

# Growth kinetics of GaN thin films grown by OMVPE using single source precursors

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## ABSTRACT

We report the growth kinetics of GaN thin films using the single source precursor bisazido dimethylaminopropyl gallium (BAZIGA) in a cold wall reactor. Transparent, smooth, epitaxial (FWHM of the  $\alpha$ -GaN 0002 rocking curve = 129.6 arcsec) and stoichiometric GaN films were grown on *c*-plane Al<sub>2</sub>O<sub>3</sub> substrates in the temperature range of 870 – 1320K and high growth rates were obtained (up to 4000 nm/hr). Film growth was studied as a function of substrate temperature as well as reactor pressure. Although high quality films were obtained without using any additional source of nitrogen such as ammonia, we have investigated the effect of ammonia on the growth and properties of the resulting films. The films obtained were characterized by XRD, RBS, XPS, AES, AFM, SEM and the room temperature PL spectroscopy of GaN films grown exhibited the correct near band edge luminescence at 3.45 eV.

## INTRODUCTION

The nitrides GaN, AlN, InN and their ternary alloy systems AlGaIn and InGaIn are very promising materials for applications in green/blue light-emitting diodes and semiconductor lasers<sup>[1]</sup>. The commercial growth of high quality epitaxial group-III nitrides by organometallic vapor phase epitaxy (OMVPE) is based on the co-pyrolysis of metal alkyls MR<sub>3</sub> (M = Al, Ga, In, R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, <sup>t</sup>Bu) and NH<sub>3</sub>. But high temperatures are involved in this process for the effective activation of NH<sub>3</sub> (>773K for InN<sup>[2]</sup>, >1173K for AlN and GaN<sup>[3]</sup>).

Many efforts have been undertaken to substitute the ineffective nitrogen source (NH<sub>3</sub>) using alternative precursors based on the concept of preformed direct M-N bonds in the precursor molecule. Such precursors for the growth at a lower V/III ratio and milder growth conditions were achieved with many compounds for instance hydrazine (N<sub>2</sub>H<sub>4</sub>), 1-1-dimethyl hydrazine (M<sub>2</sub>NNH<sub>2</sub>), phenyl hydrazine (PhNH-NH<sub>2</sub>), hydrazoic acid (HN<sub>3</sub>)<sup>[6-8]</sup> and also alkyl amines (RNH<sub>2</sub>, R = <sup>t</sup>Bu, <sup>i</sup>Pr)<sup>[9]</sup>. But the disadvantages of these precursors are their toxic and explosive nature as well as carbon incorporation into the resulting films. Besides these compounds, some group-III metal amido compounds such as [R<sub>2</sub>GaNH<sub>2</sub>]<sub>3</sub> (R = Et, Me) and [Ga(NR<sub>2</sub>)<sub>3</sub>]<sub>2</sub> (R = Et, Me) are interesting as single source precursors (SSP). However these precursors are only used with limited success in terms of the achieved film properties<sup>[10]</sup>. The azides such as [R<sub>2</sub>GaN<sub>3</sub>]<sub>x</sub> (R = Cl, H, Et, Me) are possible candidates as SSP and have been already used successfully to grow GaN<sup>[11]</sup>. The azide group combines a pre-formed strong Ga-N bond with a reduced number of undesired Ga-C and N-C bonds to minimize the carbon incorporation during film growth. But the disadvantage with these precursors are their air sensitivity and explosivity. To find an alternative to these problems we concentrated our research on the growth

of epitaxial GaN films using the novel Lewis-base stabilized organometallic azide compound of the type  $(N_3)_aM[(CH_2)_3NMe_2]_{3-a}$  ( $M = Al, Ga, In$  and  $a = 1, 2$ ). These SSP's are non-pyrophoric, non-explosive and yield epitaxial GaN films under moderate conditions. The successful growth of GaN and InN films was already reported earlier using a simple horizontal hot wall CVD reactor<sup>[12-14]</sup>. In this paper we report the study on the growth kinetics of GaN from the precursor  $(N_3)_2Ga[(CH_2)_3NMe_2]$  (bisazido dimethylaminopropyl gallium, BAZIGA) in a horizontal cold wall CVD reactor.

