CHAPTER 2
GROWTH OF GaN NANOWIRES WITH DIFFERENT III/V RATIO AND STUDY OF ELECTRON-PHONON COUPLING

2.1 Introduction

Group III nitrides attract remarkable attention because of their tunable electronic and optical properties by appropriate alloy formation. Due to the extensive reduction of extended defects in 1D nanostructures, III-nitride based nanowires (NWs) have emerged as ideal candidates for building blocks of nanoscale electronic and optoelectronic devices such as LEDs, laser diodes, photodetectors ranging from infrared to ultraviolet regime.\textsuperscript{1-3} The III-nitride NW heterojunctions also find application for high electron mobility transistor and high efficiency solar cells.\textsuperscript{4,5} The performance of such highly efficient nanoscale electronic and optoelectronic semiconductor devices depends on the dopants and defects, which control the carrier density as well as carrier mobility. Among the commonly known native point defects such as N vacancy ($V_N$), O in the lattice site of N ($O_N$) and Ga vacancy ($V_Ga$) in unintentionally doped GaN, $O_N$ is a ubiquitous inevitable impurity in group III nitride. In the literature, the concentration of unintentional O impurity in GaN films is reported to be order of $10^{17}$-$10^{21}$ cm$^{-3}$, which results in tuning the net carrier concentration of $10^{16}$-$10^{20}$ per cubic cm.\textsuperscript{6,7} The free charge carriers can interact with the basic interactions of exciton or lattice vibrations, which in turn influence the optical and electrical properties in the semiconductor. The electron-phonon interactions in GaN films are well studied by varying the extrinsic doping concentration.\textsuperscript{8} Different kinds of interactions are possible with different lattice vibrations in GaN. The nonpolar transverse optical (TO) phonons, interact with electrons by means of deformation-potential (DP), while the polar longitudinal optical (LO) phonons interact with electrons by
means of Coulomb interactions known as Fröhlich interaction (FI).\textsuperscript{8,9} The plasmon coupled LO phonon modes are studied by analyzing Raman spectra of GaN, revealing the strong electron-phonon coupling in the system with different carrier density.\textsuperscript{10-13} Nevertheless, there is hardly any study on the effect of native defects ($V_N$, $O_N$, $V_{Ga}$) in unintentionally doped GaN and resultant free carriers on electron-phonon coupling in GaN NWs using optical spectroscopy.

The present chapter is devoted to the growth of GaN NWs with different native defect density and study of the electron-phonon coupling in these NWs. GaN NWs were grown using atmospheric pressure chemical vapor deposition (APCVD) technique under variable precursor flow rates to manipulate the defect induced free charge carrier concentration. Detailed Raman and photoluminescence (PL) spectroscopic studies were performed to explore the electron-phonon interactions induced by native defects.

2.2 Atmospheric Pressure Chemical Vapor Deposition

CVD is the technique in which the deposition of solid materials occurs at high temperature by means of chemical reactions. Usually, the material synthesized via CVD technique is crystalline as the growth occurs in the thermodynamically equilibrium condition. The CVD method can be classified based on different parameters. The main parameters are pressure, wall and substrate temperature, nature of precursor, and gas flow state and mode of activation. CVD is a promising method for its cost-effectiveness and large-scale growth of NWs.\textsuperscript{14,15} In the CVD technique, NW growth is normally performed by following the well-established vapour-liquid-solid (VLS) growth mechanism. We have chosen CVD process as commercially viable growth of GaN NWs where the large area of deposition can be facilitated.
The following are the major steps involved in the CVD process,\(^4\)

- Convective and diffusive transport of reactant species to the reaction zone,
- Transport of the reactant products from the chemical to the substrate surface,
- Chemical reactions of these species at the substrate surface by means of adsorption, diffusion, and desorption processes leading to nucleation,
- Further rational attachment of reactant species leading to the growth of nuclei,
- Transport of volatile substances and the byproducts of reaction away from the reaction zone.

The experimental setup for CVD varies depending upon the requirements. If the chamber is maintained at atmospheric pressure during the deposition time, the method is called atmospheric pressure chemical vapor deposition (APCVD). The experimental setup used for the growth of GaN NWs in the VLS mechanism,\(^{14,16}\) is shown in figure 2.1.

