Plasma-assisted molecular beam epitaxy of NiO on GaN(00.1)

Cite as: J. Appl. Phys. 127, 015306 (2020); https://doi.org/10.1063/1.5129881
Submitted: 04 October 2019. Accepted: 16 December 2019. Published Online: 06 January 2020

Melanie Budde, Thilo Remmele, Carsten Tschammer, Johannes Feldl, Philipp Franz, Jonas Lähnemann, Zongzhe Cheng, Michael Hanke, Manfred Ramsteiner, Martin Albrecht, and Oliver Bierwagen
Plasma-assisted molecular beam epitaxy of NiO on GaN(00.1)

Cite as: J. Appl. Phys. 127, 015306 (2020); doi: 10.1063/1.5129881
Submitted: 4 October 2019 · Accepted: 16 December 2019 · Published Online: 6 January 2020

Melanie Budde,1,a) Thilo Remmele,2 Carsten Tschammer,1 Johannes Feldl,1 Philipp Franz,3 Jonas Lähnemann,1, Zongzhe Cheng,1 Michael Hanke,1 Manfred Ramsteiner,1 Martin Albrecht,2 and Oliver Bierwagen1,b)

AFFILIATIONS
1Paul-Drude-Institut für Festkörperelektronik, Leibniz-Institut im Forschungsverbund Berlin e.V., Hausvogteiplatz 5-7, 10117 Berlin, Germany
2Leibniz-Institut für Kristallzüchtung, Max-Born-Str. 2, 12489 Berlin, Germany

a)Electronic mail: budde@pdi-berlin.de
b)Electronic mail: bierwagen@pdi-berlin.de

ABSTRACT
The growth of NiO on GaN(00.1) substrates by plasma-assisted molecular beam epitaxy under oxygen-rich conditions was investigated at growth temperatures between 100 °C and 850 °C. Epitaxial growth of NiO(111) with two rotational domains, with epitaxial relation NiO(1\(\frac{1}{2}2\)10) \parallel GaN(110) and NiO(10\(\frac{1}{2}2\)1) \parallel GaN(110), was observed by X-ray diffraction and confirmed by in situ reflection high-energy electron diffraction as well as transmission electron microscopy (TEM) and electron backscatter diffraction. With respect to the high lattice mismatch of 8.1% and a measured low residual tensile layer strain, growth by lattice matching epitaxy or domain-matching epitaxy is discussed. The morphology measured by atomic force microscopy showed a grainy surface, probably arising from the growth by columnar rotational domains visible in TEM micrographs. The domain sizes measured by AFM and TEM increase with the growth temperature, indicating an increasing surface diffusion length. Growth at 850 °C, however, involved local decomposition of the GaN substrate that leads to an interfacial \(\beta\)-Ga\(_2\)O\(_3\) \(\parallel 201\) layer and a high NiO surface roughness. Raman measurements of the quasiforbidden one-phonon peak indicate increasing layer quality (decreasing defect density) with increasing growth temperature.

Published under license by AIP Publishing. https://doi.org/10.1063/1.5129881

I. INTRODUCTION

The transparent wide bandgap (3.7 eV) 1 material nickel oxide (NiO) crystallizes in the rock salt crystal structure. Stoichiometric NiO is considered insulating, whereas unintentional \(p\)-type conductivity is induced by Ni vacancies formed under certain growth conditions. Intentional Li-doping has been shown to create \(p\)-type conductivity in a controlled way. NiO is antiferromagnetic with a Néel temperature of about 525 K, below which the crystal structure is slightly distorted with angles of \(\geq 90.1^\circ\) instead of 90°. However, this minor deviation from the perfect cubic structure can be neglected for our study.

Its properties make NiO an interesting material for many GaN-based applications: Heterojunction \(p\)-NiO/\(n\)-GaN diodes and normally-off operating heterojunction field-effect transistors (HFETs) have been investigated based on the equivalent work function of NiO and GaN. Furthermore, NiO has been used as a stable hydrogen reduction catalyst to enhance the efficiency of GaN-based water splitting and protect the GaN from decomposition during this process. Finally, NiO is a potential antiferromagnetic pinning layer in (GaN-based) spintronic devices.

