

Observation of crossing pores in anodically etched *n*-GaAs

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Pores in GaAs in the micrometer range and oriented in $\langle 111 \rangle$ directions have been observed during the anodization of GaAs in aqueous HCl electrolytes. A direct evidence of pores intersection is presented which is a very promising feature for three-dimensional micro- and nanostructuring of III-V compounds for the production of photonic materials. © 2001 American Institute of Physics. [DOI: 10.1063/1.1350433]

Over the last years, porosity emerged as a promising and cost-effective approach for engineering certain characteristics of semiconductor materials. In particular, pore formation allows to fabricate semiconductor structures with large spatial variations of the dielectric properties. Porous Si is a prime example for this: two-dimensional photonic band gap crystals have been recently fabricated by introducing an array of ordered parallel pores in bulk material; the ordered distribution of pores being defined by photolithography.¹ Obviously, manufacturing of three-dimensional (3D) photonic crystals would require a controlled modulation of the pore diameter or, in a more complex geometry, formation of crossing pores along definite crystallographic directions. Although crystallographically oriented pores were reported for some of the III-V compounds (see Ref. 2, and references therein), no evidence of their crossing with subsequent continuation of their growth along the initial directions has been obtained. In this work, we present experimental data on pore growth in *n*-GaAs along well defined $\langle 111 \rangle$ crystallographic directions, and crossing of pores following different $\langle 111 \rangle$ directions under anodic etching of *n*-GaAs in a HCl-based solution.

(100)-oriented GaAs substrates were cut from the liquid-encapsulated Czochralsky-grown Si-doped ingots with a free electron concentration $n = 10^{18} \text{ cm}^{-3}$ at 300 K. The anodization was carried out in an electrochemical double-cell as shown in Fig. 1. A four electrode configuration was used: a Pt reference electrode in the electrolyte, a Pt reference electrode on the sample, a Pt counter electrode, and a Pt working electrode. The electrodes were connected to a Keithley 236 Source Measure Unit. The temperature was kept constant at $T = 23^\circ \text{C}$ with the help of a Julabo F25 thermostat.

The electrolyte was pumped continuously through both parts of the double cell with the help of a peristaltic pump. All equipment involved in the experiments was computer controlled. The area of the sample exposed to the electrolyte

was 0.12 cm^2 . The anodic etching was carried out using 5% HCl aqueous electrolyte at low-current densities in galvanostatic regimes.

After electrochemical etching, fresh cleavages were prepared and studied using a scanning electron microscope (SEM) operating at 10 kV. Figure 2 shows a cross-sectional SEM image taken from a sample anodized at $j = 4 \text{ mA/cm}^2$ in 5% HCl aqueous electrolyte. As can be observed, the angle between the directions of pore growth (marked by arrows) and the direction perpendicular to the surface ($[100]$ -direction in this case) is 54° . Thus, the two directions of pore growth can be assigned to $[111]$ and $[1\bar{1}\bar{1}]$ ones. The intersection of these $[111]$ and $[1\bar{1}\bar{1}]$ oriented pores is most likely the reason for the formation of the visible terraces as a result of the cleavage. Apart from that, the analysis of the SEM micrograph presented in Fig. 2 shows the existence of sets of pores oriented along $[1\bar{1}\bar{1}]$ and $[11\bar{1}]$ crystallographic directions. Enlarged images of such pores cut by the plane of the cleavage are illustrated in Figs. 3(a) and 3(b). The pores show a triangular cross section; the pore walls are

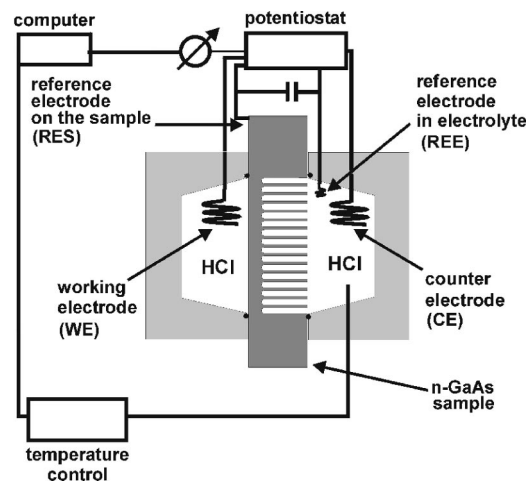


FIG. 1. Schematic illustration of the double-room electrochemical cell.

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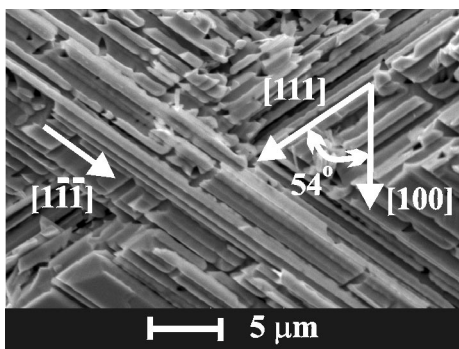


FIG. 2. SEM cross-sectional view of anodically etched *n*-GaAs in 5% HCl aqueous electrolyte at $j=4 \text{ mA/cm}^2$. Directions of pore growth make an angle of 54° with the direction perpendicular to the surface.

formed by $\{112\}$ planes. The formation of triangular pores introduces a second anisotropy of the electrochemical etching in GaAs (besides the preferred directions in $\langle 111 \rangle$). In analogy to findings concerning the H passivation of pore walls in Si,³ it may be concluded that $\{112\}$ planes are the most stable, i.e., most easily passivated set of planes, enveloping $\langle 111 \rangle$ directions.

