Molecular Beam Epitaxy of Nonpolar Cubic $Al_xGa_{1-x}N$/GaN Epilayers

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ABSTRACT

Cubic $Al_xGa_{1-x}N$ films were grown by molecular beam epitaxy on freestanding 3C-SiC (001) substrates with an Al mole fraction of x=0 to 0.74. Using the intensity of a reflected high energy electron beam as a probe we find optimum growth conditions of c-AlGaN when a one-monolayer gallium coverage is formed at the growing surface. Clear reflection high energy electron diffraction oscillations during the initial growth of $Al_xGa_{1-x}N$/GaN layers were observed. We find that the aluminium mole fraction is only determined by the aluminium flux, and that the $Al_xGa_{1-x}N$ growth rate is independent on the aluminium content. Atomic force microscopy exhibits smooth surfaces with a RMS roughness of about 5 nm on 5x5 μm^2 areas. Cathodoluminescence spectroscopy revealed clear band edge emission up to an aluminium mole fraction of x=0.52, showing a linear relation between the band gap energy and the Al composition.

INTRODUCTION

Group III-nitrides crystallize in the stable wurtzite structure or in the metastable zincblende structure. An important difference between these material modifications is the presence of strong internal electric fields in hexagonal (wurtzite) III-nitrides grown along the polar c-axis, while these "build-in" fields are absent in cubic (zincblende) III-nitrides. Since polarization fields can limit the performance of devices some attention has been focused recently on the growth of wurtzite structures with nonpolar orientations e.g., growth along *a, m* or *R* directions [1-3] and also on cubic nitrides [4-5]. The cubic III-nitride polytype is metastable and can only be grown successfully in a narrow window of process conditions [6]. For the fabrication of electronic devices it is essential to realize $Al_xGa_{1-x}N$ epilayers with a well defined Al mole fraction x which determines e.g. the barrier height of heterojunctions.

In this paper we report on investigations of the growth parameters of cubic $Al_xGa_{1-x}N$ (c-$Al_xGa_{1-x}N$) layers with optimized structural perfection. The Ga coverage of the surface during growth of c-$Al_xGa_{1-x}N$ films was measured and the dependence of the Al mole fraction and the growth rate on the Al flux was investigated. The RMS roughness of c-$Al_xGa_{1-x}N$ was measured at different Al contents and the dependence of the c-$Al_xGa_{1-x}N$ band gap energy on the Al mole fraction was determined.

EXPERIMENT

All cubic $Al_xGa_{1-x}N$ films were grown using a Riber 32 MBE unit. Thermal effusion cells were used for the evaporation of group-III elements. For the activation of nitrogen an Oxford Applied Research HD-25 rf-plasma was used. The films were grown on freestanding 3C-SiC (001) substrates. Prior to growth, the substrates were subjected to an aluminium deoxidation process at 800 °C using an Al-flux with an beam equivalent pressure of $8.2*10^{-8}$ mbar. Following this step, a 300 nm thick GaN buffer layer was grown at 720°C. Finally, a series of $Al_xGa_{1-x}N$ films, about 50 nm to 600 nm thick, were grown at the same temperature. During the growth of all these films, the nitrogen plasma conditions were kept constant at 260 W rf power and 0.4 sccm N_2 flow equal to an active nitrogen flux of $F_N=2.2*10^{14}$ $cm^{-2}s^{-1}$. The growth was continuously monitored *in situ* by reflection high-energy electron diffraction (RHEED) with a 16 keV electron-beam at an incidence angle of 1.3°. The intensity of the RHEED pattern was recorded using a digital RHEED analysis system. The arrival rate of the group-III atoms was determined by measuring the beam equivalent pressures (BEP) prior to growth, using a nude ionization gauge placed at the substrate position. The impinging flux F_i^{imp} of species i (in $cm^{-2}s^{-1}$), is given by [7]:

$$F_i^{imp} = C_i \frac{P_i}{\sqrt{m_i k_B T_i}} \tag{1}$$

where P_i is the measured BEP, m_i is the atomic mass, and T_i is the vapor temperature, which is assumed equal to the corresponding effusion cell absolute temperature. The constant C_i reflects the ionization gauge sensitivity factors for gallium and aluminum as well as geometrical factors related to placing the ion gauge in the exact position of the substrate.

