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Growth Mode Transition of Crysto and Curro Pores in III-V Semiconductors

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The formation of crystallographically oriented and current line oriented pores in n-type InP is reviewed and compared to other semiconductors in the light of some new results. A model for the formation of crystallographically oriented pores is presented that reproduced salient features of this pore type rather well. Impedance data together with their model-based evaluation are given and discussed. Some self-organization features of current line oriented pores and their possible relation to self-induced or externally triggered growth mode transitions between the two pore types conclude the paper.

Introduction

The growth mode transition between crystallographically oriented (crysto) pores to current-line oriented (curro) pores in III-V semiconductors (InP, GaP, GaAs) remains one of the most interesting phenomena in the field of electrochemically etched porous semiconductors. Even though a considerable amount of work has been performed (1 - 3), a consistent theory for the growth mode transition does not yet exist. In this work some new findings with respect to this topic in InP will be presented and discussed with regard to older results and other semiconductors.

The two pore types mentioned above may not be the only pore types in InP (or other III-V semiconductors); at least some mixtures or intermediate structures ("currystos") between crysto and curro pores exist, if not truly other types, for example if liquid ammonia is used as electrolyte (4). However, crysto and curro pores are the dominating species at least in InP, and they are found in a surprisingly large range of electrolytes including acidic electrolytes like diluted HCl (1, 5 - 8), almost pH-neutral "salt-water" (9), alkaline electrolytes like KOH (10, 11) and liquid ammonia (4). While GaAs so far produced only crysto pores, both kinds are known from GaP (1, 12), which also supports a new kind of pores with rectangular cross-section as shown by the Erlangen group (13) that seems to combine features of both crysto and curro pores. The few pore etching experiments with regard to II-VI semiconductors (9) also show typical curro pores in CdSe and ZnSe, plus yet another new pore type (three-dimensional fractal pores in ZnSe (14)).

The extensive literature to macropores in Si (for reviews see (1, 15 - 25) is almost completely centered on pores that would be termed crysto pores in this context. However, true curro pores as well as mixes have been reported, too (24): moreover, in (24) a claim was made that at least some macropores in p-type Si are actually current line pores and not crystallographically oriented pores as implicitly assumed.

While in some of the cases mentioned above only one pore type was observed, the crysto – curro issue also includes the transition between those two basic pore types either self-induced or externally triggered. Pore growth mode transitions also might be seen in a more general context (with crysto-curro transitions being a special case), in particular in

the light of recent findings in Si (24, 26, 27); in (27) a first attempt was made to look at this phenomenon in a systematic way.

The crysto – curro issue is thus a quite general feature of pore etching in semiconductors, and a complete understanding of the underlying mechanisms would be an important step in the ongoing attempt to understand pore etching in semiconductors. While this goal has not yet been reached, some progress in the general direction will be reported in what follows. In particular, experiments dedicated to increase the size of curro pores in InP, in-situ-FFT impedance spectroscopy, and first results from an attempt to simulate crysto pore growth will be given.

Crystallographic Pores

The distinctive features of crystallographic pores are:

