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## **Evaluation of the chemical and optical perturbations** 1 induced by Ar plasma on InP surface

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- 12

#### Abstract 13

14 Interfaces are of primary importance in heterostructures. We propose here an innovative methodologic development to access the chemical information in depth and, more 15 especially, at buried interfaces. This specific approach is based on the combination of Glow 16 Discharge Optical Emission Spectroscopy (GD-OES) plasma profiling, enabling to quickly 17 and precisely reach buried interfaces, with X-Ray Photoelectron Spectroscopy surface 18 analyses, bringing an accurate determination of the composition and the chemical 19 environments. The representativeness of the crater chemistry is therefore a critical issue. On 20 InP substrate, the fine examination inside the GD-OES crater reveals surface modifications, 21 22 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 23 modifications thanks to a multi-technique approach, with an important contribution of 24 Spectroscopic Ellipsometry measurements. A crater regeneration strategy, by means of a 25 nano-chemical etching, is proposed and also assessed by the same analytical pathway, proving 26 the recovery of the initial InP properties. 27

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<sup>2</sup> 

# 30 I. INTRODUCTION

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Access to the chemistry of buried interfaces is a key parameter in the comprehension 32 of heterostructures properties and can be reached through a lot of different experimental 33 techniques<sup>1-3</sup>. Recently we developed a combination of Glow Discharge-Optical Emission 34 Spectrometry (GD-OES) depth profiling and X-Ray Photoelectron Spectroscopy (XPS) 35 surface characterization<sup>4</sup> to precisely determine the chemistry at interfaces buried at several 36 micrometers, in a reasonable acquisition time. GD-OES profiling is used as a very efficient 37 and quantitative method (after intensities calibration on standards) to determine atomic 38 concentration profiles of thin films stacks. When arriving close to a critical interface, GD-39 OES can be stopped and relayed inside the etched crater by a sequential XPS analysis, 40 assisted or not with Ar or  $Ar_n^+$  ion profiling in order to be as close as possible to the interface 41 thanks to XPS profiling. This analytical strategy strongly refines the chemical profile 42 accuracy on both sides of interfaces of interest as it additionally brings the direct atomic 43 composition and the chemical environment information in the same experimental sequence<sup>4</sup>. 44 45 This combination is therefore particularly well adapted to perform an efficient and complete characterization of heterostructures. Nevertheless, a main question relative to this GD-46 OES/XPS coupled approach concerns the integrity of the information inside the GD-OES 47 crater, which condition the representativeness of the XPS interpretation of the chemistry at 48 buried interfaces. Thus, a systematic control of the crater surface physico-chemical properties 49 50 is necessary to ensure the reliability of the relay between GD-OES and XPS. Surface modifications observed when stopping the plasma etching differ with the nature of the 51 material. Therefore they have to be considered case by case to determine, if necessary, the 52 best physical or chemical procedure to recover the initial information. This knowledge is 53 essential to further implement consistent GD-OES/XPS coupling and perform an advanced 54 chemical characterization of more complex blocks such as heterostructures. 55

To evaluate the modifications inside the GD-OES crater, a multi-technique approach is 56 employed to determine the chemical (XPS, Energy-Dispersive X-Ray Spectroscopy -EDS-), 57 morphological (Scanning Electron Microscopy -SEM-), microstructural (Electron Back-58 Scattering Diffraction –EBSD-) and optical Spectroscopic Ellipsometry (SE) characteristics of 59 the surface and sub-surface. Among this set of techniques, SE is less usually employed for 60 such a study and we will emphasize its added value. SE represents an efficient nondestructive 61 characterization method, particularly well adapted to material surfaces and thin films 62 analyses<sup>5</sup>. SE is a perfect optical tool to detect even slight surface evolutions, due to different 63 kinds of perturbations. Indeed, SE can be used to qualitatively detect evidences of plasma 64 induced modifications and the subsequent effect of the chemical engineering necessary to 65 remove the perturbed surface layer, therefore enabling the step by step<sup>6,7</sup> monitoring of the 66 surface evolutions. Moreover, through an adapted modeling step, it provides quantitative 67 68 optical data linked to such modifications. The optical SE responses also allows an autonomous diagnosis directly related to chemical features<sup>5</sup>. However the determination of 69 perfect surface optical parameters needs some physical constraints, as for example minimal 70 surface roughness<sup>8</sup>. Semi-quantitative or quantitative SE interpretation will then depend on 71 the morphological consideration onto the surface. 72

The present work focuses on the evaluation of the GD-OES crater perturbation on one 73 specific III-V material: InP. Evolutions of optical parameters are determined with SE, directly 74 implemented in the crater, just after GD-OES profiling stop (corresponding to the XPS relay 75 step in our GD-OES/XPS combined approach) as well as after wet chemical treatments 76 77 dedicated to the GD-OES crater regeneration. InP is one of the most studied III-Vs semiconductor, especially under reactive conditions<sup>9</sup>, and its SE response has been largely 78 described in many different situations on well-defined surfaces<sup>10–14</sup>. Providing quantitative 79 information about the GD-OES crater impact is therefore a very interesting challenge for SE. 80

