

Measurement and analysis of dynamic impedance spectra acquired during the oscillatory electro-dissolution of p-type silicon in fluoride-containing electrolytes^{a)}

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Using dynamic multifrequency analysis (DMFA), we investigated the oscillatory reaction dynamics that govern the anodic electro-dissolution of p-type silicon in fluoride-containing electrolytes, in which the anodization of silicon is followed by the chemical etching of the oxide layer. By applying a constant voltage to the silicon electrode, stable oscillations are found in the presence of an external resistance. The dynamic impedance spectra acquired through DMFA were fitted to a suitable electrical equivalent circuit. In doing so, it was possible to investigate the temporal evolution of the kinetic parameters throughout the formation and dissolution of the silicon oxide.

Being one of the most important semiconductor/electrolyte interfaces, the anodic electro-dissolution of silicon in fluoride-containing media has been well investigated since the 1950's. Yet, many aspects of the electro-dissolution dynamics remain unclear, among them the current oscillations that occur for potentials more positive than approx. 3 V, as first reported by Turner in 1958¹. In this potential range the silicon surface is covered by an oxide layer, which is continuously formed at the silicon/silicon-oxide interface and etched by the fluoride species at the silicon-oxide/electrolyte interface. As summarized in chapter 5 of reference² several attempts have been made to connect the oscillations to changes in the oxide properties, the most widely discussed mechanisms are based on stress-induced cracks in the oxide film³, morphological changes⁴, or electrical breakdown⁵. However, studying transient voltage oscillations during galvanostatic silicon anodization in fluoride-free electrolyte with advanced equipment available nowadays, Proost and co-workers⁶ could rule out essentially all of the proposed mechanisms. In particular in-situ thickness and stress measurements as well as high-resolution

TEM and AFM showed that the oscillations were not stress induced, nor were they accompanied by significant changes in surface roughness or the formation of nano-sized pores or cracks. Furthermore, the characteristic sudden changes in potential occurred at different electric field strength across the film, which speaks against an electrical breakdown as origin of the oscillation. Instead, they argue that the oscillations are connected to a "sudden dissipation of accumulated charge". Further insight that helped clarifying discrepancies in the literature and getting a more concise picture came from studies concerning the classification of the oscillatory behavior. Depending on the experimental conditions, different kinds of oscillations were identified⁷, among them the period-1 low- and high-amplitude oscillations, which are assumed to be linked to different electrochemical processes⁸. Low-amplitude oscillations appear to be simpler from a mechanistic point of view, since they can be characterized by fewer degrees of freedom, as compared to high-amplitude oscillations. From ellipsometric intensity measurements the thickness change of the oxide layer could be extracted and correlated to the current density, revealing that neither the reaction valency nor the etch rate are independent degrees of freedom. The fact that the current density could be ascribed fully to the thickness variation of the oxide implies that only one of these four quantities (current, oxide layer thickness, reaction valency and etch rate) represents a true degree of freedom. Since any oscillation requires two true degrees of freedom, any further progress in understanding the origin of the dynamic instability is not possible without revealing the nature of the second independent variable. Therefore, it would be desirable to prove the dynamic processes occurring in the system at different time scales simultaneously. This is possible by performing multisine dynamic impedance measurements covering a large range of frequencies, which represent an efficient method to describe

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the underlying physical processes of the oscillatory dynamics.

In this work we show the measurement and fitting of dynamic impedance spectra by means of dynamic multi-frequency analysis (DMFA), a method that we have recently proposed for the extraction of dynamic impedance spectra^{9,10} and which is based on multisine perturbation and digital quadrature filtering. In contrast to standard stationary impedance spectroscopy, DMFA does not require a steady-state behavior of the system in the time domain⁹. With the help of DMFA, impedance spectra that cover a large range of frequencies become accessible at each point in the time domain in the oscillatory region of the system. The extracted temporal development of the kinetic parameters is discussed in relation to the oscillating current.

