Self-Induced Voltage Oscillations during Anodic Etching of n-InP and Possible Applications for Three-Dimensional Microstructures

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Voltage oscillations were observed during anodic etching of (100)-oriented n-InP substrates in an aqueous solution of HCl at high constant current density. Under certain conditions, the oscillations lead to a synchronous modulation of the diameters of pores on large areas of the samples which indicates a correlation between the phases of the oscillations in the pores. These self-induced diameter oscillations may be useful for three-dimensional microstructuring of n-InP and thus for the design and fabrication of new photonic materials.
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With the discovery of intense visible photoluminescence in porous Si,[1] electrochemical etching has become an important technological tool for controlling the properties of semiconductor materials. In particular, the formation of ordered arrays of parallel pores would allow one to fabricate two-dimensional (2D) photonic band-gap crystals.[2] Such photonic crystals have been previously produced using macroporous Si, the ordered distribution of pores being defined by photolithography.[3] At present considerable research efforts are focused on the design and preparation of three-dimensional (3D) photonic crystals. The pronounced anisotropy of III-V compounds[4] with respect to chemical etching makes them promising in this regard. In this paper we report on the possibility of 3D structured pores in n-InP linked to self-induced voltage oscillations observed during electrochemical etching of (100) oriented substrates under galvanostatic conditions.

Self-induced voltage oscillations at constant current, and current oscillations at constant voltage, are known and have been investigated in Si in the electropolishing regime.[5-10] However, oscillations under pore formation conditions have not been observed so far in Si. While this does not necessarily imply that no current oscillations are locally present, it does demand that possible local current oscillations at the pore tips as postulated by the current burst model are not phase correlated.[10-12] In n-InP, we show that the self-induced voltage oscillations result from an interaction of neighboring pores which may spread by percolation, and the pores grow in a correlated (or synchronized) fashion.

(100) oriented n-InP wafers cut from Czochralski grown Si-doped ingots were used in this work. Two types of wafers with free carrier concentrations $n_1 = 1.5 \times 10^{16}$ cm^{-3} and $n_2 = 3 \times 10^{17}$ cm^{-3} at 300 K were studied. The anodization was carried out for 10 min in an electrochemical double cell as described in Ref. 13. The hole supply is due to the reverse current of the junction and may involve avalanche break-through effects. 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 was kept constant at $T = 23°C$ with the help of a Julabo F25 thermostat.

The electrolyte was pumped in a continuous mode through both cells by means of peristaltic pumps. The equipment used in the experiments was computer controlled. The area of the sample exposed to the electrolyte was 0.12 cm^2. The anodic etching was carried out in 5% HCl aqueous electrolyte at the constant current density of 100 mA/cm^2. The morphology of the porous layers was analyzed with a scanning electron microscope (SEM).

In the etching experiments carried out under galvanostatic conditions an interesting behavior of the voltage measured between the n-InP sample with $n_1 = 1.5 \times 10^{16}$ cm^{-3} and a Pt electrode in the electrolyte (RES and REE)[13] was found. At the beginning of the anodization process, the voltage increased monotonously from 0 to ~60 V. After reaching the maximum value, the voltage started to oscillate, as illustrated in Fig. 1a. The cross-sectional SEM of a porous sample obtained under these etching conditions is shown in Fig. 1b. The diameter of the pores is strongly modulated, the observed local increases in the pore diameter are called pore "nodes". It is apparent that nodes of different pores are correlated as a function of depth by the "trajectories" connecting nodes immediately obvious to the eyes of the observer. A comparative analysis of Fig. 1a and b shows that each line of nodes is directly coupled to one voltage maximum. Consequently, there is a direct relation between the peaks seen on the voltage/time diagram (Fig. 1a) and the formation of pore nodes. The voltage maxima and the corresponding pore nodes are marked in Fig. 1a and b as "P1" ... "P22" (note that Fig. 1b shows only the nodes from "P4" to "P22"). It appears that the natural frequency of the system is ≈100 mHz and is fully expressed only at the end of the etching experiment (inset of Fig. 1b), while at the beginning an oscillation cycle is only seen occasionally.

The correlation between the voltage maxima and pore nodes offers the possibility to calculate the rate of pore growth. From Fig. 1a one can calculate the time interval between two voltage maxima, while from Fig. 1b it is possible to estimate the growth of the pores during the period involved.

Figure 2 shows that the rate of pore growth decreases from nearly 10 μm/min at the beginning to approximately 5 μm/min at the end of the etching experiment. The retardation of pore growth, despite the fact that the electrolyte was continuously pumped through the cell, may be caused by the increasingly difficult transport of chemical species from and to the pore tips by diffusion. At the beginning of the experiment (etching in the vicinity of the initial surface) more oxide dissolving species were available for the dissolution while in depth the number of oxide dissolving species provided by the process of diffusion decreases and, as a consequence, the dissolution rate goes down.

