Investigations on the Growth of AlN Heterostructures for UV Emitting Devices

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We report on the metalorganic vapor phase epitaxial (MOVPE) growth of AlN films on sapphire substrates. The effect of precursor flow rate and nucleation layer (NL) on the film quality was investigated. The films were characterized using AFM, XRD and PL. We could realize AlN films with very smooth surfaces and narrow symmetric XRD peaks indicating low screw/mixed type dislocation densities in the films. Moreover, PL spectra showed a very strong luminescence, confirming high crystalline quality of the optimized AlN films.

1. Introduction

AlGaN as a wide band gap semiconductor material has found increasing scientific and practical interest in the last few years. This is, in large part, due to its use in UV light emitting diodes (LEDs) as well as laser diodes (LDs). A common method in realizing high quality AlGaN epilayers with high Al content is to grow on AlN epilayers—serving as a template. The AlN templates are transparent for UV-LEDs based on $Al_xGa_{1-x}N$. The goal in this work is to realize high quality AlN films—suitable for AlGaN-based UV-B and UV-C LEDs—using metalorganic vapor phase epitaxy (MOVPE).

All samples investigated in this study were grown on (0001) sapphire substrates in a low pressure horizontal reactor (Aixtron AIX-200/4 RF-S). Trimethylaluminum (TMAl) was used as group-III precursor and ammonia as group-V precursor. Moreover, the investigated films have been grown by using a TaC coated graphite susceptor. This so called *high temperature setup* is capable of reaching temperatures up to about 1400 °C in our MOVPE reactor whereas the conventional *low temperature setup*—SiC coated graphite susceptor—can reach temperatures up to about about 1200 °C.

The growth of high quality AlN is much more challenging compared to GaN. Al has a higher sticking coefficient than Ga and the parasitic pre-reactions of the precursors are stronger in the case of MOVPE of AlN. Hence, these issues result in higher dislocation densities and poorer surface properties in AlN epilayers compared to the case MOVPE of GaN, causing deficiency of emitting devices grown on top of such templates. In this work we have investigated the effect of the TMAl flow rate and NL layer deposition temperature on the AlN epilayer properties.

2. Variation of TMAl Flow Rate

A lower growth rate may result in films with higher crystal qualities. At very high growth rates, there is not enough time for ad-atoms to make a complete AlN monolayer before the next atomic layer starts to grow on top. Conversely, at sufficiently low growth rates, there is an increase of capture time of ad-atoms to find suitable points to reside within the crystal structure. According to the work of Xie et al. [1], a strong improvement of crystal quality was achieved by reducing the TMAl flow rate. Therefore, we investigated the effect of the TMAl flow rate on the growth properties of our AlN films.

Table 1: The notable growth characteristics of AlN epilayers grown with different TMAl flow rates. TMAl molar flow rates here correspond to 25, 13 and 7 sccm gas flow from a bubbler kept at 17 °C. NH_3 molar flow corresponds to 240 sccm gas flow. The last column indicates the ratio between defect luminescence and NBE luminescence.

Sample	TMAl (µmole/min)	NH_3 (mmole/min)	$T_{proces.}$ (°C)	Thickness (nm)	Def. lum./NBE lum.
T1191AbH	3	10.7	1200	500	41
T1190AbH	5	″	″	″	18.3
T1166AbH	10	″	″	″	18.5

Table 2: Low temperature AlN:O nucleation layer conditions for investigations of AlN epilayers growth. For oxygen doping a mixture of oxygen and nitrogen was used. The carrier gas was hydrogen.

$T_{proces.}$ (°C)	Pressure (hPa)	TMAl (µmole/min)	NH_3 (mmole/min)	$N_{99.7}O_{0.3}$ (sccm)	Thickness (nm)
805	80	2.35	5.6	10	15

Three AlN samples have been grown at a process temperature[2] of 1200 °C with a film thickness of about 500 nm (see Table 1). The reactor pressure during the growth of these AlN epilayers was chosen to be 35 hPa which is much lower than the typical reactor pressures applied to the growth of GaN films. Lower reactor pressures mean faster gas flows and hence less time for undesired parasitic reactions in the gas phase above the substrate. These AlN films (500 nm thick) have been grown on an oxygen doped AlN nucleation layer (NL) (Table 2). The growth of AlGaN on such a NL results in high quality AlGaN films [2], and therefore it may be also suitable for the growth of high quality AlN films as well. The deposition temperature of such nucleation layers was lower than that of the sequential AlN films in order to accommodate the large lattice mismatch between the sapphire and AlN film.