Two series of $Al_xGa_{1-x}N$ epilayers were realized, one with a coverage of 1 monolayer (ML) Ga on the growing surface, a second one having a Ga coverage exceeding 1 ML. Details of the procedure of the Ga-coverage measurements are given in the next chapter.

The AlN mole fraction x of our c-$Al_xGa_{1-x}N$ films was determined *ex situ* by high resolution X-ray diffraction (HRXRD). Using appropriate standards, we estimate the error of the AlN mole fraction to be less than 1 %. The growth rate was obtained *in situ* from RHEED intensity oscillations and the film thickness was determined *ex situ* by optical reflection measurements. The results of the two methods agreed within $\Delta d = 10$ nm. The surface morphology was inspected with an atomic force microscope (AFM). Room temperature cathodoluminescence (CL) spectra of the c-$Al_xGa_{1-x}N$ layers were measured using an acceleration voltage of 10 kV.

RESULTS AND DISCUSSION

It is well established [6] that the optimum conditions for the epitaxial growth of c-$Al_xGa_{1-x}N$ are mainly determined by two parameters, the surface stoichiometry and the substrate temperature. Both parameters are interrelated; therefore an in-situ control of both, substrate temperature and surface stoichiometry is desirable and has been achieved by monitoring the MBE growth process by RHEED. The study of the surface reconstruction behaviour was one of the key issues in understanding the c-III nitride growth. First principle calculations by Neugebauer et al. [8] showed that all energetically favoured surface
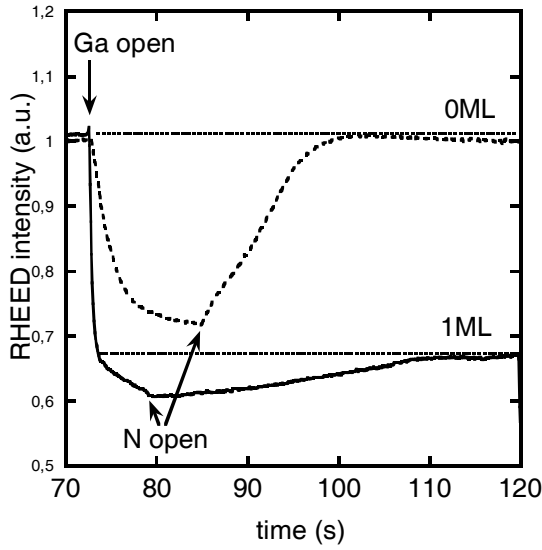
Fig. 1 *The intensity of the zero order RHEED reflexion measured during the initial growth of c-GaN.*
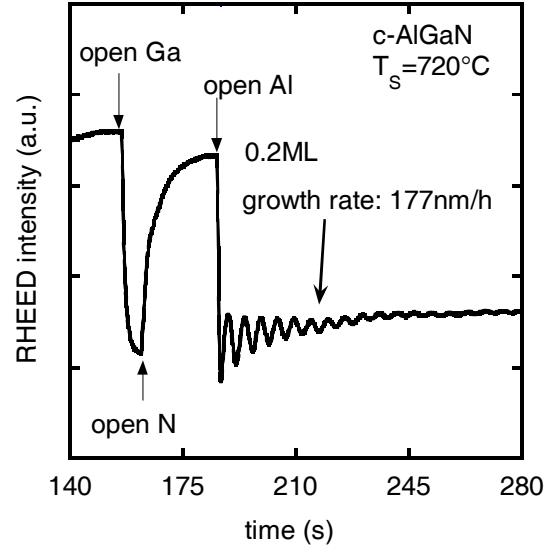
Fig. 2 *RHEED intensity measured during the initial growth of c-Al$_{0.25}$Ga$_{0.75}$N. After opening the Al shutter.*

modifications of the polar (001) c-GaN surface are Ga-stabilized and therefore optimum growth conditions were expected under slightly Ga-rich conditions.

The Ga-coverage during c-AlGaN growth was obtained by measuring the intensity of the reflected electron beam ((0,0)-streak RHEED intensity). The relation between the reflected intensity and the Ga-coverage was obtained by the following calibration procedure: When we expose a AlGaN surface which is kept at growth temperature to a Ga-flux we observe a decrease of the RHEED intensity up to a saturation value, which is related to the impinging Ga flux and the substrate temperature. With the known value of the Ga-flux and the transient time of the RHEED intensity we were able to estimate the amount of adsorbed gallium and establish a relation between the relative variation of the RHEED intensity and the adsorbed Ga-layer.

