#### Pore Etching in Compound Semiconductors for the Production of Photonic Crystals

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### ABSTRACT

Ordered arrays of pores in Si provided the first (two dimensional) photonic crystals with bandgaps in the  $\mu$ m region. The paper explores the potential of pore etching for two- and threedimensional photonic crystals in GaAs, InP, and GaP. A striking feature of pore etching in III-V semiconductors is the strong tendency to self-organization and pattern formation. As an example, self-organized well-defined pore lattices ( $a = 100 \text{ nm} - 1 \mu \text{m}$ ) can be made in InP. All materials show self organized diameter oscillations, often synchronized over large distances between pores. Extremely strong diameter oscillations are observed in GaAs. Pores in all materials tend to grow in <111> directions, but can be induced to grow in the direction of current flow, too. These features can be used to produce two- and three dimensional photonic crystals. The latter goal might be achieved by switching periodically between different pore morphologies with depth, or by modulating the diameter with depth - always helped by the tendency to self organization. Self organization, however, will not lead to perfect crystal structures; lithographically defined nucleation is needed and has been tried. First results show that there are pronounced differences to what is known from Si. While the production of externally defined photonic crystals in the sub um region appears to be feasible, the strong tendency to self organization must be taken into account by matching internal time and length scales to the desired external ones.

#### INTRODUCTION

The first two-dimensional photonic crystal with a band gap in the  $\mu$ m region and with defined defects was made from porous Si [1,2]. Meanwhile porous Al<sub>2</sub>O<sub>3</sub> is also considered an attractive material for photonic crystal purposes [3]. In both cases the pores were etched electrochemically.

The aim of the present paper is to explore the potential of electrochemical pore etching for the production of photonic crystals, in particular with respect to III-V compound semiconductors. The possibilities for two- and three-dimensional pore crystals will be discussed separately, including some relevant aspects of Si pore crystals.

It is important to note in this context that pore etching in Si is far from being fully understood, and even less is known about pore etching in other semiconductors. While there are plenty of experimentally observed phenomena, some of which appear to hold promise for photonic crystals, the full potential of pore etching can only be utilized, if the basic processes responsible for pore formation are understood as will be shown below.

While Si is an ideal material for making pore crystals from the viewpoint of cost, size and perfection, its major disadvantages are: i) large absorption below  $\lambda = 1100$  nm, ii) indirect band gap, i.e. no optical activity, iii) pore lattice constants below about 800 nm are difficult to obtain and below about 500 nm it was not possible so far [4, 5].

III-V compounds, on the other hand, always contain defects like dislocations and are relatively expensive, but they offer optical activity. Moreover, achievable pore geometries are much closer to what is desired for photonic crystals with band gaps in the near or visible spectrum, as will be shown in this paper.

In addition, porous III-V compounds show some very peculiar and highly interesting optical properties in their own right. In particular, porous GaP under certain circumstances not only exhibits a hundred fold increase of cathodoluminescence band-gap radiation, but also an about hundred fold increase in the second harmonic generation, cf. [6]. Porous InP, on the other hand, shows strongly decreased optical activity under electron beam irradiation than bulk InP.

In what follows we will discuss pore crystal formation under the headings two- and three dimensional crystals, but this is just a loose guideline because there are many intermediate stages of pore morphologies.

## SOME REMARKS TO PORE ETCHING IN GENERAL

Loosely speaking, what is required for making photonic pore crystals in general are individual pores with well defined morphologies (tending towards "perfect", i.e. smooth walls with defined and constant cross sections) and adjustable diameters that can be grown in pre-determined periodic arrangements with lattice constants that can be adjusted between about 100 nm and several  $\mu$ m.

In other words, we want to impress *external* length scales on a system that must have some *intrinsic* length scales on its own because otherwise no pores would grow in the first place. In pore-lingo, we want to grow so-called *macro*pores, (mesopores being smaller than 50 nm, and micropores referring to <10 nm structures). In n-Si this can and has been done for lattice constants > 500 nm, utilizing electrochemical etching of *n-type Si* in *aqueous electrolytes* under *backside illumination*. In short-hand, we produced *n-macropores*(*Si/aqu/bsi*). The backside illumination in this case ensures that the holes needed for the electrochemical dissolution will reach the tips of growing pores first, thus stabilizing the growing pore.