According to the XRD investigations, although the (002) reflections of this series of samples were very narrow—with an FWHM below 50 arcsec—the asymmetric (102) reflections

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[2] $T_{proc.}$ denotes the process temperature which is the temperature measured from the back side of the rotation tray by using a pyrometry system. In other word, this does not indicate the true temperature on top side of the susceptor or wafer surface ($T_{surf.}$).

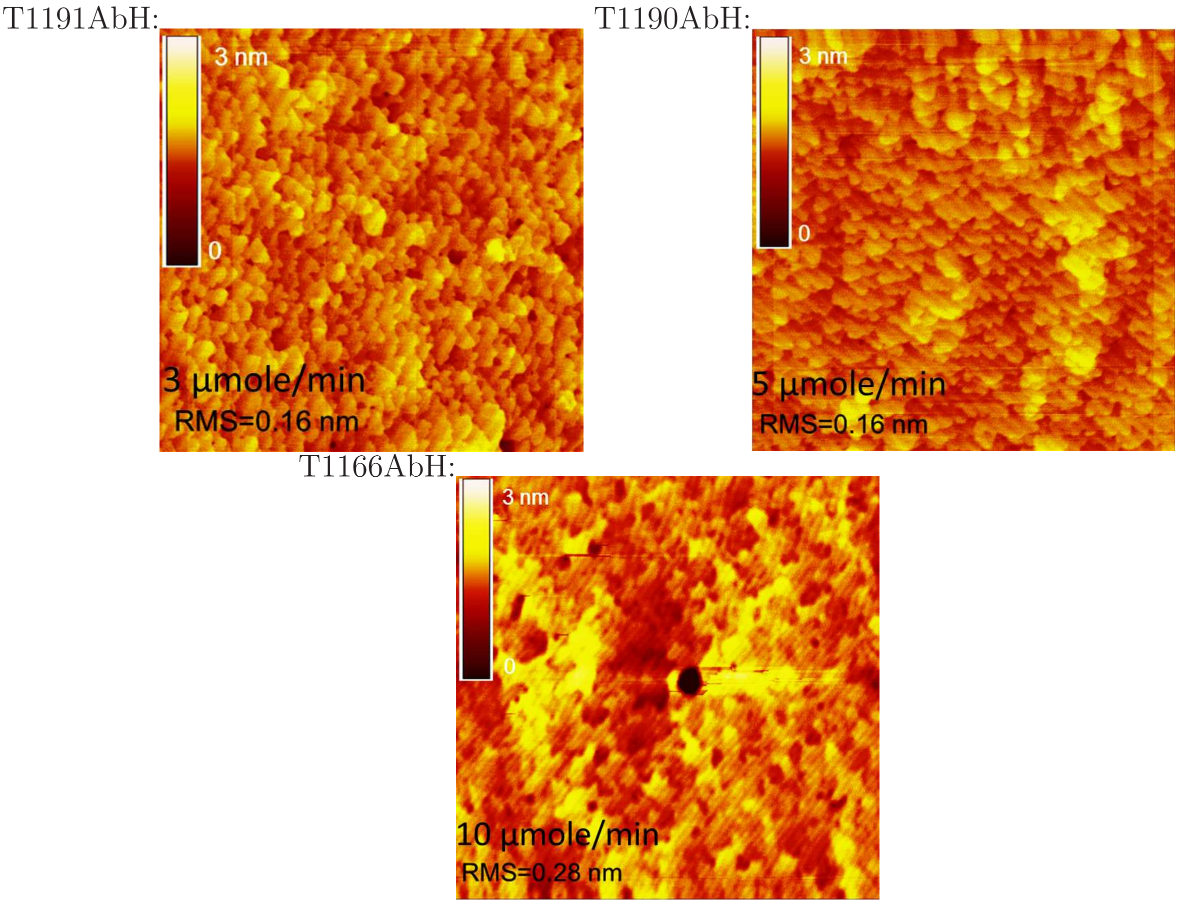

Fig. 1: $2 \times 2\,\mu m^2$ AFM investigations on the samples shown in Table 1 with different TMAl flow rates.

were very broad—approximately 5000 arcsec. Moreover, an intense defect related blue luminescence was visible in all samples. The sample grown with the lowest TMAl flow rate was the worst sample in this respect. The surface properties were visibly improved in the samples grown with reduced TMAl flow (T1190AbH) in which both big and small surface pits fairly disappeared (Fig. 1). In the sample with the lowest TMAl flow (T1191AbH), however, the small surface pits appeared again. The growth rate of these films show a linearly increasing trend with the increase of the TMAl flow rate as expected (see Fig. 2). Nevertheless, the growth rate is well below the predicted mass transport line which can be attributed to material loss due to gas phase pre-reactions on the heated susceptor during the growth process.

