Impact of intermediate high temperature annealing on the properties of AlN/sapphire templates grown by metalorganic vapor phase epitaxy

Sebastian Walde*, Sylvia Hagedorn, and Markus Weyers

Ferdinand-Braun-Institut, Leibniz-Institut fuer Hoechstfrequenztechnik, Gustav-Kirchhoff-Straße 4, 12489 Berlin, Germany

E-mail: sebastian.walde@fbh-berlin.de

Received November 16, 2018; revised February 12, 2019; accepted February 23, 2019; published online April 16, 2019

In this work, we investigate AlN/sapphire templates grown by metalorganic vapor phase epitaxy (MOVPE) subjected to an intermediate high temperature annealing (HTA) step at different AlN film thicknesses. To avoid cracking of the MOVPE layers during HTA at 1700 °C these layers have to be grown under low incorporation of tensile strain. For each sample the growth is stopped at a certain thickness between 230 nm and 1.2 μm followed by HTA. X-ray rocking curve FWHM of 0002 and 10–12 reflections lead to an estimation of threading dislocation densities (TDD) as low as 6 × 10^6 cm^-2 for the thickest AlN layers of 880 nm and 1.2 μm after annealing. For all layer thicknesses MOVPE growth is subsequently continued to a total AlN layer thickness of 1.5 μm to reach for a smooth surface. The change of the AlN strain state after HTA leads to an increased wafer curvature at room temperature and compressive strain in the subsequently grown AlN layers increasing the wafer bow at room temperature. Hence, to serve as a base layer, e.g. for ultraviolet light emitting diodes, a trade-off between low TDD, surface smoothness and wafer bow has to be found. © 2019 The Japan Society of Applied Physics

1. Introduction

AlGaN-based ultraviolet (UV) light emitting diodes (LEDs) in the UVB (315–280 nm) and UVC (280–200 nm) spectral range offer applications in various fields such as phototherapy, water disinfection, biochemical agent detection, gas sensing etc.1–3 AlN/sapphire templates grown by metalorganic vapor phase epitaxy (MOVPE) are typically used as pseudo substrates, since AlN bulk substrates still suffer from limited size (<2") and high costs. However, this technique leads to a high threading dislocation density (TDD) of about 10^10 cm^-2 at growth start at the AlN/sapphire interface due to the lattice mismatch between AlN and sapphire. Such threading dislocations cause non-radiative recombination in the active region of LEDs which limits the internal quantum efficiency. It is therefore necessary to reduce the TDD below 10^6 cm^-2 to enable high efficiency UV LEDs.4 To reduce the TDD in the AlN/sapphire template different approaches have been developed in the last years, e.g. nitridation of the sapphire,5,6 pulsed growth7 and epitaxial lateral overgrowth.8–10 For these methods dislocation density reduction down to 10^6 cm^-2 is usually achieved for AlN layer thicknesses >4 μm. However, it would be advantageous to obtain a low TDD already at thinner layer thicknesses, since thick AlN layers will result in large wafer curvature due to the thermal mismatch between AlN and sapphire. Thick AlN/sapphire templates (~5 μm) normally show curvature values of around ~170 km^-1 (convex) at room temperature, which will further be enlarged by compressive AlGaN heterostructure overgrowth. The curvature translates into a huge wafer bow leading to inhomogeneous heat coupling to the substrate holder during heterostructure growth and thus inhomogeneous growth conditions. Large bow also causes serious problems in the UV LED chip process, for example in lithography.

A promising approach to achieve high quality AlN/sapphire already for thin layers (<2 μm) is the high temperature annealing (HTA) of MOVPE-grown17 or sputtered18,19 AlN layers at elevated temperatures around 1700 °C presented by Ref. 20. High efficiency UVC LEDs on such layers were recently demonstrated by our group. However, cracking of layers during annealing can be a problem as shown by Ref. 21 for a 1 μm thick sputtered AlN/sapphire layer grown under tensile strain.

In this study, we investigate HTA of MOVPE layers with different thicknesses and the subsequent growth on such annealed layers. The aim of this study is to avoid layer cracking during HTA and provide low TDD, atomically smooth AlN layers with reduced wafer bow for devices like UV LEDs.

