phys. stat. sol. (a) **197**, No. 1, 186–191 (2003) / **DOI** 10.1002/pssa.200306497

Voltage oscillations – an emergent property at high density pore growth

S. Langa[*, 1, 2], **J. Carstensen**[1], **M. Christophersen**[1], **I. M. Tiginyanu**[2], and **H. Föll**[1]

[1] Materials Science, Faculty of Engineering, University of Kiel, Kaiserstr. 2, 24143 Kiel, Germany
[2] Laboratory of Low-Dimensional Semiconductor Structures, Technical University of Moldova, Stefan cel Mare av., 168, MD-2004 Chisinau, Moldova

Received 11 March 2002, accepted 30 November 2002

PACS 81.05.Ea, 81.05.Rm, 82.45.Mp

The paper addresses macroscopic voltage oscillations observed during anodic etching of pores in n-InP [1] and GaP [2]. These oscillations always occur concurrently with the modulation of pore diameters which are synchronized on large areas of the samples. The observed macroscopic voltage oscillations represent a kind of pattern formation of the system at high pore density which does not occur when the pore density is low and no interaction between pores is present. The voltage oscillations obtained at different temperatures and current densities are analyzed in time and space, including Wavelet transformations. A model of these macroscopic voltage oscillations will be presented, which is based on the basic principles of the current burst model [3] developed for Si and which can be successfully applied to III–V compounds, too.

1 Introduction Pore formation by means of electrochemical etching is an effective and inexpensive method for obtaining novel structures in semiconductors [4, 5]. However, in order to take full advantage of the electrochemical methods, a good understanding of the processes, which are taking place at the semiconductor/electrolyte interface during pore formation, is required. The Si/electrolyte interface is by far the most investigated in this regard. The huge amount of experimental results available concerning porous Si triggered a wealth of models attempting to explain pore formation mechanisms in Si [6–10]. Most models are trying to explain only a limited number of pore features and morphologies, obtained at a limited region in parameter space. Therefore, most models are severely limited in their predictive power and cannot be easily applied to the peculiarities of pore etching in III–V compounds. On the other hand, the current burst model takes a broader approach and strives to understand all possible kinds of pore morphologies observed not only in Si, but also in other semiconductors, from a generalized point of view. The current burst model is essentially a generalization of a stochastic model used with some success to explain the current-voltage oscillations in the Si–HF system [11] and relies on interaction and correlations between essentially stochastic basic dissolution events termed "current bursts". In what follows, we will briefly develop a model explaining the voltage oscillation accompanied by pore diameter oscillations based on an extension of the current burst model to n-InP.

2 Experiment All experiments were performed in a Teflon electrochemical double cell using a four electrode configuration: working electrode (WE) and sense electrode (SE) – on the sample, counter electrode (CE) and reference electrode (RE) – in the electrolyte. The current was flowing through the

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[*] Corresponding author: e-mail: sla@tf.uni-kiel.de, Phone: +49 431 880-6181, Fax: +49 431 880-6178

0031-8965/03/19705-0186 $ 17.50+.50/0

WE-CE electrodes, whereas the voltage was measured between SE and RE. The double cell was used in order to obtain a good backside contact and thus the usual In-Ga/sample contact was replaced by an electrolyte/sample forward biased junction.

The potentiostat/galvanostat was custom designed for experiments at high current densities and can deliver up to 250 mA and ±80 V. The temperature of the electrolyte was kept constant at preset values by means of a Julabo F25 thermostat. The potentiostat/galvanostat and the thermostat were both computer controlled. Peristaltic pumps were used to pump the electrolyte continuously from the Teflon containers through both rooms of the electrochemical double cell.

In the experiments (100)- and (111)-oriented n-InP samples were used, with doping levels of $n = 3 \times 10^{17}$ cm^{-3} and $n = 10^{16}$ cm^{-3}, respectively. The area of the samples exposed to the electrolyte was 0.2 cm^2. Aqueous HCl electrolyte solutions at different concentrations were used.

