

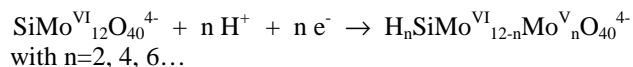
Localized photoetching of n-InP, at open-circuit potential

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In the manufacture of (opto)electronic devices, the etching of semiconductor (SC) compounds is an important step. Wet etching can be performed, more often it is due to the anodic dissolution of the SC (hole consumption). It can be carried out, in the dark, either at open circuit potential in the presence of an oxidizing agent or under anodic polarization in an indifferent electrolyte. Localized etching can be achieved using light of energy greater than the SC band gap to create electron-hole ($e^- - h^+$) pairs. Under these conditions, the SC photodissolution is obtained under applied potential to prevent the occurrence of electron-hole recombination. However, SC photoetching can also be managed under electroless conditions, especially in the presence of an oxidizing agent which prevents electron-hole recombination by picking up some electrons from the conduction band or from surface states of the SC. This ensures that some photogenerated holes are available to trigger the SC dissolution.

In this communication, we will present an unusual etching agent which allows one to photoetch n-InP at rest potential (without applied potential). This oxidizing agent is a heteropolyanion, a silicomolybdate ion which has Keggin structure : $\alpha\text{-SiMo}_{12}\text{O}_{40}^{4-}$. In strong acidic solutions, it can be reduced according to the following reaction :



At rest potential, in the dark, neither n-InP nor p-InP samples are etched in the presence of $\text{SiMo}_{12}\text{O}_{40}^{4-}$ ions. Whereas under illumination ($h\nu > 1.35\text{eV}$), n-InP undergoes an anodic dissolution process (Fig. 1). These observations are summarized in the drawing shown in Fig. 2.

In order to specify the mechanism which occurs at the InP/SiMo₁₂ solution interface, electrochemical studies have been performed on n- and p-type InP electrodes, first, in the dark then under illumination.

At a p-InP electrode, in the dark, no reduction current is observed. $\text{SiMo}_{12}\text{O}_{40}^{4-}$ ions are not reduced (Fig. 3, solid line). Under illumination ($h\nu > 1.35\text{eV}$), the reduction of $\text{SiMo}_{12}\text{O}_{40}^{4-}$ is effective, some reduction waves are observed on the J(E) curve (Fig. 3, dashed line). From these results, we can conclude that, at the InP surface, the reduction of $\text{SiMo}_{12}\text{O}_{40}^{4-}$ takes place by capture of electrons from the SC conduction band.

We will see that the mechanism of the charge transfers should involve surface states of the SC.

The global reactions which occur at the n-InP/SiMo₁₂ illuminated interface can be represented as :

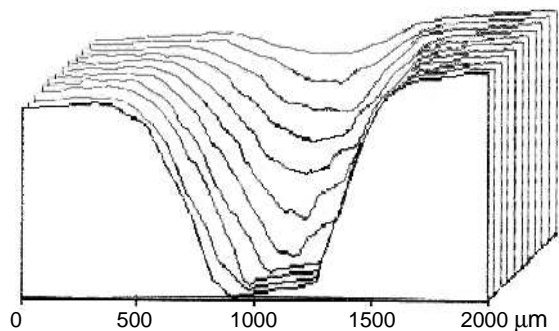
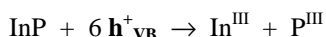
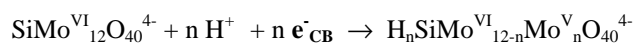


Fig. 1: 3D etching profile obtained after applying He-Ne laser irradiation for 3 hours to an n-InP sample immersed in $5 \times 10^{-3}\text{M SiMo}_{12}\text{O}_{40}^{4-}$, 3M HCl solution.
Pit depth : 30 μm .

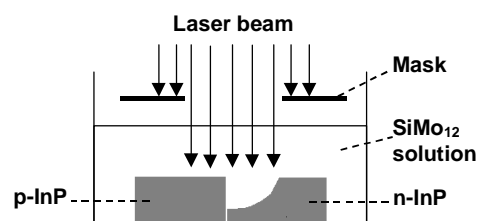


Fig. 2 : Schematic experiment which underscores photoetching of n-InP and its selective etching with respect to p-InP, in the presence of $\text{SiMo}_{12}\text{O}_{40}^{4-}$ ions.

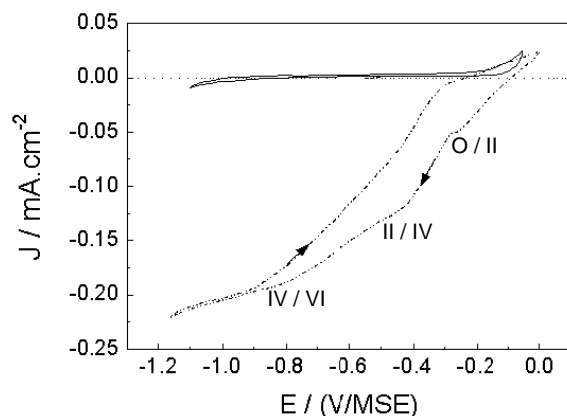


Fig. 3 : Current density vs. potential curve obtained at a p-InP electrode. Electrolyte : $10^{-4}\text{M SiMo}_{12}\text{O}_{40}^{4-}$, 0.5M H_2SO_4 . $\omega = 1$ rps. (—) : in the dark, (---) : under illumination.