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The growth rate evolution versus substrate temperature and V/III ratio during GaN MBE using ammonia

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The growth rate evolution versus V/III ratio and substrate temperature was studied by means of optical reflectivity during MBE of GaN layers using NH_3 as nitrogen source. The GaN desorption becomes observable at temperatures above 800°C and causes the reduction of growth rate accompanied with the surface roughening at temperatures above 850-870°C. Unlike GaAs, which evaporates in accordance with the action mass law, the desorption rate of GaN is found to be almost independent of V/III ratio within the N-rich growth conditions. The activation energy for GaN desorption during the growth is found to be (3.2±0.1) eV. This value is very close to the activation energy for free evaporation. At V/III ratio values exceeding 200 the GaN growth rate reduction caused by violation of the molecular flow regime is observed. The Mg-doped samples grown under these extreme conditions tend to have improved acceptor activation and thus p-type conductivity.

1 Introduction

The group III nitrides are the subject of permanent interest during last decade due to their outstanding properties for optoelectronics. The current progress in this field is based on development of heterostructure growth techniques such as MOCVD [1] [2] and MBE [2] [3] [4]. The latter, however, remains rather sophisticated in literature due to a number of difficulties concerning the problem of proper active nitrogen sources, lower deposition temperatures, doping limitations etc.. The concept of deposition at higher V/III ratios, recently developed for an ammonia based process [5], seems to be very promising with respect to improvement of GaN structural and electrical properties. It is believed that both V/III ratio and deposition temperature (T_s) are the key kinetic parameters to obtaining nitride layers of proper quality by MBE. Dependencies of the growth rate on these parameters are also very important in determining the upper temperature limit for MBE growth, since GaN thermally decomposes in high vacuum at lower temperatures than in most MOCVD systems. Held *et.al.* [3] have proposed the idea that GaN desorption under growth conditions should obey the action mass law, but there were no experimental data concerning that point. Grandjean *et.al.* [6] have recently reported experimental data indicating that GaN evaporation under NH_3 flux deviates from the thermodynamic behavior, but experiments under growth conditions were not carried out in this work.

Here we report on results of the study of GaN growth kinetics by MBE using NH_3 cracking. The desorption rate of GaN during the growth was *in situ* measured by the optical reflectivity as function of substrate temperature and V/III ratio, and then compared with the free evaporation rate. Growth rate evolution under extremely high NH_3 flux was studied at intermediate temperatures.

2 Experimental

The growth of GaN layers was carried out in ATC-EPN2 system specially designed for nitride epitaxy. Standard effusion cells were used as group III and dopants elemental sources while a flow of purified ammonia served as the nitrogen source. The main novel solution is the system used to allow variation of the V/III ratio over the wide range. The common situation is that hydrogen originating from ammonia cracking on heated surfaces is poorly pumped by the turbomolecular pums usually used in MBE systems. It causes the NH_3 flow rate to be limited by the total pressure in the system. To eliminate this factor the sample heater unit is water cooled so that the NH_3 cracking takes place practically at the substrate

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only. Furthermore, reinforced pumping system and the specific arrangement of the ammonia inlet have made it possible to reach V/III ratios up to 1000 while keeping GaN growth rate of 1 µm/h under a total pressure of 10^{-3} Pa .

Sapphire (0001) wafers with Mo-metallized backside were used as substrates and placed on In-free holders. The substrate temperature wes measured by both pyrometer and thermocouple, calibrated in a separate experiments by additional thermocouple mounted on the surface of a test GaN sample (accuracy of calibration was not worse than ±10°C). Thermocouple readings were primarily used for the temperature determination, while a pyrometer was employed to control the transient processes. The absolute values of the incident fluxes were calibrated using a Bayard-Alpert gauge equipped by the shield with an aperture corresponding to the sample diameter and placed at the sample position. Growth rate and surface roughness were monitored *in situ* by optical reflectivity using a 633nm He-Ne laser in a manner similar to Grandjean *et. al.* [4] [5] [6].

Sapphire substrates were annealed in high vacuum and nitridated in ammonia flow at ≈950°C. Then a GaN 25nm buffer layer was deposited at ≈490°C and annealed under NH_3 flux at ≈900°C. The following growth of GaN layers was carried out at T_s and V/III ratio varied in ranges 750-930°C and 10-800, respectively. Typical values of the growth rate at moderate substrate temperatures were 1.2-1.6 µm/h (for the growth rate 1.2µm/h and V/III ratio=100; absolute values of Ga and NH_3 fluxes are about $1.5\cdot10^{15}\,cm^{-2}\cdot s^{-1}$ and $1.5\cdot10^{17}\,cm^{-2}\cdot s^{-1}$, respectively).