In summary, we could realize high quality AlN films based on an oxygen doped AlN nucleation layer. These AlN films have very smooth and (almost) pit-free surfaces in addition to very low level of mixed/screw type dislocations. Nonetheless, more optimization steps are necessary to reduce effectively the high level of twist and other types of crystal imperfections in our AlN films. For this purpose, we have optimized the nucleation layer deposition temperature as described in the next section.

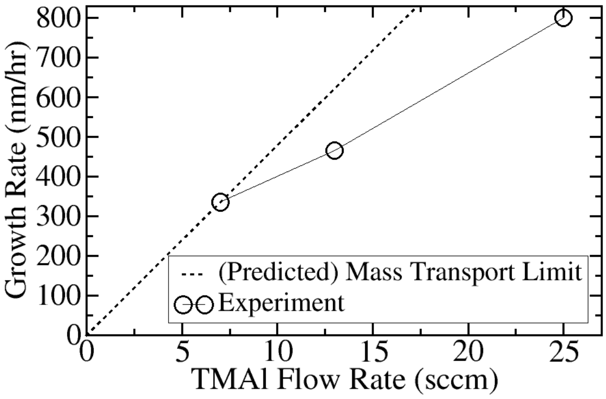

Fig. 2: Growth rate of the samples with different TMAl flow rates (Table 1).

3. Importance of the Nucleation Layer in AlN Epi-Films

It is expected that the nucleation layer (NL) plays an important role in reducing—or introducing—crystal imperfections in the epitaxial films as also observed by many groups in III-V nitrides, see e.g. [4–7]. As mentioned earlier, our NL is a thin AlN layer doped with oxygen. In this section, we tried to optimize the NL growth conditions starting from the NL deposition conditions for our high quality GaN films [3] as presented in Table 3 in order to grow AlN films. We investigated mainly the deposition temperature of the NL on the quality of AlN films. The nucleation layer deposition temperature ($T_{\text{surf.}}$) was varied between 825 and 890 °C (Table 3)[3]. About 500 nm thick AlN was grown with TMAl and ammonia molar flow rates (gas flow rates) of 10 µmole/min (25 sccm) and 10.7 mmole/min (240 sccm), respectively. The process temperature for growth of the AlN film was set to 1200 °C.

Table 3: Low temperature AlN:O nucleation layer conditions optimized for our high quality GaN to be adopted for AlN films. For oxygen doping a mixture of oxygen and nitrogen was injected into the reactor.

Pressure (hPa)	TMAl (µmole/min)	NH_3 (mmole/min)	$N_{99.7}O_{0.3}$ (sccm)	Thickness (nm)
80	4.7	11.2	10	25

We compare five samples having about 500 nm thick AlN grown on the NL as listed in Table 4. Moreover, Table 4 presents the FWHMs of the (002) and (102) reflections which were used to estimate the dislocation densities based on XRD investigations in our AlN films, as depicted in Fig. 4.

Generally, the investigated samples in this section exhibit a reduced defect luminescence to

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[3] Surprisingly, despite the process temperature for both samples T1374AHa and T1249AHa was set to be 845 °C, the difference in wafer surface temperatures was 40 °C. Considering that sample T1374AHa has been grown two months after the other sample, this shows the importance of *in-situ* true surface temperature measurements in MOVPE reactors to assure the repeatability/reproducibility of the grown epilayers.

