3114 *Chem. Mater.* **2010,** *22,* 3114–3120
DOI:10.1021/cm100035a

CHEMISTRY OF MATERIALS
Article

Fully Protective yet Functionalizable Monolayer on InP

Anne-Marie Gonçalves,*[‡] Nicolas Mézailles,[§] Charles Mathieu,[‡]
Pascal Le Floch,[§,†] and Arnaud Etcheberry[‡]

[‡]*University of Versailles St Quentin-en-Yvelines, Institut Lavoisier de Versailles, UMR-CNRS 8180, 45, Avenue des Etats-Unis, 78035 Versailles Cedex, France, and* [§]*Laboratory "Hétéroéléments et Coordination", École Polytechnique, UMR-CNRS 7653, Route de Saclay, 91128 Palaiseau cedex, France.* [†]*Deceased.*

Received January 5, 2010. Revised Manuscript Received April 7, 2010

A novel protective monolayer film on an *n*-InP semiconductor is obtained using a controlled photoelectrochemical process performed in liquid ammonia. Using a submillicoulombs per square centimeter spent charge and using a low current density ($< 10\ \mu A/cm^2$) in an innovative photoassisted galvanostatic mode, a novel passivation process with ultrathin film growth was successfully employed. The nature of the resulting monolayer which has a polyphosphazene-like structure is studied by X-phoelectron spectroscopy. The proof and reproducibility of the thickness and chemical composition are clearly evidenced by XPS analyses. The perfect coverage of the InP matrix by this thin film is revealed by electrochemical experiments and XPS data. The presence of amino groups in the film offers a unique opportunity for further functionalization, as exemplified by the first chemically controlled coordination of Pt(II) centers onto the protective layer. The stability of the covered InP substrate as well as of the passivated film upon functionalization is again demonstrated by XPS analyses. Without this protective film, the immersion of a bare InP substrate in a K_2PtCl_4 solution leads to the formation of metallic Pt clusters on the surface concomitant with the oxidation of the InP substrate.

Introduction

The integration of III−V semiconductors into attractive electronic devices is at the center of thorough research, as shown by patent activity. Present and future electronics and nanotechnology are indeed reflected in the widespread interest in III−V devices.[1−6] III−V optoelectronic interest is essentially based on adaptable optical properties, high switching speeds, and low supply voltages. The integration of high-speed InP devices into elemental semiconductors such as Si and Ge has therefore attracted a great deal of interest, the final goal being the design of hybrid structures capitalizing the best properties of each component.[7,8] Compared to silicon, better electrical characteristics, such as high electron saturation velocity and high thermal conductivity, make InP an efficient candidate for electronic devices such as heterojunction bipolar transistors (HBT), metal−insulator−semiconductor field-effect transistors (MISFETs), electron mobility transistors in their traditional (HEMTs) and pseudomorphic (PHEMTs) forms, microwave diodes, optoelectronic devices, sensors, data storage devices, and biomedical applications.[9,10] Nevertheless, in contrast to silicon, InP and InP-based devices suffer from interfacial or surface chemical instabilities because of spontaneous surface oxidation and related side reactivity. Optoelectronic and electrical properties are then drastically affected because of the high resulting density of traps at the insulator−semiconductor interfaces or surfaces. Several attempts to stabilize the surface chemistry of InP have already been made using a wet process, for instance, inorganic sulfite chemistry[11] or ruthenium deposition.[12] An improvement in the InP electrical properties is observed only in the early stages after the passivating treatment. Rapidly, the air aging of the semiconductor surface leads to an uncontrolled formation of surface oxides correlated to a degradation of the surface network and in turn to the loss of the desired electrical properties.[13,14]

---

*To whom correspondence should be addressed. Fax and telephone: + 33 (0) 1 39 25 44 19/18. E-mail: goncalves@chimie.uvsq.fr.

(1) Algra, R. E.; Verheijen, M. A.; Borgström, M. T.; Feiner, L. F.; Immink, G.; Van Enckevort, W. J. P.; Vlieg, E.; Bakkers, E. P. A. M. *Nature* **2008**, *456*, 366.
(2) Snaith, H. J.; Zakeeruddin, S. M.; Schmidt-Mende, L.; Klein, C.; Grätzel, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6413.
(3) Yu, H.; Li, J.; Loomis, R. A.; Wang, L. W.; Buhro, W. E. *Nat. Mater.* **2003**, *2*, 517.
(4) Duan, X.; Huang, Y.; Cui, Y.; Wang, J.; Lieber, C. M. *Nature* **2001**, *409*, 66.
(5) Quake, S. R.; Scherer, A. *Science* **2000**, *290*, 1536.
(6) De la Rue, R. M. *Science* **1999**, *286*, 2459.
(7) Lauhon, L. J.; Gudiksen, M. S.; Wang, D.; Lieber, C. M. *Nature* **2002**, *420*, 57.
(8) Bakkers, A. P. A. M.; Van Dam, J. A.; De Franceschi, S.; Kouwenhoven, L. P.; Kaiser, M.; Verheijen, M.; Wondergem, H.; Van der Sluis, P. *Nat. Mater.* **2004**, *3*, 769.
(9) Woodall, J. M. *Science* **1980**, *208*, 908.
(10) Kogelnik, H. *Science* **1985**, *228*, 1043.
(11) Jeong, Y. H.; Jo, S. K.; Lee, B. H.; Sugano, T. *IEEE Electron Device Lett.* **1995**, *16*, 109.
(12) Bose, D. N.; Ramprakash, Y.; Basu, S. *Mater. Lett.* **1989**, *88*, 364.
(13) Wu, Y. Q.; Xuan, Y.; Shen, T.; Ye, P. D.; Cheng, Z.; Lochtefeld, A. *Appl. Phys. Lett.* **2007**, *91*, 022108/1.
(14) Zhao, H.; Shahrjerdi, D.; Zhu, F.; Kim, H. S.; Ok, I.; Zhang, M.; Yum, J. H.; Banerjee, S. K.; Lee, J. C. *Appl. Phys. Lett.* **2008**, *92*, 233508/1.

