

Fundamental Materials-Issues involved in the Growth of GaN by Molecular Beam Epitaxy

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Abstract

Gallium nitride is one of the most promising materials for ultraviolet and blue light-emitting diodes and lasers. Both Molecular Beam Epitaxy (MBE) and Metal-Organic Chemical Vapor Deposition (MOCVD) have recently made strong progress in fabricating high-quality epitaxial GaN thin films. In this paper, we review materials-related issues involved in MBE growth. We show that a strong understanding of the unique meta-stable growth process allows us to correctly predict the optimum conditions for epitaxial GaN growth. The resulting structural, electronic and optical properties of the GaN films are described in detail.

Introduction

The fabrication of high-quality single crystal GaN has been a formidable challenge to researchers to date. In order to produce GaN, it has been experimentally realized that high temperatures, activated nitrogen species and/or high nitrogen pressures are necessary to overcome the large kinetic barriers of formation. For this reason, conventional bulk and thin-film growth technologies which are commonly-used to produce III-V semiconductors such as GaAs and InP can not all be directly transferred to GaN production. Only the MOCVD technique operates under analogous principals when growing GaN and other III-V semiconductors. In this report, we highlight the important issues involved in the MBE growth process which we have reported in journal articles.^{1,2} We also include more detailed characterization of the films using a number of techniques including Transmission Electron Microscopy (TEM), ion-channeling Rutherford Backscattering (RBS), Cathodoluminescence (CL), and Photoluminescence (PL)

Standard bulk growth techniques such as Czochralski, Bridgeman and Float-zone are not practical alternatives for the growth of GaN because experimental techniques have not been developed which can contain the high equilibrium nitrogen pressures at the melt temperature. In fact, even when contained at pressures possible with diamond anvil cell technology, melting of GaN has not been achieved. Single crystals have been produced by solution growth in a predominantly Ga melt under high pressure (~ 2 GPa) and high temperature (~1500 C) conditions.³

In contrast to bulk growth, the successful use of both MBE and MOCVD to fabricate high-quality epitaxial GaN thin films by a large number of groups is striking. MOCVD is grown under conditions which GaN is the stable phase.(Fig. 1a) Typically pressures of 0.1-1.0 atmospheres and temperatures of ~1300 K are used. Since the growth temperature is less than 50% the theoretically-predicted melt temperature (2793 K)⁴, the kinetic barriers of epitaxial growth may be limiting the quality of the growing film. For comparison, device quality GaAs is fabricated using MOCVD at ~950 K which is ~63% of the melting temperature(1511 K).

Chemistry of GaN Growth by MBE

Essential conditions for growth: In contrast to all III-V MOCVD growth and MBE growth of conventional III-V compounds, MBE growth of GaN occurs under metastable conditions. Fig. 1b shows the equilibrium phase diagram for the reaction of Ga(l) and N₂(g) to form GaN(s), as well as the conditions under which successful MBE growth occurs.¹ The figure clearly shows that the conditions of growth fall below the critical stability line(solid line). This indicates that

additional energy is required to drive the forward synthesis reaction. The use of a more reactive species such as activated nitrogen or nitrogen ions provides sufficient energy to form GaN.¹

Since the growth occurs in the unstable region of the phase diagram, decomposition will also occur during growth.¹ Fig. 2 compares the rate at which nitrogen ions arrive at the growing