Experiments on GaAs growth were carried out in ATC-EP3 system, conventionally designed for arsenide MBE. A 0.5µm GaAs buffer layer was grown on GaAs (001) substrate at 600°C. Ga flux was calibrated at this temperature and kept at 1ML/s. Growth rate was measured *in situ* by a RHEED oscillation registration system based on a CCD-camera and appropriate hardware and software. Substrate temperature was carefully controlled by thermocouple and pyrometer readings. It was further calibrated by both GaAs (001) native oxide removal point (580°C) and by AlAs surface phase diagram [7]. GaAs desorption rates were measured under incident arsenic flux varied in the range 1.5-5 ML/s at substrate temperatures 630-750°C. To increase accuracy of results all the measurements were made within the same epitaxy process.

3 Results and discussion

The V/III ratio is one of the most important growth conditions in MBE of $A^{III}B^{V}$ compounds. In the particular case of nitride epitaxy using NH_3 this value, determined from the incident fluxes F_{NH_3}/F_{Ga}, must be distinguished from so-called "effective" ratio due to the low efficiency $\alpha^0_{NH_3}$ of ammonia cracking. The $\alpha^0_{NH_3}$ can be easily determined from the experimental dependence of the growth rate on F_{NH_3}/F_{Ga}. The plot of GaN growth rate (v_g) versus V/III ratio at moderate substrate temperatures (<850°C) is shown in Figure 1. The vertical grid labeled "I" marks well-known transition between Ga-rich and N-rich growth regimes ($F_{Ga} \approx \alpha^0_{NH_3} \cdot F_{NH_3}$) [3] [5]. It's easy to see that $\alpha^0_{NH_3}$ ≈0.05 in our experiments, what agrees well with results of Held *et. al.* [3]. The region of higher V/III ratios is less reported in literature. One can see that on the right from the grid labeled "II", the growth rate essentially decreases despite the strong N-rich conditions. Obviously, the upper limit of V/III ratio reachable in MBE is limited by the molecular flow regime. In our growth chamber geometry the NH_3 beam equivalent pressure near the substrate is about 10^{-1}-10^{-2} Pa in the region near grid "II" on Figure 1 (while the total pressure in chamber is about 10^{-3}Pa), and the free path length for Ga atoms is as low as a few centimeters. So Figure 1 shows that the molecular flow regime can be extended up to V/III ratios as high as 200 without remarkable v_g reduction in our experiments.

It should be noted that growth at V/III ratios exceeding 200 is still possible and just requires increased effusion cell fluxes to compensate their dissipation by the NH_3 flow. It was found that Mg-doped samples grown under these extreme conditions tended to have improved acceptor activation. Hole concentrations in GaN:Mg layers grown at substrate temperatures 800-850°C and V/III ratios 50-100 were usually about $(1\text{-}3)\cdot10^{17}cm^{-3}$, while values $(3\text{-}7)\cdot10^{17}cm^{-3}$ were obtained under V/III≈500 and growth rate kept at 1.0-1.2 µm/h. At present we study this quite important effect and hope to report results in near future.

The growth temperature (T_s) is known to be next critical parameter in respect of crystal quality and surface roughness. Due to MBE environment a remarkable desorption of GaN takes place at substrate temperatures sufficiently lower (≥800°C) as compared to the MOCVD. The growth rate of GaN as well as surface roughness depending on the T_s can be clearly monitored by optical reflectivity (Figure 2). At T_s>850-870°C the fading of average reflected intensity is observed accompanied with the growth rate reduction (Figure 3), most

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probably due to GaN desorption appearance. In this case the desorption rate (v_d) is the difference between the initial (v_g^0) and reduced (v_g^r) values of the observable growth rate:

$$v_d = v_g^0 - v_g^r$$

The main peculiarity observed is that the desorption rate shows no remarkable dependence on the V/III ratio in a rather wide range (Figure 3), i.e. within the region between grids “I” and “II” on Figure 1. If the action mass law were correct for GaN desorption, a four-fold increase of the V/III ratio would cause sufficient changes (more than 30%) in the Ga desorption rate. In contrast, we have not observed any changes within the experimental error.

