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Invited paper

Spectroscopic Ellipsometry Analysis of Rapid Thermal Annealing Effect on MBE Grown $GaAs_{1-x}N_x$

Nebiha Ben Sedrine, Jaouher Rihani, Jean-Christophe Harmand, and Radhouane Chtourou

Abstract—We report on the effect of rapid thermal annealing (RTA) on $GaAs_{1-x}N_x$ layers, grown by molecular beam epitaxy (MBE), using room temperature spectroscopic ellipsometry (SE). A comparative study was carried out on a set of $GaAs_{1-x}N_x$ as-grown and the RTA samples with small nitrogen content ($x = 0.1\%$, 0.5% and 1.5%). Thanks to the standard critical point model parameterization of the $GaAs_{1-x}N_x$ extracted dielectric functions, we have determined the RTA effect, and its nitrogen dependence. We have found that RTA affects more samples with high nitrogen content. In addition, RTA is found to decrease the E_1 energy nitrogen blueshift and increase the broadening parameters of E_1, $E_1+\Delta_1$, E_0' and E_2 critical points.

Keywords— $GaAs_{1-x}N_x$, optical constants, optoelectronic device, rapid thermal annealing, semiconductors, spectroscopic ellipsometry.

1. Introduction

Recently, the nitrogen containing GaAs alloys are intensively studied since these semiconductors have a promising potential for optoelectronic device applications due to their unique electronic and optical properties especially in the telecommunication wavelength range [1]–[3]. However, an increase in nitrogen incorporation needed to achieve the desired bandgap energy, has been found to cause a degradation in the material quality [4]–[6]. Post-growth treatments, such as rapid thermal annealing (RTA), on $GaAs_{1-x}N_x$ materials were largely studied using either photoluminescence (PL) [7], [8] or high-resolution X-ray diffraction (HRXRD) [9] in order to improve the material quality.

However, an undesirable effect is often induced: a shift toward the blue of the emission peak is observable as RTA proceeds. In previous works, spectroscopic ellipsometry (SE) was used for the GaAsN material to investigate the nitrogen effect on GaAs host matrix [10], [11]. Very recently, Pulzara-Mora *et al.* [12] studied the growth temperature (from 420 to 600°C) effect of GaAsN on GaAs substrate by photoreflectance (PR) spectroscopy and phase modulated ellipsometry (PME), and established the corresponding growth mode. In a previous work [12], we have reported results relative to RTA effect on the $GaAs_{1-x}N_x$: the accurate optical constants, and the decrease of the E_1 transition energy nitrogen dependence.

In this work, we study the rapid thermal annealing effect using room temperature spectroscopic ellipsometry technique on $GaAs_{1-x}N_x$ ($x = 0.1\%$, 0.5% and 1.5%) layers grown by molecular beam epitaxy (MBE) on GaAs substrate. The study will lead us to accurately determine the RTA effect on the samples, using the fitting analytic line shapes to the dielectric function imaginary part second derivatives, by the way of the critical points parameters (broadenings Γ_1, $\Gamma_{\Delta 1}$, Γ_0', Γ_2 and amplitudes A_1, $A_{\Delta 1}$, A_0', A_2) nitrogen dependence.

2. Experiment

The study is based on $GaAs_{1-x}N_x$ ($x = 0.1\%$, 0.5% and 1.5%) samples grown on (001) GaAs substrate by MBE equipped with a radio-frequency (RF) plasma as nitrogen source. The samples consist of a GaAs buffer layer and a 0.1–0.2 μm $GaAs_{1-x}N_x$ layers grown at 450°C. Rapid thermal annealing was performed for 90 s under N_2 flow ambient at 680°C. The crystal quality and the nitrogen content of the samples were determined from HRXRD measurements.

Spectroscopic ellipsometry measurements were performed at room temperature using an automatic ellipsometer SOPRA GES5. The system uses a 75 W xenon lamp, a rotating polarizer, an autotracking analyzer, a double monochromator, and a photomultiplier tube as detector. Data were collected in the 1.6–5.5 eV energy range with a step of 5 meV, at incidence angle of 75°. Spectroscopic ellipsometry determines the complex reflectance ratio ρ defined in terms of the standard ellipsometric parameters ψ and Δ as

$$\rho = \frac{r_p}{r_s} = (\tan\psi)e^{i\Delta}, \qquad (1)$$

where r_p and r_s are the reflection coefficients for light polarized parallel (p) and perpendicular (s) to the sample's plane of incidence, respectively.