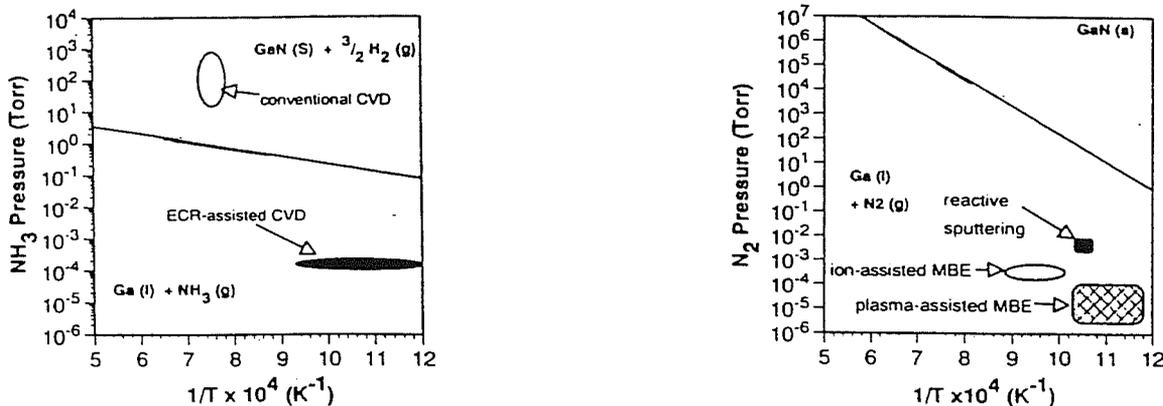


Fig. 1. Phase diagram for the reactions: (a) $\text{Ga (l)} + \text{NH}_3(\text{g}) \rightarrow \text{GaN (s)} + \frac{3}{2} \text{H}_2(\text{g})$ and (b) $\text{Ga (l)} + \frac{1}{2} \text{N}_2(\text{g}) \rightarrow \text{GaN (s)}$. Also shown are typical gas pressure and substrate temperature used for the successful production of GaN. From Ref. 1.

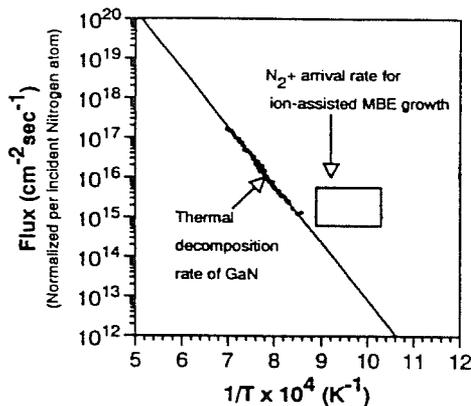


Fig. 2. A comparison of the flux of N_2^+ at the growth surface during MBE growth and the N_2 flux from the experimentally-determined sublimation rate⁵ of GaN in vacuum. From Ref. 1.

GaN surface with the rate of thermal decomposition, as measured by Munir and Searcy.⁵ Note that film growth by MBE only occurs when the rate of arrival of the activated species (i.e. the maximum rate at which the forward reaction could occur) is greater than the thermal rate of decomposition (the minimum rate at which the reverse reaction could occur). As is illustrated, the growth process is controlled by a competition between the forward reaction which depends on the arrival of activated nitrogen species at the growing surface and the reverse reaction whose rate is limited by the unusually large kinetic barrier of decomposition of GaN.¹

Experimental parameters of growth

Substrate temperature: The effect of substrate temperature on the electrical properties of the GaN films is shown in Fig. 3.¹ Consistent with our analysis, the large kinetic barrier of decomposition allows crystalline film growth up to substrate temperatures of approximately

800 °C. As the temperature was reduced to 600 °C, the carrier concentration decreased to $10^{14}/\text{cm}^3$ and the mobility rose to $1200 \text{ cm}^2/\text{V sec}$. This is strong evidence that at the higher substrate temperatures, the enhanced rate of decomposition results in the formation of a significant concentration of the auto-doping donor levels, presumably the non-stoichiometric defect, V_N . For substrate temperatures below 600 °C, epitaxial films are not obtained, presumably because the thermal energy was not sufficient to overcome the kinetic barriers of compound formation and epitaxial growth.

Plasma/Ion energy: The requirement that activated Group V species are present during the growth of GaN by MBE is distinctly different than that for other III-V compounds such as GaAs and InP. This requirement may limit the quality possible with this technique due to

