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► **To cite this version:**

Solène Béchu, Céline Eypert, Anais Loubat, Jackie Vigneron, Sofia Gaiaschi, et al.. Evaluation of the chemical and optical perturbations induced by Ar plasma on InP surface. *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics*, 2019, 37 (6), pp.062902. <10.1116/1.5121897>. <hal-03116617>

HAL Id: hal-03116617

<https://hal.science/hal-03116617v1>

Submitted on 20 Jan 2021

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Evaluation of the chemical and optical perturbations induced by Ar plasma on InP surface

Solène Béchu^{1,2,a)}, Céline Eybert³, Anais Loubat², Jackie Vigneron², Sofia Gaiaschi³, Patrick Chapon³, Muriel Bouttemy², Arnaud Etcheberry²

¹ *Institut Photovoltaïque d'Ile-de-France (IPVF), 18 Boulevard Thomas Gobert, 91120 Palaiseau, France.*

² *Institut Lavoisier de Versailles (ILV), Université de Versailles Saint-Quentin-en-Yvelines, Université Paris Saclay, CNRS, 45 avenue des Etats-Unis, 78035 Versailles, France,*

³ *HORIBA Scientific, 14 Boulevard Thomas Gobert, Passage Jobin Yvon, CS 45002, 91120 Palaiseau, France*

^{a)} Electronic mail: solene.bechu@uvsq.fr

Abstract

Interfaces are of primary importance in heterostructures. We propose here an innovative methodologic development to access the chemical information in depth and, more especially, at buried interfaces. This specific approach is based on the combination of Glow Discharge Optical Emission Spectroscopy (GD-OES) plasma profiling, enabling to quickly and precisely reach buried interfaces, with X-Ray Photoelectron Spectroscopy surface analyses, bringing an accurate determination of the composition and the chemical environments. The representativeness of the crater chemistry is therefore a critical issue. On InP substrate, the fine examination inside the GD-OES crater reveals surface modifications, both chemical, morphological and optical, and as a consequence the need to regenerate the initial chemical information. We present here a study dedicated to the evaluation of those modifications thanks to a multi-technique approach, with an important contribution of Spectroscopic Ellipsometry measurements. A crater regeneration strategy, by means of a nano-chemical etching, is proposed and also assessed by the same analytical pathway, proving the recovery of the initial InP properties.

30 I. INTRODUCTION

31

32 Access to the chemistry of buried interfaces is a key parameter in the comprehension
33 of heterostructures properties and can be reached through a lot of different experimental
34 techniques¹⁻³. Recently we developed a combination of Glow Discharge-Optical Emission
35 Spectrometry (GD-OES) depth profiling and X-Ray Photoelectron Spectroscopy (XPS)
36 surface characterization⁴ to precisely determine the chemistry at interfaces buried at several
37 micrometers, in a reasonable acquisition time. GD-OES profiling is used as a very efficient
38 and quantitative method (after intensities calibration on standards) to determine atomic
39 concentration profiles of thin films stacks. When arriving close to a critical interface, GD-
40 OES can be stopped and relayed inside the etched crater by a sequential XPS analysis,
41 assisted or not with Ar or Ar_n⁺ ion profiling in order to be as close as possible to the interface
42 thanks to XPS profiling. This analytical strategy strongly refines the chemical profile
43 accuracy on both sides of interfaces of interest as it additionally brings the direct atomic
44 composition and the chemical environment information in the same experimental sequence⁴.
45 This combination is therefore particularly well adapted to perform an efficient and complete
46 characterization of heterostructures. Nevertheless, a main question relative to this GD-
47 OES/XPS coupled approach concerns the integrity of the information inside the GD-OES
48 crater, which condition the representativeness of the XPS interpretation of the chemistry at
49 buried interfaces. Thus, a systematic control of the crater surface physico-chemical properties
50 is necessary to ensure the reliability of the relay between GD-OES and XPS. Surface
51 modifications observed when stopping the plasma etching differ with the nature of the
52 material. Therefore they have to be considered case by case to determine, if necessary, the
53 best physical or chemical procedure to recover the initial information. This knowledge is
54 essential to further implement consistent GD-OES/XPS coupling and perform an advanced
55 chemical characterization of more complex blocks such as heterostructures.

