Self-induced Oscillations in Si and Other Semiconductors

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This is the draft of this published paper:

H. Föll, J. Carstensen, and E. Foca, "Self-induced oscillations in Si and other semiconductors", *Int. J. Mat. Res.* **2006(7)** (2006)

Abstract

Some metals share an elusive property with Silicon (and other semiconductors): They may exhibit strong self-induced current oscillations during anodic dissolution in electrochemical experiments. While this feature, as well as related features concerning self-organization at reactive solid-liquid interfaces, is still not well understood, the so-called “current-burst model” (CBM) of the authors succeeded in reproducing many effects quantitatively that have been observed at the Si electrode. The CBM assumes that current flow through the electrode on a nm scale is inhomogeneous in both time and space; a single CB is a stochastic event. Current oscillations in time and space result from interactions in space or time of single CBs. The paper outlines the basics of the model and gives results of Monte Carlo simulations concerning stable and damped oscillations for the current and, as a new feature, for the voltage. With the CBM a kind of “nano”-electrochemistry is introduced; its strengths, weaknesses, and possible implications for other electrochemical phenomena and for other materials are briefly discussed.

1. Introduction

While it is safe to say that Silicon and Iron are the best investigated materials on this planet, it would be premature to conclude that all "simple" properties of these crystals are well understood. The definition of "simple" at this point means that the outcome of simple experiments can be predicted - at least qualitatively. This includes experiments that practically everybody can perform in no more than a kitchen environment. One experiment meeting these criteria would be to immerse a piece of (p-type) Si in a water–mouthwash mixture while applying an anodic voltage (positive pole on the Si) of a few Volts from a battery. Until a few years ago, nobody who did not have information from previous experiments could predict the outcome of this particular experiment. Moreover, the person doing the experiment would most likely be rather amazed of what he or she would have observed.

A scientifically trained person would then choose to conduct this experiment with well defined parameters: An electrolyte containing, e.g. HF at a certain concentration (since it is the fluorine contained in mouthwash that is the "active" ingredient in the experiment), a potentiostat or galvanostat supplying a constant voltage or current relative to some reference electrode, Si samples with various doping levels, crystal orientation and minority carrier lifetimes. The minority carrier generation, e.g., by illumination or breakdown would be controlled, the temperature would be kept constant - and so on. The experimenter might also choose to use other semiconductors, e.g. Ge or the III-V's, or even metals like Fe or Ni. In short: the experimenter would perform electrochemical experiments.

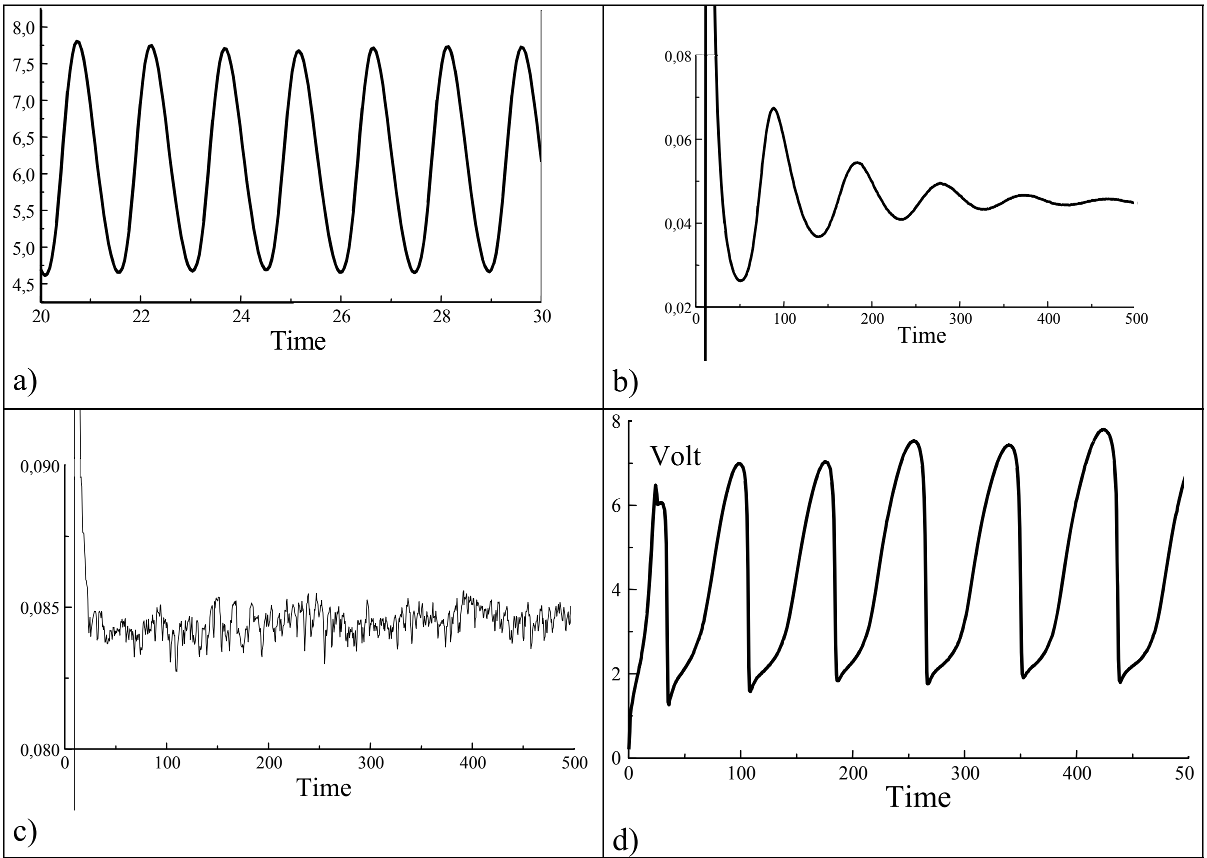
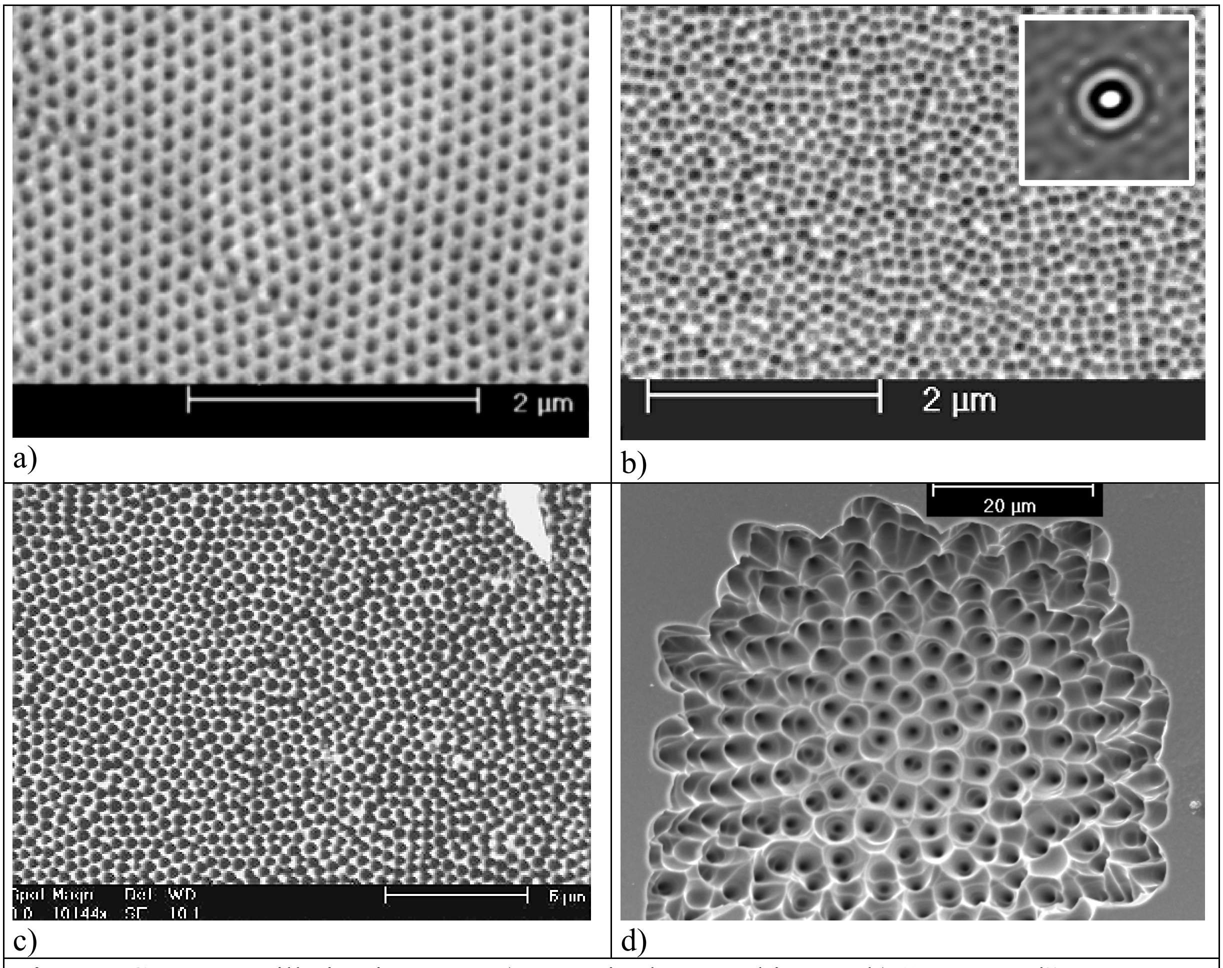


