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Fast growth of smooth AlN in a 3×2" showerhead type vertical flow MOVPE reactor

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The conditions required for high growth rate of AlN in a 3×2' showerhead type vertical flow metalorganic vapour phase epitaxy (MOVPE) reactor are studied. It was found that at the standard growth conditions (low V/III, 50 mbar, 1110°C, H_2), growth rate linearly increases with the trimethylaluminium (TMAl) flow rate until about 280 µmol/min with some drop of precursor utilisation efficiency at higher pressures. While the pre-reaction of TMAl with NH_3 at 140 µmol/min of TMAl is still not a major issue, it is not possible, however, to maintain a smooth AlN surface morphology during this "fast" growth. To suppress the surface morphology deterioration, the growth pressure required optimisation. An increase of growth pressure, to 75 mbar, was found to be critical to grow 20+ µm of smooth AlN at a rate of about 3.6 µm/h on bulk AlN substrates.

Keywords: A1. Surface morphology; A3. Metalorganic vapour phase epitaxy; B1. Nitrides; B2. Semiconducting aluminium compounds

III-nitrides with high aluminium contents are a natural choice for building material of deep ultraviolet (DUV) light emitters. Being grown by MOVPE on foreign substrates they often suffer from high densities of dislocations that have a strong negative impact on the device performance and reliability. Since bulk AlN substrates grown by physical vapour transport (PVT) became available on the market, this issue can be greatly overcome. These allow homoepitaxial growth with low extended defect densities, but the PVT growth of bulk AlN typically produces material with high point defect concentrations due to almost unavoidable impurity incorporation leading to a limited transparency in the DUV [1]. In AlGaN-based light emitting diodes (LEDs), the light extraction has as a rule to be realised through the substrate due to difficulties in AlGaN *p*-doping [2] and necessity of using non-UV transparent

p-GaN as a top contacting layer. This leads to a limited applicability of bulk PVT grown AlN, especially in the shortest accessible wavelength range (220-260 nm).

One of the possible solutions in this situation is growth of relatively thick AlN layers on top of the PVT AlN before the actual device heterostructure. In this case the PVT AlN can be removed from backside by grinding/polishing or potentially other separation method until the epitaxial material, which being MOVPE grown, is relatively free of the high concentration of point defects and thus essentially transparent nominally to the AlN bandgap energy. This, however, requires growth of relatively thick layers of at least 20-50 μm, which is several times thicker than what can be typically grown by MOVPE. A normal growth rate that can be comfortably applied to grow AlN in a vertical flow showerhead-type MOVPE reactor is about 1 μm/hour [3], [4], and thus 20-50 μm of material would mean 20-50 hours of growth, which is unacceptably long. Previously quite fast rates of Al(Ga)N growth were demonstrated in specially designed MOVPE reactors [5], including high temperature ones [6], [7]. For more standard MOVPE reactors, fast growth rates are also achievable at extremely low V/III ratios (1.5–2), but the surface morphology was reported to be an issue [8]. In this study we investigated possibility to grow AlN in our showerhead type vertical flow 3×2" MOVPE reactor at three times faster rate in comparison to our standard growth [4].

Our base growth parameters are as follows: TMAl flow of 60 sccm/min (≈ 47 μmol/min), V/III ratio of 25, total growth pressure p = 50 mbar, temperature T_g = 1110°C, H_2 up to 8 slm of total flow, showerhead–susceptor gap of 11 mm. The peculiarities of AlN growth on sapphire and other details can be found elsewhere [4]. In this study, the growth rate (GR) was varied by supplying TMAl with an increased rate while keeping ammonia flow fixed (thus decreasing V/III ratio). Another varied parameter was pressure. Test samples were grown on *c*-sapphire wafers (2" in diameter, 430 μm-thick, single side polished, nominally no miscut with respect to *c*-axis) with the final growth at optimised parameters on a bulk PVT grown AlN wafer from HexaTech Inc (25 mm in diameter, 550 μm-thick, single side polished,

c-axis ±1°). The samples were characterised by in-situ optical reflection, ex-situ optical, scanning electron and atomic force microscopies and X-ray diffraction.

