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

Solène Béchu,1,2,a) Céline Eybert,3 Anais Loubat,2 Jackie Vigneron,2 Sofia Gaiaschi,3 Patrick Chapon,3 Muriel Bouttemy,2 and 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

(Received 29 July 2019; accepted 10 September 2019; published 30 September 2019)

Interfaces are of primary importance in heterostructures. The authors propose here an innovative methodologic development to access the chemical information in depth and, especially, at buried interfaces. This specific approach is based on the combination of glow discharge optical emission spectroscopy (GD-OES) plasma profiling, enabling one 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 the InP substrate, the fine examination inside the GD-OES crater reveals surface modifications, chemical, morphological, and optical, and, as a consequence, the need to regenerate the initial chemical information. The authors present here a study dedicated to the evaluation of those modifications thanks to a multitechnique approach, with an important contribution of spectroscopic ellipsometry measurements. A crater regeneration strategy, by means of a nanochemical etching, is proposed and also assessed by the same analytical pathway, proving the recovery of the initial InP properties. Published by the AVS. https://doi.org/10.1116/1.5121897

I. INTRODUCTION

Access to the chemistry of buried interfaces is a key parameter in the comprehension of heterostructure properties and can be reached through a lot of different experimental techniques.1–3 Recently, we developed a combination of glow discharge optical emission spectrometry (GD-OES) depth profiling and x-ray photoelectron spectroscopy (XPS) surface characterization4 to precisely determine the chemistry at interfaces buried at several micrometers, in a reasonable acquisition time. GD-OES profiling is used as a very efficient and quantitative method (after intensities calibration on standards) to determine atomic concentration profiles of thin film stacks. When arriving close to a critical interface, GD-OES can be stopped and relayed inside the etched crater by a sequential XPS analysis, assisted or not with Ar or Ar+ ion profiling in order to be as close as possible to the interface, thanks to XPS profiling. This analytical strategy strongly refines the chemical profile accuracy on both sides of interfaces of interest, as it additionally brings the direct atomic composition and the chemical environment information in the same experimental sequence.4 This combination is, therefore, particularly well adapted to perform an efficient and complete characterization of heterostructures. Nevertheless, the main question relative to this GD-OES/XPS coupled approach concerns the integrity of the information inside the GD-OES crater, which condition the representativeness of the XPS interpretation of the chemistry at buried interfaces. Thus, a systematic control of the crater surface physicochemical properties 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 material. Therefore, they have to be considered case by case to determine, if necessary, the best physical or chemical procedure to recover the initial information. This knowledge is essential to further implement consistent GD-OES/XPS coupling and perform an advanced chemical characterization of more complex blocks such as heterostructures.

To evaluate the modifications inside the GD-OES crater, a multitechnique approach is employed to determine the chemical [XPS, energy-dispersive x-ray spectroscopy (EDS)], morphological [scanning electron microscopy (SEM)], microstructural [electron back-scattering diffraction (EBSD)], and optical spectroscopic ellipsometry (SE) characteristics of the surface and subsurface. Among this set of techniques, SE is less usually employed for such a study, and we will emphasize its added value. SE represents an efficient nondestructive characterization method, particularly well adapted to material surfaces and thin film analyses.5 SE is a perfect optical tool to detect even slight surface evolutions, due to different kinds of perturbations. Indeed, SE can be used to qualitatively detect evidence of plasma induced modifications and the subsequent effect of the chemical engineering necessary to remove the perturbed surface layer, therefore enabling the step by step6,7 monitoring of the surface evolutions. Moreover, through an adapted modeling step, it provides quantitative optical data linked to such modifications. The optical SE responses also allow an autonomous diagnosis directly related to chemical features.5 However, the determination of perfect surface optical parameters needs some physical constraints, for example, minimal

Note: This paper is part of the Conference Collection: 8th International Conference on Spectroscopic Ellipsometry 2019, ICSE.

a)Electronic mail: solene.bechu@uvsq.fr
II. EXPERIMENT

GD-OES experiments are performed using a pulsed RF glow discharge optical emission spectroscope (GD-PROFILE 2, HORIBA Scientific) equipped with the DiP (differential interferometry profiling). Samples are sputtered with a pulsed Ar plasma of up to 120 s according to the following parameters: 650 Pa, 30 W, and 3000 Hz. The DiP module gives access to a direct and continuous measurement of the crater depth during the GD-OES analysis (i.e., depth versus sputtering time) and allows to stop at specific depths. This accessory uses an interferometric method with a red laser diode at 633 nm (that generates no perturbation of the GD-OES analysis, as there are no spectroscopic lines of interest in this spectral region) and measures the relative phase shift between the crater and the surface close to the crater. For nontransparent materials, such phase shift can be directly linked to the crater.15