2. Experimental methods

The AlN/sapphire templates were grown in an AIX2400G3HT MOVPE planetary reactor with a capability for 11 × 2 inch wafers using c-plane sapphire with 0.2° nominal offcut towards the m direction as substrate material. We used the standard precursors TMAl and NH₃/H₂ served as carrier gas and a reactor pressure of 50 mbar was kept constant during growth. Before growth, the surface was cleaned by a thermal treatment under hydrogen at process temperature TProc = 1145 °C for 10 min. For growth, firstly a 50 nm thick standard nucleation layer was deposited on the sapphire at process temperature TProc = 980 °C and an input group V to group III (V/III) ratio of 4000.22 Nucleation was followed by AlN growth at temperatures above TProc = 1140 °C and V/III ratios between 30 and 540 by changing the NH₃ flow from 250 to 4250 sccm at constant TMAl flow of 400 sccm. HTA was done in a sintering oven in N₂ atmosphere at a total pressure of 1000 mbar in face-to-face configuration of the samples following.23 Heating up was performed with 5.5 °C min^-1 before temperature was kept constant at 1700 °C for 3 h. The temperature was adjusted by a thermocouple close to the heater.

MOVPE growth was monitored by a LayTec EpiCurveTT in situ metrology system measuring 405 nm reflectance and curvature of the wafers. X-ray diffraction rocking curves were measured with a Philips X’Pert Pro system including a fourfold 220 Ge monochromator. Aperture on the source side was 0.5 mm × 5 mm and the acceptance angle in front of the
detector was 1°. The surface morphology was investigated by light microscopy with Nomarski contrast and atomic force microscopy (AFM) in contact mode.

3. Results and discussion

3.1. Annealing of thin MOVPE layer
We investigated HTA of a thin (350 nm) AlN layer on sapphire grown by MOVPE. After thermal cleaning of the sapphire and 50 nm AlN nucleation the following 300 nm AlN was grown at 1180 °C and V/III ratio of 30. These growth conditions lead to growth of a smooth layer showing clear Fabry–Perot oscillations and an average value of 0.13 for the 405 nm reflectance [Fig. 1(a)]. The curvature [Fig. 1(b)] of the wafer strongly increases during growth indicating build-up of high tensile strain which is commonly observed for MOVPE growth of AlN/sapphire. Due to the thin layer thickness the X-ray rocking curve FWHM (XRC-FWHM) for the 10–12 reflection of 1700 arcsec is relatively high. However, the XRC-FWHM of the 0002 reflection of 100 arcsec is already quite low indicating low tilt of the nucleation islands. From the XRC-FWHM a TDD of $3 \times 10^{10}$ cm$^{-2}$ was estimated following.23,24) After annealing at 1700 °C for 3 h the XRC-FWHM are reduced to values of 50 arcsec and 450 arcsec for 0002 and 10–12 reflection, respectively. The estimated value for the TDD of $2 \times 10^{10}$ cm$^{-2}$ reveals a reduction of the TDD by approximately one order of magnitude. However, light microscopy imaging (Fig. 2) shows cracks on the surface over the full 2 inch wafer after annealing. This cracking is based on the high tensile strain state of the layer before annealing indicated by the increase in concave curvature during growth [Fig. 1(b)]. Due to the thermal mismatch between AlN and sapphire resulting in higher expansion of the sapphire compared to the AlN layer during annealing the tensile strain increases until it partially relaxes via generation of cracks. Cracking of layers after HTA was also observed by Ref. 21 for sputtered AlN layers of 1000 nm with incorporated tensile strain. The cracking makes the 300 nm MOVPE layer unusable as a template for UV LEDs although the TDD was reduced by one order of magnitude due to HTA. To avoid cracks during HTA lower tensile strain in the initial MOVPE layers is desired.