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

- 93 II. EXPERIMENTAL
- 94

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

106	XPS surface chemical analyses are carried out with a Thermo Electron K-Alpha $^+$
107	spectrometer using a monochromatic Al-K $\alpha$ X-Ray source (1486.6 eV). The X-Ray spot size
108	is 400 $\mu$ m. The Thermo Electron procedure was used to calibrate the K-Alpha <sup>+</sup> 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 <sup>®</sup> 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  $0.72 \,\mu$ m, measurement time 1s) at ambient temperature.
- 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

The main information achieved with GD-OES profiler are the in-depth profile of the 139 different elements present inside the etched layer as well as the different positions of the 140 interfaces when they are crossed during profiling of heterostructures. In present case, the 141 142 sample is only constituted of bulk InP. The GD-OES profile performed on InP is displayed in Fig. 1. a. and shows an expected constant atomic ratio (In/P = 1), whatever the depth of the 143 crater. Before reaching the sputtering stationary state, a specific transient zone is observed 144 (several seconds at the beginning of the experiment) due to surface contamination. 145 Thanks to the DiP module, the sputtered depth is also accessible. Here, a quasi-linear 146 relationship between the DiP thickness measurement and the plasma exposure time is 147 measured, in agreement with a quasi-constant etching rate (Fig. 1. b.). Up to 10 µm of InP are 148

profiled in 120 seconds. Using the DiP tool, the etching time can be converted in etched depth

and the precise localization in depth of a buried interface is made easier.



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

156 The main issue concerns now the surface state inside the GD-OES crater bottom. From previous studies on semi-conductors (Cu(In,Ga)Se<sub>2</sub>, III-V binary compounds...)<sup>4,16</sup>, we 157 have shown that the plasma shut down is a critical step and leads to more or less significant 158 chemical, optical and structural modifications, which depend on the nature of the layer. In the 159 case of Cu(In,Ga)Se<sub>2</sub> when stopping the plasma sputtering, we have shown the presence of a 160 161 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 process (redeposition) and air exposure (oxidation). This overall examination of the crater 163 164 surface is therefore imperative to determine if an intermediary step is required to eliminate this layer and access to the original chemical information by XPS. 165

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.



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

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

- 190 modifications are typically observed when amorphization occurs, as already suggested for
- 191 different bombardments<sup>17</sup> and other III-V materials<sup>16</sup>.
- 192

Photopeaks	InP surface		GD-OES crater		
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	
In4d <sub>5/2</sub> - 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 <sub>3/2</sub> - InP <sub>ox</sub>	20.0	0.68	19.9	0.96	
P2p <sub>3/2</sub> - InP	128.5	0.70	128.6	1.02	
P2p <sub>1/2</sub> - 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	

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

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  $1.00 \pm 0.03$  to  $1.40 \pm 0.03$  (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).

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

everywhere. The composition determined by XPS is averaged over 400 µm and therefore doesnot enable to separate the contributions of this heterogeneous surface.

Complementary EDS measurements (interaction volume around 1µm) informs at a 208 209 higher lateral resolution but deeper in the volume. Those results (Table 2) confirm the In enrichment, with a ratio up to  $1.81 \pm 0.03$  on the balls and ratio of  $1.02 \pm 0.03$  outside the 210 balls coherent with the InP matrix. Thus, In enrichment can be attributed to the presence of 211 such balls, explaining also the XPS In/P ratio of 1.40. This is also confirmed by local 212 characterization using Auger nano-probe showing a higher In content on the balls but also that 213 the balls are not only composed of metallic In as the In-MNN Auger fingerprint, different 214 from the InP one, is nevertheless not perfectly similar to the In metallic one<sup>18</sup> (Fig. 2 c.). 215

216





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

<sup>220</sup> 

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

		Ratios	InP surface		G	GD-OES crater		
			XPS	XPS EDX	XPS	EDX		
			MB			Ball	Outside	
		In/P	1.00	0.96	1.40	1.81	1.02	
227								
228								
229	2. (	Optical mod	lifications					
230		SE is an excel	lent tool to a	ussess the differ	rent perturbation	ons induced	l by the GD-O	)ES
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.							

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



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

Optical indexes  $\langle n \rangle$  and  $\langle k \rangle$  evolutions between freshly deoxidized InP unperturbed 240 surface and GD-OES crater bottom are displayed in Fig. 4. The optical indexes of deoxidized 241 InP surface are in good agreement with literature<sup>19</sup>. After GD-OES plasma stop, modifications 242 all over the energy range are shown, with an apparent position shift to lower energy values for 243 E1 and E2 transitions (respectively from 3.25 eV to 3.1 eV and 4.8 eV to 4.65 eV). We also 244 note a negative pseudo <k> for the energy under the InP band gap value. It could be explained 245 246 by a refractive index of the top layer higher than the InP substrate one, which is confirmed by modeling (respectively at E=0.85eV, the effective refractive index of the top layer is 3.96 247 versus 3.17 for the InP substrate one). 248

249



#### 250

FIG. 5. Fit Results (Is, Ic)=f (E) obtained for the GD-OES crater surface, with Is =  $\sin 2\psi . \sin \Delta$ and Ic =  $\sin 2\psi \cos \Delta$  (a.) and optical indexes <n> and <k> for metallic In (b.).