Initially, the AlN growth rate as a function of TMAl flow rate was studied to determine possible limits of efficiently utilising precursors in our vertical flow 3×2" MOVPE reactor. It was found (Fig. 1, curve *1*) that up to six times higher than our standard flow rate (360 sccm/min ≈ 280 μmol/min) results in a proportionally faster growth rate (up to ≈7.8 μm/hour) confirming that the TMAl-NH_3 pre-reaction [9], [10] reported to happen during AlN growth is still marginal in this regime. Then AlN surface morphology was considered for the different growth rates (Fig. 2). While a smooth surface was maintained during growth of ~2.5 μm AlN using our standard conditions (Fig. 2, curve *2*), a gradual deterioration of in-situ reflectance was observed at TMAl×3 growth (Fig. 2, curve *3*). Ex-situ optical microscopy confirmed a surface morphology developed in the form of islands (not shown), making these conditions obviously not suitable for growth of thick AlN.

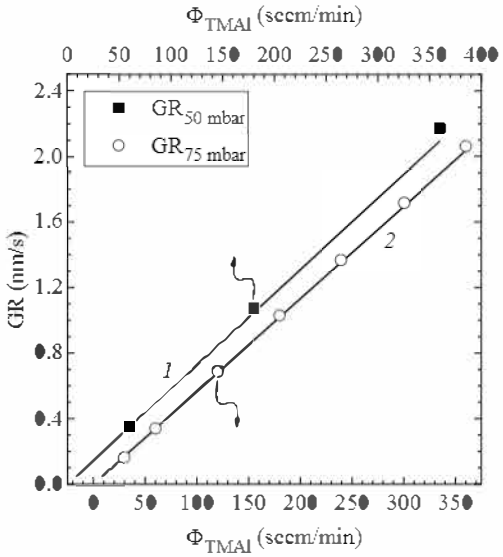


Fig. 1. Growth rates (GRs) estimated from in-situ reflectance data for different growth conditions. The solid lines show linear increases based on GRs at TMAl = 60 sccm/min. Note that plots for datasets *1* and *2* have *x*-axes shifted relatively by 25 sccm/min.

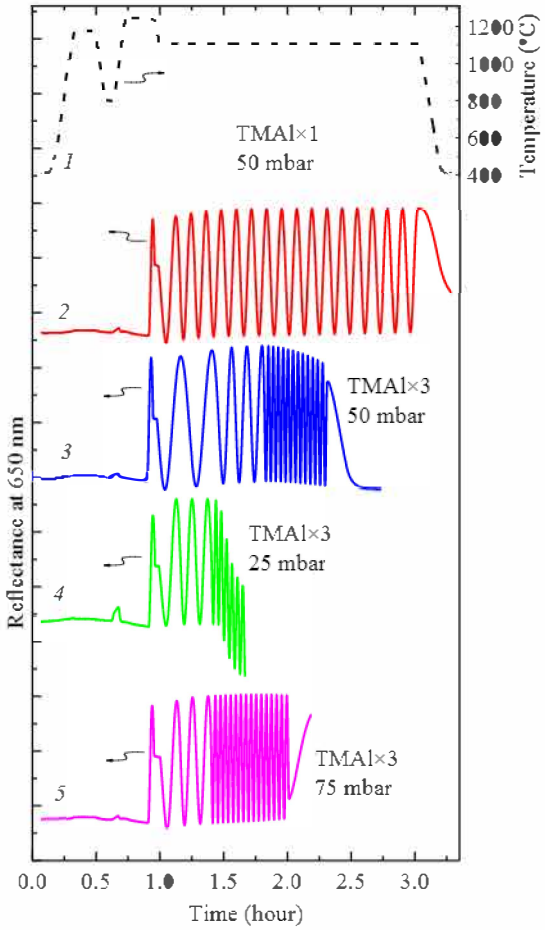


Fig. 2. In-situ temperature (curve *1*) and reflectance (curves 2-5) of AlN samples grown at different conditions. Note that curve *1* (the temperature profile during growth) corresponds to only the reflectivity profile of curve *2*.

