



## New insights into the oxidation rate and formation of porous structures on silicon



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### ABSTRACT

The rate of oxide formation on silicon was investigated by *in situ*  $I-V$  measurements, one after the other within 300 s, and as a result the current or  $I-V$  gap was used to compare the relative oxidation rate during pore formation at different anodizing currents. The study was based on the electrochemical etching of p-type silicon using HF electrolyte treated with surfactant to obtain pores with straight walls. The study showed that the rate of oxidation during the formation of macropores, which have straight walls and relatively deep structures, decreases as the pores grow down with time, where it shows that the etching rate decreases as the pores grow deep. However, electropolishing resulted in a relatively high and constant rate of oxide formation with time. These observed properties are related to the expected diffusion limitation of oxide-forming ( $\text{OH}^-$ ) molecules, which reach the electrolyte-pore tip while etching occurs. Anodic oxide formation rate at the electrolyte-pore tip, which was created under complex kinetic conditions, depends on the pore structure, pore depth, diffusion rate of oxide-forming species, and anodizing current. The fast  $I-V$  method is an advanced approach and can be used to study pore formation mechanisms in different semiconductor materials.

### 1. Introduction

The discovery of porous silicon (PS) has opened the door for various silicon structures where the pores give rise to interesting physical properties, which can be used in photonic applications [1–3], sensors [4,5], micromechanics [6], energy conversion [7,8], biotechnology [9,10] and related issues. With regard to such novel applications and interrelated physical properties, understanding the electrochemical process at the silicon-electrolyte interface is crucial. Since the beginning of the science of PS, in the mid of the last century, efforts have been made to understand the mechanism of pore formation. In 1990, Lehmann and Föll discovered that very regular arrays of macropores with extremely large aspect ratio could be obtained in n-Si/hydrofluoric acid (HF) system, and some of the scientific details were explained in their studies [11]. Later, in 1994, Propst and Kohl showed that macropores in p-type silicon could be etched as well, where they used HF in acetonitrile and moderately doped p-type wafers. These and other related earlier studies provide vital inputs to the science and application of PS. Yet, the electrochemistry of silicon remains a challenging research field as there remains a considerable number of unanswered questions [12,13], such as the many features of anodic dissolution, the reactions kinetic governing the dissolution of silicon, rates of carrier transport in the silicon semiconductor, oxidation of silicon, and mass transport in

the electrolyte [2].

In the past years, PS has been investigated by various ways to address the many opened questions in the electrochemistry of pore formation. For example, oxide formation has been a several years' concern mainly for the current burst model. The rate of oxide formation during etching for different pore types, different morphology and electropolishing is one crucial issue to be addressed in PS. The way in which the rate of oxide formation proceeds when pores grow deep and during a transition between porous (macro- and nanopores) and electropolishing is also one major question to be investigated.

*In situ* monitoring of pore growth is needed to obtain direct information during the growth of pores and the related electrochemical oxidation at the Si-electrolyte interface. However, there is no ideal *in situ* measurement due to the complexity of observing within the pores at the Si-electrolyte interface. Until now, dual-mode fast-Fourier transform impedance spectroscopy (FFT-IS) is the only method that can contribute to *in situ* monitoring [14]. The common single  $I-V$  characteristics of Si in HF acid solution have been used to characterize porous and electropolishing regimes of p- and n-type Si for more than 25 years. However, there is a need to advance the  $I-V$  characterization method; therefore, it is extended as an *in situ* method to study the rate of oxide formation in a better way. Here, as a solution, a new approach hereafter referred to as “fast  $I-V$  curve” measurements method is

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developed, which is designed to obtain two *in situ*  $I$ - $V$  measurements within a short time (300 s) – fast  $I$ - $V$  method. Compared to the first  $I$ - $V$  measurement, the second  $I$ - $V$  measurement shows the displacement of current (in mA/cm<sup>2</sup>) for each corresponding voltage. Considering that oxide formation commonly occurs during the macropore formation process, one can assume that the gap between forward and reverse fast  $I$ - $V$  curves is caused by the oxide. Thus, the current gap between the two  $I$ - $V$  measurements relates to the rate of current-driven formation of oxide. Indeed, the dissolution at the electrolyte-pore tip interface is caused by oxidation or electrocorrosion followed by dissolution of the silicon created between the two measurements. Thus, the fast  $I$ - $V$  measurement is a unique *in situ* method, and it has the potential for use in advanced analysis of the underlying growth mechanisms of pores and in automatic monitoring of pore growth.

The rate of oxide formation is affected by the diffusion limitation of oxide-forming (OH<sup>-</sup>) molecules, and the diffusion can depend on the pore type, pore etching depth and pore morphology. Therefore, the *in-situ* fast  $I$ - $V$  measurements were related to scanning electron microscope (SEM) images of pore morphology and pore type. Thus, the fast  $I$ - $V$  curves were used to offer comparative data related to the rate of oxide formation as a function of pore depth/time while etching occurs, where the current gap depends on the morphology, anodizing current, and type of porous/electropolishing regimes.