Fig. **1** Stable (a) and damped (b) current oscillations of a Si electrode held at constant voltage. In c) "colored noise" is shown; all current densities in mA/cm^2. d) illustrates voltage oscillations obtained for constant current conditions.

While this has been done for many years and a large body of data and understanding has been assembled, the outcome of certain experiments was still not predictable a few years ago. The keyword in this context is "pore etching in semiconductors"; but this will not be the focus of this paper (cf. the recent reviews and books [1 - 5] in this context). Here we concentrate on one particular topic: Self-induced current (or voltage) oscillations in time and space.

Our kitchen experiment, employing a constant (battery) voltage of, say, 6 V, with some luck would have produced a current that oscillates for hours in ways shown in Fig. **1**.

Similar behavior could be observed with some metal electrodes including Fe [6], and already Faraday some 170 years ago was aware of this effect [7]. If the experiment did not produce oscillations, chances were good that it produced a Si surface that showed interference colors since a thin (and transparent) layer of so-called microporous Si (we adopt here the IUPAC definition [8], where "micro" refers to pores with seizes up to 10 nm, "meso" to sizes between 10 nm and 50 nm, and "macro" to everything above 50 nm), [9 - 11] was formed in a still not well understood dissolution process. If we do the slightly more sophisticated experiments described above, we also may find self-induced current oscillations in space as shown in **Fig. 2**.

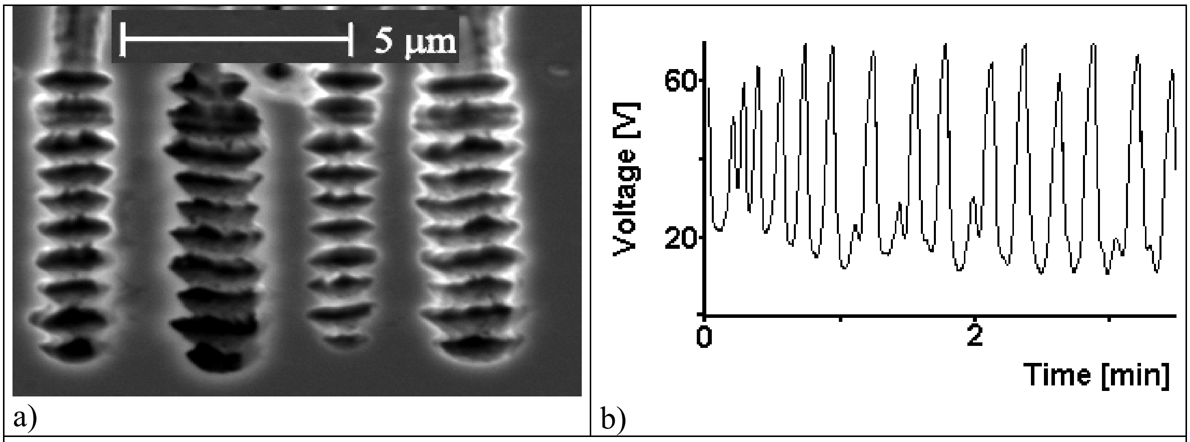


a) b) c) d)

Fig. 2 Current oscillation in space. a) Pore single crystal in InP. b) "Frustrated" pore structure in Si; the inset shows the autocorrelation functions. c) Short range ordering of pores in Si. d) Random pore arrangement in Ge within a pore domain.

Current oscillations in space simply mean that the local current on the specimen surface oscillates along any line – while the external current (and / or the voltage) might be perfectly constant. In two dimensions this implies that current maxima and minima are distributed on some kind of periodic lattice. Since a chemical process always accompanies current flow across a liquid-solid interface, and since this process under anodic conditions is invariably the dissolution of the sample, areas of large local current flow will simply lead to pore formation. **Fig. 2** shows SEM pictures of pore arrays with various and interesting degrees of lattice perfection that can be understood as the results of current oscillations in space. While **Fig. 2a)** shows a self-induced pore single crystal in InP and thus rather "good" current oscillations in space, **Fig. 2b)** appears to show a random pore arrangement in Si. However, the arrangement is far from being random! If we measure the probability of finding another pore at a certain distance and angle (via doing an autocorrelation analysis), we obtain the calculated autocorrelation function akin to a "diffraction" pattern in the inset. While there is no angular correlation for the next neighbors, the second next neighbors are arranged in a clear 12-fold symmetry. In other terms: What was obtained is a kind of "frustrated" crystal on a macroscale that "tries" to have the four-fold symmetry of the underlying {100} Si crystal and at the same time a hexagonal close-packed structure. While frustrated crystals are well known for spin arrangements in ferromagnetic materials or in the mineralogy of, e.g., silicates [12, 13], we believe that this pores-in-Si arrangement is the first example of such a structure on a macroscale – and an observation that most certainly would not have been predicted by scientists form "first" or even "second" principles alone. **Fig. 2c)** shows rather good short range order of pores in Si, and **Fig. 2d)** finally shows a truly random or amorphous arrangement of pores within a domain in Ge [5, 14], but it is clear that there is still some short-range order, and one might still be justified to some extent to use the term "current oscillations in space". In fact, there are even two major wavelengths: the average distance between the domains and the average distance between the pores in a domain.

To make the matter a bit more complicated, we may observe more types of self-induced system oscillations; **Fig. 3** shows examples. In **Fig. 3a)** we see diameter oscillations of pores in an InP single pore crystal that not only start and stop in a somewhat stochastic manner (i.e. without giving any intentional "signal" from the outside) and are obviously synchronized, but are accompanied by oscillations of the external voltage (under galvanostatic conditions); **Fig. 3c).**



a) b)

Fig. 3 a) Self-induced diameter oscillations in pores (organized in a single 2-dim. crystal in InP). b) Voltage oscillations always accompanying diameter oscillations.

The examples given could be augmented by many more instances of self-induced oscillations in other (semiconductor) materials, but are deemed sufficient to illustrate the point made in the beginning: These self-induced oscillations were not predictable, i.e. understood on any level until a few years ago – and much about this behavior is still not understood today. However, understanding these self-induced oscillations clearly will be at the root of a better understanding of all properties of the reactive current-carrying solid-liquid interface, and the remainder of this paper will report about the progress that has been made more recently.