The deterioration of AlN surface morphology is often associated with the TMAl-NH_3 parasitic pre-reaction, and the mechanism of the roughening is the formation of AlN particles in the vapour in addition to the surface growth, which in falling to the growth surface provides additional nucleation centres [11]. At the same time, the pre-reaction is known to be stronger at higher pressures [9]. Taking into account these two facts, we carried out a growth run at a reduced (down to 25 mbar) pressure and increased TMAl

flow. Counter to expectation, the corresponding sample exhibited even faster roughening (Fig. 2, curve *4*) at the TMAl×3 growth. Interestingly, the observed in Fig. 2 surface morphology deterioration is up to some level reversible i.e. when the GR is reduced and/or pressure increased the surface becomes smooth again.

As a result, reactor pressure was increased (initially to 75 and then up to 150 mbar in 25 mbar steps) to investigate its effect on the surface morphology at the TMAl×3 growth conditions. At 75 mbar (slightly higher than our standard pressure), the in-situ reflectance did not deteriorate during the growth of 2.7 µm thick AlN layer (Fig. 2, curve *5*) and no surface features were observed with Nomarski interference optical microscopy, except some cracks (not shown), which typically appear only for layers grown on sapphire at standard conditions up to thicknesses of above 3 µm. The XRD quality of the smooth sample was found to be somewhat worse than what typically achievable at the standard conditions: 002 ω-scan FWHM 305 arcsec (vs. 260 arcsec) and 101 ω-scan FWHM 810 arcsec (vs. 550 arcsec). This means that the dislocation annihilation rate is seemingly lower in the case of the fast growth compared to the standard growth conditions. These two drawbacks, however, are expected to be not critical when AlN is grown homoepitaxially on bulk AlN, which is an ultimate target of the study.

Further increase of pressure (up to 100 mbar) led to an apparently slightly poorer in-situ reflectance (not shown), and in this case the parasitic reaction between TMAl and ammonia could be considered to be the main reason of the apparent surface roughening since a sublinear increase of growth rate in comparison to increase of TMAl flow rate was detected (Tab.). However, in spite of further reduction in GR at both Φ_{TMAl} = 60 sccm/min and Φ_{TMAl} = 180 sccm/min (Fig. 3) and more pronounced GR sub-linearity with the three times increased TMAl flow (Table 1), which mean even stronger pre-reactions, no deterioration of in-situ reflectance was observed at pressures of 125 and 150 mbar and TMAl×3 conditions (not shown). From this observations one can conclude that at least a moderate pre-reaction does not lead to significant surface morphology deterioration in this type of MOVPE reactors.

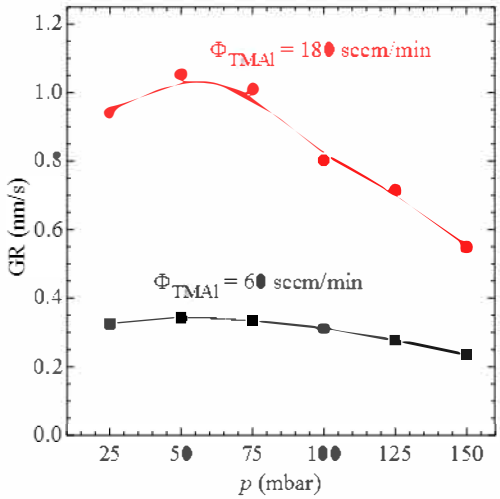


Fig. 3. Reactor total pressure dependences of GR at different TMAl flows. The solid lines represent a guide to the eye.

Table 1. Summary of the fast growth at different reactor pressures.

Pressure, mbar	Surface morphology	$\frac{\text{Growth rate at TMAl×3}}{\text{Growth rate at TMAl×1}}$ ratio
25	Quick degradation	2.91
50 (std.)	Moderate degradation	3.07
75	No degradation	3.04
100	Slight degradation?	2.58
125	No degradation	2.59
150	No degradation	2.34

To see what happens to the surface morphology on the nanoscale, scanning electron microscopy (SEM) was applied to the sample grown at the standard pressure with three times increased growth rate (Fig. 4). SEM micrograph of the sample reveals its surface morphology developed in the form of hexagonally shaped islands with the average diameter of ~0.5 μm and scattered randomly distorted hexagonal pits. SEM does not allow identification of any surface features of the smooth samples grown both at 50 mbar with the standard TMAl flow rate and at 75 mbar with the three times increased TMAl flow rate (not shown).