## EXPERIMENT

For GaN film deposition, a horizontal low pressure cold wall CVD reactor (base pressure:  $10^{-6}$  Torr) was fabricated (Fig. 1). It consists of a quartz tube about 50 cm in length and 2.5 cm in diameter. The substrates are placed on a SiC coated graphite susceptor at the center of the tube. For the substrate heating, an inductive heating arrangement was used monitored by a radiation pyrometer. During the heating process the outer wall of the central part of the quartz tube was cooled by water. Using this set up temperatures up to 1473K could be attained. Attached to the quartz tube are the precursor vaporizer heated by means of an air bath and a glass trap cooled with liquid nitrogen. To generate the necessary vacuum, a turbo-molecular pump backed up by a rotary pump was used. The reactor pressure during the CVD process was regulated using a motor driven throttle valve and mass flow controllers were used to control the flow of different gases. For GaN film deposition, epi-polished c-plane  $Al_2O_3$  substrates as large as 1 x 1 cm were used. Before loading it into the reactor, the substrates were degreased in trichloroethylene, etched in a mixture of  $H_2SO_4 / H_3PO_4$  (3:1) at 353K and rinsed with water and acetone. After the etching and cleaning process the substrates were pre-treated under vacuum for several hours (12 h) and subsequently annealed at 1323K with hydrogen (10 sccm) for 1 hour. Following this annealing, the substrates were nitridated with ammonia (40 sccm) at 1223K for 30 min. The vaporizer temperature was maintained at 353K for all depositions. Finally the vaporizer valve was opened to start the deposition which lasted normally for 45 min. High purity nitrogen (40 sccm) was used as a carrier gas to transport the precursor to the reaction zone. The deposition temperature was varied in the range of

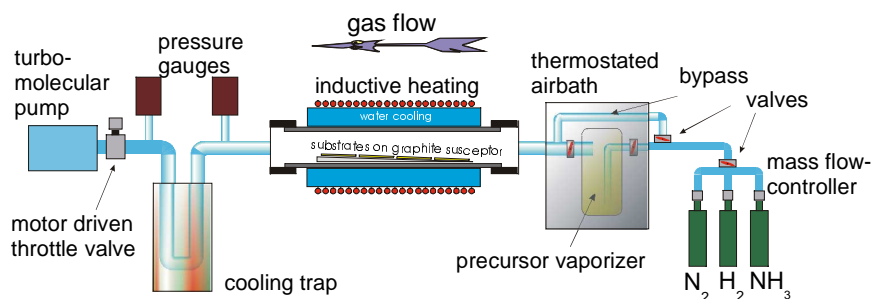


Fig. 1) Schematic of the cold wall CVD reactor

773 – 1323K, the reactor pressure between 0.080 – 100.0 mbar. To investigate the influence of ammonia as a reactive gas to the growth process, ammonia flow rates were varied at different temperatures and pressures. The crystalline properties of the obtained films were investigated in detail by x-ray diffraction studies using a D8-Advance Bruker ax diffractometer and a high resolution D8-Discover Bruker ax diffractometer. The  $2\Theta$ - $\Theta$  scans, rocking curves, pole figures, reciprocal space mappings and reflectometry measurements were carried out. The film composition was determined by Rutherford Back Scattering (RBS) using the instrument of DTL (Dynamitron Tandem Laboratory), X-ray Photoelectron Spectroscopy (XPS) as well as Auger Electron Spectroscopy (AES) using the equipment from FISIONS. The optical properties were studied by room temperature Photoluminescence (PL). The surface morphology was investigated with Atomic Force Microscopy (AFM) using a Nanoscope Multimode III scanning probe microscope (Digital Instruments) and Scanning Electron Microscopy (SEM) using an equipment from LEO. The film thickness was analyzed by AFM, using a TOPOMETRIX microscope.

## RESULTS AND DISCUSSION

The primary goal was to grow epitaxial GaN films using BAZIGA with  $N_2$  as inert carrier gas but without any additional nitrogen source such as ammonia. In fact this was achieved successfully. The films were grown without any buffer layers except that the substrates were nitridated with ammonia. It was found that at temperatures below 973K the films were predominantly amorphous. X-ray diffractograms showed a broad 0002  $\alpha$ -GaN reflection with low intensity. At higher temperatures crystalline  $\alpha$ -GaN was found with a sharp 0002  $\alpha$ -GaN reflection and high intensity. It was also found that the crystal quality and the signal intensity was clearly improved with increasing pressure due to the decreasing growth rate. At low reactor pressures (0.080 mbar) growth rates of the order of 4500 nm/hr were obtained whereas higher reactor pressures (8.000 mbar) resulted in growth rates of the order of 2000 nm/hr. Besides the reactor pressure, the growth rate