XPS surface chemical analyses are carried out with a Thermo Electron K-Alpha® spectrometer using a monochromatic Al-Kα x-ray source (1486.6 eV). The x-ray spot size is 400 μm. The Thermo Electron procedure was used to calibrate the K-Alpha® spectrometer by using metallic Cu and Au samples as internal references (Cu 2p_{3/2} at 932.6 eV and Au 4f_{7/2} at 84.0 eV). High energy resolution spectra are acquired using a constant analyzer energy mode with 10 and 0.05 eV as the energy step size. Data are processed using the Thermo Fisher Scientific Avantage® data system. XPS spectra are treated using a Shirley background subtraction, and XPS compositions are deduced using the sensitivity factors and the inelastic mean free paths from Avantage library associated to the spectrometer and the corresponding transmission function.

Spectroscopic ellipsometry measurements are performed using a phase modulated spectroscopic ellipsometer (UVISEL+, HORIBA Scientific) over the spectral range of 0.6–6.5 eV at an angle of incidence of 70°. Modelings are performed with DELTAPI 2 software.

Secondary electron micrographs (SEM), elemental (EDS), and microstructural (EBSD) analyses are performed using a JEOL JSM 7001F microscope with a patented “in-lens” Schottky field emission gun (FEG) equipped with an OXFORD Aztec EDS-EBSD system. SEM and EDS imaging analyses are realized at 10 kV accelerating voltage and 10 mm working distance, EBSD at 5 kV.

Auger characterizations are performed with a JEOL JAMP 9500F Auger nanoprobe also equipped with a patented “in-lens” Schottky FEG and a hemispherical analyzer. Experiments are carried out at 20 kV, 10 nA, a tilt angle of 0° leading to 12–15 nm spot size, and the maximal analyzed depth being inferior to 4–5 nm. Spectra are acquired with a spectral resolution of dE/E = 0.5%.

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

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

III. RESULTS AND DISCUSSION

A. Modifications induced by GD-OES

The main information achieved with the GD-OES profiler is the in-depth profile of the different elements present inside the etched layer as well as the different positions of the interfaces when they are crossed during profiling of heterostructures. In the present case, the 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 crater. Before reaching the sputtering stationary state, a specific transient zone is observed (several seconds at the beginning of the experiment) due to surface contamination.

Thanks to the DiP module, the sputtered depth is also accessible. Here, a quasilinear relationship between the DiP thickness measurement and the plasma exposure time is measured, in agreement with a quasiconstant etching rate [Fig. 1(b)]. Up to 10 μm of InP are profiled in 120 s. Using the DiP tool, the etching time can be converted to etched depth, and the precise localization in the depth of a buried interface is made easier.

The main issue concerns now the surface state inside the GD-OES crater bottom. From previous studies on
semiconductors [Cu(In,Ga)Se$_2$, III-V binary compounds, etc.], we have shown that the plasma shut down is a critical step and leads to more or less significant chemical, optical, and structural modifications, which depend on the nature of the layer. In the case of Cu(In,Ga)Se$_2$, when stopping the plasma sputtering, we have shown the presence of a superficial perturbed layer at the bottom of the crater inherent to the plasma/material interaction (formation of metallic droplets, specific morphology, etc.), the stop of the dynamic process (redemption), and air exposure (oxidation). This overall examination of the crater surface is, therefore, imperative to determine whether an intermediary step is required to eliminate this layer and access to the original chemical information by XPS.

1. Surface modifications

Comparing the physicochemical properties of a pristine unexposed InP surface and the one obtained in the GD-OES crater is, thus, of primary importance. The modification of chemical environments as well as quantitative composition can be obtained through XPS measurements, which will serve here as a preliminary diagnosis tool.
First, it has to be noted that no shift of the photopeaks energy position is visible either for P2p or for In4d (Table I). On both spectra, oxide traces are present at a similar level as outside the crater, due to time transfer inside the XPS analyses chamber. However, these traces are minimized regarding the InP surface, since the different oxide contributions start to grow after 30 min of air exposure. The In metallic site presents a more critical reactivity. Indeed, In metal is very sensitive to air oxidation, but thanks to our fast transfer (less than 5 min air exposure), the surface modifications are, thus, minimized. Moreover, a large broadening of the full width at half maximum (FWHM) is visible (Table I) for both photopeaks, increasing 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 (spectra modeling not shown here). These FWHM enlargements are accompanied by the disappearance of the spin orbit feature for both chemical elements [Figs. 2(a) and 2(b)]. These modifications are typically observed when amorphization occurs, as already suggested for different bombardments and other III-V materials.\(^{16}\)

As observed in Figs. 3(b) and 3(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 in Fig. 3(b) and enlarged in Fig. 3(c)], small balls of 10–20 \(\mu\)m diameter appear inside the crater. Second, the roughness is modified [labeled 2 in 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 \(\mu\)m and, therefore, does not enable to separate the contributions of this heterogeneous surface.

