Morphology, interface polarity and branching of electrochemically etched pores in InP

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The 3-dimensional morphology of individual pores grown in InP(001) by electrochemical etching, their interface polarities and their branching behavior have been investigated by transmission electron microscopy (TEM) in various crystal lattice projections and by convergent-beam electron diffraction (CBED). Pores start to grow irregularly shaped with preferential orientation perpendicular to the surface. Following this nucleation layer long straight pores with triangular cross-section grow deep into the crystal along inclined \(\langle 111\rangle_B\) directions. Along the pore axis the pore diameter oscillates. The morphology of the pore tips can be described approximately by a chain of interconnected tetrahedrons bounded by \{111\}_A\)-facets. Some pores show additional \{001\} facets at the transition regions between the tetrahedrons. With increasing distance from the pore tips the mean pore diameters increase and the pores approach the shape of open prismatic channels with channel walls that are bounded, on the average, by \{112\}-planes. Self-assembling pore branching in all four \(\langle 111\rangle_B\) crystal directions leads to 3-dimensional pore arrangements which are of considerable interest for the fabrication of photonic crystals. – We discuss the observed pore morphologies within the framework of a model that describes the pore formation as an interplay of dissolution and surface passivation with the surface passivation being affected by the crystal polarity of the material.

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1 Introduction

Electrochemically etched pores in semiconductors have been the subject of intense research since the discovery of macropores in Si in 1990 [1] and of luminescent microporous Si in 1991 [2]. Since then various applications of porous semiconductors have been suggested, among these the use of periodic pore arrays as photonic band gap material (“photonic crystals”) [3, 4]. Most of the research work done so far has focused on the semiconductor Si because of the importance of this material in microelectronics. The mechanisms controlling the electrochemical pore etching in Si are now quite well understood allowing the pore sizes, the pore morphology and the three-dimensional arrangement of pores to be tuned over a wide range of dimensions and geometries (see [4] and references therein).

Since a few years also pores in the III–V compound semiconductors GaAs, GaP and InP are receiving increasing interest [5] triggered by the observation of interesting optical phenomena, like birefringence in porous InP at wavelengths suitable for optical communication systems [6, 7], pronounced photoluminescence shifts in InP showing long straight pores [8] and the strong enhancement of blue and ultraviolet

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luminescence in porous GaP [9]. Furthermore, a future perspective is the integration of photonic crystals based on porous compound semiconductors into optoelectronic devices. InP is the most promising material in this respect since the typical dimensions of pores and of pore arrays are in a range appropriate for photonic crystal applications in the visible spectral range [10].

Electrochemically etched pores in III–V semiconductors generally fall into one of two distinctly different groups: current line pores and crystallographically oriented pores, abbreviated here to “current pores” and “crystallographic pores”, respectively. Current pores follow the flow of the current, i.e. they are perpendicular to the equipotential surfaces in the sample. These pores are therefore mostly perpendicular to the sample surface [5, 8, 11]. However, their direction can be tuned to some extend by patterning the surface with metallic masks thus changing the electric field distribution in the near-surface region [12]. Crystallographic pores are largely controlled by the different dissolution rates of crystal facets and therefore follow low-index crystal directions and often show faceted pore walls [5, 13]. Crystallographic pores generally occur at small current densities whereas current pores develop at larger current densities [5]. The only pore growth direction reported for crystallographic pores in III–V semiconductors is \(\{111\}\)B reflecting the polar crystal structure of the material (cf. Chapter 2). 3-dimensional pore arrays have been found and have been attributed to a self-assembled repeated branching of crystallographic pores into the four equivalent \(\{111\}\)B directions [5]. For GaAs periodic 3-dimensional pore arrays (“domains”) formed from a single primary pore have been observed [5] suggesting that self-assembled branching of crystallographic pores may be exploited for the fabrication of photonic crystal structures. However, a detailed microscopic investigation of the branching of crystallographic pores in III–V semiconductors and an understanding of the factors governing the self-assembled branching is still missing.