3. Results and Discussion

The imaginary part ε_2 of the pseudo-dielectric function spectra covering the photon energies range of 1.6–5.5 eV for rapid thermal annealed $GaAs_{1-x}N_x$ ($x = 0.1\%$, 0.5% and 1.5%) samples compared to the reference sample GaAs ($x = 0.0\%$) and shifted for clarity, are plotted in Fig. 1. The pseudo-dielectric function is obtained by assuming the samples as bulk, and can be obtained by using an analytical

relation to the experimentally measured data. This can be used as a rough estimation of the nitrogen incorporation effect in $GaAs_{1-x}N_x$. However, the nitrogen induced effect on our samples has already been studied [11] which was in good agreement with previous reports [10]. In Fig. 1, four peaks are clearly observed at 2.9, 3.1, 4.5 and 4.8 eV, which correspond, respectively, to the E_1, $E_1+\Delta_1$, E_2 and E'_0 transitions.

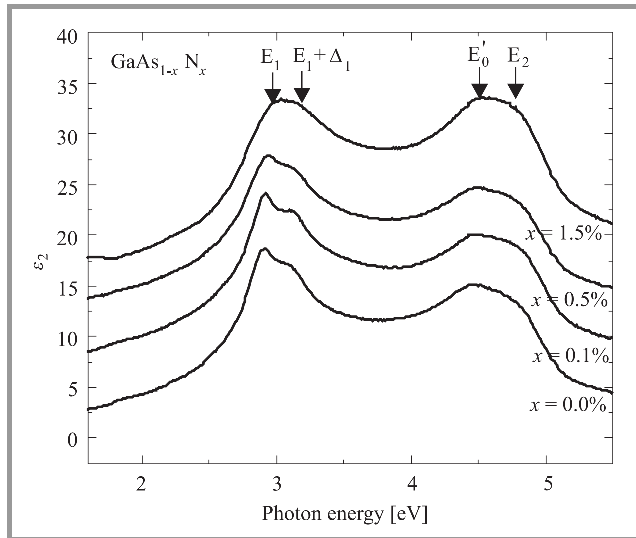


Fig. 1. Pseudo-dielectric function imaginary parts of the RTA $GaAs_{1-x}N_x$ layers compared to GaAs. The spectra of the samples with $x = 0.1\%$, 0.5% and 1.5% are shifted for clarity by 5, each.

We have reported in a previous work [13] on the $GaAs_{1-x}N_x$ optical constants, that we accurately extracted using the Newton-Raphson method applied to the four-phase model (ambient –oxide – $GaAs_{1-x}N_x$ layer – GaAs substrate), together with a conventional SE analysis. The oxide in the model used there was assumed to be the GaAs native oxide. The procedure was performed for both as-grown and RTA samples with (x = 0.1%, 0.5% and 1.5%). We presented the refractive indices (n) and absorption coefficients (k) of the as-grown and RTA $GaAs_{1-x}N_x$ (x = 0.1%, 0.5% and 1.5%) layers resulting from the best-fit model analysis. We have found that, in the visible energy range, it appears that a small decrease of the refractive index (n) of about 0.4 and 0.15, respectively, for samples with x = 0.1% and 0.5% is noted by annealing.

However, an opposite largest effect (increase of the refractive index of about 0.7) is observed for the sample with the highest nitrogen content ($x = 1.5\%$). For the absorption coefficients (k), the same behavior is observed in the high energy side; an improvement of the absorption coefficient by the annealing treatment is clear for the 1.5% nitrogen sample. These behaviors versus annealing can allow us to conclude that RTA seems to affect more the highest nitrogen containing $GaAs_{1-x}N_x$ material, leading to an improvement of the complex refractive index reaching the values of diluted $GaAs_{1-x}N_x$ alloys (under 1% of nitrogen).

