Refractive indexes and extinction coefficients of n- and p-type doped GaInP, AlInP and AlGaInP for multijunction solar cells

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ABSTRACT

The optical properties of p-type, n-type and nominally undoped $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ layers have been determined in a wide spectral range. The layers under study have been chosen with compositions and dopant concentrations which make them interesting for their use in III-V multijunction solar cells. The layers have been measured by variable angle spectroscopic ellipsometry and, irrespective of composition and doping, their optical response has been modelled using the same model dielectric function consisting of two asymmetric Tauc-Lorentz oscillators and a 3D- M_0 Adachi term. The results show that transition energy values change with layer composition, whilst for layers of the same material (i.e. GaInP or AlInP), the band-gap transition energy E_0 shows a strong dependence on the order parameter. The refractive indexes and extinction coefficients deduced from the ellipsometric data have been used to fit reflectance measurements for the same layers and an excellent agreement has been achieved, thus validating the model dielectric function proposed for this kind of materials.

1. Introduction

Ternary and quaternary III-V alloys such as $\text{Ga}_x\text{In}_{1-x}\text{P}$, $\text{Al}_x\text{In}_{1-x}\text{P}$ and $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ are widely used in many optoelectronic devices. In particular, $\text{Ga}_x\text{In}_{1-x}\text{P}$ is a key material for the top cell in triple junction solar cells [1]. $\text{Al}_x\text{In}_{1-x}\text{P}$ and $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ have emerged as potential candidates with bandgaps above 2.0 eV that can be used as top cells in multijunction solar cells with more than 3 junctions [2–5]. Moreover, $\text{Al}_x\text{In}_{1-x}\text{P}$, $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ and $\text{Ga}_x\text{In}_{1-x}\text{P}$ are usually employed as passivating and barrier layers in III-V solar cells, namely, front/back surface fields and buffer or nucleation layers with thicknesses ranging from tenths to hundreds of nanometers and up to the micrometer range (i.e. as in compositionally graded buffer layers in metamorphic structures). Even in cases where they act as photovoltaic inactive layers, their impact on light transmission to the underlying layers is not negligible. Therefore, the knowledge of the optical properties of $\text{Ga}_x\text{In}_{1-x}\text{P}$, $\text{Al}_x\text{In}_{1-x}\text{P}$ and $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ is of paramount importance for the development of III-V multijunction solar cells. In fact, analytical models [6] and drift-diffusion simulators typically used to predict solar cell performance require reliable optical constants (wavelength dependent refractive index and absorption coefficient) of the materials to improve their accuracy [7].

The optical behaviour of lattice matched $\text{Ga}_x\text{In}_{1-x}\text{P}$ and the quaternary $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ films has been extensively studied using a variety of experimental techniques [8–16]. However, very few of these works have correlated the material optical properties with dopant type and level [14,15]. $\text{Al}_x\text{In}_{1-x}\text{P}$ has attracted much less attention from the scientific community, although excellent reports have been published in the last years [17–19]. More recently, the study of the optical properties of lattice mismatched III-V alloys has been addressed, thus extending the compositional range for which data are available [20]. It is well known that the electrical and optical properties of solar cells are dependent on the growth conditions (temperature, V/III ratio, growth rate, etc.), doping level and dopant type. Growth conditions may induce different degrees of CuPt-type ordering on the group III-sublattice of the (Al)GaInP alloys [21]. In essence, CuPt-type ordering describes a superlattice of alternating Ga- and In-rich {111} planes (i.e., for the case of GaInP, $\text{Ga}_{0.5(1-\eta)}\text{In}_{0.5(1+\eta)}\text{P}/\text{Ga}_{0.5(1+\eta)}\text{In}_{0.5(1-\eta)}\text{P}$, where η is defined as the order parameter). For a completely disordered material $\eta = 0$, whereas for a completely ordered material $\eta = 1$, although, so far, only experimental values as high as $\eta = 0.6$ have been reported for GaInP grown using Metal Organic Vapour Phase Epitaxy (MOVPE) [22,23]. The degree of order modulates, among others, the energy bandgap (E_g) of the alloy [14,21,24,25]. In this respect, a decrease in the order parameter (low η) leads to a higher E_g .

In spite of the extensive literature in the field, most of the existing works have studied $\text{Ga}_x\text{In}_{1-x}\text{P}$, $\text{Al}_x\text{In}_{1-x}\text{P}$ and $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ layers with an intrinsic doping which does not correspond to the typical doping values (and thus degree of disorder) used in conventional III-V solar cells. Therefore, the determination of the optical constants of III-V phosphide-based materials with the typical doping levels and growth conditions applied in the fabrication of multijunction solar cells is essential to improve the accuracy of the models used to predict the solar cell performance.

