



Electrochemical Formation of Porous GaP in Aqueous HNO₃

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Porous gallium phosphide was produced by anodic etching of n-type GaP in an aqueous solution of 1 M HNO₃. At potentials lower than 15.5 V, yellow porous samples were obtained, of which the pore size was around 45% larger than the pores obtained in 0.5 M H₂SO₄. At potentials around 15.5 V electropolishing occurred. No pores formed when GaP was etched at potentials in this range. At potentials higher than approximately 15.5 V the current density increased strongly with increasing potential, and very large pores formed. It was found that NO₃⁻ and SO₄²⁻ only play a role in the chemical dissolution of the oxide layer that forms during etching.

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Gallium phosphide is transparent for light in the yellow and red part of the visible spectrum ($\lambda > 0.55 \mu\text{m}$). This absence of optical absorption, together with its very high refractive index ($n = 3.3$),¹ makes GaP a fascinating material for optical applications in the important wavelength range, $0.55 < 1.1 \mu\text{m}$, a range where Si shows strong absorption. Because light can be scattered strongly inside porous GaP, Anderson localization² can appear. In this way light can be locked up in the material, and released at will, by, for example, changing the refractive index of the GaP using two-photon absorption.³⁻⁵ Our group is a pioneer in the field of porous GaP formation.⁶⁻⁸ However, Anderson localization of visible light has not yet been observed.

Porous GaP is formed by the electrochemical anodic etching of single-crystalline n-GaP wafers in an aqueous electrolyte. The diameter of the pores formed depends on the current density; the larger the current density the larger the diameter of the pores.^{7,8} Until now solutions of H₂SO₄ have mostly been used for the formation of strongly scattering samples of porous GaP. When GaP is electrochemically etched in H₂SO₄ the current density reaches a maximum at a certain potential (see Fig. 1). Above this potential no porous GaP is formed.⁷⁻⁹ Therefore the range in pore size of the porous GaP that can be made using H₂SO₄ as an electrolyte is limited. We investigated the usability of aqueous HNO₃ as an electrolyte for the formation of porous GaP that has a larger pore size, and therefore achieved a higher scattering strength than has been obtained before.^{6,7}

Experimental

All experiments were performed in the dark, on n-type, (100)-oriented, S-doped GaP with a dopant density of $1\text{--}5 \cdot 10^{17}/\text{cm}^3$. The semiconductor was placed in a polytetrafluoroethylene (PTFE) holder that was designed to make an electrical connection to the back side using a copper plate, and simultaneously protect the semiconductor from making contact with the electrolyte. A circular area with a diameter of 7.2 mm (surface area 0.41 cm^2) was left open to expose the GaP to the electrolyte. A potential difference was applied between the semiconductor working electrode and a platinum counter electrode having a surface area of approximately 2 cm^2 . Aqueous solutions of 1 M HNO₃ and 0.5 M H₂SO₄ were used as electrolyte. A plot of the current through the GaP was measured as a function of the applied potential, while scanning the potential between 10 and 20 V, with a scan rate of 50 mV/s. Samples were etched in the above described solutions at potentials of 13, 14, 15, 16, and 17.6 V (17.6 V only for 1 M HNO₃), until a charge density of 10 C/cm² was reached (5 C/cm² for the sample etched at 17.6 V to prevent it from destruction). The samples were subsequently cleaved and analyzed using a JEOL 5610 scanning electron micro-

scope (SEM). Pore diameters were measured, using a vernier scale, from SEM pictures printed at a size that just fit on A4-sized paper ($29.7 \times 21.0 \text{ cm}$). The diameter of 10 pores was measured, and a mean value was calculated. The thicknesses of the porous layers were also measured from SEM pictures. The porosity of a layer can be defined as the fraction of empty space in the layer. For every molecule of GaP that is dissolved, six holes are used.¹⁰ Bulk GaP contains $2.47 \cdot 10^{22}$ units GaP per cm³. Hence 1 C dissolves an amount of GaP that fits in a space with a surface area of $1 \times 1 \text{ cm}$ and a height of 421 nm. With this knowledge, Eq. 1 can be derived for the porosity of a porous GaP layer

$$P = \frac{0.421C}{d} \quad [1]$$

In this equation P is the porosity, C the charge density through the sample in C/cm², and d the thickness of the porous layer in micrometers. The porosities of the obtained layers were calculated using Eq. 1.

