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Modelling electrochemical current and potential oscillations at the Si electrode

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This paper is dedicated to the memory of Volker Lehmann, one of the pioneers of semiconductor electrochemistry, who died under tragic circumstances in July 2006. He will be remembered as a good friend and an excellent researcher, whose work will inspire and guide us for many years to come

Abstract

The paper presents a deep and detailed but comprehensive analysis of the electrochemical current and potential oscillations at the Si– HF interface. Calculations and simulations are based on the so-called current burst model (CBM), which allows to calculate all local electrode features, e.g., current, potential, oxide thickness, interface roughness or capacitance as a function of time. The CBM is introduced in unparalleled detail and its application here is extended to the simulation of various observed oscillatory phenomena at the Si– HF interface taken from the literature. Apart from a detailed analysis of current oscillations in various modes, potential oscillations could be simulated for the first time, too. A new evaluation tool for parameter maps obtained by the simulation is introduced that yields, e.g., correlation lengths for certain domain features. The strengths and limitations of the CBM are discussed and analyzed with respect to other qualitative and quantitative models.

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1. Introduction

Almost half a century has passed since microporous silicon was first observed by Uhlir [1]. Since then, about 4000 papers were published in the field, in particular after Canham discovered in 1990 that microporous Si shows strong luminescence at room temperature [2]. The discovery of macropores by Lehmann and Föll in 1990 [3] also precipitated much interest, and various technical applications of porous Si have surfaced or are proposed, cf. e.g. [4–6].

Many models dealing with the mechanisms of pore formation have been proposed [3,7–17], and a good understanding of some mechanisms has been achieved.

However, there are also still many open questions, in particular if pore etching in other semiconductors like III–V materials [4] or Ge [18] is addressed.

The many open questions in this field are not surprising, considering that one of the most remarkable features of Si electrochemistry, namely self-induced potential or current oscillations, has never been fully understood. These "electrode oscillations" are easily observed in the external circuits in parts of the electropolishing regime and thus are not usually associated with pore growth. However, pore etching in III–V semiconductors may be accompanied by strong potential oscillations [19], and more recently similar observations have been made during Si pore etching [20] and Ge pore etching [18].

This may be seen as an indication that pore etching and self-induced current/potential oscillations are somehow connected, a viewpoint that has been advanced by some of the authors before [21]. Be that as it may, the

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self-induced current or potential oscillations of Si electrodes in usually aqueous HF electrolytes are interesting enough in their own right, and this paper attempts to demonstrate that many features of these oscillations can be quantitatively understood on the base of the so-called current burst model (CBM) [22] introduced before by two of the authors.

In this paper, we extend earlier modelling work [22] not only to larger sample areas, but cover several new topics like potential oscillations under galvanostatic conditions, induced current oscillations, and driven oscillations in some detail for the first time.

"Oscillating electrodes" were noted about 150 years ago by Faraday [23] and are rather common in electrochemistry. Oscillations were found in such systems as, e.g., Ni and Fe electrodes in H_2SO_4 solution [24–28], Cu in HCl [29–31], iron in chloride solutions [32], to name just a few. Several theoretical models were formulated that tried to explain oscillating electrodes and chemical oscillations in general [33–35].

It is not possible in a short space to do justice to all previous efforts that have been targeted at unravelling the mechanism behind the Si electrode oscillations, in particular because most mechanisms proposed were qualitative or addressed some but not all features of the general phenomena. Nevertheless, in what follows we attempt to cover prior work to a reasonable extent, in particular if it relates to the topics addressed in this paper.

Turner reported current oscillations at the Si electrode in the Si/HF system for the first time in 1958 [36]. His main interpretation was that above a certain potential and below a certain value of the electrolyte concentration, the HF concentration at the anode surface is too small to allow the divalent direct dissolution of silicon. Turner was aware that an "electropolishing film" is formed during oscillations, and considered this film to be SiO₂. While Turner was essentially correct in his interpretation, the mere presence of a (always uninterrupted) SiO₂ film during dissolution is not sufficient to produce oscillations. Nevertheless, it is now generally accepted that almost exclusively tetravalent dissolution takes place in the oscillation regime; i.e. dissolution essentially proceeds by current-driven SiO₂ formation and purely chemical SiO₂ dissolution.

In 1988, Gerischer and Lübke [37] related oscillations of the current density under a constant potential to the periodic growth and dissolution of a SiO₂ layer at the Si/HF interface. They postulated the existence of a "suboxide" SiO_{2-x} between the SiO₂ and Si. As the oxide becomes thicker, the composition of the total oxide layer is closer to SiO₂. The oxide was supposed to grow by field-assisted oxygen ion diffusion through the oxide towards the SiO₂– SiO_{2-x}/Si interface. In essence they proposed a nonlinear relation between oxide formation and its dissolution as the cause for the oscillating current density.

Again, this point of view is reasonable, and some nonlinear behaviour could lead to oscillating solutions of a system of reaction equations. However, there are three basic problems with this approach and other models proposed later, that are worthwhile to be outlined at this point in order to facilitate a critical discussion:

- Even if some oscillating reaction driven by the local current does take place locally, it is rather unlikely that all area increments on the electrode will stay in phase without some synchronizing mechanism. Small local variations in, e.g., electrolyte flow, temperature, potential or current density will destroy any initial phase coherence. Given only some oscillating reaction in the form of "micro-oscillators" (a term coined later by Chazalviel et al. [38]), at best a damped oscillation could be observed ending in a constant (if somewhat noisy) current resulting from the superposition of many micro-oscillators with random phases. Any detailed model therefore must include some mechanism that keeps the oscillations in phase on at least a substantial part of the sample surface.
- 2. Even if there are nonlinearly coupled reaction equations (in particular if some autocatalytic mechanism is involved), not all of them will produce oscillations, or oscillations as observed with a Si electrode. The wellknown Belousov–Zhabotinsky reaction [39] by now has many brethren showing beautiful chemical oscillations; but this kind of chemical oscillation is still more of a curiosity and not a paradigm for electrode oscillations. Moreover, differential equations for the reaction kinetics are not always well suited to describe stochastic phenomena as, e.g., current flow through fluctuating pores in an oxide.
- 3. Postulating some kind of oscillating balance between oxide formation and dissolution, while not wrong, does little to explain what is really happening. In other words: qualitative models might be very helpful in approaching the oscillation phenomena, but will by necessity fall short of providing an in-depth understanding of the mechanism involved.

With this remarks in mind, the many models proposed after Gerischer and Lübckes paper [37], can be put in a better perspective.

Föll in 1991 invoked electron tunnelling and electronic oxide breakdown under large electrical fields as an essential factor for the Si electrode oscillations [40]. The model could produce local oscillations, but lacks a synchronization mechanism and is purely qualitative. However, it introduced for the first time the particular stochastic component of local oxide breakdown, occurring with a certain probability that is determined by the local field strength, as the reason for local current oscillations or micro-oscillators.

Eddowes in 1990 proposed the idea that the second current peak in the voltammogram of the Si/HF system marks the point where an oxide of different stoichiometry (or state) is formed during electropolishing [41]. Smith and Collins enlarged on that idea, postulating a "hard" oxide for high potentials, and a "soft" oxide for low potentials, respectively [42]. Their speculation is based on the fact that the potential at the Si/SiO_2 interface changes as a function of the oxide type that is exposed to the HF at any instance in time. Assuming that the "hard" oxide dissolves less quickly than the "soft" oxide, scenarios can be constructed that lead to current oscillations. Again, there is some merit in this proposal, but as before it lacks a synchronization mechanism and is purely qualitative.

A big step forward was made 1992 by Chazalviel and Ozanam [38,43,44]. They studied current oscillations under constant potential conditions, but also with superimposed sinusoidal excitation and sharp steps [45]. In contrast to many workers in the field who reported long-lasting oscillations, they claim that "natural" oscillations are always damped on relatively short time scales. Stable oscillations were only obtained via external excitations of the system, e.g. by a sinusoidal modulation of the applied potential, which lead them to consider the Si/HF system as a kind of resonant system reacting to external stimuli rather than a self-oscillating system. The authors are among the first who proposed the existence of micro-oscillators on the electrode, which they considered to be organized in small selfoscillating areas or domains of constant oxide thickness, randomly distributed on the electrode, and suggested that macroscopic oscillations will be detected in the external circuit if these domains (or at least a majority of them), will synchronize. Ozanam et al. then made an attempt for a quantitative description of these oscillating domains together with relevant experimental results in 1993 [46] and arrived at a typical domain size of about 100 nm. Realizing that oscillations are organized in domains and will not be "visible" if the domain size is much smaller than the sample size was a major insight. However, the model did not explain the physical reasons for oscillations or for the synchronization.

Lewerenz and Aggour [47] proposed a model in 1993 that explains the oscillations on the basis of fluctuating pores in the oxide that essentially conduct the local current. Their paper also tries to explain the observed frequency dependence of oscillations on the pH of the solution and the applied potential. Their model seems to be the first one that includes the large volume change from Si to SiO_2 upon reaction, and a postulated interaction of the resulting stress and strain in the SiO2 film with the dissolution process. Lewerenz and Aggour then invoked stressinduced point defect generation as the cause for pore formation and preferential local dissolution of the oxide as the cause of the oscillations. Oscillation parameters like frequency, amplitude, shape and their dependence on external parameters like potential, pH, HF concentration or temperature, are, in principle, functions of the number of point defects and pores, their spatial distribution, radii and dissolution rate. In other words, specific oxide properties depend sensitively on electrochemical parameters, and these oxide properties are the cause for the oscillations. Later, Grzanna et al. [48,49] presented a sophisticated mathematical analysis based on variants of this model, which quantitatively reproduced many observed features. They included the necessary synchronization feature, but as a kind of free parameter with no direct physical justification. In the newest version of this model [50], two kinds of oxide are invoked and (compressive) stress-induced formation of microcracks plays a major role.

In 1996, Lehmann conducted major experimental work that also looked at potential oscillations under galvanostatic conditions (a feature not much investigated before). He tried to explain his results by enlarging on the ideas of Eddowes [41] that predicted the existence of two kinds of the oxide, but also introduces the notion of "flat" and "rough" oxide [51]. The main argumentation line in this work is based on the supposition that the oxide dissolution rate is not constant in time. The transition from flat (dense) oxide obtained close to the Si/SiO_2 to rough (less-dense) oxide, induces also a change in the ionic permeability and the etch rate. On a pure Si surface the oxide grows homogeneously as long as its dissolution rate is smaller than the formation rate and this homogenous oxide growth also leads to the synchronization of the oscillations. Reaching a certain thickness, the oxide will undergo a transition from dense to less dense or flat to rough, and this causes a strong drop in the potential and fast dissolution of the less-dense oxide forming a porous layer of SiO₂. After the less-dense layer is etched away, the dense part of the oxide is exposed to the electrolyte and process starts again. The model is completely qualitative and therefore has little predictive power. Nevertheless, the notion of rough and flat oxides has some merit for modelling, and the experimental results pose a big challenge for quantitative models.

In contradiction to other authors, Parkhutik and Matveeva find long lasting potential oscillations at the Si electrodes, however in electrolytes with drastically reduced SiO₂ dissolution rates [52]. They ascribe these sustained oscillations essentially to mechanical changes in the oxide layer. The SiO₂ grows until a certain thickness limit is reached when it will de-attach from the substrate by some lift-off, causing a strong drop in the potential. Beneath the disattached oxide a new oxide layer forms and the process continues. The authors claim that X-ray investigations showed a perfect accordance between the number of oscillations and the lifted-off layers. While this mechanism is possible and might be observed under special conditions, it is not the general cause of Si electrode oscillations and moreover purely qualitative. Some related work [53] studied the nature of chaotic and ordered oscillations and invoked porous oxide formation as part of the oscillating mechanism, but remained qualitative and did not offer new insights.

