Surface photovoltage study of GaInNAs layers for photovoltaic applications

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Abstract. The optical and carrier transport properties of GaInNAs layers grown by molecular beam epitaxy on n-GaAs substrates are studied by surface photovoltage (SPV) spectroscopy combined with photoluminescence (PL) measurements data. The SPV spectra clearly show a red shift of the band gap energy with respect to the band gap of GaAs, which is in line with the PL results. The combined analysis of the SPV amplitude and phase spectra has allowed determining the residual doping type in the layer. The minority carrier diffusion length was assessed by means of the method called “constant SPV”.

1. Introduction
Dilute nitrides form a novel class of semiconductor alloys, which has emerged from the conventional III-V compounds by incorporating a small amount of nitrogen. The interest in these compounds is due to their potential to alter the energy band gap and the lattice constant, which creates additional flexibility desired in many applications such as multijunction solar cells [1], heterojunction bipolar transistors [2] and high-speed photodetectors [3]. Different experimental techniques have been used to investigate such materials. However, surface photovoltage (SPV) spectroscopy has been relatively rarely applied [4–7], although it provides information on the optical absorption spectrum and carrier transport in the sample [8]. To partially fill this gap we present an original study of the optical and electronic properties of GaInNAs layers based on SPV spectroscopy, combined with photoluminescence (PL) results.

2. Experimental
The samples under study were grown by molecular beam epitaxy (MBE). They consisted in an n-GaAs substrate (350 μm), an n-GaAs buffer (200 nm) and a nominally undoped Ga₁₋ₓInₓN₀ₓAs₀₋ₓ dilute nitride layer of 1000 nm. The doping for n-GaAs was 5×10¹⁷ cm⁻³. The nominal content of In and N was y ~ 0.06 and x ~ 0.02, respectively.

The SPV measurements were performed at room temperature using the metal-insulator-semiconductor operation mode of the SPV technique [8]. The probe electrode was a semi-transparent SnO₂ film evaporated on the bottom surface of a quartz glass. The excitation was performed using a 250 W halogen lamp along with a SPEX grating monochromator (f=0.25 m, 600 gr/mm) and an optical

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chopper (94 Hz). The light wavelength was scanned from high to low values. The photon flux was kept constant ($\approx 10^{14}$ cm$^{-2}$s$^{-1}$) by adjusting the position of a neutral density filter with variable optical density according to the signal of a spectrally flat Golay detector (Oriel IR50). The probe signal with respect to the ground was fed to a high-impedance unity gain buffer and then measured by a Lock-in amplifier (SR830). The reference signal from the optical chopper defined the zero value of the SPV phase. For that purpose we took all precautions to eliminate undesired phase shifts, following the procedures described in [9]. More details about the SPV set-up and measurement procedure can be found in [9,10].

PL spectra were measured at room temperature with Accent RPM 2000 PL mapper by using 532 nm laser excitation.

3. Results and discussions

Figure 1 represents typical SPV amplitude and phase spectra measured with light excitation from the layer side. The sharp increase of the amplitude around 1150 nm corresponds to the onset of the band-to-band transitions in GaInNAs. The band gap assessed from Tauc plot is $E_g = 1.08$ eV. Therefore, the band gap shift $\Delta E_g$ with respect to the band gap of GaAs (1.42 eV) is 0.34 eV. Figure 1 represents also the PL spectrum of the same sample. The band gap value estimated from the SPV data is close to the PL peak position (1.117 eV) indicating a good agreement between the two techniques.

To explain the spectral behaviour of the SPV amplitude we take into account that the SPV phase is in the 4th (2nd) quadrant when electrons move toward the bulk (surface) and/or holes move toward the surface (bulk) [9,10]. This is usually the case where the energy band bending at the surface/interface is upward (downward) in the direction from bulk to surface. In the present case the energy band bending at the interface GaInNAs/n-GaAs is upwards due to the different doping (i-n junction), the space charge region (SCR) being mostly in the lower-doped GaInNAs layer. The SPV generated there has phase in the 4th quadrant in accordance with the expectations. The phase and amplitude in figure 1 change monotonically with decreasing the wavelength, the phase values being in the 4th quadrant. The phase values remain in the 4th quadrant for wavelengths down to 500 nm (not shown here), where the

