A comparison of pores in silicon and pores in III–V compound materials

M. Christophersen¹, S. Langa^{1, 2}, J. Carstensen^{*, 1}, I. M. Tiginyanu², and H. Föll¹

¹ Materials Science, Faculty of Engineering, University of Kiel, Kaiserstr. 2, 24143 Kiel, Germany
² Technical University of Moldova, Chisinau, Moldova

Received 11 March 2002, accepted 30 September 2002 Published online 9 May 2003

PACS 61.43.Gt, 82.45.Mp, 85.85.+j

This paper compares the morphologies of porous silicon and porous III–V compounds and discusses their growth mechanisms. Looking into the fine structure of pores, in silicon (meso)pores with intercalating octahedra are prevalent, while in III–V compounds chains of tetrahedra are observed. The anisotropic properties of pore growth in all materials can be understood considering the role of surface states in the band gap and the anisotropy of the passivation of these states which leads to an "aging" effect of the surface. In III–V compounds, and for the first time in silicon, the strong interaction of pores during their growth has been found. In InP as well as in silicon these interactions lead to self-induced diameter modulations. To achieve this effect in Si requires the etching conditions to be comparable to those in the III–V compounds.

1 Introduction Porous silicon has been studied in numerous papers, see [1], mainly due to the photoluminescence properties of microporous silicon. Its preparation, generally based on electrochemical etching in a hydrofluoric acid containing electrolyte, is now controlled up to a remarkable level of reproduction. Another growing area of interest is macropores, first described in 1990 by Lehmann and Föll, obtained using back-side illumination for n-type silicon in an aqueous hydrofluoric electrolyte [2]. The first macropores in p-type Si were found by Propst and Kohl in 1994 using an organic electrolyte [3]. In the last few years many kinds of meso- and macropore morphologies have been obtained in n-type and p-type Si under many, sometimes quite different, etching conditions.

In contrast to silicon, most pore etching in III–V compounds has been done on highly doped n-type material and only occasionally on low doped n-type material, while no pores were found in p-type material (for the single exception with p-type, see [4]). Meso- and/or macropores, but never micropores, have been found so far in n-type GaAs [5], GaP [6], InP [7, 8], and GaN [9], with varying morphologies, but mostly aligned in the $\langle 111 \rangle$ directions.

The formation of pores in the III–V compound semiconductors has been discussed in the framework of the mechanisms suggested for Si. Most of the papers concerning pore formation, cf. [6], agree that the space charge region around the pores, avalanche breakdown effects, and preferred nucleation at defect sites play an important role. Because most of the experiments have been performed on highly doped n-type material, the necessary holes are assumed to be always generated by field induced avalanche breakdown. Defects like dislocations reduce the critical electric field strength for hole generation and thus encourage pore nucleation.

^{*} Corresponding author: e-mail: jc@tf.uni-kiel.de, Phone: +49 431 880-6181, Fax: +49 431 880-6178

New kinds of pores in silicon and in III–V compounds have been found recently [9–11], starting again a discussion on the detailed formation mechanism of pores in semiconductors [12]. Few papers exist which compare pore formation mechanisms or the morphologies of pores in silicon with the pores in III–V compounds. Ross et al. [12] compared the morphologies of pores in GaAs and silicon, while Chazalviel et al. [13] claim the applicability of their diffusion instability model, originally introduced for silicon, also to pores in III–V compounds. In this paper some new pore morphologies obtained in compound semiconductors will be compared to their counterparts (partially new) in Si, resulting in new general concepts for anodic etching of semiconductors.

2 Experiments Silicon specimens (n-type, $2-6 \Omega$ cm, $\{100\}$; p-type, $1-16 \Omega$ cm, $\{100\}$) were etched under the following conditions: 4 V etch bias, and galvanostatic current densities between 4 and 10 mA/cm²; illumination of the sample from the front side in the case of n-type silicon. The illumination was computer controlled to maintain constant current densities. For the generation of breakthrough pores no illumination of the sample was used – a galvanostat was used to obtain a constant current of 4 mA/cm². The electrolyte was 4–10 wt% HF in water (always with the addition of NCW 1001 from Wako Chemicals as a tenside for better wetting). The temperature of the electrolyte was fixed at 20 °C, and the etch time was 60 min for all experiments. For some experiments, instead of water, the organic solvent dimethylformamide (DMF) was used.

