Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Direct correlations between XPS analyses and growth film by chronopotentiometry on InP in liquid ammonia (−55 °C)

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ARTICLE INFO

Article history:
Received 24 December 2015
Accepted 2 March 2016
Available online xxx

Keywords:
Passivation
Semiconductor electrochemistry
Galvanostatic methods
InP
Liquid ammonia
XPS

ABSTRACT

This paper is based on the understanding of the formation of a reproducible polyphosphazene-like film (—[(H_2N)—P=N]$_n$—) obtained on InP by anodic treatment in liquid ammonia. The approach is innovative as it combines indications from the coulometric charges and the related chemical information from XPS analyses. Anodic charges are accurately monitored by galvanostatic treatment between 0.05 mC cm^{-2} and 12.5 mC cm^{-2}. XPS investigation of the treated surfaces demonstrates the presence of an anodic film on InP. Whatever the spent charge, the specific P_{2p} and N_{1s} signals agree with the growth of an ultra-thin phosphazene layer. From 0.25 mC cm^{-2} to 12.5 mC cm^{-2}, a quasi constant XPS response is revealed without thickening of the film. However a gradual chemical evolution of the modified surface is clearly observed for the lower anodic charges (from 0.04 mC cm^{-2} to 0.5 mC cm^{-2}). In this case, the surface is entirely recovered by the film as soon as 0.25 mC cm^{-2} is consumed at the interface. Same atomic surface ratios are indeed revealed indicating that a constant chemical composition is consistent with a polyphosphazene film. On the basis of atomic surface ratios evolutions determined by XPS, a mechanism of the film growth is deduced. It requires a nucleation step which is followed by a phosphazene coalescence phenomenon in the two dimensions of the surface. A final phosphazene monolayer film is suggested if a sufficient anodic charge spent at the interface is considered, allowing a quantitative discussion related to electrochemical and XPS data.

1. Introduction

Monitoring efficiently the surface chemistry of semiconductors is still a challenge for a lot of semiconductors devices with high added value whose performances depend essentially on surface passivation states. This is true for III–V semiconductors (III–Vs) such as InP and InP-based devices which suffer from interfacial or surface chemical instabilities due to spontaneous surface oxidation and related side reactivity. Optoelectronic and electrical properties are then drastically affected due to the high resulting density of traps at the insulator/semiconductor interfaces or surfaces. The stakes are high if we consider the integration of III–V's on large scale silicon platforms and device scaling to nanometer range. As a consequence, questions related to III–V passivation remains on the front page again [1,2]. Among all methods for surface passivation, electrochemical technique can be an effective way [1].

In aqueous medium, electrochemical techniques can be used to control the growth of various oxide compositions on InP surface [1,3–5]. Depending on the applied electrochemical parameters (current density, interfacial potential), different anodic films can be grown on InP in aqueous media [6,7]. The use of non-aqueous solvents provides a larger potential window to the electrochemical response of semiconductors (SC). However, in past decades, many electrochemical studies in non-aqueous solvents have been revealed to be ruled by moisture, *i.e.* side water chemistry (see *e.g.* Ref. [8]). As a solvent, liquid ammonia (NH_3 *Liq.*) has found a distinguished place in electrochemical studies of semiconductors. In NH_3 *Liq.*, chemical environment is obviously different from water, since their dielectric constant, viscosity coefficients are strongly different [9]. Compared to other non-aqueous solvents, liquid ammonia provides a better control of water traces [10]. Moreover, its electrochemical decomposition does not induce "side reactions" which could contaminate the electrode surface. Indeed, ammonia anodization leads to the formation of N_2 while its reduction to hydrogen evolution in acidic and neutral pH is established [11]. As a consequence electrochemistry in liquid ammonia differs strongly from than occurs in aqueous solution but also in classical organic solvent.

In liquid ammonia (−55 °C), the chemical passivation of InP (-*n* and -*p* types) was carried out under anodic overvoltage as

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http://dx.doi.org/10.1016/j.apsusc.2016.03.019
0169-4332/

well in the dark as under illumination [12,13] in acidic medium. The crucial step is the extraction of InP sample from the solvent from −55 °C to ambient temperature. This stage can be monitored by moving carefully the semiconductor from the solvent under an argon stream. In acidic NH_3 *Liq*., whatever the electrochemical technique used (cyclic voltammetry, chronopotentiometry, potentiometry) the formation of a polyphosphazene-like film was shown on the surface [12,13]. Polyphosphazenes are rich chemical compounds in which phosphorus atom is doubly bounded to nitrogen and two reactive functions are also bounded to this same phosphorus [14]. The phosphorus of the polyphosphazene-like film on InP involves also two reactive functions. One corresponds to the matrix of InP and the other to an amino group which provides the formation of the primary stable inorganic hybrid structure on InP [12]. This film opens a new way for further functionalization, as demonstrated by the chemically controlled coordination of Pt(II) [12]. The opportunity of substituting chloride on the phosphazene backbone by abundant and relevant functional groups leads to a rich and active chemistry [14]. Moreover, the perfect coverage of the surface by the polyphosphazene-like film is revealed by XPS analyses since no degradation of the film chemistry is shown as well by XPS as photo-luminescence and electrochemistry [12,15]. The high chemical stability of the passivated surface offers new opportunities for III-Vs integration in electronic devices. Phosphorus nitride insulating films as chemical passivation layers on InP seem to be very attractive to realize MISFETs with high channel electron mobilities and low interface state densities. Even if the proof of the stability of polyphosphazene-like film and the functionalization opportunities are demonstrated, the growth of the passivated film is still unknown. According to the electrochemical technique used (cyclic voltametry, chronoamperometry), the polyphosphazene-like film requires an anodic charge widely variable, from 7 mC cm^{-2} to 22 mC cm^{-2} [12,16]. The understanding of the growth mechanism is crucial to extend this promising passivating process to other III–V and also II–VI semiconductors. In this paper, lower anodic charges are explored using galvanostatic technique. According to the anodic charge spent at the interface, the chemical evolution of the surface is carried out by XPS analyses to follow the different stages until a complete passivation of the surface by the polyphosphazene film.

