Progress in III–nitrides: Process issue and purity perspective

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Abstract. The growth of good quality layers of gallium nitride (GaN) as suitable for epitaxial growth is of great technological importance. Chloride vapour phase epitaxy (Cl–VPE) has been employed to grow good quality layers of GaN. The grown layers have been extensively characterized for their structural and optical properties. MOVPE grown GaN layers have been used to address process issues on device structuring and fabrication. GaN samples with different transition metal dopants have been synthesized and their usefulness as semi-magnetic materials, which are also identified as dilute magnetic semiconductors (DMS), have been evaluated. Better results have been obtained on the magnetic characteristics of GaN with ruthenium as the dopant. Nano dimensional structures of GaN have been obtained with excellent control of the growth parameters.

Keywords. Gallium nitride; chloride vapour phase epitaxy; nano gallium nitride; semi-magnetic materials; dilute magnetic semiconductors.

1. Introduction

Recent advances in nitride based white light sources and on electronic devices that can operate at high temperatures have enthused researchers to work more vigorously on different aspects of III–nitrides such as gallium nitride (GaN), indium nitride (InN) and aluminium nitride (AlN). The recent report on the reduced band gap value of InN owes much to the control on the purification and deposition process. Hence, InN based alloy systems have opened up excellent new possibilities on solar cell fabrication and on newer device structures.

The availability of an appropriate substrate for epitaxial growth is crucial to the practical application of new semiconductor materials. The factors determining the appropriateness include crystallographic, physical, chemical, and economic parameters.

The major objective of the investigation is to develop gallium nitride (GaN) device quality layers and evaluate their characteristics. We have designed and fabricated the vapour phase epitaxy system (VPE) for the growth of gallium nitride (GaN). GaN samples with different transition metal dopants have been synthesized and their usefulness as semi magnetic materials, which are also identified as dilute magnetic semiconductors (DMS), have been evaluated using vibrating sample magnetometer (VSM) measurements. Ruthenium doped GaN shows better promise as a DMS material. GaN has been synthesized through a reaction between metal Ga and NH_3 in the temperature range 900–950°C. The reaction period has been varied from 4–12 h and it was found that the synthesis carried

out at 950°C for 8 h yielded very excellent GaN. Synthesized GaN powder has been characterized by XRD, which reveals the hexagonal structure. The process had also been used for synthesis of GaN with dopants such as manganese, ruthenium and chromium.

2. Gallium nitride synthesis and chloride vapour phase epitaxy growth

Gallium nitride was synthesized with and without dopants such as chromium, manganese, magnesium and ruthenium of different concentrations and the details including the characterization of the same has already been reported (Senthil Kumar *et al* 2000).

The VPE system mainly consists of a reaction chamber, single zone furnace, ammonia gas purifier and gallium tri chloride (GaCl_3) cell assembly. The experimental set up is shown in figure 1.

As the growth was a high temperature process, the reaction chamber was made out of a quartz tube of length, 90 cm, wall thickness, 2 mm and diameter, 70 mm. Both ends of the tube were made out of SS assembly with 2 ports on one end and three ports on the other end. One end of the quartz was used for the flow of GaCl_3 vapour and nitrogen gas and another end of the reactor tube was used for ammonia gas, exhaust and substrate holder set up.

The furnace was interfaced with a computer for controlling the temperature. The controlling thermocouples, chromel alumel, were placed inside the muffle along with the reaction chamber i.e. outside the quartz reaction chamber, so that the temperature difference between the actual growth position and the thermocouple sensing position was minimized.

Ammonia gas was purified with a system that consisted of molecular sieves, which was a palladium and silica based compound, to remove moisture, carbon monoxide and carbon dioxide. The purified ammonia was expected to be of electronic grade. For the actual experiment the quartz reaction chamber was inserted into the muffle and fixed exactly in the horizontal position with the help of adjusting screw from outside. After purification the ammonia gas flow was monitored and varied with the help of an ammonia gas flow meter. The GaCl_3 cell assembly was made of quartz tube and SS. The crystalline GaCl_3 was heated and melted by an electric heater immersed in liquid paraffin. The GaCl_3 vapour was transported to the reactor by the nitrogen carrier gas. The nitrogen gas was also used to dilute the ammonia and to increase the total gas flow rate. Both the GaCl_3 cell temperature and the flow of nitrogen gas controlled the supply of GaCl_3 . Mass flow controller and solenoid valves controlled the flow rate of the carrier gas. The experimental conditions were optimized for getting good epitaxial layers of GaN on sapphire substrates (Varadarajan *et al* 2004a,b).

