

Facts and challenges in the electrochemistry and wet surface chemistry of silicon

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The second half of the twentieth century has seen the advent of silicon as the key material of microelectronics. Though the most critical processing steps in established silicon technology are performed in dry conditions, this has stimulated interest in the electrochemistry and wet surface chemistry of that material.

Well-known features of silicon are its highly electropositive character and the ion- and electron-blocking properties of its oxide, which make the electrical passivation of its surface very easy. Silica is virtually insoluble in all but fluoride electrolytes. However, the silicon/silica interface, especially when obtained by anodic oxidation, usually bears electronic interface states and fixed charges, which make it inappropriate for the elaboration of field-effect transistors (MOSFETs). For that reason, high-temperature thermal oxidation under optimized conditions has remained as the only effective route for the elaboration of MOSFETs. However, though it has not emerged as a practical method, anodic oxidation in ultrapure water has been shown to lead to interfaces of a comparable electronic quality [1].

The most important finding of the last fifty years on the wet surface chemistry of silicon is probably the fact that dissolution of the native oxide in fluoride medium leads to a silicon surface terminated with hydrogen [2] (not with fluorine, the naive expectation!), which stands exposure to ambient atmosphere on an hour time scale. This hydrogenated silicon surface exhibits a very low density of interface states and can be obtained atomically flat on (111) wafers, which leads to enhanced stability [3]. This behavior has been rationalized in the framework of a pH-dependent chemical/electrochemical etching mechanism [4]. Upon applying a positive potential to a p-Si electrode in fluoride electrolyte, silicon dissolution takes place. At moderate potential, the surface remains essentially hydrogen-terminated, and the material is dissolved partially, leading to the formation of a layer of porous silicon, a material which has attracted a high interest due to its original and tailorable properties [5].

At higher potentials, anodic dissolution in fluoride electrolytes leads to complex voltammograms exhibiting several very reproducible features, namely two electropolishing plateaus separated by a broad current maximum [6]. A lot of information has been accumulated on the properties of the interface in these regimes. It is generally accepted that the first plateau corresponds to formation of a wet oxide/hydroxide, and the second plateau is associated with the appearance of a dry oxide underneath the wet one.

In the region of the second plateau, (typically above 3 V potential), the electrochemical system tends to exhibiting an original oscillatory behavior: The system is self-oscillating in the presence of a series resistance; however, if such a resistance is absent, the current under potentiostatic conditions is stable, but the impedance exhibits a *resonant behavior* at the oscillation frequency and at its overtones. This original behavior has been attributed to the presence of an oscillation at the local scale: As long as the local oscillators are not synchronized, a constant average current is observed, but a potential excitation tends to bring them into phase,

leading to a resonant response at the frequencies present in the spectrum of a local oscillator [7]. Several models have been proposed to identify the very origin of the oscillation, but this remains as yet a conflicting issue.

At still higher potentials, a porous oxide is formed, whose thickness may reach up to a few micrometers. This oxide is mesoporous but may exhibit macrostructures. Interestingly, it also exhibits a stratified structure, which has been shown to be related with the oscillatory behavior observed above 3 V potential.

The electrochemistry of silicon in non-aqueous non-fluoride media is hampered by the need to rigorously exclude water, which can lead to oxidation, interface states and ultimately passivation of the surface. However, alcohols and especially methanol have been found to lead to “good” interfaces, allowing for the elaboration of efficient and stable photoelectrochemical cells [8]. This specific behavior has been shown to be due to a chemical modification of the surface by grafting of methoxy groups [9]. A wealth of other surface modifications have been explored in the last 15 years, using chemical and/or electrochemical routes. Among those, one may cite the cathodic grafting of aromatic groups from diazonium precursors, the anodic grafting of alkyl groups from Grignard precursors, or the chemical grafting of alkyl or substituted alkyl groups by hydrosilylation of alkene or alkyne precursors. The latter method is of special interest, because it allows for the immobilization of complex chemical or biochemical species on the silicon surface, opening the route to the elaboration of chemical and/or biochemical sensors [10]. Also, an ultrathin organic layer may be considered as a means for interfacial-oxide growth inhibition during the deposition of high-K oxides on silicon for next generation MOSFETs [11].

After over 50 years of work, the electrochemistry of silicon is still presenting several challenging issues. Obtaining chemically resistant, electronically clean (no surface states within the band gap) and thermally stable organic modifications appears as a Holy Grail for the sensor and high-K oxide applications. Though the inherent tendency of silicon to surface oxidation has led many researchers to regarding diamond or silicon carbide as more promising materials, we do think that silicon is still alive in this context. On the other hand, there are several open issues of high fundamental interest. The formation mechanism of porous silicon has led to many suggestions, but a general agreement on the subject is still lacking. The oscillation mechanism, though of more academic interest, is also a controversial issue. We believe that a clear understanding of these matters should not be dissociated from the understanding of the electrochemical behavior of silicon as a whole: Especially, one has to account for the complex shape of the voltammograms, a work that is presently underway.

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