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# Structural study of porous silicon and its oxidized states by solid-state high-resolution $^{29}$Si NMR spectroscopy

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$^{29}$Si nuclear magnetic resonance spectra were measured to characterize porous silicon structures. $^{29}$Si nuclei close to surface were selectively detected both in cross-polarization and non-cross-polarization spectra. The spectra were different from those for amorphous silicon and amorphous hydrogenated silicon. Therefore porous silicon is different from amorphous materials in the structural character. The resonant peaks were, however, much broader than the peaks observed for crystalline silicon. There exists distribution of bonding conformation in the porous silicon layer. The origin of the linewidth in the NMR spectra has been discussed. The contribution of each broadening mechanism to the width has been estimated theoretically and experimentally. The $^{29}$Si NMR spectra for oxidized porous silicon species have been assigned as follows: $-50$ ppm due to $O_2SiH_2$, $-85$ ppm due to $O_3SiH$, $-111$ ppm due to $SiO_2$, and $-101$ ppm due to $Si(OH)_x$ or $^{29}$Si located between $O_ySiH_x$ and $SiO_2$. The signals of $SiH_x$ species have been assignable to $-85$ and $-94$ ppm; however, further study should be done for the detailed assignment. [S0163-1829(98)03426-2]

## I. INTRODUCTION

Porous silicon (PS) is prepared by anodic oxidation of a single crystalline wafer in HF-based solutions.[1] The physical properties of PS structures span a wide range with pore dimensions of about 3 nm to 1 $\mu$m or more, and average porosities in the range of 0.1–0.9, depending on etching conditions, dopant type, and concentration.[2] The recent discoveries of the visible photoluminescence[3] and the electroluminescence[4] at ambient temperature have attracted great interest because they may lead to a Si-based optoelecronic technology. Since PS has potential applications in microelectronics industries and as a ''host matrix'' for metals and catalysts, more detailed studies should be performed about the structure of PS itself.

X-ray diffraction (XRD) provides information about long-range order. A PS layer was found to be a monolithic single crystal by XRD.[5–8] X-ray multicrystal diffractometry revealed that the PS layer has a slightly larger lattice spacing than Si substrate: a small lattice expansion of PS.[5–8] The powder XRD of PS shows peak broadening. Lehmann *et al.* attributed the cause to reduced size and lattice distortion of the crystallite.[9]

Large surface area of PS enables us to investigate the PS surface using transmission Fourier transform infrared (FTIR) spectroscopy; the passivation of PS has been extensively studied.[10–16] The surface is passivated with hydrogen: $SiH_x$ ($x=1$, 2, and 3) and/or $O_ySiH_x$ ($x=1$ and 2, $y=2$ and 3) species. The assignment has been discussed, but there are differences in the detail between researchers.

Solid-state high-resolution nuclear magnetic resonance spectroscopy reveals the local structure at the site of a nucleus. NMR is in contrast to XRD in this respect. Measurements by an ordinary one-pulse cycle give information about nuclei having a short relaxation time. The cross-polarization (CP) technique enables the selective detection for the nucleus in the vicinity of a proton. The presence of hydrogen near the surface and the absence in the bulk permit the selective observation for PS surface by CP measurements. Recently, NMR measurements of PS have been reported;[17–20] however, the spectra have not been interpreted in detail.

In this paper, we report solid-state high-resolution $^{29}$Si NMR spectra of as-prepared and oxidized PS samples. A combination of various techniques was used to obtain different spectra for each sample. The first aim is to clarify the bonding structure of PS from the chemical shift and the full width at half maximum (FWHM) of the spectra. Comparison with amorphous silicon ($a$-Si), amorphous hydrogenated silicon ($a$-Si:H), and crystalline silicon ($c$-Si) revealed the structure of PS. In addition, the selective detection of the surface region was done by the CP technique. Supplementary measurements of XRD patterns and FTIR spectra were performed to characterize the PS structure.