Complementary EDS measurements (interaction volume around 1 \(\mu\)m) inform at a higher lateral resolution but deeper in the volume. Those results (Table II) confirm the In enrichment, with a ratio of up to 1.81 ± 0.03 on the balls and a ratio of 1.02 ± 0.03 outside the balls coherent with the InP matrix. Thus, the In enrichment can be attributed to the presence of such balls, explaining also the XPS In/P ratio of 1.40. This is also confirmed by local characterization using the Auger nanoprobe showing a higher In content on the balls but also that the balls are not only composed of metallic In as the In-MNN Auger fingerprint, different from the InP one, is nevertheless not perfectly similar to the In metallic one\(^{18}\) [Fig. 2(c)].

Figures 3(d) and 3(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.

### Table II. Comparison of In/P ratio with two quantitative techniques: XPS and EDS (measured at 10 kV).

<table>
<thead>
<tr>
<th>Ratios</th>
<th>InP surface</th>
<th>GD-OES crater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XPS</td>
<td>EDX</td>
</tr>
<tr>
<td>In/P</td>
<td>1.00</td>
<td>0.96</td>
</tr>
</tbody>
</table>

2. **Optical modifications**

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

Fig. 3. SEM images of the InP surface (a), the GD-OES crater (b), In metallic ball inside the GD-OES crater (c), and EBSD Kikuchi patterns for the InP surface (d) and GD-OES crater (e).
Fig. 4. Optical indexes \(\langle n\rangle\) and \(\langle k\rangle\) of the InP deoxidized surface (blue) and GD-OES crater surfaces (green).

Optical index \(\langle n\rangle\) and \(\langle k\rangle\) evolutions between freshly deoxidized InP unperturbed surface and the GD-OES crater bottom are displayed in Fig. 4. The optical indexes of deoxidized InP surface are in good agreement with the literature. \(^{13}\) After GD-OES plasma stops, modifications all over the energy range are shown, with an apparent position shift to lower energy values for E1 and E2 transitions (respectively, from 3.25 to 3.1 eV and 4.8 to 4.65 eV). We also note a negative pseudo-\(\langle k\rangle\) for the energy under the InP bandgap value. It could be explained by a refractive index of the top layer higher than the InP substrate one, which is confirmed by modeling (respectively, at \(E = 0.85\) eV, the effective refractive index of the top layer is 3.96 vs 3.17 for the InP substrate one).

The attempt of SE modeling inside the crater is performed as shown in Fig. 5(a), with a Maxwell Garnet Effective Medium Approximation, \(^{19}\) in agreement with SEM images showing small quantities of In balls at the surface and, then, an inhomogeneous surface. This model of \(I_s = \sin 2\psi \sin \Delta\) and \(I_c = \sin 2\psi \cos \Delta\) presents the advantage to perform better simulations in this case than the effective medium approximation one, especially at a low energy range. The proposed model is a one layer model on a deoxidized InP substrate. The layer is described by a mixture of two components to take account for the roughness observed at the surface: metallic In (for the In balls) and InP substrates. No voids are used here, as the In enriched balls are considered inside the InP substrate and not placed on top of the surface. Regarding metallic In, as far as we know, only a few publications deal with SE. \(^{20}\) We then have determined our proper value using the SE measurement performed on a pure In ingot, beforehand dipped in 6M HCl solution to prepare the surface. The deduced optical indexes \(\langle n\rangle\) and \(\langle k\rangle\) are shown in Fig. 5(b). Note that they are in reasonable agreement with the literature. \(^{20}\)

The performed modeling results [Fig. 5(a)] present two areas of interest. The first one is the sub-bandgap area (photon energy \(<1.34\) eV), with a good agreement between modeled and experimental data, especially for \(I_s\). The second one is regarding the E1 and E2 transitions where values do not converge. This can be easily explained by the different components that were considered inside our model. Indeed, a combination of metallic In and InP substrates in the overlayer contribution is a too simple approximation. While a metallic In component is perfectly justified, a more appropriate choice to model the external InP component has to be considered. Obviously, the external InP is perturbed, and this perturbation must be considered optically. XPS measurements clearly display that the chemical response of InP is modified. The loss of the spin orbit splitting of the P2p level is a clear indication that the perturbation of 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 magnitude inserted inside the model is in good agreement with the one observed in XPS (few nanometers). Indeed, the SE modeling result shows a layer of 4.4 nm thick with a volume fraction of 12% metallic In and 88% InP substrates. Ratios between metallic In and InP substrates are also in good agreement.