To control the architecture of 3D pore structures, etching conditions which provide crossing of pores and their continued growth along the initial directions must be maintained. Figure 4 illustrates an example of the intersection of two pores oriented along $[111]$ and $[1\bar{1}\bar{1}]$ directions. Somewhat surprisingly, the intersection has no influence on the pore shape, the size, and the direction of subsequent propagation. This important finding demonstrates that anodic etching may be a suitable and unique tool for the production of 3D micro- and nanostructured III–V compounds, e.g., for photonic crystals applications. Nevertheless, in addition to pore interconnection a photonic crystal requires a very high level of uniformity,⁴ which was not possible to achieve in our experiments because the pores start to grow (nucleate) randomly.

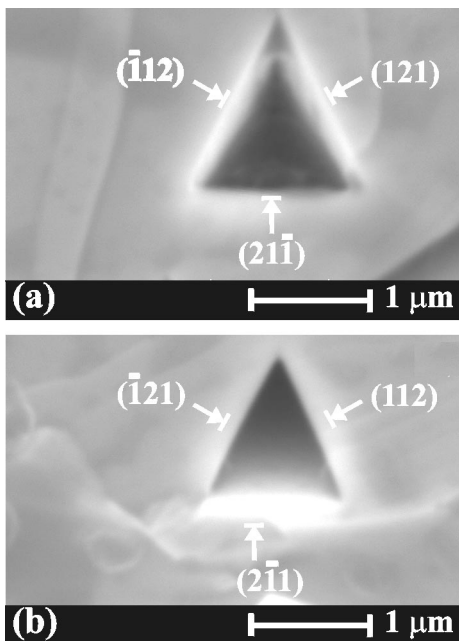


FIG. 3. SEM micrographs of $[1\bar{1}\bar{1}]$ (a) and $[111]$ (b) oriented pores cut by the plane of the cleavage

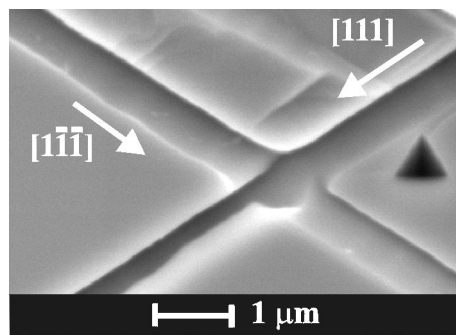


FIG. 4. Intersection of $[111]$ and $[1\bar{1}\bar{1}]$ oriented pores in anodically etched (100) *n*-GaAs.

Since the dissolution is stimulated by defects^{5,6} and/or illumination,⁷ it is expected that a predefined nucleation and thus a controlled intersection of the pores can be provided by conventional lithographic means followed by a conventional chemical treatment to generate small pits (defects) or by proper front side illumination of the sample at the beginning of the anodization.

The crossing of the pores is somewhat unexpected because according to the existing models,^{7–9} the formation of pores in *n*-type semiconductors is a self-adjusted process controlled by the distribution of the electric field at the semiconductor-electrolyte interface. The pores may branch and form porous domains, but both individual pores and domains should be separated by walls with characteristic dimensions of twice the thickness of the surface depletion layer.^{6,10} These observations have been argued supposing that when a wall becomes too thin, it can no longer support a field perpendicular to the surface which is sufficiently high for anodic hole generation, so that etching stops.^{10,11} On the other hand, crossing suggests that, independent of the distance separating two neighboring pores, there are sufficient holes at least to initiate the rate-limiting step of the dissolution reaction. The oxidation intermediates produced by this initial reaction are usually considered as surface states with energy levels above the valence band edge¹² and can be further easily oxidized by injection of an electron in the conduction band by tunneling and do not need anodically generated holes. Thus, in spite of the fact that the field strength decreases when the space charge region of two pores overlaps, it is still high enough to support the dissolution leading to intersection.

The observation of crossing pores in single crystalline *n*-GaAs suggests that the depletion layers may be overcome also in other materials. Our experiments were carried out under conditions of strongly anisotropic etching along guidelines adopted from the “current burst model” proposed for pore formation in Si.¹³ The strong influence of the crystal anisotropy under those conditions probably plays also a major role in the crossing of pores and subsequent continuation of the growth along the same crystallographic directions. Further research efforts are required in order to elucidate the mechanism of dissolution in this case.

In summary, anodic etching of *n*-GaAs(100) in aqueous solution of HCl was found to produce well formed pores aligned along $[111]$, $[1\bar{1}\bar{1}]$, $[1\bar{1}1]$, and $[11\bar{1}]$ crystallographic directions. Crossing pores were observed with per-

fect morphology both before and after their intersection, allowing the generation of 3D pore lattices. These results demonstrate that pore etching is a promising method for designers in need of 3D micro- and nanostructuring of III–V compounds for the production of photonic materials.

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