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Freestanding two inch c-plane GaN layers grown on (100) γ-lithium aluminium oxide by hydride vapour phase epitaxy

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(100) γ-lithium aluminium oxide substrates of two inch diameter were fabricated from crystals grown by the Czochralski technique. Onto these substrates c-plane GaN with a thickness of about 200 µm has been grown by hydride vapour phase epitaxy in a horizontal AIX HVPE reactor. The GaN layer spontaneously separates from the bottom lithium aluminium oxide substrate during the cool-down resulting in complete freestanding 2 inch GaN wafers.

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1 Introduction

Freestanding 2 inch GaN substrates for epitaxy of nitride layer structures are of crucial importance for improved device operation for example in case of blue laser diodes and UV LEDs. Although GaN substrates have successfully been grown by hydride vapour phase epitaxy (HVPE) their availability is still limited. When the widely used sapphire and SiC substrates are applied for the fabrication of GaN substrates separation of the layer from the initial substrate without breakage is a challenge due to the strong bowing stemming from the differences in the thermal expansion coefficients. Preferably, the GaN layer should separate from the substrate already during the growth procedure. The substrate (100) γ-lithium aluminium oxide ($LiAlO_2$) with space group $P4_12_12$, a = b = 0.5169 nm, and c = 0.6268 nm [1] can inherently offer such a separation mechanism due to its low thermal stability above 900 °C. For c-plane GaN the orientation relationship GaN(0001)||$LiAlO_2$(100), GaN[11.0]||$LiAlO_2$[001] with –1.4% mismatch, and GaN[1-1.0]||$LiAlO_2$[010] with –6.3% mismatch holds. The larger mismatch in b-direction was found to be accommodated due to coherent tilt [2]. However, on (100) $LiAlO_2$ the growth of c-plane and m-plane GaN has been observed as well. Recently, the growth of 40 µm thick freestanding c-plane GaN layers using an MOVPE growth start followed by HVPE layer growth in a special hybrid H-MOVPE reactor was reported [3]. It was stated there that typically c-plane results from growth using MOVPE while MBE yields m-plane GaN. However, more precisely, the resulting orientation relationship seems to primarily depend on the growth conditions in the nucleation phase since c-plane GaN was grown with MBE [2] and m-plane GaN was grown by MOVPE [4] and by HVPE [5] whereas c-plane GaN grown by HVPE directly on (100) $LiAlO_2$ has not been reported so far.

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In this paper it is demonstrated that freestanding c-plane GaN-layers of 2 inch can be obtained by HVPE growth and self-separation due to the decomposition of the starting $LiAlO_2$ substrate.

2 Experimental

$LiAlO_2$ single crystals of 2 inch diameter and 80 mm length were grown using the Czochralski technique with rf-induction heating. Pre-dried powders of 4N purity Li_2CO_3 and 5N purity Al_2O_3 were mixed in the stoichiometric ratio and gradually sintered up to 1000 °C for about 40 h. Due to the high melting temperature of about 1700 °C a crucible with 100 mm diameter and 100 mm height and an active afterheater made of iridium were used. To reduce the strong selective evaporation of Li_2O from the melt and from the grown crystal a steep axial temperature gradient had to be applied. The pulling rate was 1.5 mm h^{-1} and the rotation rate was 10 min^{-1}. Flowing argon was used as the growth atmosphere. The crystals were pulled along the [100] orientation. After grinding of primary (001) and secondary (010) flats, the ingot was sliced, lapped and chemomechanically polished resulting in 2 inch wafers (100) γ-$LiAlO_2$ of 0.4 mm thickness. HVPE growth was performed in an horizontal AIX-HVPE reactor described in [6]. $LiAlO_2$ wafers were annealed with NH_3 in a N_2/H_2 atmosphere at 800 hPa typically for 15 min at temperatures varied from 870 °C up to 910 °C which results in surface nitridation [3]. After cooling down to 600 °C under nitrogen a low-temperature nucleation layer of about 70 to 80 nm thickness was grown with a V/III ratio of 50. The layer thickness was adjusted using a Laytec EpiSense in-situ reflectometer and AnalysR program. Afterwards, the nucleated substrate was heated up to 990°C under NH_3 and recrystallized for about 2 min at a total pressure of 200 hPa. Subsequently, about 10 µm GaN were grown under N_2 carrier gas with a V/III of 20 at a rate of about 50 µm/h. Thick GaN layers were grown with rates of 150 to 200 µm/h at temperatures of 1010 °C to 1040 °C with a H_2:N_2 - carrier gas composition 1:1 to avoid cracking [7] for typically 1 hour. The GaN layer was cooled down to 700 °C with NH_3 stabilization. The freestanding GaN layers of around 200 µm thickness and the cracked residues of the $LiAlO_2$ starting substrates were unloaded below 250 °C. SEM and thin film X-ray diffractometry (TFXRD) of nucleation layers were applied in order to verify a proper nucleation and recrystallization for subsequent c-plane GaN growth. The thickness of the freestanding GaN layer was determined gravimetrically or with a micrometer screw. Results of CL and PL measurements are published elsewhere [8]. Standard characterization techniques, i.e. optical microscopy, XRD, AFM, SEM, and SIMS were applied. The determination of the threading dislocation density was performed by XRD and photoenhanced chemical etching.