While there are many (hotly debated) intrinsic length scales operative during electrochemical dissolution, cf. [4, 7, 8], the most important one in this case is the width of the space charge region. Achievable lattice constants thus are essentially limited by the useable range of doping, and structures below 500 nm are not accessible [5, 9] because the doping level cannot be raised too much without loosing some other required properties (e.g. large minority carrier diffusion length). This space charge limitations hold for all semiconductors. So although in silicon it is not reasonable to go to much smaller wavelength due to the onset of strong absorption overcoming space charge region limits is part of the game and Fig. 1a shows an example of pmacropores(Si/aqu) with a large lattice parameter due to large pore diameters, while Fig. 1b shows the smallest macropores obtained so far in Si by utilizing p-type Si and an optimized organic electrolyte, i.e. we are looking at p-macropores(Si/org) in this case. No illumination is needed for hole generation in this case and the space charge region width is no longer the decisive intrinsic length.



**Figure 1** Example of pore crystals produced in Si. a) With rather large lattice constant, and b) with the smallest lattice constant produced so far (minimum distance between pores = 200 nm).

The pores in Fig. 1b, however, are obviously far from being perfect and this pore crystal would not be a good photonic crystal. What the picture indicates, however, is that some kind of chaotic or stochastic (i.e. not very regular) oscillation of pore diameters occurs which we will interpret as an expression of some self organization or pattern formation that takes place in this system and that introduces some intrinsic length scale (wavelength of the oscillations) together with an intrinsic time scale (frequency of the oscillations). This is a feature that is very dominant also in III-V compounds.

#### TWO DIMENSIONAL PORE CRYSTALS IN III-V COMPOUNDS

Producing two-dimensional pore crystals in particular requires i) "good" single pores growing with constant diameter and without branching, ii) defined growth direction (preferably) perpendicular to the sample surface, and iii) organization into a crystal either by *extrinsic* (i.e. lithographically defined) nucleation or by *intrinsic* self organization.

The crystallography of macropore growth thus must be addressed first, and it will be found to be rather peculiar. The major findings up to date are shown in **Table I** (including some properties not discussed here; for details see [12]. While in Si all <100> and (surprise!) <113> directions are the preferred directions for macropore growth, the polar nature of III-V compounds strongly favors the so-called <111B> directions which are just four out of the available eight directions [10]. In other words, pores only grow in e.g. [111], but not in [-1-1-1].

Торіс	Si				GaAs	n-GaP	n-Inp
Doping	n	р	n <sup>+</sup>	$\mathbf{p}^+$	<b>n, n</b> <sup>+</sup>	<b>n, n</b> <sup>+</sup>	<b>n</b> , <b>n</b> <sup>+</sup>
Pore	micro	micro					
geometry	meso	meso	meso	meso	meso	meso	meso
	macro	macro	macro		macro	macro	macro
Growth	100	100	100	100	111B	111B	111B
direction	113	113	113	113		current	current
(macro/meso)	fractal					line	line
Hole	bsi	doping	avalan.	doping	avalan.	avalan.	avalan.
supply	fsi				No definite effects of frontside		
	avalanche				illumination		
Stopping	111	111	111	111	111A	111A	111A
planes					112	112	112
	Chains of octahedrons		?	?	Chains of tetrahedrons		

**Table I** Some salient features of pore formation in Si and III-V compounds. Abbreviations and explanations:  $bsi/fsi = backside/frontside illumination; (111A/B} refers to the polarity of the {111} planes; A = group III element layer, B = group V element layer. "Stopping planes" means the crystallographic planes often (but not always) encountered as pore walls. "Current line" means an orientation of pore growth parallel to the flow of current (see Fig. 3 and 4).$ 

However, at least GaP and InP show a second kind of pore growth direction which is simply the direction of the current flow (perpendicular to the equipotential lines), independent of the crystal orientation. We will call pores growing in a crystallographic direction "crystallogaphically oriented pores" or "crysto pores" for short, and the other kind "current line oriented pores" or "curro pores". No curro pores have been observed so far in Si.

