Doping effects on the composition, electric and optical properties of MBE-grown 1.1 eV GaNAsSb layers

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ABSTRACT

Dilute nitrides based on GaAs constitute a family of compounds whose main characteristic is the band-gap tunability, depending on the nitrogen content. In this work we have focussed our attention on the indium free dilute nitrides, i.e. GaNAsSb with a bandgap around 1.1 eV, to study the effects that has doping on the crystalline structure, electrical and optical properties of the material. For such purpose, p-doped and n-doped GaNAsSb layers were grown by Molecular Beam Epitaxy and characterized using X-ray diffraction, spectroscopic ellipsometry and photoreflectance among other techniques. The GaNAsSb optical properties match the double Band-Anticrossing model which is the proposed one to explain the dilute nitride band structure. However, the determined optical bandgap value does not follow any trend with doping, neither with concentration nor type. This is related with doping effects on the crystalline quality and layer composition, thus inducing a Sb gradient along layer thickness together with variations in N and Sb concentrations for different doping levels. Besides these structural variations, the complex refraction index, Hall mobility and carrier concentration as a function of temperature have been determined for these GaNAsSb layers.

Keywords: dilute nitrides, optical properties, doping effects, MBE growth, band structure, HRXRD

1. INTRODUCTION

Dilute nitride semiconductors have attracted a great research interest since their initial development in the 1990s [1-3], because of their physical properties, which may open their use in many device applications. In particular, GaNAsSb is a type of dilute nitride which has demonstrated its suitability as a ~ 1 eV bandgap material, provided the partial substitution of As anions by N and Sb [4, 5]. This fact allows its incorporation in many types of electronic and optoelectronic devices such as near infrared photodetectors [6-9], photoconductive switches [10, 11], heterojunction bipolar transistors [12, 13], lasers [14, 15], etc. Other works have used GaNAsSb for building a subcell in III-V multijunction solar cells for both space and terrestrial applications [16-18], or even as a tandem solar cell on top of a silicon substrate [19]. However, the wider exploitation of dilute nitrides such as GaNAsSb is being restricted because of the difficulty in achieving high quality materials. Hitherto, the best approach to achieve the highest performance has been to epitaxially grow the material and perform a post-growth annealing. Nowadays, Molecular Beam Epitaxy (MBE) is the growth technology which, after an annealing process, results in the best dilute nitride quality in comparison with, for example, Metal Organic Vapour Phase Epitaxy (MOVPE) [20, 21]. In addition to these difficulties to achieve high quality GaNAsSb, there is also a lack of wide and accurate data for most of its fundamentals properties. In particular, there are very few works describing the effects that extrinsic doping has on GaNAsSb [22]. This is of paramount importance since the performance of most optoelectronic devices is ruled by doping. However, the inclusion of dopants in the GaNAsSb crystalline lattice could give rise to a variety of structural defects that may alter the inherent material characteristics, as it was demonstrated for GaInNAs layers [23].

Accordingly, the goal of this paper is the determination of the main electro-optical properties of GaNAsSb layers as a function of doping level and dopant type. We have focused in the doping level range going from 10^{17} to 10^{18} cm⁻³ for both, n and p-type, since they are the typical values in several optoelectronic devices such as solar cells. A complete characterisation of doped GaNAsSb layers has been accomplished, including Secondary Ion Mass Spectrometry and High Resolution X-ray Diffraction analysis, allowing identification of the consequences that extrinsic n- and p-doping has on the layer microstructure. Spectroscopic ellipsometry, photorefectance, transmittance and Hall effect measurements have been used in order to determine the electro-optical properties of these doped epitaxial layers.

2. EXPERIMENTAL

2.1 Sample Growth

1 μm -thick GaNAsSb layers were grown on semi-insulating (100) GaAs substrates using Molecular Beam Epitaxy (MBE). A Radio Frequency (RF) nitrogen plasma and a valved effusion cell with cracking zone were used respectively as sources of nitrogen and antimony [24, 25]. Be and Si were used as p-type and n-type dopants, respectively. The GaAs substrate orientation ensures the incorporation of Si as a donor [26]. Samples were grown at a RF plasma power of 200 W while the substrate temperature was 420-460°C. The N_2 gas flow in the plasma source was set to 0.25 sccm. The beam equivalent pressure of the Sb flux was $\sim 1.2 \times 10^{-7}$ torr. Under these growth conditions, $\sim 2.4\%$ of nitrogen and 6.5% of Sb were expected to incorporate into the GaNAsSb layers [11]. The nominal doping levels were determined by comparison of the dopant cell temperatures during GaAs and GaNAsSb doped layers growth. After the growth of GaNAsSb, a 50 nm-thick $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ layer is deposited. Subsequently, the samples were *in-situ* annealed at 700°C for 5 minutes. After that, the $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ layer is removed using an HF etching process. Table 1 gathers sample identification as well as basic information concerning layers doping.

Table 1. MBE-grown sample description showing their nominal doping levels as well as the thicknesses measured by SEM. The target thickness for all samples was 1 μm .

Sample No.	Polarity	SEM Thickness (nm)	Nominal Doping level (cm^{-3})
$p1 \times 10^{17}$	p-type	990	1×10^{17}
$p5 \times 10^{17}$	p-type	974	5×10^{17}
$p1 \times 10^{18}$	p-type	1020	1×10^{18}
$n1 \times 10^{17}$	n-type	980	1×10^{17}
$n5 \times 10^{17}$	n-type	1000	5×10^{17}
$n1 \times 10^{18}$	n-type	990	1×10^{18}

2.2 Equipment for characterization of layers

Scanning electron microscopy (SEM) images for measuring the layer thickness were acquired on a Helios Nanolab 650 Dual Beam Scanning Electron Microscope from FEI with a Schottky field emission source. Secondary Ion Mass Spectrometry (SIMS) measurement was undertaken on advanced CAMECA tools at Loughborough Surface Analysis in the UK. Carrier density, resistivity and mobility were determined by Hall effect measurements and Electrochemical Capacitance-Voltage (ECV) profiling measurements using a WEP Control CVP21 tool. High resolution X-ray diffraction (HRXRD) measurements were made in a PANalytical X'Pert PRO MRD equipment, using Cu-K α 1 ($\lambda=1.540598\text{\AA}$) radiation, a parabolic mirror plus an asymmetric 4-bounce Ge 220 monochromator, and a PIXcel detector. The diffractograms were analysed using dynamical diffraction theory. X'PertEpitaxy v.4.1 of PANalytical B.V. software was used for diffractogram simulations.

