

## MICROTEXTURE AND LATTICE DISTORTION OF P-TYPE POROUS SILICON LAYERS PRODUCED BY ELECTROCHEMICAL ANODIZATION

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### ABSTRACT

The lattice distortion and the texture of porous silicon ( PS ) layers, formed on p-type silicon ( 100 ) wafers (  $0.02 \Omega\text{cm}$  ) with various current densities, have been investigated by mainly diffraction techniques including X-ray diffractometry and electron diffraction/microscopy. The natures of pores in PS layers were also characterized by the gas adsorption method. Pore morphology and lattice distortion of PS layers depended on pore size, and small pores showed more intricate morphology showing branches on the sides than large ones. The lattice expansion of PS layer was found to be an intrinsic nature, which was generated during anodization. When PS layers were produced with high current densities, remaining silicon parts showed large lattice distortions. X-ray precise measurements of PS layers revealed that, when PS layers were anodized with higher current densities, remaining silicon parts were heavily distorted during anodization and thus took a microtexture composed of small block-like grains which were formed on account of large stresses caused during anodization, and that remarkable stress relaxation took place for self-supported PS layers. It was also shown that the lattice expansion was strongly related to the amount of hydrogen gas produced during anodization process, supporting that hydrogen chemisorbed or bonded to Si atoms on pore surfaces is attributed to the lattice expansion.

### INTRODUCTION

Porous silicon ( PS ) is obtained by anodic oxidation of silicon in concentrated hydrofluoric acid ( HF ) solution. The formation of PS depends on the doping level of the silicon wafer and electrochemical parameters; HF concentration and current density ( or voltage ) applied. It clearly appears that the porous texture or microstructure of PS is first of all determined by the nature and level of the semiconductor doping, and the porosity and pore sizes can be changed by the anodization conditions [1,2] . The PS layer was found to be a monolithic single silicon with a lattice spacing slightly larger than that of the original silicon substrate [3-7] in the direction normal to the substrate. To the authors's knowledge there has been a few systematic studies concerning the relation between the lattice distortion and microstructure of PS layer. The present authors [8,9] 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 the lattice expansion and microstructure of PS layers formed on p-type silicon wafers. Ito et al. [10] showed experimentally and theoretically that the structural change of PS is strongly dependent on foreign atoms such as H and O atoms chemisorbed or bonded Si atoms on the pores PS layers. Recently, Kim et al. [11] proposed another model for lattice expansion in PS layers stored in air at room temperature. The mechanism of the lattice distortion, however, has not been established yet. Further detailed studies must be done to investigate the lattice distortion of PS layer with reference to the microstructure of remaining silicon parts.

Recently, isolated fine silicon rods in PS layers were reported to be used as quantum wire arrays [12,13]. In those studies, visible light emission was demonstrated for PS layers which were prepared by electrochemical anodization followed by chemical dissolution during immersion in the electrolyte. The microstructure of such PS layers, however, has not been investigated directly, although a model of microstructure was proposed for PS layer. Such a structure model has not been confirmed yet. In fact, proposed structure was very different from that previously observed by the present authors [8,9]. In order to use PS as such quantum devices, further detailed features of microstructure and lattice distortion of PS layers as well as preparations conditions suitable for defining networks of isolated silicon rods in PS layers must be investigated.

In this paper, we describe experimental results concerning pore morphology of PS layers produced on p-type silicon (100) wafers which were anodically oxidized with various current densities. In addition, the lattice distortion including the lattice expansion of PS was investigated precisely by means of X-ray diffraction techniques, together with the measurements of porosity, specific surface area and mean pore radius. From X-ray measurements, a model was proposed to explain the degradation of crystallinity in PS layers produced with high forming current densities. A relationship between the crystallinity of remaining silicon parts and the light emission is briefly discussed on the basis of experimental results.