253

The attempt of SE modeling inside the crater is performed in Fig. 5 a., with a Maxwell 254 Garnet Effective Medium Approximation<sup>20</sup>, in consistency with SEM images showing small 255 quantities of In balls at the surface, and then, an inhomogeneous surface. This model of Is = 256  $\sin 2\psi \cdot \sin \Delta$  and Ic =  $\sin 2\psi \cdot \cos \Delta$ , presents the advantage to perform better simulations in this 257 case than the effective medium approximation one, especially at low energy range. The 258 proposed model is a one layer model on a deoxidized InP substrate. The layer is described by 259 a mixture of two components to take account for the roughness observed at the surface: 260 metallic In (for the In balls) and InP substrate. No voids are used here as the In enriched balls 261

are considered inside the InP substrate and not placed on top of the surface. Regarding
metallic In, as far as we know, only few publications deal with SE<sup>21</sup>. We then have
determined our proper value using SE measurement performed on a pure In ingot, beforehand
dipped in 6 M HCl solution to prepare the surface. The deduced optical indexes <n> and <k>
are shown in Fig. 5 b. Note that they are in reasonable agreement with the literature ones<sup>21</sup>.

The performed modeling results (Fig. 5 a.) present two areas of interest. The first one 267 268 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 where values do not converge. This can be easily explained by the different components that 270 271 were considered inside our model. Indeed, combination of metallic In and InP substrate in the over-layer contribution is a too simple approximation. While a metallic In component is 272 perfectly justified, a more appropriate choice to model the external InP component has to be 273 274 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 apparent surface amorphization is in progress, even if our first approximation of the order of 278 279 magnitude inserted inside the model is in good agreement with the one observed in XPS (few nm). Indeed, the SE modeling result shows a thickness layer of 4.4 nm with a volume fraction 280 of 12% metallic In and 88% InP substrate. Ratios between metallic In and InP substrate are 281 also in good agreement with the SEM observation (Fig. 3 b.) showing the presence of random 282 In metal balls at the surface. 283

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

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

290

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

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

298

### 299 1. Chemical regeneration

300

Several chemical treatments can be applied in order to succeed to perform a nano-301 chemical regeneration<sup>18</sup>. However, depending on the nature of the studied semi-conductor, the 302 formulation has to be adapted. The first attempt to retrieve the chemical information was 303 performed through a dipping in HCl 2 mol.L<sup>-1</sup> during 2 minutes, as this is known to be a good 304 InP deoxidation can be achieved in HCl<sup>22</sup>. However, as observed on Fig. 6 (semi-regenerated 305 crater), the chemical treatment is not sufficient to obtain a total regeneration, as for P2p and 306 In4d the spin orbit splitting is not fully recovered, the FWHM broadening still visible and the 307 308 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 immersion time is prolonged up to 15 minutes. In this case, at the XPS scale a perfect 310 regeneration of the chemical environment is shown with the reemergence of both photopeaks 311

spin orbit splitting is clearly visible (Fig. 6, regenerated crater) as well as a narrowing of the





324

# 325 2. Optical regeneration

326

In Fig. 7, the optical indexes evolutions are displayed in function of the chemical treatment regeneration. Similar trends are observed between the recovery of the optical parameter and the chemical ones presented in the previous paragraph. After the short immersion time (2 min dipping in HCl), this intermediate step of regeneration is not sufficient to completely remove the perturbation induced at the end of GD-OES sequence. However, once a 15 minutes dipping is performed, the optical indexes <n> and <k> are similar to the
initial InP pristine substrate, bringing evidence of a renewed InP surface.

334



335

FIG. 7. Optical indexes (<n> and <k>) of pristine InP (blue) and GD-OES crater surfaces
before (green) and after chemical regeneration in HCl 2 mol.L<sup>-1</sup> 2 min (yellow) and 15 min
(purple).

339

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

343

# **IV. SUMMARY AND CONCLUSIONS**

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

characterization tools is their total complementarity bringing an accurate diagnosis of the 352 353 surface modification nature, structuration and organization. Both XPS and SE results suggest that a very thin external surface layer is present but, in both cases, with a part of the responses 354 355 linked to the InP substrate contribution. On one hand, XPS demonstrates that the surface is In rich, amorphous, present a new metallic component in relation with its specific morphology. 356 357 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 suggest that the surface layer is thin (few nanometers) and inhomogeneous in agreement with 360 361 SEM observations evidencing heterogeneities at the surface.

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

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

383

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