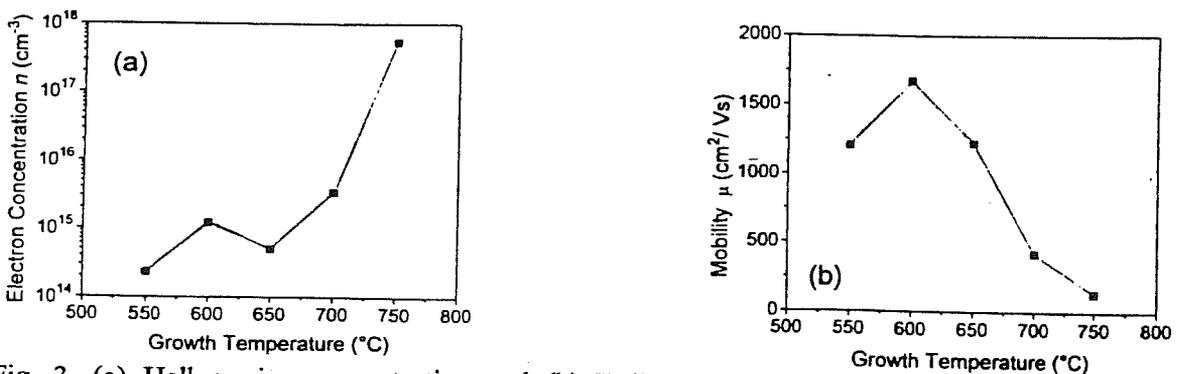


Fig. 3. (a) Hall carrier concentration and (b) Hall mobility versus growth temperature for unbiased undoped n-GaN films. From Ref. 2.

several different processes. The reverse decomposition rate can be significantly enhanced by the impinging flux of energetic ions, electrons, atoms and molecules.¹ Also, damage can be produced by energetic species, resulting in defects in the growing film.² Brice et. al.⁶ reported that subsurface damage is found when ions with kinetic energies of ~3 times the cohesive energy of the film.⁶ This is on the order of ~20 eV for GaN. Also, the presence of the ion beam or plasma results in much less stringent control of contamination due to sputtering of absorbed gas and the system components.

In order to minimize ion-impact damage and decomposition during the film growth, a source which can produce a high flux of activated species with a small, but well defined, kinetic energy is required. A Kauffman Ion Source is used for these experiments because it superior to ECR sources for the production of low-energy monoenergetic species. In order to reduce the kinetic energy of the impinging ions with a Kauffman Ion Source, the substrate to anode potential should be kept small. The minimum anode potential of + 30 V combined with a substrate bias of + 18 V is expected to reduce the impinging N_2^+ ion kinetic energy to ~10 V. Because the Kauffman source typically uses a tungsten filament for the production of the plasma and a nickel or carbon grid for the extraction of the ions, it is inherently higher in contamination. An activated ion source which can produce a high-flux low-energy monoenergetic ion-beam with low levels of contamination is clearly needed in this field.

When the substrate bias was used in combination with low temperature and high N_2^+ flux, p-GaN was obtained without intentional doping.² Hall measurements indicate a hole concentrations of $5 \times 10^{11} \text{ cm}^{-3}$ and hole mobilities of over $400 \text{ cm}^2/\text{V s}$ at 250 K. These electrical parameters compare quite well with values for GaAs when adjusted for the strength of

the electron-phonon coupling and the Debye temperature, despite the higher level of impurities in our ion-beam MBE system compared to conventional GaAs MBE and the wider x-ray peaks of the GaN films.

Properties of the epitaxial films

In this section, we give a brief overview of the properties of the films grown in our laboratory.

Structural Properties: Θ - 2Θ X-ray diffraction data (Fig. 4a) indicate that the films are single phase with the hexagonal structure and the c-axis is parallel to the growth direction.

Fig. 5a shows the RBS channeling yield as a function of depth when the beam is aligned perpendicular to the film. The channeling data for bulk GaAs is also plotted for comparison. Note that the 200 nm closest to the surface show a low minimum yield (5%), indicating a reasonably perfect crystal. The significant slope starting at 200 nm indicates that the material contains a significantly larger density of extended defects closer to the substrate/semiconductor surface. The TEM study described below indicates the density and nature of the extended defects responsible for this observation. Off-axis X-ray Φ -scans (Fig. 4b) and off-axis RBS channeling data (Fig. 5b) show that the film is well-oriented in-plane, indicating the films are single crystalline.

