

Title	Electrochemical formation of nanoporosity in n-InP anodes in KOH
Authors	Buckley, D. Noel;O'Dwyer, Colm;Lynch, Robert P.;Quill, Nathan
Publication date	2011-01
Original Citation	Buckley, D. N.,O'Dwyer, C.,Lynch, R. P.,Quill, N. (2011) 'Electrochemical Formation of Nanoporosity in n-InP Anodes in KOH'. ECS Trans, 35(8), pp.29-48. doi: 10.1149/1.3567735
Type of publication	Article (peer-reviewed)
Link to publisher's version	http://ecst.ecsdl.org/content/35/8/29 - 10.1149/1.3567735
Rights	© The Electrochemical Society, Inc. 2011. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in Buckley, D. N.,O'Dwyer, C.,Lynch, R. P.,Quill, N. (2011) 'Electrochemical Formation of Nanoporosity in n-InP Anodes in KOH'. ECS Trans, 35(8), pp.29-48. doi: 10.1149/1.3567735
Download date	2026-09-19 17:44:53
Item downloaded from	https://hdl.handle.net/10468/990



UCC

University College Cork, Ireland
 Coláiste na hOllscoile Corcaigh

Electrochemical Formation of Nanoporosity in n-InP Anodes in KOH

D. N. Buckley, C. O'Dwyer, R.P. Lynch¹ and N. Quill

*Department of Physics, Materials & Surface Science Institute, University of Limerick,
Ireland*

¹Present Address: *Polish Academy of Sciences, Warszawa*

We review our recent work on anodic formation of nanoporosity in n-InP in aqueous KOH. Typically, a nanoporous sub-surface region is formed beneath a thin, dense near-surface layer. Atomic force microscopy (AFM) shows pit formation on the surface in the earlier stages of etching, and transmission electron microscopy (TEM) shows individual nanoporous domains separated from the surface by a thin InP layer. Each domain develops from a surface pit. We developed a model based on propagation of pores along the $\langle 111 \rangle_A$ directions. The model predicts porous domains with a truncated tetrahedral shape and this was confirmed by scanning electron microscopy (SEM) and TEM. Pores are cylindrical and have well-developed facets only near their tips. No porous layers are observed at a KOH concentration of 1.1 mol dm^{-2} or lower. Linear sweep voltammograms (LSVs) show a pronounced anodic peak corresponding to the formation of the porous region. We describe a technique to deconvolute the effects of potential and time in LSVs and explain their shape and their relationship to porous layer formation.

Introduction

There has been considerable research, both fundamental and applied, on porous semiconductor formation.¹⁻⁸ Much of the research on porosity in compound semiconductors has been on gallium arsenide⁸⁻¹² and indium phosphide.¹³⁻¹⁶ It has been shown that pore growth is affected by electrolyte concentration^{13,17,18} as well as substrate type¹⁹, orientation²⁰ and doping density.²¹ Considerable progress has been made in understanding the basic mechanisms of pore formation in silicon under electrochemical conditions, and several pore formation models have been proposed to account for the range of observed pore types.²²⁻²⁵ The mechanism of pore formation in III-V semiconductors has also been investigated.⁹⁻¹⁶

Anodic etching of n-type semiconductors does not readily occur in the dark since it requires holes in the valence band. At highly positive potentials, however, tunneling of carriers across the depletion layer can occur and the resulting holes in the valence band enable etching to take place.²⁶ Since tunneling is sensitive to the surface condition of the semiconductor, this type of anodic etching is often localized, thereby giving rise to the formation of porous structures.

Nanoporous structures can be formed in compound semiconductors by anodic etching under either acidic or alkaline conditions. In this paper, we will review our recent work^{13,16,27-41} on n-InP in aqueous KOH.

Experimental

Typically, the working electrode consisted of polished (100)-oriented sulfur-doped n-type indium phosphide (n-InP) grown by the liquid-encapsulated Czochralski (LEC) method and supplied by Sumitomo Electric. As-received polished wafers had an essentially featureless surface when viewed at a magnification of 1000X under an optical microscope with Nomarski interference contrast (i.e. a typical surface finish for substrates for epitaxial growth). The nominal density of surface defects of the LEC wafers, as characterized by the etch-pit density (EPD), was in the 10^3 cm^{-2} range or lower. Wafers were cleaved into coupons (typically $\sim 5 \text{ mm}$ square) along the natural $\{110\}$ cleavage planes and an ohmic contact was made by alloying indium to the back of the coupons. The back and the cleaved edges were isolated from the electrolyte by means of a suitable varnish. The electrode area was typically 0.2 cm^2 . A conventional three-electrode cell configuration was used employing a platinum counter electrode and saturated calomel electrode (SCE) to which all potentials are referenced. All electrochemical experiments were carried out at room temperature and in the absence of light.

A CH Instruments Model 650A Electrochemical Workstation interfaced to a Personal Computer (PC) was employed for cell parameter control and for data acquisition. All linear potential sweep (LPS) experiments were carried out at a scan rate of 2.5 mV s^{-1} . Transmission electron microscopy (TEM) samples were prepared as previously described³⁶ using a FEI 200 FIB workstation and examined using a JEOL 2000 TEM operating at 200 kV. Cleaved $\{011\}$ cross-sections were examined using a Hitachi S-4800 field emission scanning electron microscope (SEM) operating at 5 kV unless otherwise stated. Crystallographic directions were determined by reference to the primary (0 $\bar{1}\bar{1}$) and secondary (0 $\bar{1}$ 1) flats of the supplied wafers (identified using a standard wet chemical⁴² etch to reveal the $\langle 111 \rangle_A$ faces).

Results and Discussion

1. Electrochemical Etching and TEM Examination of Cross-Sections

Fig. 1(a) shows a linear sweep voltammogram (LSV) of an n-InP electrode in 5 mol dm^{-3} KOH and Fig 1(b) shows an LSV of a similar n-InP electrode in 1 mol dm^{-3} KOH at the

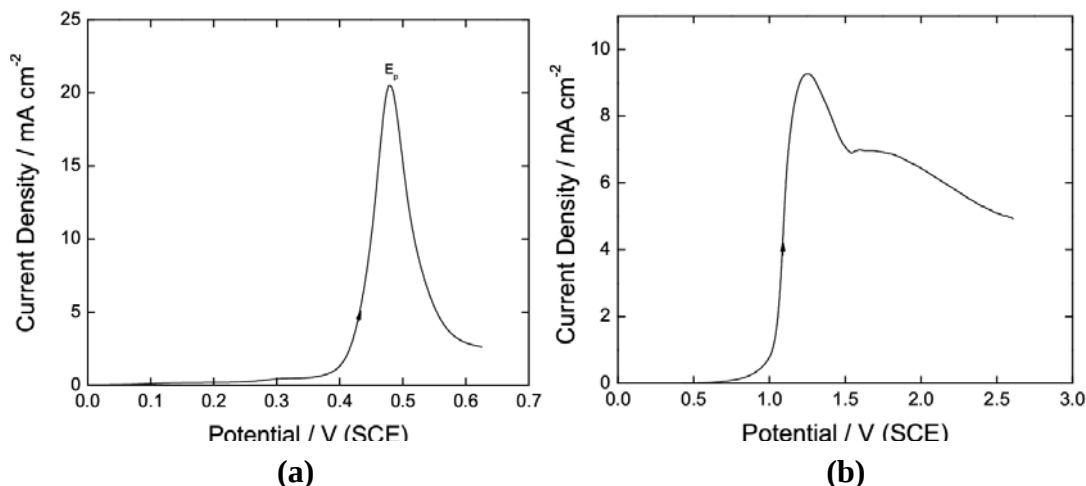
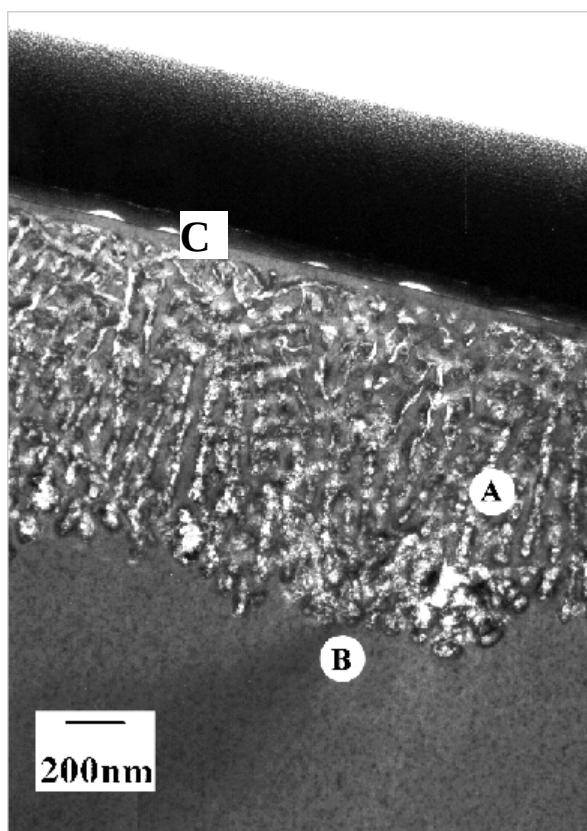
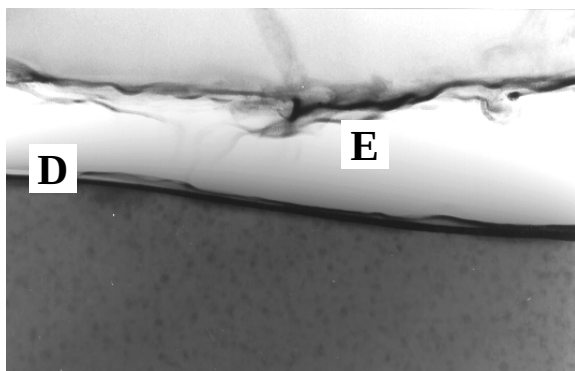


Figure 1. LSV at 2.5 mV s^{-1} of an n-InP electrode with a carrier concentration of $\sim 3 \times 10^{18} \text{ cm}^{-3}$ in (a) 5 mol dm^{-3} KOH and (b) 1 mol dm^{-3} KOH.

same scan rate (2.5 mV s^{-1}). A significant anodic process clearly occurs in both cases leading to a peak at 0.48 V in (a) and at $\sim 1.25 \text{ V}$ in (b).