The layer optical properties were characterized in a Semilab GES-5E variable angle spectroscopic ellipsometer (SE) in the region from 230 to 1630 nm (approximately 5.4 to 0.76 eV), with the use of a two detector configuration, a CCD for the UV and optical region and an InGaAs detector for the Near Infrared (NIR) region. The spot size of the ellipsometer is approximately 400 μm . The incident angle varies between 60° and 75° and measurements were made in several points for every sample showing no differences among them. Measurements of the polarization state (ψ , Δ) of a collimated beam light after impinging the sample have been made at room temperature.

Room-temperature photoreflectance (PR) was used in order to probe the critical points of the band structure GaNAsSb layers as a function of doping levels. Measurements were performed at different pump-beam penetration lengths, using the 325 nm line of a 15 mW HeCd laser and the 632.8 nm line of a 17 mW HeNe laser as pump beams, mechanically chopped at 777 Hz. The light of a 250 W quartz-tungsten-halogen (QTH) lamp was dispersed with a 1/8 monochromator and used as probe beam. The direct reflectance of the probe beam impinging on the sample, containing average (dc) and modulated (ac) components, was detected with a cooled InGaAs detector and a Si-photodiode, connected to a preamp (Keithley) and a lock-in amplifier (Stanford) at the reference chopping frequency. The PR signal is defined as the spectral ratio between ac and dc components. Transmittance (T) and reflectance (R) of the dilute nitride samples were characterized with a PerkinElmer Lambda 1050 spectrophotometer.

3. RESULTS AND DISCUSSION

In order to understand the results obtained from the electro-optical characterization, it is compulsory to know the composition of the GaNAsSb compound and the doping variations across the layers. Therefore, this section is divided in two subsections, namely, the first one devoted to determine the structural characteristics and the related electrical properties of the dilute nitride samples, and a second one for the optical characterization itself.

3.1 Structural and electrical characterization

Samples were first examined through SEM images (see Figure S1 in Supplemental Material). For all of them, sample surface was rather flat and their cross-sections had a homogeneous appearance. The measured thicknesses were very close to the nominal 1 micron (see Table 1).

A first approximation to GaNAsSb layer composition and doping level has been addressed using SIMS measurements. The constituent concentrations along the whole layer thickness show different profiles. The most striking finding is that Sb concentration is not constant along the layer thickness, except for sample $p1 \times 10^{17}$, namely, the lower doped of the p-type samples, and the only one for which growth temperature was 420°C. For the rest of the samples, Sb concentration shows a decreasing profile going from the GaAs substrate to the layer top surface, irrespective of dopant type (see Figure 1 and Supplemental Material, Figure S2). On the contrary, N exhibits a rather constant profile for all the samples (Figure 1).

Figure 1. As (red line), Sb (black line) and N (blue line) profiles corresponding to the sample $p1 \times 10^{18}$.

Concerning the dopant profile, the p-type lower doped samples, $p1 \times 10^{17}$ and $p5 \times 10^{17}$, exhibit a constant amount of Be dopant along the layer thickness (Figure 2(a)). There is just a Be accumulation at the interface between the GaNAsSb and the GaAs substrate, which is more important as the total dopant amount in the layer increases. For the $p1 \times 10^{18}$ sample, Be amount increases towards the top surface, except for the already mentioned dopant accumulation at the interface. The amount of dopant in these p-doped samples is always smaller than the nominal doping, as deduced from the SIMS data (Table 2). On the other hand, for the n-doped samples, $n1 \times 10^{17}$, $n5 \times 10^{17}$ and $n1 \times 10^{18}$, the Si profiles are rather flat (Figure 2(b)), no matter the dopant amount, and the Si dopant amounts deduced from SIMS results are higher than nominal values (see Table 2). At the interface between dilute nitride layer and GaAs substrate (right side in the figures), dopant amount exhibits an initial increase followed by an abrupt decrease, afterwards, Si concentrations reach the mean value observed along the whole layer thickness. Actually, we have no explanation for the abrupt peak in the Si profiles at the interface between the GaNAsSb layer and the GaAs substrate.

Figure 2. Be dopant concentration profile for the p-doped samples (a). Red, blue and green curves account for the $p1 \times 10^{17}$, $p5 \times 10^{17}$ and $p1 \times 10^{18}$ samples, respectively. Si dopant concentration profile for the n-doped samples (b). X-axis corresponds to sputtering time, in such way that left side in the graphics is the sample surface, while right side is the interface with GaAs substrate. Magenta, navy and wine curves account for the $n1 \times 10^{17}$, $n5 \times 10^{17}$ and $n1 \times 10^{18}$ samples, respectively.

However, the dopant total amount supplied by SIMS along the layer thickness differs from the effective (electric) doping level measured by Hall effect and ECV. In order to understand the different doping level values achieved from different techniques, it is customary to mention here

that SIMS measurements detect the global amount of dopant atoms in the layer. ECV can provide reliable values of carrier concentration but electrically active defects can affect the CV signal. Hall technique deals with electrical resistivity and not with counting atoms and its transformation to carrier concentration depends on the Hall factor that strictly is material dependent. Due to the inherent cons of these well established measurement techniques, we have used the three ones in order to have a more robust crosscheck method. Accordingly, in the case of dopants, the doping levels shown in third column of Table 2, correspond to the global amount of Be (p-type) and Si (n-type) atoms in these GaNAsSb layers. As it can be seen in Table 2, values obtained from electrical measurements do not match neither the intended doping level during the layer MBE growth, nor the dopant amount as deduced from SIMS data. Concerning the effective doping level achieved in the layers, two different tendencies have been revealed. For the p-type doped layers, doping level values obtained from Hall effect and ECV techniques do not differ very much between them, and they always exceed the dopant amount determined after SIMS measurements (Figure 2(a)). This fact points to an unintentional p-doping in the GaNAsSb layers as it was described previously for similar samples [22], in such a way that the total doping level would be the sum of both intrinsic (unintentional) and extrinsic doping. Besides, the unintentional doping would also hinder the incorporation of extrinsic atoms acting as p-dopant in the lattice, as the SIMS results suggest. The intrinsic doping seems to be directly related to the extrinsic dopant concentration in the lattice, according to the figures in Table 2, which suggests an increment in the unintentional doping level as the extrinsic dopant quantity does. The origin of this unintentional doping could be related to defects associated with the beryllium incorporation. Besides, an additional source of unintentional doping could be structural defects inherent to the material growth as it has been reported in some other dilute nitride layers [27-30].