So far, NiO on GaN has been grown by electron-beam evaporation, RF magnetron sputtering, or metal organic chemical vapor deposition (MOCVD). In addition, growth by MOCVD on AlGaN is reported, reducing the lattice mismatch from about 8% to 5%. While plasma-assisted molecular beam epitaxy (PA-MBE) is a well-suited method to grow high-quality oxide layers and interfaces, this method has not been reported for the growth of NiO on GaN. We have previously reported on the PA-MBE of NiO on MgO substrates for a wide range of growth parameters (temperature, oxygen flux, etc.).
In the present study, we investigate the properties of NiO thin films grown by PA-MBE on GaN(00.1) substrates as a function of growth temperature. In particular, the epitaxial relationship between the two materials, the accommodation of the lattice mismatch, and the effect of the growth temperature on layer and interface quality are analyzed. Different methods were used to measure the structural properties of the films, allowing one to compare their advantages and disadvantages.

II. EXPERIMENT

NiO was grown by PA-MBE on 2-in. (00.1)-oriented gallium nitride templates manufactured by “Kyma Technologies.” The templates consist of a sapphire substrate (α-Al₂O₃), an AlN buffer, and a GaN layer. Substrate heating was improved by sputter-coated Ti on the rough backside to absorb the radiation from the heating filament. Five substrate heater temperatures, measured by a thermocouple between the substrate and heating filament (100 °C, 300 °C, 500 °C, 700 °C, and 850 °C), were used to investigate their influence on the NiO layer. Throughout this report, the corresponding samples are named S100, S300, S500, S700, and S850, respectively. Ni was sublimed from an effusion cell at a temperature of 1380 °C, since staying below the melting point of Ni (1455 °C) is important to protect the Al₂O₃ crucible of the effusion cell from breaking upon resolidification of Ni. For the resulting beam equivalent pressure (BEP), which is proportional to the particle flux, was measured by a nude filament ion gauge positioned at the heating filament. Five substrate heater temperatures, measured by a thermocouple between the substrate and heating filament (100 °C, 300 °C, 500 °C, 700 °C, and 850 °C), were used to investigate their influence on the NiO layer. Throughout this report, the corresponding samples are named S100, S300, S500, S700, and S850, respectively. Ni was sublimed from an effusion cell at a temperature of 1380 °C, since staying below the melting point of Ni (1455 °C) is important to protect the Al₂O₃ crucible of the effusion cell from breaking upon resolidification of Ni. For the resulting beam equivalent pressure (BEP), which is proportional to the particle flux, was measured by a nude filament ion gauge positioned at the substrate location and then removed before growth. For 1380 °C, a Ni BEP of about 8.5 × 10⁻⁹ mbar was measured for all growth runs. Activated oxygen was provided by passing 0.5 standard cubic centimeters per minute (sccm) of O₂ through an RF-plasma source run at an RF-power of 300 W, resulting in an oxygen BEP of 1.5 × 10⁻⁶ mbar and oxygen-rich growth conditions. In our study on MgO, we found plasma activated oxygen to yield significantly smoother NiO layers than molecular oxygen. For growth, the Ni shutter was opened first and oxygen was introduced after 60 s. The total growth time was 5000 s for all samples. As a comparison, one sample without Ni preflow, named S500*, was grown at 500 °C. During growth, the crystallinity and morphology was assessed in situ by reflection high-energy electron diffraction (RHEED).

After growth, different ex situ methods were used to investigate the layer properties. X-ray diffraction (XRD) measurements in a 4-circle lab-diffractometer using Cu Kα radiation were conducted to investigate the epitaxial relationship between substrate and layer by a combination of symmetric on-axis 2θ – ω scans (out-of-plane orientation) and a skew symmetric off-axis -scan (in-plane relationship). The Laue oscillations visible in the symmetric on-axis 2θ – ω scan around the NiO peak are used to determine the layer thickness. In addition, synchrotron-based XRD 2θ – ω scans at grazing-incidence, measured at the PHARAO facility as described in Ref. 15 as described in Ref. 19, were used to extract the in-plane lattice parameter from the peak position of the NiO(220) reflection referenced to that of the GaN(11.0) reflection.

