Self-organized growth of single crystals of nanopores

S. Langa^{a)}

Faculty of Engineering, Christian-Albrechts-University, Kaiserstr. 2, D-24143 Kiel, Germany and LDSS Laboratory, Institute of Applied Physics, Technical University of Moldova, Stefan cel Mare 168, MD-2004, Chisinau, Moldova

I. M. Tiginyanu

Institute of Applied Physics, Technical University of Moldova, Stefan cel Mare 168, MD-2004, Chisinau, Moldova

J. Carstensen, M. Christophersen, and H. Föll Faculty of Engineering, Christian-Albrechts-University, Kaiserstr. 2, D-24143 Kiel, Germany

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Self-organized single crystalline two-dimensional hexagonal arrays of pores in InP semiconductor compound are reported. We show that the self-arrangement of pores can be obtained on *n*-type substrates with (100) and (111) orientations. The long-range order in pore distribution evidenced in (100)InP samples proves to be favored by the so-called nucleation layer exhibiting branching pores oriented along $\langle 111 \rangle$ directions. The combination of long-range order with self-induced diameter oscillations is shown to be promising for nonlithographic growth of three-dimensional pore crystals. © 2003 American Institute of Physics. [DOI: 10.1063/1.1537868]

The impact of porosity on the properties of semiconductor materials depends upon the size, shape, density, and spatial orientation of pores. In particular, precise engineering of pore architecture was shown to lead to the occurrence of photonic band gap in macroporous Si.¹ A strongly enhanced optical second harmonic generation was recently observed in porous GaP with triangular prism like nanopores.² Porous matrices were found to contribute to the formation of superior electrical and emission characteristics of polymersemiconductor nanocomposites promising for display applications.^{3,4} Over the last years, considerable efforts were focused on nonlithographic growth of two dimensional (2D) arrays of nanopores for manufacturing cost-effective nanotemplates. Self-organized 2D crystals of pores were so far observed only in Al₂O₃, but always in the form of polycrystals.^{5–8} In this work, nonlithographic growth of 2D single crystals of nanopores with lattice constant as small as 100 nm is presented using electrochemical dissolution of InP. Moreover, when etching occurs at constant current density, three-dimensional (3D) pore crystals are produced due to self-induced oscillation of pore diameters.

(100)- and (111)-oriented substrates of *n*-InP single crystals with 500 μ m thickness and free electron concentration ranging from 10¹⁷ to 10¹⁸ cm⁻³ were used. The electrochemical etching was carried out in HCl-based solutions as described elsewhere,⁹ the area of the samples exposed to the electrolyte was 0.2 cm². A scanning electron microscope (SEM) operating at 10 kV was used to analyze the morphology of the porous samples.

Two types of distinctly different pores were evidenced. The first type of pores growing in $\langle 111B \rangle$ directions will be called "crystallographically oriented pores" or "crysto pores." The "B" refers to the inequality of $\langle 111 \rangle$ directions in III–V crystals and in case of InP it designates the direction running from the In layer to the P layer via one straight bond. Curro pores seem always to need crysto pores for nucleation, i.e., they cannot grow by themselves from the beginning of the etching process. The thickness of the crysto pore layer necessary to induce curro pores depends upon substrate orientation and electrolyte composition. For (111) oriented samples and less oxidizing electrolytes (e.g., HCl diluted



FIG. 1. SEM micrograph taken from (100) InP sample exhibiting curro pores (overview of a cleavage). The inset shows curro pores in the upper part, and crysto pores oriented along $\langle 111B \rangle$ directions in the lower part.

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Generally speaking, crysto pores grow at relatively small anodic current densities (less than 10 mA/cm²), while at large current densities the second type of pores, called "current line oriented pores" or "curro pores" for short, are observed (Fig. 1). Curro pores do not branch and grow in the direction of current flow, i.e., perpendicular to the equipotential lines and thus perpendicular to the sample surface except at the edges of the etched area where they bend smoothly around the corner. Crysto pores, on the other hand, have a strong tendency for branching, in particular if the sample is (100) oriented, and this includes also branches that grow upwards towards the initial surface. The inset in Fig. 1 illustrates both pore types in a (100)-oriented specimen where a switch over from curro pores to crysto pores was initiated by an externally induced decrease of the current density from 500 to 0.5 mA/cm^2 .

