

## Combined hydride and metal organic vapor-phase epitaxy of GaN on sapphire

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We describe a method to produce GaN epitaxial layers in a single chamber where a low-temperature buffer layer is deposited using metalorganic vapor-phase epitaxy (MOVPE), followed by conventional hydride vapor-phase epitaxy (HVPE) of GaN at higher temperatures. While a typical 12  $\mu\text{m}$  sample is investigated here, the GaN film thickness can vary between 2 and 200  $\mu\text{m}$ , with HVPE growth rate ranging from 5 to 60  $\mu\text{m}/\text{h}$ . Cross-sectional transmission-electron microscope images show a dense network of mixed dislocations, whose density is significantly reduced after 6  $\mu\text{m}$  to the high  $10^7 \text{ cm}^{-2}$  range. 10 K photoluminescence shows bound exciton dominated emission associated with the *A* and *B* valence bands and phonon replicas. No yellow emission is observed. This versatile process can be extended to produce additional device layers by MOVPE.

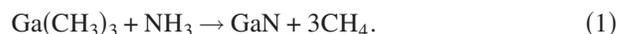
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Although the development of commercial-scale, bulk GaN crystal growth technologies continues, significant impediments remain, even without regard to cost.<sup>1,2</sup> While progress continues, it is currently simply not feasible to produce large quantities of bulk GaN, as its tendency to dissociate at elevated temperatures requires extremely high nitrogen overpressures to remain stable. Techniques such as flux growth help but the problem remains daunting, especially on a commercial scale.<sup>3,4</sup> This has led to the advancement of alternative “pseudobulk” techniques to produce GaN wafers for wide-band gap nitride-based electronics and optoelectronics. This is accomplished by heteroepitaxial growth of a thick GaN layer onto a non-native substrate, such as  $\text{Al}_2\text{O}_3$ , SiC,  $\text{LiAlO}_2$ , Si, or GaAs. This pseudobulk layer may be utilized as a GaN template still attached to the heterosubstrate or, it may be removed to form a free-standing substrate.<sup>5</sup> To produce thick high quality GaN layers, hydride vapor phase epitaxy (HVPE) is a favored method as it has the dual advantage of a low materials cost and high growth rates, sometimes reported in excess of 100  $\mu\text{m}/\text{h}$ .<sup>6,7</sup>

Vapor-phase heteroepitaxy of GaN onto non-native substrates typically employs a low temperature buffer layer, allowing for high-quality GaN epitaxy on large mismatch substrates. The buffer layer is a thin amorphous GaN layer deposited at approximately 500 °C, and recrystallized at the regular growth temperature. The metalorganic precursors, for example, trimethylgallium  $\text{Ga}(\text{CH}_3)_3$  (TMGa) are useful for the low-temperature buffer layer because, unlike the metal-hydride reaction, the source material does not need to be heated above the low-temperature buffer layer temperature. Thus, in metalorganic vapor-phase epitaxy (MOVPE) it is easy and efficient to produce the low-temperature buffer layer as part of the standard crystal growth process.

In this letter, we report the use of a novel hybrid growth system to produce high quality GaN films.<sup>8</sup> The growth process utilizes sequential growth in MOVPE and HVPE and can be cycled as necessary. Since the sign of the change in free energy with temperature is opposite for MOVPE and HVPE, a dual heating system is required to insure the substrate is respectively hotter or colder than the surrounding surfaces. Here, we demonstrate a low-temperature buffer layer produced in MOVPE mode, followed by GaN growth produced in HVPE mode. High resolution x-ray diffraction (HRXRD), 10 K photoluminescence (PL), and transmission-electron microscopy (TEM) analysis shows that even for the relatively thin epitaxial thickness reported here (12  $\mu\text{m}$ ), this hybrid method yields very high quality epitaxial layers.

