In situ investigation of porous anodic films of silica

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Received 11 March 2002, accepted 30 November 2002
Published online 29 April 2003

PACS 73.40.Mr, 78.30.Am, 78.60.Fi, 82.45.Cc

The electrochemical behaviour of p-type silicon in dilute fluoride electrolyte has been investigated in a potential range extending up to +100 V vs SCE. Beyond the known range where the system is prone to exhibiting an oscillatory behaviour (3–8 V), two marked current rises are observed, at around 10 V and 20 V. Evidence for electronic transport through the oxide is given by the appearance of two distinct electroluminescence bands, a red band above 10 V, and a “blue” band above 20 V. The observation of strong gas evolution above 20 V confirms that in this potential range transport through the oxide is mainly electronic. However, in the range 10–20 V, no gas evolution is seen and electrochemical impedance indicates that the oscillatory behaviour somewhat survives. Furthermore, the electrical thickness of the oxide film appears one order of magnitude lower than its thickness determined by infrared spectroscopy, which proves that the oxide film is largely porous. The appearance of this porosity is associated with the sharp increase in current around 10 V. Direct scanning-electron-microscopy observation of the oxide film indicates a close similarity with porous alumina formed in similar conditions, which suggests that ordered structures may be realisable in this system.

1 Introduction

The thin film of silicon dioxide present at the surface of silicon during its anodic dissolution in dilute fluoride electrolytes has been a subject of strong scientific interest: it appears at weakly positive potentials, which sets the end of the porous silicon formation regime and the onset of electropolishing. At more positive potentials (3–8 V), it leads to an intriguing resonant regime, which can be ascribed to the presence of a sustained current oscillation on the microscopic scale [1]. However, the origin of this oscillation cannot as yet be regarded as fully understood [1–5]. For fundamental purposes, it is then of interest to investigate the behaviour of this system at still higher potentials [6]. On the other hand, since silicon dioxide is a good blocking oxide, it could lead to behaviours similar to aluminium oxide, that is, formation of ordered porous mesostructures at high positive potentials, which would be of interest for nanotechnology [7]. We have then undertaken a study of the anodic dissolution of silicon in a dilute fluoride electrolyte, trying to characterise the oxide film in this regime, using several characterisation techniques: voltammetry, electrochemical impedance, in-situ infrared (IR) spectroscopy and electroluminescence, and ex-situ scanning electron microscopy (SEM).

2 Experimental

Our samples were cut from p-Si single-crystals [(111), 0.5 \(\Omega\) cm and (100), float-zone, 3–8 \(\Omega\) cm], polished and provided with Au + 1%Al diffused Ohmic back contacts. For the voltammetry, electrochemical impedance and electroluminescence experiments, samples were shaped as 4 mm

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diameter disks and mounted as rotating electrodes in a three-electrode cell. For the in-situ IR measurements, samples were shaped as multiple-total-internal-reflection trapezoids \((15 \times 15 \times 0.5 \ \text{mm}^3, 45^\circ \text{ bevels})\) and mounted in a circulation cell, by applying the trapezoid against an aperture in the cell wall, with a 10 mm diameter O-ring seal [8]. Samples for SEM were mounted with wax in a polytetrafluoroethylene holder, leaving a 5 mm diameter area unprotected, and held by the connecting wire in a circulation cell, a geometry which allowed fast removal of the sample under potential and immediate rinsing in bidistilled water. All our cells were made of plastic (polyvinylchloride or polytrifluorochloroethylene) and were equipped with a Pt-wire counter electrode and an Ag/AgCl (in saturated KCl) reference electrode. The cell for preparation of SEM samples could be cooled down to 0 °C. Our electrolytes were prepared from Millipore water, 1 M NH\(_4\)Cl supporting salt, and variable added amounts of HF and NH\(_4\)F. The total fluoride concentration \(c_F\) was in the range 0.05 M to 0.3 M.

3 Results

In the following, we will successively present our results on voltammetry, electroluminescence, electrochemical impedance, in-situ IR spectroscopy, and the SEM observations.