The film domain structure and orientation was investigated by electron backscatter diffraction (EBSD) measurements in a scanning electron microscope fitted with an EDAX-TSL EBSD detector using an acceleration voltage of 15 kV. Atomic force microscopy (AFM) in the peak force tapping mode using a Bruker “Dimension edge” with the “ScanAsyst” technology was used to analyze the surface morphology and domain size. Cross-sectional transmission electron microscopy (TEM) was used for detailed investigations of the domain structure of the NiO layers, the interface to the GaN substrate, and the strain state of the layers. For this purpose, cross-section samples were prepared by polishing on diamond lapping films, followed by Ar ion milling with 4 kV down to 200 V acceleration voltage to minimize amorphous surface layers. Finally, quality investigations were performed using the forbidden one-phonon-Raman peak as we have previously described for NiO on MgO. For this purpose, Raman spectra were recorded at room temperature in backscattering geometry using the 325 nm line of a Cd-He ion laser.

III. RESULTS AND DISCUSSION

A. Epitaxial relation

Figure 1(a) shows the on-axis 2θ – ω scan of sample S500 (grown at 500 °C) for 2θ between 15° and 100°. The presence of a strong NiO(111) peak and the absence of other NiO peaks for this and all other investigated samples [shown in Fig. 1(b)] indicate the NiO out-of-plane direction to be [111] and the corresponding out-of-plane epitaxial relation

\[ \text{NiO}(111) \parallel \text{GaN}(00.1). \]

(1)

The other (GaN, AlN, and Al₂O₃) peaks can be assigned to the template structure of the substrate.
Distinct Laue oscillations are visible, which suggest a sufficiently smooth interface and surface for all samples. However, for S850, a strong reduction of the oscillations indicates a rougher interface at this growth temperature. Compared to the (111) reflex of bulk NiO ($d_{NiO}^{bulk} = 0.4176$ nm), the NiO(111) peak of the S100 sample is shifted to lower angles, which indicates tensile strain with a lattice constant around $0.419$ nm. Compressive out-of-plane strain is expected due to the Poisson effect and the higher lattice constant of the substrate surface lattice. The higher lattice constant for S100 could arise, for example, from defects or the low grain size (see below). The peaks of the samples grown at higher temperatures are shifted to higher angles, indicative of compressive strain with an out-of-plane lattice constant down to $0.416$ nm. The in-plane epitaxial relationship of the GaN/NiO samples was determined by Φ-scans of the two skew symmetric reflections GaN(10.1) and NiO(002). The result for S500, representing all samples, is shown in Fig. 2. The GaN(10.1) reflection shows a sixfold rotational symmetry as expected from the hexagonal wurtzite-structure. However, the NiO(002) peak also shows a sixfold rotational symmetry despite the expected threefold one of the (111)-oriented rock salt structure. This observation indicates an epitaxial growth with the formation of two domains rotated by $60°$ with respect to each other. Similar intensities of the two domains indicate a homogeneous distribution of both.

As the peaks of layer and substrate are at the same Φ angles, the following in-plane epitaxial relationship of both NiO domains, with respect to the GaN substrate, can be defined:

\[ \text{NiO}(1\bar{1}0) \parallel \text{GaN}(1\bar{1}0) \] (domain 1),  
\[ \text{NiO}(10\bar{1}) \parallel \text{GaN}(1\bar{1}0) \] (domain 2).

In fact, the two domains could already be identified during growth by the spotty RHEED patterns arising from simultaneous transmission diffraction of the electron beam through the asperities of multiple domains. The superposition of the diffraction spots of the two domains, taken along the GaN(11.0) azimuthal direction, is shown in Fig. 3. The patterns also indicate a two domain growth of NiO and are marked by green and blue circles.

A schematic cross section illustrating the two domains of NiO on GaN can be seen in Fig. 4. For the diagram a N-terminated GaN surface was assumed, since the NiO layer should start with Ni due to the oxygen-free start of our growth process. This growth of two rotational domains is expected as a result of the different rotational symmetries of substrate (sixfold) and layer (threefold) and has also been observed for the growth of MgO(111) on ZnO(00.1) by Saitoh et al. or for NiO(111) on Al₂O₃(001) by Lee et al.

The theoretical in-plane mismatch between NiO and GaN can be derived from the basis vectors $a_{Ni} = 2.95$ Å and $a_{N} = 3.19$ Å of the two domains, taken along the GaN(11.0) azimuthal direction, is shown in Fig. 3. The patterns also indicate a two domain growth of NiO and are marked by green and blue circles.

FIG. 2. XRD Φ-scan for S500 of tilted lattice planes as indicated in the legend.