Accordingly, the purpose of this paper is to determine the optical constants (refractive index and absorption coefficient) by variable angle Spectroscopic Ellipsometry (SE) of $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$, $\text{Al}_{0.53}\text{In}_{0.47}\text{P}$ and $(\text{Al}_x\text{Ga}_{1-x})_{0.51}\text{In}_{0.49}\text{P}$ lattice matched to GaAs (hereafter referred to as GaInP, AlInP and AlGaInP, respectively) for different doping levels and dopant types – and subsequent order parameter – as the ones typically used for III-V solar cells. It is known that CuPt-type ordering induces a symmetry lowering and therefore a small birefringence in the layer dielectric function in the near-bandgap spectral region [26]. However, such a fine analysis is beyond the scope of this article and anisotropy was not taken into account in the data treatment to calculate the optical constants as previous works proved the suitability of the isotropic approximation for similar III-V layers [9,14,15,17,18].

Complementary characterization techniques such as X-ray diffraction (XRD), Raman spectroscopy, Scanning Electron Microscopy (SEM), Photoluminescence (PL), are used to determine thicknesses, order parameter and composition of the layers which are required to carry out the analysis. The comparison of the reflectance obtained from the deduced optical constants with experimental data along a wide spectral range, is used to validate the model describing the optical behaviour of the layers. The results of the paper are also useful for devices other than solar cells, such as LEDs, lasers, etc and will contribute to extend knowledge on the optical properties of the aforementioned materials.

2. Experimental

For this study, a batch of GaInP and AlInP structures, plus a AlGaInP one, were epitaxially grown on (100) GaAs wafers misoriented 2° towards the nearest (111)A plane in a low pressure horizontal Aixtron MOVPE reactor (AIX-200/4). Trimethyl-gallium (TMGa), trimethyl-indium (TMIn), trimethyl-aluminium (TMAI), phosphine (PH_3) and arsine (AsH_3) were the sources used for the GaAs, GaInP and AlInP layers. Dimethylzinc (DMZn) and ditertiarybutylsilane (DTBSi) were used as dopant sources. Growing conditions were chosen in order to get layers with the typical doping levels and compositions actually used in III-V multijunction solar cells. Two GaAs layers were grown in such a way that they sandwiched the GaInP, AlInP or AlGaInP layer that will be the object of this study. A buffer GaAs layer, 500–1000 nm thick, is grown on the substrate before the phosphide layers while a thin GaAs cap layer finishes the stack to protect the phosphide layers that will be analysed in this paper. Prior to the optical characterization, the cap layer was chemically etched using $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (2:1:10) (see Fig. 1).

The thickness of the layers of interest was measured by in situ reflectometry during the epitaxial growth and confirmed by SEM once the layer was grown. The reflectometry tool is an EpiRAS 2000 instrument from Laytec. SEM equipment is a FEI Helios Nanolab 650 Dual Beam

microscope. The dopant concentration in the layers was measured by electrochemical capacitance–voltage (CV) profiling using a WEP Control CVP21 tool. The mismatch between the layer of interest and the substrate was analysed by a QC2a X-Ray Diffractometer Bede Scientific XRD.

PL measurements were performed at 20 K excited with a 532 nm laser at 26 mW. Raman spectroscopy measurements were conducted to determine differences in the ordering parameter among layers with the same composition. The equipment is a Raman Confocal Microscope Invia Reflex from RENISHAW, using Ar 514.5 nm (12 mW) as excitation line. Spectral resolution achieved was 1 cm^{-1} by selecting a 1800 l/mm grating and a slit opening of 50 μm . Spectra were acquired in back-scattering geometry at room temperature. The dielectric response of the layers has been characterized in a Semilab GES-5E variable angle spectroscopic ellipsometer in the region from 233 to 984 nm (approximately 5.3–1.26 eV) at room temperature. The layers were analysed with a microspot configuration with a spot size of approximately 400 μm and angular aperture of 4.25° , the angle of incidence was varied between 60° and 75° . Specular reflectance was performed on a Perkin Elmer Lambda 1050 UV/VIS/NIR WB InGaAs Spectrometer with defined angle of incidence and reflection of 6° . Reflectivity simulations have been performed by using the generalized matrix method [27]. The structure used in the simulations is exactly the one depicted in Fig. 1. An incoherent optical behaviour was assumed within the substrate due to its large thickness ($350 \pm 25\text{ }\mu\text{m}$) while the other layers were treated coherently. No roughness was assumed in any layer due to the specular behaviour of the samples.