Most of the microscopic investigations of pores in semiconductors have been carried out by scanning electron microscopy (SEM) which allows a fast characterization of pores and pore arrays at various magnifications. However, the use of SEM for characterization of crystallographic pores is limited because of the lack of direct crystallographic information (orientation of crystal facets, sign of the crystal polarity, …) in SEM images. Moreover, it is difficult to deduce 3-dimensional morphologies of pores and of pore junctions from SEM images if the pores are small (<100 nm). Transmission electron microscopy (TEM) enables a much more detailed characterization of pore structures owing to the higher spatial resolution of this technique and the availability of important additional crystallographic information in electron diffraction patterns. Application of TEM methods to crystallographic pores in Si allowed for the first time to reveal the 3-dimensional morphology and the branching behavior of pores in this material [14, 15]. Moreover, the observation of thin oxide layers at the pore interfaces directly contributed to the present understanding of the mechanisms leading to the formation of crystallographic pores in Si [14, 15].

In the present paper, results of a detailed TEM investigation of 3-dimensional arrays of crystallographic pores in InP are presented. Pores and pore junctions have been studied in different crystal projections allowing to reveal their three-dimensional morphology. By application of a recently developed convergent-beam electron diffraction (CBED) method for reliable polarity determination [16, 17] the relationship between the pore morphology and the crystal polarity of InP has been determined locally for the first time. The results confirm our models of pore growth in III–V semiconductors and provides new insight into the details of pore branching which is the basic process governing the formation of three-dimensional arrays of crystallographic pores for future photonic crystal applications.

2 Experimental details

In order to achieve crystallographic pores in n-type InP(001) \((n = 10^{17} \text{ cm}^{-3})\) electrochemical pore etching of polished InP wafers has been performed under anodic etching conditions in a 5 wt% aqueous HCl solution at 20 °C at a current density of 4 mA/cm². In order to improve the homogeneity of pore nucleation the experiments were started with a voltage spike of 40 V for half a second. For the TEM investigations electron-transparent specimens have been prepared in [001] plan-view geometry, as \(\langle 110\rangle\) cross-sections and as sections of various crystal orientations (\([101], [111]\)) using the bevel polishing technique.
The pore arrangement and morphology, the interfaces of pores and their relationship to the polar crystal structure have been investigated by the methods of transmission electron microscopy (TEM) and by convergent-beam electron diffraction (CBED). The experiments were performed using a Philips CM 30 transmission electron microscope at 300 kV.

To be consistent with previous work [5] we use the following notation for describing polar directions and polar faces in the InP crystal (cf. Fig. 6c): the four crystal directions pointing from an In atom to the next-nearest P atoms are termed $\langle 111 \rangle$B (and correspondingly the four directions pointing from a P atom to the next-nearest In atoms $\langle 111 \rangle$A). $\{111\}$A and $\{111\}$B describe the $\{111\}$ surfaces which are terminated by In atoms and P atoms, respectively, and are also assigned to the normal surface vectors pointing out of the corresponding surfaces. Notice that in this notation the direct space vectors $\langle 111 \rangle$A and the reciprocal space vectors $\{111\}$A are anti-parallel (Fig. 6c).

For determination of the crystal polarity of InP we applied a CBED method [16, 17], which we recently developed as an extension of an earlier method [18] established for polarity determination of GaAs and other zincblende compounds with a small mass difference of the constituting atoms. In our method the sign of the crystal polarity is deduced from the contrast differences in two CBED patterns taken under 4-beam dynamical diffraction conditions. Important for a reliable polarity determination is an appropriate choice of the excited reflections and of the sample thickness range. The reliability of the method under these conditions has been demonstrated first by dynamical contrast simulations [19] and later by a detailed comparison of experimental and simulated CBED patterns [16, 17].