All of these models strive to explain all of the observed oscillatory behaviour of the Si electrode in a HF based electrolyte. However, most models are essentially restricted to current oscillations. While it may appear that a model that "explains" current oscillations will automatically also explain potential oscillations, this is not really the case – potential oscillations need more ingredients than just a working current oscillation model, as will be shown in this paper. Moreover, there are many blatant or subtle contradictions between the models proposed, e.g., some authors insist that only damped oscillations exist, while others claim that they have found stable oscillations for reasonably long times. While most models are purely qualitative, even most of the more quantitative models remain at a theoretical level without reproducing measured results, the only exceptions are found in [48,49] and the related papers.

The general lack of detailed microscopic (actually nanoscopic) mechanisms that produce micro-oscillators and some degree of synchronization in most models more or less automatically preclude the generalization of these models to other aspects of semiconductor electrochemistry, most noteworthy current oscillations in space otherwise known as self-ordered pore arrays [54]. There is a deep connection between the formation of self-ordered pore arrays (cf. e.g., the papers on pore single crystals in InP [55] or GaP [56]) as an expression of synchronized current oscillations in space, or "noisy" arrangements of pores with a strongly prevalent spatial frequency (=average distance), and the same phenomena in time as discussed here. Obviously, "current or potential in time oscillation" models with at least a clear option of generalization to "current or potential in space oscillation" would be of interest.

In 1998, the "current burst model" (CBM) was cursorily published [22]; it is the base of the present paper. The CBM was the first fully quantitative model that predicted many features of experimentally observed current oscillations [57] in a "bottom-up" way by simulating electrode reactions with a Monte Carlo approach on a nm scale.

2. Current burst model for the oscillation regime

2.1. General remarks

In order to emphasize the quintessence of the current burst model (CBM) we will begin with the (by now mostly accepted) "axiom" or fundamental assumption that the current through a Si electrode is neither homogenous in space, nor in time. Considering that Si dissolution in general involves at least three reactions (current-driven direct dissolution and oxide formation; purely chemical oxide dissolution), which in a strict sense cannot take place at exactly the same place at exactly the same time, this is a logical necessity. Of course, on slightly larger space and time scales the reactions involved could average to a smooth behaviour describable by differential equations, but here we will argue that at least in the oscillatory regime of the current (I)-potential (V) characteristics this is not the case. The postulated inhomogeneity in space and time follows rather directly from the following set of assumptions, which constitute the essentials for the application of the current burst model to electrode oscillations in time:

- 1. The electrode is completely covered with a (thin) oxide having some (non-uniform) thickness distribution at all times.
- 2. Charge transfer from the Si to the electrolyte is localized in space and time; a single localized charge transfer process is called a current burst (CB). Its initiation or nucleation occurs with a certain probability W(E(r)) at some point (or better pixel with a typical dimension of (1.5×1.5) nm²) at the position r as a function of the local field strength E(r). The probability W(E) increases for increasing field strength or decreasing local oxide thickness s(r). Note that the vector properties of E and r are of no consequence in this context and we will drop the bold font in what follows.
- 3. The total charge transferred in a CB produces only oxide in the form of an "oxide bump". The lateral extension of this oxide bump is assumed to be comparable to its thickness. In the simplest approximation the total oxide produced is contained in a sphere.
- 4. Local current flows only during the "on" phase of a CB, and the local oxide thickness increases accordingly. The local field strength thus decreases, and current flow will stop with a certain probability R(E(r)); i.e. the CB is turned "off". The field strength required for turning a CB off is generally lower than for turning it on; meaning that there is a certain hystereses in the process. Local current flow in a CB thus lasts for a certain average time t_{CB} defined by the parameters of the system, and in particular by the two probability functions W(E) and R(E).
- 5. The locally produced oxide dissolves continuously in the HF, the field strength increases, and the process cycle starts again. The oxide dissolution will take place for some average time t_{dis} , after which a new CB and thus a new local cycle will start. The sum of both times defines the time constant or lifetime $\tau_{CB} = t_{CB} + t_{dis}$ of a CB (which is, of course, a property only meaningful as an average quantity for many CBs). It is important to note that the CBM thus introduces intrinsic time constants into the otherwise static electrochemical system Si/HF.

It is clear that within these assumptions any current flowing through oxides lacking perfect thickness uniformity will be automatically localized in space, i.e. will only be initiated in regions where the oxide thickness happens to be small enough. Since the oxide thickness in any given pixel is fluctuating – it decreases because the oxide dissolves in HF and increases because of anodic oxidation during current flow – the current in a given pixel will be "on" or "off" in some characteristic yet stochastic pattern in time, and therefore will also be localized in time.

Individual CBs may and will differ in their size, duration, total charge transferred, etc., but for what follows it will be sufficient to consider just averages, i.e. treat all CBs as identical. The sum of all individual CBs active at any given time then defines the total current flowing through the electrode at this instant.

If current bursts just happen at a purely random fashion, i.e. an individual current burst is not correlated at all to other CBs, the density of CBs in space and time will average to constant values, and on a macroscopic scale a constant current leading to electropolishing is observed. However, as will be shown in what follows, if there are some interactions between individual next-neighbour CBs correlations may result that lead to oscillations of the CB density in time, in space, or in both. The macroscopic counterparts of these correlations are current oscillations in time, pores (=current oscillations in space), or both. Interactions between neighbouring CBs may happen in two extremes: Interaction in space, i.e. the probability for nucleating a CB at r is influenced somehow by what is going on in the neighbourhood, or interaction in time, i.e. the probability for nucleating a CB at r at the time t is influenced somehow by what has happened at r before. In what follows we will enlarge on this, but it is helpful to keep in mind that the CB model intrinsically predicts oscillations and pore formation if there are interaction mechanisms leading to correlations between CBs. This is not to say, however, that all oscillatory phenomena and all pores are only due to CB interactions.

In this paper, we focus on oscillations in time, and for that it is enough to have some interaction between neighbouring CBs [54]. The necessary mechanism for this interaction is an intrinsic part of the CBM, already contained in the set of assumptions given before, and easy to conceive as will be shown below.

2.2. Implementation of the CBM in a Monte Carlo simulation tool

It remains to cast the current burst model into a form accessible for calculations. The mathematical tool chosen is a Monte Carlo simulation, and in the rest of this section the basic formalism necessary to implement the algorithms will be introduced and discussed to some extent.

First, we consider only very low HF concentrations and p-type Si for the sake of simplicity. In this case the oxide layer always covering the electrode has a thickness *s* that is smaller than about 10 nm at all times (avoiding possible effects due to mechanical stress), but still large enough at all times to avoid noticeable electron tunnelling effects (not producing oxide). Any external potential or anodization potential U_{an} to the electrode (corresponding to the potential measured in actual experiments between the sense electrode and the reference electrode) then will drop across this SiO₂ layer (and to some extent in the adjacent electrolyte).

The basic assumptions of the CBM as implemented in a Monte Carlo program then can be formulated as follows: The electric field strength $E(r_p)$ across the oxide film at a pixel with an area $A_p = (1.5 \times 1.5) \text{ nm}^2$ at $r_p = \text{pixel number or coordinate is given by}$

$$E(r_{\rm p}) = \frac{U_{\rm an}}{s(r_{\rm p})} \tag{1}$$

An "ionic" breakdown event will occur in that pixel with a certain probability $W(r_p)$, forming a "channel" through the oxide layer and driving oxygen ions towards the Si/SiO₂ interface where they will be consumed in the chemical reaction that results in SiO₂. While it may appear a bit simplistic to calculate the electric field strength via Eq. (1), considering that the oxide thickness is not constant, this approach is nevertheless justified in retrospect because the system tends to behave rather homogenously, i.e. the oxide roughness is sufficiently small on a scale comparable to its thickness.

The probability function $W(r_p)$, and $R(r_p)$ for the reverse effect, are the only critical inputs into the CBM. They are derived as follows: Below a certain critical minimum thickness of the oxide s_{min} (or above a certain critical field strength E_{max}) the probability for starting a CB is 1. For field strengths below E_{max} , W(E) decreases to zero within some interval ΔE_{max} as shown in Fig. 1. For R(E) similar considerations apply, with a minimum field strength E_{min} necessary to stop a CB with probability 1.

The use of probability functions is necessary because electrical breakdown events always have a stochastic character for many possible reasons. The most important one is that the critical field strengths for breakdown events of any kind are always tied to the local oxide "quality", a parameter hard to define structurally, but nevertheless existent and of prime importance, e.g. in microelectronics.

The probabilities W(E) and R(E) for the nucleation or closing of a CB, respectively, are defined as follows:

$$W(E) = \begin{cases} \exp -\left(\frac{E_{\max} - E}{\Delta E_{\max}}\right)^2 & \text{for } E \leq E_{\max} \\ 1 & \text{for } E > E_{\max} \end{cases}$$
(2)

$$R(E) = \begin{cases} \exp -\left(\frac{E - E_{\min}}{\Delta E_{\min}}\right)^2 & \text{for } E \ge E_{\min} \\ 1 & \text{for } E < E_{\min} \end{cases}$$
(3)

The task thus is to find reasonable values for E_{max} and E_{min} together with reasonable values of the ΔE 's. Since breakdown of "electronic" SiO₂ is a very well known effect, occurring at field strengths around roughly 10 MV/cm in



Fig. 1. Graphical representation of two examples for the probability functions for turning a current burst on (triangles) or off (squares), respectively.

"good" thermal oxides, this gives a first order-of-magnitude for the critical field strength values. Moreover, since it is quite likely that the ionic breakdown postulated here is a consequence of an electronic breakdown damaging the oxide and inducing ionic breakdown, this value even suggests itself. While the kind of ionic breakdown suggested here might be a novelty, it is not a really new, because it is well known (and has been recently demonstrated again [58]) that current flow does occur through oxide layers with finite thicknesses.

The four constants E_{max} , ΔE_{max} , E_{min} , ΔE_{min} in the probability function are the main parameters of the CBM, they simply reflect the uniformity and quality of the oxide. A representative graph of the probability functions as used for most of the simulations (vs. oxide thickness *s* instead of *E*) is shown in Fig. 1.

For an ideal oxide the graphs should be step functions; and it is of course possible to run the simulations for this case, too. However, oscillations in certain cases are not possible if the probability functions are too "hard"; and the slope at W(E) = 1/2 must be seen as an important system parameter. Formally, at least three numbers (for symmetric probability functions) are needed, which refer indirectly to oxide properties.

As discussed in the introduction part of this paper, numerous authors claim the existence of two types of oxide: oxide and "suboxide", soft and hard oxide, flat and rough oxide, etc. At this point we may take that as an indication that one number is deemed not to be sufficient for describing all oxide properties, and that the approach taken here is sound. For our model we chose $E_{\text{max}} = 3.5 \times 10^7 \text{ V/cm}$ and $E_{\text{min}} = 5 \times 10^7 \text{ V/cm}$ for all simulations if not stated otherwise. These values resulted from a comparison of many simulations to experiments [22] and are in the general range known from electrical breakdown of thin oxide films [59]. The ΔE values defining the slope are variables, but generally are found between 0.1 and 0.2 V/nm depending on the system (or oscillation type) to be modelled.

It is worthwhile to point out that this part of the CBM is fully compatible with a well-known und powerful tool in, e.g., fracture mechanics, known as weakest-link theory or simply as Weibull statistics [60].

After the CB nucleation, the local oxide thickness will increase in the pixel where the nucleation took place, but also in neighbouring pixels. The growing oxide bump has some lateral extension either due to oxygen diffusion in the Si–SiO₂ interface, to some lateral movements of the breakdown channel (akin to the "dancing" of microflashes below an electrode), or to both. The total amount of oxide produced is directly given by the total amount of charge transferred in a CB on average – and vice versa. Assuming a spherical geometry of the oxide bump, which suggests itself because it follows the equipotential lines and thus constant field strength lines of the system as shown in Fig. 2, the average amount of charge Q_{CB} transferred in a CB is given, and so is the average current $I_{CB} = Q_{CB}/$



Fig. 2. Schematic drawing of the electrical field lines and the equipotential planes around a current burst imagined as an ion-conducting channel in the oxide layer.