3.1 Voltammetry

A typical voltammogram of p-Si in a dilute fluoride electrolyte (1 M NH\(_4\)Cl + 0.025 M NH\(_4\)F + 0.025 M HF, i.e., \(c_F = 0.05 \text{ M}, \text{ pH} \approx 3\)) is shown as Fig. 1. In addition to the two well known current maximums at \(V = 0 \text{ V}\) and \(V = 1.5 \text{ V}\), which mark the boundaries of two electropolishing plateaux, it exhibits two steep current increases at around \(V = 10 \text{ V}\) and \(V = 20 \text{ V}\). Two new plateaux appear in between. The current density of the plateau between 10 V and 20 V is an increasing function of fluoride concentration, whereas that of the plateau beyond 20 V is weakly dependent on the electrolyte composition [9]. Marked gas evolution is observed at the electrode in the region of the last plateau (i.e., above 20 V). This is plausibly oxygen evolution associated with high-field electronic conduction through the oxide layer. Note that this curve, recorded at a potential sweep rate of 10 mV/s, represents a steady state (the same curve is observed on the back sweep): in this electrolyte the oxide dissolves at a rate on the order of a few Å/s; hence, for a slow enough sweep rate, the state of the interface (current, amount of oxide) is fully determined by the potential.

3.2 Electroluminescence

A weak electroluminescence is observed in the presence of the anodic current. Its intensity increases dramatically with increasing potential. Typical spectra are shown in Fig. 2.

![Fig. 1](image1.png)

**Fig. 1**

Voltammogram of p-Si (111) in \((c_F = 0.05 \text{ M}, \text{ pH} \approx 3)\) electrolyte (electrolyte composition 1 M NH\(_4\)Cl + 0.025 M NH\(_4\)F + 0.025 M HF). Rotating disk electrode. Rotation rate 300 rpm. Scan rate 20 mV/s. Only the positive scan is shown (the negative scan is closely similar). Notice the well known shape up to 8 V, and the two sharp current rises near 10 V and 20 V.

![Fig. 2](image2.png)

**Fig. 2**

Typical electroluminescence spectra. Same electrolyte as Fig. 1. Notice the change in shape and increase in intensity associated with the increase of potential.
For potentials below 20 V, the spectrum is peaked in the red. At higher potentials, a broad blue component appears, and increases in intensity, finally overcoming that of the red component. A more detailed report on these electroluminescence bands, together with experimental details, has appeared elsewhere [9]. As discussed there, the increase in luminescence intensity with increasing potential must be associated with the gradual change of the current-flow mechanism through the oxide from ionic to electronic. At potentials below 20 V, the electronic part of the current may consist of holes created by field-induced neutralisation of positively charged defects in the vicinity of the Si/SiO$_2$ interface [10], and the red electroluminescence may originate from oxygen-deficient regions in that zone. At potentials above 20 V, the current is more plausibly dominated by electrons and holes created by avalanche in the oxide, the broad “blue” electroluminescence being associated with two-step electron-hole recombination at defects. From a general viewpoint, we retain that the presence of an electroluminescence signal can be taken as an indication that part of the electric current through the oxide is electronic.

3.3 Electrochemical impedance Typical electrochemical impedance spectra are shown in Fig. 3. In the 10–20 V range, they exhibit some similarity with the spectra obtained in the 3–8 V potential range. Namely, the complex shapes near 0.1 Hz associated with an oscillation on the microscopic scale [1] are still present, though less sharp than in the 3–8 V range. The characteristic frequency $f_0$ (taken as the frequency where the admittance modulus is maximum) appears to increase around 8–10 V, at the same time as the current density, and it keeps following the behaviour $f_0 \propto J/V$ observed in the lower potential range [1]. In some electrolytes, the series resistance may even be sufficient to turn this resonant behaviour into self oscillating, as it has been reported for the 3–8 V range [11]. Such is the case near 20 V in the voltammogram of Fig. 1. We cannot say whether these resonant features are still present above 20 V, because we have not been able to extract reliable impedance data in the presence of the strong noise associated with oxygen gas evolution.

The high-frequency part of the spectrum ($f > 10$ Hz) has been fitted using a three-element equivalent circuit (resistance of the electrolyte in series with a capacitance/constant-phase-element parallel combination). The obtained capacitance is expected to represent that of the oxide layer. It may be used for a determination of its thickness, if one assumes that the dielectric constant of amorphous silica ($\varepsilon = 4$) is an appropriate value. In the 3–8 V region, this capacitance decreases with increasing potential. However, it becomes almost potential independent beyond 10 V. Its value, of about 0.5 µF/cm$^2$, corresponds to an “electrical thickness” of the oxide layer on the order of 10 nm.

