Gas source molecular beam epitaxy of high quality $Al_xGa_{1-x}N$ $(0 \leqslant x \leqslant 1)$ on Si(111)

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Layers of $Al_xGa_{1-x}N$, with $0 \leqslant x \leqslant 1$, were grown on Si(111) substrates by gas source molecular beam epitaxy with ammonia. We show that the initial formation of the Si–N–Al interlayer between the Si substrate and the AlN layer, at a growth temperature of 1130–1190 K, results in very rapid transition to two-dimensional growth mode of AlN. The transition is essential for subsequent growth of high quality GaN, $Al_xGa_{1-x}N$, and AlGaN/GaN superlattices. The undoped GaN layers have a background electron concentration of $(2-3)\times10^{16}$ cm^{-3} and mobility up to (800 ± 100) $cm^2/V\,s$, for film thickness ~2 μm. The lowest electron concentration in $Al_xGa_{1-x}N$, with $0.2<x<0.6$, was $\sim(2-3)\times10^{16}$ cm^{-3} for 0.5–0.7-μm-thick film. Cathodoluminescence and optical reflectance spectroscopy were used to study optical properties of these $Al_xGa_{1-x}N$ layers. We found that the band gap dependence on composition can be described as $E_g(x)=3.42+1.21x+1.5x^2$. p–n junctions have been formed on crack-free layers of GaN with the use of Mg dopant. Light emitting diodes with peak emission wavelength at 3.23 eV have been demonstrated. © *2001 American Vacuum Society.* [DOI: 10.1116/1.1377590]

I. INTRODUCTION

Structures based on GaN and $Al_xGa_{1-x}N$, prepared on sapphire, are being developed for photodetectors[1–4] and light emitting diodes operating at wavelengths shorter than 360 nm. Many of these applications would benefit from $Al_xGa_{1-x}N$-based heterostructures grown on Si. Silicon is a very attractive substrate for the growth of GaN-related materials since large diameter wafers are available, having relatively high thermal conductivity and low cost. However, while some work has already been done to prepare $Al_xGa_{1-x}N$ on Si(111) by molecular beam epitaxy (MBE),[5–9] investigation of the crack formation process, dopant incorporation, and behavior of band gap versus composition in the range of Al content $x_{AlN}>0.6$ are still not well understood.

Two growth nucleation methods are known to be effective for epitaxial nitride layers on Si substrates. The first method is carried out on the Si(111)-7×7 reconstructed surface[10–13] at a temperature below 830 °C. The procedure includes deposition of a few Al monolayers on the Si surface before the growth of AlN, to prevent the formation of the amorphous SiN_x. After that, the Al is nitrided and epitaxy of AlN is initiated. The second method, the formation of AlN at a temperature higher than that of the 7×7–1×1 surface reconstruction transition, relies on the formation of a Si–N–Al interlayer and the subsequent epitaxy of AlN.[14]

This work describes the preparation of AlGaN over the entire range of the AlN content. We also discuss the investigation of growth mechanisms leading to the suppression of cracks, effective dopant incorporation, and the preparation of light emitting diodes.

II. EXPERIMENTAL DETAILS

$Al_xGa_{1-x}N$ films, with $0 \leqslant x \leqslant 1$, were grown by gas source molecular beam epitaxy (GSMBE) with ammonia on oriented n- and p-type Si(111) substrates. The substrates were prepared by wet chemical etching.[14] The effects of growth conditions on the surface morphology, homogeneity of the film thickness, and the structure of epitaxial layers have been studied using 10 kV reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), atomic force microscopy (AFM), x-ray diffraction, secondary ion mass spectroscopy, cathodoluminescence (CL), and optical reflectivity. Electrical parameters were investigated by capacitance–voltage (C–V), thermoprobe, and Hall measurements. Epitaxial layers grown on nitridated sapphire substrate[15] were used for Hall measurements.

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Ammonia was introduced into the growth chamber through a mass-flow controller operating in the range of 50 sccm. The temperature was measured by a pyrometer, corrected for the emissivity of the substrate. The layers of AlN were grown in the temperature range of 860 ± 30 °C. Layers of GaN and AlGaN were grown at 780 ± 20 °C.[9,16] Si and Mg were used as dopants to obtain *n*- and *p*-type conductivities.

