

Formation of Finite Porous Layers during Anodization of n-InP in Aqueous KOH Electrolytes

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The variety of semiconductors that can be rendered porous electrochemically includes GaAs¹ and InP² to name but a few. Under some conditions, porous layers of arbitrary thickness can be formed.³ However during anodisation of InP in KOH, layer formation terminates at a finite thickness.⁴ These layers are constructed from domains of $\langle 111 \rangle_A$ crystallographic pores. Initially, the domains have triangular (01 $\bar{1}$) and 'dove-tail' (011) cross-sections and rectangular profiles when viewed in (100) planes parallel to the electrode surface.⁵ Each domain is connected to the surface by an individual channel, and eventually these domains merge to form a continuous porous layer, beneath a thin (~40 nm), dense near-surface layer of InP.⁶

When InP is anodised in KOH the $\langle 111 \rangle_A$ pore propagation occurs in a similar manner to pore propagation during anodisation of InP in aqueous acidic electrolytes.^{2,3} However, in KOH the pore propagation spontaneously halts both in linear-potential-sweep (LPS) and potentiostatic experiments resulting in a rapid decrease in current density. In this presentation we will describe the cessation of this pore propagation and propose an explanation for why the pore propagation ceases. We support our explanation with a model for the diffusion of material through the porous networks, along with *in-situ* optical and *ex-situ* electron microscopy observations of the precipitates.

Our model of diffusion within the porous networks is based on the expansion and merging of domains of $\langle 111 \rangle_A$ pores beneath the electrode surface, as we described previously.^{6,7} The model indicates the OH⁻ concentration near the pore tips does not differ much from the bulk value even just before the cessation of etching and consequently the etch mechanism is not expected to change significantly as pores increase in length. Furthermore, once a complete porous layer has formed, the model predicts that further thickening of the layer should not result in any significant increase in the diffusive flux through the pores; *i.e.* the vast majority of the increase in the rate of transport of etch products through a surface pit occurs as individual domains are expanding and not as the continuous layer is thickening.

We will show the largest products-concentration gradient within each porous domain should occur across the pit at the electrode surface and that once precipitation of products begins it should spread rapidly throughout the network of pores connected to the respective pit in the

electrode surface. This process should lead to the formation of precipitates on the electrode surface also – due to the expansion of material precipitating within the pores – resulting in precipitation and the termination of pore propagation spreading to porous networks of neighboring pits.

Scanning electron microscopy images of cross-sections of samples anodised for different durations will be used to support our theory that the formation of precipitates, both within the porous networks and on the electrode surface, occurs rapidly and at the same time as the cessation of porous layer growth. In addition, the formation of these deposits on electrode surfaces and the change in refractive index of the porous layer will be shown by *in-situ* optical microscopy⁸ (*e.g.* Fig. 1) to coincide with the rapid decrease in current density corresponding to the cessation of pore propagation.

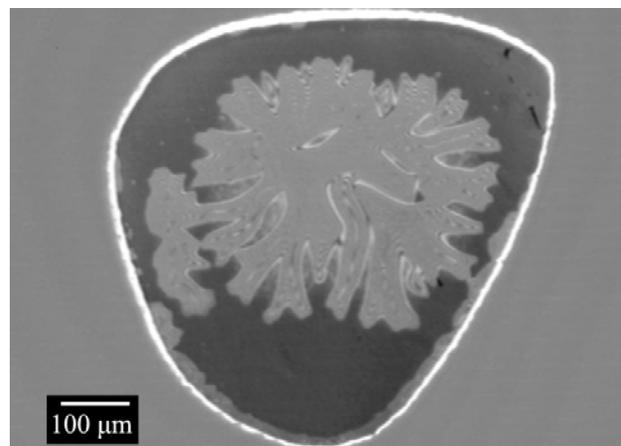


Fig. 1 Background-subtracted image of n-InP under Köhler illumination ($\lambda_K=530$ nm) at 0.31 V (SCE), *i.e.* as the current decreases (due the cessation of $\langle 111 \rangle_A$ pore propagation), during an LPS from 0 V at 2 mV s⁻¹ in 5 mol dm⁻³ KOH. The interference fringes, arising from the different thickness of the layer being deposited on the electrode surface, can clearly be seen.

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