Summary

Dilute nitride alloys, obtained by incorporating a small amount of nitrogen in III-V semiconductors, have attracted a considerable interest in the past few years. Alloying of conventional III-V semiconductors with N results in a large band-gap bowing and thus offers an interesting route to control optical properties. This unique property made this alloy a promising material for several applications ranging from infrared and mid-infrared laser diodes to multi-junction photovoltaic solar cells. While originally expected to be easy to realize, the actual fabrication of such alloys by employing crystal growth techniques has been challenging in practice. A major challenge for the realization of these alloys is the extremely low equilibrium N solubility in III-V semiconductors. Other challenges include large spatial composition fluctuations and the tendency for phase separation and 3D island growth. While numerous experimental efforts have been devoted to overcome these challenges, an understanding of the basic reasons leading to these growth difficulties is so far lacking.

In order to enhance N incorporation, improve quality, and control the local order of atoms, a theoretical understanding of the basic physical mechanisms that control the growth of III-V dilute nitride alloys at the atomic level is therefore crucial. State-of-the-art first-principles (*ab-initio*) simulations provide a powerful and a promising approach to achieve this goal. To accurately describe these multi-component alloys, large-scale simulations are highly desirable. However, performing growth simulations for a realistic system size fully based on *ab-initio* methods is computationally prohibitive. The main objective in this thesis is therefore the development of the necessary methodologies and concepts that allow us to overcome this challenge and obtain an accurate understanding and predictions based on small-scale atomistic simulations.

In the first part we address the issue of limited N solubility and discuss approaches to increase it. Particularly, we focus on the possibilities offered by enhanced surface solubility and how it can be employed in practice. By calculating the detailed stability phase diagrams for N substitutions in bulk GaAs and InAs and at surfaces and subsurfaces using *ab-initio* thermodynamics combined with Monte-Carlo simulations we provide an accurate measure of N concentration as a function of growth conditions and determine the solubility limits. Contrary to bulk, we find that the solubility of N at surfaces is significantly larger and shows a complex behavior as a function of growth conditions. Based on these results, optimal growth conditions for N incorporation and the kinetic pathway that should be employed to achieve maximum N concentration are predicted.

After that we focus on surface kinetics. Specifically, in a first step we concentrate on achieving a complete understanding of the diffusion of the N adatoms at the GaAs surface, which turns out to be a particularly challenging problem. The complex diffusion behavior leads for the first

time to the breakdown of the conventional approaches and methods usually employed to analyze diffusion. Based on a careful analysis we identify the underlying reasons and develop appropriate techniques to overcome this problem. In a second step we consider the possible kinetic pathways for surface/subsurface incorporation of N. We examine these pathways in detail and determine the associated barriers and the corresponding reaction rates under typical growth temperatures. Based on these results and with the help of kinetic Monte Carlo simulations we are able to fully analyze and understand N diffusion and their incorporation mechanisms. In contrast to what was previously believed, we find that the subsurface incorporation of N cannot be realized under typical MBE growth conditions, while their incorporation at the topmost surface layer is easily achievable.

Important consequences are realized based on these results. First, by revealing the functional N incorporation mechanism and based on the solubility phase diagrams, the growth conditions that should be employed in practice to achieve the highest N concentration are identified. A second consequence is that by additionally understanding the interaction behavior between In and N atoms in the quaternary dilute nitride alloys we are able to identify the driving mechanisms for the puzzling compositional correlations and anitcorrelations. This work allows to achieve a full understanding of the growth of dilute nitride alloys for the first time. We note that the methods derived and employed here are general – the alloy system studied here thus provides a prototype for understanding other highly-mismatched multi-component systems that are difficult to describe by conventional theoretical approaches.