Table 2. Nominal doping level and measured doping level as deduced from SIMS data (mean value along layer thickness) considering that all dopants are activate. Effective doping level as measured by Hall effect and ECV techniques is also included although some measurements did not render a reliable value for some layers (n.a.). Resistivity and mobility have been calculated from Hall effect measurements data.

Sample No.	Nominal Doping level (cm ⁻³)	Doping level (cm ⁻³) (SIMS)	Doping level (cm ⁻³) (Hall effect)	Doping level (cm ⁻³) (ECV)	Resistivity (Ω×cm) (Hall effect)	Mobility (cm ² /Vs)
p1×10 ¹⁷	1×10 ¹⁷	0.5×10 ¹⁷	1.3×10 ¹⁷	n.a.	0.65	72
p5×10 ¹⁷	5×10 ¹⁷	1.6×10 ¹⁷	3.8×10 ¹⁷	5×10 ¹⁷	0.24	69
p1×10 ¹⁸	1×10 ¹⁸	3×10 ¹⁷	7.7×10 ¹⁷	8×10 ¹⁷	0.13	64
n1×10 ¹⁷	1×10 ¹⁷	1.5×10 ¹⁸	1.2×10 ¹⁷	7×10 ¹⁷	0.20	266
n5×10 ¹⁷	5×10 ¹⁷	6×10 ¹⁸	1.0×10 ¹⁷	7×10 ¹⁷	0.46	128
n1×10 ¹⁸	1×10 ¹⁸	1.25×10 ¹⁹	n.a.	n.a.	n.a	n.a.

For the n-type doped layers, the effective doping level is quite similar for the two samples where it could be measured, however, the values obtained are rather different depending on the characterization technique. In any case, the effective doping level is at least one order of magnitude lower than the dopant amount deduced from SIMS measurements (Figure 2(b)). Therefore, most of these Si atoms would not be effectively incorporated into the GaNAsSb lattice as it has been described for n-type GaInNAs alloys [23], and could give rise to several types of defects. In parallel, the extrinsic n-dopants could be partially compensated by the aforementioned unintentional p-type doping, which seems to be inherent in these layers [22]. It is worth mentioning here that the doping levels obtained after electrical characterization are very similar for the n1×10¹⁷ & n5×10¹⁷ layers, which points to a possible effective n-doping saturation in these layers for these relatively high silicon concentration in the lattice [23].

Table 2 also gathers the electrical parameters deduced from Hall effect measurements at T=300 K. For p-type doped layers, mobility diminishes with doping level and exhibit values quite similar to those seen for Mg doped GaInNAs [31], and slightly lower than for Be doped GaInNAs [32]. After all, p-type GaNAsSb mobility is around half-one third the range of p-type GaAs mobility. For the n-doped samples, mobility dramatically decreases with the silicon concentration (values obtained after SIMS), despite the effective doping level is the same for samples n1×10¹⁷ and n5×10¹⁷, and their values are similar to Si-doped GaInNAs [32, 33], but they are more than ten times lower than those typical of GaAs. No ohmic contact on the most n-doped sample, n1×10¹⁸, were possible to achieve in order to measure Hall, what could be also explained by a huge resistivity produced by defects, as we will explain below this paragraph. The low values of electron mobility (in comparison with the theoretical limit around 1000 cm²/Vs for dilute nitrides [34], which

has been practically achieved with Te-doping GaInNAs [31]), could be related with Si-N induced cluster scattering or compensation defects [35].

The Hall data of mobility and carrier concentration in figures 3(a) and (b), respectively, show the clear difference between the temperature behaviour of n- and p-type samples. In order to evaluate the mobility dependence with temperature, we consider different scattering mechanisms. The resultant carrier mobility can be given by the Mattiessen's rule:

$$\mu_{tot} = \left(\sum_i \frac{1}{\mu_i} \right)^{-1}$$

where μ_i is the mobility limited by the i th scattering mechanism which can be written as:

$$\mu_i = C_i T^\alpha$$

where C_i is a constant of the i th scattering mechanism and α is a positive or negative number which is characteristic of the scattering mechanism [36]. Therefore, we can determine the main scattering mechanisms in the samples by analyzing the temperature dependence of carrier mobilities by a parameter-fitting process which results in the value of α .

In the p-doped samples the hole mobility is higher than the electron mobility in n-doped samples at low temperatures. Similarly, the p-type carrier concentration is much higher than the corresponding n-type for the same nominal conditions (Table 2 and Figure 3(b)). The hole mobility exhibits an almost negligible temperature dependence below $T=150$ K and then decreases with increasing temperature with temperature dependence between $T^{0.5}$ and $T^{0.7}$ for the three samples suggesting an alloy-scattering limited mobility ($\propto T^{1/2}$) [32]. The electron mobility exhibits a strong ionized impurity scattering temperature dependence ($\propto T^{3/2}$) for the $n5 \times 10^{17}$ sample ($T^{1.4}$) while for $n1 \times 10^{17}$ the dependence is decreased to $T^{0.7}$. So one needs to consider additional scattering mechanisms, which result in a weaker temperature dependence of electron mobility. For this, we could consider an additional component ($\propto T^0$). The temperature-independent scattering mechanism is typically assigned as a neutral impurity scattering which is usually observed at relatively low temperatures <100 K as we can see in Figure 3(a) for the lower n-doped sample, $n1 \times 10^{17}$, when almost all the shallow donors and acceptors are thermally frozen [32]. This could be related to a lower [N]/[Sb] ratio of $n1 \times 10^{17}$ with regard to $n5 \times 10^{17}$, as Table 3 will show. We anticipate here that, as it will be described along with HRXRD results, the higher the Si

concentration, the higher the N composition of the GaNAsSb. Therefore, the intense n-type mobility decrease from $n1 \times 10^{17}$ to $n5 \times 10^{17}$ could be explained in terms of the presence of N and Si atoms which may exist in the form of Si-N complexes [37], and also by resonant scattering induced by N-related states [38]. In the case of p-type doping, the higher the doping the lower the nitrogen concentration, as Table 3 will show. Therefore, hole mobility of Be-doped GaNAsSb is insensitive to nitrogen as it happens for Be-doped GaInNAs [32]. The weak temperature dependence of electron mobility at ambient temperatures can be explained in terms of both the N-related compositional fluctuation with highly localized states close to the conduction band (CB) edge, and non-substitutional N defects such as N-N split interstitials and N-As split interstitials [39, 40], which may trap the carriers and act as ionized impurity scattering centres, leading to further reduction in electron mobility.