FIG. 3. RHEED image of a GaN/NiO sample. The domains for the different diffraction spots are defined using the diffraction pattern simulation of "Web-EMAPS". The patterns also indicate a two domain growth of NiO and are marked by green and blue circles.

FIG. 4. Diagram of the growth of NiO on GaN by two domains. The resulting domain boundary is marked. The atoms are marked by colors, where O is red, Ni is gray, N is blue, and gallium is green.
the NiO and GaN surface unit cells. Thus, the in-plane strain for lattice matching epitaxy (LME) calculated by\cite{27}

\[ \epsilon_{\text{LME}} = \frac{a_{\text{substrate}}}{a_{\text{layer}}} - 1 \] (4)

would result in a tensile strain of $+8.1\%$, which is in the critical range ($7\%–8\%$) for LME.\cite{27} LME describes a one-to-one matching of lattices in pseudomorphic growth. At a critical thickness, dislocations formed at the growth surface can glide to the interface to relax the layer. For a higher mismatch ($>7\%–8\%$), the growth mechanism “domain matching epitaxy” (DME) has been proposed by Narayan and Larson,\cite{27} which describes the growth by coinciding super cells (SCs) of the surface unit cells of the film and substrate. SCs are created by multiplying the surface unit cell (SUC) to create a better matching. For DME, the residual strain is calculated by\cite{27}

\[ \epsilon_{\text{DME}} = \frac{n \cdot |a_{\text{substrate}}|}{m \cdot |a_{\text{layer}}|} - 1. \] (5)

Here, $m$ is the number of Ni SUCs, which are needed for the SC, and $n$ is the number of needed N SUCs. [To ensure tensile strain to be positive we changed the definitions Eqs. (4) and (5) compared to Ref. 27.]

The lowest residual tensile strain between NiO and GaN can be achieved for $m = 14$ and $n = 13$, leading to a strain of $0.41\%$. Thus, a super cell is approximately 4 nm large and can be described by

\[
\begin{align*}
{a}_{SCN} &= 13 \cdot {a}_N, \\
{b}_{SCN} &= 13 \cdot {b}_N.
\end{align*}
\]

Here, $a_{SC}$ and $b_{SC}$ are the vectors of the created SC. An in-plane schematic of the created SC ($m = 14$, $n = 13$) is shown in Fig. 5(green). The same SC can be created by a $60^\circ$ rotated Ni SUC, which only leads to a small difference in the definition of the SC but creates the same misfit of $0.41\%$ (red). The advantage of DME growth is that the misfit dislocation network is established so early in the growth that no threading arms are generated in the layer above. Layers grown by LME, in contrast, typically possess threading arms of the dislocation halfloops needed for establishing misfit dislocation segments at the interface.\cite{27}

1. Transmission electron microscopy

Cross-sectional TEM of S100, S700, and S850 is used to investigate the possible creation of interfacial oxides, the grain sizes, and the epitaxial relationship between substrates and layers. Mainly, columnar grains with NiO(110) || GaN[11.0] are found for all growth temperatures, confirming the orientations observed in XRD [see Eqs. (2) and (3)] and RHEED. The existence of the two different domains is confirmed by the observation of mirrored [002] directions for the grains illustrated by arrows in Fig. 6. Occasionally, NiO(112) || GaN[11.0] grains can also be seen in the TEM images. This orientation is still consistent with NiO(111) growth and a rotation angle of $30^\circ$ with respect to the other grains. The absence of any NiO(002) reflections between the substrate reflections in the $\Phi$-scan (cf. Fig. 2), however, suggests only a minor fraction of those $30^\circ$ rotated NiO grains.

2. Electron backscatter diffraction

Alternatively, EBSD measurements confirm the (111) out-of-plane direction of the NiO film and the presence of twin domains rotated by $60^\circ$. The probing depth of EBSD is $\approx 20$ nm, and for thinner films, the GaN Kikuchi pattern is superimposed on the NiO pattern. Therefore, we chose the thickest NiO layer S300 ($d_{XRD} = 20.9$ nm) for the EBSD investigation (cf. Table II).

