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PRESSURE CONTROLLED GaN MBE GROWTH USING A HOLLOW ANODE NITROGEN ION SOURCE

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ABSTRACT

GaN films were grown on sapphire substrates at temperatures below 1000 K utilizing a Hollow Anode nitrogen ion source. A Ga flux limited growth rate of ~ 0.5 µm/h is demonstrated. Active utilization of strain and the assistance of a nitrogen partial pressure during buffer layer growth are found to be crucial issues that can improve the film quality. The best films exhibit a full width at half maximum of the x-ray rocking curves of 80 arcsec and 1.8_5 meV for the excitonic photoluminescence measured at 4 K. A Volmer-Weber three dimensional growth mode and the spontaneous formation of cubic GaN inclusions in the hexagonal matrix are observed in the investigated growth temperature range. It is argued that this growth mode contributes to a limitation of the carrier mobility in these films that did not exceed 120 cm^2/Vs though a minimum carrier concentration of ~ 10^{15} cm^{-3} was achieved.

INTRODUCTION

In recent years, GaN thin film growth was developed in an unprecedented short time [1-3]. At present, films grown by metal-organic chemical-vapor deposition (MOCVD) or related techniques exhibit the best physical properties that allow for the fabrication of LED's, and for the development of power devices and laser diodes. In addition, growth of GaN thin films by molecular beam epitaxy (MBE) was successful [4, 5]. In contrast to MOCVD, a MBE growth process can exploit deviations from thermodynamic equilibrium that may help to increase doping levels or to grow AlN/InN/GaN quantum well structures of quality. However, GaN thin films are grown at temperatures that are low compared with the melting point of the material ($T_{growth} < 0.5\ T_m$), though absolute growth temperatures are high (typical: MBE growth at 1000 K; MOCVD growth at 1300 K). This, together with the lack of lattice matched substrates makes the growth of GaN thin films a rather complex process. Additional complications arise for the MBE growth process. These range from technical limitations imposed by the development of reliable nitrogen sources that can give growth rates > 1µm/h to the lack of basic understanding of thin film growth at low temperatures.

In this paper we demonstrate that a hollow anode ion source (HA-CGD), utilizing a constricted dc glow discharge nitrogen plasma, allows for a reliable MBE growth of GaN thin films. The unprecedented low kinetic energy (~ 5 eV) of the activated nitrogen ions minimizes ion damage of the growing films. For the present study, a Ga flux limited growth rate of ~ 0.5 mm/h was used. We expect to realize growth rates > 1 µm/h in the near future. These properties distinguish the HA-CGD nitrogen source from commonly used ECR and RF sources. Those suffer in addition from a more complex design which makes them more susceptible to failure during operation. We demonstrate that our films compare in several aspects very well with state-of-the-art MOCVD grown films. In addition, we show that at growth temperatures below 1000 K hexagonal (2H) and cubic (3C) GaN can be grown and that a Volmer-Weber three dimensional (3D) growth mode results in films being composed of oriented sub-grains. It is argued that their shape, size and coalescence is limited by the diffusion of Ga ad-atoms, depending on strain and growth temperature.