3.4 IR measurements Typical in-situ IR spectra as a function of potential are shown in Fig. 4. In order to extract a quantitative measurement of the oxide thickness, the vSiO bands have been fitted and the results analysed according to the method described in [3]. However, at potentials above 10 V the resulting thicknesses came out too large to justify the use of a linear approximation (i.e., IR absorbance is no longer proportional to oxide thickness). We have then nu-
Numerically simulated absorption spectra of an oxide film, using the known optical constants of amorphous SiO$_2$, and used the obtained absorption/thickness curve to correct our results for the non linearity [9], a correction amounting to $\sim 30\%$ for our thickest oxide. This procedure would be perfectly rigorous if the oxide film were made of dense, dry, pure amorphous silica, which obviously is not the case. Due to these problems, the film thickness determined by this procedure is somewhat underestimated.

As shown in Fig. 5, the obtained thickness exhibits marked increases at around the same potentials where sharp current increases are observed, i.e., around 10 V and 20 V (compare with Fig. 1). The oxide film is estimated to be several hundreds of nanometers thick at 80 V potential. Furthermore, the broadening of the $\nu$SiO bands indicates some degradation of oxide quality, as compared to the 3–8 V range, and the tilt of the baseline at potentials above 30 V stands as an indication of roughening of the interface.

The oxide thickness as determined from the high-frequency interface capacitance has also been plotted in Fig. 5. The two determinations are in fair agreement at potentials up to 5 V (though some minor deviations have been noticed and are discussed in the literature [10, 12]), but disagree by about an order of magnitude in the 10–20 V range. This discrepancy, whose onset in the 5–8 V range was already noticed by Bailes et al. [12], will be addressed in the discussion.

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**Fig. 4** In-situ IR spectra as a function of potential, for p-polarisation. The reference spectrum was taken at $-0.2$ V (oxide-free interface). Same electrolyte as Fig. 1. For clarity, the spectra have been shifted by increments of 0.3. Notice the increase and change in shape of the $\nu$SiO bands, the negative $\text{H}_2\text{O}$ contributions (loss of electrolyte replaced by the oxide) and the sloping baseline (surface roughness) for potentials above 30 V.

**Fig. 5** Oxide thickness (a) as deduced from the IR measurements (data of Fig. 4) and (b) as deduced from the high-frequency interface capacitance (data of Fig. 3). Notice the strong mismatch for potentials above 10 V.

**Fig. 6** Potentiodynamic current/potential curve recorded on a positive potential sweep (same electrolyte as Fig. 1, here $T = 4$ °C). Notice the two current peaks (here at 8 V and 24 V) associated with the increases in oxide thickness near 10 V and 20 V. The two small bumps at 11 V and 15 V are due to a weak current oscillation triggered by the potential sweep. Preparation of the SEM samples was made after such a sweep. The sweep was stopped at the potential of interest and the potential was kept there for 5 min.
3.5 SEM observations The main motivation for the SEM observations was to investigate whether a porosity of these thick oxide films can be evidenced directly. For the aim of comparing oxides formed at different potentials, a well-defined procedure was used. The surface of a fresh sample was first etched for 10 min in the dilute fluoride electrolyte by cycling the potential in the 0–5 V range. Then, the nominal potential $V_0$ for thick-oxide formation was imposed after a fast sweep from 0 to $V_0$ (sweep rate 0.5 V/s, see Fig. 6). Polarisation at $V_0$ was maintained for 5 min. The sample was then removed under potential, rinsed three times in bidistilled water and blown dry. Transfer from the electrolyte to the first water bath was made in less than a second, so that negligible oxide dissolution can occur. For the oxide layers grown at potentials above 35 V, eye observation allowed a quick check of thickness homogeneity, since these layers exhibit interference colours. As it is known that better-quality porous alumina is obtained at low temperature, some of the present experiments were made in a cooled cell (4 °C). On the voltamograms, this resulted in a significant decrease of the current below 20 V, as compared to the experiments at ambient temperature.

A typical recording of the current during the potential sweep preceding the 5 min anodisation is shown in Fig. 6. An interesting aspect of this recording is the presence of two peaks in the regions where the oxide film is known to undergo fast thickening, namely here at 8 V and 24 V. The presence of these peaks (as compared with Fig. 1) is obviously due to the fast potential sweep rate. The area under the peaks gives a charge on the order of 40 mC/cm$^2$ and 200 mC/cm$^2$, respectively. For an ideally compact stoichiometric oxide, these figures would correspond to thickness increases of 30 nm and 150 nm, respectively, in fair agreement with curve (a) in Fig. 5. An interesting by-product of this experiment is then a confirmation of the IR data on oxide thickness.

