Porous Silicon Carbide and Gallium Nitride

Epitaxy, Catalysis, and Biotechnology Applications

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Preface

Single crystal semiconductors can be etched electrochemically in an electrolyte such as dilute hydrofluoric acid. Illumination is often required to provide the positively charged holes necessary for oxidation. This process, known as photo-electrochemical (PEC) etching, can result either in a relatively featureless, two-dimensional (electro-polishing) or complex, three-dimensional porous morphology. Pore dimensions can range from nanometer to millimeter-scale by varying the etching conditions.

PEC etching has allowed porous morphology in a variety of semiconductors. Perhaps the best known is porous silicon, which was studied intensely during the 1980s and 1990s [1]. When excited by an electric current or using incident blue light, porous silicon emits intense red light. In contrast, the 1.1 eV band gap of bulk (i.e. nonporous) silicon corresponds to a wavelength in the near infrared, and even at this energy, bulk silicon is a poor light emitter as it has an indirect band gap. Intense visible emission from porous silicon has attracted great interest. Despite much research, the precise mechanism for the light emission is still controversial. Moreover, persistent degradation effects in the emission intensity have hampered device development. Nevertheless, other applications have been successfully explored. Porous Si remains a very interesting prototypical porous semiconductor.

This volume deals largely with the properties and application of porous silicon carbide (SiC), which, in single crystal form, has a relatively high bond strength. It has been commercially available in multi-centimeter diameter crystalline wafers and boules for only the past two decades. All the SiC polymorphs have large 3.0±0.3 eV band gaps, which together with high bond strength make them suitable for high power and/or high temperature applications.

The very high thermal conductivity and close lattice match to gallium nitride (GaN), another wide band gap semiconductor, has recently
prompted SiC usage as substrates for blue through UV optical emitters, and for very high frequency electronic applications (wireless communications, radar, etc.). It should be noted that GaN is not commercially available as a single crystal substrate.

SiC can be made porous using PEC etching [2], although in contrast to silicon it is not an efficient light emitter. This volume describes various other applications of the material as explored during 2001–2006 under a Defense University Research Initiative on Nanotechnology (DURINT) program entitled ‘Nanoporous Templates for Large Defect Reduction in SiC and GaN, Nanocatalysis, Magnetic Clusters, and Biotechnology’. This program dealt with topics including the epitaxial growth of SiC and of GaN on porous SiC, utilizing the large surface area of porous materials for catalytic applications, and biotechnology applications in which free-standing porous SiC is used as a semi-permeable membrane for sampling proteins and other macromolecules.

Chapter 1 deals with porous SiC formation mechanisms. A wide range of morphologies are found depending on etching conditions and dopant type and concentration of the initial SiC. One morphology explored extensively is a narrow columnar one with 10–100 nm diameter pores, normal to the surface, and depths of hundreds of micrometers. Such layers can be made free standing by separation from the underlying material through application of a current pulse.

Processing steps required for application of porous SiC in electronic devices are described in Chapter 2, including doping via diffusion, thermal oxidation and contact deposition. Epitaxial growth of SiC on porous substrates, both SiC and Si, is discussed in Chapter 3. Pores may help reducing dislocations or strain, thereby improving the properties of epitaxial layers grown on porous substrates. The low cost and large area of porous silicon substrates make them attractive for SiC epitaxy. The porosity provides one mechanism of accommodating the lattice mismatch between the Si and the SiC.

Porous GaN can be produced without using electrical excitation as described in Chapter 4. As for porous SiC, there is potential for using the porous GaN as a substrate for homo-epitaxial growth of GaN. Other applications with strong potential include chemical sensors, with the large surface area of the porous material providing enhanced sensitivity of such devices.

Chapters 5–8 discuss uses of porous SiC, and porous intermediate layers of other materials, as substrates for GaN epitaxy. The lattice mismatch between GaN and SiC leads to dislocations in GaN films, and use of a porous template offers a mechanism for reducing the dislocation density.
As for Ge on Si [3], growth conditions are chosen which favor nucleation only on regions between the pores. With further deposition three-dimensional islands allow strain relaxation by elastic deformation, followed by island coalescence. The density of inter-island dislocations can be orders of magnitude less than in films grown on nonporous substrates.


Important electrical properties of porous SiC are discussed in Chapter 9. Not surprisingly, porous SiC has a higher specific resistivity than its host crystals. More significantly, pores appear to trap charge carriers, which renders p-SiC semi-insulating. Such effects strongly influence the use of porous material as electrical sensors.