When anodizing n-InP samples with the higher electron concentration $n_2 = 3 \times 10^{17}$ cm^{-3}, voltage oscillations with nearly the same constant frequency of 100 mHz were also observed, as shown in Fig. 3a. The amplitude of the oscillations varies considerably
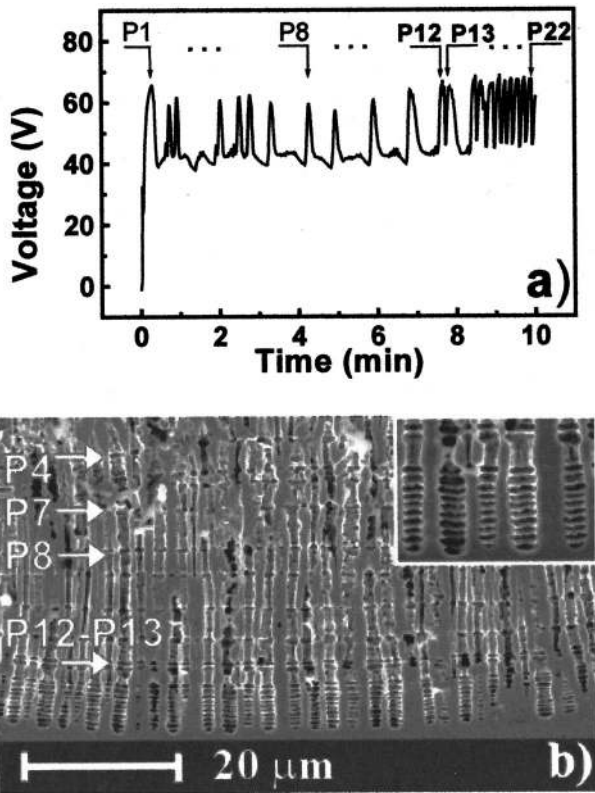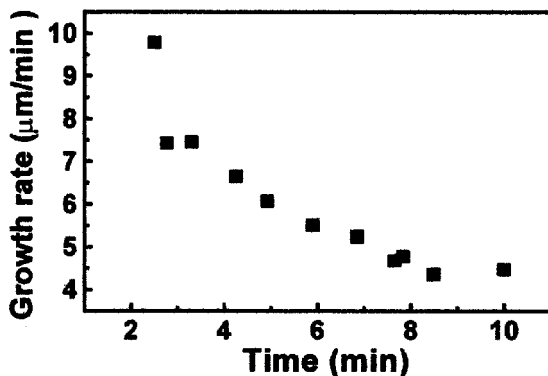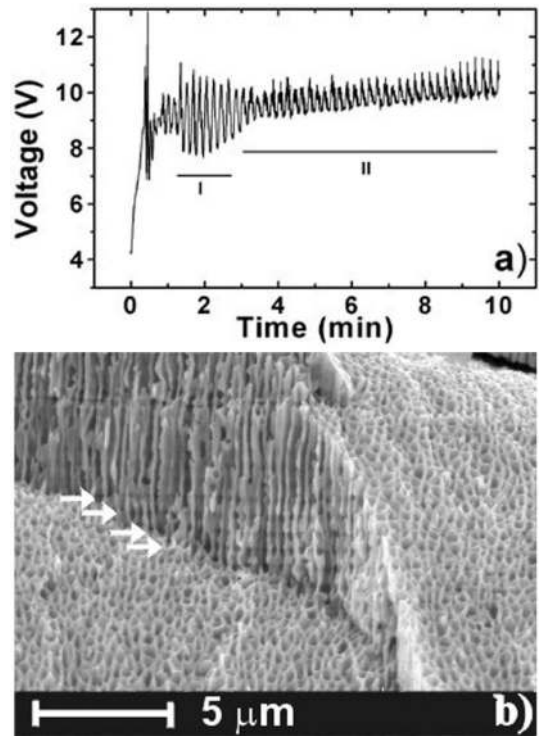
Figure 1. Data taken from an InP sample with $n_1 = 1.5 \times 10^{16}$ cm^{-3} anodized at a current density $j = 100$ mA/cm^2. (a) Voltage oscillations, (b) cross-sectional SEM of the sample; the inset is the magnification of the nodes at the bottom of the porous layer.

Figure 3. Data taken from an InP sample with $n_2 = 3 \times 10^{17}$ cm^{-3} anodized at a current density $j = 100$ mA/cm^2. (a) Voltage oscillations, (b) SEM image.

during the time of anodization. High amplitude voltage oscillations (region I in Fig. 3a) can be traced to a synchronous modulation of the pore diameters. In this case, the SEM images in cross section show weak horizontal trajectories, illustrated in Fig. 3b. Both horizontal trajectories (marked by arrows) in cross section and the morphology of the porous layer as a function of depth can be seen. As expected, the layer morphology does not depend much on the depth of the pores; the correlation between pores, however, seems to be lost at larger depths.

A detailed SEM from a cross section taken from an area corresponding to region II with smaller voltage amplitudes (Fig. 3a) is shown in Fig. 4. Only a small part of the pores shows synchronous modulation of their diameters under the etching conditions involved

and trajectories are not apparent. This does not necessarily indicate a total loss of synchronization between pores, however, because the correlation may either be too weak to be directly visible or it may only occur in regions not contained in the picture.

