The Effect of Nitrogen Ion Damage on the Optical and Electrical Properties of MBE GaN Grown on MOCVD GaN/sapphire Templates

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ABSTRACT

We have established a correlation between localized states responsible for mid-gap optical emission and film mobility of GaN grown under different nitrogen conditions. By imposing a deflector voltage at the tip of the plasma source, we varied the ion/neutral flux ratio to determine how N ions affect mid-gap luminescence and electrical mobility. Low energy electron-excited nanometer scale luminescence (LEEN) spectroscopy in ultrahigh vacuum (UHV) showed mid-gap emission intensities in the bulk that decreased in the ratio, 50 : 1.3 : 1 with increasing deflector voltage. Hall measurements indicated over a factor of two increase in mobility, and a factor of 8 decrease in residual charge density with increasing deflector voltage. The correlation of optical and electrical properties with a reduction in N ion flux suggests the primary role of native defects, such as N or Ga vacancies, in the mid-gap emissions.

INTRODUCTION

Advanced heterostructures based on GaN are increasingly viewed as the materials system of choice for implementing light emitting diodes, solar blind photo detectors, solid state lasers, and high power microwave devices. The performance of these devices is critically dependent upon control of point defects and dislocations in order to make full use of these new materials. While impressive achievements have already been made, the electrical and optical properties of the nitrides remain relatively poorly controlled. A deeper understanding of fundamental growth parameters is still necessary to realize the continued improvement of these devices based on the nitrides.

The nitrogen source of choice for the production of state-of-the-art GaN by molecular beam epitaxy MBE is the RF plasma source [1,2]. While GaN films made using this source are superior to others, the material quality is dependent on many variables including: RF power, RF frequency, nitrogen flow rate, and the ratio of group III to group V fluxes. Because of the many parameters involved when using a plasma source to grow GaN, it's difficult to isolate any one parameter as being of fundamental importance to the production of defect free, single crystal layers. Of particular concern in this article is the sensitivity of the growth to the ratio of N ions to neutral atomic species in the N flux. Different plasma sources are known to have a complex mixture of N components with widely varying amounts of ions, atomic N, and meta stable molecular N species[3,4]

By placing a perpendicular electrostatic potential at the tip of the plasma gun source, ions are deflected away from the growth path. In this way, we can directly observed the effect of the N ion/neutral ratio on material quality. In this work, we directly measured the impact on the electrical and luminescence properties of GaN by reducing the N ion/neutral flux ratio using an electrostatic voltage at the tip of the N source.

EXPERIMENT

We examined 1 μm thick GaN specimens grown by MBE on substrates composed of 3 μm of GaN grown by Metal-organic chemical vapor deposition (MOCVD) on sapphire. The substrate temperature during the GaN growth was 750 °C. A plasma source from SVT Associates, Inc. was used to produce the active nitrogen, in which the RF power and nitrogen flow rate were 250 W and 2.5 sccm, respectively, and the plate voltage at the tip of the plasma gun was varied between 0 and 700 V. The specimens were exposed to ambient conditions, then transferred back into UHV to perform LEEN. For the LEEN measurements, we used an electron gun with an energy range of 0.5 - 4.0 keV, emission current of 0.2 - 2 μA, and a spot size of 0.5 mm to generate optical emission at constant incident power. A Peltier cooled, S-20 photomultiplier collected the light over a spectral range of 1.40 - 3. 75 eV, and the detector output was obtained using standard lock-in techniques. The incident angle of the electron beam was set at 45°, enhancing the surface sensitivity of the measurement relative to normal incidence excitation. All LEEN measurements were made at room temperature.

RESULTS AND DISCUSSION

Ex situ atomic force microscopy (AFM) measurements were performed on the MBE grown GaN as well as the MOCVD GaN pseudo-substrate. All samples were extremely smooth with long, double steps pinned by threading dislocations observed on the MOCVD GaN surface, and stepped mounds 3 - 5 nm high on the surface of the MBE GaN. By applying the plate voltage, the film had noticeably less excess Ga droplets on the surface, and looked remarkably similar to the optimal MBE GaN grown under Ga rich conditions observed by Tarsa *et al* [2]. As shown in Table I, measurements of the specimens as a function of applied plate voltage show a factor of two increase in mobility and an almost order of magnitude decrease in residual electron density at the highest plate voltage. This indicates a significant improvement in the electrical quality of the material after reduction of the ion flux. While we cannot discount the effect of the MOCVD GaN, since we measure the overall sum of the conducting layers, the trend is clear, the reduction in ionized N has increased the conductivity of MBE epilayer.

Table I. Electrical properties of GaN grown with successively greater plate deflection voltage. As the plate voltage is applied, the mobility increases, and correspondingly, the residual charge density decreases. All Measurements were made at 300K.