The electro-dissolution of p-type silicon was investigated under anodic voltages in a fluoride-containing aqueous electrolyte using a three electrode set-up with a rotating disk electrode configuration (AFM-SRCE, Pine Research Instrumentation, Inc.) in a custom made, gas tight, polymethylmethacrylate (PMMA) cell with two compartments. The 5 mm diameter p-type silicon disk working-electrode with a resistivity of $\rho = 5 - 25 \Omega\text{cm}$ was prepared as explained in reference¹¹. A Pt wire was used as counter electrode, while a Hg/Hg₂SO₄ electrode served as reference electrode. All potentials are reported vs. SHE.

The electrolyte was prepared using 0.06 M NH₄F, 142 mM H₂SO₄ and ultra-pure water, yielding a pH of 1 in accordance with dissociation constants found in the literature¹² and the potential was controlled via a SP-300 potentiostat (Bio-Logic Science Instruments). An external resistance equal to 10 k Ω was placed in series with the working electrode. A 2-channel waveform generator (Keysight) was used to generate the multisine perturbation which was added to the potential control of the potentiostat. In order to record the response of the system, a 2 channel oscilloscope (4262 PicoScope, Pico technology) was connected to the output of the potentiostat, where Matlab scripts were used to analyse the data¹⁰. The dynamic impedance spectra were acquired at a rotation speed of 500 rpm and a polarization potential of 8.64 V vs. SHE, to which the multisine perturbation was added. The multisine signal contained 39 frequencies ranging from 17 kHz to 680 mHz with an amplitude of 300 mV peak-to-peak, and a base frequency equal to 170 mHz. Although the amplitude of the multi-frequency signal is quite large, we verified before that no secondary harmonics were present in the output signal. A total of 2000 impedance spectra were extracted. The fitting of the impedance spectra was performed using suitable Matlab scripts, according to the algorithm presented in reference⁹.

Cyclic voltammetry (CV) of the p-type silicon sample in contact with the 0.06 M NH₄F solution was performed at a scan rate of 20 mVs (Figure 1). According to the literature^{13,14} this CV can be divided into three

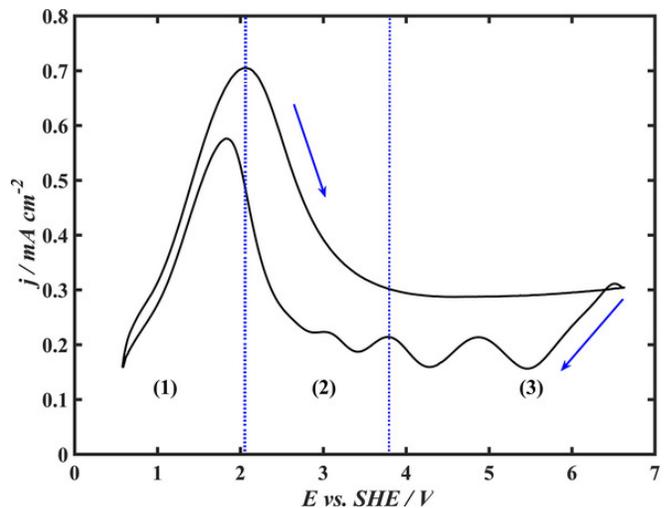


FIG. 1. CV of the electro-dissolution reaction of a p-type silicon sample in an electrolyte containing 0.06 M NH₄F-ions (pH 1) at a scan rate of 20 mV/s, arrows indicating the scan direction.

regions: The region to the left of the maximum of the current (2.06 V vs. SHE), the region where the current is decreasing with increasing voltage and the region where the current has reached a plateau. The first region is the electropolishing region of the silicon electro-dissolution. In the second region the oxide grows faster than its chemical dissolution rate, resulting in a thin oxide film. In the third region low-amplitude, self-sustained, natural oscillations, as shown in Figure 2a, can be observed when inserting an external resistance in series. We use the term natural oscillations to distinguish the oscillations obtained from potentiostatic experiments from those extracted from DMFA. The latter was performed by imposing a multisine signal on sustained low-amplitude oscillations. All frequencies contained in the multisine signal are integer multiples of a base frequency, f_b , which was chosen to be equal to 170 mHz, to avoid interferences with the Fourier spectrum of the natural oscillations with a frequency, f_{osc} , of about 20 mHz. Since the natural oscillation is very slow with respect to the ac components, the data can be analysed with the same equivalent circuits used in classical stationary impedance spectroscopy⁹. Following the procedure in reference¹⁰, we extracted 2000 dynamic impedance spectra in the time domain from the bare data by using a quadrature filter with a bandwidth equal to 170 mHz. In literature it was reported that electro-dissolution of p-type silicon proceeds uniformly across the electrode surface, at least down to the μm scale¹⁵. In Figure 2b four impedance spectra are shown, taken at four points along the natural oscillation, as indicated in Figure 2a.

