Mechanisms of Two Different Macroporous Structure Formation Observed in Anodization of p-Type Silicon

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Formation mechanisms of macropore-like structure filled with micropores (skeleton structure) and conventional macroporous structure (macropores being not filled with micropores) are studied. By controlling the current density and HF concentration in the electrolyte solution, it has been clarified that the skeleton structure is formed under conditions where the bulk HF concentration is higher and the current density is lower. Porous silicon prepared under such conditions does not have oxidized silicon at the bottom of pores. This suggests that the mechanism of the skeleton structure formation is totally different from that reported for the explanation of conventional macropore formation. In this study we propose a model for skeleton formation based on hole-supply in a silicon electrode.

**Keywords**: Silicon, Anodization, Macropore, Porous Silicon

1. Introduction

Porous silicon is a well-known porous electrode that is produced by electrochemical dissolution of a silicon wafer in HF solutions. Controllability in pore size enables lots of applications. 3 In the present study, we focus our attention on the formation of macroporous silicon. The mechanism of macroporous silicon formation has intensively been studied by several groups. Most of the approaches for understanding macropore formation in silicon were based on nonlinear dynamics that is very much different from micro and mesoporous silicon formations. Of these, the mechanism proposed by Föll et al. has been widely accepted as the probable mechanism that is so-called “current burst model.” 4-10 They have been successful in explaining the electrochemical oscillation during silicon anodization as well as macropore formation on the surface of silicon. In the model, the participation of oxidized silicon at the bottom of macropores plays a central role. The coexistence of bare and oxidized silicon surface is the key to understand the mechanism.

In earlier studies, formation of porous silicon that has a macroporous framework filled with microporous silicon was reported. 5,11,12 We refer to the macroporous silicon filled with micropores as skeleton structure. Chazalviel et al. studied the skeleton structure, and explained the mechanism by considering the ratio of the resistivity of the electrode and the electrolyte solution. 4 Since the macroporous framework of the skeleton and conventional macroporous silicon look very similar to each other, the formation mechanisms of the structures have been thought to be similar or common. 11

In the present paper, the optimum conditions for the skeleton structure as well as conventional macroporous silicon are experimentally examined. It reveals that the condition for skeleton structure formation is totally opposite to that of conventional macroporous silicon formation in terms of the local HF concentration at the surface. The mechanism of skeleton formation is discussed based on the diffusion of holes in silicon.

2. Experimental

Single crystalline p-type Si(100) wafers with a resistivity of 10-20 Ω cm were purchased from Electronics & Materials Corporation Limited. All wafers were rinsed in acetone and ultra pure water, and afterward dipped in 5 wt.% HF aqueous solution to remove the native oxides in advance of sample preparation. A two-electrode setup with a platinum rod serving as the counter electrode was used for anodization of silicon. The ohmic contact was achieved by painting Ga-In alloy on the backside of the wafer with a Cu current collector. The electrolyte solution was a mixture of aqueous HF solution (47 wt.% HF), ultra pure water and 2-propanol (PrOH) with a composition of 5:6.29 (8 wt.% HF), 8:6.26 (12 wt.% HF), 10:6.24 (15 wt.% HF), 14:6.20 (20 wt.% HF) or 22:6.12 (30 wt.% HF) in volume. Note that utilization of PrOH is a well-known strategy to produce macroporous structure in anodization of silicon. Thus, we adopt PrOH as the solvent of HF solution. 13 Anodization was carried out at various current densities as given in the figure captions. The duration of the anodization was tuned so that the total electric charge was constant at 50.4 C cm−2.

The porous structures were observed using a field emission-type scanning electron microscope (SEM, JSM-6500 FE, JEOL Ltd., Tokyo, Japan).

3. Results and Discussion

Effect of HF concentration on the morphology of porosified silicon was examined first. The current density was fixed and the concentration of HF was changed from 8 wt.% to 30 wt.% Fig. 1 illustrates the cross-sectional images of p-type silicon after anodization for 60 min at 14 mA cm−2. When the HF concentration is relatively low such as 8 wt.% and 12 wt.%, conventional macropores are formed. The pore walls look very straight from the bottom to the pore opening. With increasing the HF concentration, the direction of the pore growth is destabilized and the pore morphology becomes non-straightforward. In 20 wt.% and 30

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wt.% solution, macroporous framework is filled with micropores. Namely the skeleton structure is formed under high HF concentration conditions (Fig. 1g).

The effect of current density on the porosification was also investigated in 30 wt.% HF solution (Fig. 2). At current densities less than 28 mA cm$^{-2}$, the cross-sectional views clearly show the skeleton structures. The macroporous framework completely disappears at intermediate current densities of 140 mA cm$^{-2}$, but a uniform microporous silicon is formed. Interestingly, the microporous silicon disappears again when applying much higher current densities of 700 mA cm$^{-2}$. Conventional macroporous silicon is formed on the surface in a solution with a high HF concentration at high current densities. It should be noted that there exist two schemes for oxidation of silicon. Namely, two-electron (divalent) and four-electron (tetravalent) oxidation schemes are expected in anodization of silicon. Two-electron oxidation results in micropore formation with the pore wall terminated with Si-H bond. On the other hand, four-electron oxidation leads to the formation of macropore whose pore tips dissolve via formation of oxidized silicon. Thus, the amount of silicon dissolved is not constant among the conditions shown in Fig. 2 although the total charge is constant. Similar experiments were performed at various current densities and HF concentrations. Fig. 3 summarizes the types of pores formed under given conditions. The conventional macroporous silicon tends to be formed at conditions higher current densities and lower HF concentrations. These conditions correspond to the diffusion-limitation of HF during the anodization. Under the conditions, electropolishing of silicon partially occurs. On the other hand, the skeleton structure is formed under conditions totally opposite to the macropore formation in terms of local HF concentration at the surface. Namely it is obtained under conditions with lower current densities and higher HF concentrations.