Chapter 10 presents theoretical work on the origin of magnetism in Mn- and Cr-doped porous GaN with promise towards a room temperature dilute magnetic semiconductor, an essential component for spintronic applications. The large surface areas of porous material allow very high concentration of surface-specific atomic arrangements to be formed. Extensive computations have been performed on (Ga,Mn)N and (Ga,Cr)N systems from zero-dimensional clusters to one-dimensional nanowires, nanotubes, and nanoholes, two-dimensional surfaces and thin films, and three-dimensional crystals.

Chapter 11 presents and discusses porous SiC use in catalysis for which the large porous film surface areas are again clearly useful. SiC’s high chemical bond strength allows its use at high temperature and renders it resistant to oxidative erosion.

Finally, Chapter 12 describes initial studies on biological applications of porous SiC. Free-standing porous membranes are explored as particle-size-selective semi-permeable membranes for filtering of macro (bio-) molecules. SiC’s hardness makes it chemically inert and bio-compatible (e.g. coating on stents [6]).

REFERENCES


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Porous SiC Preparation, Characterization and Morphology

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1.1 INTRODUCTION

The production and investigation of porous semiconductors began in the 1950s at Bell Laboratories with work by Uhlir Jr [1] and Turner [2] on Si and Ge and at the Westinghouse Research Laboratories by Faust Jr [3] for SiC. Technological interest began with the discussion of the process of insulation by porous oxidized Si in the 1970s [4]. Interest in porous Si exploded in 1990 when Canham [5] at RSRE in the UK discovered that highly porous layers of Si excited by a blue laser emit readily visible red light at room temperature. The origin of this above band gap luminescence was a topic of heated controversy for several years. We became interested in the possibility of blue shifted luminescence into the ultraviolet (UV) in porous SiC, and began to collaborate with Joseph Shor and colleagues, who were actively investigating electrochemical etching...
of SiC at Kulite Semiconductor products and Columbia University [6]. They successfully fabricated porous SiC [7,8], but initial cathodoluminescence results [9] in 1994 did not convincingly reveal the desired effect. Further low temperature photoluminescence and cathodoluminescence measurements did not resolve this issue. However, we [10] found a dramatic effect of porosity on the reststrahl band of thick p-type 6H-SiC layers observed using room temperature infrared (IR) reflectance. A simple effective medium model, chosen to incorporate the porous morphology, accounted for the observed spectral features. Subsequently, these effects have been observed in several other porous polar semiconductors and explained using similar models. Spanier and Herman [11] published further work on the IR reflectance of porous SiC. We ceased our optical investigations of porous SiC in 1995.

Our interest in porous SiC was renewed in 2000, based on some interesting work in the intervening years, which has been reviewed by Saddow et al. [12]. We set up a laboratory for fabricating porous SiC by (photo)electrochemical etching. We discovered (or rediscovered, in some cases) about ten distinct morphologies in 4H-, 6H- and 3C-SiC, as well as GaN layers [13]. This chapter focuses on the two morphologies we have investigated most thoroughly: the layered triangular and the nanocolumnar morphologies. For each case, we discuss the fabrication and characterization, followed by discussion of the formation mechanism.

1.2 TRIANGULAR POROUS MORPHOLOGY IN n-TYPE 4H-SiC

The ‘triangular’ porous morphology may be manufactured from highly doped hexagonal Si-face 4H-SiC by photoelectrochemical etching (PECE) [14]. A small number of Si-face 6H-SiC samples was also studied and revealed no significant difference from 4H-SiC. The observed morphology is explained based on the crystallography and a model for the semiconductor/electrolyte interface.

1.2.1 Crystal Anodization

The electrochemical etching, with the intent of making the etched semiconductor porous, is performed in the anodic regime, so that positive charge is collected at the semiconductor–electrolyte interface. In order to increase the speed of the anodization process, electrical bias is applied to the sample through ohmic contacts. To protect the ohmic contacts on the
POROUS SiC PREPARATION

back as well as the edges during the anodization procedure, the samples are masked using Apiezon black wax. The experiments described here were performed in aqueous 5% HF solution mixed with ethanol in the ratio HF:ethanol = 1:1 (measured by weight).