Results

In Fig. 1 the current densities through GaP samples etched electrochemically in 1 M HNO₃ and 0.5 M H₂SO₄ are plotted as a function of the applied potential V . The scan directions are indicated by arrows. Figure 1 shows that when HNO₃ is used as an electrolyte, at potentials above approximately 15.5 V (which we call the onset potential in the rest of this paper) the current density increases dramatically with increasing potential. Current oscillations appear in the back scans. When H₂SO₄ is used as an electrolyte, the GaP passivates at potentials above approximately 16.5 V. A protective oxide layer forms which prevents the dissolution of more GaP, and thus the development of current.⁷⁻⁹ During the back scan this protective layer dissolves in the electrolyte, and eventually the current returns. The potential at which the current returns during the back scan depends on the dissolution rate of the oxide and the rate at which the potential is scanned.⁸

In Fig. 2 the current density during etching is shown as a function of time for a sample etched in 1 M HNO₃ at 14 V (below the onset potential), at 16 V (near the onset potential), and at 17.6 V (above the onset potential). At potentials below the onset potential the current density increases slowly until a steady state is reached. This is a different behavior from the electrochemical etching of GaP in H₂SO₄, where the current density reaches a maximum and then drops to a slightly lower value.⁷ When GaP is etched in H₂SO₄ the pore formation starts at specific points at the surface. The pores, which only etch at the pore tips, spread out and form hemispherical porous regions underneath the surface of the sample. In this way, an unetched top layer forms on the sample. When the pore fronts meet, the current density is at a maximum. As the etching continues, the hemispherical domains grow into each other, and the porous GaP/bulk GaP interface becomes flat, thereby decreasing its surface area.

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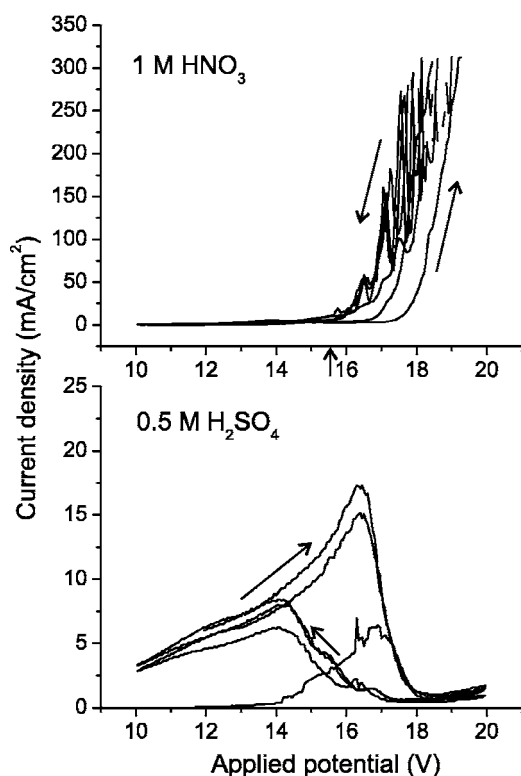


Figure 1. Current-potential curve of n-type GaP in 1 M HNO_3 and 0.5 M H_2SO_4 . The scan direction is indicated by the arrows in the plots. Note the large differences in the current densities. When HNO_3 is used, passivation does not occur, but the current increases strongly at potentials above the onset potential of 15.5 V, indicated by the arrow on the x-axis of the upper plot. When H_2SO_4 is used the GaP is passivated at potentials above approximately 16.5 V, causing the current to drop.