Figure 3. (a) Comparison of the mobilities for p- and n-doped samples. Straight lines illustrate temperature dependence. (b) Comparison of carrier concentrations for p- and n-doped samples. (c) Carrier concentration and mobilities for the n-doped samples. Linear fittings allow to extract the activation energy. (d) Carrier concentration for the p-doped samples. Linear fittings allow the

extract the activation energy.

The Arrhenius plot of the free-electron concentrations and mobilities for n-doped samples are shown in Fig. 3(c). The electron concentrations and mobilities drop with decreasing temperature and both remain almost constant below ~ 100 K. A first order approach of the compensation doping level can be established by comparing the electron concentrations at both 300 and 90K [32], whose difference results in around 10^{17}cm^{-3} doping compensation/traps. The observed dependence of electron concentration for $T > 100$ K would be due to thermal activation of the transition between these trap states of energy E_T and the CB edge. As we can see from Figure 3(c), the activation energy $E_A = 35.8$ meV for both n-type samples ($n1 \times 10^{17}$ and $n5 \times 10^{17}$) is twice and triple, respectively, of the thermally activated energy for the mobility (19.8 and 11.7 meV), which can be partially explained by a dislocation scattering model [41]. Besides, the $E_A = 35.8$ meV agrees reasonably with the $E_A = 40\text{--}50$ meV found for Si doped GaInNAs [32]. A similar analysis for the p-type samples in Figure 3(d) shows a much lower activation energy ranging from 3 to 7 meV for the whole 10^{17}cm^{-3} range which demonstrates a much more easy Be doping than the Si one in GaNAsSb.

It has become clear that not all the Si impurities are activated to generate free carriers in GaNAsSb. This can be explained by the coexistence of Si-N complexes, which are known to decrease both the electron concentration and electron mobility [32]. This fact can explain why we cannot achieve an ohmic contact for sample $n1 \times 10^{18}$ because of both an intense decrease of mobility together with a reduced free electron concentration. The completely different behaviour between hole and electron concentrations and mobilities as a function of temperature denotes the tremendous impact that doping has on the GaNAsSb properties.

In order to determine the GaNAsSb composition of the samples we have carried out HRXRD measurements. Taking into account the results obtained from SIMS presented above, the HRXRD data analysis is funded in some assumptions such as, N content is constant along the layer thickness, and Sb content is decreasing when going from the substrate to the top surface.

Since GaNAsSb is a quaternary alloy and its lattice constant depends on several parameters, a recently published approach [42] for HRXRD structural characterization based on diffraction dynamical theory [43] has been used for data analysis. It consists of the analysis of the measured 004 reflection rocking curves, which are continuously correlated with calculations of the bandgap

energy for the different samples and compared with the experimental results obtained from ellipsometry (that are described below). In the calculations of bandgap energy, all necessary parameters of multicomponent alloys were estimated from HRXRD results using the Vegard's law. The change of the GaNAsSb bandgap induced by the presence of Sb in the crystal, was calculated according to a nonlinear approximation considering the bowing parameter. The band anticrossing (BAC) model was applied in order to calculate the changes of the conduction band due to the presence of nitrogen atoms in the alloy. The biaxial strain was calculated based on the Pikus-Bir Hamiltonian and the energy shifts and splitting of the valence band into heavy and light holes, caused by hydrostatic and shear stresses, were also considered. The initial GaAs material parameters, such as valence band energy, elastic stiffness constants, deformation potentials, lattice parameters as well as bowing parameters, were taken from literature [44]. More detailed information about this structural characterization algorithm can be found in Pucicki et al. [42].

All the samples, except $p1 \times 10^{17}$, show asymmetrical 004 reflection peaks which points to a non-homogeneous composition along the layer thickness, in accordance to what has been revealed by SIMS results. Figure 4 shows both, the experimental and simulated 004 reflection rocking curves corresponding to the samples $p1 \times 10^{18}$ & $n1 \times 10^{17}$.

Figure 4. 004 reflection $\omega/2\theta$ scans corresponding to samples $p1 \times 10^{18}$ (a) and $n1 \times 10^{17}$ (b). Black lines correspond to simulated rocking curves obtained from HRXRD data analysis.

The HRXRD analysis output is the composition along layer thickness for every sample, which have been gathered in Table 3. The obtained Sb concentration profiles reproduce the SIMS results (see

Figure S2 in Supplemental Material). The only layer where Sb content can be considered constant is $p1 \times 10^{17}$, i.e. the p-type lower-doped sample and the only one grown at 420°C. For the rest of the samples, Sb concentration profile decreases when going from substrate to sample surface. For the p-doped samples $p5 \times 10^{17}$ & $p1 \times 10^{18}$ and the lower doped n-type sample ($n1 \times 10^{17}$), Table 3 shows antimony extreme values at the GaNAsSb/GaAs interface (maximum) and at the top GaNAsSb layer surface (minimum). For the higher doped n-type samples ($n5 \times 10^{17}$ & $n1 \times 10^{18}$), the total layer thickness can be divided into 2 sublayers. In the sublayer nearest to the substrate, Sb concentration profile is concave, while in that on top of the former one, it can be considered constant (Table 3). Taking into account the SIMS results (see Table 2), this kind of behaviour may suggest that the higher growth temperature together with the dopant concentration in the layer, irrespective of type and of its effective role as electric dopant, are the responsible of the Sb concentration profile indicating a possible competition of dopants to reach Sb substitutional positions.

It is important to note that all these layers were grown using the same conditions for the N_2 plasma source and Sb flux, therefore, the same amount of N and Sb was expected to be incorporated in the layers (2.4% N, 6.5% Sb). According to our HRXRD results, this is no longer true and sample composition varies along layer thickness, which matches with what has been seen in similar dilute nitrides layers [45]. Regarding N content, it seems that p-type doping hinders N incorporation into the GaNAsSb layer. Concerning n-doped samples, no clear conclusion can be extracted since the effective doping seems to be rather similar for the samples in which it could be determined. However, N amount increases as the detected Si concentration after SIMS measurements does. Very similar conclusions can be extracted for Sb incorporation into the GaNAsSb layer. Sb amount decreases as p-dopant concentration increases. However, the ratio between both anion contents keeps the same value for all the p-type doped samples and the lower n-doped layer. Similar value is also obtained for one of the sublayers (namely, the closer to the surface) in which the $n5 \times 10^{17}$ & the $n1 \times 10^{18}$ samples can be divided. This figure could account for the inherent difficulties for achieving a desired composition in GaNAsSb doped layers and the influence that doping exerts on N and Sb incorporation into the layer. At the same time, the variations in N content for the n-doped samples have been shown as impacting the mobility values, thus illustrating the close interdependence between structural and electrical properties for this kind of materials.