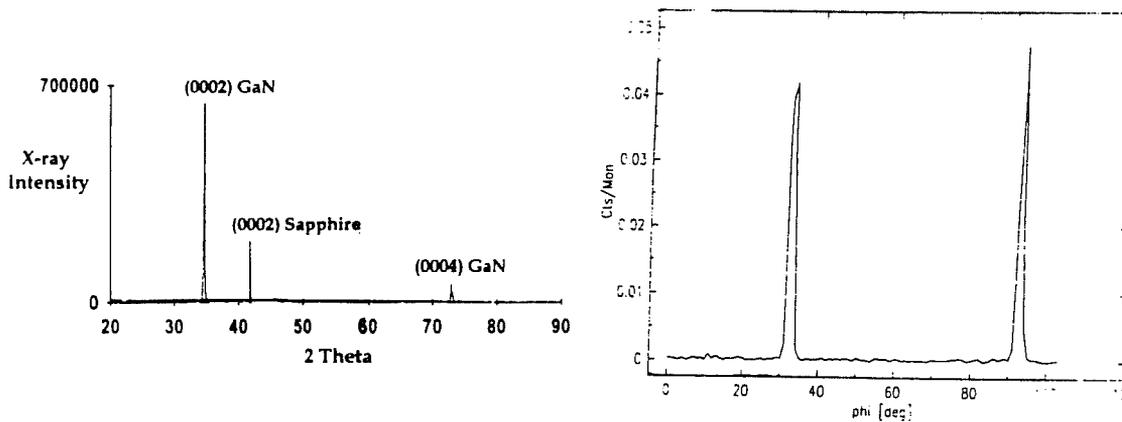


Fig. 4. X-ray diffraction data. (a) Θ - 2Θ scan illustrating that the GaN films are predominantly c-axis oriented and (b) Φ -scan for the $(1\bar{1}0)2$ diffraction condition illustrating that there is a high degree of in-plane epitaxy (i.e. a-b plane) with no detectable high angle grain boundaries.

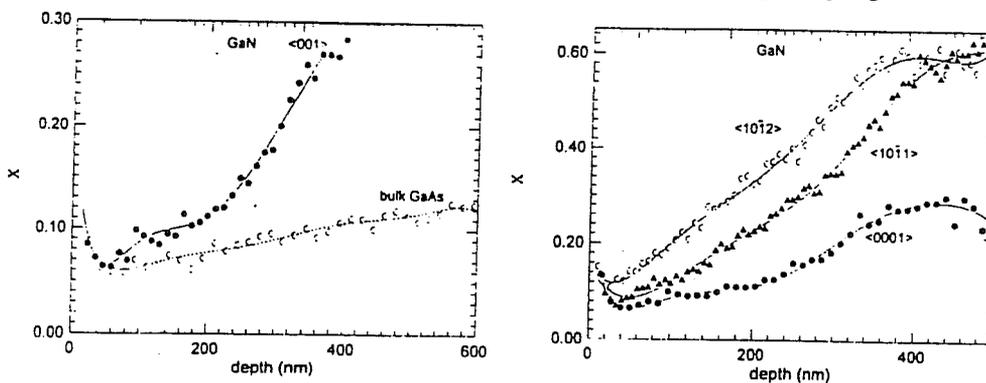


Fig. 5. RBS channeling yield for the beam directed along the normal (001) direction (a) and along off-axis $(10\bar{1}2)$ and $(10\bar{1}1)$ directions (b).

Transmission Electron Microscopy of plan-view and cross-section samples confirm the conclusions from the RBS study that the GaN thin films are high quality crystalline material. A Topcon 002B microscope was used for the TEM studies. The high resolution micrograph (Fig. 6a) from a plan-view sample shows the six-fold symmetry characteristic of the hexagonal structure. Diffraction patterns obtained from the plan-view samples indicate that the thin films are monocrystalline. The (1 $\bar{1}$ 00) planes of the GaN layers are parallel to the (2 $\bar{1}$ $\bar{1}$ 0) sapphire planes with [0001] Al₂O₃ || [0001] GaN and show about 13% mismatch between these two materials, as predicted theoretically from bulk lattice constants.

The most common defects in the GaN layers are low angle grain boundaries. The average grain size is on the order of 800 nm. In cross-sectioned samples, a significant concentration of two other defects are also found. Fig. 6b is a high resolution micrograph which shows both of these defects. The defects perpendicular to the interface are twins and are initiated at the interface and extend through the entire layer thickness. Their width is of the order of 8-10 nm and the distance between them is about 20 nm. Their contrast disappears for the (0001) diffraction vector. These defects appear to be the same as the double positional boundaries described by Paisley and Davis⁷. Image simulation is in progress in order to determine the detailed atomic nature of these defects.