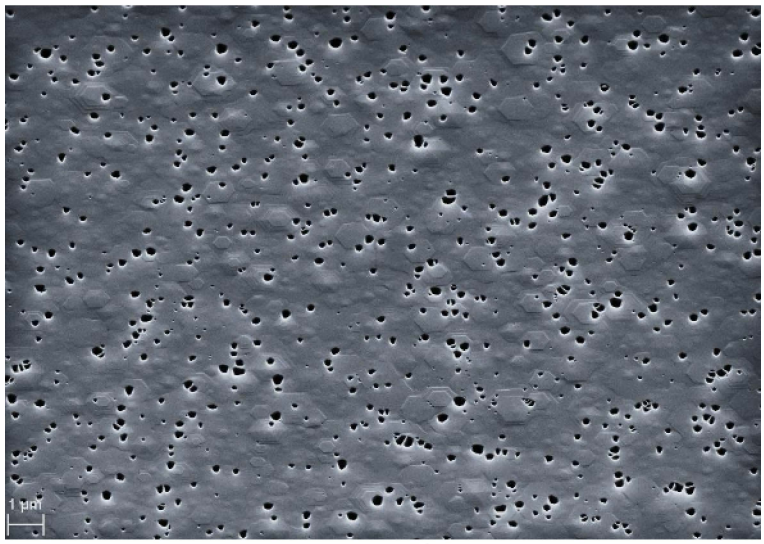
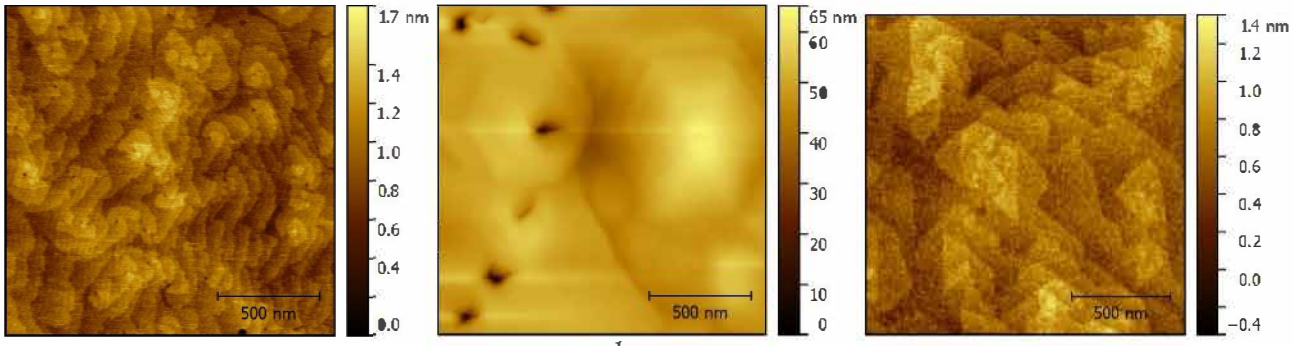


Fig. 4. SEM micrograph (45° tilted view) of 2.5 µm-thick AlN layers grown at our standard pressure of 50 mbar and the three times increased growth rate.

Additionally atomic force microscopy (AFM) was applied to the three mentioned above samples (Fig. 5). The sample grown at the standard conditions shows a surface morphology typical for a step flow growth mode i.e. distinct single bilayer steps between terraces are clearly visible (Fig. 5, *a*). While sapphire wafers with nominally no miscut were used here, the steps between terraces are provided by a spiral growth around screw dislocations (seen as dark dots in the figure). The three times increase in growth rate changes AlN surface morphology quite significantly, particularly inducing 3D growth (hexagonally shaped islands as was already seen from the SEM above) and decorating cores of (most probably screw/mixed type) dislocations with quite large V-pits (Fig. 5, *b*). A 50% increase in reactor pressure again changes the surface morphology quite strongly, returning the growth mode back to a step flow regime with terraces of even larger average width in comparison to the sample grown at our standard conditions. A root mean squared (RMS) roughness of about 0.20 nm was estimated for both smooth samples while that of the sample with its surface decorated with pits and islands was found to be of 5.4 nm. It should be noted that in contrast to the RMS roughness of the smooth samples, the last value should not be interpreted as an ultimate characteristic of the corresponding growth conditions (fast

growth rate, 50 mbar) as it is expected to increase further for thicker samples grown using these conditions.



