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Investigation of melt-grown dilute GaAsN and GaInAsN nanostructures for photovoltaics

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Abstract

The present work demonstrates the possibility to use liquid phase epitaxy to incorporate nitrogen in epitaxial GaAsN/GaAs and GaInAsN/GaAs heterostructures, including nanoscaled ones. The structures are grown from Ga - and GaIn - melts containing polycrystalline GaN as a nitrogen source. The red shift of the absorption spectra corresponds to nitrogen content in the epitaxial layers near or less than 0.2 at %. Photoluminescence spectra of dilute nitride GaAsN and GaInAsN show emission from localized nitrogen states - N-nanoclusters of more than two N atoms. These studies show that the melt grown dilute GaAsN and GaInAsN nanostructures can be used for solar cells with extended long wavelength edge.

keywords: liquid phase epitaxy, GaAsN; GaInAsN; photoluminiscence

1. Introduction

Nanostructures for photovoltaics containing dilute III-nitrides, such as GaAsN and GaInAsN, are of considerable current interest for applications in modern multijunction solar cells extending their long wavelength edge. The content of a very low – less than 1% - molar fraction of GaN in GaAs leads to substantial changes in optical absorption and radiation spectra, reducing the effective band gap. Some features in the spectra show presence of N-containing nanoclusters in the solid solutions.

Technologically, the incorporation probability of nitrogen in GaAs is very small and it strongly depends on the growth conditions. Delute GaAsN - based solid solutions and heterostructures have been first grown by

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metaloorganic vapor-phase epitaxy (MOVPE) and molecular-beam epitaxy (MBE). Only one group, Dhar et al. [1], has reported on liquid-phase epitaxy (LPE) growth of these compounds. In this paper we study the optical properties of GaAsN and GaInAsN layers grown by LPE on GaAs substrates at different temperatures. One important feature is that GaInAsN quaternary solid solutions can have a perfect lattice match to a GaAs substrate with an appropriate In-to-N ratio in the solid solution.

2. Experimental procedure

GaAsN and GaInAsN compounds were grown by the horizontal graphite slide-boat technique for LPE on (100) n-type GaAs:Si. A low-temperature LPE version, presented by Andreev et al. [2] and Milanova and Khvostikov [3], was used. Epitaxial layers were grown 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 the studied layers. Nanoscaled epitaxial layers, 200 - 800 nm thick, were grown at initial temperatures in the range of 560 - 660ºC at a cooling rate of 0.5 ºC/min. The technological conditions of the as grown samples are summarized in Table 1.

Table 1.Growth conditions of the investigated samples

Sample	E66 GaAs	E68 GaAsN	E70 GaAsN	E72 GaAsN	E74 GaInAsN	E75 GaInAsN
T º C	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 double beam UV-VIS spectrophotometer UV-3600 Shimadzu. 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 488 nm Coherent 12 W Argon laser were obtained at 5 K. They were analyzed with a Jobin-Yvon Spectrometer HR460 and a multichannel CCD detector (2000 pixel).

2. Results and discussion

2.1. Absorption spectra discussion:

Figures 1 a, b show the transmission spectra of several GaAsN and GaInAsN layers compared with the reference GaAs sample E66. The insets show the behaviour of the normalized curves in a broader range. It is seen that the absorption edge for all N-containing nanoscaled layers is red shifted compared to the GaAs one. The red shift increases when the growth temperature of the samples decreases. This fact is in accordance with the effect of the growth temperature on N concentration in GaAsN reported by Toivonen et al. [4], thus confirming the incorporation of nitrogen at our growth conditions. The red shift of the absorption spectra observed in fig. 1, according to Tisch et al. [5], corresponds to nitrogen content in the epitaxial layers near or less than 0.2 at %.

