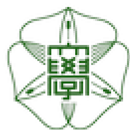
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Title	X-ray photoelectron spectroscopic studies of the chemical nature of as-prepared and NaOH-treated porous silicon layer
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Citation	Applied Physics Letters, 62(14), 1676-1678 https://doi.org/10.1063/1.109597
Issue Date	1993-04-05
Doc URL	http://hdl.handle.net/2115/50251
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Type	article
File Information	APL62-14_1676-1678.pdf

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X-ray photoelectron spectroscopic studies of the chemical nature of as-prepared and NaOH-treated porous silicon layer

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(Received 11 September 1992; accepted for publication 4 January 1993)

The effect of various surface treatments of a porous silicon layer (PSL) including etching in NaOH solution on the chemical nature of the surface was studied using x-ray photoelectron spectroscopy. As-prepared PSL, which is formed by anodic oxidation of silicon in ethanolic HF solution, is covered with silicon oxide. NaOH treatment removes the surface oxide almost completely. Chemical states of surface silicon at the NaOH-treated PSL surface are very close to that at the HF-treated silicon surface. Surface oxygen on the NaOH-treated PSL surface seems to be in the form of Si-OH.

The recent discovery of visible light emission from a porous silicon layer (PSL) at room temperature opened a new era for the application of silicon to optoelectronic devices. The electronic properties of silicon bulk cannot explain the above phenomenon as silicon has the indirect band gap of 1.06 eV. One explanation recently proposed for the visible luminescence is based on the nanometer-size crystalline structure of PSL. The structure can exploit quantum confinement effects which are responsible for the band gap widening and the increase of the probability of a direct band gap recombination.[1] On the other hand, contribution of surface chemical species such as silicon oxide to the luminescence has also been pointed out.[2] Despite a large amount of the experimental results on the luminescence from PSL samples prepared and treated in various ways, the chemical nature of the surface of PSL is not clear. To investigate the mechanism of the luminescence from PSL, information on the chemical nature of the PSL is very important. Furthermore, extensive studies revealed that the luminescence properties depend on the subsequent chemical treatments of PSL such as the etching using HF and various hydroxide solutions.[3,4] The etching process should change not only the structure of the PSL but also the chemical nature of the surface. The investigation on the chemical nature of such surfaces is also indispensable.

In this work we studied the chemical structures of the surface of HF-treated silicon and electrochemically prepared PSL by using x-ray photoelectron spectroscopy (XPS). The effect of the subsequent NaOH treatment was also investigated.

Polished *p*- and *n*-type single crystal silicon wafers with the resistivity of <0.01 and 2 Ω cm, respectively, were used in this study. The wafers were cleaned first in acetone to remove organic impurities. After being rinsed with water purified by Milli-Q system, the samples were immersed in ethanolic hydrofluoric acid (10%) for 1 min (HF treatment) and then rinsed with water immediately after the HF treatment. An ohmic contact was formed using In-Zn alloy on one side of the sample. A Teflon vessel was used as an electrochemical cell and was cleaned by immersing in a mixture of sulfuric acid and nitric acid for 1 h then in boiling water for 1 h. While anodic oxidation of *p*-type silicon was carried out at a constant current density of 30 mA/cm^2 for 700 s in the dark, *n*-type silicon was anodized with a current density of 5 mA/cm^2 for 600 s under illumination with a 30 W tungsten lamp as a light source. Some of the anodized samples were immersed in aqueous 1 M NaOH solution for 20 s (NaOH treatment). Both as-prepared PSL and NaOH-treated PSL samples were rinsed with water just after the preparation or treatment and dried under a pure nitrogen gas flow. It was confirmed that both the as-prepared and NaOH-treated PSL samples show electroluminescence (EL) in a visible region in electrolyte solution such as 1 M Na_2SO_4.[5] EL of porous Si in electrolyte solution has been already reported by various groups[6–8] and is more reproducible than PL because the measurements are carried out at the surface under well-defined conditions.

