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# Phase separation in thick InGaN layers – A quantitative, nanoscale study by pulsed laser atom probe tomography

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## Abstract

Pulsed laser atom probe tomography was employed to study 300 nm thick $In_{0.25}Ga_{0.75}N$ layers grown on a GaN buffer layer. The unique three-dimensional data provided by atom probe tomography revealed a complex microstructure in the InGaN formed by indium-rich columns and plates adjacent to strongly indium-depleted regions. This complex indium-related domain structure is likely to represent the early stages of spinodal decomposition occurring during layer growth. The interface with the buffer layer is characterized by the absence of this microstructure and a generally more homogeneous indium distribution. Also, a significantly reduced InN mole fraction was found in that region. Both are believed to be a result of the interfacial misfit strain, which suppresses phase separation and impedes indium incorporation during growth, which is termed the compositional pulling effect.

*Keywords:* Compound semiconductors; Indium gallium nitride; Spinodal decomposition; Phase separation; Atom probe

## 1. Introduction

The (III)-nitride materials have been receiving enormous attention in recent years. Their appeal is that the alloys of the three nitrides GaN, InN and AlN allow the fabrication of materials covering an extremely wide range of band gap energies. For opto-electronic applications this means that alloys of these three materials cover the entire technically relevant wavelength spectrum. Alloying GaN with indium leads to materials that can be used to fabricate devices that emit blue and green light, a wavelength range not normally covered by other semiconductor materials. Cutting-edge applications include green and blue light emitting diodes, lasers and microwave transistors [1–3]. Ternary nitrides form the active layers in (III)-nitride based opto-electronic devices, for example quantum well structures, since they are found to significantly improve the efficiency and quality of LEDs and laser diodes [1,4].

Generally one needs to distinguish between thin, pseudomorphically strained, i.e. substrate coherent, InGaN layers and thick substrate incoherent layers. InGaN quantum well structures fall within the first category and there has been spirited debate as to why the quenching of luminescence in the presence of high dislocation densities is much weaker than for other compound semiconductors. A common explanation is that the charge carriers are somehow localized and thus non-radiative recombination at dislocations is significantly reduced. Initially, mainly based on transmission electron microscopy (TEM) observations, it was widely argued that these localization centres could be indium-rich clusters or even quantum dots within the quantum wells [5]. However, some studies questioned this in the light of experiments showing that prolonged exposure to high energy electron beams may provoke indium clustering [6–8]. It was suggested that nanoscale fluctuations in the quantum well width could instead localize the carriers [7,9]. Another interesting aspect is the thermodynamics of InGaN alloys. Initially Ho and

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co-workers [10] predicted that bulk InGaN alloys have a large positive mixing enthalpy and are unstable over most of the compositional range. Consequently, a wide miscibility gap should exist in the pseudo-binary GaN–InN phase diagram [10], apart from some edge solubility, and InGaN might undergo phase separation. Later Karpov [11] and Liu et al. [12] considered strain effects, for example, the misfit strain from the substrate can increase the energy for phase separation, shifting the miscibility gap to higher InN mole fractions, resulting in an extended compositional range with full miscibility [11]. Hence, assuming the formation of indium-rich InN quantum dots within quantum wells seems somewhat questionable [12]. In thin constrained InGaN layers thickness- and strain-dependent effects are strongly evident. Recent work by Zhang et al. on $In_{0.14}G_{0.86}N$/GaN quantum wells with thicknesses of 2.5, 5 and 7 nm showed the first signs of phase separation only in the thickest quantum wells, where the misfit strain is more relaxed [13].

For thick, relaxed InGaN layers with dislocations and thicknesses larger than the critical thickness the previously mentioned miscibility gap fully applies and phase separation into GaN and InN-rich phases is expected to occur over a wide range of compositions [12] and growth temperatures. Depending on the position in the pseudo-binary phase diagram those phases can form via crystallization and growth or spinodal composition [10,12].

For a better understanding of device functionality and systematic material engineering, full quantification of the nature and extent of phase separation is needed, as a function of layer thickness, indium content and growth conditions.

Atom probe tomography (APT) is a unique technique in the armory of microscopy techniques. It relies on the very well controlled field evaporation of surface atoms from a sharp, needle-shaped specimen. Atoms released from the surface are ionized, pass through a time of flight mass spectrometer and impact on a position-sensitive detector. The ion flight times, the detector coordinates and the sequence in which the ions arrive on the detector are fed into software-based reconstruction algorithms [14] that produce the typical three-dimensional (3-D) chemical maps of the field evaporated specimen volume. These datasets can possess picometre accuracy [15], rendering APT the highest resolving tomographic method available to date. The technique is unique in providing direct chemical analysis of materials at the single atom level. It therefore avoids many of the difficulties associated with the interpretation of indirectly gained quantitative data from, for example, electron microscopy techniques.

Conventionally atom by atom removal from the specimen surface is triggered by high voltage pulses, which are only applicable to materials of high electrical conductivity like metals and alloys. In order to study semiconductor materials these voltage pulses are replaced by ultra-short laser pulses, which is referred to as pulsed laser atom probe tomography (PLAPT), first developed in the early 1980s [16,17] and employed in early pioneer semiconductor analyses [18–21]. Later, in the early 2000s [22], the concept of PLAPT was revisited and sophisticated solid-state lasers with pulse widths of a few picoseconds, sufficiently high pulse repetition frequencies and stability have been implemented in the latest atom probe instruments [23]. This, together with the development of sophisticated focused ion beam sample preparation methods [24–26], can certainly be considered as the most important evolutionary steps in atom probe tomography without which the studies described in this publication would not have been possible. Since then, contemporary PLAPT has been applied to a variety of different materials that had originally been inaccessible to APT. One of these growing fields is semiconductor analysis, ranging from silicon-based materials and device structures [27,28] to nanowires [29,30], magnetic semiconductors [31] and compound semiconductor nanostructures [32–35]. Contemporary PLAPT has also already been used to study InGaN materials, in particular focusing on the issue of indium clustering in InGaN quantum wells [7,36–39]. This study moves on from these earlier PLAPT investigations of thin, highly constrained InGaN layers to thick, partially relaxed layers in order to shed light on the phase separation phenomena expected to occur in such materials.

## 2. Experimental

The material investigated in this study was derived from a family of similar materials described by Rao et al. [40]. It was grown by metal–organic chemical vapour deposition in an Aixtron AIX 200 RF horizontal reactor. Growth of the InGaN was carried out at a temperature of 880 °C, a growth rate of 300 nm $h^{-1}$, with nitrogen as the carrier gas. As the substrate an ∼900 nm thick GaN buffer layer was grown on a 2 in. (0 0 0 1) sapphire substrate at 1170 °C. The InGaN layer had an approximate thickness of 300 nm and its nominal composition was determined by Rutherford backscattering spectroscopy (RBS) to be approximately $In_{0.25}Ga_{0.75}N$.

Atom probe specimens were produced normal to the growth plane, employing focused ion beam lift-out and annular milling procedures [24]. The lift-out procedure was slightly modified in order to avoid inclusion of the sapphire substrate in the lift-out wedge, which would have introduced an additional interface region that might contribute to premature specimen failure. Extra care was exercised to minimize ion beam damage by means of ex situ sputter deposition of an ∼200 nm gold and in situ ion beam deposition of an ∼100 nm tungsten–carbon layer on top of the specimen surface. A final, low ion beam current clean-up step [26] was conducted in order to remove damaged surface layers from the specimen needle.

All atom probe studies were conducted with a pulsed laser, energy compensated, local electrode atom probe LEAP™ 3000X HR, manufactured by Cameca (formerly