## EXPERIMENTAL

The CZ-silicon samples used to prepare PS were (100) p-type boron-doped wafers of  $0.02\Omega\text{cm}$ , produced. A 100 nm thick film of aluminum was deposited on the back of a wafer ( $20\text{mm} \times 20\text{mm} \times 0.6\text{mm}$ ) by conventional vacuum evaporation, which ensured a uniform current distribution during electrochemical anodization. Anodization was performed without special illumination in an electrolyte solution (HF:  $\text{H}_2\text{O}$  :  $\text{C}_2\text{H}_5\text{OH}$  = 1: 1: 2) with various current densities of 10 to 300  $\text{mA}/\text{cm}^2$ . In this study, a reaction cell shown in Fig. 1 was used. This cell was easier to

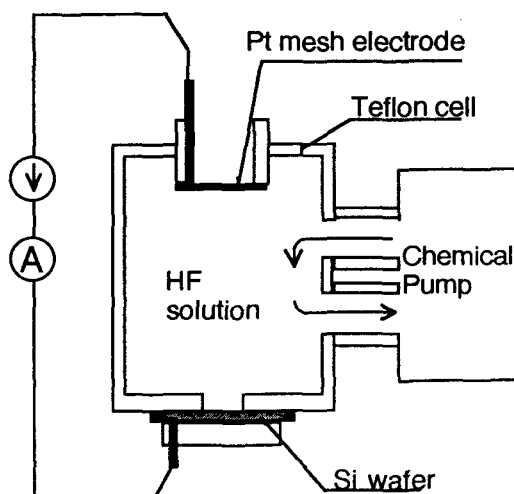


Fig.1 Experimental cell

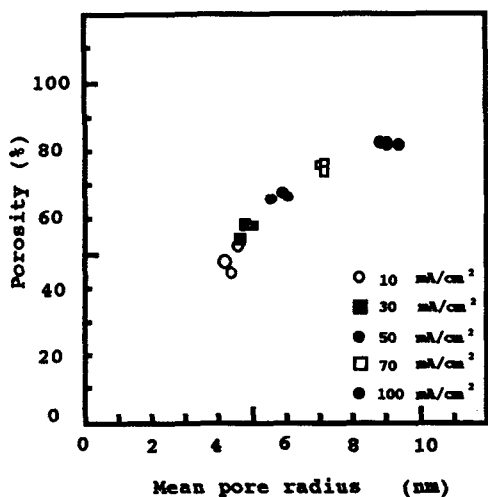


Fig.2 Porosity as a function of mean pore radius for PS layers prepared on p-type silicon (100) wafers ( $0.02 \Omega\text{cm}$ ) anodized with various forming current density

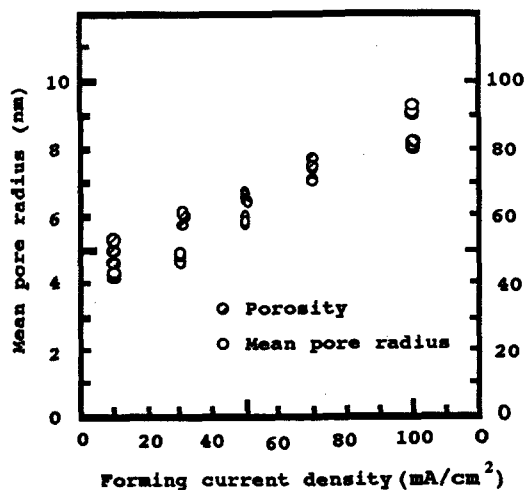


Fig.3 Mean pore radius and porosity as a function of forming current density.

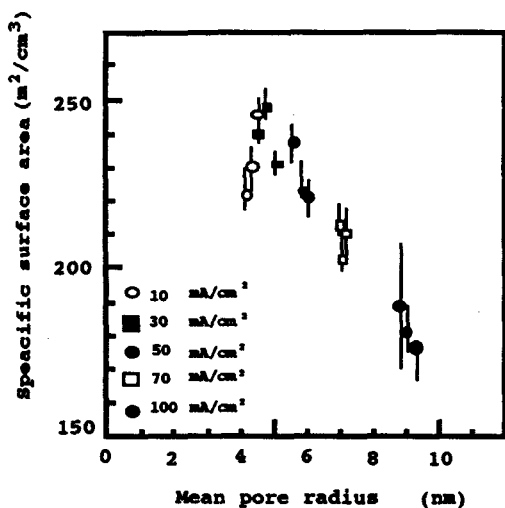


Fig.4 Specific surface area as a function of mean pore radius for PS layers anodized with various current densities.