(a)



(b)

Figure 2. TEM images of n-InP with a carrier concentration of $\sim 3 \times 10^{18} \text{ cm}^{-3}$ after an LPS at 2.5 mV s^{-1} (a) from 0 V to 0.63 V (SCE) in $5 \text{ mol dm}^{-3} \text{ KOH}$ and (b) from 0 V to 1.3 V (SCE) in $1 \text{ mol dm}^{-3} \text{ KOH}$. The amorphous deposit E was added during specimen preparation for TEM.

After anodization, the electrodes were examined using TEM. The resulting micrographs in Fig. 2 show that the anodic processes are remarkably different in the two different concentrations of KOH. Fig. 2(a) shows that anodization in $5 \text{ mol dm}^{-3} \text{ KOH}$ results in the formation of a nanoporous layer. In contrast, Fig. 2(b) shows that there appears to be little change in the electrode after anodization in $1 \text{ mol dm}^{-3} \text{ KOH}$ other than a thin ($\sim 25 \text{ nm}$) surface film, as marked at D.

Fig. 2(a) is typical of what is observed when highly doped n-InP is anodized in KOH in the concentration range $2\text{--}10 \text{ mol dm}^{-3}$. A porous region A extends into the InP substrate B and is capped by a thin (in this case $\sim 40 \text{ nm}$), near-surface layer C of unmodified InP. The thickness of the nanoporous region is generally uniform although in some cross-sections the interface with the substrate is characteristically found to be non-planar. The average pore width and inter-pore distances in Fig. 2(a) are similar ($\sim 40 \text{ nm}$) to one another as well as to the thickness of the near-surface layer.

Careful examination of TEM images shows that the near-surface layer contains a sparse distribution of localized channels from which the underlying pores appear to emanate. It is assumed that both the porous layer and the channels through the near-surface layer are filled with electrolyte, which connects the porous structure with the bulk electrolyte. This enables ionic current to flow and electrochemical oxidation of InP to

proceed, thus providing a mechanism by which the porous layer can grow.

Also in experiments at constant potential, a nanoporous region forms beneath a thin near-surface layer, similar to that described above for linear potential sweep (LPS) conditions. The pore size as well as the pore morphology varies somewhat with potential. Similar observations have been reported for InP electrodes anodized galvanostatically in HCl based electrolytes.^{15,43}

2. Surface Examination by Atomic Force Microscopy (AFM)

Further evidence for the existence of channels through the near-surface layer was obtained from AFM examination of the surface of electrodes after anodization³⁷. The AFM image, Fig. 3(a), following an LPS from 0 V to 0.425 V clearly shows an etch pit that has formed on the surface. Fig. 3(b) shows a line scan across the pit in Fig. 3(a). Although the AFM cannot accurately profile deep pits, we can see that the diameter of the pit is ~ 50 nm in agreement with cross-sectional TEM images³⁶. Similar pits were observed in AFM images obtained in other LPS experiments with upper potentials in the range 0.4 V to 0.53 V and in experiments at constant potentials.

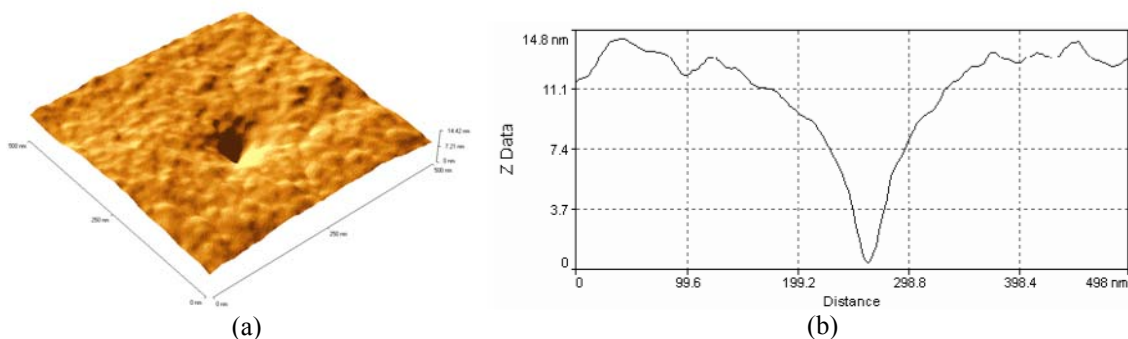


Figure 3. (a) AFM image of the surface of an InP electrode after LPS at 2.5 mV s^{-1} in 5 mol dm^{-3} KOH from 0 V to 0.425 V (SCE); (b) line scan through pore shown in (a). The carrier concentration is $\sim 3 \times 10^{18} \text{ cm}^{-3}$.

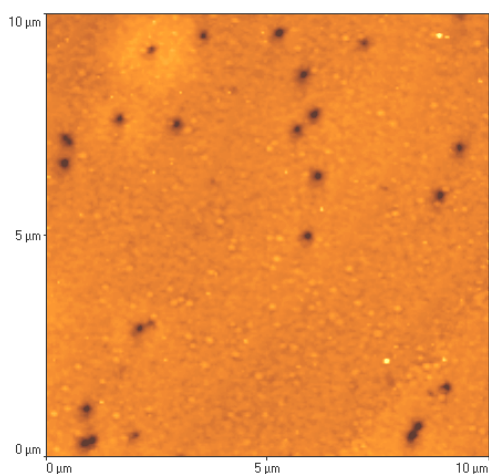


Figure 4. AFM image of the surface of n-InP (carrier concentration $\sim 3 \times 10^{18} \text{ cm}^{-3}$) after an LPS from 0 V to 0.48 V (SCE) at 2.5 mV s^{-1} in 5 mol dm^{-3} KOH.

Estimates were made of the density of pits on electrode surfaces from lower magnification AFM images. A typical image is shown in Fig. 4 after an LPS from 0 V to 0.48 V (corresponding to the current peak). The density of pits on the surface is $2.3 \times 10^7 \text{ cm}^{-2}$ in this case. Estimates of pit density were similarly obtained for other upper potentials and the results are plotted in Fig. 5. It is clear that the rising side of the current peak corresponds to a progressive increase in density of surface pits; when the current maximum is reached, no further significant increase in pit density is observed.

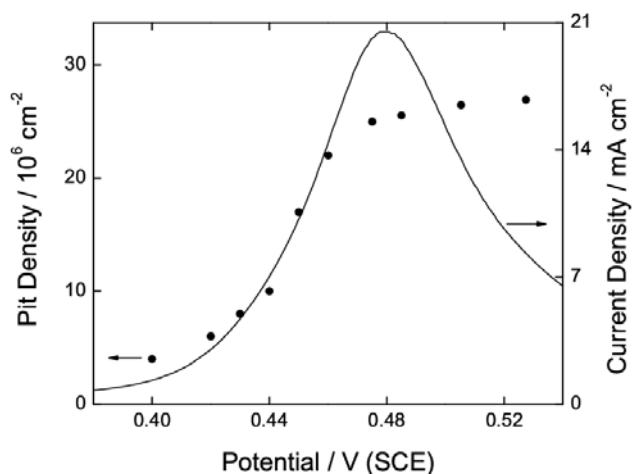


Figure 5. Areal density of surface pits (●) on n-InP electrodes, following an LPS from 0 V (SCE), plotted against the upper potential. The line shows the corresponding LSV. The carrier concentration is $\sim 3 \times 10^{18} \text{ cm}^{-3}$. The scan rate was 2.5 mV s^{-1} and the electrolyte was $5 \text{ mol dm}^{-3} \text{ KOH}$. Pit densities were determined from $10 \mu\text{m} \times 10 \mu\text{m}$ AFM images.

3. Formation of Porous Domains

In order to investigate the mechanism by which porosity develops, LPS experiments were carried out to upper potentials below the peak and the electrode was then cross-sectioned and examined. A TEM micrograph of such a cross-section (Fig. 6) shows that individual triangular nanoporous domains have formed. These are separated from the surface by a thin ($\sim 40 \text{ nm}$) dense near-surface layer A, as was observed for the more fully developed nanoporous layer. Thus, it appears that the development of porosity begins with individual porous domains, each originating from a single channel through the near-surface layer. These domains eventually merge to form a porous layer.

