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The pH response of the InP/liquid ammonia interface at 223 K: A pure nernstian behavior

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ABSTRACT

Liquid ammonia (NH_3 *liq.*) provides an original electrochemical environment onto semiconductors electrodes (SC). Its particular interest is that water influences can be neglected in opposition to a lot of non-aqueous other solvents. Fundamentals electrochemistries of the SC are related to the energy diagram of the interface. In this paper it is established into NH_3 *liq.*, on both types, on p- and n-InP by flat band potential (V_{fb}) measurements. The V_{fb} are determined over the whole range of pH that reaches 33 pH units in this non-aqueous solvent. InP exhibits a pure nernstian behavior with a specific 44 mV/pH slope at 223 K. This is particular compare to the "under nernstian" dependency, observed in water onto InP. The actual band positions are related to the initial chemical state of the InP surface, since oxide free surfaces and thin native oxide covered surfaces differ slightly. Reproducible contrasted results from the acid–base equilibrium, which is supported by the V_{fb} according to the pH, for singular interfacial chemistry. This aspect is confirmed by XPS measurements performed before and after InP immersion into NH_3 *liq*. They establish the perfect stability of the initial chemical composition of the semiconducting surface in contact with NH_3 *liq.* whatever its pH conditions. NH_3 *liq.* appears as an inert solvent which is able to create an acid–base equilibrium onto InP surfaces. Each InP surface chemistry support its own linear V_{fb} *vs.* pH variation. In NH_3 *liq.*, the poor water control on the building of the Helmholtz layer is well shown by the perfect V_{fb} alignment position from the intermediated pH buffered solution obtained from the addition of tetraethyl ammonium hydroxide ($(Et)_4N^+,OH^-$) dissolved in water (20%).

1. Introduction

The establishment of the semiconductor/solution interfaces induces complex interfacial phenomena which leads to equilibrium the energy diagrams of the resulting interfaces. This fundamental concept of semiconductor electrochemistry has been extensively studied through couples of semiconductors and solvents [1]. Each interface has their suitable characteristics which depend on the initial surface chemistry of the immersed semiconductor, on the nature of the solvent. The resulting chemical and physical interactions act for the interface formation. Among the numerous interactions, one of the key phenomena, are the local acid–based reactions supported by the surface lattice in front of the solvent. The more obvious expression of this interaction is observed through the V_{fb} *vs.* pH dependencies that are observed for most of the semiconductors. For III–Vs, it is reported that acid–base interactions play an important role in the interface building [1,2].

When pH parameters keep a main role at the interface, more or less established nernstian behaviors are observed for the V_{fb} dependencies with the pH. Depending on the SC, constant variations can be detected in the whole pH range or in partial pH ranges as well in aqueous solvent [1] as in non-aqueous solvent [2]. The V_{fb} dependency with the pH is directly linked to an evolution of the potential drops through the Helmholtz layer which is ruled by the local acid–base equilibrium [1], evolution which is associated to the charge balance inside the interface.

Such equilibrium makes inquiries about the chemical composition of the semiconductor surface. In the literature, lot of examples of acid–base equilibrium at the semiconductor interface are related to an oxide (or hydroxide) surface [1–6] interface in aqueous solvents. This is obviously the case of semiconductor oxides like ZnO, TiO_2, SnO_2, WO_3, where the interaction of their surfaces sites with H_3O^+ or OH^-, modified the structure of the electrical double layer as the pH of the solution change [1]. The type of variations differs from one oxide to another but all have marked pH sensitivities.

Among III–Vs, freshly etched GaAs, presents a good linear variation of the V_{fb} [7] in the whole range of pH in aqueous media [1]. The expected and unique slope of $-RT/F$ i.e. 60 mV/pH unit at room temperature, suggests a stable acid–base equilibrium at the interface. The nature of the associated interfacial chemistry is not well established even if *in situ* IR spectroscopy of the interface of GaAs/0.5 M H_2SO_4 or GaAs/6 M HCl shows only the presence of adsorbed water

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[7]. In opposite, InP, presents an "unexpected" slope of 40 mV [3] if we consider the whole pH range. Two nernstian V_{fb} behaviors were nevertheless observed for limited ranges of pH (0–4) and (8–14) while in the neutral pH range a non-nernstian variation was still detected. These behaviors revealed that a pure nernstian evolution depends essentially on the pH stability of the surface chemistry which supports the acid–base equilibrium [3]. According to the pH ranges, two different chemical compositions of InP surface were indeed determined by XPS chemical analyses. Either in acidic pH range (0–4) or basic pH range (8–14) a chemical composition close to a bare InP surface was determined, while a presence of a oxide mixture and hydroxide was analyzed only in neutral pH range [3]. How can we explain the nernstian potential variation observed onto a bare surface in aqueous media? Our previous work revealed therefore the ability of an acid–base equilibrium in a bare InP surface [3]. The question which must be considered is a nernstian V_{fb} variation can also occurred onto a bare InP surface without oxide (or hydroxide) as intermediate supports of acid–base equilibrium.