This causes the current density to drop slightly. When GaP is anodically etched at potentials lower than the onset potential in HNO_3 a smooth, bright yellow, porous layer is formed. The fact that the current density does not reach a maximum means that either the pores form everywhere at the surface, or the distance between the

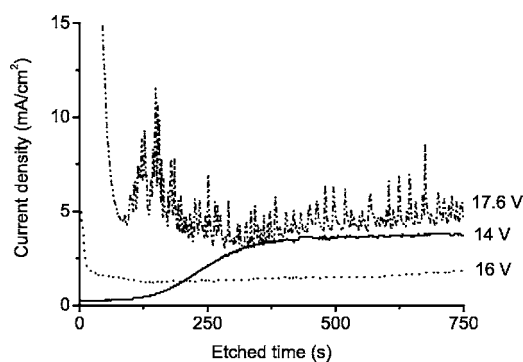


Figure 2. Current-time curves of n-type GaP etched at different potentials in 1 M HNO_3 .

porous regions is initially much smaller than when H_2SO_4 is used, and the maximum in the current density becomes invisible. Investigation of SEM pictures of samples that were etched for a short time in HNO_3 shows that indeed porous regions are formed very close to each other, and a top layer develops.

At potentials close to the onset potential the current density is initially high and drops to a value lower than the current density during etching at a lower potential. The surface of the sample became rough, but no porous layer was formed. At potentials above the onset potential the current density was initially very high and dropped fast. During etching many spikes can be seen in the current density vs time plot. The minimum current density when etching at potentials above the onset potential was higher than the minimum current density that was reached when potentials at or below the onset potential were applied. A bright yellow powder consisting of porous particles detached from the sample during etching, and the sample emitted visible light. This phenomenon was discovered and described by Van Driel et al.¹¹ Gas evolution from the sample is clearly visible during etching. The rate of gas formation as well as the intensity of the emitted light increase with increasing potential.

Examples of porous layers formed in 1 M HNO_3 at various potentials are shown in Fig. 3. An unetched top layer can clearly be seen, indicating that the etching starts at pits and the pores spread out under the sample surface, as is the case when GaP is electrochemically etched in H_2SO_4 . At potentials far beneath the onset

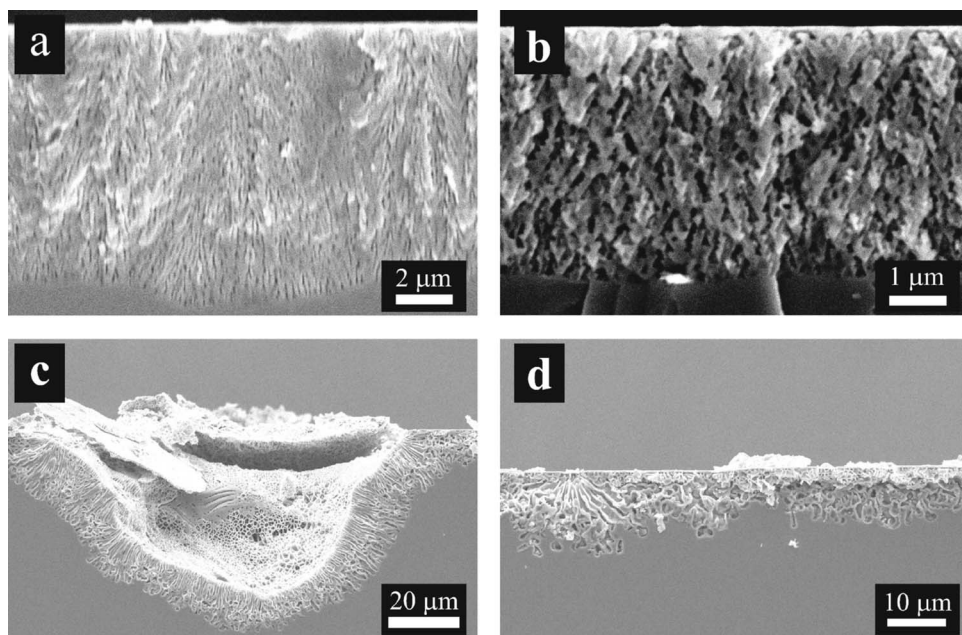


Figure 3. Side views of GaP samples etched in 1 M HNO_3 at potentials of 13 V (a), 15 V (b), and 17.6 V (c, d). Because at 17.6 V the morphology depended strongly on the location on the sample, two pictures from different locations on the same sample are shown. Samples were etched until a charge density of 10 (a,b) or 5 (c,d) C/cm^2 was reached.

