

## Why are XPS analyses of III-V semiconductors suitable after electrochemical treatments in liquid ammonia (223K) ?

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Electrochemical studies in liquid ammonia have been proved to be helpful for understanding anodic interfacial processes onto III-V semiconductors electrodes, since  $\text{NH}_3$  is a very weak proton donor. Among all non-aqueous solvents, liquid ammonia appears to be unique both for its similarities to water and its own chemical properties. It provides a larger potential window to electrochemical responses and the part played by water can be discarded at the interface. Moreover its strong basicity, and its large pH range (33 units) allow to detect proton contribution during electrochemical processes. All these properties make liquid ammonia the most appropriate non aqueous solvent for discerning electrochemical processes in aqueous medium.

Even if electrochemical measurements are perfectly reproducible and significant, the detection of a chemical change of the composition of the semiconductor surface is necessary to support electrochemical conclusions. XPS chemical analysis is one of the most appropriate analysis surface technique. XPS measurements are often used after electrochemical process in aqueous medium and provide a efficient coupling technique. A rigorous procedure was already required to transfer samples, from aqueous medium, toward X-ray photoelectron spectroscopy analyzer. In addition to these usual precautions, there is a strong variation of temperature from 223 K to 293 K for samples from liquid ammonia. Until reaching the room temperature, the chemical surface of the sample can be modified by water condensation, which can induce surface reactions. A rigorous procedure was settled for samples from liquid ammonia treatment.

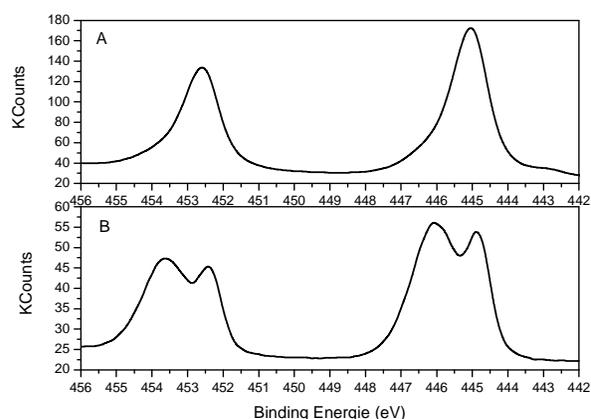
Semiconductors were chemomechanically polished with bromine/methanol (1% $\text{Br}_2$  in volume), rinsed with methanol and chloride acid (2M), and finally dried under an argon stream before the UHV transfer. No surface oxides were present after this chemical treatment. After dipping samples into liquid ammonia, and dried under an argon stream and isolated from oxygen, not much additional oxides surface were detected by XPS. Moreover, the presence of nitrogen is negligible. Consequently, the transferring procedure is suitable for XPS analysis.

The anodic electrochemical behavior of III-V semiconductors in liquid ammonia is remarkable (InP, GaAs). Two simultaneous reactions occur through an anodic peak on the one hand and through an unlimited current of semiconductor dissolution on the other hand. In contrast to aqueous media, the oxidation of the solvent occurs during the anodic treatment. A passivation occurs through the anodic wave and the resulting film involves the formation of strongly adsorbed atoms of nitrogen, intermediates from ammonia oxidation, which can behave as site poison at the interface during nitrogen evolution [1,2].

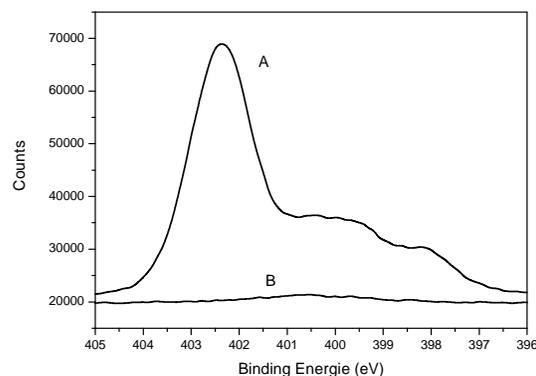
XPS analysis have been performed after anodic electrochemical treatments of semiconductor electrodes. The same rigorous transferring procedure was used like for semiconductor samples. The chemical surrounding was strongly perturbed after the anodic treatment (**Fig.1**). An enrichment of the V element was generally observed. The presence of nitrogen was detected (**Fig.2**), and III and V elements were clearly oxidized. The formation of "amide" complexes can be assumed, associated with oxidized matrix elements. Thus, these intermediaries have been detected from XPS analysis during the anodic treatment.

## References

- [1] A-M. Gonçalves, C. Mathieu, M. Herlem and A. Etcheberry. *Electrochimica Acta* **46** (2001) 2835.
- [2] O. Seitz, C. Mathieu, A.M Gonçalves\*, M. Herlem, A. Etcheberry . "Interfacial anodic behaviors of n- and p-GaAs semiconductors in liquid ammonia at 223K" (submitted, *Journal of Electrochemical Society*)



**Fig 1** : In 3d XPS spectra from an n-InP electrode after immersion in liquid ammonia without (A) and with (B) anodic treatment.



**Fig 2** : N 1s XPS spectra from an n-InP electrode after anodic treatment in liquid ammonia (A). Nitrogen is quasi-absent without the anodic treatment (B).