The anodization of the compound semiconductors was carried out in an electrochemical double cell made of Teflon which is advantageous for a good ohmic back-side contact. The electrolytes consisted of 5–10 wt.% of HCl or H₂SO₄ in distilled water. Potentiostatic as well as galvanostatic experiments have been performed without illumination. n-Type GaAs ($n = 10^{17}-10^{18} \text{ cm}^{-3}$ or $\approx 0.02 \Omega$ cm, {100} and {111}) and InP ($n = 10^{16}-10^{18} \text{ cm}^{-3}$, or $\approx 0.01 \Omega$ cm {100}) samples have been anodized. Galvanostatic current densities were between 8 and 100 mA/cm²; the high currents were used to etch current line pores in InP and tetrahedron like pores in GaAs. The temperature of the electrolyte was controlled at 20 °C. The pore morphologies were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3 Experimental results The morphology of "breakdown" pores (i.e. meso- or macropores obtained under avalanche breakdown conditions which is what we must compare in the first place) generally is heavily dependent on crystallography [14]. In Si, these pores often consist of interconnected octahedral voids – independent of the electrolyte, cf. Fig. 1. However, breakdown pores etched in organic electrolytes exhibit sharper structures than those from aqueous electrolytes. The tips of the octahedra point in the $\langle 100 \rangle$ directions and the walls consist of $\{111\}$ planes, so obviously the $\{111\}$ planes are most stable against electrochemical dissolution. This crystallographic directions are even found in apparently straight $\langle 100 \rangle$ oriented pores: at high magnification the pore walls often consist of facets with $\{111\}$ surfaces (Fig. 1).



Fig. 1 TEM micrograph. Breakthrough pores in moderately doped n-type silicon consist of intercalated octahedra: a) aqueous electrolyte; b) organic electrolyte.



Fig. 2 First multilayer pore structure in a III–V compound ((100) n-InP, $n = 1.3 \times 10^{18}$ cm⁻³, 5 wt% HCl) by stopping the etching. An etch stop for 30 s leads to the formation of a new nucleation layer. An etch stop of 2 s would lead to the formation of a smaller nucleation layer.

In InP and GaP two different types of pores are found: (i) "crystallographically oriented" and (ii) "current line" oriented pores as shown in Fig. 2 for InP where this feature is particularly pronounced. At high current densities the crystallographically oriented pores serve as (always required) nucleation sites for the current line oriented pores. At lower current densities the crystallographically oriented pores may evolve into two types: straight pores in the $\langle 111 \rangle$ B direction, and chains of tetrahedral pores as shown in Fig. 3a for pores in GaAs – obviously corresponding to the octahedral pore chains in silicon. The walls of the tetrahedra consist of $\{111\}$ A surfaces only (i.e. the $\{111\}$ plane terminating in group III atoms); three of them are clearly visible in Fig 3a. The tetrahedra grow in the $\langle 111 \rangle$ B direction. The straight $\langle 111 \rangle$ B growth direction and the $\{111\}$ A planes of the pore walls, the triangular cross section of straight pores must consist of $\{112\}$ planes as shown in Fig. 3b. Stable growth of straight $\langle 111 \rangle$ B pores can only be obtained at low current densities. Upon increasing the current density, they switch into chains of tetrahedra in GaAs and into current line oriented pores in InP.



Fig. 3 SEM micrograph. Breakthrough pores in highly n-type GaAs consist of intercalated tetrahedra.



Fig. 4 Pores in InP. This pore can show self-induced voltage pore diameter modulations in a galvanostatic experiment. Depending on the pore density an interaction of these modulations can occur: a) interaction; b) no interaction.

In InP crystallographically oriented pores are small and intercalating tetrahedral voids are not as easily identified as in GaAs, but a comparable structure to silicon is present in current line oriented pores (cf. Fig. 4b). Upon increasing the current density, a self-ordering phenomenon is found: the octahedra begin to grow synchronized as shown in Fig. 4a, resulting in an oscillation of the voltage at constant current conditions. With this result as guidance, such self-induced synchronized diameter modulations could now also be found in p-type silicon under high current conditions (Fig. 5a, aqueous electrolyte with 10 wt% HF, 8 mA/cm²), and in n-type silicon using front-side illumination (Fig. 5b, organic electrolyte with 4 wt% HF, 4 mA/cm²).

