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Growth and formation of hybrid structures on InP by alternated anodizations in aqueous media and liquid ammonia

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Abstract

Results about electrochemical anodic passivation of indium phosphide formed sequentially in two electrolytes with contrasted properties are reported for the first time. Using a galvanostatic method, oxidation of the InP surface has been formed initially at pH 9 with a current density of 0.2 mA cm^{-2}, while the anodization was achieved under illumination in liquid ammonia by cyclic voltammetry. Capacitance−voltage measurements in aqueous media coupled with cyclic voltammetry in liquid ammonia indicate the covering level of the two kinds of anodic layers, whereas XPS analysis gives access to chemical composition of hybrid structures. As a first result, the different measurements reveal the great stability of anodic oxide in liquid ammonia, at each step of oxide coverage. As a second result, the formation of a mixed layer with both oxide and ‘‘P−N’’ terminations has been evidenced by XPS. A new route of InP passivation was clearly established by this alternated anodization process. ***To cite this article: A.-M. Gonçalves et al., C. R. Chimie 11 (2008).***

Résumé

Pour la première fois, l’anodisation électrochimique du phosphure d’indium a été réalisée successivement dans deux électrolytes très différents : le milieu aqueux et l’ammoniac liquide. L’anodisation de InP est d’abord réalisée à pH 9 par voie galvanostatique en appliquant une densité de courant de 0,2 mA cm^{-2}. Le traitement se poursuit dans l’ammoniac par voltamétrie cyclique sous éclairement. Les mesures de capacité interfaciale réalisées en milieu aqueux et la voltamétrie cyclique effectuée dans l’ammoniac liquide ont permis d’évaluer le taux de recouvrement des différents films anodiques. Les analyses spectroscopiques de surface (XPS) ont quant à elles permis d’accéder à la composition chimique des surfaces ainsi traitées. Le premier résultat majeur est la mise en évidence de la grande stabilité, dans l’ammoniac liquide, du film d’oxyde réalisé en milieu aqueux. Cette stabilité est vérifiée quel que soit le taux de recouvrement de l’oxyde à la surface Hd’InP. Le deuxième résultat majeur est la mise en évidence par XPS d’une structure hybride en surface, combinant à la fois des oxydes et des terminaisons de type « P−N ». Une nouvelle voie de passivation Hd’InP est ainsi obtenue par des traitements électrochimiques alternés. ***Pour citer cet article : A.-M. Gonçalves et al., C. R. Chimie 11 (2008).***

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1. Introduction

In aqueous media, electrochemical methods can be used to control the growth, on InP, of different kinds of oxide structures [1–5]. In particular, at pH 9, the growth and formation of thin $InPO_4$-like anodic films have been evidenced [6–8]. By modifying the anodization parameters (*i.e.* current density and treatment time), the oxide coverage can be controlled from an island stage up to a complete covering by a homogeneous layer with good electrical blocking properties [6–8].

Anodic treatment can be carried out in true water-free conditions when using high-purity (electronic grade quality) liquid ammonia (NH_3 liq.). As a polar solvent, NH_3 liq. exhibits unique physical properties such as low viscosity, allowing better conductivity than in aqueous media. Compared to water its low dielectric constant makes liquid ammonia a poorly dissociating solvent. Ammonia molecules are therefore available for chemical interfacial processes onto semiconductors. Thus, a new interface is expected due to oxygen-free surfaces and an interfacial electrochemistry ruled by ammonia molecules. A reproducible thin passivated film involving phosphazene terminations has recently been evidenced by XPS analyses and stability tests. A specific "P–N" surface chemistry was evidenced and associated with a phosphinimidic amide-like electrodeposition [9,10]. The efficiency of this new passivation route was supported by the high stability of the complete covering thin film, since no air ageing effect is detected on the InP surface [9,10].

The aim of this present work was, on the one hand, to investigate in liquid ammonia the chemical stability of anodic oxides prepared in aqueous media and, the other hand, to combine the good electrical blocking properties of this oxide layer with specific "P–N" surface bonds resulting from anodic treatment in liquid ammonia.

2. Experimental

n-InP wafers with a (100) orientation were purchased from InPact Electronic Materials, Ltd, with a doping density of 10^{18} cm^{-3}. The wafers were cut into small squares (0.5×0.5 cm^2). Prior to use, semiconductors were chemomechanically polished with a solution of bromine in methanol (2%), and rinsed with purest methanol and dried under an argon stream [4,8,11–13]. In order to remove residual oxides, samples were dipped for a few minutes in 2 M HCl just before the experiment [8,14,15].

The electrochemical set-up was a classical three-electrode device, using a 283 EG&G potentiostat–galvanostat. Anodic treatments were initially done in an aqueous borate buffered Tritisol (Merck) solution, at pH 9, using a classical three-electrode configuration with a Mercury Sulfate Electrode ($E_{MSE} = +0.65$ V/SHE) as reference and a large Pt counterelectrode. Oxidation treatments in aqueous media were carried out by applying a constant anodic current density, $J_a = 0.2$ mA cm^{-2}. Treatment durations varying from 1 s to a few minutes were applied. Capacitance measurements *vs.* potential, $C(V)$, were used to probe the oxide covering level. $C(V)$ measurements were carried out in the dark, before and after oxidation treatments, in aqueous media, with a linear potential scan of 10 mV/s. The sinusoidal modulation frequency was set at 1107 Hz and the peak-to-peak amplitude at 20 mV.

Ammonia condensation, from gaseous ammonia ("electronic grade" from Air Liquide), was provided by a glass column assembly and required a low operating temperature under atmospheric pressure [16]. An electrochemical cell filed up with 150 cm^3 of liquid ammonia was maintained at 223 K in a cryostat. The acidic medium was obtained by addition of 0.1 M NH_4Br (purest available quality from Aldrich). All potentials were measured *vs.* a silver reference electrode (SRE) [17]. The electrochemical set-up was also a classical three-electrode device, with a linear potential scan of 20 mV/s. Current–voltage curves were performed under illumination using an optical fiber with a tungsten lamp. After the anodic treatment in NH_3 liq. at open circuit, InP was rinsed in purest liquid ammonia and the sample was then transferred towards an XPS analyzer using a procedure avoiding any air contamination [10].

XPS analysis was performed on a V.G-Escalab 220 iXL, spectrometer. A focused monochromated X-ray beam (Al Kα) was used for excitation. For detection a constant analyzer energy mode was used, with pass energy of 8 or 20 eV. Photoelectrons were collected perpendicularly to the surface. Calibration of the