3 Results

Characteristic for InP are the excellent self-assembling properties of pore growth along certain crystal directions forming a 3-dimensional array in a layer of several $\mu$m thickness near the substrate surface. An overview of the pore arrangement at a lower magnification is shown by the scanning electron micrograph of a (110) cleavage plane (Fig. 1). The contrast lines inclined from the (001) surface correspond to pores oriented along $\langle 111 \rangle$ crystal directions. On the length scale revealed by SEM such pores form a rather uniform two-dimensional pattern which extends about $\sim 15 \mu m$ deep into the substrate depending on the pore growth duration. The dark contrast dots correspond to pores that intersect the cleavage plane. In a layer below the surface about $2 \mu m$ thick the pore arrangement differs from that in the bulk. In this near-surface layer the pores appear to be preferentially aligned perpendicular to the surface.

Figure 2a shows a TEM-BF image of the sample surface in plan-view geometry. The image depicts nucleation sites of pores (bright square holes) and an irregular two-dimensional network of shallow etch-trenches. The pores possess $\{100\}$ facets and are embedded in shallow edge-pits, which are elongated along one of the in-plane $\langle 111 \rangle$ directions (see inset). Figure 2b shows a (110) cross-sectional TEM-BF
image of the near-surface layer. In this layer the pores possess a rather irregular shape with preferential orientation perpendicular to the surface in accordance with the contrast in the SEM image (Fig. 1). According to the common convention (cf. Chapter 1) such pores can be classified as current pores even though they show crystallographic contrast features (e.g. triangular contrast) and occasionally show branching. However, in contrast to the branching of crystallographic pores (see below), the pore branching in the near-surface layer is unspecific in the sense that it cannot be ascribed to the presence of crystallographically equivalent pore growth directions. At the lower interface of the layer there is an abrupt transition from current line pores to crystallographic pores, which branch into the inclined \(\langle 111\rangle\)-directions.

Figure 3 shows an example of the growth directions and the branching of crystallographic pores and their relationship to the polarity of the InP crystal. The bright-field image of a (101) bevel-polished specimen (Fig. 3a) depicts the tip region of a pore with pore branching. It becomes obvious from this example that (101) bevel-polished specimens are advantageous for such investigations since pore growth along two \(\langle 111\rangle\)-directions, \([1\bar{1}1]\) and \([\bar{1}11]\), are contained within the thin TEM foil and can be investigated by TEM over large distances. The tip of the long pore points into the bulk of the substrate (so called type-I pore) whereas the tip of the pore branch (upper right) points towards the substrate surface (so called type-II pore). The relationship between growth direction and crystal polarity has been deduced from an analysis of CBED patterns taken under two excitation conditions which have been chosen to be symmetric to the \{020\}-plane (Chapter 2). The CBED patterns are depicted with correct orientation with regard to the bright-field image. From the asymmetry of the contrast within the \{020\} diffraction discs the sign of the polarity or, in other words, the spatial orientation of the polar atom arrangements of the crystal may be determined \[16, 17\]. The result of this analysis is displayed as the projected atom arrangement for one unit cell. The growth directions of both pore branches are the \(\langle 111\rangle\)B-directions. The \([\bar{1}11]\) and \([1\bar{1}1]\) growth directions pointing into the bulk of the substrate belong to type-I pores whereas the \[111\] and \([\bar{1}1\bar{1}]\) growth directions pointing towards the surface belong to the type-II pores. This situation is depicted also as stereographic projection (Fig. 3c) where the growth directions of type-I pores and type-II pores are marked by \(\bigotimes\) and \(\bigodot\), respectively. The figure shows also the crystallographic projections which are useful for an investigation of pore morphologies and the \{101\}-plane of the bevel polish (Fig. 3a).