3. Results

The basic characterization results of the nine layers grown for this study have been gathered in Table 1. For each type of sample, this table includes the doping type, doping concentration and layer thickness as measured in situ with EpiRAS, and *ex-situ* through SEM. Some other structural characteristics of the layers have also been included. Fig. 2 shows an example of a SEM cross-section image. As can be seen, the GaAs buffer layer is slightly recognizable, while an abrupt interface with the layer under study is clearly visible for all the structures.

3.1. Structural characterization

XRD measurements were performed in order to obtain the lattice mismatch between the semiconductor layers (GaInP, AlInP) and the GaAs substrate. The determination of their lattice constants can be calculated by:

$$a[\text{Ga}_x\text{In}_{(1-x)}\text{P}] = xa[\text{GaP}] + (1-x)a[\text{InP}] \quad (1)$$

where a_{GaP} and a_{InP} are the lattice constants of GaP and InP. For $x = 0.516 = X_{\text{LM}}$ (lattice matched) at 25°C , the GaInP layer has a lattice constant of 0.56532 nm and it will be lattice matched to the GaAs substrate [28]. The lattice mismatch is calculated by:

$$a \frac{[a_{\text{GaInP}}] - a[\text{GaAs}]}{a[\text{GaAs}]} \% \quad (2)$$

As can be seen in Table 1, most of the layers are lattice matched to GaAs, just the undoped GaInP layer shows a slight mismatch in agreement with [28]. For the AlGaInP layer, the peak shift to that of the GaAs substrate ($\Delta\theta = 80''$) shows again a good lattice matching, but due to complexity of lattice mismatch calculations for quaternaries elements, only a rough estimate of the Al quantity around 10–20% (i.e. $(\text{Al}_{0.15}\text{Ga}_{0.85})_{0.51}\text{In}_{0.49}\text{P}$) can be made.

The estimation of the order parameter for the GaInP layers was performed, as in previous works, from PL measurements at 20 K [29,30]. The relation between the order parameter, η , and the energy bandgap (i.e. peak energy from low temperature PL measurements) is described by:

Fig. 1. Sketch of the semiconductor structure after chemical etching of the cap layer, prior to the optical characterization.

Table 1

Brief summary of the different layers analysed in this work. Dopant type is indicated between brackets; n^+ , p^+ denote highly doped layers for the same semiconductor material while u means nominally undoped. Composition, lattice constant and lattice mismatch of GaInP and AlInP layers are also included.

Layer	Dopant concentration (cm^{-3})	Thickness (nm) EpiRAS/SEM	Ga or Al composition	Lattice parameter ($\text{\AA}$)	% lattice mismatch to GaAs substrate
GaInP (u)		503/500	0.487	5.665	0.210%
GaInP (n)	4.7×10^{17}	566/566	0.512	5.655	0.030%
GaInP (p)	3.1×10^{16}	1093/1096	0.511	5.655	0.030%
GaInP (p^+)	1.6×10^{17}	455/450	0.521	5.650	0.056%
AlInP (n)	3.8×10^{17}	240/240	0.534	5.652	0.016%
AlInP (n^+)	5.6×10^{18}	423/420	0.537	5.651	0.038%
AlInP (p)	1.4×10^{17}	534/538	0.534	5.652	0.016%
AlInP (p^+)	9.4×10^{17}	660/660	0.540	5.650	0.059%
AlGaInP (p)	1×10^{18}	383/380			

$$E_g(\eta) = E_g(\eta = 0) - \eta^2 \Delta E_g \quad (3)$$

where $E_g(\eta = 0)$ is the bandgap of the fully disordered layer, 2.010 eV [10] and ΔE_g is the bandgap reduction of the fully ordered alloy, which has been experimentally determined to be 471 meV [22].

The order parameter obtained for our GaInP layers was very similar for all of them, ~ 0.56 , which is considered highly ordered (being $\eta = 1$ fully ordered, while $\eta = 0$, fully disordered [30]). Unfortunately, the AlInP bandgap determination from PL measurements is not straightforward since our AlInP composition makes the lowest energy inter-band transition indirect.

