Hydride Vapor-Phase Epitaxy of c-Plane AlGaN Layers on Patterned Sapphire Substrates

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Growth of AlxGa1−xN layers by hydride vapor-phase epitaxy on patterned sapphire substrates is investigated. The pattern consists of honeycombs which by their orientation and size promote the formation of coalesced c-plane-oriented AlxGa1−xN layers with reduced crack density. The orientation of parasitic crystallites in the honeycomb openings is investigated using scanning electron microscopy and electron back-scatter diffraction. Crystallites with their [11.0] and [52.3] directions parallel to the vertical growth direction of the Al0.3Ga0.7N layer are observed and successfully overgrown by a 20-μm-thick fully coalesced c-plane-oriented layer.

Key words: AlGaN, PSS, HVPE, pseudosubstrates

INTRODUCTION

Group III nitride semiconductors form a material system that is successfully applied for an increasing number of high-frequency, high-power electronic and various optoelectronic applications.1–3 AlxGa1−xN alloys permit the fabrication of ultraviolet (UV) light-emitting devices with shorter wavelengths by increasing the Al content. However, the quantum efficiency decreases with increasing emission energy, mainly due to a reduced radiative recombination efficiency.4,5 Substrates with reduced threading dislocation densities allow for higher internal quantum efficiency. This is known for UVA-LEDs with emission from 340 nm to 400 nm which benefit from homoepitaxial growth on GaN substrates6 and UVC-LEDs with emission from 210 nm to 280 nm showing optimum performance for homoepitaxial pseudomorphic growth on AlN substrates.7 However, UVB-LEDs emitting in the range of 280 nm to 340 nm suffer from the lack of suitable substrates for homoepitaxy and are thus difficult to fabricate with competitive quantum efficiencies. Thick AlxGa1−xN layers in the medium composition range with x from 0.3 to 0.7 can be grown by hydride vapor-phase epitaxy (HVPE),8 and their use as pseudosubstrates promises to close this gap. However, such pseudosubstrates are not yet available, mostly because of practical challenges such as the availability of suitable reactors, parasitic reactions,9 inhomogeneous Al incorporation at facets, cracking of AlxGa1−xN layers grown on foreign substrates,10 or distortion of the surface by prevailing misoriented crystallites from trenches of patterned sapphire substrates.11 It has already been shown that Al0.45Ga0.55N layers with smooth, non-disturbed surfaces can be grown successfully up to thicknesses of 40 μm on trench patterned sapphire substrates (PSS) by optimization of the miscut of the sapphire substrate, of the AlCl3 pretreatment, the growth of an AlN buffer layer, and the growth conditions.12 However, buried cracks which were mostly oriented along (1120)AlGaN, i.e., perpendicular to the ridges, were found by plan-view cathodoluminescence in such layers. The aim of this study was to find a way to reduce anisotropy and overall crack formation by further optimization of PSS and growth parameters with the aim of obtaining pseudosubstrates for LEDs in the UVB range around 300 nm.
EXPERIMENTAL PROCEDURES

PSS were prepared using I-line stepper lithography with 8-μm-thick KMMP 1005 resist on a c-plane sapphire substrate with misorientation of 0.25° toward (1100). The honeycomb-like pattern was etched using a BCl3-based inductively coupled plasma reactive ion etching (ICP-RIE) process in a SENTECH SI 500 ICP. The hexagonal cells exhibit ridge sidewalls with orientation close to (1010) sapphire with angles to the c-plane surface of about 83°. The cells have a maximum opening of about 8 μm, ridge widths of about 1.5 μm, and depths of about 4 μm. A series of samples of AlGaN layers with different growth times up to 2 h were prepared on PSS of 16 mm × 16 mm size using a modified horizontal Aixtron HVPE reactor. The reactor consists of quartz with separated metal sources of liquid Ga operated at 850°C and solid Al operated at 550°C. GaCl and AlCl3 are formed by reaction with HCl and mixed before reaching the substrate surface. Ammonia was provided by a separate line to minimize prereactions. Experiments were performed with sample rotation of about 30 rpm. The surface was pretreated using AlCl3 flow for 15 min, and an AlN layer was grown as described in Ref. 10. The AlGaN layers were grown at 1100°C and 400 hPa. The aluminum content was determined by high-resolution x-ray diffraction (HRXRD) assuming complete relaxation of the AlGaN layers, which are well above the critical layer thickness. The average layer thickness was determined gravimetrically taking into account the composition and in addition from scanning electron microscopy (SEM) cross-section micrographs. Nomarski microscopy and SEM were applied for surface inspection. Optical properties and composition homogeneity were investigated using low-temperature cathodoluminescence (CL). X-Ray diffraction and electron back-scatter diffraction (EBSD) were used to assess the structural properties.

