A CRITICAL COMPARISON BETWEEN MOVPE AND MBE GROWTH OF III-V NITRIDE SEMICONDUCTOR MATERIALS FOR OPTO-ELECTRONIC DEVICE APPLICATIONS

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ABSTRACT

A systematic study of the growth and doping of GaN, AlGaN, and InGaN by both molecular beam epitaxy (MBE) and metal-organic vapor phase epitaxy (MOVPE) has been performed. Critical differences between the resulting epitaxy are observed in the p-type doping using magnesium as the acceptor species. MBE growth, using rf-plasma sources to generate the active nitrogen species for growth, has been used for III-Nitride compounds doped either n-type with silicon or p-type with magnesium. Blue and violet light emitting diode (LED) test structures were fabricated. These vertical devices required a relatively high forward current and exhibited high leakage currents. This behavior was attributed to parallel shorting mechanisms along the dislocations in MBE grown layers. For comparison, similar devices were fabricated using a single wafer vertical flow MOVPE reactor and ammonia as the active nitrogen species. MOVPE grown blue LEDs exhibited excellent forward device characteristics and a high reverse breakdown voltage. We feel that the excess hydrogen, which is present on the GaN surface due to the dissociation of ammonia in MOVPE, acts to passivate the dislocations and eliminate parallel shorting for vertical device structures. These findings support the widespread acceptance of MOVPE, rather than MBE, as the epitaxial growth technique of choice for III-V nitride materials used in vertical transport bipolar devices for optoelectronic applications.

INTRODUCTION

The recent development of III-V Nitride semiconductor devices for optoelectronic applications has been driven by improvements in the epitaxial growth of these semiconductor materials. Heterostructures have been fabricated across a range of AlN-GaN-InN compositions with bandgaps ranging from 6.2 eV (ultraviolet) to 1.9 eV (red) for LED, laser diode, and photodetector applications [1,2]. Heterostructure epitaxy has traditionally been performed using either MBE or MOVPE in many semiconductor material systems [3,4]; however, most of the recent device application demonstrations for III-V nitrides have used MOVPE, particularly in the commercially driven work at Nichia Chemical and Cree Research [5,6]. MBE growth for optoelectronic device applications has lagged behind. Initially, this was attributed to the unavailability of an appropriate source of active nitrogen species for MBE [1]. Through the development of nitrogen rf plasma sources for MBE, the quality of the resulting epitaxial layers has improved [7,8,9,10]. Despite these advances, demonstration of high quality vertical devices such as laser diodes or high brightness LEDs grown by MBE has not occurred [8,11].

In this work, we compare the growth of III-V nitride materials by MBE and MOVPE in order to examine the fundamental differences in the epitaxial growth and the influence on resulting devices. We have studied three areas of critical importance for light emitting devices.

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First is the difference in the epilayer growth morphology; second is the doping of GaN with magnesium for p-type conductivity; and finally, the deposition of InGaN quantum wells with compositions in the visible emission range. This comparison provides a twofold benefit of identifying critical areas for further exploration in crystal growth and deepening the understanding of the underlying physical processes at work in successful epitaxial deposition.

EXPERIMENTAL PROCEDURE

MOVPE growth was performed in a vertical flow rotating wafer (up to 2000 rpm) system designed and built at NCSU. A radiatively heated substrate mount, of original high reliability design, can achieve temperatures up to 1200°C, as measured by an optical pyrometer. 50-mm diameter sapphire wafers were used as the base substrate with a typical low temperature GaN nucleation layer. Trimethylgallium (TMGa), trimethylaluminum (TMAl), trimethylindium (TMI) and ammonia were used as precursors with nitrogen and hydrogen carrier gases at a reactor pressure of 76 Torr. Silane and bis(cyclopentadienyl) magnesium were used as dopant sources. Growth temperatures for GaN ranged from 1060°C to 1130°C. The conditions resulted in 2D epitaxial growth at rates of 1-2 µm/hr. InGaN growth was conducted in a manner similar to Yoshimoto at temperatures from 725°C to 800°C [12].