The complex variation of V_{fb} with the pH, reflects the complex surface chemistry of InP surface immersed into water. It is disquieting that the perturbed part of the V_{fb} variation overlaps with the pH range for which stabilities of InP oxides are clearly demonstrated. It is also interesting to point out that the oxide behaviors on GaAs are different in the same pH range. So to progress in this complex interfacial it is interesting to explore the responses of other interfaces. Non-aqueous solvent can be a suitable opportunity to modify the surface interaction that governs the interface building, allowing comparison that enriches our understanding of the interfacial structure. In past decades, many electrochemical processes have been studied in no aqueous solvents [8,9] but liquid ammonia (NH_3 *liq.*) appears to be among the most relevant to investigate original SC/electrolyte interfaces. Indeed, compared works performed in NH_3 *liq.* and water, for the oxygen reduction onto GaAs or InP suggest that the electrochemical behavior of semiconductors in NH_3 *liq.* can be considered as under water-free conditions [10–12]. Moreover surrounding influences at the interface semiconductor/electrolyte are obviously different from water, since their dielectric constant, viscosity coefficient are also strongly different [10]. Nevertheless electrochemical processes can be compared since similar physical and chemical properties are still observed. Particularly, both solvents are protic and polar. In comparison to aqueous media, specific mechanisms at the interface have been already reported from the high stability of intermediaries [11,12]. In this non-aqueous solvent, NH_4^+ ion is the strongest acid, and NH_2^- ion is the strongest base [10]. At room temperature NH_3 *liq.* is a very strong basic solvent [13–15] (10^{11} times stronger than water), and is a very weak acid (10^{29} times weaker than water) [10]. In NH_3 *liq.* few is known about the variation of the V_{fb} variation *vs.* pH. Such as wide pH range (33 pH units) is experimentally accessible it is fascinating and original to test the V_{fb} behavior of the same InP surfaces as the ones used for experiments in water. The challenge is to provide different data to discuss the fundamentals of InP/electrolyte interfaces.

InP material can be easily deoxidized by a mechanochemical etching although a small carbon pollution could be detected [3]. This deoxidized surface is enough stable to be handled without oxide during several minutes as shown from our previous works [16,17]. Thus we used as well bare InP samples as oxidized InP semiconductors coated with native oxides resulting from ageing in air. Like in aqueous electrolyte, the energy diagram of III–V semiconductors like InP can be determined using electrochemical capacity measurements in NH_3 *liq.* solutions [3].

The chemical composition of InP surface was analyzed by XPS before and after its immersion in NH_3 *liq.* What V_{fb} variations are observed onto a bare or oxidized InP surface in NH_3 *liq.* electrolyte? Using this non-aqueous solvent, do we confirm that an acid–base equilibrium can occur onto a bare InP surface?

2. Experimental

InP semiconductor (n- and p-types) wafers with a ⟨1 0 0⟩ orientation were purchased from MCP Electronic Materials, Ltd. A doping density of 10^{17}–10^{18} cm^{-3} was used. The wafers were cut into small squares (0.5 cm × 0.5 cm). Oxide free InP surfaces were prepared using an initial mechanochemical polishing with methanol bromide solution (2%) followed by a thoroughly methanol rinsing. Just before experiment the surface is dipped in 2 M HCl solution then washed in pure DI, finally dried using ultra pure argon stream and immediately immersed in NH_3 *liq.* Electrochemical experiments, in NH_3 *liq.*, are performed using a classical three-electrodes configuration. A large surface platinum foil is used as counter electrode. All potentials were measured *vs.* a silver reference electrode (SRE) [18]. All experiments have been done in the dark, using a 273A EGG potentiostat/galvanostat. The capacitance–voltage ($C(V)$) measurements have been carried out in the dark, before and after illumination of the InP surface, using a Fabelle-CNRS potentiostat and a lock in amplifier (EG&G 5208) in a classical three electrode set-up. Before $C(V)$ measurements, the illumination of the semiconductor was performed uniformly all over the immersed surface. The frequency is set in the 207–4107 Hz range (generally 1107 Hz).

Before the transfer towards X-ray photoelectron spectroscopy analyzer, samples are handled under a solution drop protection that is tangentially dried by an Argon stream. Sample handling for the UHV transfer is performed sheltered from air under N_2 purified atmosphere. The duration between the end of the polarisation and the full drying of the surface is about 2 min. The XPS analyses are performed on an Escalab 220 i XL, V.G. spectrometer. A focussed monochromated X-ray beam (Al Kα) was used with a beam size settled either at 100 μm or in the mm range, depending on the illumination size of the spot. Constant analyzer energy mode was used with pass energy of 8 eV or 20 eV. The photoelectrons are collected perpendicularly to the surface.

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 [18]. The connection of a mercury column provides a simple control of the pressure in the glass column assembly. The electrochemical cell was filled with 150 cm^3 of NH_3 *liq.* and was maintained at 223 K in a cryostat for experiment. The deoxygenating of the medium was performed under an argon stream to avoid oxygen contamination during the electrochemical measurements. All chemicals (purest available quality) were obtained from Prolabo. At 223 K, the auto-protolyse constant of NH_3 *liq.* [10] is equal to 10^{-33}. The acidic ammonia solution was obtained by condensing ammonia on dry NH_4Br which is soluble in NH_3 *liq.* [18]. The acidic pH in NH_3 *liq.* was determined from the logarithm of NH_4^+ concentration [10]. Consequently, pH = 0, referred to NH_3 *liq.* pH scale, corresponds to a concentration of NH_4^+ equal to 1 mol L^{-1}. The alkaline media was obtained from potassium amide solution which was *in situ* obtained by addition of weighed amounts of potassium [19]. Consequently, pH 33, referred to NH_3 *liq.* pH scale, corresponds to a concentration of NH_2^- equal to 1 mol L^{-1}. A large range of pH domain (33 pH units) can be explored in NH_3 *liq.*

Mott–Schottky plots were determined from strong acidic pH (0–1 and 2,3) and strong alkaline pH (30–31 and 33). These pH, referred to NH_3 *liq.* pH scale, were obtained in acidic media from a concentration of NH_4Br equal to 1 M, 10^{-1} M, 5×10^{-3} M and in basic media from a concentration of NH_2^- respectively equal to 1 M, 10^{-2} M and 10^{-3} M.

Unbuffered media, can be also provide using pure NH_3 *liq.* but we succeed also to obtain a buffered neutral medium (pH = 16.5) from