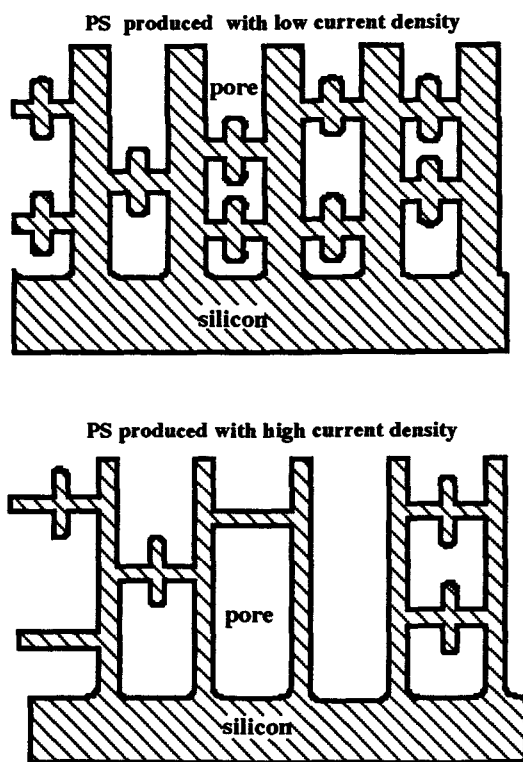


Fig.5 A model for morphology of PS layer

use than that used in the previous study [8,9] because of reduction of sample preparation time; In this cell, only a part of silicon wafer was exposed to the electrolyte solution and anodized, and no covering tape was used to protect an extra part of silicon wafer from anodization.

Infrared spectroscopy was performed to confirm that anodization was well done under suitable conditions. Similar infrared absorption features to the previous [8,9] were obtained for all the PS layers examined. The PS layers produced using the above conditions showed color changes from bluish-gray to dark golden brown with increasing the porosity. In this study, preliminary verification of visible light emission was carried out using He-Cd laser. In most cases, anodized wafers were dried in vacuum just after anodization without rinsing in alcohol nor in wafer and then were left in vacuum until individual measurements; It has been already confirmed that such sample treatment did not disturb the crystalline quality of PS layer [9].

The crystalline quality (or crystallinity) as well as the lattice spacing of PS layers was investigated by means of X-ray multi-crystal diffractometry at room temperature. 400 reflection curves from the lattice plane parallel to the Si (100) surface were mainly measured using a (111, 400) setting monochromator of silicon with Cu K $\alpha$  radiation. Some of them were also investigated by means of X-ray multi-crystal diffractometry of a (111, 400, 400, 400) setting, with the specimen as the third crystal and the analyzer as the fourth crystal, using Synchrotron Radiation (SR) at PF in KEK, Tsukuba, Japan.

In order to characterize the pore morphology of PS layers, specific surface area and pore size distribution were measured by means of the conventional BET (Brunauer-Emmett-Teller) [14] and BJH (Barrett-Joyner-Halendra) [15] methods, respectively, for self-supported PS layers. In this study, the mean pore radius was defined as a value calculated by assuming that all the pores are cylinders, and the porosity was defined as the percentage of void volume in PS layers. Of course, this evaluation may lead to some uncertainty in the absolute value, but in all case, values obtained by this method allow for comparison between different samples. Microstructure of PS layers was also investigated by cross-section TEM (XTEM) and high resolution SEM (HRSEM) observation. The results were interpreted with reference to those obtained by the gas adsorption method.

## RESULTS AND DISCUSSION

### Morphology of Porous Silicon

The porosity and the specific surface area were examined in terms of the mean pore radius for PS layers prepared with different forming current densities. The reaction time was 1 h (except 2h in the case of 10 mA/cm<sup>2</sup>), and thus the thickness of PS layer was slightly different from each other. Figure 2 shows that the porosity increases from about 50% up to 80% when the current density is raised from 10 mA/cm<sup>2</sup> to 100 mA/cm<sup>2</sup>. The pore size and the porosity increase regularly with the forming current density, as shown in Fig. 3. In this connection, the specific surface area decreases monotonously with increasing the mean pore radius, as shown in Fig. 4. It should be noted here that, when the mean pore radius became twice larger than the initial size, the specific surface area decreased to about 80% of the initial one with 1.6 times larger porosity. In the BJH method, the mean pore radius is evaluated on an assumption that all the pores are cylinders. Therefore, we cannot expect an increase in pore radius

accompanied with a decrease in specific surface area, because when pore radius becomes twice larger than the initial one, porosity must be four times larger and specific area should be about twice larger. This is not the case. These features may result in a speculation that pores do not take any cylindrical shape but small pores exhibit more complicated morphology than large ones, as shown by a structure model in Fig. 5.

