In situ Characterization of MOCVD Growth by High Resolution X-Ray Diffraction

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X-ray diffraction is used for the *in situ* characterization of the growth of cubic GaN by metalorganic chemical vapor deposition. Our setup permits the simultaneous measurement of a wide angular range and requires neither goniometer nor exact sample positioning. Time-resolved measurements during growth give access to film thickness and growth rate as well as information on the chemical composition of ternary compounds. Additionally, the relaxation of the crystal lattice during heteroepitaxial growth of GaN on AlGaN can be measured directly.

Introduction

In situ monitoring and process control is an increasingly important point for the epitaxial growth of semiconductor layers. In high vacuum environments, reflection high energy electron diffraction (RHEED) is well established and provides real time information about growth rate and surface reconstruction. Metalorganic chemical vapor deposition (MOCVD), the favorite growth technique for industrial production of compound semiconductors, operates near atmospheric pressure and has to rely on techniques which are not sensitive to the presence of a gas atmosphere in the reactor. Optical methods such as spectroscopic ellipsometry (SE) [1], [2], reflectance difference spectroscopy (RDS) [3], [4] or laser reflectometry have been developed for that purpose. Most of the information needed for growth control can however only be accessed through models and careful calibration of the device and none of these methods gives direct access to structural parameters of the sample.

Our intent was to show that X-ray diffraction (XRD), a powerful tool for *ex situ* characterization, can also be used for real time measurements during MOCVD growth. It provides detailed information on the crystallographic structure of the growing layers. Up to now, synchrotron radiation was necessary to perform measurements with both time and angular resolution [5] – [8]. Our setup has the advantage that neither a goniometer nor exact sample positioning are required and it is compact enough to be attached to an industrial size MOCVD reactor. We have applied this method to monitor the growth of cubic GaN yielding information on growth rate, ternary compound composition, strain relaxation and thermal expansion.

Experimental

Our MOCVD system is an AIXTRON AIX 200 RF-S horizontal flow reactor designed for nitride compound semiconductor growth. Trimethylgallium (TMGa) and Ammonia (NH_3) are used as Ga and N precursors, respectively, and N_2 and H_2 as carrier gases. The sample is mounted on a graphite susceptor which is inductively heated by a radio-frequency (RF) generator. Beryllium windows were mounted to the top and lateral reactor viewports to allow the passage of the incident and diffracted X-ray beam, respectively. The X-ray system consists of a standard Cu X-ray ($\lambda_{CuK\alpha}$= 1.5418 Å) source and a position sensitive detector which permits the simultaneous acquisition of an angular

range of about 2°. The main difference to conventional systems lies in the fact that neither a goniometer nor exact sample positioning are required. The diffraction angle will be called $\Delta\varepsilon$ to reflect the fact that relative measurements were performed. The angular resolution of this system is mainly dependent on the distance between sample and detector and can be adjusted to the desired accuracy and angular range.

All overgrowth experiments were performed on cubic GaN (001) templates which were grown on GaAs (001) substrates by molecular beam epitaxy (MBE) [9]. The size of these samples was about 1 cm^2 and the thickness of the MBE GaN layer around 400 nm. Prior to introduction into the MOCVD reactor, all samples were cleaned in a sequence of Acetone, Ethanol and Methanol to remove organic surface contaminations. Sample heating and cooling was done in N_2 atmosphere to ensure inert conditions. An additional surface cleaning step had to be performed in the reactor before growth initiation to remove native oxide layers. Pre-running H_2 gas for 30 s at growth temperature etched the topmost layer of the template and created a bare GaN surface. The growth process was performed under H_2 ambient with a constant NH_3 flux of 5.56×10^{-3} mol/min at temperatures ranging between 700 °C and 800 °C. The TMGa flux was varied between 8.837×10^{-6} mol/min and 7.953×10^{-5} mol/min to test the dependence of the growth rate and to determine a stable growth regime. Similar parameters were used for the growth of a GaN layer on an AlGaN/GaN template containing 14% Al.

Results and Discussion

Time-resolved measurements yielded diffraction spectra in an angular range of about 2° with a temporal resolution of 2 s. Figure 1 (a) shows typical spectra of the GaN (224) diffraction peak as acquired during the growth of c-GaN on an MBE template. The spectrum at t = 0 s represents the XRD signal of the MBE template at growth temperature. Due to the lattice mismatch of about 20% between GaAs and GaN, the substrate peak is out of range of our setup. This data was used to determine the thickness of the growing layer as the intensity of the diffraction peak is linearly dependent on its thickness for thin epitaxial films. The solid lines in the figure are fits using a pseudo-Voigt function which gave the peak intensity, position and full width at half maximum (FWHM) of the curve. The intensity from the MBE layer alone was taken as a reference for thickness calculations. Deviations from the linear behavior were found for thicknesses above 1.5 µm, when the intensity began to saturate due to the fact that the path length of the X-rays in the sample approached the extinction length. Layer thicknesses were cross-calibrated with optical methods to verify the values found by XRD.
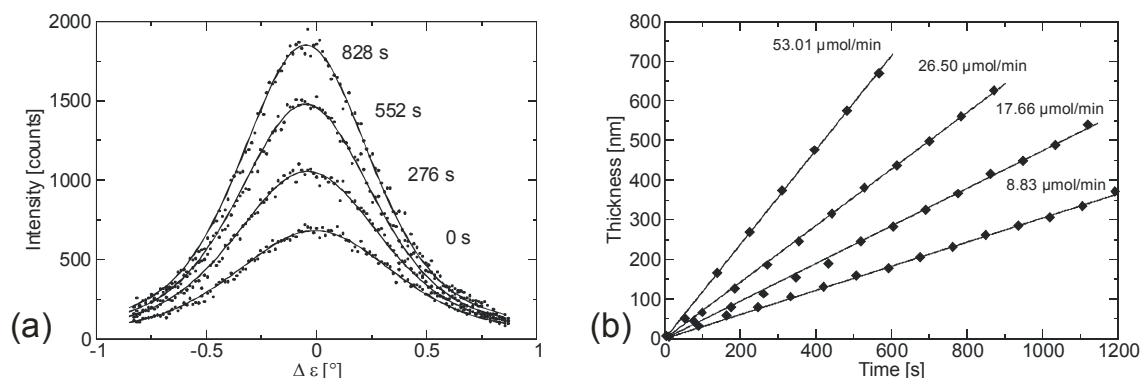

