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Analysis of porous silicon formation process using infrared absorption spectroscopy and Monte Carlo simulation

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1. Introduction

It is well known that the structure of PS fabricated strongly depends on the applied electrode potential as well as the electrical resistivity and type (p or n) of a Si electrode itself [1]. Depending on the anodization condition, the diameter of pores varies over a wide range from the nanometer size to the micron size. Therefore, the anodization technique may be applied to the fabrication of nanostructures. In order to control the position of pores on the nanometer scale, it is necessary to elucidate the mechanism of formation of PS. Several models have been proposed for the formation mechanism of PS. Among them, diffusion limited aggregation (DLA) model yields a good structural correspondence to cross-sectional transmission electron microscopy (XTEM) images of PS [2]. However, the DLA model cannot explain the crystallographic orientation dependence of PS formation [3] and the detailed chemical state of pore surfaces. In this study, we have investigated in-situ and in real time the chemical state of Si electrode surfaces during anodization in a HF solution using infrared absorption spectroscopy in the multiple internal reflection geometry (MIR-IRAS). We determined the densities of hydrides, SiH_x ($x=1-3$), on the electrode surface. In order to clarify the etching process on the atomic level, we carried out a simulation using the Monte Carlo method, in which we assume that the etching rate of each hydride species depends on the type of hydride (SiH , SiH_2 , or SiH_3).

2. Experimental results

Figure 1 shows IR spectral changes of a Si(100) electrode surface which was anodized in a HF solution with respect to a spectrum which was observed in pure water before anodization as shown at the bottom. In the spectrum before anodization, a peak at about 2110 cm^{-1} , which is due to the stretching mode of dihydride (SiH_2) species, is dominant. This indicates that the Si(100) electrode surface before anodization was mainly terminated by SiH_2 . Immediately after applying an anodic potential of $0.2\text{ V}_{\text{RHE}}$ to the Si electrode, the peak at 2110

cm^{-1} decreased its intensity, and instead, a new peak appeared at about 2070 cm^{-1} , which is due to the stretching mode of monohydride (SiH^*) species bound to another hydride species [4]. These facts suggest that SiH_2 species on the topmost layer of the Si electrode surface was removed, and that SiH^* species was generated on the second layer. With further anodization, the peak intensity of SiH_2 species started to increase again, and then all the hydride species (SiH , SiH^* and SiH_2) gradually increased their peak intensities. We interpret that an increase in the surface area of the Si electrode due to pore formation caused an increase in the density of surface hydride species.

In Fig. 2, we plot the surface densities of hydride species (SiH , SiH^* and SiH_2) as a function of the charge density transferred to the electrode. The evolution of the density of surface hydride species reflects the PS formation process on the atomic scale; it reflects how a surface Si atom with different number of hydrogen atoms bound to it, is etched away during the course of PS

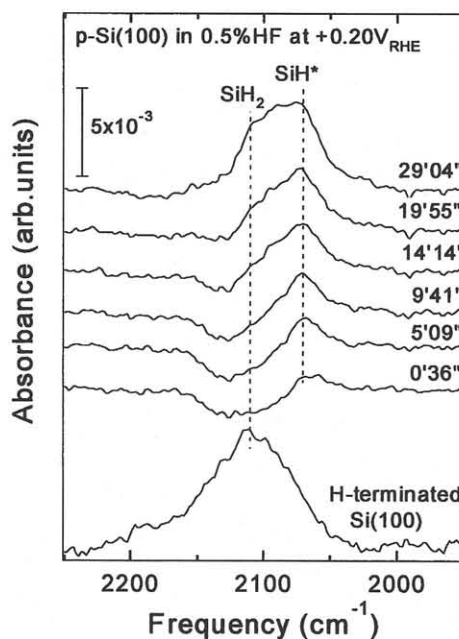


Fig.1. IR absorption spectra of Si electrode surfaces anodized in a 0.5 % HF solution at the potential of $0.20\text{ V}_{\text{RHE}}$.