- Their growth direction is strictly a crystallographic direction. In III-V semiconductors and, as far as is known, in II-VI semiconductors, so far always <111>B has been found as growth direction (with the exception of the rectangular pores in GaP that are growing in <110> directions (13)). In Si, the major growth directions of crysto pores are <100> and <113> (28, 29), for Ge <100> and <111> have been found (23).
- Pore walls consist of "stopping planes", i.e. planes that are not or only slowly dissolved and the pore thus consists of a facetted tube. On a closer look, crysto pores are actually a sequence of either tetrahedrons for <111> pore directions, i.e. for the bulk of the III-V's (30), or octahedrons for <100> directions, i.e. for Si (31) that are connected like pearls on a string. The sidewalls then consist of {111} planes. The tetrahedrons / octahedrons may show considerable overlap (32, 33) (cf. Fig. 1a) and at lower magnification the pore may actually appear to have smooth walls (with, e.g., {112} pore walls (32) for <111>B pores).
- The formation mechanism of crysto pores relies on two ingredients: i) local production of the holes needed for dissolution at the pore tips by some junction breakdown mechanism (avalanche or tunneling), and ii) strong passivation of the pore walls allowing the formation of a space charge region (SCR) around the pore. The second ingredient may well be the more important one for pore formation as will become clear from the simulation model described below.
- The crysto pore size in InP in the sense of its (average) diameter is rather constant (within a factor of 2 3) and not, as one could expect, tied to the critical field strength needed for junction breakdown. It increases somewhat with pore depth or time, due to leakage currents causing lateral growth (32) and seems to be smaller in alkaline electrolytes (11). For pure crysto pores it is essentially a function of the size of the tetrahedrons formed and thus given by the passivation kinetics of the pore wall or rather tetrahedron walls (cf. (30, 31)), which appears to be rather insensitive to the electrolyte composition. The doping level has some influence, because it controls the size of the SCR. However, no systematic study with respect to crysto pore size has been done so far.



Figure 1: a) TEM picture of a sequence of overlapping tetrahedra in InP (cf. (32)). b) Crysto pore formed by a string of tetrahedra in GaAs. Nucleation layer in InP followed by a thin layer of crysto pores (not visible) and curro pores showing domains in the nucleation layer. For details see text. d) TEM picture of nucleation layer for crysto pores at high magnification (cf. (32)).

- Crysto pores branch in all 4 <111>B directions until the current density at pore tips is small enough. This leads to pore growth not only into the depth of the sample but also towards the surface.
- The nucleation of crysto pores may not be uniform and it might require some nucleation layer that is not well characterized at present, cf. **Fig. 1c, d** and (34). In the case of GaAs, nucleation of crysto pores is preceded by some lateral etching producing grooves on the surface as described in (1).
- So far it was not possible to induce nucleation by some lithographically provided mask (see below).
- There is little self-organization among crysto pores.

Recently an attempt has been made to model some of the pertinent features of crysto pores; details are given in (35, 36). A three-dimensional Monte Carlo model as illustrated in **Fig. 2** with about 1 billion voxels reproduced the experimental findings for a reasonable set of assumptions and parameters, including the pore density oscillations; for details cf. (35, 36) and forthcoming publications. Three assumptions have been made. i)

The valence of the dissolution process is constant, ii) The branching probability of a pore is proportional to the current density j_{tip} at the pore tip (with different probabilities for branching at pore tips and from pore walls). iii) Pore growth stops if the pore tip approaches a pore wall of another pore.



Figure 2: Simulation array of the Monte-Carlo-Simulation model. On top, the nucleation points for pores can be observed, which lead to downward growing pores (left hand side) and subsequently to upward growing pores (right hand side). A three-dimensional crysto pore structure evolves.

The model needs a nucleation scenario as input, but otherwise reproduces many features of crysto pores with good accuracy; for example the weak oscillation pore density with depth as found in (32, 35). **Fig. 3** compares two experimental results with simulations. In **Fig. 3a** examples of the crysto pore structure in (100) n-type InP obtained for relatively low current densities of 0.4 mA/cm² and a 5 wt. % HCl electrolyte (1.4 M), branching probability ratio: $k_{tips} / k_{walls} = 100$ is shown in cross-section. Downwardly branching pores show up with their triangular cross-section as shown in the inset. While experiment and simulation agree rather well, the simulation of a typical growth domain as found in GaAs (1) (and in InP) in **Fig. 3c,d** is even more striking. In this case the current density of 80 mA/cm² is rather high, the ratio of the branching probabilities was adjusted to $k_{tips} / k_{walls} = 1$.

