Molecular beam epitaxy growth and properties of GaN, Al$_x$Ga$_{1-x}$N, and AlN on GaN/SiC substrates


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The thin film growth of GaN, AlGaN, and AlN on GaN/SiC substrates by molecular beam epitaxy (MBE) has been studied. The GaN/SiC substrates consisted of 3-μm-thick GaN buffer layers grown on 6H-SiC wafers by metal organic vapor phase epitaxy (MOVPE) at Cree Research, Inc. A radio frequency plasma source was employed to generate active nitrogen species for MBE growth. The high quality of the MBE grown GaN epilayers was evident from the intense room temperature photoluminescence (PL) dominated by a sharp band-edge peak at 3.409 eV having a full width at half maximum (FWHM) of 29.7 meV and the double-crystal x-ray rocking curve (0002) diffraction peak having FWHM as narrow as 156 arcsec. Vertical cross-section TEM clearly showed these MBE grown GaN epilayers to have replicated the quality of the underlying MOVPE grown GaN buffer layer on SiC. The room temperature PL spectra from Mg doped p-type films showed a dominant peak at 3.2 eV. Al$_x$Ga$_{1-x}$N films were also grown on GaN/SiC substrates. Two-dimensional nucleation and growth was monitored by reflection high energy electron diffraction for GaN, Al$_x$Ga$_{1-x}$N, and AlN epilayer deposition, and featured (2×2) surface reconstruction during the growth of GaN/AlN strained layer superlattices. Light emitting diodes (LEDs) based on vertical Al$_x$Ga$_{1-x}$N/GaN double heterostructures have been demonstrated for the first time using MBE grown III–V nitrides on conducting GaN/SiC substrate materials. The typical turn-on voltage among these LEDs was 3.2 V. The forward bias voltage was 4.7 V at 20 mA. The peak wavelength of the electroluminescence (EL) spectrum was 400 nm at 77 K. These results demonstrate that MBE may be used to produce GaN, Al$_x$Ga$_{1-x}$N and AlN based epitaxial structures which are comparable in crystalline quality to those grown by MOVPE. © 1996 American Vacuum Society.

I. INTRODUCTION

The III–V nitrides are promising materials for high temperature electronic and UV/blue/green optoelectronic applications which would use the wide range of direct energy band gaps of these materials: from 1.9 eV (InN), to 3.4 eV (GaN), to 6.2 eV (AlN). Key issues in the successful III–V nitride growth by molecular beam epitaxy (MBE) include: improving the growth rate which has typically been 0.04–0.15 μm/h (Refs. 1–5) [although Moustakas and Molnar reported growth rates as high as 0.65 μm/h for semi-insulating GaN grown by electron cyclotron resonance (ECR) MBE (Ref. 1)]; detailed understanding of the active nitrogen generated by plasma sources, and controlling the mechanisms and kinetics of MBE growth of GaN using plasma sources. This article reports the work at North Carolina State University (NCSU) on the growth of high quality GaN, Al$_x$Ga$_{1-x}$N, and AlN films on GaN/SiC substrates. The GaN films were grown homoepitaxially by rf plasma-assisted MBE on 3-μm-thick GaN buffer layers previously grown on 6H–SiC substrates prepared by MOVPE at Cree Research, Inc. We have circumvented the problems associated with heteroepitaxial nucleation of GaN on highly lattice-mismatched substrates such as sapphire or SiC by using this homoepitaxial approach, and have instead concentrated on the issues associated with the MBE growth process itself. We employed rf plasma-assisted MBE instead of the commonly used ECR plasma-assisted MBE to generate beams of active nitrogen for film growth. Rf plasma source have previously been successful in generating active nitrogen for the MBE growth of GaN and InN at rates of 0.2 μm/h as well as for the p-type doping of ZnSe films. Using this configuration, the MBE growth of very high quality GaN and Al$_x$Ga$_{1-x}$N layers, Al$_x$Ga$_{1-x}$N/GaN multiple quantum well (MQW) structures, GaN/AlN strained layer superlattices, and blue-violet light emitting diodes based on double heterostructures of Al$_x$Ga$_{1-x}$N/GaN have been achieved.

II. EXPERIMENTAL DETAILS

The GaN films were grown using a three-chamber MBE system. The first chamber was an MBE growth chamber which accepted substrates up to 75 mm in diameter, had ports for up to ten MBE source ovens, and was equipped with reflection high energy electron diffraction (RHEED).
The second chamber was used for plasma cleaning of substrates. The third chamber was designed for the chemical analysis of substrate and epilayer surfaces at temperatures up to 800 °C using Auger electron spectroscopy. The three chambers were interconnected by an ultrahigh vacuum (UHV) sample transfer system. This system allowed for the preparation and analysis of substrate surfaces, the controlled growth of epitaxial layers, and the chemical analysis of final epilayer surfaces all in vacuo.