Two dimensional pore crystals in III-V compounds thus require either samples oriented in {111B} or the production of curro pores. Both approaches can be used, Fig. 2 shows crysto pores in GaAs and in InP (random nucleation).



Figure 2 Pores in <111B> directions in (111)-oriented a) n-GaAs, b) n-InP.

No sustained attempts have been made so far to use extrinsic nucleation to force the pores into a two dimensional crystal; the only exception can be found in [11]. However, two-dimensional self-organized pore crystals formed by curro pores can be obtained in InP which provides a splendid example to demonstrate the potential and the difficulties of making photonic crystals from porous semiconductors.

In short, for relatively large current densities curro pores can be obtained that exhibit a strong tendency to form a close packed arrangement with lattice constants ranging from 50 nm to 2  $\mu$ m and typical dimensions of a few lattice constants - there is short-range order only (Fig. 3a). However, upon optimizing the etching conditions, in particular with respect to the voltage, long range order may evolve and a single crystal (albeit full of defects) formed by curro pores results, cf. Fig 3c). That a single crystal is formed at least over distances of several 1000 lattice constants is demonstrated by the Fourier transform of the image (i.e. the diffraction picture) shown in the inset which was obtained from an area of approximately 100 x 100  $\mu$ m<sup>2</sup>. This is a unique finding that has not been observed before in ordered pore arrays, e.g. in Al<sub>2</sub>O<sub>3</sub>.



**Figure 3** Current line oriented pores in InP (the nucleation layer on top has been polished off). a) Short range ordering only, b) cross section with diameter oscillations, c) single pore crystal; the inset shows a Fourier transform obtained from a much larger part of the crystal than the section shown.

Looking at a cross section of an InP self-organized pore crystal, two outstanding features are visible: i) the curro pores (and thus the pore crystal) always form from a nucleation layer of crysto pores, and ii) the pores show self-induced phase-coupled diameter oscillations (accompanied by external voltage oscillations if the etching is performed under constant current conditions).

Space does not allow to discuss the obviously complicated mechanisms of self organization on various levels (for more details the reader is referred to [4, 12]), suffice it to mention the most important findings:

- i) Short range order is induced by pore-pore interactions via overlapping space charge regions. Under galvanostatic condition, this induces phase coupling of diameter variations between the pores, voltage oscillation, and by feed back, the formation of a large pore domain where pore growth is globally synchronized.
- ii) Long range order is impressed on the system by the effects of multiple branching of the crysto pore nucleation layer which induces a certain alignment of the tips of the crysto pores in a <110> direction – see Fig. 4 and Fig. 5.



**Figure 4** Cross sections through (100) samples. a) Very long curro pores (grown in about 15 min vs. roughly 8 hrs for a corresponding Si case). b) Detail of nucleation layer. c) Detail of a).



**Figure 5** Branching within the nucleation layers of curro pores produces pore tip domains with <110> preferences. Secondary branches grow upward. a) (100) oriented n-InP; b) (111) oriented n-InP;

A single crystal will only form if both processes are optimized and while first attempts obviously were successful, the available parameter space has not been probed in depth so far.

Some conclusions can be drawn with respect to the formation of pore crystals good enough for photonic crystal purposes: i) The formation of perfect two dimensional pore crystals in InP with lattice constant ranging from below 50 nm to  $\mu$ m by lithographic means is almost certainly possible. ii) However, the intrinsic lattice constant of the pore crystal must be closely matched to the extrinsic one because otherwise (unlike in Si!) parasitic random nucleation most likely will overrule the extrinsic pattern definition. iii) While the intrinsic system dynamics as expressed in the diameter oscillations can be suppressed, it might also be used for "open loop" control (also known as a special kind of chaos control) to force the system on perfectly synchronized pore growth conditions. In Si, such an approach succeeded in forcing "bad" pores with many branches into "good" pores which only showed some diameter modulation following the external enslavement [4].



**Figure 6** Diameter oscillations: a) Crysto pores in (100) GaAs; self induced and not synchronized), b) Curro pores in (100) GaP; self induced and synchronized.