To clarify this point, a direct comparison with other $A^{III}B^V$ compounds is needed. GaAs is the well-known case for applying a thermodynamic approach to successful simulation of surface processes under an MBE environment [8] [9] [10]. It was shown that both the action mass law and exact mass balance equations are correct on GaAs surface at high temperatures [11]. One can also find some experimental data on GaAs desorption rate versus substrate temperature in the literature [12] [13]. In this work we have carefully measured the GaAs growth rate versus substrate temperature under different incident arsenic fluxes in a manner mentioned above. To our best knowledge, this kind of measurements was carried out for the first time. Results presented in Figure 4 clearly show that even doubling of V/III ratio sufficiently reduces GaAs desorption rate. Data calculated in a manner similar to [11] are also presented as solid lines on Figure 4 and confirm a good correlation with the action mass law.

The direct comparison with GaAs shows that the GaN desorption strongly deviates from the thermodynamic behavior. On the other hand, measurements of GaN evaporation rates at different temperatures and calculations made in terms of kinetic model [6] shows the remarkable effect of ammonia flux on v_d in the region of lower F_{NH_3}, i.e. close to free evaporation conditions. In this respect, to compare carefully our data with previously published ones, we have studied free evaporation of GaN layers by optical reflectivity. We have observed reflectivity oscillations (Figure 5) indicating the smoothness of the initial layer and the layer-by-layer evaporation mode. The GaN free evaporation rates as well as desorption rates evaluated from Figure 3 are summarized in Figure 6 and Figure 7. The well-known data obtained by Munir and Searcy [14] and confirmed by Held *et.al.* [3] are also plotted on Figure 6 as solid line. One can see that

a) GaN free evaporation data is well correlated with the solid line (the activation energy is about 3.25eV);

b) the activation energy for GaN desorption (3.2±0.1 eV) is almost the same as for free evaporation;

c) GaN desorption rate is lower than the free evaporation rate but remains almost independent on V/III ratio within the N-rich growth regime.

On Figure 7 our data extracted from Figure 6 for the substrate temperature (875±5)°C are compared with data of Grandjean *et. al.* [6]. One can see that in both cases the GaN free evaporation rate is higher than the GaN desorption rate under NH_3 flux. On the other hand, there is a remarkable quantitative discrepancy between our data obtained during the growth and the data obtained during GaN evaporation under NH_3 flux [6]. This discrepancy concerns both the average level of desorption rate and the slope of experimental plots.

Grandjean *et.al.* [6] in their paper discussed the data slope in detail. They asserted that the experimental desorption rate dependence on the NH_3 flux (except its smallest values) is weaker than expected from theoretical estimations. Further, experimental data fitting by the kinetic model was reached assuming that the nitrogen atoms accumulated in the adsorption layer block the available adsorption sites [6]. In this case, further increase of NH_3 incident flux becomes less efficient, because the blocking adsorption site mechanism prevents NH_3 cracking.

We guess that our data don’t correlate with such a model, because the blocking adsorption site mechanism could be realized without GaN growth rather than during the growth, when the growing surface is permanently renewed. But then the desorption rate should be much more dependent on the NH_3 flux (i.e. the slope of experimental data on Figure 7 should be greater) during the growth, while we haven’t observe any remarkable slope at all.

4 Summary

In summary, we have studied by optical reflectivity measurements the kinetics of GaN free evaporation and desorption during the MBE growth over wide ranges of substrate temperatures and V/III ratio. Free evaporation rates agree well with the data observed by other authors. GaN desorption rate during the growth is found to be lower than free evaporation rate, but unlike GaAs, it shows no remarkable dependence on V/III ratio under N-rich conditions. As compared with GaN evaporation

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under NH_3 flux [6], our results obtained during the growth show qualitative agreement, but essential quantitative discrepancy. The activation energies for GaN free evaporation as well as for desorption during the growth, are found to be almost the same - (3.2±0.1) eV. At V/III ratio values exceeding 200 the GaN growth rate reduction caused by violation of molecular flow regime is observed. The Mg-doped samples grown under these extreme conditions tended to have improved acceptor activation and thus p-type conductivity.

