Hydrogen Evolution on InSb Semiconductor in Liquid Ammonia (223 K)

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Abstract

The cathodic electrochemical behavior of InSb was studied in liquid ammonia. In neutral unbuffered media, in spite of strong negative polarization no electrochemical modification of the interface was observed. However, in acidic media, a cathodic decomposition was detected after scanning InSb in the potential range of hydrogen evolution. Hydrogen embrittlement results from a strong interaction of hydrogen radical (H$^{\cdot}$) and indium surface. A coated film of indium results from this cathodic decomposition.

Keywords: semiconductor III-V, InSb, hydrogen evolution, cathodic decomposition.

Introduction

The reaction of hydrogen evolution has never lost its interest in electrochemical research. Like for metal electrodes, the knowledge of each step of the reaction is necessary to understand the behavior of semiconductor electrodes (SC). Thus, this reaction has been studied extensively in the area of the electrochemistry of SC electrodes. Semiconductors surface transformation obtained by radio frequency (RF) hydrogen plasma expositions, annealing under hydrogen pressure or exposure under ultra-height vacuum (UHV) demonstrates the crucial role of hydrogen bond with the semiconductor surface [1-6]. Electrochemical techniques are relevant *in situ* tools which are appropriate to study how hydrogen evolution can induce a semiconductor cathodic decomposition. Hydrogen evolution occurs through a two-electrons step mechanism and leads to the formation of adsorbed H$^{\cdot}$. The interaction of H$^{\cdot}$ and the semiconductor

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surface involves the embrittlement of the crystal lattice surface which is attributed to its cathodic decomposition. The magnitude of the resulting interaction between H· and the compound governs the magnitude of the surface transformation. Therefore, the surface stability of the III-V compounds depends on the nature of the bond between the hydrogen radical (H·) and the material.

This reaction is generally studied in aqueous media. However, among non aqueous solvents, liquid ammonia is unique on the one hand by its similarity to water (both are protic), on the other hand by its strong basicity. At room temperature liquid ammonia is a very strongly basic solvent [7] (10^{11} times stronger than water) and it is a very weak acid (10^{29} times weaker than water): ammonium ion is the strongest acid. Thus, the conditions of hydrogen evolution are completely different from those encountered in water, where the protons are solvated by H_2O. In liquid ammonia, without protons or proton donors in the medium and in spite of a strong negative polarization, no cathodic decomposition is detected. Studies in liquid ammonia demonstrated clearly the necessity of protons to induce the cathodic decomposition of InP; indeed, it occurs in the potential range where protons are reduced and the intermediate In-H· seems to induce the cathodic decomposition [8]. In this case a characteristic anodic peak is observed in the following positive potential scan and it is associated to the anodic dissolution of the indium surface; this results from a strong interaction between the hydrogen atom and the InP surface. Hydrogen evolution may be an unique and original way to observe the influence of very different chemical surroundings. Therefore, comparative studies of this reaction onto various semiconductors electrodes may be a convenient way to classify the compound reactivity towards hydrogen evolution. In this paper the cathodic electrochemical behavior of InSb was studied both with protons and without protons in the medium.

Experimental

Ammonia (electronic quality) was obtained from «Air Liquide». All chemicals, KBr, NH_4Br and $InBr_3$ were of the highest purity and purchased from «Aldrich». The acidic medium was obtained by addition of NH_4Br. In liquid ammonia, protons are solvated by the ammonia molecule. Thus NH_4^+ is the strongest acid in liquid ammonia. For low concentration of NH_4Br, the electrical conductivity of the solution is provided by KBr. A neutral unbuffered media was obtained from 0.1 M of KBr.

Electrochemical measurements were performed at -50 °C under an argon stream which provides oxygen free conditions. The electrochemical equipment used has been already described [9,10]. All potential-intensity curves were performed with a scan rate of 20 mV/s. The potential reference was a silver wire placed in a separate compartment. It was used as silver reference electrode (SRE). Semiconductors were purchased from MCP Electronic Materials Ltd with an orientation of (100). The SC electrodes were small squares of 0.5 cm^2. Prior to use the semiconductor surfaces were polished with 1vol % bromine/methanol, rinsed with methanol and then dried under an argon stream.