All impedance spectra consist of a semicircle followed by a straight line. While the radius of the semicircle is in anti-correlation with the natural current oscillation (it reaches its maximum when the current reaches its minimum and vice versa), the straight line does not follow

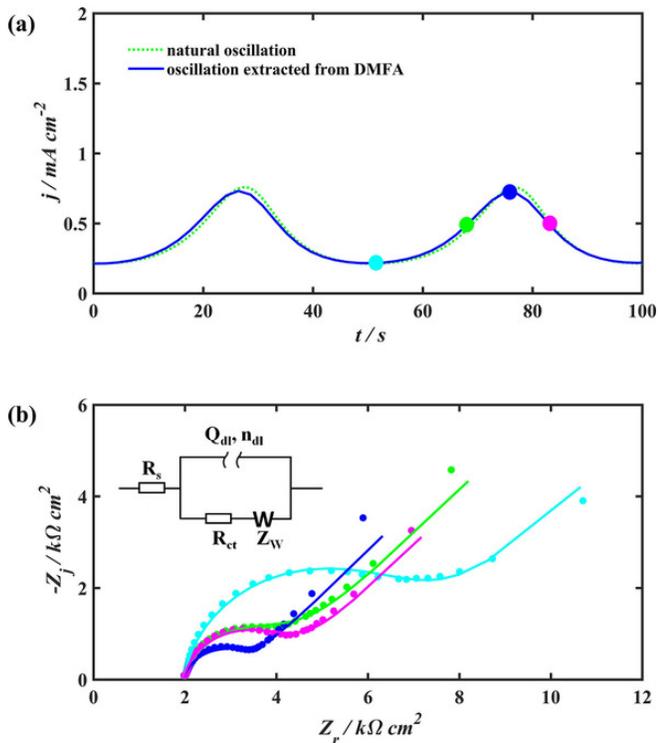


FIG. 2. (a) Sinusoidal low-amplitude current oscillations observed at a potential of 8.64 V vs. SHE and an external resistance of 10 k Ω as well as current oscillations extracted from DMFA. (b) Dynamic impedance response at different parts of the oscillation, as indicated by the circles in (a) and the corresponding fitted spectra, as well as the used fitting circuit.

an immediately recognizable trend. The shape of the impedance spectra suggests that they could be fitted by a simple Randles circuit, as shown in Figure 2b (continuous lines)¹⁶. It is important to note that we did not aim to represent the real physico-electrochemical properties of the system, instead the circuit was used as an assembly of reasonable fitting parameters, which can be considered a first approach to develop the proper reaction mechanism. The fitting was performed considering the condition of continuity and smoothness of the parameters, according to the procedure described in reference⁹. The Nyquist plots show that the quality of both recorded spectra and fitting is very good (χ^2 equal to $3.05 \cdot 10^{-4}$). To describe the non-ideal capacitive behaviour of the anodic silicon oxide, which we attributed to disk current density distribution¹⁷, the capacitance was replaced by a constant phase element (CPE), which is represented by the parameter Q_{dl} and its corresponding phase angle, n_{dl} . R_s is given by the sum of the solution resistance and the external resistance. We assumed R_s to be constant. By data fitting a value of R_s equal to $1.97 \text{ k}\Omega \text{cm}^{-2}$ was obtained, which is almost identical to the external resistance ($1.96 \text{ k}\Omega \text{cm}^{-2}$). n_{dl} was found to attain values between 0.88 and 0.90, thus indicating that the behaviour of the CPE is close to the one of a pure capacitor¹⁸.