To make the InP substrate suitable for its incorporation into (opto)electronic devices, its chemical surface has to be protected from oxidation and readily functionalized. The challenge in obtaining actual passivation using a wet treatment still exists. Remarkable potentialities of liquid ammonia (NH_3 liq.) have been recently reported through unusual anodic electrochemical mechanisms on III−V semiconductors. For high anodic current densities (> 2 mA/cm^2), both original porosification of the InP surface and stoichiometric ammonia oxidation were evidenced.[15,16] Using cyclic voltammetry experiments, an anodic passivation effect was achieved in NH_3 liq. It gives rise to a specific "P−N" chemistry on the modified surface.[16] Nevertheless, this vain attempt by cyclic voltammetry did not provide a perfect control of the modified surface. In contrast, a galvanostatic mode should provide quantitative formation via a novel passivation process of InP in NH_3 liq. In this paper, our goals are manifold. We proposed to limit the insertion of nitrogen to only the uppermost layer of InP, relying on the simultaneous InP dissolution and ammonia oxidation to yield a protective monolayer. This new challenge is to perform on the uppermost InP layer a chemistry based on nitrogen regulated at a molecular scale, supported by an accurate quantification of electron and chemical exchanges at the interface. This controlled transformation would be the equivalent of the classical anodic oxide growth in water. To reach this ambitious goal, we used a controlled galvanostic mode assisted by light to suit a more efficient passivation treatment. In a recent paper,[17] preliminary results seemed to offer further opportunities by a rough and approximate galvanostatic mode. In this paper, first, a rigorous and well-established galvanostatic treatment, combining low-imposed current regimes and assistance by light soaking, provides for the first time a perfect controlled passivation film. Second, the precise chemical nature of the resulting protecting film is to be uncovered by a quantitative XPS determination. Third, the protective monolayer would ideally provide a platform for further functionalization.

The requirements that are to be met are therefore stringent. The InP surface was 100% protected from oxidation not only for the short periods of time but also for extended periods of time, and the protective layer should provide a platform for further functionalization without damaging the underlying III−V lattice to guarantee and to maintain (opto)electrical performances. Both goals are reached since a novel passivation route is established, and the resulting support allows the first successful functionalization of an InP surface.

Experimental Methods

n-InP semiconductor wafers, with a ⟨100⟩ orientation, were purchased from InPact Electronic Materials, Ltd., with a doping density of 10^{18} cm^{-3}. InP electrodes, small squares of 0.5 cm × 0.5 cm, were then fabricated. Prior to being used, they were chemomechanically polished with a solution of bromine in methanol (2%), rinsed with the purest methanol, and dried under an argon stream. To remove residual oxides, samples were dipped for a few minutes in 2 M HCl[18] just before the experiment in liquid ammonia. Condensation of ammonia, from gaseous ammonia ("electronic grade" from Air Liquide), was performed in a glass column assembly, and a low operating temperature (210 K) under atmospheric pressure was required.[19] A volume of 150 cm^3 of liquid ammonia was condensed and maintained at 223 K in a cryostat. The de-aeration of the medium was performed via an argon stream. An optical fiber was immersed in the cryostat and connected to a tungsten lamp which allowed the illumination of the sample through the electrochemical cell.

Note that at room temperature liquid ammonia is a very strongly basic solvent (10^{11} times stronger than water) and a very weak acid (10^{29} times weaker than water).[19] The addition of 0.1 M NH_4Br (purest available quality from Aldrich) provided a constant pH as well as the conductivity of the medium. A pH of 1 is then expected in the NH_3 liq. pH scale. All potentials are measured versus a silver reference electrode (SRE).[15,16] A large smooth platinum electrode was also used as a counter electrode. The galvanostatic setup, for performing anodization, used a classical three-electrode configuration, controlled by a Parstat 2273 potentiostat-galvanostat. After the electrochemical treatment, the sample was rinsed via a long immersion in the purest liquid ammonia (without a conducting salt). After the rinsing step (at least 30 min), the semiconductor was analyzed by XPS, using a transfer procedure limiting any air contamination [16].