![Figure 2.1. Schematic of APCVD system used for the growth of GaN NWs.](image)

The major components of the APCVD system are listed below with the specific functionalities.
(i) Horizontal tube furnace: A horizontal tubular furnace was used as an energy source to carry out the chemical reaction. The important parameters of the furnace are listed below.

Maximum temperature: 1200 °C

Temperature control: Proportional-integral-derivative (PID)

Temperature accuracy: ±1 °C

Heating element: SiC

Thermocouple: S-type

(ii) Reaction chamber: The quartz tube of length ~110 cm and diameter of 2.5 cm was used as the reaction chamber. The solid precursors were kept inside the tube using the ceramic boat and the gaseous precursors could pass through the gas delivery system.

(iii) Vacuum system: The reaction chamber was connected to a mechanical rotary pump for the pre-evacuation. The chamber was capable to be evacuated up to a pressure of 1E-3 mbar. The chamber pressure was measured using the Pirani gauge and mechanical gauge for the low and high-pressure regimes, respectively.

(iv) Gas delivery and control system: The delivery system included the transport of precursor gas along with the carrier gas. In the present study, reactive NH₃ (99.999%) was used as precursor gas along with carrier gas Ar. The gas flow was controlled using the mass flow controller (MFC). Both the gases could flow through different MFC and mixed together before entering to the reaction chamber.
2.3 Vapor-Liquid-Solid Mechanism: Growth of Nanowires

In the VLS mechanism, the metal catalyst forms liquid alloy droplets at a high temperature by adsorbing vapor components. Due to the fluctuation of temperature or vapor pressure, the alloy is further supersaturated; i.e. it becomes a solution in which the actual concentration of the components is higher than the equilibrium concentration. It then drives the precipitation of the component at the liquid-solid interface to achieve minimum free energy of the alloy system. Accordingly, 1D crystal growth begins and it continues as long as the vapor components are supplied. As vapor (carrying solid components), liquid (catalyst alloy), and solid (precipitated one-dimensional structures) phases are involved in the growth process (schematic in Fig. 2.2), it is known as the VLS mechanism.

![Figure 2.2. Schematic of different steps involved in the VLS mechanism.](image)

2.4 Synthesis of GaN Nanowires

GaN NWs were synthesized by APCVD technique using VLS process. Au catalyst was deposited on Si substrates using thermal evaporation technique (12A4D, HINDHIVAC, India). These substrates were annealed for making the Au nanoparticles (NPs) at a temperature of 900 °C for 10 min. Ga metal (99.999%, Alfa Aesar) as precursor, NH₃ (5 N pure) as reactant
and Ar (5 N pure) as carrier gases were used for the growth process. The Si substrate with Au NPs was kept upstream of a Ga droplet (~200 mg) in a high pure alumina boat (99.95%), placed inside a quartz tube. The temperature of the quartz tube was raised to a growth temperature of 900 °C with a ramp rate of 15 °C per minute. Growth was carried out for 180 minutes with different flow rates of NH₃ and by keeping a constant amount of Ga (200 mg) in the reaction chamber. Sample S1 was grown under N rich condition by flowing 50 sccm of NH₃ without any carrier gas. On the other hand, samples S2 and S3 were grown under N reduced environment by NH₃ flow rate of 10 sccm and diluted with the carrier Ar gas of 10 and 20 sccm, respectively.

2.5 Morphological Analysis

The typical field emission scanning electron microscopy (FESEM) images of as-grown GaN NWs from sample S1-S3 are shown in figure 2.3a-c respectively. The Au NPs at the tip show that the NWs are grown in the VLS process. The FESEM micrograph of sample grown under N rich condition (S1) shows very rough and non-uniform surface morphology for the as-grown NWs having a size distribution of ~80-120 nm with a less growth rate of ~ 0.5 μm/hr (Fig. 2.3a). On the other hand, the NWs grown under N reduced conditions (S2 and S3) show a quite smooth and uniform surface morphology with a growth rate ~2 μm/hr and size distribution of ~60-120 nm (Fig. 2.3b) and ~60-150 nm (Fig. 2.3c) for S2 and S3, respectively. The reduction in the growth rate for sample S1 can be attributed to the self-nitridation of Ga source in case of N rich condition. In other words, the growth rate is impeded with the formation of a thin nitride layer on the top surface of the Ga source and the observation is consistent with the earlier report.
Figure 2.3. Typical FESEM images of GaN NWs of samples (a) S1 (b) S2, and (c) S3. Insets showing the high magnification images of as-grown NWs.

