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High-quality AlN grown on a thermally decomposed sapphire surface

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ABSTRACT

In this study we show how to realize a self-assembled nano-patterned sapphire surface on 2 inch diameter epi-ready wafer and the subsequent AlN overgrowth both in the same metal-organic vapor phase epitaxial process. For this purpose in-situ annealing in H_2 environment was applied prior to AlN growth to thermally decompose the c-plane oriented sapphire surface. By proper AlN overgrowth management misoriented grains that start to grow on non c-plane oriented facets of the roughened sapphire surface could be overcome. We achieved crack-free, atomically flat AlN layers of 3.5 μm thickness. The layers show excellent material quality homogeneously over the whole wafer as proved by the full width at half maximum of X-ray measured ω-rocking curves of 120 arcsec to 160 arcsec for the 002 reflection and 440 arcsec to 550 arcsec for the 302 reflection. The threading dislocation density is $2 * 10^9$ cm^{-2} which shows that the annealing and overgrowth process investigated in this work leads to cost-efficient AlN templates for UV LED devices.

1. Introduction

In recent years AlGaN based diodes that emit light (LEDs) in the UVC and UVB spectral range attracted increasing attention. The development is driven by the high potential of such devices for, e.g., water purification [1,2], plant growth stimulation [3], gas sensing [4,5] and non-line-of-sight communication [6]. The best substrate choice for epitaxial growth of such devices would be AlN bulk material. Unfortunately, bulk AlN substrates with suitable diameter of at least 2 inch and transparency for wavelengths below 260 nm for bottom up devices are not readily available. Since sapphire is available at relatively low costs and transparent for UV light, a widely used approach is to realize pseudo-substrates that consist of AlN grown by metal-organic vapor phase epitaxy (MOVPE) on sapphire. Unfortunately, due to the large in plane lattice mismatch between AlN and sapphire of about 11%, AlN immediately forms 3-dimensional islands on the sapphire surface. During island merging twist and tilt components are balanced by formation of threading dislocations (TD). These TDs can propagate into the active regions of subsequently grown UV LED structures and can act as centers for non-radiative recombination. Therefore AlN layers with low threading dislocation density (TDD) in the range of 10^9 cm^{-2} or below [7] are required.

AlN grown directly on planar sapphire usually exhibits TDDs of more than 10^{10} cm^{-2}. To lower the TDD several approaches are used. As TDD can be reduced with increasing layer thickness due to dislocation annihilation, the main issue is a careful strain management to avoid layer cracking during growth of thick (>1 μm) AlN layers. One approach is to intentionally apply layer roughening and subsequent surface smoothing by proper choice of growth parameters, e.g. by varying the V/III ratio [8] which leads to TDDs (calculated from FWHM of X-ray rocking curves [9]) of $2.5 * 10^9$ cm^{-2}. Another technique comprises sapphire surface nitridation prior to AlN growth [10]. Thereby the layer roughening and strain relaxation is introduced by simultaneous nucleation of Al- and N-polar domains. Layers with TDD of $2 * 10^9$ cm^{-2} were grown by this method. Unfortunately, the polarity of the growing AlN is highly sensitive towards humidity, oxygen and carbon in the reactor environment [11,12]. Hence the growth start on nitridated sapphire is hard to control especially if there are parasitic deposits, quartz ware and carbon present in the reactor. A more effective decrease of TDD compared to the above-mentioned growth on planar sapphire can be reached by epitaxial lateral overgrowth (ELO) of patterned AlN/sapphire templates. There the spatial extension of the defect-rich AlN/sapphire interface is intentionally decreased. Hence, the strain introduced by the heteroepitaxial growth is reduced and dislocations that propagate in growth direction can bend towards free surfaces and annihilate with increasing layer thickness. Therefore, patterned AlN/sapphire substrates are often used to benefit from the advantages of the ELO principle TDD of down to $3 * 10^8$ cm^{-2} in the lateral grown regions can be reached [13]. Also the growth of AlN directly on patterned sapphire has been already demonstrated [14,15], but is more frequently affected by misaligned AlN growth and coalescence problems. Compared to the growth on planar sapphire, the growth

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on patterned (AlN/)sapphire can lead to much lower TDDs. Anyway, the usual surface patterning processes involve photolithography. Hence, they are relatively expensive. A cost efficient sapphire patterning process for lowering the strain during AlN growth, preferably applied in-situ prior to growth is desired. Tajima et al. [16] realized such a process in a hydride vapor phase epitaxy reactor by annealing of 100 nm thin pre-deposited AlN layers on sapphire at 1450 °C. Due to the high temperature voids are formed at the AlN/sapphire interface by sapphire decomposition. Unfortunately, such high temperatures cannot be reached with many conventional MOVPE reactors.

In 2012 Kumagai et al. [17] published their research on the impact of gaseous environment and temperature in an MOVPE reactor on the morphology of sapphire surfaces. They showed that sapphire decomposition in H_2 already occurs at temperatures above 1200 °C. These are temperatures that can easily be reached by conventional MOVPE machines. It has been reported that decomposed sapphire causes defective AlN growth [18]. Our study sheds light on the reasons and shows that partial decomposition of sapphire surfaces can be used as a cost-efficient in-situ patterning process prior to AlN growth using an optimized multi-step growth process. Thick, crack-free and smooth AlN layers with TDD of $2 * 10^9$ cm^{-2} across a whole 2 inch wafer can be obtained by this technique in a conventional multiwafer MOVPE reactor.