The functionalization of the resulting film was conducted by its immersion in an aqueous solution of K_2PtCl_4 (3 mmol/L). The chemical modifications of the InP surface were then analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo electron VG-ESCALB 220i XL system. High-resolution XPS conditions have been used, in a constant analyzer energy mode with a pass energy of 8 or 20 eV. The monochromatic Al Kα line or Al Kα line of a dual anode was used as X-ray excitation. Large X-ray spots (3 mm) were usually used to explore the surface. The homogeneity of the surface modification was also controlled on lines by using small X-ray spots (100 μm). Spectrometer calibration was performed using the manufacturer's procedure, which was completed by a self-consistent check on sputtered copper and gold samples, based on the ASTM E902-94 recommendation. The value of the $Au_{4f}{}^{7/2}$ binding energy is 84 eV.

Results and Discussion

1. Controlled Photoanodic Surface Treatment.

To limit the *n*-InP dissolution close to a single atomic layer, in NH_3 liq., a very weak electrochemical treatment must be applied at the interface.[20,21] To perform the anodic treatment, we used a galvanostatic mode over a low current density range (1, 5, and 10 μA/cm^2) under illumination. To ensure a weak surface modification, low coulometric

---

(15) Gonçalves, A. M.; Santinacci, L.; Eb, A.; Gerard, I.; Mathieu, C.; Etcheberry, A. *Electrochem. Solid-State Lett.* **2007**, *10*(4), D35.

(16) Gonçalves, A. M.; Seitz, O.; Mathieu, C.; Herlem, M.; Etcheberry, A. *Electrochem. Commun.* **2008**, *10*, 225.

(17) El Ali, O.; Gonçalves, A.-M.; Mézailles, N.; Mathieu, C.; Le Floch, P.; Etcheberry, A. *ECS Trans.* **2009**, *19*, 235.

(18) Simon, N.; Quach, N. C.; Gonçalves, A. M.; Etcheberry, A. *J. Electrochem. Soc.* **2007**, *154*, H340.

(19) Jander, J. *Anorganische und allgemeine Chemie in flüssigen Ammoniak. Part I, Friedr.*; Vieweg & Sohn: Braunschweig, Germany, 1966.

(20) Gonçalves, A. M.; Santinacci, L.; David, C.; Mathieu, C.; Herlem, M.; Etcheberry, A. *Phys. Status Solidi A* **2007**, *204*, 1286.

(21) Eb, E.; Gonçalves, A. M.; Santinacci, L.; Mathieu, C.; Etcheberry, A. *Phys. Status Solidi C* **2008**, *5*, 3484.

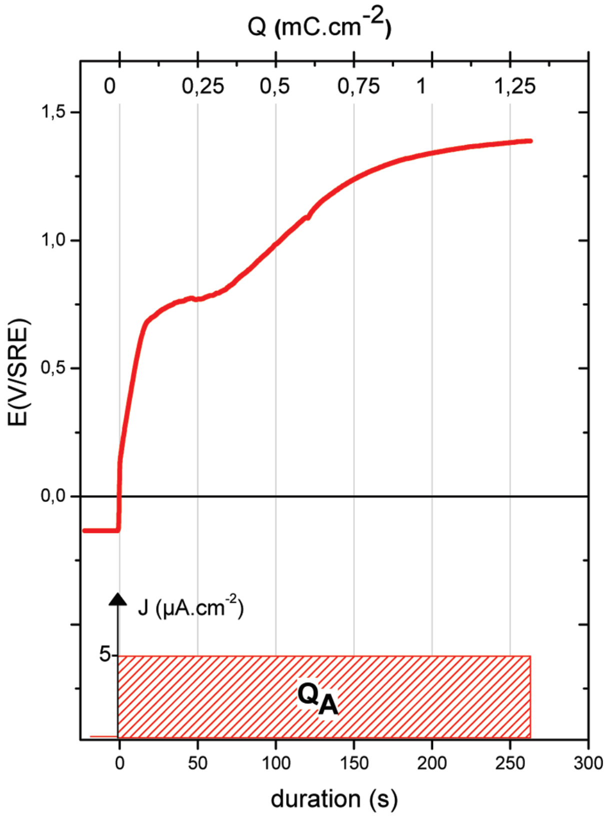


Figure 1. Interfacial potential evolution of *n*-InP in acidic NH_3 liq. (T = 223 K, [NH_4Br] = 0.1 M) for a galvanostatic treatment corresponding to 5 μA/cm^2. The controlled electrochemical process occurs under illumination and for a low coulometric charge (Q = 1.3 mC/cm^2) providing weak surface dissolution.