This calibration was used to measure the Ga-coverage during c-GaN and AlGaN growth. Figure 1 shows the RHEED intensity measured after opening the N shutter with the Ga flux on. From the decrease of the RHEED intensity after opening the nitrogen shutter we were able to measure the Ga-coverage during growth with an accuracy of 0.1 ML. Stoichiometric growth of c-GaN was realized, when no drop in the RHEED intensity (dotted line) was observed after opening the N shutter, whereas c-GaN growth with 1 ML coverage was defined by a certain drop in the intensity (solid line).

The total Ga flux for GaN growth under one monolayer excess Ga conditions is given by:

$$F_{Ga,1ML}^{imp}(GaN) = F_{Ga,0ML}^{imp}(GaN) + F_{Ga}^{1ML,cov} = \frac{F_{Ga}^{inc}(GaN)}{s_{Ga}} + F_{Ga}^{1ML,cov} \qquad (2)$$

where $F_{Ga,1ML}^{imp}$ is the impinging Ga flux for Ga growth with 1 ML coverage, $F_{Ga,0ML}^{imp}$ is the corresponding flux for stoichiometric growth, $F_{Ga}^{1ML,cov}$ is the Ga flux necessary for the coverage of 1 ML, and F_{Ga}^{imc} is the incorporated Ga flux and s_{Ga} the sticking coefficient, respectively.

After the determination of the fluxes $F_{Ga,0ML}^{imp}$ and $F_{Ga}^{1ML,cov}$ by the experiment described above, the impinging Al and Ga fluxes for the growth of a c-Al$_x$Ga$_{1-x}$N alloy with 1 ML
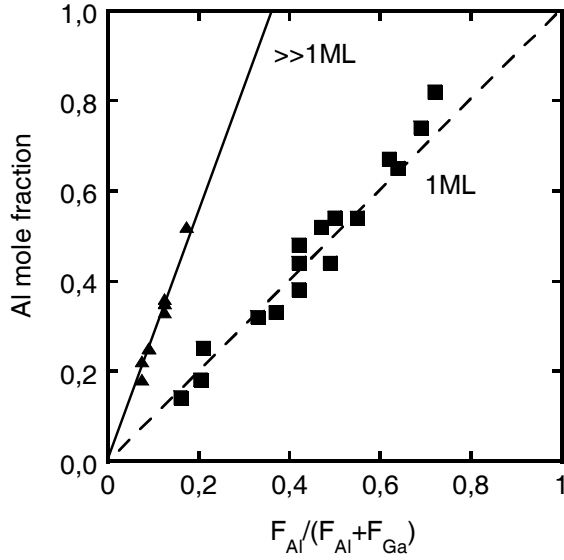
Fig. 3 *Relation between the Al mole fraction x of c-Al$_x$Ga$_{1-x}$N and the ratio of Al-flux to the total metal flux for films grown under 1ML and exceeding 1ML (>>1ML) Ga coverage. The mole fraction x was determined by HRXRD.*
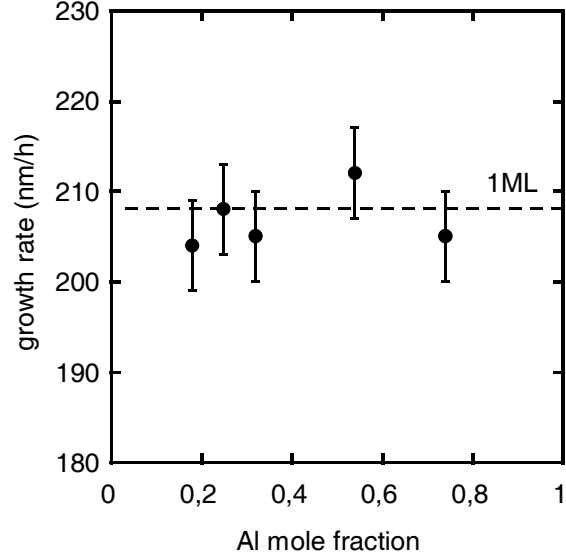
Fig. 4 *Growth rate of c- Al$_x$Ga$_{1-x}$N derived from the RHEED oscillation period and optical thickness measurements for x between 0 and 0.74. The layers were grown using a constant nitrogen flux of $F_N=2.2*10^{14}cm^{-2}s^{-1}$.*