Table 3. Nitrogen and antimony content deduced from HRXRD data analysis. Concerning antimony content, values on the left correspond to the content at the sample surface, (as in the Figure 1, 2 and S2) while value on the right is the content at the GaNAsSb/GaAs interface.

Sample No.	Layer thickness (nm)	Nitrogen content (%)	Antimony content (%)	[N]/[Sb]
p1×10 ¹⁷	1000	2.40	8.15	0.29
p5×10 ¹⁷	1000	1.97	7.25 – 6.00	0.29
p1×10 ¹⁸	1000	1.85	6.40 – 5.72	0.30
n1×10 ¹⁷	1000	1.70	5.90 – 4.60	0.30
n5×10 ¹⁷	700 (upper sublayer)	1.83	4.55	0.33
	300 (lower sublayer)		6.60 – 4.55	0.40
n1×10 ¹⁸	750 (upper sublayer)	1.95	5.00	0.31
	250 (lower sublayer)		7.60 – 5.00	0.39

Reciprocal Space Mappings (RSMs) from the asymmetrical reflections 115 and 224 have been recorded in order to explore the layer relaxation degree. For each sample, very similar RSMs were obtained for both reflections. Figure 5 shows those from 115 reflection corresponding to samples p1×10¹⁷ and n1×10¹⁷. i.e. the lower doped ones for both p and n-type, respectively. According to these figures, all the layers are completely stressed, i.e. the layer relaxation degree is null. The diffuse scattering surrounding the main peaks is quite high for all the samples suggesting a high defect density in these layers, which is probably related with N and dopant incorporation into the lattice, in the first case due to its bigger anion size as compared to As³⁺ and Sb³⁺ [46]. The presence of such high defect density is probably on the origin of the low values for mobilities and carrier concentrations found for these samples, as it has been described in former pages.

Figure 5. RSMs corresponding to 115 reflection of the $p1 \times 10^{17}$ (a) and $n1 \times 10^{17}$ (b) samples.

3.2 Optical characterization

3.2.1 Ellipsometry

The general procedure for making ellipsometric data analysis begins with a proposed layered structure where the thicknesses and optical behaviour of each layer can be treated as known parameters or as the final result of the fitting procedure. The schematic structure for the studied samples consists in 3 layers, namely; 1) the top one is an oxide layer due to atmosphere exposition; 2) the second one is the GaNAsSb layer, where both, thickness and optical behaviour are considered as unknown, though in this case, the layer thickness measured in SEM images has been used as input data; and 3) the third layer is the GaAs substrate, whose optical parameters have been taken from database/deduced from experimental data fitting (see Figure 6).

Figure 6. Sketch of the layer stack model used for the ellipsometry data fitting (not to scale).

In this paper, the GaNAsSb layers have been modelled following the model of dielectric function proposed by Adachi [47] to describe the real and imaginary parts of the dielectric function of III-V binary semiconductors (GaAs and GaSb among others). The same model proved its ability to fully describe GaAs optical behaviour by Ozaki et al. [48], and it was later extended by Rakic et al. [49] for aluminium arsenide, AlAs. GaNAsSb electronic structure should share common features with the GaAs and GaSb ones since these semiconductors order accordingly to the same crystalline structure. The model is Kramers-Kronig consistent and accounts for the various inter-band transitions between the valence and conduction bands which are considered as critical points (CPs)

in the dielectric function spectrum. The experimental data is thus fitted through various CPs along the measured spectra. Each CP is associated to a mathematical function which extends along the whole measured energy range. In the model proposed by Adachi for GaAs, the first one (lowest transition energy) is a 3D M_0 contribution (Adachi 3D, three-dimensional oscillator), then, a 2D M_0 (Adachi 2D, bi-dimensional oscillator) accounts for the indirect transitions E_1 , and after that, the higher energy transitions are modelled using damped oscillators (Adachi DHO) [48]. However, the inclusion of N and Sb in the GaAs crystalline structure induces both, the valence band (VB) and conduction band (CB) splitting, which has been explained using a double BAC model [50]. Therefore, new transitions are expected to be detected in the SE signal among the splitted sublevels. Following the works of Ben Sedrine et al., these transitions are labelled as E_+ and $E_\#$, and they are assigned to transitions from the E_+^{SO} and the E_-^V sublevels in the valence band, to the upper sublevel in the conduction band [51, 52].

According to these premises, the model proposed to fit our SE GaNAsSb layer data contains three 3D M_0 oscillators, which account for the lowest energy transitions in the Γ point, E_0 (the fundamental bandgap), E_+ and $E_\#$. A 2D M_0 oscillator represents the main contribution of the indirect transition E_1 , while an additional damped oscillator has been included in the fit to describe the $E_1+\Delta_1$ transition. The rest of the higher energy transitions, E_0' and E_2 will be described using damped oscillators. For a detailed explanation of these GaAs transitions the reader is referred to [53]. The sum of the parameters associated to describe each oscillator (transition energy, width, etc.) and layer thickness leave 34 fitting parameters (see Table S1 in the Supplemental Material) to give rise to the real and imaginary parts of the complex dielectric permittivity, ϵ_1 and ϵ_2 . In the Supplemental Material, reader can identify the way each oscillator contributes to the global sample optical behaviour in terms of ϵ_1 and ϵ_2 (Figure S3).

The most relevant fitting results are gathered in Table 4, where the energies of the inter-band transitions associated to each oscillator are shown. The lowest energy oscillator, E_0 , is associated with bandgap transition. The energy values found for these transitions are very similar for all the samples, and no clear tendency has been found for increasing dopant concentration. For p-type doped samples, along the series $p1 \times 10^{17}$, $p5 \times 10^{17}$ and $p1 \times 10^{18}$, two opposite tendencies would compete, since and increasing dopant quantity tends to lower bandgap value, but the associated decreasing N and Sb content would enlarge it. In that sense, the small enlargement of the E_0 transition when going from $p1 \times 10^{17}$ to $p5 \times 10^{17}$ accounts for the preponderant role of the smaller N

and Sb content in the second sample, while the small diminution observed for $p1 \times 10^{18}$ sample as compared to $p5 \times 10^{17}$, tell us that doping effect is a bit stronger in this case. In the n-doped samples, the effective doping level is very similar for the $n1 \times 10^{17}$ and $n5 \times 10^{17}$ samples and, therefore, the very small bandgap diminution in the last one should be attributed to the higher amount of both N and Sb in the $n5 \times 10^{17}$ sample (see Table 3). Concerning $n1 \times 10^{18}$ sample, no effective doping level could be measured. This fact, together with the bandgap enlargement observed for this sample in spite of the higher N and Sb contents, suggest that dopant has not been incorporated as an effective donor in this sample, as we have advanced in Section 3.1.

