Abstract No. 2792

Electrochemical behavior of InSb semiconductor in liquid ammonia (223 K)

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In comparison to aqueous media, few studies have been done in non aqueous solvent. However they give their greatest importance in relation to interfacial semiconductors reactions. They provide a larger potential window to electrochemical responses and the part played by water can be minimized at the interface semiconductor/non aqueous solvent. Among all them, liquid ammonia appears to be unique both for its similarities to water and its own chemical properties.

Among III-V semiconductors (InP, GaAs, GaP), InSb is distinguished by a energy gap seven time lower (0.2 eV instead of 1.4 eV). However, can the same electrochemical behavior be considered since the element III is common to InP? Can the presence of antimony change the anodic behavior ?

Protons are often implied in many interfacial electrochemical processes. An obvious way to understand these complex electrochemical processes is to isolate the effects of protons. The interesting point in using liquid ammonia is that a large range of pH is available: 33 pH units. This large pH range allows to study electrochemical processes as well with as without proton contribution. Electrochemical cathodic decomposition was not evidenced in basic pH even after the contact of InSb with the solvated electron. However in acidic medium, hydrogen evolution leads to the cathodic decomposition of InSb (**Fig. 1**) [1], like InP semiconductor, according the following reactions:

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

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

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

During the reverse scan an anodic peak emerges resulting from the dissolution of indium film surface. In spite of an energy gap different, a strong interaction of In-H· also involves the semiconductor cathodic decomposition like onto InP [2].

In recent years, studies have demonstrated that the photocorrosion of GaAs [3] is ruled by traces of water in methanol. In opposition to other non-aqueous solvents, liquid ammonia provides a better control of water traces. It was obtained from electronic grade and the dissolution of alkaline metals removes the last traces of water by using a double condensation. The role of water could be really discarded at the interface. Then an original anodic behavior was observed on other III-V semiconductors (GaAs, InP, GaP) in liquid ammonia. Before the unlimited anodic current corresponding to the semiconductor dissolution an anodic wave was detected which involves the oxidation of liquid ammonia. Therefore amide complexes (of In^{3+} as well of Sb^{3+}), which are precursors of nitride compounds could be expected at the interface [4].

In contrast to these III-V semiconductors, the anodic treatment of InSb (**Fig. 2**) points out the electrochemical behavior of the element V (antimony). Scanning a determined anodic range of current, a cathodic wave as well its corresponding anodic wave appears after several scans.

The same coulometric charge was observed after stabilization of both waves (anodic and cathodic). These two electrochemical processes are clearly linked. Like other III-V semiconductors (GaAs, GaP, InP), a chemical contribution of the solvent during its oxidation also can be considered. In order to isolate the antimony contribution, electrochemical studies have been performed using as well antimony metal as antimony salt in liquid ammonia.

References

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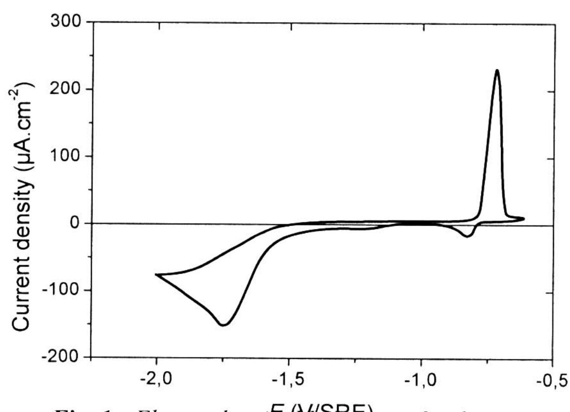

Fig. 1 : *Electrochemical behavior of Indium element from InSb semiconductor in acidic liquid ammonia (223 K)*

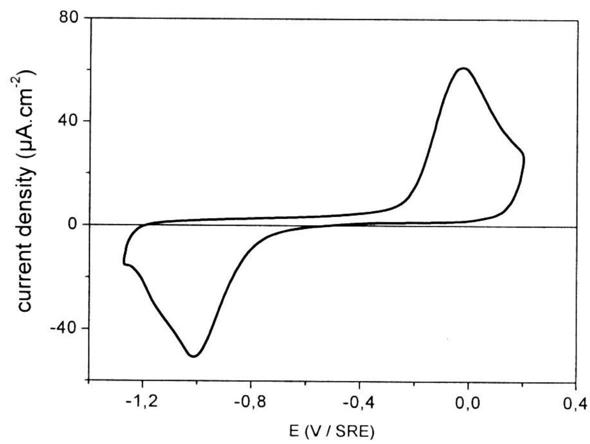

Fig. 2 : *Anodic electrochemical behavior of InSb semiconductor in acidic liquid ammonia (223 K)*