Oscillations at the Si/electrolyte contact: Discretization of phase oscillators

J Grzanna and H J Lewerenz
Helmholtz Zentrum Berlin for Materials and Energy, Hahn-Meitner Platz 1, D-14109 Berlin, Germany
E-mail: grzanna@helmholtz-berlin.de

Abstract. The origin of sustained current oscillations at the Si/electrolyte contact is not fully understood. Oscillatory functions are regarded which describe the oscillating oxide thickness at the silicon electrode. We consider an initially vanishing two-dimensional time dependent function which oscillates between a minimum and a maximum oxide thickness at each location of the electrode. The function is continuous except at single points of the electrode at which the oxide thickness drops deeply due to the formation of nanopores in the oxide. The oscillatory function is represented by a set of infinite (infinitesimal) oscillators. The mathematical model is based on the fact that it is sufficient to register the oscillators only one time per \( i \)-th cycle at their minimum or when the phase of the oscillator equals \( i \cdot 2\pi \). In phase-space representation, the passing of the phase trough the \( i \cdot 2\pi \) planes leads to oscillator density functions \( p_i(t) \) which define the (differential) number of oscillators passing their minimum at the \( i \)-th time at the time \( t \). Two consecutive oscillator density functions are connected by an integral equation representing a Markov process. Together with a local model for the oxide microstructure, a fit of the model parameter to the measured current is possible. The result is that the existence of two types of oxides (with different nanopore densities) can explain sustained current oscillations and, further, it is possible to calculate the mean nanopore distance in both types of oxide.

1. Introduction
Oscillatory processes are observed in almost any field of science. The oscillatory behaviour of silicon electrodes has been reported about two decades ago [1]. In photo-electrochemistry and electrochemistry, oscillatory behaviour has been extensively studied on Si photo-electrodes [2]. Several models were developed based on self-oscillating domains [3], oxide-induced interfacial stress [4] and the so-called current bursts [5]. The observation of nano-dimensioned pores, fluctuating with the phase of the oscillating (photo)current of Si electrodes immersed in dilute ammonium fluoride solutions motivated the further development of the original stress model, also to spatial resolution, by applying cellular automates [6-8]. In section 2, the basics of the oscillatory process are presented. The discretization of the used phase oscillators is illustrated in section 3 and finally the fit to measured data is discussed in section 4.

2. The oscillatory process
The relation between the oxide evolution at the electrode and the considered two-dimensional time dependent oscillating function \( d(t,x,y) \) is shown in figure 1 in which \( d \) denotes the oxide thickness, \( t \)
the time, \( x,y \) the spatial coordinates at the electrode, and \( i \) the cycle (Si layer) number. The basic process at the surface of the Si electrode is characterised by a cyclic oxidation (figure 1b) of a small silicon layer (with a thickness of ca. 10 nm) and the following removal of the oxide by etching (figure 1c-d). The oxide thickness evolves not uniformly at the electrode due to cracks and nanopores at the oxide (figure 1b-d) which result from stress due to the lattice mismatch between silicon and its oxide. Hence the oxidation can proceed at different layers (cycles) at the same time. The introduced function \( d \) reflects the dynamics of the oxide thickness and oscillates between a minimum and maximum value (figure 1, bottom). At the left hand side of a single minimum value of \( d \), the oscillation process is in a different (neighbouring) cycle relative to the right hand side (figure 1d).

![Figure 1. Relation between the oxide thickness evolution at the electrode at the top and the oscillating function \( d(t,x,y) \) at the bottom.](image)

The mathematical model is based on the fact that it is sufficient to register the time \( s \) at which \( d \) equals the minimum value at the location \((x,y)\). At this time \( s \) (which depends on \((x,y)\)), the oxide starts to grow (figure 1a, d) and during the (constant) oxide growth time an anodic current \( E_i(t-s) \), whose duration is short with regard to the oxide etching time, flows [4, 7]. Then, the total current can be calculated by superposition of all elementary current peaks \( E_i(t-s) \) [4].