56 To evaluate the modifications inside the GD-OES crater, a multi-technique approach is
57 employed to determine the chemical (XPS, Energy-Dispersive X-Ray Spectroscopy –EDS-),
58 morphological (Scanning Electron Microscopy –SEM-), microstructural (Electron Back-
59 Scattering Diffraction –EBSD-) and optical Spectroscopic Ellipsometry (SE) characteristics of
60 the surface and sub-surface. Among this set of techniques, SE is less usually employed for
61 such a study and we will emphasize its added value. SE represents an efficient nondestructive
62 characterization method, particularly well adapted to material surfaces and thin films
63 analyses⁵. SE is a perfect optical tool to detect even slight surface evolutions, due to different
64 kinds of perturbations. Indeed, SE can be used to qualitatively detect evidences of plasma
65 induced modifications and the subsequent effect of the chemical engineering necessary to
66 remove the perturbed surface layer, therefore enabling the step by step^{6,7} monitoring of the
67 surface evolutions. Moreover, through an adapted modeling step, it provides quantitative
68 optical data linked to such modifications. The optical SE responses also allows an
69 autonomous diagnosis directly related to chemical features⁵. However the determination of
70 perfect surface optical parameters needs some physical constraints, as for example minimal
71 surface roughness⁸. Semi-quantitative or quantitative SE interpretation will then depend on
72 the morphological consideration onto the surface.

73 The present work focuses on the evaluation of the GD-OES crater perturbation on one
74 specific III-V material: InP. Evolutions of optical parameters are determined with SE, directly
75 implemented in the crater, just after GD-OES profiling stop (corresponding to the XPS relay
76 step in our GD-OES/XPS combined approach) as well as after wet chemical treatments
77 dedicated to the GD-OES crater regeneration. InP is one of the most studied III-Vs semi-
78 conductor, especially under reactive conditions⁹, and its SE response has been largely
79 described in many different situations on well-defined surfaces¹⁰⁻¹⁴. Providing quantitative
80 information about the GD-OES crater impact is therefore a very interesting challenge for SE.

81 The SE goal is to inform about the possible modifications induced by the plasma etching,
82 their nature and, if possible, the amount of external material impacted by such modifications.
83 SE measurements combined with XPS characterization inside the crater could provide a
84 quantitative description of the perturbations induced or not (stoichiometry, surface oxidation,
85 effective perturbed depth, presence of post etching film, etc). The use of other easier
86 characterizations techniques (SEM, EDS, EBSD) is also an important purpose to completely
87 understand the perturbation nature. The robustness of this multi-technique approach will be
88 discussed and particularly the autonomy of the SE as an efficient probe to show the
89 perturbation induced by the plasma etching. After the initial crater examination, the question
90 of the crater bottom recovery is detailed. The efficiency of wet chemical engineering is
91 studied and again the capability of SE to demonstrate that the crater cleaning is effective is
92 demonstrated.

93 **II. EXPERIMENTAL**

94
95 GD-OES experiments are performed using a pulsed RF glow discharge optical
96 emission spectroscopy (GD-PROFILER 2, HORIBA Scientific) equipped with the DiP
97 (Differential Interferometry Profiling). Samples are sputtered with a pulsed Ar plasma up to
98 120 seconds according to the following parameters: 650 Pa, 30 W and 3000 Hz. The DiP
99 module gives access to a direct and continuous measurement of the crater depth during the
100 GD-OES analysis (i.e. depth vs sputtering time) and allows to stop at specific depths. This
101 accessory uses an interferometric method with a red laser diode at 633 nm (that generates no
102 perturbation of the GD-OES analysis as there are no spectroscopic lines of interest in this
103 spectral region) and measures the relative phase-shift between the crater and the surface close
104 to the crater. For non-transparent materials, such phase shift can be directly linked to the
105 crater ¹⁵.

106 XPS surface chemical analyses are carried out with a Thermo Electron K-Alpha⁺
107 spectrometer using a monochromatic Al-K α X-Ray source (1486.6 eV). The X-Ray spot size
108 is 400 μm . The Thermo Electron procedure was used to calibrate the K-Alpha⁺ spectrometer
109 by using metallic Cu and Au samples internal references (Cu 2p_{3/2} at 932.6 eV and Au 4f_{7/2} at
110 84.0 eV). High energy resolution spectra are acquired using a Constant Analyzer Energy
111 (CAE) mode 10 eV and 0.05 eV as energy step size. Data are processed using the Thermo
112 Fisher Scientific Avantage[©] data system. XPS spectra are treated using a Shirley background
113 subtraction and XPS compositions are deduced using the sensitivity factors and the inelastic
114 mean-free paths from Avantage[©] library associated to the spectrometer and the corresponding
115 transmission function.