It has been reported that local electropolishing at the pore bottom plays a role in the formation of the conventional macroporous silicon. Electropolishing generally occurs under conditions where fluoride species are depleted at the silicon surface. This results in the tetravalent indirect dissolution of silicon via the formation of oxidized silicon, followed by the chemical etching of the oxidized silicon. If fluoride species are available enough, divalent direct dissolution of silicon occurs. The conditions for conventional macropore formation shown in Fig. 3 are in good agreement with previous studies. Although several feedback mechanisms have been proposed for the oxide mediated pore formation, they are not applicable to the skeleton structure formation. This is because the formation of silicon oxides is not expected in high HF concentration and low current density conditions. Actually, the valence of the dissolution reaction calculated by the gravimetric method reached $\sim 2$ when the skeleton structure was prepared. Although the skeleton structure shows

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**Fig. 1** Cross-sectional views of p-type silicon anodized at 14 mA cm$^{-2}$ for 60 min. Concentration of HF was tuned as (a) 8 wt.%, (b) 12 wt.%, (c) 15 wt.%, (d) 20 wt.% and (e) 30 wt.%. Magnified images of a macropore (b) and a macroporous framework filled with microporous silicon in (e) are shown in (f) and (g). Part of the images are reproduced with permission from ECS Trans., 50, 61 (2013). Copyright 2013, The Electrochemical Society.

**Fig. 2** Cross-sectional views of p-type silicon anodized in 30 wt.% HF solution. Current density for the dissolution reaction is controlled at (a) 7.0 mA cm$^{-2}$ for 120 min, (b) 28 mA cm$^{-2}$ for 30 min, (c) 140 mA cm$^{-2}$ for 6 min, and (d) 700 mA cm$^{-2}$ for 1.2 min so that the total charge is kept at 50.4 C cm$^{-2}$. Part of the images are reproduced with permission from ECS Trans., 50, 61 (2013). Copyright 2013, The Electrochemical Society.
a macroporous framework, the valence of the dissolution indicates no contribution of the tetravalent oxidation scheme. This is highly expected since the macroporous framework is filled with "microporous silicon." Mechanisms for conventional macropore (with being not filled with micropore) formation are proposed based on the simultaneous occurrence of the divalent and tetravalent oxidation schemes. Thus, the destabilization for the skeleton structure must have a different origin from the conventional macroporous silicon formation.

To understand the instability for the emergence of the macroporous framework in the skeleton structure, we focus our attention on the uniform microporous layer formation at intermediate current densities in the highly concentrated HF solution. The formation of the uniform microporous silicon layer means that the instabilities for the spontaneous formation of a conventional macroporous layer as well as the skeleton structure are not expected under these conditions. The system is under a stable condition although the system is not in the thermodynamic equilibrium. The downward bending of the band structure is expected at the equilibrium condition of moderately or low doped p-type silicon. With increasing the overvoltage (the current density) to the anodic direction, the band bending changes to the flat band and finally to accumulation of holes. Fig. 4 shows the relationship between the band structures of low-doped p-type silicon, together with the expected profiles of HF concentration in the vicinity of the surface. At the applied potential near the equilibrium, holes are depleted, and thus the diffusion current of holes mainly limits the current of the electrochemical cell (Fig. 4 (a) and (d)). On the contrary, at the higher current density, the potential applied to silicon is expected to be higher than the flat band potential (Fig. 4 (c) and (f)). In these cases, holes are accumulated at the surface, and thus the electrochemical reaction is limited by the concentration of HF in the electrolyte solution.

Then, let us compare the case of intermediate current density. At a certain applied potential, the flat band is achieved in the silicon electrode. In the case of high HF concentration, the HF concentration in the vicinity of the surface is not low enough to reach the diffusion limitation of HF. Under this condition, holes and HF are not depleted at the silicon surface. This suggests that the system is not destabilized under this condition. As a result, the uniform microporous layer is formed. However, in the case of low HF concentration, HF in the vicinity of the surface might be almost depleted (Fig. 4 c). In such a case, the system is in the similar condition to the high applied potential (Fig. 4 c and Fig. 4 f) in terms of the depletion of HF. According to this mechanism, the macroporous morphology should change directly from the skeleton to the conventional macroporous structures in the case of low HF concentration.

4. Summary

Formation of skeleton structure in p-type silicon anodization was studied. The instability for the skeleton structure is caused by the diffusion–limitation of holes in silicon under the applied potential below the flat band potential. This study shows that formations of the skeleton and macroporous structures obtained
in p-type silicon anodization are explained by distinctly different mechanisms. The clarification of these mechanisms is of importance for further understanding of porous silicon formation from the nonlinear dynamical viewpoint.

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