CHAPTER 2

GROWTH OF GALLIUM NITRIDE EPILAYERS BY
CHLORIDE VAPOUR PHASE EPITAXY (Cl-VPE)
TECHNIQUE AND THEIR CHARACTERISATION

2.1 INTRODUCTION

The ability to produce new-high performance semiconductor devices is one of the factors on which the future growth of solid - state electronics depends. This requires the development of new semiconductor materials and ability to grow special structures, particularly those with very thin layers. Epitaxial, or the growth of single crystalline epitaxial layers, has become a major technique for the production of many types of device-quality semiconductor materials. Much progress in semiconductor technology during last two decades has been based on epitaxial technologies in the development of the quality, and the success of advanced multi layered structures and devices depend mainly on the epitaxial techniques used to grow them.

2.2 ADVANTAGES OF EPITAXIAL GROWTH

The epitaxial layers have better structural and electrical properties than the bulk ones. This is mainly due to the fact that, in epitaxy, the growth is carried out at temperatures several hundred degrees lower than melting point of the compound or alloy. This decrease in growth temperature accounts for the observed decrease in the concentration of both chemical and crystalline defects as compared with the material grown from a nearly
stoichiometric melt. At lower temperature the melt is subjected to less chemical contamination by dissolution or diffusion from the surrounding container. Also concentration of the lattice vacancy is expected to decrease at lower temperatures. Advantages of epitaxial growth, with reference to above facts are such as (1) the ability to control material thickness and carrier concentration, (2) the possibility of growing p-n junctions and other multilayer structures, (3) superior electrical, properties due to the lower defect densities in the epitaxial material particularly minority carrier.

2.3 EPITAXIAL TECHNIQUES

Epitaxial growth can be achieved from solid-phase, liquid-phase, vapor – phase and molecular-beam deposition. Vapour phase growth is by far the most widely used technique for semiconductors. It consists of oriented crystal growth of a material transported from the gas phase onto a suitable solid substrate.

Vapour phase growth is the condensation of the material from its own vapours, as in an evaporation-condensation process. However, the term is commonly used to describe all epitaxial growth processes involving transport from the gas phase, whether the gaseous medium actually contain vapours of the crystallizing material or simply a mixture of gaseous reactants capable of undergoing chemical conversion at the solid surface to yield the epitaxial layer. In fact the most commonly employed techniques for semiconductor epitaxy correspond to the later case, where a gaseous compound or combination of compounds is transported to the vicinity of the solid surface, at which point a chemical reaction occurs which results in formation and deposition of the semiconductor material.
2.4 VAPOUR PHASE EPITAXY (VPE)

VPE systems are particularly employed in mass production of electronic device because of their proven low-cost high throughput, in addition of their capability of growing advanced epitaxial structures. The fundamental reason for their success is due to the ease of dealing with low and high vapour pressure elements. This is achieved by using specific chemical precursors, in the form of vapour, containing the desired elements. These precursors are brought into the reactor by a suitable carrier gas and normally mixed shortly before reaching the substrate, giving rise to the nutrient phase of the crystal growth (Fornari 2003). The release of the gas elements necessary for the construction of the crystalline layer may occur at the solid-gas interface or directly in the gas phase, depending on the type of precursors and on the thermodynamic conditions.

2.5 GaN FILM GROWTH BY VAPOUR PHASE EPITAXY

The growth of epitaxial films by VPE (Maruska and Tietjen 1969), until the early 1980s, VPE was considered as a popular method for the growth epitaxial layers of gallium nitride. This technique was largely abandoned in the early 1980s because of an apparent inability to reduce the native defect concentration to non-degenerate levels. This was presumed to be due to the nitrogen vacancy defect, which would be thermodynamically favored at the high growth temperatures typically used in HVPE GaN growth. This interpretation predominated in spite of reports of nondegenerate films grown by HVPE (Ilemgems 1972) and careful growth studies which suggested that incorporation behavior of this donor was inconsistent with a nitrogen vacancy defect (Seifert et al 1981).
The nature of chemistry involved in GaN growth by HVPE technique differs from other III-V semiconductors. For instance, in GaAs growth halide vapour phase epitaxy, which uses the halide of the group V precursor AsCl$_3$ instead of its hydride AsH$_3$, thermal dissociation of the arsenic compound results in the formation of As$_4$ and As$_2$ molecules, which typically remain volatile and chemically reactive and thus participate in the film growth. In HVPE GaN, NH$_3$ is used as a source of nitrogen rather than nitrogen halide (NC1$_3$), which is highly explosive. In this process the thermal dissociation of NH$_3$ results in the formation of N$_2$ molecules which are extremely stable and essentially underactive at the temperatures of interest (Molnar et al 1997, Lee and Harris 1996 and Dwikusuma et al 2003). In fact, the viability of HVPE GaN growth lies in the relatively sluggish disassociation of NH$_3$, which enables the effective transport of reactive nitrogen to the growth surface. Hydride VPE (HVPE) and Chloride-VPE (Cl-VPE) operate in a very similar manner and can be described by the final reaction as,