116 Spectroscopic Ellipsometry measurements are performed using a Phase Modulated
117 Spectroscopic Ellipsometer (UVISEL+, HORIBA Scientific) over the spectral range 0.6-
118 6.5eV at an angle of incidence of 70°. Modelings are performed with DeltaPsi 2 software.

119 Secondary Electron micrographs (SEM), elemental (EDS) and microstructural (EBSD)
120 analyses are performed using a JEOL JSM 7001F microscope with a patented "in-lens"
121 Schottky Field Emission Gun (FEG) equipped with an OXFORD Aztec EDS-EBSD system.
122 SEM and EDS imaging analyses are realized at 10 kV accelerating voltage and 10 mm
123 working distance, EBSD at 5kV.

124 Auger characterizations are performed with a JEOL JAMP 9500F Auger nano-probe
125 also equipped with a patented "in-lens" Schottky Field Emission Gun (FEG) and a
126 hemispherical analyzer (HAS). Experiments are carried out at 20 kV, 10 nA, tilt 0° leading to
127 12-15 nm spot size, the maximal analyzed depth being inferior to 4-5 nm. Spectra are
128 acquired with a spectral resolution $dE/E=0.5\%$.

129

130 The micro photoluminescence (PL) measurements are performed using a confocal
131 Raman Microscopy system (Xplora PLUS, HORIBA Scientific), using a laser diode at 532
132 nm (laser diameter of 0.72 μm , measurement time 1s) at ambient temperature.

133 All transfers between GD-OES and surface (XPS, AES, and SEM) measurements are
134 performed in less than 5 min.

135 .

136 III. RESULTS AND DISCUSSION

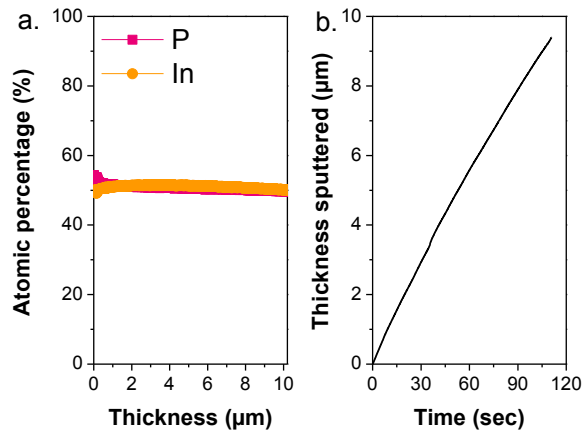
137

138 A. *Modifications induced by GD-OES*

139 The main information achieved with GD-OES profiler are the in-depth profile of the
140 different elements present inside the etched layer as well as the different positions of the
141 interfaces when they are crossed during profiling of heterostructures. In present case, the
142 sample is only constituted of bulk InP. The GD-OES profile performed on InP is displayed in
143 Fig. 1. a. and shows an expected constant atomic ratio ($\text{In/P} = 1$), whatever the depth of the
144 crater. Before reaching the sputtering stationary state, a specific transient zone is observed
145 (several seconds at the beginning of the experiment) due to surface contamination.

146 Thanks to the DiP module, the sputtered depth is also accessible. Here, a quasi-linear
147 relationship between the DiP thickness measurement and the plasma exposure time is
148 measured, in agreement with a quasi-constant etching rate (Fig. 1. b.). Up to 10 μm of InP are
149 profiled in 120 seconds. Using the DiP tool, the etching time can be converted in etched depth
150 and the precise localization in depth of a buried interface is made easier.

151



152

153 FIG. 1. GD-OES depth profile (atomic percentage vs thickness) for an InP layer (a.) and
 154 corresponding DiP measurement of the thickness sputtered over plasma exposure time (b.).

