High-temperature annealing of AlN films grown on 4H–SiC

Cite as: AIP Advances 10, 125303 (2020); doi: 10.1063/5.0027330
Submitted: 5 October 2020 • Accepted: 9 November 2020 •
Published Online: 1 December 2020

F. Brunner,[1,a)] L. Cancellara,[2] S. Hagedorn,[1] M. Albrecht,[2] and M. Weyers[1]

AFFILIATIONS

[1] Ferdinand-Braun-Institut, Leibniz-Institut fuer Hoechstfrequenztechnik, Gustav-Kirchhoff-Str. 4, 12489 Berlin, Germany
[2] Leibniz-Institut für Kristallzüchtung Berlin, Max-Born-Straße 2, 12489 Berlin, Germany

[a)] **Author to whom correspondence should be addressed:** frank.brunner@fbh-berlin.de

ABSTRACT

The effect of high-temperature annealing (HTA) at 1700 °C on AlN films grown on 4H–SiC substrates by metalorganic vapor phase epitaxy has been studied. It is shown that the structural quality of the AlN layers improves significantly after HTA similar to what has been demonstrated for AlN grown on sapphire. Dislocation densities reduce by one order of magnitude resulting in 8×10^8 cm^{-2} for a-type and 1×10^8 cm^{-2} for c-type dislocations. The high-temperature treatment removes pits from the surface by dissolving nanotubes and dislocations in the material. XRD measurements prove that the residual strain in AlN/4H–SiC is further relaxed after annealing. AlN films grown at higher temperature resulting in a lower as-grown defect density show only a marginal reduction in dislocation density after annealing. Secondary ion mass spectrometry investigation of impurity concentrations reveals an increase of Si after HTA probably due to in-diffusion from the SiC substrate. However, C concentration reduces considerably with HTA that points to an efficient carbon removal process (i.e., CO formation).

Ultrawide Bandgap (UWBG) Semiconductors offer new opportunities for electronic, optical, or sensing applications. One of the most promising UWBG materials is AlN that provides an extremely high critical electrical field (>15 MV/cm[1]) due to its room-temperature bandgap of 6.2 eV. In the case of AlN-based high-power transistors, this offers a high breakdown voltage strength.[2]

Since the homoepitaxial growth of AlN thin films is hampered by the unavailability of large diameter AlN substrates, the heteroepitaxial growth on suitable foreign substrates is the subject of ongoing research. Here, the combination of AlN and SiC benefits from a low thermal expansion mismatch and a high thermal conductivity of both semiconductors. The latter property is highly beneficial for efficient heat dissipation in high-power III-N transistors.

Despite a comparatively low lattice mismatch, the epitaxial growth of AlN on 4H–SiC results in a high dislocation density (typically above 10^9 cm^{-2}) and suffers from a strong tendency to form small pits.[3,4] Different approaches to improve the structural quality of AlN on SiC have been reported, mostly based on high-temperature growth in combination with a proper substrate treatment.[5,6] As published by Chen *et al.*,[7] a structurally improved AlN–SiC interface shows up a route to minimize buffer trapping issues in AlGaN–GaN HFETs.

High-temperature annealing (HTA) has been reported to recrystallize sputtered AlN-on-SiC.[8] The structural properties of such annealed layers improved considerably, as it was also published for AlN-on-sapphire templates by Miyake *et al.*[9]

In this work, the effect of high-temperature face-to-face annealing of Metalorganic Vapor Phase Epitaxy (MOVPE)-grown AlN layers on 4H–SiC substrates is investigated. Characterization of morphological and structural properties as well as the initial defect and impurity state is the focus of this study.

Epitaxial growth was carried out in a modified AIX2600G3-HT "planetary" and a vertical closed-coupled showerhead (CCS) Metalorganic Vapor Phase Epitaxy (MOVPE) system, both configured for high-temperature growth. Trimethylaluminum and ammonia have been used as precursors in a hydrogen atmosphere. Both systems are equipped with EpiCurveTT *in situ* metrology sensors, which give access to the emissivity-corrected susceptor surface temperature (T_s). Substrates used were 100 mm diameter on-axis 4H–SiC with Si-face cmp epi-ready polishing. We did not apply any

chemical pre-treatment before epitaxy. The typical growth parameters for AlN were a reactor pressure of 50 mbar and a low V/III ratio between 30 and 100 in both types of reactors.