 $\tau_{\rm CB}$ and current density $j_{\rm CB} = Q_{\rm CB}/A_{\rm p}\tau_{\rm CB}$ (referred to the area $A_{\rm p}$ of one pixel) of a CB with respect to the average cycle time $\tau_{\rm CB} = t_{\rm CB} + t_{\rm dis}$.

However, for the Monte Carlo simulation only the current density j_a for the active phase of the CB is needed, and that value is not easily obtained, since τ_{CB} in our case of low HF concentration is dominated by the time t_{dis} it takes to dissolve the oxide again. This is a direct consequence of the CBM: since the current density in a CB is by definition far larger than the macroscopic current density, and since the over-all oxide production from the macroscopic current density must be equal to the over-all oxide dissolution in all cases where the average oxide thickness stays constant, the oxide dissolution time or "off" time t_{dis} of a CB must exceed the oxide production time or "on" time t_{CB} by far. Computing t_{CB} and then j_a from the known total cycle time, while possible in principle, therefore will not give good values, and an independent way of arriving at j_a is needed. In Ref. [22], a value for the current $I_a = 0.1$ fA and not for the current density of a CB has been introduced, based on independent experimental observation and since this value gave good results, it will be used throughout this paper, too. While I_a or j_a is in principle determined by known system parameters, it must be seen as approximation in the CBM and therefore to some extent as a fit parameter.

After some oxide has been grown in the active phase of a CB, it will dissolve purely chemically with an effective dissolution rate α that depends on the "trivial" parameters HF concentration, pH, temperature, roughness of the oxide surface, and "oxide quality". It is thus impossible to find one precise value of α for the system under investigation, but in a sufficiently close approximation α is known well enough. Here we take a value of 0.04 nm/s for the

conditions specified. Note that the effective dissolution rate depends on the oxide roughness, rough oxides dissolve faster than smooth ones for the same nominal dissolution rate α . This effect is implemented in the program: by interpolating the effective area between three node points or pixels with different oxide thicknesses, a net or effective dissolution rate automatically results. This effective dissolution rate thus depends on the oxide roughness; it is generally

the oxide roughness oscillations. Whatever the precise shape of the oxide bump will be, and however long it takes to produce it, the electric field during its growth decreases at most until the lower limit $E_{\min} = U_{an}/s_{\max}$ defined above has been reached and the CB has been turned off with a probability of 1.

larger than the nominal rate, and it oscillates parallel to

By now quantitative relationships for a "micro-oscillator" or CB have been defined, the first needed ingredient for any oscillation model. It was claimed already that the second necessary ingredient, a synchronization mechanism, is an intrinsic part of the CBM and thus needs not to be added to the CBM. There is, however, a third ingredient that has not been discussed so far but is also present: desynchronization or negative feed-back, i.e. a mechanism that tends to destroy correlations between CBs. While this may appear counterintuitive, it is known from general considerations of pattern formation including oscillations that a de-synchronization mechanism is often needed if selforganized structures with a certain complexity are to evolve from stochastic processes [61]. Only the interplay of synchronization and de-synchronization (also called positive and negative feedback) tends to produce complex patterns; synchronization alone would either produce fully expressed oscillations or none at all. As will be shown, de-synchronization is also an intrinsic feature of the CBM that only needs to be noticed, but then must be implemented in the Monte Carlo program.

We will now discuss the mechanisms of synchronization and de-synchronization in more detail, because they apply not only to the simulation of oscillations, but also to more general simulations of stochastic processes on Si electrodes.

A synchronization mechanism in the context of this paper thus is any interaction that leads to some synchronization of the "on" or "off" state of (neighbouring) CBs. It expresses itself by strengthening the oscillations produced in the model; de-synchronization, contrariwise, is the term used for effects that tend to damp those oscillations. Obviously, local current oscillations with random "on" times (and "off" times then t_{CB} seconds later), or random phases in more conventional albeit not strictly precise terms, will not lead to macroscopic oscillations, but to a constant current. The term "oscillation" in this context does not imply a well-defined sinusoidal time dependence of the current but more generally any (stochastic) current (or potential) variation where an average frequency, amplitude and phase can be defined in a meaningful way. CBs in some defined area will give exactly that behaviour; a CB thus is nothing but a local current oscillator.

Macroscopic oscillations thus demand some degree of synchronization, i.e. a not too small fraction of the CBs present in a given time interval must be "in-phase" or at least phase correlated to some extent, i.e. starting and stopping within a not too large time interval. Again, no "perfect" synchronization is needed, and whatever synchronization there is must not necessarily occur on the whole sample surface in order to produce macroscopic oscillations. It is entirely possible that some degree of synchronization only occurs in areas of finite size, which are called domains. The average size of such domains introduces an intrinsic length scale l_{Do} into the system, and strong macroscopic oscillations will only be observed if $l_{\rm Do}$ is in the order of the specimen size. At this point the definition of a domain agrees with those given before, in particular by Ozanam et al. [46], since areas with constant oxide thickness within the CBM are more or less "automatically" also areas with phase-correlated currents. Note, however, that the older concepts of domains need to be enlarged upon later on.

One might distinguish two basically different synchronization mechanisms: Indirect (static) synchronization resulting from fixed system conditions, and direct (dynamic) synchronization, resulting from the processes themselves by some form of interaction. The most trivial example for indirect synchronization is a perfectly homogeneous system: If all conditions everywhere on the sample are exactly the same at the beginning of the experiment, exactly the same will happen everywhere at any instance in time. What one CB does, is what all do. Just having local oscillators then would produce oscillations. However, if the underlying micro-oscillators have a stochastic component (e.g. the probability functions W(E) and R(E) for CBs), those oscillations would be damped with a time constant intrinsic to the stochastics of the micro-oscillators. Moreover, in real experiments local conditions like e.g. electrolyte flow are never exactly the same; this also tends to destroy any initial static synchronization. We will therefore not consider static synchronization anymore. In order to exclude the transient effects of static synchronization, all Monte Carlo runs are started with a random distribution of the oxide thickness (which is not the same as random phases of CBs at the starting point, however).

Dynamic synchronization is far more powerful, and already contained in the CBM, as outlined before. It results in an easily understandable fashion from the overlap of oxide bumps of neighbouring CBs as illustrated in Fig. 3a.

The highly schematic picture shows what happens if a CB forms between the oxide bumps of its neighbours-tobe. Even if the time for its nucleation is independent from that of its neighbours, it will clearly switch off earlier than it would have done without the oxide bumps of the neighbours, since it does not have to produce as much oxide for this as an isolated CB. In formal language, its switching-off time is now correlated to what is going on in its neighbourhood. If this correlation is strong enough, stable oscillations will result [54].



Fig. 3. Schematic representation of the synchronization (a) and desynchronization (b) mechanisms contained in the CBM. In (a) it can be seen that the "switching-off" time of current burst CB3 is correlated to those of CB1 and CB2. (b) Shows schematically the voltage losses around an active CB, decreasing the nucleation probability of new CBs in the neighbourhood.

Note that while the oxide grows essentially into the depth of the Si in the form of a semi-sphere, the concomitant volume expansion by a factor of two automatically produces a spherical shape and at the same time a certain roughness of the interface and the oxide surface. While the purely chemical oxide dissolution will smooth the oxide surface, the Si-SiO₂ interface retains its roughness in the quiescent phase of the oscillations, and the CBM, if correct, must automatically produce the correct (=measured) roughness values without any further adjustments. It is not necessary to incorporate this interaction into the Monte Carlo model - it will evolve by itself since everything needed is already in place. In this context, it is important to realize that this correlation per se does not depend on the exact shape of the oxide bump; we thus chose the simplest shape, a sphere.

It is not clear at this point that this next neighbour interaction is sufficient to produce large-scale synchronization, but as has been shown before and will be shown here, it will be a sufficient condition if the CB density is large enough to overcome some percolation threshold. It is also important to note here that within the CBM a "non-oscillating" electrode doesn't imply the absence of CBs but rather the absence of synchronization between the CBs. Contrariwise, an oscillating electrode of some kind does not imply that its properties can be explained by some CBM since there are many oscillating electrochemical systems where it is quite likely that other mechanisms are the decisive factors, e.g. mechanical stress [52] or gas evolution; cf. also the excellent review [61] for a general view at oscillations.

As stated before, the CBM also contains an intrinsic de-synchronization mechanism. However, contrary to the synchronization mechanisms, de-synchronization must be coded into the algorithm. The de-synchronisation mechanism is based on the fact that the current density around an active CB is very large and localized, and this will lead to a decrease in the anodization potential across the oxide layer; a simple model for this, employing (nearly) hemispherical symmetry, is illustrated in Fig. 3b. The current density j(r) in the electrolyte "on top" of an active CB then decreases $\propto r^{-2}$ and the electric field lines in crosssection will show a cylindrical geometry as schematically shown in Fig. 2. This determines the form of the newly growing oxide as outlined before and favours the spherical shape of the bumps. The potential decrease in the vicinity of an active CB leads to a decrease in the electric field strength in its neighbourhood (it may be even zero), which in turn decreases the life time t_{CB} of already existing CBs and decreases the probability for the nucleation of a new CB. This effect tends to destroy correlations (CBs tend to be "loners") and thus leads to desynchronisation.

For a quantitative evaluation we consider that the current I_a flowing during the active phase of a CB through any equipotential surface at distance r from the CB is by definition $I_a = I_{CB} \cdot t_{dis}/t_{CB} = j_a \cdot A_p/\pi d^2$. With

 $j_{a}(r) = \sigma \cdot E(r) \tag{4}$

and σ = conductivity of the electrolyte, one can define the potential loss on the sample surface at a distance *r* from an active CB as:

$$U = \int_0^r E(r) \,\mathrm{d}r = \int_0^r \frac{I_{\rm CB}}{\sigma \pi r^2} \,\mathrm{d}r = -\frac{I_{\rm CB}}{\sigma \pi r} \tag{5}$$

The potential loss ΔU_{an} in the electrolyte is thus approximately given by the relation:

$$\Delta U_{\rm an} = -\frac{B}{r} \tag{6}$$

with $B = I_{CB}/\sigma\pi$ being some experimental constant that can be in principle determined. However, as in the case of the current density in the active phase of a CB, *B* is to some extent an adjustable parameter. In our case, we found that a value for *B* of 0.2 V nm (corresponding to the approximate electrolyte conductivity σ of about 5×10^{-4} S cm⁻¹) was best suited for the qualitative and quantitative reproduction of the experimental results. In principle, effects like the Nernst potential, caused by strong concentration gradients of the oxidative species due to a high current through the open channel of the CB, should also be considered, but are neglected for the time being.

Of course, the simple 1/r dependence of the potential loss $\Delta U_{\rm an}$ leads to arbitrarily large potential losses for $r \to 0$, which make no sense as soon as $|\Delta U_{\rm an}| > U_{\rm an}$. This problem is remedied by setting $\Delta U_{an} = -U_{an}$ in all pixels where the calculated ΔU_{an} is larger than the actual potential U_{an} , i.e. zero field strength conditions are assumed. Nevertheless, in potential loss maps, the calculated ΔU_{an} is displayed because it gives a better representation of the system dynamics and in particular because it is a direct measure of the number of active CBs. In a physical interpretation, areas with $\Delta U_{an} > U_{an}$ in potential loss maps denote diffusion limitation of the current – the potential needed to drive the actual current is larger than the potential available. In other words, the cluster of CBs that would drive ΔU_{an} into unphysical values cannot draw a total current equal to the sum of the standard CB current.

With the data and relations given at this point, almost all ingredients for a Monte Carlo program capable of simulating current flow through a Si electrode held at constant potential in the oscillation regime have been described in sufficient detail to emulate the results given in the next paragraphs. Only for galvanostatic experiments a somewhat more sophisticated approach is needed (e.g. how to keep the potential constant or how to deal with charging/ discharging the oxide capacitor), which will be described later.