^{a)}Electronic mail: sla@tf.uni-kiel.de

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FIG. 2. SEM images of pore arrays in InP (top views): (a) nucleation layer of crysto pores; (b) polycrystal of curro pores; and (c) single crystal of curro pores. In case of (b) and (c) the images were taken after removal of the nucleation layers. The insets show the two dimensional Fourier transforms.

with organic solvents) it proves to be thinner in comparison to that inherent to (100) samples or pore etching in more oxidizing electrolyte (e.g., HCl diluted with H_2O).

Characteristic top views of the pore arrangements in samples etched at high voltage (U)/current densities (j) are shown in Fig. 2. What "high" or "low" means depends somewhat on the doping level, temperature etc.; at 20 °C, for example, U = (5-9) V and j = (0.4-0.6) A/cm² are considered high values for $n = 10^{18}$ cm⁻³.

Decreasing the doping level, porous structures with average pore diameter starting from about 50 nm up to 1 μ m can be obtained. The substrate doping influences also the rate of pore etching. At the beginning of the process, for instance, the etching rate equals 50 μ m/min for $n = 10^{18}$ cm⁻³, U = 5 V, and 5% HCl aqueous solution. In spite of the fact that the etching rate decreases with time due to diffusion limitations,¹⁰ the morphology of pores remains nearly unchanged even when etching pores through the complete wafer. Note that etching is extremely fast and it takes only one hour to etch pores through a wafer of 500 μ m thickness. The general findings as illustrated in Fig. 2 are the following.

- (a) Randomly distributed nanopores on the sample surface showing the nucleation layer of the crysto pores which always form first. The inset shows the direct Fourier transform or "diffraction image" of a picture including at least 500×500 pores (the picture shown, for sake of clarity, is only a small part of the analyzed area). It clearly demonstrates that there is no visible ordering in the primary nucleation of crysto pores and this is true under any conditions.
- (b) Curro pores with short range ordering. Perfect domains or grains with an average size of roughly six lattice constants, arranged in a hexagonal close packed structure, are observed. The Fourier transform (see inset) proves the formation of pore polycrystals.
- (c) Curro pores with long range ordering. The Fourier transform, which was taken from an area of about Downloaded 16 Jan 1003 to 034.235.242.173. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp



FIG. 3. Schematic outline of multiple branching of crysto pores. A part of the secondary branches grow upwards towards the specimen surface. The alignment of pore end points along one $\langle 110 \rangle$ direction causes the tendency of different domains to exhibit the same spatial distribution of curro pores leading to the formation of 2D single crystals of pores.

 500×500 lattice constants (much larger than the section shown), clearly indicates monocrystallinity despite many lattice defects. This specimen thus represents the first single crystal of pores ever made without lithographic means.

The best single crystals of pores with aspect ratio as high as 5×10^3 are achieved at optimum values of the applied voltage and electrolyte concentration (U=7 V; 7.5% HCl); deviations in either direction lead to a decreased tendency for ordering. The following two ingredients are needed to account for the self-organized 2D ordering of pores.

- A repulsive pore-pore interaction that induces short order. This allows for the formation of small ordered domains with a close packed structure.
- (ii) Some global guidance that induces domains formed independently on many parts of the sample to assume the same general orientation or, in other words, the processing conditions should provide a kind of epitaxy on a macroscopic scale.

The required repulsive pore-pore interaction is relatively easy to understand, it will occur if at large pore densities the space charge regions surrounding the pores start to overlap. The epitaxy component is much harder to understand. It is unlikely to result directly from the underlying crystals lattice, because pore ordering is best developed in (100)-oriented crystals and it is hard to imagine how a substrate with fourfold symmetry induces a hexagonal structure.