coverage can be adjusted using the relations:

$$F_{Al}^{imp}(AlGaN) = \frac{x * F_{Ga}^{inc}(GaN)}{s_{Al}} \tag{3}$$

$$F_{Ga,1ML}^{imp}(AlGaN) = \frac{(1-x) * F_{Ga}^{inc}(GaN)}{s_{Ga}} + F_{Ga}^{1ML,cov} \tag{4}$$

Figure 2 shows the variation in the RHEED intensity during the initial growth of a c-Al$_{0.25}$Ga$_{0.75}$N layer. When the nitrogen shutter was opened with Ga on, an increase of the RHEED intensity was observed, indicating a GaN growth with a Ga-coverage of about 0.2 ML. When the Al shutter was opened the RHEED intensity dropped revealing a 1 ML metal coverage of the surface. Weakly damped RHEED oscillations were observed, indicating a two dimensional Al$_{0.25}$Ga$_{0.75}$N growth mode at substrate temperatures of 720 °C with a growth rate of 177 nm/h. Since the energy E^{AlN}=2.88 eV of Al-N bonds [9] exceeds that of Ga-N with E^{GaN}=2.24 eV [9], we suppose that the excess metal is gallium and all the Al atoms are incorporated in the growing layer

The relation between the ratio of the Al-flux over the total metal-flux versus the Al mole fraction x of the epilayer is depicted in Fig. 3. We find that x is proportional to the Al flux for the samples grown with 1 ML and more then 1ML Ga-coverage, respectively, indicating that indeed Al is preferentially incorporated. For the films deposited with 1 ML coverage a one to one relation between the flux ratio and the Al content was observed, whereas for the coverage exceeding 1 ML the slope was larger than 1 due to the larger total metal flux.

The growth rate of c-Al$_x$Ga$_{1-x}$N films was measured for a wide range of the Al mole fraction x. The data were summarized in Fig. 4. Within the experimental error the growth rate
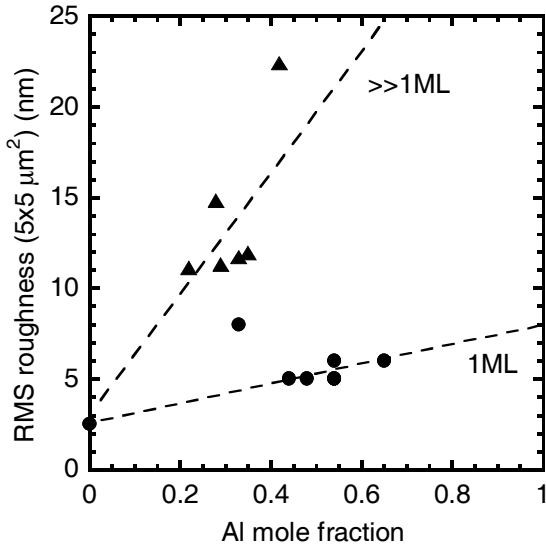
Fig. 5 *RMS surface roughness of different c-Al$_x$Ga$_{1-x}$N layers with an Al mole fraction between x=0 and x=0.74. Layers were grown under 1ML Ga- coverage (circles) and more than 1ML Ga-coverage(triangles).*

showed no variation for x between 0 and 0.74. This behaviour is in contrast to that of h and c-InGaN where the growth rate depends strongly on the In flux [10, 11].

The influence of the Al flux (i.e. the Al mole fraction) on the roughness of c-Al$_x$Ga$_{1-x}$N layers is depicted in Fig. 5. We find that the RMS-roughness measured on a 5x5 µm^2 area is about 5 nm and independent of the Al mole fraction when the films are grown under a Ga-coverage of 1 ML (circles). With increasing coverage (>>1 ML) a strong increase of the RMS roughness with the Al content was observed (squares). The values increased from 2.5 nm (GaN) to 22.5 nm (Al$_{0.44}$Ga$_{0.56}$N) most likely due to the formation of Ga droplets on the surface.

