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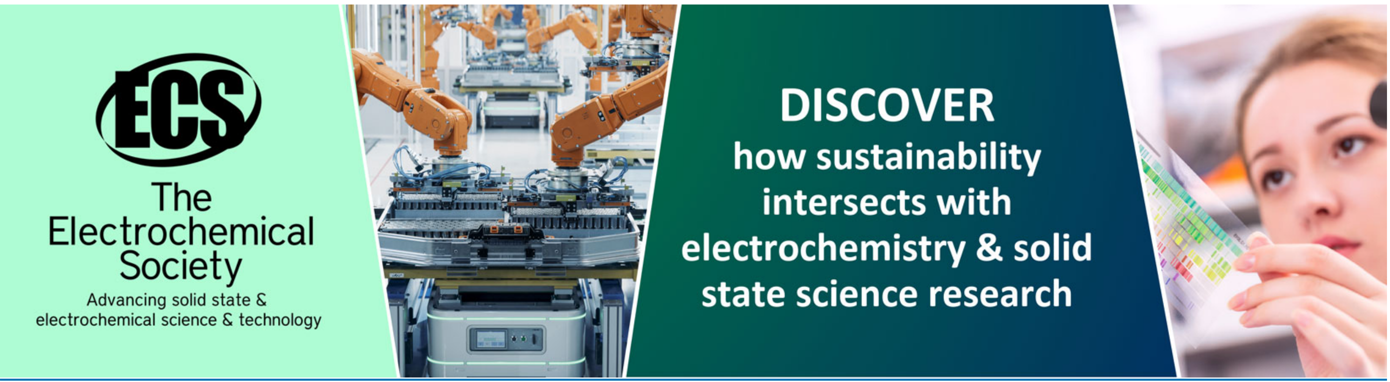

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# Dilute GaAsN and GaInAsN grown by liquid phase epitaxy

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**Abstract.** Dilute III-nitrides, such as GaAsN and GaInAsN, are of considerable current interest both from a fundamental point of view and for applications in solar cells, GaAs-based long-wavelength photodetectors and diode lasers. The addition of nitrogen leads to material properties that deviate strongly from those expected for conventional III–V solid solutions.

The possibility was investigated to use liquid phase epitaxy to incorporate nitrogen in epitaxial GaAsN/GaAs and GaInAsN/GaAs heterostructures. The structures were grown from Ga- and Ga-In- melts containing powder GaN as a nitrogen source. The initial growth temperature was varied in the range 560ºC - 660ºC. The low temperature growth favors nitrogen incorporation in the epilayers. The optical transmission and photoluminescence spectra of a set of structures grown at different temperatures were studied showing ternary and quaternary dilute nitride solid solutions with nitrogen content about 0.2 at.%. The photoluminescence spectra show emission from localized nitrogen states as well.

## 1. Introduction

The III–V–N semiconductor solid solutions have attracted a great deal of attention because of their interesting physical properties and potential applications in optoelectronic devices and multi-junction solar cells. One technologically important feature of GaInAsN quaternary solid solutions is that they can have a perfect lattice match to a GaAs or InP substrate with an appropriate ratio of indium-to-nitrogen fractions, thus avoiding the growth problems encountered in strained layers, such as the ternary GaAsN and GaPN semiconductors.

Technologically, the incorporation probability of nitrogen in GaAs is very small and strongly depends on the growth conditions. GaAsN-based solid solutions and heterostructures are first grown by metaloorganic vapor-phase epitaxy (MOVPE) [1] and molecular-beam epitaxy (MBE) [2]. Only one group, Dhar et al. [3], has reported liquid-phase epitaxy (LPE) growth of these compounds. The advantages of the LPE are its simplicity, low cost and ability to produce materials of high quality.

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In this paper, we show the possibility to use liquid phase epitaxy to incorporate nitrogen in epitaxial GaAsN/GaAs and GaInAsN/GaAs heterostructures and study the optical properties of GaAsN and GaInAsN LPE layers grown at different temperatures.

## 2. Experimental procedure

Epitaxial layers of GaAsN and GaInAsN, 0.2-0.8μm thick, were grown in a conventional horizontal sliding boat LPE reactor on (100) oriented n-type GaAs:Si substrates from Ga- or mixed Ga-In melt. Polycrystalline GaAs and powder GaN were used as an As and N sources, respectively. The N content in the melt was 1.5 at.% for all layers studied. Epitaxial layers were deposited at different initial temperatures in the range 560-660 ºC at a cooling rate of 0.5 ºC/min. The technological conditions of the as-grown samples are summarized in table 1. The layers were not subsequently annealed.