3.2. Impact of strain in the AlN starting layer
AlN layers of different thicknesses with reduced tensile strain were grown by using the method of roughening and subsequent smoothing of the surface to achieve 1.5 μm crack free AlN on sapphire. The growth process is interrupted at the 5 marked positions for subsequent HTA.
This growth process enables crack free AlN/sapphire over the full wafer up to a thickness of at least 1.5 μm. To investigate HTA of different layer thicknesses (230–1150 nm) the growth was interrupted at the positions 1–5 marked in Fig. 3(a). For the first two layer thicknesses AFM topograms [Figs. 4(a.1) and 4(a.2)] show that the layers are not closed but feature holes which have a larger diameter for the thicker layer. This corresponds to the roughening of the layer in the reflectance measurement [Fig. 3(a)]. Since the high V/III ratio promotes growth of the nucleation islands in c-direction their coalescence is inhibited and thus a porous layer forms. When the V/III ratio is ramped down to 30 lateral growth is promoted and consequently the layer starts to coalesce. This can be observed in the AFM image of the 660 nm thick layer [Fig. 4(a.3)] by a reduction of the hole density. For 880 nm [Fig. 4(a.4)] the layer is fully coalesced growing in step flow growth mode. At 1150 nm [Fig. 4(a.5)] step flow growth continues leading to further smoothing of the layer. The roughening-smoothing process is also indicated by the rms values of the AFM images in Figs. 4(a.1)–4(a.5). The rms roughness increases from 3.4 up to 4.1 nm during roughening and decreases down to 0.2 nm during smoothing.

3.3. HTA of MOVPE thickness series

The five samples with layer thicknesses between 230 and 1150 nm were annealed at 1700 °C for 3 h in the same annealing process. The XRC-FWHM of 0002 and 10–12 reflections for the as grown layers and after HTA are plotted in Fig. 5. Before annealing, one can see a decrease in the XRC-FWHM with increasing layer thickness. This can be explained by the mutual annihilation of threading dislocations with increasing layer thickness during growth. After HTA the XRC-FWHM of the 0002 reflection vary only slightly [Fig. 5(a)] while a distinct reduction of the XRC-FWHM of the 10–12 reflection for all layer thicknesses is observed [Fig. 5(b)] indicating lower TDDs. However, the samples with lower initial TDD after 3 h of HTA reach a state of saturation in which due to the higher average distance of the dislocations mutual annihilation is not probable any more. This leads to comparable XRC-FWHM for the higher layer thicknesses (880 nm + 1150 nm) corresponding to TDDs of $6 \times 10^8$ cm$^{-2}$. The AFM topograms of the layers after HTA can be seen in Figs. 4(b.1)–4(b.5). Before coalescence [Figs. 4(b.1)–4(b.3)] the holes of the layers become slightly bigger during annealing. Additionally, especially for the coalesced layers [Figs. 4(b.4)–4(b.5)] a redistribution of the surface steps can be observed. During annealing the atoms on the surface can move and accumulate at the step edges forming step bunches and thus the layers get rougher. This effect is comparable to step bunch formation during growth under low supersaturation conditions. The increase in diameter of the holes that are still present after HTA in the layers with 230 to 660 nm thickness [Figs. 4(b.1)–4(b.3)] can be explained by redistribution of material from the hole edges and formation of more extended stable AlN sidewall facets.