The second type of defects observed in cross-section samples form domains terminated by stacking faults parallel to the (0001) growth surface. Their contrast disappear for the diffraction vector parallel to [$\bar{1}$ 010]GaN. In the area close to the interface, the distance between the stacking fault is of the order of 50 nm and this distance increases to 200 nm when the GaN layer thickness is larger than 300 nm. The smaller concentration of these defects away from the substrate/semiconductor interface can explain the RBS data that indicates the crystal quality improves near the surface of the film.

Optical properties: Fig. 7 shows cathodoluminescence spectra for typical undoped (a) and Mg-doped (b) samples at 90 K. For the undoped sample, the spectrum is dominated by near-band edge exciton emission at 362 nm (3.43 eV). Note the absence of significant emission from deep-levels. In the Mg-doped sample, the near-band edge emission at 372 nm (3.33 eV) is associated with donor-acceptor pair transitions. Also, a strong emission from deep levels is observed at 550 nm (2.2 eV). Other groups typically report emission at similar energies, even in undoped films. The physical origin of this defect has not been directly identified, although our data suggests the presence of Mg during growth can induce the formation of this deep defect.

Electrical properties; Achieving p-type doping: Diffusion of Mg into unintentionally doped n-type GaN films resulted in conversion to p-type material.² The films were grown at 600 °C without substrate bias. The diffusion was performed in a sealed ampoule for 80 hours at atmospheric N₂ pressures and 800 °C. Hall measurements at room temperature indicated a hole concentration of 2x10¹⁶/cm³ and a mobility of 12 cm²/Vs at room temperature. Higher diffusion temperatures resulted in the removal of the film by decomposition and evaporation. Lower diffusion temperatures were not successful in converting the material to p-type.

Finally, a Knudsen cell for direct in-situ co-evaporation of Mg was used.² At a Mg source temperature of 180 °C and a substrate bias of 18 V, the films were found to exhibit hole conduction. Hall measurements indicated a hole concentration of 2x10¹⁷ /cm³ and hole mobilities of <1 cm²/V s at room temperature.