2.6 Compositional Analysis

The X-ray photo electron spectroscopy (XPS) study was carried out to estimate the Ga/N ratio in NWs for all the samples. Typical XPS spectra for the samples are shown in figure 2.4 for different elements. The peak centered at \(~19.4\) eV corresponds to the binding energy of the electron in \(3d\) electronic state of Ga. Similarly, N \(1s\) level is observed at \(~397\) eV from the de-convolution of a broad peak, which is considered as a combination of N \(1s\) and Ga \(LMM\) Auger transitions. Along with the peaks corresponding to Ga and N, a peak at \(~531\) eV was also observed and was attributed to O \(1s\).\(^{18,19}\) The presence of O peak in the XPS study shows that the unintentional incorporation of O in GaN may have occurred during the APCVD growth process, as the base vacuum of the chamber and purging of precursor gases are inadequate to reduce the presence of O. Other sources like substrate and quartz tube can also contribute to the O contamination. However, the relative variation of atomic percentages (at.\%) of O from sample S1 to S3 represents its contribution from the GaN lattice. The at.\% of Ga, N and O are calculated from the area under the curves and are tabulated in table 2.1.\(^{20}\)
Table 2.1. Atomic percentage of the elements calculated from XPS spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ga (at. %)</th>
<th>N (at. %)</th>
<th>O (at. %)</th>
<th>Ga/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>29.9</td>
<td>41.8</td>
<td>28.3</td>
<td>0.715</td>
</tr>
<tr>
<td>S2</td>
<td>27.9</td>
<td>40.1</td>
<td>32.0</td>
<td>0.696</td>
</tr>
<tr>
<td>S3</td>
<td>26.7</td>
<td>39.9</td>
<td>33.4</td>
<td>0.670</td>
</tr>
</tbody>
</table>

XPS analysis shows a decrease in both Ga and N at.% and an increase in O at.% from sample S1 to S3. Surprisingly, less amount of Ga at.% was observed in the sample S3, which was grown under N reduced, (i.e. Ga rich) condition. However, the observed increase in O at.% from sample S1 to S3 could be due to the reduction in the N concentration during their growth.

![Figure 2.4. Typical XPS spectra of different elements and its characteristic electronic transitions for samples (a)-(c) S1, (d)-(f) S2 and (g)-(i) S3 deconvoluted with a Shirley type background (red line) correction.](image)
Hence, it may be emphasized that since S3 is grown under less concentration of NH$_3$, the amount of O involved in the growth process is expected to be high by forming O$_N$ point defects and 2O$_N$ defect complex in GaN.$^{21}$ Furthermore, the excess O$_N$ defects enhance the V$_{Ga}$ density by forming V$_{Ga}$-3O$_N$ defect complex,$^{21}$ and hence a reduction in Ga at.% is observed in the XPS analysis. Moreover, we calculated Ga to N ratio (Ga/N) in all the samples and the ratio for sample S1 ($\sim$0.715) is found to be close to the stoichiometric value of unity.

2.7 Characteristics of Electron-Phonon Coupling in Raman Spectra

The typical Raman spectra are shown (Fig. 2.5) for the NW samples grown under different N concentration. In case of a wurtzite hexagonal structure, group theory predicts eight sets of phonon normal modes at the Γ-point, namely, $2A_1 + 2E_1 + 2B_1 + 2E_2$. Among them, one set of $A_1$ and $E_1$ symmetry modes are acoustic, while the remaining six modes ($A_1 + E_1 + 2B_1 + 2E_2$) are optical. Each one of $A_1$ and $E_1$ optical modes split into LO and TO modes due to their polar nature of vibration.$^{13,22}$