3. Structural, optical and electrical properties of VPE grown GaN thin films

High resolution X-ray diffraction (HRXRD) results of the GaN layers, which are grown at different temperatures are shown in figure 2. The films are found to have completely *c*-axis orientation in the normal direction without any meaningful trace of differently aligned planes. This observation shows that the basal planes of these films and sapphire substrate are parallel to each other (GaN (0001) and Al_2O_3 (0001)). The peak intensities increase with increase of growth temperature. The FWHM of the GaN layers grown at 990°C is about 0.213° . The XRD peaks observed in this study are in good agreement with the values reported earlier (Yang *et al* 2000; Heinke *et al* 2000; Narayanan *et al* 2001). Figure 3 shows the θ -scan of the VPE layer (grown at 990°C) of GaN ($\bar{2}203$) plane, which is used to determine the in-plane orientation. Only one set of reflection peaks from ($\bar{2}203$) plane has been observed with 60° spacing. This indicates that the GaN films grown on sapphire are single crystal (Varadarajan *et al* 2003).

Figure 1. Schematic apparatus of the GaN Cl-vapour phase epitaxy system (MFC, mass flow controller; SV, solenoid valve).

Figure 4 shows the Raman spectra of the Cl-VPE grown GaN layers at different temperatures. The spectra show two Raman modes, E_2 (high) and A_1 (LO) at frequencies 577 and 752 cm^{-1} , respectively along with sapphire substrate peaks. There is a considerable change in the peak intensity of E_2 (high) and A_1 (LO) Raman modes of GaN layers observed for various growth temperatures (Varadarajan *et al* 2004a).

Room temperature (300 K) and low temperature (20 K) PL spectra were recorded for the GaN epilayers grown at different growth temperatures using He-Cd laser as the

excitation source (345 nm). PL spectra for GaN grown at 925°C and 950°C exhibit deep level yellow line (YL), blue band (BB) and band edge (BE) emissions at peak energies of 2.46, 3.19 and 3.45 eV, respectively. For the origin of YL, there are many reasons reported in the previous works: residual impurities such as oxygen, native defects such as vacancies, antisites and extended defects such as dislocation and domain boundaries. Nevertheless, the exact origin and mechanism of the YL emission is still not yet clearly understood and hence under debate. Our PL measurements show that the intensity of YL emission increases as growth temperature decreases. On the other hand, for the film grown at 990°C, the band edge emission is sharp, whereas the deep level yellow emission is greatly suppressed as shown in the inset of figure 5a. This means that the optical properties of the GaN films greatly depend on the growth temperature. The FWHM of the GaN layers grown at 990°C is about 60 meV.

The low temperature (20 K) photoluminescence (PL) spectra recorded for the films is shown in figure 5(b). At low temperature the signals are more energetically resolved and the peak intensities (YL, BB and BE emissions) are very high and also sharp when compared to the room temperature PL measurements. The FWHM of the GaN layers grown at 990°C is about 40 meV.

Scanning electron microscopy (SEM) (Leica Stereoscan 440) was used to characterize the surface morphology of GaN films grown at different growth temperatures and are shown in figure 6. Surface morphology of the sample grown at 925°C is shown in figure 6(a). It was observed

Figure 2. HRXRD pattern for GaN films on sapphire substrate.

Figure 3. f -scan of the GaN ($\bar{2}203$) plane.

Figure 4. Room temperature Raman scattering spectrum of GaN epilayer grown at different temperatures.

that the sample consisted of GaN crystalline islands. These islands did not coalesce and there are holes all the way to the substrate. As the growth temperature was increased to 950°C (figure 6b), crystallite islands were reduced and the surface became smoother; however, grooves and microholes were observed. Figure 6(c) gives the surface features of GaN grown at 990°C, which has the smoothest and the flattest surface.

SEM observations have been substantiated with the results obtained from other analysis. Hence, it is certain that the reaction temperature plays a very important role in the growth of GaN.

VPE GaN films are commonly unintentionally *n*-type doped and exhibit free carrier concentration in the range between $2 \times 10^{17} \text{ cm}^{-3}$ and $1 \times 10^{19} \text{ cm}^{-3}$. In our present work, the GaN film grown at 990°C exhibit low carrier concentration and also high mobility among the three

layers. The measured values for CI-VPE grown layers are given in table 1.

