CHAPTER 4

GROWTH OF GaN NANOTIPS USING Ga AND GaN POWDER SOURCE

4.1 INTRODUCTION

GaN thin film growth is an important focus of current research because of their potential applications in UV, blue emitters, detectors, high-speed field-effect transistors, and high temperature electronic devices (Mohammad et al 1996, Morkoc et al 1995, Ponce et al 1997). Low-dimensional quantum-confinement structures are crucial for understanding fundamental concepts underlying the observed electronic, optical, and mechanical properties of materials. They can also be used as interconnects in microelectronic devices. Using density-functional calculations, Lee et al (1999) suggested that the GaN bandgap should increase with decreasing GaN nanotube diameter and such properties are useful for the bandgap engineering. One-dimensional structures (nanowires or nano-rods) of gallium nitride are known to have great prospects in fundamental physical science and novel technological applications (Morkoc et al 1995, Ponce et al 1997). Because of the large band gap and structural confinements of nanostructures, for example, the fabrication of visible and UV optoelectronic devices with relatively low power consumption is potentially feasible (Lieber et al 1998, Nakamura et al 1994).

Low electron affinity value of GaN (2.7-3.3 eV) compared to CNTs and ZnO can be used as an efficient field emitter. Hesegawa et al (2005)
reported field emission from polycrystalline GaN nanorods grown on Si and molybdenum (Mo) sheets prepared by molecular beam epitaxy (MBE) technique. Chen et al (2007) reported field emission properties from oriented bicrystalline GaN nanowire arrays on Si by catalytic carbon thermal reduction process. GaN field emission pyramids growth on sapphire substrate by selective-area metalorganic chemical vapor deposition is also reported (Underwood et al 1998). Wang et al (2009) reported field emission property from amorphous GaN thin film fabricated by pulsed laser deposition. The field emission properties of polycrystalline GaN layers grown on polycrystalline Mo substrate by gas source MBE was studied (Yamanaka et al 2002). Czarczynski et al (1999) observed field emission characteristics from GaN layers grown on Si by MOVPE. All the reported methods used were expensive to grow GaN nanostructures for field emission displays. The self assembled simple and inexpensive CVD method is presented here for the growth of GaN nanotips on sapphire substrate for field emission applications.

4.2 EXPERIMENTAL DETAILS

The growth was performed using GaN powder as a source, which was synthesized by nitridation of Ga-EDTA Complex. The detailed experimental procedure was discussed in chapter two about the synthesis of GaN nanocrystalline powders. XRD and FTIR analysis were carried out to confirm the crystal structure and phase purity of the synthesized GaN nanocrystals. GaN nanotips have been grown in a horizontal reactor with resistive heating. The growth process was carried out in ammonia ambient, passing through the growth cell placed inside the reactor on an alumina boat. A mixture of liquid Ga and self synthesized GaN nanocrystals were used as source to grow GaN nanotips. The experiments show that use of pure Ga as the source provides maximum growth rates but results in poorer temporal and spatial stability of source operation. In turn, use of pure GaN powder leads to
partial decomposition of the source material into the liquid (Ga) and vapor (N\textsubscript{2}) phases starting immediately after the beginning of the growth process. The source boat was placed in a temperature gradient zone, so that there appears a certain temperature difference $\Delta T$ between the source and the substrate. This temperature difference serves as the driving force for Ga transport inside the growth cell and GaN crystallization on the substrate. The distance between the source and the substrate was varied from 2 to 10 cm. Temperatures of the source and substrate was controlled by high precision temperature controllers.

\textbf{Figure 4.1} Self assembled CVD experimental setup for the growth of GaN nanotips

The diagram of the self assembled experimental setup for the growth of GaN nanotips is shown in Figure 4.1. From the direction of the gas flow, the system consists of one gas cylinder (N\textsubscript{2}), with a flow meter having adjustable precision valves at the inlet, single tubular furnace, a quartz tube, a glass bubbler with liquid ammonia, and a glass bottle with water to absorb the residual NH\textsubscript{3}. A\textsubscript{1} and A\textsubscript{2} are the interfaces of quartz and stainless steel (SST).
flanges. A O-ring is placed at the interface. The quartz and SST flanges are then tightened by screws. A₁ is used for loading and unloading samples. All the other connections are standard connectors. The exhaust gas is filled into the glass bottle where NH₃ will be dissolved in water and H₂SO₄ then flows into the open atmosphere. The single zone furnace is one meter long; its stable temperature zone was 10 to 15 cm. The alumina boat holding the substrates and the source, placed at the constant temperature zone. The position of the boat together with the distance between the substrate and the source can be adjusted if the temperature gradient is used. The growth procedure is as follows.

