

# Morphology of porous *n*-GaP anodically formed in different mineral acids

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**Abstract** *n*-type GaP(100) was anodized in H<sub>2</sub>SO<sub>4</sub>, HF, HCl, HBr, HI, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> in order to obtain porous structures. Remarkable differences in the morphology were found when anodisation was carried out under comparable electrochemical conditions. Etching in HF led to a statistically porous structure, but no evidence for higher ordering was obtained. Etching in HCl solutions caused a localized attack of the surface leading to porous insular areas. In HBr highly defined rectangular pores grow perpendicular to the (100)-surface forming several  $\mu\text{m}$  thick well defined porous layers. In HI pores are aligned parallel to equipotential lines along defects. Pore formation in H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub> can lead to highly complex ordered structures. Clearly the work shows that the formation of porous *n*-GaP is strongly dependent on the anion present in the electrolyte.

**Keywords** Gallium phosphide · Electrochemical etching · Porous semiconductors · Pore morphology

## Introduction

Etching tunnels in GaP were reported in the early 1970s when Chase and Holt tried to thin GaP for TEM investigations [1]. Since then, aside from silicon, several compound semiconductors were successfully porosified by a localized electrochemical dissolution process. The most prevalent ones in literature are *n*-GaAs [2] and *n*-InP [3]. As recently as in 1996 porous GaP was rediscovered by Ern  et al. [4, 5] who published detailed work of the pore formation and pore propagation during anodization of *n*-type GaP electrodes in 0.5 M

H<sub>2</sub>SO<sub>4</sub>. Up to now, only scarce knowledge can be found in literature about other suitable electrochemical etchants for GaP which lead to a porous structure. Merely KOH, chlorine gas in methanol or HF in ethanol is mentioned as further etchants for obtaining porous GaP [1, 5, 6–11]. Pure chemical etchants generally consist of oxidizing species in acidic or alkaline solution to remove the amphoteric gallium oxide layer which is formed during anodization of GaP. Other electrochemical etchants are mainly used for polishing (for solution compositions see Ref. [10] and references therein).

Most common pore growth models on semiconductors [12–14] discuss the effect of the semiconductor parameters such as doping, type, width of space charge layer and electrical treatment, voltage or current density on pore morphology. The effect of the electrolyte nature is mostly neglected. Particularly, models developed on III-V materials [14] that essentially distinguish between two forms of electrochemical etching that is crystallographic etching and current line oriented etching do not consider the species present in the electrolyte.

As the vast majority of investigations of porous GaP was carried out in H<sub>2</sub>SO<sub>4</sub> electrolytes we aim in the present work at an extension of this knowledge by an evaluation of the behavior of GaP in mineral acids and other common etchants. In the present paper we screen several acids (HF, HCl, HBr, HI, H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub>) for their influence on the pore growth morphology.

## Experimental

For our experiments we used 500  $\mu\text{m}$  thick *n*-type gallium phosphide wafers, provided from MTI crystal Corp. The wafers have a (100) surface orientation and a sulphur donor concentration of  $2\text{--}8 \times 10^{17} \text{ cm}^{-3}$ . The wafers were cut into

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$6 \times 6 \text{ mm}^2$  pieces. Prior to each experiment the samples were degreased by successively sonicating in acetone, isopropanol and methanol and rinsed with pure water. Back contact to the GaP samples was established by smearing In/Ga-eutectic on the backside. By means of a copper plate the samples were pressed against the *O*-ring of an electrochemical cell leaving a circular area of  $0.13 \text{ cm}^2$  exposed to the electrolyte. All experiments were carried out with the *n*-GaP working electrode in a three-electrode setup with a platinum gauze as counter electrode and a silver-silver chloride electrode as a reference electrode. Therefore all potentials are given in reference to silver-silver chloride. All etching experiments were performed under ambient conditions in different electrolytes in the dark of a steel box which also acts as a Faraday cage. The electrodes were connected to a Jaisle IMP88PC-200V potentiostat which was driven by a Prodis 1/16I and controlled by a computer with home-written software. Scanning electron micrographs were obtained using a Hitachi S4800 microscope.