2.3. Basic results and interpretation of simulations with the CBM

The software allows for in situ maps (i.e. while the program runs) of the morphology of the SiO_2/HF and SiO_2/Si interface, as well as for calculations of the local oxide thickness, potential losses and other parameters. This information is displayed (and stored in the memory of the PC) in the form of maps accompanied by histograms as illustrated in Fig. 4a. With a certain periodicity (usually every 20 ms) the content of these maps is updated (the "time frame" for an individual calculation is 5 ms); from all the data the dynamics of the system can be retraced and displayed as a "movie". This is quite instructive; examples will be placed in the Internet. The cycle time used for updating the content of the maps, and hence the information about the state of the system, can be decreased if necessary, but this will result in longer simulation times, and a compromise between the information quantity and quality must always be found.

The results of *one* simulation run with one set of input parameters provide the following primary and secondary entities, usually plotted as colour coded maps with histograms for full quantization:



Fig. 4. Examples of maps generated for one time frame in a simulation run (a). On the oxide thickness map some "smooth" subdomains are schematically indicated. The mottled areas can also be considered to be subdomains. The voltage loss map in this case shows directly the location of active CBs as indicated. For each calculated oxide thickness map the average free autocorrelation function (AFAF) is calculated (black curve) and subsequently fitted (red curve) (b).

- Macroscopic current density $j_{an}(t)$ (or potential $U_{an}(t)$) in all modes (from strong stable oscillations to constant values) as a function of the major conditions like constant (or modulated) potential or current, HF concentration and temperature.
- Oxide thickness maps as a function of time. From this, secondary oxide characteristics can be obtained, e.g.
 - Capacity of the SiO₂ layer (with Helmholtz layer and SCR capacity usually neglected).
 - Roughness of the oxide thickness as a function of time.
 - Roughness of the SiO₂ surface as a function of time.
 - Roughness of the Si–SiO₂ interface as a function of time.
 Correction factors for converting globally measured
 - Correction factors for converting globally measured capacitances (proportional to $1/\langle s \rangle$) to the real capacitance (proportional to $\langle 1/s \rangle$).
 - Autocorrelation functions with regard to the oxide thickness, which in turn allows to extract certain correlation lengths *l* and sizes of correlated areas *F*.
- Special maps indicating e.g. the potential losses on the electrode surface. Those maps allow to obtain the number of active CBs because potential drops are additive.
- Capacitive currents or potential drops in global series resistors as a function of time.
- Additional parameters as a function of time, e.g. the number of CBs nucleated or extinguished in a given time interval.

From a sequence of simulation runs with systematically varied parameters (e.g. potential, current, temperature, electrolyte concentration, serial resistance), the following information can be quantitatively deduced as a function of the variable chosen:

- General shape (e.g. sin, saw tooth, etc.), amplitude and frequency of oscillations.
- Decay constant of damped oscillations.
- General *IV* characteristics for the range of the potential where the basic limitations still apply (e.g. closed oxide).
- Mean oxide thickness, capacitance, and roughness.
- Correlation lengths.

Fig. 4a illustrates the possibilities of the model with respect to maps. It shows four (especially "simple") representative maps generated at the minimum of strong stable current oscillations (similar to the ones shown in e.g. Fig. 5). By definition, pretty much the whole area of the sample then must be one domain, i.e. all of the current flowing locally has (about) the same phase. However, looking at the picture, it is clear that the postulated domain has an internal structure with respect to the oxide thickness, the interfaces and the potential losses, and that the current flowing is strongly localized in the three active areas shown in the potential loss map.

At this point it is necessary to make clear what is meant by "phase" with respect to CBs and as applied to the phase of the current or better the (oscillating) resistance regulating the current flow in a domain, since current flow in the CBM model is inherently inhomogeneous in time and space. For this, the total time or "lifetime" τ_{CB} of a CB defines the phase scale: a phase of 360° then corresponds to τ_{CB} , and most of this time the CB is "off", as pointed out before. This definition allows to assign phases to electrode areas where temporarily no current is flowing and thus provides a link to the old (and somewhat naïve) picture of domains, where a domain was defined as an area where the (spatially uniform) current has (about) the same phase and magnitude everywhere. Note also, that this definition correlates the oxide thickness to the phase, albeit in a somewhat indirect way. Moreover, defining phases relative to CBs, makes immediately clear that there must be a considerable spread of CB phases in a domain because otherwise the macroscopic current resulting from synchronized CBs would consist of sharp pulses with the frequency $1/\tau_{CB}$. The half-width of a current peak in $j_{an}(t)$ is therefore a direct measure of the strength of the synchronization. In what follows, phases are always defined as CB phases.

In principle, this definition would allow to generate maps of the local current magnitude and phase by a Hilbert transformation of the temporal-spatial resistance distribution; and those maps would show the domains more directly than the maps provided so far. However, since τ_{CB} is an average property and thus not well defined for a single CB, this is not a trivial task and the necessary routines have not yet been implemented.

For lack of a better term, and to facilitate the description of the results of a simulation run, the structures visible within the sample-size domain in Fig. 4 will be called subdomains; as it will turn out, there are characteristic features associated with these subdomains outlined in the picture. We will now address the question of what exactly constitutes a domain and how domains develop in time. This has not been discussed in detail in any previous publication, and we will now give a detailed description of what constitutes a domain based on our results:

- (i) domains may be multiply connected and frazzled-looking with no obvious boundaries in the maps provided. The boundary, as e.g. in the case of magnetic domains, is a continuous transition from one phase to another one or to random phases.
- (ii) Actual current flow within one domain is spatially rather inhomogeneous and concentrated in "active" areas (visible especially well in the potential loss maps). However, with the phase definition from above, the (CB) phase within a domain is still about the same.
- (iii) While the current in a domain does oscillate in time, the necessary changes of the size and location of the active (and by default passive) areas produce rather non-uniform sub-structures = sub-domains within the domain.



Fig. 5. Example of a fairly stable current oscillation at $U_{an} = 6$ V together with four screenshots of the oxide thickness and the voltage losses at the times indicated. The large bars in the histograms at the end of the scale show the sum of all values outside the range and are thus not "real". The time development of the four most important fit parameters for the AFAF are shown, too; for details refer to the text.

- (iv) Other parameters, like the oxide thickness, show pronounced structures within a domain, too.
- (v) While there is a meaningful linear size obtainable from the maps (the correlation length of synchronization), it is not necessarily coupled to the domain area size.

The domains described in this way can do everything the simple "classic" domains can do, but avoid many conceptual difficulties that would arise with the more naïve picture. The domains defined here thus are closer to reality, but not as easily visualized as "classical" domains.

Looking at the subdomains in Fig. 4 one realizes that they consist mostly of areas where current flow is (and recently was) concentrated ("active" subdomains), and areas where oxide dissolution dominates ("passive" subdomains). The first kind, by the very nature of CBs, produces rough structures (varicoloured or mottled areas); the latter results in quite smooth parts (unicolour). Besides quite different appearances, all subdomains have about the same phase (as defined above) and wander around within the large domain, producing well-defined average properties of the large domain at all times.

In other words, the internal structure of a domain that determines how a domain changes its phase with time is far better visible than the domain itself - and far more interesting!

Some features of subdomains can be assessed by routines described later, most prominently the size of subdomains as expressed in correlation lengths. In Fig. 4, some of such correlation lengths are indicated, they will be discussed in detail in Section 4.

2.4. Calculation of secondary quantities

The most important quantity that is calculated in the simulation program at each time instance is the local oxide thickness. This value can be used to calculate secondary measurable quantities of the system and to observe their dynamics. Supposing that D(s) is the fraction of the surface covered with an oxide of thickness *s*, the mean oxide thickness $\langle s \rangle$ then is

$$\langle s \rangle = \int s D(s) \, \mathrm{d}s \tag{7}$$

and the integration runs always over the whole area. Another important electrode parameter is the roughness Yof the oxide, which has been (indirectly) determined in some experiments by measuring the capacitance C(t) of the system based on in situ ellipsometry [62,63] (and references therein). Y is calculated according to

$$Y = \int |s - \langle s \rangle |D(s) \,\mathrm{d}s \tag{8}$$

The capacitance C of the oxide layer; easily measured, is practically completely given by the oxide thickness (distribution) and the mean dielectric constant of the oxide via

$$C = \varepsilon \varepsilon_0 \int \frac{1}{s} D(s) \, \mathrm{d}s = \varepsilon \varepsilon_0 \left\langle \frac{1}{s} \right\rangle \tag{9}$$

with ε = dielectric constant of the oxide and ε_0 = electric susceptibility of vacuum.

Of course, the roughness of the oxide – electrolyte interface and the roughness of the oxide – Si interface can be calculated, too. The latter is quite similar to the total oxide roughness given above. While the roughness of the Si–SiO₂ interface is not (yet) measurable, some quite revealing in situ measurements of the SiO₂ surface have been made; however on a scale considerably coarser than the one given here [62].

Some quantitative comparisons of experimental findings and results of CBM have been made before [64], the agreements were not only rather perfect but showed that the interpretation of capacitance measurements in terms of a "two oxide" model given in [51] were based on equating the proper average $\langle 1/s \rangle$ with $1/\langle s \rangle$, which is not correct for the roughness actually observed or calculated with the CBM.

The various maps generated by the CBM contain far more information than can be captured by calculating averages over map parameters. A first attempt has been made to extract some quantitative information about the spatial structure of mapped quantities, in particular for the oxide thickness maps, by using autocorrelation methods. The so-called "average free autocorrelation function" (AFAF) was calculated for all oxide maps obtained. The AFAF is defined as:

$$AFAF(\Delta) = \frac{1}{L} \int_0^L [s(x) - \langle s \rangle] [s(x + \Delta) - \langle s \rangle] dx$$
(10)

where Δ is a spatial displacement between two points on the electrode, *L* is the lateral size of the simulated electrode (i.e. 300 nm in our case), $\langle s \rangle$ is the average value of the function s(x), i.e. the mean oxide thickness, and *x* is a space coordinate (i.e. on the oxide map in our case).

For this class of problems, i.e. for the determination of correlation lengths for some patterns, it is common to use the standard autocorrelation function (ACF). However, in our case the average oxide thickness changes between time frames, and these changes are comparable to the thickness changes in the subdomains. The ACF is therefore not the best tool for this purpose. It is advantageous to resort to the average free autocorrelation function (AFAF) as defined in Eq. (10). The AFAF essentially measures the average magnitude of the correlation of two points separated in space by a distance Δ ; i.e. the probability of finding the same oxide thickness at this distance. From the data obtained correlation lengths can be extracted that provide information about the dynamical behaviour of subdomains over time, i.e. the changes in areas primarily growing or dissolving oxides.

The AFAF is "easily" calculated, i.e. it does not take much processing time. But since it is still a function and not a number, it is still not sufficient for plotting relevant parameters as a function of time. In order to do this, the calculated AFAFs need to be fitted with a suitable function that contains correlation lengths as desired parameters. The best fitting function for this purpose is defined as

$$f(x) = A(t)\cos[k(t)x - \varphi(t)]\exp\left(-\frac{x}{\psi(t)}\right) + B(t)\exp\left(-\frac{x}{\chi(t)}\right) + O(t)$$
(11)

where A(t), B(t), k(t), $\varphi(t)$, $\psi(t)$, $\chi(t)$, O(t) are the fitting parameters. The first term in the sum contains a cosine function, which, being periodic in space and time, attempts to describe the oxide roughness found in the active subdomains producing growing oxide. The correlation length, i.e. the average size of these subdomains is given by $\psi(t)$. The second term describes the "smooth" subdomains where oxide dissolution takes place; its correlation length is given by $\chi(t)$.

The correlation lengths $\psi(t)$ and $\chi(t)$ thus give the average length over which subdomains extend. The parameters A(t), B(t) have a more complex nature. While they include the surface fractions of growing and dissolving subdomains, respectively, they might also include a measure for the oscillation amplitude. However it is rather difficult to quantify these parameters separately, which in turn makes it difficult to give a full interpretation of A(t) and B(t). Later in the text, these parameters will be referred to as "surface fractions" only, but are not used in any depth for the interpretation of the results. The parameter k(t)contains information about the roughness in the growing subdomain. The parameters $\varphi(t)$, O(t), which describe a certain phase lag and an offset, seem to have no particular significance but are simply needed for a better fit.