2. Setting the Stage

In order to define the topic more precisely, it is necessary to point out that there are many oscillatory processes observed at an electrode (with or without current flowing), and that many of these processes are understood in some detail. We thus are neither dealing with variants of non-linear reaction kinetics with the Belousov-Zhabotinsky reaction as the paradigmatical examples [15, 16], nor with oscillations observed on non-reacting interfaces, i.e. during gas evolution [17, 18]. Moreover, we will also exclude oscillations mechanisms based on "mechanics", e.g. the stress-induced "periodic" flaking or blistering of e.g. anodic oxides [19, 20].

Here, we only treat the case of an anodic dissolution process that proceeds via the formation and concomitant dissolution of a (thin) oxide. While this is a certain restriction, it still leaves plenty of room for a plethora of experimental observations that does not fit into the categories excluded. Moreover, we will only look at the Si case. The reasons are simple: A Si electrode – in contrast to e.g. a Fe electrode – is perfectly homogeneous and free of defects like grain boundaries or dislocations that will always lead to averaged and thus "smeared-out" properties. Studying oscillatory behavior in its many expressions is therefore far easier in Si than in most other materials.

Fig. 1 already illustrated the major current and voltage oscillation phenomena of the Si electrode. In **Fig. 1b)** damped oscillations are shown; the related time constant τ_d for damping introduces a second characteristic time besides $\tau_{osc} = 1/f_{osc}$ (f_{osc} = frequency of oscillations). Both time constants show a clear dependence on the system variables: they increase linearly with the applied voltage, for example.

Fig. 1d) illustrates voltage oscillation obtained if a constant current is impressed on the system. Voltage oscillations do not follow straight-forward from current oscillations since the voltage is an extensive variable (there is the same voltage or potential at any point of arbitrarily large samples if we neglect lateral currents for the time being) while the current is intensive (it could have any value at a given point; only the sum of all local currents is a given for a given area). This is also born out by the experiment: The shape of the voltage oscillations is more involved, they are more difficult to keep stable, and they often show a run-away behavior; i.e. the average voltage keeps raising until some fuse blows.

Fig. 1d) shows a constant but noisy current, which, as a Fourier transform would show, has a spectral peak at just that frequency that would have been predicted from extrapolating f_{osc} from measured values to the parameter used in this experiment. This is a crucial observation that is illustrated in a more clear-cut way once more in **Fig. 4**. Shown is a measured current voltage characteristic of the Si -HF system that will show stable current oscillations at voltages above about 4 V. At certain points of this characteristic the otherwise constant voltage was sinusoidally modulated with a bunch of frequencies with identical and small amplitudes. The resulting current response was measured and plotted (via a FFT routine) as gray bars in the spectra shown in the inserts of **Fig. 4**. Significant current responses at frequencies not contained in the modulating signal (neither directly nor as sum or difference) were plotted as darker lines. Hard- and software had to be built for these experiments, and proper care must be taken to employ this FFT variant of otherwise well-known impedance spectroscopy without unduly disturbing the system to be characterized.

Considering the log scale of the response spectra, there is ample evidence for the presence of strong oscillatory behavior even in those parts of the characteristics where the external current is practically noise-free and constant. Moreover, whatever the oscillatory mechanism might be, it must have a strong non-linear component since frequencies not contained in the disturbance signal are very pronounced in the system answer right at the expected "resonance" frequency, i.e. the frequency extrapolated to the chosen voltage from the measured frequencies of stable oscillations at higher voltages.

There are many more experimental results from scores of researchers, providing, e.g., data about the surface roughness and its changes during an oscillation period [21], the average thickness of the oxide and its changes during an oscillation period [22, 23], the behavior of the capacitance, and, directly connected, the apparent oscillations of the dielectric constant of the oxide [24], or the amount of charge stored in the Si - SiO_2 interface during an oscillation period [25 - 27].

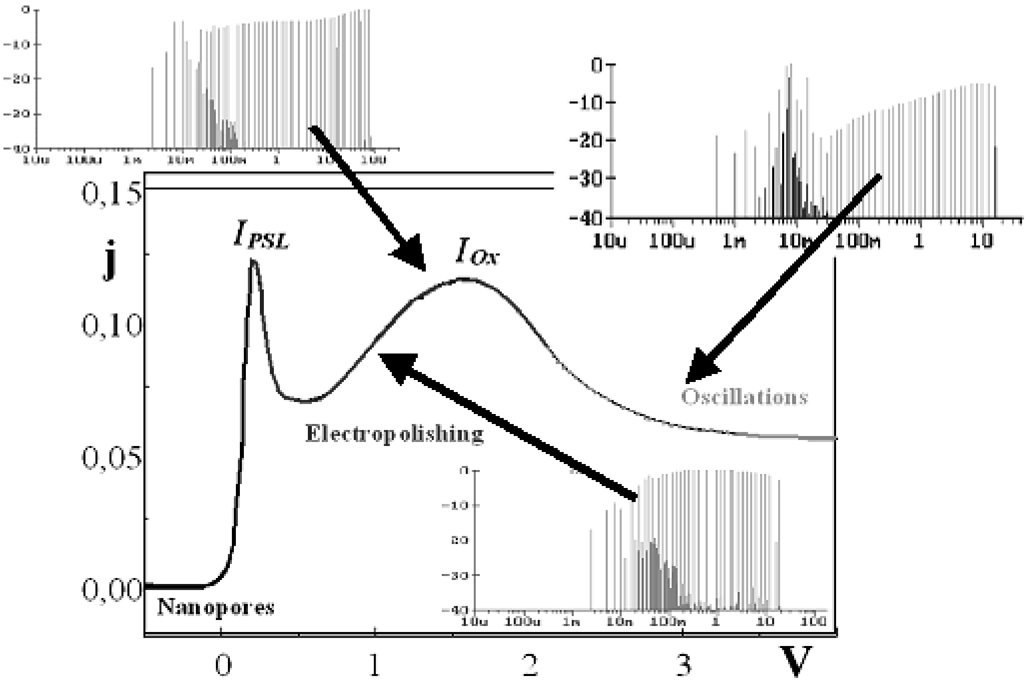


Fig. 4 Current response at three points of the *IV* characteristics of p-type Si at frequencies from about 1 mHz to 10 Hz or 100 Hz to harmonic disturbances of the voltage with identical amplitudes at the frequencies indicated by the bars. Surplus lines (producing darker areas) are strong non-linear responses. Note the (0 - -40) dB scale of the spectra.

There are also many qualitative models for this oscillatory behavior that were proposed on the base of specific experiments [28 - 32]. However, none of these models had much predictive powers, and from today’s understanding of the topic, most are obsolete. It were Chazalviel and Ozanam [33] who first produced a major insight into the problem. From a detailed analysis of experimental data they concluded that current oscillations are primarily local events, and that the external current would only oscillate if sufficiently many local oscillators were in phase or synchronized. Only parts or domains of the sample area might contain synchronized oscillators, and the domain sizes relative to the sample size together with their time development would determine the kind of oscillation – stable, damped, or colored noise.

This “top-down” model contained a certain stochastic element and provided a framework for future models that must be met. However, Chazalviel and Ozanam did not provide the necessary “bottom-up” parts, namely a mechanism for local oscillators, a mechanism for their synchronization, and conditions for the degree of synchronization possible in some relevant point in parameter space.

The first “bottom-up” model that could quantitatively reproduce many experimental data while conforming to the framework spelled out in [33], was the so-called “current burst model first introduced by the authors [3, 25, 34, 35] . In what follows, the basics of the current burst model will be introduced and discussed, followed by new results, a discussion of strengths and weaknesses, and an outlook.