Table I. Pore diameters (in nm) of porous GaP formed in HNO₃ and H₂SO₄ as a function of the applied potential.

Potential (V)	1 M HNO ₃	0.5 M H ₂ SO ₄
13.0	63.4 ± 16.7	66.1 ± 18.7
14.0	82.6 ± 17.9	54.3 ± 12.9
15.0	142 ± 39.1	97.9 ± 17.6
17.6	599 ± 202 ^a	No pore formation

^a At this potential the pore morphology varied quite considerably with the location on the sample.

potential, the pores are narrow and long, and branching did not occur very often (Fig. 3a). At higher potentials, slightly below the onset potential, branching occurred more frequently, and the pores are more pyramid-shaped (Fig. 3b). The walls of the pores are now determined by $\langle 111 \rangle$ planes in the GaP crystal.¹² For potentials below the onset potential the shape, size, and density of the pores obtained in HNO₃ at a certain potential are comparable to the shape of the pores obtained in 0.5 M H₂SO₄ at the same potential. At potentials above the onset potential, the pores are very irregularly distributed, and also the size distribution of the pores is very broad. The pore sizes range from several 100 nm to several micrometers. Figure 3c and d show examples of pores formed at a potential of 17.6 V. The pores are clearly much bigger than the pores formed at lower potentials. In many places, craters were formed because porous GaP had detached from the surface. This sample was etched until 5 C/cm² had passed through it, to prevent its total destruction.

The dimensions of the pores are shown in Table I. At a potential of 16 V no pores were formed in both 1 M HNO₃ and 0.5 M H₂SO₄. The pores formed in H₂SO₄ at a potential of 13 V are wider than the pores formed at a potential of 14 V. The reason for this is unclear. As can be seen from Table I, the use of HNO₃ instead of H₂SO₄ increased the maximum obtainable pore size by approximately 45%. At high potentials the pores are much more evenly distributed in the porous layer than the pores formed in H₂SO₄. The porosities of the layers are shown in Table II. From this table it can be seen that the porosities of the porous samples that were etched in HNO₃ are higher than the porosities of the samples that were etched in H₂SO₄. From enhanced backscatter and total transmission data (not shown), we infer that despite the increased pore size and porosity, the optical properties of the samples etched in HNO₃ were not significantly altered with respect to the optical properties of samples etched in H₂SO₄.

Discussion

During the electrochemical etching of GaP at potentials below the onset potential, we assume that two competing reactions occur, in analogy with the model proposed by Zhang et al.¹³ for the electrochemical formation of porous Si: (i) the direct dissolution of GaP (which leads to porous GaP), and (ii) the formation of gallium oxides.

At potentials below the onset potential, the direct dissolution of GaP is the most common reaction, and a uniform, yellow layer of porous GaP is formed, as described in Ref. 7, 8, and 12.

At potentials close to the onset potential, the oxidation of GaP is thought to be the prevalent process. Because the initial GaP surface is bare, containing only a thin layer of native oxides that are easily dissolved in HNO₃, the current density is initially high. Gallium oxide is produced slowly and forms a thin layer at the surface. This layer is attacked by the NO₃⁻ in the electrolyte, and rapidly dissolves chemically. This is called transpassive dissolution, which is a well-known phenomenon in metal dissolution.¹⁴ Because the formation and etching of the oxide layer occur at approximately the same rate, a constant low current flows. The surface of the sample roughens, but no porous GaP is formed. A similar mechanism is responsible for the electropolishing of Si in HF-containing aqueous solutions.¹⁵

Table II. Porosities (in %) of porous GaP layers formed in HNO₃ and H₂SO₄ as a function of the applied potential.

