Study of melt-grown GaAsN and InGaAsN epitaxial layers

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Abstract. This paper presents investigation of electronic transport properties of GaAsN and InGaAsN epitaxial layers with low nitrogen content, the so called dilute nitrides, grown by liquid-phase epitaxy (LPE). The layers up to 2 microns thick have been grown from Ga- and In-rich melt at different initial epitaxy temperatures in the range 660 - 620 °C. Polycrystalline GaN has been used as a source for nitrogen. As grown, unintentionally doped GaAsN and InGaNAs are n-type with free carrier concentrations one order of magnitude higher than those for the reference nitrogen free undoped GaAs and InGaAs layers. Lattice matched to GaAs substrate InGaAsN layers exhibit Hall mobility values higher than 2000 V/cm\textsuperscript{2}s

1. Introduction

The quaternary solid solution InGaAsN proposed by Kondow [1] for the realization of long wavelength lasers based on GaAs has attracted considerable attention during the last few years. Numerous laboratories have demonstrated that the optical energy-gap of GaNAs decreases substantially when small amounts of N are incorporated into the solid. More importantly, InGaNAs alloys can be grown lattice-matched to GaAs because In and N have opposing strain effects on the lattice (N adds tensile strain, In - compressive). Using this quaternary system, it should also be possible to engineer a strain-free graded band gap base layer.

The incorporation of small quantity of nitrogen into GaAs also deteriorates the crystalline and optoelectronic properties of the dilute nitride materials, including reduction of the photoluminescence intensity and life-time, decreasing of electron mobility and increasing in the background carrier concentration. Even for the low N content the concentration of N interstitial is the major defect formed in nitride-arsenides due to the large size mismatch between the As and N atom. The existence of high density of N interstitials and Ga vacancies in the as-grown structures will significantly affect device performance, since they would introduce band-gap levels affecting the carrier collection and recombination in transport process. GaAsN- based solid solutions and heterostructures are primarily grown by metalorganic vapor-phase epitaxy (MOVPE) [2, 3] and molecular-beam epitaxy (MBE) [4, 5], but the material quality has been inferior to that of GaAs. Recently chemical-beam epitaxy (CBE) has been developed in order to improve the quality of the grown layer [6], but to date it has remained a challenge to grow dilute nitride materials for photovoltaic (PV) application. We propose low-temperature LPE [7] as a new growth method for...
these dilute nitrides. Moreover, it is a challenge to demonstrate thick, lattice-matched and of high electrical and structural quality InGaAsN layers needed for development of multijunction solar cells. In this work, our focus is specifically on LPE growth conditions of thick InGaAsN films on GaAs (001) substrates with a polycrystalline GaN as N source.

2. Experiment
A series of GaAsN and InGaAsN epilayers have been grown on semi-insulating (100) GaAs substrates. The crystal growth is performed in a horizontal quartz tube using a graphite boat designed for 10×15 mm² substrate. Pure 99,9999 Ga and 99, 9999 In were used as solvents, and polycrystalline GaN and GaAs were used as sources for N and As, respectively. Epitaxial InGaAsN with In- content in the layer lower than 0.1 at% which acts as isovalent dopant were grown from Ga+(5-10%) In- melt. In order to obtain ternary and quaternary InGaAs and InGaAsN alloys with a few percent In content the growth was done from 80%In +20%Ga melt. Prior to growth, substrates were etched in 5H₂SO₄: H₂O₂: H₂O for 4 minutes and rinsed in deionized water. The charged boat was heated for 1 hour at 800 °C in order to reduce the contamination and to homogenize the melt. The layers with thicknesses of 1-2 µm were grown in the temperature interval of 10°C from initial epitaxy temperatures varying in the range 660-620 °C at a cooling rate of 0.6 °C/min.

The values of composition parameters x and y of the epitaxial In₀.₇Ga₀.₃N₀.₂As₀.₈ layers were determined by X-ray microanalysis and X-ray diffraction (XRD) methods.

The Hall electron mobility and free carrier concentration were measured in the temperature range 80-300K by conventional Van der Pauw method on layers grown on 5x5 mm² semi-insulating GaAs substrates.

3. Results and Discussion
Epitaxial GaAsN and InGaAsN layers grown from Ga and Ga+(5-10%)In -melt with 1.5 at.% GaN content from 660 °C initial epitaxy temperature are with thicknesses of 1 µm and N content in the layers varies from 0.1 at. % for GaAsN to about 0.2 at. % for InGaAsN layers. The presence of 5-10% In in the melt enhances the incorporation of N in the grown layers.

Figure 1. Free carrier concentration as a function of inverse temperature for as grown GaAs, GaAsN and InGaAsN layers grown from Ga-rich solution.
Figure 1 shows the temperature dependence of the Hall-concentration $n_H$ on reciprocal temperature for as grown GaAsN (sample E44) and InGaAsN (sample E87) layers in comparison with undoped GaAs (sample E43). It is seen that all samples are of n-type and for layers containing nitrogen electron concentration increases about one order of magnitude. This could be explained by the assumption that nitrogen behaves mainly as an isoelectronic donor, which arises from the local heterojunction scheme GaAs-GaN according to Belliache et al [8]. The N-related point defects and Ga- vacancies have a dominant role on electrical properties and increase the background concentrations.