3 Experimental observations of voltage oscillations

Up to now external voltage oscillations in the pore formation regime have been observed in n-InP and n-GaP. Evident correlation between voltage oscillations and pore diameter modulation in n-InP are presented in Ref. [1]. Examples of voltage oscillations in GaP and corresponding weak pore diameter modulations are presented in Fig. 1. Voltage oscillations have been observed in (100) as well as in (111) oriented samples. More than that, it seems that there is no difference between the oscillations observed on two differently oriented samples. The reason for this is that oscillations are always observed while the so called current line oriented (CLO) pores grow, whose main characteristic is that they do not have preferential crystallographic directions of growth but always grow perpendicular to the surface of the sample. It is therefore not surprising that the oscillations do not show peculiarities related to the crystallographic orientation of the samples either.

It is evident that the self induced external modulations of voltage and diameter are directly related to the mechanism of pore formation; investigations of the oscillations thus may lead to a better understanding of the pore formation mechanisms. The usual method of investigating oscillating signals is Fourier analysis, yielding a frequency spectrum, but giving no information about the changes of frequency with time. In contrast, by means of the so called Wavelet transformation (a kind of time-resolved Fourier transformation) [12], it is possible to investigate how the frequency spectrum is changing in time.

Figure 2a presents the voltage oscillations observed during galvanostatic etching of (100)-oriented n-InP; Fig. 2b shows the corresponding Wavelet transformation map. The *X* and *Y* axes in Fig. 2b show time and frequency, respectively. The positive direction of the *Y*-axes points towards the lower frequencies. The black region in the Wavelet map (see the white solid line) represents the dominant frequency of the signal which decreases in time from nearly 100 mHz at the beginning of the experiments to about

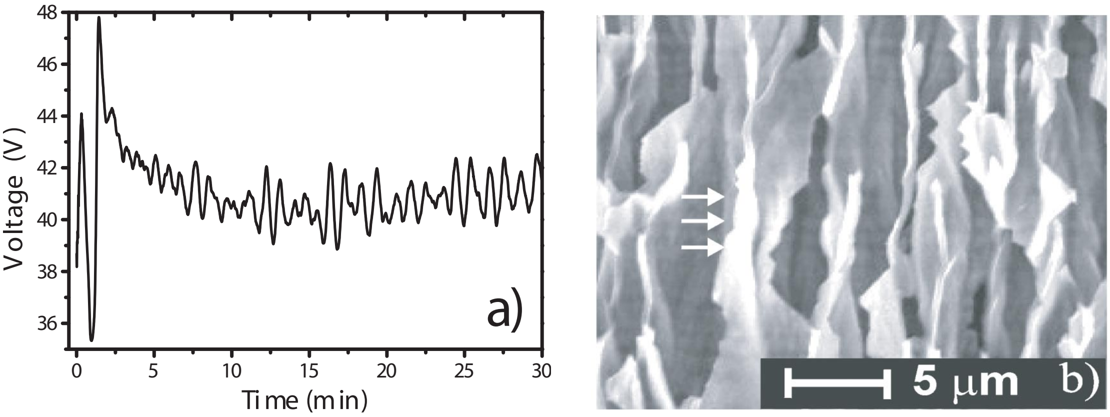

Fig. 1 a) Time dependence of self-induced voltage oscillations in GaP. b) SEM image in cross-section taken from a sample anodized galvanostatically (j_1 = 100 mA/cm^2 for 30 min). The arrows show weak synchronized pore diameter modulations.