## II. EXPERIMENTAL

A PS layer was obtained by electrochemical anodization of a boron-doped $p$-type Si(100) wafer (resistivity 10–20 $\Omega$ cm) at constant current density. On the back surface of the Si wafer, Al was evaporated, followed by annealing at 400 °C for 30 min under vacuum in order to make an ohmic contact. The electrolyte used was 20 wt. % HF solution. Before anodization, the Si wafer was rinsed with acetone and dipped for a few minutes in the HF solution. The anodization current density and anodization time were 10 mA cm$^{-2}$ and 8 h, respectively. The current density was increased to about 1 A cm$^{-2}$ for a few seconds at the end of the anodization in order to put into an electropolishing regime. This produced a free-standing PS layer. In order to avoid oxidation, the PS was dried by blowing Ar gas without any rinse. The film was about 200 $\mu$m in thickness and 84% in porosity, measured by gravimetric measurements. The Hall-Williamson plot[9,21] of XRD patterns for as-prepared PS showed that the particle size was 8 nm and that the change in lattice constant due to

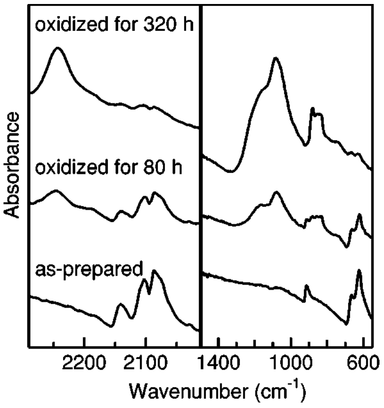

FIG. 1. Transmission FTIR spectra of as-prepared and oxidized PS samples.

stress was ±0.02. The PS was then ground into powder. A PS sample was oxidized in a water-saturated atmosphere at 50 °C. It was placed in a container with a lid where distilled water was filled at the bottom to keep the humidity saturated, and the container was set in a thermostat.

Transmission FTIR spectra were measured by means of a JASCO FT/IR-5M spectrometer. The data were averaged over 16 times and the resolution of 4 cm$^{-1}$ was used. $^{29}$Si NMR spectra were recorded on a JEOL JNM-GX400 NMR spectrometer operating with a $^{29}$Si resonance frequency of 79.3 MHz. The $^{29}$Si chemical shifts reported in this paper were referred to tetramethylsilane (TMS). Polydimethylsilane was used as the external second reference; the $^{29}$Si chemical shift was taken to equal to $-34.0$ ppm from TMS. A rotor was made of zirconia and the rotation speed was about 6 kHz for magic-angle spinning (MAS). A cross-polarization technique was used between $^{29}$Si and $^{1}$H nuclear spins with dipolar-decoupling (DD) of $^{1}$H spins in cases of necessity. Unless the conditions are especially mentioned, the contact time was 5 ms and the recycle time was 15 s for CP measurements; whereas an ordinary one-pulse cycle was used, in which the recycle time was set at 60 s and the flip angle of the $^{29}$Si pulse at about $\pi/2$ for non-CP measurements. Except measurements using the CP technique, a spectrum of a rotor was subtracted from an obtained spectrum in order to eliminate the background.

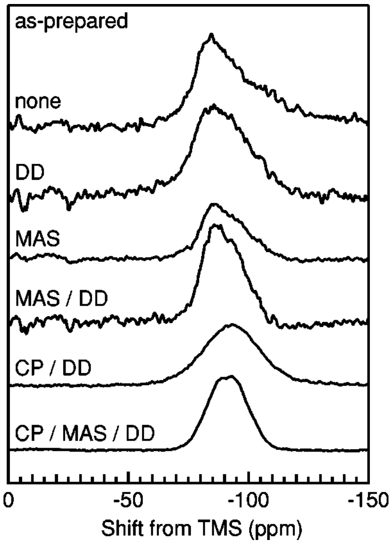

FIG. 2. $^{29}$Si NMR spectra of as-prepared PS. CP, MAS, DD denote cross-polarization, magic-angle spinning, and dipolar-decoupling, respectively. The notation of ''none'' in the figure denotes using no CP, MAS, or DD.