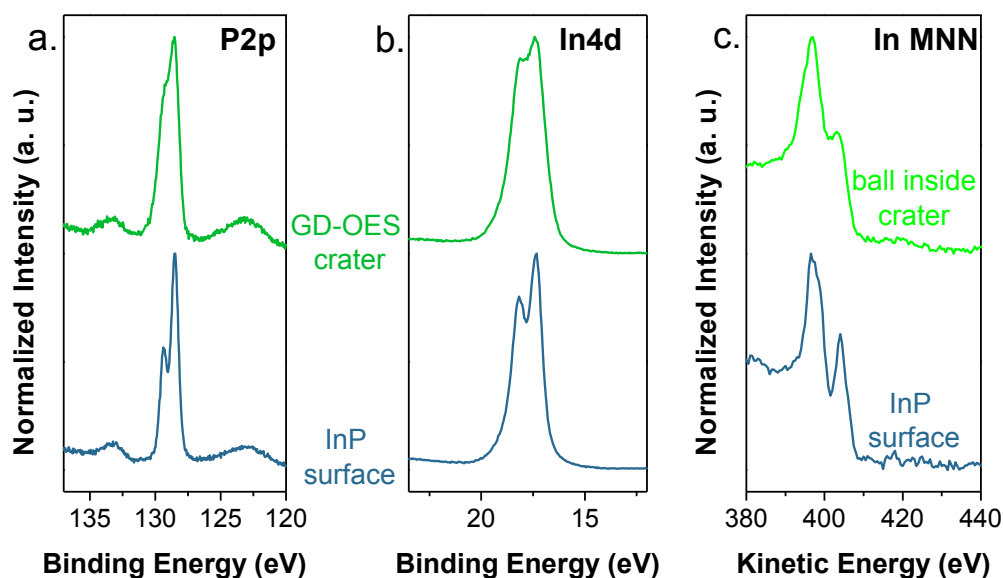
155

156 The main issue concerns now the surface state inside the GD-OES crater bottom.
 157 From previous studies on semi-conductors (Cu(In,Ga)Se₂, III-V binary compounds...)^{4,16}, we
 158 have shown that the plasma shut down is a critical step and leads to more or less significant
 159 chemical, optical and structural modifications, which depend on the nature of the layer. In the
 160 case of Cu(In,Ga)Se₂, when stopping the plasma sputtering, we have shown the presence of a
 161 superficial perturbed layer at the bottom crater both inherent to the plasma/material
 162 interaction (formation of metallic droplets, specific morphology...), the stop of the dynamic
 163 process (redeposition) and air exposure (oxidation). This overall examination of the crater
 164 surface is therefore imperative to determine if an intermediary step is required to eliminate
 165 this layer and access to the original chemical information by XPS.

166

167 1. Surface modifications

168 Comparing the physico-chemical properties of a pristine unexposed InP surface and
 169 the one obtained in the GD-OES crater is thus of primary importance. Modification of
 170 chemical environments as well as quantitative composition can be obtained through XPS
 171 measurements, which will serve here as a preliminary diagnosis tool.



173

174 FIG. 2. XPS high energy resolution spectra of P2p (a.) and In4d (b.) photopeaks obtained on
 175 InP for an unperturbed surface (blue) and inside the GD-OES crater (green). Corresponding In
 176 MNN Auger transitions recorded at local scale using the Auger nano-probe outside (blue) and
 177 inside the crater (green) on specific features illustrated on Fig 3 b. and c.

178

179 Firstly, it has to be noted that no shift of the photopeaks energy position is visible
 180 either for P2p or for In4d (Table 1). On both spectra, oxide traces are present at a similar level
 181 as outside the crater, due to time transfer inside XPS analyses chamber. However, those traces
 182 are minimized regarding the InP surface, since the different oxide contributions start to grow
 183 after 30 minutes of air exposure. In metallic site presents a more critical reactivity. Indeed, In
 184 metal is very sensitive to air oxidation, but thanks to our fast transfer (less than 5 min air
 185 exposure), the surface modifications are thus minimized. Moreover, a large broadening of the
 186 Full Width at Half Maximum (FWHM) is visible (Table 1) for both photopeaks, increasing
 187 from 0.68 ± 0.05 to 0.96 ± 0.05 eV for In4d and 0.70 ± 0.05 to 1.02 ± 0.05 eV for P2p
 188 (spectra modelling not shown here). These FWHM enlargements are accompanied with the
 189 disappearance of the spin-orbit feature for both chemical elements (Fig. 2 a. and b.). These

190 modifications are typically observed when amorphization occurs, as already suggested for
 191 different bombardments¹⁷ and other III-V materials¹⁶.

192

193 TABLE 1. Evolution of the fitting parameters of In4d and P2p photopeaks.

Photopeaks	InP surface		GD-OES crater	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
In4d _{5/2} - InP	17.3	0.68	17.4	0.96
In4d _{3/2} - InP	18.2	0.68	18.3	0.96
In4d _{5/2} - InP _{ox}	19.1	0.68	19.0	0.96
In4d _{3/2} - InP _{ox}	20.0	0.68	19.9	0.96
P2p _{3/2} - InP	128.5	0.70	128.6	1.02
P2p _{1/2} - InP	129.4	0.70	129.5	1.02
P2p _{3/2} - InP _{ox}	133.0	0.70	133.0	1.02
P2p _{1/2} - InP _{ox}	133.9	0.70	133.9	1.02