There are two ways to produce a substantial anodic current. One way is to apply a large positive, or reverse, bias so that dielectric breakdown occurs and electrons from the ions in the electrolytic solution tunnel into the semiconductor. Voltages may range from 10 up to 100 V. The resultant structures are dendritic, sinuous, and columnar. The other way is to apply a moderate reverse bias, from 1 to 3 V, accompanied by UV light illumination (from which the term photoelectrochemical etching originates). The UV light of above photon band gap energy generates electron–hole pairs. The electrons are swept away by the electric field into the bulk of the semiconductor, while the holes rush to the surface where they participate in the electrochemical reaction.

To make porous 4H-SiC of triangular morphology, we employed the second approach. As a UV light source one can use a Hg arc lamp. Filters and dichroic mirrors are recommended to attenuate visible and IR components of the radiation from the source. The UV light intensity was \( \sim 160 \text{ mW/cm}^2 \) as measured by a thermopile-type power meter. The electrochemical etching is conducted in a three-electrode cell where the SiC crystal serves as the working electrode. The current is controlled either potentiostatically (constant potential) or galvanostatically (constant current) with a potentiostat/galvanostat. In the potentiostatic mode, the voltage applied to the cell should not exceed 3 V. When the galvanostatic mode was used, the fixed current density ranges from 1 to 5 mA/cm\(^2\) so that the corresponding applied voltage would not exceed about 3 V in order to minimize breakdown effects.

After anodization, samples are carefully removed from the bath and cleaned in acetone to remove the black wax mask. As an alternative, trimethylchloroethylene may be used. Plan-view and cross-sectional imaging is performed by scanning electron microscopy (SEM). The 8-bit gray scale [intensity ranges from 0 (black) to 255 (white)] digital SEM pictures are then processed by imaging software to obtain the pore size and porosity. The porosity is estimated from cross-sectional images by integrating the area occupied by the pores.

1.2.2 Description of the Porous Structure

Figure 1.1 shows a series of cross-sectional SEM images of porous 4H-SiC \( (n \sim 6 \times 10^{18} \text{ cm}^{-3}) \) taken at different depths from about 5 to 55 \( \mu \text{m} \).
Figure 1.1  Sequence of cross-sectional images of a 56 μm thick porous vicinal Si-face 4H-SiC sample of triangular morphology. In the sequence, (a) corresponds to the top of the film, (e) to the bottom. The distance $d$ from the front surface and the corresponding porosity $P$ are: (a) $d = 5 \mu m$, $P = 0.28$; (b) $d = 15 \mu m$, $P = 0.23$; (c) $d = 30 \mu m$, $P = 0.16$; (d) $d = 40 \mu m$, $P = 0.12$; (e) $d = 55 \mu m$, $P = 0.08$. Reproduced from Y. Shishkin et al., J. Appl. Phys., 96(4), 2311–2322. Copyright (2004), the American Institute of Physics
below the surface. The morphology seen on Figure 1.1 was obtained in 8°-offcut Si-face 4H-SiC porous samples made by UV-photoassisted electrochemical etching at a voltage of +3 V. The particular surface exposed to the imaging by fracturing the sample is the (1\overline{2}10) plane. The sample is organized into a stack of planar layers. When viewed from the (1\overline{2}10) direction, a tilt of about 8° of the layered structure relative to the normal to the front surface is seen (image not shown). A similar layering of pores is seen also in 3.5°-offcut 6H-SiC.

In photoelectrochemically etched n-type crystals, the porosity is rarely uniform throughout the porous layer. The porosity is largest at the surface and gradually decreases with depth. This is illustrated in Figure 1.1. As can be seen, not only the porosity changes but also there is a distinctive development of the triangular pore shape. Figure 1.1(e), taken near the interface between the porous layer and the substrate, shows that small oblong channels form in an orderly fashion. They are arranged in an array with rows separated by about 30 nm with the distance between pores also about 30 nm on average. The pore width at this stage is 5–10 nm. A porous film produced under similar conditions for 2 min, whose thickness was later measured to be 3 \( \mu \)m, exhibited only structure resembling Figure 1.1(e). This indicates that Figure 1.1(e), taken at the bottom of a 56 \( \mu \)m thick porous film (etched for 5 h), portrays the initial stage of the triangular pore development.

