Characterization of Porous Silicon Layers by means of X-ray Double-crystal Diffractometry

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(111) and (100) p-type silicon wafers of 0.55 to 33 Ωcm resistivities were anodized in 50 wt% HF solution and formed porous silicon layers were investigated by using X-ray double-crystal diffraction techniques. The porous layer is shown to be a monolithic single crystal, and its lattice spacing is slightly larger than that of the unanodized substrate, resulting in elastic bending of the wafer. The difference in lattice spacing between the porous layer and the substrate was nearly identical independent of wafer orientation and wafer resistivity. The crystal lattice of porous silicon layer is found to be elastically distorted predominantly in the direction normal to the wafer surface. The lattice spacing of porous layer increased slightly with time and the crystalline quality degraded. The results suggest that stresses, generated by the growth of native oxide layers on pore surfaces, are responsible for the elastic lattice distortion of porous layer. It is also shown that the crystalline quality of the porous layer produced on the (111) wafers appears superior to that of the (100) wafers for all the wafer resistivity studied.

KEY WORDS: X-ray diffraction; porous silicon; anodization; crystal perfection.

1. Introduction

Oxidized porous silicon layers can be effectively used for the full dielectric isolation of devices in very large scale integration.1-3 Therefore, formation conditions and relevant physical properties of porous silicon layers have been investigated extensively.4-13 As a result, the porosity and mean pore radius in porous layer were found to be strongly affected by wafer resistivities and by anodization conditions including the forming current density and the concentration of hydrofluoric acid solution. Microstructures of porous layers have been investigated with cross-section transmission electron microscopy and X-ray diffraction4,7,10,11; the crystalline quality of porous layer formed on the (100) wafers of 0.01 Ωcm resistivity was superior to that on the wafers of more than 0.1 Ωcm resistivity.

Crystalline properties of porous layers have been also investigated by means of X-ray diffraction14-19; Barla et al.16,17 examined the porous layers produced on the (100) p-type silicon wafers of 0.38-mm thick having a resistivity of 0.01 Ωcm, and demonstrated that the layers are monocrystalline and they are expanded with respect to the substrate, resulting in elastic bending of the wafer. Young et al.20 also examined both heavily and lightly doped (100) silicon wafers (p-type wafers of 0.01 Ωcm and of 0.1 to 25 Ωcm resistivities), and reported that the crystal lattice of a porous layer was tetragonally distorted and the change in lattice spacing of the porous layer was about ten times smaller on the heavily doped wafers than on the lightly doped wafers.

Nevertheless, the previous X-ray studies were not always carried out under well-defined conditions and thus no detailed data concerning rocking curves from porous layers have been reported yet. In these studies, heavily doped (100) wafers of 0.01 Ωcm resistivity were extensively examined; no particular attention was paid to the differences in features between the (100) and (111) wafers. However, for further application of porous silicon layers to integrated circuits, more extensive investigations of crystalline properties of porous layers are required. In the present study, therefore, porous layers formed on (100) and (111) wafers of 0.55 to 33 Ωcm resistivities were investigated in detail by means of well-defined X-ray double-crystal goniometry, which is a powerful tool for appropriate and non-destructive characterization of the crystalline properties of porous layers. This paper describes preliminary results on crystalline properties of porous silicon layers, and the lattice distortion of the porous layer is also discussed.