194

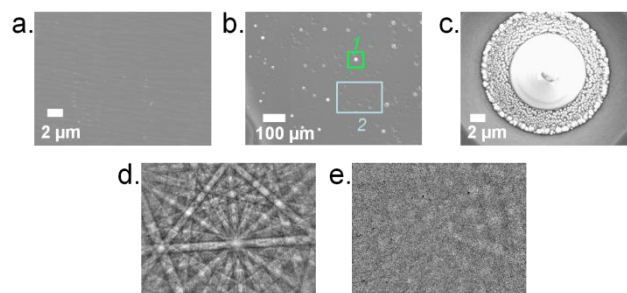
195 Regarding the quantitative aspect, interesting evolutions are also noticed. Indeed, In
 196 surface enrichment is evidenced through XPS measurements, with In/P ratios evolving from
 197 1.00 ± 0.03 to 1.40 ± 0.03 (Table 2). This suggests that when stopping the RF plasma
 198 sputtering process In metallic sites are created at the surface and some P (lighter) is
 199 preferentially released. This is only inherent to the process stop since no preferential
 200 sputtering is observed during dynamic profiling (Fig. 1).

201 As observed on Fig. 3 b. and c., after GD-OES sputtering, the crater surface has a
 202 specific morphology compared to a pristine InP surface (Fig. 3 a). Two types of defects are
 203 observed. First, (labeled 1 on Fig. 3 b. and enlarged in Fig. 3 c.) small balls of 10 to 20 μm
 204 diameter appear inside the crater. Secondly, the roughness is modified (labeled 2 on Fig. 3 b.)
 205 inside the GD-OES crater, with the presence of small circular impacts, randomly distributed

206 everywhere. The composition determined by XPS is averaged over 400 μm and therefore does
207 not enable to separate the contributions of this heterogeneous surface.

208 Complementary EDS measurements (interaction volume around 1 μm) informs at a
209 higher lateral resolution but deeper in the volume. Those results (Table 2) confirm the In
210 enrichment, with a ratio up to 1.81 ± 0.03 on the balls and ratio of 1.02 ± 0.03 outside the
211 balls coherent with the InP matrix. Thus, In enrichment can be attributed to the presence of
212 such balls, explaining also the XPS In/P ratio of 1.40. This is also confirmed by local
213 characterization using Auger nano-probe showing a higher In content on the balls but also that
214 the balls are not only composed of metallic In as the In-MNN Auger fingerprint, different
215 from the InP one, is nevertheless not perfectly similar to the In metallic one¹⁸ (Fig. 2 c.).

216



217

218 FIG. 3. SEM images of InP surface (a.), GD-OES crater (b.), In metallic ball inside the GD-
219 OES crater (c.) and EBSD Kikuchi patterns for InP surface (d.) and GD-OES crater (e.).

220

221 Fig. 3 d. and e. show the EBSD results and the evolution of the Kikuchi patterns for an
222 InP surface before and after GD-OES sputtering. The disappearance of such patterns after the
223 sputtering (Fig. 3 e.) is another proof of the surface amorphization.

224

225 TABLE 2. Comparison of In/P ratio with two quantitative techniques: XPS and EDS (measured
 226 at 10 kV).

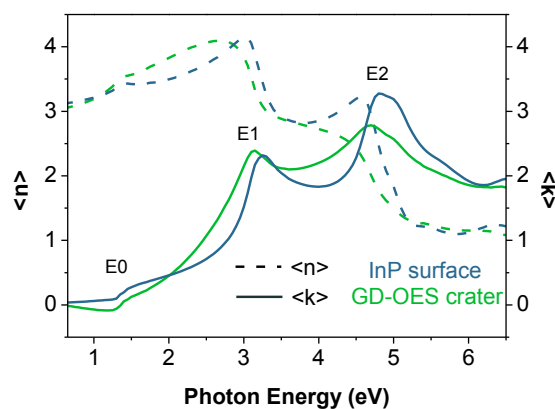
Ratios	InP surface		GD-OES crater		
	XPS	EDX	XPS	EDX	
				Ball	Outside
In/P	1.00	0.96	1.40	1.81	1.02

227

228

229 **2. Optical modifications**

230 SE is an excellent tool to assess the different perturbations induced by the GD-OES
 231 interruption. Firstly, our experiments have shown that SE measurements are perfectly
 232 repeatable inside the GD-OES crater, whatever the profiling duration performed,
 233 demonstrating that the final surface evolution at the end of the plasma sequence is the same
 234 regardless the depth reached by the profiling sequence. It is a post RF plasma etching steady
 235 state.