While similar expressions of self induced pore crystal formation has not been observed (so far) in Si, GaAs, and GaP, the latter material at least shows crysto and curro pores and self-induced synchronized diameter oscillations, while Si, re-investigated with the InP results as a guide line, could be induced to exhibit self-induced synchronized diameter oscillations [12].

A variant of 2D pore crystal with some overlap to 3D crystals are 2D crystals with periodically modulated pore diameters. They may be obtained in several ways; most directly by external modulation of the pore diameter during the growth of a 2D pore crystal, cf, [5]. In Si this has been tried and found to be quite difficult mainly because the system often reacts in a strongly nonlinear fashion to changes in the etching current *I*. In other words, the I(t) profile is not necessarily found in the variation of the pore diameter *d* with depth *z*. This is not surprising, considering that in all materials investigated so far it has been found that pore growing systems have intrinsic time constants, expressed, e.g. in the diameter oscillations shown in Fig. 6 for GaAs and GaP. With the strong degree of self organization present in InP, it was possible to obtain for the first time a completely self organized 3D crystal as shown in a collage giving some perspective in Fig. 7.

Considering that the pores are arranged as a single (but defective) crystal in the x-y-plane with a lattice constant between 50 nm and 1  $\mu$ m, this is the best approach to a large 3D photonic pore crystal far below the 1  $\mu$ m range obtained so far. With proper external stabilization of the pore arrangement and tight control of the growth conditions including outside current modulations, perfect 3D crystals appear to be within reach.

A way of producing so called 2.5D pore crystals is to induce sudden transitions between curro pores and crysto pores while growing a 2D crystal. In InP this is comparatively easy, Fig. 8 shows some results.



Figure 7 First 3D single pore crystal obtained by self organization.



**Figure 8** Periodical switching from curro pores to crysto pores by current density modulation in InP: a) Switch over from curro pores to crysto pores; extremely planar interfaces are possible b), defined 2.5D crystal obtained by periodically switching from curro pores to crysto pores and back.

# THREE DIMENSIONAL PORE CRYSTALS IN SI AND III-V COMPOUNDS

There are two basic possibilities to produce 3D pore crystals: i) Use the anisotropic pore growth mode, and ii) use a two stage process. The first approach employs the crystallographic equivalence of three <113> directions of {111} oriented samples in Si, or of the 4 <111> directions in {100} oriented III-V compounds; the second approach was not yet successful. For the III-V compounds, however, recent research has shown that pores will only grow in the two <111B> directions. In the first case with an interpenetrating network of pores in three <113> directions, an orthorhombic crystal should result which, as shown by calculations will produce a full photonic band gap. This structure has been dubbed "Kielovite" honoring its origin in the city of Kiel.

A full 3D structure with an interpenetrating network of pores in four <111> directions would produce a cubic structure (called "Moldavite" [13]) which most likely, however, does not exhibit a photonic band gap in all directions. The photonic properties of the subset with pores only in two of the four <111> directions are not clear at present.

One attempt has been made to produce an extrinsically nucleated 3D crystal for the GaAs case as shown below; a randomly nucleated Si <113> structure is shown for comparison. Again, the system shows some dynamic behavior on its own (here the quasi periodic branching of side pores. Preliminary results indicate that periodic modulations of external parameters as, e.g., the current or voltage with the right frequency, may suppress branching or even induce it at the right moment.



**Figure 9** Pores in <113> directions in Si. b) Schematic representation of pores growing along <111B> directions from a (100) surface; c,d) Plane and cross section views of the first experimental results on lithographically patterned (100) n-GaAs. The uniformity of the structure is lost in the depth due to high branching rate of the pores.

# CONCLUSIONS

Growing pores in III-V semiconductors (and Si) must be perceived as operating a highly non linear dynamic system that has intrinsic lengths and times scales which may express themselves by pattern formation including fully self organized three dimensional single crystals. Lattice constants and pore diameters far below  $1\mu$ m are easily achieved in III-V semiconductors (in contrast to Si). Attempts to induce order by lithographically defined pore nucleation are bound to fail if the external geometry is not matched to the internal system geometry and dynamics. However, controlling the system from the outside based on an understanding of the system behavior appears to be possible and opens the route to two and possibly three dimensional photonic crystals in optoelectronic materials with band gaps in the infrared or even optical range of the spectrum.

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