We have analyzed the RTA effect on the dielectric function $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$ which is closely related to the material band-structure. An accurate determination of the interband transition energies (or critical points – CP's) was

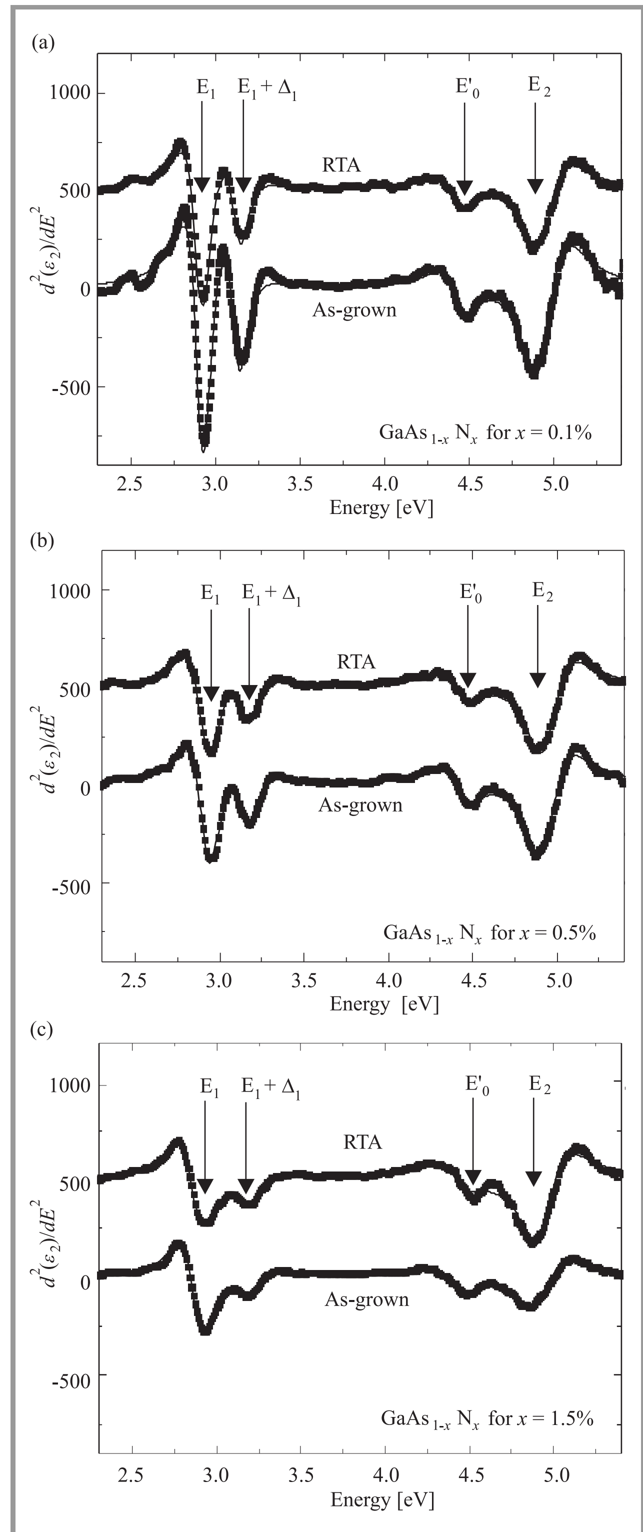


Fig. 2. Second derivative of the dielectric function imaginary parts for as-grown and after RTA $GaAs_{1-x}N_x$ samples: (a) $x = 0.1\%$; (b) 0.5%; (c) 1.5%. Scatters (solid lines) refer to experimental (best-fit calculated) spectra.

performed by fitting analytic line shapes to the numerically calculated dielectric function imaginary part second derivatives. For small nitrogen content, like in GaAs at room temperature [14], the derivative spectra in the vicinity of the critical points (E_1, $E_1+\Delta_1$, E_2 and E_0') can be assumed as two-dimensional line-shapes:

$$\frac{d^2\varepsilon}{dE^2} = \sum_{j=1}^{N}\left[A_j e^{i\phi_j}(E-E_{cj}+i\Gamma_j)^{-2}\right], \qquad (2)$$

where: A_j is the amplitude of the critical point, E_{cj} its energy, Γ_j is a broadening parameter, and ϕ_j a phase angle. In Fig. 2 [13], the best-fit calculated $d^2\varepsilon_2(E)/dE^2$ spectra (solid lines) from Eq. (2) are compared to the numerically second-derivatives extracted results (scatters) using the Levenberg-Marquardt regression algorithm. In order to improve the quality of the fit, peaks (j) were fitted simultaneously by taking A_j, E_{cj}, Γ_j and ϕ_j as free parameters.