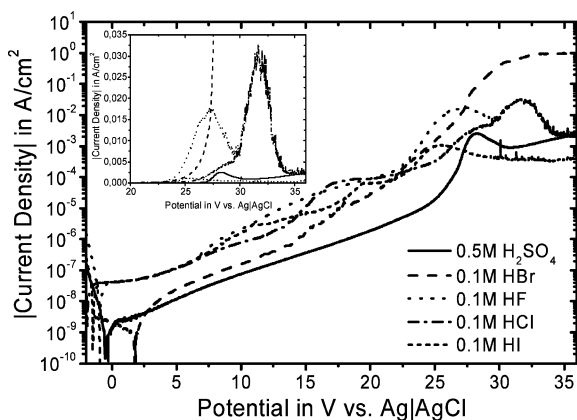
## Results and discussion

To obtain preliminary information of the effect of a specific electrolyte on the electrochemical behaviour of *n*-type GaP polarization curves were acquired (Fig. 1). We included  $\text{H}_2\text{SO}_4$  in our experiments to obtain a reference to this well investigated case [4, 5, 7, 15–19]. Consistent with earlier work in  $\text{H}_2\text{SO}_4$  [15] an active-passive transition at about 28 V is observed during anodization. From Fig. 1 it is clear that an essentially similar polarization behaviour is observed also in most of the halide containing electrolytes. At low anodic potentials a *n*-type GaP electrode behaves in the dark like a reverse biased diode. Therefore a relatively low current density can be observed in the polarisation curve for low anodic

potentials. There is a slight current increase which may be ascribed to leakage or the fact that an applied electric field lowers the work function which results in a higher current flow. In  $\text{H}_2\text{SO}_4$  this blocking-state region covers a range from the open circuit potential up to a distinct potential where significant current increase sets in (at about 24 V). The sudden increase in current density can be ascribed to breakdown effects of the depletion layer such as avalanche breakdown or interband tunnelling (Zener tunneling). In the  $\text{H}_2\text{SO}_4$  electrolyte the current density drops again to lower values at the passivation potential ( $U_{\text{pass}}$ ) of about 28 V. Previously, this effect has been ascribed to gallium oxide formation on the surface [15]. However, the amphoteric oxide layer is not entirely stable in the  $\text{H}_2\text{SO}_4$  electrolyte but undergoes a slow chemical dissolution [15]. A porous GaP structure can be observed for anodization in the potential range between the breakdown potential and the repassivation potential. First pores are found once the breakdown potential is passed, therefore this potential value often was termed PFP (Pore Formation Potential) [2].

For the polarization curves of GaP in HF, HCl and HI electrolytes the polarization curves exhibit essentially the same features as the polarization curve in  $\text{H}_2\text{SO}_4$  electrolyte. At lower anodic potentials but still within the blocking regime the current density increases only slowly. It is also obvious from the polarisation curves that the current densities in  $\text{H}_2\text{SO}_4$  electrolytes within the blocking regime are reproducibly lower by about one or two orders of magnitude compared to halide ion containing electrolytes. This may lead to two different effects: either the dissolution of GaP is faster in these electrolytes or it is a current contribution due to the oxidation of halide ions to molecular halogens at the semiconductor-electrolyte interface. The latter was obviously the case for HBr and even stronger and at a lower potentials for HI because of a visible colouring of the electrolyte. After polarisation in HCl sometimes chlorine gas could be smelt. These findings lead to the conclusion that the measured current density in the blocking regime has a contribution from electrochemical oxidation of electrolyte species. Once chlorine, bromine or iodine molecules are formed one has to take into account the possibility of chemical etching of the surface [5, 17, 20].

A marked current increase can be observed once the PFP is passed in a potentiodynamic scan. Therefore we assume that accelerated dissolution occurs in these electrolytes. In all halide ion containing solutions except for HBr an active-passive-transition ( $U_{\text{pass}}$ ) could be observed. This indicates that the behaviour in  $\text{H}_2\text{SO}_4$ , HF, HCl and HI is somehow comparable. In contrast to this behaviour, no passivation of the GaP surface could be observed in HBr. At higher anodic potentials ( $>30 \text{ V}$ ) the current density levels off and remains quite constant at a high level of about  $1 \text{ A/cm}^2$ —possibly the current becomes transport limited. Characteristic potentials



**Fig. 1** Polarisation curves of *n*-GaP (100) in 0.5 M  $\text{H}_2\text{SO}_4$ , 0.1 M HF, 0.1 M HCl, 0.1 M HBr and 0.1 M HI. The scan rate is in all cases 20 mV/s in the anodic direction. The inset shows a linear plot of the polarization curves to visualize the active-passive transitions for all acids except for HBr