Results and Discussion

The electrochemical behavior of InSb was studied in neutral unbuffered media from –0.3 V to –2.4 V in the dark (Fig. 1). The formation of the solvated electron was observed at –2.4 V and also its reversible oxidation [8]. In spite of a smaller energy gap (0.75 eV), the formation of the solvated electron occurred at the same potential than InP or GaAs [8-11]. The solvated electron is the strongest reducing agent in liquid ammonia. However, no modification of the electrochemical behavior was detected by cyclic voltammetry. Indeed, during the reverse positive potential scan, no oxidation wave was detected in spite of strong negative polarization. The same experiment was performed in acidic media. Considerably before the formation of the solvated electron, a cathodic wave was observed from –1.6 V (Fig. 1). This cathodic current increased with the acidification of the media. Therefore, this current was associated to the hydrogen evolution. Like on n-InP, the peak potential of proton reduction was located at –1.8 V. The same peak potential was observed for both semiconductors in spite of an energy gap strongly different. After scanning the potential range of proton reduction, an anodic peak was clearly observed at –0.7 V. This anodic wave increased with the time of polarization in the potential range of hydrogen evolution (Fig. 2).

This anodic peak is clearly connected to the cathodic treatment in the potential range of proton reduction (Fig. 3A). In order to determine from what was originated this anodic peak, a solution of InBr$_3$ was reduced in acidic media on InSb electrode. Before hydrogen evolution a cathodic wave appeared from –1.2 V. The current density of this cathodic wave depends on the InBr$_3$ concentration. Therefore, it results from the reduction of In^{+3} cations. During the reverse scan, the anodic peak located at –0.7 V strongly increased (Fig. 3B). The reduction of In^{+3} solution provides a proof that the anodic wave is originated by the dissolution of a coating indium film onto the InSb

electrode. In acidic liquid ammonia, we demonstrated that the electrodeposition of indium can be indeed performed as on smooth platinum electrode as on the InP semiconductor [8]. This electrodeposition occurs before hydrogen evolution and provides the formation of a coated film of indium onto the InP electrode. During the reverse positive scan, the oxidation of this film clearly occurs [8]. Without In^{+3} cations in solution (from $InBr_3$), an anodic wave was observed after polarisation of InSb in potential range of hydrogen evolution.
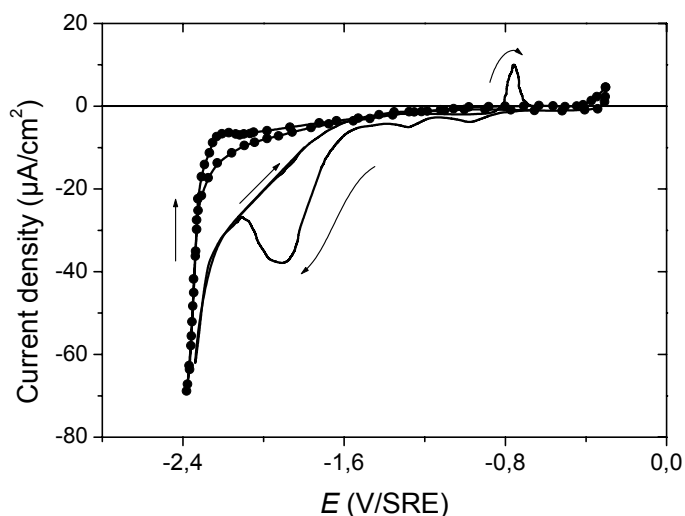