3. The Current Burst Model

The current burst (CB) model introduces a kind of paradigm change to the usual way of envisioning current flow through a sold-liquid interface. Before it will be introduced, it is worthwhile to look at the ”old” paradigm and its consequences for modeling electrode oscillations. So far, current flow through the interface is pictured as continuous in space and time with changes that can be described by differential quotients. The proper description of the system dynamics than is by differential equations. Accordingly, in trying to understand self-induced electrode oscillations, much time was “wasted” in searching for some reaction kinetics, describable by differential equations, which could produce current oscillations. This is a difficult task as Frank pointed out already in 1978 [36], since oscillatory behavior could only be expected under a very restrictive set of conditions. What makes the problem even more difficult is the fact that finding suitable differential equations for oscillatory behavior would not even have been sufficient! Since unavoidable local differences in electrolyte flow, sample uniformity, contacts, etc. provide slightly different local conditions on the sample surface, slight differences in local oscillation frequencies would sooner or later lead to a loss of coherence and a randomizing of phases. At best a damped oscillation could be produced in this way. Experiments, on the other hand, showed stable oscillation going on for hours.

Even if one leaves the confines of differential equation modeling, the need for some synchronization mechanism that ensures matched phases across large distances (typically 1 cm or more) will persist. In retrospection, the need for a synchronization mechanism turns out to be the difficult part of modeling electrode oscillations.

The new paradigm of the current burst model is simple: Charge transfer (and thus current flow) through the solid liquid interface is localized in space and time and occurs in a stochastic manner. At least for the Si case, it is a logical consequence of the dissolution mechanism on an atomic or nm scale. From many measurements it is known that Si dissolution proceeds by three gross reactions: Direct dissolution ($Si + x\,h^+ - y\,e^- \Rightarrow Si^{4+}$), oxidation ($Si + 4h^+ + 2\,O^{2-} \Rightarrow SiO_2$), and oxide dissolution ($SiO_2 + 6HF \Rightarrow H_2SiF_6 + 2H_2O$). Logic dictates that on an atomic scale these three processes cannot occur on exactly the same place at exactly the same time. However, on slightly large scales everything could average out to smooth behavior. The current burst model, however, simply assumes that the three basic processes must still be treated separately on a somewhat larger, i.e. nanometer scale. If we envision a small area on the sample surface (about 1 nm^2; a “pixel” for the Monte Carlo calculations described later) that at $t = t_0$ is covered with a thin oxide (thickness d; typically a few nm), and held at the external voltage U_{ex}, we have the following chain of events:

i) The oxide carries the field strength $E_0 = d_0/U_{ex}$ which is too small to induce current flow. The oxide dissolves at a constant rate more or less given by the HF concentration, the temperature T and the oxide “quality”; the field strength thus increases about linearly with time.

ii) At some time t_1 the oxide will suffer field strength dependent “ionic breakdown” that produces a nm-sized “channel” allowing oxygen and / or OH ions to reach the Si. Rapid oxidation occurs within some nm around the channel. The breakdown event is stochastic in nature, i.e. it is described by a probability function as shown in **Fig. 5a).** Exactly how this ionic breakdown occurs is somewhat unclear, but details are not necessary for modeling. It may well be, for example, that an electronic breakdown akin to the well-known breakdown of gate oxides in MOS transistors occurs first, and that the structural damage produced by such a breakdown triggers the ionic breakdown. In fact, for quantitative modeling we use the known breakdown parameters of an electronic breakdown.

iii) A small current yet a large current density now flows locally, producing an oxide "bump". Since the Si in SiO_2 occupies about twice the volume as compared to the Si crystal, this oxide bump is felt at both interfaces: Si – SiO_2, and SiO_2 – electrolyte as shown in **Fig. 5b).** The current flow through the ion-conducting channel spreads out in the Si and the electrolyte and produces sizeable and, given the conductivities of the Si and the electrolyte, easily calculated ohmic losses. The concomitant local voltage drop around an active current burst thus lowers the probability for the nucleation of other current bursts in its neighborhood in a predictable way.

iv) During the growth of the oxide bump, the field strength drops and finally becomes too small to support current flow. The channel "closes" and current flow stops; again in a stochastic way determined by a probability function. The hysteresis contained in the choice of the probability functions is necessary and expected: it needs a larger field strength to induce current flow than to stop it – as in any "arcing" or plasma discharge device.

v) Some time has passed and the pixel now is "at rest". Its oxide thickness has a certain computable value d_1 and carries a field strength $E_0 = d_1/U_{ex}$. A full cycle has closed and we are back at the beginning, just with a somewhat altered value of the oxide thickness.

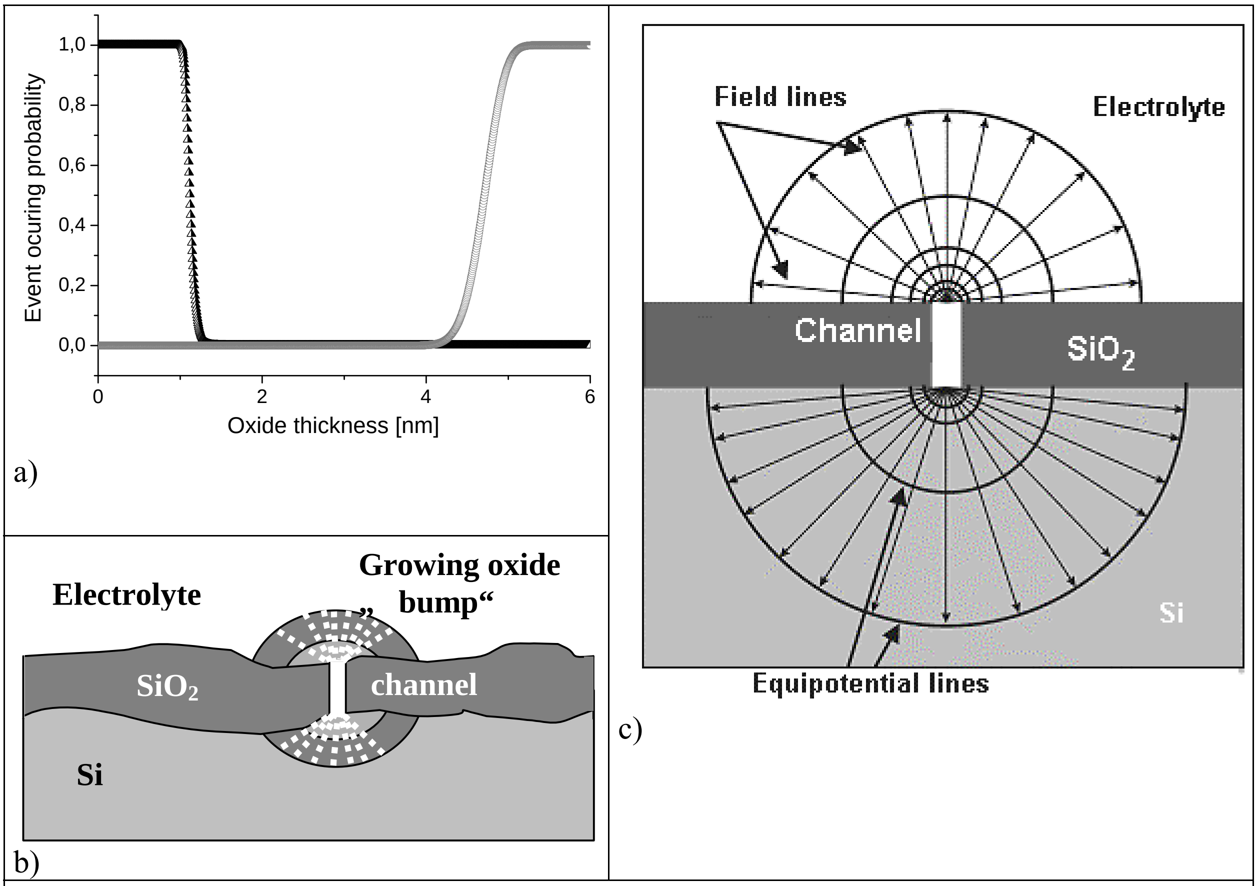


Fig. 5 a) Probability functions for an ionic breakdown to start (triangles) and to stop (circles). b) Formation of an oxide bump (very schematic). Note that the oxide formed needs to be porous to some extent to allow current flow. c) Semi sphere approximation to field distribution around a current burst.