2. Experimental Procedures

2.1. Sample Preparation

The microstructure of porous layer is characterized mainly by the porosity and the pore size which are strongly dependent on the anodization condition as well as wafer resistivity.4-13 In order to clarify the influence of the wafer nature on the porous microstructure, in this study (100) and (111) wafers with a variety of resistivities were anodized under an identical anodization condition with a current density of 100 mA/cm² in an electrolyte solution of 50 wt% HF. Three kinds of p-type wafers were prepared in a size of about 20 mm × 20 mm × 0.55 mm: (a) (111) wafers...
of 18 Ωcm resistivity, (b) (100) wafers of 0.55 Ωcm resistivity, and (c) (100) wafers of 33 Ωcm resistivity. These wafers were assumed almost the same in lattice spacing independent of the resistivity. Two kinds of cell, I and II, as shown in Figs. 1 and 2, respectively, were used for anodization. For selective anodization, the wafer surface except a region to be anodized (5 mm × 5 mm for the cell I and 13 mm in diameter for the cell II) was masked with a piece of acid-proof and insulating adhesive tape. A very thin aluminum-alloy layer was formed on the back surface of the wafer so that the anodic current distributes uniformly. The anodized wafers were dried and then kept in a desiccator until measurement. The thickness of the porous layer was measured on a cross section of a cleaved sample under a differential interference microscope. It was found that the thickness of porous layer was proportional to the anodization time and the mean formation rate of porous layer was about 5 μm/min for both cells. The porosity of porous layer was not measured, but it was inferred to be in a range of 50 to 60% from the experimental conditions previously reported.9,10

2.2. Characterization by X-ray Diffraclometry

X-ray double-crystal diffractometry was employed to measure reflection rocking curves from the porous layers of about 15 μm thick. The curves were usually measured after 24 h from anodization. The measuring time was 30 to 60 min. A probing X-ray beam was prepared with CuKα radiation by a (111, –111) channel-cut silicon monochromator and in some cases by (111) and (100) silicon monochromators. The rocking curves from the porous layers were measured mainly with the reflection planes parallel to the wafer surfaces (the symmetrical Bragg case). The area illuminated by the highly collimated incident beam was limited by slits to be approximately 0.2 mm in width and 2 mm in height in order that the measured rocking curve profile should not be affected by the wafer bending. In most cases, the central part of anodized area was examined. The wafer bending was determined from the angular separation between Kα1 and Kα2 peaks which were always observed in the non-parallel setting. Several of the wafers were also examined by means of X-ray reflection and transmission topography.

3. Experimental Results and Discussion

3.1. General Features of Rocking Curves

Typical rocking curves from anodized (111) and (100) wafers are reproduced in Figs. 3 and 4. In the parallel setting for the (111) wafers shown in Fig. 3, two distinct peaks usually appear: one at a lower angle side is associated with the porous layer, and the other at a higher angle associated with the substrate silicon. This indicates that the porous layer is a monolithic single crystal and has a slightly larger lattice spacing than the substrate, thus being under compressive stress. In Fig. 3(a), the measured full width at half maximum (FWHM) of the peak for the silicon substrate, 10.7°, was comparable to that of the unanodized silicon peak, 8.8°, indicating that the measured rocking curve profile was not strongly affected by the wafer bending under the present experimental conditions. The rocking curve from the porous layer shown in Fig. 3 is found to be composed of a sharp peak and a diffuse peak: The sharp peak is considered to be related to a spatially coherent crystalline part where the dynamical diffraction phenomena are not strongly perturbed, and the FWHM of the peak directly gives information on crystalline quality of the porous layer. On the other hand, the diffuse peak is thought to be attributed to X-ray diffraction from an assembly of small silicon crystallites (or mosaic crystals) which gives rise to peak broadening. When the wafer was rotated around the normal of the wafer surface by 180°, almost the same diffuse peak profile was observed. Therefore, the diffuse peak may be attributed mainly to the differences in lattice spacing of such small crystallites. From the
angular separation between the two peaks, the difference in lattice spacing between the porous layer \((d_p)\) and the substrate \((d_s)\), \((d_p-d_s)/d_s\) is found to be in the order of \(10^{-4}\), which is comparable to the difference in lattice spacing for heteroepitaxial layers such as ZnSe films grown on GaAs crystals.\(^{37}\)

In the non-parallel \((111, -400)\) setting shown in Fig. 4, four peaks including two additional peaks due to the \(K\alpha_2\) radiation are usually observed. Each peak is shown to be strongly distorted and broadened by the wavelength dispersion due to successive diffraction. In this case, however, the wafer bending caused by the formation of porous layer can be evaluated from the angular separation between \(K\alpha_1\) and \(K\alpha_2\) peaks diffracted from the silicon substrate; the difference between theoretical and observed values is associated with the wafer bending. The details of the characteristic crystalline properties of porous silicon layers are described below.