2. Experimental

An AIX2400G3HT metal-organic vapor phase epitaxy multiwafer (11 × 2 inch) reactor was used to deposit AlN on c-plane oriented sapphire substrates. The nominal offcut of the epi-ready sapphire was 0.2° towards m-plane orientation. All annealing and growth processes were monitored in-situ by a LayTec EpiCurveTT metrology system. The process temperature T_{proc} was measured pyrometrically on the backside of the susceptor. Hence, due to the temperature gradient towards the cooler front side of the sample holder the temperature of the substrates during annealing and growth is expected to be about 50 °C lower than T_{proc}. Annealing of sapphire was done at T_{proc} = 1290 °C with only H_2 as ambient gas. AlN was grown from the standard precursors TMAl and NH_3 with only H_2 as carrier gas. For the AlN growth start we always deposited a 50 nm thick standard nucleation layer (NL) at T_{proc} = 980 °C and a group V to group III ratio (V/III) of 4000 [19]. Then AlN is deposited at T_{proc} > 1160 °C at growth rates up to 1.6 μm/h.

The material properties were investigated by X-ray diffraction measurements (XRD) using a Philips X'Pert Pro system. For low diffraction volume like nanometer-scale islands we use the XRD powder setup with a Goebel mirror on the source side and a parallel plate collimator in front of the detector to obtain high diffraction intensities. To investigate the material quality of the MOVPE grown AlN layers, an XRD geometry with a fourfold 220 Ge monochromator and 0.5 mm × 5 mm aperture on the source side and a slit with an acceptance angle of 1° in front of the detector was applied. The morphology of the sample surfaces was imaged by atomic force microscopy (AFM) and cross-sections were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For the cross-sectional TEM analysis specimens were prepared in two zone axes, [1–100]AlN and [11–20]AlN.

3. Results and discussion

3.1. Sapphire annealing

Firstly, the aim of our study was to apply a nano-scale structure to the smooth epi-ready sapphire surface. Therefore, sapphire was annealed in the MOVPE reactor under in-situ monitoring (Fig. 1a). During heating up to T_{proc} = 1290 °C the 405 nm reflectance from the sample surface stays constant at 0.08 until a temperature of T_{proc} = 1200 °C is reached. From that temperature on and during the 20 min annealing step at constant T_{proc} the 405 nm reflectance decreases down to 0.05. Hence the surface undergoes a roughening during the annealing step.

AFM (Fig. 1b) reveals holes with maximum diameter of 300 nm and hills with maximum diameter of 200 nm and up to 10 nm height as reasons for the decreased reflectance. Hence, the nano-scale patterning of the sapphire surface was successfully reached by thermal decomposition of the sapphire surface in H_2 environment. Akiyama et al. [20] and Kumagai et al. [17] suggest the following chemical reaction to govern the thermal sapphire decomposition:

$$Al_2O_3(s) + 3H_2(g) = 2Al(g) + 3H_2O(g)$$

Unfortunately, taking only this process into consideration we cannot explain the generation of hills on the c-plane sapphire surface (Fig. 1b). Therefore we investigated the annealed sapphire by XRD using symmetric powder diffraction geometry with coupled 2θ/ω (Fig. 1c). Despite of the expected low diffraction volume the 10–10 AlN and 0002 AlN peaks can clearly be identified. Consequently there is already c-plane oriented AlN (as desired for growth on c-plane sapphire) but also m-plane (10–10) oriented AlN present on the surface. According to Kumagai at al. [17] this can typically be observed for sapphire annealed in an environment of H_2 and N_2 mixture. Since we used only H_2 as annealing environment nitrogen must have been provided unintentionally by decomposition of parasitic AlN deposits that are always present in the MOVPE reactor. Probably the decomposition of the polycrystalline deposits takes place following the same chemical reaction that is suggested in literature [21] for decomposition of different AlN polarities (x between 0 and 3):

$$AlN(s) + (x+3)/2H_2(g) = AlH_x(g) + NH_3(g).$$

On one hand the consequence is that the thermal decomposition of the sapphire surface cannot be applied in our MOVPE reactor without causing an unintentional pre-deposition of undesired non-c-plane oriented AlN nucleation sites. On the other hand unintentionally deposited c-plane oriented AlN islands can partially prevent the c-plane oriented sapphire surface from decomposition and hence enable the subsequent MOVPE growth of well aligned c-plane oriented AlN. In our MOVPE reactor we were able to establish reproducible conditions for sapphire independent from reactor history. This conditioning was done by heating the reactor at T_{proc} = 1250 °C for 30 min and a subsequent pre-deposition of 4 μm AlN at T_{proc} = 1180 °C using V/III = 30.

3.2. Growth start on thermally decomposed sapphire

The annealed sapphire (Fig. 1b) and an epi-ready sapphire wafer for comparison were overgrown with 50 nm AlN-NL and 650 nm AlN at a V/III ratio of 30 and T_{proc} = 1180 °C. The AFM image of the layer on the annealed wafer (Fig. 2a) shows that there is still a high density of holes and hills comparable to the density observed after sapphire annealing (Fig. 1b). The surface hills after growth of 650 nm AlN exhibit a maximum height of 25 nm. Notably most of the hills are located close to a hole. A closer investigation of the sample surface by SEM (Fig. 2b) indicates incomplete coalescence especially around misoriented surface areas as causes of the distorted surface. The image shows tilted hexagonal columns with impeded coalescence at the columns' sidewalls. In comparison AlN grown on sapphire without the 20 min annealing step exhibits an atomically smooth surface as proved by the AFM measurement in Fig. 2c. We presume that the tilted sidewalls of the holes that are formed during thermal sapphire decomposition