$$\text{GaCl}_3 + \text{NH}_3 \rightarrow \text{GaN} + 3\text{HCl} \quad (2.1)$$

However, the precursor for generating gallium chloride is different in both the techniques. In HVPE of GaN, the gallium source is gallium monochloride (GaCl), which is stable only at temperatures above 600°C and is produced by the reaction of liquid gallium with HC1 gas (Jacob et al 1977, Fornari et al 2001). The supply of GaCl is controlled by the gallium cell temperature and the flow rates of HCl gas and H$_2$ carrier gas. The use of highly corrosive HCl gas, which can quickly destroy reactor equipment if care is not taken to avoid leaks to air. To circumvent this problem, several researchers have chosen pre-synthesized GaCl$_3$ instead of HCl gas (Nickl et al 1974, Tsuchiya et al 1996 and Topf et al 1998).
In Cl-VPE gallium trichloride (GaCl\(_3\)) is used as the Ga source, due to its high vapour pressure. Thus it is evident that there are no fundamental differences between HVPE and Cl-VPE. The use of mono-halide (GaCl) or tri-halide (GaCl\(_3\)) is the main difference between HVPE and Cl-VPE, respectively. In this study, we used gallium trichloride as the Ga source, ammonia for nitrogen, gases were used as the nitrogen precursor and carrier gas respectively.

2.6 SEQUENCE EVENTS IN VAPOUR PHASE EPITAXIAL GROWTH

In vapour phase epitaxy with open flow systems, a carrier gas containing the reactive species is forced to flow past the substrate. At the substrate surface the species undergo a sequence of chemical reactions leading to extension of the substrate lattice and formation of products which must have the vicinity in order for the process to continue.

The sequence of steps which is generally assumed to occur during vapour phase epitaxial growth is as follows:

1. Transport of reactants to the epitaxial growth region
2. Transfer of reactants to the surface region
3. Adsorption of reactants
4. Surface process including reaction, surface diffusion, and site incorporation
5. Desorption of products
6. Transfer of products to main gas stream
7. Transport of products away from epitaxial growth region
These sequences are shown schematically in Figure 2.1. The factors which influence the growth rate and material composition are the vapour flows, pressure and the temperature, all of which can be precisely controlled. Depending upon the sources and the reactor type, one can distinguish between two special cases of VPE, namely hydride/chloride vapour phase epitaxy and metalorganic vapour phase epitaxy MOVPE). The former one uses inorganic sources and the reactor is a hot wall reactor, the latter one uses fully or partly organic sources and is a cold wall reactor.

Figure 2.1 Schematic description of the sequence of steps in a VPE process
2.7 GROWTH OF GaN BY CHLORIDE VAPOUR PHASE EPITAXY (Cl - VPE)

2.7.1 Single Zone Furnace

As the growth occurs at high temperature, the reaction chamber is made out of a quartz reactor of length 90 cm, wall thickness 2mm and diameter 70 mm. The single zone furnace consists of a suitable resistive heating arrangement. A ceramic muffle of length 80 cm has been used for winding the heating element. There are two thermocouples, one to control the furnace temperature, mounted at the middle of the ceramic tube near the growth zone and the other thermocouple is mounted inside the quartz tube, very close to the boat, to monitor the growth temperature more accurately.

2.7.2 Gallium Tri Chloride (GaCl\textsubscript{3}) Cell Assembly

The GaCl\textsubscript{3} cell assembly is made up of a quartz tube. The crystalline GaCl\textsubscript{3} in the cell is melted uniformly by liquid paraffin bath, in which it is immersed. An electric heater maintains the paraffin bath at a suitable temperature in the range of 353-423K.