While it is legitimate to have some doubts about the usefulness of describing a "picture" by 7 fit parameters, the procedure does make some sense; note that for one simulation run some of the information contained in several thousand maps can now be condensed into the time behaviour of these 7 parameters. The snapshots of the oxide thickness shown in Fig. 5, and some of the following pictures together with the analysis based on the AFAF should be sufficient to prove the merit of the approach presented here.

3. Current oscillations

3.1. General results and representations

In this chapter, we will present simulations that were done under potentiostatic conditions; i.e. constant external potential, partially because the results presented here are new and/or from a larger area than earlier simulation runs [65,22], partially to introduce important features of the simulations and their interpretation for the most simple case. The CBM produces features more complex than envisioned in its conception (as a good model should) and the results of a simulation may not only be unexpected and in need of an interpretation, but will tend to change the simplistic viewpoint that went into the initial model construction.

The "standard" system modelled consisted of a p-Si electrode with (100) surface orientation. The HF electrolyte concentration was chosen to be 0.024 mol L⁻¹. According to our experiments this corresponds to an etching rate of 0.04 nm/cm²; this value being close to the one calculated by Sere et al. [66]. Different anodization potentials ranging from 3.5 to 8 V, with an increment of 0.5 V, were used. The area covered by the simulation was (300 × 300) nm² at a pixel size of 1.5 nm. The first or primary quantities of interest are simply the current density vs. time curves, i.e. $j_{an}(t)$, which allows by "inspection" to deduce the oscillation frequency v_{osc} and period $T_{osc} = 1/v_{osc}$ and the damping time constant τ_{D} .

Fig. 5 shows a typical result for 6 V anodization potential. The simulation yields pronounced current density oscillations as illustrated in the graph; also shown are four "snapshots" or "screenshots" of the oxide thickness and the potential losses taken at four characteristic times in the oscillation cycle as indicated. These screenshots were chosen to illustrate the initiation and synchronization of the CBs as well as the relatively quiescent state. Again, the whole area constitutes pretty much one "classical" domain by definition, simply because we have strong oscillations with currents close to zero in the minimum.

A new cycle will start with the nucleation of single and mostly uncorrelated CBs in the low current phase as soon as the oxide has been sufficiently thinned by chemical dissolution; this is clearly visible at t = 421 s (a situation similar to the one shown in Fig. 4). The synchronization or phase correlation of the spatially separated CB clusters or subdomains is a direct result of the rather uniform starting conditions. While this would be a static synchronization in the sense introduced in Section 2, it is a direct consequence of a dynamic synchronization, taking place during the previous current cycle. By now the reader should be aware of the fact that any linear description of what is going on encounters the "egg and hen" problem – there is no clear cause – effect relation, but a closed "logical circle".

As the oxide thinning continues, a rapidly increasing number of CBs is initiated and some dynamic synchronization takes place, e.g. at t = 318 s. Areas of still thinning oxide (blue) separate from areas of oxide growth (yellow) - clearly visible in the histogram. Nevertheless, the phase as defined before is similar everywhere. Note, for example, that in "phase space" the dark blue parts in the oxide thickness map (CB about to start) signify a phase comparable to the yellow area (CB almost over). Synchronization occurs because the CBs in active subdomains all turn off at about the same time by the mechanism discussed in Section 2, leaving back a passive subdomain that will quickly turn "unicolour" by the smoothing action of oxide dissolution. The current in this time frame is partially carried by CBs that have been initiated earlier but are still active, but is mostly due to CBs initiated within the time frame considered. Close inspection of the oxide thickness maps (also in the other figures containing those maps) show that there are always small areas of very thin oxide ("blue dots") in an active subdomain. This results from the de-synchronizing mechanism discussed before, which tends to prevent the nucleation of new CBs close to an active one because there is a reduced or even vanished electrical field, and thus allows severe thinning by chemical dissolution between active CBs. It is important to note that within an active subdomain there is a lot of "activity" on small scales in space and time that cannot be captured by a few screen shots, but presently only by movies and, to a much smaller extent by the correlation lengths obtained from the fitting routine described below.

At the peak of the current (t = 363 s), the average oxide thickness has considerably increased but there are still thin patches that can initiate the new CBs. Nevertheless, the rate of "old" CBs being extinguished now becomes larger than the initiation rate. On the downward slope of the current the production rate of new CBs is far smaller than the stopping rate of old ones, the current drops sharply. Simultaneously the oxide thickness starts to decrease because chemical dissolution now removes more oxide than is produced. It is interesting in this context to compare the situations at the current amplitude midpoints in the upward and downward part (t = 318 s and t =380 s), where the current is identical, but the maps rather different. This is due to the fact that in the upward part the current is mostly due to CBs that start in this time frame, whereas in the downward part it is mostly carried by "old" CBs.

Chemical etching smoothes the relatively rough oxide as can be clearly seen in the t = 421 screenshot. Conditions are now rather uniform, even if one started from a random oxide thickness distribution, and this helps to keep the process synchronized.

What can be seen in the oxide thickness maps of Fig. 5 by visual inspection (particularly well in the screenshot at 421 s) are the "smooth" and "rough" areas or subdomains, correlated to mainly oxide dissolution and oxide production via active CBs. The potential loss maps show that even more pronounced (with oxide-growing "rough" areas always "red-shifted" with respect to the background). It is evident (in particular with the 380 s potential loss map) that the two kinds of subdomains are rather irregular or non-circular; the correlation length thus is not a measure of their area. Increasing correlation lengths (as shown later) therefore may only indicate that subdomains are getting somewhat more "roundish", but not necessarily bigger.

At and after the current maximum, the active subdomains percolate and produce a large new passive subdomain pretty much identical at this point with the domain itself, which will get smoother (with respect to the oxide thickness distribution) during the downward turn of the current because the oxide dissolution smoothes the surface, and some newly nucleated CBs remove particularly thin parts. Together, a rather narrow oxide thickness distribution results as shown at t = 421 s, which provides the uniform background into which new small and sufficiently synchronized active CB subdomains develop in the next cycle. Synchronization of the spatially separated CB clusters or subdomains comes from rather uniform starting conditions – and this brings us back to the beginning of the cycle as described above.

The correlation length (CL) for the growing domains behaves in a quite similar way; it oscillates almost in phase with the current density. Up to the current peak at t = 363 s the CL increases, indicating a continuous increase of newly nucleating CBs. The decrease in the current density, which is caused by more CBs turning off than on, is also perfectly correlated with the decrease in the CL for growing domains. An aberrant behaviour, however, expresses itself in the intermediate CL peak at the current minimum. This most likely relates to the nucleation of new CBs in areas, which until this moment underwent only dissolution and where no CBs could nucleate since the potential losses from the neighbouring CBs were too strong. However, even after this intermediate peak the CL will decrease again, and this is caused by the fact that the next batch of freshly nucleated CBs are very strongly localized and too far away from each other to be closely correlated.

The CL for the dissolving domains is essentially anticyclic, which is what would be expected. Its time sequence also shows some finer structure related to the CB dynamics, but we will refrain form a detailed discussion at this point. Suffice it to mention that the data compression as described in the foregoing does allow to a certain extent to arrive at a better interpretation of what is actually going on.

Fig. 5, for the sake of completeness, also shows the time development for the surface fractions as defined before. While quite intriguing curves resulted, their interpretation will not be attempted here.

3.2. Damped current oscillations

Having progressed to this point, it is now of interest to look at the simulation of damped current oscillations, which must, by definition end in a loss of synchronization and the presence of several domains with random phases. One example is shown in Fig. 6.

On a first glance, nothing resembling "naïve" domains is visible. On a second glance, keeping in mind what has been pointed out before, and just looking at the potential loss maps, one sees that there is indeed a large frazzled domain in the map related to the second current maximum, 149 s. The areas in bright red (and the areas in dark blue!) have comparable phases and percolate. In the fourth current maximum 365 s, carrying only about 60% of the maximum current, the red – dark-blue "domain" is decidedly smaller and the connected greenish areas – correlated to domains with other phases – are larger.

Both correlation lengths oscillate weakly while macroscopic oscillation in the current density can still be observed, and then become stationary. Their behaviour during the oscillations is similar to that discussed for the stable oscillations, although both parameters are very noisy. Due to comparatively lower anodization potential, the overall number of active CBs on the surface is also smaller, which clearly leads to smaller CLs.

Once the oscillations are damped, both CLs come to the same value and exhibit no clear macroscopic oscillation, just as the current density does. At this point the whole surface is oscillating at random phases (equivalent to many domains). This is also very nicely pictured by the potential losses maps taken at different (still slightly visible) peaks in the damped region of the current density.

At this point it becomes clear that a discussion of simulation results in the framework of simple "classical" domains does not do justice to what really is going on at the electrode, and this justifies the deeper concept of domains and especially subdomains as presented in Section 3.

It remains to be seen if (difficult to calculate) maps of the CB phases will produce clearer visual images of the domains, but to some extent this is a moot question. Everything of physical interest is already contained in the data, and all measurable quantities are easily derived as will be shown in what follows.

3.3. Potential dependence of prime quantities

The nucleation of a new CB will generate potential losses in its neighbourhood according to Eq. (6) and thus



Fig. 6. Damped current oscillations with snapshots of the oxide thickness and the voltage losses; the time development of the correlation lengths and the subdomain surface fractions are also given.

lower the electric field strength in its surroundings as shown in the potential loss maps in several figures. According to Eq. (2), this decreases the probability for the nucleation of a new CB, or the lifetime of an existing CB, respectively. This implies that the degree of synchronization depends on the average number of active CBs, or, since active CBs carry all the current, the average current. Weak synchronization will lead to damped oscillations, described by exponential decay of the amplitudes with a time constant τ_d , and this is what will be observed at the onset of oscillations around the current minimum after the Iox peak. However, it is a well established experimental observation that increasing the anodization potential, while hardly changing the average current, leads to more stable oscillations, i.e. the damping time constant τ_d will increase substantially with increasing potential.

The CBM should reproduce this behaviour without any additional adjustment. That this is indeed the case is shown

in Fig. 7a. The current vs. time results are shown for three values of the potential, and from a number of simulations at various potentials the oscillation period $T_{\rm osc}$ and the damping time constant $\tau_{\rm d}$ have been extracted and plotted. Starting with strongly damped oscillations for $U_{\rm an} = 3.5$ V, the oscillations become rather stable at $U_{\rm an} = 5.5$ V and beyond.

The oscillation period increases linearly with the applied potential; this is shown in Fig. 7b, together with the damping time constant in Fig. 7c. These results are in good agreement with measured ones as shown in Fig. 7d and e taken from [67].

It remains to interpret the potential dependence of the damping time constant, a quantitative result that the model produced "automatically". In this case it is easy: For all else being equal, a higher anodization potential increases the nucleation probability for new CBs and decreases the stopping probability for existing CBs. In other words, the effects of the de-synchronization mechanism are smaller



Fig. 7. Current density oscillations as a function of the applied voltage. Current density vs. time showing damped oscillations with different degrees of damping (a). Following anodization voltage was used: solid line 3.5 V; dotted line 4.5 V; dashed line 5.5 V. Oscillation period T = 1/v; increasing linearly with time (b). Decay time constant τ_d of the oscillations (c).

and this favours synchronization. All else, of course, remains not equal if the potential is raised, but whatever happens in a more subtle way and influences the synchronization/de-synchronization behaviour (e.g. changes in the thickness distribution of the oxide and the frequency of the oscillations) will be "automatically" taken care of by the CBM.

As can be seen from Fig. 7c, oscillations decay more or less instantaneously below a minimum potential of about 4.5 V, after that τ_d increases linearly. At least for the parameter space scanned here, oscillations are never undamped (in accordance with [68]), although it may take many oscillation periods before that becomes noticeable.