Note that the model is essentially of the "current burst" (CB) type (37). In other words, current flow is not uniform in time but occurs in "bursts" that are governed by some probability function. The CB model implemented in this case is simpler than the full-fledged CB model employed to model oscillatory phenomena at the Si electrode (38) but maintains the essential stochastic component.



Figure 3: Comparison of observed (a) and simulated (b) crysto pore structures from a uniform (random) nuclei distribution. b) From just one nucleation point pore domains result as shown in c) for GaAs, with the simulated structure in d).

Nucleation of crysto pores in general is not well understood. While rather uniform and easy nucleation is often found in Si and InP, the opposite is true for Ge and GaP, with GaAs being a kind of intermediate case. The two examples shown in **Fig. 1c,d** for InP serve only to show that the surface layer shows nucleation structures with a texture that changes at some kind of domain boundaries, and that fully developed crysto pores might be preceded by a thin nucleation layer of heavily branched pores with no clear expression of <111> directions. On occasion (in particular at high current densities), this nucleation layer may switch to curro pores without forming "proper" crysto pores first; an example is given in **Fig. 4a**. The doping of the sample also appears to influence nucleation, While the mostly used more heavily doped InP samples show rather uniform pore structures, this is not true for lightly doped samples, **Fig. 4** gives an example. Initiating etching

proved to be difficult in this case; the (curro pore) obtained in this case is reminiscent of structures in Si (39).



c)

Figure 4: a) Curro pore formation without well-developed crysto pores at high current densities. b), c) Pore structure in lightly doped n-type InP $(2 \cdot 10^{15} \text{ cm}^{-3})$. c) shows an overview, b) some detail of c) at a depth around 150 µm.

Given the points made above, it cannot be expected that the initial nucleation of crysto pores would follow some lithographically defined structure. One experiment undertaken in this vein (unfortunately) proved this assumption to be correct, **Fig. 5** shows some results. The idea was to see if - against expectations - one could nucleate curro pores with the desired spacing directly without the (crysto) nucleation layer. As it turned out, this was not possible. A number of crysto pores or their predecessors nucleated at each opening in the mask (usually at the edge as can be seen from **Fig. 5a**, and while

curro pores formed after about 2 μ m, the original structure was completely lost. This underscores once more that curro pores need some diffusion limitation that is provided by first forming crysto pores.



Figure 5: a) Nucleation of (crysto) pores at the openings of the mask; typically at the edge. b) Pore structure obtained with the mask.

Considering that crysto pore growth starts with some as yet unspecified nucleation phase and then proceeds by continued branching until the current density at the pore tip is below some limit, it is clear that crysto pore growth only achieves some "steady state" for low current densities and after some time. If a steady state cannot be achieved, a transition to curro pore occurs. In-situ FFT IS data, always averaging over many pores, must thus be expected to show some complex time behavior as long as steady state is not established.



Figure 6: Equivalent circuit diagram used for fitting impedance data. The three $RC = \tau$ components are particular important for the three growth modes as indicated. R_S is the series resistance of the system.

The equivalent circuit in **Fig. 6** described by **Eq. 1** gives a rather perfect fit to typically more than 10000 IS spectra obtained in a crysto pore etching experiment.

$$Z(\omega) = R_{s} + \frac{1}{\frac{1}{R_{1}} + i\omega C_{1} + \left(R_{2} + \frac{1}{i\omega C_{2}}\right)^{-1}} + \frac{R_{3}}{1 + i\omega R_{3}C_{3}} \qquad [1]$$



Figure 7: Time dependence of the three important resistances from the equivalent circuit shown in Fig. 6. Together with the other 8 curves not shown here, the 4 time regimes emerge as indicated.

In total, 7 parameters can be extracted (4 resistances and 3 capacities) as a function of time, and thus also the three time constant $\tau_i = R_iC_i$. Together with the time dependence of the potential U(t) for a galvanostatic experiment, a first picture for what happens during pore growth emerges. Fig. 7 shows just three out of the 11 curves obtained, which allow to make a distinction between four crysto growth modes (indicated by the times when they occur in Fig. 7): Nucleation (t_1) , branching mainly at pore tips (t_2) , branching mainly from pore walls (t_3) and steady state with little branching (t_4) .