**Fig. 2** a) Plan-view TEM bright-field image of the top surface showing nucleation sites of pores. b) TEM bright-field image of a (110) cross-section sample showing the pore alignment in and below the nucleation layer.
Fig. 3  Relationship between the pore growth directions and the crystal polarity of InP: a) TEM bright-field image of a pore in a (101) bevel-polished specimen and CBED-patterns for determination of the crystal polarity. The result of the polarity analysis is depicted by the projected unit cell. The pore growth directions of both pore branches correspond to \(\langle 111\rangle\)B crystal directions, defined by the directions pointing from an In-atom to the neighboring next-nearest P-atom (cf. Fig. 6c). b) Schematic drawing showing the four possible \(\langle 111\rangle\)B pore growth directions. Two directions, \([\overline{1}1\overline{1}]\) and \([11\overline{1}]\), occur for pores that grow into the sample (“type-I pores”), the other two directions, \([11\overline{1}]\) and \([\overline{1}1\overline{1}]\), occur for pores that grow back towards the surface (“type-II pores”). c) Stereographic \([001]\) projection indicating various crystal projections which are particularly useful for studying the pore morphology. The growth directions of type-I pores (\(\bigcirc\)) and type-II pores (\(\bigotimes\)) are also indicated. A (101) section contains two pore growth directions, so that corresponding bevel-polished (101) TEM specimens are well-suited for analyses of pore morphologies and of pore branching (cf. Fig. 3a, Fig. 4).

Fig. 4  TEM bright-field images of a (101) bevel polished sample showing the morphology of a pore at different distances from the pore tip (left). Along the pore growth axis the pore diameter oscillates. The oscillation amplitudes slightly decrease with increasing distance from the pore tip while the pore diameter slowly increases. Multiple pore branching can be seen in the third and forth image (see arrows).
As mentioned before the (101)-bevel polish technique allows to prepare TEM foil specimens of thicknesses of a few 100 nm that completely contain the crystallographic pores over lengths of more than 20 µm. Figure 4 shows TEM micrographs of sections of one pore that has been investigated over a total length of ~17 µm (distances given indicate the lengths of pore sections not displayed). The investigation yielded the following characteristic morphological properties of pores: a) The pore diameters increase continuously with increasing distance to the pore tip, for the case shown from ~50 nm in the tip region to ~140 nm at ~17 µm distance to the pore tip. b) The pore diameters oscillate along the extension of the pores. Characteristic of these oscillations are facets near the pore tips and weaker undulations of the pore walls at larger distances from the tip. These morphologies will be discussed in more detail later (Figs. 5, 6). c) Repeated branching along other <111>B-directions is initiated along such longer pores. The example of 3-fold branching (Fig. 4, third micrograph) shows the branching of a type-II pore from the type-I pore, the subsequent branching into a type-I pore followed by the subsequent branching into a type-II pore (arrows). Pore branching and the morphology of pore junctions will be discussed in more detail later (Figs. 7, 8).

The morphology of different pore tips in different crystal projections is shown by the TEM bright-field micrographs in Fig. 5. The pronounced step-like faceting of tip regions in <111>-projections is given in Fig. 5a and b together with the polar atom arrangements of the InP crystal (as so called dumbbell structure) as obtained from CBED analysis (cf. Fig. 3). The dominating facets of the upper part are of {111}A type, indicating that the inner pore surface is terminated by In atoms. The smaller facets in-between are often {001}-planes and as such are non-polar surfaces (Fig. 5b). The faceting of the lower pore wall sections appears less clear since the chosen imaging condition does not allow for an edge-on projection of the facets. Figure 5c shows a pore tip ending within the TEM foil (upper right) and the cross-section of a pore that has penetrated the TEM foil (lower left). The TEM bright-field image has been taken with a [220]-reflection under two-beam conditions in a projection along the pore axes. The
pore cross-sections are triangular with edges parallel to the traces of \{112\}-crystal planes. The pore tip shows a triangular thickness fringe system indicating a tetrahedron-like tip shape. The thickness contours at the pore which penetrates the foil indicate that the diameter changes across the TEM foil thickness, in agreement with the observation of oscillating pore diameters described above. Figure 5d shows a TEM micrograph taken in a \(\langle 112\rangle\)-zone axis orientation and shows crystallographic pores with axes which are inclined with respect to the TEM plan-view specimen. Moreover, the directions of the \(\langle 111\rangle\) pore axes are inclined with respect to the \(\langle 112\rangle\) incident electron beam direction by about 18°. In contrast to the plan-view specimen prepared from the top-layer regions (Fig. 2a), this specimen from deeper layers has been prepared by thinning the material from two sides. The micrograph reflects a pore contrast which is typical for this projection geometry: the pores appear as chains of triangle-shaped interconnected voids with longer \{111\}A facets which are imaged edge-on (cf. also Figs. 5a, b, 6a).

