Mechanism and dissolution rates of anodic oxide films on silicon

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ABSTRACT

The electropolishing of p-type silicon has been investigated over a wide range of wafer conductivities (p^- to p^{++}) and HF concentrations (0.01–15 wt%) by potentiodynamic polarization. The rate of oxide dissolution was determined from the plateau current density observed in the electropolishing region of the *IV* curve; i.e. where the growth and dissolution rates of the anodic oxide film are equal. The *IV* curves of silicon are reminiscent of a corrosion process control by the dissolution of a salt film in which the rate of reaction is controlled by the removal of dissolved products away from the surface rather than reactants to the surface as previously proposed. For the silicon anodic oxide films this can be by either mass transport or further chemical reaction with HF species in solution. It is shown that this means the dissolution rate should be described by:

$$\text{Dissolution rate} = \frac{DK_{sp}[\text{HF}]^2}{\delta} + \frac{k}{A}K_{sp}[\text{HF}]^6$$

This relationship is shown to hold for the whole concentration range investigated. Because hydrofluoric acid is a weak acid this rate equation converts to a cubic equation when written in terms of the total HF concentration as opposed to only the HF species, but in this form the connection with the dissolution mechanism is lost.

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1. Introduction

Silicon dioxide's excellent dielectric properties mean that it is widely used in the manufacturing of microelectronics. Usually thermal oxides, either grown thermally in dry O_2 or in a wet H_2O vapour atmosphere at temperatures above $900\,^\circ$C, are used [1]. However thermal oxidation has two main drawbacks; high thermal budget that inevitably leads to a smear-out of steep doping profiles and the restriction that thermal oxide can only be formed on bulk or polysilicon substrates [2]. Alternative methods of oxide formation such as chemical vapour deposition, liquid phase deposition and electrochemical anodization offer the advantage of a lower deposition temperature compared with thermal oxidation [1,2]. Anodic silicon oxides are usually formed in wet etchants based on HF [3].

The microelectronic industry also has a need to remove or thin silicon oxide layers and this is usually achieved by dipping in HF solutions. The high electronegativity of fluoride allows the strong Si—O bond to be broken. As a possible mechanism it has been proposed that the HF molecules react at the silicon surface by adsorption to the lattice Si—O bonds rather than by adsorption to the silicon hydroxyl groups terminating the silicon oxide surface

[5]. Several equations are available to describe the dissolution rate of thermal oxides in different electrolytes [6,7]. Nevertheless, these equations tend to be empirical, typically cubic functions of the HF concentration, so provide little insight into reaction mechanisms.

Because the electrical performance of an anodic oxide is inferior to a thermal oxide, device-related applications of anodic SiO_2 are limited to cases where the thermal budget is crucial, e.g. nuclear radiation detectors [4]. As a result of the limited applications, research on the anodic oxide dissolution rates has also been limited compared with that for the dissolution of thermal and CVD formed oxides. Nevertheless, it is generally estimated that the dissolution rates of anodic oxide films are two orders of magnitude larger than the rates for thermal oxides [8–11]. For example, in 1% HF aqueous solutions the dissolution rates for thermal and anodic oxides have been reported to be 3.0 and 300 nm/min (0.05 and 5 nm s^{-1}) respectively [12].

Electrochemical potentiodynamic polarization experiments are an attractive way to study both the growth and dissolution mechanisms of anodic oxide films on silicon. HF does not dissolve bulk silicon at any appreciable rate, therefore within the electrochemical polishing region the anodic oxide dissolution rate should be related to the anodic oxide formation rate, which in turn is given by the anodic current density [9]. That is to say the anodic oxide dissolution rate should be related to the current density in the electropolishing region.

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Table 1
Resistivities and doping densities of the p-type silicon wafers used.

Dopant level (cm^{-3})	Resistivity (Ω cm)
8×10^{19}	0.0015
2×10^{19}	0.004
5.5×10^{17}	0.05
9.5×10^{16}	0.2
3.2×10^{16}	0.5
3.5×10^{15}	4
6.5×10^{14}	10

In this paper, current–voltage (*IV*) curves for p-type silicon in HF are measured over a wide range of both wafer resistivity and electrolyte concentration in order to investigate the relationship between anodic oxide dissolution rate and HF electrolyte concentration. Based on the data obtained a possible mechanism for the rate determining step in the oxide dissolution process is proposed.

2. Experimental

The p-type silicon wafers used were boron doped with (1 0 0) orientation and resistivity ranging from $1.5 \times 10^{-3}\,\Omega$ cm to $10\,\Omega$ cm, as determined via 4-point probe measurements (Table 1). The wafers were cleaved into $1\,cm \times 1\,cm$ and the native oxide removed in 10 vol% HF, after which GaIn eutectic was applied to the back surface to ensure an Ohmic contact.