MBE growth was performed in an EPI Model 930 system using elemental group III and dopant sources. Rf plasma sources were used to generate the active nitrogen species. Pre-nucleated GaN/SiC substrates were used for the MBE deposition. Growth temperatures ranged from 750°C to 900°C for GaN and 670°C to 700°C for InGaN resulting in growth rates of 0.4-2 µm/hr. A modulated beam technique was used to grow InGaN as previously described [11].

The MOVPE and MBE were connected as a multichamber UHV cluster tool. This allows for the growth of sophisticated heterostructures with specific layers grown in either the MBE or MOVPE system where applicable. Characterization of epitaxial layers included: scanning electron microscopy using a JEOL JSM6400 SEM, photoluminescence (PL) using a 12 mW He-Cd laser source, and Nomarski microscopy using an Olympus BX60 microscope and image capture system. Vertical cross section samples were studied in a Topcon 002B Transmission Electron Microscope (TEM) with $g=(1\bar{1}00)$ at 200 kV.

LED samples were prepared following standard lithography techniques and using Ni/Au and Ti/Al as p-type and n-type contact metals, respectively.

RESULTS AND DISCUSSION

Epitaxial Layer Surface Morphology and Magnesium Doping

The surface morphology of epitaxially grown GaN exhibits an obvious difference between MOVPE and MBE deposited material. As shown in the SEM micrograph in Figure 1a, undoped or n-type doped MBE grown GaN exhibits a “wormy” structure. This surface structure has been previously reported and the degree of texture can be minimized, although not eliminated, through changes in the nitrogen plasma source operating conditions [8,9,10,13,14]. The MOCVD grown undoped material is smooth and uniform as shown in Figure 1b.

Magnesium was used as a p-type dopant for both MBE and MOVPE grown of GaN. For MOVPE growth, the surface of p-type material is smooth and featureless. However, in MBE growth, there is a dramatic change in surface texture with the evolution of a faceted surface with increasing magnesium flux as shown in Figures 1c and 1d. Cross sectional TEM studies revealed the facet morphology to be related to the pre-existing dislocation structure [4].