Based on the experimental results of our characterizations Fig. 6 summarizes the pore morphologies in the tip regions by idealized drawings. Figure 6a shows a model which describes the pores as tetrahedral-like voids bounded by \{111\}A-facets and interconnected with each other along a \{111\}B-direction. The \(\langle 110\rangle\)-projection (right) depicts the transitions of the interconnected voids, allowing also for a smoothing of the edges near the transitions between the interconnected voids. This model describes the mor-
Fig. 7  Left: Pore branching imaged by TEM in four different crystal projections. The pore intersects the (111) TEM foil perpendicularly (top left image), and the cross-section appears triangular-shaped. The small pore starting from one of the corners of the intersecting pore shows a narrow neck. Right: Three-dimensional idealized model of the pore branching using truncated tetrahedra as structural units (cf. Fig. 6a).

In summary, the morphology of pores is characterized by oscillations of the pore diameters with amplitudes that decrease with the distance from the pore tips. These oscillations are due to, in parts, undulations or due to facets. The pore cross-sections are in all cases triangle-shaped (cf. Figs. 5c, 7, 9a, b). Hence, with increasing distance to the pore tips the pores take the shape of open prismatic channels with channel walls that are bounded, on the average, by facets with orientations near {112}.

The formation of a 3-dimensional pore array results from repeated branching of pores along the different ⟨111⟩B directions. The detailed morphology of the pore branching could be deduced from TEM investigations in different crystal projections. Figure 7 shows as example TEM bright-field images of the branching of a pore of different projections and the corresponding projected 3-dimensional morphology of the pore branching as schematic drawing. The branching of a larger pore (shown as triangle-shaped cross-section with edges nearly parallel to traces of ⟨112⟩ planes in ⟨111⟩ projection) into a small pore (Fig. 7, upper left) is characterized by a narrow neck region near the nucleation site of the small pore, followed by a subsequent widening of the pore diameter. The narrow neck region of the pore near its nucleation site has been observed in many cases and is typical for the branching of pores (see also Figs. 3a and 8, for instance). Tilting the TEM foil into the different neighbouring zone axes of type ⟨110⟩ and ⟨112⟩ allows to determine the nucleation site and the pore growth directions. From such experiments
we are able to conclude that the pore branches nucleate at one of the tips of the pore tetrahedra and then grow along the corresponding $\langle 111 \rangle$B directions (cf. Fig. 7, right).

Our TEM investigations of different pore branches clearly demonstrate that all conceivable combinations of pore growth directions, i.e. type-I pores and type-II pores (cf. Fig. 3b), exist, for instance, branchings $I \rightarrow II$ (Figs. 3a, 4), $II \rightarrow I$ (Fig. 4), $I \rightarrow I$ (not shown), and $II \rightarrow II$ (Fig. 7). No systematic differences among the pore branchings are observed. These observations lead to the conclusion that the branching of pores is largely independent on its position relative to the initial substrate surface.

An example of branching into two small pores growing along $\langle 111 \rangle$B directions is shown in Fig. 8. In principle, the case of simultaneous branching into three small pores initiated at the tetrahedra tips (see model, Fig. 7) is also conceivable, however, has not been observed so far.