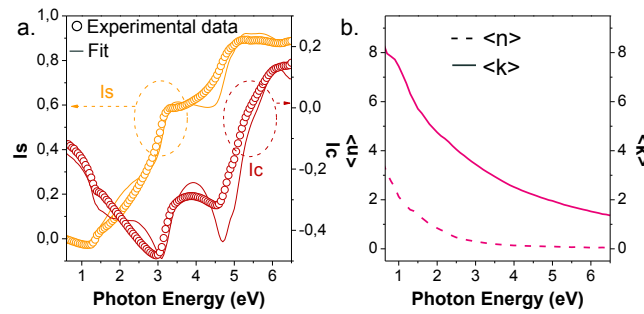
236

237 FIG. 4. Optical indexes (<n> and <k>) of InP **deoxidized surface** (blue) and GD-OES crater
 238 surfaces (green).

239

240 Optical indexes $\langle n \rangle$ and $\langle k \rangle$ evolutions between freshly deoxidized InP unperturbed
 241 surface and GD-OES crater bottom are displayed in Fig. 4. The optical indexes of deoxidized
 242 InP surface are in good agreement with literature¹⁹. After GD-OES plasma stop, modifications
 243 all over the energy range are shown, with an apparent position shift to lower energy values for
 244 E1 and E2 transitions (respectively from 3.25 eV to 3.1 eV and 4.8 eV to 4.65 eV). We also
 245 note a negative pseudo $\langle k \rangle$ for the energy under the InP band gap value. It could be explained
 246 by a refractive index of the top layer higher than the InP substrate one, which is confirmed by
 247 modeling (respectively at $E=0.85\text{eV}$, the effective refractive index of the top layer is 3.96
 248 versus 3.17 for the InP substrate one).

249



250

251 FIG. 5. Fit Results $(I_s, I_c)=f(E)$ obtained for the GD-OES crater surface, with $I_s = \sin 2\psi \cdot \sin \Delta$
 252 and $I_c = \sin 2\psi \cos \Delta$ (a.) and optical indexes $\langle n \rangle$ and $\langle k \rangle$ for metallic In (b.).

253

254 The attempt of SE modeling inside the crater is performed in Fig. 5 a., with a Maxwell
 255 Garnet Effective Medium Approximation²⁰, in consistency with SEM images showing small
 256 quantities of In balls at the surface, and then, an inhomogeneous surface. This model of $I_s =$
 257 $\sin 2\psi \cdot \sin \Delta$ and $I_c = \sin 2\psi \cdot \cos \Delta$, presents the advantage to perform better simulations in this
 258 case than the effective medium approximation one, especially at low energy range. The
 259 proposed model is a one layer model on a deoxidized InP substrate. The layer is described by
 260 a mixture of two components to take account for the roughness observed at the surface:
 261 metallic In (for the In balls) and InP substrate. No voids are used here as the In enriched balls

262 are considered inside the InP substrate and not placed on top of the surface. Regarding
263 metallic In, as far as we know, only few publications deal with SE²¹. We then have
264 determined our proper value using SE measurement performed on a pure In ingot, beforehand
265 dipped in 6 M HCl solution to prepare the surface. The deduced optical indexes $\langle n \rangle$ and $\langle k \rangle$
266 are shown in Fig. 5 b. Note that they are in reasonable agreement with the literature ones²¹.

267 The performed modeling results (Fig. 5 a.) present two areas of interest. The first one
268 is the sub band gap area (photon energy <1.34 eV), with a good agreement between modeled
269 and experimental data, especially for Is. The second one, regarding the E1 and E2 transitions
270 where values do not converge. This can be easily explained by the different components that
271 were considered inside our model. Indeed, combination of metallic In and InP substrate in the
272 over-layer contribution is a too simple approximation. While a metallic In component is
273 perfectly justified, a more appropriate choice to model the external InP component has to be
274 considered. Obviously the external InP is perturbed and this perturbation must be considered
275 optically. XPS measurements clearly display that the chemical response of InP is modified.
276 The loss of the spin orbit splitting of the P2p level is a clear indication that the perturbation of
277 the outer part of the InP layer has to be considered. A suitable model to take account of this
278 apparent surface amorphization is in progress, even if our first approximation of the order of
279 magnitude inserted inside the model is in good agreement with the one observed in XPS (few
280 nm). Indeed, the SE modeling result shows a thickness layer of 4.4 nm with a volume fraction
281 of 12% metallic In and 88% InP substrate. Ratios between metallic In and InP substrate are
282 also in good agreement with the SEM observation (Fig. 3 b.) showing the presence of random
283 In metal balls at the surface.