![Fig. 5. In-plane schematic of the two possible super cells to achieve a misfit strain of only 0.41% between GaN and NiO by domain matching epitaxy. Ni atoms are marked in gray, and the N atoms in blue. The same coloring is used for the SUCs.](image)

![Fig. 6. Cross-sectional TEM image of S700 showing the two rotational NiO(110) || GaN[11.0] domains. The different rotations are indicated by the different (002) directions. A red dashed line indicates the interface between GaN and NiO.](image)
Examples of Kikuchi patterns recorded for the two twin orientations are given in Fig. 7. The Kikuchi bands used to index the pattern are marked by colored lines. As expected for crystal twins, both patterns share several of the main bands but also contain distinctive bands indicative of the respective in-plane orientation. Nevertheless, each of the patterns also contains weak bands from the opposite direction as highlighted by the dashed lines in Fig. 7. In fact, the domain size derived from the transmission electron micrographs (see Table II) between 10 and 25 nm, depending on the growth temperature, is on the order of the lateral resolution of the EBSD measurements, which explains the overlapping of the Kikuchi patterns. A further consequence of this small grain size is that maps of the in-plane orientation obtained from an automatic indexing of the Kikuchi patterns recorded when stepping the electron beam over the sample surface lead to a misrepresentation of the domain size as discussed in the supplementary material.

B. Strain

The in-plane lattice parameter of the NiO films in S100–S700, measured by grazing-incidence XRD at room temperature, was used to calculate the in-plane strain $\varepsilon_{\parallel}(RT)$ in these films. The results are shown in Table I. Besides the in-plane strain at growth temperature $\varepsilon_{\parallel}(T_g)$, the calculated strain also includes the thermal strain $\varepsilon_T$ arising during cooldown to room temperature after sample growth as a result of the different thermal expansions of GaN and NiO $[\varepsilon_{\parallel}(RT) = \varepsilon_{\parallel}(T_g) + \varepsilon_T]$. Thermal strain can be estimated from the thermal expansion coefficients for the two

| $T_g$ (°C) | $\varepsilon_{\parallel}(RT)$ (%) | $\Delta T$ (K) | $\varepsilon_T$ (%) | $\varepsilon_{\parallel}(T_g)$ (%) |
|------------|-------------------------------|----------------|-------------------|-------------------------------|
| 100        | 0.06                          | −75            | 0.02              | 0.04                          |
| 300        | 0.59                          | −275           | 0.06              | 0.53                          |
| 500        | 0.42                          | −475           | 0.11              | 0.31                          |
| 700        | 0.47                          | −675           | 0.16              | 0.31                          |

The resulting values for $\Delta T$ and $\varepsilon_T$ can be found in Table I. Sample S850 was excluded from strain evaluation, since the decomposition of the GaN substrate and the interfacial oxide (see Sec. III E) prevents a meaningful comparison with the other samples. Samples grown between 300 °C and 700 °C show a similar strain $\varepsilon_{\parallel}(T_g)$ for their growth temperature. The values are comparable with the residual strain by DME growth of 0.41%. However, since relaxation is a gradual process, which can lead to small residual strain even for thicknesses above the critical thickness, LME cannot be excluded. S100 shows a much lower in-plane strain, indicating an almost relaxed layer. This could be created by a change in the relaxed lattice constant of the layer due to the higher defect density, as it was already mentioned for the out-of-plane strain (see Sec. III A) and will be further discussed within the Raman results.

From high-resolution transmission electron microscopy (HRTEM) images, the strain can be estimated by the geometric phase analysis.35 In particular, dislocations have a characteristically strong and localized bright-dark contrast at their cores originating from the change from high compressive to high tensile strain. Taking a look at the strain map of S700 by TEM, a clear misfit dislocation network can be seen at the interface (see Fig. 8), indicating...
an almost relaxed NiO layer which appears darker due to the narrower spacing of the NiO lattice compared to GaN used as reference. The sample S100 shows the same network (see Fig. S2 in the supplementary material). In the GaN [11.0] projection, for every 13th GaN(11.0) plane, an additional NiO(110) plane is expected in relaxed NiO. Therefore, about every 2 nm, a dislocation contrast in the geometric phase analysis of the HRTEM pattern occurs. While the GaN(11.0) planes are parallel to the NiO(110) planes, there is no low index lattice plane in the NiO layer parallel to the GaN(11.0) planes. Instead, one can see a continuation of GaN(11.1) planes by NiO(111) and NiO(002) planes with an inclination of around 6.5° for relaxed NiO(111) on GaN(00.1). In this case, NiO will have an additional (111) plane compared to the number of GaN(11.1) planes around every 3 nm, when viewed in the GaN[11.0] direction, respectively, for the NiO(002) plane. Again, the strain analysis shows dislocation contrasts with this spacing at the interface. One should mention that for such narrowspaced misfit dislocation networks, the characterization of the dislocation types is ambiguous in wurtzite materials, especially with dislocations running transversely to the projection direction causing a distortion of the high resolution pattern at the interface, which hinders a direct interpretation of the pattern in our case. However, the dislocation network can either occur due to relaxation above the critical thickness or as a result of the growth by DME. The small domain sizes make it impossible to differentiate between the two modes by analyzing the threading dislocation density.