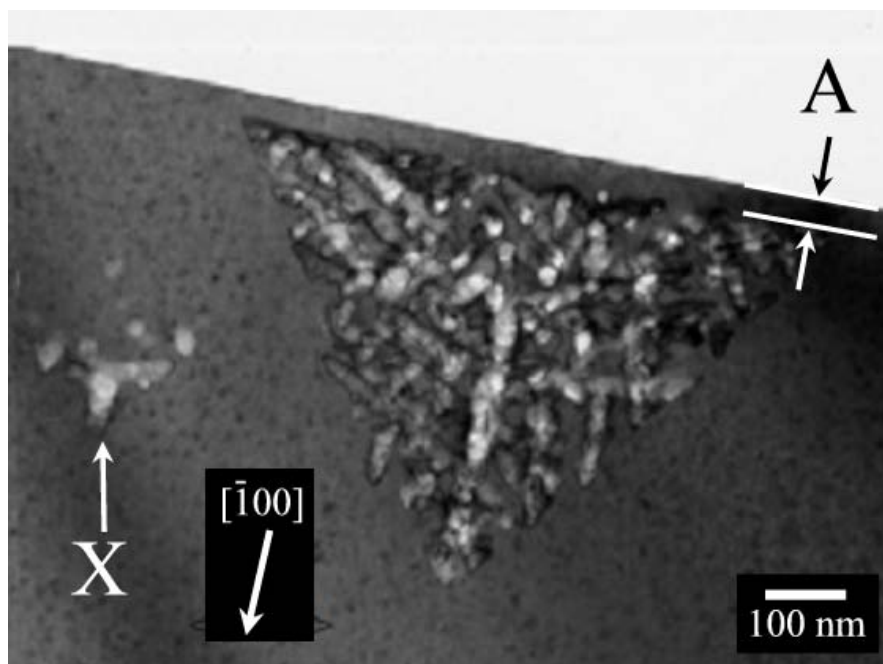


Figure 6. Cross-sectional TEM image of n-InP after an LPS from 0.0 to 0.44 V (SCE) in $5 \text{ mol dm}^{-3} \text{ KOH}$ at 2.5 mV s^{-1} . The carrier concentration is $\sim 3 \times 10^{18} \text{ cm}^{-3}$. The TEM slice is $\sim 100 \text{ nm}$ thick; the $[\bar{1}00]$ direction is shown by an arrow.

4. Domain Shape

4. 1. Model

In III-V semiconductors the $\{111\}$ B planes (e.g. the phosphorous planes in InP) are commonly found to be fast-etching in electrochemical pore formation^{44,45} as well as in wet etching^{42,46-50} and photoelectrochemical etching.^{51,52} This means that the direction of etching (i.e. the direction in which an etch-front moves or a pore propagates) is $\langle 111 \rangle$ A. A model for this behavior was proposed by Gatos and Levine^{53,54} and supported by the subsequent work of Holt.⁵⁵

We therefore consider preferential growth along the $\langle 111 \rangle$ A directions of pores originating at a surface pit and show how we can deduce the shape of the resulting porous domains. In order to do this, it is useful to first consider the hypothetical case of pores originating at a point in the interior of a crystal and advancing only along the $\langle 111 \rangle$ A directions. If branching of pores does not occur and if, at any given time, all pores grow at the same rate, then after a time t pores will have grown an equal distance l along each of the four $\langle 111 \rangle$ A directions. These primary pores will form the vertices of a tetrahedron, and if branching occurs along the $\langle 111 \rangle$ A directions, the interior of this tetrahedron will fill completely with pores. However, during anodic etching the domain originates not from a point in the bulk of the semiconductor but from a point near the surface of the electrode, and therefore only one half of the tetrahedron

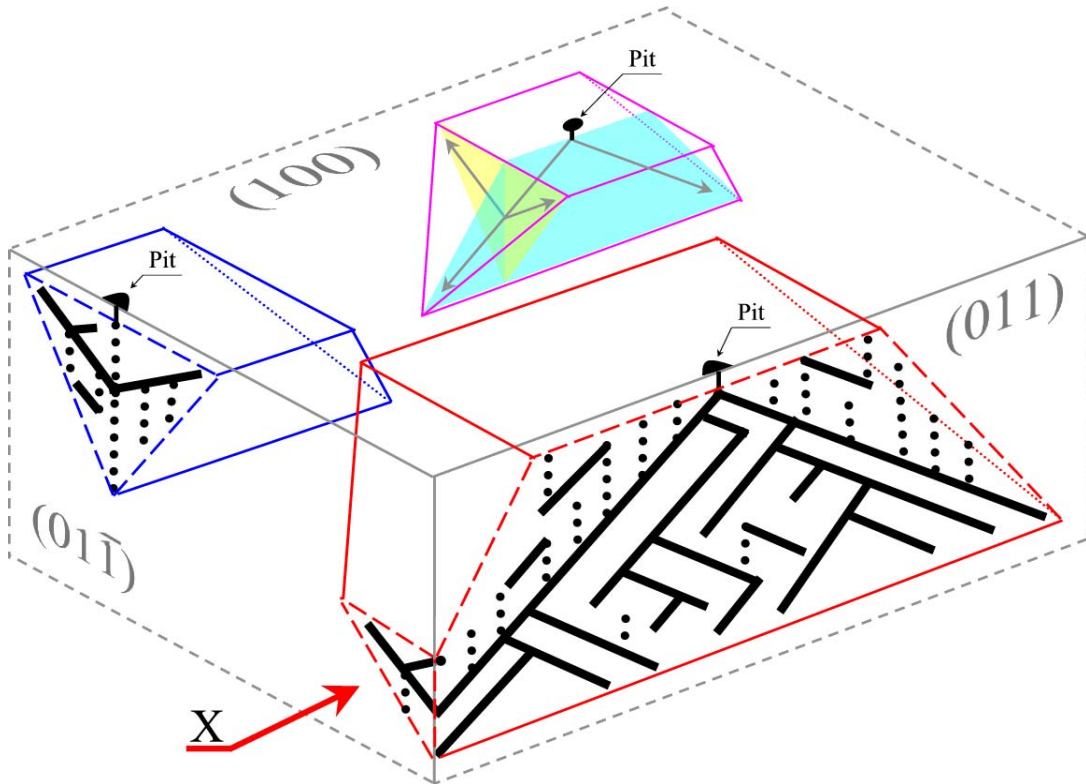


Figure 7. Isometric drawing of porous domains predicted for pore growth along the $\langle 111 \rangle$ A directions. The trapezium-shaped and triangular cross-sections in the (011) and (01 $\bar{1}$) cleavage planes, respectively, are shown. Where the (01 $\bar{1}$) cleavage plane intersects a domain near one of its vertices, the resulting small triangular cross-section (X) appears at a distance from the surface: an example is seen at X in Fig. 6.

can be formed. As shown in Fig. 7, the truncated tetrahedral shape produced according to this model has trapezium-, triangle- and square-shaped cross-sections in (011), (01 $\bar{1}$) and (100) planes, respectively.

4.2. Cross-Sectional Electron Microscopy

To test this model, electron microscope images of anodized electrodes were taken in three orthogonal views: the (100) surface plane, the (011) cleavage plane (parallel to the primary flat of the wafer) and the (01 $\bar{1}$) cleavage plane (parallel to the secondary flat). Fig. 8 shows an SEM (011) cross-section from the early stages of anodization. A trapezium-shaped nanoporous domain (indicated by the dotted line) is observed. The domain is separated from the surface by a layer of dense InP (at A). The similarity to the trapezium-shaped domain cross-section in the (011) plane in Fig. 7 is clearly evident. Primary pores extend downwards along the $\langle 111 \rangle_A$ directions from a point near the surface to the bottom corners of the trapezium (see the pore marked 'B' on the left and a similar pore symmetrically on the right) Other pores branch downwards along the $\langle 111 \rangle_A$ directions from the primary pores and fill the region between the primary pores. In contrast, the region between the primary pores and the near-surface layer has few in-plane pores and is occupied mainly by holes. These holes can be seen in the (011) cross-section of the schematic in Fig. 7 and are the cross-sections of $\langle 111 \rangle_A$ pores growing in orthogonal (01 $\bar{1}$) planes.

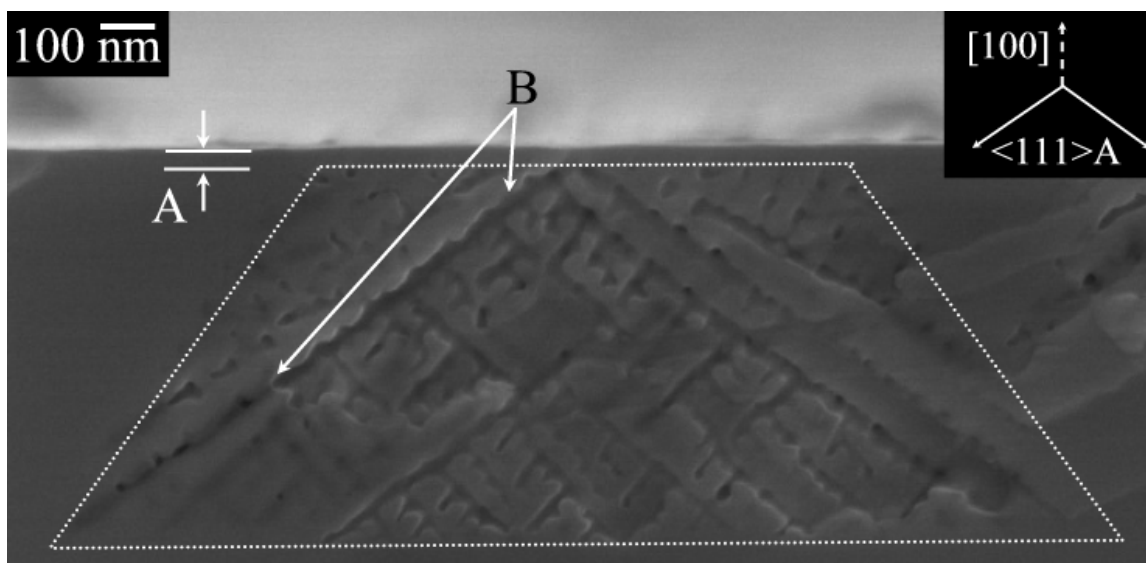


Figure 8. Cross-sectional SEM image of InP cleaved along the (011) plane following an LPS from 0 to 0.44 V (SCE) at 2.5 mV s^{-1} in 5 mol dm^{-3} KOH. Pore growth along the $\langle 111 \rangle_A$ directions to form a trapezium-shaped domain can be discerned.