Table 4. Energies of the interband transitions, associated to each oscillator as deduced from SE data fitting.

	Unit	SAMPLE					
		$p1 \times 10^{17}$	$p5 \times 10^{17}$	$p1 \times 10^{18}$	$n1 \times 10^{17}$	$n5 \times 10^{17}$	$n1 \times 10^{18}$
Law parameters		Critical points position (or oscillator position)					
Adachi 3D 1 (E_0)	eV	1.11(3)	1.12(8)	1.11(4)	1.09(9)	1.08(5)	1.15(8)
Adachi 3D 2 (E_+)	eV	1.87(6)	1.90(8)	1.78(0)	1.72(4)	1.82(0)	1.81(5)
Adachi 3D 3 ($E_\#$)	eV	2.38(7)	2.44(1)	2.36(5)	2.38(3)	2.39(9)	2.39(3)
Adachi 2D (E_1)	eV	2.72(3)	2.75(8)	2.72(3)	2.74(3)	2.76(9)	2.74(5)
Adachi DHO 1 ($E_1 + \Delta_1$)	eV	3.07(2)	3.10(1)	3.03(8)	3.06(5)	3.10(8)	3.00(3)
Adachi DHO 2 (E_0')	eV	4.40(9)	4.44(0)	4.45(2)	4.46(6)	4.44(4)	4.43(6)
Adachi DHO 3 (E_2)	eV	4.77(6)	4.81(2)	4.80(2)	4.82(5)	4.80(4)	4.79(1)
Fit quality							
R^2 (ψ, Δ 0.75 – 5.5 eV)		0.993	0.998	0.996	0.996	0.994	0.994
RMSE		1.608	0.937	1.304	1.251	1.674	1.596

The energies of the transitions named E_+ and $E_\#$ should increase as N content increases [51]. For p-type samples there is a drastic diminution in N concentration for $p5 \times 10^{17}$ and $p1 \times 10^{18}$ samples, as compared to $p1 \times 10^{17}$ (see Table 3). Therefore, the small enlargement observed for both E_+ and $E_\#$ transition energies in $p5 \times 10^{17}$ should be attributed to a more important doping effect for this sample. However, the diminution observed for $p1 \times 10^{18}$ sample compared to $p5 \times 10^{17}$ would agree with the N content diminution. An enlargement of the E_+ transition energy is noticed for the $n5 \times 10^{17}$ and $n1 \times 10^{18}$ samples, when compared to $n1 \times 10^{17}$ sample. Since the effective dopant level are very similar for $n1 \times 10^{17}$ and $n5 \times 10^{17}$ samples (see Table 2), this enlargement should be explained in terms of the higher N amount for the more (nominally) doped samples (see Table 3).

E_1 and $E_1+\Delta_1$ transition energy variations among the different samples are similar to those described for E_+ and $E_\#$. Their values are smaller than those found for the GaAs matrix (2.91 and 3.14 eV, respectively) [48], though their diminution is not as important as for the lower energy transitions. Finally, E_0' and E_2 transitions (4.45 and 4.77 eV respectively for GaAs) get not affected neither by N and Sb inclusions, nor by dopant incorporation.

The dielectric function ε obtained after SE data fitting, is directly related with the complex refraction index (n , k) through a very simple relationship. The complex refractive index has been deduced from the fit results for the six samples and it is presented in Figure 7. As it could be expected, there are very few differences among the different samples and they concentrate in selected regions of the spectrum (see insets). For the refractive index, there are small differences in the low wavelength region and in the small feature appearing in the bandgap region (around 1100 nm). In this same region differences in the extinction coefficient are evidenced. The behaviour of this last parameter in this spectrum region is directly connected with the bandgap value through the absorption coefficient. As it has already discussed for Table 4, variations in N and Sb content, as well as doping, are responsible of the energy inter-band transitions shifts observed in these GaNAsSb layers. Therefore, for example in the bandgap region, no clear tendency with doping for the value of the fundamental transition (E_0) can be observed neither for p-type nor for n-type doped samples. Moreover, the dependence of the rest of the inter-band transition energies with N and Sb contents is not the same as for the bandgap transition. As we have demonstrated in the former Section 3.1, N and Sb contents differ from one sample to another. For these reasons, the refractive index and extinction coefficient lines intersect among them along the whole energy range.

Figure 7. Real, n (a) and imaginary part k (b) of the complex refractive index along the measured energy range for all the samples. Insets show the bandgap energy region.

3.2.2 Photoreflectance

Two sets of measurements with different pump wavelengths, 325 and 632.8 nm, were recorded for all samples (Figure 8). Experimental data obtained with 325 nm excitation wavelength show no features corresponding to the GaAs substrate, as a result of shallow penetration of the pump beam and low values of photogenerated minority carrier diffusion length within the GaNAsSb layers (Figure 8 left). Under these conditions, the observed PR signal originates from the modulation of the front surface space charge region (SCR) of GaNAsSb (highlighted in green as indicated in the schematics). The situation is different under 632.8 nm excitation wavelength, when the probe reveals signatures from both the front and rear surfaces of the GaNAsSb layers, together with signatures from the GaAs substrate (the latter highlighted in grey in Figure 8 right).

Concerning the data obtained under 325 nm pump, we can observe different PR-signal to noise ratios between p-type and n-type samples, similar to the case, e.g., of bare GaAs wafers. It is worth mentioning here that according to XRD data analysis all samples were fully strained, and the RSMs do show significant defect densities or structure alterations in any GaNAsSb layer, regardless of doping type. The lower PR signal intensity obtained from p-doped layers, like in the case of GaAs, is not related to an eventual deterioration of the crystalline quality of these layers, but instead to a reduced magnitude of the surface band bending in p-type samples, as compared to n-type ones. Such an asymmetry in the photovoltage developed under pump excitation as a function of doping type is likely the result of Fermi-level pinning off-midgap at the free surface of the layers.

