Real-time investigations of GaN metal-organic chemical vapor deposition using synchrotron radiation

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Introduction

We have applied synchrotron x-ray analysis techniques to probe the film and surface structure during metal-organic chemical vapor deposition (MOCVD) of GaN. The evolution of surface structure and morphology were measured in real time using grazing incidence x-ray scattering (GIXS).

Although most previous *in situ* studies of surface structure and morphology during crystal growth have been performed in vacuum environments, chemical interactions between the vapor phase environment and surface play a critical role during MOCVD growth. For example, the competition between deposition rates, surface diffusion rates, and nucleation and propagation of atomic steps on the surface determines the surface morphology during crystal growth (i.e., the homoepitaxial growth mode). In particular, with rapid surface diffusion and low deposition rates, a smooth surface remains smooth as existing steps simply propagate across it in step-flow growth. For slow diffusion and high deposition rates, the surface roughens in a three-dimensional (3-D) growth mode. At intermediate growth and diffusion rates, two-dimensional islands alternately nucleate and coalesce on the surface. It is clear that these rates will be affected by the surface chemistry and structure as determined by the gas composition, flow rate, pressure, substrate temperature, impurity level, etc. However, there have been few *in situ* measurements of atomic-scale surface structure during MOCVD growth because few surface analysis techniques are compatible with this vapor phase environment.

Methods and Materials

Real-time x-ray measurements were carried out using a vertical-flow MOCVD chamber mounted on a 'z-axis' surface diffractometer designed for *in situ* GIXS studies [1] at BESSRC-CAT 12-ID-D beamline and shown in Figure 1. A relatively high x-ray energy of 24 keV (0.5166 Å) was used to penetrate the 2 mm-thick quartz walls of the chamber. In addition to the x-ray probe, the chamber also has capabilities for *in situ* normal incidence optical interferometry. Precursors used for growth experiments are trimethylgallium (TMG) and ammonia (NH_3). We also explored the effect of silicon and oxygen impurities by introducing disilane and O_2. To observe atomic-scale changes in surface morphology during growth, we measured features in the scattering pattern known as crystal truncation rods (CTR). The x-ray CTR intensity is a sensitive measure of atomic-scale roughness.

Results and Discussion

We have mapped the equilibrium surface structure of GaN (0001) as a function of temperature and ammonia partial pressure [2]. We found that in the region most relevant to MOCVD growth, a simple model can be used to describe the effect of vapor-phase chemistry on surface structure [3]. Studies of film growth behavior elucidated the effects of various processing parameters on growth rates. Under certain conditions, intensity oscillations were observed corresponding to the completion of each monolayer during layer-by-layer growth. Transitions between step-flow, layer-by-layer, and 3-D growth modes were observed and mapped as a function of process conditions. We determined the growth mode as a function of temperature, growth rate, and ammonia partial pressure [4]. We also studied the effect of silicon and oxygen impurities. While the introduction of oxygen has minimal effect on growth modes, we found that the presence of silicon has a large effect, analogous to surfactant effects observed in epitaxial growth on close-packed metal surfaces [5].

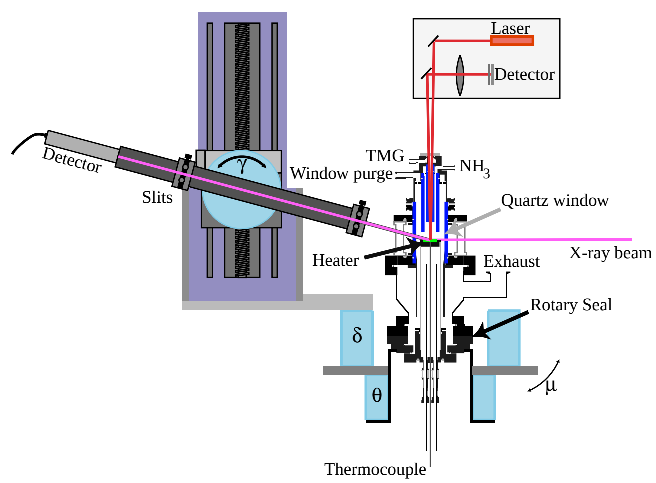

Figure 1: Vertical-flow MOVCD chamber.

Acknowledgments

This work is supported by the State of Illinois under HECA; the U.S. Department of Energy, BES-W-31-109-ENG-38; and the National Science Foundation under Grant DMR-9704201.

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