In order to estimate the porosity, the pixels of the gray-scale images are thresholded so that those corresponding to a pore on the image are assigned the value 0 (black), and the pixels corresponding to the solid the value 1 (white). The total area occupied by the black pixels \( S_{\text{black}} \) can be calculated [15]. Then the porosity \( P \) is estimated by taking the ratio of \( S_{\text{black}} \) to the total area of the cross-sectional image. Here, it is assumed that the areal porosity for a particular cross-section equals the volume porosity for the channel pore structure. For Figure 1.1(e), the porosity \( P \) obtained by this method is 0.08.

As the anodization process continues, the channels quickly pierce the crystal in directions perpendicular to the \( c \)-axis. The non-basal plane walls of every channel begin to flatten out [Figure 1.1(d)] to follow crystallographic planes tilted at about 60° relative to the basal plane. One can clearly distinguish triangular shapes. Figure 1.1(b) and Figure 1.1(c) represent the continuing pore development as the channel walls become more distinct quasi-equilateral triangles. Their characteristic shape suggests anodization anisotropy, i.e. not all the directions in the crystal are equivalent in terms of the PECE. The tendency of the pores not to propagate normal to the [0001] direction suggests that the (0001) basal plane
Figure 1.2  Plan view image of a 4H-SiC Si-face sample, off-cut 8° towards [12\textoverline{1}0], photoelectrochemically etched to obtain the triangular porous morphology. About 2 μm of material was removed by RIE prior to imaging. The exposed channels apparently propagate preferably along \langle 1\textoverline{2}10 \rangle directions. Reproduced from Y. Shishkin \textit{et al.}, \textit{J. Appl. Phys.}, 96(4), 2311–2322. Copyright (2004), the American Institute of Physics

possesses an etch-stop character. The largest triangles are on Figure 1.1(a) corresponding to the top of the porous film. Here, the porosity $P$ is estimated to be about 0.28. At this point we note that the experiments have shown so far no, or very little, porosity gradient in p-type SiC in which the etching is performed without light assistance [16].

Figure 1.2 is a plan view SEM image of a porous sample similar to the one shown in Figure 1.1 but processed for 15 min by reactive ion etching (RIE) with SF$_6$ plasma to perform the plan view SEM analysis. Figure 1.2 shows how a vicinal basal plane appears with roughly 2 μm removed by RIE. Compared with the non-RIE surface, which had just occasional circular openings, one can now see channels which tend to propagate parallel to the basal plane. The channels branch out, wriggle, and occasionally intersect each other. There seems to be a slight preference in the channel propagation along \langle 1\textoverline{2}10 \rangle directions, which are indicated by the arrows in Figure 1.2. The particular \langle 1\textoverline{2}10 \rangle direction towards which the 8° miscut was made is indicated.

If the C-face (000\textbar{1}) is anodized, conical pores with triangular cross-sections are observed, but the pores are not arranged into arrays of planes (images not shown). The conical pores intersect, forming an overall spongy network. Even though their typical size is very similar to that
of the triangular channels, it is clear that Si-terminated and C-terminated surfaces etch differently.

The observed differences in the etching of (0001) and (000\bar{1}) crystal faces suggest etching experiments on non-basal planes. In these cases the electric field is applied parallel to the basal plane. Figure 1.3 shows an example of a front surface of a (1\bar{1}00) 4H-SiC sample after UV photoassisted anodization. The front surface of an etched (1\bar{2}10) sample looks similar within the resolution limits of the SEM. The surface morphology is described by layered triangular pits of average size of 30–40 nm observed all over the surface. The fact that the surface pits have a defined geometrical shape as well as their self-regulating character again point out anodization anisotropy.

The non-basal samples were also sectioned for analysis. Figure 1.4 shows an example for which a 4H-SiC (1\bar{1}00) oriented sample has been fractured to expose the (1\bar{2}10) plane. The crystal is seen to be divided into 35–50 nm thick layers. Each layer contains triangular cavities 30–40 nm in size. When the image in Figure 1.4 is rotated 90° clockwise, a similarity to the cross-sectional images of the (0001) etched samples can be seen. The size and the shape of the triangular pores and their general planar layout on the fractured surface are identical. The similarity is striking given the fact that during etching the electric field is applied parallel to the basal plane and consequently perpendicular to the field applied to etch the sample in Figure 1.1.
Figure 1.4 Cross-sectional image of a porous (1\overline{1}00) 4H-SiC sample. The surface shown in the image is a \{1\overline{1}210\} plane. When rotated, it resembles the cross-sectional images of vicinal Si-face samples. Reproduced from Y. Shishkin et al., J. Appl. Phys., 96(4), 2311–2322. Copyright (2004), the American Institute of Physics.