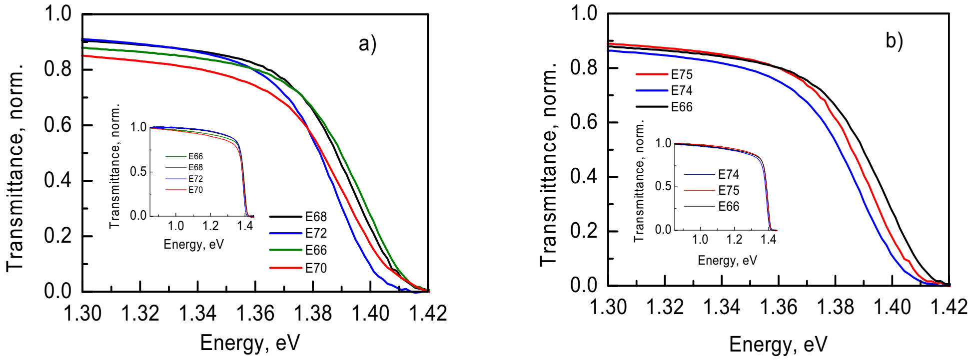

Fig. 1 Normalized transmission spectra of layers a) GaAsN/GaAs samples, b) GaInAsN/GaAs samples

2.2. PL spectra discussion

Fig. 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 the 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 and they are observed in similar N-containing GaAs-based structures, as published by Dhar et al.[1], Makimoto et al.[6] and Zhang et al. [7]. Some authors, e.g. by Toivonen et al. [4] attribute them as due to free-to-impurity recombination.

A broad emission band at 1.3 - 1.5 eV is observed in the spectrum of the N-containing sample E72. The same band but with relatively lower intensity is observed in the spectra of the other N-containing samples E68 - E75 also shown in fig. 2. This emission band is the only “individual” announcement of the N-content in the epitaxial layers studied. A very weak, near the noise level, this emission band is observable in the spectrum of the reference sample E66. For sample E70 the intensity of the 1.3 - 1.5 eV emission band is comparable with the intensity in the reference sample E66.

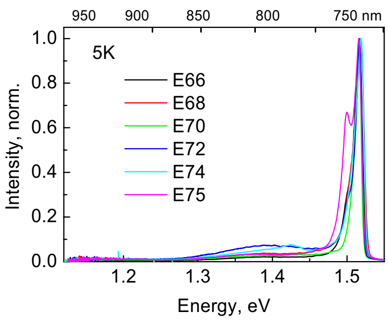

Fig.2 Low temperature PL spectra of all samples

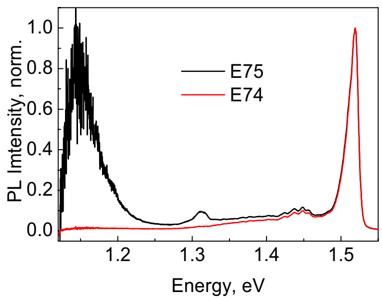

Fig.3 PL spectra of GaInAsN/GaAs samples

In the emission spectra of the quaternary GaInAsN layers we observe a set of 4 or 5 relatively narrow emission bands situated in the range 1.42 - 1.48 eV, shown in Fig. 3 for sample E74 and E75. These “peaks” appear on the high-energy slope of the above discussed broad 1.3 - 1.5 eV emission band and they support the assumption that the added In increases the optical activity of the nitrogen in the GaAs layers. Similar sets of 5 peaks in the same spectral region are reported by Makimoto et al. [6] and Zhang et al. [7] and they are assigned– simultaneously with the peaks at 1.518 eV - to an excitonic activity of N - 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 $1.5x10^{19}$ 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.

Additionally, bands at 1.32 eV are observed in the emission spectra of GaInAsN layers - fig. 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-nanoclusters of more than two N atoms. The lowest-energy emission band observed in the GaInAs layer is at 1.15 eV - sample E74, fig. 3. Similar bands are reported by Toivonen et al. [4] and by Fan et al. [10], also for QW structures.

3. Conclusion

Dilute GaAsN and GaInAsN 200 – 800 nm layers for application in multiheterojunction solar cells are grown on GaAs substrates by low-temperature LPE using powder GaN as a nitrogen source. The absorption edge of all N-containing samples is red shifted compared to the GaAs one corresponding to about 0.2 at % N in the solid. 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 attributed to N-nanoclusters of more than two N atoms and is an evidence that the added indium in the solid increases the optical activity of the nitrogen in the GaAs layers.

Acknowledgements

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