## III. RESULTS

Figure 1 shows transmission FTIR spectra of as-prepared and oxidized PS samples. The peak locations and the bond assignments are as follows:[10,11] 630 cm$^{-1}$ due to Si-H bending, 680 cm$^{-1}$ due to Si-$H_2$ wagging, 850 cm$^{-1}$ due to Si-O-Si symmetric stretching and/or O-Si-H deformation, 910 cm$^{-1}$ due to Si-$H_2$ scissors bending, 1100 cm$^{-1}$ due to Si-O-Si antisymmetric stretching, 2090 cm$^{-1}$ due to Si-H stretching, 2100 cm$^{-1}$ due to Si-$H_2$ stretching, 2140 cm$^{-1}$ due to Si-$H_3$ stretching, 2190 cm$^{-1}$ due to Si-H stretching in $O_2$Si-$H_2$, and 2250 cm$^{-1}$ due to Si-H stretching in $O_3$Si-H. As-prepared PS was brown in color and had strong absorption at 630–680 cm$^{-1}$, sharp absorption at 910 cm$^{-1}$, and distinctive triplets around 2100 cm$^{-1}$. All the peaks are related to Si-$H_x$ species. This result means that as-prepared PS is not oxidized and does not contain oxygen as long as the sample is measured by FTIR spectroscopy. After the PS was oxidized for 80 h, the color was changed to whitish brown. The intensity of absorptions assigned to Si-$H_x$ decreased. Broad absorptions appeared at 1100 and 850 cm$^{-1}$ due to Si-O-Si antisymmetric stretching and Si-O-Si symmetric stretching and/or O-Si-H deformation, respectively. The absorption at 2250 cm$^{-1}$ with a small shoulder at 2190 cm$^{-1}$ due to $O_y$Si-$H_x$ species was observed. These absorptions relate to silicon oxides. Further oxidation for 320 h brought the increase in the intensity of the absorption for oxide-related species, whereas the absorptions due to Si-$H_x$ disappeared. PS oxidized for 320 h was covered with $O_y$Si-$H_x$ and $SiO_x$ species. The PS was brownish white in color.

A preliminary measurement of a MAS $^{29}$Si NMR spectrum for a ground silicon wafer used for the preparation of PS was performed. A very sharp resonance at $-81$ ppm was observed as expected for the highly ordered material. The peak had a FWHM of 1 ppm. This result is consistent with those by other authors.[17,22] The FWHM of 3 ppm was observed without MAS.

Figure 2 shows $^{29}$Si NMR spectra of as-prepared PS. Table I summarizes the peak positions and linewidths. A

TABLE I. Summary of the $^{29}$Si NMR spectra for as-prepared PS. Notations in the table are as in Fig. 2.

| Measuring mode | Peak (ppm) | FWHM (ppm) |
|---|---|---|
| CP/MAS/DD [a] | $-93$ | 20 |
| CP/DD | $-93$ | 27 |
| MAS/DD | $-85$ | 19 |
| MAS | $-85$ | 20 |
| DD | $-85$ | 24 |
| none | $-85$ | 24 |

[a] The structured spectrum consisting of two peaks at $-85$ and $-94$ ppm with FWHM's of 11 and 14 ppm was observed.

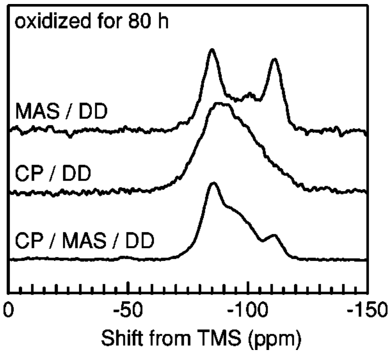

FIG. 3. $^{29}$Si NMR spectra of PS oxidized for 80 h. Notations are as in Fig. 2.

peak with the position of −93 ppm and FWHM of 20 ppm appeared in the CP/MAS/DD spectrum. A detailed insight led to a structured spectrum with two peaks. Separating the spectrum into two Gaussian profiles revealed that it showed peaks at −85 and −94 ppm with FWHM's of 11 and 14 ppm, respectively. The peak position and the FWHM were −93 ppm and 27 ppm, respectively, in the CP/DD spectrum. For the non-CP technique, the spectra had peaks at −85 ppm. The FWHM's were 19, 20, 24, and 24 ppm for MAS/DD, MAS, DD, and "none", respectively, where none denotes using no CP, MAS, or DD. For the "none" spectrum, the spectrum showed a tail in the upfield region.

