# Incorporation of nitrogen in melt grown GaAs♣

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Group III-V-nitrides, the so called dilute nitrides, are promising materials for multi-junction solar cells, telecommunications, heterojunction bipolar transistors and high frequency (THz) applications. The introduction of a tiny fraction (~1 %) of nitrogen in GaAs or GaP induces a decrease of the band gap energy and a deformation of the conduction band structure, which extends the range of its applicability. In the present work, we demonstrate the possibility of incorporating nitrogen in melt-grown GaAs layers. The dilute gallium arsenide-nitride layers were grown on GaAs substrates by liquid-phase epitaxy, using polycrystalline GaN as a source of nitrogen in the melt. Characterisation of the structural and electrical properties was done by XRD, XPS analysis, FTIR spectra and Hall effect measurements in the range 80-300K.

## 1. Introduction

Considerable interest in III-V-N dilute nitride thin film alloys, such as GaAsN, is due both to their fundamental physical properties and potential device applications [1]. The substitution of a few percent of As atoms in GaAs by N atoms leads to a strong reduction in the band gap energy. This characteristic makes GaAsN alloys very attractive for application in multi-junction solar cells, extending the wavelength range further into the infra red. Metal-Organic Chemical Vapour Deposition (MOCVD) and Molecular Beam Epitaxy (MBE) are the commonly used methods for dilute nitride alloy growth.

The addition of nitrogen to GaAs reduces the optoelectronic quality: it decreases the electron mobility, the photoluminescence intensity and lifetime, and brings about an increase in the background carrier concentration [2-4]. Even for low N contents in as-grown samples, the N interstitials are the major defect formed in nitride arsenides, due to the large size mismatch between the As and N atoms. At low concentrations, N incorporation has proven problematic [5, 6] for III-V –N alloys, and it remains a challenge to demonstrate 3-4 microns thick high quality dilute nitride epilayers for solar cell applications.

In this paper, the incorporation of nitrogen in $GaAs_{1-x}N_x$ layers several microns thick, grown from a melt, using polycrystalline GaN as a nitrogen source, is studied.

## 2. Experimental

The $GaAs_{1-x}N_x$ layers were grown in a conventional horizontal liquid phase epitaxy (LPE) reactor used for the fabrication of multilayer III-V solar cell heterostructures. No special baking of the system was done before epitaxy. The layers were obtained on (100) semi-insulating or on n+ GaAs substrates. The starting materials for the solutions consisted of 99.999 % pure Ga, polycrystalline GaAs and GaN. The charged boat was heated at 780°C for 1 h in a purified $H_2$ gas flow, in order to dissolve the source materials and decrease the contaminants in the melt. Two series of samples were grown from different initial epitaxy temperatures of 700 and 660 ºC. The crystallization was carried out from supersaturated melts of 10 ºC with 1 at. % GaN content for 20 minutes, at a cooling rate of 0.8ºC/min.

X-ray diffraction (XRD) measurements were performed using a Bruker AXS D8 Advance diffractometer with a copper anode.

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Absorption Fourier Transform Infrared (FTIR) measurements were made on a Shimadzu FTIR spectrophotometer IR PRESTIGE-21.

The Hall mobility and carrier concentration in the layers were measured by the Van der Pauw Hall technique on $5 \times 5$ mm$^2$ square samples, with alloyed indium ohmic contacts.

X-ray photoelectron spectroscopy (XPS) was employed to study the nitrogen bonding configurations and the influence of annealing on the nitrogen concentration. Some of the GaAs$_{1-x}$N$_x$ layers were annealed in a flow of 100% nitrogen for 10 min at 750°C. XPS analysis was performed using an ESCALAB II (VG Scientific) spectrometer.

## 3. Results and discussion

Figs. 1 a) and b) show the High Resolution XRD (004) scan spectra of undoped GaAs and GaAs$_{1-x}$N$_x$ layers, grown on semi insulating GaAs substrates. The spectrum of the undoped sample is typical of monocrystalline GaAs material. For the GaAs$_{1-x}$N$_x$ sample, the N content determines the line shape of the main peak: it manifests itself as a broad shoulder evolving into a weak separate peak shifted to the right from the (004) GaAs substrate reflection (Fig1 b).
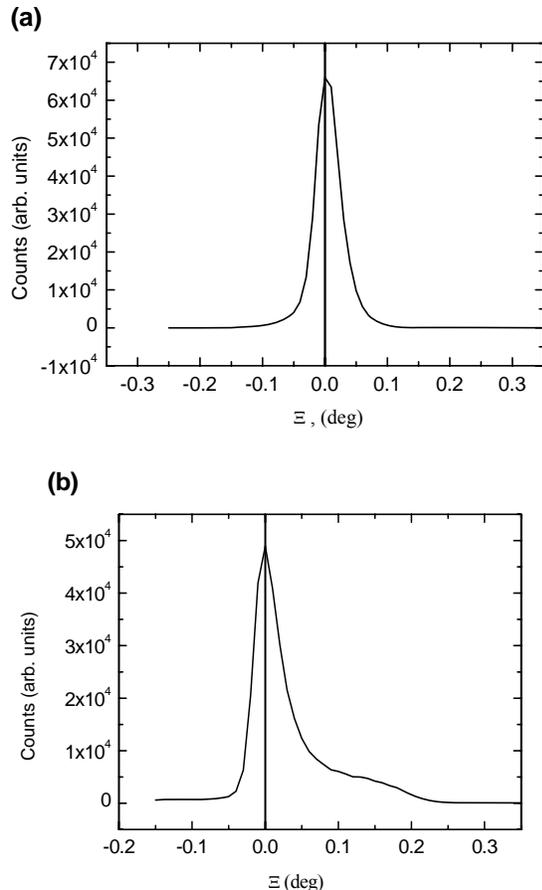
**(a)**