The chain of events described above can be "easily" implemented in the form of a Monte Carlo program. The dissolution rates of the oxide, the oxide formation rate for a certain current, the conductivities and resulting ohmic losses etc. are well known (up to a point), and suitable values can be selected. The only ingredients not known with sufficient precision are the two probability functions for the opening and closing of active channels; these two functions are fundamental assumptions of the model. Everything else must be seen as approximations to known properties. In the context of the well-known electric breakdown of "dry" oxides the two probability functions for ionic breakdown shown in **Fig. 5a**), while still not justified from first principles, appear at least to be rather reasonable.

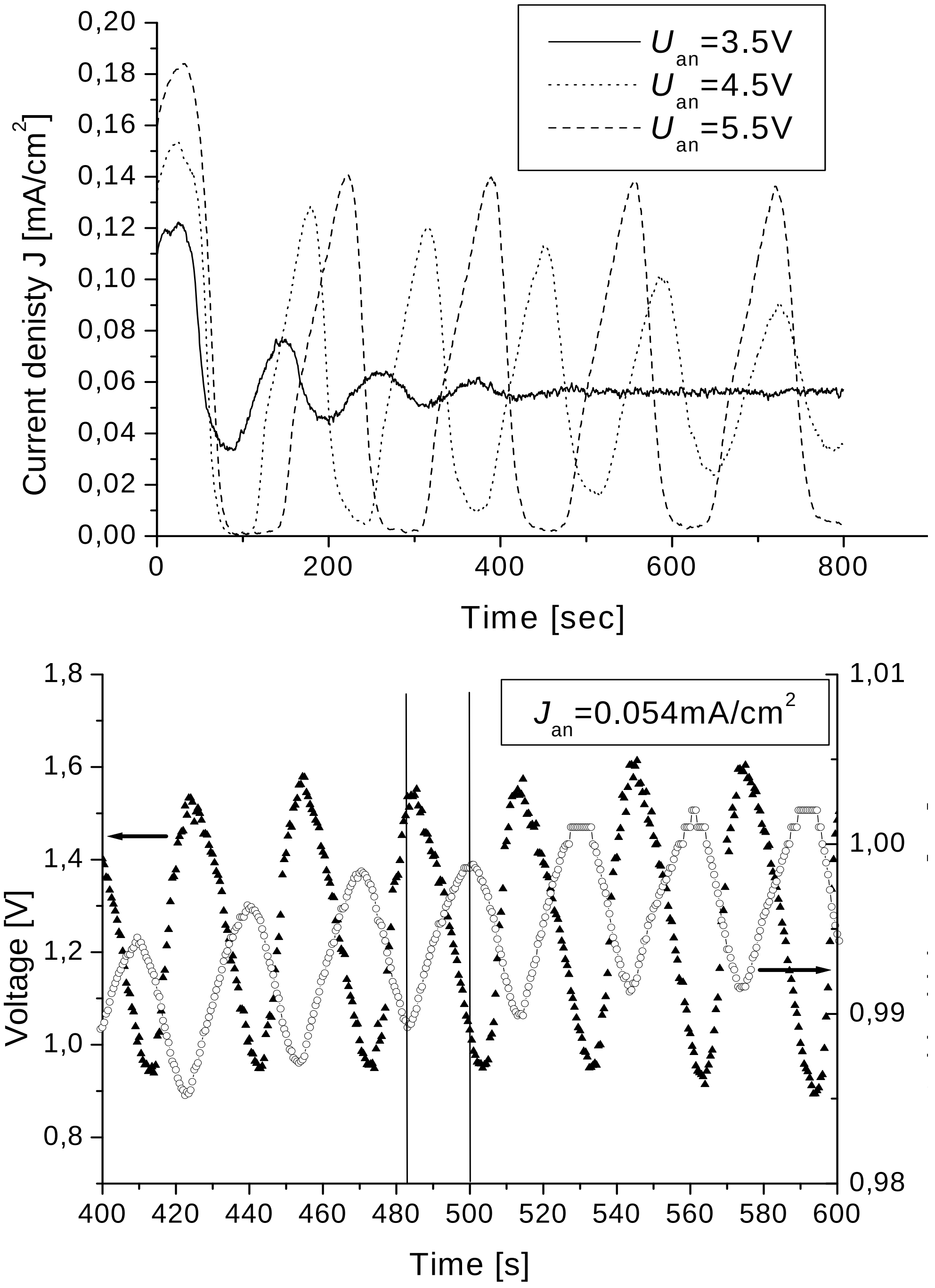


Fig. 6 Simulated current oscillations (up) for three voltages showing increasing damping with decreasing voltage and simulated voltage oscillations (down) and concomitant oxide thickness oscillations.

An implementation of the model for a sample size of (100 x 100) nm does indeed reproduce all observations with respect to current and / or voltage oscillations; **Fig 6** gives some examples. Before discussing these results in more detail, a puzzle of sorts needs to be addressed: While current bursts provided the needed local (stochastic and digital on/off) oscillators with some average frequency, no synchronization mechanism was introduced in the model. Nevertheless, stable oscillations can be obtained, which are only possible if the phases of these local oscillators stay synchronized over many cycles. The CB model thus must have some intrinsic synchronization mechanism that is contained in the description above, but not directly apparent.

A more detailed inspection reveals that synchronization, i.e. a *correlation* between current bursts *in time*, will occur as soon as individual current bursts *interact in space*. This is easily visualized: If, for example, a new current burst nucleates sufficiently close to an older one, i.e. if it "feels" its neighbors, it will turn itself off somewhat earlier than in isolation because it needs to produce less oxide before the critical field strength is reached – it simply uses some of the oxide produced by the neighbors. Its turning-off time thus is somewhat earlier, i.e. closer to the turning off time of its neighbors. More generally speaking, an interaction in space produces a correlation in time, and this correlation may spread by percolation and mature into a more or less pronounced synchronization of a certain area of the sample – the domains postulated by Chazalviel and Ozanam [33] are quite naturally and intrinsically produced.

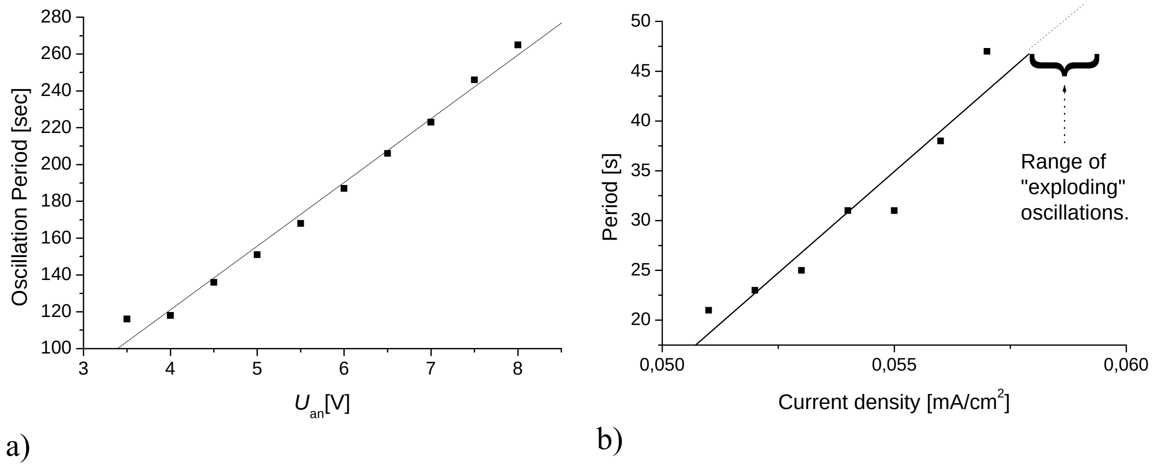
Synchronization thus is indeed an intrinsic feature of the current burst model. The degree of synchronization, the size of the synchronized domains, and the development in time result from the input parameters without any further assumptions or modifications of the model. This is a very special feature of the current burst model not found in other models, e.g. in the model of Lewerenz, [37, 38], which has emerged during the last few years and is presently the only competing quantitative model for oscillation phenomena on electrodes.

