Separation of Structural Defects in MOCVD Grown GaN and AlN Films on c-Plane Sapphire by HRXRD

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ABSTRACT

A novel triple-axis diffractometer equipped with a parabolically curved graded multilayer, which replaces the conventional analyzer crystal, is used to characterize structural properties of epitaxial GaN and AlN films grown on c-plane sapphire. From the angular broadening of the symmetric rocking curves, the lateral correlation length and the tilt angle is obtained by two independent methods. Additionally, the measurement of asymmetric reflections yields further information concerning the anisotropic dislocation structure in hexagonal GaN. For AlN, the out-of-plane disorder (tilt) is such small that coherent X-ray scattering from individual crystallites is observed. Despite the poor epitaxial quality with respect to the in-plane orientation (twist), the angular broadening of X-ray rocking curves remains small. The AFM images and the XRD measurements of asymmetric reflections confirm the high degree of the in-plane rotational disorder (twist).

INTRODUCTION

Epitaxial layers of group-III nitrides are most commonly grown on c-plane sapphire Al₂O₃(0001) as substrate material. Although, high dislocation densities, tilted and twisted growth, and small crystallites are well known characteristics of this heteroepitaxial system [1,2], the feasibility of GaN based electronic and optoelectronic devices has been demonstrated in the last years [3-5]. For the characterization of epitaxial layers, the double-crystal X-ray diffractometry is a well established method. However, an application of this measurement technique in the field of group-III nitrides is problematic due to two reasons. Because of the hexagonal symmetry of group-III nitrides, an anisotropic distribution of dislocations is expected and the broadening of the rocking curve is affected by several structural imperfections (wafer bending, mosaicity, heterogeneous strain, small correlation lengths parallel and normal to the substrate surface) causing the intrinsic width of Bragg peaks to broaden. For the analysis of such layers which exhibit a large divergence in the diffracted X-ray beam, a triple-axis diffractometer was developed [6, 7]. This instrument combines a
two-crystal four-reflection (+,-,-,+) monochromator with an analyzer crystal (one, two or three reflections). Thereby, the large acceptance angle of the detector is limited to a few arcsec only. With triple-axis diffractometry it is possible to resolve different contributions to Bragg peak broadening in different directions of the reciprocal space without the drawbacks of a triple-crystal diffractometer (alignment, crystal matching) [6,7] or a system with a slit system as secondary optics (loss in intensity and/or resolution) [8].

In this study, a new technique is proposed to limit the acceptance angle of the detector. The conventional analyzer crystal is replaced by a parabolically curved graded multilayer mirror and a detector slit positioned at the parabola focus. Especially for the analysis of layers exhibiting a poor epitaxial quality, where investigations are time consuming or call for synchrotron radiation, this method has advantages compared to a conventional triple-axis diffractometer equipped with an analyzer crystal.

EXPERIMENTAL

1 μm thick GaN films were grown on c-plane sapphire by MOCVD at a temperature of 950 °C with a 15 nm thick GaN buffer layer using triethylgallium and ammonia. For the deposition of AlN, for which ammonia and tritertiarybutylaluminum were used, the growth temperature was 1050 °C. The AlN films were also grown with a 15 nm thick GaN buffer layer. The layer morphology was investigated by atomic force microscopy (AFM) (Digital Instruments Nanoscope IIIa).

