## Single crystalline 2D porous arrays obtained by self organization in n-InP

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Self organization is a rather common phenomenon during pore formation in III–V semiconductors. The so called tetrahedron-like pores, the domains of crystallographically oriented pores in n-GaAs, or the macroscopic voltage oscillations in n-InP at high constant current densities are examples of a self organization process. In this paper we will discuss two-dimensional arrays of pores in n-InP with the unique property that they may form a *single* crystal as a result of a self organization process. The reasons for this long range order and its dependence on the etching conditions will be discussed.

**1 Introduction** Self organization of stochastic events is known in all fields of science, even including the social "sciences", and an increasing number of phenomena is understood as a result of self organization processes. Therefore it is not surprising that self organization has also been observed during pore formation processes in semiconductors or other materials [5–7]. The essence of self organization is that structures or patterns emerge without explicit input or constraints from outside the system [1, 2]. Patterns can evolve in space and/or time, can maintain a stable form, or can show transient phenomena.

In our case the components of the system are the pores which "interact" via the space charge regions surrounding each pore. As a result, pore arrangements with local or even long range order can be obtained as will be shown in this paper.

**2 Experiment** The experiments were performed in a Teflon electrochemical double cell using a four electrode configuration. The double cell was used in order to obtain a good backside contact and thus the usual In-Ga/sample contact was replaced by an electrolyte/sample contact.

The custom-built potentiostat/galvanostat can deliver up to 250 mA,  $\pm$ 80 V, and the temperature of the electrolyte was kept constant at T = 20 °C by means of a Julabo F25 thermostat. Both the potentio-stat/galvanostat and the thermostat were computer controlled. Peristaltic pumps were used to pump the electrolyte continuously through the electrochemical cell.

(100) and (111) oriented n-InP samples at a doping level of  $n = 10^{18}$  cm<sup>-3</sup> were used. The area of the sample exposed to the electrolyte was 0.2 cm<sup>2</sup>. Aqueous HCl solutions at different concentrations were employed.

**3 Results and discussion** In contrast to pore formation in n-Si, where a back side illumination technique is applicable, the only effective mechanism for generating holes required for electrochemical dis-

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Fig. 1 Ordered distribution of CLO pores after the nucleation layer has been mechanically removed with (a) lattice constant of  $a \approx 200$  nm. (b)  $a \approx 800$  nm.

solution during the pores formation process in III–V compounds is junction breakdown or "breakthrough". The pores in III–V compounds therefore should be compared to the so-called "breakthrough" pores in Si. Two completely different types of pores have been observed in n-InP up to now: crystallographically oriented pores and current-line oriented pores.

The pores belonging to the first group are usually obtained at "low" voltage/current densities and "low" is a relative measure tied to the doping level of the samples, e.g. for  $n = 10^{18}$  cm<sup>-3</sup>, j < 10 mA/cm<sup>2</sup> is "low". Pores obtained in this way, like most breakthrough pores in Si, are always crystallographically oriented (CO), exhibiting a high level of anisotropy. They do not only grow along definite crystallographic directions,  $\langle 111 \rangle$  directions, they also have triangular shapes exposing  $\{112\}$  planes [8, 9] which is a second anisotropy feature. It should be noted that in polar crystals like the III–V semiconductors not all eight  $\langle 111 \rangle$  directions are equivalent from the electrochemical point of view. Only the four so called  $\langle 111 \rangle$  B directions are preferential dissolution directions.

The second type of breakdown pores, called current line oriented pores (CLO), begins to grow only at relatively high current densities (e.g. for  $n = 10^{18}$  cm<sup>-3</sup>, j > 10 mA/cm<sup>2</sup>) and does not have preferential directions of growth [4]. They are usually found to grow perpendicular to the surface of the sample independent of the specimen orientation, but closer analysis shows that they grow in the direction of current



**Fig. 2** Cross sections through (100) samples. a) Very long CLO pores following a nucleation layer. b) Detail of nucleation layer. (c) Switch over from CLO pores to CO pores upon reducing the current density.

flow which is usually perpendicular to the sample surface except at the edges of the etched area. Depending on the etching conditions, CLO pores may still retain a triangular cross section, but often the shape tends to become round.

An important feature of the CLO is that they self organize locally into a closed packed (hexagonal) lattice. Domains of a perfect pore lattice can be easily distinguished. Such domains with a hexagonal arrangement of the pores with two different lattice constants are presented in Fig. 1.

