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Molecular beam epitaxy of free-standing wurtzite $Al_xGa_{1-x}N$ layers

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ABSTRACT

Recent developments with group III nitrides present $Al_xGa_{1-x}N$ based LEDs as realistic devices for new alternative deep ultra-violet light sources. Because there is a significant difference in the lattice parameters of GaN and AlN, $Al_xGa_{1-x}N$ substrates would be preferable to either GaN or AlN for ultraviolet device applications. We have studied the growth of free-standing wurtzite $Al_xGa_{1-x}N$ bulk crystals by plasma-assisted molecular beam epitaxy (PA-MBE). Thick wurtzite $Al_xGa_{1-x}N$ films were grown by PA-MBE on 2-in. GaAs (111)B substrates and were removed from the GaAs substrate after growth to provide free standing $Al_xGa_{1-x}N$ samples. X-ray microanalysis measurements confirm that the AlN fraction is uniform across the wafer and mass spectroscopy measurements show that the composition is also uniform in depth. We have demonstrated that free-standing wurtzite $Al_xGa_{1-x}N$ wafers can be achieved by PA-MBE for a wide range of AlN fractions. In order to develop a commercially viable process for the growth of wurtzite $Al_xGa_{1-x}N$ substrates, we have used a novel Riber plasma source and have demonstrated growth rates of GaN up to 1.8 μm/h on 2-in. diameter GaAs and sapphire wafers.

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1. Introduction

At present there is great interest in the development of ultraviolet (UV) light sources for solid-state lighting, optical sensors, surface decontamination and water purification. UV disinfection is one of the most promising methods for water treatment. Unlike chemical water treatment it will be fast and easy to use and will not require hazardous materials. 250 nm deep ultra-violet (DUV) light attacks the DNA of micro-organisms. Until recently the main UV sources for such applications were mercury lamps, however, these lamps are fragile, have a limited lifetime and present a disposal problem due to the toxic mercury.

Recent developments with group III nitrides allows researchers world-wide to consider $Al_xGa_{1-x}N$ based LEDs as possible new alternative DUV light sources. If efficient devices can be developed they will be easy to use, will potentially have a long life time, will not be fragile and will be suitable for battery operation allowing their use in remote locations. The first UV LEDs are now being successfully manufactured using the $Al_xGa_{1-x}N$ material system. DUV LEDs require $Al_xGa_{1-x}N$ layers with compositions in the mid-range between AlN and GaN. For example for efficient water purification the $Al_xGa_{1-x}N$ LEDs need to emit in the wavelength range 250–280 nm. However, there are significant differences in the lattice parameters of GaN

($a \sim 3.19$ Å and $c \sim 5.19$ Å) and AlN ($a \sim 3.11$ Å and $c \sim 4.98$ Å) [1]. Therefore $Al_xGa_{1-x}N$ substrates would be preferable to those of either GaN or AlN for deep ultraviolet device applications, that has stimulated an active search for methods to produce bulk $Al_xGa_{1-x}N$ substrates with variable AlN content.

MBE is normally regarded as an epitaxial technique for the growth of very thin layers with monolayer control of their thickness. However, we have recently used MBE for bulk crystal growth and have produced layers of zinc-blende GaN up to 100 μm in thickness [2–4]. We have also demonstrated the scalability of the process by growing free-standing zinc-blende GaN layers up to 3-in. in diameter.

We have shown that our newly developed PA-MBE process for the growth of bulk zinc-blende GaN layers can also be used to achieve free-standing wurtzite $Al_xGa_{1-x}N$ wafers [5,6]. Thick wurtzite $Al_xGa_{1-x}N$ films with an AlN content, x, from 0 to 0.5 were successfully grown by PA-MBE on 2-in. GaAs (111)B substrates.

In this paper we will describe our recent results in development of our PA-MBE approach for the growth of free-standing wurtzite $Al_xGa_{1-x}N$ bulk crystals.

2. Experimental details

Wurtzite (hexagonal) GaN and $Al_xGa_{1-x}N$ films were grown on different substrates by plasma-assisted molecular beam epitaxy (PA-MBE) in a MOD-GENII system [2–6]. 2-in. diameter sapphire and GaAs (111)B substrates were used. The active nitrogen for the

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growth of the group III-nitrides was provided by RF activated plasma sources. We compared different nitrogen plasma sources for the growth of thick wurtzite GaN and $Al_xGa_{1-x}N$ films including a standard HD25 plasma source from Oxford Applied Research and a modified novel high efficiency plasma source from Riber.

A GaAs buffer layer was grown on the GaAs (111)B substrates in order to improve the properties of the $Al_xGa_{1-x}N$ films. A thin GaN buffer was deposited before the growth of the $Al_xGa_{1-x}N$ layers of the desired composition. All the $Al_xGa_{1-x}N$ layers were grown under strongly group III-rich conditions in order to achieve the best structural quality layers. In the current study the $Al_xGa_{1-x}N$ layers were grown at temperatures of ~ 700 °C.