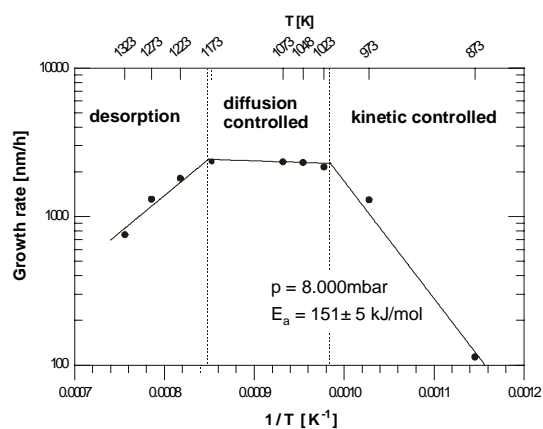


Fig. 2) Arrhenius-plot at 8.000 mbar without  $NH_3$

strongly depends on the substrate temperature because of surface reactions and altered reaction pathways. From the Arrhenius-plot (Fig. 2) the temperature dependence of the growth rate can be clearly seen. The growth rate at lower temperatures indicates a thermally activated deposition kinetics. To determinate the activation energy ( $E_a$ ) for the linear portion of the curve in the kinetic controlled part at lower temperatures, the Arrhenius equation  $G = A \cdot \exp(-E_a/RT)$

was used, where  $G$  is the growth rate,  $A$  is the Arrhenius pre-exponential factor,  $R$  is the gas constant and  $E_a$  the activation energy that is the rate limiting process under the given conditions. For all depositions a reactor pressure of 8.000 mbar was adjusted. It was found that in the temperature range of 870 – 1020K the GaN film growth is associated with an activation energy of  $151 \pm 5$  kJ/mol. The maximum growth rate of 2500 nm/h was obtained in the temperature range of 1020 – 1175K. In this range, the growth rate shows nearly no temperature dependence that means the growth is only controlled by the diffusion of the precursor molecule fragments to the substrate surface. At temperatures over 1175K the growth rate decreases because of desorption and depletion processes consistent with the typical behavior of a CVD process. To investigate the influence of ammonia as a reactive gas to the growth kinetics, an Arrhenius-plot under the same conditions (8.000 mbar reactor pressure and 363K vaporizer temperature) but with additional  $\text{NH}_3$  (40 sccm) was carried out. Under these conditions some differences were observed and it was found that the slope of the kinetically controlled regime is lowered by more than half yielding an activation energy of  $E_a = 65 \pm 5$  kJ/mol. A temperature range of 870–1060K for the kinetically controlled regime was obtained. Thereby the kinetically controlled regime is extended to higher temperatures than in the previous case where no  $\text{NH}_3$  was used. The growth rate was also reduced and the highest growth rate of the order of 1000 nm/h was obtained in the range of 1060 – 1175K. The growth rate drops off again at temperatures greater than 1175K. In addition to the reduction in  $E_a$  and growth rates, the crystalline quality of the resulting films were poorer when compared to those obtained without  $\text{NH}_3$  under similar CVD conditions. To study the effect of  $\text{NH}_3$  on the crystalline quality, several  $\alpha$ -GaN films were deposited at a reactor pressure of 8.000 mbar and a substrate temperature of 1073K with increasing ammonia flow. The film properties were determined with x-ray diffraction (XRD) and it was found that the obtained films were epitaxial due to the fact that the diffractograms showed only the 0002 reflection and also confirmed from their pole figure measurements (Fig. 4). To investigate the crystalline quality, rocking curves of the 0002  $\alpha$ -GaN reflection have been carried out. Fig. 3 shows the variation of FWHM (as determined by x-ray rocking curves) of the epitaxial  $\alpha$ -GaN films with increasing ammonia flow rates. It is to be noted that the FWHM of the 0002 GaN rocking curves strongly depends on the flow rate of  $\text{NH}_3$ . With

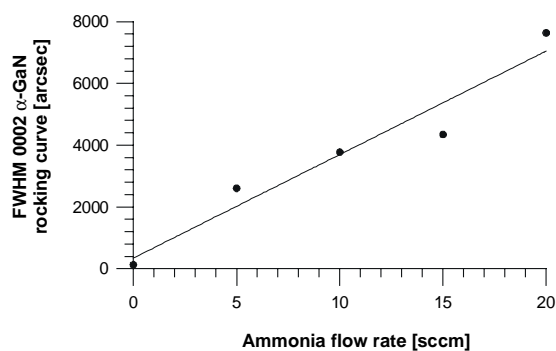


Fig. 3) Variation of FWHM with  $\text{NH}_3$  flow rates

increasing  $\text{NH}_3$  flow, the FWHM increases. Without ammonia a FWHM of 129.6 arcsec was achieved. This is to our knowledge the best ever reported value for the epitaxial films obtained from single source precursors without any additional source for nitrogen. As illustrated in Fig. 3, with increasing ammonia flow rates, the crystal quality becomes poorer. The pole figure measurement (Fig. 4) was