The high-temperature setup of the CCS system allows for a surface temperature of T_s = 1350 °C, which is about 150 K higher compared to the temperature routinely achieved in the planetary system (T_s ~ 1200 °C). Growth rates in the range of ~1.7 μm/h were used in the CCS reactor, applying a showerhead gap of 7 mm. In the planetary reactor, the growth rates are limited to about 1.1 μm/h due to a stronger tendency for gas-phase pre-reactions and a resulting loss of TMAl at the growth surface. All layers investigated are between 0.7 μm and 0.9 μm thick. High-temperature annealing up to a temperature of 1700 °C for 3 h was done in an N_2-purged oven at atmospheric pressure with face-to-face surface stabilization.

A high-resolution x-ray diffractometer (Malvern-Panalytical X'Pert MRD) with Cu-K_α radiation was employed to evaluate the structural parameters of the III-nitride layers. Estimation of structural defects such as a-type (edge) and (a + c)-type (mixed edge and screw component) dislocations from the characteristic broadening of symmetric and asymmetric Bragg reflections has been adapted from Ref. 10.

An atomic force microscopy (AFM) system (Bruker Dimension Edge) was employed to characterize the surface morphology. Transmission electron microscopy (TEM) was done in an aberration-corrected FEI Titan 80-300 operated at 300 kV. Diffraction contrast micrographs were taken in the dark-field mode using the ⟨11-20⟩ and ⟨0002⟩ g-vectors to distinguish a-type, c-type, and (a + c)-type threading dislocations (TDs). Secondary ion mass spectrometry (SIMS) measurements were performed using a CAMECA IMS-4fE6 with a Cs^+ primary beam at RTG Mikroanalyse GmbH Berlin.

AFM (1 × 1 μm^2) topograms of the surface morphology in the as-grown state and after HTA are shown in Fig. 1. The characteristic features of the as-grown surface are pits (holes) of irregular shape with a density between 10^5 cm^{-2} and 10^9 cm^{-2}. Particularly, for thinner layers, these pits are arranged along step edges,[3] which points to the model of growth suppression at oxygen-terminated step edges as proposed by Nakajima *et al.*[4] In addition, interfacial dislocations along the step edges of the SiC substrate have been associated with surface pits.[11] The fact that the pits are formed on the SiC surface at the beginning of growth is confirmed by TEM measurements showing dislocations that open up into nanotubes as well as dislocation bunches below the v-shaped surface pits [Fig. 3(c)].

High-temperature treatment at 1700 °C for 3 h results in the removal of these pits [Fig. 1(b)] without changing the step-terrace structure of the surface. On the other hand, AlN layers grown at 1350 °C do not show pits already after growth (AFM view graph not shown here). In that case, either surface contamination with O is reduced or the increased adatom mobility provides a sufficient lateral growth rate to close pits during layer growth.[12]

Figure 2 shows the change of XRD peak broadening of the skew-symmetric 302 reflection upon annealing of 0.8 μm thin AlN/4H–SiC films in comparison to AlN grown on c-sapphire. The sample grown at 1200 °C has an as-grown FWHM value in the order of 1350 arc sec, which corresponds to an edge dislocation (a-type and a + c type) density in the order of 1 × 10^{10} cm^{-2}. While this

