

Mechanism of Anodic Formation of Porous InP

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There is considerable interest in the electrochemical formation of porosity in semiconductors. Much of the work has focused on silicon but investigations of pore formation in III-V compounds such as GaAs^{1,2} and InP³⁻⁵ have also been reported recently. It has been suggested that controlled modulation of the pore diameter and pore growth direction in such structures could lead to photonic band gap applications. However, only limited investigations of the mechanism of pore initiation and growth in III-V semiconductors have been reported. In this paper we report an investigation of the mechanism of formation of porous InP during anodization in KOH electrolytes.

Electrodes consisted of (100)-oriented S-doped n-InP with a carrier concentration of $\sim 4 \times 10^{18} \text{ cm}^{-3}$. Experiments were carried out in a conventional three-electrode electrochemical cell in dark conditions at room temperature.

We have recently reported³ the formation of a porous sub-surface region in InP electrodes anodized in KOH electrolytes in the concentration range 2 - 5 mol dm⁻³. Interestingly, transmission electron microscopy (TEM) cross-sections show a thin non-porous region, $\sim 40 \text{ nm}$ in thickness, between the porous region and the electrode surface. Careful TEM examination shows evidence of channels through this non-porous layer but these appear to be sparsely distributed. Further evidence of the presence of such channels has been obtained by atomic force microscopy (AFM) of the surface.

When the potential of an InP electrode in a KOH solution (2 - 5 mol dm⁻³) is swept in the anodic direction, a current peak is obtained after which the current decreases to a low value. Cross-sectional TEM of electrodes subjected to a potential sweep past this peak shows a porous sub-surface region of fairly uniform thickness, typically $\sim 600 \text{ nm}$ for 5 mol dm⁻³ KOH. We suggest that electrochemical etch processes leading to generation of this porous layer occur at the advancing tips of electrolyte-filled pores in a network which is connected to the bulk electrolyte via a limited number of channels through the otherwise dense near-surface layer. Consequently, these channels have a critical role in the evolution of the porous region.

In order to elucidate the formation process of porous InP, experiments were carried out in which the potential sweep was stopped before the current peak was reached and the electrode was examined by cross-sectional TEM. A typical micrograph for such a cross-section cleaved along the (110) plane is shown in Fig. 1. A porous domain with a triangular cross-section is clearly observed, separated from the surface by a non-porous region $\sim 40 \text{ nm}$ in thickness. It is suggested that this porous domain originated from a single channel through the near-surface layer.

These domains were also observed in plan-view TEM micrographs obtained by ion-milling the surface of samples to a depth of $\sim 100 \text{ nm}$. A typical micrograph

obtained in this way is shown in Fig. 2 for a sample similar to that in Fig. 1. Development of the porous region appears to occur via the formation of multiple domains of this type. TEM examination was also carried out on samples obtained at other stages of the potential sweep. The mechanism of porous layer formation will be discussed in the light of these results.

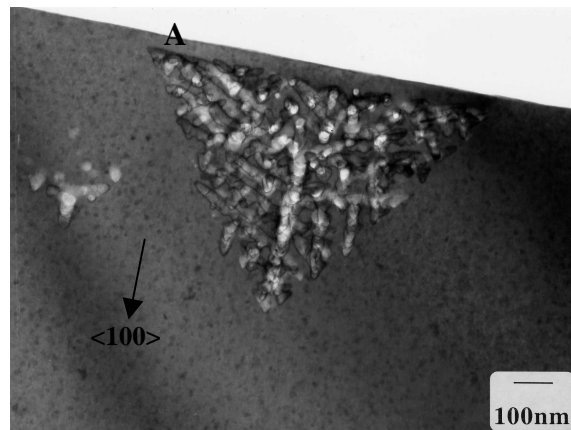


Fig. 1 Bright field TEM of a cross section of an InP electrode after a potential sweep from 0.0 to 0.44 V (SCE) in 5 mol dm⁻³ KOH. The plane of the micrograph is (110). A single porous domain is clearly visible.

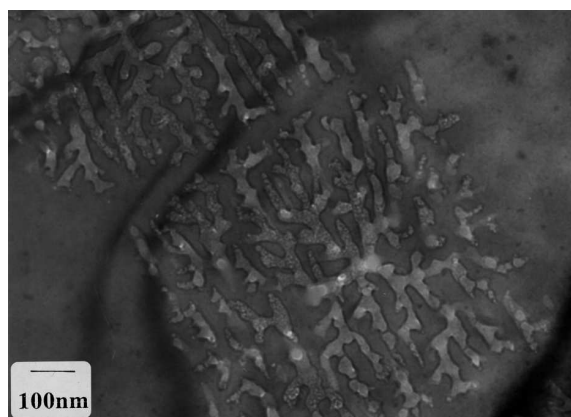


Fig. 2 Plan view bright field TEM image of a section through a porous InP layer $\sim 100 \text{ nm}$ below the surface of the electrode. Anodization conditions were the same as in Fig. 1. The plane of the micrograph is (100). Two nearby porous domains are visible.

References

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