3. Discretization of phase oscillators

The oscillating function \( d \) is described by a set of infinite oscillators. Each oscillator is dedicated one-to-one to an infinitesimal point \((x,y)\) of the electrode surface domain \( \Omega \subseteq \mathbb{R}^2 \). With

\[
d(t,x,y) = \cos(q(t,x,y) + \pi) + \frac{1}{2} (d_{\text{max}} - d_{\text{min}}) + d_{\text{min}} \quad \text{for} \quad i2\pi \leq q(t,x,y) \leq (i+1)2\pi, i = 0,1,2,...
\]

the oscillatory process is described by a two-dimensional time depending phase function \( q(t,x,y) \). Due to equation (1), \( q \) propagates monotone increasing (with variable shape) in the phase-space \( \Phi = \{(x,y,q) \mid (x,y) \in \Omega, q \in \mathbb{R}_+ \} \). If an oscillator passes its minimum at the \( i \)-th time, the phase equals \( i2\pi \). Due to the above mentioned basics, it is sufficient to register the time \( s \) at which the phase passes the so-called snap-shot screens \( S_i = \{(x,y,i2\pi) \mid (x,y) \in \Omega \} \) that are planes in \( \Phi \) with a phase difference of \( 2\pi \). The latter corresponds to a discretization of the phase (oscillators) because only the multiple of \( 2\pi \) is considered and not the continuum. The passing of the phase through each snap-shot screen \( S_i \) is described by a density function \( p_i(t) \) of oscillators which defines the
differential number of oscillators passing their minimum simultaneously at the time \( t \) at the \( i \)-th time. For the calculation of \( p_i(t) \), firstly the intersection \( \Gamma_i(t) = \{(x,y) | (x,y) \in \Omega \text{ and } q(t,x,y) = i \pi \} \)

\[
\pi \phi_{yt} = \Omega \in \Gamma \subseteq \Gamma
\]

\[\begin{array}{c}
\partial \phi \\
\partial t
\end{array} = \sqrt{\left( \frac{\partial \phi}{\partial x} \right)^2 + \left( \frac{\partial \phi}{\partial y} \right)^2} = \tan \alpha
\]

**Figure 2.** The passing of the phase \( q(t,x,y) \) through \( S_i \) (here the \( (x,y) \) plane) is shown.

between the phase \( \phi \) and \( S_i \) is determined. \( \Gamma_i(t) = \Gamma_i^{\text{string}}(t) + \Gamma_i^{\text{area}}(t) \) subdivides into strings (contour lines of \( \phi \)) and to areas at which the phase equals \( i \pi \). Normally such areas does not exist \( (\forall i \pi \text{ area} \subseteq \Gamma \text{ are empty}) \) but we consider here also the possibility that some few \( \Gamma_i^{\text{area}}(t) \) are not empty for \( j = 1 \text{ for } m \). Assuming the phase \( \phi \) passes completely the \( i \pi \)-screen \( S_i \) during the time interval \( [t_i^\text{min},t_i^\text{max}] \), we get the factorization \( \Omega = \bigcup_{\in [t_i^\text{min},t_i^\text{max}]} \Gamma_i(t) \). Secondly, the incremental velocity of a string is calculated. The string of intersection between \( \phi \) and \( S_i \) moves at the \( i \pi \)-screen with the incremental velocity of

\[
\frac{\partial r}{\partial t}(t,x,y) = \frac{\partial \phi}{\partial t} \left( \frac{\partial \phi}{\partial r} \right)^{-1} = \frac{\partial \phi}{\partial t} \left( \frac{\partial \phi}{\partial x} \right)^2 + \left( \frac{\partial \phi}{\partial y} \right)^2 \right)^{-1/2}
\]

for \( (x,y) \in \Gamma_i^{\text{string}}(t) \)

\[\text{(2)}\]

