Current-Line Oriented Pore Formation in n-InP Anodized in KOH

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Current-line Oriented Pore Formation in n-InP Anodized in KOH

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Previously, we have demonstrated the formation of crystallographically oriented (CO) porous layers in KOH electrolytes with concentrations varying from 1 mol dm^{-3} to 17 mol dm^{-3} [1] and temperatures ranging from 10^{o}C to 50^{o}C [1] in n-InP electrodes of differing carrier concentration [2]. These pores were shown to originate from pits in the electrode surface [3] and grow along the <111>A crystallographic directions forming tetrahedral porous domains [4]. Pores formed in InP in other electrolytes, most commonly HCl [5-6], exhibit crystallographic growth at low overpotentials but switch their orientation to match the direction of the current flow at higher overpotentials. In this paper we describe the observation of current-line oriented (CLO) pore morphology in KOH electrolytes for the first time.

We will describe the formation of CLO pores, which were observed while investigating the effect of temperature and electrolyte concentration on porous etching in KOH. CLO pores were formed at the highest and lowest concentrations in which pore formation occurs (<2.5 mol dm^{-3} and >17 mol dm^{-3}) at a temperature of 10^{o}C. CLO pore etching was performed at potentials ranging from about 0.6 to 1.0 V (SCE).

In the early stages, the pore orientation was partially crystallographic with some branching visible and typical pore widths of the order of 40 nm. As the porous layer thickened, the growth direction became less crystallographically oriented and the pores began to widen. Finally, fully CLO pores were formed. Typical CLO porous layers reached a depth of between 5 and 6 µm before etching was irreversibly terminated. The porosity of the layers was typically found to be between 60% and 70%.

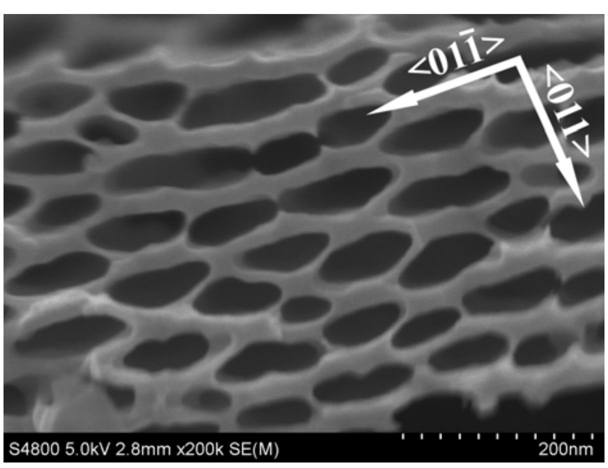

Fig. 1: Cross sectional SEM micrograph of the (100) plane of an InP sample anodized at 0.9 V(SCE) in 17 mol dm^{-3} KOH at 10^{o}C. The pore growth direction is perpendicular to the image plane.

Observation of the CLO pore cross section showed it to be approximately elliptical, with typical pore diameters of 70 to 140 nm measured along the <01$\bar{1}$> direction. These pore widths were 2.5 times larger than those measured along the perpendicular <011> direction (see Fig. 1). It will be proposed that even though the direction of pore etching is predominantly determined by the current lines, there is still a preference for etching along the two <111>A directions which point down towards the bulk substrate, leading to pore widening along those directions and the observed elliptical cross section. Pore widening cannot occur along the other two <111>A directions because of the high density of pores. Fig. 1 also shows that some pores are seen to 'merge' along the <01$\bar{1}$> direction. A similar 'pore crossing' phenomenon has been observed in GaAs [7] but not, to our knowledge, in InP.

For CO pore growth in KOH, the thinnest pores and lowest porosities occur at 9 mol dm^{-3} [1]. As the concentration is either increased or decreased from 9 mol dm^{-3}, the pore width and porosity both increase. Wider pores and a correspondingly greater degree of porosity are also seen at lower temperatures. This suggests that CLO pore formation is the result of a critical porosity or pore width being reached. Pores which have an orientation between that of CO and CLO pores can be formed at low temperatures and intermediate concentrations of KOH. However, fully CLO pores have only been observed at low temperature and at the lowest and highest ends of the KOH concentration range, where porosity and pore widths are high. This can be understood by considering that at higher porosities and pore widths, pore branching is restricted due to overcrowding. The thinning pore walls should also be completely depleted of carriers, leading to pore growth occurring exclusively in the direction of available holes.

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