1. Before heating the furnace, The quartz tube is purged with N₂ Gas to remove residual oxygen from the tube.

2. When the tube is purged for 10 minutes, the furnace will be heated to the growth temperature. When the furnace temperature is increased to the growth temperature, the gas cylinders will be open and the flow rates will be adjusted to the standard rates. The two-way switching-valve will be bypass to the NH₃ bubbler then the growth begins.

3. Growth of GaN nanotips on sapphire is carried out at a temperature of 1000 °C for a period of 1 h. The temperature difference between the source and substrate is approximately 10 - 15 °C. The sapphire substrate is cleaned with organic solvents and acids prior to the growth. Then the source container is filled with Ga and GaN powder and kept it into the reactor together with the substrate. Later the reactor was purged with nitrogen gas to remove the residual oxygen and the reaction zone will be heated upto the growth temperature.
with desired ammonia flow. The growth was carryout for a period of 1h. After the growth, temperature was brought down to 500 °C followed by nitrogen purging up to room temperature.

(4) The switching valve will be adjusted in order to achieve the N\(_2\) pressure. When the growth time is over, then the furnace is cooled down to the room temperature. At the same time, the two-way switching valve is switched to side N\(_2\) with the closing of the NH\(_3\) gas.

(5) The reactor is purged with N\(_2\) until the furnace temperature reaches to room temperature.

The grown GaN nanotips were characterized by X-ray diffraction, room-temperature photoluminescence, scanning electron microscopy and atomic force microscopy. Field emission characteristics were also studied.

4.3 GROWTH MECHANISM

Several methods are viable for the synthesis of 1D nanostructures, including thermal and pulsed laser induced evaporation, chemical vapour deposition and molecular beam epitaxy. Thermal evaporation is typically a high temperature vapour process used for deposition of high melting point materials, where a significant amount of energy is required to break strong chemical bonds. Pulsed laser deposition is a versatile technique in which a solid phase material is evaporated through high energy laser pulses. Even though the local temperature during a pulse is very high, the overall temperature of the source material is fairly low, when compared to the thermal evaporation process. MBE is based on the thermal evaporation of the
phase-forming elements under high vacuum conditions, which react on a substrate surface to form the desired crystal lattice. CVD techniques probably allow for the highest variability of deposition parameters. The chemical reactions involved in the precursor-to-material conversion can include thermolysis, hydrolysis, oxidation, reduction, nitration and carbonation, depending on the precursor species used. Once the gaseous species are in proximity to the substrate or the surface itself, they can either adsorb directly on the catalyst particle or on the surface. Diffusion processes as well as the concentration of the adsorbents (supersaturation) are responsible for the growth of a solid phase at the catalyst–surface interface. In the early 1960s Wagner and Ellis described the growth of micrometer-sized Si whiskers/wires with hemispherical or truncated tips of similar radial dimension, also known as vapour–liquid–solid (VLS) mechanism (Wanger et al 1964).

GaN nanostructure synthesis mostly involves one of two typical growth mechanisms. The vapor–liquid–solid (VLS) mechanism utilizes a transition metal catalyst while the vapor–solid (VS) mechanism relies on direct crystallization from the vapor. For VLS the dominant morphology is generally nanowire because nucleation and growth are determined by a liquid catalyst particle. However, undesired contamination can occur from the catalyst. In contrast, morphologies such as e.g., nanobelts, are possible due to the absence of constraints by the catalyst in the case of VS growth. Furthermore, the growth scheme is simple, and contamination can be avoided. In the absence of metal catalysts, the vapour–solid or self-catalytic growth mechanism has been mainly used for synthesis of metal oxide and some semiconductor nanostructures. In the present method Ga act as a self catalyst for the growth of GaN nanotips on sapphire substrate. In all cases the growth front plays a crucial role in the adsorption of atoms or phase-forming species. The front can be very rough (poorly arranged atomic positions and the
presence of defects) which promotes the sticking of diffusing species and nucleation. An ideal crystal facet contains only a few nucleation centers and potential desorption events of diffusing species are likely due to low binding energy. In this respect, the presence of defects, such as screw-dislocations, is mandatory to continuously provide atomic steps, where the diffusing species can bond. Pure vapour transport synthesis is a re-sublimation event and the material morphology is governed by process parameters, such as substrate temperature, gas-phase composition and overall pressure. This synthetic strategy allows the synthesis of nanostructures. The nucleation step could be induced by defects on the growth front which exhibit a rounded shape or by sequential incorporation of charged species on nuclei combined with the formation of low energy facets or catalytic growth (self-catalytic or metal induced), followed by VS growth to attain the most favored nanostructure under given experimental conditions (Barth et al 2010).