We have found [13] that the best-fit critical point energies show a very small dependence of $E_1+\Delta_1$, E_2 and E_0' upon annealing, however, a notable effect on the E_1 interband transition is observed: RTA decreases the E_1 nitrogen dependence. From the fit curvatures that match well with the extracted experimental results, we can also deduce the RTA effect on the critical points amplitudes A_j and broadening parameters Γ_j. Tables 1 and 2 show the best-fit broadening parameters (Γ_1, $\Gamma_{\Delta1}$, Γ_0' and Γ_2) for the E_1, $E_1+\Delta_1$, E_0' and E_2 critical points, for as-grown and RTA $GaAs_{1-x}N_x$ ($x = 0.1\%$, 0.5% and 1.5%) samples. A clear increase of the broadening parameters upon annealing is noted for each nitrogen composition, reaching about 10 meV for the $\Gamma_{\Delta1}$ corresponding to the 1.5% sample. Lautenschlager *et al.* in [14] studied the effect of temperature on the broadening parameters of GaAs; they have noted a linear increase for temperatures above 300K.

Table 1
The broadening parameters for the E_1, $E_1+\Delta_1$, E_0' and E_2 critical points, for as-grown samples $GaAs_{1-x}N_x$: $x = 0.1$, 0.5 and 1.5% (errors obtained from the fitting procedure are given in parentheses)

Energy [eV]	$x = 0.1\%$	$x = 0.5\%$	$x = 1.5\%$
Γ_1	0.088 (0.002)	0.109 (0.002)	0.120 (0.002)
$\Gamma_{\Delta1}$	0.087 (0.003)	0.097 (0.005)	0.136 (0.007)
Γ_0'	0.122 (0.008)	0.134 (0.007)	0.182 (0.008)
Γ_2	0.164 (0.003)	0.165 (0.003)	0.187 (0.004)

Table 2
The broadening parameters for the E_1, $E_1+\Delta_1$, E_0' and E_2 critical points, for RTA samples $GaAs_{1-x}N_x$: $x = 0.1$, 0.5 and 1.5% (errors obtained from the fitting procedure are given in parentheses)

Energy [eV]	$x = 0.1\%$	$x = 0.5\%$	$x = 1.5\%$
Γ_1	0.095 (0.001))	0.113 (0.002)	0.129 (0.003)
$\Gamma_{\Delta1}$	0.089 (0.003)	0.102 (0.005)	0.149 (0.009)
Γ_0'	0.129 (0.009)	0.150 (0.009)	0.192 (0.009)
Γ_2	0.165 (0.003)	0.170 (0.003)	0.190 (0.003)

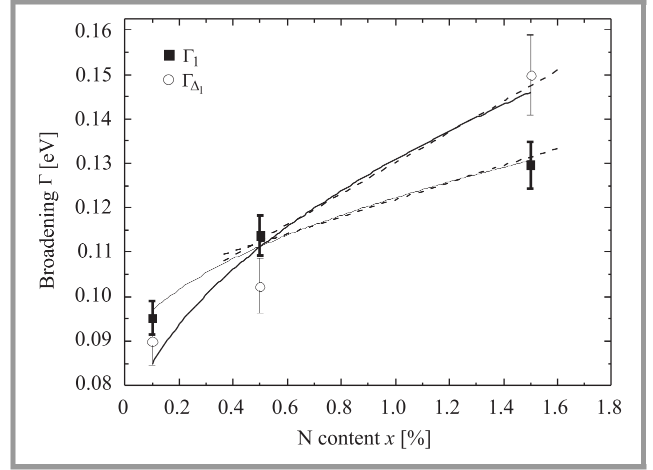


Fig. 3. The broadening parameters Γ_1 and $\Gamma_{\Delta1}$ for the E_1, $E_1+\Delta_1$ critical points, respectively, versus N molar fraction x (x = 0.1, 0.5 and 1.5%) for RTA samples. The symbols represent the results of fitting Eq. (2) to the second derivative of the experimental spectra. The full line represents the square-root-like dependence of Γ. The additional dashed line represents the nearly linear increase of Γ above 0.4% N molar fraction x.

