high) mode frequency for the bulk GaN, illustrates [Fig. 3.24(c)] that strain free GaN phase is intensely distributed along the surface region with a contrast in the core region due to strain accumulation. A differential image [Fig. 3.24(d)], obtained by comparing the 2D mapping of peak intensity corresponding to observed \(E_2\) (high) mode at 569 cm\(^{-1}\) and the shifted peak at 587 cm\(^{-1}\) depicting the strained region in the core, is also shown as further evidence.

3.4.2.4 Photoluminescence Study:

RT micro-PL spectra of a single nanotip and NPs show strong emission in the photon energy in the range of 3.0 - 3.6 eV [Figs. 25(a,b)]. All the observed emission lines possess a broad and asymmetric line shape with weak band-edge-emissions.

![Typical micro-PL spectrum](image)

Fig. 3.25 Typical micro-PL spectrum shows for (a) nanotips and (b) NPs; Inset in a) shows the PL spectrum at the base region of nanotips.
The peak at 3.54 eV for the nanotip corresponds to $I_2$ emission line of WZ-GaN which is blue shifted by 80 meV with a broad line shape of ~105 meV [Fig. 3.25(a)]. Such a shift in this system is not expected due to quantum confinement effect. However, PL line shift and additional broadening possibly arises due to strain in the system.$^{30}$ The relation between the change in the excitonic PL, $\delta E$ (meV) and biaxial stress $\sigma$(GPa) is estimated to be $\delta E=(20\pm3)\sigma$. Thus, a compressive stress of 4 GPa in the nanotip is estimated. This is in close agreement with the previously calculated value of compressive stress using a Raman shift of $E_2$(high) mode. The $I_2$ line in the PL spectrum of GaN NPs shows a broad line shape (~124 meV) with a blue shift of 30 meV. Since the NPs are grown in the vapor phase without using any substrate, the effect of stress is ruled out. The ambiguity of the observed blue shift, broad line width and the asymmetric line shape of the $I_2$ line of the NPs may be attributed to small sized crystallites. In addition, strong broad bands centered at 3.29 and 3.27 eV are observed for the nanotip and NPs, respectively, with similar line widths of ~134 MeV. The peak at 3.29 EV of the nanotip has been assigned to the FB emission line. The FB transition is mediated by the free to a deep acceptor (DA) state. This possibly stems from Ga vacancy ($V_{Ga}$) formed under N-rich condition and will be discussed later. However, additional peaks appearing in the spectra of NPs belong to various electronic origins. The peaks centered at 3.27 eV and 3.128 eV are due to recombination of neutral donor acceptor pairs ($D^0A^0$) and their LO phonon replica ($D^0A^0$-LO), respectively.$^3,19$ Additional peak at 3 eV may be assigned to a blue band (BB). The well-known yellow band centered at 2.2 eV is not noticeable in both these samples, indicating high purity and crystallinity. Overtones of LO phonon modes upto 3rd-order are also observed in the right arm of the PL spectra [Figs. 3.25(a,b)]. Higher order phonon modes arise due to strong electron-phonon coupling mediated Frolich interaction with excitations above the band gap (325 nm, ~3.81 eV). This supports the above argument of higher crystalline quality in the nanostructures. On the other
hand, PL spectrum [inset in Fig. 3.25(a)] from the base region of the nanotip shows a broadband emission around 3.1 eV. It is observed from EDX and Raman study (data not shown)\textsuperscript{3} that the base region of the nanotip is Ga rich and contains oxide phases. Significant amount of nitrogen vacancies (V\textsubscript{N}) is present in the base region, which act as shallow donors. The transition from a shallow donor state (V\textsubscript{N}) to a deep acceptor state is expected to occur around 3.26 eV in case of GaN epilayers.\textsuperscript{19,31} Nevertheless, it is assigned to DAP recombination lines after taking into account the transition from a shallow donor state V\textsubscript{N} to a deep acceptor state, such as, V\textsubscript{GaO,N} type defect complex present in the nucleating region. The broad DAP line is red shifted by 100 MeV indicating presence of significant amounts of defect in the base region. Nevertheless, oxide related native defects might have supported the foundation of strong nucleation sites for nanotips as incubation time with low N\textsubscript{2} concentration is found to be high in the initial stage for a low ramping rate. The issue will be further elaborated in the subsequent paragraph.