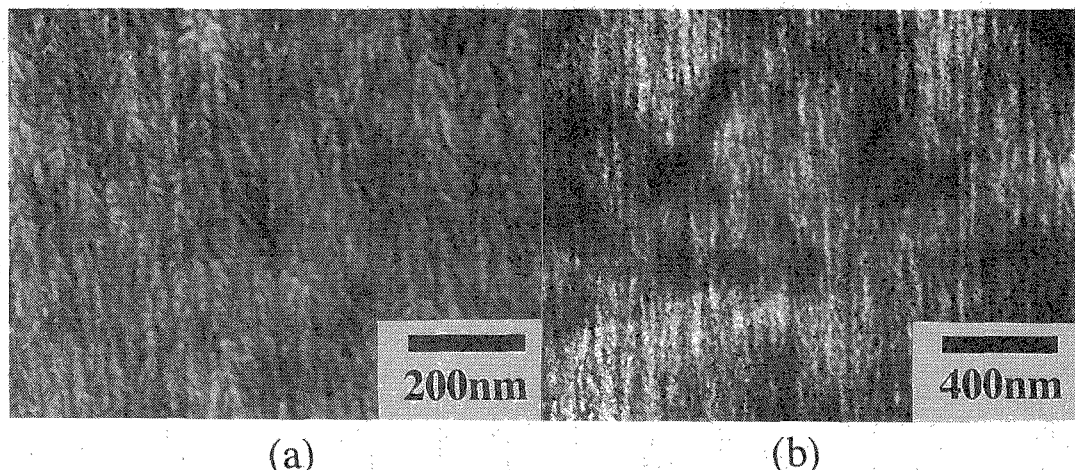


Fig.6 Cross-section TEM observation for ps layers produced with different current densities. (a)  $30 \text{ mA/cm}^2$  and (b)  $100 \text{ mA/cm}^2$ .

The above speculation was also confirmed by XTEM observations. Figure 6 reproduces cross-sectional transmission electron micrographs for two PS layers formed with different current densities. The results of the gas adsorption showed that PS layer formed at  $100 \text{ mA/cm}^2$  has a distribution of pore radius varying from 4 to 11 nm with a peak at 6 nm, while PS layer formed at  $30 \text{ mA/cm}^2$  has a distribution from 3 to 5 nm with a peak at 4 nm. Although a large number of pores are overlapped with each other on the electron micrographs, many branches and buds are seen on the pore sides. It appears that remaining silicon parts look like fir trees having many branches emerging at wide angles in three dimensions to the main trunks. This result is consistent with the microstructure of PS layer observed by HRSEM, as shown in Fig. 7. Observed pore radii, although they were difficult to estimate even from the observations by HRSEM and by

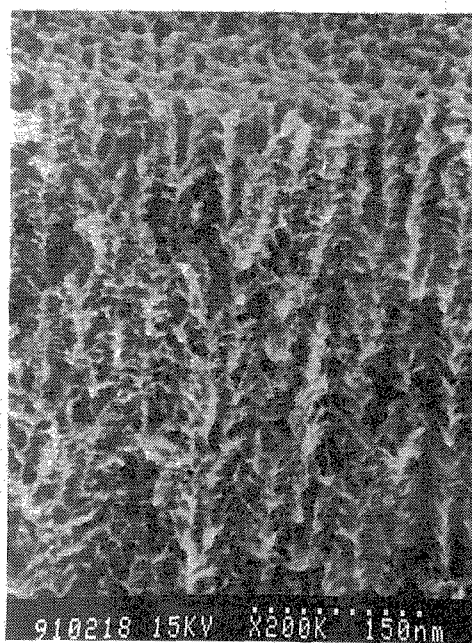


Fig.7 HRSEM showing the microstructure of PS layer. Remaining silicon parts look like fir trees having interacting branches on the main trunks.

XTEM, appear comparable with the peak-values of pore size distribution. Many observations of PS layers showed that small pores exhibit slightly more intricate morphology than large ones. In this study, the depth dependence of morphology in PS layers was not examined, although it can be expected from anodization process. This point must be further investigated in detail.

### Lattice Distortion and Crystalline Quality of PS Layer

In this study, the lattice distortion of PS layer was defined by  $(d_p - d_s) / d_s$ , where  $d_p$  and  $d_s$  are respectively the interplanar spacings of the PS layer and the silicon substrate [7,8], and directly evaluated from the peak-positions of corresponding rocking curves measured by X-ray diffractometry for PS layers formed on the silicon wafers. The crystalline quality of PS layer was also evaluated from the width of the rocking curve; particularly, the full width at half maximum (FWHM) which can provide information of the crystal perfection.