On a somewhat more sophisticated level of model evaluation, it becomes clear that besides a locally acting "driving" force for synchronization, a de-synchronizing "force" is also needed. Only the interplay between synchronization and de-synchronizing can produce stable "mixed" states; if there would be only synchronization, the system would tend to be either fully synchronized, or not at all. The de-synchronizing "force", it turns out, is simply the voltage drop in the environment of an active current burst, decreasing the likelihood that close neighbors will appear and interact and thus provide synchronization.

4. Results

While current oscillations could be obtained already in the earlier version of the current burst model, some other properties, in particular voltage oscillations, proved to be harder to obtain. Meanwhile, however, after reprogramming the model for more powerful hardware, most observed properties can now be modeled quantitatively without adjusting parameters other then the probability functions for CB turn-on and turn-off. In what follows some results will be presented including new results that have not been published before.

Fig. 7 shows some quantitative data concerning the two essential time constants $\tau_{\mathrm{osc}} = 1/f_{\mathrm{osc}}$ for the oscillation frequency and τ_{d} for the damping as extracted from many simulation runs as a function of the applied voltage. The agreement with experimental values is excellent; but will not be presented here. Damping simply results form insufficient synchronization by current burst interaction. Oscillations then are simply a remnant of initially identical starting conditions; and the damping time constant describes how long it takes the system to "forget" its initialization.



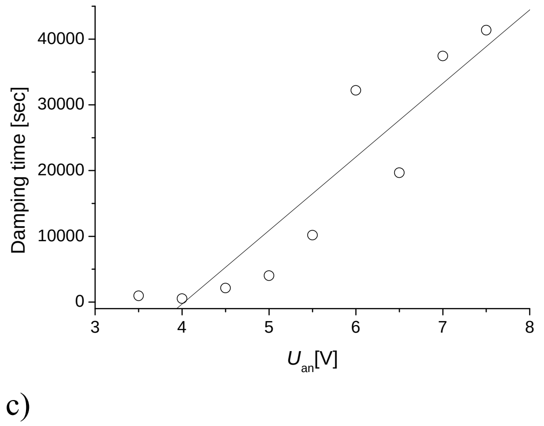
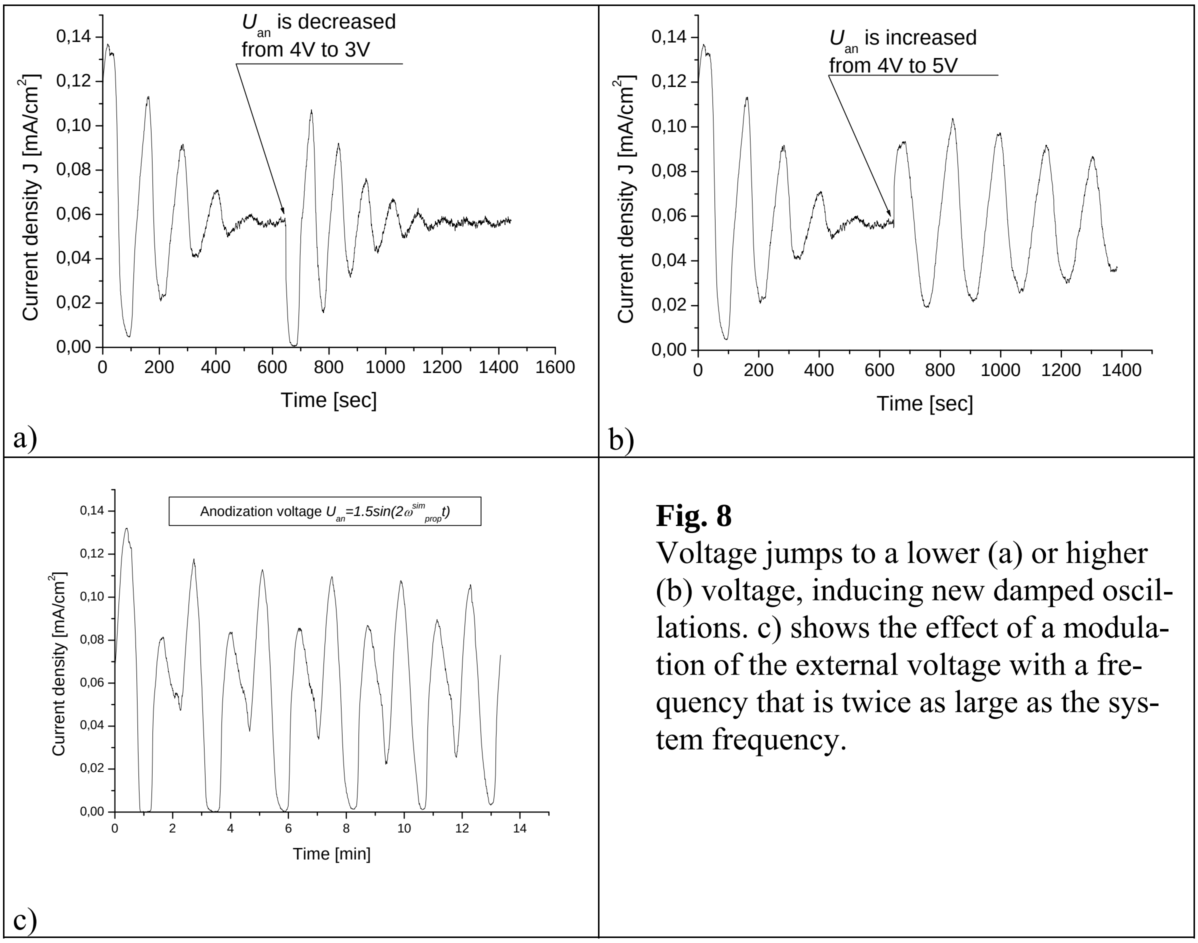


Fig. 7
Oscillation time constant for current oscillations (a) and voltage oscillations (b) as well as the damping time constant for current oscillations calculated as a function of the applied voltage.

Fig. **8** shows the system response to external disturbances. In **Fig**. **8a)** and **b)** a voltage jump to a lower or higher voltage, respectively, is implemented: again showing expected results fully compatible with experiments.

Following an oscillation cycle frame by frame produced movies that visualize directly the switch-over from randomness to synchronization, the smoothness or roughness of the surface and interface, the formation of (small) domains etc. **Fig. 9** gives some still frames of relevant events. While movies cannot be published in print, they can be viewed in the internet [39]. From those “movies” quantitative data can be extracted, e.g. with regard to the roughness of the interfaces, the (average) oxide thickness, and the capacity of the system – parameters that also can be measured. However, care has to be taken with respect to global measurements. In-situ ellipsometry, for example, used to measure the average oxide thickness provides only $<d>$, the mean thickness of the oxide. If that value is used to calculate the capacitance C as proportional to $\varepsilon_r/<d>$ (with ε_r = dielectric constant of the oxide) and compared to direct measurements, it follows that the dielectric constant of the oxide layer must oscillate, too. This, however, is an artifact of the measurement technique. If instead of $1/<d>$ the proper value $<1/d>$ is used – which is easily obtained from the model – the measured capacitance is fully reproduced for a constant ε_r.