All experiments confirm that the degree of ordering scales to some extent with the thickness of the crysto pore nucleation layer. It is thus reasonable to assume that this layer, though nucleated without any ordering [see Fig. 2(a)], induces the epitaxy of the curro pore layer. Indeed, multiple branching of one crysto pore will result in a whole set of pores from one root ancestor which are no longer distributed at random but aligned along one intersection of inclined $\{111B\}$ planes with the surface, for $\{100\}$ surfaces this is a $\langle 110 \rangle$ direction. The end points of the set of pores originating from one primary pore form a domain and serve as the nuclei for a corresponding domain of curro pores (Fig. 3). Thus, there is a certain tendency for globally ordered curro pore



FIG. 4. (a) Self-induced synchronized diameter oscillations of curro pores in a (111)-oriented sample. (b) Example of well developed voltage oscillations always observed together with synchronized pore diameter oscillations.

growth in a kind of graphoepitaxy if there are well developed crysto pore domains.

The voltage influences pore ordering in two opposing ways. While the space charge region and thus the tendency to short range ordering increases with increasing voltage, the thickness of the crysto pore nucleation layer decreases; for decreasing voltage the effects are reversed. At voltages too low we therefore lose short range ordering, at voltages too large, the global ordering is missing. Suffice it to mention that all other observations support this model; there is, however, much room for further investigations.

Both crysto and curro pores show manifestations of pattern formation; the more spectacular cases are obtained from curro pores. If the experiment runs under constant current density, spontaneously starting and ending voltage oscillations often occur which are always tied to pore diameter oscillations that are synchronized on a large area of the sample, most likely everywhere. While only rather irregular oscillations have been observed so far,¹⁰ optimized conditions lead to very regular pore diameter and voltage oscillations as shown in Fig. 4 and clearly demonstrate the perfect synchronization between the pores on large area.

These voltage oscillations can be understood if the current and current density within one pore are naturally oscillating in a stochastic (i.e., random) way as was proposed for Si and GaAs.^{11,12} A constant external current then can only be obtained under two conditions.

- (i) The current in individual pores oscillates with random phases with respect to many other pores; the total current then averages to a constant value and the voltage can be fairly constant, too.
- (ii) All (or at least a large majority) of the pores are phase locked and thus synchronized which would produce a macroscopic current oscillation. Constant current con-

ditions then can only be maintained if the voltage oscillates accordingly. Intermediate situations are not allowed since the voltage can only have one value at any given time, i.e., small synchronized domains needing an oscillating voltage cannot exist in a sea of unsynchronized pores requiring a constant voltage.

The essential ingredient is the necessity to have an intrinsically oscillating current within one pore (which is another feature of self-organization); and this is a direct consequence of the current burst model proposed earlier for the electrochemical dissolution of Si.¹³ The reason for the phase locking between pores at high pore density resulting in a large synchronized domain is the overlapping of the space charge regions surrounding each pore. This puts constraints on the intrinsic diameter oscillations tied to current oscillations and induces the feedback that is needed to start synchronization and thus large-scale voltage oscillations.

We described an effective technological approach for growing 2D single crystals of nanopores with aspect ratio as high as 5×10^3 . When the growth of 2D single crystals of pores is combined with synchronized diameter modulation inducing additionally a periodicity in z direction, fully selforganized 3D pore crystals can be produced in InP. Note that similar trends in pore etching were evidenced by us for other semiconductor compounds such as GaP and GaAs. The obtained results do not only provide particularly noteworthy instances of self-organized pattern formation allowing for 2D and 3D nanostructuring, but demonstrate that it is possible to produce single crystals of nanopores for various applications (e.g., in nanotemplates for nanofabrication) without employing lithography or other prepatterning techniques. Moreover, they indicate that pore etching, or more generally, the electrochemistry of semiconductors does have a stochastic component which is not contained in the conventional view of electrode processes.

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