This interpretation agrees well with the independent results obtained form the Monte Carlo model. The next step in modeling crysto pore formation would be to identify the physico-chemical processes behind the components of the equivalent circuit, but presenting and discussing the present speculative efforts in this vein would go beyond the scope of this paper. It is clear that R_2 is only important at the beginning of the experiment and thus most likely associated to the nucleation process. R_1 decreases as branching slows down whereas R_3 increases and then stays roughly constant, indicating steady state.

Current Line Pores

The distinctive features of current line pores are:

- Growth direction is in the direction of current flow or at right angles to the equipotential planes. Under uniform etching conditions away from the sample boundaries, the current flow is perpendicular to the surface and curro pores then appear to grow in the crystallographic direction perpendicular to the surface (usually a low-indexed direction). A distinction between the two types might then be impossible without further data.
- If current flow is very inhomogeneous for whatever reason (e.g. because nucleation occurs only at some widely spaced points), very irregular structures might be obtained that are nevertheless still curro pores. Fig. 8 gives some examples.
- The decisive intrinsic length scale is foremost the space charge region width d_{SCR} , which gives directly the distance between curro pores or the pore wall thickness. The curro pore diameter often also is in the order of d_{SCR} but may be considerably larger, too. It is sensitive to many parameters including the flow rate of the electrolyte (see below).
- The formation of curro pores relies on only one ingredient: Chemical passivation of the pore walls breaks down (or becomes sufficiently weak) because of diffusion limitation by the nucleation layer (= crysto pores). Pore growth essentially proceeds by direct dissolution but without the strongly crystallographically dependent passivation of pore walls. Pore walls are mainly stabilized by the overlapping of the space charge regions of neighboring pores typically ordered in a hexagonally closed packed arrangement.
- At least for some length of time pore growth proceeds in or close to steady-state conditions, and this is reflected by the impedance data.
- Curro pores cannot nucleate directly and always need some precursors, usually crysto pores that provide for diffusion limitation of the passivating species.
- There are many self-organized structures resulting from the interaction between curro pores via the SCR between the pores.



a)

b)

Figure 8: a) "Hedgehog" structure of curro pores obtained for point-like nucleation with pores growing in all directions. b) Waveguide structure (cf. (40)) obtained for linear nucleation; overview left; detail (showing initial crysto pores) on the right.

The fact that the remaining semiconductor between curro pores is an insulator allows to predict that III-V or II-VI membranes with curro pores will be good piezoelectric materials in contrast to bulk samples where the piezo voltage is short-circuited by the low resistance of the semiconductor (41).

SCR "filled" pore walls provide for a strong coupling between neighboring pores and this is the reason for the many self-organization effects observed with curro pores. Besides the formation of single curro-pore crystals and synchronized pore diameter oscillations described before in some detail (42, 43), a new effect that will be called "pore bundle oscillations" has been reported more recently (24). Fig. 9 shows this effect on an unusually large scale. Obviously, the current density in a pore bundle oscillates in anti-phase to its neighbors, causing "antiphase" oscillations of the pore bundle diameter.

A similar effect has been observed recently in Si for single macropores and termed anti-phase oscillations in view of the fact that the diameters of single pores oscillate in "antiphase" as shown in **Fig. 9c**. Note that from a top view, the structure of the Si pores is "frustrated" (for details see (24)), since this kind of oscillations cannot be obtained in a hexagonal close-packed symmetry. This is also true for the pore bundles here, which have a one-dimensional symmetry (i.e. they look the same on any plane parallel to the one shown but different at right angles).



Figure 9: a) Overview of pore bundle oscillations with a wavelength of about 70 μ m. b) Detail of a). c) Antiphase oscillations of macropores in Si (cf. (26)).