### 3.2. Lattice Spacing and Crystalline Quality of Porous Layers

Table 1 summarizes the characteristics of rocking curves for the examined wafers. For the \((111)\) wafers, the porous layers produced in the cell I have a slightly larger lattice spacing than those produced in the cell II. This is probably due to the differences in structural property of porous layers produced by the two types of cell. As additional evidence, X-ray topographs of the porous layers produced in the cell I showed irregular image contrasts throughout the anodized area, while those in the cell II showed a fairly uniform image.

On the contrary, all the porous layers produced in the cell II appear to have nearly the same order of lattice spacing independent of both orientation and resistivity, although the measured values are in wide scatter. This result is similar to that obtained from lightly doped wafers of 1 to 23 \(\Omega\)cm resistivities.\(^{10,15}\) The above result suggests that the wafer resistivity is not necessarily the primary factor determining the lattice spacing of porous layer. The lattice spacing of porous layer has been reported to be proportional to the porosity of layer.\(^{14}\) Therefore, it is considered that the porosity of the porous layers are nearly the same and thus the mean pore size is almost similar. This, however, does not necessarily mean that the structural features are always identical for all the porous layers produced in the cell II: In fact, the FWHM of the porous layer, as shown in Table 1, and the diffuse peak profile, as shown in Fig. 3, are different among wafers. This suggests that, to characterize the porous silicon layers, diffraction information other than the lattice spacing differences such as peak profile should be also taken into account.

In this work, diffraction peaks from porous layers appear distinctly: The observed narrow peaks indicate that the crystalline quality of the porous silicon layer is inferior to that of the silicon substrate but is
not strongly degraded. This is contrast to the results obtained by cross-section transmission electron diffraction studies. The difference may be explained by considering that, in case of transmission electron diffraction of thin films, internal stresses caused by the constraint of surrounding materials are removed and as a result the porous structure including micro pores can change into a modulated microstructure which gives rise to diffuse scattering in electron diffraction patterns. Furthermore, the porous layers of the (111) wafers exhibited fairly narrow diffraction peaks, while those of the (100) wafers showed broad peaks with increasing resistivity, as shown in Table 1. This result indicates that the crystalline quality of porous layers formed on the (111) wafers is superior to that on the (100) wafers. This was also confirmed in the parallel (400, –400) setting, which is more sensitive to the lattice distortion than the non-parallel (111, –400) setting because of the small reflection angular range and the elimination of wavelength dispersion (Fig. 5). The degradation of crystalline quality of the (100) porous layer is probably attributed to a small Young’s modulus of porous silicon layer; Young’s modulus for directions within the (100) silicon planes is much smaller than that within the (111) planes, and thus it is expected that the (100) porous layer also can have a smaller modulus than the (111) porous layer and can be more heavily deformed by the compressive stress due to the difference in modulus. Further detailed examinations should be made on this point.

Changes in crystalline property with time were also examined. A (111) wafer, as shown in Fig. 3(a), was examined again after aging about one week from the initial test. The result is reproduced in Fig. 3(b). A comparison between Figs. 3(a) and 3(b) shows an increase in lattice spacing of the porous layer in aging. The FWHM of the substrate peak remains almost constant but the porous layer peak increases slightly in FWHM, and decreases in height. This indicates that the porous layer is gradually deformed under increasing compressive stress, thus resulting in degradation of crystalline quality. According to the previously reported results, a native oxide is thought to grow on the pore surfaces as well as on wafer surface. Therefore, an enhancement of diffuse scattering around the porous layer peak may be attributed to an increase in the number of small distorted silicon crystallites produced by the oxide.