Potential (V)	1 M HNO ₃	0.5 M H ₂ SO ₄
13.0	45	40
14.0	58	45
15.0	93 ^a	45

^a The high value for the porosity was probably caused by underetch.

At potentials above the onset potential, oxides are formed at a higher rate. The oxide layer can now form faster than it can be removed by the electrolyte. When the oxide layer reaches a certain thickness it will break down due to either internal stress or the high electric field. Holes will form in the oxide layer, exposing small patches of bare GaP to the electrolyte solution. Due to the high electric field the current density at these locations is initially very high, and a large amount of GaP will dissolve, yielding the big pores shown in Fig. 3c. Because of the high positive potential at the surface of the sample, the water in the electrolyte is oxidized and oxygen bubbles form. When these bubbles detach from the surface, the local current density also changes.

Due to the big pores, the porous layer is structurally very weak, causing it to fall apart and yielding the yellow powder that was observed. Eventually an oxide layer will form again on the remaining GaP and the local current density will drop. However, new holes will also form in the oxide layer. The formation of gas bubbles and the electrical breakdown of the oxide layer explain the current oscillations during the potentiostatic etching of GaP in 1 M HNO₃ at potentials higher than the onset potential (Fig. 2).

Tables I and II show that the diameters of the pores, as well as the porosities of the porous GaP formed in HNO₃ are higher than those of GaP that is anodically etched in H₂SO₄. A significant discovery is that, because the shape of the pores that are formed at potentials below 15.5 V in HNO₃ and H₂SO₄ are comparable, it can be concluded that the SO₄²⁻ and NO₃⁻ ions only play a role in the chemical formation and dissolution of the oxide layers that are formed during the etching, and not in any electrochemical process. This is in strong contrast with the results obtained when GaP is electrochemically etched in aqueous HBr solutions, which can result in the formation of very long, oblong-shaped pores.¹⁶ The bigger pores in the samples that were etched in HNO₃ are the result of the faster removal of oxides in this electrolyte.

Optical measurements did not show a significant decrease of the mean free path of visible light in the samples described in this paper, which means the light is not stronger scattered in these samples than in samples obtained before using H₂SO₄. This is probably due to the fact that although the pore diameters are larger, the porosity of the porous layer is also higher, which means that the walls between the pores are thinner than in samples formed in H₂SO₄. In order to optimally scatter the light, the walls between the pores should not be too thin. However, it is an open question what the optimum relative sizes of the pores and the pore walls should be.

Conclusions

Gallium phosphide can be made porous by electrochemical etching in aqueous HNO₃ solutions. At low potentials the pores that are formed are quite similar in shape, but around 45% bigger than pores formed in aqueous H₂SO₄ solutions. Optical measurements performed on samples etched at low potentials in 1 M HNO₃ did not show significantly altered optical properties compared to samples that were made using H₂SO₄. This is probably caused by the fact that although the pores are a bit bigger than the pores formed in H₂SO₄, the porosity is also higher, which means that the thickness of the walls between the pores is relatively thinner than when H₂SO₄ is used in the formation of the porous GaP. This has a detrimental effect on the light scattering properties of the sample. To

make samples in which Anderson localization can occur it is necessary to increase the distance between the pores. At high potentials, passivation, like in aqueous H_2SO_4 , does not take place, but the current density increases strongly with the applied potential. A small electropolishing regime exists near the onset potential. When GaP is etched anodically in 1 M HNO_3 at potentials higher than this onset potential, very large pores develop. This can be explained by the different rates at which the oxide layers that are formed during etching are dissolved in the electrolyte solutions. The ions SO_4^{2-} and NO_3^- only play a role in the chemical formation and dissolution of the oxide layer that is formed during the etching of the GaP, and not in any electrochemical process. During etching the sample emits light, and oxygen gas evolution takes place. A yellow porous powder detaches from the sample during etching at high potentials.

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