Figure 3 represents the increase of the broadening parameters Γ_1, $\Gamma_{\Delta1}$ for the RTA samples versus nitrogen content x. Both Γ_1 and $\Gamma_{\Delta1}$ show a root-square-like dependence on x, following $y = a + b\sqrt{x}$ and the corresponding constant prefactors a and b, obtained using the Levenberg-Marquardt regression algorithm, are given in Table 3. We found that our results are in good agreements with the work of Tish *et al.* [15] for $GaAs_{1-x}N_x$ samples grown by metal organic vapor phase epitaxy (MOVPE). For N content below 0.4%, we note a strong increase of the broadening parameters Γ_1, $\Gamma_{\Delta1}$ of about 10 meV per 0.1% nitrogen. However, for higher nitrogen content, the broadening linearly increases ($y = cx + d$), and the corresponding constant prefactors c and d, obtained using the Levenberg-Marquardt regression algorithm, are given in Table 3. For our MBE-grown $GaAs_{1-x}N_x$ samples, the same trend of

Table 3
Values for the constant prefactors (a and b) for the square-root-like dependence of Γ_1 and $\Gamma_{\Delta1}$ ($y = a + b\sqrt{x}$) and (c and d) for the linear fit ($y = cx + d$) corresponding to the E_1, $E_1+\Delta_1$ critical points (errors obtained from the fitting procedure are given in parentheses)

Parameter	a [eV]	b [eV]	c [eV]	d [eV]
Γ_1	0.085 (0.004)	0.373 (0.046)	1.9 (0.2)	0.103 (0.002)
$\Gamma_{\Delta1}$	0.064 (0.008)	0.672 (0.076)	3.5 (0.2)	0.095 (0.002)