4. Device processing and fabrication issues on MOCVD grown GaN layers

Metal–GaN contacts have been fabricated on MOCVD grown GaN epitaxial layers. NEXAFS measurements have been used to understand the electronic structure of Ti/*n*-GaN interface through Ti K-edge absorption spectra. Ti/*n*-GaN contacts with different Ti thicknesses when annealed at 900°C for short duration forms TiN on GaN surface by creating highly electron concentrated region in GaN layer, which might be the reason for the low resistance of Al/Ti/*n*-GaN ohmic contacts. Pd/*n*-GaN Schottky barrier diodes (SBDs) have been fabricated. Schottky

Figure 5. (a)–(b) RT and LT PL spectra of GaN/Al₂O₃ grown at different temperatures.

Figure 6. Surface morphology of the GaN films grown at (a) 925°C, (b) 950°C and (c) 990°C.

Table 1. Electrical properties of the Cl-VPE GaN layers grown at different growth temperatures.

Growth temperature (°C)	Resistivity (ρ) (Ω cm)	Carrier concentration (cm^{-3})	Mobility (μ) (cm^2/Vs)
925	8.7×10^{-1}	12.27×10^{18}	64.01
950	5.06×10^{-2}	10.07×10^{17}	72.45
990	2.11×10^{-3}	6.02×10^{17}	83.03

parameters like barrier height, ideality factor and saturation current density have been evaluated from I - V measurements to characterize the Pd/GaN interface.

The ramp SBDs direction is from negative to positive bias. GaN MFS structures have been established on n -GaN by using barium titanate (BaTiO_3), a ferroelectric material, as an insulating layer deposited by sol-gel technique. Composition of the deposited ferroelectric layers has been analysed using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDX) analysis. Al/ BaTiO_3 /GaN MFS structures were fabricated (Senthil Kumar *et al* 2002a,b) by using thermally evaporated aluminum (Al) as gate electrode. An inversion behaviour of GaN MFS structures has been attained in capacitance-voltage (C - V) measurements for a applied voltage of 5 V due to the high dielectric constant and large polarization field of the ferroelectric layer whereas GaN MIS structures with conventional oxides require a high voltage (above 10 V) which is incompatible with other electron devices. The stability of the BTO films has been investigated using bias stress measurements. The 1 MHz capacitance-voltage plot of Al/ BaTiO_3 /GaN MFS structure is shown in figure 7.

5. Nanocrystals of gallium nitride

GaN nano materials have interesting and potentially important applications as exemplary materials to new theoretical concepts and for practical applications. Such devices would be wonderful test beds for studying quantum effects in one-dimensional structures. On the other side, growth of larger diameter rods could be very useful for optical devices and electronic applications. One gram of pure metal gallium, 1 g of gallium nitride doped with manganese and 10 g of B_2O_3 are mixed in an alumina boat and placed in a quartz reactor. The quartz reactor is kept inside a double zone furnace. Sapphire (0001) substrate was initially cleaned using manganese sulphate and placed near the alumina boat. The furnace was heated to 950°C. Nitrogen was allowed to flow over the gallium surface from the start of the experiment. After reaching 950°C, liquid ammonia was placed in a bubbler (1 h) across the nitrogen gas tube from the inlet of the quartz reactor. Nitrogen gas was used as the carrier gas to allow the ammonia molecule into the reaction zone. The dimen-

Figure 7. MHz capacitance-voltage plot of Al/ BaTiO_3 /GaN MFS structures.

sion of the nanowire varies depending upon the ammonia flow rate.

6. Summary

Wurtzite GaN films have been grown on sapphire substrates at different growth temperatures ranging from 925–990°C. HRXRD spectrum for the film grown at 990°C exhibits a sharp peak of wurtzite GaN (0002) and the sapphire substrate. Raman study establishes the good crystallinity of the GaN films. Raman frequency of E_2 and A_1 (LO) modes of GaN is related to the vibrational modes of hexagonal GaN. The film grown at 990°C shows a clear band edge emission at 3.45 eV and very weak emissions related to defects (YL and BB). SEM analysis has been carried out on GaN samples prepared at different growth temperatures. The film grown at 990°C show a smoother surface morphology. Hall measurements show that the film grown at 990°C has high mobility and lower carrier concentration compared to the films grown at 925°C and 950°C. It is concluded that higher growth temperature ($\sim 990^\circ\text{C}$) is an very important processing parameter to obtain good quality crystalline GaN films.

GaN doped with ruthenium has been observed to be a more effective DMS material. Gallium nitride nano structures have been realized on sapphire substrates and the growth morphology had been evaluated in terms of the process parameters.

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