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Growth of free-standing wurtzite AlGaN by MBE using a highly efficient RF plasma source

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Ultraviolet light emitting diodes (UV LEDs) are now being developed for various potential applications including water purification, surface decontamination, optical sensing, and solid-state lighting. The basis for this development is the successful production of $Al_xGa_{1-x}N$ UV LEDs grown by either metal-organic vapor phase epitaxy (MOVPE) or molecular beam epitaxy (MBE). Initial studies used mainly sapphire as the substrate, but this result in a high density of defects in the epitaxial films and now bulk GaN or AlN substrates are being used to reduce this to acceptable values. However, the lattice parameters of GaN and AlN are significantly different, so any AlGaN alloy grown on either substrate will still be strained. If, however, AlGaN substrates were available, this problem could be avoided and an overall lattice match achieved. At present, the existing bulk GaN and AlN substrates are produced by MOVPE and physical vapor transport, but thick free-standing films of AlGaN are difficult to produce by either method. The authors have used plasma-assisted MBE to grow free-standing $Al_xGa_{1-x}N$ up to 100 μm in thickness using both an HD25 source from Oxford Applied Research and a novel high efficiency source from Riber to provide active nitrogen. Films were grown on 2- and 3-in. diameter sapphire and GaAs (111)B substrates with growth rates ranging from 0.2 to 3 μm/h and with AlN contents of 0% and ~20%. Secondary ion mass spectrometer studies show uniform incorporation of Al, Ga, and N throughout the films, and strong room temperature photoluminescence is observed in all cases. For films grown on GaAs, the authors obtained free-standing AlGaN substrates for subsequent growth by MOVPE or MBE by removing the GaAs using a standard chemical etchant. The use of high growth rates makes this a potentially viable commercial process since $Al_xGa_{1-x}N$ free-standing films can be grown in a single day and potentially this method could be extended to a multiwafer system with a suitable plasma source.
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I. INTRODUCTION

Ultraviolet light emitting diodes (UV LEDs) are now being developed for various potential applications including water purification, surface decontamination, optical sensing, and solid-state lighting. The basis for this development is the successful production of $Al_xGa_{1-x}N$ UV LEDs grown by either metal-organic vapor phase epitaxy (MOVPE) or molecular beam epitaxy (MBE). The required wavelength for the different applications varies, but, for example, in water purification, LEDs emitting in the wavelength range 250–280 nm are required.[1] This in turn means that films with different Al content are required with relatively low dislocation density. UV LEDs grown on sapphire have a high defect density which in turn limits their efficiency, so lattice matched substrates of AlGaN would be ideal. At present, both free-standing bulk GaN and AlN can be grown by MOVPE, hydride vapor phase epitaxy, and physical vapor transport methods; however, their lattice parameters are significantly different.[1] This has led to the search for methods to produce $Al_xGa_{1-x}N$ substrates of arbitrary Al content.[2,3]

Typical growth rates in MBE are about 0.5 μm/h, so the growth of thick free-standing substrates requires many hours of continuous MBE operation. Using plasma-assisted MBE (PA-MBE), we were nevertheless able to produce 3-in. diameter zinc-blende layers of GaN on (001) GaAs substrates up to 100 μm in thickness with up to 200 h continuous MBE operation.[4] Free-standing GaN films were obtained by removing the GaAs substrate using a standard chemical etch. The same method was also used to grow free-standing wurtzite $Al_xGa_{1-x}N$ wafers on (111) GaAs with compositions from 0% to 50% AlN content.[5] However, this is both an expensive and time consuming process; therefore, to make this a viable commercial process, much higher growth rates are needed, and ideally, the time for MBE growth needs to be less than 24 h operation. The main limit to growth rate comes from the supply of active nitrogen from the RF plasma source, so improving the efficiency of the plasma source is a key requirement.