Fig. 8 gives some examples for the average oxide thickness, the oxide roughness and the specific capacitance for damped oscillations (a)-(c) and stable oscillations (d)-(f). The slight difference in phase of the oxide roughness oscillations and current density oscillations Fig. 8a and d is important. The maximum in the oxide roughness coincides with the maximum of the active CB number (not displayed) – as it should. A large density of CBs will always induce faster synchronization as compared to a smaller density. The minima in the current and the oxide roughness coincide rather well, indicating that as soon as the current drops, i.e. active CBs "die" and hardly any new ones are nucleated, the dissolution of the oxide is the predominant oxide modifier in the system. This will smooth the oxide surface (but not the interface) and the roughness will decrease – a fact that is clearly seen in Fig. 8a and d.

3.4. Current oscillations induced by extrinsic synchronization

Insufficient direct or dynamic synchronization leads to damped oscillations as pointed out in Section 2. Experimentally it was shown that oscillations could be restarted after they vanished by suddenly changing the applied potential to a higher or lower value [43].

This experiment is easily implemented in the CBM; Fig. 9 shows some simulation results. A typical (damped) oscillation for 4 V is started and run until it has all but disappeared. Then the potential is either decreased to 3 V (Fig. 9a), or increased to 5 V (Fig. 9b). In both cases the system starts to oscillate again, just as found in experiments [68].

Again, the model reproduces the experimental reality, but now this needs to be interpreted. From the viewpoint of the CBM both results are easy to understand. A damped oscillation finally results in some relatively constant density of CBs over time with random phases. If the potential is suddenly decreased, active CBs will stop prematurely, and new ones will not be nucleated. The current drops to (almost) zero, because most current bursts stop at the same time – i.e. they are now synchronized. Activity starts again as soon as the oxide has thinned down sufficiently, and since this process homogenizes its thickness to some extent, many CBs start within a narrow time frame, i.e. they are synchronized once more.

If the potential is increased, the situation is even more straightforward. Once the potential is increased to 5 V, the "history" of the CBs on the electrode surface is not so important any more. Most CBs will keep "burning", and new ones are nucleated right away. The current will immediately increase; it will come down, as discussed before, as soon as a synchronized domain has formed. Again, the electrode has been reset to the conditions typically prevalent at the start of a 5 V cycle.

Chazalviel and Ozanam [38] explain this (and other) oscillatory phenomenae as a result of some "resonance" effect that is taking place at the electrode under perturbation. The results presented here reproduced the measure-



Fig. 8. Calculations of the oxide roughness Y (a) and (d), average thickness $\langle s \rangle$ (b) and (e), and capacitance C (c) and (f). Considered are damped oscillations (a-c) and stable oscillations (d-f). All the plots also contain the current density curve (dashed line).

ments shown in [68]. The term "resonance" with all the implications it carries is not needed, however, to understand the phenomenon.

3.5. Forced current oscillations

So far, strict potentiostatic conditions were used; at best the potential was changed in sudden jumps. Considering the electrode as a system of stochastic micro-oscillators with a certain (average) time constant $1/v_{osc}$, new effects can be expected if the potential is not kept constant but is modulated with a (cycle) frequency $\omega_{mod} = 2\pi v_{mod}$ of its own, e.g. sinusoidally as

$$U_{\rm an} = U_{\rm an} + \Delta U_{\omega} \sin \omega_{\rm mod} t \tag{12}$$

For all following simulations and experiments the amplitude ΔU_{ω} is chosen to be 1.5 V whereas ω_{mod} is a multiple of the intrinsic oscillation frequency $2\pi v_{\text{osc}}$; i.e. the oscillation frequency obtained for constant anodization potential (4 V in the case shown here).

Fig. 10a and b show a direct comparison of "simple" oscillations from the simulations and an experiment at a

potential of $U_{an} = 4$ V. The two oscillation frequencies are $v_{osc} = 9 \text{ mHz}$ for the simulation and $v_{osc} = 20 \text{ mHz}$ for the experiment. The difference is trivial; it would be no problem to match the simulated frequency to the observed one, but that is not the issue here. In both cases the oscillations essentially disappear after 4-6 cycles; which is more important here than a perfect match of the frequency. The modulations used in the simulation and the experiment refers to the intrinsic frequency of each case. The results can be seen in Fig. 10c and d. In both cases the current density oscillations will couple to the external frequency, and the oscillations now become stable in time, albeit on occasion only after a short transitory period in the experimental case. This transitory period (most pronounced in Fig. 10d) may simply be due to a kind of "initialization" of the real Si surface, which is covered with a native oxide and possibly some organic residue that need to be removed first.

Fig. 10e and f show the current density oscillations when the anodization potential is modulated with half the frequency of the intrinsic oscillations. The resulting oscillation contains both frequencies in some kind of beat pattern. The

Fig. 9. Voltage changes induce new oscillations. Decreasing the voltage by 1 V (a), increasing the voltage by 1 V (b).

same can be observed in Fig. 11g and h, where the anodization potential is modulated with twice the intrinsic frequency. Some beating is observed for all modulation frequencies ω_{mod} , harmonics were chosen here to maximize the effect of producing more stable oscillations by modulations.

The detailed experimental conditions used for the measurements in Fig. 10 can be found in [69]; essentially an HF(aq) electrolyte concentration of 0.024 mol L⁻¹, was used for (100) p-type (20–30) Ω cm Si sample of 1 cm² area with a metallization layer on the back ensuring a good ohmic backside contact. In comparison to the simulations, where the sample area is set to be (300 × 300) nm² = 0.09 µm², the area used in the experiments is several orders of magnitudes larger. Keeping this in mind, together with consideration of the usual scaling problems for this kind of simulation (see also the discussion), the agreement is quite good.

4. Potential oscillations

4.1. General remarks

Potential oscillations, i.e. oscillations measured between the reference electrode and the sense electrode on the sample backside, can occur at a Si/HF interface under galvanostatic conditions, i.e. for a constant anodization current. This fact already proves that the physical mechanism behind the oscillations must be more complicated than a "simple" positive/negative feedback stochastic oscillator running in an area of the global characteristics where a differential negative resistance is observed [70]. That is also the reason why stable potential oscillations are relatively hard to obtain, as also shown indirectly by the relatively small number of published papers dealing with this topic. For high anodization currents [52,53] and an "exotic" electrolyte [71] not containing HF, Parkhutik found long lasting stable oscillations [72]. Lehmann investigated the potential and the oxide thickness oscillations at relatively high electrolyte concentrations [51,15].

Potential oscillations are qualitatively quite different from current oscillations for a variety of reasons that are cursorily given and compared in Table 1. Assumed is a certain capacity C of the system and a certain total series resistance $R_{\rm S}$.

The table contains a few self-explanatory points, but mainly serves to point out the major difference of potential oscillations to current oscillations and to introduce some of the finer points for the implementation of the CBM as mentioned in Section 2.

- (i) The potential is an intensive variable; it does not depend on the sample size. More simply put, the potential, in a first approximation, is the same everywhere at the sample surface at any instance in time as long as no lateral currents are flowing. This does not contradict the de-synchronization mechanism introduced in Section 2, which firstly introduces only deviations from an equipotential surface on a nanoscopic scale by allowing lateral current flow components, and secondly is an expression of what may happen if one looks beyond a first approximation.
- (ii) The current still could have any arbitrary local value, but the sum of the current over all pixels must be constant at all times.
- (iii) The oxide capacitor *C*, as defined and calculated in Section 3.3, draws a displacement current j_{cap} , which must be included in the current flow balance. For current oscillations, shown in Section 3, j_{cap} was neglected since it is quite small. For potential oscillations, it must be included, however, and this provides another feedback mechanism.
- (iv) The potential or potential $V_{\rm SiO}(x,y)$ at the sample surface is not identical to the external potential $U_{\rm an}$, but always diminished by $R_{\rm ser}I_{\rm an}$ i.e. the potential drop in the total series resistor. It is also varying laterally around active CBs due to the mechanism discussed before. For the same reason $R_{\rm ser}$ is not an absolute constant but depends somewhat on the number of active CBs and thus provides another feedback mechanism that can be crucial for the occurrence of oscillations (cf., e.g. [70]). The part of $R_{\rm S}$ coming from the electrolyte conductivity, etc., was of small importance for the results shown here (and in Section 3) and will

Fig. 10. Simulated (left column) and measured (right column) current density oscillation for forced oscillations and an average anodization voltage $U_{an} = 4$ V. Reference with zero amplitude, i.e. no modulation (a) and (b). Modulation frequency $\omega = 2\pi v_{osc}$ (c) and (d). Modulation frequency $\omega = \pi v_{osc}$ (e) and (f). Modulation frequency $\omega = 4\pi v_{osc}$ (g) and (h).

thus be neglected, while the CB-related part is fully accounted for.

(v) The basic mechanisms for the synchronization (or phase correlations) of CB's due to local interactions have not changed under galvanostatic conditions; they are still due to local interactions. Current oscillations would result, and that can only be avoided by changing the potential "in reverse": if the current tends to go up, the potential must come down and vice versa. This is what a galvanostat does (which is nothing but a constant potential source with a hardware feedback control loop) and that is what the

Fig. 11. The first simulated voltage oscillations at a Si electrode. Stable voltage oscillations for an anodization current of $J_{an} = 0.054 \text{ mA/cm}^2$ (a). Voltage oscillations at slightly different (see inset in (b)) anodization currents (b)–(d), the time period 150–250 s (c), the 500–600 s interval (d).

Table 1 Comparison of galvanostatic and potentiostatic conditions for electrode oscillations

Parameter	Current oscillations	Potential oscillations
Total current density j_{an}	$j_{\rm an} = j_{\rm an}(t)$	$j_{an} = \text{const.}$
Local current density $j_{loc}(x, y, t)$	$CBs \Rightarrow j_{an}(t) = \sum j_{loc}(x, y, t)$	CBs $\Rightarrow j_{an}(t) = \sum j_{loc}(x, y, t)$ i.e. local currents still oscillate!
External potential $U_{an}(t)$	$U_{\rm an} = {\rm const.}$	$U_{\rm an} = U_{\rm an}(t) = V_{\rm SiO}(x, y, t) + R_S I_{\rm an}$
Local potential on the Si surfaces	The potential is the same everywhere at some distance from the sample surface (=equipotential surface),	
$V_{\rm SiO}(x,y,t)$	but lowered considerably on the Si surface in the vicinity of active CBs	
Correlations between	Random phases: $I_{an} = \text{const.}$	Random phases: $U_{an} = \text{const.}$
CB micro-oscillators	Phase coupling: $I_{an} = I_{an}(t)$	Phase coupling: $U_{an} = U_{an}(t)$
Displacement current density j_{cap}	$j_{\rm cap} \approx U_{\rm an} \cdot {\rm d}C/{\rm d}t$	$j_{\rm cap} \approx C \cdot \mathrm{d}U_{\rm an}/\mathrm{d}t$
-	Unimportant	Important
Basic oscillation mechanism	CB interaction	CB interaction
	\Rightarrow Synchronization and de-synchronization	\Rightarrow Synchronization and de-synchronization
	\Rightarrow Domain formation	\Rightarrow Domain formation
	$\Rightarrow j_{an}$ oscillations	\Rightarrow Resulting j_{an} oscillation suppressed by potential oscillations
Shape	Simple, sinusoidal	More complex, saw-tooth, double peak,
Run-away effects	No; $j_{an}(t)$ is always self-limiting	Yes; U_{an} may exceed all limits. New effects
Experiment	Stable oscillations easy to obtain at all HF	More difficult to obtain, especially at small HF conc.
	conc.	

CBM does for galvanostatic "experiments" with a software feedback loop.

(vi) While there is always some well defined average current for any (reasonable) potential applied to the system, the reverse statement is not true: Currents fed into the system that are too large will grow more oxide than can be dissolved by the HF at any condition. Galvanostatic conditions then necessitate continuous potential increases, i.e. a steady state in the form of stable oscillations, damped oscillations, or no oscillations but constant potential, is never reached. The system virtually "explodes" (sometimes experimentally, too, if no external fuse blows and a sufficiently powerful potentiostat is used).