2.7.3 Ammonia Gas Purifier

The purifier parts consist of molecular sieves, which is a palladium and silica based compound, to remove moisture, carbon monoxide and carbon dioxide from the ammonia gas. The purified ammonia is of analytical grade. After this online purification of ammonia gas, the flow is monitored using an ammonia gas flow meter in standard liter per minute (slm).
Figure 2.2  Schematic apparatus of the GaN Chloride-vapour phase epitaxy (Cl-VPE) system

NH$_3$ – Ammonia, SV – Solenoid Value, MFC- Mass Flow Controller, N$_2$ – Nitrogen, GaCl$_3$ – Gallium Tri Chloride
2.8 EXPERIMENTAL PROCEDURE

Growth conditions for the growth of GaN using GaCl$_3$ and ammonia precursor and the reactions are investigated. In view of the high quality GaN growth, it is understood that careful cleaning the substrates prior to loading into the substrate holder is an important issue because the quality of the grown layer (desired morphology and good optical property) depends on this process and also the reproducibility of results. Sapphire Al$_2$O$_3$ (0001) substrates were degreased in trichloroethylene (TCE), acetone, methanol and de-ionized water in sequence for about 10 minutes. After completing the organic cleaning processes, in order to remove residual damage and scratches on the surface, the substrates were chemically etched with HCl + H$_3$PO$_4$ (3:1) solution heated at 353K for 15 minutes.

Cleaned sapphire substrates are again rinsed thoroughly in de-ionized water. A quartz plate of 8cm$^2$ area was used as the substrate holder, located at an optimized distance from the GaCl$_3$: NH$_3$ mixing zone. Substrates of 1 cm$^2$ area are used per run and are placed lengthwise along the deposition zone. Considerable variation on the deposition is observed between layers grown in a single run with respect to the position of the substrate. It is observed that GaN layer deposits always in the region closer to the GaCl$_3$: NH$_3$ mixing zone. After loading the substrates, the reactor is purged with nitrogen gas. Subsequently, the substrate was heated to the desired growth temperature and GaCl$_3$ is supplied using nitrogen carrier gas. The nitrogen source, NH$_3$ is not stable at high temperature and will thermally decompose to nitrogen and hydrogen gases.

Hence, most of the ammonia will decompose to nitrogen and hydrogen at that elevated temperature in thermodynamic equilibrium. The H$_2$ gas, produced from the thermal decomposition of ammonia, will promote the
reduction of GaCl\textsubscript{3} to GaCl. If hydrogen reduction of GaCl\textsubscript{3} is not completed, the remaining GaCl\textsubscript{3} can react with ammonia via the following reaction

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\text{GaCl}_3 + \text{NH}_3 \rightarrow \text{GaN} + 3\text{HCl}
\]  (2.2)

No low temperature buffer layer is used in these experiments. Typical N\textsubscript{2} flow rate for GaCl\textsubscript{3} transport was 100 sccm. During the process 2.0 slm of N\textsubscript{2} were introduced into the reactor zone and the growth temperature is maintained at 1263K. To our knowledge there is lot of reports on the growth of GaN by this technique by varying the growth temperature. So here we studied the experiment by varying the ammonia flow rate in the range of 3 to 5 slm. The ammonia flow rate was varied in the range of 3 to 5 slm. Ambient pressure inside the reactor is maintained at one atmosphere for all the experiments.

It is obvious that there are no ideal crystals in reality and all crystals grown by any technique contain some defects, impurities and inhomogeneities. Most of the physical properties are sensitive to the deviation from ideality therefore, generally the characterization of the grown crystals is a necessity. The assessment of crystalline perfection is essential of epitaxial layer provides information on the processes that occurred during growth. The demand for layers of the highest quality is increasing and only systematic characterization enables the crystal grower to optimize the growth parameters in order to obtain better results. An epitaxial layer characterized by a description of its chemical composition, of its defects and of spatial distribution of these features. It is very vital to know the degree of purity and perfection of epilayers to interpret structure dependent properties and in order to determine whether the material can be successfully employed in the experiments or device fabrication. GaN being a technologically important material has elicited a large degree of characterization studies (Akasaki and