In attempting to understand this phenomenon it is important to realize that curro pores can neither cross each other nor branch, and this necessitates that they are always coupled: what one pore does for whatever reason determines what its neighbors must do and vice verse. For example, one curro pore cannot change its direction; this can only be done in a collective. This "explains" to some extent why a pore bundle oscillation, if started somehow, must continue for some time or depth. The puzzle is the wavelength of the oscillations shown in **Fig. 9**, since it does not scale with any of the known intrinsic length scales of the electrochemical system like d_{SCR} , critical radius of curvature etc. (cf. (1)). The experiments suggest that it is tied to inhomogeneities of the primary nucleation, possibly to the domains mentioned above, and that the pumping of the electrolyte is a decisive ingredient in this case.

The geometry of curro pores is directly tied to the width of the space charge region d_{SCR} as pointed out before, as far as the pore wall thickness is concerned, and to several parameters, as far as the pore diameter is concerned. For the relatively high-doped samples, used in most studies, pore diameters in the (50 – 200) nm region resulted. For

some possible applications larger diameters are desired and an attempt was made to produce large diameter curro pores by using low-doped InP. This proved to be surprisingly difficult, however: **Fig. 4** gives an example. Excessively high voltages (> 100 V) were needed to induce current flow, nucleation was always very inhomogeneous, and often no clear pore structures could be obtained. Therefore attempts were made to increase just the diameter, while keeping the thin pore walls unavoidable in medium to high-doped samples. This approach worked to some extent, **Fig. 10** shows results.



Figure 10: a) Curro pores in InP with large diameters. a) Cross section; b), c) top view of two different samples (after removal of the nucleation layer).

The curro pore diameter proved to be a function of many parameters, in particular the inducement of uniform nucleation by, e.g., a series of voltage steps at the beginning of a (potentiostatic) experiment. The following empirical relation for the pore diameter d_{Pore} has been found for an n-InP {100}, specimen with $N_{\text{Doping}} = 5.4 \cdot 10^{17} \text{ cm}^{-3}$, processed in a 2 wt % HCL electrolyte + a variable small amount of H₂SO₄ at 20 °C.

$$d_{\text{Pore}} \propto (j \cdot c_{\text{Ox}} \cdot PS)/c_{El}$$
 [2]

with j= current density (around (60 - 80) mA/cm², c_{Ox} = concentration of the oxidizing species (H₂SO₄), *PS* = pump speed (settings at the electrolyte pump), and c_{El} concentration of the dissolving species (HCl). While this result, in particular the dependence on c_{Ox} , is in accordance with predictions from the current burst theory in particular as far as the oxidizing part is concerned (cf. (22)), it should be emphasized that the dissolution chemistry is at present not very well established. The dissolution valence, for example, has only been addressed quite recently by the Versailles group.

Impedance data obtained during curro pore growth provide a rather clear picture of what is going on; for details see (44). All data can be fitted very well by **Eq. 3**, that describes besides a general series resistance R_S the series connection of two simple *RC* circuits with a third *R* in parallel to a Warburg impedance (44).

$$Z(\omega) = R_s + \frac{R_1}{1 + i\omega\tau_1} - \frac{R_2}{1 + (1 + i)\sqrt{\omega\tau_2}} + \frac{R_3}{1 + i\omega\tau_3}$$
[3]

The last (R_3) component is related to the unavoidable nucleation via crysto pore formation necessary for curro pores and thus not important in this context. The Warburg impedance describes diffusion through the length of the pore, and the R_1 term describes



the reaction at the interface. Fig. 11a shows this relation between equivalent circuit components and physico-chemical processes schematically.

Figure 11: a) Processes in curro pore etching and their schematic relation to the components of the equivalent circuit. b) The product of the etching current and R_1 shows a nearly constant voltage in steady-state etching. Three out of 7 curves from the impedance data showing the development of R_2 , the associated time constant τ_2 and the Warburg parameter σ .