Figure 7 shows typical SEM pictures of the surface of such samples after anodisation at 35 V, 50 V and 70 V. The oxide layer is clearly porous, with a porosity of ~15%, a characteristic pore diameter of ~20 nm and a typical pore spacing of ~100 nm. Notice that the oxide between the pores seems itself built from elementary globules of typical size 20 nm. Comparison of the three pictures suggests that the characteristic lengths, and especially the pore spacing, slightly increase with increasing anodisation potential. No good pictures have as yet been obtained for potentials below 30 V. The oxide thickness may be obtained from side views on cleaved samples. Thicknesses of a few hundred nm for 30 to 100 V formation potentials are obtained, in good agreement with the IR determination.

Fig. 7 SEM pictures of a p-Si surface anodised for 5 min at 35 V a), 50 V b) and 70 V c) at 4 °C in the same electrolyte as Fig. 1. Notice the globular structure of the oxide between the pores, and the slight increase in characteristic globule size and pore spacing from a) to c).
4 Discussion  The SEM observations bring clear cut evidence for oxide porosity, at least for formation potentials above 30 V. For lower potentials, the SEM resolution is not sufficient to observe distinct structures. However, when potential rises in the 8–10 V region, the large increase in oxide thickness, as determined by IR spectroscopy, is in apparent contradiction with the small nearly constant value deduced from the high-frequency capacitance of the interface. This discrepancy can be taken as evidence for a porosity of the oxide: the infrared absorbance measures the total amount of oxide, whereas the capacitance only depends on the thickness of the compact part of the film, the porous part being short-circuited by the electrolyte inside the pores. The most plausible picture is that of a thin compact layer right on the silicon surface, of a thickness ~10 nm, and a much thicker porous layer on top of the compact layer. The presence of pores in the low potential range (3–8 V) has already been invoked, in connection with the oscillation mechanism [4, 13]. Though in our opinion this suggestion still requires experimental confirmation, the present data clearly demonstrate that such pores are present above 10 V.

Our results bring several new elements for the fundamental understanding of the anodic dissolution of silicon. Since the oscillating tendency survives in the range 10–20 V, and the relation \( f_0 \propto J/V \) still holds, it seems plausible that the charge-transport mechanisms through the oxide are the same all the way from 3 V through 20 V. This is in line with the observation that oxygen evolution is seen only above 20 V. Electronic current through the oxide then appears as a minority transport mechanism below 20 V. The change of behaviour around 10 V would be just a change in morphology, the oscillating domains giving rise to a fully developed porous structure. On the other hand, the change of behaviour around 20 V appears associated with a change from ionic transport to electronic transport through the oxide. This is plausibly associated with the high electric field and high potential drop (more than twice the bandgap of SiO\(_2\)), allowing for avalanche breakdown of the oxide film. The associated increase in oxide thickness would then result from the increased defectivity of the oxide. Though our data may be helpful for clarifying the unresolved issues in Si dissolution, they are clearly calling for further investigations.

The interest of the porous oxide for applications largely depends on the possibility to grow ordered arrays of pores. Though the aspect of Fig. 7 is very disordered, the orders of magnitude for pore size and pore spacing are rather similar to those found for porous alumina. Despite the more complex electrochemical behaviour of silicon, this suggests that the underlying mechanisms of formation may be similar, so that conditions of ordered pore growth may not be out of reach. This again calls for more investigations on this system.

5 Conclusion  The oxide film at the surface of silicon during electropolishing in fluoride electrolytes becomes porous at potentials above 10 V. Two new electrochemical regimes appear (10–20 V and 20–100 V). The appearance of the first regime at ~10 V corresponds to the morphological transition to a thick porous oxide. The appearance of the second regime at ~20 V corresponds to an increase of the electronic contribution to the mechanism of current flow through the oxide layer, leading to strong oxygen evolution. In relation with this electronic transport mechanism, a red electroluminescence and a blue electroluminescence appear during the anodisation. A fingerprint of the oscillating regime of Si dissolution survives at least up to 20 V. Though the morphology of the porous oxide appears disordered, the characteristic sizes are of the same order of magnitude as for porous alumina. This suggests that it may be possible to form ordered mesostructures of porous silica.

Acknowledgment  The authors are indebted to Sven Matthias and Jinsub Choi for technical assistance.

References