4 Discussion

4.1 Aging concept/passivation mechanism While at high current densities the semiconductor surface is completely covered with oxide, at low current densities most of the semiconductor surface will be in direct contact to the electrolyte. It is well known that, after chemical dissolution stops, the free surface will passivate, i.e. the density of surface states reduces as a function of time, which in turn increases the stability of the surface against further electrochemical attack. For silicon, for example, the passivation of a $\{111\}$ crystallographic surface is faster and leads to a higher degree of perfection than for a $\{100\}$ surface. In other words, there is a selective aging of surfaces leading to a self-amplifying dissolution of $\{100\}$ surfaces (which will become pore tips) and a preferential passivation of $\{111\}$ surfaces (which will become pore targe). This probably explains why under optimized chemical conditions with an extremely large passivation difference between $\{111\}$ and $\{100\}$ surfaces a self-organized growth of octahedral cavities occurs in silicon. As soon as the complete surface of a cavity consists of $\{111\}$ pore walls



Fig. 5 a) Pores in p-type silicon. Used electrolyte was 7 wt% HF in an aqueous solution. A very high pore density can be achieved by 4 mA/cm². A starting interaction of the pores in the form of a self-induced diameter oscillation can be seen. b) Pores in n-type silicon under front-side illumination. Under constant front-side illumination in an aqueous electrolyte (4 wt% HF, 4 V, 4 mA/cm²) self-induced diameter changes can be found.



Fig. 6 Schematic outline of the formation of octahedra in silicon. Some stages of the formation of a breakthrough pore are shown in a), b) and c). d) The starting wall passivation.

which are effectively passivated, it is easier to start a new cavity at a $\langle 100 \rangle$ tip of the old cavity. Since the current density at the walls of the new and therefore small cavity is always large, no surface passivation will occur until the surface again becomes large enough to allow for a selective passivation of different crystallographic planes. This growth mechanism leads to an oscillation of both the current through each pore and the diameter of each pore (for details about the oscillation of the current, see [15]). The mechanism of forming intercalated octahedra and the starting wall passivation is shown schematically in Fig. 6.

The passivation is a kind of chemical passivation of the semiconductor surface. During the etching process surface states are present at the semiconductor/electrolyte interface. These states can reduce the width of the space charge region, and lead to a self-enhancement effect for the electrochemical reactions at the pore tips (as described in [16]). Owing to the interacting of the surface states and the space charge region the chemical passivation and the electronic passivation have the same meaning: enhancement of the electrochemical reaction at the pore tip, where passivation is not so active.

In the case of a compound semiconductor, the surface aging of III–V compounds is more complicated since two different {111} surfaces exist, e.g. in GaAs the {111} A planes are Ga-rich and the {111} B planes are As-rich. Only the {111} A planes appear as stopping planes while the $\langle 111 \rangle$ B directions are preferentially dissolved. In consequence, in III–V compounds tetrahedra bounded by the four {111} A planes and pores growing into $\langle 111 \rangle$ B directions are etched instead of octahedra. Further the surface chemistry of silicon and the III–V compounds is different. In silicon the passivation is probably by H termination of the silicon surface. For example in GaAs probably Cl is passivating the pore walls.

A rather spectacular consequence of the surface aging concept is demonstrated in Fig. 2 for InP. Changing the current density periodically from high values to zero, a layered structure of crystallographically oriented and current line oriented pores results. The crystallographically oriented pores always precede the current line oriented ones. Just stopping the current for one second, the surface has already been passivated so effectively that the old current line oriented pore tips cannot serve as nucleation sites for the new pores. A nucleation layer of crystallographically oriented pores forms just as before the beginning of the experiment.

4.2 Lateral interaction of pores A lateral interaction of pores can occur by a next neighbor interaction due to an overlap of the space charge region. In order to describe the current flow through a large number of pores electrically connected in parallel, we define the serial resistance R(t) of each pore

$$R(t) = \frac{\rho(t) \, l(t)}{A(t)} \,,$$

where $\rho(t)$ is the effective specific resistance at a pore tip, l(t) the length and A(t) the chemically active area at the pore tip of a pore. Owing to the (quasi)periodic nucleation of new cavities, $\rho(t)$ will periodically increase and decrease as a consequence of surface aging. For the total electric effect of a large number of individually oscillating pores connected in parallel, three different regimes exist: - At constant voltage conditions (potentiostatic control) the current through each pore will oscillate. If the pores grow independently of each other (which so far they always do) there exists no phase coupling of the individual oscillations and the overall current averages in time to a fairly constant value.

- For galvanostatic control we have to distinguish between two cases:

1. At low pore densities there are no restrictions for the pore diameter, i.e. the area A(t) may increase freely.

2. At high pore densities the increase of the diameter is restricted by the neighboring pores, and thus the area A(t) is limited.