Thick (~ 10 μm) $Al_xGa_{1-x}N$ layers were grown by MBE on GaAs substrates and the GaAs was subsequently removed using a chemical etch (20 ml H_3PO_4:100 ml H_2O_2) in order to achieve free-standing $Al_xGa_{1-x}N$ wafers. From our previous experience with MBE growth of zinc-blende GaN [2–4], such a thickness is already sufficient to obtain free-standing GaN and $Al_xGa_{1-x}N$ layers without cracking and at the same time it does not require very long growth runs. To increase the thickness even further to 50–100 μm is merely a technical task, which we have shown earlier is possible. Therefore, for this demonstration of the feasibility of the method, we have chosen to grow the majority of the bulk wurtzite $Al_xGa_{1-x}N$ layers ~ 10 μm thick.

The structural properties of the samples were studied in-situ using reflection high-energy electron diffraction (RHEED) and after growth ex-situ measurements were performed using X-ray diffraction (XRD). To investigate the optical properties of free-standing $Al_xGa_{1-x}N$ layers we have studied photoluminescence (PL) and cathodoluminescence (CL). The PL was excited by a quadrupled tuneable ps Ti:Sapphire laser operating at 190–330 nm. The CL was measured using a telescopic collection system on field emission gun scanning electron microscope [7].

We have studied Al incorporation in the $Al_xGa_{1-x}N$ layers by secondary ion mass spectrometry (SIMS) using Cameca IMS-3F and IMS-4F systems and by electron probe microanalysis (EPMA) using a Cameca SX100 apparatus.

3. Results and discussion

At the first stage we carried out PA-MBE growth of thin (~ 1 μm) wurtzite $Al_xGa_{1-x}N$ layers on two-in. diameter (111)B GaAs substrates for AlN fractions ranging from 0 up to 0.5. This substrate orientation was chosen in order to initiate the growth of the hexagonal phase of material. Wurtzite GaN buffers, of thickness ~ 50 nm, were deposited before the growth of all the $Al_xGa_{1-x}N$ layers. As expected, in 2θ–ω XRD plots, with increasing Al content we observed a gradual shift of the position of the $Al_xGa_{1-x}N$ XRD peak to higher angle. PL and CL studies confirmed an increase of the band gap of $Al_xGa_{1-x}N$ layers with increasing Al content.

Based on these results then grew ~ 10 μm thick wurtzite $Al_xGa_{1-x}N$ layers under similar growth conditions with x ranging from 0 up to 0.5. Fig. 1 shows a 2θ–ω XRD plot for a 10 μm thick free-standing wurtzite $Al_xGa_{1-x}N$. The GaAs substrate had been chemically removed from the substrate after growth. In XRD studies we have observed a single peak at ~ 35 degrees, which is the correct position for a wurtzite $Al_xGa_{1-x}N$ layer. Using Vegard's law, we can estimate the composition of the $Al_xGa_{1-x}N$ layer shown in Fig. 1 to be $x\sim 0.1$. The value of AlN fraction in this $Al_xGa_{1-x}N$ layer was also confirmed by EPMA measurements. From high resolution XRD scans we can estimate the zinc-blende fraction, which in this case was below our detection limit ($<0.1\%$). It is important to note that for $Al_xGa_{1-x}N$ layers with a similar composition ($x\sim 0.1$), but with a thickness of only ~ 0.5 μm the FWHM was similar. This data confirms that we are able to sustain the same good structural quality of wurtzite $Al_xGa_{1-x}N$ layers, whilst increasing the thickness from the very thin layers up to

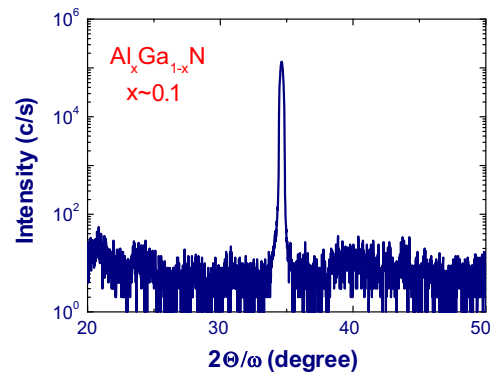**Fig. 1.** A 2θ–ω XRD scan showing the 0002 peak at the centre of a ~ 10 μm thick 2-in. diameter free-standing wurtzite $Al_xGa_{1-x}N$ layer with composition $x\sim 0.1$.