![Figure 1. Typical SPV amplitude (circles, left axis) and phase (line, right axis) spectra measured with excitation from the layer side. The PL spectrum of the same sample is presented by squares.](image-url)
absorption is much closer to the surface. All this leads to the conclusion that the surface SCR gives SPV signal with phase in the 4th quadrant, too and the two signals (from surface and interface) add constructively. Schematically this is shown in figure 2 using the vector model for SPV [10]. According to this model, the SPV vector has a magnitude equal to the amplitude of the SPV signal and an angle with respect to the X-axis equal to the SPV phase. In figure 2 are represented the SPV vectors corresponding to the SPV signals from the GaInNAs/n-GaAs interface (vector A1) and from the GaInNAs surface (vector A2), as well as the overall measured signal (vector A = A1 + A2). The two SPV vectors form an acute angle, therefore their sum is larger than each of them. One observes a continuous increase of the SPV amplitude with decreasing the wavelength, due to the increase of the GaInNAs optical absorption coefficient. This is accompanied with a continuous anti-clockwise change of the SPV phase towards -0 degrees. The fact that the SPV signal from the GaInNAs surface has phase in the 4th quadrant means that the energy band bending at the surface is upwards. This is typical for n-type semiconductors. Thus, we conclude that the nominally undoped GaInNAs layer has n-type residual conductivity.

Figure 2. Schematic representation of the SPV vectors corresponding to the SPV signals from the interface (A1), surface (A2) and the overall SPV vector (A=A1+A2) for excitation with wavelength around 1050 nm.

At around 900 nm the SPV amplitude starts increasing faster, while the phase starts increasing slower. This feature is observed in all the spectra measured with different photon fluxes. To explain it the following discussion is proposed. For wavelengths below 900 nm (1.377eV) n-GaAs can already absorb photons, as can be seen from the SPV spectrum of n-GaAs presented in figure 3. Assuming a value around 10^4 cm^{-1} for the absorption coefficient of GaInNAs in this energy range, means that the 1000 nm layer still transmits around 30% of the photons to reach the interface, where the band bending in n-GaAs is also upward. So, n-GaAs starts absorbing light and contributing to the SPV signal, too. This generates another SPV signal with vector in the 4th quadrant, thus leading to a stronger overall SPV signal, which is seen as a faster increase of the amplitude in figure 1. To account for the slower anti-clockwise change of the phase in this range, we can use again figure 2, but in this case, vector A2 will corresponds to the signal from GaInNAs and vector A1 – to the signal from n-GaAs. One can assume that the SPV vector related to n-GaAs (A1) is closer to -90 degree than the SPV vector related to GaInNAs (A2), as shown in figure 2. It is easy to understand that increasing A1 will effectively slow down the anti-clockwise rotation of the overall SPV vector (A) and in the same time will increase its magnitude. If this mutual position of the SPV vectors is correct, it means that the SPV process related to GaInNAs is faster than the one related to n-GaAs (vector closer to -0 degrees means faster process
Such statement is in agreement with the shorter recombination time in dilute nitrides as compared to GaAs, reported in the literature [11].

![Figure 4. SPV amplitude (symbols, left axis) and phase (line, right axis) spectra of the sample from figure 1 excited from the substrate side.](image)

To check the above conclusions we turned the sample so that the excitation is from the substrate side. Figure 4 represents the SPV spectra measured in this case at the same experimental conditions. The slope in the amplitude around 1150 nm gives the same value of the GaInNAs band gap. The SPV signal in this range mainly comes from the GaInNAs interface SC. The phase is in the 2nd quadrant because the band bending at the interface is now downward, that is opposite to the previous case (same sample looked from the opposite side). On the other hand the surface of the GaAs substrate has an upward band bending because of the n-type doping. After 950 nm the signal decreases quickly, reaches a minimum at 900 nm and increases again. The phase quickly jumps clockwise toward the 4th quadrant and reaches values around -40 degrees. This behavior is explained by the inclusion of the SPV signal from the n-GaAs substrate with phase in the 4th quadrant on top of the signal from the interface. The interplay of these two SPV signals with nearly opposite phases leads to the minimum in the amplitude spectrum and the phase jump observed around 900 – 920 nm. For wavelengths below 900 nm the SPV process from the n-GaAs surface dominates and the SPV amplitude spectral shape is similar to that of n-GaAs shown in figure 3.