III. RESULTS AND DISCUSSION

Epitaxial growth of AlN is usually initiated with a few monolayers (2–3 ML) of Al.[10–14] It is generally believed that this results in the formation of the Al–Si γ phase, thus preventing the formation of amorphous silicon nitride. Subsequent exposure to N would result in formation of the Si–Al–N interface, allowing for epitaxy of AlN. However, the details of this mechanism are not clear. Due to a large misfit between AlN and Si there is no possibility for formation of pseudomorphic AlN layer, even if all Al atoms are bonded to Si at the interface. Only islands of relaxed Si–Al–N can be formed by exposure to nitrogen.[11] These islands cannot produce complete coverage of the Si surface, resulting in openings in which active nitrogen can react with Si and form Si–N bonds.[11] This process would thus result in the presence of islands of AlN and Si–N at the surface of Si. Such a surface exposed to fluxes of Al and active nitrogen should produce domains of AlN with different surface polarities. This is similar to the growth of GaAs on Si(001), where both polarities of GaAs are produced.[17] However, high quality films of AlN were obtained with this nucleation procedure when the growth was initiated at low temperature and continued at higher temperature under large III/V flux ratios.[18] This suppresses either the Al- or N-terminated islands, depending on the choice of fluxes.

To improve the nucleation process we carried out growth experiments on Si(111) substrates, leading to complete surface coverage with the Si–N–Al interlayer. This was done by exposing the surface to alternating fluxes of Al and active N.

We began the growth process at high (>830 °C) temperature, where formation of the Al–Si γ phase is impossible due to the short lifetime of Al atoms on Si, by a brief exposure of the surface to NH_3. At this point RHEED shows the presence of an ordered periodic structure on (111) silicon, which we attributed to strongly bound layer of chemisorbed N atoms (Fig. 1). RHEED shows that the surface layer is ordered and two dimensional. This observation is consistent with the superstructure reported on the surface of hexagonal silicon nitride.[19]

A typical RHEED pattern due to formation of ordered surface structure is shown in Fig. 1. Following Ref. 19, we suppose that this structure can be attributed to a 4×4-reconstructed surface of SiN_x crystal at the growth temperature. This superstructure generates 8×8 reconstruction at room temperature. The inset of Fig. 1 displays the LEED pattern of the ordered SiN_x surface, which is in agreement with results of scanning tunneling microscopy and LEED investigation.[19]

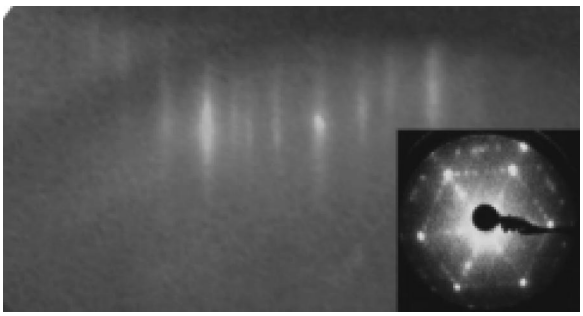


FIG. 1. RHEED picture of partially nitrated Si(111) surface at growth temperature and LEED pictures of partially nitrated Si(111) surface at room temperature.

Once the ordered structure of the type shown in Fig. 1 is formed, the surface is exposed to the flux of Al. This results in the formation of Si–N–Al islands, in agreement with previous observations, separated by the clean surface of Si. This surface is then exposed to active nitrogen, resulting in the formation of Si–N bonds over the clean Si surface. A second exposure to Al flux increases the surface coverage of Si–N–Al. This process of alternating exposure to Al and N is carried out several times, until a complete surface coverage with the Si–N–Al phase is obtained. At this point the growth surface is free of SiN_x.

By initiating the growth of AlN at a high temperature, it ensures that Al atoms form chemical bonds only with nitrogen atoms bonded to Si. Such a Si–N–Al interlayer would provide strongly oriented films with definite Al polarity. After formation of this layer is completed, growth of AlN can be started by simultaneous exposure to fluxes of Al and ammonia. The AlN and the subsequently grown GaN or AlGaN show good crystalline properties, atomically smooth surfaces, and are free of cracks. Using this procedure we were able to grow AlGaN over the entire range of composition, from GaN to AlN, on Si substrates.