3.2. Raman spectroscopy

Raman spectra of the different layers show typical features of GaInP and AlInP grown on GaAs. GaInP layer spectra look very similar for all the layers, irrespective of doping type and level (Fig. 3 left). InP-like (~ 325 (TO) and ~ 355 (LO) cm^{-1}) and GaP-like LO (~ 380 cm^{-1}) modes can be easily identified in the graph [31] and references therein. InP-like TO mode is forbidden in the zincblende structure for backscattering from [001] planes, however, it is clearly visible in both, GaInP and AlInP spectra. According to PL measurements, the order parameter is rather high for these GaInP samples, which induces a symmetry lowering to point group C_{3v} and thus boosts the InP-like TO mode [32]. An estimate of the intensity of the InP-like modes through the $I(\text{TO})/I(\text{LO})$

Fig. 2. Scanning electron microscope images of a) GaInP(p), and b) AlInP(n^+) layers.

Fig. 3. Left, GaInP layers Raman spectra: black line, undoped (u) sample; green line, n-doped layer (n); magenta lines, p-doped layers, dashed line corresponds to the less doped one (p), while solid line is the spectrum of the more doped layer (p⁺). Right, AlInP layers Raman spectra: blue lines are the spectra from the p-doped layers and red lines correspond to n-doped layers. Again, dashed lines are used for the less doped samples ((n) and (p)) while solid lines for the more doped layers ((n⁺) and (p⁺)). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Fig. 4. Sketch of the layer stack model used for the ellipsometry data fit (not to scale). Notice how the GaAs buffer grown on top of the GaAs substrate is not taken into account since it does not affect the ellipsometry fit.

ratio, suggests that order parameters for all doped samples are very similar and slightly smaller than that of the undoped GaInP [33]. This reduction of the order parameter associated with doping could be also the reason for the small frequency redshift noticeable in GaP-like LO mode for the doped samples [34,35].

Raman spectra of AlInP layers show some differences among layers (Fig. 3 right). The InP-like TO mode is visible in all sample spectra, however, its intensity differs from one sample to another. As for the GaInP samples, its presence it is related to a symmetry lowering due to CuPt-type ordering. Therefore, order parameter would have different value for each AlInP layer, being AlInP (n⁺) the more ordered layer. The intensity ratio $I(\text{TO})/I(\text{LO})$ for InP-like modes increases following the sample sequence (p) < (n) < (p⁺) < (n⁺), which is in agreement with dopant concentration irrespective of type (see Table 1). Conversely to what has been observed for our GaInP layers, increasing doping strongly affects order parameter and it enhances CuPt ordering in these AlInP layers. Around 450 cm⁻¹, AlP-like modes appear [36–38]. Noticeable differences deserve reader attention. First of all, for the less doped p-type sample, an important frequency blueshift occurs. This could be related to what has been detected for the InP-like modes, where for the AlInP (p) layer, TO mode intensity is lower than that of the LO one. In that sense, AlP-like mode peak would be dominated by LO contribution for the less doped p-type AlInP layer, while for the rest of the samples, TO contribution would be the most important, suggesting again that the less p-doped AlInP layer presents the lower degree of CuPt ordering among these layers. Due to the absence of GaP-like modes, it is possible to detect one of the alloy-induced (AM) modes, AM₃, around 410 cm⁻¹ region [38]. These AM modes are strongly

dependent on the value of the ordering parameter and contribute with an asymmetric profile to the global spectrum in this energy region. The intensity of this mode, as compared with the AlP-like one, reaches a maximum value for the more n-doped sample, which again is in agreement with the findings described for the InP-like modes and supports our conclusion that this sample exhibits the highest order parameter value among these AlInP layers.

On the left side of the InP-like modes, a peak around 260 cm⁻¹ is detected. Its origin is the GaAs buffer layer [37] and it could appear due to the low AlInP absorption coefficient in this energy range.