2.9 RESULTS AND DISCUSSION

2.9.1 X-ray Diffraction Studies

X-ray diffraction is used to determine the structural property of the GaN films. The grown GaN film was characterized using D8 Brucker AXS X-ray diffractometer with Cu K$_\alpha$ source. The wurtzite structure of grown GaN epilayers at three different flow rates of ammonia gas are shown in Figure 2.3. The pattern shows sharp peak corresponding to wurtzite GaN at 34.98° for (0002) plane. The Peak at 42.5° corresponds to sapphire substrates. The calculated lattice constant is $a=3.18\ Å$ and $c=5.18\ Å$, which are in good agreement with the reported values. The analysis shows the preferential orientation for growth of GaN epilayers is c-plane. When the ammonia flow rate increases from 3 slm to 5 slm, the intensity of the peak decreases. Because the growth take place in nitrogen rich condition as flow rate increases, so there is a good possibility of Gallium related defects, may be due to the creation of Ga vacancy defects in epilayers. Hence, the quality of the grown film decreases.
2.9.2 X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) technique is used as a non-destructive experimental tool to study the local electronic and atomic structure of materials. XAS is generally characterized by very fine spectral features near the absorption edge. NEXAFS spectra provide important information about the electronic and structural properties. The energy region of 50-1000 eV above the absorption edge is referred to as the extended X-ray absorption fine structure (EXFAS). NEXAFS measurements are carried out using the facility at the Synchrotron Radiation Research Centre (SRRC), Hsinch, Taiwan, operating with an electron energy of 1.5 GeV and a maximum stored current of 200 mA. The NEXAFS spectrum at N K-edges for GaN was obtained from high energy spherical grating monochromator (HSGM) by the fluorescence mode in a vacuum chamber of $10^{-9}$ torr. Figure 2.4 shows the spectrum recorded at nitrogen K edge region for Cl-VPE grown GaN at three different ammonia flow rates (3,4 and 5 slm).
The spectral features indicates the transitions from the N 1s level to vacant low lying levels in the conduction band with 2p symmetry (Xin et al 2000). The spectral features are very much similar to that of the hexagonal GaN. The first peak at 401eV of the spectrum corresponds the transition to final states in the ‘c’ direction i.e., to states that originate from the mixing of ‘s’ and $P_z$ molecular orbital’s (Katsikini et al 1999) and is due to the $\pi^*$ resonance of molecular nitrogen trapped within the films (Ruck et al 2004). While the second peak is related to final states in the a-b plane i.e., from the mixing of $P_x$ and $P_z$ orbital. We observed that for higher flow rate of ammonia, the intensity of absorption peak decreases, which indicated that the structural quality of the film degrades.

![Graph](image.png)

**Figure 2.4** X-ray absorption spectroscopy of GaN grown at different ammonia flow rate

### 2.9.3 Optical Transmission

Optical property of the GaN film is investigated by means of transmission measurements. UV-VIS spectrophotometer (Shimadzu, model
UV-3101) was used to record the transmission spectra of the GaN layer. The halogen and deuterium lamps are used as near infrared and UV visible sources, respectively. It uses a grating type double monochromatic to disperse the beam into constituent wavelengths. The incident radiation is split into reference beam and sample beams by a chopper mirror. The reference beam is used to nullify the effect of sample mount. The wavelength resolution of the instrument is 0.1 nm. A thick aluminum plate with a hole of 1mm diameter was used as sample holder.

![Optical transmission spectrum of GaN grown at different ammonia flow rate](image)

**Figure 2.5** Optical transmission spectrum of GaN grown at different ammonia flow rate

Figure 2.5 shows the transmission spectra of the GaN epilayers grown at two different flow rate of ammonia. The sharp transmission edge located at a wavelength of 364.7 nm is assigned to the band gap of GaN. The well defined interference pattern observed in the transmission spectrum for
the flow rate of 3 slm is very good due to the difference in the refractive index between the GaN layer and the sapphire substrate, also it indicate the epilayers grown are of high quality. When the flow rate increases to 4 slm and 5 slm, the interference pattern get affected and also the percentage of transmission decreases with no shift in band edge emission. This poor transmission percentage indicates that the quality of grown epilayer gradually decreasing due to creation of defects and also due to increases in surface roughness values.