**Table 1** Passivation potentials and critical current densities for the different electrolytes

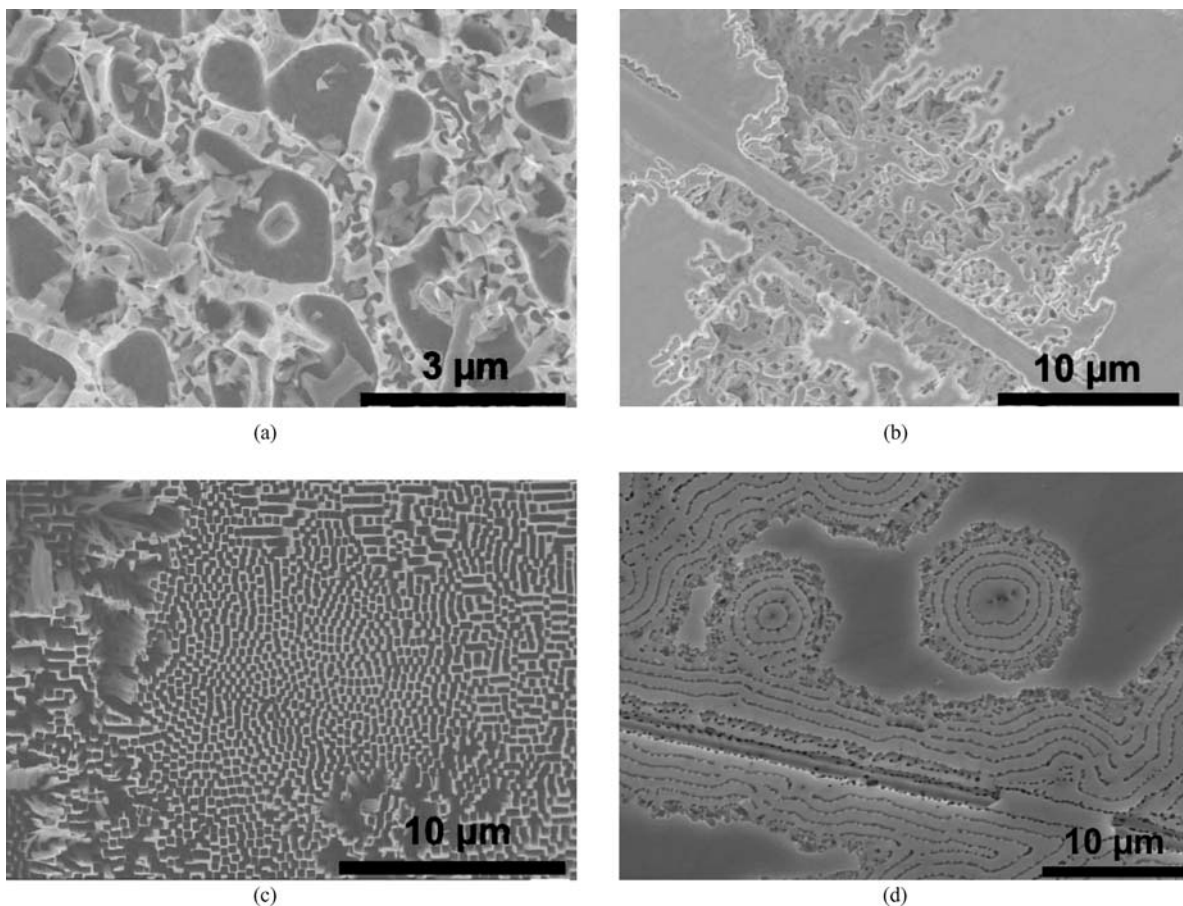
	PFP in V	$U_{\text{pass}}$ in V	$i_{\text{crit}}$ in A/cm <sup>2</sup>
H <sub>2</sub> SO <sub>4</sub>	24	28	0.0025
HF	22	27.5	0.017
HCl	25	32	0.033
HBr	20	–	–
HI	23	26	0.011

(PFP,  $U_{\text{pass}}$ ) as well as the critical current densities for the active-passive-transition which is a measure for the ease of passivation are summarized in Table 1. From these findings it is obvious that the interaction of bromide ions with the GaP-surface is different compared to other halide or sulfate ion containing etchants.