3.3. Variable angle spectroscopic ellipsometry

In order to analyze the ellipsometric data, a layer structure model is necessary. In such structure, the thicknesses and optical behaviour of each layer can be treated as known parameters or might be the outcome of a least squares fit of the experimental results to a theoretical model. In this paper the assumed layer stack better describing the semiconductor structures is shown in Fig. 4. It consists of the GaAs substrate, along with the ternary or quaternary indium phosphide layer under study and a thin oxide layer on top (see Fig. 1 right for comparison). The GaAs buffer layer between GaAs substrate and the (Al_xGa_{1-x})_yIn_{1-y}P layer of the original structures does not present any noticeable optical difference with the GaAs substrate, and therefore no distinction will be made between them. The optical characteristics of GaAs and the top oxide layer have been treated as known parameters, extracted from the database of Semilab. There are very few studies on the optical properties of the surface oxides of ternary semiconductors, one exception being a recent work on the optical characteristics of AlInP_{ox} [17]. However, it has been found that the inclusion of a specific AlInP_{ox} does not improve model fitting even for AlInP samples. Therefore, we have assumed the dielectric function of InP_{ox} as representative of the oxide formed on the top of any of the semiconductor layers studied; the specific function being that proposed by Zollner [39]. Furthermore, the first studies showed the presence of a weakly absorbing layer in the higher energy range. Unlike InP_{ox}, GaP_{ox} is transparent in the whole energy range analysed and other potential oxides exhibit higher absorptions [39]. Thus, InP_{ox} has been chosen to describe the optical properties of the top layer on all samples.

The spectra have been fitted using the same model dielectric function (MDF) for all samples, which mathematically describes the gallium/aluminium indium phosphide layers dielectric function. Several terms have to be included. There is a constant term ϵ_∞ describing the

behaviour at high enough frequencies (energies), regardless of free carrier effects. Then two asymmetric Tauc-Lorentz oscillators were included. The model combines the Tauc joint density of states for band edge [40] and the classical Lorentz broadening function. In this approach, the dispersion law parameters are A , E , C and E_g , the oscillator amplitude, peak position, width and band gap, respectively. There are two sets of these parameters, one for each Tauc-Lorentz Oscillator.

The last one is a 3D- M_0 Adachi term, which is the one that controls the optical behaviour in the vicinity of the bandgap. It accounts for the less energetic transitions between electronic bands. This type of Adachi MDF can be used to describe the spectral dependence of the dielectric constant of semiconductor crystals, when the direct interband E_0 , $E_0 + \Delta_0$ transitions are dominant [41,42]. In this approach, the dispersion mechanism includes the effect of discrete and continuum excitonic transitions. The terms to be fitted are A_0 , E_0 and Γ_0 , respectively the transition amplitude, position and broadening. Additionally A_{0x} is the 3D discrete exciton strength, G_0 is the 3D exciton Rydberg energy, A_{0c} is the 3D continuum exciton strength and E_{0c} is the ground state exciton energy, which usually is assumed to have the same value as E_0 . Together with the Tauc-Lorentz and Adachi terms, there are two thickness parameters to be fitted, the thickness of the layer under study, d_b , and that of the oxide layer on top, d_s , for a total of 17 terms to fit.

As an example of the results of the model adjustments, Fig. 5 shows the measured ellipsometric spectra composed of ψ and Δ , with angles of acquisition ranging from 60° to 75° ; the generated values after model fitting are shown as well. As can be seen, the model proposed provides a good fitting both in the transparent region (below the band gap) and in the absorbing region (above the bandgap).

Table 2 shows the best values after model fits. First two rows correspond to thicknesses of oxide (d_s) and $(\text{Al}_x\text{Ga}_{1-x})\text{In}_{1-y}\text{P}$ layers (d_b). Oxide layer thickness has very similar values to those reported in literature [11,17] except for the AlInP(p) layer. Regarding d_b values, they agree rather well with those measured by RAS and SEM. Last row in the table corresponds to the parameter that measures the goodness of fitting.

4. Discussion

All the spectra show the typical features associated with E_0 , E_1 and E_2 transitions [8,9,11,13,18], which leads to a very similar shape for all the dielectric functions along the energy range measured. Fig. 6 contains the dielectric functions, resulting from the model fit, along the whole energy range measured for all layers. They are clearly separated according to the layer stoichiometry, in the form of a noticeable shift in

Fig. 5. Variable angle measured ellipsometric spectra ψ and Δ (open symbols) and that generated after model fitting (full lines) for GaInP(p) layer.

Table 2
Analytical parameters extracted from the spectroscopic analysis, root mean square error (RMSE) shown stands for ψ and Δ representations.