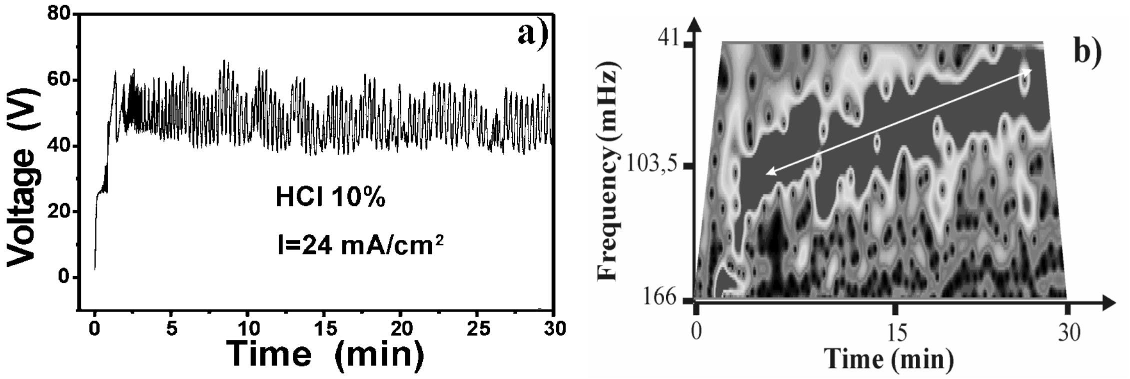

Fig. 2 Wavelet analysis of the oscillating signal. a) External voltage oscillations observed in (100) n-InP, $n = 3 \times 10^{17}$ cm^{-3}, in 10% HCl electrolyte solution, anodized at $j = 24$ mA/cm^2. b) The Wavelet transformation map. The white line shows the tendency of the dominant frequency in the signal.

40 mHz after 30 minutes of etching. A frequency decrease as the pores grow into the substrate is always observable, and its slope depends on the etching conditions, mainly on current density, temperature, electrolyte concentration, and doping level of the sample.

In order to see how the oscillation frequency depends on the etching parameters, experiments at different temperatures and external current densities have been performed. The results are presented in Fig. 3 and Fig. 4. First of all, from Figs. 3a and b it is clearly observed that the voltage oscillations are much more stable at low temperatures, and the amplitude as well as the stability of the signal is going down as the temperature is increased to $T = 20$ °C. More than that, at $j = 25$ mA/cm^2 and $T = 20$ °C, the oscillations practically disappear. Figure 4a shows how the mean oscillation frequency depends on temperature and current density.

Remarkably, the frequency of oscillations increases both by increasing the current density and by increasing the temperature of the electrolyte (Figs. 4a and b). More than that, the frequency increases linearly with the current density. This means that the charge consumed per oscillation cycle (see the slope of the curves in Fig. 4b) is constant and does not depend on the current density. However, the charge consumed per oscillation cycle is changing by increasing the temperature. Namely, at $T = 5$ °C the charge per cycle is 1.35 Q/cm^2, whereas at $T = 10$ °C the charge per cycle is 0.97 Q/cm^2.

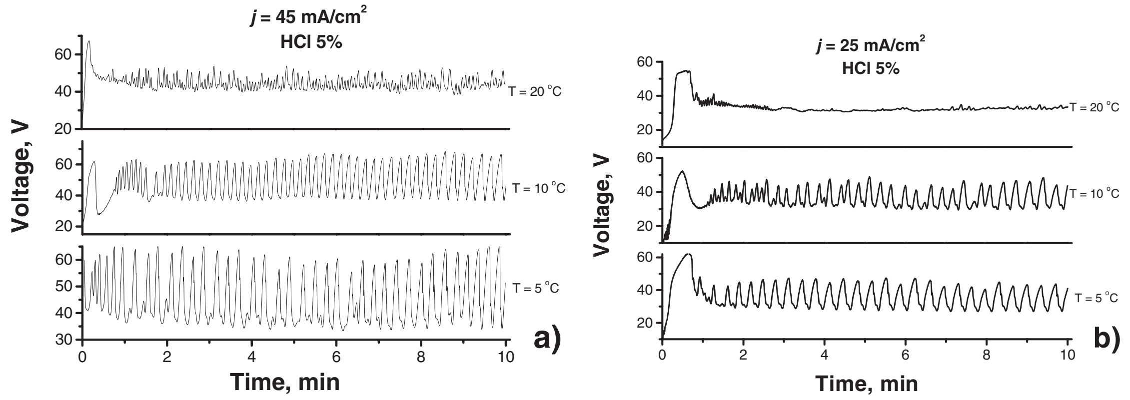

Fig. 3 (111) n-InP, $n = 3 \times 10^{16}$ cm^{-3}, in 5% HCl electrolyte solution and different temperatures. a) $j = 45$ mA/cm^2, b) $j = 25$ mA/cm^2.