a *b* *c*

Fig. 5. 1.6×1.6 μm^2 AFM scans for 2.5 μm-thick AlN layers grown at standard pressure and growth rate (*a*), standard pressure and increased growth rate (*b*) and increased pressure and growth rate (*c*).

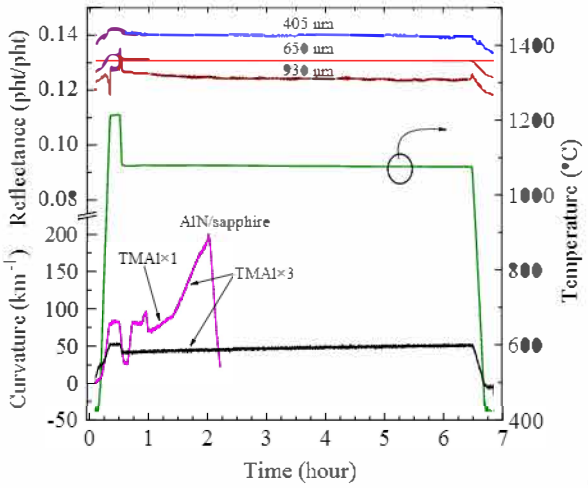
Taking into account that pre-reaction is not dominant in controlling the surface morphology in our case, another mechanism likely related to the surface growth kinetics must be responsible for the observed surface roughening. To maintain a step flow mode of AlN growth, Al adatom diffusion length should be of the order of the average terrace width. Otherwise depending on the ratio between actual and critical surface supersaturation, formation of surface nucleus within the terraces can be initiated which form additional steps acting as further nucleus for growth and leading to a transition from step flow to 3D growth mode [12]. From this point of view it is clear why the increased TMAl flow results in the observed deterioration of AlN surface morphology. The surface supersaturation is directly related to the Al vapour supersaturation defined as the relative difference between input and equilibrium partial pressures of Al [12].[12].[12].[12].[12].[12], while the former is in its turn directly proportional to the TMAl flow applied. The positive effect of the relatively weak change in total pressure (+50%) is less clear from these arguments, but it is obvious that the total growth pressure is a quite critical parameter, which needs to be accurately optimised for better control of AlN surface morphology.

Taking into account the preliminary results of fast AlN growth at different pressures on sapphire, the following growth parameters were used to grow a 20+ μm-thick AlN on a bulk AlN wafer:

140 µmol/min of TMAl, 1.165 mmol/min of NH_3 (V/III = 8.3), up to 8 slm of carrier gas (H_2), 1110°C, 75 mbar. In-situ reflectance, wafer curvature and temperature data of the corresponding growth run are presented in Fig. 6. Apparently lower in-situ growth temperature measured for the bulk AlN wafer in comparison to the sapphire wafers (see Fig. 1-Fig. 3) is due to a lower transparency of the former on the wavelength used by pyrometer for temperature estimation. Depending on substrate used, our in-situ temperature thus is either susceptor pocket bottom temperature (e.g. in case of double polished sapphire) or substrate surface temperature (in case of silicon for example) but in most cases it shows something in between. Temperature detected by a thermocouple located below susceptor was the same in all the above experiments (not shown).