Parameter	GaInP (u)	GaInP (n)	GaInP (p)	GaInP (p +)	AlInP (n)	AlInP (n +)	AlInP (p)	AlInP (p +)	AlGaInP (p)
d_s (nm)	1.9 ± 0.009		1.1 ± 0.0001	2.51 ± 0.0007	3.9 ± 0.0005	2.84 ± 0.0006	7.5 ± 0.0005	3.6 ± 0.003	2.5 ± 0.0008
d_b (nm)	528.9 ± 0.005		1076.3 ± 0.001	438.9 ± 0.004	241.7 ± 0.001	407.7 ± 0.002	544.7 ± 0.002	602.1 ± 0.002	375.5 ± 0.004
A_2 (eV)	31.6 ± 0.09		31.0 ± 2.5	38.9 ± 3.93	80.6 ± 2.9	69.8 ± 5.4	55.9 ± 4.28	67.3 ± 7.23	67.1 ± 4.7
E_2 (eV)	4.77 ± 0.01		4.81 ± 0.01	4.85 ± 0.01	4.85 ± 0.03	4.85 ± 0.02	4.91 ± 0.02	4.87 ± 0.01	4.85 ± 0.02
C_2 (eV)	21.27 ± 0.01		1.13 ± 0.04	1.25 ± 0.04	1.15 ± 0.007	1.07 ± 0.06	0.86 ± 0.06	1.04 ± 0.04	1.25 ± 0.05
E_g^2 (eV)	0.99 ± 0.04		1.0 ± 0.17	1.06 ± 0.11	2.30 ± 0.006	2.27 ± 0.238	2.12 ± 0.04	2.28 ± 0.11	1.74 ± 0.3
A_1 (eV)	47.4 ± 0.18		117.6 ± 9.69	103.5 ± 10.36	47.8 ± 1.89	59.8 ± 3.3	46.4 ± 4.2	57.9 ± 3.34	62.8 ± 3.1
E_1 (eV)	3.34 ± 0.09		3.3 ± 0.01	3.34 ± 0.01	3.8 ± 0.02	3.81 ± 0.02	3.83 ± 0.01	3.79 ± 0.08	3.48 ± 0.02
C_1 (eV)	0.89 ± 0.01		0.95 ± 0.04	0.84 ± 0.02	0.82 ± 0.03	0.85 ± 0.04	0.85 ± 0.04	0.92 ± 0.02	0.83 ± 0.04
E_g^1 (eV)	1.81 ± 0.02		2.28 ± 0.05	2.3 ± 0.04	2.06 ± 0.25	2.25 ± 0.17	2.18 ± 0.06	2.21 ± 0.05	2.02 ± 0.13
A_0 (eV ^{1.5})	8.25 ± 0.08		10.8 ± 0.9	11.6 ± 1.09	11.3 ± 0.29	19.1 ± 1.17	22.9 ± 2.8	21.2 ± 1.13	7.27 ± 0.71
E_0 (eV)	1.81 ± 0.003		1.84 ± 0.08	1.9 ± 0.15	2.53 ± 0.03	2.51 ± 0.005	2.61 ± 0.25	2.51 ± 0.01	2.05 ± 0.0037
Γ_0 (eV)	$9.4 \times 10^{-4} \pm 2.1 \times 10^{-5}$		0.15 ± 0.01	0.22 ± 0.06	0.034 ± 0.006	0.02 ± 0.0008	0.05 ± 0.01	$2.6 \times 10^{-2} \pm 0.002$	0.004 ± 0.0001
A_{0x} (eV)	0		-0.068 ± 0.006	-0.096 ± 0.008	-0.014 ± 0.006	-0.0043 ± 0.0001	$-0.017 \pm 2 \times 10^{-4}$	$7 \times 10^{-5} \pm 7 \times 10^{-6}$	$7 \times 10^{-5} \pm 7 \times 10^{-6}$
G_0 (eV)	$0.004 \pm 5 \times 10^{-5}$		0.048 ± 0.007	0.074 ± 0.0002	2.3 ± 0.14	1.8 ± 0.04	0.047 ± 0.003	1.71 ± 0.13	0.018 ± 0.003
E_{0c} (eV)	0		0.035 ± 0.004	-0.0043 ± 0.0005	-0.016 ± 0.001	-0.77 ± 0.03	$0.042 \pm 2 \times 10^{-4}$	-2.36 ± 0.27	$0.003 \pm 5 \times 10^{-4}$
e_{∞}	1.90 ± 0.01		1.66 ± 0.05	1.744 ± 0.08	1.59 ± 0.11	1.563 ± 0.09	1.494 ± 0.24	1.63 ± 0.04	$1.23 \pm$
RMSE	1.212		0.794	0.839	2.158	2.635	1.899	1.389	1.653

Fig. 6. Real and imaginary parts of the dielectric function of GaInP layers (a and c), and AlGaInP and AlInP layers (b and d), extracted after the fitting of the ellipsometric measurements. For the sake of clarity, each curve has been displaced 2 and 3 units from the lower one in the positive ϵ_1 and ϵ_2 direction, respectively.