Room temperature CL spectra of c-Al$_x$Ga$_{1-x}$N films with Al mole fractions between 0.16 and 0.52 are plotted in Fig. 6. The spectra are normalized to one and shifted linearly for a better overview. We find a clear shift of the emission peak with increasing Al-content from 3.48 eV for a Al$_{0.16}$Ga$_{0.84}$N film to 4.12 eV for a Al$_{0.52}$Ga$_{0.48}$N layer. Emission from the underlying GaN buffer (dashed line) was not observed. The CL peak energy shift vs Al mole fraction x is shown in Fig. 7.
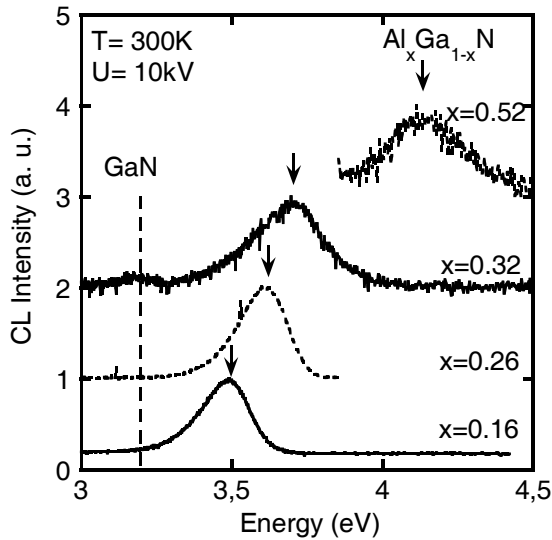

Fig. 6 *Room temperature CL spectra of c-Al$_x$Ga$_{1-x}$N layers with an Al mole fraction rangin from x=0.16 to x=0.52 indicated at the right side of the respective CL spectrum.*
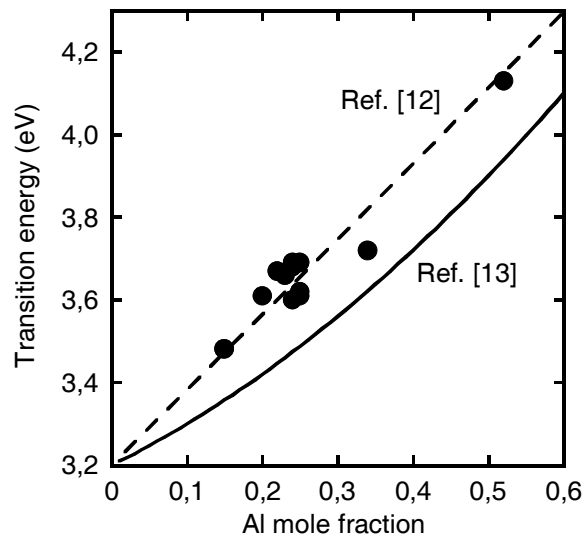

Fig. 7 *Room temperature CL peak energy of c-Al$_x$Ga$_{1-x}$N layers vs. Al mole fraction. The dashed curve shows data of from c-AlGaN (Ref. 12) the full curve are data from h-AlGaN (Ref.13).*

The CL peak energy E_{peak} increases linearly with increasing x $(0 \leq x \leq 0.52)$ yielding $E_{peak}=3.20+1.85x$ [eV] (dashed line) in agreement with the results from c-$Al_xGa_{1-x}N$ [12], in contrast to what has been observed by Koide et al. [13] (solid line) for h-$Al_xGa_{1-x}N$.

CONCLUSIONS

We have grown cubic-$Al_xGa_{1-x}N$ films $(0 \leq x \leq 0.74)$) on 3C-SiC substrates. We have employed measurements of the RHEED intensity to obtain well defined metal-rich growth conditions. The Al content of our layers was directly proportional to the Al flux while the roughness of the layers was strongly depending on the excess Ga-coverage during growth. Lowest values of the RMS roughness which was independent of the Al content x were obtained with a 1 ML coverage. Pronounced oscillations of the RHEED intensity which were observed after growth interruptions indicate predominant two-dimensional growth of our cubic $Al_xGa_{1-x}N$ films. Room temperature cathodoluminescence measurements revealed that the optical band gap of c-$Al_xGa_{1-x}N$ varies linearly with the Al mole fraction x up to x=0.52.

ACKNOWLEDGMENTS

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