For X-ray diffraction investigations, a high-resolution diffractometer equipped with an incident-beam optics consisting of a parabolically curved graded multilayer mirror [9] and a 2-crystal 8-reflection Ge(022) monochromator in (+,-,+-,+,-,+) geometry was applied. This first mirror acts as a condenser for the divergent X-ray beam emanating from the source (1.5 kW Cu anode, line focus 8 mm × 0.04 mm). With this optical element, parallel beam coupling into the monochromator crystal is obtained resulting in an intensity gain of a factor 6 compared to a system without mirror [9,10]. On the diffracted-beam side, a second parabolically curved graded multilayer was mounted on the 2θ circle in focusing geometry. In connection with a detector slit aligned to the focus of the mirror, this system replaces the analyzer crystal in front of the detector. The multilayers used consist of 50 layer pairs of equally spaced W and B₄C layers, fabricated by sequential sputtering on a (001) silicon wafer. The multilayer mirror is bent and glued to a parabolically machined backing. Peak reflectivities up to 80 % are achieved by this multilayer structure. The first mirror, used as condenser, has a focal length of 150 mm and the second mirror, positioned in the diffracted beam, has a focus length of 90 mm. In the focal plane, a detector slit of 0.015 mm width is used to limit the acceptance angle. Thereby, the acceptance angle of the detector is reduced to 80 arcsec. This value is determined by the FWHM of the transmission peak profile measured with an analyzer scan over the monochromator beam. Further details contributing to a broadening of the acceptance angle (spherical aberration, curvature and grading errors of the mirror, transversal and longitudinal displacements of the slit with respect to the parabola focus) are described elsewhere [11,12]. Fig. 1 shows the schematic setup of the triple-axis diffractometer equipped with two parabolically curved graded multilayer mirrors.
RESULTS AND DISCUSSION

GaN

Fig. 2a shows the AFM image of the GaN film exhibiting a smooth surface with a rms roughness of about 2 nm. In this image, individual crystallites cannot be observed. Performing X-ray diffraction measurements with our new triple-axis diffractometer, the recorded broadening of the rocking curve (Ω-scan) of symmetric reflections is only influenced by the distribution of the out-of-plane misorientation (tilt) and the small lateral correlation length.

AFM image of GaN grown at 950 °C on c-plane sapphire using a 15 nm thick GaN buffer layer

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Wafer bending as well as heterogeneous strain have no influence on the measured peak broadening because of the small acceptance angle of the detector [6]. Both observable broadening effects can be separated due to their different dependency on the scattering vector $|g_{hkl}|$. A distribution of the out-of-plane misorientation causes Bragg peaks to broaden into arcs. In reciprocal space, the width of this broadening is proportional to $|g_{hkl}|$ for symmetric reflections. The broadening due to small correlation lengths parallel to the substrate surface remains constant for the different values of the scattering vector. Therefore, a graphical separation of these two effects is possible by considering higher order reflections. For a linear superposition of both effects, a separation analogous to the Williamson Hall plot [13] can be performed, if $\beta_\Omega (\sin \Theta)/\lambda$ is plotted versus $(\sin \Theta)/\lambda$ for each reflection and linearly fitted (see fig. 3) according to $\beta_\Omega = 0.9/(2L_l) + \alpha_\Omega$. Thereby, $\beta_\Omega$ is the integral width (peak height and integral width define a rectangle equal in area to the peak area) of the measured profile, $\lambda$ is the X-ray wavelength and $\Theta$ is half the scattering angle.

![Graphical separation of the lateral correlation length $L_l$ and the tilt angle $\alpha_\Omega$ from the dependency of the integral width on the diffraction vector obtained from the linear fit according to the equation given in the text.](image)

From the ordinate intersection $y_0$ of the straight line, the lateral correlation length $L_l$ can be estimated. $L_l = 0.9/(2y_0)$. The slope is a direct measure for the tilt angle $\alpha_\Omega$ describing the distribution of the out-of-plane misorientation. For the investigated GaN film, $L_l$ is about 150 nm and $\alpha_\Omega$ is 0.13°. Assuming that screw dislocations with $b_s = [0001]$ determined by TEM measurements [2, 14-18] lead to a tilt of single crystallites in GaN, the screw dislocation density $N_S$ can be calculated to be $4.4 \times 10^5$ cm$^{-2}$ using the equation of Gay, Hirsch and Kelly [19]:

$$N_S = \frac{\alpha_\Omega^2}{4.35b_s^2}$$  \hspace{1cm} (1)

where $b_s$ is the Burgers vector of the screw dislocation ($|b_s| = 0.5185$ nm).