In MOVPE, a Ga-based metalorganic precursor (typically TMGa) is used, which is reacted with ammonia ( $\text{NH}_3$ ) near 1025 °C:



Because of costs and growth rate limitations, this technique is generally not suitable for the growth of a GaN layer sufficiently thick to be useful as a pseudosubstrate; it is a method better suited for growing low-temperature buffer layers and thin layers for device applications.

An alternative method for GaN growth is HVPE, an approach used for GaAs growth<sup>9,10</sup> and on occasion GaN growth<sup>11</sup> in the 1960s. In our process, the method uses two separate chemical reactions in the deposition process; first, Ga metal and HCl gas are reacted at 850 °C in an upstream reaction chamber to form volatile GaCl:



The GaCl is then transported downstream to the substrate, which is held at a typical growth temperature of 1025 °C. There it reacts with ammonia to deposit as GaN:

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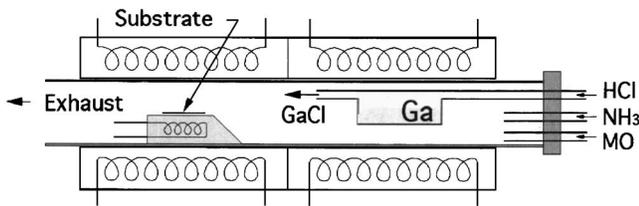
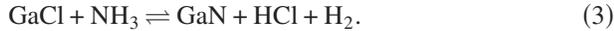


FIG. 1. Schematic of the hybrid VPE system includes an internal substrate heater, here shown as a resistive heater, and an external tube heater. In MOVPE mode, the internal substrate heater is used, in conjunction with the metalorganic source and  $\text{NH}_3$ .



The thermodynamics of reactions (1) and (3) bear some discussion. Values for the enthalpies and entropies of GaN precursor compounds have been previously reported,<sup>12</sup> and from these it is possible to calculate the free energy for reactions (1) and (3), as well as their temperature relationship. Reaction (1) is strongly exothermic, with a positive net entropy change; higher temperatures increase the driving force for this reaction to occur, and deposition occurs most favorably in the hottest region of the growth system. To reduce parasitics and gas phase reactions it is desirable that this region be the substrate area. Reaction (3) is weakly exothermic, with a negative change in entropy; as temperature increases the driving force decreases. In this case, deposition is more likely to occur in the coolest part of the growth system, within limits. HVPE is a near-equilibrium deposition method; at 1025 °C the driving force for deposition is just 3% of that for MOVPE.

HVPE is not an ideal method for producing the low temperature buffer layer. In HVPE the growth rates are high and thus the thickness of the low-temperature buffer layer ( $\approx 25$  nm) is difficult to accurately control. Furthermore, the growth chamber will have an inverted temperature profile, leading to parasitic deposition that can re-enter the gas stream upon heating. Finally, reducing the reaction chamber temperature below 800 °C favors the formation of  $\text{GaCl}_3$ , which is not desirable because the excess Cl atoms contribute to etching during growth.

Since, in an optimized MOVPE process the substrate is the hottest part of the growth system, while for HVPE the substrate should be more neutral or slightly cooler than the upstream region, these two processes are generally not compatible. We have developed a hybrid MOVPE-HVPE growth system incorporating both techniques into a single growth system. This utilizes an internal substrate heater (cold-wall heating system) for MOVPE growth, in the form of resistive heaters in the susceptor, and a hot-wall system for HVPE, using a multizone tube furnace. A schematic diagram of this system is shown in Fig. 1.