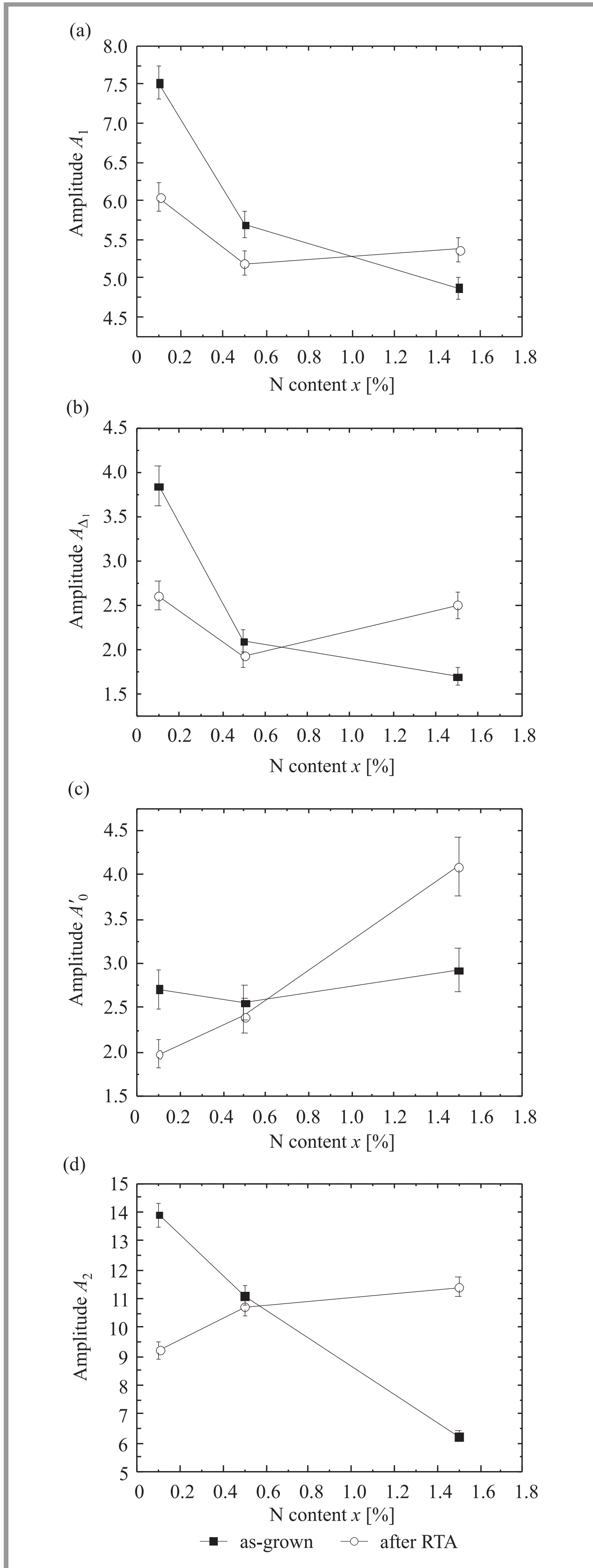


Fig. 4. $GaAs_{1-x}N_x$ critical points amplitudes (a) A_1, (b) $A_{\Delta 1}$, (c) A'_0, and (d) A_2 versus nitrogen content x ($x = 0.1\%$, 0.5% and 1.5%) results of fitting Eq. (2) to the second derivative of the experimental spectra for as-grown and RTA samples, lines are guides for eyes.

the Γ_1, $\Gamma_{\Delta 1}$ dependence versus nitrogen content x is observed. We note that the linearly increase of the $\Gamma_{\Delta 1}$ ($c = 3.5$ eV) is more than that of Γ_1 ($c = 1.9$ eV). This effect was interpreted as the consequence of an assembly of several closely spaced critical points of the $E_1 + \Delta_1$ [15].

In Fig. 4 the critical points amplitudes ($A_1, A_{\Delta 1}, A'_0$, and A_2) versus nitrogen content x, resulting from fitting Eq. (2) to the second derivative of the experimental spectra for as-grown and RTA samples, are shown. The most notable effect in these representations is the increase of the amplitude of all the critical points (A_1, $A_{\Delta 1}$, A'_0, and A_2) after annealing for the highest nitrogen containing sample ($x = 1.5\%$). We remind that the used dielectric function $\varepsilon(E)$ in the standard critical point model is given by:

$$\varepsilon(E) = \sum_{j=1}^{N} \left[C_j - A_j e^{i\phi_j} \ln\left(E - E_{cj} + i\Gamma_j\right) \right], \qquad (3)$$

where the amplitude A_j is proportional to $\varepsilon(E)$.

These behaviors versus annealing can allow us to conclude, like for the complex refractive index [13], that RTA seems to affect more the highest nitrogen containing $GaAs_{1-x}N_x$ material. Consequently, the material degradation due to high nitrogen content can be improved by RTA.

4. Conclusion

We have presented an analysis of the RTA effect on $GaAs_{1-x}N_x$ layers using room temperature SE. The study was performed on a set of as-grown and RTA (680°C for 90 s) $GaAs_{1-x}N_x$ ($x = 0.1\%$, 0.5% and 1.5%) samples. We have found that RTA post-growth treatment affects more the high containing nitrogen samples, leading to optical parameters close to those of GaAs in terms of the standard critical point model applied to the complex dielectric function: a decrease of the E_1 transition energy nitrogen dependence, an increase of the critical points amplitude. This behavior is interpreted as a better alloy uniformity and nitrogen reorganization in the $GaAs_{1-x}N_x$ layers.

References

[1] M. Weyers, M. Sato, and H. Ando, “Red shift of photoluminescence and absorption in dilute GaAsN alloy layers”, *Jpn. J. Appl. Phys.*, part 2, vol. 31, pp. L853–L855, 1992.

[2] R. Chtourou *et al.*, “Effect of nitrogen and temperature on the electronic band structure of $GaAs_{1-x}N_x$ alloys”, *Appl. Phys. Lett.*, vol. 80, pp. 2075–2077, 2002.