The XPS measurements were performed using an ESCALAB Mk II (VG Scientific Co.) equipped with XPS, ultraviolet photoemission spectroscopy, and Auger electron spectroscopy facilities. The x-ray photoelectron spectra were recorded using Mg $K\alpha$ x rays of energy of 1235.6 eV. The acceleration voltage and emission current used for generating the x-ray were 15 kV and 20 mA, respectively. Low resolution (50 eV) pass energy survey spectra were acquired over the binding energy range 0–1000 eV for all samples. In order to examine the surface in more detail, high resolution windows at 20 eV pass energy and scanning speed of 1 eV/s were also employed. The spectrum data were analyzed using a program which permits averaging of the data, background correction, determination of binding energies at the peak maximum and peak areas, and deconvolution of the overlapping peaks by Gaussians–Lorenzians fitting.

Figure 1 shows the low resolution (50 eV pass energy) XPS survey spectra for *n*-type surface of (a) HF-treated silicon, (b) as-prepared PSL, and (c) NaOH-treated PSL. O 1*s*, C 1*s*, Si 2*s*, and Si 2*p* lines are observed as the predominant ones in Fig. 1. It is clear that the oxygen level increases after anodizing treatment, i.e., PSL formation, but decreases by the NaOH treatment. The dependence of oxygen level on the treatment was the same as that at

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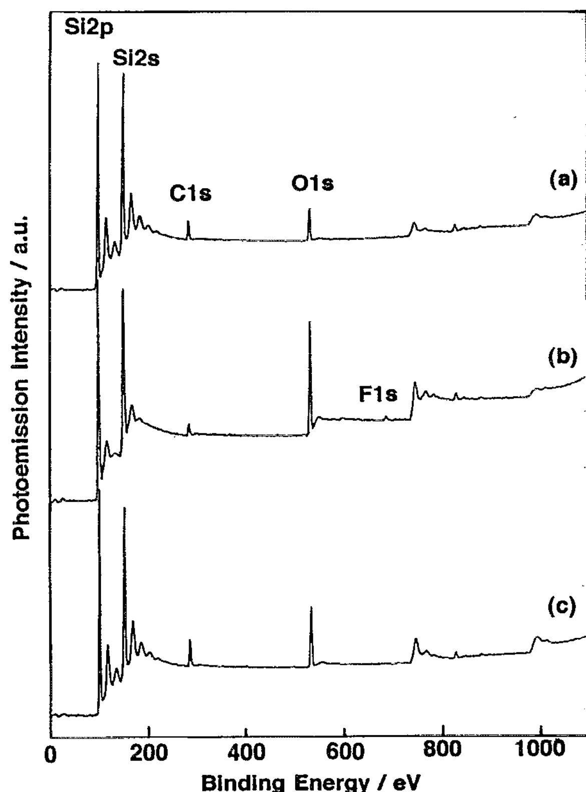

FIG. 1. XPS survey scan spectra for n-type silicon surface of (a) HF-treated silicon, (b) as-prepared PSL, and (c) NaOH-treated PSL.

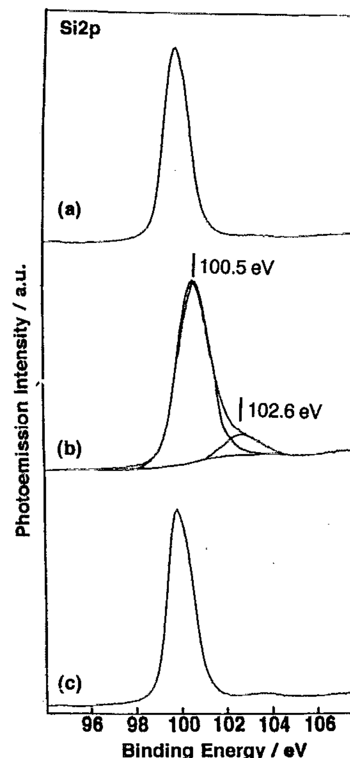

FIG. 2. Si $2p$ expanded spectra for n-type surface of (a) HF-treated silicon, (b) as-prepared PSL, and (c) NaOH-treated PSL. The deconvoluted spectrum for the as-prepared PSL is also shown in (b). Vertical lines mark the location of spectral components at 100.5 and 102.6 eV.