Figure 1.5 shows an example for which a 4H-SiC (1\overline{1}00) oriented sample has been fractured to expose a basal plane. The channeled structure of the pores can still be discerned. The arrows next to the figure show the \langle 1\overline{1}210 \rangle directions. There are no (or very few) channels aligned with \langle 1\overline{1}00 \rangle, suggesting that \langle 1\overline{2}10 \rangle are the primary directions along which

Figure 1.5 Cross-sectional image of a porous (1\overline{1}00) 4H-SiC sample. The surface shown in the image is a basal plane. Compare the wormy character of the pore channels with Figure 1.2. Reproduced from Y. Shishkin et al., J. Appl. Phys., 96(4), 2311–2322. Copyright (2004), the American Institute of Physics.
the pores prefer to propagate. Comparing the result with Figure 1.2, where we were able to look at the basal plane by means of RIE etching off the top layer, we again conclude that pores do not propagate well along the c-axis. Moreover, the direction of the electric field applied during the experiment does not seem to be a factor in the pore formation in the investigated voltage/current regime.

1.2.3 Model of the Morphology

1.2.3.1 Pore Dimensions and Porosity

One of the arguments used in the porous silicon literature to explain the typical dimension of the structures states that the pore formation is governed by the width of the space charge region formed near the semiconductor/electrolyte junction (see, for example, [17]). The argument seems to be very plausible as it works well for the mesoporous structures (10–100 nm pore size) obtained from n-type Si. The model has also been proposed for porous SiC [18] and elaborated in Shishkin et al. [14].

The width of the space charge (or, depletion) layer \( L_{sc} \) (cm) is determined by solving the Poisson equation with appropriate boundary conditions. For the case of an n-type semiconductor with a planar surface, such that \( n \approx N_d \) and \( N_d \gg N_A \), the charge density is approximated as \( \rho \approx en \). One obtains:

\[
L_{sc} = \sqrt{\frac{2\varepsilon_{sc}\varepsilon_0\phi_{sc}}{en}}. \tag{1.1}
\]

At the potential \( \phi_{sc} = 3 \) V, the width of the space charge region when the free carrier concentration is \( n = 6 \times 10^{18} \) cm\(^{-3} \) is calculated to be \( L_{sc} \sim 30 \) nm (\( \varepsilon_{sc} \) is assumed \( \sim 10 \)). As we showed in Figure 1.1(e), the average distance between the newly formed channels in the triangular pore structure obtained by PECE is 30–35 nm. The calculated value for \( L_{sc} \) then may be interpreted as a typical distance which determines the self-regulatory character of the lateral (i.e. parallel to the basal plane) pore formation process. Piercing the crystal, the channels align themselves into a network in such a way that for each given channel the onset of another channel next to it occurs at a distance where the electric field produced by the band bending vanishes, i.e. where the depletion layer ends. Such pore initiation-alignment processes happen both vertically and horizontally.
Depleted of charge carriers, the interpore spacing of a newly formed porous structure exhibits semi-insulating properties with the Fermi level of the semiconductor pinned to the surface energy levels close to the middle of the band gap [18]. Such pinning results in a different distribution of the potential at the interface as compared with a planar semiconductor/electrolyte junction without surface states. In particular, a substantial potential drop in the so-called Helmholtz region of the electrolyte occurs, which has a few nanometers thickness and is adjacent to the sample surface. The field in the semiconductor then is expected to become lower, decreasing the band bending at the surface and slowing down the charge transfer through the interface. In this regard, the stages of the pore formation can be deduced indirectly from the current versus time dependence recorded over the course of the PECE experiment. In Figure 1.6, the etching starts in the mA cm\(^{-2}\) range, which is due to the rapid pore initiation process which manifests itself in the fact that one can obtain a porous film a few micrometers thick in 1 min. The cross-sectional SEM image of such a film shows small ‘shapeless’ channels similar to what is seen in Figure 1.1(e). A rough estimate gives the total internal surface area of the pores at this stage to be 50–60 times larger than the front surface area of the sample. This turns out to be enough to substantially increase the number of collected holes. The current density quickly rises to a value

![Figure 1.6](image)

**Figure 1.6** Current density vs time for an n-type 4H-SiC sample etched at 3 V for 2 h. The sample area is \(~0.45\) cm\(^2\). Integration of the curve provides the total charge transferred during the course of the reaction leading to the estimate of porosity \(P \sim 0.2\). Reproduced from Y. Shishkin et al., *J. Appl. Phys.*, 96(4), 2311–2322. Copyright (2004), the American Institute of Physics
an order of magnitude higher than its initial value on a flat (nonporous) surface.