Fig. 9 shows an SEM image of the (01 $\bar{1}$) plane of an InP electrode in the early stages of anodization. A triangular domain cross-section can be seen, corresponding to the (01 $\bar{1}$) cross-section in Fig. 7. Vertical arrays of holes can also be seen corresponding to cross-sections in this plane of $\langle 111 \rangle_A$ pores growing down from the surface in (011) planes as observed in Fig. 8. As can be seen in the schematic in Fig. 1, the $\langle 111 \rangle_A$ directions in this plane, the (01 $\bar{1}$) plane, are upwards towards the surface (making an angle of 35.26° with it). Pores along these directions seen in Fig. 9, are similar in orientation to those

represented schematically in the $(01\bar{1})$ cross-section in Fig. 7. Thus we can see from Figs. 8 and 9 that pores grow downwards from the surface along the $\langle 111 \rangle_A$ directions in the (011) plane and upwards along the $\langle 111 \rangle_A$ directions in the $(01\bar{1})$ plane giving patterns in the SEM cross-sections very closely resembling those represented schematically in the corresponding cross-sections in Fig. 7.

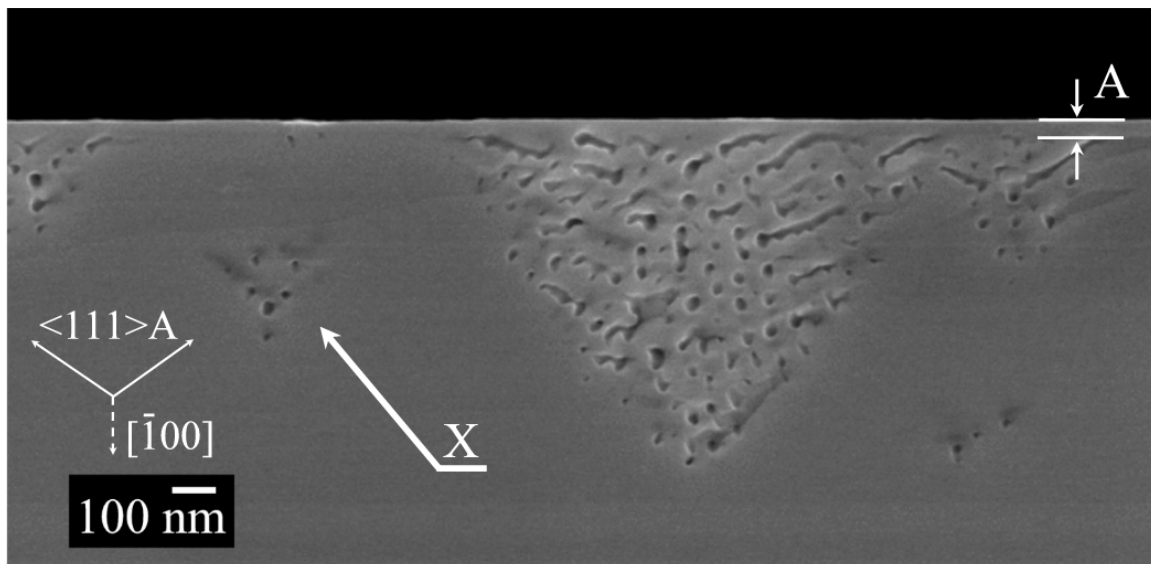


Figure 9. Cross-sectional SEM image of InP cleaved along the $(01\bar{1})$ plane (orthogonal to Fig. 8) following an LPS from 0 to 0.44 V (SCE) at 2.5 mV s^{-1} in 5 mol dm^{-3} KOH. Pore growth along the $\langle 111 \rangle_A$ directions and a triangular domain are clearly visible. A smaller domain cross-section at a distance from the surface is also visible (at X).

The TEM cross-sectional image in Fig. 6 is similar to the SEM image in Fig. 9 but the interior of the image has a different appearance. This is because a TEM image is a two-dimensional representation of a three-dimensional object—a slice of material with finite thickness. Because the image is a projection on a plane, the actual pore directions cannot be directly observed. Overlapping pores have the appearance of intersecting and pores that are growing through the volume have the appearance of growing in the plane of the image. Thus, prominent features in Fig. 6, the $[\bar{1}00]$ central axis of the domain and parallel $[\bar{1}00]$ features, which are at intervals of $\sim 40 \text{ nm}$, correspond to planes of pores growing in the orthogonal (011) planes and to the vertical arrays of holes in Fig. 9.

In both the TEM (Fig. 6) and SEM (Fig. 9) images of the $(01\bar{1})$ cross-section, a small triangular feature (marked X in each case) at a considerable distance from the surface is observed. It is clear that this is a cross-section of a domain that intersects the $(01\bar{1})$ cleavage plane close to one of its corners as shown at X in Fig. 7. This provides further confirmation that the nanoporous domains have a truncated-tetrahedron shape.

4.3. Plan-View Electron Microscopy

Fig. 10 shows a plan-view TEM image of a 100-nm-thick slice along the (100) plane taken from the surface of an electrode. A nanoporous region with a square outline is

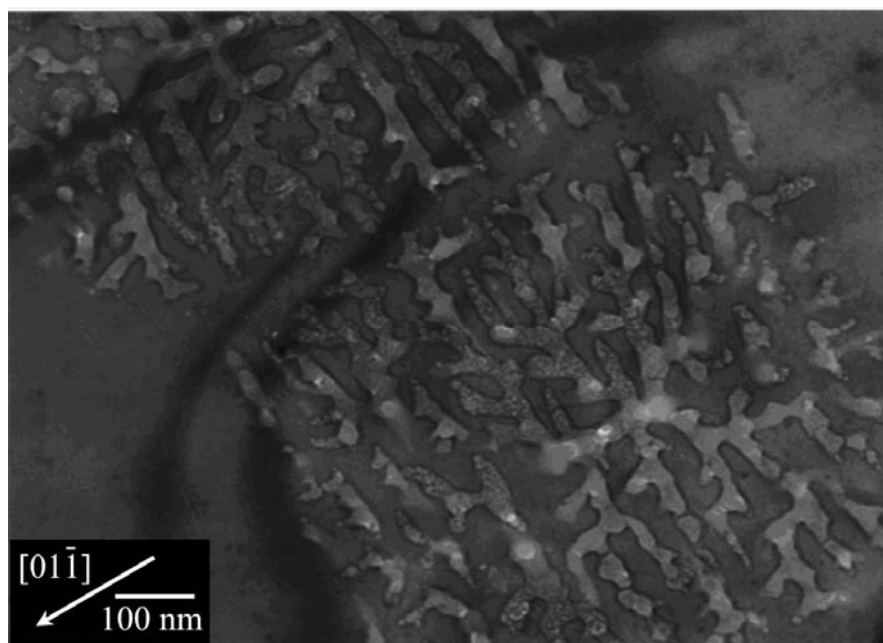


Figure 10. Plan-view TEM image of a ~100-nm-thick section taken from the surface of the same InP electrode as in Fig. 6. The plane of the micrograph is (100).

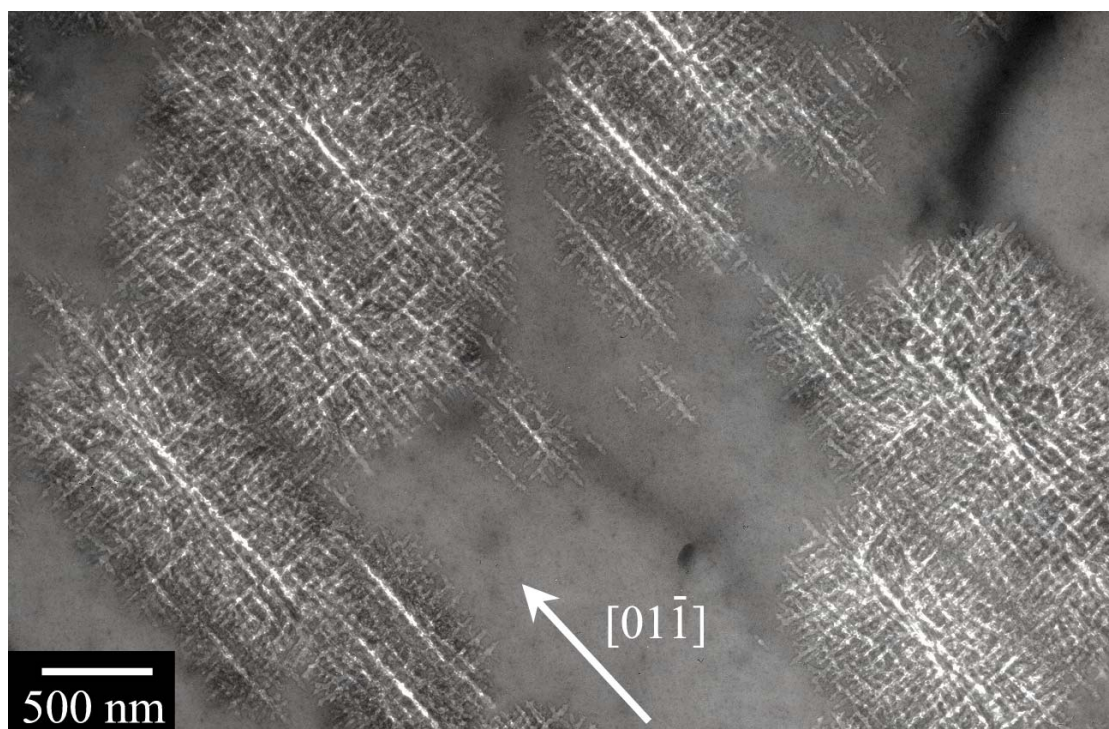


Figure 11. Plan-view TEM image of a ~400-nm-thick section taken from the surface of the same InP electrode as in Fig. 9. The plane of the micrograph is (100).

clearly visible. This is consistent with the shape of the domain in Fig. 7 which shows a square base parallel to the surface of the electrode and immediately below the near-surface layer. The porosity within the square-shaped outline of the domain base appears as a mesh of approximately orthogonal structures. These are approximately parallel to the sides of the square and correspond to the $\langle 011 \rangle$ directions. Thus, the mesh represents the projection on the (100) plane of pores along the $\langle 111 \rangle_A$ directions, again consistent with Fig. 7.