In contrast to current oscillations which may occur locally under constant voltage conditions at the pore tips (or, more generally, in arbitrarily large domains) but add up to a constant external current if the phases are distributed randomly, local voltage oscillations are not possible; the voltage along any path between the electrodes must be the same. Voltage oscillations under constant external current conditions may be understood if we assume that the current at the pore tip generally oscillates while the diameter stays nearly constant, *i.e.*, the current density oscillates too. Both assumptions, which we adopt in general without specifying the current oscillation mechanism at this point (which may be different from the oxide based Si

Figure 2. The rate of pore growth during the anodization of InP with $n_1 = 1.5 \times 10^{16}$ cm^{-3}.
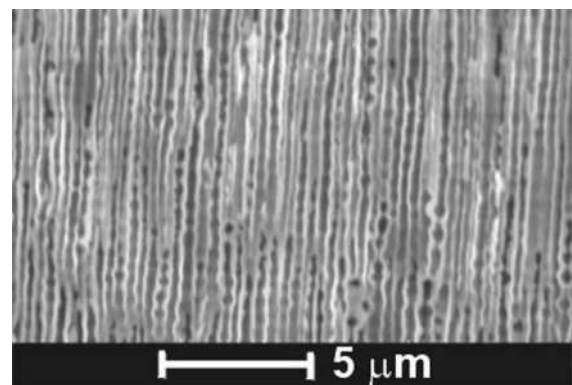
Figure 4. Cross-sectional SEM taken from an InP sample with $n_2 = 3 \times 10^{17}$ cm^{-3} anodized under conditions of small-amplitude voltage oscillations.

case), are general properties of the current burst model for Si. In equivalent circuit terms each pore may then be described by an oscillating resistor $R(t)$ with the average value $\langle R \rangle$; the total current is given by switching all resistors in parallel to the voltage/current source. As long as the phases of the oscillating resistors are uncorrelated, *i.e.*, random, the total current will have some constant average value given by $\langle I \rangle = U/\langle R \rangle$ (U = voltage).

Correlating or synchronizing the pores in some part of the sample surface (a domain) can only be done by correlating the phases of the oscillating resistors while $R(t)$ does not change (in this simple approximation). Because the total current through a domain now would no longer average out to a constant value, but would also oscillate, the constant current condition enforced by the external current source now can only be maintained if the voltage oscillates so that $I_{\mathrm{domain}} = \mathrm{const.} = NU(t)/R(t)$, where N is the number of pores in the domain. Because the current density must still oscillate, it is now required that the diameter oscillates.

This simple model explains all observations. Of course, in a better approximation one would have to describe a pore by a more complex equivalent circuit containing capacitors C; the displacement currents $I_{\mathrm{cap}} = C(dU/dt)$ must also be compensated by the voltage adjustments, causing some degree of feedback in the system. Nevertheless, the ultimate cause of the voltage oscillation are intrinsic current oscillation together with some phase coupling or correlation between pores.

This consideration, if turned around, gives a clue as to the interaction mechanism between neighboring pores. If, by random fluctuation of pore diameters, pores come close enough to experience some kind of influence on their states of dissolution, a feedback mechanism may be started that leads to phase coupling of the pore states and by percolation to the formation of a synchronized domain.

This domain, however, does not have to cover all of the specimen surface, *i.e.*, regions with uncorrelated pores may be also found. Moreover, because percolation does not have to take place at every cycle of the oscillation, especially if the general conditions are just around the percolation point of the system, somewhat irregular voltage oscillations as shown in Fig. 1a are possible. The frequency of the voltage oscillations in this model would be determined by the frequency of the current oscillations inherent in the current burst model.

It is interesting to discuss why macroscopic voltage oscillations so far have not been observed in Si while stable porous layers are developed. The reason may be sought in the high pore density which is not reachable in Si and allows for the necessary local synchronization between pores. At correspondingly high current densities on Si samples, only electropolishing occurs due to the higher stability of silicon oxide in comparison with the oxides in III-V materials.

In conclusion, anodic etching of n-InP under galvanostatic conditions at high current densities was found to be accompanied by self-induced voltage oscillations. The macroscopic voltage change results from current density oscillations occurring in single pores which are accompanied by oscillations of the diameter. The lateral interaction of pores via space charge layers most likely provides the phase coupling between pores necessary to obtain macroscopic oscillations. Without phase coupling, the macroscopic current, and thus the voltage, would be constant while the current through each pore may still oscillate. Behavior like that is predicted for Si pores by the so-called current burst model, but has not yet been directly observed. The results for InP may give a first indication that the current burst model may also be applicable to III-V compounds.

Given that the local oscillations at the pore tip may be phase correlated without external synchronization techniques, *e.g.*, by modulating the current with the oscillation frequency, three-dimensional microstructuring of the material should be fairly easy using photolithography to define the nucleation of the pores, and synchronization techniques in conjunction with optimized parameters. To explore the ramifications of this approach (*e.g.*, for the preparation of photonic crystals), further investigations into the oscillation and synchronization mechanisms are required.

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