The growth sequence was typically as follows. After cleaning, etching and loading, the 2 in. diameter (0001) sapphire substrate was heated to 1000 °C for cleaning. A 25 nm GaN buffer layer was deposited onto the sapphire at 500 °C using MOVPE. After deposition of the buffer layer, the substrate was heated using the external heater to 1025 °C for recrystallization and HVPE deposition. The HVPE growth rate was 25  $\mu\text{m}/\text{h}$ , and 12  $\mu\text{m}$  was deposited. Afterwards, the reactor was cooled to room temperature and the wafer was unloaded. The layer was mirror-smooth and shiny with no cracks. Atomic-force microscopy indicates a rms rough-

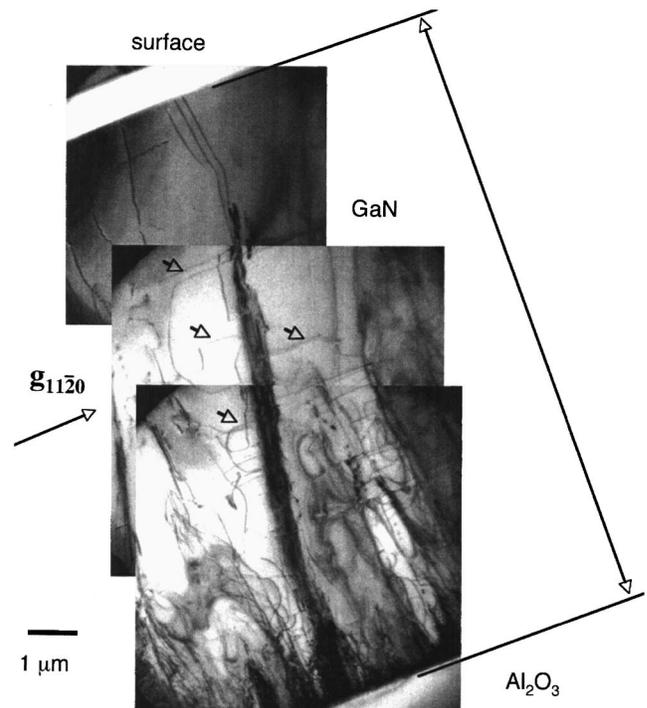


FIG. 2. Series of successive TEM micrographs taken from a 12- $\mu\text{m}$ -thick film grown on  $\text{Al}_2\text{O}_3$  (0001). The cross-sectional bright-field images are recorded with  $g=11\bar{2}0$  detecting dislocations with Burgers vector  $\mathbf{b}=\mathbf{a}$  (arrows indicate some dislocations bent in the basal plane).

ness of less than 1 nm over a  $10 \times 10 \mu\text{m}$  area.

Figure 2 shows a series of successive cross-sectional bright-field TEM images of the 12  $\mu\text{m}$  film grown with this system. There is a dense network of threading dislocations, denoted by dark lines, concentrated at the film-sapphire interface. Because most of the dislocations show curved lines and some are even bent into the basal plane (cf. arrows in Fig. 2), dislocation interaction and annihilation can efficiently proceed during growth. Therefore, within a thickness of approximately 1  $\mu\text{m}$ , the dense tangle of dislocations begins to diminish dramatically, with a density dropping into the  $10^7/\text{cm}^2$  near the surface.

HRXRD rocking curves (done with open detector and in skew geometry) for this sample exhibit a full-width at half-maximum (FWHM) of 460 and 450 for the symmetric (0002) and the asymmetric ( $20\bar{2}1$ ) reflections, respectively. The nearly equal FWHM for these reflections is consistent with the dominance of mixed dislocations in these samples as shown in the TEM (Fig. 2). For thicker layers these linewidths are further reduced; for example, for a 55- $\mu\text{m}$ -thick layer these values drop to 300 and 280 arc sec.