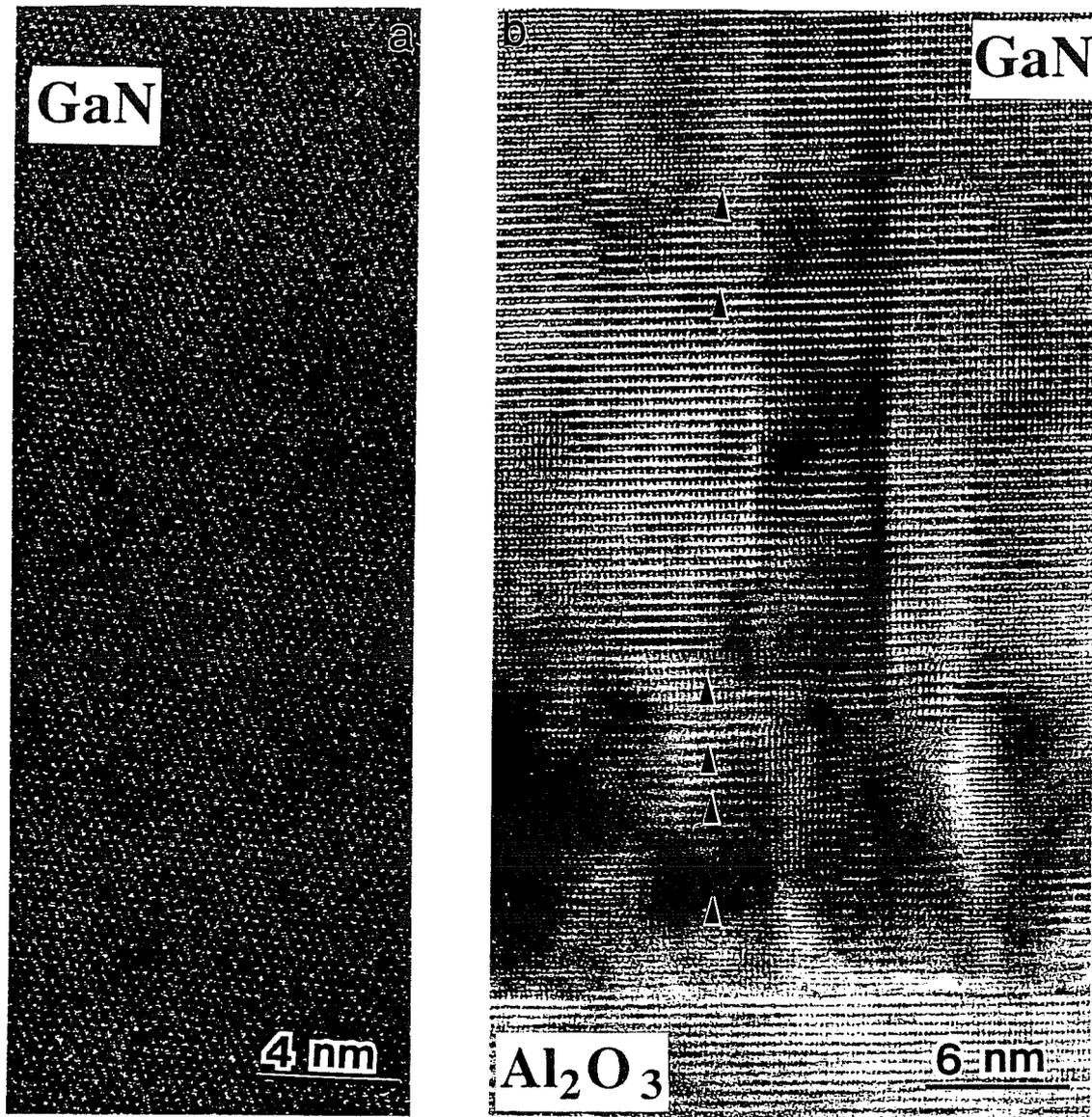


Fig. 6. (a) High resolution plan-view TEM micrograph. (b) High resolution cross-sectional TEM micrograph illustrating a defect which lies perpendicular to the substrate surface and extends throughout the thickness of the film and defects (marked by arrows) which lie parallel to the substrate surface. The concentration of the latter defect is found to decrease with distance from the substrate/film interface.

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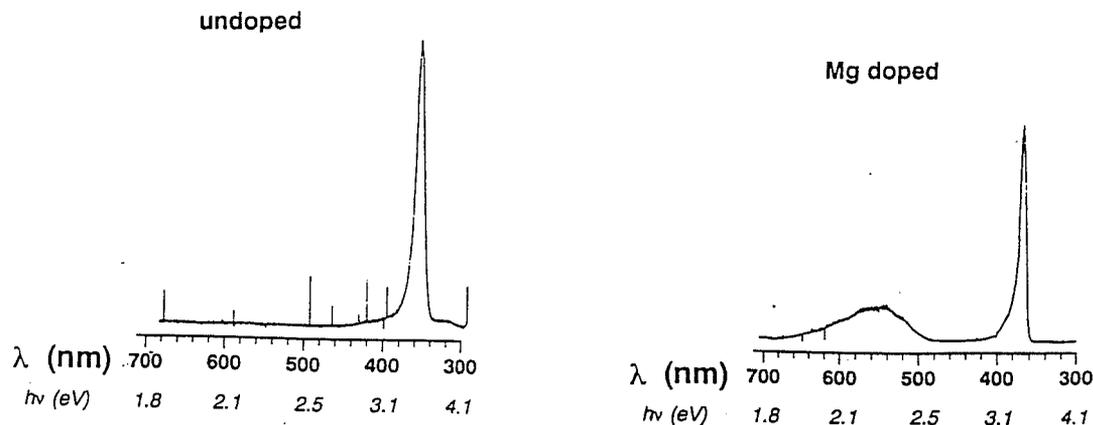


Fig. 7. Cathodoluminescence data for an undoped (a) and Mg-doped (b) GaN film at 90 K.

Summary

We show that an understanding of the unique meta-stable growth process allows us to correctly predict the optimum conditions for the epitaxial growth of GaN with MBE.¹ Using this method, high-quality GaN epitaxial thin films are routinely fabricated.² We have also demonstrated that the control of hole-doping lies primarily in reducing the defects in the base material.²

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