A second analytical method is based on the perception that small correlation lengths can be described by a Cauchy profile [20, 21] whereas the out-of-plane misorientation results in a Gaussian peak shape [19]. The
convolution of a Gaussian $G(x)$ and a Cauchy profile $C(x)$, called a Voigt function [22], can be approximated by a pseudo Voigt function $P(x)$:

$$P(x) = I_0 \left[ \eta C(x) + (1 - \eta) G(x) \right], \quad 0 \leq \eta \leq 1 , \quad (2)$$

with $I_0$ as a scaling factor. If the parameter $\eta$ of the pseudo Voigt function and the integral width $\beta_\Omega$ are determined by a least square fit, the lateral correlation length $L_{||}$ and the tilt angle $\alpha_\Omega$ can be calculated with the formulas given by DeKeijser et al. [21]:

$$L_{||} = \frac{0.9 \lambda}{\beta_\Omega \left( 0.017475 + 1.500484 \eta - 0.534156 \eta^2 \right) \sin \Theta} , \quad (3a)$$

$$\alpha_\Omega = \beta_\Omega \left( 0.184446 + 0.812692 \left( 1 - 0.998497 \eta \right)^{1/2} - 0.659603 \eta + 0.445542 \eta^2 \right). \quad (3b)$$

Applying this method to the measured GaN, a value of 190 nm for $L_{||}$ is obtained. For the tilt angle $\alpha_\Omega$, a value of 0.1° is found, from which the screw dislocation density $N_\Sigma$ can be calculated to be $2.6 \times 10^8$ cm$^{-2}$ according to eq. (1).

Since symmetric rocking curves are insensitive to pure edge dislocations with $b_E = 1/3 (\overline{1}1\overline{2}0)$ and slip planes $\{\overline{1} \overline{1} 00\}$, which is the main type of dislocation in GaN [2, 16-18, 23], $\Phi$-scans (rotation of the sample with respect to the surface normal on asymmetric reflections (diffraction vector and surface normal are not parallel) have to be performed. This type of edge dislocation leads to a distribution of the in-plane rotational disorder (twist) of individual crystallites resulting in a broadening of the $\Phi$-scans. From the measured twist angle $\alpha_\Phi$ (integral width of the performed $\Phi$-scans), the dislocation density $N_E$ for a random distribution of edge dislocations can be calculated neglecting the small broadening contributions of limited correlation lengths parallel to the substrate surface:

$$N_E = \frac{\alpha_\Phi^2}{4.35 b_E^2} \quad (4)$$

If the dislocations are piled up in small angle grain boundaries, the following equation holds [24]:

$$N'_E = \frac{\alpha'_\Phi}{2.1 |b_E| L_{||}} \quad (5)$$

$\alpha'_\Phi$ is again the measured integral width of the $\Phi$-scans. In both cases, $|b_E| = 0.3189$ nm. For $L_{||} = 150$ nm, the edge dislocation density in the GaN film under investigation is calculated to be $1.2 \times 10^{11}$ cm$^{-2}$ according to eq. (4) and $2.3 \times 10^{10}$ cm$^{-2}$ according to eq. (5). Transmission electron microscopy (TEM) measurements should give additional information, which dislocation distribution can be expected in the films under investigation. Therefore, the values for the dislocation density calculated from eq. (4) and eq. (5) are the upper and lower limit obtained by XRD, respectively. For comparison, the dislocation density in commercially available GaN based LEDs is in the range of $1 \times 10^{10}$ cm$^{-2}$ obtained by TEM [1].
AlN

Compared to the GaN film, the AlN film exhibits a different layer morphology (see fig. 2b). The layer consists of individual crystallites which are rotated with respect to the surface normal. Thus, the epitaxial relationship $(0001)\text{Al}_2\text{O}_3 \parallel (0001)\text{AlN}$, $[2\overline{1}\overline{1}0]\text{Al}_2\text{O}_3 \parallel [1\overline{1}00]\text{AlN}$ [25-28] is not strictly fulfilled for all crystallites.

Measuring the symmetric rocking curves $002$, $004$ and $006$ with the triple-axis diffractometer, some striking characteristics in the diffraction profiles can be observed (see fig. 4). The $002$ and $004$ rocking curves consist of two components: a very narrow specular component and a broad diffuse component, which is almost one order of magnitude lower than the specular one. The FWHM of the sharp peak is first of all limited by the instrumental resolution limit. In addition, for the higher order reflection $006$ the sharp component vanishes, the angular broadening of the diffuse component is almost independent of the scattering vector $|\mathbf{g}|$. This kind of broadening is mainly due to an out-of-plane disorder (tilted growth) present in the layer. For this broadening effect, the angular width of the diffuse component should decrease for higher order reflections.

