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In-situ infrared study of silicon in KOH electrolyte: Surface hydrogenation and hydrogen penetration

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ABSTRACT

The n-Si(111)/6 M KOH electrolyte interface has been investigated by *in-situ* multiple-internal reflection infrared spectroscopy, at room temperature and at 40 °C. The potential of the Si electrode was stepped successively to positive and negative values with respect to open-circuit potential, leading to surface oxidation and oxide dissolution, respectively. Infrared spectra were recorded together with the interfacial current. Analysis of the infrared spectra indicates that, following the positive potential step, the electronic state of the surface changes from accumulation to inversion and the surface termination changes from a hydrogenated state to an oxidised state. The hydrogenated state is recovered after an induction time following the negative potential step. However, hydrogen penetration into the silicon lattice is then found to take place, as indicated by the appearance of a new SiH band and a strong background absorption of electronic origin. This sub-surface hydrogenation is associated with a slow increase of the interfacial current. This process is found to be especially important at higher temperature and is attributed to the formation of microcracks partially decorated with hydrogen. These results indicate that the chemistry and morphology of a silicon electrode are not stable even in the presence of an applied negative potential.

1. Introduction

The striking orientation dependence of the chemical etching of Si in alkaline solutions forms the basis for important applications in Micro-Electro-Mechanical Systems (MEMS). The key feature here is the very low etch rate of the Si(111) surface [1–4]. On the other hand, anodic passivation of Si in alkaline solution has proved important in the field of etch-stop techniques, widely used in the fabrication of beams, membranes, and other components in MEMS devices [5,6]. These two properties have been successfully exploited in device technology [5,6].

At open-circuit potential (OCP) in alkaline solution, Si undergoes chemical dissolution giving, as products, silicate in solution and hydrogen gas [1,3,6,7]. Surprisingly, *in-situ* and *ex-situ* infrared (IR) spectroscopy has shown that, during chemical etching in NaOH and KOH solution, the surface of Si is hydrogen terminated [8–10]. The electrochemistry of p-type Si in alkaline medium looks straightforward. When the potential is scanned positive of OCP, oxidation by surface holes gives rise to an anodic current peak followed by surface passivation [11–13]. In the range negative of OCP, the cathodic current is low because of the absence of electrons in the conduction band in the dark, and the chemical etch rate is close to that measured at OCP [13,14]. For the case of n-Si, at potentials negative of OCP, a cathodic current results from hydrogen evolution due to conduction-band electrons, and the etch rate is reduced [11–13]. *In-situ* STM studies in NaOH solution showed the (111) surface to consist of atomically flat terraces with the (1×1)-H structure separated by bilayer steps [10]. At potentials negative of OCP, perfect step-flow etching is observed. At OCP, dissolution proceeds via step flow and, to a lesser extent, by pitting on the terraces [10]. Surprisingly, when the potential is scanned positive of OCP in the dark, a current peak comparable to that on p-Si is also observed, despite the absence of valence band holes [11,12,15]. This anodic current has been attributed to electron injection into the conduction band from surface states associated with intermediates of the chemical etching reaction [10,12,13]. There is evidence that electron injection also occurs to some extent with p-Si [12]. In both cases, chemical etching is suppressed as soon as anodic passivation occurs [4,12,14].

Clearly, the surface chemistry of Si in aqueous solution of high pH is complex. In an attempt to clarify the mechanisms of anodic oxidation and oxide dissolution, we have undertaken an *in-situ* IR study of these processes. In KOH and NaOH solution, chemical etching of Si(100) and Si(110) is fast and tends to give roughened surfaces [1,3,4], not suitable for an extended IR study. Consequently, we used the Si(111) surface which has added advantages for a spectroscopic investigation of anodic processes: the chemical etch rate is very low and as a result the rate of evolution of hydrogen bubbles from the surface is limited. Previous studies involving potential-step measurements with n-Si(111) have

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shown an unexpectedly long induction time for oxide film formation, a feature attractive for kinetic studies [11,15]. These various considerations led us to the choice of atomically flat n-Si(111) as the starting electrode for our study. The electrode potential was stepped repeatedly between a negative value, at which hydrogen was evolved, and a potential in the passive range, at which surface oxide was formed. In addition, the use of an n-type electrode allowed us to study the surface chemistry during the cathodic generation of hydrogen at the negative potential.

In the present paper, we describe our experiments performed in 6 M KOH solution at room temperature (RT) and 40 °C. We focus on three topics: i) changes in the electronic properties of the surface during potential cycling, as determined from the electronic absorption baseline in the IR spectra; ii) the role of hydrogen at the surface, *i.e.* oxidation and regeneration of the hydrogen-terminated surface; and iii) interaction of hydrogen with the silicon crystal. The results on oxide formation and dissolution will be reported in a companion paper [16].

2. Experimental

The IR spectra were taken in the now classical multiple-internal-reflection geometry [17]. However, the use of KOH electrolyte at temperatures above 25 °C requires the design of a specific cell, which cannot be made of glass. We have made two series of experiments: at room temperature (RT) and at 40 °C (which builds a bridge to the transient studies in the literature). In each case, the experiments were performed in the dark, in a solution of 6 M KOH (VLSI grade from Merck, Selectipur). For the room-temperature experiments, the cell was similar to that used for fluoride electrolytes [18]. Namely, it was made of polytrifluorochloroethylene with a Pt-wire counter electrode. For the 40 °C experiments, the body of the cell was machined in stainless steel, which was also used as the counter electrode. A power resistor (as the heating element) and a Pt-resistance temperature sensor were inserted in the stainless-steel block and the temperature was controlled to ± 0.1 °C through a home-designed electronic regulation. Preliminary tests indicated that stainless steel is perfectly stable at open circuit in the operating conditions, and *post-mortem* examination of our silicon samples using XPS analysis did not reveal any trace of metal contamination.