Figure 8 shows the lattice distortion as a function of current density for PS layers prepared by electrochemical anodization. The results were obtained from PS layers which were formed on substrate silicon wafers. The lattice distortion is shown to be nearly proportional to the current density below  $200 \text{ mA/cm}^2$ . Observed FWHM's were slightly wider than that of the silicon substrate, indicating that the crystallinity is not so heavily degraded. This result is the same as the previously reported result.<sup>[7]</sup> This also indicates that the lattice distortion is controllable with the current density when the nature and the level of the semiconductor dropping are given. To the contrary, for PS layers produced above  $250 \text{ mA/cm}^2$ , the lattice distortion decreases and the

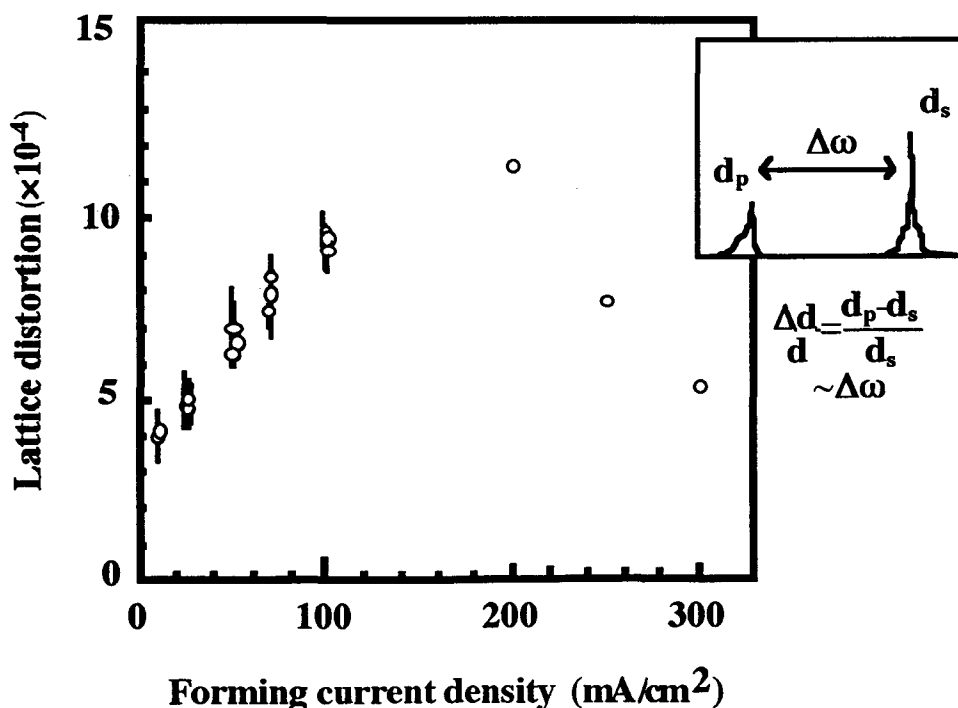


Fig.8 Lattice distortion as a function of forming current density of PS layers.

peak from PS layer becomes diffused, although the data are not shown here. This suggests that the PS layer is heavily degraded in crystallinity.

In order to elucidate the original of lattice distortion, the interplanar spacings of self-supported PS layers, which were ripped-off out of the silicon substrates by electrochemical etching, were measured in the absolute value by the Bond method [16], and corresponding lattice distortions are shown as a function of forming current density in Fig. 9. Although the lattice distortions show a wide distribution in value, they appear slightly smaller than the values evaluated from the rocking curves of PS layers shown in Fig. 8. In the present X-ray measurement, the angular separation between the two peaks from both the PS layer and the silicon substrate is related

to both the lattice expansion of PS layer and the lattice bending (or lattice curvature) resulting from stresses caused by the lattice misfit between the PS layer and the silicon substrate. Since the self-supported PS layers are free from restraint by the substrate silicon wafers, the above results indicate that the lattice expansion is mainly ascribed to an intrinsic nature of PS layer. Observed slight difference of the lattice distortion may be due to the lattice curvature of the PS/silicon system.

