Anodic behavior of III-V semiconductors (InP, GaAs) in liquid ammonia at 223K

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In aqueous media, the anodic behavior of small band gap semiconductors, such as GaAs and InP, is limited by the decomposition of the semiconductor [1]. The use of common non aqueous solvents that are never water-free leads to results ruled by traces of water [2,3]. In opposition, liquid ammonia (electronic purity) provides a better control of water traces and electrochemical reactions can be studied under water-free conditions, and without proton donor (NH_3 is a strong base, and a very weak acid). Moreover, working at low temperature (223 K) and controlling the large range of pH (33 units) may increase the lifetime of intermediaries or may evidence products of reactions.

On GaAs and InP semiconductors, in liquid ammonia like in aqueous medium, the anodic treatment leads to semiconductor dissolution, which is characterized by an unlimited current. In opposition, in liquid ammonia, an anodic peak emerges just before this unlimited current and involves an electrochemical passivation of the electrode in this range of potential [4,5] (**Fig.1**). A cathodic treatment, clearly evidenced by the existence of a new reduction peak on n-GaAs can provide the recovering of the initial electrochemical state of the electrode. The aim of this work was to determine what occurred under the anodic peak.

Our studies were performed through electrochemical studies like scan rates variations, pH control, temperature control, coulometric charge measurement coupled with quantitative chemical analysis by atomic absorption spectroscopy of III and V elements (**Fig.2**). We demonstrated that the anodic peak results from an adsorption phenomenon where ammonia oxidation clearly occurs (**Fig.3**). This work pointed out the fact, that the oxidation of the solvent can occur on a small gap semiconductor before the dissolution of the semiconductor. The formation of “nitride” intermediates can be assumed.

The same phenomenon was clearly observed on InP and GaAs semiconductor, whatever the type (n- and p-). InP studies gives the advantage that the modified surface stays electrically blocked even if the electrode has been getting out of liquid ammonia and put progressively at room temperature and in a controlled inert atmosphere. A XPS chemical analysis taking only account of the electrochemical modification can be expected.

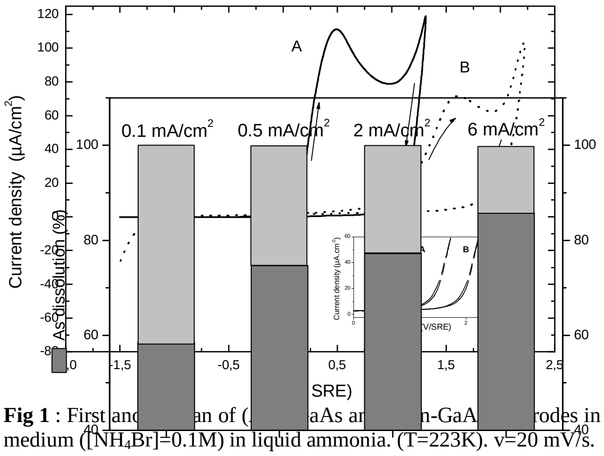

Fig 1 : First and an of (aAs ar n-GaA rodes in acidic medium ([NH_4Br]=0.1M) in liquid ammonia. (T=223K). v=20 mV/s.

Insert figure : Electrochemical behaviour of (A) p-GaAs and (B) n-GaAs electrodes in acidic medium ([NH4Br]=0.1M) in liquid ammonia (T=223K) after the first anodic scan.) v=20 mV/s.

Fig 2 : Ratio (%) between the quantity of dissolved As obtained from analysis and the one computed from anodic coulometric charge for different low current densities on p-GaAs electrodes and for a same coulometric charge of 6.8 C/cm².

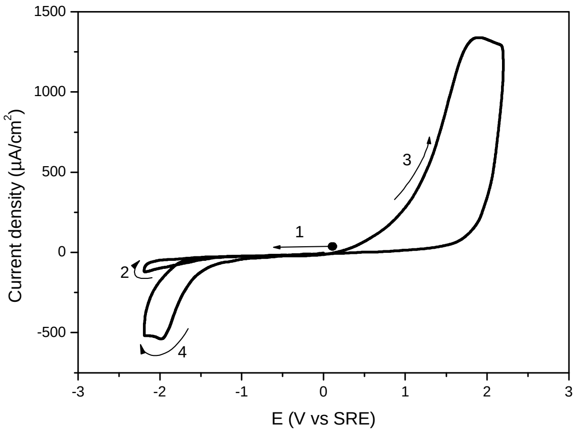

Fig 3 : In neutral unbuttered medium (0.1 M of KBr). Scan rate of 500 mV/s. First scan from 0 to –2.2 V : no cathodic wave was observed. The following second scan, from –2 to +2 V : formation of the anodic wave. The following third scan, from +2 to –2.2 V : a cathodic wave which results from the reduction of the adsorbate film.

References

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