Current Density Dependence of Microstructure and Lattice Expansion in Porous Silicon Layers Prepared by Anodization

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Microstructure and lattice expansion of porous silicon (PS) layers, formed on p-type silicon wafers $(0.02\,\Omega\text{cm})$ under various current densities, have been investigated by means of scanning electron microscopy, cross-sectional transmission electron microscopy and gas adsorption technique, and precise X-ray diffractometry. The pore morphology and lattice distortion of PS layers was dependent on pore size. Small pores showed more complicated morphology than large ones. When PS layers were produced at high current densities, remaining silicon parts showed large lattice distortions. The lattice distortion is ascribed to diffused hydrogen atoms into silicon matrix and repulsion force due to chemisorbed hydrogen atoms near pore surfaces.

1. Introduction

It has been reported that properties of porous silicon (PS) are very dependent on the type and resistivity of the original silicon substrate and on the electrochemical parameters such as current density and the concentration of hydrofluoric acid solution $^{1)}$. The PS layer was found to be a monolithic single crystal with a lattice spacing slightly larger than that of the original silicon substrate²⁻⁵). Recently, the authors⁶⁻⁷) investigated annealing effects of lattice distortion in PS layers and demonstrated that annealing in vacuum below 450°C was effective for desorption of hydrogen atoms from PS layers, and that hydrogen atoms chemisorbed around pore surfaces had strong influence on the lattice expansion of as-prepared PS layers. They also provided a consistently adequate explanation of the relationship between lattice distortion and microstructure of PS layers formed on p-type silicon wafers. The mechanism of the lattice distortion due to hydrogen atoms, however, is not yet clear. Recently, fine silicon rods in PS layers were reported to be used as quantum wire arrays8,9) In order to use PS as such quantum devices, detailed features of microstructure and lattice distortion of PS layers must be investigated.

In this study in order to gather further data of lattice distortion as well as pore morphology of PS layers, p-type silicon (100) wafers were anodically oxidized under various current densities, and the lattice distortion was examined precisely, together with porosity, specific surface area and mean pore radius. The results are used to develop a model for mechanism of lattice distortion of PS layer.

2. Experimental Procedures

Anodization of p-type Si (100) wafers (20mm x 20mm x 0.6mm in size) was carried out under conditions of various current densities. 10, 30, 50, 70 and 100 mA/cm^2 , without illumination, in an electrolyte solution of $HF:H_{20}:C_{2}H_{5}OH = 1:1:2$. A cell employed was the same in the previous study⁶⁾. PS layers of 10-50µm thick were usually produced on the matrix wafers and used as specimens for X-ray measurements and for crosssectional TEM and SEM observations. Selfsupporting PS layers of 80-200µm thick were prepared for gas adsorption measurement. In most cases, anodized wafers were dried in vacuum just after anodization, without polishing, and then were subjected to individual measurements. The lattice distortion of PS layer was investigated by means of X-ray multi-crystal diffractometry at room temperature, using a (111, 400) setting Si monochromator with $CuK\alpha_1$. In order to characterize the pore morphology of PS layers, pore size distributions and specific surface areas were measured by means of the conventional BJH and BET methods, respectively, for self-supporting PS layers. These features were correlated with forming current density. In most cases, three PS layers produced formed on the same preparation conditions. Measured data proved to show a considerably narrow distribution of values, indicating a good reproducibility.

3. Results and Discussion

Figures 1 and 2 show respectively the porosity and the specific surface area as a function of the mean pore radius for PS layers prepared under the same reaction time of 60min with different current densities, except for 120min at 10 mA/cm². It is shown that both the porosity and mean pore radius increase with increasing current density, and the specific surface area decreases monotonously with increasing the mean pore radius; when the mean pore radius became twice larger, the porosity increased by no more than 1.6 times and the specific surface areas decreased to 80 % of initial ones. This indicates that pores do not take similar morphology when they become large, and large pores take simpler shapes than smaller ones, because if a similarity in morphology was realized independent of pore size, when pores having twice larger pore radius than before are formed without any change in the number of formed pores, porosity must be four times larger and specific surface areas should be twice as large as before. This was directly confirmed by SEM and TEM observations. Here, we show the results by cross-sectional TEM observations in Fig.3: large pores produced with a current density of 100 mA/cm² show simpler pore morphology with a small number of branches than smaller pores. This suggests that, in order to form pores having simple morphology by electrochemical dissolution, it is effective to anodize silicon wafers with large current densities.

Figure 4 shows the mean lattice expansion of PS layer (the lattice distortion of remaining silicon parts) as a function of current density. The lattice distortion, defined by $(d_p - d_s) / d_s$, where dp and d_s are respectively the interplanar spacings of the PS layer and the silicon substrate, is proportional to current density, indicating that the lattice distortion of PS layer can be controlled with current density. Figure 5 shows the lattice distortion of the remaining silicon parts as a function of the pore-pore distance, which was evaluated from each measured porosity. The lattice distortion increases with decreasing the pore-pore distance, thus with decreasing the radius of remaining silicon part, indicating that the small remaining silicon parts become heavily distorted. This also suggests that remaining silicon parts are still constrained by surby the rounding silicon parts as well as matrix silicon substrate. Such in-plane strain distribution may lead to preferential dissolution between nearest neighbor pores, there-by promoting the pore-pore overlap needed to define isolated silicon wires, as proposed by Canham⁸⁾. It is expected that, if PS layers, formed by electrochemical and chemical dissolution of silicon wafers, were

composed of ideally isolated rods like quantum wire arrays, the lattice distortion of such fine rods will be reduced by an amount which is attributed to the constraint by surrounding silicon parts. It is well known that hydrogen atoms can diffuse into the matrix silicon with a diffusion constant of 5 x 10^{-15} m²/s at 293 K, and thus produce a small lattice expansion. A simple preliminary calculation shows that a change in lattice spacing, $\Delta d/d$, of 4 x 10⁻⁴ can be expected from hydrogen atoms of 0.2 at% in concentration diffused into the matrix silicon. Thus, it is said that the lattice expansion is due to both diffusion of hydrogen atoms diffused into the matrix silicon and repulsion force related with chemisorbed hydrogen atom near pore surface layers¹⁰)

4. Conclusions

The deduced conclusions are as follows: (1) The pore morphology was strongly dependent on pore size. Small pores produced at lower current densities showed large specific surface areas due to complicated pore morphology with a large number of branches. (2) The lattice expansion in PS, corresponding to the lattice distortion of remaining silicon rods, was dependent on pore size as well as on forming current density. Smaller rods were heavily distorted, indicating that nearest neighbor silicon rods are correlated with each other and constrained with surrounding rods. (3)Slight lattice expansion of PS is ascribed to hydrogen atoms diffused into the matrix silicon and hydrogen atoms chemisorbed near pore surfaces.

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Fig. 1 Porosity as a function of mean pore radius for PS's produced with various current densities.



Fig. 2 Specific surface area as a function of mean pore radius for PS's produced with various current densities.



(a) 30 mA/cm² 100nm (b) 100 mA/cm² Fig. 3 Cross-sectional TEM observations of PS's produced with different current densities.







254