**Table 1**.Growth conditions of the samples investigated.

| Sample | 66<br>GaAs | 68<br>GaAsN | 70<br>GaAsN | 72<br>GaAsN | 74<br>GaInAsN | 75<br>GaInAsN |
|---|---|---|---|---|---|---|
| T | 660 ºC | 660 ºC | 595 ºC | 560 ºC | 570 ºC | 660 ºC |

The composition dependence of the effective band-gap of the layers was investigated by optical transmission spectroscopy. Transmission spectra were measured in the spectral range 850-2000 nm by a UV-3600 Shimadzu double-beam UV-VIS spectrophotometer. In order to increase the signal-to-noise ratio, the substrates of GaAsN/GaAs and GaInAsN/GaAs heterojunction samples as well as the GaAs reference sample were thinned down to 90 μm.

The CW photoluminescence (PL) spectra under excitation of a Coherent 488 nm 12 W Argon laser were measured at 5 K. They were analyzed by a Jobin-Yvon Spectrometer HR460 and a multichannel CCD detector (2000 pixel).

## 3. Results and discussion

### *3.1. Absorption spectra discussion*

Figure 1 a), b) shows the transmission spectra of several GaAsN and GaInAsN layers respectively, compared with the reference GaAs sample 66.

It is seen that the absorption edge for all N-containing samples is red-shifted compared to the GaAs one. The red shift for the samples investigated increases when the growth temperature decreases. This

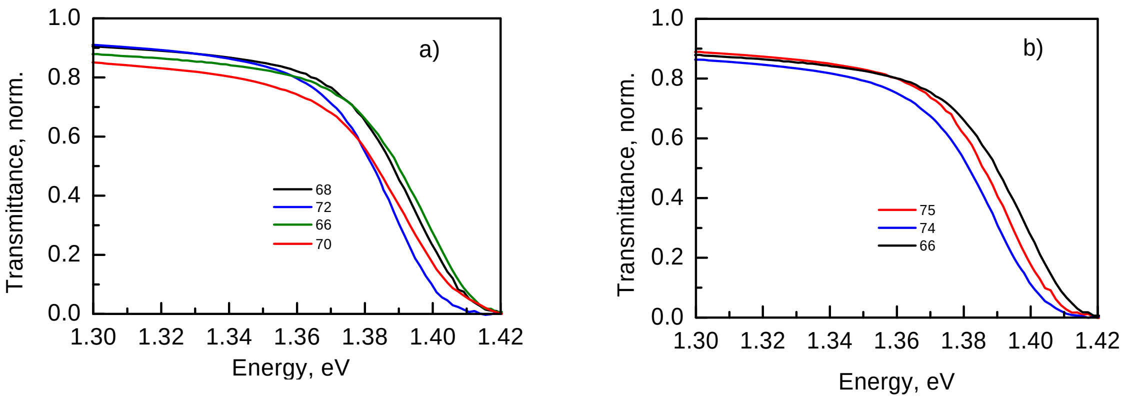


**Figure 1.** Normalized transmission spectra of a) GaAsN/GaAs samples and b) GaInAsN/GaAs samples.

fact is in accordance with the effect of the growth temperature on the N concentration in GaAsN reported by Toivonen et al. [4], thus confirming the incorporation of nitrogen under our growth conditions. According to Tisch et al. [5], the red shift of the absorption spectra observed in figure 1 corresponds to a nitrogen content in the solid solution epitaxial layers near or less than 0.2 at.%.

*3.2. PL spectra discussion*
Figure 2 shows representative PL spectra for the samples listed in table 1.

First, narrow excitonic-like emission bands near 1.52 eV are recorded in the spectra of all N-containing layers and the reference GaAs layer, as well as at 1.49 eV for sample E75. Such narrow bands are typical for intentionally undoped GaAs of relatively good quality and are observed in similar N-containing GaAs-based structures, as published by Dhar et al.[3], Makimoto et al.[6] and Zhang et al. [7]. These bands have been explained, e.g. by Toivonen et al. [4], as due to free-to-impurity recombination.