As seen in Figure 1.6, the current density reaches its maximum value of about 3 mA cm$^{-2}$ in approximately 30 min, and then gradually drops, indicating a decreasing rate of dissolution. Such a decrease in the anodic current density for SiC has also been reported in the literature [8,19]. Despite the noisy character, the current density $j(t)$ dependence in Figure 1.6 may be used to calculate the integrated charge $Q_{int} = \int j(t)dt = A \int j(t)dt$ transferred during the course of the reaction. Knowledge of $Q_{int}$ allows one to estimate the average porosity $P = V_p/V$. The total volume of the semiconductor $V$ is simply the product of the front surface area $A$ and the film thickness $d$. The total 'void' volume produced by dissolution is $V_p = N \cdot V_0$ where $N$ is the number of Si-C pairs dissolved and $V_0$ is the volume of a single Si-C pair in the SiC crystal lattice. $V_0$ is obtained from the lattice constants of 4H-SiC: $a = 3.081 \text{ Å}, c/4 = 2.52 \text{ Å}$ [20]. $N$ is $Q_{int}/e\gamma$, where $\gamma$ is the number of holes required to dissolve one Si-C pair. Combining all the terms, we write

$$P = V_p/V = V_0 Q_{int}/e\gamma = V_0 \int j(t)dt \frac{1}{ed\gamma}.$$  

(1.2)

The gravimetric measurements for 4H n-type SiC show that $\gamma$ is very close to 7, within 1% accuracy [14].

When the $j(t)$ curve (see Figure 1.6) is integrated, one gets roughly 22.3 C cm$^{-2}$. Once the porous film thickness is determined from the cross-sectional SEM measurement ($d \sim 16 \mu$m for the sample in Figure 1.6), one can obtain the value of the average porosity for the porous planar/triangular morphology obtained in n-type 4H-SiC using Equation (1.2). After inserting all the numbers, the estimated average porosity is $P = V_p/V \approx 0.20$.

SEM images have also been obtained for the above sample at 1, 4, 7, 10, 14 and 16 $\mu$m from the front surface. The resultant dependence of $P$ as a function of depth $d$ is shown in Figure 1.7. This 16 $\mu$m thick sample has a clear porosity gradient which is reflected by the decreasing values of $P$ with the increasing of $d$. If fitted to an exponential,

$$P(d) = P_0 + ae^{-bd},$$

(1.3)

the constant $b$ can be determined (values of the offset $P_0$ are negligible.). For the sample in Figure 1.7, $b = 880 \text{ cm}^{-1}$. Making a similar analysis
The porosity as a function of distance from the front surface of the sample. The porous layer was obtained in the run shown in Figure 1.6. The values of porosity are extracted from digital analysis of the SEM images. The solid line is a fit to Equation (1.3), which gives \( P = 21\% \) for the average porosity. Reproduced from Y. Shishkin et al., J. Appl. Phys., 96(4), 2311–2322. Copyright (2004), the American Institute of Physics.

for samples etched for shorter times (so that the photo-electrochemical action proceeds closer to the original, ‘starting’, surface) results in larger values of \( b \). For longer etching times used to produce thicker films, the collection of holes, on average, takes place at larger depths where the longer wavelengths of the UV light, associated with lower absorption coefficient, penetrate more efficiently. Therefore, \( b \) is a representative coefficient which takes into account the range of UV lines participating in the etching process.

The integration of the \( P(d) \) function given by Equation (1.3) gives the average porosity of the porous layer. A value of 0.21 is obtained from the data in Figure 1.7 when integration is done from 0 to \( d_{\text{max}} = 16 \mu\text{m} \). Thus, the porosity estimated from SEM images is in good agreement with the average porosity calculated using the charge transfer (\( P \sim 0.20 \)).

1.2.3.2 Model for the Pore Shape

The base of each ‘triangle’ always lies in the basal plane whereas its sidewalls are oriented about 60° relative to the base. This pore shape implies some etching relationship to the crystallographic planes of the original SiC single crystal.