RESULTS

Compared with our previous work,10,12 the pattern of the sapphire was modified from stripes along the [1100] sapphire direction with width of 6 μm and pitch of 10 μm to hexagonal cells with stripes along (1100) sapphire with width of 1.5 μm and pitch of 9 μm, as shown in Fig. 1. The flow pattern in the reactor was adjusted to achieve mirror-like surfaces for the binary compounds GaN and AlN at 400 hPa before the growth study. The composition of the AlGaN layers was determined by HRXRD from the distance between (0006) sapphire and (0002) layer reflections in ω-2θ scans to be x = 0.3 ± 0.03 assuming complete relaxation. SEM micrographs of different stages of AlGaN layer growth are depicted in Fig. 2. In Fig. 2a, b two early stages of growth are shown. The micrographs were recorded from different planes of a sample grown for 15 min with a calculated average layer thickness of about 2.5 μm. AlGaN growth takes place on ridges and in honeycombs. Two different kinds of crystallites can be distinguished within the honeycombs. While crystallites growing on (0110) sapphire, (1100) sapphire, and (1010) sapphire break through the c-plane surface of the AlGaN layer on the ridges (Fig. 2b), the smaller crystallites at (1010) sapphire, (0110) sapphire, and (1100) sapphire are less high and do not break through the c-plane surface (Fig. 2b). Above the latter positions the c-plane AlGaN layer from the top of the ridges starts to overgrow the honeycombs. After growth for 1 h resulting in an AlGaN layer of about 10 μm thickness (Fig. 2c), the c-plane surface is nearly completely closed with the exception of a few remaining pits. After about 20 μm the surface is completely closed (Fig. 2d).

EBSD investigations were performed to obtain additional information on the orientation of the crystallites growing in the honeycomb-like cells with their near-m-plane sapphire facets. Maps of orientation distribution were recorded from a sample area of about 59 μm × 44 μm in size. Representative image details are depicted in Fig. 3a, b. According to the color code inserted in Fig. 3b, the planar surface of the patterned sapphire is covered by c-plane AlGaN. In contrast, the larger crystallites growing on the three honeycomb sidewalls mentioned above share the same crystallographic direction along the surface normal, i.e., z-direction, as indicated by the same color of the crystallites in Fig. 3a, but different in-plane orientations along, e.g., the horizontal x-direction, as can be seen by the different colors of crystallites in Fig. 3b. The (0001) poles in the pole figure constructed from the EBSD measurements prove the presence of the c-plane-oriented matrix, as can be seen from the centered (0001) pole marked by the black square in Fig. 3c. Twins can be identified at the comb sidewalls with the c-axes of the crystallites inclined to the surface normal direction z, as indicated by arrows to the corresponding (0001) poles. According to the pole figures, the crystallites are oriented with their [431] hexagonal Miller indices axis along the vertical z-direction.
Pure (0001) orientation was found by EBSD analysis for the fully coalesced Al$_{0.3}$Ga$_{0.7}$N layer shown in Fig. 2d with a maximum of the misorientation angle distribution at about 0.25°. This value fits reasonably well with the full-widths at half-maximum of the x-ray rocking curves of 1470 arcsec at the 002 reflection and 1750 arcsec at the 302 reflection.

CL spectroscopy was applied at cleaved cross-sections to reveal the optical properties and compositional homogeneity across the coalesced layer. CL spectra obtained from c-plane Al$_x$Ga$_{1-x}$N grown
above a ridge (Fig. 4a) revealed an energy shift from 4.0 eV to 4.2 eV along the growth direction during the early stages of coalescence (Fig. 4b). In addition, isolated overgrown cracks were found in SEM micrographs at different positions above the PSS at cleaved cross-sections as marked in Fig. 4a.