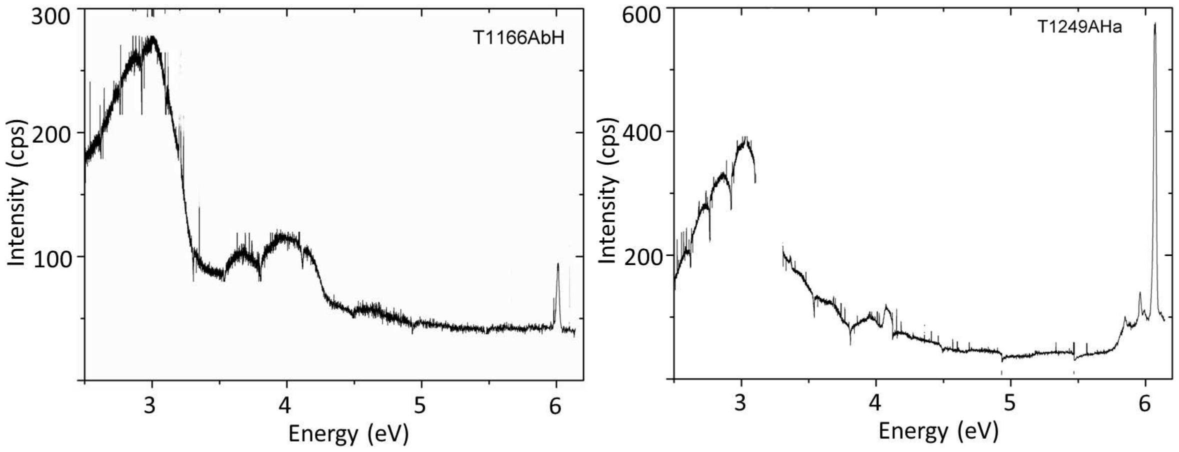

Fig. 3: PL spectra of samples T1166AbH and T1249AHa: The NBE luminescence is more intense in the sample with the NL deposited at a (process) temperature of 845 °C.

Table 4: The influence of wafer surface temperature during the NL deposition on the FWHM of (002) and (102) reflections and dominant D°X line broadening in PL of the 500 nm thick AlN films.

Sample	T_{process}	T_{surface}	(002)-FWHM	(102)-FWHM	PL-FWHM
T1346AHa	825 °C	850 °C	45”	1350”	9.2 meV
T1347AHa	845 °C	870 °C	125”	1400”	11.2 meV
T1345AHa	870 °C	895 °C	60”	1230”	8.6 meV
T1249AHa	845 °C	910 °C	60”	1600”	14.2 meV
T1354AHa	890 °C	925 °C	70”	1625”	14.6 meV

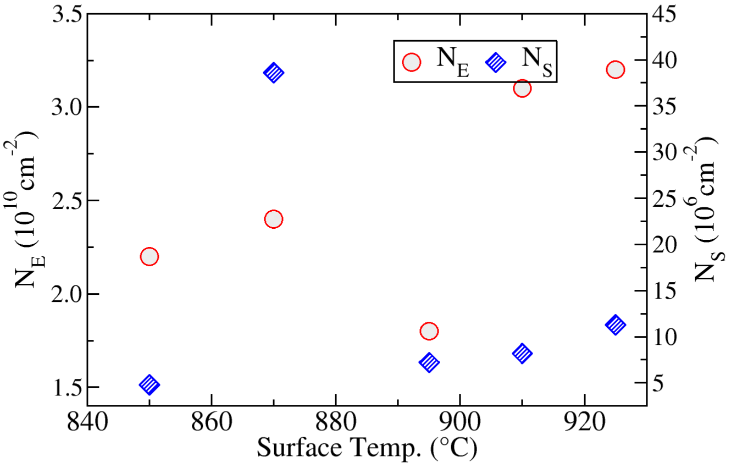

Fig. 4: The estimated screw/mix-type (N_S) and edge/mix-type (N_E) dislocation densities from XRD peak broadening, for the samples presented in Table 4.

NBE luminescence ratio compared to that of the films presented in the previous section—see Fig. 3 as an example.

The AlN epilayers with a NL deposition temperature of 895 °C (sample T1345AHa) showed the best results within this series with the narrowest (102) reflection (1230 arcsec)