Table 1. Results obtained by X-ray measurements of porous silicon layers of 15 μm thick.

| Anodizing cell type | Wafer surface | Resistivity (Ω/cm) | Reflection setting | \(\langle 2 d_2 - d_1 \rangle / d_1\) (10^-4) | FWHM of porous layer (arc sec) | FWHM of substrate (arc sec) | FWHM of virgin silicon (arc sec) | radius of curvature (mm)** |
|--------------------|--------------|-------------------|-------------------|---------------------------------|-------------------------------|-----------------------------|----------------------------|--------------------------|
| I                  | (111)        | 18                | (111, –111, 111)  | 3.40±0.30**                    | 13.9±1.0*                     | 10.2±0.4*                   | 8.8                       | –                        |
|                   | (111)        | 18                | (111, –111)       | 3.05                            | 9.3                           | 10.2                       | 8.1                       | –                        |
|                   | (111)        | 18                | (111, –111)       | 2.47                            | 9.0                           | 9.5                        | 8.1                       | –                        |
| II                 | (100)        | 0.55              | (111, –400)       | 2.73                            | 42.8                          | 30.8                       | (34)_{tot} 7             | –                        |
|                   | (100)        | 0.55              | (111, –400)       | 2.67                            | 63.2                          | 30.5                       | (34)_{tot} 12            | –                        |
|                   | (100)        | 0.55              | (400, –400)       | 2.54                            | 48.4                          | 4.5                        | 3.8                       | –                        |
|                   | (100)        | 0.55              | (400, –400)       | 2.77                            | 52.0                          | 5.3                        | 3.8                       | –                        |
|                   | (100)        | 33                | (111, –400)       | 2.56                            | ~200                          | 36.1                       | (34)_{tot} 9             | –                        |
|                   | (100)        | 33                | (111, –400)       | 2.85                            | ~200                          | 35.7                       | (34)_{tot} 12            | –                        |
|                   | (100)        | 33                | (111, –400)       | 2.37                            | ~200                          | 34.2                       | (34)_{tot} 19            | –                        |
|                   | (100)        | 33                | (400, –400)       | 2.78                            | 112                           | 6.5                        | 3.8                       | –                        |

* This value is the average of five measured values.
** These values were evaluated from the angular difference between theoretical and observed angular separations. Thus, in the present case values correspond to the lower limits and the actual values would be a little larger than the calculated values.

![Fig. 5. X-ray rocking curves from porous (100) wafers of 0.55 Ωcm in (a) and of 33 Ωcm in (b), respectively, obtained by the (400, –400) setting. The lattice distortion of the porous layer formed on the (100) wafer is exaggerated and thus the porous layer peak is broadened in comparison with the substrate silicon peak.](image-url)
growth on the pore surfaces.

3.3. Determination of the Lattice Distortion of Porous Layer

From the above experimental results for the (111) and (100) wafers, it was found that the lattice spacing of porous silicon layer was expanded with respect to the substrate and thus the porous layer was under compressive stress. Therefore, the direction of the lattice distortion was examined in more detail. For this purpose, a (111) wafer, whose surface is not parallel to the crystallographic (111) plane but is inclined by about 4° from the (111) plane in the (110) plane, was effectively used. Two geometrical settings shown schematically in Fig. 6 were used for determination of rocking curves. The setting I corresponds to an asymmetrical Bragg case where the wafer surface is not parallel to the crystallographic reflection planes and thus the features of the wafer surface can be clearly demonstrated, while the setting II is apparently identical to the symmetrical Bragg case where the wafer surface is just parallel to the reflecting planes. A comparison between the rocking curves obtained in these two settings can give available information on the direction of lattice distortion with respect to the wafer surface. The measured angular separations of 111 reflection peaks between the substrate and the porous layer were 99.3' in the setting I and 135' in the setting II.