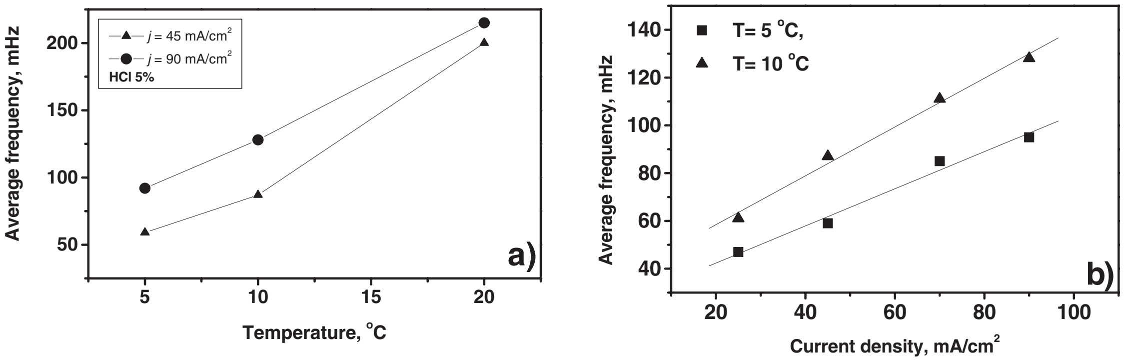

Fig. 4 Dependence of the oscillations frequency on the applied current density and temperature of the electrolyte. a) Oscillation frequency increases by increasing the temperature. b) Oscillation frequency increases linearly by increasing the current density.

4 Discussion and model The voltage and synchronized diameter oscillations can be understood in detail within the framework of the current burst model [3]. The essential features needed are

– Charge transfer across the interface is discontinuous in space and time and occurs via "current bursts" which have an intrinsically stochastic nature. A current burst may thus be considered to be a stochastic local current oscillator.

– Meso- and macropores are formed by current bursts that aggregated ("are correlated") in space due to an interaction in time between individual current bursts which is mediated by "aging" of free surfaces.

– Inside one pore the current bursts are to some extent synchronized (= correlated) in time due to an interaction in space and thus the current (and/or the current density) in a growing pore intrinsically oscillates.

Only the last point is relevant to voltage oscillations: the *current density* j_{por} at the pore tip has a strong tendency to oscillate. Oscillation in this context always means a stochastic oscillation, i.e. a falling and rising of the current with time only describable by an average frequency – not unlike waves hitting a beach. This immediately implies that a pore with a constant *diameter* must experience *current oscillations* while a pore with constant *current* must show *diameter oscillations*.

Understanding voltage oscillation is easiest by using an electrical equivalent circuit. This requires to assign an oscillating resistor $R_i(t)$ to each pore with an average value $\langle R_i \rangle$, mirroring the current oscillations. The total or external current then is given by switching all resistors/pores in parallel to the voltage/current source. Note that the voltage has always one value only at any given time, there is no such thing as local voltage variations (in contrast to the current which can vary in space and time).

Figure 5 presents a schematic representation of pores as oscillating resistors, where $R_i(t)$, I^i_{por} , j^i_{por}- are resistance, current and current density respectively at the tip of one pore; U_{ex}, I_{ex} – are externally implied current (constant) and measured voltage respectively; A_i is the surface of the pore tip; ρ_i and l_i are resist-

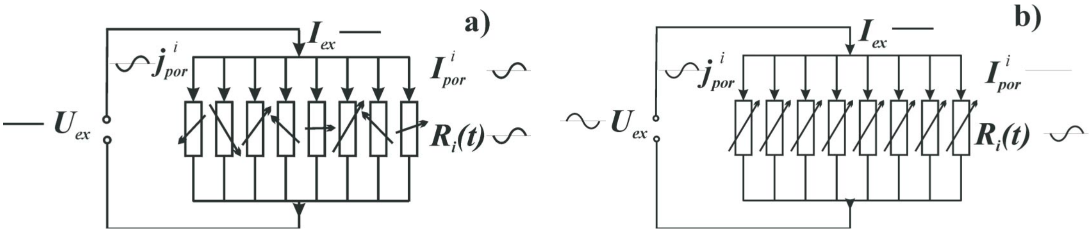

Fig. 5 A schematic representation of pores as oscillating resistors, for details see text.