Recently, Riber developed a novel plasma source (RF-N 50/63) for the growth of GaN layers at higher growth rates. The main differences were modification of the pyrolytic boron nitride crucible and an increase in the number of holes in the PNB aperture plate to 1200 with 0.3 mm diameter. Using this source, the group in Santa Barbara produced thin layers of GaN at growth rates up to 2.65 μm/h.[6] We have used a similar source in our GEN-II MBE system to obtain growth rates for bulk GaN up to 1.8 μm/h on 2-in. diameter GaAs

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(111)B and sapphire substrates.[7] By further increasing the number of holes to 5880, the group in Santa Barbara has now achieved growth rates of up to 7.6 μm/h, but with very high nitrogen flow rates of about 25 sccm.[8]

In this study, we report our recent experience in the growth of free-standing wurtzite (hexagonal) $Al_xGa_{1-x}N$ films with AlN content up to $x \sim 0.2$ by PA-MBE using this latest highly efficient Riber nitrogen plasma source. This is a first stage in developing PA-MBE technology for free-standing $Al_xGa_{1-x}N$ layers over the whole AlN composition range.

II. EXPERIMENTAL SETUP AND METHODOLOGY

Wurtzite polytype layers of GaN and $Al_xGa_{1-x}N$ were grown by PA-MBE on both (0001) sapphire and GaAs (111)B substrates in a Varian MOD-GENII MBE system. Elemental sources were used for both Al and Ga and active nitrogen was provided from two different RF plasma sources, one from Oxford Applied Research (HD25) and one higher efficiency source from Riber (RF-N 50/63). For films grown on GaAs, to avoid any thermal degradation and roughening of the substrate, the oxide was removed prior to growth by heating to ~630 °C under an arsenic (As_2) beam equivalent pressure (BEP) of approximately 6×10^{-6} Torr from a two zone arsenic cracker. The arsenic flux was stopped before growth of either GaN or $Al_xGa_{1-x}N$ layers with $x \sim 0.2$.

At the beginning of each growth before the epitaxy of AlGaN, a thin GaN buffer layer was grown under Ga-rich conditions. It is now well established that Ga-rich conditions are required to produce the best quality material for growth by PA-MBE.[9] After the thin GaN buffer layer was grown, the Al shutter was opened to form $Al_xGa_{1-x}N$ of the desired composition. The higher reactivity of Al determined the composition of AlGaN layers. For films grown on GaAs substrates, the growth temperature was limited to ~700 °C to prevent decomposition of the substrate.

Thick wurtzite AlGaN layers were grown on (111)B GaAs substrates. The GaAs substrate was removed using a standard chemical etch (20 ml H_3PO_4:100 ml H_2O_2)[7] to provide free standing AlGaN up to 100 μm thick as we have previously shown for both zinc-blende and wurtzite AlGaN.[4,5]

In situ reflection high-energy electron diffraction (RHEED) and *ex situ* x-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to investigate the structural properties of the layers. XRD measurements were performed using a Philips X'Pert MRD diffractometer. TEM samples were prepared using a combination of mechanical polishing, dimple grinding, and ion milling with an acceleration voltage of 4 kV, and the resulting samples were studied in a JEOL 4000 EX microscope.

The optical properties of the free-standing AlGaN layers were studied using photoluminescence (PL). The samples were excited using a pulsed frequency multiplied Ti-sapphire laser. The excitation wavelength was 250 nm (photon energy ~5 eV), and average excitation power density was ~2 kW/cm^2. The luminescence was collected using dispersion-free reflective optics and analyzed using a UV enhanced Ocean Optics CCD spectrometer.

The chemical concentrations of Al, Ga, N, and impurities were studied as a function of depth using secondary ion mass spectrometry (SIMS) in two commercial systems—a Cameca IMS-3F and a Cameca IMS-4F system. The samples were also studied using an Oxford Instruments Energy-dispersive X-ray spectroscopy (EDX) system for comparison.

III. RESULTS AND DISCUSSION

Before the growth of thick free-standing films, thin (~1 μm) wurtzite AlGaN layers were grown on 2 in. diameter (111)B GaAs substrates after the growth of a ~50 nm thick GaN buffer layer. Both RF plasma sources showed a RHEED pattern consistent with the growth of wurtzite GaN during the growth of the GaN buffer layer. Recent studies by TEM of the GaN/GaAs interface have shown that there are zinc-blende crystallites in the first few nanometers into the wurtzite GaN layer, which may result from As contamination. By optimizing the nucleation process, we have reduced this to a minimal amount.