![Fig. 8](image)

**Fig. 8** Two small pores emerging from a larger pore along two different $\langle 111 \rangle$B directions.

![Fig. 9](image)

**Fig. 9** Section of extended collages of TEM BF-images of type-I pores (a) and type-II pores (b) intersecting $[\overline{1}1\overline{1}]$ and $[111]$ bevel-polished samples, respectively (cf. Fig. 3b). The surface and the nucleation layer are revealed in the top parts of the images. The pores show triangular cross-sections which are rotated by $180^\circ$ relative to each other for the two pore types (insets). c) Area densities (referred to the (001)-plane) of type-I pores and of type-II pores as a function of the depth below the surface. Type-I pores growing from the surface towards the bulk of the crystal possess a considerably higher density than type-II pores growing from the bulk back towards the surface. Both densities decrease with increasing depth below the surface.
During continuous etching, the repeated branching of pores obviously leads to the self-organizing formation of a complex 3-dimensional pore arrangement in the bulk of the substrate material. The homogeneity of such pore arrangements may be characterized by the pore density and its dependence on the distance from the substrate surface. By pore density we mean the number of pores intersecting the unit area of the (001) plane. The pore densities of type-I pores and of type-II pores have been determined from two \(\langle 111\rangle\)-bevel-polished specimens. These specimens were prepared in such a way that the corresponding pore directions (of type-I or of type-II pores, respectively) were perpendicular to the TEM foil surfaces. Figure 9a and b show the corresponding BF-images of the pore layer near the upper part of the substrate. The type-I pores and the type-II pores differ from each other by the different orientation of the triangle-shaped cross-sections in these projections, pointing with their tips away or towards the substrate surface (insets). Figure 9c summarizes the quantitative evaluation of a large number of such micrographs taken from the substrate regions with pores. The density of type-I pores and of type-II pores are plotted as function of the depth. It has been accounted for that the TEM images reveal only about half of the pores present within a certain depth layer since the other part of the pores is inclined with respect to the projection direction. The density of type-I pores in the near-surface regions is higher by about a factor of 3. The densities of both types of pores decrease with increasing distance to the substrate surface. Within a narrow depth range (~2 µm wide) at the interface between the pore layer and the substrate only type A pores are observed.

4 Discussion

The results of our investigations demonstrate that information about the 3-dimensional shape of pores with dimensions in the range of 10 nm to several 100 nm, the interface polarities and the branching behavior of pores may be obtained from combining microstructure investigations by TEM in different crystal projections with crystallographic information from CBED experiments.

The local pore morphologies of crystallographically oriented pores in InP could be determined for the first time by a combination of TEM imaging in different crystal projections with a recently developed CBED technique which allows to obtain local crystallographic information about the crystal polarity [16, 17]. Our investigations show that the crystallographic pores are bounded by \{111\}A-facets in regions near the pore tips thus indicating that such facets, once developed, have the largest stability against further dissolution during electrochemical etching. For crystallographic pores our investigations revealed also that the growth occurs exclusively along the \(\langle 111\rangle\)B-directions of the InP crystals (Fig. 3). These observations are in agreement with the interpretation of results obtained from cross-section SEM investigations of electrochemically etched III–V semiconductors [5]. The observed oscillations of the pore diameters in the pore tip regions in InP are caused largely by the formation of different types of facets (Figs. 5, 6). The pore tip regions consist, in a first approximation, of interconnected tetrahedron-shaped voids with \{111\}A-faceted interfaces which are oriented in such a way that the tip of the tetrahedron at the pore tip points in a \(\langle 111\rangle\)B growth direction (Fig. 6a). Shape modifications occur during further pore growth and result in additional other types of facets, predominantly \{100\} facets, at the backside of these tetrahedrons (Figs. 5b, 6b). Pore growth during prolonged etching subsequently leads to the widening of the pore diameters and to the development of other types of facets showing smaller inclination with respect to the pore growth direction (Fig. 4). Finally the pores approach the shape of open prismatic channels with channel walls that are bounded, on the average, by facets with orientations near \{112\}. Electrochemically etched pores along \{111\} with triangular cross-section have been observed in InP before by SEM [5, 13]. However, the small pore dimensions impeded more detailed analyses of the pore morphologies by this microscopic technique. The morphologies of pores in InP are similar to those observed for electrochemically etched pores in GaAs and in Si [5, 15]. For instance, TEM investigations for Si showed that pores may consist of interconnected (truncated) octahedral voids with \{111\} interfaces [15]. SEM investigations of etched GaAs showed pores with morphologies that may be described as interconnected tetrahedral voids with \{111\}A-faceted interfaces [5]. The preferred faceting on \{111\}A and on \{001\} crystal planes has been observed also for voids which have been formed.
in the III–V compound semiconductors GaAs, GaP, and InP by high-concentration dopant diffusion [20–22].

