

Self-organized growth of single crystals of nanopores

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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 polymer-semiconductor 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 μm 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 $\langle 111 \rangle$ 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.

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/cm².

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

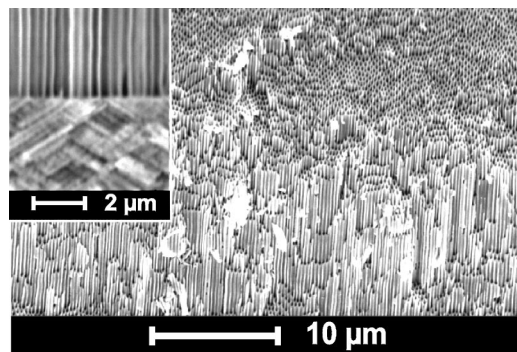


FIG. 1. SEM micrograph taken from (100) InP sample exhibiting curro pores (overview of a cleavage). The inset shows curro pores in the upper part, and crysto pores oriented along $\langle 111 \rangle$ directions in the lower part.

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