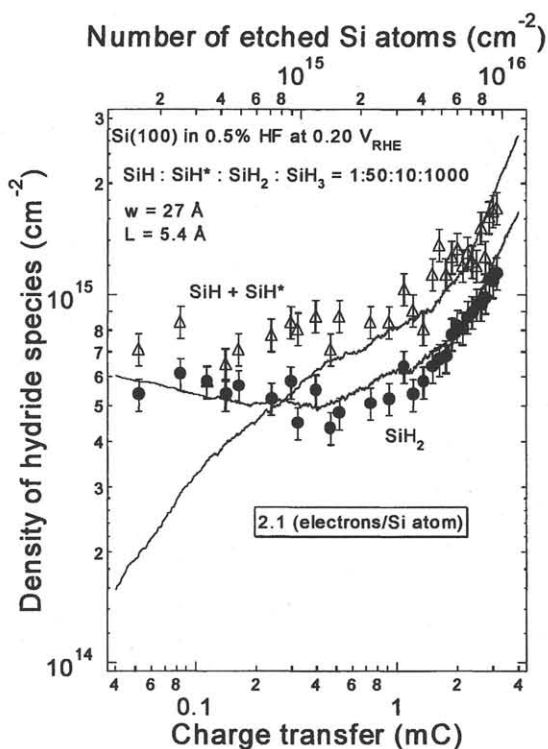


Fig.2. The evolution of hydride species densities estimated from the results of IRAS as a function of charge transfer (markers) and the results of Monte Carlo simulation as a function of etched Si atoms (solid lines).

formation. In order to explain the evolution of the surface density of each hydride species, we have carried out an etching simulation using the Monte Carlo method. In our simulation, we assumed that the etching rate for surface hydride species is different from each other, and used two additional etching parameters, which introduce effects of concentration of holes at tips of pores into our simulation: One is the depletion width or the screening distance, w , and the other is the interacting distance of surfaces, L , which is similar to the drift-diffusion length of holes or the migration length in the DLA model [2,5]. We prepared the cell of $20 \times 20 \times 40 \text{ nm}^3$ that had a diamond-structure lattice and satisfied the periodic boundary condition. In Fig. 2 we compare the results of the simulation with the experimental density of hydride species. We obtained fairly good agreement between the simulation and the experiment by assuming that the ratio of the etching rate of hydride species is $\text{SiH} : \text{SiH}^* : \text{SiH}_2 : \text{SiH}_3 = 1 : 50 : 10 : 1000$ and pores form in the vicinity of the surface of the cell, of which the diameter is approximately 3 nm, simultaneously with an increase in the density of SiH_2 species. The discrepancy between the simulation and the experiment observed for the

monohydride species density at regions of small charge transfer would be due to the roughness of the real Si electrode surface. From comparison between the simulation and the experiment, we obtained a value of approximately 2 for the number of electrons required for removal of a surface Si atom, which is in good agreement with the value of 2-3 that has previously been reported by Beal et al. [6]. This indicates that our simulation is valid and supports the assumption that the etching rate of SiH^* species on Si surfaces is higher than or equals to that of SiH_2 species. This correspondence of the simulation to the experiment is due to introduction of both dependence of the etching rate of the surface hydride species on the type of them and effects of the concentration of holes at the tips of pores into it. That is, both hydride species on the surface and the transfer of holes play the important role of the PS formation process.

3. Conclusion

We have investigated the initial stages of PS formation using MIR-IRAS. We found that etching on a Si electrode surface proceeds through the removal of SiH_2 followed by the generation of monohydride species (SiH^*). Comparison between the experiment and the Monte Carlo simulation clearly indicated that surface hydride species have quite different etching rates from each other; the etching rate of SiH^* species is higher than or equals to that of SiH_2 species and we obtained a value of approximately 2 for the number of electrons required for removal of a surface Si atom.

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