The electrochemical etching of pores in (n-type) III–V compound semiconductors has been discussed in the framework of the mechanisms suggested for Si [23, 24]. The growth of crystallographic pores is attributed to an interplay of dissolution and surface passivation with the surface passivation being affected by the crystallography of the material. At low current densities, i.e., slow dissolution, surface passivation sets in and increases the stability of certain crystallographic surfaces against further electrochemical attack. For the III–V-semiconductors {111}A-facets are most effectively passivated leading to the formation of the tetrahedron-like cavities. Further dissolution can only take place near the tips of the cavity bounded by the {111}A-facets which occasionally leads to the nucleation of a new cavity at the very tip region. As long as this cavity is small the dissolution proceeds quickly giving rise to a high current density. With increasing cavity size the local current density decreases and passivation sets in at the {111}A-facets which act as efficient stopping planes for further dissolution. This model allows to explain qualitatively our observations of pore shapes in InP near the pore tips and earlier observations of similar pore shapes in GaAs [25]. The observed widening of the pores during later etching stages, i.e., further away from the pore tips, is likely due to the transport of the electrolyte through the pore channel leading to post-etching effects. Interestingly, the triangular pore cross-section is maintained during this process indicating the importance of crystal polarity even when the {111}A planes are not the dominating facets anymore. Under this geometric restriction the widening process naturally transforms the pore geometry from that of interconnected tetrahedrons to a prismatic channel bounded by {112} planes. The weak oscillation of the pore diameter even far away from the pore tip indicates that the {112} planes themselves are not preferred pore facets, however.

Our investigations of the pore branching reveal that small pores nucleate sideways from the existing pores at sites which have evolved from the initial tetrahedron-shaped cavities (Fig. 7). Following the nucleation at the tip region of the cavities the new pores grow along one or several of the remaining \{111\}B crystal directions. In case of the pore morphologies which may be described approximately as a chain of interconnected tetrahedral cavities with \{111\}A-facets there exist three different tip sites for each tetrahedron pointing sideways into different \{111\}B directions. Similar to the nucleation of a new tetrahedron-shaped cavity at the tip of the initial pore, the nucleation of branching pores is likely to be caused by the chemical passivation of the \{111\}A-facets, as described above. Since the four tips of a tetrahedron bounded by \{111\}A-facets are equivalent from a crystallographic point of view one would expect similar probabilities of forming pore nuclei at all tips, i.e., the tip pointing in the pore growth direction and the three other tips pointing sideways. However, the space charge region around the primary pore is expected to make the nucleation of branching pores (at sideways tips) more difficult than the nucleation of cavities at the end tip of pores giving rise to forward pore growth. This may explain why branching occurs only occasionally along the pores. The typical neck formation at pore branches (Figs. 3, 7 and 8) may have its origin in the geometry of the space charge region around the initial primary pore as well.