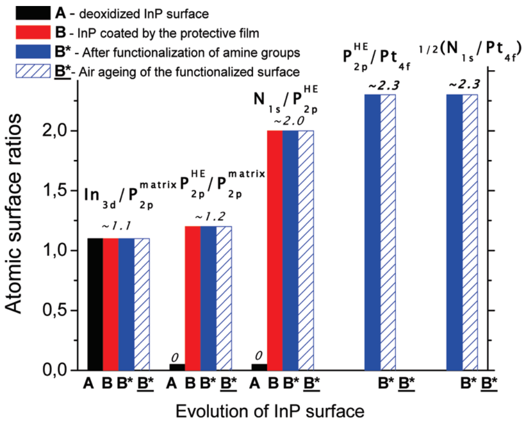


Figure 2. Significant atomic surface ratios observed for different InP surface treatments: (A) (black) onto a freshly deoxidized InP surface, (B) (red) after the anodic treatment in NH_3 liq. and air aging of the resulting surface for a long period of time (more than one year), (B*) (blue) after immersion for 16 h in a deoxygenated K_2PtCl_4 solution onto an InP surface previously treated with NH_3 liq. (B), and ($\overline{\mathrm{B}^*}$) (blue stripes) after air aging of the resulting functionalized surface (B*) for a long period of time (more than one year).

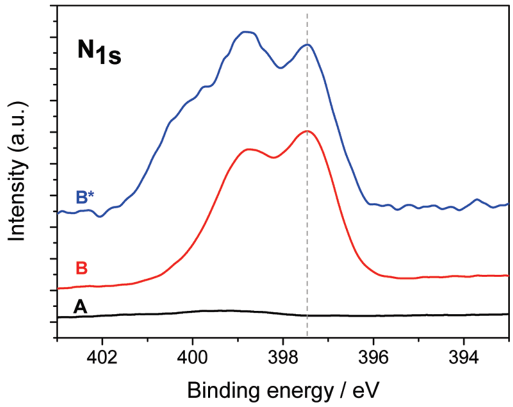


Figure 3. Comparison of XPS spectra for the N_{1s} contribution observed for different InP surface treatments: (A) (black) onto a freshly deoxidized InP surface, (B) (red) after the anodic treatment in NH_3 liq. and air aging of the resulting surface for a long period of time (more than one year), and (B*) (blue) after immersion for 16 h in a deoxygenated K_2PtCl_4 (3 mmol/L) solution onto an InP surface previously treated in NH_3 liq. (B) and after air aging of the resulting functionalized surface for a long period of time (more than one year).

charges, ranging from 0.7 to 2 mC/ cm^2, were used under potential control. As the constant anodic current is applied, a reproducible and specific variation of the interfacial potential is reported in Figure 1. From the very first 10 s, a potential step increase (approximately 0.8 V/SRE) is observed from the initial equilibrium potential (approximately −0.2 V/SRE). The resulting interfacial potential exhibits a gradual potential stabilization close to 1.4 V/SRE during the following 150 s of the controlled photoanodic treatment. An electrochemical modification of the InP−NH_3 liq. interface is therefore suggested by the striking evolution of the interfacial potential and its notable and reproducible stabilization. The evolution reproducibility is favored by the combination of the low-current regime and the light assistance that provide a regular hole collection at the interface with a lowest potential drop inside the InP space charge region.[22]

2. Film Composition. The assumption of a surface electrochemically modified was clearly demonstrated from XPS analyses. At an anodic charge of >0.7 mC/cm^2, XPS points out a constant modified chemical surface composition that obviously correlates with the interfacial potential stabilization (Figure 1). Indeed, in the 0.7−1.25 mC/cm^2 range, novel constant atomic ratios are evidenced which are associated with unsuspected additional phosphorus and nitrogen XPS contributions (Figure 2). The same ratios and new contributions are also supported by using a small X-ray spot, so notable homogeneity of the resulting surface is confirmed by XPS mapping analyses. The invariable chemical modification of the InP surface is noted B in all figures.

These specific XPS analyses are then compared to those of InP before anodic treatment (noted A in all figures; see Figure 2B vs Figure 2A). A contrasted chemical composition is strongly shown by a sample photoelectrochemically treated in NH_3 liq. In spite of the low anodic spent charges, a strong and specific nitrogen contribution (N_{1s}) is clearly evidenced after superficial electrochemical transformation of the InP electrode (Figure 3B vs Figure 3A). At the same time, for the phosphorus contribution, a new high-binding energy component appears at 133.5 eV, noted P_{2p}^{HE} (Figure 4B vs Figure 4A).

---

[22] Morrison, S. R. In *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*; Plenum Press: New York, 1980.