**(b)**



*Fig. 1. XRD spectra of n-GaAs (a) and GaAs$_{1-x}$N$_x$ (b) samples.*

The nitrogen bonding configurations in GaAs$_{1-x}$N$_x$ alloys grown by LPE have been studied using XPS. The spectra were measured over a range of binding energies from 1 to 550 eV. XPS analysis of samples that contain Ga and N is complicated, since for both commonly used x-ray source anode materials (Al and Mg), the Ga Auger peaks occur in the same region of the spectrum as the N 1*s* photoelectron peak.

The X-ray photoelectron spectra of the N 1s photoelectron and Ga LMM Auger lines, recorded from the as grown and annealed GaAs$_{1-x}$N$_x$ samples prepared in different temperature ranges, are shown in Figs. 2 and 3



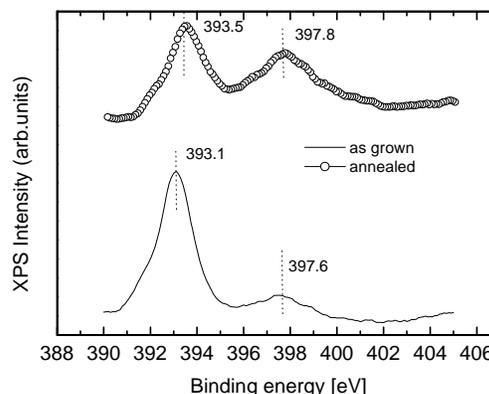*Fig. 2 XPS spectra of N 1s and Ga LMM lines from sample E 27 grown in the 700-685ºC range, as grown and after annealing*



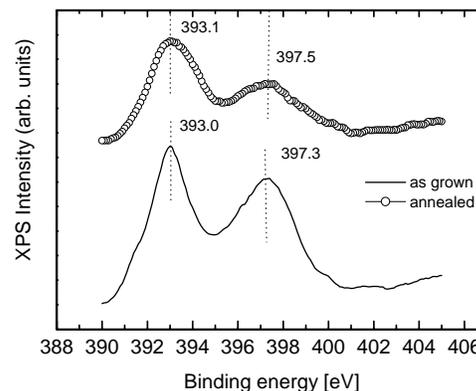*Fig. 3. XPS spectra of N 1s and Ga LMM lines from sample E 30 grown in the 660-645ºC range, as grown and after annealing*

The spectral region for as grown samples includes the low binding energy tail of a Ga LMM Auger peak centred at 393.1 eV, and the N 1s level photoemission peak at a binding energy of 397.6 eV.

The variation of the intensity of the N 1s peak with respect to the Ga LMM peaks reflects the different nitrogen contents of the samples. Sample E27 (Fig. 2), grown from a higher initial epitaxy temperature of 700 ºC exhibits a N 1s peak with lower intensity, in comparison with the N 1s peak intensity of sample E30 (Fig. 3), grown in the lower temperature range 660-645°C. Fig. 2 shows a slight increase in the intensity of the N 1s peak of sample E27 after annealing. The increased nitrogen incorporation may be due to the diffusion of N atoms from the bulk layer to the surface during annealing. For sample E30, which has higher nitrogen content, after annealing the N 1s peak decreases and broadens (Fig 3). The broad N 1s peak, centred at 397.5 eV, is attributed to superposition of N 1s and other chemically shifted components of the Ga LMM lines associated with the Ga-N bonding [7]. Annealing reduces the overall nitrogen concentration, due to out-diffusion of nitrogen, and the presence of point defects induced by the low growth temperatures promotes a change in the N-bonding configuration.
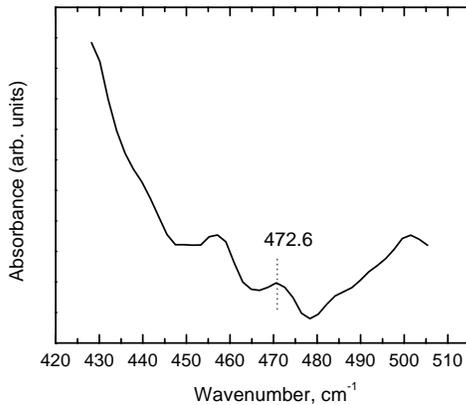
dependencies of the Hall-concentration differ more substantially. The curve for the undoped sample decreases monotonically with temperature decrease, corresponding to the temperature change of the Hall-scattering factor for prevailing impurity-scattering. The curve of the sample doped with nitrogen has the same character at higher temperatures. The numerically estimated high-temperature slopes of both curves are near 2 meV, and they do not represent an activation but only a temperature variation of the Hall-scattering factor. The $n_H(T)$ curve does not remain monotonic: at temperatures lower than 120 K it begins to grow. Such an increase in the Hall-concentration with temperature decrease is an indication of conduction via impurities.
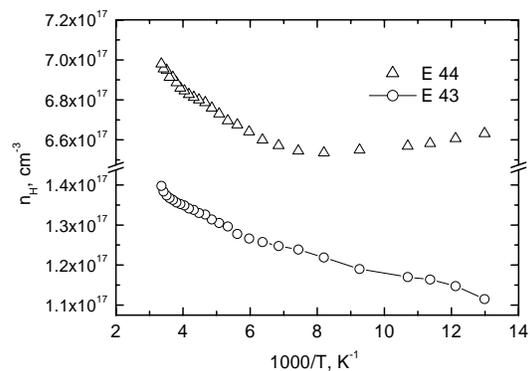