Fig. 5. Fit results \((I_s, I_c) = f (E)\) obtained for the GD-OES crater surface, with \(I_s = \sin 2\psi \sin \Delta\) and \(I_c = \sin 2\psi \cos \Delta\) (a) and optical indexes \(\langle n\rangle\) and \(\langle k\rangle\) for metallic In (b).
with the SEM observation [Fig. 3(b)], showing the presence of random In metal balls at the surface.

Note that the notion of superficial perturbation agrees with additional PL measurements. Actually, when the laser is pointed on an InP image zone without In ball, the PL signal decays in the crater by a factor of 5, which is consistent with an ultrathin 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 the metallic In screening site, the InP modified thin layer, and the InP unperturbed substrate.

B. Regeneration with nanometer scale surface dissolution

The presence of a perturbation layer at the InP surface inside the crater has been evidenced and fully characterized. The recovery of the initial properties of the semiconductor is possible through different techniques, among them is nanochemical 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, which has proven to be an efficient tool for such surface problems.

1. Chemical regeneration

Several chemical treatments can be applied in order to succeed to perform a nanochemical regeneration. However, depending on the nature of the studied semiconductor, the formulation has to be adapted. The first attempt to retrieve the chemical information was performed through dipping in 2 mol l⁻¹ HCl during 2 min, as this is known to be a good InP deoxidation that can be achieved in HCl. However, as observed in Fig. 6 (semiregenerated crater), the chemical treatment is not sufficient to obtain a total regeneration, as for P2p and In4d the spin orbit splitting is not fully recovered, the FWHM broadening still visible, and the surface not deoxidized. One of the different options considered to improve this chemical treatment is to modify the dipping duration. By conserving the same HCl concentration, the immersion time is prolonged up to 15 min. On the extreme surface (<10 nm, i.e., the XPS scale, a perfect regeneration of the chemical environment is shown with the re-emergence of both photopeaks’ spin orbit splitting, which is clearly visible (Fig. 6, regenerated crater) as well as a narrowing of the FWHM parameters (0.65 ± 0.05 for P2p and 0.66 ± 0.05 eV for In4d).

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

2. Optical regeneration

In Fig. 7, the optical index evolutions are displayed in the 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 the GD-OES sequence. However, once a 15 min dipping is performed, the optical indexes (n) and (k) are similar to the initial InP pristine substrate, bringing evidence of a renewed InP surface.

Note that, using the semiregenerated crater experimental data, the quality of the GD-OES crater bottom SE signal modeling can be improved, especially within the high energy range.

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 an 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 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 linked to the InP substrate contribution. On one hand, XPS demonstrates that the surface is In rich, amorphous, and presents a new metallic component in relation to its specific morphology. On the other hand, SE response is also consequently modified but clearly conserves an InP trend and component for the signal modeling. So, one should consider the combination of a 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 SEM observations evidencing heterogeneities at the surface.

This inhomogeneity is a strong challenge for the SE interpretation but also for the XPS one. Concerning the attempt to model the characteristic SE responses, it is evident that our simple proposition of a combined layer constituted by a metallic In and InP contribution is not enough to provide an optimal simulation. To increase the pertinence of this approach, we think that the optical constant of the outer InP would be slightly different from the perfect substrate one. The specificity of the In4d and P2p photopeaks, with broadened FWHM and subsequent spin orbit splitting loss, suggests, in agreement with EBSD 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. Nevertheless, present results clearly evidence that the qualitative comparison of the SE response is sufficient to determine whether a surface chemical modification has occurred. SE is a very efficient technique to follow in a nondestructive way and in reasonable acquisition time the variations of the optical response in relation with variation of experimental conditions. SE is easier to perform than systematic XPS characterization and offers as for XPS, the possibility to perform mapping. Going back to the present context, dealing with GD-OES and XPS 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.

ACKNOWLEDGMENTS

This work was carried out in the framework of IPVF. This project has been supported by the French Government in the frame of the program of investment for the future (Programme d’Investissement d’Avenir, No. ANR-IEED-002-01).