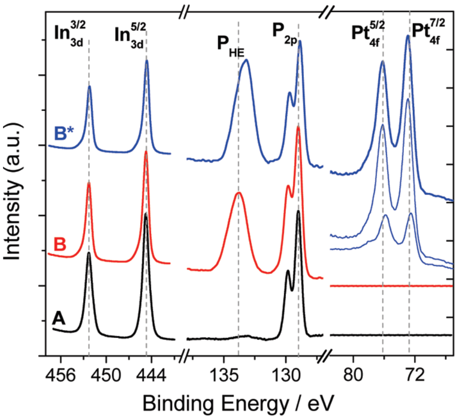


Figure 4. Evolution of indium, phosphorus, and platinum XPS spectra observed for different InP surface treatments: (A) (black) onto a freshly deoxidized InP surface, (B) (red) after the anodic treatment in NH_3 liq. and air aging of the resulting surface for a long period of time (more than one year), and (B*) (blue) after immersion for 16 h in a deoxygenated K_2PtCl_4 (3 mmol/L) solution on an InP surface previously treated in NH_3 liq. (B). Large oxidized Pt(II) peaks are centered at 72.5 eV ($Pt_{4f}^{7/2}$) and 76 eV ($Pt_{4f}^{5/2}$).The kinetic evolution of Pt(II) peaks is consecutively reported after 2, 7, and 16 h. The last reported peak (after 16 h) is also observed after an air aging of the resulting functionalized surface for a long period of time (more than one year).

In comparison to those of a bare surface, the P_{2p} spectra associated with the modified surface exhibit specific double features: the P_{2p}^{HE} high-energy one and the P_{2p}^{matrix} low-energy one. XPS analyses point out that both of these new and specific contributions (N_{1s} and P_{2p}^{HE}) are therefore exclusively related to the controlled photoanodic treatment in NH_3 liq. A constant ratio between the corrected areas of N_{1s} and the oxidized phosphorus component (P_{2p}^{HE}) of ~2.0 is always observed (see N_{1s}/P_{2p}^{HE} in Figure 2B vs Figure 2A). A perfect correlation between both of these new XPS contributions is indeed clearly established. In contrast, the In_{3d} energy contributions stay unchanged despite the NH_3 liq. treatment. XPS analyses of the starting deoxidized InP surface reveal the classical “In and P” double contributions for the indium phosphide matrix. On *n*-type samples, the $In_{3d}^{5/2}$ and $In_{3d}^{3/2}$ peaks are centered at 444.8 and 452.3 eV, respectively (Figure 4A). The concomitant phosphorus matrix contribution is observed at a lower binding energy (Figure 4A). Its double structure corresponds to the spin orbit splitting whose contributions are centered at 129 eV for $P_{2p}^{3/2}$ and 129.8 eV for $P_{2p}^{1/2}$. The area ratios of these exclusive matrix contributions, which are corrected by the sensitivity factors and the transmission parameters of the spectrometer, systematically give a predicted matrix ratio $(In_{3d}/P_{2p})^{matrix}$ of ~1.1, in full agreement with ratios observed on a deoxidized surface of InP ⟨100⟩.[18,23] Obviously, on a bare InP surface, all of the indium contribution is related to only In_{3d}^{matrix} (see In_{3d}/P_{2p}^{matrix} in Figure 2A).

In contrast to that of a bare surface, all of the indium contribution, after the controlled electrochemical process, can be as related to the matrix as the superficial electrochemical transformation of the InP electrode induced by the NH_3 liq. process. In spite of the photogalvanostatic treatment, this ratio remains constant and close to 1.1 (see In_{3d}/P_{2p}^{matrix} in Figure 2B vs Figure 2A). As a consequence, the total indium contribution detected on the modified surface is related to only the InP matrix. Most importantly for subsequent use, the high chemical stabilities of the modified uppermost layer and the buried InP surface are proved by the unchanged chemical composition even after exposure of the surface to air one year. As mentioned above, after the galvanostatic treatment, the double thin structure of indium peaks is still centered at 444.8 and 452.3 eV, which are perfectly superimposed with those of the unmodified oxide free surface (Figure 4B vs Figure 4A). On the molecular scale, XPS analyses of the phosphorus contribution showed the appearance of a high-energy peak at 133.5 eV as mentioned above. This high-energy peak is consistent with a new chemical environment of the phosphorus atoms of the surface. High-energy contributions for P_{2p} are usually related to oxide phases onto InP.[18,23] In this photoelectrochemical process, oxide phases are definitively excluded by the constant and reproducible N_{1s}/P_{2p}^{HE} ratios of ~2 (see N_{1s}/P_{2p}^{HE} ratios in Figure 2B vs Figure 2A). In this nonaqueous solvent, an oxygen−phosphorus bond in the modified surface film is therefore discarded from P atoms. In the same way, a constant $P_{2p}^{HE}/P_{2p}^{matrix}$ ratio of ~1.2 is always evidenced after the superficial electrochemical transformation in NH_3 liq. (see $P_{2p}^{HE}/P_{2p}^{matrix}$ ratios in Figure 2B vs Figure 2A). This ratio, ~1, gives evidence of a thin film covering the InP surface. This ratio is moreover outstandingly stable after air aging of the InP surface even after exposure to air for one year. The exceptional stability of these ratios ($P_{2p}^{HE}/P_{2p}^{matrix}$, N_{1s}/P_{2p}^{HE}, and In_{3d}/P_{2p}^{matrix}) proves, on one hand, the perfect coverage of the InP surface and, on the other, a constant thickness of the resulting thin film induced by the electrochemical treatment in NH_3 liq.