It goes without saying that damped oscillations, colored noise, “hidden” oscillations and so on emerge directly form the model – they simply reflect various degrees of synchronization and percolation. Much more could be that, in particular with respect to other semiconductors, extensions of the model to pore formation, or extension to other material that dissolve while forming an oxide, e.g. Fe. We will, however, rather turn to a discussion of the limitations of the CB model and to some possible generalizations.



a)

b)

c)

Fig. 8
Voltage jumps to a lower (a) or higher (b) voltage, inducing new damped oscillations. c) shows the effect of a modulation of the external voltage with a frequency that is twice as large as the system frequency.

5. Discussion and Outlook

While the current burst model was the only quantitative “bottom-up” model for electrode oscillations at its conception, one competing model has emerged in the meantime [37, 38]. While the mathematical description of this “Grzanna, Jungblut, Lewerenz” (GJL) model (Markhow chains) appears to be completely different from that of the CB model at a first glance, the two models have nevertheless much in common. Both describe oscillations as emergent phenomena of essentially stochastic events on a nanoscale, and both use the local field strength as the driving force. However, the GJL model is to some extent an “inverse” version of the current burst model: The decisive feature is not the localized rapid growth of oxide, but the localized rapid (field and/or mechanical stress assisted) dissolution. Quantitative analysis can reproduce all kinds of current oscillations rather well, but not (yet) voltage oscillations and some other features. The GJL model also needs more assumptions (e.g. effects related to stress in the oxide) than the CB model, and has no intrinsic synchronization mechanism. Synchronization must be introduced by an adjustable parameter.

Time will tell which model is closer to the truth. Both models are far from describing the full complexity of the solid-liquid interface, and some of the limitations and open questions for the current burst model will be addressed in the remainder of this paper.

So far, the current burst model is restricted to rather small current densities and therefore HF concentrations, while oscillations are observed (in fact more easily) at high current densities, too. If the program is run for larger HF concentrations, the agreement with experimental values becomes less convincing. One simple reason fore this can be found in the underlying assumption that all current produces oxide. However, for large HF concentrations and large currents, the mean oxide thickness decreases, and this must by necessity start to produce some current from electrons tunneling through the oxide with oxygen production, and not SiO_2 production, as the accompanying reaction. Since not much is known about this process, and since it is highly non-linear in nature, it is not straightforward to implement electron tunneling and oxygen production into the Monte Carlo program.

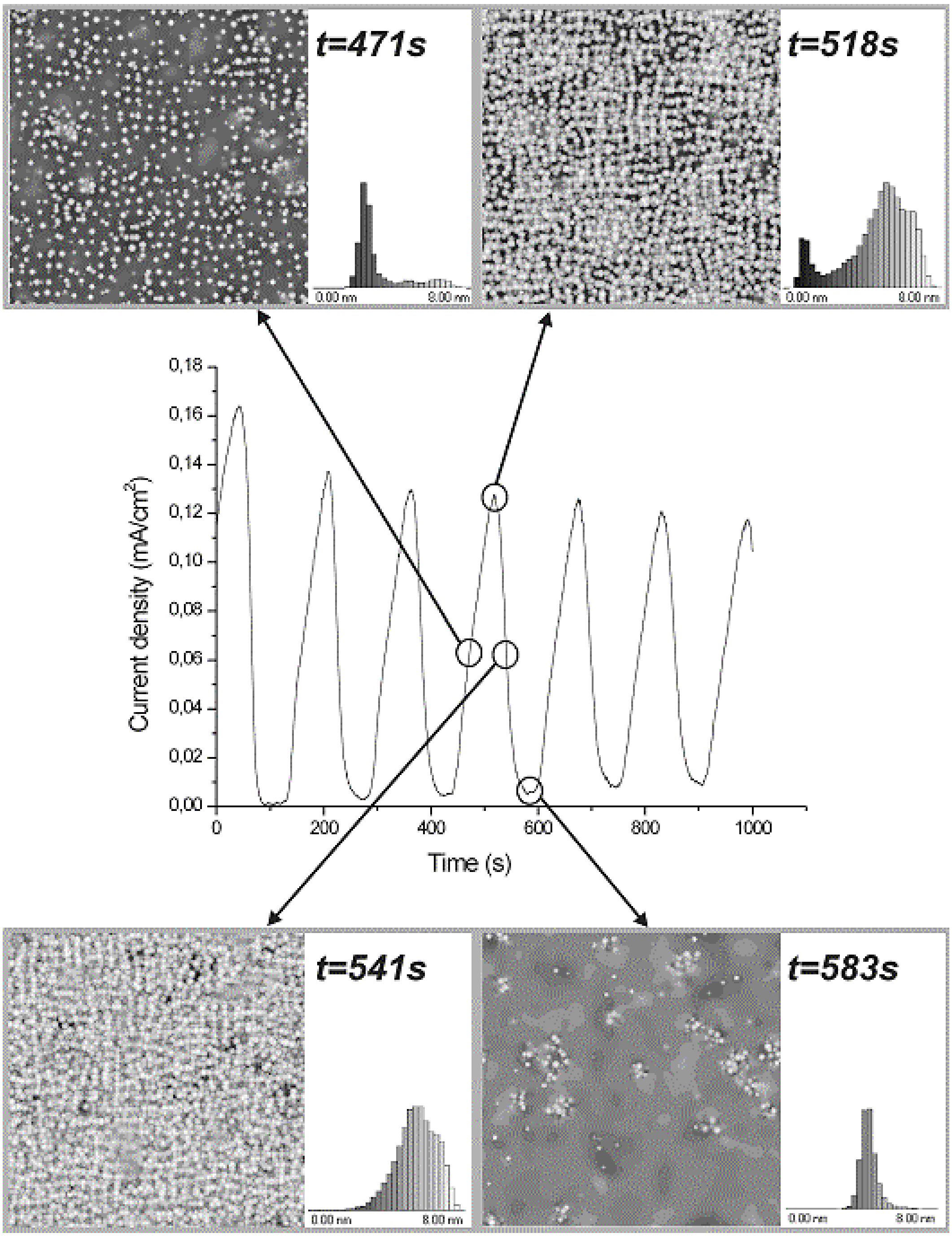


Fig. 9 "Still" frames of a simulation sequence during one current oscillation. The process starts with nucleation of single CBs (*t = 471 s; white spots*) which will synchronize in time to some extent (*t = 518 s*), and stop producing oxide (*t = 541 s*). Whenever the dissolution process dominates (*t = 583 s*) domains with the same oxide thickness form.

The oxide produced will be under mechanical stress (in addition to the electrical stress), and around an oxide thickness of about 12 nm the stress is so high that "something happens”. This might be crack formation, or flaking off, or something else. Stress, however is not directly considered in the current burst model; indirectly, however, it may be contained in the probability functions for turning a current burst on or off. If stress has more effects, and if these effects produce the effects claimed in the LJG model, remains to be seen.

There is no doubt that the oxide layer experiences rather high field strength all the time. If that leads to altered properties, e.g. accelerated diffusion of oxygen, is an open point. In any case, if oxygen diffusion would increase very rapidly for field strengths above a certain limit, the resulting effect would simply describe a current burst in other words. Again, some possible effects may already be contained in the probability functions. Other possibilities, like rapidly increasing dissolution rates with (high) field strength, would actually help to produce a local channel and thus a current burst.

There are certainly more possible effects than the ones mentioned above. Nevertheless, the many quantitatively correct results obtained so far justify the belief that the current burst model can be extrapolated to more involved situations, too.

If we look at the basic assumptions of the current burst model, the most crucial are the two probability functions for starting or stopping an active burst, and the assumption of an ionic breakdown allowing rapid transport of reactants and actants locally. While the general choice of the probability functions can and has been justified before, it turns out that their detailed shape can be crucial for the proper working of the model. As an example, while current oscillations can be modeled accurately with one set of probability functions, the modeling of voltage oscillation under otherwise comparable conditions demands a somewhat different set of functions. While this was baffling if not disappointing in the beginning, closer examination revealed that this actually should be so. The probability functions essentially represent structural properties of the oxide, and upon reflecting oxide formation conditions at constant current or constant voltage, it becomes clear that the properties of the oxides obtained must be somewhat different and thus their probability functions, too. However, at present, these functions must be seen as the adjustable and not fully justified parameters of the model.