EXPERIMENTS

GaN is grown using a refurnished Riber 1000 MBE system. A Knudsen cell is used to evaporate pure Ga (99.9999%) while the activated nitrogen is produced by the HA-CGD source with pure nitrogen gas (99.9999%) along with a Millipore nitrogen purifier. Some details of the source design are given elsewhere [6]. A dc voltage generates a glow discharge in a hollow anode ion source that is constricted to an area in the plasma chamber close to the gas exit. It is the pressure difference between the plasma chamber and the MBE growth chamber that extracts the activated nitrogen species with energies around 5 eV. Liquid nitrogen cryopanels are used during growth to obtain a base pressure in the chamber of ~ 5 x 10^{-10} Torr. A thin Titanium (Ti) layer on the back of the substrate absorbs the heat radiated from the Tungsten (W) filament heater. The temperature of the substrate is monitored with a pyrometer. 10 x 11 mm^2 c-plane sapphire substrates are used. They are degreased by boiling in acetone and ethyle alcohol for 5 minutes each and blown dry with nitrogen gas and introduced in the growth chamber via a load lock. The substrates are heated up to 700 °C for thermal desorption of surface contaminants. At this temperature, they are exposed to activated nitrogen for 10 minutes. Subsequently, a thin low temperature GaN buffer layer (~ 250 Å) is deposited on the substrate. Finally the main epitaxial layer is grown on the buffer layer during 4 hours. Typical grown conditions are: Ga source temperature: 1210 K; nitrogen flow rate: 5 - 80 sccm; buffer layer growth temperature: 773 K; main layer growth temperature: 1000 K. The nitrogen partial pressure in the chamber during growth was varied in the range 10^{-5} - 10^{-2} Torr. The strain in the layers was engineered by using buffer layers of different thickness (0-30 nm) and by variation of the III/V flux ratio during main layer growth [7]. About 100 films were grown with the HA-CGD source and the source did not fail in a single event.

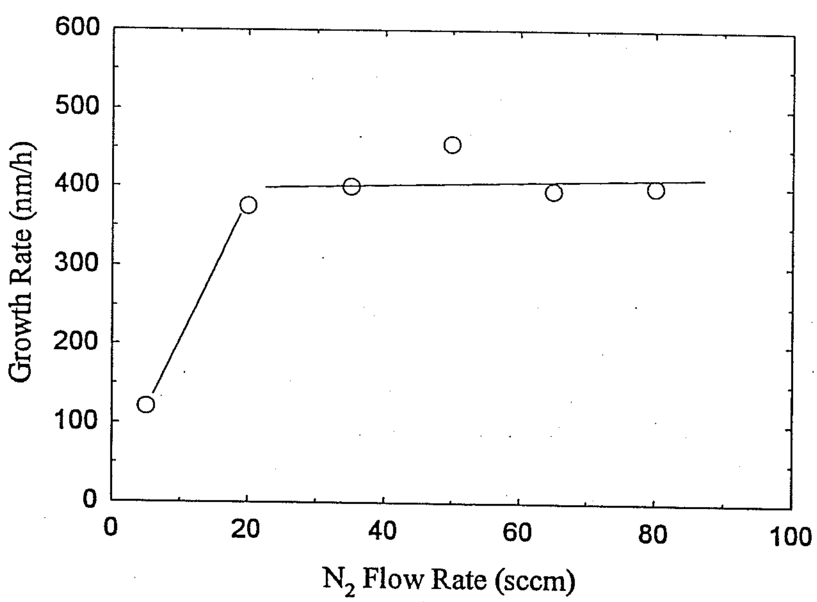


Fig. 1: Growth rate for different flows of nitrogen from the HA-CGD source. For a N-flux larger than 20 sccm the growth rate is limited by the Ga source temperature of 1210 K.

RESULTS AND DISCUSSION

In figure 1 we show that we achieved a growth rate of 400-500 nm/h that is Ga flux limited for nitrogen flows that exceed 20 sccm. The rate is determined by measuring the film thickness and for a growth time of four hours. The present design of the HA-CGD source allows for an increase of the nitrogen flow to 150 sccm. Consequently, we expect growth rates >1 μm/h to be realized in the near future.

The strain in the films was engineered by the buffer layer thickness and the composition of the film as described previously [7]. We note that in addition the nitrogen partial pressure in the growth chamber can be utilized to grow films with a smoother surface morphology. Figure 2 shows the dependence of the surface roughness on the nitrogen flow. Obviously, an increase of the nitrogen partial pressure during buffer layer growth reduces the roughness of the films considerably. A pressure of ~ 10^{-3} Torr decreases the mean free path of the activated species to source-substrate distance so that collisions with the background gas reduce the kinetic energy of the ions. This alters the structure of the buffer (nucleation) layer by forming a homogeneous layer with smaller nucleation sites.