The wafers were then mounted as the working electrode in a standard three electrode polytetrafluoroethylene (PTFE) electrochemical cell. The wafers were held vertically in position by clamping with a PTFE washer and O-ring seal that reduced the exposed surface area to $0.017\,cm^2$. A platinum mesh counter electrode and a saturated calomel reference electrode (SCE), against which all potentials here are reported, completed the cell. The SCE reference electrode was furnished with a polyethylene luggin capillary with the tip positioned at around 5 mm distance from the working electrode to minimize iR drop. The anodizing electrolyte was 0.01–15 wt% HF dissolved in a 1:1 by volume mixture of H_2O and ethanol with the addition of $0.5\,M\,NH_4Cl$ as a supporting electrolyte; the upper concentration was limited by safety considerations as HF solution above 10 wt% generate considerable amounts of toxic vapour. No external stirring was applied to solutions, i.e. static conditions were maintained. The samples were potentiodynamically polarized at a sweep rate of $5\,mV\,s^{-1}$ from $-300\,mV$ vs. SCE using the potentiostat and sweep generator components of an ACM Instruments field machine. All the *IV* curves presented are after iR compensation. Unless otherwise stated the reported current densities are taken from the forward sweeps and are the average of three runs using fresh wafers each time.

3. Results and discussion

Fig. 1 shows a typical anodic current–voltage curve for moderately doped p-silicon in 3.7 wt% HF electrolyte; the basic shape of the *IV* curves was independent of both HF concentration range (0.01–15 wt%) and wafer resistivity ($10^{-3}\,\Omega$ cm to $10\,\Omega$ cm). The *IV* curve can be divided into three potential regions: (i) at the most negative potentials the silicon is under inversion condition so very little current flows in this region; (ii) as the potential is increased the current density starts to rise as a porous silicon layer is formed with a silicon dissolution valence of two; and (iii) at high positive potentials electropolishing occurs, with a dissolution valence of four [8,13]. Within the second region the anodic current initially increases exponentially with applied potential before adopting a linear dependence, as explained elsewhere [12].

The transition from the second to third regions is marked by a peak (usually referred to as j_{ps}) followed by a relatively constant
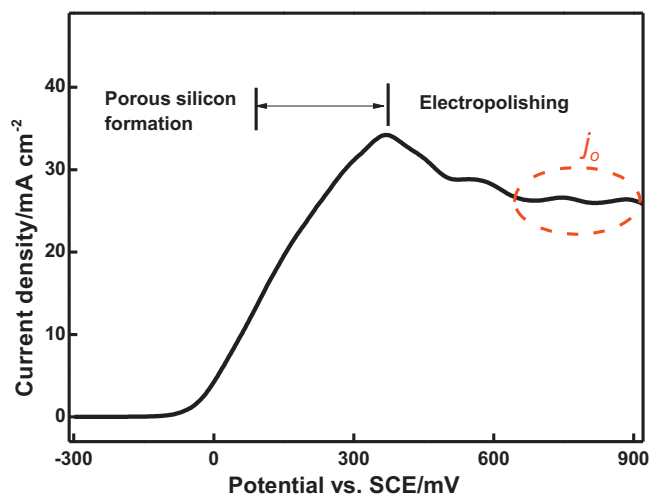

Fig. 1. Typical anodic *I–V* curve measured on a moderately doped (0.05 Ω cm) p-Si wafer in 3.7 wt% HF + 0.5 M NH$_4$Cl solution.

plateau current density (j_0), a behaviour that is reminiscent of the passivation of metals and alloys [14]. In the case of passivation, the oxide film is very insoluble in the working medium so that the plateau current density arises mainly from thickening of the passive film (along with some capacitance charging). However, in the present case SiO_2 is soluble in HF solutions so the situation is actually closer to the behaviour of the salt films that form during pitting and crevice corrosion [14]. In these cases the corrosion rate is controlled by chemical dissolution of the salt film and steady state conditions are achieved when the rate of corrosion (growth of the salt film) is equal to the film's dissolution rate, such that the observed current density reaches a plateau. That is to say it is believed that the plateau current density in Fig. 1 (marked as j_0) represents the situation where the growth and dissolution rates of the anodic oxide film on the silicon wafer are equal.

At potentials positive of the j_{ps} current peak the silicon's surface is believed to be covered by an oxide that is continuously being dissolved by the HF. The form of the oxide is still unclear with evidence for both a complete film [2] and for closely spaced islands with complete oxide coverage occurring only at the inflection point in the rise of the second electropolishing peak that appears at potentials beyond the positive limit of the present work [15]. The electropolishing process thus occurs in two steps, first the silicon electrode is anodically oxidized and then the oxide is chemically dissolved in the HF [12]. The rate of the oxide growth in the plateau region is directly proportional to the anodic current density [9]:

$$\text{Oxide growth rate} = \frac{j_0 M_w}{nF_\rho} \qquad (1)$$

where M_w and ρ are the oxides molecular weight ($60\,g\,mol^{-1}$) and density ($2.65\,g\,cm^{-3}$) respectively, n is the dissolution valence and F is the Faraday's constant. If the anodic oxide film was SiO_2 then the dissolution valance would be +4, but this is unlikely to be the case for the potential region of the present study where the oxide is believed to be in a hydroxylated form [16,17] and according to the work of Peiner and Schlachetzki [18] the dissolution valance is close to 3.5; this value will thus be used in the present work.

Tables 2 and 3 show the dependencies of the plateau current density and the calculated oxide growth rate, respectively, on HF concentration and wafer resistivity. The standard deviations in j_0 between the three runs under identical conditions were less than 7% of their mean values. It can be seen that both j_0 and the oxide growth rate increase with HF concentration and for the non-degenerate doped wafers are independent of resistivity, which is