For the two arrangements, the n-Si samples [float-zone grown, ⟨111⟩ orientation, 0.2 ± 0.05° misoriented towards the $\langle 11\overline{2} \rangle$ direction, P-doped, 130–150 Ωcm resistivity, 500 μm thickness, from ITME (Poland)], were shaped as trapezoids (20×15 mm^2, 45° bevels along the longer edges). For sample preparation, a sacrificial anodic area was implemented by scratching the surface in a region outside the IR path. The samples were then cleaned by Piranha/HF cycles and their surface was prepared atomically flat by etching in de-oxygenated NH_4F solution, as described in more detail in [19]. The samples were mounted in the cell by pressing them against a circular aperture in the cell wall with a perfluorinated elastomer 10-mm inner diameter O-ring seal. In this geometry, 10 reflections take place at the Si/electrolyte interface. Two electrical contacts to the sample were made in the upper corners, away from the optical path, by rubbing the surface with In-Ga eutectic and contacting the liquid–metal drop with a copper clip. The mercury/mercurous sulphate reference electrode, to which potentials will be referred in the following, was connected to the cell through a long polytetrafluoroethylene pipe (salt bridge). The electrochemical cell was controlled with a home-made four-electrode potentiostat. The use of two independent contacts for the working electrode (a sensing contact for the potential and the other for current flow) helps to avoid errors in the value of the potential due to poor ohmicity of the contacts and/or series resistance of the Si electrode.

The IR spectra were recorded with a Bruker Equinox 55 spectrometer (800–4500 cm^{-1} spectral range, 4 cm^{-1} resolution). The cell was mounted in a home-designed external compartment, including a rotatable grid polariser and an Infrared Associates MCT liquid-nitrogen cooled photovoltaic detector. The small magnitude of the signals required using accumulation of several interferograms, so that a spectrum could be obtained every 20–30 s. The potential was stepped successively to positive and negative values with respect to open-circuit potential, leading to surface oxidation and oxide dissolution, respectively. Each potential was maintained until the current became stable. The typical duration of such a cycle was 40–50 min at 40 °C and 2–3 h at RT. Infrared spectra were continuously recorded together with the interface current. Several such cycles were run and the results could be either considered separately for checking the reproducibility, or accumulated for improving the signal-to-noise ratio.

The spectra were converted to differential absorbance spectra by choosing a reference state (*e.g.*, the steady state at the negative potential) and calculating $(1/N)\ln[I_0(\sigma)/I(\sigma)]$, where σ is wave number, $N = 10$ is the number of useful reflections at the Si/electrolyte interface, $I_0(\sigma)$ is the raw spectrum in the reference state, and $I(\sigma)$ is the spectrum of interest. Analysis of these differential spectra was performed by using a versatile home-made fitting software. In the following, the fitting methods for each spectral range will be mentioned only briefly, the technical details being given in Appendix A.

3. Results

The results of the experiments at RT and at 40 °C turned out to exhibit marked differences, which were found to be reproducible over many experiments. For that reason, we will present them in two separate subsections.

3.1. The RT study

Fig. 1 shows a typical current transient (Fig. 1a) and the corresponding series of spectra recorded at RT upon stepping the potential from − 1.3 V to + 1.0 V and back (Fig. 1b). Here the raw IR data actually consisted of 1200 spectra, representing 3 cycles of 400 spectra each. Fig. 1b was obtained by accumulating the three cycles and taking the average of each 5 consecutive spectra. Within each cycle, the reference was taken as the average of the first 40 raw spectra, recorded just before the positive-potential step (taken as the origin of time). It is clear from Fig. 1b that potential cycling leads to many changes in the IR spectra. Among the most conspicuous features are the disappearance of the SiH surface bonds (negative band around 1900–2200 cm^{-1} associated with the formation of an oxide layer (νSiO absorption in the 900–1250 cm^{-1} region) at the positive potential, and the progressive disappearance of the oxide at the negative potential together with the restoration of the SiH surface bonds.[2] One also notices a reversible modification of the baseline. The oxide formation/dissolution will be discussed in detail in a separate paper [16]. Here, we will focus our attention on the changes in the νSiH region (1900–2200 cm^{-1}) and in the baseline. The various contributions considered are listed in Table 1.

3.1.1. Current transients

The current transient following the positive-potential step exhibits a fast and a slow component, like those reported in the literature [11,15]. However, here the current maximum is barely seen. This is plausibly due to the fact that the fast component is dominant, whereas the slow component is reduced in magnitude (~10 μA/cm^2) and extends to several hundred seconds. These latter effects can be attributed to the lower temperature (25 °C here as compared to 60 °C in Ref. [15] or 40–70 °C in Ref. [11]).

When the potential is stepped back to the negative bound, there is a weak negative current transient, the cathodic current remains very low (~− 1 μA/cm^2) for about 1000 s, then it slowly increases, and finally tends to a steady-state value of ~− 20 μA/cm^2 about 7000 s after the

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[2] The presence of two weak peaks at 2855 and 2930 cm^{-1} and other features in the 1400–1600 cm^{-1} range is due to the O-ring seal and is discussed in the companion paper [16].