Additionally, relative differences in p- and n-dopant concentrations at surface level as detected by SIMS, (see Figure 2) could also contribute to the observed differences. For the p-doped samples, dopant concentration at surface is lower than in the rest of the layer, while the opposite happens for the n-doped samples.

Figure 8. PR data corresponding to 325 (left) and 632.8 nm (right) pump wavelength. SI-GaAs substrate data have been included in both cases in the upper part for comparison purposes. Note the different energy scales for both graphics. Probed regions from GaNAsSb (green) and SI-GaAs substrate (grey) under different pump energies are indicated by the arrows.

The fundamental gap E_0 of all GaNAsSb samples is clearly resolved around 1.1 eV from measurements using 325 nm pump. At least two additional transitions of lower intensities are observed at higher energies in n-type samples, assigned to spin-orbit split of the valence band $E_0 + \Delta_0$ around 1.5 eV (also visible in two p-type samples) and the E_+ branch around 1.8 eV (see Figure 8 left), in agreement with reports on double BAC model [50]. The first of these transitions cannot be resolved in ellipsometry measurements, but second one is in agreement with SE results (Table 4). Attempts to fit the spectra of n-type samples according to Aspnes' Third Derivative Functional Form (TDFF) [54] have been carried out, as shown in Figure 9, with results collected in Table 5. Imposing an exponent factor $m=2.5$ (characteristic of 3D-parabolic critical points) on each term of the functional accounting for the observed signatures requires using four critical points for optimal fit

quality ($R^2 > 0.995$). The fourth signature employed in the fits (marked E^* in Table 5), which overlaps the fundamental transition E_0 , shows in all cases unrealistically large values of the corresponding broadening factor. Therefore, this additional signature cannot be simply attributed, at the light of these results, e.g., to the split of heavy and light holes as a result of accumulated strain, its origin being more likely related to composition inhomogeneities, which would be in accordance with the variable composition of these samples along layer thickness demonstrated after SIMS and HRXRD data analysis.

Figure 9. PR spectra (dotted) and corresponding TDFF fits (red lines) of the n-type GaNAsSb critical points.

Table 5. Results of best fits to TDFFs with exponential factor $m=2.5$ of spectra obtained from n-type doped GaNAsSb layers under 325 nm pump, including critical point (CP) energies and broadening factors of the four signatures employed: E_0 is the fundamental transition; $E_0 + \Delta_0$ is the spin-orbit split; E_+ is the high energy branch after band anticrossing; E^* is an additional unknown transition necessary for best fits.

$n1 \times 10^{17}$		$n5p1 \times 10^{17}$		$n1 \times 10^{18}$	
CP (eV)	Γ (meV)	CP (eV)	Γ (meV)	CP (eV)	Γ (meV)

E_0	1.116	64	1.140	76	1.183	89
E^*	1.231	91	1.179	245	1.345	288
$E_0 + \Delta_0$	1.467	81	1.441	99	1.456	172
E_+	1.806	59	1.812	74	1.795	72

Concerning PR measurements recorded under 632.8 nm pump, the main difference with respect to the previous case is the appearance of GaAs-related signatures from the substrate in all spectra, revealing access to the GaNAsSb/GaAs interface, in addition to the front surface. The presence of GaAs-related Franz-Keldysh oscillations (FKOs), particularly conspicuous in the case of n-type samples, unveils high electric fields present at the GaNAsSb/GaAs interfaces. The FKO-period is a direct measure of the maximum built-in field intensity in the probed space charge region [55, 56], which are related by:

$$\frac{\Delta R}{R} \propto \cos \left\{ \frac{4}{3} \left(\frac{E - E_0}{\hbar \theta} \right)^{3/2} + \varphi \right\}$$

and where $(\hbar \theta)^3 = (e\hbar F)^2 / (2\mu)$ is the electro-optic energy, φ is a phase factor related to the dimensionality of the critical point E_0 , F is the maximum intensity of the electric field, and μ is the reduced interband effective mass in the direction of the field. Imposing:

$$n\pi = \frac{4}{3} \left(\frac{E_n - E_0}{\hbar \theta} \right)^{3/2} + \varphi$$

where n is the integer index of the oscillation extrema and E_n the corresponding energy of the n -th extremum, a direct relationship between field intensity and the FKO-period follows. In this manner we have estimated a maximum field intensity present at the interfaces of n-GaNAsSb/GaAs samples of 47.3, 48.4, and 53.1 kV/cm for increasing n-doping concentration of GaNAsSb, using values of GaAs effective masses $m_e^* = 0.0655 m_0$ and $m_h^* = 0.523 m_0$. Such high field intensities detected at the GaNAsSb rear surface could be connected with the dopant and Sb-accumulation observed by SIMS (Figures 42 & S2), yet the eventual interplay is unclear.

TDFE-fitting of GaNAsSb-signatures is not properly justified on the spectra obtained under 632.8 nm pump, as according to composition deduced from HRXRD and doping profiles seen on SIMS measurements, the front and rear SCR differ in composition, doping and homogeneity (see Section 3.1). Such an approach would imply the assignment of single oscillator factors to describe critical points of varying nature as a function of location. Large values of the broadening factor already obtained from TDFE analysis of spectral signatures under 325 nm pump further hamper any

realistic attempt to resolve separate contributions in the corresponding spectra under 632.8 nm pump. Alternatively, we have used Kramers-Krönig analysis to estimate the energies of the main contributors to PR signatures as observed from PR-signal moduli of the fundamental transitions [57]. It has also been applied to p-type samples with lower signal-to-noise ratios and to 325 nm pump spectra for comparison purposes, showing a very good agreement. The fact that PR-spectra recorded under 632.8 nm pump do probe inhomogeneous and spatially different regions of the GaNAsSb layer is further supported by the observation of larger broadening factors, in comparison to those under 325 nm pump (see Table 6). The energy of the fundamental transition increases as the nominal doping of the layer does, although we must keep in mind the differences in composition (N and Sb content) among the samples, and that this factor rules also the bandgap values. The line broadening follows the same tendency, except for values obtained from 632.8 nm pump data for the n-doped samples which are very similar.