p-type substrate. At the PSL surface all the peaks were located at higher binding energy by 0.9–1.2 eV than those observed at the HF-treated silicon surface. After the NaOH treatment the peak positions became the same as those of the HF-treated surface. The shift at PSL should be due to the charging effect on the surface, suggesting that the surface of as-prepared PSL is less conducting than those of the HF-treated silicon and of the NaOH-treated PSL. The values of binding energy were corrected by considering the above energy shifts in the following discussions.

The Si $2p$ expanded spectra for n-type surface of (a) HF-treated silicon, (b) as-prepared PSL, and (c) NaOH-treated PSL are shown in Fig. 2. At the HF-treated silicon surface the spectrum has a peak at 99.9 eV. FWHM of the spectrum is $\sim$1.3 eV. Asymmetric shape of the peak indicates the Si $2p_{3/2}$-$2p_{1/2}$ spin orbit splitting which leads to double peak structure.[9] The signal is attributed to elemental silicon on the surface. Figure 2(b) shows the spectra for the as-prepared PSL. The PSL surface exhibits the chemically shifted small peak along with the strong main peak. The signal can be deconvoluted into two components at 100.5 and 102.6 eV. FWHM of the main signal at lower energy is $\sim$1.7 eV. Although the fact that the main peak is wider than that at the HF-treated silicon surface suggests the presence of Si^{n+} ($n=1,2,3$),[9] it was not considered in the deconvolution. The higher energy component can be attributed to Si^{4+}. The formation of Si^{n+} and Si^{4+} was also observed at the p-type substrate. A ratio of photoelectron intensity of Si^{4+} with respect to the total emission intensity of Si $2p$ is $\sim$0.12 and 0.9 at n- and p-type PSL, respectively. After the NaOH treatment, the small peak at higher energy is reduced remarkably and the width of the spectrum becomes the same as that of HF-treated silicon surface, as shown in Fig. 2(c). This result indicates that only elemental silicon exists on the NaOH-treated PSL surface.

The shape of the O $1s$ spectra dose not depend on the sample. A typical O $1s$ signal is shown in Fig. 3. The spectrum for the n-type as-prepared PSL has a asymmetric tail at higher energy. The signals were deconvoluted into two components at 532.7 and 534.3 eV. The main peak at 532.7 eV is attributed to the oxygen which is chemically bonded to silicon, i.e., hydroxyl group and oxide.[10] One cannot identify whether the signal is due to Si-OH or surface oxide only from the spectral analysis. The higher energy component of O $1s$ signal should be due to physisorbed water. The signal intensity at p-type PSL due to water was relatively weak compared with that at n-type PSL.

The presence of fluorine was detected only on the surface of as-prepared PSL with a weak signal at 686.6 eV corresponding to F $1s$ electron as shown in Fig. 4. The binding energy position of this peak agrees with that observed for Si—F bond formed on the Si surface etched with conc. HF,[10] suggesting that the fluorine on the PSL surface is in the form of Si—F bonds. The possibility that the peak is due to etch residue is excluded because no F $1s$ signal was observed at the HF-treated Si.

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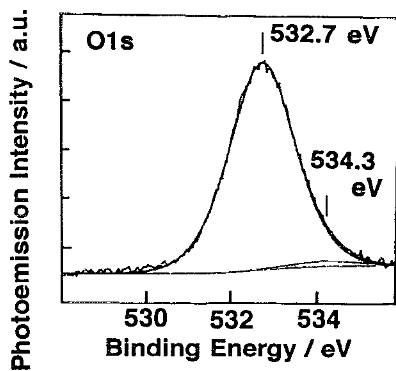

FIG. 3. O 1*s* expanded spectra for the *n*-type as-prepared PSL. Vertical lines mark the location of spectral components at 532.7 and 534.3 eV.