The oxidizing power of the electrolyte, to produce SiO<sub>2</sub>, determines the rate of pore formation [15]. Apparently, electrolytes with little or insignificant water (OH<sup>-</sup>) species have quite small oxidizing powers. Therefore, adding oxidizers has been common to increase the oxidizing power to enrich OH<sup>-</sup> species, that is, for improved oxidation and macropore formation [1,16]. Pore formation in silicon surfaces is a consequence of localized oxidation and dissolution at the anodic side while nothing occurs at the cathode. Thus, the formation of PS is an anodic dissolution process, and it consists of carrier transport in the semiconductor, electrochemical reactions at the interface, mass transport of the reactants, and reaction products in the electrolyte [17]. Mass transport, e.g., oxide-forming species, is expected to be particularly limited by pore depth while pores are growing, and electrolytes with little water or oxide-forming species have comparatively little oxidizing and as a result reduced dissolution power of silicon. Consequently, considering the mass transport, current-driven silicon oxidation and dissolution can be limited by the diffusion limitation of oxide-forming species. In other words, the rate of oxidation can increase with the increase in the number of water molecules reaching at the semiconductor-electrolyte interface [18]. The rate of oxide formation is expected to be limited in the same trend, that is, the deep region of a pore can be diffusion limited (with less oxidation rate) than the shallow portion of a pore. In turn, the diffusion rate of oxide-forming species depends on the morphology of the pores; in particular, pores with straight walls and high aspect ratio versus pores with irregular structure (e.g., spongy like, having cavity or tumbler structure). This is because the sponge or tumbler/cavity-like structure can be responsible for a better diffusion or reaching of the oxide-forming species, while the pores are growing downward. Indeed, the relative oxidation rate on such morphologically affected or irregular pore growth was studied by the fast  $I$ - $V$  method (see Ref. [19]).

The rate of diffusion of oxide-forming molecules, and as a result the rate of oxidation and dissolution, on pores with straight walls (regular or Collins structure) is completely different from that on pores with irregular structure. Here, the study is intended to investigate the rate of oxidation while pores are growing, excluding the structural effect of pores, that is, study based on cylindrical pores with straight walls excluding the already studied case of morphologically affected and irregular pores. Furthermore, the scientific and industrial community works quite more on straight-walled pores growing downward, and thus, advanced insight on the rate of oxidation while pores are growing straight down needs to be addressed. Thus, in this study, the trend oxide formation during the growth of porous structures, including

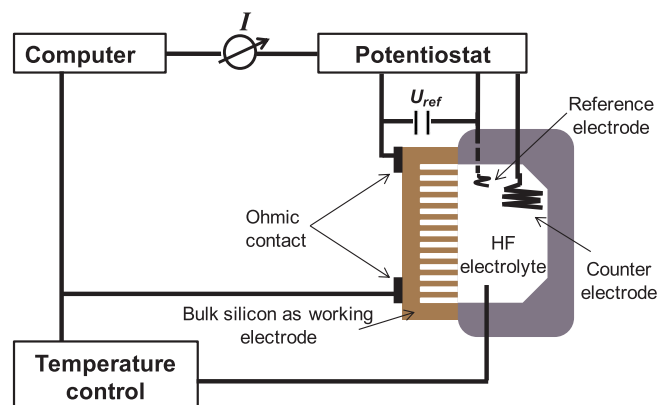


Fig. 1. Schematic illustration of the etching cell.

electropolishing, on p-type silicon is studied by the fast  $I$ - $V$  method. The use of a neutral surfactant can help in the formation of pores with straight walls and relatively high aspect ratio [20], and therefore, it has been used in this study. This study intends to gain a new insight on the relative rate of oxide formation, at the semiconductor-electrolyte interface, using the fast  $I$ - $V$  measurements at different times (pore depth, if it is not electropolishing), while etching occurs for p-type silicon with surfactant-treated HF electrolyte.

## 2. Experimental

The investigations were made on a p-type Si (100) wafer with a resistivity of 10–20 Ω·cm. The experimental setup is presented in Fig. 1 (for further details see Ref. [21]). The main parts of the setup are an electrochemical cell, potentiostat, electrolyte container, peristaltic pump (which are not shown in Fig. 1), thermostat and computer. To protect against the aggressive HF media, the etching cell and the acid container are made of Teflon. The temperature of the electrolyte is controlled by the thermostat, and the electrolyte flows from the reservoir through the cell driven by the peristaltic pump. The pumping rate and the temperature of the electrolyte was 100 rotations/min and 20 °C, respectively. The current and voltage applied to the cell are controlled by the potentiostat, which is in turn controlled by the computer. The potentiostat and correspondingly the cell have four electrodes: counter electrode (platinum electrode as cathode), working electrode (anode, which is indeed the silicon sample), reference electrode (in the electrolyte), and a sensing electrode (on the sample). The reference electrode is used to provide a non-polarizable interface for potential measurements. In the electrochemical reaction, the cathode supplies electrons to the solution and the anode removes electrons from the solution, i.e., two reactions are occurring simultaneously in an electrochemical cell -the anode (oxidation) reaction and the cathode (reduction) reaction. The Si sample was pressed against an O-ring with an etching area of 1 cm<sup>2</sup>. To get a good ohmic contact, the samples were dipped into 10% HF. After removing the oxide by scratching, to exclude the possibly left oxide, a layer of In/Ga alloy was applied to the sample for a contact. Thereafter, the samples were introduced into the cell (see Fig. 1), and the experimental parameters (current density and etching time) were computer controlled. The electrolyte containing 4 wt% HF was treated with the surfactant. The current density ( $j$ ) was constant during the experiment (except during the periodic measurement of the fast  $I$ - $V$ ) but varied from experiment to experiment between  $j = 0.1$  and  $j = 30$  mA/cm<sup>2</sup>. The etching time was adjusted to 120 min. The fast  $I$ - $V$  measurements, common/standard  $I$ - $V$  method but made two times in short time, were made (from -1.0 to 2.5 V) with a scan rate of 50 V/s. The time interval between the two fast  $I$ - $V$  measurements, one in the forward and the other in the reverse direction, was 300 s for all the experiments. The linearity of the fast  $I$ - $V$  voltage for the forward and reverse side was checked before the experiment. Thereafter, the fast  $I$ - $V$

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