The Raman spectra of NWs from all the samples were fitted with Lorentzian line shape and were analyzed for the corresponding phonon modes. As grown NWs of sample S1 (Fig. 2.5a) show the peaks centered at $\sim$567, $\sim$537, and 721 cm$^{-1}$ corresponding to Raman active $E_2$(high) phonon mode, TO and LO phonon modes of $A_1$ symmetry ($A_1$(TO)) and $A_1$(LO)), respectively. The observation confirms the presence of wurtzite GaN phase of the grown NWs.$^{13,22}$ Along with the Raman active modes, two broad peaks centered at $\sim$628 and $\sim$680 cm$^{-1}$ are assigned to the surface optical (SO) phonon modes of GaN corresponding to $A_1$ and $E_1$ symmetries, respectively.$^{21}$ An intense peak centered at $\sim$521 cm$^{-1}$ corresponds to the Si substrate on which GaN NWs are grown (Fig. 2.5a). The Raman spectra of GaN NWs of
sample S2 (Fig. 2.5b) also show similar characteristics as that of S1, along with a new peak centered at ~420 cm\(^{-1}\) which corresponds to the zone boundary (ZB) phonon mode of GaN arising due to the finite size of the crystal in the NW sample.\(^{23}\) However, the \(A_1(LO)\) symmetry phonon mode is blue shifted by ~3 cm\(^{-1}\). Whereas in case of sample S3 (Fig. 2.5c), along with an intense peak of \(E_2(\text{high})\) phonon mode, a peak corresponding to the TO mode of \(E_1\) symmetry (\(E_1(\text{TO})\)) at ~551 cm\(^{-1}\) is also observed. Moreover, the \(A_1(LO)\) mode is further blue shifted by 6 cm\(^{-1}\) as compared to that for the sample S1.

**Figure 2.5.** Typical Raman spectra of GaN NWs acquired using 514.5 nm excitation from samples (a) S1, (b) S2 and (c) S3 with Lorentzian line shape fitted. (d)-(f) Corresponding \(A_1(LO)\) mode fitted with line shape analysis. The vertical dashed line is a guide to eye for the observed blue shift of \(A_1(LO)\) mode.
2.8 Fröhlich Interaction and Deformation-Potential Involved Electron-Phonon Coupling

As discussed in Chapter 1, the electron-phonon coupling can occur either by FI and/or by DP interactions. The non-polar phonons, such as $E_2$, TO modes are mostly involved in interacting with DP, whereas polar LO phonons are involved in both FI and DP interactions.\(^8\) In the ionic crystals like GaN, the FI is dominant depending on the excitation energy. The relative strength of both FI and DP interactions by different phonon modes can be revealed by considering the ratio of Raman intensities of corresponding phonon modes.\(^24\) Since the matrix element $\langle k|H_{ep}|j \rangle$ of electron-phonon interaction ($H_{ep}$) in Raman intensity is different for different phonon modes, the ratio of Raman intensities of particular phonon modes is equivalent to the ratio of magnitudes of the corresponding matrix elements as given by equation (2.1), and hence the relative strength of the interactions.\(^24\)

$$I_{E_2,TO}/I_{1(LO)} \approx \frac{|\langle k|H_{ep}(E_2,TO)|j \rangle|^2}{|\langle k|H_{ep}(LO)|j \rangle|^2} \approx \frac{|\langle k|DP|j \rangle|^2}{|\langle k|(DP+FI)|j \rangle|^2} \quad (2.1)$$

Variations are often observed in relative Raman intensities of $E_2$(high), $E_1$(TO), $A_1$(TO) and $A_1$(LO) phonon modes in GaN, with respect to the crystal orientation, collection geometry for scattered photons, excitation energy, and presence of dopants.\(^10\)-\(^12\),\(^25\) In the present study, although the scattered photons from GaN NWs are collected in unpolarized condition and the NWs are aligned randomly on the substrate, the relative Raman intensities of $E_2$(high) and $A_1$(LO) phonon modes are found to vary among the three NWs samples (Figs. 2.5a-c). Such variations in the Raman intensity could be due to the relative strength of the electron-phonon interactions. In order to understand the strength of these interactions, the ratio of intensities of $E_2$(high) and LO phonon modes ($I_{E_2}/I_{A_1(LO)}$), and the ratio of intensities of TO and LO phonons ($I_{TO}/I_{LO}$) are estimated and compared among the three samples. The ratios
\(I_{E_2}/I_{A_1(LO)}\) for S1, S2, and S3 are found to be 0.3, 1.0, and 1.76, respectively. Whereas, the ratios \(I_{A_1(TO)}/I_{A_1(LO)}\) for S1 and S2 are 1.80 and 1.57, respectively. For the sample S3, the ratio \(I_{E_2}/I_{A_1(LO)}\) is estimated to be 0.94. The values suggest that DP interactions with \(E_2\) (high) phonons is stronger in case of sample S3 than that of the sample S1. While in case of non-polar TO phonons in III-nitrides, the contribution of DP interaction is significantly reduced as compared to \(E_2\) (high) mode leading to an overall decrease in the ratio \(I_{TO}/I_{LO}\). In this context, it may be noted that an approximately six-fold increase is observed for the ratio \(I_{E_2}/I_{A_1(LO)}\) indicating a significant role of DP in sample S3.\(^{20}\)

