

## The Cathodic Decomposition of InP followed by *in situ* Photoluminescence

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Optical characterisation, used as an *in situ* tool, provides a lot of information during electrochemical processes. Among the available techniques, Photoluminescence (PL) has a specificity on semiconductor (SC) electrodes, due to its sensitivity to several parameters of the SC/Solution interface : the space charge layer width, the surface recombination velocity of the minority carriers, the optical parameters of the interface. So, PL intensity can be very sensitive to a lot of events that happen at the interface but the difficulty is to determine what parameter plays the main role. However, by a judicious choice of the doping level of the SC, it is possible either to increase ( low density) or to decrease (high density) the contribution of the space charge layer to the total PL intensity variation. Similar considerations can be used with the surface recombination which the influence depends strongly on the variation range of its value. So for a given mechanism it is often possible to choose experimental conditions that provide the largest PL variation associated to the more interesting interfacial parameter. To illustrate these generalities we will present results about the PL intensity variations that occur during the cathodic decomposition of n-InP. The cathodic decomposition is a side phenomenon observed during the H<sub>2</sub> evolution. For InP, an In enrichment is obtained as the consequence of the surface lattice destruction. The amount of matter concerned by this transformation depends on the time and the polarisation. PL excited at very low level can be recorded at each step of the mechanism during the potential scans. The shape of the PL depends strongly on the pH of the solution in accordance with a pH dependency of the voltammograms that correspond to the different electrochemical behaviours of the In enriched surface layer . The figure 1 illustrates this remark and show the potential dependency of the PL at pH 9 when the cathodic decomposition occurs. Whatever the pH the PL-potential curves present specific behaviour in accordance with the

state of the surface. In all cases, PL responses of a surface: without cathodic decomposition, during the first scan with an H<sub>2</sub> evolution then on a decomposed surface, differ strongly, demonstrating that PL is a very sensitive tool for the interface modification. The H-surface interaction is suggested by PL enhancement; In apparition implies PL decrease; In transformation during the positive potential scan gives rise to specific PL intensity variations according to the dissolution or the transformation of the film in In(OH)<sub>3</sub> (see fig 1). All this remarks suggest that the full electrode story, since the first step of the mechanism until the strongly modified surface, can be accurately followed by *in situ* PL. So our purpose will be to described qualitatively then quantitatively the relation between the PL variation and the cathodic decomposition undergone by the n-InP surface at different pH.

Fig1: Voltammograms of cathodically decomposed n-InP; pH= 9, PL variation is recorded at the same time. Influence of the high potential limit; features on the voltammogram is associated to the anodic then cathodic transformation of the surface In film. The charge associated to the smaller cathodic peak is  $0.48 \cdot 10^{-3}$  C.