AFM image of AlN grown at 1050 °C on c-plane sapphire using a 15 nm thick GaN buffer layer.

Fig. 2b
Symmetric rocking curves 002, 004 and 006 of AlN grown on c-plane sapphire. The constant angular broadening of the diffuse component and the vanishing of the sharp component for the higher order reflection 006 is clearly visible.

An explanation for these observations is given in Miceli and Palmstroem [29]. They observed a two component rocking curve as well as an attenuation of the resolution limited component for higher order reflections in epitaxial ErAs layers grown on GaAs. The model given by Miceli and Palmstroem for rotational disorder considers the simultaneous presence of a long-range and a short-range order. The long-range order gives the specular peak and the short-range order causes diffuse scattering. Both effects are assumed to be present in unconventional mosaic crystals. This is in contrast to conventional mosaic crystals [30] where single crystallites scatter X-rays incoherently with respect to each other. In conventional mosaic crystals, a mosaic broadening of Bragg peaks is observed. If the tilt angle $\alpha_0$, which describes the disorder, is very small compared to $\alpha_0$ of a conventional mosaic crystal, individual mosaic blocks can scatter X-rays coherently with respect to each other. The reason for the small disorder is attributed to a strong substrate-layer interfacial interaction by which crystallites can be ‘bound in magnitude by the substrate’ [29]. Since a small disorder is still present, the specular component is increasingly attenuated for higher order reflections. In the case of a conventional mosaic crystal with a large tilt angle $\alpha_0$, this uncorrelated disorder prevents the appearance of a resolution limited component (distinct mosaic blocks scatter incoherently with respect to each other). In contrary, if the diffuse scattering is mainly caused by small lateral correlation lengths, the angular width of the diffuse component decreases for higher order reflections and the sharp component should also be observed for higher order reflections [29].

Performing $\Phi$-scans on asymmetric reflections, the poor epitaxial quality concerning the in-plane orientation (twist) of AlN can be demonstrated, because these profiles exhibit large widths in the range of several degrees. However, the twisted growth, also observable in the AFM image, causes a horizontal displacement, but no vertical displacement with respect to the substrate surface. The symmetric $\Omega$-scans are not influenced by this kind of rotational disorder (twist). Therefore, the sharp component can arise. If the epitaxial quality of the AlN film is only judged by the FWHM of the symmetric rocking curves, the true structural properties of the layer cannot be obtained. Only the instrumental resolution limit will be recorded. We want to particularly emphasize that the diffuse component has to be considered as well. Additionally, the measurement of asymmetric reflections has to be performed to obtain detailed information on the structural imperfections present in the AlN film.
SUMMARY AND CONCLUSION

For the characterization of heteroepitaxial GaN and AlN films exhibiting a large divergence in the diffracted beam, a new type of triple-axis diffractometer is used. It is equipped with a parabolically curved graded multilayer as secondary optics. Compared to a conventional analyzer crystal, a distinct gain in intensity is obtained with a sufficiently high resolution limit for the samples under investigation. From the broadening of symmetric rocking curves of GaN, the lateral correlation length \( L_l \) calculates to 150 nm. The density of screw dislocations with \( b_s = [0001] \) is in the order of \( 3 \times 10^8 \) cm\(^{-2} \) and the density of edge dislocations with \( b_E = \frac{1}{3}(11\overline{2}0) \) and slip planes \( \{1\overline{1}00\} \) is in the range of \( 10^9 \) to \( 10^{11} \) cm\(^{-2} \). For the AlN film, a striking anisotropy in the disorder is observed. A small out-of-plane disorder (tilt) is accompanied by a very strong in-plane rotational disorder (large twist broadening). The out-of-plane disorder is such small that coherent X-ray scattering from individual crystallites is observed. The poor in-plane orientations are also apparent in the AFM image. Further investigations will concentrate on the dislocation structure, which causes a distinct strain broadening of symmetric and asymmetric reflections for the radial scan directions.

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