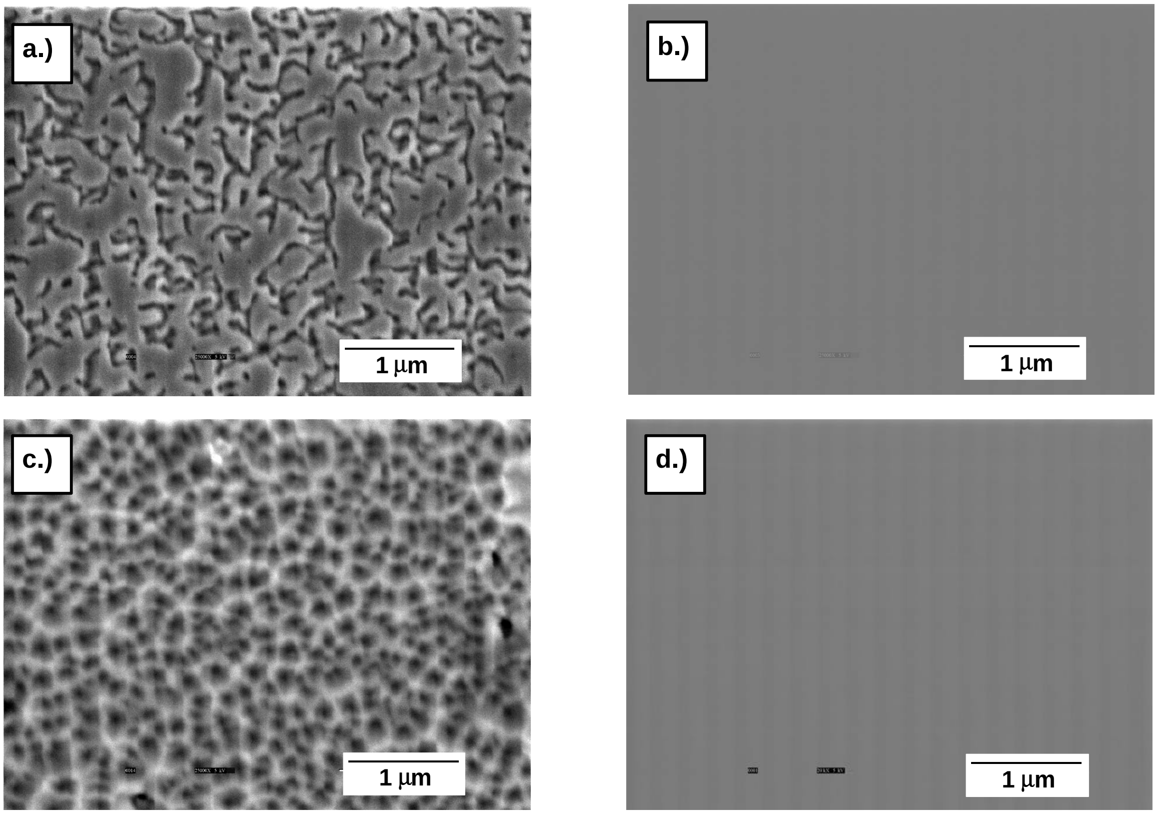

Figure 1: Scanning Electron Micrographs of as Grown Surfaces: a.) Undoped GaN by MBE; b.) Undoped GaN by MOVPE; c.) Magnesium Doped GaN by MBE; and d.) Magnesium Doped GaN by MOVPE.

The spacing of the contrast features in the plan view SEM image of this surface is consistent with a dislocation density of 10^{8}-10^{10}cm^{-2}. We feel that this segregation is related to the nature of doping in the MBE environment from a source that is at a lower temperature (300°C) than the substrate (750°C). Based on normalized flux measurements, we estimate the sticking coefficient of magnesium to be almost two orders of magnitude less than that of the gallium. As previously reported, a further increase in the magnesium flux beyond a maximum level results in a reduction in magnesium incorporation, a transformation in the growth morphology observed by RHEED to 2D, and n-type conductivity behavior [16].

Hydrogen plays an important role in the p-type doping of GaN grown by MOVPE. The formation of a Mg-H complex, with a characteristic blue PL, during subsequent activation annealing is thought to be the acceptor species responsible for p-type doping [15]. Ammonia and carrier gasses are the source of hydrogen to the MOVPE process in a viscous flow pressure regime. Although the presence of hydrogen in the molecular flow pressure regime of MBE may have some influence on the surface morphology of undoped GaN layers, addition of hydrogen to the nitrogen plasma does not provide a similar effect in the magnesium doping MBE grown GaN [16, 17]. A conversion in the PL spectrum to the characteristic blue has not been observed following post-growth annealing of MBE deposited magnesium doped material.

Though these phenomenon are still not well understood, there is a clear difference between both the incorporation and activation of magnesium doped GaN grown by MOVPE as compared with MBE. Magnesium doping by MBE results in a featured surface which would have a negative impact on optoelectronic devices grown by this technique.

InGaN Growth

The growth of InGaN layer, which have a high equilibrium vapor pressure of nitrogen, points to another significant difference between MBE and MOVPE growth. In MBE, the active species of nitrogen participating in epitaxial growth are atomic nitrogen and excited molecules, which are generated and injected from a plasma source. As a result, the dissociation pathways for nitrogen from the InGaN alloy can play a dominant role and special techniques of modulated beam growth have been employed to stabilize the growing surface and limit the precipitation of metal droplets [11]. This method results in a layered InGaN/GaN structure as shown in the TEM image of Figure 2. The defect structure replicates the defects that are present in the underlying substrate, with dislocations bridging the InGaN layered structure. This InGaN multiple quantum well test structure was grown to a 50% indium composition, and emits the green PL spectrum shown in Figure 2b. To our knowledge, this is the highest reported mole fraction of optical quality InGaN grown by MBE.