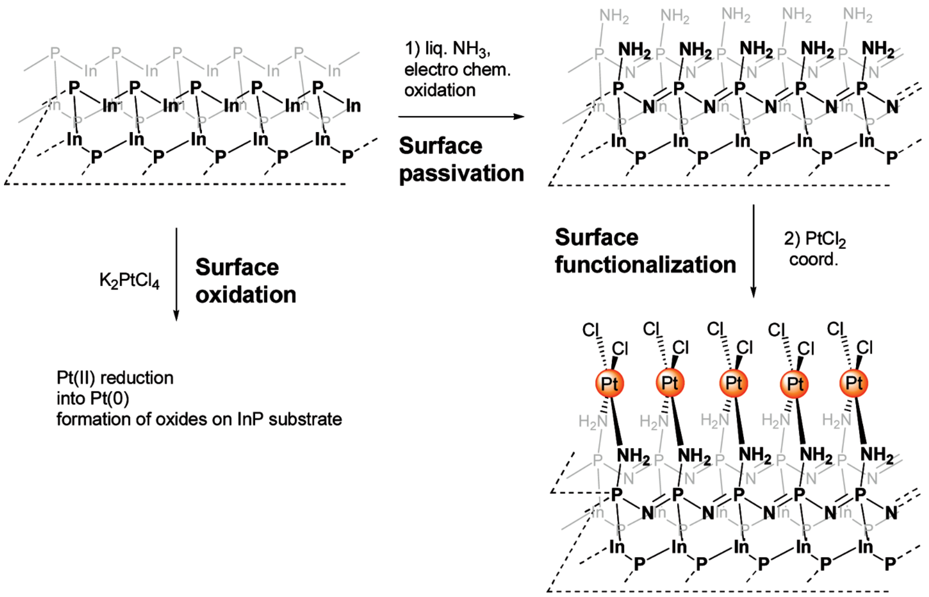
As the formation of the novel P_{2p}^{HE} contribution is concomitant with the appearance of two peaks corresponding to N_{1s}, the incorporation of nitrogen atoms into the thin film is proven. The constant N_{1s}/P_{2p}^{HE} ratios of ~2 (see N_{1s}/P_{2p}^{HE} ratios in Figure 2B vs Figure 2A) also provide evidence of the close chemical association of these two components incorporated in the thin film. Finally, the double structure of the N_{1s} peak demonstrates two different environments for the nitrogen atoms.

3. Surface Molecular Functionalization on a Stable Protective Film. Taken together, these data led us to postulate the selective and quantitative replacement of each indium center of the surface with a nitrogen atom, concomitant with the formation of a terminal $P-NH_2$ bond from each phosphorus center of the surface of the InP substrate (see Scheme 1). Importantly, this proposed chemical formula for the thin film is consistent with all the XPS data. The ultrathin perturbation of the interface agrees with the submillicouloms per square centimeter charge spent in the process. This formula is reminiscent of a polyphosphazene structure, involving a polymeric backbone consisting of formally $[P(R,R'){=}N]_n$ repeating

---

(23) Noten, P. H. L.; Van den Meeraker, J. E. A. M.; Kelly, J. J. *Etching of III-V Semiconductors: An electrochemical approach*; Elsevier Science: Amsterdam, 1991.

Scheme 1. Competitive Reactivity of Unprotected (bare surface) and Protected InP Substrates Besides an Oxidizing Solution of K_2PtCl_4



units, where R is an In center of the InP matrix and R′ is a terminal NH_2 moiety. The presence of multiple covalent bonds between In centers of the matrix and P centers of the surface is without doubt the key to the chemical stability of the thin film. At this point, however, the true nature of the terminal nitrogen moiety, although very likely, remained to be proven. On the basis of our "terminal NH_2" hypothesis, we reasoned that the film covered by amine functions would offer a unique opportunity for further surface molecular reactivity and open an entirely novel route for III−V semiconductor functionalization.

Experiments for proving simultaneously our two hypotheses were devised. These involve parallel exploration of surface reactivity of the covered InP surface by the thin film and bare InP samples with the same metal precursor, K_2PtCl_4. Indeed, only if the film contains terminal NH_2 moieties should we observe the coordination of the platinum (+II) center on the surface, since it is well-known that amino groups are efficient ligands of the $[PtCl_2]$ fragment. Furthermore, it is also well established that platinum grafting on surfaces is easily revealed by XPS analyses even at low coverages. Moreover, the different oxidation states of platinum (0, II, and IV) are defined by well-separated chemical shifts.[24] The hypothetical Pt(II) functionalization of the covered thin film onto InP (noted B* in all figures) is then compared to a surface reference state obtained by a direct reaction of $[K_2PtCl_4]$ with a bare InP surface (noted A* in all figures). The reference surfaces were again InP oxide free surfaces (noted A in all figures) obtained by suitable chemical etching.[18,23] The appropriately prepared InP samples were then immersed for at least 2 h in a deoxygenated solution of K_2PtCl_4 (3 mmol/L). The resulting samples were extracted and sheltered under a drop of solution, dipped in pure deoxygenated water, rinsed thoroughly with pure water, and dried under an argon stream before the immediate XPS transfer.