*Fig. 5. Temperature dependencies of the Hall concentration for an undoped (43) and a N-doped sample (44)*

Fig. 6 presents the temperature dependencies of the Hall-mobility $\mu_H$. The mobility of the sample doped with nitrogen is considerably lower, and it has a well expressed low-temperature decrease (scattering by impurities). The mobility maxima of both curves are almost at the same temperature with a relatively small difference of about 20K, which is an indication of scattering specificity. At a later stage, an attempt will be made for a better insight into the mobility of nitrogen-doped layers.



*Fig. 4. FTIR spectrum of a GaAs$_{1-x}$N$_x$ layer on an n- GaAs substrate*

FTIR absorption spectra of an epitaxially grown GaAs$_{1-x}$N$_x$ layer on a n-GaAs substrate were measured. A peak at 472.6 cm$^{-1}$(Fig. 4), attributed to a local vibrational mode of nitrogen at arsenic sites in GaAs [8], is clearly seen.

The electrical parameters of an intentionally undoped layer and a nitrogen-doped one, both grown on semi-insulating GaAs substrates, were measured in the temperature range 80 – 300 K, using the van der Pauw geometry.

Fig. 5 shows the temperature variation of the Hall-concentration $n_H$. It is seen that both samples are n-type and the layer containing nitrogen has a several times higher electron concentration. The temperature
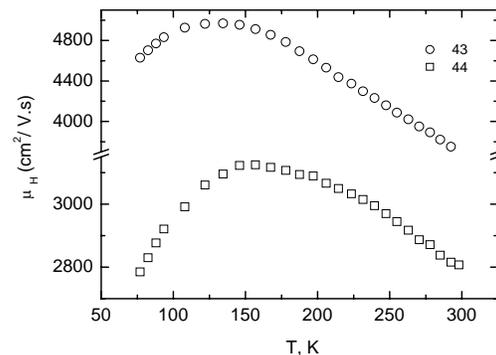
*Fig. 6 Temperature dependencies of Hall mobilities for*
*an undoped (43) and a N-doped sample (44)*

The curves of Hall concentration and mobility for both samples – intentionally undoped and nitrogen-doped –correspond to moderately doped GaAs near the degeneracy limit or higher. The sample doped with nitrogen remains n-type. The increase in the Hall concentration at high temperatures is still not an impurity activation. Nevertheless, one can suggest that in our case, nitrogen behaves mainly as an isoelectronic donor, that arises from the local heterojunction scheme GaAs-GaN according to Bellaiche et al. [9]. The calculated energy depth of this donor is greater, but its thermal ionization energy can decrease at higher concentrations, so that some of the donors could be ionized in the temperature range studied. Their concentration is probably higher than the alternative local acceptor-like levels of N predicted by Bellaiche et al. [9], if the latter have been formed at all.

The assumption of an isoelectronic donor can explain qualitively the greater slope of the low temperature mobility region of the nitrogen-doped sample.

## 4. Conclusions

The structural and electrical properties of $GaAs_{1-x}N_x$ layers grown by LPE have been studied.

The grown layers were characterized by XRD, XPS, FTIR and Hall measurements. XRD and XPS and FTIR measurements confirmed the presence of nitrogen in the layers.

A high electron concentration, (greater than $6.6 \times 10^{17}$ $cm^{-3}$) in $GaAs_{1-x}N_x$ layers, 3-4 μm thick, grown by LPE has been achieved. In comparison to undoped samples, this corresponds to a 5-6 times enhancement in the free electron concentration. The mobility values of the sample doped with nitrogen are lower than those of the undoped layers, but considerable higher than those obtained in n-type GaAsN films with similar free electron concentration, grown by MOCVD.

In order to obtain reproducible high quality dilute nitride epitaxial layers, additional studies on the alloys' growth and their properties are required.

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