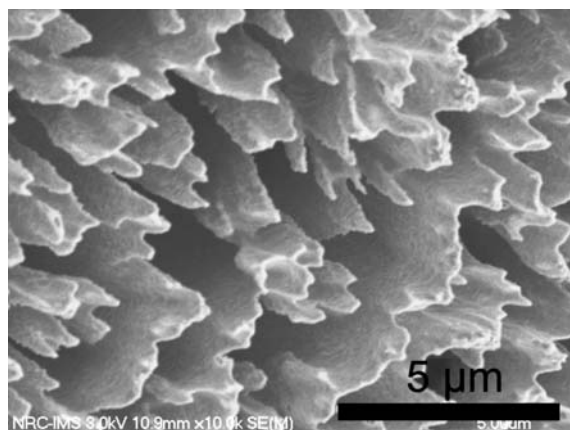
However, during etching of *n*-type GaP in all of the above listed etchants pore formation was observed. Various possibilities can be considered. Clearly an effect in HBr is that repassivation is suppressed in other words the formation of an oxide layer is hampered. This can, for example, be due

to a rapid dissolution of any oxide that should electrochemically be formed on the electrolyte surface. Another possibility is a specific reaction (adsorption) of Br<sup>−</sup> or Br<sub>2</sub>—the latter being produced in the electrolyte—with GaP. So far CV and XPS-measurements gave some indication for this idea but revealed no unambiguous proof. Furthermore bromide or bromine species can inhibit the formation of a passivating oxide layer by reaction with that. SEM investigations of the samples after polarization scans from −2 V up to the passive region with an end potential of 36 V revealed the pore morphologies for the different etchants as shown in Figs. 2(a)–(d). For comparison Fig. 3 shows current line oriented pores obtained in 0.5 M H<sub>2</sub>SO<sub>4</sub> under comparable conditions. Below the individual pore morphologies will be discussed in more detail:

Anodic etching of *n*-GaP in hydrofluoric acid was already reported previously in literature but never with any morphological images of the resulting porous structure [8, 9, 11]. From Fig. 2(a) it is apparent that after anodisation the GaP surface had an irregular appearance with pores and etch scars of various sizes and directions. There is no distinct pore morphology which could be attributed to either



**Fig. 2** Pore morphologies obtained with different halide acids after anodization from −2 V to 36 V, scan rate 20 mV/s in (a) 0.1 M HF, (b) 0.1 M HCl, (c) 0.1 M Br and (d) 0.1 M HI



**Fig. 3** Current line oriented pores obtained by anodization of *n*-GaP in 0.5 M H<sub>2</sub>SO<sub>4</sub> from  $-2$  V to 36 V, scan rate 20 mV/s

crystallographically oriented type or the current line oriented type. According to the high applied potentials and the comparatively high current densities one would rather expect current line oriented pores. Nevertheless there are some indications that a porous domain was formed previously and only the domain walls are left after finishing the polarisation scan. But surprisingly new attacked sites can be observed within those domain boundaries. Investigations of the pore initiation revealed that the pores nucleate homogeneously distributed over the surface. During nucleation not one single primary pore starts at the surface with subsequent branching of secondary pores underneath the surface as reported earlier for GaP [4, 5] but several random-like oriented interlinked primary pores form a nucleation island. From these nucleation islands branching takes place after initiation.