3 Results and discussion

Figure 1 shows a $LiAlO_2$ single crystal grown by the Czochralski technique used for the preparation of the starting wafers. The obtained $LiAlO_2$ crystals were transparent and colorless. Surface inspection of the resulting $LiAlO_2$ wafers by AFM yielded typical values of root-mean-square-roughness (RMS) of 0.10 nm with a maximum peak-to-valley height (P-V) of 1.0 nm for an area of 1x1 μm^2. The misorientation of the (100) surface determined according to [9] was below 1 degree. Typical values of the FWHM of ω rocking curves at the (200) reflection mapped over a 2 inch wafer were 62 arcsec with a standard deviation of 11 arcsec along <001> and 368 arcsec with a standard deviation of 29 arcsec along <010>.

Fig. 1 2 inch $LiAlO_2$ crystal of 80 mm length.

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Although the crystal and the wafer surface quality need further improvement compared to standard sapphire substrates the X-ray data reveal a high quality and uniformity of the boule growth and the wafers were used without any further ex-situ treatment. The low-temperature nucleation layer of some ten nm was investigated ex-situ. In Fig. 2a the SEM micrograph of the surface of an about 120 nm thick nucleation layer after recrystallization is shown. It can be seen that crystalline grains with a hexagonal surface habitus clearly dominate. The 2θ scan over a large angle range revealed a single strong peak at 34.6 degree which corresponds to the (0002) reflection of GaN as well as to the (200) reflection of the tetragonal $LiAlO_2$ (Fig. 2b). Some additional weak peaks matching with diffractions from (10-13), (11-22), (20-23), and (11-24) GaN planes indicate that small amounts of crystallites with a different orientation also exist. However, in the θ/2θ scan the additional peak at 32.4 degree with a fourfold lower intensity can be observed. This result indicates that in the buffer layer for the subsequent GaN growth a small fraction of crystallites with (10-10) orientation corresponding to m-plane GaN competes with the majority of c-plane oriented grains. For subsequent GaN growth a nucleation layer thickness of about 70 to 80 nm was found to be optimum and a recrystallization time of 2 min at about 990 °C was used without optimization.

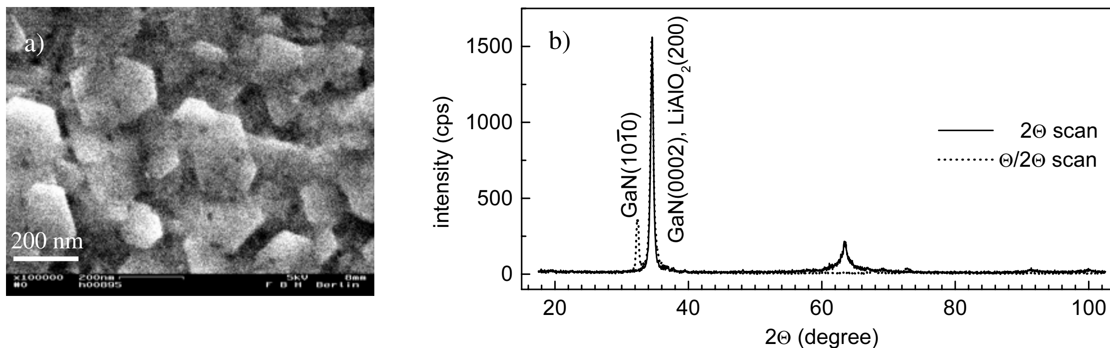

Fig. 2 Plan view SEM picture of a low-temperature nucleation layer of about 120 nm thickness after recrystallization for 5 min (a), and the corresponding 2θ and θ/2θ scans obtained by X-ray diffraction (b).