High purity (99.999 99%) Ga and Al, and very large scale integration (VLSI) grade (99.9995%) N2 gas were used as MBE source materials. High purity (99.9999%) Mg and (99,999 99%) Si were used as p-type and n-type doping sources, respectively. An Oxford Applied Research MPD21 rf plasma source was used to generate an active nitrogen flux. The rf plasma source was operated at nitrogen pressures of 5 x 10⁻⁶ to 4 x 10⁻⁴ Torr and powers of 150 to 400 W. We have previously reported high resolution emission spectroscopy studies showing that the rf plasma source emits a much larger fraction of atomic nitrogen and first-positive series excited molecular nitrogen than the ECR plasma source. The ECR source mainly emits second-positive series excited molecular nitrogen and nitrogen molecular ions when operated under the same conditions. It has also been found that high energy nitrogen molecular ions in the output of the ECR source have a negative effect on GaN film growth,6,11,12 It was therefore concluded that the nitrogen species coming out of the rf source at these powers and pressures were preferable for the growth of high-quality GaN films.

The substrates were 3-μm-thick high-quality GaN buffer layers prepared by MOVPE on basal plane 6H-SiC substrates at Cree Research, Inc. The MOVPE grown GaN layers exhibited PL spectra at 298 K dominated by near-edge emission at 3.41 eV and double-crystal x-ray rocking curves as narrow as 85 arcsec FWHM; the best FWHM ever reported for MBE grown GaN. The 0002 GaN diffraction peak with a FWHM of 156 arcsec; the best FWHM ever reported for MBE grown GaN. The 0002 GaN diffraction peak represented a superposition of diffractions from the 3-μm-thick MBE grown layer and the underlying ~3-μm-thick MOVPE grown GaN layer since diffraction from the SiC was also observed.

Vertical cross-section TEM studies were conducted on selected MBE grown GaN epilayers. The TEM photomicrograph in Fig. 2 clearly shows the MBE grown GaN layers replicating the quality of the underlying MOVPE grown GaN buffer layer. TEM studies revealed dislocation densities as low as 10⁸ per cm² in both the MBE grown GaN layer and the underlying MOVPE grown GaN buffer layer. This result provided direct evidence that, using a homoepitaxial approach, GaN grown at North Carolina State University (NCSU) by MBE was comparable in structural quality to state-of-the-art MOVPE grown GaN.

PL measurements of the GaN epilayers provided additional proof of quality. Figure 3 shows a PL spectrum for...
undoped MBE grown GaN at 295 K. This spectrum was dominated by band-edge emission at 3.409 eV. Note that the band-edge emission peak had a FWHM of only 29.7 meV, which was remarkably close to the theoretical thermal broadening at room temperature. There was also evidence in the PL spectrum at 295 K of yellow-green deep level emission near 2.2 eV.

\[ n \]-type GaN was grown using Si as the dopant. GaN was doped \( p \)-type using Mg. PL spectra from these layers shown in Fig. 4 reflect the presence of the respective dopants. The room temperature PL spectrum of an MBE grown 1-m thick heavily doped \( n \)-type GaN:Si film is shown in Fig. 4(a). The spectrum is dominated by a very intense peak at 3.39 eV, which we associated with a donor–hole \((D,h)\) optical transition. The corresponding donor activation energy for this transition \( (E_d) \) was about 19 meV for Si doped GaN. The room temperature PL spectrum for a 0.7-\( \mu \)m-thick MBE grown GaN:Mg film is shown in Fig. 4(b). The \( p \)-type characteristic of Mg doping was confirmed by thermal probe techniques. The PL emission peak at 3.25 eV was believed to be due to an electron–acceptor \((e,A)\) optical transition. This peak corresponded to an acceptor ionization energy \((E_a)\) for the Mg doped GaN of about 160 meV. Emission at 3.39 eV also can be seen. This peak was attributed to unintentional impurity donor levels.

**B. Al\(_x\)Ga\(_{1-x}\)N films and Al\(_x\)Ga\(_{1-x}\)N/GaN multiple-quantum-well structures**

The end-point composition AlN was grown as either 2-\( \mu \)m-thick buffer layers or as thin AlN/GaN strained layer superlattice structures. RHEED patterns indicated a two-dimensional growth surface for the AlN in either case. As shown in Figs. 5(a) and 5(b) a \((2\times2)\) surface reconstruction was observed during growth in both the \([1120]\) and the \([1100]\) directions. Similar to the RHEED reconstructions that were reported for the growth of GaN,\(^4,8\) this reconstruction has been designated as \((2\times2)\).