In Figure 3 the resulting fitting parameters were plotted as a function of time. R_{ct} , representing the charge transfer resistance of the process, which oscillates symmetrically and in anti-correlation with the current. This fact points out that the resistance is due to a charge transfer process. The constant phase element is coupled to the solution resistance as well as to the charge transfer resistance, therefore, the effective capacitance, C_{eff} , was calculated from Q_{dl} , R_s and R_{ct} , in order to represent this correlation¹⁸. The oscillation of C_{eff} behaves symmetrically and shows a minimum where the current density reaches the maximum. Here, it is tempting to associate the effective capacitance with the dielectric behaviour of SiO_2 , however C_{eff} does not follow the shape of Δd_{ox} (cf. Figure 3d,c), the variation of the oxide layer thickness, estimated from an integration of the current according to reference⁸. Therefore, it appears that the change in thickness of the oxide is not the only factor influencing C_{eff} . However, if we assume that the average dielectric constant of silicon oxide is equal to 3.9 and consider the average value of the effective capacitance,

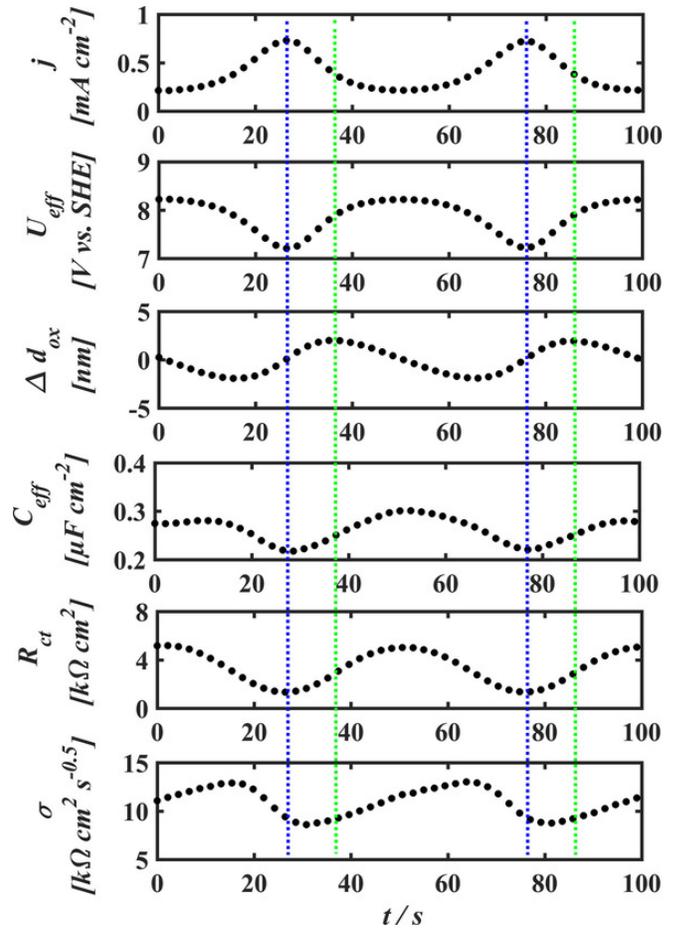


FIG. 3. Temporal development of the different kinetic parameters obtained from the measurements shown in Figure 2, the dashed guiding lines indicate the maximum of the current (blue) and the maximum of Δd_{ox} (green), respectively.

