

Theory on the correlation of localized corrosion and macroscopic oscillatory behavior at Si electrodes

J. Grzanna, H. Jungblut, H.J. Lewerenz
Hahn-Meitner-Institut GmbH
Glienicke Str. 100, 14109 Berlin, Germany

We consider current oscillations at single crystal silicon electrodes in fluoride containing solutions which are observed at higher anode potentials ($>3V$ vs. SCE). In previous publications (for instance [1-6]) the oscillatory behavior is described by chemical and electrochemical parameters which are of integral character. Differential equations are developed reflecting the relation between the parameters but the initial process for the oscillatory phenomenon remains obscure. Chazalviel [7] suggested self oscillating domains could lead to the oscillatory behavior. This idea is developed further. To illustrate the origin of the oscillation process it is necessary to separate the fundamental parameter and to consider its spatial and temporal resolved evolution. The remaining parameters should be computable from the fundamental parameter. In the presented theory [9-10] the oscillatory behavior at Si electrodes is attributed to morphological aspects (cracks and pores) of the silicon oxide layer. The local and dynamic evolution of oxide growth and its etching in domains is considered. Therefore the local thickness oscillator (oxide thickness at one point) is introduced reflecting (in the totality) the spatial and temporal resolved behavior of the oxide layer of a domain and of the hole electrode. One cycle of a thickness oscillator starts at the minimal thickness (zero thickness is not excluded) of the oxide passing the maximal oxide thickness (local growing phase) until the minimal thickness is reached again (local etching phase).

The so called synchronization state (time-dependent function) represents the fundamental parameter. During a cycle the synchronization state describes the (differential) number of thickness oscillators passing the minimal thickness simultaneously. Hence a synchronization state similar to the Dirac function represents high synchronization. The probability distribution q for the period of a thickness oscillator links two consecutive synchronization states. The synchronization state of the i -th cycle is the convolution of the $(i-1)$ -th synchronization state with q . q results from the evolution of the oxide thickness (growth and etching) in a characteristic domain during one cycle. The characteristic domain is the statistical mean (spatial and temporal) of all possible domains of the Si electrode. The common of the domains is the existence of cracks and pores in the grown oxide due to lattice mismatch between silicon and silicon oxide. The pores increase the local etch rate in his neighborhood because three dimensional etching works instead of planar etching in the absence of pores. Hence some thickness oscillators (located nearby pores) have a shorter period than the majority (located far away from pores) and consequently the resulting q is a monotone increasing function until the largest period is reached. The synchronization mechanism results from the lattice

mismatch between silicon and silicon oxide which leads to local stress around the domain just oxidized. Consequently the oxide of such stressed domains (with temporally shifted starting point) contains more cracks and pores resulting in an increased local etching rate. Synchronization occurs because the initially formed oxide is less defective (reduced stress from neighboring domains) and prevails compared to later grown oxide of the neighboring domains. Hence it is the spatial and temporal change of the etch rate which leads to synchronization, differently from assumed changes in the local oxide formation [8] which takes place in a much shorter time.

We calculate the integral chemical and electrochemical parameters such as oxide thickness, roughness, refractive index, effective etching rate or the current. The used potential and the solution composition (nominal etch rate) determine the model parameter as for instance the charge resulting from the grown oxide during one cycle, the maximal oxide thickness, the time for oxide growth, the time for planar oxide etching, and the mean pore distance in oxide with reduced stress. To calculate the integral parameters we consider the evolution of the oxide in the characteristic domain during one cycle. We assume a uniform growth of oxide at a circular characteristic domain (until the maximal thickness is reached) followed by the etching of the oxide containing a pore in the middle. Similar to the determination of q we derive for one characteristic domain the (time-dependent) integral oxide thickness D , roughness R , refractive index N , and the elementary current peak E . The elementary current peak is a decreasing function which reflects the increasing passivation behavior of the growing oxide. A convolution of the sum of all synchronization states with the elementary current peak leads to the overall current of the electrochemical system. Analogously we can calculate the other chemical and electrochemical parameters by the convolution of the sum of all synchronization states with D , R , and N . The results show that a variety of experimental data can be reproduced, such as the initial behavior, damped as well as sustained oscillations and also the synchronization of two different current peaks resulting from two different parts of a Si surface. A good quantitative agreement between experimental measurements and the corresponding simulations can be found.

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