4.4 RESULTS AND DISCUSSION

4.4.1 X-ray Diffraction Analysis

A typical XRD pattern of the resulting GaN nanotips grown on sapphire substrate is shown in Figure 4.2. The sharp diffraction peak (002) in the pattern was indexed to a be from GaN wurtzite structure (002) plane. The presence of only (002) reflection indicated the film is highly oriented along the c-axis. This was also further evident from the columnar growth observed in AFM. The diffraction at 34.36 and 41.5 are attributed to GaN layer and Al$_2$O$_3$ substrate respectively.
Figure 4.2  XRD pattern for GaN nanotips grown on sapphire substrate at 1000 °C

4.4.2 Scanning Electron Microscopy

Figure 4.3 shows the SEM image of the GaN nanotips grown on sapphire substrate. The microstructure has rod like morphologies. During the growth period of 1 h, this rod like structures probably continuously grew in length along the lateral direction to form wire-like structures. A large number of short rods like structures with diameters of several hundred nanometers are seen in the image.
Figure 4.3 SEM image of GaN grown on sapphire substrate

4.4.3 Atomic Force Microscopy

Figure 4.4 (a), (b) and (c) show typical perspective views of AFM images of GaN nanostructure grown on sapphire substrate at 1000 º C. The length and width of the nanotips are 300 and 190 nm respectively. The 3D AFM image Figure 4.4 (b) also shows that there are tip like structure at the grains. In order to produce efficient field emission of electrons, tip-like structures are usually used. More over GaN has quite rough surface and the grains protrude substantially from the surface. From the XRD and AFM results, it can be seen that the GaN film consists of single crystalline GaN nanotips. Actually, low threshold electric fields were obtained from some tip like structures for boron nitride (BN) (Sugine et al 2000), AlN (Kasu et al 2001) and GaN (Sugino et al 2001).
Figure 4.4 AFM images of 2D (a) and 3D (b and c) view of GaN nanotips

4.4.4 Photoluminescence Spectroscopy

Typical photoluminescence spectrum from GaN film recorded at room temperatures is shown in Figure 4.5. He-Cd laser working at 325 nm with an output power of 10 mW was used as an excitation source. The emission signal was collected by a SPEX 0.85-m double spectrometer and detected by a lock-in amplifier coupled with a photomultiplier tube. The PL spectra of GaN nanotips grown on sapphire substrate exhibit a strong peak emission at 367 nm, which corresponds to the band edge emission of GaN.
A broad peak at 2.28 eV can be assigned to the well-known yellow luminescence (YL) band (from 1.7 to 2.8 eV), which arises due to capture of conduction band electrons, or electrons from shallow donors (with a maximum depth of the order of the thermal energy) by a deep acceptor level with a broad energy distribution, centered at ~2.2 eV below the conduction band edge (Shalish et al 1999). This broad deep emission is usually attributed to defects caused by impurities.

![Figure 4.5 PL spectrum of GaN nanotips grown on sapphire substrate](image)

**Figure 4.5** PL spectrum of GaN nanotips grown on sapphire substrate

### 4.4.5 Field Emission

Electrons are emitted from a metal or semiconductor on applying a strong electric field by a process called “Field Emission”. The phenomenon was first reported by Wood et al (1987), subsequent field emission studies have made significant contribution to the technological advances and basic
sciences similar to other fundamental electron emission processes from solids like thermionic emission, photoelectric emission and secondary electron emission.

### 4.4.6 Fowler Nordheim (F-N) Plot

In a field emission experiment the measurable quantities are the field emission current \((I)\) and the electric potential \((V)\) applied between the cathode and the anode. \(J\) and \(E\) are related as

\[
I = JA
\]

\[
F = V
\]

where \(A\) is the emitter area and \(\beta\) is the field enhancement factor determined by the geometry of the emitter. The F-N equation takes the following form

\[
J = \frac{1.54 \times 10^{-6} \beta^2 V^2 A}{\phi t^2(y)} \exp \left[-\frac{6.83 \times 10^7 \phi^2 f(y)}{\beta V}\right]
\]

Plot of \(\ln(J/E^2)\) Vs \(1/E\) from this equation results in a straight line for metals called Fowler Nordheim plot. The field enhancement factor was determined from the slope of the \(\ln(J/E^2)\) vs \(1/E\) plot, which is given in the following form.

\[
\beta = \frac{-6.83 \times 10^7 \phi^2}{m}
\]

Here \(m\) is the slope of the F-N plot; \(\phi\) is work function of the material.
4.4.7 Importance of Field Enhancement Factor in Nano Systems

The field enhancement factor determines the size of the emitter. The nanometric dimensions of materials are excellent field emitters due to their favorable aspect ratio and size. The field enhancement of an individual nanowire is approximately proportional to the aspect ratio \( l/r \), where \( l \) and \( r \) are the length and radius of the nanowire. The high current densities and low threshold field are a result of high field enhancement factor.