In Figures 4 and 5, highly contrasted effects of a K_2PtCl_4 solution are then reported as well on a bare InP surface (noted A) as on a covered InP surface by the thin film (noted B). On a bare surface, a strong oxidation of InP is demonstrated by XPS as shown in Figure 5A*. The $In_{3d}{}^{5/2}$ and $In_{3d}{}^{3/2}$ peaks are still centered at 444.8 and 452.3 eV, respectively, but for both sublevels, a dissymmetric shape is clearly observed at the higher energy, because of new oxide phase contributions. As a consequence, for P_{2p}, a new contribution is also evidenced at the higher energy, 133.4 eV (see $P_{2p}{}^{HE}$ in Figure 5A*). The enlargement at the higher energy for In_{3d} peaks and the new contribution for the P_{2p} component are observed on an oxidized InP surface.[23] A concomitant multicontribution for $Pt_{4f}{}^{5/2}$ and $Pt_{4f}{}^{7/2}$ is furthermore detected after contact with a platinum solution (Figure 5A*). Narrow $Pt_{4f}{}^{7/2}$ and $Pt_{4f}{}^{5/2}$ peaks are clearly distinguished at low

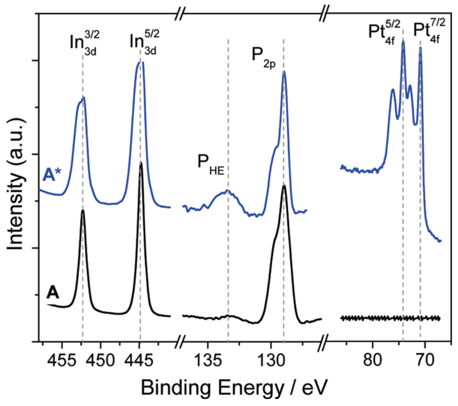


Figure 5. Evolution of indium, phosphorus, and platinum XPS spectra observed for different InP surface treatments: (A) (black) onto a freshly deoxidized InP surface and (A*) (blue) after damping InP, 2 h into a deoxygenated K_2PtCl_4 solution (3 mmol/L). Thin metallic Pt(0) peaks are centered at 71.1 eV ($Pt_{4f}{}^{7/2}$) and 74.3 eV ($Pt_{4f}{}^{5/2}$).

---

(24) Manolova, M.; Ivanova, V.; Kolb, D. M.; Boyen, H. G.; Ziemann, P.; Büttner, M.; Romanyuk, A.; Oelhafen, P. *Surf. Sci.* **2005**, *590*, 146.

energies and centered at 71.1 and 74.3 eV, respectively. These energies attest to metallic platinum found on the surface as reported in the literature.[24] Accordingly, strong chemical interfacial modifications of the initial oxide free InP surface occur in contact with the Pt(II) solution. Both Pt(II) reduction and InP oxidation are therefore simultaneously involved. This reaction is an original electroless process that coats simultaneously the surface with InP oxides and metallic Pt clusters. Near Pt(0) peaks, second very large contributions at higher energies are evidenced for each platinum peak contribution ($Pt_{4f}^{7/2}$ and $Pt_{4f}^{5/2}$). These higher-energy peaks centered at 72.5 eV for $Pt_{4f}^{7/2}$ and 76 eV for $Pt_{4f}^{5/2}$ are related to a double contribution involving equal amounts of platinum salt chloride and Pt oxide. The first contribution results from disordered adsorption phenomenon, and the second is associated with the detected electroless process.[25] As a consequence, on a bare InP surface, the aqueous neutral solution of K_2PtCl_4 behaves then as a strong chemical oxidizing reactant, leading to metallic superficial Pt clusters.

The same experiment performed on a covered thin film on InP gives rise to new and specific XPS responses (sample labeled B*). In Figure 4, resulting spectra are compared with those of the starting covered thin film (noted B) and the bare surface (noted A). Very significant information is provided by indium peaks. Although the immersion is 5 times longer than the one required to strongly modify a bare surface (Figure 5A*), indium peaks remain unchanged and can be perfectly superposed with those of the bare surface or the covered surface (Figure 4B* vs Figure 4A, and Figure 4B* vs Figure 4B). This result unequivocally establishes that the InP surface is perfectly covered and also perfectly protected by the film since no indium site is oxidized, unlike in the reference experiment (Figure 5A* vs Figure 5A).