Plate Voltage (V)	**Charge Density (10^{17} cm^{-3})**	**Mobility (cm^2/V-sec)**
MOCVD GaN	~1	600
0	8	300
500	5	500
700	1	640

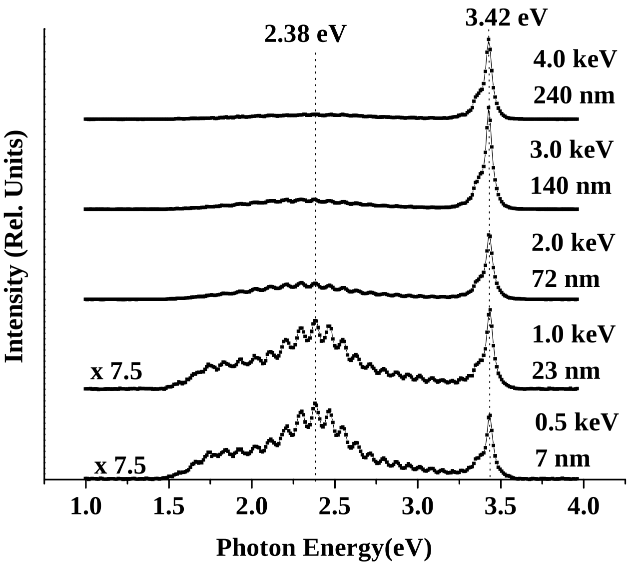

Figure 1. LEEN luminescence intensity as a function of electron beam penetration depth for GaN grown with plate voltage = 700 V. The right side of the figure indicates the beam voltage and the corresponding electron beam penetration depth in nm.

Based on calculations by Everhart and Hoff, a 0.5 keV incident electron beam energy penetrates 6 nm into GaN[5], increasing with beam energy at a rate proportional to ≈ $E^{1.67}$. By increasing the beam energy to 4.0 keV, the electron beam penetrates to a probe depth of 240 nm giving us the capability of resolving the optical properties of the GaN from 7-240 nm in this work, well within the MBE GaN. From LEEN spectroscopy of a separate MOCVD GaN control specimen, we found intense mid-gap "yellow" emission centered at 2.17 eV well into the bulk of the film. Also from the spectra, we find that the mid-gap emission exhibits intensity oscillations indicative of nm-smooth interfaces, as confirmed by the AFM measurements. In addition to the "yellow" emission, near band edge (NBE) emission at 3.42 eV is observed at a intensity ratio relative to the "yellow emission of ~ 2:1 within the bulk, along with the presence of a peak at 3.35 eV, attributed to D-A recombination. From the depth-dependent nature of the LEEN spectra, we find that the "yellow" emission persists clear up to the surface, while the NBE is almost entirely quenched by non-radiative recombination in the near surface region.

Figure 1 shows the depth-dependent LEEN from the specimen grown with plate voltage = 700 V. In comparison to the control specimen, the mid-gap luminescence is almost entirely absent within the bulk of the film (4.0 keV), and substantial NBE emission remains even in the near surface region. Secondly, there are many more intensity oscillations over a larger energy range indicative of a significantly smoother morphology and a somewhat thicker film, even though the growth conditions were the same. Furthermore, a qualitative change in the nature of the mid-gap luminescence now occurs in the near surface region below 2.0 keV (72 nm penetration depth). We see evidence that the "yellow" emission is now comprised of two peaks, one at 1.8 eV and a second at 2.38 eV. While only the specimens with a plate voltage applied showed this distinct 2.38 eV peak, in all three cases investigated, (plate voltage = 0, 500, 700 V), mid-gap emission exceeded NBE emission at the surface (0.5 keV incident energy, 6 nm probe depth). Although we might be tempted to attribute the change in shape of the "yellow" band directly to the reduction in ionized N, other groups have suggested that there are multiple channels for recombination depending upon temperature as well as growth mechnism, not just MBE grown GaN[6]

In Figure 2, we show a close-up of the NBE region for GaN grown with three different plate voltages. From the figure, it is clear that even for a small plate voltage, D-A recombination is significantly reduced.

We also see that the effect has already saturated by a 500 V plate voltage even though the electrical mobility continued to rise with increasing plate voltage. It is unclear at this time what defect is the cause of the peak, but the "yellow" emission and the D-A feature reduction are correlated in this case.