Following this initial study, we then grew thick AlGaN layers using the new Riber source with the increased number of 5880 holes in the aperture plate. Due to the finite pumping in our GEN-II system, we used nitrogen flow rates of 6 sccm compared to 25 sccm in the previous study.[8] Using lower flow rates enabled us to keep the chamber pressure to ~10^{-4} Torr and increased the time between regeneration of the cryopump.

First, we studied the growth rate of GaN as a function of Ga flux to determine the transition from N- to Ga-rich growth mode.[9] For this purpose, we grew GaN films at nitrogen flow rates of 6 sccm with an RF power of 500 W. Each sample was grown for a fixed time of 30 min on 2 in. diameter (0001) sapphire wafers. The layer thickness was measured using a standard optical interference method. Films grown under N-rich conditions were free from Ga droplets, which were clearly visible under Ga-rich conditions.[9] Figure

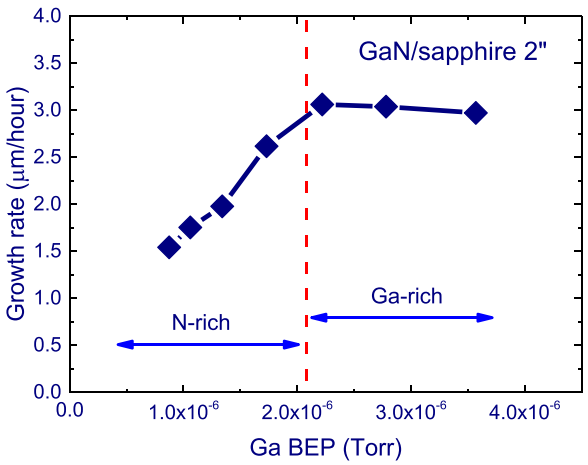

FIG. 1. (Color online) Growth rate dependence for GaN layers on 2 in. sapphire on the Ga flux for the Riber plasma source with 5880 holes in the aperture plate (6 sccm N_2 flow, 500 W, and growth time 0.5 h).

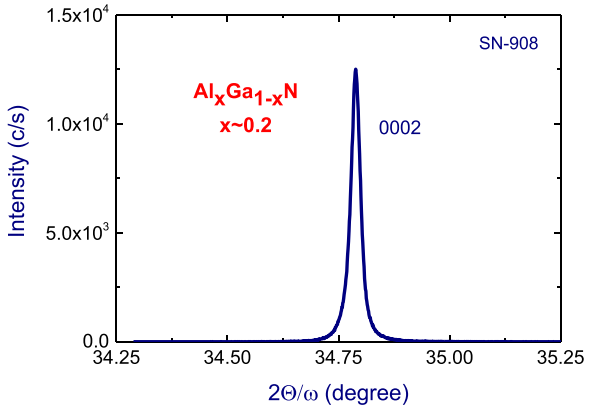

FIG. 2. (Color online) XRD scan of 2θ-ω of the 0002 peak for a wurtzite $Al_xGa_{1-x}N$ layer (x ~ 0.2, thickness ~100 μm).

1 shows that the maximum growth rate achieved in this study was ~3 μm/h, which is consistent with previous studies using the Riber source.[8]

From the above data, we determined the Ga flux corresponding to the transition from N- to Ga-rich growth. Using that information we have grown a set of $Al_xGa_{1-x}N$ layers under slightly group III-rich conditions with an AlN content of about 20 mol. % and with different thicknesses. In 2θ-ω XRD plots, we observed a shift of the $Al_xGa_{1-x}N$ peak to higher angle in comparison with a pure GaN layers, indicating a small decrease in lattice parameter in agreement with the literature.[1] As shown in Fig. 2 for a 100 μm thick wurtzite $Al_xGa_{1-x}N$ layers, we observe a single 0002 reflection at ~35°, which using Vegards law is consistent with the AlN mole fraction x ~ 0.2. This estimate of the AlN mole fraction was also confirmed by both EDX and SIMS studies. XRD measurements show that the zinc-blende content was below the detection limit (0.1%).