10 K PL spectra from the GaN epitaxial layer are shown in Fig. 3. The sample was pumped with a He-Cd laser, with a spot size of approximately 2  $\mu\text{m}$  (confocal imaging), and an excitation density of approximately 20  $\text{W}/\text{cm}^2$  (OD4) or 200  $\text{W}/\text{cm}^2$  (OD3). The collected light was dispersed in a 0.8 m spectrometer and imaged on a liquid nitrogen cooled charge coupled device (CCD) array. In Fig. 3, luminescence from the band edge spectral region (3.47–3.5 eV) dominates the spectrum and is from donor-bound exciton states and free excitons. Emission at 3.4 and 3.3 eV is from first and second phonon replica, respectively. The band edge energies are consistent with a small compressive strain of 0.1%, confirmed by Raman spectroscopy. Most importantly, there is no AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

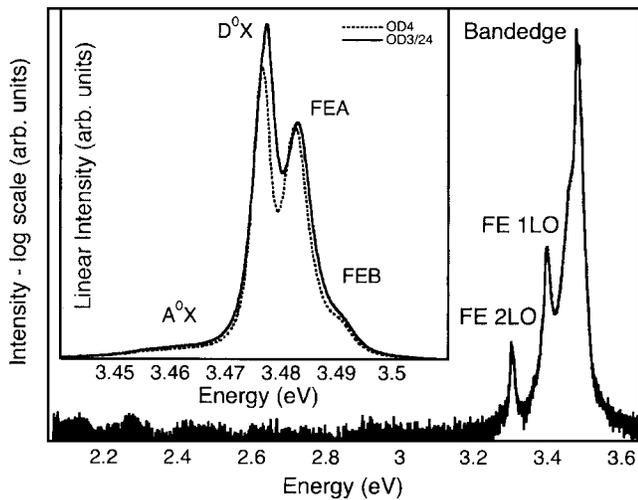


FIG. 3. 10 K PL spectra of a 12  $\mu\text{m}$  GaN epilayer. The log-scale intensity spectrum shows bandedge luminescence, and first and second phonon replicas, but no evidence of deeper emission. Inset: A linear-scale intensity spectrum of the near band edge region with lower (dotted) and higher (solid) excitation density. Dominant emission is from the neutral donor exciton ( $D^0X$ ). Free exciton emission from the A (FEA) and B (FEB) valence bands are also present, along with weak emission from a neutral acceptor bound exciton ( $A^0X$ ).

evidence of emission in the midgap, *yellow luminescence* region. In the insert of Fig. 3 a higher resolution spectrum reveals the bandedge luminescence structure. The near band edge emission is dominated by emission from excitons bound to neutral donors ( $D^0X$ ) and free exciton emission associated with the highest energy valence band, the A band (FEA). Emission from free excitons of the next valence band, the B band, is also observed. A comparison is shown between excitation densities that differ by an order of magnitude, where the higher excitation density spectrum (solid line) is scaled by 1/24. The shift in  $D^0X$  emission energy suggests that emission is from  $D^0X$  states associated with more than one type of donor. The increase in the intensity of the  $D^0X$  emission line with pump power is superlinear in the pump regime investigated here, resulting in a change in the intensity ratio of the  $D^0X$  and FEA emission lines. This suggests that the donor states could be at least partially ionized in conjunction with a deep acceptor (which we have not observed). In the low pump regime the donors would become

neutral and then attract excitons, leading to the super linear dependence of the  $D^0X$  line on the pump power.<sup>13</sup> If the  $D^0X$  is fitted as one peak, the Lorentzian linewidth is approximately 3.5 meV. The narrow emission from  $D^0X$  and FEA indicate the high uniformity of the epilayer<sup>14</sup> and the relatively low donor concentration. Additionally, there is a small signature from a neutral shallow acceptor bound exciton level at approximately 3.46 eV.

In conclusion, a novel hybrid MOVPE-HVPE growth system has been used to produce high-quality epitaxial GaN on sapphire. This combined method presents a unique cost-effective and scalable means for the production of GaN-based epilayers and devices, without the need for a separate reactor for each deposition process. Additionally, the ability to switch deposition modes makes it possible to produce an entire device structure, from the low temperature MOVPE buffer, to the thick HVPE pseudobulk layer, to the final MOVPE device layer, all in a single reactor in one growth.

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