4.4.8 Field Emission Displays

A field emission display (FED) is a low power, flat cathode ray tube type display that uses a matrix-addressed cold cathode to produce light from a screen coated with phosphor materials. A field emission display typically includes an electron emission tip configured for emitting a flux of electrons upon application of an electric field to the field emission device. An array of miniaturized field emission devices can be arranged on a plate and used for forming a visual display on a display panel. The emission tip is specifically shaped to facilitate effective emission of electrons, and may for example conical, pyramidal, or ridge-shaped in surface profile, or alternatively the tip may comprise a flat emitter surface of low work function material. In the initial FEDs, the emitters were formed of what are referred to as Spindt-type metal tips (or microtips). A main material of the metal tips is molybdenum. Recently, in a field emission display, several hundreds to thousands of micro tips or CNTs per pixel are provided as an electron emission source on a back plate of FED.

4.4.9 Field Emission Studies

Field emission characteristics of the GaN nanotips on sapphire substrate were investigated. The field emission study was performed at a base
pressure of $1.5 \times 10^{-5}$ Torr. The distance between cathode-to-anode was 150 µm. Figure 4.6 (a) shows the field emission curve of the current density as a function of electric field ($J - E$).

![Figure 4.6(a) Field emission current density as a function of the applied bias voltage for GaN nanotips grown on sapphire substrate](image)

The grown GaN nanotips show a larger threshold electric field of 8 V/µm and a lower field emission current density of 1 µA/cm². The heights of the nanotips were approximately 250 to 300 nm. The diameter of the top part of the nanotips was smaller than that of the bottom part of the nanotips. The current density of the samples show lower value compared to previous reports, which may be due to larger surface roughness and larger surface area of the nanotips.
Figure 4.6(b) F-N plot of I–V characteristics of GaN nanotips

Figure 4.6 shows the Fowler - Nordheim (F - N) plot of the J - E curves, i.e., ln(J/E²) Vs 1/E, for GaN nanotips. According to the F - N theory, the slope of the F - N plot is equal to the \(-6.83 \times 10^3 \phi^{3/2}\) (Chen et al 2007), where \(\phi\) is the work function and \(\beta\) is the field enhancement factor (Niranjan et al 2006). It is possible to estimate field enhancement factor \(\beta\) from the slope of the F-N plot, with the known work function \(\phi = 4.1\) eV). For a nanostructured emitter, \(\beta\) factor depends on the geometry of the nanostructures (aspect ratio), work function, conductivity, and nanostructure density. The higher the field enhancement factor \(\beta\) better will be the field emission. The field enhancement factor estimated from the sample is 425. For single crystalline GaN the field enhancement factor reported to be 61 and 120 for as grown smooth surface and plasma treated rough surface samples (Sugino et al 2001). It is well known that field enhancement factor \(\beta\) is decided by the aspect ratio and geometry of materials. These results indicate that the GaN nanotips have a structure that is suitable for a field emitter.
4.5 SUMMARY

A simple and inexpensive method was used to grow GaN nanotips on sapphire substrate. The self synthesized GaN powder and pure metallic Ga were chosen as source material for the growth. GaN growth has been carried out in a horizontal reactor on sapphire substrate in ammonia atmosphere at 1000 °C for a period of 1hr. The crystal structure of GaN film was confirmed by XRD. The sharp diffraction peak (002) in the pattern was indexed to a wurtzite structure. The lattice constant derived from the XRD peak positions was \( c = 5.20 \, \text{Å} \). Surface morphology of the film was observed by scanning electron microscopy and atomic force microscopy. The SEM image shows rods like structures which continuously grew in length along the lateral direction. Nanorods were tip like structure at the top edge observed from 3D AFM image. In order to produce efficient field emission of electrons, the tip-like structures are usually used. The photoluminescence spectrum of GaN nanotips grown on sapphire substrate exhibited a strong peak emission at 367 nm, which corresponds to the band edge emission of GaN. The field enhancement factor estimated by FED analysis was 425. These FED results indicate that the GaN nanotips have a structures which will be suitable for fabricating field emitter devices.