C. Surface morphology

AFM images of all samples and a clean GaN substrate as reference are shown in Fig. 9. The AFM images of the NiO layers show a morphology defined by islands. Their lateral size (SAFM), evaluated with the program "Gwyddion" by taking the average lateral size of ten islands, can be found in Table II together with the layer thicknesses measured by XRD (dXRD). In addition, the root mean square roughness (RMS), determined for 0.4 × 0.4 μm² images, is given. The film roughness of S700 is larger than that of the GaN substrate (≈0.3 nm). A clear difference in the topology can be seen for S850, showing drastically enlarged islands. Film thickness and island size were also extracted from cross-sectional TEM images as shown in Table II. The TEM image of S700 (see Fig. 6) clearly shows a columnar domain growth of the layer, correlating the formation of islands with the formation of the two rotational domains. The thickness dTEM is about 2.5 nm thicker than the thickness dXRD calculated from the Laue oscillation seen in the 2θ–ω scans (see Fig. 1). However, dXRD depends strongly on the crystal quality and includes planes with similar distances, which often leads to an underestimation of the thickness (e.g., strained interface region). The thickness of S850 could not be measured by XRD as a result of the reduced oscillation intensity. The TEM images show a variation of the thickness by ±2 nm over the sample due to roughness of surface and interface.

The domain sizes measured by TEM are much smaller than the islands measured by AFM, likely related to the convolution with the tip shape and morphology. Therefore, the AFM cannot resolve all trenches between domains, which leads to the apparent larger island size than domain size. However, AFM (surface islands) and TEM (domains) measurements show a similar trend for both methods, i.e., an increase of the domain/island size with increasing growth temperature. The sample S850 has the biggest domains (cf. Table II). The increasing domain size indicates a higher adatom surface diffusion length consistent with a higher growth temperature, as it was also observed for the growth on MgO(100). The main difference is the lateral island size. For S100–S500, the islands are smaller compared to those of S700. A drastic increase is found for S850.

### Table II. Calculated layer thicknesses from oscillation fringes in XRD on-axis 2θ–ω scans (dXRD), average island sizes (SAFM), and roughness (RMS) measured from AFM images. Results for NiO layer thickness (dTEM) and island size (STEM) from TEM images in comparison for all growth temperatures. In addition, full width at half maximum (Δω) from a Gaussian fit for all temperatures measured at the NiO (111) XRD peak.

| Tg (°C) | dXRD (nm) | dTEM (nm) | SAFM (nm) | STEM (nm) | RMS (nm) | Δω (deg) |
|--------|-----------|-----------|-----------|-----------|----------|----------|
| 100    | 17.0      | 19.5      | 35        | 10–20     | 0.35     | 0.153    |
| 300    | 20.9      | 30        | 0.93      | 0.165     |
| 500    | 17.2      | 35        | 1.30      | 0.166     |
| 500*   | 25.2      | 25.0      | 50        | 10–30     | 2.02     | 0.152    |
| 700    | 17.4      | 20.0      | 45        | 20–25     | 1.11     | 0.163    |
| 850    | 15.0      | 165       | ~120      | 2.38      | 0.722    |
D. Raman quality metrics

Figure 10 displays room temperature Raman spectra of all NiO layers excited at 3.81 eV, nearly resonant with the bandgap of NiO. The spectra exhibit peaks due to first-order (580 cm$^{-1}$) and second-order (730, 900, and 1130 cm$^{-1}$) scattering by optical phonons in NiO. Superimposed on these spectral features, the $E_2$ and $A_1$ Raman peaks of the GaN substrate are detected at 570 and 735 cm$^{-1}$, respectively. Since first-order Raman scattering by optical phonons is forbidden for the rock salt structure, the ratio between the intensities of the first-order peak at 580 cm$^{-1}$ (1P) and the second-order peak at 1130 cm$^{-1}$ (2P) from NiO has been established as a quality metrics ($Q$) for NiO films on MgO(100),\textsuperscript{15}

$$Q = \frac{I_{1P}}{I_{2P}}. \quad (7)$$

A perfect crystal is characterized by a quality index ($Q$) of zero, since $I_{1P} = 0$. The value of $Q$ increases with the density of crystal defects. In the case of NiO, a potentially desired defect could be Ni vacancies to induce $p$-type conductivity.\textsuperscript{16} Since our layers are always insulating as shown on MgO,\textsuperscript{15} the increase in the 1P peak cannot be solely related to Ni vacancies.