It was shown that PS layers composed of large pores showed slightly larger lattice distortions than those in PS layers composed of small pores. Thus, we can evaluate the lattice distortion of remaining silicon parts in PS layers: The smaller in diameter the remaining silicon parts are, the larger the lattice distortion is. This was also confirmed by investigating X-ray intensity distribution around the reciprocal lattice points for PS layer and the silicon substrate, as shown in Fig.10. The intensity distribution increases in area gradually with increasing forming current density, indicating that the lattice relaxation easily takes place with decreasing the mean radius of remaining silicon part. Figure 11 reproduces an X-ray intensity distribution from a self-supported PS layer, suggesting that the crystal lattice of self-supported PS layer is relaxed just after being ripped out of the silicon substrate. In order to explain such large stress relaxation for self-supported PS layer, a structure model was proposed, as shown in Fig. 12, on the basis of a mosaic structure resulting from stress relaxation. Remaining silicon parts are composed of many small crystallites which are mutually orientated with angular distributions (so-called mosaic structure).

In the present preliminary study, visible light emission was confirmed only for PS layers which were prepared with forming current densities higher than 250 mA/cm<sup>2</sup>. For such PS layers, the X-ray intensity around the peak for PS layer was weak and

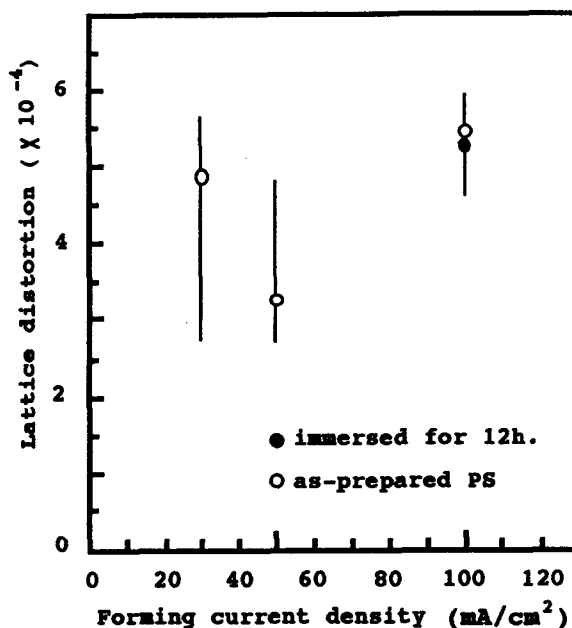


Fig.9 Lattice distortion as a function of forming current density for self-supported PS layers, evaluated from the values measured by the Bond method.

diffused, although their lattice distortion was as small as that of PS layers prepared with lower forming current densities. Observed diffused intensity may indicate that remaining silicon parts are heavily distorted to be composed of similar mosaic blocks to those in the self-supported PS layer.

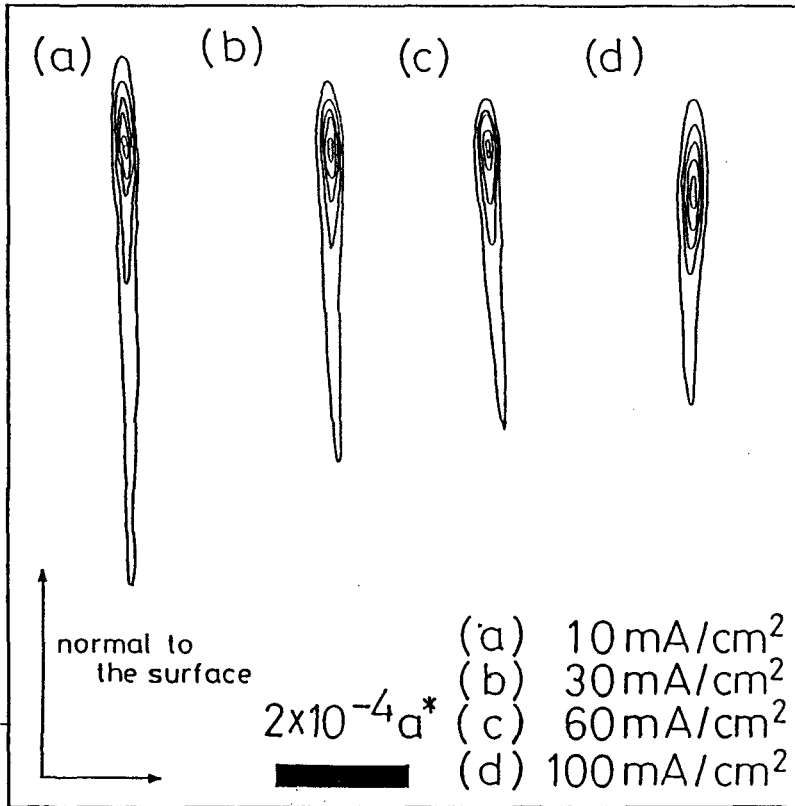


Fig.10 X-ray intensity distribution around the reciprocal lattice point for PS layers.