Figure 3 shows an XRD ω-plot for the same ~100 μm thick wurtzite $Al_xGa_{1-x}N$ layer with an AlN content ~0.2. We observed a single 0002 diffraction peak. Figure 4 presents the data for full-width-at-half-maximum (FWHM) of the 0002 peak from XRD ω-plots for several wurtzite $Al_xGa_{1-x}N$ layers as a function of their growth time. The $Al_xGa_{1-x}N$ layers were grown at a growth rate of ~2.2 μm/h

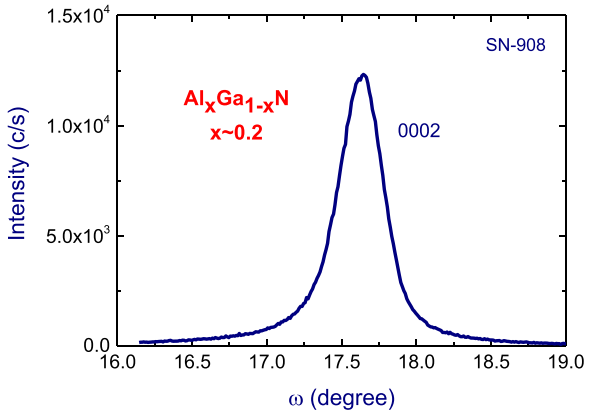

FIG. 3. (Color online) ω XRD scan of the 0002 peak for a wurtzite $Al_xGa_{1-x}N$ layer (x ~ 0.2, thickness ~100 μm).

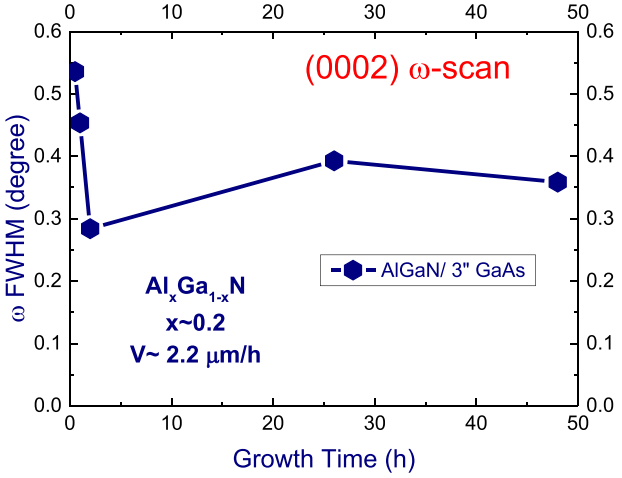

FIG. 4. (Color online) Dependence of ω XRD 0002 peak FWHM for a wurtzite $Al_xGa_{1-x}N$ layer (x ~ 0.2) on the growth time.

and with an AlN content of x ~ 0.2. The growth time was up to 48 h and the thickness of the layers was up to ~100 μm. In all of our earlier experiments with the growth of bulk zinc-blende $Al_xGa_{1-x}N$ layers, we observed degradation of the crystal quality of the layers with increasing thickness due to a gradual build up of the concentration of wurtzite inclusions in the zinc-blende matrix. In the current research, the structural quality of the wurtzite $Al_xGa_{1-x}N$ layer improves rapidly with increasing layer thickness during first few hours of epitaxy. However, the structural quality then degrades slightly during further MBE growth. This may arise because we are probably gradually shifting from the optimum Ga/N flux ratio after the first ten hours of growth, due to depletion of Ga in the 400 g SUMO Ga-cell during the long growths with high fluxes of BEP ~2×10^{-6} Torr.

Our earlier XRD studies using reciprocal space maps for ~10 μm thick free-standing wurtzite $Al_xGa_{1-x}N$ layers show that with increasing AlN content there is a gradual increase in the ω FWHM and decrease in peak intensity.[5] However, a reasonable crystal quality remains for AlN mole fractions up