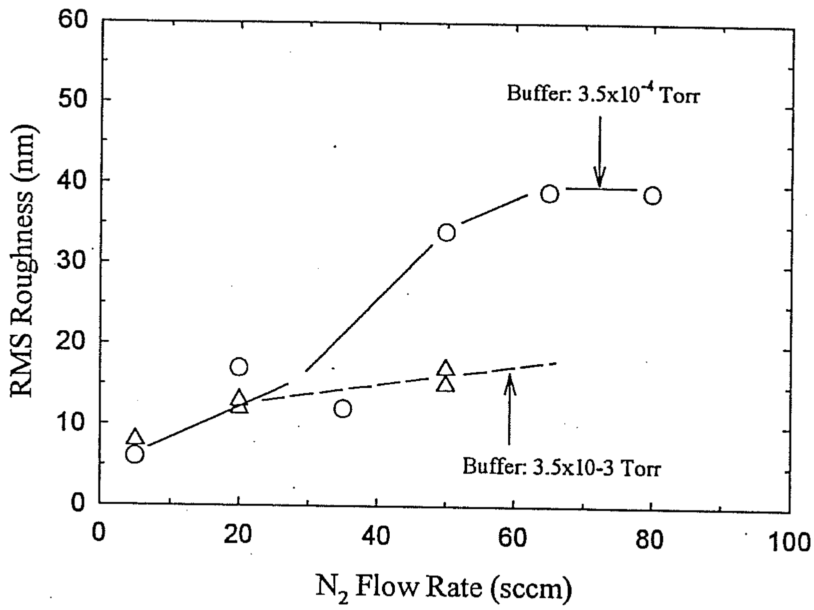


Fig. 2: Dependence of the surface roughness on the nitrogen flow realized with two different nitrogen partial pressures. Depicted are root mean square (RMS) AFM results obtained from 2 x 2 μm^2 areas.

The structural quality of the GaN films were characterized by x-ray diffraction measurements with a Siemens D5000 x-ray diffractometer containing a four bounce Ge monochromator. Typically, (0002) rocking curves exhibited a full width at half maximum (FWHM) ranging 2 to 10 arcmin depending on the growth condition. In the present study, a best value 80 arcsec was obtained. Fig. 3 shows the $\theta/2\theta$ scan of this particular GaN film grown on c-plane sapphire. The insert depicts the (0002) rocking curve. Such FWHM values are well comparable to the best heteroepitaxially grown MOCVD GaN samples.

The photoluminescence spectrum depicted in figure 4 was excited using the 325 nm line of a 50 mW HeCd laser. The luminescence light was then dispersed by a 0.85m double monochromator and detected with a photomultiplier via a lock-in technique. The sample temperature was 4 K. The spectrum is dominated by a donor bound excitonic transition at 3.468_8 eV with a FWHM of 1.8_5 meV, indicating that the layer is only slightly compressed [8]. To the best of our knowledge, an excitonic line as narrow as 1.8_5 meV has not yet been reported for heteroepitaxial GaN films. Such narrow PL lines can be obtained by engineering the strain in the material such that after the post-growth cooling the film is almost strain free.

The surface morphology of the films was investigated by a Park Scientific Atomic Force Microscope operated in air with tip force of 1 nN and a scan rate of 1 Hz. Details of the study are reported elsewhere in these proceedings [8]. No surface treatment is applied to the sample to preserve the surface features. Figure 5 depicts the surface morphology of a compressed GaN film measured by AFM as well as a cross-section transmission electron micrograph of the same sample. From the AFM image figure 5 it can be seen that the film is composed of individual large features of ~ 1 μm diameter. Such features can vary in