In the first case we find diameter modulations, but still no phase coupling between the pores. In the second case the area of the pores cannot increase freely to compensate for the reduced effective resistance $\rho(t)$. Thus the external voltage must increase to guarantee a constant external current. The voltage increase then by necessity synchronizes the phase of the growth for all pores.

This is exactly what is found experimentally: etching InP at very high current densities is accompanied by self-induced voltage oscillations (for details see [17]). Each peak in the voltage corresponds to an increase of the pore diameters for all pores as indicated by the arrows in Fig. 4.

The extremely high pore density necessary for synchronized diameter and voltage oscillations is much easier to achieve in III–V compounds than in silicon because silicon oxide is much more stable than the oxides of the other semiconductors, leading to electropolishing of the silicon surface in aqueous electrolytes at the required high current densities. However, using organic electrolytes strongly suppresses oxide formation, thus still allowing for pore formation at high current densities – provided the etching cell and the electrolyte resistance are up to the task. With this insight as a guide for optimizing electrolytic cell and electrolyte, synchronized diameter oscillation of pores in silicon could now be found for the first time (Fig. 5, see also figures in [18]).

5 Conclusions The differences in the crystal symmetry and in the passivation mechanisms of the crystal planes allow to understand the anisotropic properties of pore growth in silicon and in the III–V compounds. The aging concept can explain the formation of chains of octahedra and tetrahedra in silicon or III–V compounds, respectively. The intrinsic oscillation of the current density at each pore tip resulting from aging together with a lateral interaction between neighboring pores due to the space charge region leads directly to the self-induced diameter oscillations in InP and silicon and the concurrent voltage oscillations.

Acknowledgements We thank Prof. Dr. P. Schmuki, Prof. Dr. J.-N. Chazalviel, Prof. Dr. J. Kelly and Dr. R. B. Wehrspohn for fruitful discussions. This work was supported by the Deutsche Forschungsgemeinschaft (Förderungsnummer: FO 258/1-2).

References

- [1] R. L. Smith and S. D. Collins, J. Appl. Phys. 71, R1 (1992).
- [2] V. Lehmann and H. Föll, J. Electrochem. Soc. 137, 653 (1990).
- [3] E. K. Propst and P. A. Kohl, J. Electrochem. Soc. 141, 1006 (1994).
- [4] P. Schmuki, J. Fraser, C. M. Vitus, M. J. Graham, and H. S. Isaacs, J. Electrochem. Soc. 143, 3316 (1996).
- [5] D. J. Lockwood, P. Schmuki, H. J. Labbe, and J. W. Fraser, Physica E 4, 102 (1999).
- [6] B. H. Erne, D. Vanmacekelbergh, and J. J. Kelly, Adv. Mater. 7, 739 (1995).
- [7] P. A. Kohl, C. Wolowodiuk, and F. W. Ostermayer, J. Electrochem. Soc., 130, 228 (1983).
- [8] T. Tkizawa, S. Aria, and M. Nakahara, Jpn. J. Appl. Phys. 33, L643 (1994).
- [9] J. v. d. Lagemaat, Thesis, Utrecht (1998).
- [10] S. Langa, J. Carstensen, M. Christophersen, H. Föll, and I. M. Tiginyanu, Appl. Phys. Lett. 78, 1074 (2001).
- [11] S. Langa, I. M. Tiginyanu, J. Carstensen, M. Christophersen, and H. Föll, J. Electrochem. Soc. Lett. 3, 514 (2000).
- [12] F. M. Ross, G. Oskam, P. C. Searson, J. M. Macaulay, and J. A. Liddle, Philos. Mag. A 75, 525 (1997).
- [13] J.-N. Chazalviel, R. B.Wehrspohn, and F. Ozanam, Mater. Sci. Eng. B 69-70, 1 (2000).

- [14] M. Christophersen, J. Carstensen, S. Rönnebeck, C. Jäger, W. Jäger, and H. Föll, J. Electrochem. Soc. 148, E-267 (2001).
- [15] S. Langa, J. Carstensen, M. Christophersen, I. Tiginyanu, and H. Föll, phys. stat. sol. (a) 197, 186 (2003) (these proceedings). [16] J. Carstensen, M. Christophersen, and H. Föll, Mater. Sci. Eng. B **69/70**, 23 (2000).
- [17] S. Langa, J. Carstensen, I. M. Tiginyanu, M. Christophersen, and H. Föll, Electrochem. Solid-State Lett. 4, G50 (2001).
- [18] H. Föll, J. Carstensen, S. Langa, M. Christophersen, and I. M. Tiginyanu, phys. stat. sol. (a) 197, 61 (2003) (these proceedings).