2.9.4 Photoluminescence

Photolumiscence (PL) is a non-destructive technique to characterize the intrinsic properties like band to band edge recombination to evaluate the band gap energy, shallow defect levels like donor or acceptor levels. In this technique only radiative transition of energy levels are studied, the sample is excited with laser beam from a source with photon energy \( h\nu \) greater than the bandgap \( E_g \) such that excesses electron hole pair are created. Radiative recombination of electron hole pairs produces luminescence which is wavelength resolved by prism or grating monochromator. The luminescence signal at room temperature is dominated by Band-Band (BB) transitions and corresponds to the band gap energy of the material (Gilliland 1997). BB recombination is governed by the equilibrium energy of the free electron and free holes.

The different transitions where an electron goes from a filled valance band to an empty conduction band are possible due to the influence of an external optical energy. The recombination of an electron with a hole give rise to the luminescence signal and the process is termed as radiative. Room temperature (300 K) PL spectra are recorded for the GaN epilayer grown on sapphire substrate using He-Cd laser as the excitation source (345 nm). The
sample is mounted on a cold finger inside a close cycle helium refrigerator and the transparency of the optical quartz window is up to 2500 nm. The luminescence signal from the sample is collected and focused onto the monochromator through a biconvex lens.

Figure 2.6 Photoluminescence spectra of GaN grown at different ammonia flow rate

PL spectrum of GaN layers recorded at room temperature for a three different flow rate of ammonia gas is shown in Figure 2.6. For the flow rate of 3 slm, strong band edge emission peak correspond to GaN has been observed at the wavelength of 361.6nm. When the flow rate increase to 4 and 5 slm, there is no shift in band edge emission but strong yellow luminescence at 550 nm is observed due to increase of defects during growth process as a result the intensity of band edge emission decreases. Thus the quality of epilayer grown degrades as one increase the flow rate of ammonia.
2.9.5 Atomic Force Microscopy (AFM)

The ability of the atomic force microscopy (AFM) is to create three-dimensional micrographs with resolution down to the nanometer scale. It is an essential tool for imaging surfaces which find applications ranging from semiconductor processing to cell biology. It is a non-destructive characterization technique for quantitative surface roughness measurements. Here Atomic Force Microscopy (AFM) (Digital Nanoscope III A SPM) was used to characterize the surface morphology of GaN films grown at three different ammonia flow rate (3, 4 and 5 slm). The surface analysis of ammonia flow rate variation of GaN layers are shown in Figure 2.7.

Commonly it is very difficult to achieve a very smooth surface over a large area in chloride VPE growth of GaN films due to its high deposition and gas phase etching rates. The localized flux uniformity, flow rate and growth temperature play key roles in determining the surface morphology of GaN films. In this experiment the configuration of GaCl$_3$ and NH$_3$ nozzles and the position of the sapphire substrate were fixed to optimal positions. Surface morphology of the 3 slm ammonia flow rate sample shows layer by layer pattern, grooves and microholes have been observed at higher ammonia flow rates (4, 5 slm). These grooves and microholes decrease the band edge intensity and enhance the yellow luminescence (Oh et al 1997). From the AFM analysis, it is confirmed that higher flow rates of ammonia affect the surface morphology of GaN layer.
Figure 2.7 AFM image of the as grown GaN grown at 990°C for a different ammonia flow rate (a) 3 slm (b) 4 slm and (c) 5 slm.

2.10 CONCLUSION

The processes for the growth of GaN by a Cl-VPE have been described. The Cl-VPE is distinguished by the simplicity of design, relatively low process pressure and cost effectiveness. Wurtzite GaN film is grown on sapphire substrate at three different ammonia flow rates of 3, 4 and 5 slm. XRD conformed the wurtzite structure of GaN epilayers. If the flow rate is
increased to 4 slm, intensity of the peak decreases, which establishes that the quality of the film decreases for increasing the ammonia flow rate. X-ray absorption spectral features are very much similar to that of the hexagonal GaN. UV-transmission spectra for grown GaN films show strong effect on interference pattern with no shift in transmission band edge emission at 364.7 nm. PL spectrum shows an emission peak at 361.6 eV corresponding to the band edge emission of GaN. For higher flow rate the intensity decreases, which indicated that defect are created during growth. From the AFM analysis, it is conformed that higher flow rates of ammonia affect the surface morphology of GaN layer. That is for the 3 slm ammonia flow rate, we observed oriented symmetric gallium nitride diffraction plane. Thus we conclude that from the comparison of three flow rates of ammonia, the 3 slm flow rate yields a good crystalline GaN layers.