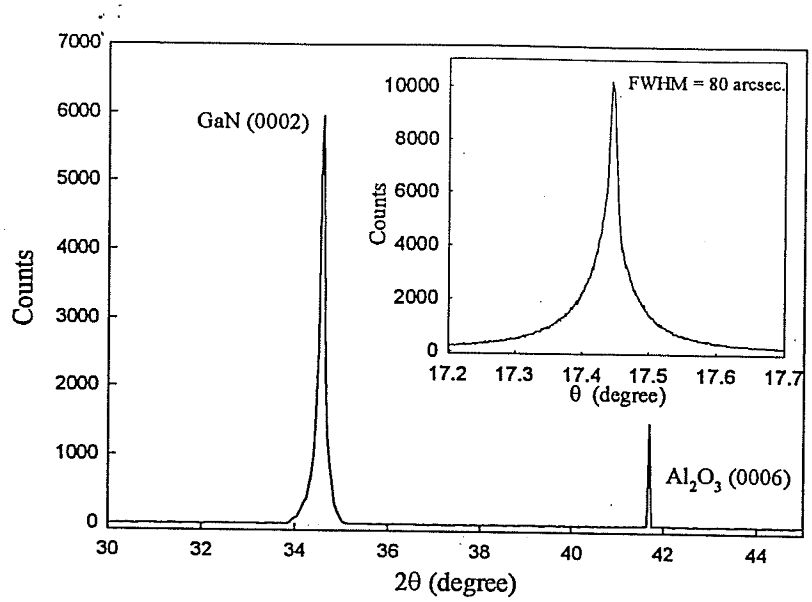


Fig. 3:
A θ/2θ scan of a GaN film grown on c-plane sapphire. The FWHM of the rocking curves is 80 arcsec, indicating an excellent structural quality.