Thirdly, we integrate the velocity of the strings and add (only in the case of \( m > 0 \)) weighted Dirac functions and get

\[
p_i(t) = \frac{1}{N_i} \int_{\Gamma_i^{\text{string}}(t)} \frac{\partial r}{\partial t}(t,x,y) \, dx \, dy + \sum_{j=1}^{m} F_i(t) \delta(t-t_j) \text{ for } t \in [t_i^\text{min},t_i^\text{max}]
\]

\[\text{(3)}\]

at which \( N_i \) is a factor to fulfill \( \int_{t_i^\text{min}}^{t_i^\text{max}} p_i(t) \, dt = \int_{\Omega} d \Omega \) (each oscillator correlates to one \( (x,y) \in \Omega \)) and \( F_i(t) \) denotes the area of \( \Gamma_i^{\text{area}}(t) \). \( p_{i-1}(t) \) and \( p_i(t) \) are connected by the two-dimensional (in \( t \) normalized) function \( q_{i-1}(t-s) \) which denotes the probability density for the period \( t-s \) of oscillators starting their \((i-1)\)-th cycle at the time \( s \). We get the Markov process \[4\] (figure 3)

\[
p_i(t) = \sum_{t_i^\text{min}}^{t_i^\text{max}} p_{i-1}(s) q_{i-1}(t-s) \, ds \text{ for } t \in [t_i^\text{min},t_i^\text{max}]
\]

\[\text{(4)}\]
\( q_{t,s}(t-s) \) is calculated as \( p_t(t) \) with the exception that \( \Omega \) is replaced by \( \Gamma_{i-1}(s) \) in the definition of \( \Gamma(t) \) and the factor \( N_i \) makes sure the normalization of \( q_{t,s}(t-s) \) in the \( \tau \) direction [6].

**Figure 3.** A sketch related to equation (4) (left) and the microscopic nanopore model (right).

### 4. Modelling sustained current oscillations

The simulation procedure entails:

i) find a kernel \( q_{t,s} \) which fulfills equation (4) with \( p_t(t) = p_{i-1}(t-T) \) (\( T \) – oscillation period) and

ii) fit the total current \( I(t) = \sum_i^{\infty} \int_{t_{i-1}}^{t_{i+1}} p_i(s) E_i(t-s) ds \) of the model to the measured current.

Figure 3 shows the case of sustained oscillations for what \( t_{i+1}^{\max} - t_{i+1}^{\min} = t_i^{\max} - t_i^{\min} \) and \( q_{t,s}(t-s) = 0 \) for all \( t \) with \( t < t_i^{\min} \) and \( t_i^{\max} < t \) are necessary conditions. Here, the shape of \( q \) is deduced from the normalized Greens function of the Helmholtz differential equation [8]. From the shape of \( q \) and the microscopic nanopore model it follows that two types of oxide (I and II) exist. We consider the \( s \) dependent oxide micro structure evolution (spatial temporal mean) during a cycle (figure 3, right). The maximum oxide life time \( t_i^{\max} - t_i^{\min} \) is determined by the maximum oxide thickness \( d^{\text{high}}(< r_{\text{max}}) \) in the case of the earlier grown oxide I with some few cracks and nanopores per area unit (see figure 3, top right). The shorter life time \( t_i^{\max} - t_i^{\min} \) of the later grown oxide II can be realized only by more cracks and nanopores per unit area. In this case, the oxide life time is determined by a smaller half pore distance \( r_{\text{min}}(< d^{\text{high}}) \) (see figure 3, bottom right) due to three dimensional etching in nanopores. Hence, the microscopic nanopore model allows (by simulating the etching) to determine the relation between the oxide lifetime \( t_i^{\max-s} \) and the mean nanopore distance \( 2r(s) \) for \( t_{i-1}^{\min} \leq s \leq t_{i-1}^{\max} \).

### 5. Conclusions

The mathematical concept to describe the oscillatory process at the Si/electrolyte contact is based on the discretization of phase oscillators which are registered at the multiple of \( 2\pi \). An integral equation describes the sequence of the resulting phase oscillator densities \( p_t(t) \) at \( i2\pi \) as a Markov process. From the kernel \( q_{t,s}(t-s) \) of the integral equation, it follows that two types of oxide with different nanopore density can explain sustained oscillations. In addition, the mean nanopore distance of the different oxide types can be calculated using the microscopic nanopore model.

**References**