[3] M. Kondow *et al.*, “GaInNAs: a novel material for long-wavelength-range laser diodes with excellent high-temperature performance”, *Jpn. J. Appl. Phys.*, part I, vol. 35, pp. 1273–1275, 1996.

[4] H. P. Xin and C. W. Tu, “GaInNAs/GaAs multiple quantum wells grown by gas-source molecular beam epitaxy”, *Appl. Phys. Lett.*, vol. 72, pp. 2442–2444, 1998.

[5] S. Francoeur *et al.*, “Luminescence of as-grown and thermally annealed GaAsN/GaAs”, *Appl. Phys. Lett.*, vol. 72, pp. 1857–1859, 1998.

[6] I. A. Buyanova *et al.*, "Mechanism for low-temperature photoluminescence in GaNAs/GaAs structures grown by molecular beam epitaxy", *Appl. Phys. Lett.*, vol. 75, pp. 501–503, 1999.

[7] L. H. Li *et al.*, "Effect of rapid thermal annealing on the optical properties of $GaAs_{1-x}N_x$/GaAs single quantum well structure grown by molecular beam epitaxy", *J. Appl. Phys.*, vol. 87, pp. 245–247, 2000.

[8] F. Bousbih *et al.*, "Effect of rapid thermal annealing observed by photoluminescence measurement in $GaAs_{1-x}N_x$ layers", *Mat. Sci. Eng. B*, vol. 123, pp. 211–214, 2005.

[9] E. Tournié, M.-A. Pinault, and A. Guzmán, "Mechanisms affecting the photoluminescence spectra of GaInNAs after post-growth annealing", *Appl. Phys. Lett.*, vol. 80, pp. 4148–4150, 2002.

[10] G. Leibiger *et al.*, "Nitrogen dependence of the GaAsN interband critical points E_1 and $E_1 + \Delta_1$ determined by spectroscopic ellipsometry", *Appl. Phys. Lett.*, vol. 77, pp. 1650–1652, 2000.

[11] N. Ben Sedrine *et al.*, "Spectrscopic ellipsometry analysis of $GaAs_{1-x}N_x$ layers grown by molecular beam epitaxy", *Mat. Sci. Eng. C*, vol. 28, pp. 640–644, 2008.

[12] A. Pulzara-Mora *et al.*, "Study of optical properties of GaAsN layers prepared by molecular beam epitaxy", *J. Cryst. Growth*, vol. 301–302, pp. 565–569, 2007.

[13] N. Ben Sedrine *et al.*, "Optical constants of As-grown and RTA $GaAs_{1-x}N_x$ layers analysed by spectroscopic ellipsometry", in *Proc. ICTON-MW'07 Conf.*, Rome, Italy, 2007.

[14] P. Lautenschlager *et al.*, "Interband critical points of GaAs and their temperature dependence", *Phys. Rev. B*, vol. 35, pp. 9174–9189, 1987.

[15] U. Tish, E. Finkman, and J. Salzman, "Fine structure of the $E_1 + \Delta_1$ critical point in GaAsN", *Phys. Rev. B*, vol. 65, pp. 153204–153207, 2002.

Nebiha Ben Sedrine was born in Tunis, Tunisia, in 1978. She received the M.Sc. degree in quantum physics from the Tunis University of Sciences in 2006. She is actually a Ph.D. student-researcher in the Laboratory of Photovoltaïc, Semiconductors and Nanostructures (LPVSN) at the Research and Technology Energy Center (CRTEn), Tunisia. She is an author and co-author of 14 scientific papers in the field of material science, optical and structural studies (ellipsometry, photoluminescence, reflectivity, microscopy), and more than 16 national and international communications. She is a member of the Société Tunisienne de Physique and the Optical Society of America.