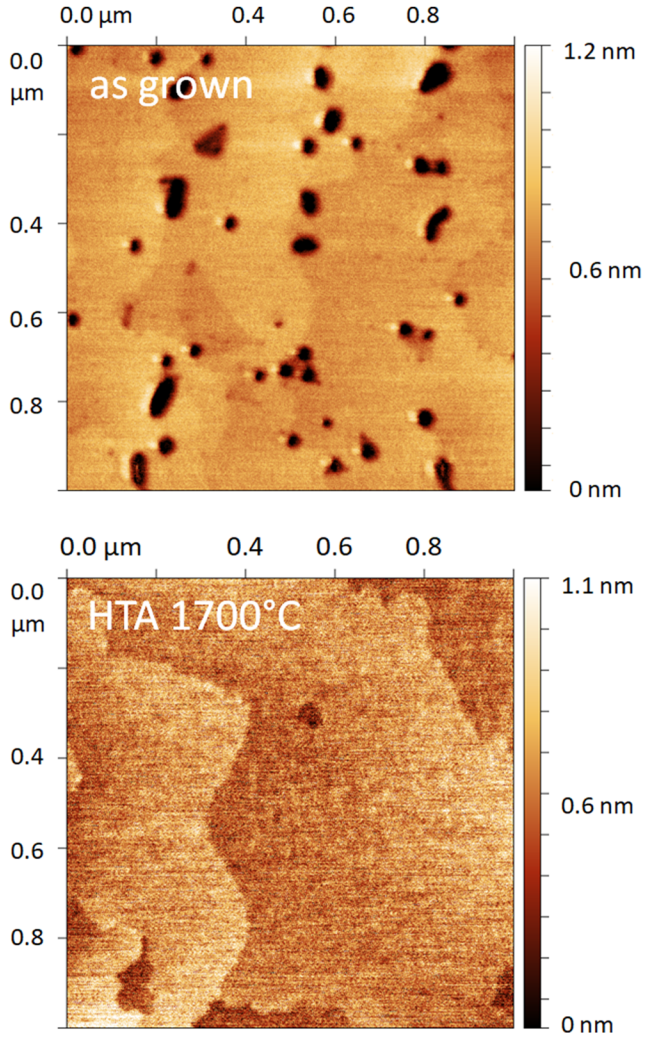

FIG. 1. 1 × 1 μm^2 AFM micrographs for an as-grown AlN film and after HT annealing. RMS roughness values are 0.8 nm (as-grown) and 0.2 nm (HTA).

value does not change up to an annealing temperature of 1500 °C, a remarkable reduction is already observed for high-temperature annealing at 1600 °C. The sample annealed at 1700 °C exhibits a FWHM value as low as 400 arc sec corresponding to an edge dislocation density of about 1 × 10^9 cm^{-2}. The improvement in structural quality with annealing temperature compares well with similar films grown on c-plane sapphire (Fig. 2). These results confirm that the mechanism of dislocation annihilation works on both substrate materials.

As shown in Fig. 2, the FWHM value of the AlN layer grown at 1350 °C in the CCS reactor reduces only marginally with the HTA treatment. Here, already the as-grown sample has a FWHM value below 600 arc sec corresponding to an edge dislocation density of about 2 × 10^9 cm^{-2}. This implies that the initial defect state is an important parameter for the thermally induced dislocation reduction. Accordingly, the more pronounced reduction of TDD of

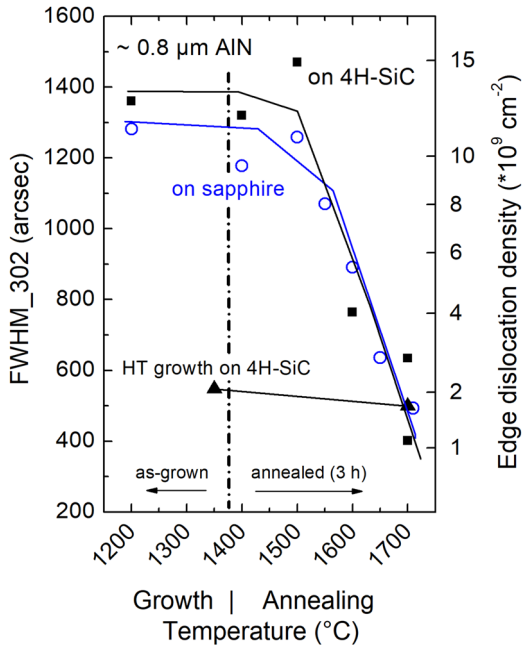

FIG. 2. FWHM values of XRD rocking curve measurements of the AlN (302) reflex as a function of annealing temperature. Right-hand axis shows the derived edge dislocation density.

sputtered AlN films[8,9] can be assigned to the very high defect density of the non-annealed samples.

The annihilation and dissociation of dislocations and nanotubes during annealing is accompanied by a slight reduction of the a-lattice constant as measured by HRXRD (from a_{ag} = 0.3116 nm to a_{HTA} = 0.3114 nm). Correspondingly, the c lattice constant increases slightly from c_{ag} = 0.4977 nm to c_{HTA} = 0.4979 nm. The c and a values of the HTA samples are close to the published values for the fully relaxed bulk material (a_{AlN} = 0.3112 nm, c_{AlN} = 0.4982 nm). This shows that the compressive strain introduced during growth as measured by *in situ* curvature sensing is completely relieved during cool-down due to a slightly lower thermal expansion coefficient of 4H–SiC compared to AlN.[6] In fact, the measured "a" lattice constants point to a slight tensile strain in the AlN film, which is relaxed by high-temperature annealing. This finding is in contrast to AlN films grown on c-plane sapphire, which are under strong compressive strain at room temperature, which even increases after HTA.[9] Here, the low thermal expansion mismatch between AlN and 4H–SiC in comparison to the AlN-sapphire material system is a major advantage.

To further investigate the microstructure of AlN films grown on 4H–SiC, cross-sectional TEM measurements were conducted. Figure 3 compares the as-grown (left side) and annealed (right side) material applying two diffraction conditions. TD densities were estimated using the cross-sectional measurements and the evaluated foil thickness by applying tilted sample measurements.

