Formation of Porous Layers with Different Morphologies during Anodic Etching of n-InP

S. Langa,^{a,b} I. M. Tiginyanu,^b J. Carstensen,^a M. Christophersen,^{a,*} and H. Föll^{a,**,z}

^aFaculty of Engineering, Christian-Albrechts-University, D-24143 Kiel, Germany ^bLaboratory of Low-Dimensional Semiconductor Structures, Institute of Applied Physics, Technical University of Moldova, MD-2004, Chisinau, Moldova

Two different morphologies of porous layers were observed in (100)-oriented n-InP anodically etched in an aqueous solution of HCl. At high current density (60 mA/cm^2) anodization leads to the formation of so-called current-line oriented pores. When the current density decreased to values lower than 5 mA/cm² the morphology of the porous layers sharply changed and the pores began to grow along definite <111> crystallographic directions.

© 2000 The Electrochemical Society. S1099-0062(00)06-078-8. All rights reserved.

Manuscript submitted June 26, 2000; revised manuscript received July 26, 2000. Available electronically September 1, 2000.

While considerable research efforts are focused on porous Si¹ and silicon-electrolyte junctions,² relatively little attention has been given to porous layer morphology in III-V compounds. Pore formation has been reported for InP in HCl,³⁻⁶ GaP in H₂SO₄ electrolytes,⁷ and for GaAs in HCl and Cl⁻ containing solutions.^{8,9}

According to preliminary investigations, the type and concentration of anions in the electrolyte,^{8,9} as well as the substrate type,¹⁰ orientation,^{10,11} and doping^{12,13} are the main parameters significantly affecting the pore growth and morphology in different semiconductor materials. Apart from that, the so-called nucleation phase of pore formation is affected by native or intentionally induced defects on the semiconductor surface. Thus, Tiginyanu *et al.* reported that preliminary MeV-ion implantation in GaP can serve as a tool for controlling the morphology of pores.¹⁴

The present paper reports on a radical change in pore morphology in n-InP substrates without using additional treatment before or during the anodization.

Wafers used in this work were (100)-oriented n-type InP, doped with Si. The concentration of free electrons in bulk material was 3 x 10^{17} 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 (REE), a Pt reference electrode on the sample (RES), a Pt counter electrode (CE), and a Pt working electrode (WE). The electrodes were connected to a Keithley 236 source measure unit. The temperature of the electrolyte was kept constant at T $= 23^{\circ}$ C with the help of a Julabo F25 thermostat only on that side of the double cell where pores were expected to grow. The electrolyte was pumped in a continuous mode through both cells with the help of peristaltic pumps. The equipment involved in the experiments was computer controlled. The area of the sample exposed to the electrolyte was 0.12 cm². The anodic etching was performed using 5% HCl aqueous electrolyte at different galvanostatic conditions. The anodized wafers were examined with a scanning electron microscope (SEM) in cross section. Additionally, the experiments were performed in the dark and the holes necessary for the dissolution of the material were generated by the breakdown of the depletion layer.

Figure 2 presents the cross-sectional micrograph of a sample anodized at 60 mA/cm² current density. Pores obtained in these conditions evidently have no specific crystallographic orientation, but rather follow some curved lines mainly oriented perpendicular to the surface. The system seems to minimize the ohmic losses by optimizing the way for the current.¹⁵ Such pores we call "current-line oriented".

- ** Electrochemical Society Active Member.
- ^z E-mail: hf@tf.uni-kiel.de

At identical conditions except for a decrease of the anodic current density of more than an order of magnitude, a totally different morphology is obtained (Fig. 3). In this case the pores prove to be strictly oriented along specific crystallographic directions. As illustrated in Fig. 3, in the cross section of the anodized sample two kinds of pores (trenches and pits) are easily distinguishable. The trenches in



Figure 1. Schematic illustration of the electrochemical double cell.



Figure 2. SEM micrograph in cross section of a sample subjected to anodic etching at current density 60 mA/cm².

^{*} Electrochemical Society Student Member.



Figure 3. Cross-sectional micrograph of n-InP anodized at current density 4.2 mA/cm^2 for 2 h. (a) Upper part of the porous layer and (b) porous layer in depth. The arrows show two preferential directions of pore growth, as described in the text.

the cross section plane are oriented in two different directions intersecting at 108° (54° with the surface normal). This suggests that the pores grow along <111> crystallographic directions. It must be noted that <111> directions were reported earlier as preferential directions of pore growth in GaAs.¹²

Analysis of the images in Fig. 3 shows that in the cross section plane two directions of growth are visible as trenches while the other two, not contained in the cleavage plane, appear as pits. According to the SEM images taken at high magnifications, these pits are triangular. Thus, formation of triangular pores introduces a second anisotropy of the electrochemical etching in InP additional to the preferential direction of growth in <111>.