$C_{\text{eff,av}} = 0.26 \mu\text{Fcm}^{-2}$, an average thickness of the oxide layer equal to 13.2 nm can be calculated, a value which is in accordance with the literature⁸. As the effective capacitance is not significantly higher than the value given by a pure dielectric behavior of the SiO_2 and in addition the change in potential drop across the Helmholtz layer is minor, we conclude that absorption phenomena and surface charging do not play a major role. Instead, we think that the behaviour of the effective capacitance is related to a simultaneous oscillation of the thickness and the dielectric constant of the oxide, the latter being due to changes in the composition and nature of the SiO_x layer. The confirmation of such hypothesis needs further evidence and is out of the scope of this work. Unlike the previous two parameters, the Warburg element, σ , which is linked to the diffusion coefficient of the electroactive species, behaves asymmetrically. This latter phenomenon generates a considerable asymmetric evolution of the impedance spectra with respect to the phase of the natural current oscillation. A variation of the rotation speed of the RDE in a range from 500 to 1000 rpm did not lead to any significant change in the impedance response. Therefore, we attributed the observed Warburg element to the transport of a reactive oxide species inside the silicon oxide layer, as opposed to transport in the electrolyte. The latter depends on the rotation speed of the RDE and was observed to influence the oscillations only at lower rotation speeds.

Though the region of diffusion is finite, the use of the Warburg element that corresponds to a semi-infinite diffusion is justified by the fact that the time constant of the diffusion is longer than the period of the lowest frequency. As mentioned above, this lower limit on the frequencies of the multisine signal is set by the Fourier spectrum of the natural oscillation. In this prescribed frequency range, the oxide layer appears to be infinitely thick to the diffusing species. The correlation between the parametric fitting given by the simple Randles circuit and the development of a physical model requires a large amount of data analysis under different experimental conditions. However, we would like to give a first hypothesis for the origin of the oscillations based on the time variation of the parameters. This hypothesis should be taken with caution, due to the non-mechanistic representation of the fitting parameters. First of all, we have to underline that the observations on the time variation of the parameters is a consequence of the oscillations (and not vice versa). While the effective capacitance and the charge transfer resistance are oscillating both with a similar shape and relative intensity variation as the current (the effective capacitance is slightly out-of-phase with the current), the time variation of the Warburg coefficient, σ , is reminiscent of an integrate-and-fire oscillation. In fact, the shape is almost triangular and the oscillations amount to less than 20 % with respect to the average (current oscillations are 50 % with respect to the average). This suggests that the solid-state mobility or diffusion coefficient of reactants, probably oxygen vacancies or defects,

is dependent on another variable, probably concentration, which causes a non-monotonic non-linearity in the behaviour of the system. We also want to stress that the value of σ and Δd_{ox} are both changing in a similar manner, although there is a clear time delay between the two curves, thus underlining the fact that the observed transport process is connected to the oxide layer and not to the liquid phase. In this context, it is noteworthy that also in reference⁶ the oscillation mechanism was suggested to be related to a diffusion process in the oxide layer, which, according to the picture of the authors, enables a charge dissipation mechanism. At present state, one should, however, be cautious with any further additional conclusions, since we consider low-amplitude oscillations while in reference⁶ a transient variant of high-amplitude oscillations was studied. Clearly further DMFA experiments under different conditions and modelling of the system are necessary to confirm this hypothesis. Yet, this powerful electro-analytical technique allowed us to monitor four kinetic parameters simultaneously with the current oscillations, demonstrating its power to study non-stationary phenomena.

In this paper we demonstrate that DMFA can be used for the investigation of the oscillatory dynamics of the anodic electrodisolution of p-type silicon in fluoride-containing media. Due to the high-quality impedance spectra that were obtained under oscillating conditions, we developed a framework that is crucial for understanding the kinetics of this complex reaction mechanism. A classic Randles circuit was used to fit the dynamic impedance spectra, which showed evidence of the asymmetric behaviour of the Warburg element, σ , around the natural oscillations in the current. The charge transfer resistance, R_{ct} , appeared to be related to a surface process, while the effective capacitance, C_{eff} , was attributed to changes in the dielectric properties and thickness of the silicon dioxide. The solid-state transport process shows an integrate-and-fire oscillation, which suggests a strong contribution of this phenomenon to the appearance of the oscillations. Further measurements need to be carried out to investigate the influence of the different experimental parameters on the reaction mechanism. However, this is an important step to a better insight in the oscillatory behaviour of silicon electrodisolution and the elucidation of the reaction mechanism.

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