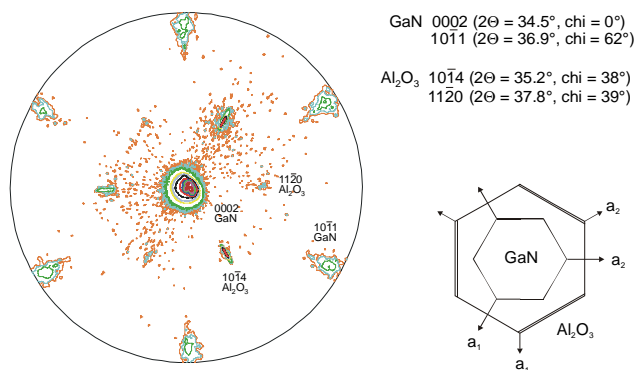


Fig. 4) Pole figure measurement and orientation of a  $\alpha$ -GaN film

setup with a fixed  $2\theta$  value of  $34.5^\circ$  and  $\omega = 17.25^\circ$  and  $\psi = 0 - 65^\circ$ ,  $\phi = 0 - 360^\circ$ . The 2-dimensional plot shows both the reflections from  $\alpha$ -GaN (0002) and (10 $\bar{1}1$ ) and from the Al<sub>2</sub>O<sub>3</sub> substrate (10 $\bar{1}4$ ) and (11 $\bar{2}0$ ) at different  $\psi$  and  $\phi$  angles. From these reflections the orientation of

the  $\alpha$ -GaN layer relative to the sapphire substrate could be determined as  $30^\circ$ . By means of these pole figure measurements as well as  $2\theta$ - $\theta$  scans and reciprocal space mappings the hexagonal symmetry of the produced GaN films was confirmed.

To investigate the role of substrate nitridation, two amorphous low temperature films (grown at 773K and 8.000 mbar) were characterized by x-ray reflectometry. It was seen that during the nitridation of the bare Al<sub>2</sub>O<sub>3</sub> substrates with NH<sub>3</sub> for 30 min, a thin layer of AlN (0.5 nm) was formed and this was verified by XPS measurements. The absence of the AlN layer on a non-nitridated Al<sub>2</sub>O<sub>3</sub> substrate was also verified by XPS. The density of the grown  $\alpha$ -GaN layer was found to be significantly lower ( $4.42 \text{ g/cm}^3$ ) than crystalline bulk  $\alpha$ -GaN ( $6.1 \text{ g/cm}^3$ ). This could be caused by incorporation of residual precursor fragments as well as structural defects. The roughness of the GaN layer was determined as  $\sim 1 \text{ nm}$  from reflectometry. This was also confirmed by AFM measurements. Crystalline high temperature films could not be characterized by x-ray reflectometry because of their higher surface roughness. The film composition was checked with RBS and XPS including nitrogen, gallium, carbon and oxygen to determine the Ga-N stoichiometry as well as the level of impurity. The RBS analysis revealed stoichiometric GaN in a "chemical sense" with a ratio of Ga and N of 1:1 without any additional oxygen. To determine possible impurities the films were analyzed by XPS. It was found that GaN films, grown at 973K, contained very small traces of carbon when grown without using ammonia and this can be accounted due to the fragmentation of the precursor leading to carbon incorporation. Whereas in GaN films grown at 1173K at 8.000 mbar reactor pressure and 363K vaporizer temperature with 20 sccm NH<sub>3</sub>, carbon was absent (Fig. 5). It was found that very small amounts of ammonia were necessary to grow GaN films free of carbon.

## CONCLUSIONS

It was demonstrated that it is possible to grow GaN films using BAZIGA as a single source precursor without any additional nitrogen source such as NH<sub>3</sub> with a high structural quality which is reasonable close to the materials grown with the standard process

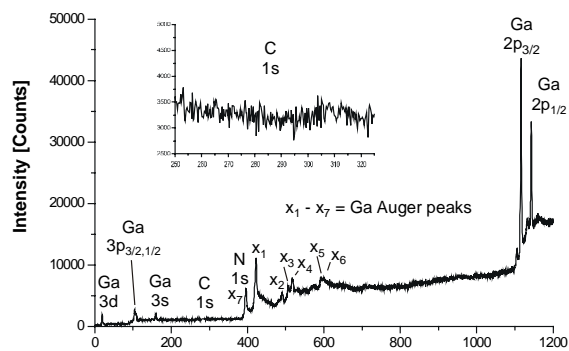


Fig. 5) XPS spektrum of a GaN film

low flow rates of  $\text{NH}_3$  (2-5 sccm) during deposition, the carbon incorporation was eliminated, but with increasing  $\text{NH}_3$  flow rates (up to 20 sccm) the crystalline quality decreased drastically.

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and exhibiting the characteristic band edge luminescence of 3.45 eV. The use of  $\text{NH}_3$  during the deposition has an important influence to the resulting film properties. It was found that the best crystalline  $\alpha$ -GaN films were achieved at higher reactor pressures (above 10 mbar) without using any  $\text{NH}_3$ . In this case very small traces of carbon could be found by XPS. Moreover using very