As can be observed from Fig. 3b, along the direction marked on the micrograph with "2" the pores are long and predominant in comparison with pores which are growing in the direction marked with "1". Figure 3b looks somehow asymmetrical taking into the account that these directions ("1" and "2") are crystallographically identical. However, Fig. 3a represents the cross section taken from the upper part of the porous layer, while Fig. 3b represents the same porous layer at a larger depth. As one can see, in the upper part of the porous layer the cleavage contains a succession of planes forming a steplike structure revealing relatively long pores in both directions. Therefore, long pores are present in both directions, but in a specific cross section plane only one direction may show long pores while in other cross section planes pores with another direction of growth from the same <111> set are predominant.

Taking into account that the results described above are reproducible, one can conclude that a gradual change of current density



Figure 4. Cross-sectional micrographs of n-InP anodized in turn at high and low current densities (60 and 5 mA/cm², respectively). (a) Upper part of the porous layer and (b) porous layer in depth.

from low to high values leads to a switch of the pore growth mechanism from being crystallographically oriented to current-line oriented. This conclusion is supported by the images presented in Fig. 4. The same n-InP sample was subjected to anodization first at high and then at low current densities. As can be seen in the cross section of the sample, a switch occurs from the current-line oriented to the crystallographically oriented pores. The upper part of the porous layer has a current-line oriented morphology and corresponds to high current density (Fig. 4a), while the lower part of the layer contains crystallographically oriented pores (Fig. 4b).

Despite the fact that the current-line oriented pores grow preferentially perpendicular to the surface, they show a pronounced instability in their direction of growth (see, for example, Fig. 2). One of the main reasons for this instability appears to be the difference between the preferential crystallographic direction of growth (<111> directions) and the direction of current-line oriented pores, *i.e.*, [100] direction in our case. This difference may act as a destabilizing factor for the direction of growth for current-line oriented pores.

Note that the instability of the direction of pore growth at high current densities is more pronounced when the anodic current through the sample is applied in pulses; this means that the current is also a factor influencing the direction of growth for the currentline oriented pores.

In conclusion, anodic etching of n-InP in HCl-based electrolyte at high current densities leads to the orientation of pores along the current lines, while anodization at low current densities provides conditions for preferential orientation of pores along four <111> crystallographic directions. When applied via lithographically defined windows, the etching of n-InP at low anodic current densities may be used to produce ordered three-dimensional structures promising for photonic applications.¹⁶ This issue is under investigation in our laboratories.

Christian-Albrechts-University assisted in meeting the publication costs of this article.

References

- 1. L. T. Canham, Appl. Phys. Lett., 57, 1046 (1990).
- 2. H. Föll, Appl. Phys. A, 53, 8 (1991).
- N. G. Fereira, D. Soltz, F. Decker, and L. Cescato, J. Electrochem. Soc., 142, 1348 (1995).
- 4. T. Takizawa, S. Arai, and M. Nakahara, Jpn. J. Appl. Phys., 54, L643 (1994).
- E. Kikuno, M. Amitti, T. Takizawa, and S. Arai, Jpn. J. Appl. Phys., 34, 177 (1995).

- A. Hamamatsu, C. Kaneshiro, H. Fujikura, and H. Hasegawa, J. Electroanal. Chem., 473, 223 (1999).
- B. H. Erne, D. Vanmeakelbergh, and J. J. Kelly, J. Electrochem. Soc., 143, 305 (1995).
- P. Schmuki, J. Fraser, C. M. Vitus, M. J. Graham, and H. Isaacs, *J. Electrochem. Soc.*, **143**, 3316 (1996).
- P. Schmuki, D. J. Lockwood, J. W. Fraser, M. J. Graham, and H. Isaacs, *Mater. Res. Soc. Symp. Proc.*, 431, 439 (1996).
- M. Christophersen, J. Carstensen, A. Feuerhake, and H. Föll, *Mater. Sci. Eng.*, *B*, 69, 70, 194 (2000).
- S. Rönnebeck, J. Carstensen, S. Ottow, and H. Föll, *Electrochem. Solid-State Lett.*, 2, 126 (1999).
- F. M. Ross, G. Oskam, P. C. Searson, J. M. Macaulay, and J. A. Liddle, *Philos. Mag. A*, **75**, 2 (1997).
- P. Schmuki, L. E. Erickson, D. J. Lockwood, J. W. Fraser, G. Champion, H. J. Labbe, *Appl. Phys. Lett.*, **72**, 1039 (1998).
- I. M. Tiginyanu, C. Schwab, J.-J. Grob, B. Prevot, H. L. Hartnagel, A. Vogt, G. Irmer, and J. Monecke, *Appl. Phys. Lett.*, **71**, 26 (1997).
- G. S. Popkirov and R. N. Schindler, *Electrochim Acta*, **39**, 2025 (1994).
- F. Müller, A. Birner, U. Gösele, V. Lehmann, S. Ottow, and H. Föll, J. Porous. Mater, 7, 201 (1998).