Figure 3 shows spectra of PS oxidized for 80 h. A small peak at −50 ppm, a relatively sharp peak at −86 ppm with a shoulder in the negative chemical shift, and a peak at −110 ppm were observed in the CP/MAS/DD spectrum. The CP/DD spectrum did not have a fine structure, but a broad line with a peak at −89 ppm and a FWHM of 28 ppm. Three peaks appeared at −85, −101, and −111 ppm in the MAS/DD spectrum.

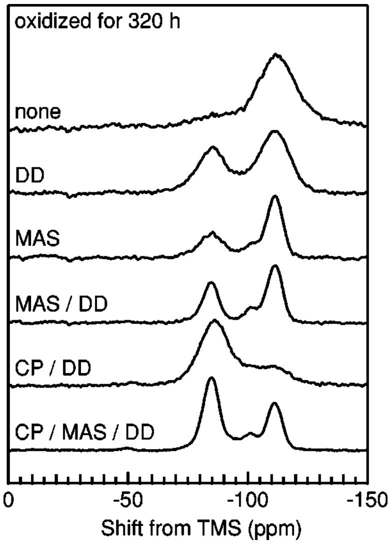

FIG. 4. $^{29}$Si NMR spectra of PS oxidized for 320 h. Notations are as in Fig. 2.

TABLE II. Summary of the $^{29}$Si NMR spectra for PS oxidized for 320 h. Notations in the table are as in Fig. 2. Only observed peaks are shown.

| Measuring mode | Peak (ppm) | FWHM (ppm) |
|---|---|---|
| CP/MAS/DD | −111 | 7 |
| | −101 | [a] |
| | −85 | 8 |
| | −50 | [a] |
| CP/DD | −111 | [a] |
| | −85 | 14 |
| MAS/DD | −111 | 8 |
| | −101 | [a] |
| | −85 | 8 |
| MAS | −111 | 8 |
| | −101 | [a] |
| | −85 | 12 |
| DD | −111 | 16 |
| | −85 | 16 |
| none | −111 | 19 |

[a] The linewidths could not be measured due to the low signal-to-noise ratio or due to broad peaks.

Figure 4 shows spectra of PS oxidized for 320 h. The summary is given in Table II. The CP/MAS/DD spectrum had a small peak at −50 ppm, a sharp peak at −85 ppm, a relatively small peak at −101 ppm, and a peak at −111 ppm. The FWHM's of the peaks at −85 and −111 ppm were 8 and 7 ppm, respectively. The shoulder observed in PS oxidized for 80 h disappeared. The ratio of the intensity at −111 ppm to that at −85 ppm increased with oxidation time. The CP/DD spectrum showed a weakened intensity at −111 ppm as compared to the CP/MAS/DD spectrum. The FWHM of 14 ppm was observed at the peak of −85 ppm.

In the MAS/DD spectrum, the peak at −50 ppm was not distinguishable owing to a low signal-to-noise ratio. Two peaks with FWHM's of 8 ppm were observed at −85 and −111 ppm and a small peak appeared at −101 ppm. The intensity at −85 ppm relatively decreased as compared to the intensity at −111 ppm in the MAS spectrum. The FWHM's were 12 and 8 ppm for the peaks at −85 and −111 ppm, respectively. Both resonances in the DD spectrum broadened to a FWHM of 16 ppm. In the "none" spectrum, the peak at −111 ppm became broader with a FWHM of 19 ppm; whereas the resonance at −85 ppm vanished.

