The Ga(In)AsN alloy has attracted considerable attention in recent years both because of practical and fundamental points of view. More recently, promising results have been obtained in light emitting devices with wavelengths in the 1.3–1.55 μm range. It is well known that the incorporation of nitrogen into GaAs causes the bulk band gap to decrease dramatically. On the other hand, due to the large lattice mismatch between GaAs and zinc-blende-type GaN, small amounts of substitutionally incorporated N will give rise to a substantial tensile strain in pseudomorphic GaNAs layers on GaAs. The most promising range of N composition in the Ga(In)NAs alloy seems to be less than 2%, where the band-gap reduction is sharp and the material quality quite good. Higher-N compositions may lead to nonrandom alloys, and photoluminescence efficiency has been observed to be severely degraded.

For the determination of the nitrogen content of Ga(In)NAs epilayers on GaAs, the x-ray diffraction (XRD) technique is often used. However, by XRD the lattice spacings are determined, and not directly the N content of the Ga(In)NAs1-x alloys. Thus, the calculation of these values requires assumptions on the variation of the lattice parameters and of the elastic constants with x. A linear interpolation (Vegard’s law) between the values of GaAs and cubic GaN has been commonly assumed to be justified. In this letter, we have measured the N content in a series of GaNAs1-x alloys (0 < x < 3%) by secondary ion mass spectroscopy (SIMS) and the lattice constant in the epilayers by XRD rocking scans. A considerable negative deviation from Vegard’s law in the variation of the lattice constant with N content is observed as N composition over 1.5%, leading to an overestimation of the nitrogen content by up to 30%.

The growth of GaNAs1-x (1000-Å-thick) samples with a 100-Å-thick cap layer and different N concentrations (0 < x < 3%) was performed in a gas-source molecular-beam epitaxy (MBE) system. Group-III fluxes are produced by thermal effusion cells, group-V flux is provided by a thermally cracking AsH3, and reactive nitrogen is provided by a radio-frequency (rf) plasma cell. The GaNAs films were grown at 440 °C to incorporate N into the GaNAs layers. The detailed growth conditions were reported in Ref. 5.

N-implanted samples were used for the calibration of SIMS measurements of nitrogen concentration in GaNAs. Nitrogen ions (14N+, 50 keV) were implanted into semi-insulating GaAs wafers at room temperature. A total N dose of 1 x 1016 ions/cm2 was implanted. SIMS measurements were provided by a VG Ionex IX70S instrument. Cs+ ions were used as primary ions and the primary ion energy used was 12 keV. The nitrogen concentration was deduced from the SIMS profile based on the signal ratio of 83 GaN/69 Ga.

For all samples, XRD rocking scans around the (004) Bragg reflections were recorded to measure the lattice constants. From reciprocal space mappings around the (115) reciprocal lattice point it was verified that all of the samples were grown fully pseudomorphic. Figure 1 shows a (004) rocking curve of a typical sample (solid line), together with a simulation in which the RADS commercial software is used based on dynamical theory (dashed line). A GaNAs peak and some thickness fringe peaks are clearly observed. This suggests that the film has a high epitaxial quality. We have measured the sample at different regions (the sample size is 1 in. in diameter) and the results are quite reproducible, indi-

![FIG. 1. XRD (004) rocking curve of a GaNAs sample (solid line). The dashed line is the corresponding simulation based on the dynamical theory.](image-url)
The physical origin of this negative deviation could be the formation of isolated interstitial nitrogen in GaNAs is unlikely because of their high formation energy in the lattice. Instead, N complexes such as As–N and N–N split interstitials are energetically favored to form, occupying a single lattice site (shown in Fig. 3). The formation of split interstitial N–As complexes induces a compressive strain in the epilayer while N–N complexes cause less tensile strain as compared to the substitutional NAs atom, as shown in Fig. 4. (The detailed results will be published in a separate paper.) Therefore, the incorporation of these non-substitutional N atoms will also contribute to the measured deviation from Vegard’s law. In addition, these defects would play an important role in carrier capture and the recombination process [e.g., act as non-radiative centers in as-grown Ga(In)NAs material on GaAs].

In summary, GaN$_x$As$_{1-x}$ epilayers on GaAs were grown by gas-source MBE using a rf plasma nitrogen source. We have performed a systematic investigation of the dependence of the lattice parameter on the N content in a series of GaN$_x$As$_{1-x}$ samples ($x < 0.03$) grown pseudomorphically on GaAs(001) substrates. A significant deviation of the lattice parameter variation in GaN$_x$As$_{1-x}$ from Vegard’s law between GaAs and GaN was observed, which leads to overestimation of the nitrogen content by up to 30%. The physical origin of the negative deviations of the lattice parameters from Vegard’s law could be mainly due to the large size mismatch between the solute and the solvent atoms. It can also be due to the nonrandom alloys (N clustering) at these higher-nitrogen concentrations, since Vegard’s law is strictly valid only if N atoms are statistically randomly distributed in the alloy formation process.

On the other hand, although most N atoms are believed to occupy predominantly the As sublattice, the N atoms might energetically prefer moving out from their substitutional to the neighboring interstitial sites as the N incorporation exceeds a certain level (this prediction has been confirmed by recent channeling experiments). Our calculations show that the formation of isolated interstitial nitrogen in GaNAs is unlikely because of their high formation energy in the lattice. Instead, N complexes such as As–N and N–N split interstitials are energetically favored to form, occupying a single lattice site (shown in Fig. 3). The formation of split interstitial N–As complexes induces a compressive strain in the epilayer while N–N complexes cause less tensile strain as compared to the substitutional NAs atom, as shown in Fig. 4. (The detailed results will be published in a separate paper.) Therefore, the incorporation of these non-substitutional N atoms will also contribute to the measured deviation from Vegard’s law. In addition, these defects would play an important role in carrier capture and the recombination process [e.g., act as non-radiative centers in as-grown Ga(In)NAs material on GaAs].

In summary, GaN$_x$As$_{1-x}$ epilayers on GaAs were grown by gas-source MBE using a rf plasma nitrogen source. We have performed a systematic investigation of the dependence of the lattice parameter on the N content in a series of GaN$_x$As$_{1-x}$ samples ($x < 0.03$) grown pseudomorphically on GaAs(001) substrates. A significant deviation of the lattice parameter variation in GaN$_x$As$_{1-x}$ from Vegard’s law between GaAs and GaN was observed, which leads to overestimation of the nitrogen content by up to 30%. The physical origin of this negative deviation could be mainly due to the formation of N-related defects in GaN$_x$As$_{1-x}$. This, in turn, has significant consequences on the correct description of the band-gap variation with nitrogen content and other physical properties.
11 W. Li and T. Rantala (unpublished).