ivity and length of the semiconductor electrolyte interface within one pore; thus

$$R_i\left(t\right)=\rho_i\,\frac{l_i}{A_i}\,.$$

As long as the phases of the oscillating resistors are uncorrelated, i.e. random, the total current will have a constant average value given by $\langle I\rangle = U_{\mathrm{ex}}/\langle R_i\rangle$, and the externally measured voltage U_{ex} will also be fairly constant (Fig. 5a). It is simple to realize that the pores will be able to correlate their oscillating phases only when they will interact or in other words will “feel” each other. A possible way of interaction between pores is via the space charge region which wraps around each of them. The interaction will be stronger and thus the synchronization easier, if the overlap is larger, i.e. if the pore density is high everything else being constant. High pore densities are relatively easy to achieve in n-InP (and GaP) but not in Si or GaAs.

In Si (and GaAs) it is not so easy to obtain very high pore densities (i.e. small diameters and small distances), and consequently synchronization between pores has never been observed until specific experiments guided by the InP findings were started [13]. In n-GaAs, self-induced diameter oscillations (resulting in chains of tetrahedra) of individual pores have been observed; they can be understood if oscillations in time of j^i_{por} occur as postulated. Again, due to the low density of pores in this material, no significant external voltage oscillations have been observed [13, 14].

Sufficient interaction between the pores under galvanostatic conditions will have an important impact on the morphological aspect of the porous layer: Pore growth now is correlated and synchronized domains appear, where the phases of the oscillating resistors (pores) and thus the diameter oscillations are correlated. However, under galvanostatic conditions, pore diameter modulations must be synchronized in just one *large* domain and always accompanied by voltage oscillations. This is so because the total current through a domain of any size would no longer average out to a constant value, but would also oscillate. The constant current condition enforced by the external current source (note the galvanostatic experiment) now can only be maintained if the voltage U_{ex} oscillates for the domain so that $I_{\mathrm{domain}} = \mathrm{const.} = N \cdot U_{\mathrm{ex}}(t)/R_i(t)$, where N denominates the number of pores in the domain.

But since there only can be *one* value of the voltage at any time at any location (and thus any resistor) of the sample, *all* domains must by synchronized, meaning there can only be *one* domain and $I_{\mathrm{domain}} = I_{\mathrm{ex}}$ (Fig. 5b). Voltage oscillations thus simply occur to suppress the current oscillations inherent in pore growth; they are needed to maintain galvanostatic conditions in synchronized pore arrays.

It is important to realize that despite a constant current, the current *density* at the pore tips still must oscillate. This necessitates an oscillation of the area A_{i} and thus of the diameter–whenever voltage oscillations are observable then synchronized pore diameter oscillations *must* occur, too. It is equally important to realize that if the current or the current density in a single pore oscillates for whatever reason, the above conclusions are unavoidable. While the current burst model gives a *specific* reason for current oscillations in a pore, *any* reason for current oscillations will be sufficient to trigger the voltage oscillations if the pores interact.

Space does not allow to discuss the frequency and its dependence on current density and temperature. Suffice it to mention that the data observed agree completely with qualitative predictions from the current burst model. In particular, the “conservation of charge” within one cycle, is an immediate consequence of current burst properties; increasing the temperature just reduces the difference in selective passivation of crystallographic planes. As a result no pronounced cavities with crystallographically oriented walls can form, i.e. a reduced intrinsic current oscillation for each pore is found, and thus the tendency for voltage oscillations is reduced leading to lower amplitudes of the externally measured voltage.

5 Conclusions Voltage oscillations observed in n-InP at constant high current densities can be explained by means of a simple model that only requires that the current density at each pore tip oscillates in time and that there is a next neighbor interaction between individual pores. The current burst model provides for the current density oscillations, while pore interaction is unavoidable if the density is large enough. The observed dependence of the oscillation frequency on current density and temperature is understandable within the model presented.

Acknowledgements This work was supported by the Deutsche Forschungsgemeinschaft (DFG) under the grants No 436 MOL 113/2/0-1 and FO 258/4-1.

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