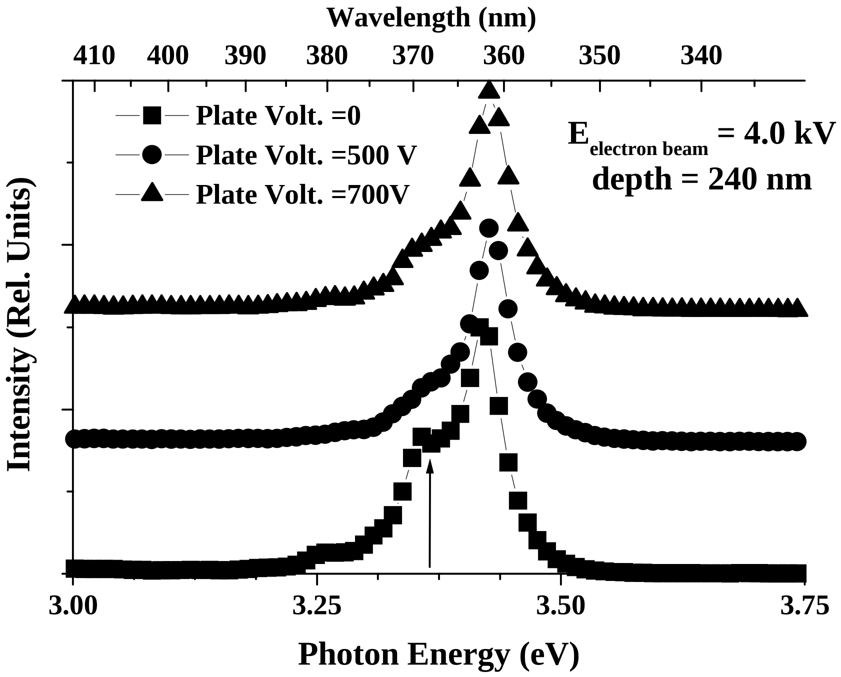

Figure 2. Close up of the band edge showing the reduction of the D-A peak as a function of plate voltage applied to the N beam flux during GaN growth. Spectra are offset for clarity.

In a direct comparison of the luminescence as a function of plate voltage, Figure 3 shows that the NBE at 3.42 eV increased as the mid-gap emissions at 1.8, 2.17, and 2.38 eV decreased. Also from figure 3, we see that GaN grown with no plate voltage emits in the yellow with an intensity over 50 times greater than GaN grown with a plate voltage of 700 V.

Considerable debate continues as to whether native defects or impurities are responsible for this mid-gap emission in GaN, and whether these emissions correlate with electrical properties. It is highly desirable to understand the atomic nature of these defects in order to prevent them from occurring on a consistent basis. It has been noted that the “yellow” emission is far less intense in GaN grown by hydride vapor epitaxy (HVPE) compared to GaN grown either by MOCVD or by MBE [7]. In the HVPE case no ionized species are involved, therefore we exclude ionized extrinsic species as the source of the “yellow” emission. While we cannot exclude the possibility that the incorporation rate of extrinsic impurities might be dependent upon the ionized N arriving at the growth front, we believe a much simpler, direct explanation is the ionized N itself is primarily responsible for the “yellow” emission in GaN. The LEEN spectra highlight the role of *native defects* such as N or Ga vacancies, possibly complexed with other impurities such as carbon or oxygen, in causing the “yellow” emission. Furthermore, the correlation of mid–gap spectral emission with electrical properties indicates the major role such defects have on overall transport properties.

CONCLUSIONS

We have established a correlation between localized states responsible for mid-gap optical emission and film electrical properties in MBE GaN grown using varying N active species. By reducing the N ion flux, we have observed a significant improvement in electrical mobility, a reduction in the residual charge density, a reduction in D-A pair recombination, and a reduction in mid-gap “yellow” luminescence by over a factor of fifty. This correlation between improved optical and electrical properties with the growth process suggests that the “yellow” luminescence is primarily due to intrinsic defects related to the specifics of growth process.

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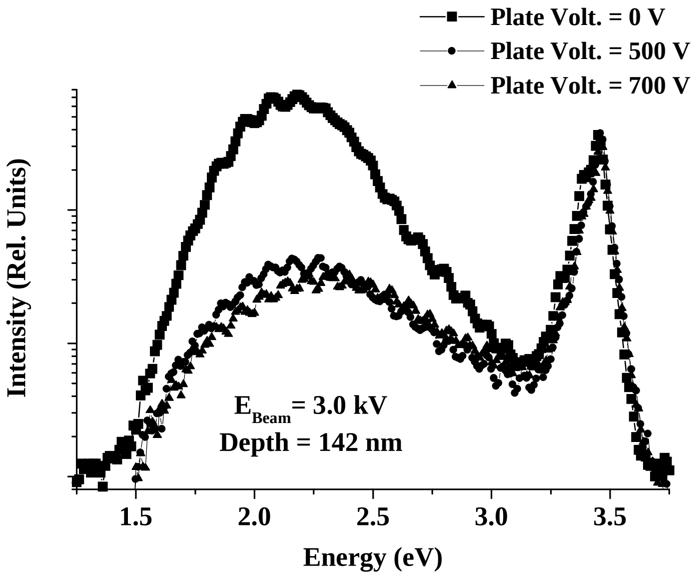

Figure 3. Comparison of LEEN spectra for GaN grown as a function of plate voltage. At an electron beam energy of 3.0 keV, the beam penetrates to a maximum depth of 140 nm, comparable to the penetration depth of a He-Cd laser.

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