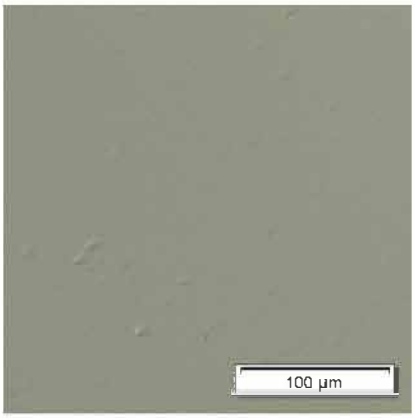
As expected, the slope of wafer curvature during the fast growth was found to be much lower in comparison to AlN grown on sapphire (shown in Fig. 6 for reference) allowing for a low absolute value of wafer curvature and resulting in no crack formation over whole wafer. The absence of the oscillations in the in-situ reflectance is due to the homoepitaxial growth and thus due to reflectance only from the top (growing) surface with no reflectance from the substrate/epitaxial layer interface to interfere with.

Analysing the reflectance data (almost no change in the reflectance signal) one can conclude that during the growth, the layer remained fairly smooth. A slight reduction of reflectance still observed is due to development of a number of local macroscopic surface defects during the growth rather than due to a gradual overall surface smoothness deterioration as was confirmed by the Nomarski interference contrast optical microscopy (Fig. 7). These local defects seem to be a consequence of initial surface defects due to non-optimal sample preparation for growth. No additional chemo-mechanical polishing was applied to the PVT AlN wafer prior growth to refresh its surface and only the standard chemical cleaning (treatment successively in hot acetone, isopropyl alcohol, HCl and buffered HF) was applied. Nevertheless, by the results obtained, the used growth conditions has been proven to be suitable ones for the fast growth rate of about 3.6 µm/hour and has allowed maintaining of a smooth surface for an AlN layer in excess of 20 µm in thickness.



a

Fig. 6. In-situ monitoring data of the 20+ µm-thick AlN sample grown on a bulk PVT-AlN wafer at 75 mbar. An in-situ curvature curve for an AlN/sapphire is given for comparison.



b

Fig. 7. Nomarski interference contrast optical microscopy image of the 20+ µm-thick AlN sample grown on a bulk PVT AlN wafer at 75 mbar.

The crystalline quality of the grown sample was assessed by measuring its symmetric (002) and skew symmetric (101) XRD rocking curves (Fig. 8). In both cases the obtained linewidths were found to be slightly narrower (002: 22", 101: 17") in comparison to those measured prior growth (002: 30", 101: 20"). In other words, the superior crystalline quality of PVT-AlN substrate is successfully translated to the newly grown material.

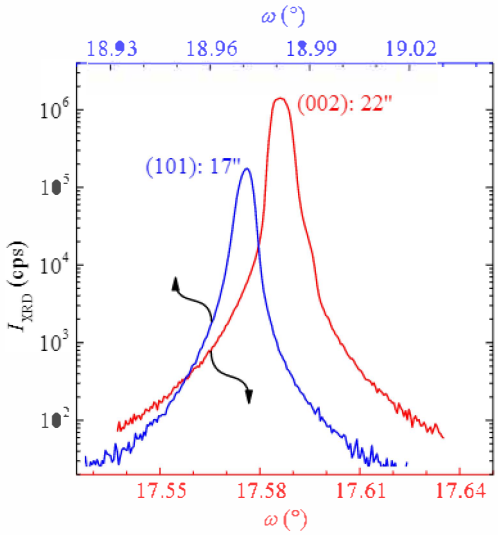


Fig. 8. XRD data for the 20+ μm-thick AlN sample grown on a bulk PVT-AlN wafer.

In conclusion, prospects of using of standard 3×2" close coupled showerhead type MOVPE reactor for fast (> 3 μm/hour) AlN growth are considered. It was found that the parasitic pre-reaction between TMAl and ammonia at typical AlN growth conditions (V/III ≤ 25, 1110°C, 50 mbar, H_2) is insignificant when AlN is attempted to be grown at the rate of up to about 7.8 μm/hour. However, at a growth rate about twice as our reference "slow" growth rate, AlN surface roughness becomes an issue. An increase of reactor pressure to 75 mbar was found to be critical to maintain smoothness of the AlN surface at 3.6 μm/hour growth rate. The optimised growth parameters were used for growth of more than 20 μm-thick AlN homoepitaxially on a bulk PVT AlN wafer. As a result, an MOVPE-PVT AlN template with a smooth surface morphology and crystalline quality not worse than that of the original PVT AlN wafer was prepared.

Acknowledgments

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