It is well known that *p*-type conductivity in nitrides occurs when Mg is incorporated into Ga-substitutional sites.[20] It is also known that superior incorporation of Mg should take place on a metal-terminated surface.[21] The stoichiometry of the growth surface is thus important. We optimize the NH_3/Ga flux ratio and the substrate temperature for the doping process, with the goals of reaching the two-dimensional growth mode and creation of the desired Ga-substitutional sites on the growing surface. The parameter window that yields the stoichiometric surface with a two-dimensional periodicity, corresponding to a bilayer structure, is quite narrow and different for different growth rates. Figure 2 shows the typical evolution of GaN and AlGaN growth rates versus NH_3 flux. The growth rate progresses until the V/III ratio is saturated for constant volume of the incident flux of group III materials. The turning points demonstrate V/III ratio close to unity and the boundary between Ga-rich and N-rich conditions. This growth optimization was carried out at the substrate temperature below 800 °C. The optimization of the V/III ratio during the growth of AlGaN shows unexpected behavior. In this experiment, sources of Ga and Al were kept

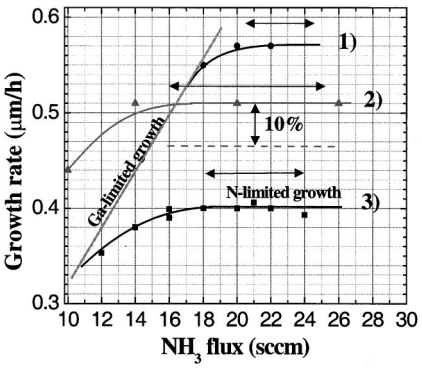


FIG. 2. Growth rate of GaN and $Al_xGa_{1-x}N$ vs NH_3/Ga flux ratio.

at a constant temperature. By measuring growth rates of GaN and AlN as a function of ammonia flux, the expected AlGaN growth rate could be estimated (shown by a dashed line) and compared to the experimental value. The growth rate of AlGaN is higher, under N-rich conditions, than the expected growth rate.

The difference between the measured and calculated growth rates is about 10%. This can be explained by the enhanced cracking efficiency of ammonia in the presence of Al. The possible influence of increased cracking efficiency on the quality of AlGaN, and its role in the doping efficiency, is still under study, but it is clear that this effect makes *p*-type doping AlGaN more difficult.

The results of band gap measurements of AlGaN by optical reflectance are illustrated in Fig. 3. In addition, Fig. 3 also shows absorption data obtained on AlGaN samples grown by MBE on sapphire[22] and CL data obtained on our layers grown on Si.[9] The three sets of data show the same band gap dependence on composition, described by $E_g(x) = 3.42 + 1.21x + 1.5x^2$. The bowing coefficient $b = 1.5$ eV is close to that determined previously for AlGaN prepared on different substrates, by a variety of growth methods.[9,22–24] This value of b is larger than that predicted from the lattice constant difference between GaN and AlN, and may be due

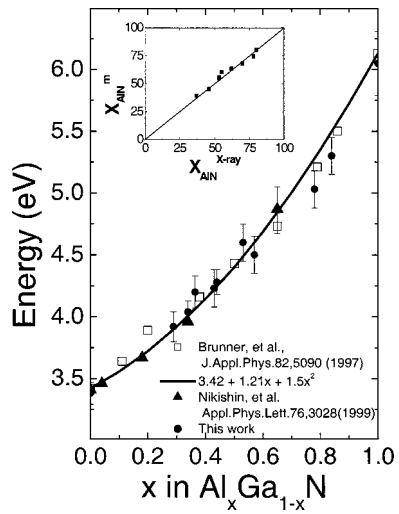
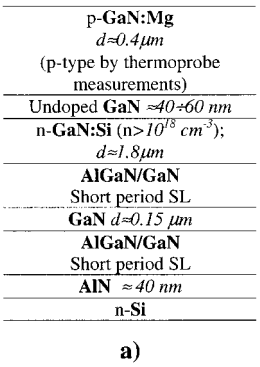
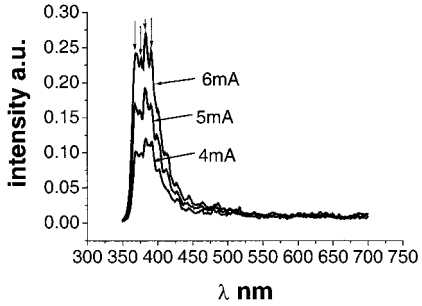


FIG. 3. Band gap dependence of $Al_xGa_{1-x}N$ layers vs the composition.



a)



b)

FIG. 4. Cross section (a) and electroluminescence spectra (b) of GaN LED.

to a large scattering potential for electrons in this alloy system.[24] The inset of Fig. 3 shows the relationship between lattice constant measurements, by x-ray diffraction and x-ray fluorescence measurements. Agreement between the methods is clear. The CL peak wavelength of the bandedge emission varied from 3.406 eV (364.0 nm) for GaN to 4.98 eV (249.0 nm) for $Al_{0.8}Ga_{0.2}N$. Agreement between optical reflectance and CL measurements was also observed. This result is consistent with the low carrier concentration of our layers. Hall and C–V measurements show electron concentrations in the alloy in the range of $(10^{16}–10^{17})$ cm^{-3}. The lowest electron concentration in $Al_xGa_{1-x}N$, with $0.2<x<0.6$, was about $(2–3)\times10^{16}$ cm^{-3}. The best undoped GaN samples show residual electron concentrations of $(2–3)\times10^{16}$ cm^{-3} and Hall mobilities of 800 ± 100 cm^2/V s, at room temperature.