Applying this metrics to the NiO layers grown on GaN, we find a reduction of $Q$ with increasing growth temperature (cf. the inset in Fig. 10), indicating a decrease in the density of crystal defects. This trend is consistent with an increasing domain size, meaning a reduction of grain boundaries (see TEM images) and an increased adatom surface diffusion length with the increasing growth temperature. Although the domain size of S850 is relatively large, its quality index is almost the same as that of S700. Probably, the quality of S850 is reduced by the interfacial oxide grown under those conditions (see Sec. III E). This influence can be seen in the FWHM measured by a rocking curve of the NiO(111) peak. S100–S700 show values around 0.16°; S850, however, shows a $\Delta \theta$ of 0.72°. The results and different trends from the two methods show again the higher sensitivity of Raman on the crystal imperfection of a thin layer. As already observed in Ref. 15, XRD ($\omega$/$\omega$) is mainly influenced by the interface structure. Compared to the $Q$ of NiO on MgO(100) (<0.2) and FWHM (0.05°–0.07°) grown under the same conditions, the values are higher for NiO on GaN, which is likely related to the formation of rotational domain grain boundaries on hexagonal GaN. In the case of the cubic MgO(100) substrate, no domains have been observed.\textsuperscript{15} Nevertheless, a high temperature is again beneficial for the growth of a high-quality layer.

E. Interfacial oxide and Ni preflow

During oxide growth, unintentional oxidation of the substrate can lead to an additional interfacial oxide layer at the substrate surface. For example, Tsai et al. have suggested the formation of an insulating Ga$_2$O$_3$ layer during PA-MBE of Sb-doped SnO$_2$ at increased growth temperature as cause for the drastically increased contact resistance to the underlying GaN-based LED structure.\textsuperscript{13} As explained in Sec. II of our study, a layer of Ni was grown in the first minute without oxygen to avoid this problem. The XRD measurements of S100–S700 (cf. Fig. 1) did not show any signature of Ga$_2$O$_3$, nor did the TEM images show an interfacial oxide layer. At the highest investigated growth temperature, 850°C for S850, however, the 2$\theta$–$\omega$ scan (see Fig. 11) shows additional features around 58.38° and 82.52°. These can be assigned to the (603) and (804) reflections of the (201)-oriented $\beta$-Ga$_2$O$_3$—the same orientation that has been observed for intentionally grown $\beta$-Ga$_2$O$_3$ films on GaN(00.1) by Nakagomi et al.\textsuperscript{35} The (201) and (402) peaks are
not visible in our scan. However, the (402) could be hidden under the NiO(111) shoulder. [An additional reflection around 51.6° in S850 could be related to (601) oriented \( \beta \)-Ga\textsubscript{2}O\textsubscript{3}.] TEM images confirm the formation of a \( \approx 10 \) nm – thick, inhomogeneous, interfacial Ga\textsubscript{2}O\textsubscript{3} layer in S850 as shown in Fig. 12. Furthermore, the TEM image shows a local decomposition of the GaN substrate, responsible for a rough GaN and NiO surface.