The density of a-type and (a + c) mixed-type dislocations reduces from 1.2 × 10^{10} cm^{-2} to 8 × 10^{8} cm^{-2} after high-temperature annealing [Fig. 3(b)]. These values show a good agreement with the estimation from XRD (Fig. 2) and with published data for HTA-AlN grown on sapphire.[13] Furthermore, the densities of c-type and (a + c) mixed dislocations are reduced by one order of magnitude (from 1.0 × 10^{9} cm^{-2} to 1 × 10^{8} cm^{-2}) after HTA.

Comparing Figs. 3(c) and 3(d), it can be seen that nanotubes and dislocation bunches dissolved or changed into voids with

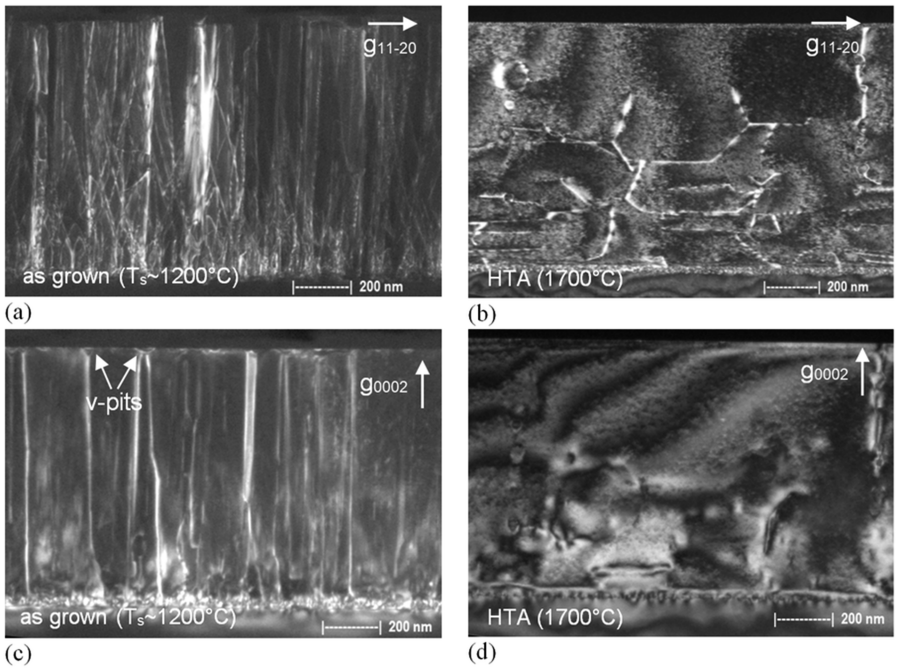

FIG. 3. Cross-sectional dark-field TEM analysis for as-grown [(a) and (c)] and HT-annealed [(b) and (d)] samples. [(a) and (b)] a-Type and (a + c) mixed dislocations are illuminated (g parallel to ⟨11-20⟩). [(c) and (d)] c-Type and (a + c) mixed dislocations are visible (g parallel to ⟨0002⟩). In (c), v-pit termination of nanotubes at the surface is marked.

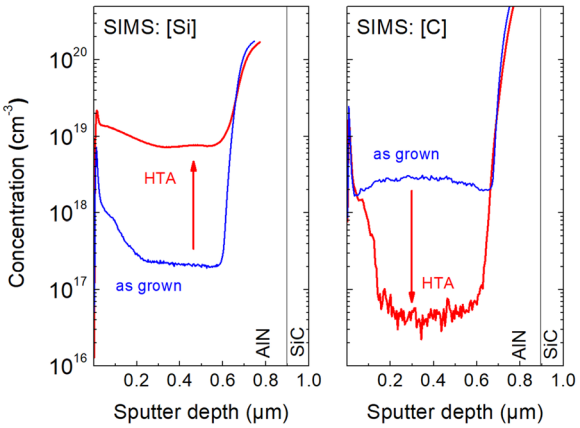

FIG. 4. SIMS depth profiles of Si (left) and C (right) concentration in as-grown and annealed AlN films.

annealing, which confirms the AFM result of a reduced surface pit density.