284 Note that the notion of superficial perturbation agrees with additional
285 Photoluminescence (PL) measurements. Actually, when the laser is pointed on an InP image
286 zone without In ball, the PL signal decays in the crater by a factor of 5 which is consistent

287 with an ultra-thin superficial PL dead layer. However it is important to point out that all
288 optical responses, and particularly the SE one, agree with a complex situation mixing metallic
289 In screening site, InP modified thin layer and InP unperturbed substrate.

290

291 ***B. Regeneration with nanometer scale surface dissolution***

292 The presence of a perturbation layer at InP surface inside the crater has been
293 evidenced and fully characterized. The recovery of the initial properties of the semi-conductor
294 is possible through different techniques, among them nano-chemical engineering. This
295 intermediary step is therefore mandatory to validate the sequential analyses operated by GD-
296 OES and XPS coupling. The resulting surface is presented using not only XPS but also SE,
297 who has proved to be an efficient tool for such surface problematic.

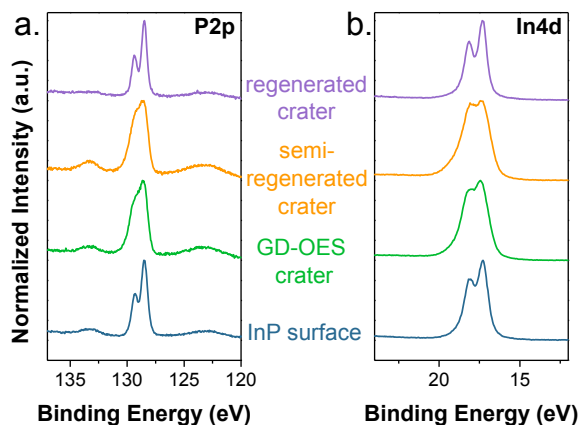
298

299 ***1. Chemical regeneration***

300

301 Several chemical treatments can be applied in order to succeed to perform a nano-
302 chemical regeneration¹⁸. However, depending on the nature of the studied semi-conductor, the
303 formulation has to be adapted. The first attempt to retrieve the chemical information was
304 performed through a dipping in HCl 2 mol.L⁻¹ during 2 minutes, as this is known to be a good
305 InP deoxidation can be achieved in HCl²². However, as observed on Fig. 6 (semi-regenerated
306 crater), the chemical treatment is not sufficient to obtain a total regeneration, as for P2p and
307 In4d the spin orbit splitting is not fully recovered, the FWHM broadening still visible and the
308 surface not deoxidized. One of the different options considered to improve this chemical
309 treatment is to modify the dipping duration. By conserving the same HCl concentration, the
310 immersion time is prolonged up to 15 minutes. In this case, at the XPS scale a perfect
311 regeneration of the chemical environment is shown with the reemergence of both photopeaks

312 spin orbit splitting is clearly visible (Fig. 6, regenerated crater) as well as a narrowing of the
313 FWHM parameters (0.65 ± 0.05 for P2p and 0.66 ± 0.05 eV for In4d).



314
315 FIG. 6. XPS high energy resolution spectra of P2p (a.) and In4d (b.) photopeaks obtained on
316 InP for an unperturbed surface (blue) and inside the GD-OES crater before (green) and after
317 chemical regeneration in $\text{HCl } 2 \text{ mol.L}^{-1}$ 2 min (yellow) and 15 min (purple).

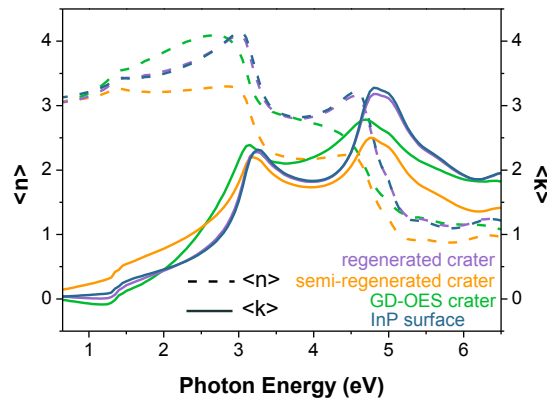
318
319 After the 15min treatment, the surface morphology and crystalline properties are
320 similar to the one presented Fig 3 a. for bare deoxidized InP substrate. In-rich balls have
321 totally disappeared. This is consistent with the photopeaks fingerprints presenting well
322 defined doublets and the In/P XPS ratio of 1.02 ± 0.03 as expected for a pristine
323 homogeneous InP surface.