![Figure 2.6. Comparison of typical excitation (514.5, 488, and 325 nm) dependent Raman spectra of NWs of sample S3.](image)

Further, the excitation energy dependence of electron-phonon interactions in the GaN NWs of sample S3 was studied by collecting the Raman spectra of NWs using three excitation wavelengths of 514.5, 488, and 325 nm for understanding the presence of FI in these samples. A comparison of the typical Raman spectra of sample S3, excited by three wavelengths is shown (Fig. 2.6). The relative intensity ratios of \((I_{E_1(TO)}/I_{A_1(LO)})\) are estimated to be 1.21, 1.00, and 0.35, respectively for the three wavelengths. The values clearly show that the LO phonons
are strongly interacted by the combination of FI and DP interactions when the excitation source is close to the resonance condition of GaN.

2.9 Defect Induced Free Carrier Plasmon-Phonon Coupling

The observed shift in $A_1$(LO) phonon mode of NWs from samples S1 to S3 (Figs. 2.5d-f) may be due to the interactions among LO phonons and free charge carriers in the samples, as such shift is not possible in $A_1$(LO) phonons alone if it is associated with strain, or as an effect of temperature. Further, considering the similar experimental conditions for all the samples in the present study, with identical lattice mismatch due to Si substrate and a constant low power laser excitation of <1 mW, the shift cannot be attributed to the strain effect to a particular phonon mode or temperature effect. However, for semiconductors, especially in ionic solids the polar LO phonons strongly interact with the free charge carriers such as electrons present in the system by means of Fröhlich interaction. As revealed from the XPS studies, the GaN NWs are expected to possess different doping concentration leading to a variation in the carrier concentration as a function of native defects present in the system. The defect induced free charge carriers thus can strongly interact with LO phonons, resulting in the blue shift of $A_1$(LO) phonon modes from samples S1 to S3. By analyzing the line shape of the coupled plasmon-phonon modes, it has been shown that the free carrier density can be calculated, considering the DP and FI in Raman scattering cross-section.

The Raman scattering intensity ($I(\omega)$) as a function of phonon ($\omega$) and plasmon ($\omega_p$) frequency is described by

$$I(\omega) \propto A(\omega) \times \text{Im}\left[\frac{-1}{\varepsilon(\omega)}\right]$$

(2.2)
where $A(\omega)$ is the correction factor by DP and FI in terms of Faust-Henry coefficient (C), TO phonon ($\omega_{TO}$) and LO phonon ($\omega_{LO}$) frequencies, plasmon damping constant ($\gamma$), and phonon damping constant ($\Gamma$), and $\varepsilon(\omega)$, being the dielectric function, is described as

$$
\varepsilon(\omega) = \varepsilon_{\infty} \times \left\{ 1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{LO}^2 - \omega^2 - i\omega \Gamma \omega} \right\} \frac{\sigma^2}{\sigma^2 + i\omega} \right\} \quad \text{…………………………. (2.3)}
$$

The line shape of $A_1$(LO) phonon modes of the three NWs samples (Figs. 2.5d-f) were fitted using the equation (2.2), by adjusting the fitting parameters $\omega_p$, $\gamma$, $\Gamma$, and $C$. From the fitted values of $\omega_p$, $\gamma$ and using the effective mass of the electron ($m^*$) in GaN, the carrier concentration $n_e = (\omega_p^2 \varepsilon_{\infty} m^*) / 4\pi e^2$ and mobility $\mu_e = e/m^* \gamma$ of the NWs were estimated and tabulated (Table 2.2).