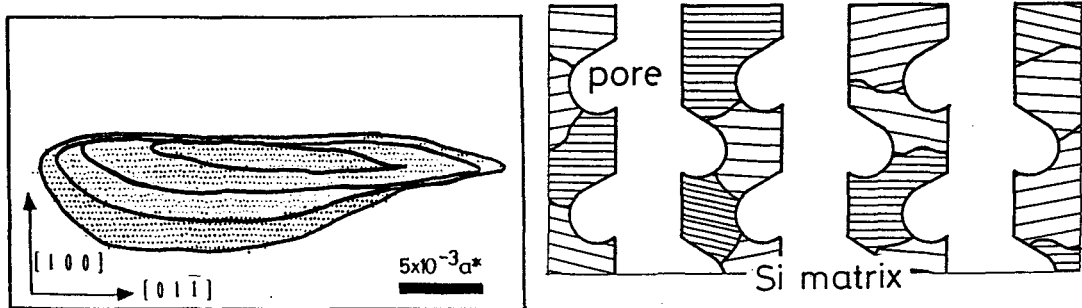


Fig.11 X-ray intensity distribution around the reciprocal lattice point for self-supported PS layer

Fig.12 A model of self-supported PS layer.



### Effect of Dissolution on Microstructure and Lattice Distortion

In order to realize physical isolation of remaining silicon parts, Canham immersed as-anodized PS layers in the electrolyte [1,2]. In this study the natures of thus prepared PS layers were also investigated. Figure 13 shows the porosity and the specific surface area as a function of the immersing time. After 3 h quiescent immersion both the pore size and the specific surface area exhibited appreciable changes and then slow changes were followed, whereas porosity remains almost unchanged independent of the immersing time. In this connection, microstructural changes were also examined by HRSEM. In this study, however, no consistently adequate explanation of all the above experimental results was obtained, because it was very difficult to take clear pictures of immersed PS layers on account of heavy charge-up; Pore surfaces were still covered with some reaction products, probably being passivated. Such reaction products may have influence on the value of the total volume, and thus may in a small change in porosity. In this study, we can say that ideally isolated silicon rods less than  $0.02\Omega\text{cm}$  in PS layers are not easy to be fabricated by only immersing in the electrolyte solution.

Figure 14 shows that the lattice distortion of such PS layers slightly decreases with the immersing time. The FWHM of PS layers hardly changed with immersing time, but the peak profile always appeared asymmetry in intensity. After 12 h

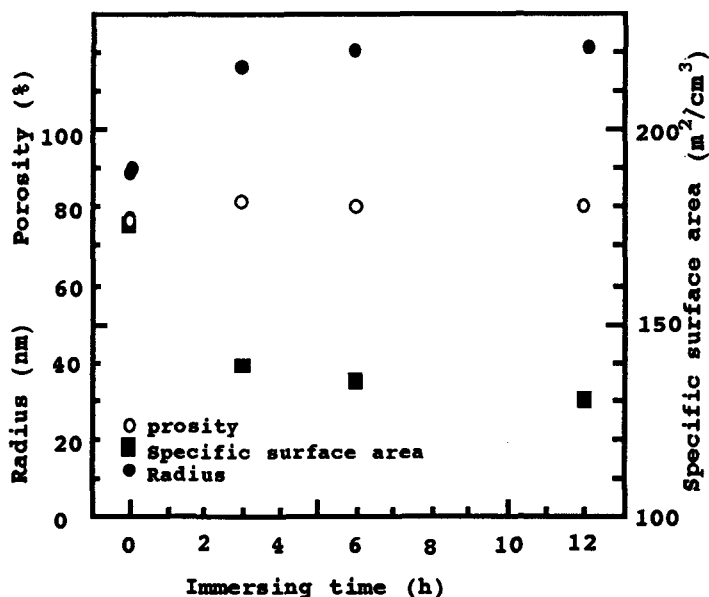


Fig.13 Pore radius, porosity and specific surface area as a function of the immersing time in the same electrolyte solution.