The above angular difference can be explained by a hypothesis that the porous layer is elastically distorted predominantly in the direction normal to the wafer surface. When the lattice spacing difference (Δd) is in the direction normal to the wafer surface inclined by θ from the normal of the (111) planes, the angular separation between the two peaks, is given approximately by

\[
\theta - \theta_0 \text{(in rad)} = \left( \frac{\Delta d}{d} \right) \cos \theta \cdot \tan \theta - \left( \frac{\Delta d}{d} \right) \sin \theta \cdot \cos \theta,
\]

where, \(\theta_n, \theta_p\): the reflection angles of the substrate and the porous layer, respectively

the first term in the right-hand side: the component of lattice spacing difference

the second term in the right-hand side: the component of lattice inclination for the measured reflecting planes.

In the setting II, the first term is significant but the second term can not contribute because the inclined surface rarely affects the reflection conditions. In the present case, θ is about 4°. The measured angle, 135°, in the setting II gives a value of Δd/d and thus the theoretical angular separation in the setting I is given by 97.7°. This value is in good agreement with the measured value, 99.3°. Therefore, it is concluded that the lattice distortion is predominantly in the direction normal to the wafer surface. This elastic lattice distortion was also confirmed by the experimental findings that the crystal lattice planes such as (331) and (224) planes inclined to the wafer surface are rotated by an amount according to the above lattice distortion. It has been reported that the porous layer of the (100) wafer is tetragonally distorted. Consequently, combining these results, we can say that the crystal lattice of the porous layer is elastically distorted predominantly in the direction normal to the wafer surface without regard to its crystallographic orientation.

The above results are well explained based on the idea of Young et al. as follows: Native oxides are produced on the pore surfaces as well as on the wafer surface. As a result of the volume expansion during oxidation, the remaining silicon part, i.e., the above-mentioned spatially coherent crystalline part, is under compression. The porous layer itself is constrained by the substrate only on the interface of porous layer and silicon and is free to expand in the direction normal to the wafer surface. Thus the stress acting on the porous layer results in an elastic distortion normal to the wafer surface. The porous layer is still in a compressive state in the direction parallel to the surface, thereby resulting in wafer bending and also resulting in broadening of the FWHM of porous layer peak. An assembly of slightly distorted small crystallites produced in the vicinity of the pores during oxidation can give rise to diffuse scattering around the porous layer peak.

Fig. 6. Geometrical arrangements for X-ray measurements of lattice distortion of a (111) porous wafer. The setting I corresponds to an asymmetrical Bragg case, while the setting II corresponds apparently to the symmetrical Bragg case where the reflecting planes are parallel to the wafer surface. The angular difference observed in the two settings can give information on the direction of the lattice distortion.
4. Summary and Conclusions

Porous silicon layers formed on the (111) and (100) p-type wafers were studied by X-ray diffraction techniques. The following results were obtained:

(1) Porous silicon is a monolithic single crystal and its crystalline quality is inferior to that of the silicon substrate but is not strongly degraded. Its lattice spacing is slightly larger than that of the substrate, and thus the porous layer is expanded with respect to the substrate, resulting in wafer bending.

(2) The porous silicon layers produced under the same anodization condition show nearly an identical lattice spacing difference, irrespective of resistivity and wafer orientation. However, structural features of porous layers are characterized not only by the lattice spacing difference between the substrate and the porous layer but also by the FWHM and the diffuse scattering profile of the porous layer peak. The diffuse scattering around the porous layer peak is attributed mainly to the lattice spacing differences among small crystallites produced in the vicinity of the pores.

(3) The crystal lattice of porous silicon layer is elastically distorted in the direction normal to the wafer surface without regard to its crystallographic orientation.

(4) The porous silicon layer on the (111) wafer seems to have a better crystalline quality than that on the (100) wafer independently of wafer resistivity.

(5) The lattice spacing of porous silicon layer increased with time and the crystalline quality degraded with increasing compressive stress. This change is attributed to the formation of native oxide layers on the pore surfaces.

However, in order to evaluate crystalline qualities including microstructural features of porous layer, more extensive investigations such as X-ray measurements of fluctuation in both lattice spacing and inclination of lattice planes of spatially coherent crystalline parts should be made, together with the analysis of the origin of diffuse scattering around the porous layer peak. In that case, cross-section transmission electron microscopy of porous layers which is now in plan will be informative.

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