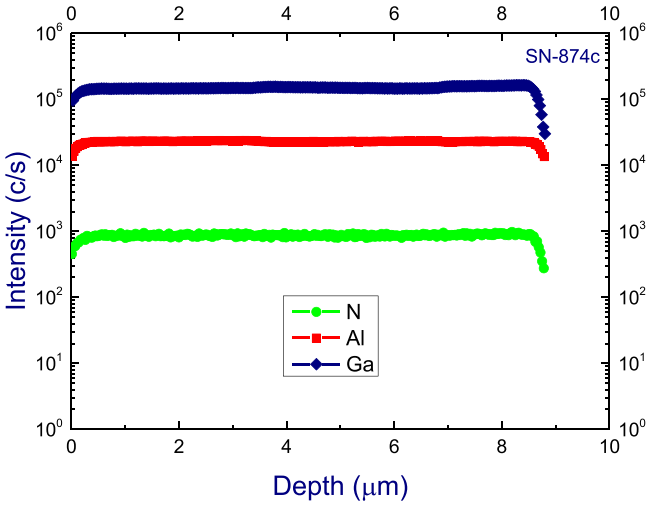

FIG. 5. (Color online) SIMS profiles for Al, Ga, and N for a w-$Al_xGa_{1-x}N$ layer (x ~ 0.2).

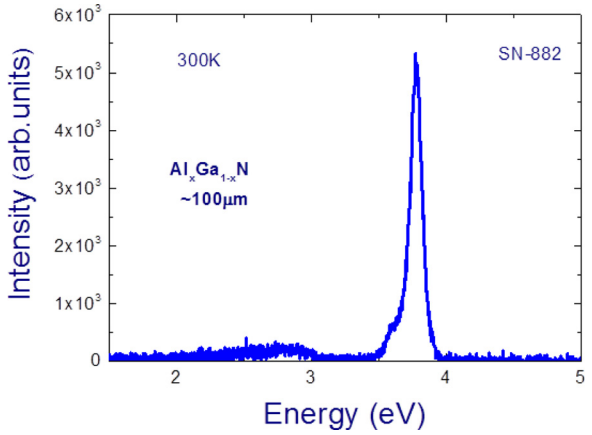

FIG. 6. (Color online) Room temperature PL of wurtzite $Al_xGa_{1-x}N$ layer ($x \sim 0.2$, thickness $\sim 100\ \mu m$).

to $x \sim 0.5$. We intend to study the MBE growth with the highly efficient nitrogen source of free-standing wurtzite $Al_xGa_{1-x}N$ layers with the AlN content higher than $x \sim 0.2$ in the near future.

As SIMS studies show in Fig. 5, the Al, Ga, and N profiles are uniform with depth within experimental error. For example, Ga and Al SIMS signal intensities are 146 018 and 23 188 counts per second (c/s) at a SIMS profile depth of 2 μm and are 145 530 and 23 296 c/s at a depth of 6 μm, respectively. The profile is from the center of the film, and there may be small variations of Al:Ga concentration as a function of radial position. There was no significant As detected in the SIMS profiles. In Fig. 5, we show data for a relatively thin $\sim 9\ \mu m$ thick $Al_xGa_{1-x}N$ layer in order to decrease the SIMS sputtering time, but the general trends will remain valid for the thicker layers.

PL studies show an increase in room temperature peak energy with increasing AlN content again as previously observed in the literature.[1] Figure 6 shows that we observe strong room temperature luminescence from the surface of a 100 μm thick layer, suggesting the sample is of good optical quality. The energy of the PL peak is about 100 meV lower than expected for $Al_{0.2}Ga_{0.8}N$, assuming zero bowing factor, which suggests the peak may be due to donor–acceptor pair recombination.

IV. SUMMARY AND CONCLUSIONS

We have studied the growth of free-standing wurtzite (hexagonal) $Al_xGa_{1-x}N$ films by PA-MBE using the latest model of highly efficient Riber nitrogen plasma source. We have grown $Al_xGa_{1-x}N$ layers with controlled AlN content of $x \sim 0.2$ and thicknesses up to 100 μm on (111)B oriented GaAs substrates. Films can be removed chemically from the GaAs substrate and with thicknesses greater or equal to 50 μm can be handled without cracking to provide free-standing $Al_xGa_{1-x}N$ substrates. Using the novel RF plasma source enables us to grow such $Al_xGa_{1-x}N$ films on 2 and 3 in. diameter GaAs in 24 h making this a potentially viable commercial process.

ACKNOWLEDGMENTS

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