Current line oriented pores obtained in galvanostatic experiments usually exhibit strong diameter oscillations due to the current synchronization of neighboring pores [3], whereas at potentiostatic conditions (and optimized electrolyte concentration) the pore diameters are constant. Therefore a domain of current line oriented pores obtained at potenstiostatic conditions can be regarded as a nearly perfectly arranged hexagonal 2D pore array.

An important feature to note is that in n-InP even at very high current densities (high constant voltages) always both types of pores are present if aqueous HCl solutions are used, because then the prevalent CLO pores are always preceded by CO pores. The latter act as a nucleation layer (NL), which is followed by a stable pore growth layer of CLO pores. The nucletaion layer is nearly absent if organic HCl solution or mixtures of HCl and  $H_2SO_4$  are used for etching; on {111} oriented samples it is generally thinner. An example showing a pronounced nucleation layer followed by very long CLO pores is shown in Fig. 2a and b.

The necessity of a nucleation layer to precede CLO pores in aqueous HCl solutions can be also proved by switching the anodization current on and off (Figs. 2 c and 3). The general finding is that a process interruption (current off) for 0.5 min is enough for the system "to loose its memory". When the current is switched on again, a new nucleation phase is required, i.e. a new nucleation layer with CO pores emerges before the transformation to CLO pores. Note that this fact is not understandable in any static pore formation model where the equilibrium structure, once reached, should be maintained under all conditions. This observation, however, fits exactly in the general scheme of the current burst model because in the current-free phase the pore tips become passivated and the self ordering process of current bursts has to be started again.

By means of current switching a succession of CO/CLO pores can be easily obtained (Fig. 3) which provides a modulation of the third dimension in an otherwise two dimensional crystal and thus the very first three dimensional pore crystal in n-InP.

In aqueous HCl solutions the thickness of the nucleation layer depends on the electrolyte concentration and voltage/current applied to the sample; it increases slightly by increasing the electrolyte concen-



**Fig. 3** a) Three dimensional pore crystal with periodic switches between CO and CLO pores. b) Detail of CLO pores. c) CO pores (taken from a thick layer).

tration and by decreasing the voltage/current. In order to see the arrangement of the CLO pores, the nucleation layer should be removed.

As can be observed from Fig. 1, there is no defined correlation between the individual domains, i.e. each of them is arbitrarily oriented in respect to its neighbors. The entire porous array (all the domains) can be regarded as a polycrystalline structure, even so the transition between domains or grains is rather smooth. A suitable method for checking the degree of crystallinity is a Fourier Transform (FT) analysis, amounting to taking a diffraction picture.

FT analysis was used for both kinds of pore arrays: the CO pores as seen on the surface of the sample, and the CLO pores after the nucleation layer has been mechanically removed. Large areas of the porous arrays were chosen for the FT analysis (at least 200 lattice constants). Figure 4a shows a SEM picture that was taken from the surface of the anodized sample; the inset shows the FT "diffraction" picture (frequency spectrum) taken from an area of  $512 \times 512$  pixels. The spatial frequency spectrum obtained is a highly diffuse spot, characteristic for a random arrangement of the nucleated pores.

However, the situation changes if the FT is taken from a CLO pore layer (Fig. 4b). In this case the spatial frequency spectrum shows a diffuse ring. From diffraction theory it is known that such patterns are obtained both from amorphous as well as polycrystalline materials. As long as there are relatively sharp next neighbor distances, the frequency domain pattern from an amorphous material looks similar to that from polycrystalline material, but the rings are broader and there is no speckle for amorphous ones. From the inset in Fig. 4b it is evident that the ring in our case is also diffuse, i.e. is broad, and it can be concluded that in Fig. 4b the porous structure is closer to an amorphous structure with some short range order than to a true polycrystal.

However, the arrangement of the current line oriented pores can be further improved if the etching conditions are optimized. Fig. 4c shows a relatively large area of a pore array obtained under optimized conditions. The FT pattern of this picture, presented in Fig. 4c, shows evident spots exhibiting clearly the six fold symmetry of a closed packed structure (the small distortions are due to the specimen tilt in the





SEM). The presence of spots instead of rings in the frequency domain pattern is undoubtedly a sign for a long range order, or in other words this is a *single crystal* formed by pores. To the best of our knowledge, this is the first such crystal obtained by self organization. However, the monocrystalline structure is far from being perfect, i.e. it has a high number of defects which make the spots diffuse.