324 325 2. Optical regeneration

326
327 In Fig. 7, the optical indexes evolutions are displayed in function of the chemical
328 treatment regeneration. Similar trends are observed between the recovery of the optical
329 parameter and the chemical ones presented in the previous paragraph. After the short
330 immersion time (2 min dipping in HCl), this intermediate step of regeneration is not sufficient
331 to completely remove the perturbation induced at the end of GD-OES sequence. However,

332 once a 15 minutes dipping is performed, the optical indexes $\langle n \rangle$ and $\langle k \rangle$ are similar to the
333 initial InP pristine substrate, bringing evidence of a renewed InP surface.

334



335

336 FIG. 7. Optical indexes ($\langle n \rangle$ and $\langle k \rangle$) of pristine InP (blue) and GD-OES crater surfaces
337 before (green) and after chemical regeneration in $\text{HCl } 2 \text{ mol.L}^{-1}$ 2 min (yellow) and 15 min
338 (purple).

339

340 Note that using the semi-regenerated crater experimental data, the quality of the GD-
341 OES crater bottom SE signal modeling can be improved by, especially within the high energy
342 range.

343

344 IV. SUMMARY AND CONCLUSIONS

345 By combining mainly SE and XPS characterizations, assisted by other techniques such
346 as SEM, EDS, EBSD, Auger and PL measurements, we show that a complete evaluation of
347 the chemical and optical modification of an InP surface after the interruption of a RF Argon
348 plasma / InP surface interaction can be performed. The first important result pointed out in
349 this work is that whatever the etching time the plasma leaves similar final surface states. This
350 surface is specific of the plasma surface interaction and the GD-OES stop configuration and
351 reproducible from one InP sample to another. The interest of combining XPS and SE

352 characterization tools is their total complementarity bringing an accurate diagnosis of the
353 surface modification nature, structuration and organization. Both XPS and SE results suggest
354 that a very thin external surface layer is present but, in both cases, with a part of the responses
355 linked to the InP substrate contribution. On one hand, XPS demonstrates that the surface is In
356 rich, amorphous, present a new metallic component in relation with its specific morphology.
357 On the other hand, SE response is also consequently modified but clearly conserves an InP
358 trend and component for the signal modelling. So, one should consider the combination of a
359 surface layer and a substrate response to describe surface inside the crater. Such observations
360 suggest that the surface layer is thin (few nanometers) and inhomogeneous in agreement with
361 SEM observations evidencing heterogeneities at the surface.

362 This inhomogeneity is a strong challenge for the SE interpretation but also for the XPS
363 one. Concerning the attempt to model the characteristic SE responses, it is evident that our
364 simple proposition of a combined over layer constituted by a metallic In and an InP
365 contributions is not enough to provide an optimal simulation. To increase the pertinence of
366 this approach, we think that optical constant of the outer InP would be slightly different from
367 the perfect substrate one. The specificity of the In4d and P2p photopeaks, with broadened
368 FWHM and subsequent spin orbit splitting loss suggests, in agreement with EBSD
369 characterization showing the disappearance of the Kikuchi patterns, that the outer InP layer is
370 different. So, a specific model for this outer InP contribution has to be developed.
371 Nevertheless, present results clearly evidence that the qualitative comparison of the SE
372 response is sufficient to determine if a surface chemical modification has occurred. SE is a
373 very efficient technique to follow by a non-destructive way and in reasonable acquisition time
374 the variations of the optical response in relation with variation of experimental conditions. SE
375 is easier to perform than systematic XPS characterization and offer as for XPS, the possibility
376 to perform mapping. Going back to the present context, dealing with GD-OES and XPS

377 coupling, the last point demonstrated in this paper is the SE capability to be a privileged tool
378 to evaluate not only the perturbation but also the regeneration of the surface. In this work,
379 regeneration was performed ex situ using a wet chemical treatment and characterized ex situ
380 as well. A fine optimization of this procedure can be envisaged by performing SE in a liquid
381 cell (mainly used for kinetic purpose) containing the sample immersed, and bringing in situ
382 surface evolution.

383

384 ACKNOWLEDGMENTS

385 This work was carried out in the framework of IPVF. This project has been supported by the
386 French Government in the frame of the program of investment for the future (Programme
387 d'Investissement d'Avenir – ANR-IEED-002-01).

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