The arrows in Fig. 2 show growth conditions for GaN and AlGaN corresponding to the maximum Mg incorporation rate of $\sim3\times10^{20}$ cm^{-3}. At these conditions we measured hole concentration $p=(0.7–1)\times10^{18}$ cm^{-3} and mobility $\mu_p=50\pm10$ cm^2/V s at room temperature. Maximum hole concentration, which was achieved under Ga deficient conditions, is 2×10^{18} cm^{-3} for GaN:Mg and 5×10^{16} cm^{-3} for $Al_{0.05}Ga_{0.95}N$:Mg. All Mg-doped samples showed *p*-type conductivity as grown. No improvement in Mg activation was observed in postgrowth annealing experiments. Moreover, such annealing changed the conductivity type from *p* to *n*, in agreement with Ref. 25. Details of Mg and H distribution in GaN and AlGaN layers are discussed elsewhere.[26]

Light emitting diode (LED) structures with total thicknesses ~2.5 μm were grown in the two-dimensional growth

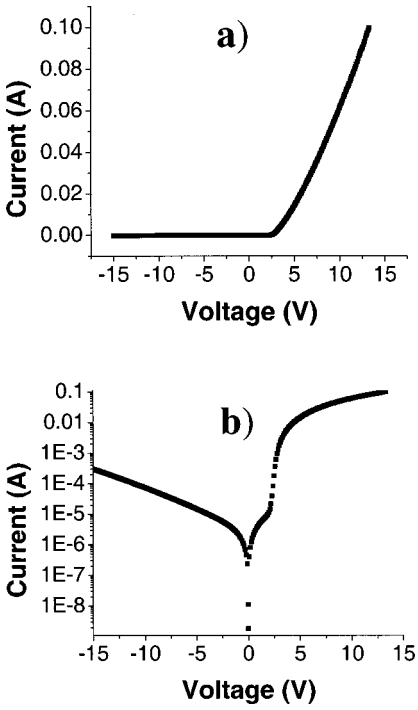


FIG. 5. *I–V* of GaN LED.

mode at ~800 °C and GaN growth rate of ~0.7 μm/h. No crack formation was observed. Root-mean-square surface roughness measured by AFM was ~0.7 nm for areas 20 μm×20 μm. A cross-section of the LED structure consisting 40 nm AlN layer/buffer superlattice of undoped (AlGaN/GaN)/undoped 0.15 μm GaN spacer/buffer superlattice of undoped (AlGaN/GaN)/1.8 μm of Si-doped GaN/10 nm of undoped GaN/0.5 μm of Mg doped GaN is shown in Fig. 4(a). *p*-type contacts were made with InZn alloy annealed at 400 °C for 2–5 min. Large area gold contact was used at the backside of low-resistivity *n*-Si substrate. The room temperature electroluminescence spectra are shown as a function of current in Fig. 4(b). The emission was dominated by a peak at ~380 nm ($h\nu_{max}$~3.23 eV). This value is close to that observed from LEDs grown by plasma-assisted MBE[27] and GSMBE with ammonia on sapphire.[28] We believe that slightly long wavelength emission peak position of our LED compared with single, λ~365 nm,[7] and double, λ~360 nm[5] GaN/AlGaN LED heterostructures grown on Si substrates can be attributed to radiative recombination in the undoped *n*-GaN and Mg-doped *p*-GaN layers close to the *p–n* junction area. We estimate the hole concentration in the *p*-GaN layer at ~$(3-5)\times10^{17}$ cm^{-3}. The spectra show Fabry–Perot interference fringes, consistent with flat epitaxial interfaces.[28]

A typical room temperature current–voltage (*I–V*) curve from a vertical geometry LED is shown in Fig. 5. Under forward bias, diodes start to emit at ~3.6 eV. At reverse bias, leakage currents at −10 V were in the 10–100 μA range, for different diodes.

In summary, we describe growth procedures resulting in high quality AlGaN on Si substrates. Gas source MBE growth under stoichiometric conditions allowed us to control electrical properties of layers and structures. Light emitting diodes based on GaN grown on Si operate at low currents and forward voltage.

ACKNOWLEDGMENTS

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