

## Ag Electrodeposition on n-InP followed *in situ* by photoluminescence

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The metal electrodeposition onto III-V semiconductors depends on the surface defects, and on the interaction between the adsorbed metal atom and the semiconductor. The nucleation step governs the rules of the growth mode and the quality of the metal film. In this work, silver is deposited onto n-InP in acidic media for various cathodic polarizations, and in electroless conditions as well. The photo-luminescence response is directly linked to the metal surface coverage and is very sensitive to the nucleation step. The initial process of Ag electrodeposition was investigated using electrochemical techniques, photoluminescence and scanning electronic microscopy (SEM). Electroless deposition depends on the initial surface of n-InP involving difficulties to obtain reproducible results. When the initial nucleation leads to a homogeneous surface coverage, the nuclei growth and clusters gathered to formed inhomogeneous aggregate. This phenomenon is due to the very weak interaction energy between the adsorbed silver atoms and n-InP.

More reproducible and controlled results, with generally better adhesion features, occur under polarization. The electrodeposition of silver on n-InP is followed by photoluminescence, monitored at 880 nm (fig 1). Greater nuclei density is obtained by nucleation under more negative polarization. The solvent reduction limits the extent of the negative polarization at -0.8 V/MSE. For various polarization times the photoluminescence decrease is reported as a function of the corresponding anodic charge of the deposited silver ( $Q_{ox}$ ) (fig.2). Two growth modes have been evidenced: the first one, corresponding to the linearity of the  $I_{PL}/I_{PL}^0$  decrease with  $Q_{ox}$ , occurs within the first 10 minutes of Ag electro-deposition. In this range, after the oxidation of the silver deposit, the photoluminescence intensity is restored up to 90% of its initial value. A good correlation is obtained between  $Q_{ox}$  and the charge amount of the reduced silver,  $Q_{red}$ . These results can be explained by the nucleation step leading to a 2D growth linked to the Ag surface coverage of n-InP. During the first 10 minutes of Ag electrodeposition, the photoluminescence intensity decreases relatively quickly, and the Ag cluster density increases as it is shown in fig.3. Longer electrodeposition implies loss of the linearity between the  $I_{PL}$  decrease and  $Q_{ox}$  and loss of the correlation between  $Q_{ox}$  and  $Q_{red}$ . The oxidation charge is lower than the reduction charge and the initial photoluminescence intensity is never recovered after many oxidation cycles. This behavior can be interpreted as a second growth mode corresponding to a 3D mode with a perpendicular growth which increases the amount of silver deposit, but does not change as much as the photoluminescence signal does. This second step leads to the formation of the homogeneous Ag film.

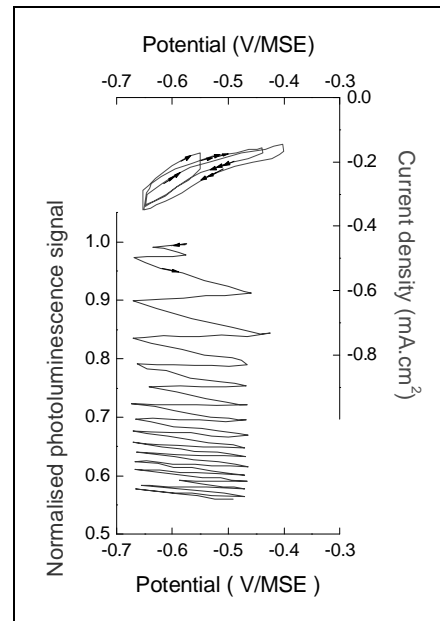


Fig.1: Ag electrodeposition onto n-InP, followed by photoluminescence, monitored at 880 nm ( $H_2SO_4$  0.5M,  $Ag^+$   $10^{-3}M$ ).

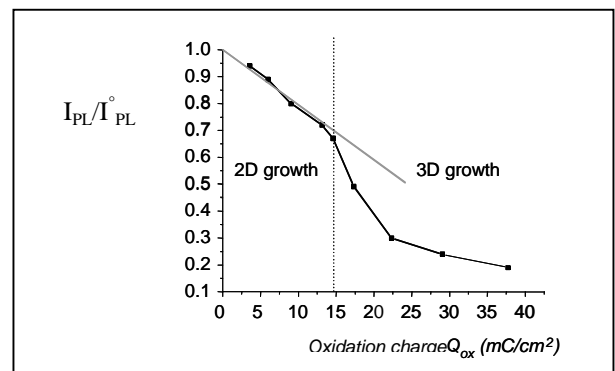


Fig.2: photoluminescence decrease as a function of the amount of oxidation charge of the deposited silver performed at  $V=-0.8V/MSE$ .

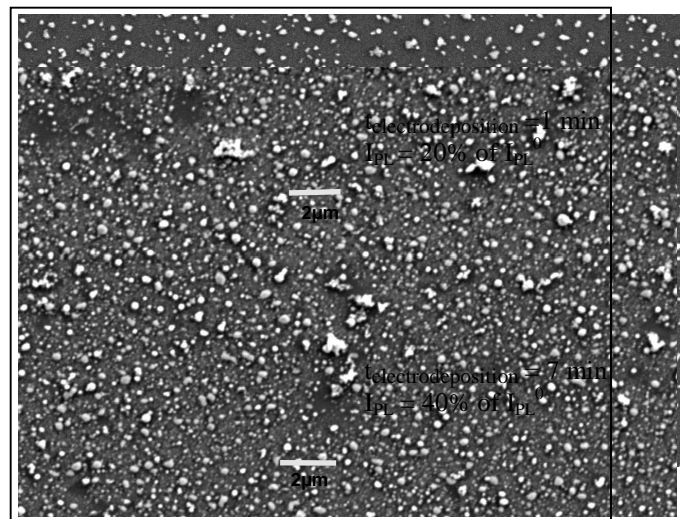


Fig.3: SEM observations of Ag electrodeposition at  $V=-0.8V/MSE$  in  $H_2SO_4$  0.5M  $Ag^+$   $10^{-3}M$