![Figure 1](image)

**Figure 2.** Temperature dependence of Hall electron mobility for GaAs (squares), GaAsN (circles), InGaAsN (triangles)

Figure 2 presents the temperature dependencies of the Hall-mobility for the same samples E43, E44 and E87. The mobility of the samples doped with nitrogen (E44 and E87) is considerably lower due to space charge scattering contributions induced by N-related defects added to well-known scattering mechanisms such as phonon and ionized impurity scattering. It is seen a well expressed low-temperature mobility decrease which could be explained by the temperature dependence of the GaAs conduction band edge energy, which is closer to the N defect levels at lower temperatures, increasing the scattering cross-section.

Another series of lattice matched InGaAsN and metamorphic InGaAs and InGaAsN layers were grown from In-rich melt. An intentionally undoped InGaAs layer and nitrogen doped one were grown under the same growth condition in the range 650-640 °C. X-ray microanalysys data show that In content in nitrogen free InGaAs layer is 3.75 at. % in the solid, while for N-doped layer it sharply decreases to 1.3 at.%. This result indicates that GaN in the melt suppresses the incorporation of In in Ga sub-lattice during epitaxial growth. These layers were lattice mismatched with rough surface as shown in figure 3a which makes it difficult to remove the melt from the surface after epitaxy. Lattice matched InGaAsN with In content of 3.47 at. % were grown at lower epitaxy temperatures in the range 620-610 °C. They exhibit smoother growth surfaces due to the lack of a highly dislocated region (figure 3b).

The log of free carrier concentration $n_H$ vs. reciprocal temperature for intentionationally undoped metamorphic InGaAs (sample E93) and lattice matched InGaAsN (sample E97) are plotted in the figure 4. For for N-containing films, two distinct temperature regimes with different temperature dependence of $n_H$ are observed. Hall-concentration decreases as the temperature decreases down to
about 200 K, indicating the presence of thermally activated deep donor levels within the dilute nitride bandgap. The saturation of $n_H$ at low temperature ($T < 200K$) is attributed to fully ionized shallow donors. This temperature dependence of the $n_H$ is similar to that observed in n-type AlGaAs and attributed to the co-existence of a shallow donors and a deep DX-center donors [8,9]. In our case this behavior could be explained by the presence of two donor levels in the InGaAsN bandgap, one being a shallow N isoelectronic donor and the second a thermally activated deeper donor, presumably N-related deep-level defects typically associated with different N-N pair and N-cluster states [10,11].

In the case of InGaAs layer, $n_H$ decreases almost linearity in the explored temperature range, 80 to 300K, typical for slightly degenerate III-V semiconductors. The deviation from linearity is due to the background N- doping of this layer grown at the same graphite boat as N-doped layers.

The temperature dependence of Hall mobility for undoped InGaAs E93 and InGaAsN E97 layers grown from In-solution is similar to those for the layers grown from Ga-rich solution as it is shown in figures 5a and 5b.

The mobility of the metamorphic InGaAs structure (E93) is low, down to 500 cm$^2$/V.s, since it possibly contains threading dislocations of high density and the latter causes relatively poor material quality. High values over 2000 cm$^2$/V.s for Hall mobility exhibits the lattice matched to GaAs.
Figure 5a. Hall mobility as a function of temperature for undoped InGaAs (E93) sample

Figure 5b. Hall mobility as a function of temperature for lattice matched InGaAsN (E97) sample

substrate InGaAsN sample E97. These values are about the theoretical limit predicted by Fahy and O’Reilly [12] and the highest reported for lattice matched thick InGaAsN layers.

4. Conclusions

Dilute nitride GaAsN and InGaAsN epitaxial layers have been grown by LPE using polycrystalline GaN as a source for nitrogen. The layers grown from Ga-rich melt are with 0.1-0.2 at. % N content in the solid. Hall measurements reveal sharply increase of free carrier concentrations about one order of magnitude and decrease of Hall mobility for nitrogen doped samples in comparison with undoped GaAs.

Metamorphic and lattice matched InGaAsN layers with 3-4 at. % In content in the solid have been prepared from In-rich melt. Temperature dependent electronic transport measurements show a thermally activated increase in free carrier concentration at measurement temperatures higher than 200 K, suggesting the presence of a carrier trapping level below the GaAsN conduction band edge. The mobility for metamorphic layers is low (about 500 cm$^2$/V.s) possibly due to high density threading dislocations. Lattice matched InGaAsN with In content of 3.47 at % have been grown in temperature range 620-610 °C from 80%In+20%Ga melt. The measured Hall mobility values over 2000 cm$^2$/V.s are the highest reported to date for thick InGaAsN layers lattice matched to GaAs substrate.

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