3.4.3 Polarity Driven Growth Mechanism:

It is observed that the Ga/N ratio in the vapor phase plays an important role in determining the resulting morphology of nanotips and NPs.\textsuperscript{23-26} During the vacuum annealing of Ga precursor and subsequent increase in temperature from 800 to 900 °C at 200 mbar pressure, nano-sized Ga liquid droplets might have formed around the source material. This is supported by the recent reports, where small uniform sized Ga droplets have been used as an effective catalyst for the growth of the aligned SiO\textsubscript{2} NW.\textsuperscript{32} Weak Ga-Ga bond, the longest liquid range and high vapor pressure of Ga might have helped the nucleation process. In the present study, different ramping rates of temperature of the reactor have been used in order to control incubation time of incoming adatom species. These are detrimental in controlling the size for forming nano-sized Ga droplets. These nano-droplets of Ga are likely to be used as nucleating center for formation of nanotips and NPs.\textsuperscript{25} In case of nanotips, the slow ramping
rate of temperature of the reactor (~15 °C/min) leads to formation of large Ga droplets of size ~1-20 μm as a result of self-agglomeration process. Energy stored in the defects and dangling bonds on the surface of Ga droplets might act as possible nucleating centers for the growth of GaN phase. In addition, it is observed that the formation of a dilute amount of oxide phase at the nucleation site is also occurring during slow ramping rate that cannot be avoided as nitride formation temperature at ~900 °C is delayed. During this process the residual and the adsorbed O₂ species from the alumina surface reacted simultaneously and helped in the nucleation process with a formation of complex oxy-nitride phase.⁵³ There are several reports exits based on oxide assisted nucleation process for the growth of GaN nanostructures.⁵³,⁵⁴ Reduction or conversion of Ga₂O₃ phase to GaN phase at moderator temperature between 900-950 °C, is also reported during ammoniation process.⁵⁵ Being a low symmetric crystal oxide phase, Ga₂O₃ accelerates the nucleation process. Upon increasing the local ambient from Ga rich to N₂ rich condition, the oxygen contents reduced subsequently. It can be stated alternatively, that the N₂ overpressure may have helped in the nucleation of GaN inhibiting the further formation of oxide phase. The sub-micron sized GaN column grows from the GaN seeds in a diffusion limited self-agglomeration process promoted possibly by high vapor pressure of Ga and slow ramping rate towards reaction temperature.⁵⁶ Furthermore, the conically shaped nanotips grow smoothly over the GaN column up to several millimeters. The growth is favored in the longitudinal direction due to the fact that vapor pressure at the conical-shape convex surface of the nanotips is much higher than that on the top-edge.⁵⁶ The growth, can possibly, be explained by VS mechanism which is very sensitive to gas phase kinetics during the growth process.

The observed conical shape of nanotip morphology can further be elucidated by considering the characteristic length scale of polar surface with respect to different reaction conditions (either Ga-rich or N-rich). It is observed that Ga-rich condition results in a broad
polar faces while in N-rich condition, morphology mainly contains rough surfaces and facets.\textsuperscript{23-26} Ga-stabilized polar surfaces play an important role during GaN growth because Ga atoms have a significantly lower diffusion barrier on this polar surface.\textsuperscript{8} The effective diffusion length of Ga reactant on the Ga-stabilized polar surface is sensitive to the chemical environment. If an excess N reactant is available, as in N-rich condition, the free surface diffusion of Ga is disrupted owing to the formation of Ga-N covalent bonds which ultimately inhibits Ga diffusion length.

However, a rapid ramping rate (about 3 times more than that used in case of nanotip growth) of the temperature of the reactor is employed in the formation of NPs. The rapid ramping rate of the temperature on the substrate reduces the effective adatom migration period. This hinders self-agglomeration, and limits the size of Ga droplets to a smaller size than what is encountered during nanotip growth. Meanwhile, NH\textsubscript{3} is introduced before the small Ga droplet ripens into big cluster and helps in the nucleation process at the vapor phase itself. This occurs before the onset of incubation time. Thus, small Ga droplets react with NH\textsubscript{3} in forming a large number of GaN islands and subsequent formation of NPs in the N-rich condition.