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FIGURES

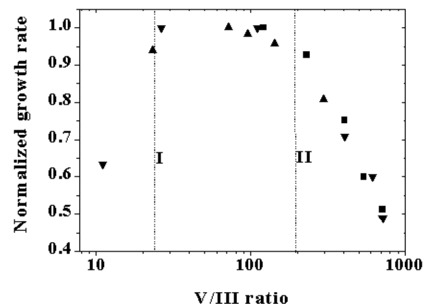

Figure 1. GaN growth rate versus V/III ratio at substrate temperature 830°C. The different symbols shows data for different samples at similar conditions. **I**- the Ga-rich / N-rich transition; **II**- the molecular flow regime limitation

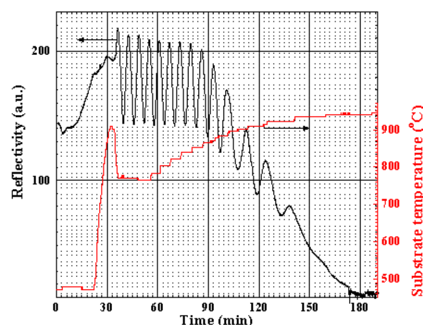

Figure 2. Reflectivity oscillation during GaN growth at different substrate temperatures

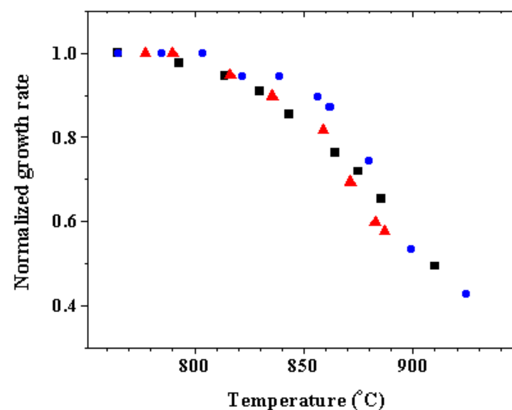

Figure 3. GaN growth rate versus substrate temperature. V/III ratio: blue sircles -40; black squares - 95; red triangles - 165

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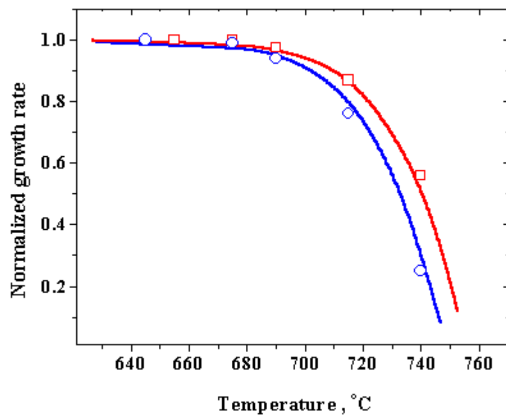

Figure 4. GaAs (001) growth rate versus substrate temperature. V/III ratio: blue circles - 2, red squares - 4.

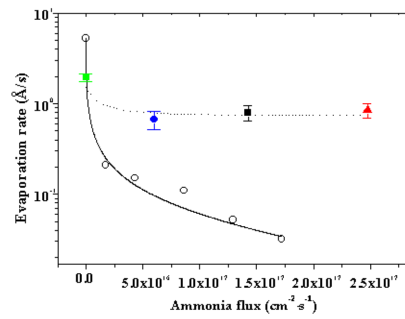

Figure 7. GaN evaporation rate versus ammonia flux at substrate temperature (875±5)°C. Our experimental points are marked by the same symbols as on Figure 6, dotted line is guided for eye. Open circles and solid line represent experimental and calculated data [6], respectively.

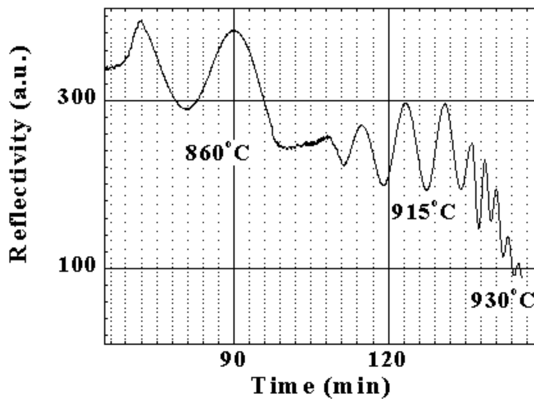

Figure 5. Reflectivity oscillations during GaN free evaporation in vacuum

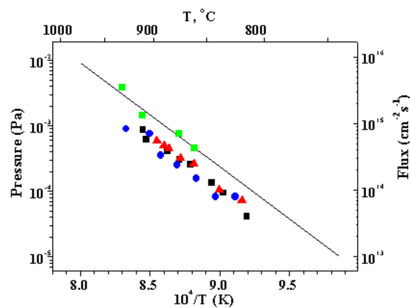

Figure 6. GaN free evaporation rate and desorption rate during the MBE growth. Green squares - free evaporation; solid line represents data of Munir and Searcy [14]; desorption rate under V/III ratio: blue sircles -40; black squares - 95; red triangles - 165.

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