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Porous semiconductors exhibit new and unexpected properties as compared to the bulk materials. In III-Vs, many, many new features with respect to optical properties emerged during the last few years for

certain pore morphologies. While pore etching is a complicated process, only poorly understood at present, it has a definite potential to produce materials with engineered properties.

Engineering porous III-Vs

Electrochemically etched nanopores in Si have caused quite a stir in the scientific community after the discovery of their luminescent properties in 1990 [1]. Some 10 years later, however, first applications of porous Silicon are not using luminescent nanoporous Si, but meso- and macro pores structures for a large variety of available or envisioned products, for a recent review see [2]. An international conference is now devoted to porous semiconductor science and technology. From 191 papers in 2002, 178 dealt with porous Si, 8 with porous III-Vs, and 5 with more 'exotic' porous semiconductors like GaN, Graphite, SiGe, and TiO₂.

In other words, porous III-V compounds so far received far less attention than porous Si. Part of the disparity is due to their relative uselessness for biological or MEMS applications, and the comparatively high prices for as-grown materials.

However, it is also far more difficult to master the electrochemistry of III-Vs than that of Si (which is mysterious enough in some parts). The situation has started to change in recent years; and a host of interesting results with respect to porous III-V compounds has been obtained. The authors have recently reviewed porous III-V compounds in detail [3], and here a brief overview will be given.

Generally, there are two large areas of interest: first the production of porous III-Vs, and second the characterisation of the properties of porous III-Vs. The focus of this overview will be on making pores, but only after giving a short list of some of the most spectacular properties of porous III-Vs.

Some properties of porous III-Vs

Pores quite generally break the symmetry of the host lattice, and this will be felt by all properties that involve part of the crystal larger than the typical pore size (as given by the mean diameter of pores and the mean distance between pores). Phonons and photons thus might be affected by mesopores and macropores (short for pores with sizes in the 2-50nm range and above 50nm respectively). For nanopores (officially called micropores; size range < 2 nm), direct size confinement effects, ie. quantum wire and quantum dot effects can be expected, on a somewhat larger scale, free and bound excitons or polaritons may feel the changed structure.

In addition, the large surface area may change the properties, eg. by changing the generation and recombination behavior; and transport properties in general will be changed by the porous structure.

The changed symmetry can induce dramatic property changes. Most conspicuous, perhaps, is the more than hundred-fold increase of the optical second harmonic generation in porous GaP, occurring concomitantly with pore-induced birefringence [4]. This would allow so-called phase matching of the second harmonic (SH) and thus the prospect of frequency doubling crystals having an efficiency much larger than the ADP or KPD crystals presently used.

Another property changed by factors >> 10 is cathodoluminescence (CL). While porous InP shows severely decreased CL, porous GaP exhibits far stronger CL from porous regions compared to the bulk

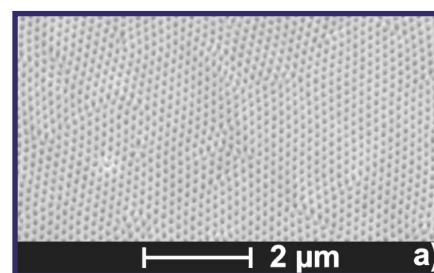
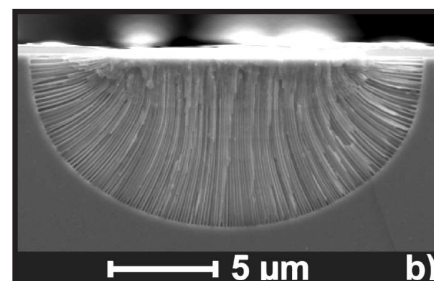


Figure 1. Some characteristic examples of pores in various III-V substrates;
a) Self-arranged single crystalline pore array in InP;



b) Waveguide like porous structures in InP. The current line oriented pores (low refractive index) surround a region with a high refractive index;

(see Figure 1d); GaAs appears to show enhanced CL, too, but there are no studies of comparison between morphology and CL.

The precise behavior found may strongly depend on pore geometry and morphology. Pores with circular cross section show far smaller SH enhancement than pores with triangular cross section. While observations of this kind may be used as a guidance for model development, it is fair to say that the phenomena mentioned are not well understood at present.

Without going into details, some more properties of porous III-Vs will be mentioned:

- Self-arranged single pore crystals on InP suitable for photonic crystal applications (Figure 1a).