Finally, the ionic breakdown and the directly correlated formation of an oxide bump may be seen as a model part that has some arbitrariness to it. While this is certainly true, recent experiments on the anodic oxidation of Si [40] may be viewed as a direct confirmation of the ionic breakdown/oxide bump concept. During anodic oxidation under certain conditions, a large voltage drives a current through a Si-electrolyte system where the only possible reaction is oxidation and oxygen formation – there is no HF and thus no oxide dissolution. Within the current burst model one would expect that oxide bumps are formed, which however cannot dissolve, but pile up (with new bumps forming because weak parts between bumps may mechanically crack, admitting electrolyte to the interface. Be that as it may, pictures at high magnifications of the oxide layer invariably show it to consists of lumps or sphere-shaped bumps loosely connected (**Fig. 10**). The current burst model explains this rather neatly; no other suggestion for an alternative formation mechanism has been made as of now.

Finally, some speculations of possible extensions of the current burst model shall be made. First, it is clear that it can be immediately used for any dissolution process proceeding via oxide formation and oxide dissolution – as long as a closed oxide layer is encountered. Electrode oscillations are then an intrinsic property of this three stage process, emerging as soon as synchronization becomes strong enough. We don’t hesitate to claim that many oscillations phenomena observed on e.g. metal electrodes will find their basic explanation here.

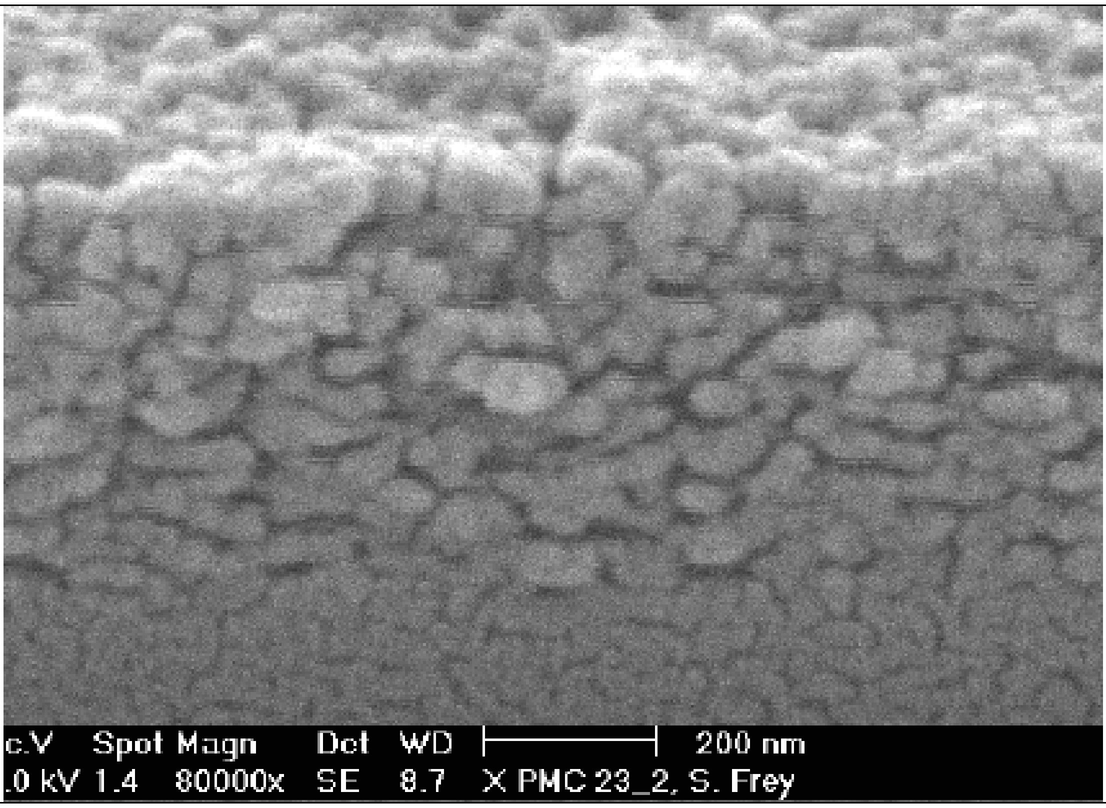


Fig. 10 Oxide “bumps” produced during anodic oxidation of Si.

Synchronization or *correlation* of CBs *in time* emerged from an *interaction* of current bursts *in space*. It is tempting to ask if this statement can be reversed. Interaction in time simply means that the nucleation probability of a current burst in a given pixel depends to some extent on how long ago another current burst was found in this pixel. Indeed, if one makes such an assumption, correlations in space may occur. Much simplified: if the interaction is positive, i.e. it is more likely to nucleate a current burst if there has been another one shortly before, a qualitative analysis shows that current bursts now may correlate in space, i.e. cluster, and thus produce oscillations of the current in space expressed as macropores. If the interaction is negative, meaning that it is less likely to nucleate a current burst on the side of recently decreased old one, we will automatically obtain micropores.

If we assume that during the growth of macropores each pore contains one synchronized domain of CBs, a direct interaction of these buried domains with each other is impossible. In each pore the current oscillates, but since the phases are random, the total current can be easily kept constant. However, as soon as the pore spacing becomes so small that the space charge regions around individual pores start to overlap, the pores will “feel” each other and synchronization between the oscillating domains at the tips of individual pores may occur. This leads to an interesting new situation: if the external current is kept constant, synchronized current oscillations are not possible – instead the voltage must now oscillate, and it must do this everywhere on the sample. This leaves only two possibilities. The phases of the current oscillations are either completely random, or completely synchronized all over the sample. The resulting large voltage oscillation amplitudes induce some diameter oscillations of the pores; and that is what has been shown in **Fig.** 3.

Finally, if we assume that any “passive” layers on electrodes are overcome by current bursts as soon as the field strength exceeds some limit, many phenomena encountered during pore growth in semiconductors can be understood in a qualitative way. This is particularly true for the passivating hydrogen layer always covering Si surfaces exposed to acids that are not carrying currents. A current burst then will be more complicated, first dissolving Si directly, followed by oxidation producing a bump and finally oxide dissolution. While quantitative details of this mechanism still need to be worked out, its semi quantitative version has been successfully used to elucidate properties of pore growth in semiconductors.

6. Summary

The current burst model combines elements of semiconductor physics, electrochemistry, and stochastic physics to a new paradigm of nano-electrochemistry. The basic assumption is that current flow through a reactive solid-liquid interface is inhomogeneous in time and (nanometer) space, i.e. that it proceeds via current bursts. The only basic assumptions of the CB model are the probability functions for a CB to start and to stop. Using this model it was possible to fully understand and to simulate quantitatively the oscillatory behavior of Si electrodes in a HF containing electrolyte. Oscillatory phenomena, are it current oscillations in time or space (i.e. pores), voltage oscillations in time, or more complicated behavior, essentially are an emergent property of interactions between CBs. Interactions in space produce correlations in time; if the degree of correlations or synchronization is large enough, macroscopic oscillations result. Monte Carlo simulations for Si dissolution via oxide formation could reproduce many experimental observations in great detail. Interactions in time will produce current oscillations in space, i.e. pores; but quantitative details need yet to be worked out.

Extension of the CB model to materials other then Si or to chemical processes more complex than oxide formation / dissolution are straight forward, but not yet implemented. Nevertheless, there I little doubt that the CB model can also explain oscillatory phenomena observed on other semiconductors or even metal electrodes.

Acknowledgement: The authors gratefully acknowledge contributions and discussions with Drs. S. Frey, G. Hasse, G. Popkirov, and a fruitful and frank exchange of ideas with Drs. Grzanna, Jungbluth and Lewerenz.

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