In hindsight, it is far easier to conceive of electrode oscillations not as current or potential oscillations per se, but as electrode impedance oscillations, which, together with external series resistances and feedback loops, lead to the effects observed under the conditions chosen.

It is worthwhile to mention that pronounced potential oscillations have also been found during pore growth; the earliest and most detailed work was published for InP, together with a first simple "resistor" model [21] based on CB dynamics. While this approach was (and is) valid for potential oscillations occurring if the current flows through pore tips exclusively, it is not sufficient to describe the potential oscillations occurring during electropolishing as is the case here.

4.2. Results of simulations

Simulating potential oscillations with the CBM should be possible in principle, because the basic claim of the CBM is that it contains all necessary ingredients for all electrode phenomena found within the confines of the model as discussed in Section 2. Nevertheless, the algorithms have to be changed to account for the constant current condition, and some finer points like the charging/ discharging of the oxide capacitor via the dC/dt term, and in particular via the dU/dt term, which is no longer zero, should be considered. In short, the following measures were taken:

- For every time frame (typically 5 ms) the total current was compared to the preset current; deviations cause a matching potential change for the next time frame. For reasonable time frames this causes rather noisy constant current conditions and introduces a kind of "numerical" time constant that acts like a capacitor. This is essentially what a potentiostat does, too, except that its operation is far smoother than the simulation.
- The capacitive displacement current as defined above was included in the simulation.
- The probability curves for switching CBs on and off had to be slightly modified – they have to be somewhat "softer" compared to the potentiostatic case.

Putting everything together, it was possible for the first time to simulate potential oscillations at the Si electrode; a typical result is shown in Fig. 11.

The necessary change of the probability functions was a bit puzzling at first, but appears to be a logical necessity upon closer inspection: As discussed earlier, the probability functions not only define the dynamics of the CBM, but are also directly related to the oxide quality. During the current oscillations, the mean oxide thickness values are always well above 2 nm, however, this is not the case for the potential oscillations [15], where the oxide thickness locally and temporarily reaches values as small as 0.7 nm. This magnitude is already comparable to the suboxide thickness; suboxide here meaning basically a different form of SiO₂ at the Si–SiO₂ interface. Independent of the peculiar properties of the suboxide, the breakdown properties of sub-nm oxides must be expected to be different from that of "thick" generic anodic SiO₂ and that must change the probability functions in the "softer" direction. In essence, it was necessary and sufficient to shift the stopping probability function in Fig. 1 in the direction of the higher oxide thickness, i.e. the magnitude of ΔE_{\min} in Eq. (4) was set to 0.1 V/nm.

Fig. 11a shows simulated (nearly) stable potential oscillations at a current density of $j_{an} = 0.054 \text{ mA/cm}^2$. Although the amplitude of the oscillations is slowly increasing with time, the frequency and average potential remain rather constant. Fig. 11b-d demonstrate the sensitivity of this type of oscillation to small changes in the current density. For $j_{an} = 0.05 \text{ mA/cm}^2$ (filled squares curve) the oscillation is heavily damped and disappears after a few cycles, while for $j_{an} = 0.051 \text{ mA/cm}^2$ and $j_{an} =$ 0.054 mA/cm^2 (empty squares and circles, respectively) stable oscillations are obtained. For $j_{an} = 0.058 \text{ mA/cm}^2$ (empty triangles) so-called "exploding" oscillations result - the potential increases steadily beyond any limits. Three time cuts are shown in Fig. 11b-d rather than one curve so as not to obscure details. Note that at 0.05 mA/ cm² the oscillations disappeared after less than 100 s, but that an increase of the current density of just 2% will cause oscillations stable for at least 800 s. An interesting behaviour can be observed for the oscillation at $j_{an} =$ 0.058 mA/cm^2 . It exhibits a relatively stable oscillatory behaviour during the first 120 s, at least with regard to the frequency. Somewhat later it looses its "monochromatic" behaviour and becomes "coloured" and unstable, i.e. it oscillates with several frequencies until it is just "noisy". This is a hallmark of insufficient synchronization of the CBs caused by the fragmentation of the surface in domains that are in different phases at any instance of time (e.g. mostly dissolving oxide or mostly growing oxide).

In general, the behaviour shown in Fig. 11b-d is compatible with the experimental findings that stable potential oscillations are very difficult to obtain, especially at very low electrolyte concentrations. According to Hasse [67] and Prange [73] stable potential oscillations are found in a very narrow current interval. Usually a change in the anodization current within 10% will lead to either strongly damped or "exploding" oscillations, a feature that is essentially reproduced in the simulation results presented here. Hasse [67] had to apply a constant current of 0.12 mA/ cm^2 for about 60 s first, followed by a decrease of the current to the "working" level of 0.04 mA/cm² in order to be able to obtain stable potential oscillations. Prange [73] and Lehmann [15] used highly concentrated electrolytes (\sim 5 wt% HF), where it is somewhat easier to produce potential oscillations.

An analysis of the oscillation period over a narrow interval of current densities, i.e. $J_{an} \in [0.05; 0.06 \text{ mA/cm}^2]$ shows that with increasing anodization current the oscillations period will increase as well, as shown in Fig. 12a. In order to have some assessment of this, a linear fit of the average potential as a function of time was made; the slope of these fit curves is shown in Fig. 12b. Damped oscillation would exhibit a negative slope, while zero slope indicates the range of stable oscillations; slopes > 0 indicate "exploding" oscillations. The results confirm once more that the range for stable oscillation is indeed very narrow, and that a small change in the current will drive the system in a nonstable oscillatory state.

Fig. 12. The oscillations period $T_{\rm osc} = 1/v_{\rm osc}$ as determined from the time interval from 100 to 600 s (a). Slope of the average voltage (linear fit) slopes > 0 indicate "exploding" oscillations (b).

As in the case of current oscillations, the CBM model simulations allow to extract many more quantitative data. Fig. 13a shows the mean oxide thickness for the "standard" potential oscillation at $J_{an} = 0.054 \text{ mA/cm}^2$ at high resolution in the time interval 400-600 s. together with the potential oscillations for reference. As one can see, the mean oxide thickness oscillates with the same period as the potential; the only difference being that the oxide oscillation is advanced in phase. Lehmann observed a phase difference between the mean oxide thickness and the potential experimentally [15]. Another important simulation result is that the mean oxide thickness never reaches zero, which is also in full accordance with the measured data [15]. Fig. 13a. It shows a very weak variation of the oxide thickness, i.e. peak-to-peak amplitudes of about 0.01 nm, furthermore the average oxide thickness does not vary significantly, at least in the range of stable oscillations.

Fig. 13b shows the behaviour of the oxide thickness for the full time scale for two distinct anodization currents, i.e. $J_{an} = 0.054 \text{ mA/cm}^2$ (stable) and $J_{an} = 0.05 \text{ mA/cm}^2$ (strongly damped). In contrast to the stable oscillations, the oxide thickness will continuously decrease for the damped case, arriving at an oxide thickness less than 0.65 nm, which is deemed an unphysical value and causes the simulation program to simply stop (as indicated in Figs. 11b and 13b).

Very small values for the oxide thickness as presented in Fig. 13b indicates that the capacitive effects outlined above can become large. Generally, the total current, i.e. the anodization current at the electrode, is always given by

Fig. 13. Voltage oscillations together with oxide thickness oscillation at anodization current $J_{\rm an} = 0.054 \text{ mA/cm}^2$ (a). The left ordinate axis belongs to the voltage, the right one to the oxide thickness. Oxide thickness oscillations belonging to damped and stable oscillations, respectively (b). Oscillation of the capacitive current, after a FFT filtering, together with the oxide capacitance at $J_{\rm an} = 0.054 \text{ mA/cm}^2$ (c).

$$J_{\rm an} = J_{\rm cap} + J_{\rm ox} \tag{13}$$

and the oxidation current J_{ox} will be given by the algebraic sum of the active CBs times their specific current I_{CB} at any specific instance in time, i.e.

$$J_{\rm ox} = \frac{\sum_{n} I_{\rm CB_n}}{A_{\rm electrode}} \tag{14}$$

where *n* is the number of the CBs and $A_{\text{electrode}}$ is the area of the electrode. From the definition of a capacitance C = Q/U (Q = charge stored in C at U) it follows for the capacitive current density $J_{\text{cap}} = dQ/dt$

$$j_{\rm cap} = \frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}C}{\mathrm{d}t}U + \frac{\mathrm{d}U}{\mathrm{d}t}C \tag{15}$$

Relation (13) will add the desired capacitive effects to the model. The parameter C in Eq. (15) is the oxide capaci-

tance, which in turn depends on the oxide thickness; which is continuously calculated by the simulation program at any instance in time. C can thus easily be calculated (assuming a dielectric constant of $\varepsilon = 3.9$ and the capacitive effects are thus intrinsically contained in the CBM).

Fig. 13c gives an idea of the magnitude of the capacitive effects; it shows the calculated capacitance and the capacitive current for the standard case $J_{an} = 0.054 \text{ mA/cm}^2$ in the time interval between 270 and 400 s. The oscillatory behaviour of the capacitance and the capacitive current is clearly visible, although the current curve is very noisy (here plotted after a FFT filtering). The capacitive current is in the order of 10^{-4} mA/cm^2 and thus at least two orders of magnitude smaller as the anodization current; it is, however, underestimated due to numerical idiosyncrasies explained The capacitive behaviour, however, is part of a feedback cycle and an absolute "must" in order to bring the electrode into the oscillatory state. While this may appear astonishing, turning off the capacitive effects produces "exploding" oscillations only.

4.3. Interpretation and more detailed simulations

As before, all kinds of maps can be produced, most interesting here are oxide thickness maps and potential losses as shown in Fig. 14. Again, the model may be "smarter" than its creators, meaning that it produces results that were not predicted and that need retrospective interpretation. Fig. 14 shows a case in question, namely a small section of the mean oxide thickness curve for the standard case of $J_{\rm an} = 0.054 \text{ mA/cm}^2$ taken from Fig. 11a together with the potential curve, the correlation lengths and the surface factions, and snapshots of the oxide thickness distribution at the times indicated on the potential curve. Each oxide thickness map is accompanied by a histogram, displaying quantitatively the oxide thickness distribution. In the first map, taken at 284 s (before the potential reaches its minimum), significant differences in the oxide thickness can be seen and the thicker areas correlate loosely with the areas containing active CBs as shown in the potential loss maps. At this moment a given number of CBs are active and

Fig. 14. A sequence of oscillations at $J_{an} = 0.054 \text{ mA/cm}^2$ (the complete oscillation can be seen in Fig. 11a). Snapshots of the oxide thickness distribution at different points on the oscillation phase as well as the fitting parameters for the AFAF are given.

produce oxide. As time progresses (t = 293 s), the mean oxide thickness increases while the potential decreases. This is simply due to CBs still "burning" and producing oxide, even if the potential decreases. At the same time, new CBs nucleate in the thin areas; as a consequence, the potential loss map shows active CBs in the same area as in the time frame considered before, but also new active areas. As time progresses, too many CBs stop and the potential has to go up again. The active areas now correlate visibly but not perfectly with the areas that were quiet before.

As can be seen, the relation between active regions and passive regions in the potential loss maps is roughly the same in all screenshots – as it should be. Moreover, on any point of the electrode we have local current oscillations that are synchronized to such an extent that the galvanostatic condition, averaging the current to I_0 at any point in time, can only be maintained by potential oscillations.

Of particular interest is the relation between the potential variation and the change in the oxide thickness for "exploding" oscillations. This can be seen in Fig. 15 where

the potential development for an anodization current $J_{\rm an} = 0.058 \text{ mA/cm}^2$ is shown. The difference between the anodization current $J_{an} = 0.058 \text{ mA/cm}^2$ for this case and for the $J_{an} = 0.054 \text{ mA/cm}^2$ producing the rather stable oscillations in Fig. 14 is 0.004 mA or 6.9%. Nevertheless, about 2000 additional CBs are needed at any time to carry the additional current. The system now is no longer able to dissolve the additional oxide produced by these 2000 additional CBs and the mean oxide thickness increases slowly with time as can be seen directly from the histograms. More over, the "camel-back" distribution of oxide thickness with maxima at thin and thick oxides that is always present for stable oscillations (cf. Fig. 14) disappears and gives place to a bell-shaped distribution with a maximum that increases with time. Note that the oxide thickness scales are different in Figs. 14 and 15: On the scale shown in Fig. 15, the oxide thickness screenshots in Fig. 14 would look rather monochrome.