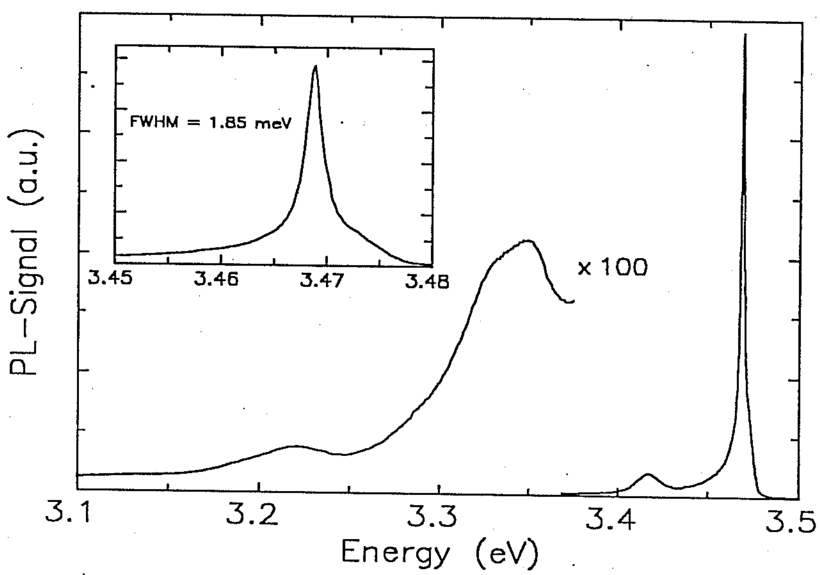
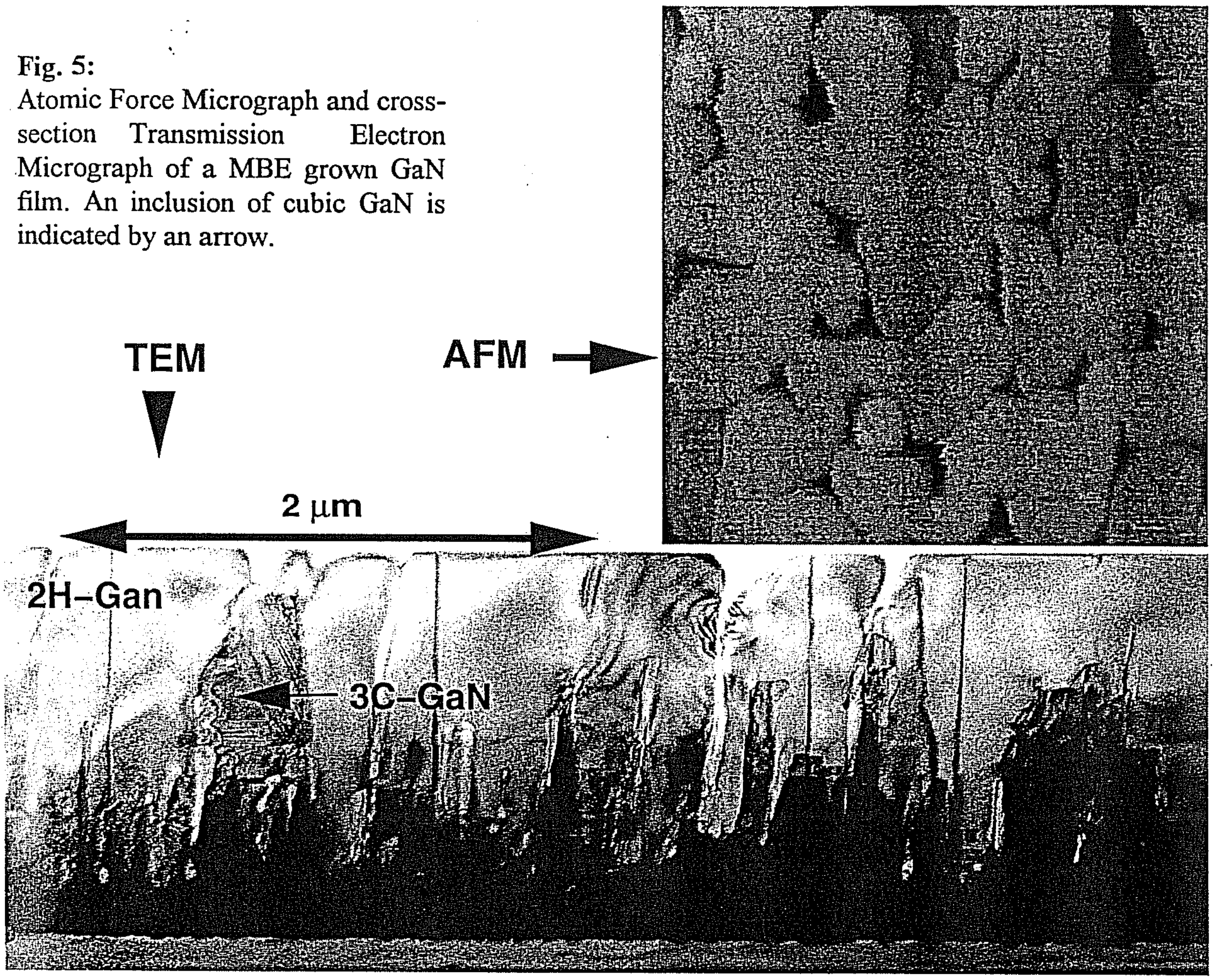


Fig. 4:
PL spectrum of a MBE grown sample, taken at 4 K. For the donor bound exciton we measured a line width (FWHM) of 1.85 meV. The line width at room temperature is 60 meV.

size, shape and coalescence depending on the growth temperature and on strain [8]. To the best of our knowledge, all MBE films grown in this temperature range exhibit similar surface structures. We argue that the formation of such structures is due to the low growth temperature. The corresponding TEM image reveals that the film is composed of individual but oriented column-like grains. In this particular example the sub-grains do not even coalesce. The grain size appears to be limited by surface diffusion of Ga adatoms [8]. These growth conditions lead to a very efficient reduction of the dislocation density close to the substrate/film interface. Consequently, individual sub-grains are almost dislocation free at the top of the layers. The surface is atomically flat as a result of the compressive strain in the sample. Closer inspection of the TEM image reveals inclusions with 60° and 120° angles, see figure 5. High resolution TEM (figure 6) confirms that such inclusions are cubic GaN crystals in the hexagonal matrix. The occurance of the cubic phase was found to decrease with increasing nitrogen flow, indicating that Ga-rich growth conditions favor the formation of cubic GaN. However, varying the composition of the films influences the strain in the layers so that it is not possible to exclude an impact of strain on the formation of the cubic phase. The

Fig. 5:
Atomic Force Micrograph and cross-section Transmission Electron Micrograph of a MBE grown GaN film. An inclusion of cubic GaN is indicated by an arrow.



observation of the cubic inclusions in areas close to the top of the layer also suggest their spontaneous formation.

