Surface photovoltage and photoluminescence study of thick Ga(In)AsN layers grown by liquid-phase epitaxy

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Abstract. We present an experimental and theoretical study of Ga(In)AsN layers with a thickness of around 1 μm grown by liquid-phase epitaxy (LPE) on n-type GaAs substrates. The samples are studied by surface photovoltage (SPV) spectroscopy and by photoluminescence spectroscopy. Theoretical calculations of the electronic structure and the spectral dependence of the dielectric function are carried out for different nitrogen concentrations using a full-band tight-binding approach in the sp3d5s*N parameterisation. The SPV spectra measured at room temperature clearly show a red shift of the absorption edge with respect to the absorption of the GaAs substrate. This shift, combined with the results of the theoretical calculations, allows assessing the nitrogen concentration in different samples. The latter increases with increasing the In content. The analysis of the SPV phase spectra provides information about the alignment of the energy bands across the structures. The photoluminescence measurements performed at 2 K show a red shift of the emission energy with respect to GaAs, in agreement with the SPV results.

1. Introduction
The addition of nitrogen in small concentrations is known to shift the absorption edge of III-V materials to longer wavelengths, which makes dilute III-V nitrides promising materials for advanced optoelectronic devices [1]. The commonly used fabrication methods for dilute nitrides are molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD). Another technique, liquid-phase epitaxy (LPE), has recently shown promise in obtaining high-quality dilute nitride layers with low defect concentrations for optoelectronic applications [2,3]. In contrast to other epitaxial methods, the crystallization at LPE growth is carried out under near equilibrium conditions, which provide a high-quality material in terms of lifetime, mobility and absence of defects in the epitaxial layers. However, since LPE has rarely been used for growing this type of materials, the data for the
structural, optical and electronic properties of LPE-grown Ga(In)AsN alloys are still scarce. Therefore, these materials need to be extensively studied in comparison with materials fabricated by more conventional techniques like MBE and MOCVD.

Among the experimental techniques applied to dilute nitrides, surface photovoltage (SPV) spectroscopy has been relatively rarely used [4,5] although it provides information on the optical absorption spectrum and carrier transport in the sample [6]. Besides, the few reported SPV studies on dilute nitrides only concern MBE or MOCVD grown samples. The present contribution partially fills this gap by presenting an original study of the electronic and optical properties of LPE-grown Ga(In)AsN layers based on SPV spectroscopy, combined with photoluminescence (PL) and semi-empirical tight-binding calculations.

2. Experimental
A series of GaAsN and GaInAsN epitaxial layers were grown by the horizontal graphite slide-boat technique for LPE on (100) n-type GaAs:Si (~10^{18} cm^{-3}) substrates. A flux of Pd-membrane purified hydrogen at atmospheric pressure was used for the experiments. No special baking of the system was carried out before epitaxy. The starting materials for the solutions consisted of 6N pure solvent metals Ga, In and of polycrystalline GaAs and GaN with a purity of 5N. Ternary GaAsN compounds were grown from Ga-rich solution, and quaternary GaInNAs with low In content were fabricated from mixed In+Ga melt. The N content in the melt was 0.5 at % for all grown layers. The 1-2 µm thick epitaxial layers were grown from initial epitaxy temperature varying in the range 620-570 °C at a cooling rate of 0.8 °C/min for 3-4 minutes. The layer thicknesses and composition were determined using a LYRA I XMU (Tescan) scanning electron microscope equipped with an energy dispersive X-ray (EDX) microanalyzer (Quantax, Bruker) in the Laboratory of Material Technology, Department of Solid State Physics and Microelectronics, Sofia University. The In content in the GaInAsN layers varied in the range 0.01-0.02 depending on the melt composition and epitaxy temperatures. Hall measurements revealed n-type doping of the layers in the 6-7×10^{17} cm^{-3} range.

The SPV spectra were recorded at room temperature using the metal-insulator-semiconductor operation mode of the SPV technique [6]. A 250 W halogen lamp along with a SPEX grating monochromator (f = 0.25 m, 600 gr/mm) and an optical chopper (94 Hz) were used for illumination. The probe electrode was a semitransparent SnO_2 film evaporated on the bottom surface of a quartz glass. A sheet of mica (15µm) was placed between the probe and the sample. The probe signal with respect to the ground was fed to a high-impedance unity gain buffer and then measured by an SR830 lock-in amplifier. The photon flux was kept constant (=1.5×10^{14} cm^{-2} s^{-1}) within ± 0.5 % for all wavelengths by positioning a neutral density filter with a variable optical density. The reference signal from the optical chopper defined the zero value of the SPV phase. More details about the SPV experimental set-up and measurement procedure can be found in [7]. The spectral resolution of the measurements was limited to 10 meV, which determined the precision of the energy positions presented below.

The photoluminescence was measured at 2 K. The sample was excited by a CW Ar-ion laser at the wavelength of 351 nm (3.53 eV) and a power of ~3 kW/cm^2. A CCD camera was used for detection.