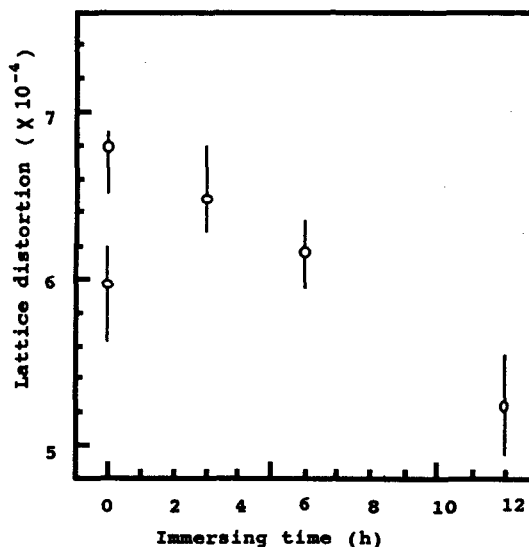


Fig.14 Lattice distortion of immersed PS layer as a function of the immersing time, evaluated by the same way as the previous one.

immersion PS layer exhibited almost the same FWHM as that from the silicon substrate, and no subsidiary diffuse intensity was detected in the low-angle side around the peak. To the contrary, as-anodized PS layers always showed asymmetric diffuse intensity around the peak [8,9]. From summarizing the results, the decrease of lattice distortion of PS layers can be interpreted by considering that remaining silicon parts, after chemically dissolved for 12 h, were almost completely released from surrounding interconnecting branches belong to the other trunks and the crystalline quality was improved. However, this point must be further investigated in detail.

### Origin of Lattice Expansion of PS layer

It was shown that PS layer is a monolithic single crystal with a slightly larger lattice spacing than that of the silicon substrate, and that such lattice expansion is attributed to an intrinsic nature of PS layer. It was also found that the lattice expansion was linearly related to the forming current density, thus the amount of hydrogen gas evolved during anodization. These results support that the cause of lattice expansion has been already generated during anodization.

The above results also suggest that the model for the origin of lattice expansion proposed by Kim et al. [11], which is concerned with the strain in PS layers stored in air at room temperature, is essentially different from the model proposed by the authors [8,9]. It has been reported that the as-anodized PS is almost completely covered with hydrogen atoms, which are automatically chemisorbed to Si atoms on the pore surfaces during anodization [17,18]. In this study this was also confirmed. The existence of hydrogen atoms may result in being free from large amounts of impurities and thus clean pore surfaces. In the present infrared spectroscopy, only adsorption spectra related to Si-Si, Si-H and Si-O bonding were seen. Considering that the decrease of strain on annealing in vacuum is related to the desorption of chemisorbed hydrogen atoms from Si atoms on pore surface, we can say that the lattice expansion of PS layer is attributed to the formation of Si-H bonding during anodization.

It is well known that hydrogen atoms can diffuse into matrix silicon with a diffusion constant of  $5 \times 10^{-15} \text{ m}^2/\text{s}$  at 293 K. In addition, chemically activated hydrogen atoms which were produced during anodization are considered to easily diffuse into the remaining silicon part. A simple preliminary calculation shows that a change in lattice spacing of  $4 \times 10^{-4}$  for silicon can be expected from hydrogen atoms of 0.2 % in concentration diffusing into the matrix silicon.

Consequently, it appears likely that the lattice expansion is mainly due to diffusion of hydrogen atoms into the remaining silicon parts and repulsion force related with chemisorbed hydrogen atoms near pore surface is secondarily contributed to this lattice expansion [18].

## CONCLUSIONS

Microstructure and lattice distortion were investigated for as-anodized PS layers and also PS layers subjected to successive chemical dissolution. The main conclusions are:

- 1) The pore morphology was strongly dependent on pore size. Small pores produced at low current density showed large specific surface area related to intricate pore

morphology having a large number of branches extended in three dimensions, and large pores have simple pore morphology.

2) The lattice expansion of PS layer is an intrinsic nature and the cause of such lattice expansion was generated during anodization accompanied by hydrogen evolution. It appears likely that the lattice expansion is mainly due to diffusion of hydrogen atoms into the remaining silicon parts.

3) Isolated silicon rods in PS layers ( less than  $0.02\Omega\text{cm}$  ) were not easy to be fabricated by only immersing in the electrolyte solution, although the crystallinity of remaining silicon part was strongly improved.

4) P-type PS layers formed with forming current densities higher than  $250\text{ mA/cm}^2$  exhibited visible light emission, although very weak, when irradiated by He-Cd laser. A direct relationship between the crystallinity of PS layer and the visible light emission was not obtained, but it seems likely that very small crystallites are related to the visible light emission of PS layer.

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