Figure. 1. Electrochemical behavior of InSb in liquid ammonia (223 K) in the dark from –0.5V –2.4V. [KBr] = 0.1 M, V = 20 mV/s.-●- :in neutral unbuffered medium;─ : in acidic medium $[NH_4Br] = 3 \times 10^{-3}$ M.
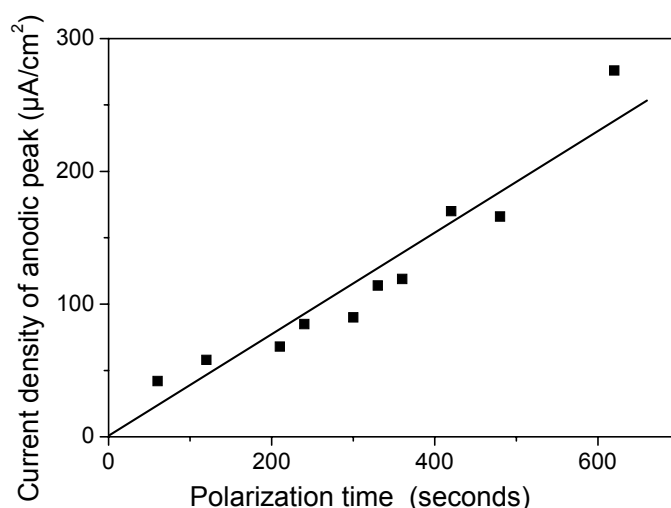
Figure 2. Liquid acidic ammonia (223 K) in the dark [KBr] = 0.1 M, $[NH_4Br] = 3 \times 10^{-3}$ M, v = 50 mV/s. Increase of anodic peak located at –0.7 V/SRE against polarisation time of InSb at –2.0 V/SRE.
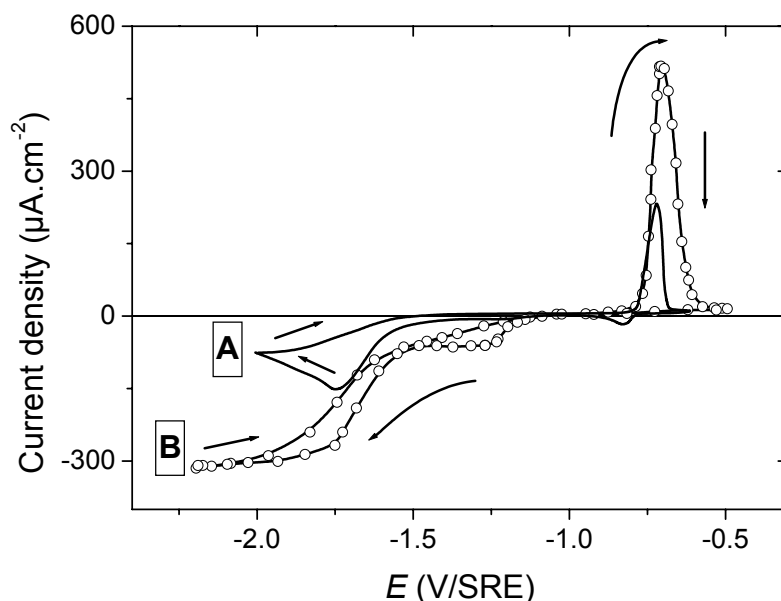
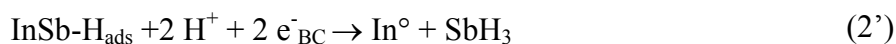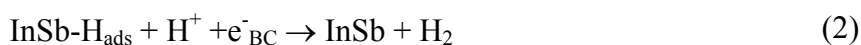**Figure 3**. In the dark, electrochemical behavior of InSb in liquid ammonia (223 K), from –0.5 V to –2.2 V. [KBr] = 0.1M, [NH$_4$Br] = 2.2×10^{-3}M, V = 20mV/s. A: Without InBr$_3$ and after 8 min at –2 V (hydrogen evolution); B: After reduction of InBr$_3$ solution.[InBr$_3$] = 5×10^{-3} M

Therefore, this anodic wave results also from the oxidation of indium coated film onto InSb semiconductor. The same anodic peak was observed on n-InP semiconductor when it was polarized on the potential range of hydrogen evolution [8]. This anodic peak resulted from the cathodic decomposition of InP [8]. Like in the InP electrode, hydrogen evolution involves the cathodic decomposition of InSb. Moreover no cathodic decomposition of InSb was observed on unbuffered media. The lack of protons or proton donors can't involve the cathodic decomposition of InSb. Only the hydrogen evolution onto InSb semiconductor induces a brittleness of the lattice. Like in the InP semiconductor, hydrogen evolution also induces the cathodic decomposition of InSb, according to the following reactions (1) and (2'):

$$InSb + H^+ + e^-_{BC} \rightarrow InSb\text{-}H_{ads} \qquad (1)$$

$$InSb\text{-}H_{ads} + H^+ + e^-_{BC} \rightarrow InSb + H_2 \qquad (2)$$

$$InSb\text{-}H_{ads} + 2 H^+ + 2 e^-_{BC} \rightarrow In^\circ + SbH_3 \qquad (2')$$

Like InP semiconductor, the cathodic decomposition induces the formation of a coated indium film onto InSb surface. This film was stable and its anodic dissolution was observed like onto InP semiconductor. The similarities between InP and InSb emphasize the strong interaction of In-H· with the SC surface that leads to the semiconductor cathodic decomposition. In opposition to InP, InSb semiconductor provides also to characterize the electrochemical behaviour of element V, the antimony. The electrochemical feature of antimony was clearly distinguished from indium [12].

Conclusion

Like on InP semiconductor, no cathodic decomposition of InSb was observed without protons on the media. As soon as hydrogen evolution occurred, a cathodic decomposition of InSb was observed. In spite of the difference in gap energy, the peak potential of hydrogen evolution was the same (-1.8 V/SRE) on both semiconductors. Moreover, the interaction of the hydrogen radical (H·) and the indium surface involves like onto InP, the cathodic decomposition of InSb.

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