Due to the thinness of the slice in Fig. 10, only the near-surface part (i.e. the square base) of the porous structure can be observed. When a thicker slice is examined it is possible to view the overall outline of domains in plan-view and not just the base of the domain. Fig. 11 shows such an image where some of the domains are small enough to be completely within the thickness of the TEM slice. (The section thickness is ~ 400 nm which is thicker than some, but not all, of the domains at this stage of etching.) In this image it can be seen that the domains are terminated at points in the long direction and by flat edges in the short direction, similar to the outline of a ship's deck and corresponding to the overall domain shape of a truncated tetrahedron (see Fig. 7). Again, the pores within the domains are aligned in a mesh along the $\langle 011 \rangle$ axes corresponding to planes of pores growing along the $\langle 111 \rangle_A$ directions.

4.4. Surface Imaging by SEM

Fig. 12(a) is a SEM secondary-electron image of the surface of an electrode that has been anodically etched. The electron energy is sufficiently high (20 keV) to allow both the surface and near sub-surface features of the electrode to be examined. As previously observed by AFM¹⁶ the etching has caused small pits to appear in the surface. As observed in Fig. 12(a), these pits are approximately circular with a typical diameter of 20 nm.

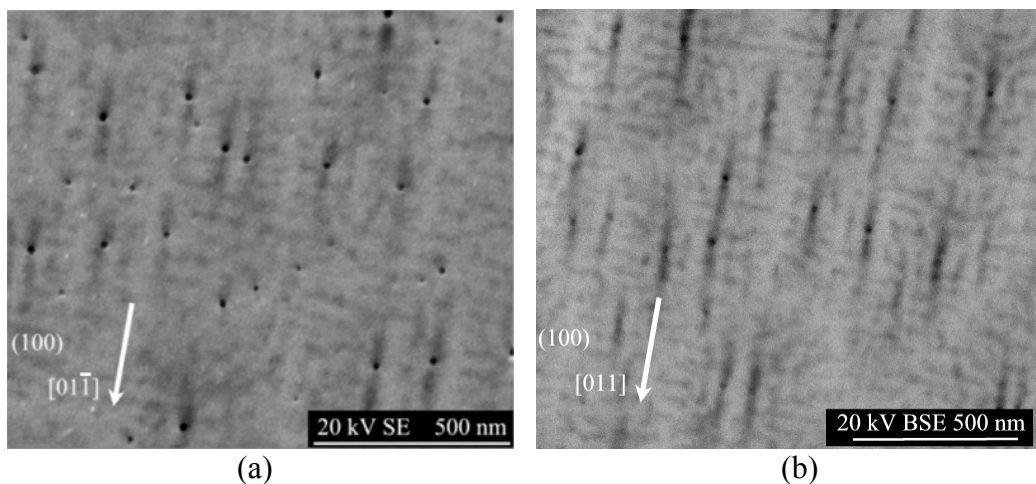


Figure 12. (a) Secondary-electron and (b) backscattered-electron SEM images of (100) InP surface following a LPS from 0.0 to 0.537 V (SCE) in 5 mol dm^{-3} KOH at 2.5 mV s^{-1} . Both images were taken at 20 kV allowing surface pits and some sub-surface features to be visible.

Fig. 12(b) is a SEM backscattered-electron image of the same electrode. The image highlights sub-surface structures similar to the structures that are visible in Fig. 12(a) as pronounced dark primary stripes pointing from the surface-pits along the $[01\bar{1}]$ and $[0\bar{1}1]$ crystallographic directions, and less pronounced secondary stripes extending orthogonally away from the primary stripes. This mesh of orthogonal stripes along the $\langle 011 \rangle$ axes of the image corresponds to the $\langle 011 \rangle$ structures seen in TEM plan views (Fig. 10). They are the projections in the (100) plane of pores along the $\langle 111 \rangle_A$ direction.

4.5. Comparison of Experimental and Theoretical Domain Shapes

Fig. 13 shows a schematic representation of domain cross-sections predicted (Fig. 1) for the two orthogonal $\{011\}$ planes that contain the central $[100]$ axis of a domain. Each of the schematics shows the outline of a domain that has grown for a time t from an originating point just beneath the surface. After a time t , the main pores in a domain (running from the central point to a vertex) will have grown a length, l . Since l is along a $\langle 111 \rangle$ direction, the domain depth b and the width of the domain base c (half the length of the long edge of the trapezium) are the components of l along the $\langle 100 \rangle$ and $\langle 011 \rangle$ directions, respectively. Thus, l is the diagonal of a cube of side b , and c is the diagonal of the cube face. It follows that

$$b = l\sqrt{1/3}$$

$$c = l\sqrt{2/3} = b\sqrt{\frac{3}{1}}\sqrt{\frac{2}{3}} = b\sqrt{2}$$

and the side a of the cross-section is

$$a = \sqrt{b^2 + \left(\frac{c}{2}\right)^2} = \sqrt{b^2 + \frac{b^2}{2}} = b\sqrt{3/2}$$

Thus, the predicted value of the width-to-depth ratio is $\frac{c}{b} = \sqrt{2} = 1.414$. Similarly, the ratio $\frac{a}{c} = \frac{\sqrt{3/2}}{\sqrt{2}} = 0.866$. These ratios are valid for any $(01\bar{1})$ domain cross-section but they are only valid for (011) domain cross-sections that include the central axis of the domain (where a cleave contains the surface pit of the domain).

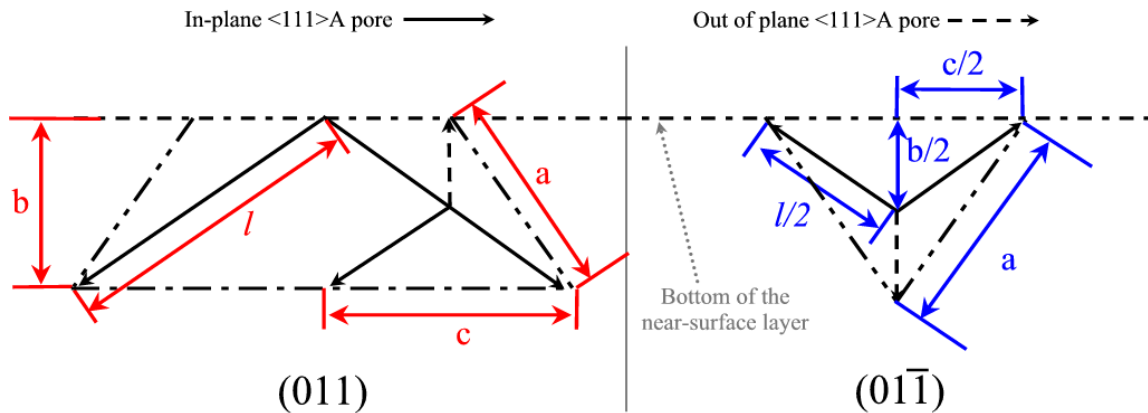


Figure 13. Schematic representation of $\{011\}$ cross-sections along the central $[100]$ axis through a domain from Fig. 7.