Interestingly, we can notice a unique relationship among the Ga and N flux rates, growth orientation and the resulting morphologies of nanotips and NPs. HRTEM data reveal that the nanotips growth occurs along [0001] polar direction (Fig. 3.2\textsuperscript{1}). The characteristic length of the polar surface of the base region is ~20 μm. However, after a typical distance from the base region (≥ 1μm) the surface layers of the nanotips are mostly non-polar. It is basically dominated by (10\textoverline{1}0) planes [Fig. 3.2\textsuperscript{1}(c)]. The polar surface is found to shrink gradually towards the tip region. This variation of growth orientation is strongly supported by our growth conditions in which Ga and N flux rates have been altered after a typical incubation time of ~ 10 min during the growth. In case of nanotip growth, the reaction
condition is initially Ga-rich which favors growth of polar surfaces. This can be explained by the fact that the interaction between adsorbate and surface is predominately realized by very weak delocalized metallic Ga-Ga bonds, which are isotropic with low diffusion barriers \( \approx 0.4 \) eV along the (0001) polar surface.\(^{23-26}\) However, anisotropic and differential growth orientations with the shrunken polar surface is expected when the reaction condition becomes relatively N-rich upon \( \text{NH}_3 \) flow. It is known that N-rich condition increases the nucleation rate of GaN due to the higher strength of the Ga-N bond and shorter diffusion length of Ga than that of Ga-Ga bond. Therefore, the Ga atoms will be bonded to N atoms before they complete their migration to step edges, to promote 3D growth and introduce roughness.\(^{10,25}\)

Apart from this, recently first principle calculation by Lymperakis et al.\(^{37}\) have revealed that N-rich condition promotes island nucleation and the Ga adatom incorporation is more probable on the (0001) polar surface than that of other non-polar surface (\( a \)- and \( m \)-planes). Thus, the diffusion-induced mechanism of adatom migration on the polar surface promotes faster material transport occurring from the side facets (non-polar surface) towards the top. Thus, the higher nucleation rate towards the top is expected to stimulate and favors the axial growth over radial growth for the nanotips.\(^{38}\) In other words, the observed nanotip morphology can be thought of driving by the strain, as indicated from the Raman [Fig. 3.24(a)] peak positions shift, in the system appearing due to the differential growth rate among competitive facets.

To summarize our model, three important consequences can be listed. These are 1) incubation time, 2) anisotropy of diffusion and 3) rate limiting factor of Ga and N adatoms in polar (0001) and non-polar (10\( \bar{1} \)0) surfaces of GaN facets play significant roles in deciding the final morphology of nanotips [schematic in Figs. 3.26(a,b)] and NPs [schematic in Figs. 3.26(c,d)]. Molecular N flux is found to have a stronger influence on the growth rate than nucleation.\(^{3}\) It is also found that few nanotips have branches at the end of the tip during
longer (3 h) growth period. These branches may be due to the formation of facets that occurs during N-rich condition [schematic in Fig. 3.26(a)]. On the other hand, NPs grown initially in N-rich condition, show appearance of nanometric seeds with a multitude of facets as shown in figure 3.26(c). These facets are made up of non-polar surfaces of (10\overline{1}0), (1\overline{1}20) and (1\overline{1}00) [Fig. 3.26(d)]. Such phenomena limit isotropic growth that invariably results in platelet morphology.

![Schematic showing the possible growth mechanism of GaN nanotips and NPs in different Ga-rich and N-rich growth conditions.](image)

Apart from NWs, nanotips and NPs, other forms of GaN nanostructures, namely, core-shell Ga$_2$O$_3$@GaN microbelts and GaN nanotubes are described in the subsequent chapters.

**3.5. Summary:**

High yield single crystalline GaN NWs of varying morphology are synthesized employing standard VLS mechanism in the CVD system. Various process parameters are optimized to realize NWs of particular morphology, including hexagonal, triangular,
wurtzite/zinc-blende biphase, and square shaped forms. A simple steady state model has been used to correlate the nanowire growth morphology with the catalyst droplet size. The detailed morphological and structural studies are performed by FESEM and HRTEM. Phonon spectra of GaN NWs reveal the presence of dominating WZ phase in all the as-grown samples. Surface optical modes associated with the surface modulation in GaN NWs are identified and validated with the theoretical calculation. The as-grown NWs show strong band edge luminescence and hence can be used as ideal materials for optoelectronics and sensor applications.

On the other hand, catalyst free vapor-solid process is employed for the growth of single crystalline GaN nanotips and nanoparticles. The nanotips nucleate in the Ga-rich condition and get converted to N-rich condition as the reaction moves forward. N\textsubscript{2} overpressure is proposed to play an important role in the nucleation of GaN phase inhibiting the further formation of oxide phase nucleated during long incubation time with the slow ramp rate for nanotips. The conical shape of the nanotips is explained in terms of reduced surface diffusion length in the N-rich condition than that of Ga-rich core region. Unidirectional growth of the nanotips is proposed to be driven by the strain developed due to the differential growth rate among different competitive facets. On the other hand, nanoparticles are nucleated initially in N-rich condition with the relatively smaller incubation time that does not favor formation of facets, and consequently limits the growth. The ability to control growth of nanotips and nanoparticles stemming via self-catalyzed process is expected to be advantageous in realization further complex structures.

3.6 Reference:


