C. R. Chimie 16 (2013) 34–38

Contents lists available at SciVerse ScienceDirect

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Stability of InP oxide versus solvated electrons in liquid ammonia

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ARTICLE INFO

Article history:
Received 12 December 2011
Accepted after revision 24 January 2012
Available online 3 March 2012

Keywords:
Non-aqueous solvent
Liquid ammonia
III-V semiconductor
Solvated electron
Interface
Oxide surface

ABSTRACT

In alkaline aqueous medium (pH 9), potassium ferricyanide was used as an oxidizing agent on InP. This electroless process was successfully controlled by capacity measurements, AFM and XPS analyses. For the first time, the chemical stability of the oxide has been studied against the strongest reducing agent in liquid ammonia (−50 °C): the solvated electron. It was obtained in two ways; an electroless process which involved the addition of metallic potassium and by cathodic galvanostatic treatment on InP in neutral medium. As a first result, the electroless process required a strong rinsing step of the surface by pure liquid ammonia. As a second result, the galvanostatic process gave also promising results. A significant decrease of the amount of oxide was evidenced by capacity measurements, AFM and XPS analyses.

1. Introduction

Indium phosphide is an attractive material for high-speed optoelectronic devices. Its integration in electronic devices is, however, still complex due to chemical instabilities of the InP surface. In aqueous media, many works have been performed to control the growth of different kinds of oxide structures on InP by electrochemistry [1–4]. In particular, at pH 9, the growth and formation of thin $InPO_4$-like anodic films has been evidenced [5–8]. According to the anodization parameters (i.e. current density and treatment time), the oxide coverage could be controlled from an island stage up to a complete covering by a homogeneous layer with good electrical blocking properties [6,8].

However, the etching of the oxide layer becomes also a crucial step when no interesting properties are evidenced. The dissolution of the semiconductor (SC) involves generally its oxidation. Two mechanisms are distinguished: either an electrochemical oxidation or a chemical oxidation process. Both techniques have made a significant contribution to the research and development of III-V devices [4,9]. In practice, the chemical etching is still a complex multi-step reaction involving surface bonded atoms. In addition, a strong anisotropy is often observed [10]. This process inhibits, then, a homogeneous dissolution of the oxide surface. In contrast to the chemical process, the electrochemical technique involves the injection of holes in the valence band of the semiconductor [11]. The electrochemical process can be performed in two ways. The first way involves the polarization of the interface SC/electrolyte using an external circuit. The second requires a strong oxidizing agent in solution. Since this electroless method does not require an electrochemical cell and voltage source, it is more attractive for many applications [4].

This work is a further contribution to this research. This study is divided in two parts. In the first part, the formation of an oxide on InP is controlled using an electroless process in aqueous solution. In the second part, the chemical stability of the resulting oxide is studied in liquid ammonia (NH_3 *Liq.*) against the strongest reducing agent: the solvated electron.

2. Experimental part

InP-*n* semiconductor wafers with a <100> orientation were purchased from InPact Electronic Materials, Ltd.

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doi:10.1016/j.crci.2012.01.010

A doping density of 10^{18} cm^{-3} was used. 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 (10%), and rinsed with purest methanol and dried under an argon stream [6–8]. In order to remove residual oxides, samples were dipped for a few minutes in 2 M HCl [6–8,12]. In aqueous media, potassium ferricyanide (3×10^{-1} M) was dissolved in alkaline solution (pH 9). This solution was the oxidizing electrolyte. The electrochemical studies were performed in a borate buffered Tritisol (Merck) solution at the same pH, using a classical three-electrode device. The mercury sulfate electrode (MSE = +0.65 V/SHE) was used as a reference electrode and a large Pt electrode as a counter electrode. Capacitance-measurements versus potential, *(C-V)*, were used to probe the oxide covering on InP. Differential capacitance voltage *(C-V)* measurements were carried out in the dark, after the oxidation treatments of InP in the oxidizing electrolyte (pH 9). The sinusoidal modulation frequency was set at 1107 Hz.

Ammonia (electronic grade) was purchased from Air Liquide. The cell and equipment for condensing ammonia have already been described [13]. The volume of liquid ammonia was approximately 150 cm^3 and the cell was maintained at 223 K in a cryostat. The neutral media was obtained by addition of KBr (0.1 M) providing also the conductivity of the electrolyte. All potentials were measured vs. a silver reference electrode (SRE) [14]. The deaeration of the medium was performed under an argon stream. The electrochemical set-up was also a classical three-electrode device, using a PARSTAT 2273 potentiostat. Solvated electrons were obtained from two mechanisms. The first was the reaction of an alkali metal (potassium) with liquid ammonia [15]. The second was a cathodic galvanostatic treatment on InP in neutral medium [16]. X-ray photoelectron spectroscopy analyzer (XPS) were performed on an Escalab 220 i XL, V.G. spectrometer. A focused monochromated X-ray beam (Al Kα) was used for excitation. For detection constant analyzer energy mode was used, with pass energy of 8 or 20 eV. Photoelectrons were collected perpendicularly to the surface. Calibration of the spectrometer was done using the E902-94 ASTM procedure. The surface roughness was characterized by AFM using a contact and mapping mode (D300, Digital instrument, WsXM software). Each stage was analyzed: the initial surface of InP, the oxidized InP surface and after solvated electrons effect on the oxidized InP surface.

3. Results and discussions

The ferricyanide ion was used as a strong oxidizing agent in alkaline solution at pH 9. This oxidizing agent was reduced by injections of holes in the valence band of InP [4,7]. In parallel, the oxidation of InP was then resulting from the migration of holes to the surface due to the electrical field on the space charge layer. By damping the semiconductor in the potassium ferricyanide solution, InP was oxidized from one hour to 16 hours. This open circuit oxidation of InP was a really attractive process since no electrochemical cell and voltage source were required. The sample was properly removed from the potassium ferricyanide solution (pH 9) to a buffered borate electrolyte (pH 9). Before this transfer, a rinsing step of InP with deionized water was required to avoid a contamination from ferricyanide ions. The oxide on InP was characterized by capacity measurement using Mott-Schottky relation ($C^{-2} = f(V)$). During the capacity measurements, a potential drop across the oxide/InP interface. The variation of the potential was used as an in situ probe of the oxide density on InP. Before and after InP oxidation, a parallel positively shift of $C^{-2}(V)$ plots was observed. A significant variation of the flat band potential (≈ 400 mV) was evidenced, with a good stability over time (Fig. 1). The linearity of the plots is kept until 30 min. The linearity of C^{-2} *(V)* plots suggests that only a modification of the space-charge capacitance could explain dependences of C^{-2} *(V)* [4]. However, we cannot omit that an extra potential drop can appear in the oxide layer or in the Helmoltz layer [4–11]. This phenomenon has already been observed on InP using also a buffered solution at pH 9 [7]. The parallel shift of C^{-2} *(V)* plots was associated to the formation of oxide islands on InP. However, some deviation from the linearity was observed for a longer time (1 and 16 h). This behavior can suggest a limitation of growth oxide on InP [7]. The surface of InP can be entirely covered with oxide. A notable modification of InP surface was then revealed after the electroless oxidation process. From constant capacity measurements, a good stability of this surface modification was evidenced.

In order to reveal this surface transformation, the chemical composition of the surface was analyzed by X-ray photoelectron spectroscopy (XPS) (Fig. 2). Reproducible In3d (In3d$_{5/2}$ and In3d$_{3/2}$) and P2p (P2p$_{1/2}$ and 2p$_{3/2}$) photoelectron peaks were obtained for different samples. In3d and P2p peaks were compared before and after the oxidizing treatment on InP. New contributions, positively shifted to higher energy were observed for In3d and P2p. They were associated with oxidized phases on InP such as

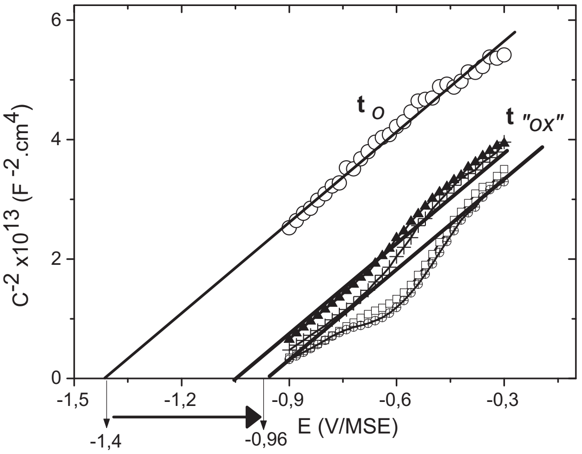

Fig. 1. Mott-Schottky interfacial capacitance ($C^{-2} = f(V)$) on *n*-InP in alkaline buffered aqueous solution at pH 9 in the dark. **t**$_O$: initial state of the surface. **t** $_{\text{"}Ox\text{"}}$: after the oxidation treatment of InP surface (1 h) in the ferricyanide aqueous solution at pH 9. Resulting $C^{-2} = f(V)$ for different period in the buffered solution (▲: 15 min, +: 30 min, ▣: 1 h, ○: 16 h).