**Table 2.2.** Carrier concentration and mobility of the samples calculated from line shape analysis of the coupled LO phonon mode.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ga/N ratio</th>
<th>$n_e$ (cm$^{-3}$)</th>
<th>$\mu_e$ (cm$^2$.V$^{-1}$.s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.715</td>
<td>$4.4 \times 10^{16}$</td>
<td>443</td>
</tr>
<tr>
<td>S2</td>
<td>0.696</td>
<td>$1.6 \times 10^{17}$</td>
<td>234</td>
</tr>
<tr>
<td>S3</td>
<td>0.670</td>
<td>$6.8 \times 10^{17}$</td>
<td>57</td>
</tr>
</tbody>
</table>

The estimated $n_e$ and $\mu_e$ values of the three samples show the increase in $n_e$ from $4.4 \times 10^{16}$ cm$^{-3}$ for sample S1 to $6.8 \times 10^{17}$ cm$^{-3}$ for S3, whereas $\mu_e$ is found to decrease from 443 cm$^2$.V$^{-1}$.s$^{-1}$ for S1 to 57 cm$^2$.V$^{-1}$.s$^{-1}$ for S3. Although, the NWs are not extrinsically doped with any dopants such as Si ($n$-type dopant), the increase in the values of $n_e$ further confirms the presence of native donor defects such as V$_N$ and O$_N$. In GaN, the native defects like V$_{Ga}$, V$_N$, O$_N$ and the defect complexes 2O$_N$, V$_{Ga}$-O$_N$, and V$_{Ga}$-3O$_N$ are known to form acceptor, donor or double donor states, respectively. $^{27,28}$ The increase in the density of donor states over acceptors are
thus responsible for increase in the free carrier concentration for the NWs of S3 as compared to that of S1. Similarly, the reduction in mobility of GaN NWs from S1 to S3 can also be attributed to the increase in the defect density in S3 as compared to that of the S1. Furthermore, the variations of $n_e$ and $\mu_e$ with respect to Ga/N ratios in NWs are analyzed (Fig. 2.7) to understand the role of native defects in electron-phonon coupling with respect to growth parameters of NWs. The increase in carrier concentration and the decrease in mobility with decreasing Ga/N ratio were observed in the GaN NWs. The NWs having Ga/N ratio close to the stoichiometric values (0.715) are found to have the lowest carrier concentration ($4.4 \times 10^{16}$ cm$^{-3}$) and highest mobility ($443$ cm$^2$.V$^{-1}$.s$^{-1}$). On the other hand, the NWs having lowest Ga/N ratio (0.670) are found to possess the large carrier concentration ($6.8 \times 10^{17}$cm$^{-3}$) with very low mobility ($57$ cm$^2$.V$^{-1}$.s$^{-1}$). The off-stoichiometry of Ga/N ratio in NWs enhanced the presence of native defects $V_N$, $V_{Ga}$ which contributed to the resultant free charge carrier concentration in the NWs. In addition, the increase in O impurities with off-stoichiometry further enhanced the carrier density due to the formation of $O_N$ donors, resulting in the large net charge carrier.

Figure 2.7. Variation of free carrier density and carrier mobility with respect to Ga/N ratio in GaN NWs.
concentration in NWs of sample S3. Due to enhanced scattering among large carrier density and scatting between free carriers and native defects in NWs, the charge mobility is lowest in the NWs having off-stoichiometry.\textsuperscript{29,30} The XPS results of Ga/N ratio and O impurities in GaN NWs, and the Raman spectroscopic analysis of variations in $n_e$ and $\mu_e$, strongly emphasizes the role of native defects in electron-phonon coupling which can vary with growth parameters, even without the extrinsic doping in NWs.

2.10 Native Defects Originated Optical Transitions and Corresponding Electron-Phonon Coupling Characteristics

The presence of native defects and their role in electron-phonon coupling during the radiative transitions in GaN NWs were investigated using PL spectroscopy. An ultra violet (UV) laser of 325 nm wavelength was used to excite the NWs and the emission spectra were recorded at room temperature (300K) and at 80K. The PL spectra of samples S1, S2, and S3 collected at 300K (Figs. 2.8a-c), and 80K (Figs. 2.8d-f) are shown. The luminescence from the NWs of sample S1 at 300K, shows a broad band between 3.0-3.6 eV (Fig. 2.8a). A clear splitting of the broad band is observed on cooling the sample to 80K (Fig. 2.8d). The peak around 3.51 eV corresponds to the emission due to the recombination of electron-hole pairs from a free exciton (FE). Along with the FE emission, the emission peaks around 3.47, and 3.27 eV are also observed in the PL spectra. The peak at $\sim$3.47 eV corresponds to the emission due to radiative recombination of electron-hole pairs from excitons, bound to the sallow donor (DBE) states created by $V_N$ and $O_N$.\textsuperscript{31} The peak around 3.27 eV is attributed to recombination of the donor-acceptor pair (DAP), due to a transition of electrons from a shallow donor state ($V_N$, $O_N$) to a deep acceptor state of $V_{Ga}$. A broad peak situated between 2.7-3.0 eV, in the low temperature PL spectra (Fig. 2.8d) corresponds to the blue luminescence (BL), which is often
observed in undoped GaN and is assigned to the defect transitions involved by shallow acceptors ($V_{Ga}$) and deep donors ($V_N$).$^{21,31}$