The dependence of the spectra for as-prepared PS and PS oxidized for 320 h on the contact time in the CP/MAS/DD technique was observed. The result of PS oxidized for 320 h is shown in Fig. 5. In the spectra for as-prepared PS (not shown here), the shape of spectra was little influenced by the contact time, although the signal intensity increased with the contact time, except the change from 0.2 to 0.5 ms. The exception was reported by Petit *et al.*[20] Increasing the contact time shifted the peak downfield slightly: −93 and −88 ppm for the contact time of 1 and 10 ms, respectively. This is because the ratio of two signals consisting of the spectra is dependent on the contact time. In PS oxidized for 320 h (Fig. 5), the intensity increased with contact time. The abovementioned exception was true of the signal at −85 ppm. The reason for the phenomenon has not been clarified. Comparison between the spectra revealed that the transfer rate of the $^{1}$H polarization was the most rapid for the peak at −85 ppm,

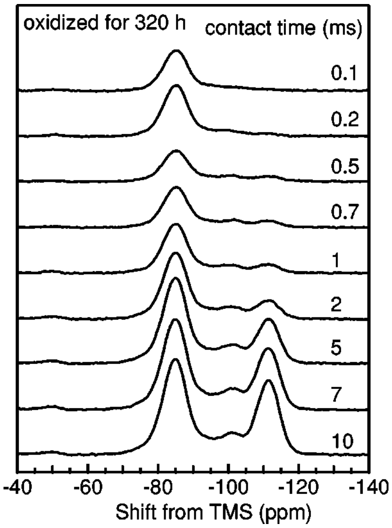

FIG. 5. $^{29}$Si CP/MAS/DD NMR spectra of PS oxidized for 320 h at various contact times.

the slowest for the peak at $-111$ ppm, and in between for the peak at $-101$ ppm.

## IV. DISCUSSION

Generally, there are two possible mechanisms that cause the shift of an NMR spectrum: the chemical shift due to the bonding structure and the Knight shift due to the interaction with charge carriers. First, we discuss the Knight shift; subsequently the chemical shift is debated.

The Knight shift of boron-doped *c*-Si has been studied.[23] The Knight shift is not observed for Si with a dopant concentration of $10^{15}$ cm$^{-3}$. The dopant concentration used for the preparation of PS was about $10^{15}$ cm$^{-3}$.[24] The band gap of PS is larger than that of silicon due to quantum size effects[3,25] and the formation of PS causes the dopant dissolution into HF solution.[26] These phenomena weaken the interaction with charge carriers. Therefore the Knight shift need not be taken into consideration.

Another piece of evidence for the absence of the Knight shift is as follows. We measured $^{29}$Si NMR spectra for PS prepared from a heavily boron-doped silicon (resistivity 0.0015–0.003 Ω cm), where the dopant concentration was $5\times10^{19}$ cm$^{-3}$.[24] No major difference was observed in the spectra, although mixing the PS with NaCl during the measurements was needed to avoid discharge caused by its good conductivity. The conductivity of the PS is much better than that of PS in this study. These results demonstrate that the Knight shift is negligible. Similarly, the effect of dopant is negligible.

Comparison between the CP/MAS/DD and the MAS/DD spectra for the same samples revealed that no major difference was found, except those in the low signal-to-noise ratio of the MAS/DD spectra and the relative intensity between peaks. A slight peak shift in the MAS/DD spectrum for as-prepared PS was caused by the change of the relative intensity between two peaks around $-90$ ppm. Both CP/MAS/DD and MAS/DD spectra showed the same peak positions. Therefore all signals originate from $^{29}$Si in the vicinity of surface. The same consideration was given by Pietraß *et al.* although their discussion was based on the long spin-lattice relaxation time of *c*-Si.[18] Nuclear relaxation must occur more efficiently near the surface than in the bulk. One of the potential relaxation mechanisms is the dipole-dipole interaction with electrons in dangling bonds. The electron spin density of as-prepared PS, determined by electron spin resonance measurements, is on the order of $10^{16}$ cm$^{-3}$.[27,28] The density is too low to affect the NMR spectra and to contribute to the relaxation of $^{29}$Si. Thus other mechanisms, e.g., the dipole-dipole interaction with the proton, contribute to the relaxation.

TABLE III. Summary of the $^{29}$Si NMR peak positions and the assignments.

| Configuration | Peak (ppm) |
|---|---|
| SiH$_x$ [a] | $-94$, $-85$ |
| SiO$_2$ | $-111$ |
| [b] | $-101$ |
| O$_3$SiH | $-85$ |
| O$_2$SiH$_2$ | $-50$ |

[a] The detailed assignments have not been attained.