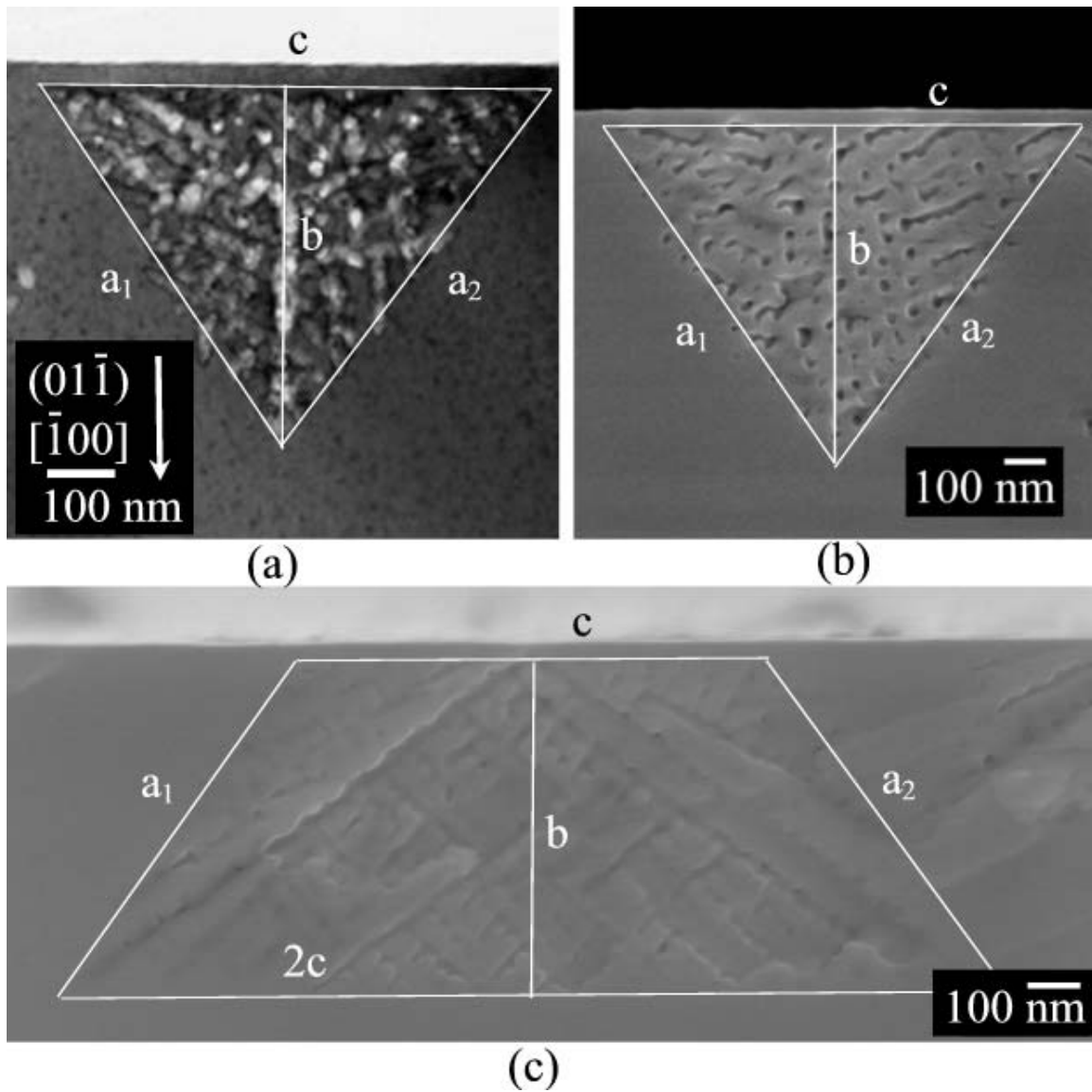


Figure 14. Micrographs showing where the measurements for Table 1 were obtained. (a) TEM image in Fig. 6; (b) SEM image in Fig 9; and (c) SEM image in Fig 8.

Measurements taken from TEM and SEM $\{011\}$ domain cross-sections (see Fig. 14) are shown in Table 1. The ratios of these values are also shown along with the corresponding theoretical values. It can be seen that there is excellent agreement between the experimental and theoretical values. This is strong evidence that the images of domains obtained by TEM and SEM are cross-sections of square-based truncated tetrahedral domains resulting from the propagation of pores from individual pits preferentially along the $\langle 111 \rangle_A$ directions.

Table 1. Comparison of experimental and theoretical ratios for the dimensions of porous domains. The superscript letters a, b and c, refer to the respective images in Fig. 14.

	Measured Value / nm (Triangle, TEM) ^a	Measured Value / nm (Triangle, SEM) ^b	Measured Value / nm (Trapezium, SEM) ^c	Predicted Value
a_1	794	949	787	$l\sqrt{1/2}$
a_2	805	978	783	$l\sqrt{1/2}$
b	650	785	643	$l\sqrt{1/3}$
c	919	1111	903	$l\sqrt{2/3}$
$2c$	n/a	n/a	1810	$l\sqrt{8/3}$
$\frac{c}{b}$	1.413	1.415	1.404	1.414
$\frac{2c}{(2 \times b)}$	n/a	n/a	1.407	1.414
$\frac{a1}{\langle c \rangle}$	0.863	0.854	0.870	0.866
$\frac{a2}{\langle c \rangle}$	0.876	0.880	0.866	0.866

5. Propagation of Pores

In Fig. 8, two primary pores that have grown all the way through the porous layer from a pit in the surface are clearly visible. These pores have propagated preferentially along the $\langle 111 \rangle_A$ directions. The pores appear to have a uniform width: there is no evidence that the pores are wider closer to the surface. This suggests that pore growth occurs only at the pore tips with no subsequent widening due to etching at the walls of the electrolyte-filled pores.

Other (shorter) pores are also visible. They are generally along the $\langle 111 \rangle_A$ directions but deviate somewhat from these directions in places. Where pores are in close proximity to each other they have diverged, and when growing towards each other they have avoided crossing. This tendency of pores to grow around obstacles is frequently observed in

micrographs. The cause is discussed briefly below: a detailed discussion can be found in ref. 40.

Observations of pore cross-sections in SEM and TEM images suggest that pore tips are pyramidal in shape with $\{111\}$ A internal faces. Despite the tip shape, the pore cross-sections are round and the pore width is constant regardless of distance from the tip, *i.e.* the pores are cylindrical in shape. The $\{111\}$ A faces near the tip are revealed due to fast etching of loosely bound $\{111\}$ B phosphorus atoms. This process results in removal of planes of atoms parallel to the $\{111\}$ A facets beginning with an indium vacancy in a $\{111\}$ A face. A vertex is therefore maintained where the three $\{111\}$ A facets intersect; this, in turn, maintains the electric field near the tip due to the high surface curvature in this region. To the rear of the tip, the electric field decreases below the threshold value required for etching and the locus of the threshold electric field is such that the resulting pore cross-section is approximately circular.

Where the availability of carriers is reduced near one side of a pore tip, etching is reduced at that side, causing pore growth to deviate from the $\langle 111 \rangle$ A direction. This also results in changes in the shape of a tip and the channel that is left in its wake. Such reductions in the availability of carriers can occur where the depletion region surrounding the tip overlaps another region that is depleted of carriers, *e.g.* during the formation of a pit in the electrode surface or when a pore tip is close to an existing pore or to the near-surface layer.

6. Effect of Electrolyte Concentration

LSVs of n-InP in 10 mol dm⁻³ KOH show a single anodic current peak at 0.41 V. As the concentration of electrolyte is decreased, the peak increases both in current density and in charge and shifts to more positive potentials. At 2 mol dm⁻³ the initial peak is followed by additional partially resolved, broader peaks but, with further decrease in concentration, individual peaks are eventually no longer discernable. Porous layers are observed in SEM cross-sections following LPSs and the porous layer thickness increases significantly with decreasing concentration of KOH, reaching a maximum value at ~2.2 mol dm⁻³. At concentrations less than 1.8 mol dm⁻³ the layer thickness decreases sharply. No porous layers are observed at a concentration of 1.1 mol dm⁻² or lower.

A gradual increase in layer porosity with decreasing electrolyte concentration, from ~18% at 10 mol dm⁻³ to ~40% at 2 mol dm⁻³, is observed. It is also observed that the pore width increases with decreasing concentration from ~17 nm at 10 mol dm⁻³ to ~62 nm at 2 mol dm⁻³. Correspondingly, the inter-pore spacing decreases with decreasing concentration from ~40 nm at 10 mol dm⁻³ to ~15 nm at 2 mol dm⁻³.

During the gradual transition from porous to non-porous etching, as the concentration is decreased, pore diameters become wider and pore walls become narrower until eventually anodization simply results in a rough surface that appears to become smoother at lower concentrations. The transition from porous to non-porous etching is shown in a typical series of SEM images in Fig. 15.