Note that the double contribution of the P_{2p} region also remains unchanged and indistinguishable from those observed on the covered thin film (Figure 4B* vs Figure 4B). The corrected intensity ratio of the indium signal with this P_{2p} is still 1.1 (see In_{3d}/P_{2p}^{matrix} in Figure 2B*). These observations led us to conclude that units of InP from the matrix are definitively not available and that covalent bonding between the InP outer layer and the protective monolayer is thus very robust. Even if the InP substrate is protected from oxidation, a platinum species is firmly bonded to the passivated film. A kinetic evolution of the platinum content is indeed observed, and a saturation of platinum grafting on the passivated surface is evidenced after reaction for 16 h (Figure 4B*). No metallic platinum is detected, and only platinum salt contributions are evidenced at the high energy: $Pt_{4f}^{7/2}$ and $Pt_{4f}^{5/2}$ peaks associated with Pt(II) are detected at 72.5 and 76 eV, respectively. The Pt(II) coordination sphere is therefore maintained. We can propose, in good agreement with literature,[24] that these contributions are related to the coordination of $PtCl_2$ to NH_2 sites available on the passivated film. Finally, formation of platinum oxide via an electroless process can also be excluded as proven by the very unfavorable oxygen balance obtained by XPS analyses. The electronic structure of the film is drastically modified by coordination of the [$PtCl_2$] fragment as shown by the following data. First, the high-binding energy peak centered at 133.5 eV for the P_{2p}^{HE} component bonded to nitrogen is now slightly but significantly shifted to a lower energy (see P_{2p}^{HE} on Figure 4B* vs Figure 4B), suggesting that the chemical environment of P_{2p}^{HE} is modified during the functionalization of the film.

The second important result concerns the nitrogen atoms. In the InP passivated film, the N_{1s} spectrum is fitted by two components with the same areas (Figure 3B). While the N_{1s} peak centered at 397.5 eV remained unmodified upon functionalization, a large distortion of the N_{1s} contribution centered at 398.7 eV is clearly detected, showing that only one of the two nitrogen atoms undergoes an important modification of its chemical environment (Figure 3B*). Finally, the third piece of important information is provided by the atomic surface ratios. The fact that the two ratios, In_{3d}/P_{2p}^{matrix} and $P_{2p}^{HE}/P_{2p}^{matrix}$, remain constant even after air aging of the functionalized platinum surface (Figure 2B*) confirms that the chemical bonding between the film and the InP surface is not altered. Moreover, we also note that the ratio between the corrected areas of N_{1s} and P_{2p}^{HE} is always close to 2.0 as in the starting passivated material (Figure 2B vs Figure 2B*). Overall, these results prove the perfect coverage of the InP matrix by a protecting yet functionalizable monolayer. As a consequence, with the protective film on the InP surface, the aqueous solution of K_2PtCl_4 is used as the root of film functionalization.

The accurate chemical nature of this layer is revealed by the ratios of the electronically modified atoms (P and one of the two N atoms of the surface) with the Pt center. The P_{2p}^{HE}/Pt_{4f} ratio of 2.3 clearly indicates that two phosphorus atoms per [$PtCl_2$] fragment are involved in the hybrid structure (Figure 2B*). The same accurate ratio is obtained taking into consideration half of the nitrogen surface in the hybrid structure [see $1/2(N_{1s}/Pt_{4f})$ in Figure 2B*]. We can state that two amino groups, directly bounded to the P atoms, are now coordinated per platinum center. On the grounds of the gathered results, a novel stable hybrid structure is evidenced. It results from a InP pavement by polymeric polyphosphazene[26] units on which [$PtCl_2$] fragments are coordinated to form square planar d^8 complexes. An idealized view of this designed hybrid architecture of the ultrathin polyphosphazene film on the InP matrix is reported in Scheme 1.

Conclusions

The controlled photoelectrochemical anodic treatment of the InP surface using NH_3 liq. leads to the formation of a novel stable protective thin film which is a remarkable polyphosphazene-like network. This significant support

---

(25) Manandhar, S.; Kelber, J. A. *Electrochim. Acta* **2007**, *52*, 5010.

(26) Allcock, H. R. *Chemistry and Application of Polyphosphazenes*; John Wiley and Sons: New York, 2003.

through its amine function provides also a powerful entry for the elaboration of functionalized and highly stable materials. The quality and reproducibility of the passivation are reached by the combination of imposed low anodic currents and assisted soaking light. A resulting quantitative surface modification can be claimed by the use of this very weak growing condition. Competitive experiments between the resulting thin film and a bare InP surface clearly support the protective efficiency and robustness of the thin film toward the oxidizing platinium solution. This chemical protection, at a molecular scale, establishes that the InP surface is perfectly covered by the efficient protective film. The resulting covalent bonding between the InP matrix and the film is very strong. In contrast, on a bare InP surface, the surface oxidation is unavoidable. Significantly, we show here, for the first time, that this protective layer on InP can also be functionalized by the successful and almost quantitative coordination of [$PtCl_2$] fragments. In turn, this proves the proposed structure of the film to be a phosphazene network in which the surface is paved with reactive NH_2 moieties. The evidence of the polyphosphazene film molecular reactivity opens a completely novel route for III−V semiconductor functionalization. These results open the way for a systematic investigation of the reactivity of this protected film toward organic or inorganic fragments and to the elaboration of optoelectronic devices through molecular grafting. Studies in this direction are currently ongoing in our laboratories.