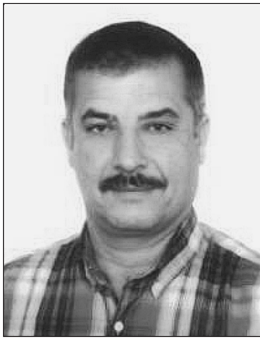
e-mail: bsnebiha@yahoo.fr
e-mail: nebiha.bensedrine@crten.rnrt.tn
Laboratory of Photovoltaïc, Semiconductors
and Nanostructures (LPVSN)
Research and Technology Energy Center (CRTEn)
BP. 95, Hammam-Lif 2050, Tunisia

Jaouher Rihani was born in Beja, Tunisia, in 1978. He received the M.Sc. degree in quantum physics from the Tunis University of Sciences in 2004. He is actually a Ph.D. student-researcher in the Laboratory of Photovoltaïc, Semiconductors and Nanostructures (LPVSN) at the Research and Technology Energy Center (CRTEn), Tunisia. He is an author or co-author of 7 scientific papers in the field of material science, optical and structural studies (ellipsometry, photoluminescence, reflectivity, microscopy). He works as an Assistant at the Gafsa University of Sciences, Tunisia, since 2007.

e-mail: rihani_jaouher@yahoo.fr
e-mail: jawher.rihani@crten.rnrt.tn
Laboratory of Photovoltaïc, Semiconductors
and Nanostructures (LPVSN)
Research and Technology Energy Center (CRTEn)
BP. 95, Hammam-Lif 2050, Tunisia

Jean-Christophe Harmand obtained his Ph.D. in physics at the University of Paris 7, France, in 1988 for his work on GaAlAs/GaAs HBTs. From 1988 to 1990, he was at the Optoelectronic Research Laboratory of Matsushita (Osaka, Japan), where he was involved in studies on metamorphic AlGaInAs/GaAs HEMTs. He obtained state-of-the-art transport properties in these lattice-mismatched heterostructures. His expertise in molecular beam epitaxy being recognized, he was recruited at CNET/France Telecom to study the growth of III-V materials for micro- and optoelectronics, from 1990 to 1999. In 2000, he joined a new laboratory created by the CNRS: the Laboratory for Photonics and Nanostructures (LPN), where he conducts epitaxial growth research. Following pioneering works, he also initiated in France the catalyzed growth of III-V nanowires. At the national level, he is actually leading a GdR (group of research) on Semiconductor Nanowires and Nanotubes bringing together researchers from about 30 laboratories. He is an author and co-author of about 170 scientific papers and 60 communications in the fields of III-Vs materials and devices (index H = 23). He holds 8 patents.

e-mail: jean-christophe.harmand@lpn.cnrs.fr
Laboratory for Photonics and Nanostructures (LPN)
CNRS Route de Nozay
91 460, Marcoussis, France



Radhouane Chtourou received his Master's degree in physics at the Faculty of Sciences of Tunis in 1983, his M.Sc. degree in solid-state physics in 1985. During the period 1986–1988, he was a physics teacher at the Nefta High School in the south of Tunisia. During 1988–1998, he joined the Raman Spectroscopic Laboratory of the Faculty of Sciences of Tunis. He was physic sciences Assistant between 1988–2003 at the Medjez-Elbab Engineering Institute. He obtained his Ph.D. in physics at the University of Tunis Elmanar in 1997. He obtained his University Habilitation degree in 2003 for his work of optical properties of semiconductors photonic crystals, electronic and optical properties of GaAsN alloys. During the period 1998–2003, he set up the Laboratory of the Semiconductor Physics at the Preparatory Institute of Scientific and Technical Studies of La Marsa in Tunis. Since 2003, he joined the Laboratory of Photovoltaïc, Semiconductors and Nanostructures (LPVSN). Prof. Chtourou is the Head of the Semiconductor Nanostructures Group. His research is currently focused on studies of electronic and optical properties of photonic crystals based on silicon and porous silicon, on gas bidimensional electrons in the III-V hetero-structures, and III-V semiconductors alloys for optoelectronic applications. He is the author of more than 40 scientific papers and 100 international communications. He is an active member of the Société Tunisienne de Physique.

e-mail: radhouane.chtourou@inrst.rnrt.tn
Laboratory of Photovoltaïc, Semiconductors
and Nanostructures (LPVSN)
Research and Technology Energy Center (CRTEn)
BP. 95, Hammam-Lif 2050, Tunisia