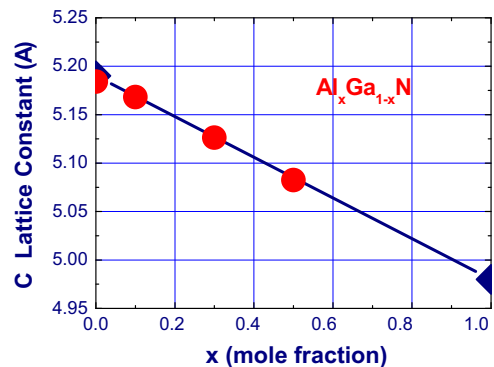**Fig. 2.** C-lattice constants for 10 μm thick wurtzite $Al_xGa_{1-x}N$ layers with the different AlN contents.

~ 10 μm. This is a very significant result, because it shows that MBE can be a viable method for the growth of bulk free-standing wurtzite $Al_xGa_{1-x}N$ crystals.

From XRD data the dependence of the lattice constants for $Al_xGa_{1-x}N$ were measured as a function of the AlN content and the results for c-lattice are shown in Fig. 2. The estimated $Al_xGa_{1-x}N$ composition data were later confirmed by EPMA studies. On the figure we have also plotted c-lattice constants for GaN and AlN [1] and a linear estimate for $Al_xGa_{1-x}N$ alloys c-lattice constants using Vegard's law. Fig. 2 shows that c-lattice parameter for free-standing $Al_xGa_{1-x}N$ layers decreases linearly with decreasing AlN content in good agreement with Vegard's law.

We have investigated reciprocal space maps and rocking curves for this series of samples and observed a gradual increase in FWHM ω and decrease in XRD peak intensity with increasing AlN fraction in $Al_xGa_{1-x}N$ layers from 0 to $x\sim 0.5$. The intensity of the XRD peak is still strong and the FWHM ω is relatively narrow for all $Al_xGa_{1-x}N$ layers, which confirms that MBE can be used as a method for the growth of bulk wurtzite $Al_xGa_{1-x}N$ crystals for a wide range of the Al compositions.

The depth uniformity of Al incorporation into the $Al_xGa_{1-x}N$ layers was studied using SIMS. Fig. 3 shows SIMS profiles for Al, Ga, As and N at the centre of free-standing $Al_xGa_{1-x}N$ layer with $x\sim 0.3$ on the side previously in contact with the GaAs substrate. After sputtering through the initial GaN layer we have observed a uniform distribution of Al, Ga and N within the bulk of $Al_xGa_{1-x}N$ layers with different AlN fractions. There is no significant As incorporation into the bulk of $Al_xGa_{1-x}N$ layers, which was confirmed by the fact that the As signal is at the background level of the SIMS system.

In order to study the lateral distribution of the elements across the 2-in. diameter $Al_xGa_{1-x}N$ wafer, we have performed EPMA studies on the surface of the $Al_xGa_{1-x}N$ crystal previously attached
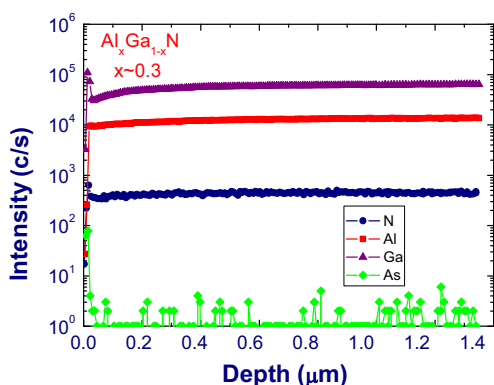
Fig.3. SIMS profiles for Al, Ga, As and N at the centre of free-standing wurtzite $Al_xGa_{1-x}N$ layer with a composition $x\sim0.3$ on the side previously in contact with the GaAs substrate.

Fig. 4. Growth rate for GaN layers grown on 2-in. sapphire substrates using the different Ga fluxes.

Fig. 5. Thickness of wurtzite GaN layers grown on 2-in. GaAs (111)B substrates as a function of the growth time.

to the GaAs substrate. We were able to achieve a uniform distribution of Al content across the diameter for the central part of the 2-in. $Al_xGa_{1-x}N$ wafer. However, close to the edge of the wafer the Al distribution becomes less uniform, with the maximum Al content close to the edge of the wafer. This is similar to EPMA results from zinc-blende $Al_xGa_{1-x}N$ wafers and can be attributed to the strong dependence of the Al incorporation on the group III:N ratio during MBE [5,6]. In our case we have slightly more group III-rich conditions at the edges of the 2-in. wafer due to temperature non-uniformity.

The maximum GaN and $Al_xGa_{1-x}N$ growth rate in our MBE system is limited by the efficiency of our HD25 nitrogen plasma source. In the current MBE configuration the maximum growth rates for HD25 were less than 1 µm/h. Recently, Riber has developed a novel plasma source for the fast growth of GaN layers. Riber have modified the construction of the source and optimised the pyrolytic boron nitride (PBN) crucible and PBN aperture arrangement. The first tests of the novel Riber source were performed for the growth of very thin GaN layers grown for 5 min on small wafers [8]. The authors of that work demonstrated that with this novel source it was possible to achieve GaN growth rates up to 2.65 µm/h [8].