Fig. 1:   (a) *In situ* XRD spectra from the GaN (224) reflection acquired during the MOCVD growth of c-GaN on c-GaN. Numbers on the right side give the time after growth initiation. The integration time was 30 s each. (b) Thickness of the MOCVD layer as a function of time for different TMGa fluxes.

The thickness data was used to calculate the growth rate of the MOCVD film, as shown in Fig. 1 (b), where the layer thickness is plotted against the growth time for different fluxes of TMGa. The slope of the curves is equivalent to the growth rate.

During heating and cooling of the sample in the reactor, a shift of the GaN peak was measured due to thermal expansion. A calculation of the thermal expansion coefficient yielded a value of 5.0×10^{-6} K^{-1}, which is consistent with previously reported results [10], [11].

A frequent application of *ex situ* X-ray diffraction is the determination of ternary compound compositions and strain in epitaxial layers [12]. *In situ* measurement of these parameters is highly desirable to ensure proper device operation. To demonstrate this feature, we used an MBE-grown AlGaN/GaN template with initial thicknesses of 250 nm GaN and 440 nm AlGaN and deposited a c-GaN layer on the AlGaN film. *In situ* XRD spectra are shown in Fig. 2 (a), and two peaks could clearly be distinguished. During growth, the intensity of the AlGaN peak remained constant, while the GaN peak continued to increase. The spectrum could again be fitted with the sum of two pseudo-Voigt functions to determine the exact size and position of both peaks. From their angular separation, the AlN content was determined to be 14% using Vegard's law.
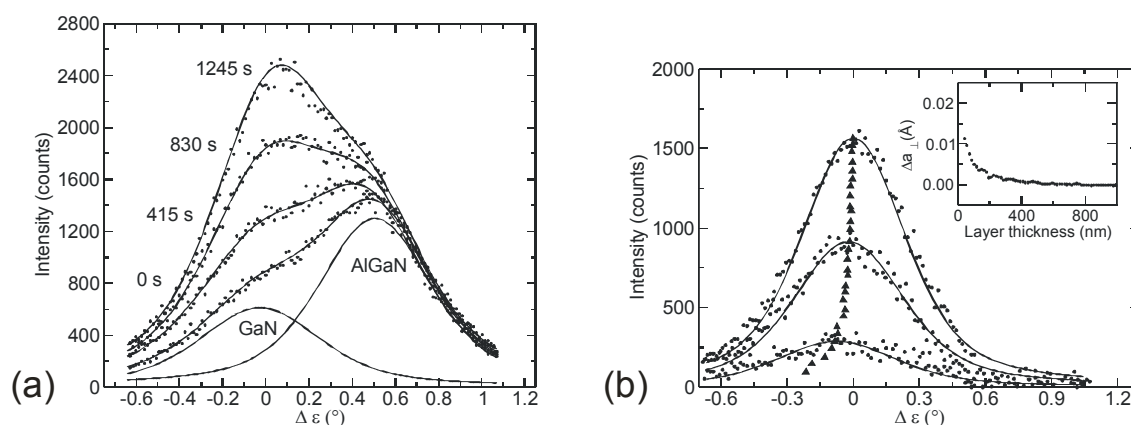

Fig. 2: (a) *In situ* XRD spectra acquired during the growth of GaN on an AlGaN/GaN template. The solid lines represent fits using pseudo-Voigt functions. (b) Difference spectra obtained by subtracting the template signal from the current spectrum. The inset shows the change in the vertical lattice parameter as calculated from the shift of the GaN peak.

To evaluate the strain in the GaN layer, difference spectra relative to the template signal were calculated as shown in Fig. 2 (b). In this case, only the peak of the MOCVD layer is found. The angular shift of the peak position can be interpreted as a change in the vertical lattice parameter of the growing layer. The equilibrium lattice constant of $Al_{0.14}Ga_{0.86}N$ (4.50 Å) is slightly smaller than that of GaN (4.52 Å) yielding an initially compressively strained epitaxial layer. This leads to an expansion in the vertical direction, which is monitored by our setup. The inset of Fig. 2 (b) shows the change in the vertical lattice constant ($\Delta a_{\perp}$) as a function of layer thickness. The data shown in this figure can however only give qualitative information about the relaxation process, as the peak represents a convolution of the whole MOCVD layer.

Conclusion

We have successfully demonstrated the application of high resolution X-ray diffraction for the *in situ* monitoring of MOCVD growth. Measurements on cubic GaN yielded in-

formation about the layer thickness and growth rate as well as on ternary compound compositions and strain relaxation. We think that this method can provide the crystal grower with valuable complementary information on the state of the crystal lattice, which is not available with current optical methods. An application to other material systems like hexagonal GaN, III-V compounds or SiGe could provide new insights on growth processes and is currently under investigation.

Acknowledgements

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