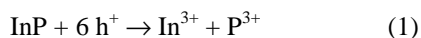


## Cathodic behavior of n-InP electrodes modified by thin and superficial anodic oxides

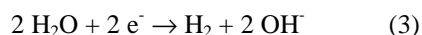
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Anodic oxides performed on n-InP with an applied potential and illumination, exhibit important blocking properties against holes transfer from the valence band (VB). In this work, we focussed our attention on the blocking properties of these anodic oxides against electron transfer from the conduction band (CB). Therefore, the electron transfer which occurs during a characteristic cathodic reaction, *i.e.*, hydrogen formation associated with semiconductor (SC) decomposition, has been studied for photo-oxidized surfaces. The cathodic behavior of n-InP previously photo-oxidized has been compared to the behavior of a non-oxidized SC surface. Our purpose is to study both the anodic oxide blocking properties and the cathodic decomposition modification of surfaces covered with anodic oxide. The modified InP electrodes have been obtained by photo-oxidizing the SC surfaces at  $E = -0.2\text{V/MSE}$  assuming the following equation:

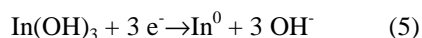


In our operating conditions (pH 9), a controlled oxide growth occurs leading to the formation of a mixed In-P oxide layer with a composition close to  $\text{InPO}_4$ . Concerning the cathodic behavior on a non oxidized surface, the SC decomposition occurs at  $E_{\text{app}} < -1.7\text{V/MSE}$  as a side reaction with  $\text{H}_2$  evolution :

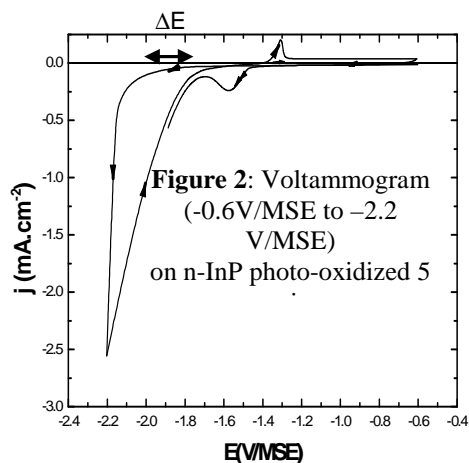
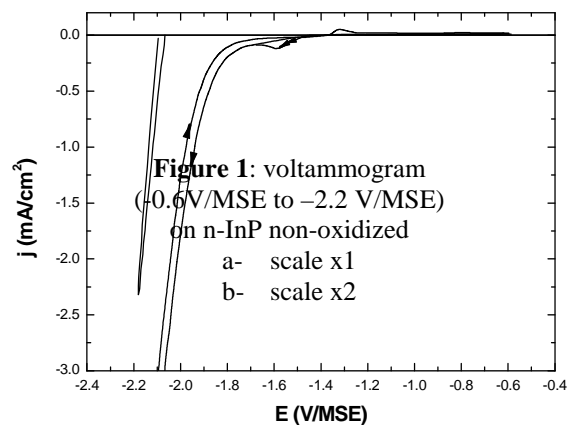


During the following positive scan, an anodic peak appears, at  $-1.3 \text{V/MSE}$ , followed by a current plateau, corresponding to:  $\text{In}^0 + 3 \text{OH}^- \rightarrow \text{In}(\text{OH})_3 + 3 \text{e}^-$  (4)

The second negative potential sweep exhibits a cathodic peak at  $E = -1.6 \text{V/MSE}$  corresponding to :



By comparing the voltammograms obtained on modified electrodes (fig.2) and clean InP surface (fig.1) significant differences have been noted: Firstly, the cathodic current drops down at higher negative polarizations for modified electrodes. Secondly, an important hysteresis is observed during the first cathodic sweep, suggesting the transformation of anodic oxide initially present at the SC surface. To quantify these phenomena, the coulometric charges involved in different process (reactions 1 to 4) were measured and compared.



Our work evidences a complex cathodic behavior for electrodes covered with oxides. During a first stage, the anodic oxide decomposition is the only one reaction which takes place at the SC interface. The presence of an overpotential ( $\Delta E$ ) evidences the oxides blocking properties toward  $\text{e}^-$  transfer. Then, when the anodic oxide is completely decomposed, a second stage happens corresponding both to SC decomposition and to  $\text{H}_2$  evolution. This electrochemical approach will be completed with XPS analysis.