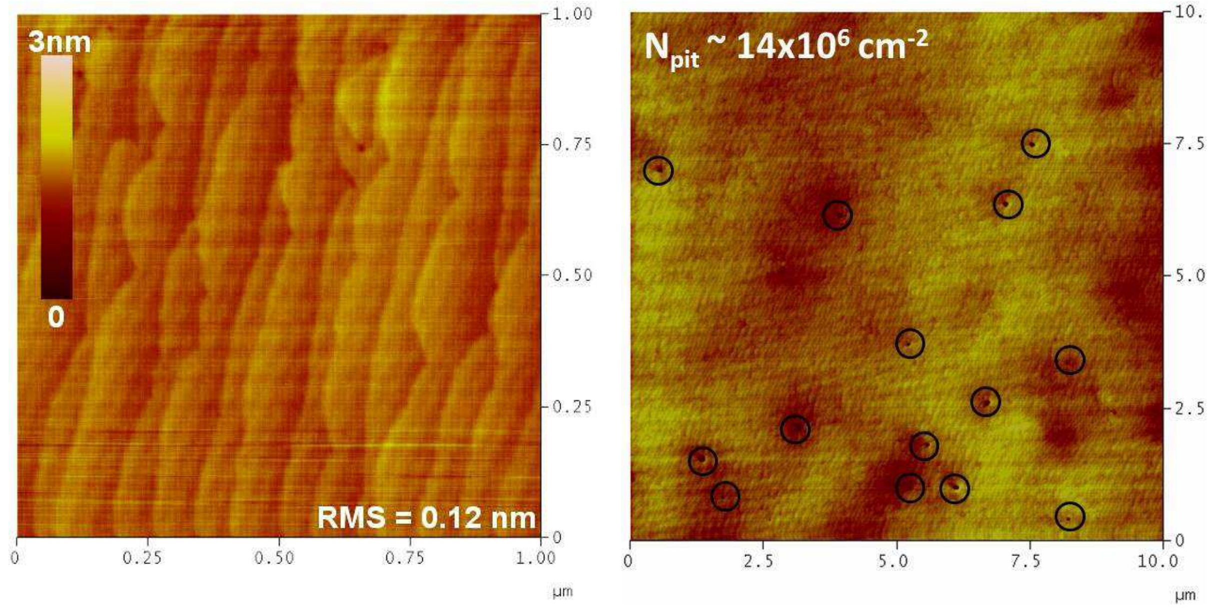

Fig. 5: 1×1 µm^2 and 10×10 µm^2 AFM investigations of the surface of a 500 nm thick AlN film (sample T1345AHa) grown on a NL deposited at a temperature of 895 °C.

corresponding to an estimated edge-type dislocation density of 1.8×10^{10} cm^{-2}. This sample also shows the narrowest PL peak (8.6 meV). This can be compared to 2 µm thick high quality AlN films from Onuma *et al.* [12] with an estimated edge-type dislocation density of 1×10^9 cm^{-2} in which the D°X line was 12 meV broad. There are several reports on recording narrower D°X lines in PL spectra of AlN films [8–11], nonetheless, those films were grown homoepitaxially (on AlN substrates) and therefore, they have much lower dislocation densities compared to our heteroepitaxial growth process. Sample T1345AHa exhibits also excellent surface properties with a surface RMS roughness of ≈ 0.1 nm (see Fig. 5). In this sample, the surface morphology is dominated by in-phase wandering steps and terraces [13]. The step heights are approximately 0.25 nm, corresponding to one mono-layer of AlN. Moreover, there are few pits visible in 10×10 µm^2 AFM scans on the surface of this sample (Fig. 5). The pit density fits very well with the screw/mix type dislocation density in this sample (Fig. 4).

4. Conclusion

MOVPE growth of AlN was investigated in this work. We demonstrated that a low temperature AlN NL doped with oxygen is a very suitable NL to realize AlN films with very low levels of screw/mixed dislocations. By further optimizations of the NL deposition temperature, we observed a huge reduction of lattice twist corresponding to a reduction of mixed/edge-type dislocations. PL investigations showed a very intense and narrow NBE luminescence confirming the high quality of our AlN epi-films. The AlN films in our work are about 500 nm thick. Based on the work of S.B. Thapa [14], we expect that an increase of the AlN epilayer thickness results in further reduction of edge-type dislocations. Moreover, future work will include growth at higher temperatures on the NL optimized in this work. This will certainly require lower V/III ratios to suppress parasitic gas phase reactions.

Acknowledgment

The assistance of Haoyuan Qi in characterization of the samples and respective evaluations is gratefully acknowledged. The author would like to thank B. Neuschl and K. Thonke from Institute of Quantum Matter (Semiconductor Physics Group) in University of Ulm for PL investigations. This work was financially supported by the German Federal Ministry of Education and Research (BMBF) within the framework of the "Deep UV-LED" project.

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