![Figure 2.8](image)

*Figure 2.8.* Typical PL spectra of GaN NWs of samples (a) S1, (b) S2 and (c) S3, collected at room temperature and their corresponding (d)-(f) low temperature (80K) spectra, respectively.

The PL spectra of sample S2 show a FE emission at ~3.51 eV along with DAP (~3.31) peak which is blue shifted by 40 meV as compared to that of the sample S1 at 80K (Fig. 2.8e). The new emission peak observed around 3.22 eV, which is ~ 90 meV less in energy as compared to the DAP peak, is attributed to the LO phonon replica of DAP (DAP-LO).$^{21,31}$ In addition to the LO-phonon replica of DAP, a sharp resonance Raman line of $A_1$(LO) phonons in PL spectra further confirmed the presence of electron-phonon coupling, as observed in Raman spectroscopic investigations of the samples. The sample S3 emitted the luminescence due to DBE (3.47 eV), and a DAP transition along with its LO phonon replica (DAP-LO)
around 3.19 eV (Figs. 2.8c and 2.8f). However, the luminescence due to FE emission is not observed even at 80 K. The spectra also showed a strong BL peak around 2.9 eV at low temperature. The quenching in luminescence originating due to FE emission is observed with decrease in Ga/N ratio of NWs sample S1 to S3.

The PL study provides clear evidence of the presence of native defects (V_N, O_N, and V_Ga) in GaN NWs having different Ga/N ratios, as supported by XPS analysis. Since, the carrier concentration is expected to be higher in the samples grown under N reduced condition (S2 and S3), which favors the formation of native defects, the electron-phonon interaction is strengthened in these samples and consequently a phonon replica (DAP-LO) was observed in the PL spectra collected at both room temperature (Figs. 2.8b and 2.8c) and low temperature (Figs. 2.8e and 2.8f). In general, FE and DBE cannot be observed for semiconductors at room temperature. However, we can observe these luminescent peaks in case of GaN, as the exciton bound to the donor (arising due to N vacancy (V_N)) is having energy ~64 (±10) meV,\(^{32}\) which is far above the room temperature thermal energy of 25 meV. The PL spectra collected from samples S2 and S3 also show Raman mode corresponding to \(A_{1g}(LO)\) phonon along with its second order mode both at room temperature (Figs. 2.8b and 2.8c) and low temperature (Figs. 2.8e and 2.8f) as well. However, there is no signature of LO phonon modes in the PL spectra of sample S1. The observation of optical phonon modes in PL spectra of samples S2 and S3, further confirms the strong electron-phonon coupling induced by Fröhlich interaction near resonance condition, in the presence of a large number of carriers originating from native defects in these NWs.
2.11 Conclusion

GaN NWs having different Ga/N ratio were grown by changing the flow rate of NH$_3$ in APCVD technique. Compositional analysis by X-ray photoelectron spectroscopy revealed the presence of different Ga/N ratios in the samples, with sample grown under N rich condition showing composition close to the stoichiometric ratio. Raman spectroscopic analysis revealed different strength of interaction of phonon modes with the lattice deformation potential and Coulomb type Fröhlich interaction for the samples with different Ga/N ratio. The influence of native defect induced carriers on Raman spectra were confirmed from the observed blue shift of $A_1$(LO) mode with decreasing Ga/N ratio. The carrier concentration and mobility of the GaN NWs were calculated from the line shape analysis of the plasmon coupled phonon modes. The sample with least value of Ga/N ratio showed the highest carrier concentration and the lowest carrier mobility as compared to that the sample close to the stoichiometry, caused by the presence of higher native defect density in the former. PL study exhibited the phonon replica, as well as both the first and the second order optical $A_1$(LO) phonon modes, which further confirm the presence of strong electron-phonon coupling for the samples grown under N reduced conditions.

2.12 References


H.-J. Choi, Semiconductor Nanostructures for Optoelectronic Devices (Springer, 2012)