To assess the minority carrier diffusion length in the GaInNAs layer SPV measurements with low photon flux were carried out. For that purpose the method called “constant SPV” or “method A” [8,12] was applied. Although there have been numerous SPV investigations of the minority carrier diffusion length in different materials (see [8] and references therein), this method has been rarely applied to GaInNAs [13]. The method is based on a solution of the continuity equation and two highly reasonable assumptions as follows: i) the SPV is a monotonous function of the excess carrier concentration and ii) the surface recombination velocity is constant if SPV is constant. It consist of keeping the SPV constant for several wavelengths by changing the photon flux \( \Phi \). Under such conditions one can show that [8,12]

\[
\Phi(\lambda) = \text{const} \left( \frac{1}{\alpha(\lambda)} + L \right),
\]

where \( \alpha \) is the absorption coefficient, \( L \) is the diffusion length and \( \lambda \) is the wavelength. By plotting \( \Phi(\lambda) \) as a function of \( 1/\alpha(\lambda) \) a straight line is obtained, which intercepts the abscissa at \(-L\). Eq.(1) holds
under the following constraints concerning $L$, $\alpha^{-1}$, the majority carrier density $n_0$, the sample thickness $d$ and the SCR width, $w$ [8,12]: i) $\Delta p \ll n_0$ (low injection level); ii) $\alpha^{-1} \ll d$ (the illumination of the back SCR can be neglected); iii) $w \ll L$, $w \ll \alpha^{-1}$ (the diffusion carrier transport is the major contribution to the SPV signal, and iv) $L/d < 1/4$ (the influence of the back SCR can be neglected).

As a first approximation for the absorption coefficient spectrum of GaInNAs we took that of GaAs at 300 K and translated it in energy by 0.32eV so that the band gap becomes 1.10 eV. To fulfil condition i) we used a filter that decreased the excitation by an order of magnitude and kept SPV=0.51 mV during the measurements. Concerning condition ii) we used wavelengths in the range 900 – 1030 nm for which $\alpha^{-1} < d = 1 \mu$m but stopped at 900 nm to avoid absorption in GaAs. For those values of $\alpha^{-1}$ (0.5 – 0.8 $\mu$m) the illumination of the back SCR cannot be completely neglected. However, as explained above, the SPV signals from the surface and from the interface add constructively and therefore the influence of the back SCR should not be crucial for the final result. Concerning condition iii) $w$ of the back SCR was assessed to be $< 0.24 \mu$m from the difference of the Fermi levels in GaAs and GaInNAs, and assuming $10^{16} \text{cm}^{-3}$ residual n-type doping of GaInNAs. The width of the surface SCR should be of the same order of magnitude or less. Thus, condition iii) is not fully satisfied, but still $w$ is less than $\alpha^{-1}$ and $L$. As to condition iv), the ratio $L/d$ was around 0.35. Taking into account the discussion in [8] (p.125) we can conclude that this value is satisfactory for the assessment of the diffusion length.

Figure 5 shows the result ($L = 350 \text{ nm}$) obtained with the above procedure. The error in the $L$ value calculated using the standard errors of the least square fit coefficients and considering the two ultimate cases for the slope of the straight line is quite small $\pm 5 \text{ nm}$. However, other uncertainties come from the unknown GaInNAs absorption coefficient, the influence of the back SCR, the close values of $w$, $\alpha^{-1}$, and $L$, and the neglect of the reflectivity spectrum. Therefore, the obtained $L$ value is regarded only as estimate of the hole diffusion length in the GaInNAs layer.

**Conclusion**

An original SPV spectroscopy study of MBE grown undoped GaInNAs dilute nitride layers is carried out combined with PL results. A reduction of the band gap energy with respect to the band gap of GaAs is evidenced in accordance with the PL results. N-type residual doping in the layers is found from the combined analysis of the SPV amplitude and phase spectra. This way a simple and contactless way is shown for determining the residual doping type of nominally undoped layers grown on substrates with
known doping type. The hole diffusion length in GaInNAs is estimated by means of the “constant SPV” method. The study highlights the potential of the SPV spectroscopy for studying dilute nitride materials.

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