[b] Si(OH)$_x$ or $^{29}$Si located between O$_y$SiH$_x$ are reasonable, although we have not found the conclusive configuration.

The assignments of $^{29}$Si NMR spectra have been proposed. Petit *et al.*[20] tentatively identified the structured spectra for as-prepared PS using the chemical shift of silane oligomers. Chang *et al.*[17] assigned the peaks on the basis of a comparison with the infrared spectra and the correlation of chemical shifts for other materials. However, detailed assignments have not been achieved. We discuss the assignment by comparison with the infrared spectra. The results of Chang *et al.*[17] and chemical shift for other materials are also used to clarify the assignments.

There appear six resolvable bonding configurations in the $^{29}$Si spectra: signals at $-85$ and $-94$ ppm due to SiH$_x$ species which originally exist in as-prepared PS (Fig. 2, Table I) and at $-50$, $-85$, $-101$, and $-111$ ppm due to the oxidized species (Fig. 4, Table II). The assignments are summarized in Table III. The peak at $-50$ ppm was very weak, although the intensity was considerably strong in the results of Chang *et al.*[17] The strong absorption at 2190 cm$^{-1}$ was observed in FTIR spectra for PS prepared by Chang *et al.*[17] The weak absorption for the PS oxidized for 320 h in Fig. 1 reveals that the signal at $-50$ ppm is related to the absorption at 2190 cm$^{-1}$: O$_2$SiH$_2$. The difference in FTIR and NMR spectra is caused by the conditions for the sample preparation: the drying and oxidation techniques.

The dependence of the spectra for oxidized PS on the contact time in Fig. 5 explains that the distance to $^1$H is shortest from $^{29}$Si for $-85$ ppm, longest for $-111$ ppm, and in between for $-101$ ppm, since the efficiency of CP is proportional to the inverse sixth power of the distance between the two spins. The signal at $-85$ ppm in the oxidized state is assigned to O$_3$SiH corresponding to FTIR absorption at 2250 cm$^{-1}$. Chemical shifts of quartz and cristobalite are found at $-107$ and $-110$ ppm, respectively.[29] Therefore the signal at $-111$ ppm is due to SiO$_2$. The signal at $-101$ ppm may arise from Si(OH)$_x$ species or $^{29}$Si located between O$_y$SiH$_x$ and SiO$_2$.

TABLE IV. Possible broadening mechanisms of $^{29}$Si resonance line for PS samples and estimated linewidths caused by them.

| Mechanism | Linewidth [a] | Method of elimination |
|---|---|---|
| Dipole-dipole interaction with $^{1}$H | $<6$ kHz | DD (MAS)[c] |
| Dipole-dipole interaction with $^{29}$Si | $<100$ Hz | MAS |
| Chemical shift anisotropy | 3–7 ppm | MAS |
| Bulk magnetic susceptibility | $<1$ ppm | MAS |
| Separation of bonding configurations [b] | 9 ppm | impossible |
| Dispersion of bonding conformations | 7–14 ppm | impossible |

[a] The linewidth expressed in unit of ppm are proportional to the applied magnetic field, while those in Hz are independent of the field.

[b] Only as-prepared PS shows the linewidth.

[c] MAS can eliminate the linewidth less than rotation speed of the rotor.

Adding hydrogen bonded to $^{29}$Si shifted the chemical shift upfield in the assignments of SiH$_x$ species:[17] the chemical shift of SiH is more positive than that of SiH$_2$. However, contradictory assignments were proposed by Petit *et al.*[20] Their assignments were alike based on the comparison between other silicon materials. The present system of as-prepared PS is essentially a continuous network composed of Si and H and the nature may differ from an isolated small molecule. The $^{29}$Si resonance peak position for $a$-Si:H shifts to more negative values with increasing hydrogen concentration.[30–33] The signals due to the SiH$_x$ species for PS are observed at $-85$ and $-94$ ppm; however, further study should be performed for detailed assignments.