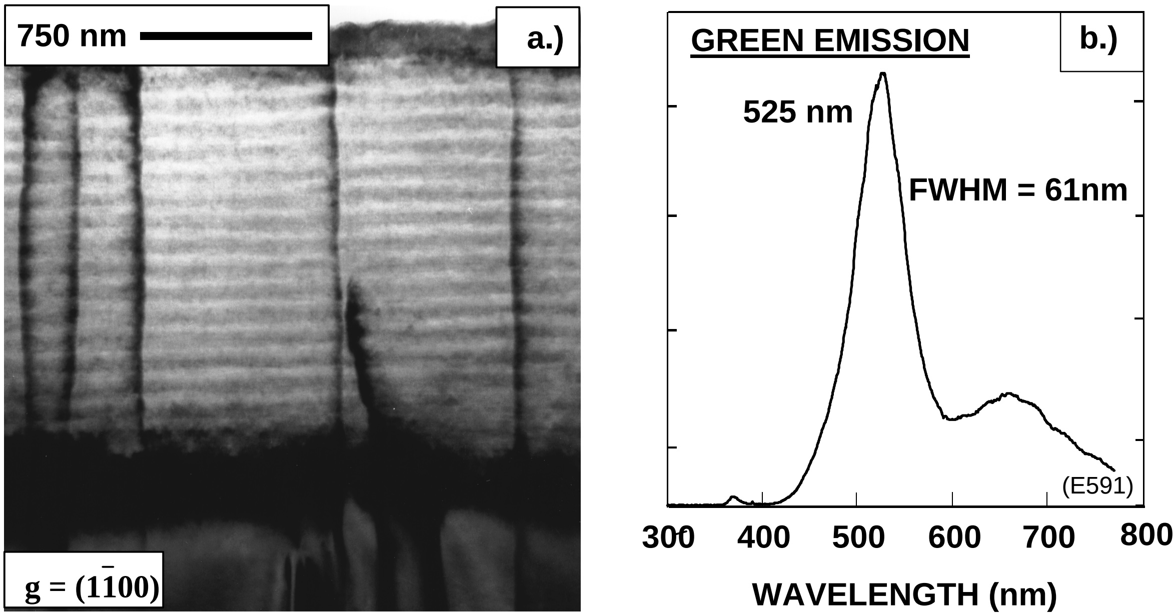

Figure 2: MBE Grown InGaN MQW Structure a.) Cross Sectional TEM Image (200 kV) and b.) Room Temperature PL Spectrum

In MOVPE, ammonia is thermally dissociated during growth and is the source of active nitrogen. While a ratio of TMI to TMGa of 10 is necessary to achieve the desired InGaN alloy compositions, it is possible to directly deposit high quality InGaN by MOVPE [12]. Using these methods, blue and green LED's have been commercially produced by MOVPE [5].

The use of ammonia as the source for active nitrogen plays another important role by providing hydrogen to the MOVPE process. Hydrogen appears to passivate the threading dislocations during MOVPE growth and render them electrically neutral. Adding hydrogen to the nitrogen plasma does not appear to produce a similar beneficial effect in MBE [16].

InGaN Quantum Well Light Emitting Diodes

LED test structures were fabricated from MOVPE and MBE grown material. Test structures were single quantum well devices with similar doping levels and compositions. As shown in Figure 3a and 3b, InGaN alloys that emit light in the blue and violet region of the spectrum have been grown. Note the two orders of magnitude difference in forward current for luminescence to be the clearly visible in room light, from 50mA for the MBE grown structure down to only 0.5 mA for the MOVPE grown material. Higher current is consistent with the presence of parallel conduction pathways shorting across the MBE grown LED structure.

Another significant difference between MBE and MOVPE grown LEDs is the typical current-voltage (I-V) characteristics shown in Figures 3c and 3d. MBE grown diodes exhibit a rather low reverse breakdown voltage. The IV characteristics for the MBE grown diode are as would be expected for a diode with shorting pathways parallel to the diode junction. We feel this to be the critical difference limiting MBE grown vertical device structures. While high quality InGaN can be deposited by MBE, the pre-existing dislocations, ranging in density of 10^8-10^{10}cm^{-2}, are replicated and act as parallel shorting pathways in MBE grown device structures. This is exactly the behavior expected in a traditional semiconductor, such as GaAs, possessing a high dislocation density. Fortunately, in the MOVPE growth environment, dislocations are rendered electrically neutral, perhaps due to the presence of hydrogen from the dissociated ammonia. As a result, diode structures which are free of parallel conduction pathways can be grown by MOVPE and the fabrication of vertical device structures is possible, even with dislocation densities as high as 10^8-10^{10} cm^{-2}.