The potential loss maps look rather similar in both cases – as they should, considering that almost the same

Fig. 15. "Exploding" voltage oscillations for $J_{an} = 0.058 \text{ mA/cm}^2$ with oxide thickness snapshots at different moments on the oscillations curve.

current is flowing in both cases. Movies of the potential loss, however, are quite different in the oscillation regime and in the non-oscillating part. While in the former case the active (yellowish) regions move in a more orderly fashion over the sample surface, their behaviour in the latter case is more hectic and random.

Fig. 14 shows part of the reference case for stable oscillations between 280 and 330 s at $J_{an} = 0.054 \text{ mA/cm}^2$; the potential together with the correlation lengths parameters is plotted. It can be seen that the correlation length $\psi(t)$ for the growing oxide subdomains has a considerable phase lag compared to the correlation length $\gamma(t)$ of the oxide dissolution subdomain, and that the minimum on the potential curve coincides with the minimum of the correlation length for the growing subdomain. The potential increase is obviously connected to the correlation length increase of the subdomains where the oxide growth takes place. This is a supplementary proof that the increase in the potential is caused by the need to start new CBs on the electrode surface. The increase of the correlation length $\chi(t)$ in parallel to $\psi(t)$ indicates that on the first phase of the potential increase new CBs nucleate indeed, but dissolution still is the predominant process.

The $\chi(t)$ curve starts to descend at about the inflection point of the upwards part of the potential oscillation. This is easy to understand. At the inflection point the potential reached a value that favours both the nucleation of new of CBs and the "burning" of the already existing CBs (i.e. it "keeps alive" the CBs); the growing subdomains thus expand at the expense of the oxide dissolving subdomains. The correlation length $\chi(t)$ of the dissolving subdomains therefore decreases. Contrariwise, the correlation length $\psi(t)$ of the growing subdomains does not simply increase, but fluctuates at a high level because there is no strong correlation between the "old" and the "new" areas. After some time, the cycle will repeat as discussed. Even though the $\gamma(t)$ and $\psi(t)$ curves tend to have the same behaviour in time, the exact shape is very different for each oscillation period. This is a supplementary argument that the processes at the electrode surface are very stochastic on a microscopic scale, but can nevertheless lead to the same macroscopic behaviour. Analyzing the "exploding" oscillations obtained for $J_{an} = 0.058 \text{ mA/cm}^2$ and shown in Fig. 15 provides new insights and justifies claims made before. In this case, the average value for $\chi(t)$ increases linearly, whereas $\psi(t)$ remains almost constant. While the oscillation has all but disappeared in the potential curve, it is still present in both correlation lengths, in particular in $\chi(t)$. However, the $\chi(t)$ curve shows clear signs of frequency doubling, and the $\psi(t)$ curve already oscillates rather "chaotically" and this may be taken as evidence that the loss of clear potential oscillations could also be interpreted as a transition from order to chaos. Be that as it may, the increase of the correlation length of oxide dissolving subdomains in perfect harmony with the potential increase shows directly that the oxide dissolving subdomains become rounder, more compact, because they cannot grow substantially in size. Knowing this, it can be clearly recognized in the maps of Fig. 15. This implies that it becomes increasingly more difficult for CBs to nucleate in, or penetrate into these areas; instead the potential has to go up to keep a constant number burning. In the active areas, the CB activity is visibly more hectic and random – and that is exactly what was claimed above for what one would see in a movie.

While many more examples could be given, it should be clear by now that the present implementation of the CBM goes far in simulating the Si electrode behaviour in the oscillatory regime of the characteristics and that useful data compression routines have been found and applied.

5. Discussion

5.1. Merits and limits of the current-burst model

It is clear from what has been presented that the currentburst model can quantitatively reproduce many, if not all, observed features of current and potential oscillations at a Si electrode in diluted HF; in particular potential oscillations under galvanostatic conditions. Competing models, e.g., [48–50] so far could not produce as many phenomena, are inherently more complicated and somewhat vague about the physical mechanisms behind the parameters considered.

The CBM is based on just one basic assumption or "axiom" - the probability functions for starting and stopping a CB – and many approximations. The basic assumption is rather natural, however, since it is generally accepted that current will start to flow before the oxide thickness is zero. However, tying current flow in a unique and reversible way to the oxide thickness (e.g. assuming that the current density is proportional to some (negative) power of the oxide thickness), will always produce a steady-state configuration with a constant oxide thickness, independent of the starting distributions of the oxide thickness. A non-linear or stochastic component is needed in relating oxide thickness and current, and the choice of some "ionic breakdown" probability is not unreasonable. Considering that this is the usual assumption for electronic breakdown, and considering that it might well be the electronic breakdown that triggers the ionic breakdown as pointed out in [74], the basic assumption of the CBM appears reasonable.

Another option would be "mechanical" oxide breakdown, e.g. crack formation somehow tied to the oxide thickness in a non-linear and stochastic way with some consequences for current flow. This is the approach tried in [50]. While this works, too (but to a far smaller extent then the CBM), it needs far more assumptions (including unphysical ones like crack formation in layers under compressive stress) and many approximations are needed, as well as an adjustable parameter.

The approximations of the CBM contain the exact numerical values of essentially uncritical numbers like the dissolution speed of SiO_2 in HF of a given concentration, or the current in a CB, some rather uncritical omissions like the capacitive effects for potentiostatic current oscillations; but also omissions of potentially important effects like mechanical stress in the oxide, electron tunneling through the oxide, diffusion limitations, Nernst potentials induced by concentration gradients or local pH variations produced by local current fluctuations.

It is worthwhile at this point to discuss the limitations, assumptions and approximations of the CBM more closely. There are presently essentially two physical limitations and two modeling limitation: The physical limitations are: (i) the surface of the Si must be covered with oxide at all times, and (ii) all current produces oxide. While deviations from those conditions encountered in experiments will probably not change the over-all behavior very much, the algorithms presently used might produce "artifacts".

The modeling limitations first concern low values of the HF concentration or the current density; as before the algorithms used might produce artifacts for physically harmless situations encountered at larger HF concentrations. Second, the numerics involved in any Monte Carlo program do not allow simple scaling to larger sample areas. A simulation run of a $(1 \times 1) \mu m^2$ sample takes 20 days or so, and realistic sample sizes are out of reach.

While the physical limitation and the modeling limitation with respect to the sample size are more or less trivial, the HF concentration issue is critical.

It is easy to run the program for increasingly larger HF concentrations, but then the spread in oxide thickness increases. Temporarily and locally the thickness may reach values as low as 0.65 nm with no CB nucleation because of the de-synchronizing effects of active CB's nearby; in this case the program simply stops. While in physical reality this may happen without major changes in what is generally going on, new effects could and would take place that are not yet part of the CBM. Electron tunneling through very thin oxides, with oxygen and not SiO₂ production as the concomitant chemical process, is a safe bet. However, since tunneling is highly non-linear in nature, an implementation into the Monte Carlo program is not straightforward. Moreover, if the oxide disappears completely, direct dissolution via CBs through a hydrogen passivation "barrier" may take over for a short time; again a process that is not yet part of the program.

Oxide thicknesses in excess of roughly 10 nm may also be encountered within the available parameter space, in this case stress-induced effects may occur, including extremes like (periodic) flaking off of the oxide as observed in [52]. Again, while physically simple, this is not straightforward to implement in the simulation, in particular because it is not quite clear what will happen. Simply postulating crack formation in an oxide that is under compressive stress as the major mechanisms behind microoscillators and synchronization as done in [50] appears far-fetched and not very likely. We are thus left with a slightly paradoxical situation. While the physics of the CBM or simply of the general situation tends to imply that more effects come into play at larger HF concentrations, i.e. everything gets far more complicated, experiments seem to indicate the opposite: it is far easier to find strong stable current and especially potential oscillations at large HF concentrations. This might be seen as an indication that at least some of the many possible effects discussed above may be neglected, or that they simply provide for positive feedback, strengthening synchronization, without changing the basic mechanisms all that much. It goes without saying that all the effects mentioned must be considered, at last in principle, in all competing models, too.

On the other hand, some effects discussed in the literature like field-enhanced diffusion of oxygen in SiO_2 layers or enhanced SiO_2 dissolution at high field strength are already included in the CBM. If the oxide at some point (x, y) is a bit thinner than on average and the effects mentioned become noticeable, it will simply produce a CB somewhat earlier than without these effects and thus change the distribution function somewhat. Since the distribution functions are, to some small extent, free parameters of the system, any such effects, if existent, are already included.

As pointed out before, the CBM is based on Monte Carlo simulations and therefore restricted to small sample sizes that can be handled by standard hardware. The parameters were selected in such a way that oscillations resulted, but that does not necessarily imply that this set of conditions would produce oscillations on a typical (1×1) cm² sample. However, since the simulations on (200×200) nm² sized "samples" agreed rather well with experimental results obtained for the parameter set used as far as it could be compared, the size problem may not be all that serious.

5.2. Possible extensions of the CBM and future work

It is tempting to extend the CBM to other phenomena encountered in electrochemistry, it is, however, too early to make definite claims. The following list therefore must be seen as tentative; while the effects mentioned might find explanations in terms of suitably modified CBM, there might be other explanations, too.

Effects under anodic oxidation conditions: In [58,75] some new phenomenae with respect to anodic oxide formation were reported. In particular, a steady-state anodic oxide was found with peculiar micro- and macrostructure. Viewed under high magnifications, the oxide seems to be composed of spherical particles with diameters of some 10 nm. This would just be what would be expected as a result of one CB for the conditions given. If interpreted in this way, the active phase of a current burst would lead to rather violent local oxide formation, producing $[H^+]$, and thus increasing the local pH value considerably. This in turn slows oxide dissolution; it may not take place at

all during the oxide formation [76]. This is a feature that is certain to occur and it can easily be incorporated in the program code; it will be interesting to see how this pHbased feedback mechanism will change the results already

obtained. Pore formation in anodically etched semiconductors often produces rather regular structures, up to self-organized single pore crystals [77]. This may be seen as a current oscillation in space instead of in time. While this fact by itself is not linked in an obvious way to the CBM, the additional observation of strong current or potential oscillations often occurring ion parallel to strong current oscillations in space (i.e. well expressed pore patterns) [77,78,56], does give a strong hint that some CBM related mechanism is at work; cf., e.g., [74,79], where some more speculations about possible connections have been made.

In this context, it is worthwhile to mention that any barrier to current flow, not just SiO₂, might induce CB behaviour. In particular, current flow through hydrogen passivated Si surfaces might follow CB patterns; with probability functions that also contain the crystallographic orientation of the surface as a parameter. While a mechanism based on this goes a long way to explain certain features of pore growth in Si (cf. [54]), it is purely qualitative at present and not necessarily the only possible explanation. It is worthwhile to point out here, that an extension of the CBM to pore growth is simple in principle, but rather difficult to implement quantitatively because only a full threedimension treatment of the dissolution process could do justice to this problem.

As has been shown, current flow via the CBM does not always produce oscillations, then the CBM model therefore should be able to reproduce the current – potential characteristics of the Si–HF system at least in that part where the basic assumptions are met. First attempts in this direction were met with some success; however, the limitations of the present software as discussed above also become quite clear. While it will take a dedicated effort to move the CBM in this direction; the authors feel quite confident that it would be met with success.

Last, it shall be mentioned that any material that dissolves anodically via oxide formation might be doing this via CBs. In other words, oscillatory phenomena observed during the anodic dissolution of metals might also be due a CB mechanism. However, it is also quite possible that the unique qualities of SiO₂ restrict the CBM to Si only. Time and more research will tell.

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