Dilute nitride InGaAsN and GaAsSbN layers grown by liquid-phase epitaxy for photovoltaic applications

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Abstract. Dilute nitride InGaAsN and GaAsSbN layers are grown by low-temperature liquid-phase epitaxy (LPE) on GaAs substrates and characterized in view of application in solar cells. The composition of the layers is determined by energy-dispersive X-ray spectroscopy. X-ray photoelectron spectroscopy measurements confirm the Sb content and provide information about the chemical bonding of the N atoms. The band gap values at room temperature assessed from surface photo-voltage and photoluminescence measurements are in good agreement. The experimental results show that the layers exhibit reproducible properties, including a good optical quality and a photosensitivity red limit extended in comparison to GaAs down to about 1.33 – 1.37 eV for InGaAsN and 1.19 – 1.23 eV for GaAsSbN layers. The results obtained highlight the capacity of the LPE for growing dilute nitride layers with good optical quality for photovoltaic applications.

1. Introduction
Quaternary InGaAsN, GaAsSbN dilute nitrides have attracted recently considerable attention due to their advantages for solar cells applications [1–3]. They are a novel class of semiconductor materials, which has emerged from the conventional III – V compounds by incorporation of a small amount of nitrogen in the crystal lattice. It has been found that the substitution of group V anions in III – V compounds with small fractions of nitrogen leads to a significant change in their electronic properties, in particular, narrowing the band gap and shifting the absorption edge to the longer wavelengths [4]. These compounds offer the possibility of engineering their band gap and lattice constants, which creates an additional flexibility desired in a variety of applications in advanced optoelectronic devices [5]. However, the incorporation of nitrogen into the crystal lattice creates a high density of N-related clusters and point defects in the grown structures, which significantly affects a device performance [6,7]. For InGaAsN compounds, the local ordering has a great impact on the band gap formation and on the optical properties [3,8]. GaAsSbN compounds contain only one element from group III and their electronic structure is less dependent on the entire configuration

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compared to InGaAsN. The advantages of this system are the absence of In-related defects and the possibility to achieve operation at longer wavelengths with lower N concentration. Furthermore, the conduction and valence band energies can be adjusted independently, while keeping the lattice-matching to GaAs [9,10]. This quaternary system has been much less investigated as compared to quaternary InGaAsN compounds, but, like them, it also suffers from poor optical properties and abnormal band structure due to N-related defects.

The epitaxial growth of dilute nitride bulk layers remains a great challenge because of the low incorporation efficiency of N into the growing crystal, the large lattice constant difference between nitrides and arsenides and the high local strain near N atoms. This is why the growth conditions are crucial for the quality of the epitaxial layers. Conventional fabrication methods, such as molecular beam epitaxy and metalo-organic chemical beam deposition operating under extreme non-equilibrium conditions favor the formation of various defects responsible for many of the anomalous optical and transport properties of dilute nitride alloys [6,7]. In contrast to other epitaxial methods, the crystallization in liquid phase epitaxy (LPE) is carried out under near equilibrium conditions and has recently shown promise in obtaining high-quality dilute nitride layers in terms of mobility and lack of defects in the epitaxial layers [11].

In this work, we investigate the incorporation of nitrogen into InGaAs and GaAsSb alloys during LPE growth. The local bonding of nitrogen in the material is studied by XPS. Photoluminescence (PL) and surface photo-voltage (SPV) spectroscopy at room temperature are used to study the optical quality and electronic band structure of the as-grown dilute nitride InGaAsN and GaAsSbN alloys.

2. Experimental

The epitaxial layers were grown in a conventional horizontal LPE reactor using the piston boat technique on an (100) n-type GaAs substrate. A low-temperature variant of the LPE method was used in order to avoid phase separation as a result of nitrogen incorporation [12]. However, at temperatures lower than 600 °C a large miscibility gap exists for Ga-rich compounds in the In-Ga-As and Ga-As-Sb system [13]. The technological conditions were carefully chosen in order to grow monocrystalline InGaAsN and GaAsSbN layers lattice-matched or with small mismatch to the GaAs substrate. The starting materials were Ga, In, Sb metals solvent and polycrystalline GaAs and powder GaN were used as sources for As and N. InGaAsN layers with a thickness of 1 μm were grown from an In-rich (90% In +10% Ga) solution in the temperature interval 555 – 552 °C at a cooling rate of 0.5 °C/min. The crystallization of GaAsSbN layers with the same thickness was carried out from a mixed (95% Ga +5% Sb) melt in the temperature interval 560 – 545°C at a cooling rate of 0.8 °C/min. The thickness of the layers was measured on cross-section by scanning electron microscopy (SEM) (Tescan LYRA IXMU). The In and Sb content in the InGaAsN and GaAsSbN samples determined by energy dispersive X-ray spectroscopy (EDX) (Quantax, Bruker) was about 3% and 6.8%, respectively. In order to assess the chemical bonding of the N atoms and their concentration in the alloys, X-ray photoelectron spectroscopy (XPS) was used.