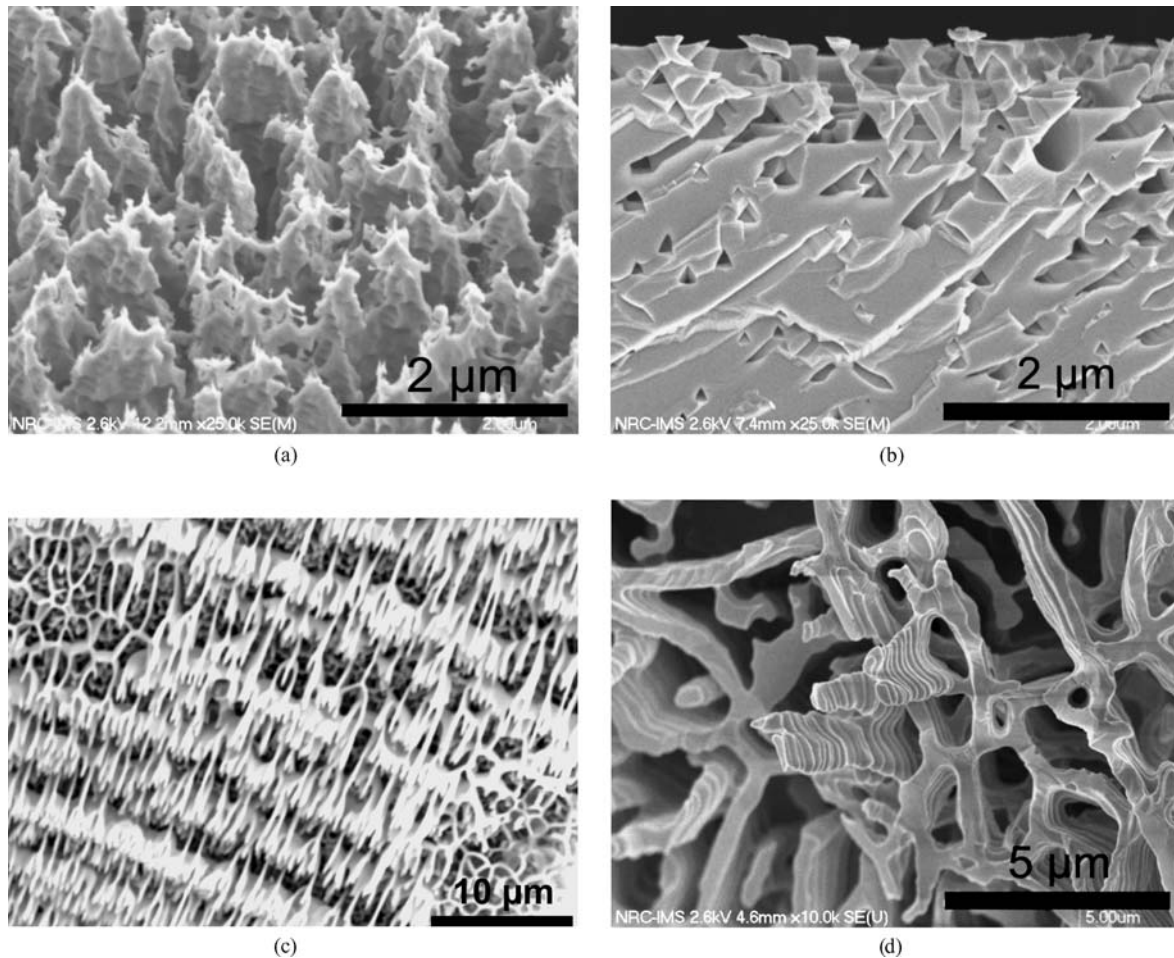
Anodisation of *n*-type GaP in 0.1 M HCl leads to an insular porous structure with crystallographically oriented pores. No homogeneous pore nucleation occurred. The porous islands are randomly distributed all over the surface and there is an undercutting of the surface with obviously crystallographically oriented pores emanating from these islands. This resulted in an undulating interface between the bulk material and the porous layer. These islands are different to the porous domains reported by Ern e et al. [4, 5] in this respect that Ern e's domains are confined by domain boundaries which develop during the overlapping of the charge carrier depletion zones of two adjacent domains. In the present case with HCl the boundary of these porous islands are superficially more or less frayed (see upper right corner in Fig. 2(b)). The ligament of obviously unattacked surface across the center of Fig. 2(b) is a slight scratch which remained from polishing the wafer. Obviously porosification sets in beside these mechanically induced defects within the deformation zone. This is in contrast to earlier findings during etching in H<sub>2</sub>SO<sub>4</sub> [4, 5], where it was stated that pore formation starts at defect sites. More recent work on Si and InP [21, 22] show that inducing defects into a surface can have electrochemically

activating or deactivating character. Possibly the pore formation is favoured in the surrounding zone of a defect because mechanical tensile stresses may lower the activation energy for bond breaking. Directly in the defect compression stresses are prevalent due to the former compressive scratching.