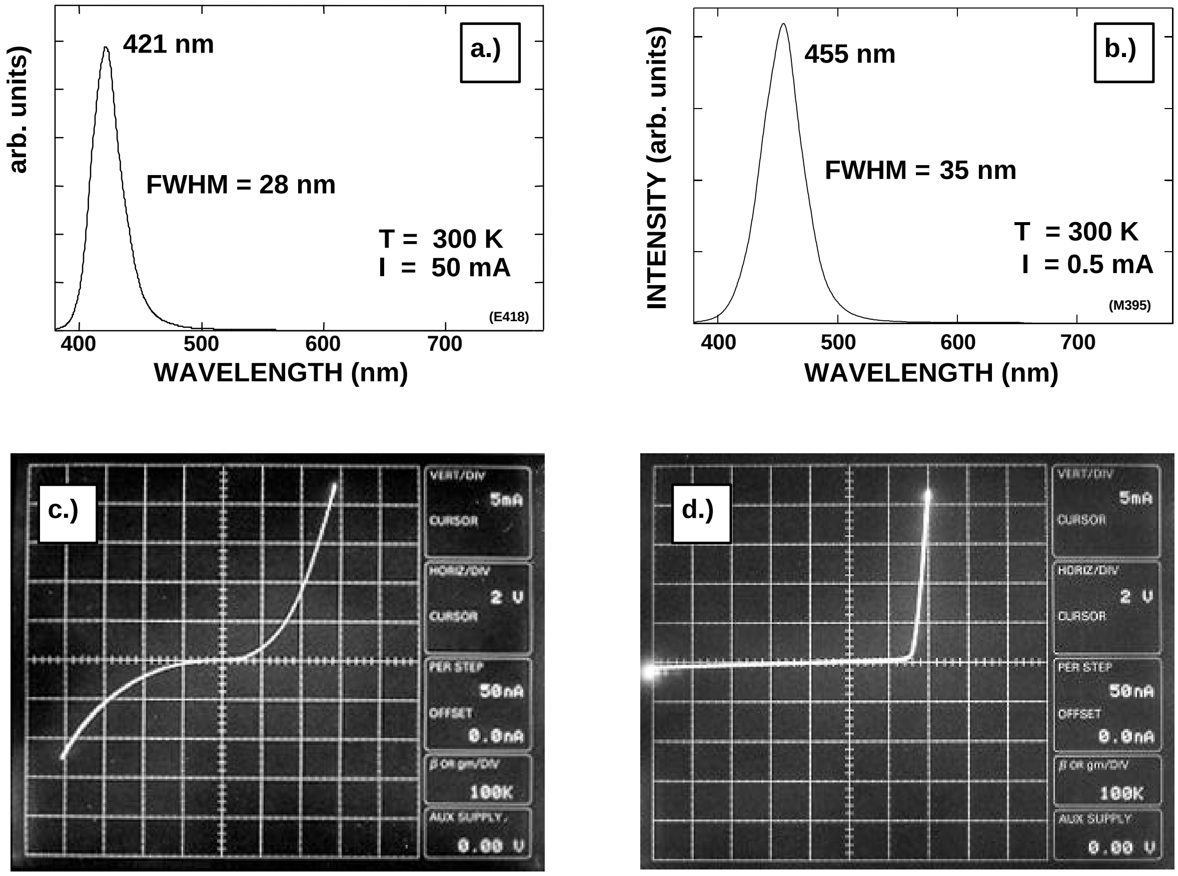

Figure 3: Spectrum for InGaN quantum well LEDs grown by a.) MBE and b.) MOVPE. I-V curve trace for LEDs grown by c.) MBE and d.) MOVPE. Note the substantially lower forward current and reduced breakdown voltage for the MOVPE grown LEDs.

CONCLUSIONS

We have compared the growth of III-V nitride materials by MBE and MOVPE. Critical differences exist in the p-type doped GaN material. A textured surface evolves for MBE grown GaN:Mg, which may be related to the pre-existing dislocation density of the material coupled with difficulties in depositing magnesium with its high vapor pressure at this growth temperature. Although InGaN can be grown by either method with a bandgap tailored to emit light in the visible range of interest for devices, the presence of a high density of shorting dislocations across the diodes limits InGaN QW LEDs grown by MBE. This is the significant factor limiting MBE growth and allowing the successful implementation of MOVPE for III-V nitride optoelectronic applications.

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