Our SEM cross-sectional images show that the etching rate, defined as the thickness of a porous layer etched per unit time, is a factor of
two larger for a \{1\bar{2}10\} plane than for a \{1\bar{1}00\} plane under identical conditions. This fact supports our observation deduced from Figure 1.2 that the \{1\bar{2}10\} surface is less resistant to electrolytic attack. Qualitatively, this can be explained by the fact that, in hexagonal polytypes, \{1\bar{2}10\} surfaces have a higher surface energy than the \{1\bar{1}00\} surfaces \[21\]. It is reasonable to assume that those directions will be chosen for the pore growth which are easier to etch. The surfaces of low energy are the ones which ‘survive’ the etching and the channel pore patterns are formed.

Even though the etch rate difference between an a-face \{1\bar{2}10\} and a p-face \{1\bar{1}00\} provides the possibility for the channel formation, it is not sufficient to explain the triangular shape. Pores form by an oxidation of the surface silicon and carbon atoms with the immediate removal of the oxidized species into the electrolytic solution. Therefore, in order to investigate the issue of a particular plane’s etching inertness, one has to make an assumption that the oxidation is substantially weaker on Si-rich surfaces of SiC as compared with the C-rich ones. The basis for this statement depends upon experiments on the oxidation of the Si- and C-faces of SiC, in which the polar character of the silicon–carbon bond \[22\] was first suggested to be responsible. Muelhoff et al. \[23\] reported different oxidation rates for (0001) and (000\bar{1}), i.e. Si-rich and C-rich, surfaces for thermally oxidized SiC. The oxidation of a Si-terminated surface proceeds at a much slower rate. Although the oxidation chemistry in aqueous environment is likely somewhat different from that reported in Muelhoff et al. \[23\], in which dry oxygen was used, the rate of oxidation for the (000\bar{1}) surface is still larger by at least a factor of two than that of the (0001) surface when water vapor is used for oxidation. Consequently, the pore shape in a SiC crystal is greatly affected by the surface polarity. Since we have already shown the etch-stop character of the (0001) plane, a silicon-terminated surface, we propose that the surfaces which make up the sidewalls of our triangular channels are silicon-rich etch-stop surfaces also.

Let us now examine the lattice structure of 4H- and 6H-SiC polytypes. Having established the preference for triangular pore propagation along \{1\bar{2}10\} directions, the logical thing to do would be, looking along a \{1\bar{2}10\} direction, to find those surfaces which are terminated with silicon atoms. Figure 1.8 shows a schematic view of a 4H-SiC crystal lattice as seen from a \{1\bar{2}10\} direction. The zigzagged lines connecting silicon atoms (lighter shaded dots) make up the surfaces of the walls forming a triangle. Two of the thick solid lines represent the (1\bar{1}0\bar{2}) and (1\bar{1}0\bar{2}) planes. We propose that, like the (0001) surface, the (1\bar{1}0\bar{2}) and (1\bar{1}0\bar{2})
surfaces are also nominally terminated with silicon atoms. The counterparts (1102) and (1102) are then terminated with carbon atoms. An oxidation experiment conducted on 6H-SiC using (1103) and (1103) surfaces, which are somewhat similar to the respective (1102) and (1102) surfaces in 4H-SiC, confirms the model [24]. Despite the lack of data on 4H-SiC, we are confident that silicon termination makes the (1102) and (1102) surfaces behave like etch-stops under anodization conditions, similar to the (0001) face. Therefore, the sides of each triangle are made of surfaces corresponding to the (1102) family of planes. This fact plus preferential pore propagation along the (110) directions create the necessary environment for the observed triangular-channeled structural pore shape.

Next we determine the angle of inclination $\theta$ of the triangular sides of the pores, assuming the {1102} planes to be the walls of these triangles. One way of doing this is to determine the components of the reciprocal lattice vector (1102) in terms of the basis vectors of the real space $\hat{x}$, $\hat{y}$, and $\hat{z}$ [14]:

$$\langle 1\overline{1}02 \rangle = 1 \cdot \hat{b}_1 - 1 \cdot \hat{b}_2 + 2 \cdot \hat{b}_3 = -\frac{4\pi}{a\sqrt{3}} \hat{y} + \frac{4\pi}{c} \hat{z}. \quad (1.4)$$