It is worth investigating the crystallinity of PS in terms of NMR. X-ray diffraction reveals the bulk crystallinity, whereas NMR gives information in the vicinity of the surface. $^{29}$Si NMR spectra of $a$-Si[22] and $a$-Si:H[30–35] have been studied. The MAS spectrum of $a$-Si had a signal with a peak at $-38$ ppm and a FWHM of 81 ppm.[22] The spectra of $a$-Si:H vary in the peak location and FWHM, depending on the conditions for sample preparation. The CP/MAS/DD spectrum of reactively sputtered $a$-Si:H without SiH$_2$ showed a peak at $-62$ ppm with a FWHM of 52 ppm, whereas a peak at $-75$ ppm with a FWHM of 50 ppm was obtained in the spectrum of $a$-Si:H containing 70% of the H in the SiH$_2$ configuration.[31] The glow-discharge $a$-Si:H with and without SiH$_2$ exhibited peaks at $-50$ and $-42$ ppm, respectively, in the CP/MAS/DD spectra.[30] Increasing hydrogen concentration, i.e., increasing hydrogen in the clustered region, shifted the peak upfield.[32,33] The CP/MAS/DD spectra had FWHM's of 51–58 ppm, depending on deposition conditions; the peaks became broader and FWHM's were 78–96 ppm without MAS.[30,32] In addition, the effect of dangling bonds on $a$-Si and $a$-Si:H spectra is negligible.[22,32]

The FWHM of spectra for as-prepared PS were less than 27 ppm. The value is much lower than the FWHM of $a$-Si:H and $a$-Si. The chemical shift of as-prepared PS differs markedly from the value of $a$-Si and $a$-Si:H, although major elements are the same: silicon and hydrogen. These differences show that PS has the crystalline structure near the surface. However, spectra of PS are much broader than that of $c$-Si which has no distortion. There exists distribution of bonding conformation in the vicinity of the PS surface.

Various techniques have been employed to obtain $^{29}$Si NMR spectra. Such experiments enable us to identify the mechanism of the line broadening, which includes information on the electronic and bonding structures. Possible broadening mechanisms in the present system are the dipole-dipole interaction ($^{29}$Si-$^{1}$H, $^{29}$Si-$^{29}$Si), chemical shift dispersion due to bonding configurations and conformations, chemical shift anisotropy, and bulk magnetic susceptibility. They are summarized in Table IV. MAS can eliminate broadening due to chemical shift anisotropy and bulk magnetic susceptibility. Broadening due to the dipole-dipole interaction disappears at spinning rate greater than the linewidth. Broadening due to $^{29}$Si- $^{1}$H dipole-dipole interaction can be eliminated using DD. However, it is impossible to eliminate broadening due to dispersion of chemical shift. The linewidth originated from each mechanism is estimated by theoretical calculation and experimental results as described below.

Chang *et al.*[17] pointed out the possibility that more than one distinct bonding configurations exist in each peak. However, such a feature was not observed in CP/MAS/DD spectra, except in the spectrum of as-prepared PS. The estimated separation due to the bonding configurations is about 9 ppm in as-prepared PS.

The broadening due to bonding conformations is observed in CP/MAS/DD spectra. The FWHM ranges from 7 to 14 ppm. The linewidth is determined by the deviation of electron distribution, which is produced by the dispersion of bonding conformation. The estimation using the diamagnetic shielding due to electrons[36] brings about a deviation of $\pm 0.05$ electron units from the linewidth of 10 ppm due to bonding conformations. The value is about one-fourth of that of $a$-Si (around $\pm 0.2$).[37] Assuming that the strength of the dispersion is proportional to the deviation of charge at the nucleus, the dispersion of bonding conformation for PS is found to be about $\pm 2\%$ since the dispersion for $a$-Si is about $\pm 8\%$.[37] The deviation includes contribution due to bonding length and angle. The dispersion near the surface is roughly the same as that in the bulk.