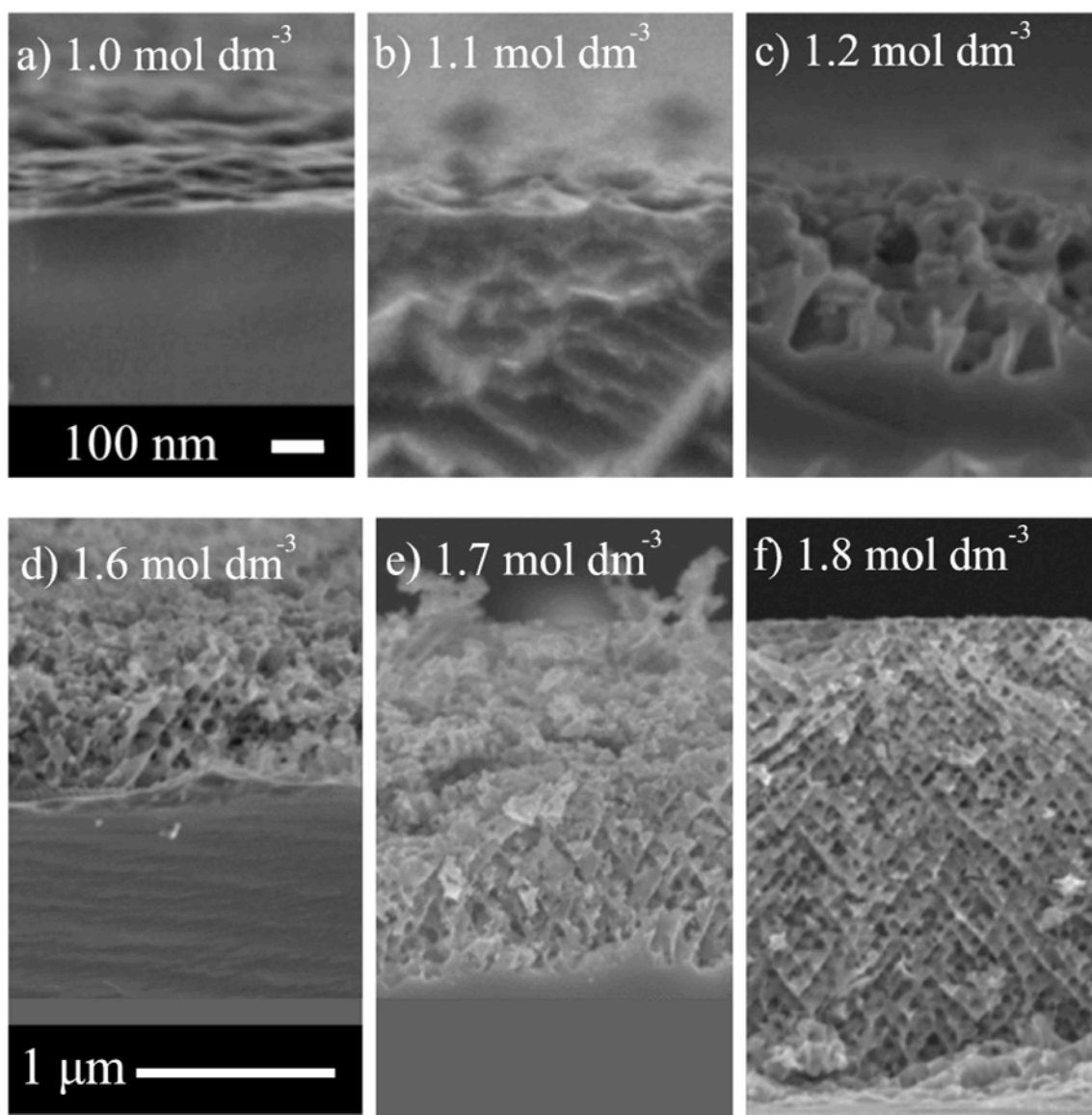


Figure 15. Cross-sectional SEM images of InP electrodes following a LPS from 0.0 to 0.75 V (SCE) at 2.5 mV s^{-1} in KOH solutions of the concentrations shown.

7. Deconvolution of the Effects of Time and Potential

We developed a technique to deconvolute the effects of potential and time in cyclic voltammograms (CVs) and LSVs and explain their shape and their relationship to porous layer formation. This technique analyzes the instantaneous value of the rate of change of current with respect to time and potential by measuring the forward and reverse slopes of CVs during porous layer formation. A series of cyclic voltammograms is obtained with a range of upper potentials. The slopes of the forward and reverse curves are estimated at the point of potential reversal on each CV. From this data, the rates of change of current with voltage and with time respectively, $(\partial I/\partial E)_t$ and $(\partial I/\partial t)_E$, are estimated.

Characteristic voltammograms are observed for n-InP anodes with different carrier concentrations. At a carrier concentration of $\sim 3 \times 10^{18} \text{ cm}^{-3}$, electrodes exhibit only a

single current peak on the forward sweep. A typical curve is shown in Fig 16. The estimated rates of change of current with voltage and with time, $(\partial I/\partial E)_t$ and $(\partial I/\partial t)_E/v$ respectively, are also shown. It can be seen that, in this case, the effect of time dominates

At a carrier concentration of $\sim 5 \times 10^{18} \text{ cm}^{-3}$, the voltammetric response shows two distinct current peaks on the forward potential sweep. Analysis of $(\partial I/\partial E)_t$ and $(\partial I/\partial t)_E/v$ shows that, in the potential region of the first peak, porous layer growth is predominantly a function of time. Thus, the porous layer continues to grow if the potential is swept to, and held, at values in this range. This peak occurs due to the merging of porous domains (growing both vertically and laterally) into a continuous porous layer. An ‘ohmic’ increase in current after the first peak can similarly be shown to be due to the vertical growth of the fully formed porous layer.

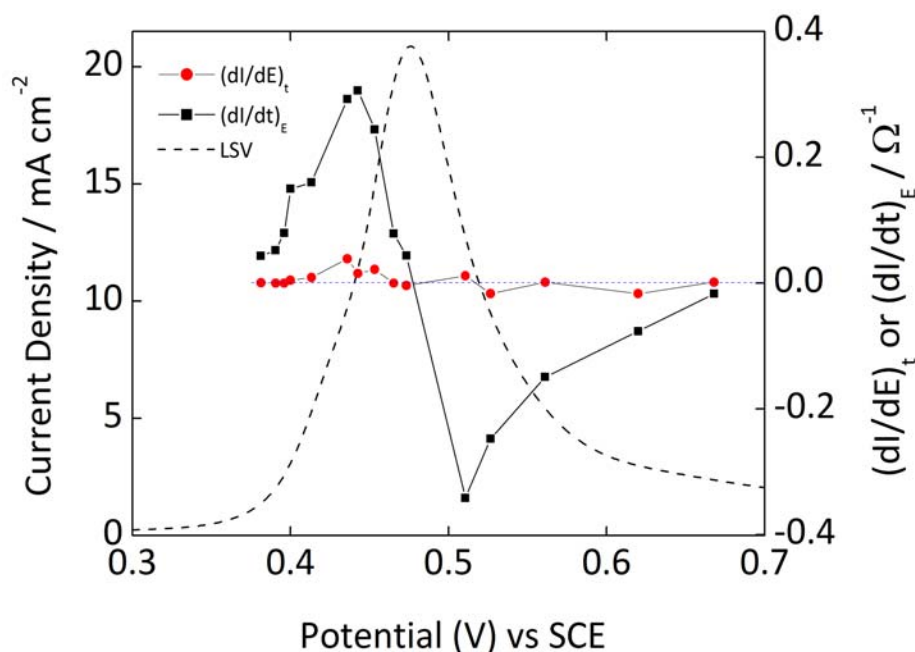


Figure 16. Potential dependence of $(\partial I/\partial E)_t$ and $(\partial I/\partial t)_E/v$ for a voltammogram (shown) of an n-InP electrode (carrier concentration $\sim 3 \times 10^{18} \text{ cm}^{-3}$) in 5 mol dm^{-3} KOH at a scan rate of 2.5 mV s^{-1} . The values for $(\partial I/\partial t)_E$ as calculated are divided by the scan rate v so as to have equivalent units to $(\partial I/\partial E)_t$.

Conclusions

Anodization of highly doped n-InP in aqueous KOH results in the formation of a nanoporous sub-surface region beneath a thin (typically $\sim 40 \text{ nm}$) dense near-surface layer. LSVs show a pronounced anodic peak corresponding to the formation of the porous region.

In the earlier stages of etching, AFM shows pit formation on the surface and TEM shows individual nanoporous domains, separated from the surface by a thin InP layer. Each domain develops by directionally preferential pore propagation from an individual surface pit. As they grow larger, domains merge to form a continuous nanoporous layer.

We developed a model of porous structure growth based on propagation of pores along the $\langle 111 \rangle_A$ directions. The model predicts porous domains with a truncated tetrahedral shape, having trapezium-, triangle- and square-shaped cross-sections in the (011), (01 $\bar{1}$) and (100) planes, respectively. This was confirmed by SEM and TEM. Cross-sectional SEM images show that pores originating from surface pits propagate along the $\langle 111 \rangle_A$ directions while TEM images show projections of $\langle 111 \rangle_A$ pores. Domain outlines observed in both TEM and SEM images are as predicted and the aspect ratios of the observed domains are in excellent agreement with those predicted by the model.

Pores are cylindrical and have well-developed facets only near their tips. Each pore tip is the apex of a pyramid formed by three $\langle 111 \rangle_A$ facets. Pore growth occurs only near the tips, where the electric field is high. Growth direction can deviate from $\langle 111 \rangle_A$ when the availability of holes is reduced at one side of a tip.

Porous layer thickness increases significantly with decreasing concentration of KOH, reaching a maximum value at $\sim 2.2 \text{ mol dm}^{-3}$. At concentrations less than 1.8 mol dm^{-3} the layer thickness decreases sharply. No porous layers are observed at a concentration of 1.1 mol dm^{-2} or lower.

We developed a technique to deconvolute the effects of potential and time in LSVs and explain their shape and their relationship to porous layer formation.