Single epilayers of Al\(_x\)Ga\(_{1-x}\)N were grown by MBE on GaN/SiC substrates. These layers were deposited under conditions similar to the growth of the GaN films. The Al composition was controlled by adjusting the flux ratio between the Ga and Al sources. During growth of the Al\(_x\)Ga\(_{1-x}\)N films, streaky RHEED patterns were observed in both the \([1120]\) and the \([1100]\) directions indicating a two-dimensional growth surface as shown in Figs. 5(c) and 5(d). During the cooldown following the growth of AlGaN, a sharp \((3\times3)\) reconstruction was observed in both the \([1120]\) and the \([1100]\) directions. We designated this pattern as \((3\times3)\) reconstruction and is shown in Figs. 5(e) and 5(f).

A representative PL spectrum at 295 K for a 1.2-\( \mu \)m-thick undoped MBE grown Al\(_x\)Ga\(_{1-x}\)N epilayer is shown in Fig. 6(a). The emission spectrum is dominated by a high intensity band-edge emission at 3.690 eV with a FWHM of 79.5 meV.
This peak corresponded to an Al mole fraction of $x = 10\%$ if a linear variation in Al$_x$Ga$_{1-x}$N band-edge energy with Al composition is assumed.

Al$_x$Ga$_{1-x}$N/GaN MQW structures consisted of five 50 Å GaN quantum wells separated by four 100 Å Al$_x$Ga$_{1-x}$N barriers grown on GaN/SiC substrates. The MQW structure was capped with a 500-Å-thick Al$_x$Ga$_{1-x}$N layer. As shown in Fig. 6(b), PL emission was observed from both the Al$_x$Ga$_{1-x}$N capping layer and the GaN QWs. The relative PL peak intensities depended on the thickness of the Al$_x$Ga$_{1-x}$N capping layer. The peak associated with the GaN QWs occurred at 3.435 eV, corresponding to a 26 meV shift in energy up from the value observed for a single layer of GaN (see Fig. 3). This energy shift was attributed to the combined effects of strain and quantum confinement, as has been reported by Krishnankutty et al. for GaN/AlGaN MQW structures grown by MOVPE on sapphire.\(^{13}\)

**C. Al$_x$Ga$_{1-x}$N/GaN double heterostructure LED**

Double heterostructure (DH) LEDs based on Al$_x$Ga$_{1-x}$N/GaN were grown by MBE. The GaN active region was co-doped with Si and Mg to create an emission center based on donor–acceptor pair recombination. The LEDs were fabricated using photolithography and dry etching techniques to define 200×200 μm mesas. Electrical contacts to the p-type layer were obtained by evaporating 100×100 μm Ni/Au contact pads. The bottom n-type layer was contacted by depositing Ni onto the back side of the conducting GaN/SiC substrate. This vertical structure is distinguished from previously reported MBE grown GaN LEDs, which required two top contacts because the sapphire substrates which were used were insulating.\(^{11}\)

Room temperature current–voltage characteristics of a typical DH LED are shown in Fig. 7. The device had a turn-on voltage of 3.2 V and a forward voltage of 4.7 V at 20 mA. The LED emitted blue-violet light from 77 K to room temperature. The peak wavelength of the electroluminescence (EL) was 400 nm at 77 K, as shown in Fig. 8. At 160 K, the peak wavelength...
shifted to 390 nm. At room temperature, however, the emission is quite broad and included emission from deep level states.

Additional work is under way at NCSU to improve the efficiency of MBE grown LED devices and to shift their EL spectrum into the blue/green region of the visible spectrum.

IV. CONCLUSIONS

High quality GaN, Al$_{x}$Ga$_{1-x}$N, and AlN films were grown by MBE using GaN/SiC substrates. The benefits of MBE growth using MOVPE grown GaN buffer layers on basal plane 6H-SiC were clearly shown in this study. MBE grown GaN films exhibited remarkably intense photoluminescence dominated by a sharp band-edge peak at 3.409 eV with a FWHM less than 30 meV at room temperature. Double-heterostructure LED devices based on Al$_{x}$Ga$_{1-x}$N/GaN were successfully fabricated and tested. These devices displayed a turn-on voltage of 3.2 V and a forward-bias voltage of 4.7 eV at 20 mA. The peak wavelength of the light output was at 400 nm at 77 K. These are the first vertical structure LEDs made from GaN based materials using MBE on conducting SiC substrates. This work demonstrated the feasibility and benefit of using conducting GaN/SiC substrates for the MBE growth of such devices.

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