After recrystallization a GaN layer of about 10 µm was grown without hydrogen in the carrier gas. Fabry-Perot-oscillations observed with the in-situ reflectometer indicated smooth layer growth. But such thin GaN films of some µm thickness were found to be cracked and peeled off as flakes or foil pieces during the cool down making their characterization inconvenient or impossible. Continuation of the growth for thick layers at 1010 °C with hydrogen in the carrier gas yielded 2 inch GaN layers with thicknesses of over 100 µm with cracked residues of the $LiAlO_2$ remaining on the backside. Eventually, longer growth times with elevated temperatures led to the complete separation of the GaN layer from the $LiAlO_2$ substrate during the cool down procedure. Li and O indiffusion into the backside of the GaN layer found by SIMS indicated also the decomposition of $LiAlO_2$ at the interface by the release of volatile Li_2O. Figure 3 shows such a freestanding 2 inch GaN substrate of 200 µm thickness. The surface is locally smooth as indicated by an rms-roughness of only 0.4 nm determined by AFM over 10x10 μm^2 in the transparent center part. The overall macroscopic morphology is wavy as can be seen from the photograph. Moreover, the edge of the wafer appears black due to dense v-pits. Their density decreases rapidly from the edge to the center. This indicates a lack of lateral uniformity that can reasonably be explained by the crossed geometry of the inlets of NH_3 and GaCl. The incident light is deflected out by these v-pits

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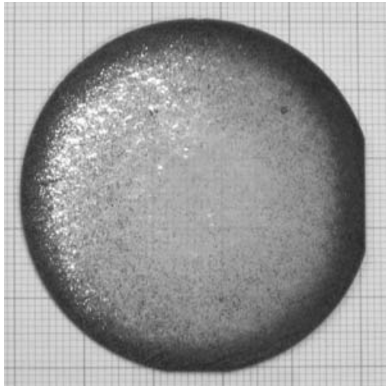

Fig. 3 Freestanding 2 inch GaN wafer.

which were found to be partly more than 100 µm deep and are therefore thought to originate already during the initial growth steps. This is supported by the observation that the rotational symmetry of the v-pit distribution was lost when the rotation was switched off during the nitridation only. Moreover, the v-pits cover the whole wafer if the NH_3 flux is switched off during the nitridation. Table 1 gives some XRD results from ω-rocking curves of 230 µm thick GaN layers on substrates from the same $LiAlO_2$ crystal and surface treatment for different nitridation times. The results indicate a reduction of mosaicity from the sample backside to the frontside but also from the edge to the center. Conversion of the FWHM values into dislocation densities [10] reveals that the GaN crystal quality still needs to be improved. For 15 min nitridation this conversion yields edge and screw dislocations of $9x10^9$ cm^{-2} and $3x10^9$ cm^{-2}. Also the density of threading dislocations of $6x10^{10}$ cm^{-2} determined from etch pits by selective photoenhanced etching supports this finding.

Table 1 XRD results from ω-rocking curves of 230 µm thick freestanding GaN layers.

Nitridation time (min)	FWHM-(0002) reflection (arcsec)			FWHM-(30-32) reflection (arcsec)	
	Backside	Frontside		backside	Frontside
	Center	Center	near edge	center	Center
10	1908	1371	1577	1501	889
15	1911	1270	1690	1591	1144
20	1803	1407	1597	1746	748

Nevertheless, the spread of tilt even from the backside traced by the (0002) reflection is always lower than the published best value of 2222 arcsec for a 40 µm thick GaN layer grown by the hybrid H-MOVPE process [3]. Best values of FWHM obtained here are 1180 arcsec in the ω-scan and 380 arcsec in the ω/2θ-scan at the (0002) reflection which show the superior crystal quality of the freestanding GaN wafers grown directly by HVPE in comparison to those reported in [3].

4 Summary

It was shown that freestanding 2 inch c-plane GaN wafers of good crystal quality can be grown directly on epi-ready (100) $LiAlO_2$ substrates obtained from Czochralski boule growth. The key for the required orientation relationship is found in the proper growth start employing surface nitridation and the growth of a low-temperature nucleation layer. Taking advantage of the limited thermal stability of $LiAlO_2$, separation of the GaN layer from the starting substrate occurs during the cool down after proper exposure to high temperatures for a sufficient time used for GaN growth. Although further optimization is still neces-

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sary the results as a proof of principle demonstrate the high potential of $LiAlO_2$ substrates for the fabrication of GaN wafers in a single process step for subsequent device structure growth.

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