2. Experimental

n-InP semiconductor wafers with a <100> orientation were purchased from InPact Electronic Materials, Ltd. Doping density of 10^{18} atoms cm^{-3} were used. The wafers were cut into small squares (0.5×0.5 cm^2). Prior to use, *n*-InP was chemomechanically polished with a solution of bromine in methanol (1%), rinsed with methanol, and dried under an argon stream. Before each anodic treatment the sample is immersed in HCl 1 M to perform a good desoxidation of the surface. Gaseous ammonia was directly condensed in the electrochemical cell at low temperature and atmospheric pressure [17]. In order to ensure this, the electrochemical cell was plunged directly into a Dewar flask containing a combination of acetone and dry ice which is kept at constant T° around −65 °C. The glass column vacuum was obtained using a primary pump. A mercury column, which was combined to the vacuum column, was used as a pressure control, and as a safety valve. The electrochemical glass cell was connected to the vacuum column. The volume of liquid ammonia inside the cell was nearly 150 cm^3. After ammonia condensation the semiconductor was immersed in the electrochemical cell which was kept at low temperature (−55 °C) in a cryostat. The illumination of InP was provided by a halogen lamp thanks to the use of an optical fiber. The deoxygenation of the medium was performed under an argon stream to avoid parasitic reaction during the anodic electrochemical treatment.

Ammonium bromide with a concentration of 0.1 M, (purest available quality from Aldrich) was added to the medium. It provided as well the conductivity of the medium as a pH equal to 1 referred to the pH scale in NH_3 *Liq*. [9,18]. As a consequence, the flat band potential of InP was kept constant under this buffered acidic conditions [10]. All potentials were measured against a pseudo silver reference electrode (SRE) [17,18]. The electrochemical set-up was a classical three-electrode device. Electrochemical measurements were performed with a 2273 Partstat potentiostat. Various current densities were applied at the interface InP/NH_3 *Liq*. using galvanostatic technique under illumination to follow the gradual formation of the anodic polyphosphazene-like film on *n*-InP. The applied current densities were at least five times lower than the resulting photocurrents for the same flux conditions. In this way, holes were only photogenerated when anodic currents were kept constant under illumination. As a consequence , no overvoltage was observed avoiding then the InP porosification phenomena for which non-photogenerated holes were involved [19]. At room temperature, InP samples are thoroughly rinsed afterwards with deionized water. InP samples are then carefully placed in the transferred box to XPS chamber. With this type of transfer device (under argon), oxygen contamination is minimized. XPS analyses were performed on an K-Alpha spectrometer thermo electron. The monochromatic AlKα line was used as X-ray excitation (1486.6 eV) with pass energy of 20 eV to obtain high resolution spectra. Large X-ray spots (400 μm) 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. XPS atomic compositions as peak fitting are achieved using the Avantage software developed by Thermo Scientific.

3. Discussion

For monitoring the evolution the formation of the polyphosphazene-like film, various anodic current densities (from 1 μA cm^{-2} to 50 μA cm^{-2}) are applied at the interface InP/NH_3 *Liq*. Whatever the constant currents, reproducible and specific variations of the interfacial potential are reported in the Fig. 1I. As soon as the current density is applied, a step increase of the potential is observed from the open circuit potential (−0.2 V *vs*. SRE). The potential spike is then followed by two consecutive stationary potential features. The presence of two potential plateaus reveals at least two electrochemical steps during the formation of the polyphosphazene-like film [16]. Same final potentials are reached whatever the applied current density. Indeed the first stationary potential is around 0.35 V *vs*. SRE while the second is about 1.35 V *vs*. SRE. This fact is even more significant as the same electrochemical mechanism can be assumed whatever the applied current. However, the duration of the first potential plateau depends on the applied current density. The higher the current density, the less is the duration of the plateau. The duration of the first plateau is about 10 s for J = 50 μA cm^{-2}, while 50 s is required for J = 10 μA cm^{-2} and 100s for J = 1 μA cm^{-2}. Under illumination, galvanostatic treatments involve only photogenerated holes because the photocurrent is at least five times higher for the same flux condition. As a consequence under illumination, a low band bending is observed [20]. In this way, InP dissolution can be prevented as possible since the electrical field in the space charge layer becomes weaker than in the dark [20]. As a result,

Please cite this article in press as: A.-M. Gonçalves, et al., Direct correlations between XPS analyses and growth film by chronopotentiometry on InP in liquid ammonia (−55 °C), Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.03.019