DISCUSSION

The modified PSS using a honeycomb-like structure with (1010)_{sapphire} sidewalls provides advantages compared with a stripe pattern because it is easier to fabricate stable narrow ridges which minimize crack formation on the ridges. This sidewall orientation promotes lateral overgrowth by relatively rapidly propagating \{1120\}_{AlGaN} and \{1122\}_{AlGaN} facets. Three different orientations of group III nitride nucleation on (1100)_{sapphire} have been reported so far: \{1100\}_{GaN}, \{1013\}_{GaN}, and \{1122\}_{GaN}.\textsuperscript{14} Crystallites with the former two orientations are expected to be trapped in the honeycomb opening. Off-orientation of 0.25° towards (1100) of the sapphire substrate\textsuperscript{12} and a proper surface treatment at the start of growth were found to avoid the formation of undesired, \{1122\}-oriented nuclei. Crystallites with habits according to \{1013\} orientation with respect to (1010)_{sapphire}, (0110)_{sapphire}, and (1010)_{sapphire} can be observed in Fig. 2a. These crystallites are aligned with the [11.0] axis along the vertical z-direction.\textsuperscript{14} However, there are also larger crystallites on the other three m-plane sidewalls which show prevailing facets tilted towards the surface by about 25° with respect to the m-plane sapphire facets on which they started. They disturb the lateral overgrowth by the c-plane-oriented material from the top of the adjacent ridges (Fig. 2a, b). Fortunately, these larger crystallites are subsequently overgrown by the c-plane-oriented Al_{0.3}Ga_{0.7}N layer entering from the three remaining facets above the \{1013\}-oriented crystallites (Fig. 2b, c). It was found from EBSD analysis (Fig. 3) that these larger crystallites are aligned with the [52.3] axis along the vertical z-direction, which does not correspond to any of the three orientations commonly observed on m-plane sapphire.\textsuperscript{14} Since three sidewalls behave as expected for m-plane sapphire surfaces, it can be assumed that the remaining (0110)_{sapphire}, (1100)_{sapphire}, and (1010)_{sapphire} surfaces support a coherently tilted growth of group III nitride layers. Investigation of the cross-sections by SEM and CL revealed a shift of the near-band-edge emission from 4.0 eV to 4.2 eV during the first three micrometers of growth of the c-plane-oriented Al_{0.3}Ga_{0.7}N layer above the ridge area (Fig. 4). Changes of emission energies of exciton-related recombinations of group III nitride layers on sapphire due to strain are usually up to about 10 meV.\textsuperscript{15} Therefore, it is assumed that the greater energy shift found here arises from an increase of the AlN fraction x from 0.27 to 0.36.\textsuperscript{16} A reasonable explanation is the enhanced incorporation of gallium on non-c-plane facets as long as the coalescence process proceeds. Similar observations have been reported for epitaxial lateral overgrowth (ELOG) of AlGaN by metalorganic vapor-phase epitaxy (MOVPE).\textsuperscript{17} However, an increasing Al content during growth is undesired as it leads to incorporation of additional tensile strain into the layer and supports formation of cracks during growth, which are still found in the Al_{0.3}Ga_{0.7}N layer of 20 μm thickness in Fig. 4a. It is expected that also local strain variations at boundaries of differently oriented grains could contribute to crack formation. The impact of such buried grains on the width of rocking curves should decrease with increasing layer thickness, since the used x-rays probe only a few μm near the surface. Cracks result in new, slightly differently oriented domains which broaden the widths of the rocking curves, and their reduction will therefore be a main subject of further growth optimization.

CONCLUSIONS

It has been shown that patterned sapphire substrates provide a base to fabricate thick Al_{0.3}Ga_{0.7}N layers by HVPE which may serve as pseudosubstrates for subsequent growth of layered structures for devices emitting in the UVB wavelength region. Honeycomb-like PSS allows for lateral overgrowth when parasitic nucleation of AlN and Al_{0.3}Ga_{0.7}N at the sidewalls is well controlled. Laterally overgrown Al_{0.3}Ga_{0.7}N layers on such PSS provide isotropic strain and composition distribution. This finding is a promising basis for further growth optimization aiming for layers without cracks, with reduced defect density, high UVB transparency,\textsuperscript{10} and sufficient thickness for surface polishing.

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