The band gap and optical absorption edge were examined by photoluminescence (PL) and surface photo-voltage (SPV) measurements at room temperature. The PL measurements were performed by means of an AvaSpec-2048TEC thermo-electrically cooled fiber-optic spectrometer equipped with a Sony 2048 CCD light detector and excited by a 50-mW 405-nm laser. The SPV spectra were recorded in the metal-insulator-semiconductor operation mode of the SPV technique using the set-up and measurement procedure described in [14]. It includes a 250-W halogen lamp along with a SPEX grating monochromator (f = 0.25 m, 600 gr/mm) and an optical chopper (94 Hz). The probe electrode was a semi-transparent SnO\textsubscript{2} film evaporated on the bottom surface of a quartz glass and separated by a sheet of mica (15 μm) from the sample, which was positioned on a copper platform. The SPV signal was fed to a high-impedance unity-gain buffer and then measured by a SR830 lock-in amplifier. The scanning was from high to lower wavelengths keeping the photon flux constant (≈10\textsuperscript{14} cm\textsuperscript{-2} s\textsuperscript{-1}) for all wavelengths.
3. Results and discussion

Figure 1 (a) and (b) presents XPS spectra of InGaAsN and GaAsSbN layers, respectively, compared to the spectrum of reference GaAs. The XPS analysis is complicated because the Ga LMM Auger and N 1s photoelectron peaks overlap when Al Kα radiation is used. In the case of InGaAsN, the comparison with GaAs referent crystal allows one to detect the N 1s core-level peak (Gaussian, FWHM of 0.8 eV) at 397.2 eV in the spectrum. This peak is partially overlapped with the contribution of the 1S final-state term in the L2M45M45 Auger process. In the ideal case, N has five different nearest-neighbor configurations for InGaAsN, and their binding energies are closely distributed in an interval of 1 eV from 397.0 eV (energy of the 4-In configuration) to 398.0 eV (energy of the 4-Ga configuration) [15,16]. Therefore, the observation of the 397.2 eV peak in figure 1a indicates that N–In is the dominant bonding configuration in our InGaAsN samples.

In the case of GaAsSbN, nitrogen can be bonded only to Ga-atoms, but the N concentration is significantly lower compared to that in InGaAsN, which makes it difficult to distinguish the N 1s line from the Ga LMM structure. To address this problem, we used a MgKα excitation source resulting in a displacement of the GaLMM structure to lower binding-energies. Nevertheless, the photoelectron background also contains a broad Ga Auger peak [17]. Its lower intensity allows one to distinguish the N 1s signal by using higher experimental parameters – pass energy, X-ray flux and registration time. The spectra of the GaAsSbN and GaAs samples are shown in figure 1(b). In their difference spectrum, a weak peak attributed to the N 1s line appears at about 398 eV. This confirms the presence of a very small nitrogen concentration in the GaAsSbN sample, at the limit of the detection sensitivity (~ 0.1 at%).

The lower N content in the GaAsSbN layers could be explained by the significantly higher incorporation efficiency of Sb atoms than those of N atoms into the As anion sublattice. In the case of InGaAsN alloys, In incorporates in the Ga-sublattice, while N incorporates in the As-sublattice. It has been found that under near-equilibrium lattice-matched LPE growth conditions, the nitrogen incorporation efficiency increases in order to compensate the compressive strain caused by the large indium atoms.

Typical PL spectra of InGaAsN and GaAsSbN layers are shown in figure 2. They reveal broad peaks of band-edge luminescence with an exponential tail at the high-energy side resulting from the Boltzmann carrier distribution. The PL peak of GaAsSbN is broader and red-shifted by 140 meV with respect to that of InGaAsN. The band gap energy values estimated from the position of the PL peaks are 1.37 eV for InGaAsN and 1.23 eV for GaAsSbN. The nitrogen content in the dilute nitride layers

![Figure 1](image1.png)

Figure 1. N1s photoelectron spectra of InGaAsN (a) and GaAsSbN (b) samples, compared to those of GaAs standard. In (a) The different peak contributions are colored in blue and their sum in red. The N 1s peak area (in the low spectrum) is filled in green. In (b) the difference between the two spectra is plotted, where the fit of the N1s peak is marked in red.

![Figure 2](image2.png)

Figure 2. Room-temperature PL spectra of InGaAsN and GaAsSbN layers.
was theoretically calculated applying the band-anticrossing model [18] with the experimentally determined values of the band gaps from the PL spectra and the measured contents of In and Sb. The composition of the investigated layers was found to be $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.997}\text{N}_{0.003}$ and $\text{GaAs}_{0.901}\text{Sb}_{0.068}\text{N}_{0.001}$.

The SPV measurements confirmed the band gap values determined from the PL spectra. Figure 3 presents the normalized SPV amplitude spectra of the GaAsSbN and InGaAsN samples compared to that of the GaAs substrate. The small undulations in the SPV spectra are due to interference effects caused by the mica sheet. The spectra reveal steep jumps of the signal, which are related to the absorption edge of the semiconductor materials. A clear red shift of the absorption edge with respect to GaAs is observed for the dilute nitride layers. These values are in good correspondence with the PL results taking into account the peculiarities of the SPV generation process [19]. A decrease in the band gap with respect to GaAs is expected due to the presence of nitrogen. However, in the case of GaAsSbN, it is larger than in InGaAsN by 140 meV. This is explained by the replacement of indium with antimony in the growth process. During the LPE growth, the active incorporation of Sb into the As-sublattice moves the edge of the valence band toward the higher energies [10], thus further decreasing the band gap.

4. Conclusions
Dilute nitride layers with compositions $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.997}\text{N}_{0.003}$ and $\text{GaAs}_{0.931}\text{Sb}_{0.068}\text{N}_{0.001}$ were grown by low-temperature LPE. Preferential In-N bonds formation in the InGaAsN layers and the presence of nitrogen of around 0.1% in the GaAsSbN compounds were identified by XPS measurements. The band gap narrowing in the grown layers relative to the band gap of GaAs was determined from PL spectra at room temperature to be 50 meV for InGaAsN and 190 meV for GaAsSbN. The higher value for GaAsSbN is due to the higher antimony incorporation efficiency into the crystal lattice of these compounds during crystallization at nearly equilibrium conditions. These results were confirmed by SPV measurements showing a red photosensitivity limit extended down to 1.33 eV for InGaAsN and 1.19 eV for GaAsSbN.

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