E_0 and E_1 transition energies for both the real and imaginary part of the dielectric function. GaInP layers feature the lowest energy transitions, whereas AlInP are the materials with the higher energies for E_0 and E_1 . AlGaInP layer features intermediate values as expected. Finally, the energy of the E_2 transition is not affected by the compositional change.

Among layers with the same composition, i.e. GaInP and AlInP, there are small differences among dielectric functions. Concerning GaInP layers, the undoped sample shows a less intense E_1 transition than the rest of GaInP layers, and the reason might be its higher lattice mismatch (see Table 2). Other remarkable behaviour is the widening of the valley between E_1 and E_2 caused by doping on the GaInP layers. There is a particular behaviour in layer AlInP(p), with a narrower and more intense transition in E_2 . Such behaviour cannot be attributed *a priori* to any of the physical properties analysed in this work, namely, doping, disorder or lattice parameter. However, the fact that this structure exhibits the thickest oxide layer could be related to this particular issue. Other possibility would be that the GaAs capping layer has not been completely removed from this structure.

There are very few sources of n and k for ternary Indium phosphide alloys, and none of them analyses doped samples. Moreover, some of them publish pseudo-coefficients ($\langle n \rangle$ & $\langle k \rangle$, or $\langle \epsilon_1 \rangle$ & $\langle \epsilon_2 \rangle$) instead of n and k , and have failed in making a separate treatment of the native oxide. This makes the comparison of the results obtained in the present work with those found in the literature a difficult task. Nevertheless, Fig. 7 shows the refractive index and extinction coefficient of GaInP (u) and AlInP (n) samples, along with the results of selected previous works. For the case of AlInP, there is a reasonable match with the recent works by Kim et al. [18], and Yuan et al. [17], being the latter the only work to make a detailed analysis of a ternary alloy oxide; on the other hand, Kim et al. present pseudo dielectric function results which have been used to deduce $\langle n \rangle$ and $\langle k \rangle$, and this is the reason for the oscillations below 2.6 eV. It can be seen that there is a significant difference with the results obtained by Kato et al. [43] (Fig. 7, top left), given that no oxide was considered in this work. Both AlInP and GaInP results match well in the bandgap region with those references that make a bandgap analysis (except for the case of Kato et al.). However, it is important to remember that none of the references includes the GaInP oxide in their analyses.

Unlike other works on the dielectric functions of these phosphide

Fig. 7. Complex refractive index obtained after the ellipsometry analysis for the GaInP (u) and AlInP (n) samples (red lines) and comparison with previous works in the literature. On the left, AlInP complex refractive indexes extracted from references [17] (green line), [18] (blue line) and [43] (black line). On the right, GaInP complex refractive indexes extracted from references [17] (green line), [11] (blue line) and [43] (black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

layers where the influence of doping is not analysed, in the present case it might be responsible for the presence of excitonic effects due to a higher availability of free carriers. This fact translates into the necessity to incorporate the excitonic parameters into the model for the doped layers (see Table 3) and can be easily visualized for the case of E_0 in the imaginary part of the dielectric function (Fig. 6c and d), for which its value is null for energies lower than that of the E_0 transition. However, a less abrupt E_0 transition due to free carrier absorption is noticeable after doping (see insets in Fig. 6c and d).

As for the dielectric functions, complex refractive indexes show very

Table 3

First direct transition energies obtained after the ellipsometric data fit for GaInP, AlInP and AlGaInP layers.

Layer	Doping	E_0 (eV)
GaInP (u)		1.81
GaInP (n)	4.7×10^{17}	1.85
GaInP (p)	3.1×10^{16}	1.82
GaInP (p ⁺)	1.6×10^{17}	1.86
AlInP (n)	3.8×10^{17}	2.56
AlInP (n ⁺)	5.6×10^{18}	2.53
AlInP (p)	1.4×10^{17}	2.59
AlInP (p ⁺)	9.4×10^{17}	2.54
AlGaInP (p)	1×10^{18}	2.04

similar features for all the layers, as it is expected from the common lattice symmetry. However, some differences can be observed for layers of the same composition. Refractive indexes for GaInP layers are shown in Fig. 8a. It is rather remarkable the fact that for the GaInP(n) and GaInP(p) layers, corresponding curves meet along the whole measured range, except for the band gap zone. Probably this is related to the equal lattice mismatch in these two layers (Table 1) and not to the free carrier density since there is a difference of an order of magnitude between them. In fact, that of the GaInP(n) layer is much closer to that of the GaInP(p⁺) layer and their refractive index curves are clearly shifted. Differences among the refractive indexes of AlInP layers are less noticeable. Concerning extinction coefficients, differences are mostly perceptible in the bandgap region, as it is stated in the insets in Fig. 8c and d.