Table 6. Fundamental transitions (E_0) and corresponding broadening factors (Γ) in the low energy range of PR spectra obtained under 325 and 632.8 nm pump, after Kramers-Krönig analysis.

sample	325 nm pump		632.8 nm pump	
	E_0 (eV)	Γ (meV)	E_0 (eV)	Γ (meV)
p1×10 ¹⁷	1.091	35	1.105	43
p5×10 ¹⁷	1.109	43	1.127	50
p1×10 ¹⁸	1.131	63	1.175	58
n1×10 ¹⁷	1.119	60	1.093	93
n5×10 ¹⁷	1.123	64	1.119	89
n1×10 ¹⁸	1.172	85	1.149	88

3.2.3 Transmittance Measurements

Bandgap values, as determined after transmittance measurements are shown in Table 7 for all the samples, as well as those obtained from photoreflectance and ellipsometry measurements. To extract the bandgap values from transmittance measurement a standard procedure described in Supplemental Material has been followed. As it was already seen during the analysis of the SE data, no clear tendency of the bandgap energy value with doping can be inferred for these samples. That

could be explained taking into account the differences in N and Sb content detected in the XRD analysis for the samples studied in this work (see section 3.1). N and Sb concentrations are key factors controlling the fundamental transition energy in this kind of materials, as much as doping level does, therefore, as explained for the SE results, the competition between these two factors is probably the origin of the absence of any tendency of the bandgap energy value with doping.

Table 7. Values of the energy of the fundamental transitions (E_0) for all the samples, as obtained by the different techniques used for optical characterization.

Sample No.	E_0 transition (eV) TR	E_0 transition (eV) PR (325 nm)	E_0 transition (eV) PR (632.8 nm)	E_0 transition (eV) SE
p1×10 ¹⁷	1.073	1.091	1.105	1.113
p5×10 ¹⁷	1.088	1.109	1.127	1.128
p1×10 ¹⁸	1.082	1.131	1.175	1.115
n1×10 ¹⁷	1.072	1.119	1.093	1.097
n5×10 ¹⁷	1.073	1.123	1.119	1.085
n1×10 ¹⁸	1.081	1.172	1.149	1.158

4. CONCLUSIONS

Doped GaNAsSb layers have been grown by MBE onto semi-insulating GaAs substrates. Growth parameters were adjusted to nominally obtain the same GaNAsSb composition for all samples. The targeted dopant levels, namely from 10¹⁷ to 10¹⁸, were chosen as they are usual in many optoelectronic devices such as multijunction solar cells.

Dopant incorporation into the dilute nitride lattice and doping effectiveness are highly dependent on the dopant type. The measured p-dopant concentration by SIMS is always lower than the targeted dopant concentration, however, the effective doping detected through electrical measurements is at least twice higher than the dopant concentration in the lattice. This fact points to an unintentional intrinsic p-doping in these samples, whose origin may lay on different crystalline defects. On the contrary, for the n-doped samples, the dopant amount in the lattice is one order of magnitude higher than the nominal doping. In spite of that, the effectiveness of the n-doping is quite low, or even null for the more (nominally) doped sample. In both cases, p- and n-doped

samples, dopant incorporation into the dilute nitride layer seems to provoke an important increase of the defects density in the crystalline lattice, as deduced from RSMs, and this could be the reason for the values and temperature dependence of the electrical parameters, mobility and resistivity. For both type of doped GaNAsSb layers, the scattering mechanisms controlling the mobility and carrier concentration have been established.

The composition of the samples is not homogeneous along the growth direction, except for the lower p-doped sample. Probably, the main reason is that for this sample, $p1 \times 10^{17}$, growth temperature was 420°C, while a higher temperature, 460°C, was used for the rest of the samples. Sb concentration varies along the layer thickness, showing a decreasing tendency going from the interface with GaAs substrate to the sample surface. For all the samples, Sb and N concentrations in the layers are different than the nominal target composition. Doping type has a clear influence on the incorporation of both anions in the crystalline lattice. For the p-doped samples, both, Sb and N contents decrease as p-dopant concentration increases. On the contrary, for the n-doped samples, Sb and N concentrations increase as the Si amount does. Degradation of electron mobility and carrier concentration for the Si-doped samples have been related with these variations in N content detected. Therefore, Si-doping of GaNAsSb is not recommendable for the 10^{17} cm^{-3} range. On the other hand, mobilities and carrier concentrations of Be-doped GaNAsSb are insensitive to N content and they exhibit similar values to those of Be-GaInNAs. All these findings are indicative of the high complexity of the growth processes in this kind of materials, in particular for n-type doped layers.

Optical characterisation of the samples has been accomplished using three different techniques, spectroscopic ellipsometry, photoreflectance and transmittance. The values obtained for the fundamental transition energy, E_0 , are very similar, around 1.1 eV, for all of them, being a bit smaller the values deduced from transmittance data. For a given sample, differences in bandgap values seen on Table 7 must be regarded as a consequence of the different techniques used to extract them. Both, SE and transmittance measurements give information of the whole dilute nitride layer optical behaviour, while PR data concern just front and rear surface space charge regions. When comparing different samples, it is worth remaining here that both, Sb amount and dopant concentration, vary from one sample to another. Therefore, bandgap values are ruled by these two issues. SE allows to explore a wide energy range where several transitions (CPs) between valence and conduction band take place. Energies found for these CPs are in accordance with literature values, even for the E_+ and $E_\#$ transitions, appearing as a consequence of N incorporation

in the dilute nitride lattice, as described in the BAC model. No clear tendency with doping has been found for any of these transitions and the same applies for the transmittance results concerning the bandgap transition. This is due to the differences in N and Sb content in the samples, which act as another regulator factor of the transition energies. PR results from 325 nm pump data evidence the differences between p- and n-type samples regarding dopant accumulation in the top layer surface, as well as the differences in composition along layer thickness. 632.8 nm pump data concerning rear layer surface are another probe of the differences between two dopant polarities. In the end, the refractive index and extinction coefficients have been determined for all the samples, in a wide energy range.

Acknowledgements

This work has been supported by the Spanish MINECO through the projects, PCIN-2015-181-C02-01, PCIN-2015-181-C02-02, TEC2017-83447-P, by the Comunidad de Madrid through the project MADRID-PV2 (S2018/EMT-4308), and by Universidad Politécnica de Madrid through the project RP 150910B12. Authors gratefully acknowledge Dr. J. M. Ripalda from Instituto de Microelectrónica de Madrid (Spain) for the technical assistance for Hall effect measurements, and technical support for HRXRD measurements from Dr. J.M. Bassas from Centres Científics i Tecnològics (CCiT) at Barcelona University (Spain).

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