To check the impurity content of the as-grown and annealed films, the SIMS depth profiles of Si and C were measured (Fig. 4). The Si concentration (Fig. 4, left) increases after annealing from 2×10^{17} cm^{-3} to 8×10^{18} cm^{-3} most likely driven by in-diffusion of Si from the SiC substrate. It should be noted that the true diffusion profile at the substrate interface is partly covered by the high Si signal stemming from the SiC matrix element. Interestingly, the C concentration (Fig. 4, right) reduces by nearly two orders of magnitude from 3×10^{18} cm^{-3} to 4×10^{16} cm^{-3} after HTA. This somewhat unexpected behavior has been validated with two independent samples. Obviously, the in-diffusion of carbon from the substrate is negligible compared to some efficient process of carbon removal. Published reports of high-temperature annealing of AlN/c-sapphire in an N_2–CO atmosphere demonstrated an increase in C concentration.[14] In our case, the annealing atmosphere was only N_2; therefore, no C incorporation from the gas atmosphere was expected. On the other hand, it can be speculated that the formation and degassing of CO plays a role in carbon removal. The oxygen concentration as measured by SIMS is in the order of 10^{19} cm^{-3}–10^{20} cm^{-3}. However, we have strong indications that the SIMS measurement of O concentration in AlN layers with a high density of pits is impaired by surface-related O and does not reflect the amount of oxygen incorporated during growth. The surface of these layers is strongly enlarged by the pits and oxygen is well known to bond to Al surface sites.

To sum up, high-temperature annealing considerably improves the structural quality of MOVPE-grown AlN layers on 4H–SiC. This effect is comparable to AlN films grown on sapphire but seems to be dependent on the initial defect density. Interestingly, the HTA process triggers the removal of carbon impurities in the layer while an in-diffusion of silicon from the substrate is observed. A related impact on AlN breakdown strength needs to be investigated; however, AlN overgrowth keeping the low defect density after HTA while reducing the Si content at the same time seems to be feasible.

This work was partly funded by the German Federal Ministry of Education and Research under Project Reference No. 16FMD02 [Research Fab Microelectronics Germany (FMD)]. We thank O. Fink for technical assistance in operating the MOVPE machine. The publication of this article was funded by the Open Access Fund of the Leibniz Association.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and from the corresponding author upon reasonable request.

REFERENCES

[1] A. G. Baca, A. M. Armstrong, B. A. Klein, A. A. Allerman, E. A. Douglas, and R. J. Kaplar, J. Vac. Sci. Technol., A **38**, 020803 (2020).
[2] A. Hickman, R. Chaudhuri, S. J. Bader, K. Nomoto, K. Lee, H. G. Xing, and D. Jena, IEEE Electron Device Lett. **40**, 1293 (2019).
[3] E. Cho, A. Mogilatenko, F. Brunner, E. Richter, and M. Weyers, J. Cryst. Growth **371**, 45 (2013).
[4] A. Nakajima, Y. Furukawa, S. Koga, and H. Yonezu, J. Cryst. Growth **265**, 351 (2004).
[5] M. Imura, H. Sugimura, N. Okada, M. Iwaya, S. Kamiyama, H. Amano, I. Akasaki, and A. Bandoh, J. Cryst. Growth **310**, 2308 (2008).
[6] C. J. Zollner, A. Almogbel, Y. Yao, B. K. Saifaddin, F. Wu, M. Iza, S. P. DenBaars, J. S. Speck, and S. Nakamura, Appl. Phys. Lett. **115**, 161101 (2019).
[7] J.-T. Chen, J. Bergsten, J. Lu, E. Janzén, M. Thorsell, L. Hultman, N. Rorsman, and O. Kordina, Appl. Phys. Lett. **113**, 041605 (2018).
[8] K. Uesugi, Y. Hayashi, K. Shojiki, S. Xiao, K. Nagamatsu, H. Yoshida, and H. Miyake, J. Cryst. Growth **510**, 13 (2019).
[9] H. Miyake, C.-H. Lin, K. Tokoro, and K. Hiramatsu, J. Cryst. Growth **456**, 155 (2016).
[10] T. Metzger, R. Höpler, O. Ambacher, M. Stutzmann, M. Albrecht, and H. P. Strunk, Philos. Mag. A **77**, 1013 (1998).
[11] H. Okumura, T. Kimoto, and J. Suda, Appl. Phys. Lett. **105**, 071603 (2014).
[12] F. Brunner, H. Protzmann, M. Heuken, A. Knauer, M. Weyers, and M. Kneissl, Phys. Status Solidi C **5**, 1799 (2008).
[13] N. Susilo, S. Hagedorn, D. Jaeger, H. Miyake, U. Zeimer, C. Reich, B. Neuschulz, L. Sulmoni, M. Guttmann, F. Mehnke, C. Kuhn, T. Wernicke, M. Weyers, and M. Kneissl, Appl. Phys. Lett. **112**, 041110 (2018).
[14] H. Fukuyama, H. Miyake, G. Nishio, S. Suzuki, and K. Hiramatsu, Jpn. J. Appl. Phys., Part 2 **55**, 05FL02 (2016).