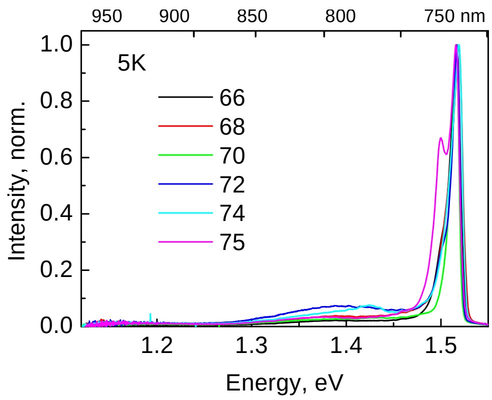


**Figure 2.** Low temperature PL spectra of all samples.

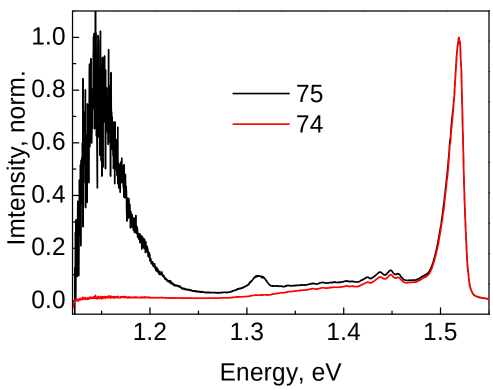


**Figure 3.** PL spectra of GaInAsN/GaAs samples.

A broad emission band at 1.3 - 1.5 eV is observed in the spectrum of the N-containing sample 72. The same band but with relatively lower intensity is observed in the spectra of the other N-containing samples 68-75 also shown in figure 2. This emission band is the only “individual” announcement of the N-content in the epitaxial layers studied and is an additional evidence for N presence in ternary or quaternary solid solutions, in accordance with the above discussed absorption spectra. Very weakly, near the noise level, this emission band is observable in the spectrum of the reference sample 66. For sample 70 the intensity of the 1.3 - 1.5 eV emission band is comparable with the intensity in the reference sample 66.

Figure 3 shows detailed emission spectra of the quaternary GaInAsN layers. We observe a set of 4 or 5 relatively narrow emission bands in the range 1.42 - 1.48 eV, shown in figure 3 for sample 74 and 75. These “peaks” grow up on the high-energy slope of the above discussed broad 1.3 – 1.5 eV emission band and support the assumption that the added In increases the optical activity of the nitrogen in the GaAs-based epilayers. Similar sets of 5 peaks in the same spectral region are reported by Makimoto et al.[6] and Zhang et al. [7];they are assigned - simultaneously with the peaks at 1.518 eV - to an excitonic activity of localized nitrogen states - a free exciton at 1.518 - 1.514 eV and an exciton bound on nitrogen as an isoelectronic impurity and on N-N pairs [6]. These excitonic lines are manifested at N-concentration in the layers up to $1.5\times10^{19}$ $cm^{-3}$. They disappear over this limit and are displaced by the wider emission band at 1.425 eV, which is assumed to belong to the GaAsN solid solution. In our case we observe the localized nitrogen states luminescence simultaneously with the “solid solution-related” 1.3 – 1.5 eV emission band.

Bands at 1.32 eV are observed in the emission spectra of GaInAsN layers - figure 3 black line. Similar emission bands are reported by Sprutte et al. [8] in QWs of GaInAsN and by Wang et al. [9] in

GaAsSbN, associated with potential fluctuations and N-clusters of more than two N atoms. The lowest-energy emission band observed in the GaInAs layer is at 1.15 eV - sample 74, figure 3. Similar bands are reported also by Toivonen et al. [4] and by Fan et al. [10] for QW structures.

## 4. Conclusion

Dilute nitride - GaAsN and GaInAsN - 0.2 – 0.8 μm thick layers are grown on GaAs substrates by low-temperature LPE using powder GaN as a nitrogen source. The heterostructures are investigated by optical transmission and photoluminescence spectroscopy. The absorption edge for all N-containing samples is red shifted compared to the GaAs one corresponding to nearly 0.2 at.% nitrogen in the solid solution. The PL spectra at 5 K show – except the GaAs-related excitonic emission bands – several emission bands at 1.3 - 1.5 eV and at 1.15 eV, attached to the ternary and quaternary solid solutions, respectively. A set of 4 or 5 relatively narrow emission bands in the range 1.42 - 1.48 eV in the PL spectra of GaInAsN layers is an evidence that the added In increases the optical activity of the nitrogen in the GaAs-based layers and that the nitrogen acts in localized states as well.

## Acknowledgments

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