We have installed this novel Riber source in our custom designed MBE system. Growth of GaN layers was performed on large area 2-in. sapphire (0001) wafers. In this study, all the GaN layers were grown for 2 h, which was significantly longer than in the earlier study [8]. The transition from N-rich to Ga-rich growth was also investigated. The N flow rate was fixed at 3 sccm, which was established to be an optimal N flow rate for efficient performance of the novel Riber source [8]. A fixed RF power of 500 W was used in all our experiments.

Fig. 4 shows the dependence of the growth rate for GaN layers grown on 2-in. sapphire for different Ga fluxes. We measured the thickness of the GaN layers after growth by an optical interference method. Under N-rich conditions we observed a clean surface and the growth rate increased linearly with increasing Ga flux. Under strongly Ga-rich growth conditions we observed Ga droplets on the surface and a fixed growth rate, so in this regime the growth is limited by the amount of active nitrogen. The dependence in Fig. 4 is in excellent agreement with the classical papers on the kinetics of PA-MBE of GaN [9]. The highest growth rate achieved under these growth conditions was 1.8 µm/h, which is in agreement with the earlier Riber results on the very thin GaN layers [8].

For the growth of free-standing GaN and $Al_xGa_{1-x}N$ layers we normally use GaAs substrates [2–4]. Therefore, we checked the performance of Riber source for the growth of GaN layers on GaAs (111)B substrates and have obtained results similar to the growth on sapphire shown in Fig. 4.

Fig. 5 shows the thicknesses of three wurtzite GaN layers grown for 2, 4 and 6 h respectively on 2 in. GaAs (111)B substrates. The N flow was kept at 3 sccm and the Ga flux was fixed at a BEP $\sim2.8\times$
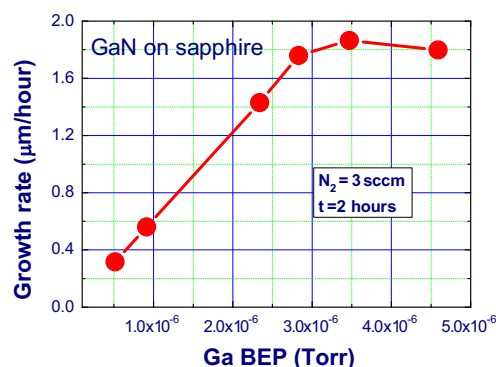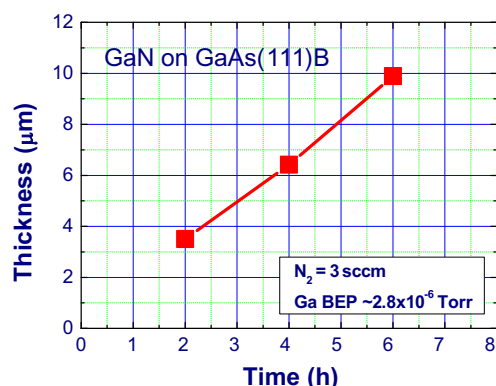
10^{-7} Torr. This Ga flux value allowed us to stay under slightly Ga-rich conditions during the growth, as can be seen from Fig. 4. We have checked the stability of the GaN growth rate during the PA-MBE process. We observed a linear increase in the GaN thickness with time as expected and so GaN layers with a thickness of ~10 µm can be obtained in 6 h. We have demonstrated previously [2–6] that for the use as a substrate the GaN layer thickness needs to be greater than 50 µm. With the new Riber source we can achieve such a thickness in less than 2 days growth, and that makes the production of wurtzite $Al_xGa_{1-x}N$ a commercially viable process.

4. Summary and conclusions

We have studied the growth of free-standing wurtzite $Al_xGa_{1-x}N$ bulk crystals by PA-MBE. Thick wurtzite $Al_xGa_{1-x}N$ films were grown by PA-MBE on 2-in. GaAs (111)B substrates and were removed from the GaAs substrate after growth to provide free standing $Al_xGa_{1-x}N$ samples. EPMA measurements confirm that the Al content is uniform across the wafer and SIMS measurement show that the composition is also uniform in depth. We demonstrated that free-standing wurtzite $Al_xGa_{1-x}N$ wafers can be achieved by PA-MBE for a wide range of AlN fractions. In order to develop a commercially viable process for the growth of wurtzite $Al_xGa_{1-x}N$ substrates, we used a novel Riber plasma source and have demonstrated growth rates of GaN up to 1.8 µm/h on 2-in. diameter GaAs and sapphire wafers.

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