The XPS spectra provide information on the chemical species on these surfaces. At the HF-treated silicon surface elemental silicon and chemically bonded oxygen were detected, but not surface bonded fluorine. These results suggest that the surface is terminated mainly with Si-H and Si-OH. The ratio of oxygen with respect to silicon at the surface was obtained by using these signal intensities.[11] Atomic ratio of oxygen to silicon at the HF-treated silicon surface is 0.073. Since there is no oxide on this sample, the ratio indicates that ~7% and ~93% of surface silicon is terminated in the form of Si-OH and Si-H, respectively. The existence of Si-OH and Si-H were confirmed by FT-IR reflectance absorption spectroscopy.

At the as-prepared *n*- and *p*-type PSL surface the Si 2*p* spectra proved the existence of Si^{4+}, i.e., oxidized silicon, suggesting the formation of silicon oxide. Atomic ratio of oxygen with silicon at *n*- and *p*-type PSL is 0.254 and 0.197, respectively. The fact that these values are larger than that of the HF-treated silicon surface can be explained by considering the formation of silicon oxide. The formation of SiO_2 at PSL on lightly doped *p*-Si was detected by XPS by Perez *et al.*[12] Actually, Si^{4+} dominates the Si 2*p* spectrum.[12] However, Vasquez *et al.* reported that only traces of O were detected by XPS at PSL prepared by immersion of *p*-Si in stain etches consisting of HF/HNO_3, $HF/NaNO_2$, or HF/CrO_3.[13] SiO_2 and siloxene derivative ($Si_6O_{3+n}H_{6-m}$) on the as-prepared PSL surface have been detected by IR and Raman spectroscopy.[2,4,14] At the PSL surface these silicon oxide species coexist with elemental silicon in the form of Si-OH, Si-H, and Si-F. The remaining Si-F at the PSL surface is considered to be in sterically hindered position against attack of water because the Si-OH formation is known as the products of hydrolysis of a Si-F bond occurring due to water exposure of the surface during rinsing process.[4]

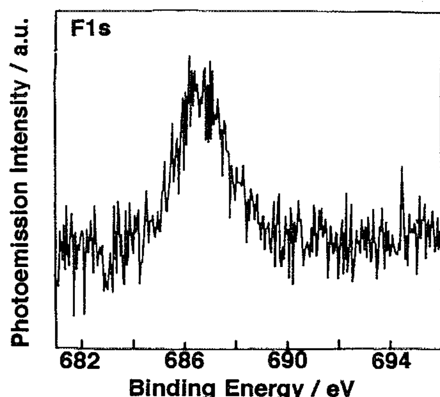

FIG. 4. F 1*s* expanded spectra for the *n*-type as-prepared PSL.

The Si 2*p* spectrum for the NaOH-treated PSL surface shows only elemental silicon, i.e., the chemical condition of the surface is almost the same as that at the HF-treated silicon surface. This result suggests that the silicon oxide was removed by the NaOH treatment. The ratios of oxygen with silicon at the NaOH-treated *n*- and *p*-type PSL are 0.147 and 0.193, respectively. These values are larger than those at the HF-treated silicon surface. At *p*-type substrate, in spite of the disappearance of oxidized silicon signal at the surface, the ratio is even comparable to that of PSL. These large ratios indicate that the amount of Si-OH bond at the surface is increased by the NaOH treatment.

In conclusion, silicon oxides such as SiO_2 and siloxene were formed on a PSL surface in the process of anodic PSL formation *n*- and *p*-type silicon in ethanolic HF solution. The NaOH treatment removes these surface oxides almost completely but increases the amount of Si—OH bond on the surface. Thus, one can investigate the PSL nature without the contribution of surface oxide after NaOH treatment or in NaOH solution. We are now evaluating the details of the EL properties as well as the morphological structure of the various NaOH-treated PSL surfaces.

We wish to acknowledge I. Saeki of Faculty of Engineering, Hokkaido University, for his help in XPS measurement and fruitful discussions. We would also like to thank S. Takada of Kawasaki Steel Company for supplying the silicon wafers used in the present study. This work was partially supported by the Ogasawara Foundation for Science and Technology.

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