Etching *n*-GaP electrochemically in 0.1 M HBr leads to an unusual self-organized pore morphology which was described previously [23]. Rectangular shaped pores can be formed. Further investigations revealed that the distribution and coverage of the surface with these pores depend strongly on the electrochemical parameters [23]. Performing only a polarisation scan from cathodic to anodic potentials until a transportation limitation is reached only some small regions underneath a lifted off nucleation layer could be observed, Fig. 2(c). The pores grow perpendicular to the surface into  $\langle 100 \rangle$ -direction. The pore walls of the rectangular pores are concluded to be (110) planes. As it was described in more detail elsewhere [23] this pore morphology can be attributed to a current line assisted crystallographic pore growth. A fine tuning of the electrochemical parameters led to larger areas of rectangular pores. Under potentiostatic conditions in 1 M HBr porous layers can grow several  $\mu\text{m}$  in length with maintaining a high degree of pore straightness [23].

The pores formed in HI are round holes with no indication of any crystallographic orientation neither in the  $\langle 111\text{B} \rangle$ -direction nor in the recently reported  $\langle 100 \rangle$ -direction. Anodizing *n*-type GaP in 0.1 M HI led to an unusual orientation of the pores around defect sites. Previously it was reported that porous domains during etching in H<sub>2</sub>SO<sub>4</sub> are formed at defects [4, 5]. The circular arrangement of pores in Fig. 2(d) is assumed to be triggered by the stress field of a dislocation which should be in the center of these rings. Therefore electrochemical etching in HI is assumed to be able to visualize equi-stress lines around mechanical defects. Here the defect itself is not attacked preferentially again. The parallel lines in Fig. 2(d) are aligned along a mechanically induced scratch. Especially at a crossing of two scratches (lower right corner of Fig. 2(d)) it is obvious how precise this arrangement is. Along the scratch the outermost layer is lifted off partially. Thus one can perform observations under the nucleation layer: remarkable is that underneath the surface no further branching of the pores occurs.

Besides the above discussed halide acid electrolytes several other electrolytes were screened in view of their ability to produce a porous structure. Several experiments in KOH with additions of halide ions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) were carried out. These alkaline solutions with or without aggressive halide ions can also lead to a porous structure. In order to achieve porosification in absence of halide ions it seems to be crucial that the pH of the electrolyte is higher than 13. Otherwise a thick oxide layer is formed on the surface preventing a homogeneous porosification of the bulk material. (see Fig. 4(a)). Experiments at different pH-values revealed



**Fig. 4** (a) Pine tree like structure of porous GaP after etching electrochemically in 1 M KOH under strong illumination, (b) GaP after anodization in  $\text{H}_3\text{PO}_4$ , (c) and (d) typical structures obtained in  $\text{HNO}_3$

that the chemical nature of the halide ion triggers the pore morphology. The pH of the electrolyte plays only a minor role and can be adjusted for fine tuning.

Anodization in  $\text{H}_3\text{PO}_4$  or  $\text{HNO}_3$  led to porous structures—typical examples are shown in Fig. 4. In 1 M  $\text{HNO}_3$  a comparatively thick porous layer is formed on *n*-GaP at very low potentials (less than 10 V). At higher potentials a tremendously fast etching process sets in that destroys the porous layer. The resulting porous patterns show sometimes quite a high regularity, Fig. 4(c), or other interesting peculiarities, Fig. 4(d). However the exact morphology was found to be of a random nature and show a low degree of reproducibility.

In summary the work clearly shows how strong the pore morphology can be dependent on the electrolyte used in the etching process. This shows that comprehensive models and concepts describing the pore formation process must include the chemical nature of the electrolyte. In other words, models entirely based on the solid-state properties of the semiconductor or a combination of the semiconductor

and electrical parameters may be used in distinct cases but need to be expanded to describe the full range of possible pore morphologies.

## Conclusion

In the present paper we screened the electrochemical and pore formation behaviour of *n*-type GaP in halide acids and other electrochemical etchants. We report the occurrence of different pore morphologies which are often specific to a certain etchant. Within this study a specific behaviour is found for bromide ions on the porosification process of *n*-type GaP leading to self-organized structures. Several other more complex self-organizing effects or self-regulating phenomena were observed especially when GaP is electrochemically porosified in HI or  $\text{HNO}_3$ .

In all, the work clearly demonstrates that the pore formation and growth on GaP strongly depends on the specific chemical nature of the electrolyte—therefore pore

formation models should take this factor into account to be comprehensive.

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