3. Theoretical calculations
The electronic structure of Ga_{1-x}In_{x}As_{1-y}N_y was calculated using the semi-empirical tight-binding method for dilute nitrides in the sp^3d_5s_1 tight-binding parameterization, including the spin-orbit coupling [8,9]. The imaginary part of the dielectric function was computed using the Fermi Golden Rule and the dipole approximation for the transition probabilities [10]. The integration over the Brillouin zone was carried out over 1.25×10^5 k-points and the spectra were smoothed out using a convolution with a Gaussian with half-width at half maximum equal to 15 meV. As the tight-binding parameters were calculated for 0 K, a temperature correction of 96.5 meV [11] was applied to compare the theoretical dielectric function to the experimental spectra. The absorption edge offset of Ga_{1-x}In_{x}As_{1-y}N_y with respect to pure GaAs was calculated using non-linear bandgap dependences.
(bending parameters) and band offsets from Ref. [11] for N and In concentrations in the expected experimental range ($x \leq 0.01; y \leq 0.1$, respectively).

**Figure 1.** SPV spectrum of a GaAsN sample (symbols) compared with the calculated imaginary part of the dielectric function of GaAs$_{1-x}$N$_x$ (lines).

**Figure 2.** Determining the bandgap of the GaAsN sample from figure 1 using the squared SPV spectrum.

4. Results and discussions

The symbols in figure 1 represent the SPV spectrum of a GaAsN sample. It is compared with the calculated imaginary part of the dielectric function of GaAs$_{1-x}$N$_x$ for $x$ ranging from 0 (right curve) to 0.01 (left curve) with a step of 0.001. The comparison shows that the N content in the experimental sample is likely to be $x = 0.001$ (0.1%). This is confirmed by the following considerations. To assess the bandgap of the material we plot the square of the SPV vs photon energy, which for the ideal case of a bulk semiconductor should give a straight line resulting from the shape of the 3D combined density of states. In the present case we consider the linear part of the obtained curve and extrapolate the straight line to find its intersection with the abscissa (see figure 2), which is assumed to be the bandgap, $E_g$. For the current sample $E_g = 1.39$ eV and therefore the bandgap shift $\Delta E_g$ with respect to GaAs ($E_g = 1.42$ eV) is 30 meV. Figure 3 shows calculated bandgap shifts as a function of the In content ($y$) in Ga$_{1-x}$In$_x$As$_{1-x}$N$_x$ for several N content values as in figure 1. For $y = 0$ (i.e. GaAsN) and $x = 0.001$, $\Delta E_g = 31$ meV in accordance with the experimental finding.

Figure 4 represents the normalized SPV amplitude spectrum of a GaInAsN sample with In content $y \approx 0.015$ (~1.5%) compared with that of the GaAs substrate. The small undulations in the spectra are due to the interference effects caused by the mica sheet. Plotting the square of the SPV vs photon energy for both curves we obtain $E_g = 1.35$ eV and $E_g = 1.42$ eV for the GaInAsN layer and the GaAs substrate, respectively, which gives $\Delta E_g = 70$ meV. Comparing the values of $y$ and $\Delta E_g$ with the curves from figure 3 we obtain $x \approx 0.002$ (~0.2%) for the N content in this sample. Similar considerations applied to samples with In content about 2% give $\Delta E_g \approx 90$ meV and therefore $x \approx 0.003$ (0.3%). In samples with 1% In content we obtain $\Delta E_g \approx 40$ meV and $x \approx 0.001$ (0.1%). The above described results lead to the conclusion that the N content in the layers increases from 0.1% to 0.3% with increasing the In content from 1% to 2%.

Figure 5 represents with stars the bandgap reduction in Ga$_{1-y}$In$_y$As due to the addition of In [11]. As can be seen, it is only 19 meV when the In content increases from 0 to 2%. The above discussed experimental bandgap shifts $\Delta E_g$ are represented with circles on the same figure. They are quite larger as compared to the shifts only due to In. Therefore, they are mainly due to the presence of N in the samples. On the other hand, the difference between $\Delta E_g$ of the GaAs$_{0.999}$N$_{0.001}$ (30 meV) and
Figure 3. Calculated bandgap shifts with respect to pure GaAs as a function of the In content (y) in Ga$_{1-x}$In$_x$As$_{1-x}$N$_x$. The dotted line corresponds to the lattice-matched condition $y = 3x$. The dashed lines mark the experimentally obtained bandgap shifts and the corresponding In contents.

Figure 4. SPV amplitude (symbols) and phase (lines) spectra of n-GaAs substrate (triangles and dashed line) and a GaInAsN sample (circles and solid line), measured at 300K.

Figure 5. Bandgap shifts as a function of In content in GaInAs [11] (stars) and GaInAsN (circles). The lines are guides for the eyes.

Figure 6. Photoluminescence spectrum of a GaInAsN sample, measured at 2 K.
5. Conclusions
An original study is presented of the optical properties of thick LPE grown Ga(In)AsN layers. The absorption features, measured by SPV spectroscopy, are compared with results obtained by tight-binding calculations. In this way, an indirect assessment of the N content in the layers is achieved. For the GaInN sample the N content is found to be 0.1%. On the other hand, with increasing the In content in the layers from 1% to 2% the incorporation of N increases from 0.1 % to 0.3%. The bending of the energy bands determined by the SPV phase spectra is found to be upward both at the surface and at the interface layer/substrate. This work demonstrates the applicability of the SPV technique as an alternative of the optical absorption spectroscopy for studying dilute nitride materials. The results obtained contribute to the better understanding of the physical properties of dilute nitrides grown by LPE and their potential for optoelectronic applications. Work is under progress for achieving GaInAsN samples with larger N contents, respectively with larger bandgap shifts.

Acknowledgements
This work was supported by the research fund of the Sofia University (contract 71/2015) and COST action 1406 MutiscaleSolar. Prof. B. Arnaudov is acknowledged for the Hall measurements and K. Genkov for the EDX measurements.

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