3.4. Overgrowth

After HTA the growth process shown in Fig. 3 was continued for all samples up to a total AlN layer thickness of 1.5 μm. XRC-FWHM of these overgrown HTA samples indicate no significant further TDD reduction. This can be attributed to the already too high average distance between the threading dislocations in the material that results in a low probability of mutual annihilation at AlN growth temperature. Exemplarily, an in situ measurement of overgrowing the 880 nm HTA AlN layer is shown in Fig. 6. For comparison a simultaneously grown 880 nm AlN layer without HTA was overgrown in the same growth run. For both samples the reflectance
measurement [Fig. 6(a)] shows the expected Fabry–Perot oscillations with an average value of 0.13 indicating growth of a smooth layer. The curvature measurement [Fig. 6(b)], however, shows a different behavior for the two samples. Firstly, before heating up, the sample with HTA exhibits a larger wafer curvature of $-60 \text{ km}^{-1}$ in comparison to $-10 \text{ km}^{-1}$ for the sample without HTA. Secondly, for the layer with intermediate HTA, the curvature value decreases during growth indicating incorporation of compressive strain rather than the usual incorporation of tensile strain observed for the sample without HTA. This observation is in agreement with previous studies of high temperature annealed samples, which showed smaller in-plane lattice constants after annealing\textsuperscript{18,31} due to relaxation of the AlN layer at annealing temperature. The smaller in-plane lattice constant leads to compressive growth under the applied growth conditions. The wafer curvature after HTA linearly increases with layer thickness (Fig. 7) reaching a constant value of about $-90 \text{ km}^{-1}$ after overgrowth up to the total layer thickness of 1.5 $\mu$m for all samples. This is the expected behavior assuming a reduced in-plane lattice constant after annealing, which is independent of the starting layer thickness. The AFM images after overgrowth [Figs. 4(c.1)–4(c.5)] clearly show that in all cases step flow growth was achieved with mostly atomically smooth surfaces. However, for the thickest layer [Fig. 4(c.5)] one can see remnants of step bunches which were generated during HTA. So the growth of additional 350 nm is not sufficient to properly smooth the surface. For 880 nm the additional growth of 650 nm is sufficient to reach an atomically smooth surface. For 660 nm some holes can be observed surrounded by an atomically
smooth surface. This can be explained by the increase of hole diameter during annealing so that some of them could not be overgrown properly. However, for the thinner layers no holes are observed after overgrowth, since in that case the diameter of the holes was smaller although the hole density was higher. So with respect to surface smoothness the overgrown layers with starting thickness of 230, 360 and 880 nm are well-suited for usage as UV LED templates. However, the TDD of the two thinner starting layers is still relatively high in contrast to the low value of $6 \times 10^8$ cm$^{-2}$ for the 880 nm starting layer. The wafer curvature after overgrowth is independent of the thickness of the starting layer and with $\sim 90$ km$^{-1}$ strongly reduced in comparison to usual values of $\sim 170$ km$^{-1}$ for thick (~5 μm) AlN/sapphire templates. So to conclude regarding the mentioned trade-off between TDD, surface smoothness and wafer bow the 880 nm starting layer works best for HTA and subsequent overgrowth to 1.5 μm yielding high quality AlN/sapphire templates.

4. Conclusions

In this study, we investigated the impact of intermediate HTA on the properties of AlN/sapphire templates grown by MOVPE. The first finding was that annealing of a layer with high incorporated tensile strain leads to cracking during annealing. Layers of different thicknesses (230–1150 nm) with reduced tensile strain were successfully annealed and overgrown without any cracking on the full 2 inch wafers. TDDs after HTA decreased with increasing layer thickness and saturated for the thicker starting layers of 880 and 1150 nm at a value of $6 \times 10^8$ cm$^{-2}$. Surface roughness increased after HTA and was consecutively reduced by further MOVPE overgrowth. Due to incorporation of compressive strain during annealing and subsequent compressive MOVPE overgrowth wafer bow increased independently of the thickness of the starting layer. The best trade-off between TDD, smoothness and wafer bow of the samples is found for the 880 nm starting layer overgrown to 1.5 μm. With TDD of $6 \times 10^8$ cm$^{-2}$, atomically smooth surface (rms = 0.3 nm) and wafer curvature of $\sim 90$ km$^{-1}$ it fulfills all criteria for a proper UV LED template.

Acknowledgments

This work was partially funded by the German Federal Ministry of Education and Research (BMBF) within the Advanced UV for Life project and by the German Research Foundation (DFG) within the Collaborative Research Center Semiconductor Nanophotonics (CRC 787). Furthermore, the authors thank Prof. Hideto Miyake for support and discussion, HTM Reetz for technical assistance of the sintering oven and Torsten Petzke for technical assistance of the MOVPE machine.