Finally, we note that our films contain significant contamination with oxygen, carbon and hydrogen (> 10^{18} cm^{-3}). In these films carrier concentrations down to 10^{15} cm^{-3} were obtained, however, the carrier mobility did not exceed 120 cm^2/Vs. Ongoing investigations indicate that the presence of the columnar structure in our films contributes to the reduction of the carrier mobility.

CONCLUSIONS

In conclusion, we demonstrate MBE growth of GaN thin films at a rate of ~ 0.5 μm/h by use of a Hollow Anode nitrogen ion source. A growth procedure has been developed that is pressure assisted and utilizes strain to engineer physical properties of GaN films. The obtained material compares well with MOCVD grown crystals as to its optical performance or its structural quality determined from the width of x-ray rocking curves. At MBE growth temperatures ≤ 1000 K a Volmer-Weber 3D growth mode is observed. As a result, the films are composed of columnar oriented sub-grains. The presence of such grains and the a large impurity content in our films may limit the carrier mobility. Spontaneous formation of the cubic GaN phase is observed if films are grown under Ga rich conditions.

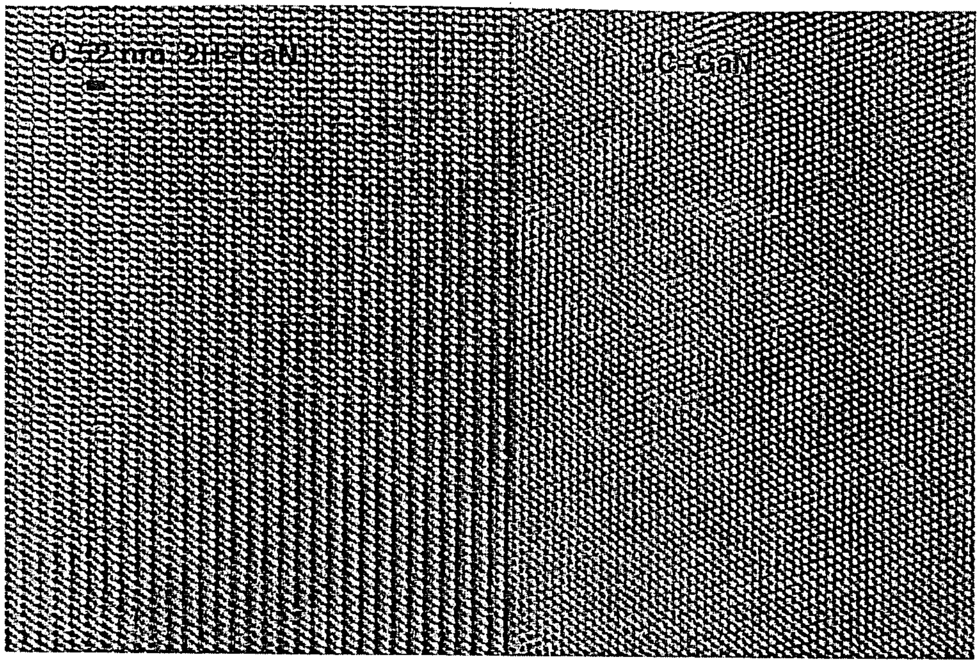


Fig. 6: High resolution lattice image of cubic (3C) and hexagonal (2H) GaN grown by MBE. Cubic GaN forms if the III/V ratio is large. Zone axes: [11-2]|||[110]

ACKNOWLEDGMENTS

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