 R_2 can be fitted very well by

$$R_2 = 29.0\Omega \left(\frac{t}{\min}\right)^{0.4},$$
[4]

which corresponds in its functionality directly to the experimentally determined pore tip growth speed given in Eq. 5 via $v_{\text{tip}} \propto 1/R_2$.

$$v_{\rm tips} = 21.4 \,\frac{\mu m}{\rm min} \left(\frac{t}{\rm min}\right)^{-0.40}$$
[5]

The foregoing consideration just serves in a spurious way to demonstrate that it is possible to move from equivalent circuit diagrams to the physico-chemical processes of interest; for details and more results the reader is referred to (44).

Intermediate Pores

It is easy to imagine some pore morphologies intermediate between crysto and curro. In Si, for example, pores that follow the current flow may consist of small tripods with "legs" extending in the crystallographic <113> direction as shown in **Fig 12a**, that stop growing at an early stage (because encountering a neighboring pore) and instead nucleate a new tripod somewhat deeper. **Fig. 12b** shows InP pores that are neither here nor there; the Versailles group has also found such "meandering" pores.

The examples given in the context of the pore nucleation (e.g. **Figs. 4a and 5b**) also show pores not quite crysto or curro. The same is true for pores found in some transition region between crysto and curro. We may conclude once more that many features of pores in semiconductors are still awaiting discovery, not to mention explanation (45).



Crysto-Curro Transitions

As a general rule, a transition form crysto to curro pores occurs if the current density at the tips of the crysto pores is larger than some steady state value of the system. If left to themselves, the pores react by branching; this goes on until the current density is low enough, followed by some kind of steady-state crysto pore growth with little branching. If that is not possible because the pore density becomes too large for further branching (i.e. the pore distance is in the order of d_{SCR}), a transition to curro pores occurs. If and when such a self-induced transition occurs thus depends on many parameters, the most important one being the current density, the initial nucleation density and uniformity, and the passivation difference between tips and pore walls (expressed in the Monte Carlo model by different nucleation probabilities for a current burst at the tip or on the side wall (then initiating branching)).

It is of interest in this context that similar transitions have recently been observed in Si (27), showing that the crysto – curro issue including the growth mode transitions transcends specific semiconductor (electro)chemistry but describes phenomena on a meta level that is common to many semiconductor pore etching situations.

A sudden increase in the current density during crysto pore growth then will trigger a sharp transition from crysto to curro (and back for a sharp current decrease). This is partially due to the fact that all pores are then induced to do "the same thing at the same time", which is possible with little geometric constraints. On contrast, if the current is gradually increased, some regions may undergo the transition ahead of others, which leads to a non-uniformity that may amplify because "latecomers" find their intended path blocked by others. **Figs. 9a** and **13b** show this indirectly to some extent: pores growing with lateral components sooner or later encounter other pores and are then forced to grow downwards. Alternatively, the system may find ways to spread non-uniformities in space and time by inducing pore bundle oscillations. **Fig. 13** shows a striking example.



Figure 13: a) About 30 externally induced crysto-curro transitions with a self-induced pore bundle oscillation in the center layers. b), c) Details of the structure. In c) it can be seen that the interface crysto-curro is rather flat; it is only the interface curro-crysto that is wavy.

Conclusion

While InP exhibits the crysto – curro topic most prominently, it is a general feature of pore etching in semiconductors and tied to the degree of wall passivation and the kinetics of passivation. In other semiconductors some parts may be lacking at present (e.g. curro pores in GaAs), but many features or subsets of the topic have been found (and, to make a prediction, will be found). In-situ FFT impedance spectroscopy proved to be very useful for developing models and theories necessary for the understanding of this topic. A Monte Carlo model for crysto pore growth based on general current burst essentials is capable of reproducing many experimentally observed features of crysto pores and thus

provides a first step for the understanding of the complete issue, in particular the growth mode transitions.

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