As can be seen, for layers with the same composition (GaInP, AlInP), the transition energies, and consequently the bandgaps, are close from one another, stoichiometry being the most important factor to

determine the energy of the E_0 transition of $\text{Al}_x\text{Ga}_{1-x}\text{InP}$ layers [8,44]. The values for this first allowed direct transition have been extracted from extinction coefficient curves. The small differences among samples with the same composition do not follow a homogeneous tendency with doping level (see Table 3).

Doped GaInP layer band gap values are higher than that of the undoped layer. This fact may be related to the small change in stoichiometry between the undoped layer and the doped ones (see Table 2), but more probably to a lowering of the ordering parameter with doping in the GaInP layer, as detected in Raman spectra. This effect has been previously reported by other authors [36,45,46]. Conversely, for the AlInP layers, the evolution of the direct band gap with doping does not show the same tendency. Irrespective of doping type, this band gap energy decreases as dopant concentration increases. The root cause of this fact is still under investigation, as we would expect the same processes that disorder the GaInP as dopant concentration increases to work in a similar way in AlInP. It might well be that the use of different substrates or slight variations in the growth conditions are behind this change in order. However, our Raman spectroscopy data show unequivocally that order increases as doping does in our samples. Coincidental or causal, it is this change in the ordering parameter, and the subsequent decrease in bandgap, what is ruling again the optical behaviour in these AlInP doped layers (as for our GaInP doped layers) and that would agree with theoretical predictions [24,25], as well as with some other works dealing with GaInP layers [14,21].

Validation of the refractive indexes obtained after the fitting of ellipsometric data has been achieved using reflectance measurements. For all the layers, the match between the experimental reflectance data and the corresponding curves simulated using the complex refractive indexes deduced from ellipsometry data analysis is very good (Fig. 9). This comparison underpins the validity of the model proposed to

Fig. 8. Refractive index and extinction coefficient of GaInP layers (a and c), and AlInP layers (b and d), extracted after the model fitting of the ellipsometric measurements. Insets show extinction coefficients in the bandgap region. Inset in d also contains the extinction coefficient corresponding to the AlGaInP layer (black line). For the sake of clarity, extinction coefficient curves have been shifted vertically in the insets.

Fig. 9. Comparison between experimental reflectance data (black symbols) and functions deduced from calculated optical parameters (red lines) for three layers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

describe the optical behaviour of these layers and reinforces its universality, since it is able to reproduce the optical response of each layer irrespective of its composition, structural characteristics and doping type and concentration.

5. Conclusions

GaInP, AlInP and AlGaInP layers have been grown by MOVPE in order to ascertain the influence of dopant type and concentration on their dielectric functions and optical properties. The layers have been grown at the same conditions that are typically employed for III-V multijunction solar cells. GaInP layers show a high order parameter, irrespective of doping. PL measurements allowed us to deduce a value on the order of 0.56 and Raman spectroscopy confirms this high ordering degree, though a bit higher for undoped GaInP layer. For AlInP layers a clear increase of η with doping level has been detected through Raman measurements. This kind of dependence is independent of doping type. The layer dielectric functions and complex refractive indexes have been extracted from the analysis of ellipsometric data. The correlation between doping and order parameter seems to be the responsible for most of the differences in the bandgap energies found for layers with the same stoichiometry (the higher the order parameter, the lower the bandgap energy). Except for these differences in the bandgap region, doping has been found to have no significant influence on the dielectric functions and optical properties of the layers, which are basically dependent on their stoichiometry. However, for GaInP layers a dependence on lattice mismatch of the refractive index values in the above bandgap region is suggested. As a final validation proof for the results, the refractive indexes and extinction coefficients deduced from the ellipsometric data have been used to fit reflectance measurements for the same layers and an excellent agreement has been achieved.

The determination of the optical parameters of III-V phosphide-based materials as a function of doping levels and ordering that we have carried out in this paper will contribute to improve the accuracy of the models used to simulate and optimise upcoming multijunction solar cell architectures.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.solmat.2017.09.028>.

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