- Current line oriented pores suitable for easy integrated waveguide like structures on InP substrates (Figure 1b).
- Intersection of crystallographically oriented pores enabling 3D microstructuring (Figure 1c).
- A strongly enhanced quantum efficiency of the photo response during pore formation in n-GaP electrodes and enormous light scattering in the porous medium.
- A sharp increase in the intensity of the photo luminescence (PL) in porous GaP along with the emergence of blue and ultraviolet luminescence.
- Evidence for birefringence in porous InP at wavelengths suitable for optical communication systems ($l = 1.55 \mu\text{m}$).
- Porosity-induced modification of the phonon spectrum in GaP, GaAs, and InP.

It is fairly certain, that more property changes will evolve as research intensifies. It is too early to speculate about uses and products; suffice it to say, that the ability to produce porous III-Vs with many different kinds of pore structures simply increases the number of available basic (bulk) semiconductors since eg. macroporous GaAs is a material with properties different from that of bulk GaAs or mesoporous GaAs.

Making porous III-Vs

Anodic etching is the most successful technique for producing pores in III-Vs (and other semiconductors). Plasma etching can produce pores, too, but in a rather limited way. A pore etching experiment thus needs an electrochemical cell plus electronics that has to meet a surprising number of requirements, details can be found in [2]. Suffice it to say that a good backside contact and precise temperature control is of importance. Prime parameters for successful pore etching is the substrate doping type and resistivity, current density, potential, and temperature, and the type of electrolyte used. Since III-Vs (in contrast to Si) will dissolve anodically in nearly all acids, the available parameter space is endless, and, if preliminary observations that very small changes in electrolyte composition may have very large effects proves to

be true, systematic work, guided by a basic understanding of the interface phenomena during etching, will be needed.

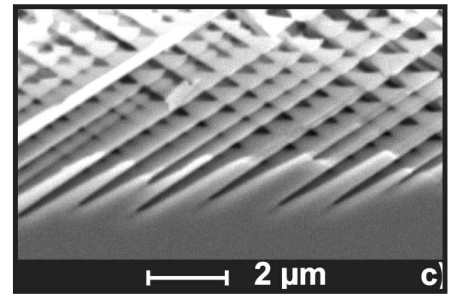
In any pore etching experiment, three phases may be distinguished:

- Pore nucleation:
- Stable pore growth:
- Instabilities and termination of pore growth after prolonged etching.

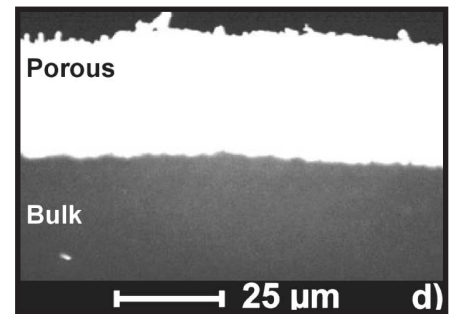
The third point, although quite interesting in practical work, is simply caused by changed conditions at the growing pore tip, deep in the substrate: Diffusive transport of reactant to and from the pore tip becomes increasingly difficult, the potential at the pore tip decreases due to a voltage drop in the pore, leakage currents through pore walls increase with pore depth, and so on. It is often necessary to compensate for these effects by suitably changing the etching conditions, but this topic will not be pursued here.

Homogeneous nucleation of pores in III-V compounds is far more difficult than in Si, but will not be pursued here. Stable pore growth in III-Vs, as far as presently known, can be summarized as follows:

- Pores grow either in $\langle 111 \rangle_B$ directions (the $\langle 111 \rangle$ direction pointing from group V to group III element along the shortest distance [3]) or in the direction of the current flow (ie. perpendicular to the equipotential planes of the electric field inside the sample). For comparison, In Si pores grow either along all $\langle 100 \rangle$ or $\langle 113 \rangle$ directions or in the direction of current flow.
- The pore geometry is influenced by many parameters, most important however, are the width of the space charge region (and thus the doping level) and the maximum curvature radius still allowing for local avalanche breakdown.
- The basic pore generation and stabilization mechanism seems to be hole generation by avalanche breakdown at the pore tip.
- The properties of III-V compounds often depend sensitively on the detailed pore structure, which in turn, reflect the concrete etching conditions.
- No pores of any kind could be obtained in p-type III-Vs so far - in marked contrast to Si.



c) 3D porous structure obtained by intersection of crystallographically oriented pores in GaAs;



d) micro-cathodoluminescence image taken from a GaP sample. A lot more light comes from a porous layer than from the bulk material.

- No nanopores could be obtained by anodic etching; again in contrast to Si and contrary to general expectations.

In conclusion, anodic etching of III-V compounds allows new materials to be obtained, exhibiting a huge diversity of optical and morphological properties, and thus opens a wide field for basic research and possible future applications.

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¹ In principle, international norms demand to call porous structures with pore sizes $< 2\text{nm}$ - microporous.