The TEM investigations of the pore branches demonstrate also that the morphology of branches is independent of the pore position in regard to the substrate surface. This result agrees with the assumption that during the etching process the voltage decrease occurs completely across the space charge region which develops around the pores independent on the position of the back side contact. This result is confirmed by the observations of all conceivable types of branching (type-I \(\rightarrow\) type-II, type-II \(\rightarrow\) type-I, type-I \(\rightarrow\) type-I, and type-II \(\rightarrow\) type-II) of pores (type-I pores growing towards the bulk, type-II pores growing towards the surface).

The quantitative investigations of the dependence of the pore densities on the depth below the surface (Fig. 9) show that type-I pores are present with considerably higher densities than the type-II pores. The origin of this result becomes clear from our investigations: type-I pores may nucleate at the interface to the nucleation surface layer while type-II pores have to nucleate from type-I pores (or from type-II pores). In addition the pore densities decrease with increasing distance to the surface so that it is more likely for growing type-II pores to interrupt their growth when approaching the space charge region of an
existing type-I pore. This explanation is confirmed by the fact that our TEM investigations for InP do not give any evidence for pore coalescence or pore crossing as observed for pores in GaAs [5].

Finally we would like to discuss briefly the microstructure phenomena observed in the near-surface layers upon electrochemical etching of InP. The near-surface layer of electrochemically etched InP samples depict both pores as well as etch pits which are bounded by crystal facets and show a preferred orientation (Fig. 2a). So far the nucleation of pores has been investigated by microscopic techniques in greater detail for GaAs [25]. The investigations for GaAs show that crystallographically oriented pores form directly at the substrate surfaces, at first in the form of pyramidal etch pits which become elongated during further etching along the [1T0]-direction because of the stability of {111}A-facets. Further etching leads to the disappearance of {111}B-facets and to growth of crystallographically oriented pores along (111)B. For InP the pore nucleation becomes effective upon applying high current densities for a short time. Therefore current line pores are formed first within a thin surface layer. The surface nucleation sites show similarities for both materials, for instance the asymmetric elongation along one of the two (110) directions (Fig. 2). Further investigations would be necessary to obtain detailed information about the pore morphology and the pore arrangements within these surface layers.

5 Summary and conclusion

The 3-dimensional morphology of individual pores grown in InP(001) by electrochemical etching, their interface polarities and their branching behavior have been investigated by transmission electron microscopy (TEM) in various crystal lattice projections and by convergent-beam electron diffraction (CBED). In a surface layer the pores show a rather irregular shape with a preferential orientation perpendicular to the surface. Starting from this layer long straight pores with triangular cross-section grow deep into the bulk of the crystal along inclined (111)B directions, defined as the directions pointing from an In atom to the next-nearest P atoms. Along the pore axis the pore diameter oscillates while the mean pore diameter increases with increasing distance from the pore tip. The morphology of many pore tips can be approximately described by a chain of interconnected tetrahedrons bounded by {111}A-facets, showing that the In-terminated {111}A-facets act as efficient stopping planes for the dissolution process. For other pores the {111}A-facets opposite to the pore tip are replaced by {001}-type facets, showing that also non-polar facets may play an important role during pore formation. With increasing distance from the pore tips the amplitude of the pore diameter oscillation decreases and the pores approach the shape of open prismatic channels with channel walls that are bounded, on the average, by {112}-facets. Branching of pores takes place by pore nucleation at sideward tips of a primary pore and generates pores that grow back to the surface along other (111)B directions. However, the number of pores growing back to the surface is considerably smaller than the number of pores growing into the bulk of the crystal. Moreover, branching does not occur at equidistant sites along a pore. This shows that the self-assembled branching of crystallographically oriented pores in InP is not yet capable of fabricating homogeneous ordered 3-dimensional pore arrangements.

The formation of ordered 3-dimensional pore arrangements in compound semiconductors is of considerable interest for the fabrication of photonic crystals. The present results may be considered as important contribution to the understanding of the fundamental phenomena governing pore formation and pore branching during electrochemical etching of semiconducting materials.

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