References

1. L. T. Canham, *Appl. Phys. Lett.*, **57**, 1046 (1990)
2. V. Lehman and H. Föll, *J. Electrochem. Soc.*, **137**, 653 (1990)
3. H. Föll, *Appl. Phys. A*, **53**, 8 (1991)
4. T. Holeç, T. Chvojka, I. Jelínek, J. Jindrich, I. Nemec, I. Pelant, J. Valenta and J. Dian, *Mater. Sci. Eng. C*, **19**, 251 (2002)
5. R. J. Martín-Palma, J. M. Martínez-Duart, L. Li and R. A. Levy, *Mater. Sci. Eng. C*, **19**, 359 (2002)
6. A. Matoussi, T. Boufaden, A. Missaoui, S. Guermazi, B. Bessaïs, Y. Mlik and B. El Jani, *Microelectronics Journal*, **32**, 995 (2001)
7. A. Jain, S. Rogojevic, S. Ponoht, N. Agarwal, I. Matthew, W. N. Gill, P. Persans, M. Tomozawa, J. L. Plawsky and E. Simonyi, *Thin Solid Films*, **398**, 513 (2001)
8. N. E. Chayen, E. Saridakis, R. El-Bahar, Y. Nemirovsky, *J. Molec. Biol.*, **312**, 591 (2001)
9. S. Langa, J. Carstensen, M. Christophersen, H. Föll, and I. M. Tiginyanu, *Appl. Phys. Lett.*, **78**, 1074 (2001)
10. G. Oskam, A. Natarajan, P. C. Searson and F. M. Ross, *Appl. Surf. Sci.*, **119**, 160 (1997)
11. M. M. Faktor, D. G. Fiddymment and M. R. Taylor, *J. Electrochem. Soc.*, **122**, 1566 (1975)

12. F. M. Ross, G. Oskam, P. C. Searson, J. M. Macaulay and J. A. Liddle, *Philos. Mag. A*, **75**, 2 (1997)
13. C. O'Dwyer, D. N. Buckley, D. Sutton, and S. B. Newcomb, *J. Electrochem. Soc.*, **153**, G1039-G1039 (2006)
14. S. Langa, J. Carstensen, I. M. Tiginyanu, M. Christophersen and H. Föll, *Electrochem. Solid-State Lett.*, **4**, G50 (2001)
15. S. Langa, I. M. Tiginyanu, J. Carstensen, M. Christophersen and H. Föll, *Electrochem. Solid-State Lett.*, **3**, 514 (2000)
16. C. O'Dwyer, D.N. Buckley, D. Sutton, M. Serantoni, and S.B. Newcomb, *J. Electrochem. Soc.*, **154**, H78 (2007)
17. P. Schmuki, J. Fraser, C. M. Vitus, M. J. Graham, H. S. Isaacs, *J. Electrochem. Soc.*, **143**, 3316 (1996)
18. P. Schmuki, D. J. Lockwood, J. Fraser, M. J. Graham, H. S. Isaacs, *Mater. Res. Soc. Symp. Proc.*, **431**, 439 (1996)
19. M. Christopherson, J. Carstensen, A. Feuerhake and H. Föll, *Mater. Sci. Eng. B*, **69**, 70, 194 (2000)
20. S. Rönnebeck, J. Carstensen, S. Ottow and H. Föll, *Electrochem. Solid-State Lett.*, **2**, 126 (1999)
21. P. Schmuki, L. E. Erickson, D. J. Lockwood, J. W. Fraser, G. Champion, H. J. Labbé, *Appl. Phys. Lett.*, **72**, 1039 (1998)
22. B. H. Erne, D. Vanmaekelbergh and J. J. Kelly, *J. Electrochem. Soc.*, **143**, 305 (1996)
23. J. Carstensen, M. Christophersen and H. Föll, *Mater. Sci. Eng. B*, **69-70**, 23 (2000)
24. S. Langa, J. Carstensen, I. M. Tiginyanu, M. Christophersen and H. Föll, *Electrochem. Solid-State Lett.*, **5**, C14 (2002)
25. S. Langa, J. Carstensen, M. Christophersen, K. Steen, S. Frey, I. M. Tiginyanu, and H. Föll, *J. Electrochem. Soc.*, **152**, C525 (2005)
26. S. M. Sze, *Physics of Semiconductor Devices* 2nd ed., John Wiley and Sons, New York (1981)
27. E. Harvey, C. O'Dwyer, T. Melly, D. N. Buckley, V. J. Cunnane, D. Sutton, S. B. Newcomb and S. N. G. Chu, in *Proceedings of the State-of-the-Art Program on Compound Semiconductors XXXV*, P.C. Chang, S. N. G. Chu, and D. N. Buckley, Editors, **PV 2001-2**, p. 87, The Electrochemical Society Proceedings Series, Pennington, NJ (2001)
28. D. N. Buckley, E. Harvey and S.N.G.Chu in *Proceedings of the 36th State-of-the-Art Program on Compound Semiconductors*, R.F. Kopf, F. Ren, E.B. Stokes, H. M. Ng, A.G. Baca, S.J. Pearton and S.N.G. Chu, Editors, **PV 2002-3**, p. 286, The Electrochemical Society Proceedings Series, Pennington, NJ (2002)
29. C. O'Dwyer, D. N. Buckley, V. J. Cunnane, D. Sutton, M. Serantoni and S. B. Newcomb, in *Proceedings of the State-of-the-Art Program on Compound*

- Semiconductors XXXVII*, P. C. Chang, W. K. Chan, D. N. Buckley, A. G. Baca, Editors, **PV 2002-14**, p. 259, The Electrochemical Society Proceedings Series, Pennington, NJ (2002)
30. D.N. Buckley, M. Serantoni, D. Sutton and S.B. Newcomb, in *Proceedings of the State-of-the-Art Program on Compound Semiconductors XXXIX*, R.F. Kopf, D.N. Buckley, F. Ren, C. Monier, K. Shiojima, A.G. Baca, H.M. Ng, T.D. Moustakas, and S.J. Pearton, Editors, **PV 2003-11**, p. 136-151, The Electrochemical Society Proceedings Series, Pennington, NJ (2003)
 31. D. N. Buckley, C. O'Dwyer, E. Harvey, T. Melly, M. Serantoni, D. Sutton and S. B. Newcomb, in *State-of-the-Art Program on Compound Semiconductors (SOTAPOCS XXXVIII) and Wide-Bandgap Semiconductors for Photonic and Electronic Devices and Sensors III*, **PV 2003-04**, pp. 48-62, The Electrochemical Society Proceedings Series, Pennington, NJ (2003).
 32. C. O'Dwyer, D. N. Buckley, D. Sutton, M. Serantoni and S. B. Newcomb in *State-of-the-Art Program on Compound Semiconductors (SOTAPOCS XXXVIII) and Wide-Bandgap Semiconductors for Photonic and Electronic Devices and Sensors III*, **PV 2003-04**, pp. 63-72, The Electrochemical Society Proceedings Series, Pennington, NJ (2003)
 33. R. Lynch, C. O'Dwyer, I. Clancy, D. Corcoran, and D. N. Buckley, in *State-of-the-Art Program on Compound Semiconductors XII and Nitride and Wide Bandgap Semiconductors for Sensors Photonics, and Electronics*, V, H. Ng and A. G. Baca, Editors, **PV 2004-06**, p. 85-95, The Electrochemical Society Proceedings Series, Pennington, NJ (2004)
 34. D.N. Buckley, C. O'Dwyer, R. Lynch, D. Sutton and S.B. Newcomb, in *State-of-the-Art Program on Compound Semiconductors XII and Nitride and Wide Bandgap Semiconductors for Sensors Photonics, and Electronics* V, H. Ng and A. G. Baca, Editors, **PV 2004-06**, pp. 103-117, The Electrochemical Society Proceedings Series, Pennington, NJ (2004)
 35. C. O'Dwyer in *State-of-the-Art Program on Compound Semiconductors XLII and Processes at the Semiconductor-Solution Interface*, P. Chang, D. N. Buckley, S. Ahmed, and K. Shiojima, Editors, **PV 2005-04**, pp. 40-63, The Electrochemical Society Proceedings Series, Pennington, NJ (2005)
 36. C. O'Dwyer, D. N. Buckley and S. B. Newcomb, *Langmuir* **21**, 8090-8095 (2005).
 37. R. Lynch, C. O'Dwyer, D. N. Buckley, D. Sutton and S. B. Newcomb, *ECS Trans.* **2**(5) 131-141 (2006)
 38. R. Lynch, C. O'Dwyer, D. Sutton, S.B. Newcomb and D.N. Buckley, *ECS Trans.*, **6**(2), 355 (2007).
 39. R. P. Lynch, M. Dornhege, P. Sánchez Bodega, H. H. Rotermund, and D. N. Buckley, *ECS Trans.* **6**(2), 331 (2007)
 40. R. Lynch, C. O'Dwyer, N. Quill, S. Nakahara, S. B. Newcomb, and D. N. Buckley, *ECS Trans.* **16**(3), 393 (2008)
 41. N. Quill, C. O'Dwyer, R. Lynch, and D. N. Buckley, *ECS Trans.* **19**(3), 295 (2009)
 42. M. Kappelt and D. Bimberg, *J. Electrochem. Soc.* **143**, 3271 (1996)
 43. G. S. Popkirov and R. N. Schindler, *Electrochim. Acta*, **39**, 2025 (1994)

44. S. Langa, J. Carstensen, I.M. Tiginyanu, M. Christophersen and H. Föll, *Electrochem. Solid-State Lett.* **5**, C-14 (2002)
45. E. Speicker, M. Rudel, W. Jäger, M. Leisner and H. Föll, *phys. stat. sol. (a)* **202**, 2950 (2005)
46. S. Iida and K. Ito, *J. Electrochem. Soc.* **118**, 768 (1971)
47. Y. Tarui, Y. Komiya and Y. Harada, *J. Electrochem. Soc.* **118**, 118 (1971)
48. S. Adachi and K. Oe, *J. Electrochem. Soc.* **130**, 2427 (1983)
49. P.H.L. Notten, *J. Electrochem. Soc.* **138**, 243 (1991)
50. I.E. Vermeir, W.P. Gomes and P. van Daele, *J. Electrochem. Soc.* **142**, 3226 (1995)
51. D. Soltz and L. Cescato, *J. Electrochem. Soc.* **143**, 2815 (1996)
52. M..M. Carrabba, N..M. Nguyen and R.D. Rauh, *J. Electrochem. Soc.* **134**, 1855 (1987)
53. H.C. Gatos and M.J. Lavine, *J. Electrochem. Soc.* **107**, 427 (1960)
54. H.C. Gatos, *J. Appl. Phys* **32**, 1232 (1961)
55. D.B. Holt, *J. Appl. Phys* **31**, 2231 (1960)