1) W. L. Morison and T. B. Fitzpatrick, *Phototherapy and Photomedicine of Skin Disease* (Raven Press, New York, 1991).
2) M. Kneissl and J. Russ, *III-Nitride Ultraviolet Emitters* (Springer, Berlin, 2016) Springer Series in Materials Science.
3) M. Wütele, T. Kolbe, M. Lipsz, A. Külberg, M. Weyers, M. Kneissl, and M. Jekel, *Water Res.* 45, 1481 (2011).
4) H. Hirayama, T. Yatabe, N. Noguchi, and N. Kamata, *Electron. Commun. Jpn.* 93, 24 (2010).
5) M. Martens et al., *IEEE Photonics Technol. Lett.* 26, 342 (2014).
6) F. Mehnke et al., *IEEE J. Sel. Top. Quantum Electron.* 23, 2000108 (2017).
7) A. Kitan, K. Balakrishnan, and T. Katona, *Nat. Photonics* 2, 77 (2008).
8) S. Y. Karpov and Y. N. Makarov, *Appl. Phys. Lett.* 81, 4721 (2002).
9) M. Kneissl et al., *Semicond. Sci. Technol.* 26, 014036 (2011).
10) M. Funato, M. Shibaoka, and Y. Kawakami, *J. Appl. Phys.* 121, 085304 (2017).
11) J. Wang, F. Xu, C. He, L. Zhang, L. Lu, X. Wang, Z. Qin, and B. Shen, *Sci. Rep.* 7, 42747 (2017).
12) H. Hirayama, T. Yatabe, N. Noguchi, T. Ohashi, and N. Kamata, *Appl. Phys. Lett.* 91, 071901 (2007).
13) H. Hirayama, S. Fujikawa, J. Norimatsu, T. Takano, K. Tsukabi, and N. Kamata, *Phys. Status Solidi C* 6, 5356 (2009).
14) V. Kueller, A. Knauer, U. Zeimer, H. Rodriguez, A. Mogilatenko, M. Kneissl, and M. Weyers, *Phys. Status Solidi C* 8, 2022 (2011).
15) P. Dong et al., *Appl. Phys. Lett.* 102, 241113 (2013).
16) S. Hagedorn, A. Knauer, A. Mogilatenko, E. Richter, and M. Weyers, *Phys. Status Solidi A* 213, 3178 (2016).
17) H. Miyake, G. Nishio, S. Suzuki, K. Hiramatsu, H. Fukuyama, J. Kaur, and N. Kuwano, *Appl. Phys. Express* 9, 025501 (2016).
18) H. Miyake, C.-H. Lin, K. Tokoro, and K. Hiramatsu, *J. Cryst. Growth* 456, 155 (2016).
19) C.-Y. Huang et al., *AIP Adv.* 7, 055110 (2017).
20) N. Susilo et al., *Appl. Phys. Lett.* 112, 041110 (2018).
21) L. Zhao, K. Yang, Y. Ai, L. Zhang, X. Niu, H. Lv, and Y. Zhang, *J. Mater. Sci., Mater. Electron.* 29, 11766 (2018).
22) O. Reentilä, P. Brunner, A. Knauer, A. Mogilatenko, W. Neumann, H. Prozenmann, M. Heiken, M. Kneissl, M. Weyers, and G. Triandl, *J. Cryst. Growth* 310, 1515 (2008).
23) P. Gay, P. B. Hirschy, and A. Kelly, *Acta Metall.* 1, 315 (1953).
24) S. R. Lee, A. M. West, A. A. Allerman, K. E. Waldrip, D. M. Follstaedt, P. P. Provencio, D. D. Koleske, and C. R. Abernathy, *J. Electron. Lett.* 2022 (2011).
25) M. Kneissl et al., *IEEE Photonics Technol. Lett.* 26, 81 (2014).
26) M. Funato, M. Shibaoka, and Y. Kawakami, *J. Appl. Phys.* 121, 085304 (2017).
27) S. Y. Karpov and Y. N. Makarov, *Appl. Phys. Lett.* 81, 4721 (2002).
28) S. Mathis, A. Romanov, L. Chen, G. Beltz, W. Pompe, and J. Speck, *J. Cryst. Growth* 231, 371 (2001).
29) B. N. Pantula, R. Dahal, M. L. Nakarmi, N. Nepal, J. Li, J. Y. Lin, H. X. Jiang, Q. S. Paduan, and D. Weyburne, *Appl. Phys. Lett.* 90, 241101 (2007).
30) I. Bryan, Z. Bryan, S. Mita, A. Rice, J. Tweedie, R. Collazo, and Z. Sitar, *J. Cryst. Growth* 438, 81 (2016).
31) R. Yoshizawa, H. Miyake, and K. Hiramatsu, *Jpn. J. Appl. Phys.* 57, 01AD05 (2018).