Monocrystallinity of the pores depends on the electrolyte concentration, on the substrate doping level, and in particular on the anodization voltage. The latter should be carefully optimized in order to obtain a long range order. For example in 5% HCl aqueous electrolytes ( $n = 10^{18}$  cm<sup>-3</sup>) the long range order is obtained at U = 6 - 7 V, whereas at lower or higher voltages the long range order disappears. These results prove that by changing the etching conditions it is possible to improve the arrangement of the pores from amorphous to high defect density monocrystalline structures.

The arrangement of the pores in a long range order is self organized which cannot be due to the percolation of next neighbor interaction, considering that all pores start to grow simultaneously. Therefore "forces" or patterns must exist that are intrinsic to the system and induce independently started domains to adjust to the same basic orientation. In order to find the "force" responsible for the long-range order, it is important to compare in more detail the samples which exhibit an amorphous structure to those with a monocrystalline structure.

Figure 5 shows SEM pictures from cross sections taken from samples with monocrystalline (Fig. 5a) and amorphous (Fig. 5b) structures of the current line oriented layer. The most evident difference between Fig. 5a and b is that in Fig. 5a the nucleation layer is more pronounced whereas in Fig. 5b the nucleation layer is practically absent. The nucleation layer thus seems to act as the template that produces a kind of epitaxial CLO layer, and this can be understood if the peculiar crystallography of the CO layer is considered.

The CO pores have a very high tendency to branch into the available  $\langle 111B \rangle$  directions, including branches growing upward [3]. This suggests that from *one* nucleation point at the surface of the sample via the branching process a set of new pore tips is generated into the substrate, in particular for {100} oriented substrates. The set of all pore tips from one root ancestor (starting point) will form a domain of nuclei for CLO pores which are to some degree aligned along  $\langle 011 \rangle$  directions as shown in Fig. 6a. Consequently, the CLO pores, which start from (some of) the tips of the CO pores, will tend to align along this  $\langle 011 \rangle$  direction. Thus all domains of CLO pores, resulting from just *one* originally nucleated CO pore, will tend to have the same global alignment. Thick nucleation layers allow for many branching events, the domains thus will be larger and the alignment tendency stronger. Figure 6b presents the same mechanism for (111) oriented samples. In this case the alignment is much weaker.

Why is long range order lost at voltages deviating from some optimum in either direction? The answer is rather simple, because two opposing factors are responsible for the long range order: local order for general close packing, and a sufficiently developed nucleation layer for global orientation of close packed domains. If one factor is too weak, no long range order will result. Now, if the anodization voltage is lower than the optimum one, the space charge region of the pores is also smaller, i.e. the interac-



**Fig. 5** (100) oriented n-InP,  $n = 10^{18}$  cm<sup>-3</sup>, 5% HCl solutions. a) At U = 6 V the nucleation layer is prominent. b) at U = 9 V no significant CO layer is present.



**Fig. 6** (online colour at: www.interscience.wiley.com) Branching within the nucleation layers of CO pores produces pore tip domains with  $\langle 110 \rangle$  preference. Secondary branches grow upward. (a) (100) oriented n-InP. (b) (111) oriented n-InP.

tion between pores decreases and the local closed packed order disappears. This insufficient interaction between pores is also expressed by their tendency to assume triangular shapes at lower voltages. On the other hand, at higher voltages (than the optimum) the thickness of the nucleation layer decreases, i.e. the domain size decreases, and as a result the tendency to global order decreases.

That this interpretation is essentially correct is also demonstrated by the fact that pore crystals with less pronounced CO nucleation layers, obtained e.g. by using organic electrolytes or {111} oriented samples, are always less perfect than their counterparts with thick nucleation layers.

The possibility to obtain long range ordered 2D porous structures without pre-structuring by means of lithography [10], seems to be a very promising feature for photonic crystal applications. More than that, by changing the doping level of the InP sample, it is possible to vary the pore diameter and pore distance significantly as already shown in Fig. 1. Changing the doping from  $n = 3 \times 10^{17}$  cm<sup>-3</sup> to  $n = 10^{18}$  cm<sup>-3</sup> increases the diameter of the pores (and thus the lattice constant) nearly four times.

**4 Conclusion** Single crystals of pores have been obtained by means of self organization processes in n-InP and that is the first instance of a single crystal obtained in this way. Perfect order was obtained within domains of a few micrometers. The global orientation of these domains is determined by multiply branched crystallographically oriented pores in the nucleation layer, which induces long range order, while the close packing on a local scale is the result of direct pore–pore interaction via the space charge region. The degree of ordering can be controlled by controlling the width of the nucleation layer, by changing the electrolyte concentration, and by the anodization voltage/current. Combining CO and CLO pores and self organization, the first three dimensional pore crystal has been obtained.

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