The CP/DD and DD spectra broaden in comparison with the CP/MAS/DD and MAS/DD spectra, respectively. The lack of MAS would bring about the broadening due to $^{29}$Si-$^{29}$Si interaction, bulk magnetic susceptibility, and chemical shift anisotropy. Broadening due to $^{29}$Si-$^{29}$Si interaction is theoretically calculated. The linewidths for $^{29}$Si-(Si)$_1$,

$^{29}$Si-(Si)$_2$, and $^{29}$Si-(Si)$_3$ are 60, 80, and 100 Hz, respectively.[38] Much weaker interaction is expected for $^{29}$Si which is not directly bonded to Si. Therefore the broadening for SiO$_2$, O$_3$SiH, and O$_2$SiH$_2$ is negligible. The linewidth due to bulk magnetic susceptibility is found to be less than 1 ppm by using Drain's equation[39] if the susceptibility of $c$-Si can be used.

The rest of the linewidth increase is almost attributed to chemical shift anisotropy, ranging from 3 to 7 ppm. Broadening due to chemical shift anisotropy of PS is much less than that for $a$-Si:H.[30,32] Chemical shift anisotropy reflects the symmetry of electron distribution around silicon nuclei. The difference demonstrates that PS is not amorphous and that the electron distribution around $^{29}$Si for PS is rather symmetrical. The linewidth of $c$-Si NMR spectra increased by 2 ppm without MAS. The broadening due to $^{29}$Si-$^{29}$Si interaction is 120 Hz (1.5 ppm) since $c$-Si has the $^{29}$Si-(Si)$_4$ bonding configuration.[38] The broadening due to bulk magnetic susceptibility is less than 1 ppm.[39] Therefore the broadening due to chemical shift anisotropy for $c$-Si is negligible. This means that the electron distribution is less symmetrical for PS surface than for $c$-Si.

In the ''none'' spectrum for PS oxidized for 320 h (Fig. 4, Table II), the intensity at $-85$ ppm was very weak. The signal is assigned to O$_3$SiH. Broadening due to $^{29}$Si-$^{1}$H interaction can be estimated by theoretical calculation. The $^{29}$Si bonded to $^{1}$H has the large linewidth, ranging from 3 (SiH) to 6 kHz (SiH$_3$).[38] Much weaker interaction is expected between $^{1}$H and $^{29}$Si which is not directly bonded to $^{1}$H, since the interaction rapidly decreases with increasing distance. Therefore the signal due to SiO$_2$ was not much influenced by DD: a slight increase in the linewidth to 19 ppm.

## V. CONCLUSION

We have measured the $^{29}$Si NMR spectra for as-prepared and oxidized PS samples to characterize the PS structure. $^{29}$Si close to PS surface was selectively detected both in CP and non-CP spectra. The Knight shift was negligible. The NMR spectra were not influenced by dopant and dangling bonds. The NMR spectra were different than those for $a$-Si or $a$-Si:H. Therefore PS has a structural character different from amorphous materials. However, there exists a distribution of bonding conformation in the PS layer, resulting in the broadening of the spectra.

The $^{29}$Si NMR spectra were assigned based on the comparison with FTIR spectra, the chemical shifts of other silicon materials, and the results of other researchers. The dependence of the intensity on the contact time was also employed for the assignments. The assignments of oxidized species are as follows: $-50$ ppm due to O$_2$SiH$_2$, $-85$ ppm due to O$_3$SiH, $-111$ ppm due to SiO$_2$, and $-101$ ppm due to Si(OH)$_x$ or $^{29}$Si located between O$_y$SiH$_x$ and SiO$_2$. The signals of SiH$_x$ species are assignable to $-85$ and $-94$ ppm, although further study should be done to assign the spectra completely.

The origin of the linewidth in the NMR spectra was discussed. The contribution of each broadening mechanism to the width was estimated theoretically and experimentally: $^{29}$Si-$^{1}$H interaction (less than 6 kHz), $^{29}$Si-$^{29}$Si (less than 100 Hz), bulk magnetic susceptibility (less than 1 ppm), chemical shift anisotropy (3–7 ppm), and dispersion of bonding conformation (7–14 ppm). The dispersion gave information about the structure of the PS surface. The dispersion of bonding conformation ($\pm 0.02$) is roughly the same as that in the bulk determined by XRD.

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