A reference growth of NiO at 500 °C without initial Ni deposition (S500*) did not show interfacial Ga\textsubscript{2}O\textsubscript{3} in the HRTEM image (see Fig. S2 in the supplementary material) either. These results suggest the formation of an interfacial Ga\textsubscript{2}O\textsubscript{3}-layer to be caused by the decomposition of GaN as a result of elevated growth temperature (and subsequent oxidation of the free Ga) rather than the pure presence of oxygen. Fernández-Garrido et al. have shown a GaN decomposition in vacuum to start at surface temperatures of about 700 °C, which would mean lower growth temperatures of the NiO layer can prevent the formation of interfacial Ga\textsubscript{2}O\textsubscript{3}. Regarding the layer quality, Raman results (cf. Fig. 10), as well as the FWHM (cf. \( \Delta \omega \) in Table II), show similar values compared to S500. The values even indicate a slight enhancement of the quality without a Ni preflow. In particular, the FWHM shows the lowest value of 0.152 comparable to the one of S100. On the other hand, an increase of the roughness and islands size is observed. In summary, besides increased layer roughness neither reduction of the quality nor formation of a Ga\textsubscript{2}O\textsubscript{3} interlayer was found for S500*. Since a Ni preflow is not needed to avoid the oxidation of the GaN substrate and can even lead to surface traps in it,\textsuperscript{27} we do not recommend a Ni preflow as it was used in this study for most samples.

IV. SUMMARY AND CONCLUSIONS

NiO growth by PA-MBE on GaN(00.1) was studied at growth temperatures ranging from 100 °C to 850 °C. XRD measurements of the films showed the formation of epitaxial NiO(111) for all growth temperatures. As expected for the growth of layers with threefold rotational symmetry on a sixfold rotationally symmetric substrate, two types of columnar, 10–25 nm-wide rotational domains, rotated by 60° with respect to each other were identified by XRD, RHEED, TEM, and EBSD. The resulting out-of-plane and in-plane epitaxial relations of cubic NiO on wurzite GaN are NiO(111) || GaN(00.1) and NiO(1 ꞏ T0)( || GaN(1 ꞏ 00) (for domain 1) or NiO(1 ꞏ T0)( || GaN(1 ꞏ 00) (for domain 2). In contrast, on the isostructural cubic MgO(100) substrate, NiO(100) grows without rotational domains, demonstrating the importance of symmetry for epitaxial growth. The layers on GaN are nearly relaxed with an in-plane tensile strain below 1%. TEM confirms layer relaxation at the interface by the formation of a closely-spaced dislocation network. Even though the mismatch between NiO and GaN is 8.1%, a growth by domain-matching-epitaxy can neither be proven nor excluded as the relative small domain sizes hinders an analysis of the threading dislocation densities. A clear formation of interfacial Ga\textsubscript{2}O\textsubscript{3} was found at the highest growth temperature of 850 °C, whereas no Ga\textsubscript{2}O\textsubscript{3} was detected at growth temperatures of 700 °C and below, suggesting thermal decomposition of the GaN substrate as the cause of interfacial Ga\textsubscript{2}O\textsubscript{3} formation rather than the sole exposure of the GaN to oxygen plasma. AFM measurements showed a 3D dominated surface with islands increasing in size with increasing growth temperature. The film grown at 850 °C was significantly rougher than all other films as a result of the inhomogeneous interfacial oxidation of the GaN.

For quality evaluation, the area ratio between the forbidden one-phonon Raman peak and the allowed two-phonon Raman peak was used, indicating the lowest concentration of parity-breaking defects for S700. Compared to our results for NiO grown on isostructural cubic (and almost lattice matched) MgO(100), the quality is drastically reduced, likely due to the domains and related domain boundaries. A frequently used indicator of dislocations is the XRD \( \omega \)-rocking curve of the film peak, which is typically wider for a larger concentration of dislocations due to the increased tilt mosaic they cause.\textsuperscript{36} All investigated films have very similar rocking curve widths with the narrowest ones exhibited by S100 and S300*.

Fernández-Garrido et al.\textsuperscript{36} identified 700 °C as the critical temperature for GaN desorption, giving it as an upper limit for high-quality oxide layers on this substrate. This situation is similar to the growth on MgO, where the onset of magnesium diffusion from the substrate into the NiO film defined an upper limit of the growth temperature.\textsuperscript{15} A lower limit was not found on both substrates, showing epitaxial NiO layers even down to 20 °C for the investigations on MgO. In addition, on GaN, the lowest roughness and XRD \( \omega \)-rocking curve widths were measured for 100 °C, which could be beneficial for devices at the expense of lower grain sizes and higher density of parity-breaking defects.

SUPPLEMENTARY MATERIAL

See the supplementary material for a detailed discussion about the analysis of the EBSD pattern and for TEM images from S100 and S500*.

ACKNOWLEDGMENTS

We would like to thank H.-P. Schönherr for MBE support and O. Brandt and V. Kaganer for helpful discussions. This work was performed in the framework of GraFOx, a Leibniz ScienceCampus...
