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Light-emission phenomena from porous silicon: Siloxene compounds and quantum size effect

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It has long been argued whether the luminescent mechanism of anodized porous silicon is mainly due to the chemical compounds such as siloxene derivatives, or the quantum size effect. We performed a comprehensive study using atomic force microscope, infrared transmission, Raman scattering, and photoluminescence measurements in terms of various annealing temperatures. Low - temperature photoluminescence spectra have also been observed. This leads us to conclude that not only the siloxene derivatives but also the quantum size effect gives the luminescence in porous silicon. The previous pseudopotential calculations are used for the explanation of our experimental results.

I. INTRODUCTION

The mechanism for the light emission from porous silicon layers (PSL) has been intensively investigated since Canham[1] observed its strong luminescence from anodically dissolved silicon wafers in HF solution at room temperature. The quantum size effect which produces the efficient luminescence at sizes smaller than 30 Å formed during the anodization process of silicon wafers has been suggested by many workers.[2–6] On the other hand, several workers have suggested that the light emission is mainly due to the chemical compounds such as siloxene derivativies which have long been known as chemiluminescent materials.[6–11] Molecular excitations from SiH_n formed on the silicon surface were also proposed for the strong light emission from porous silicon.[12]

Recently, van der Walle and Northrup[13] performed pseudopotential calculations for a silicon-hydrogen compound, consisting of a stacking in the [111] direction of double layers of silicon terminated with H atoms or OH groups. Both cases showed direct transition from calculations of matrix elements where the direct band gaps are 2.75 eV for slabs with H termination, and 1.7 eV for slabs with OH termination.

The mechanism for the light emission of porous silicon layers is still uncertain partly because the physical properties of PSLs are strongly sample-dependent. The microstructures of PSLs studied using Raman scattering by several authors appear to be amorphous (*a*-) Si, crystalline Si or even mixtures of *a*- and microcrystalline Si.[14–16] In this study we have investigated the surface structure using atomic force microscope (AFM), and correlated with results of infrared (IR) absorption, Raman scattering, and photoluminescence (PL) measurements. All the measurements have been done as a function of annealing temperature to clarify a role of the chemical compounds formed on the surface of the porous silicon layer. PL measurements have been further carried out at low temperatures.

II. EXPERIMENT

The porous silicon layers (PSLs) were formed by anodizing *p*-type Si (100) wafers with resistivity 6–9 Ω cm in HF-ethanol solutions ($HF:H_2O:C_2H_5OH=1:1:2$). Wafers were anodized under two different conditions. For one type of PSL, called PSL1, the anodization time and anodic dissolution current density were 5 min and 20 mA/cm^2, respectively. For the other type of PSL, called PSL2, they were 45 min and 20 mA/cm^2, respectively. The PSLs were chemically dissolved in 48% HF solutions for an hour. These samples were then oxidized in air by heating for 30 min in an electrical furnace at 200, 400, 600, and 700 °C. AFM, IR, and PL measurements were performed after each treatment. AFM images were obtained using Park Scientific Instrument (autoprobe) with 10 μm scanner. IR transmission spectra were taken using Perkin-Elmer IR spectrometer (Model 683). PL and Raman spectra were taken with typical Raman scattering equipment.[17] Low temperature PL measurements were carried out using a variable temperature optical cryostat.

III. RESULTS AND DISCUSSION

Figure 1 illustrates the AFM images of PSL2 under various conditions. From the optical microscopic view, the surface of the as-anodized PSL samples looks very shiny with dark brown color. However, the surface is microscopically severely corrugated with heights smaller than 90 Å as shown in Fig. 1(a). With HF treatment for an hour this surface becomes dim and is heavily stressed. Figure 1(b) shows deep crests as high as 1000 Å, which is quite different from that of an as-anodized condition. This can be interpreted as follows.

During the anodization of silicon, the holes are accumulated on the silicon surface since the silicon substate is positively polarized. The dissolution of silicon is reported to be carried out through one particular mechanism of the following two reaction mechanisms, depending on the anodizing

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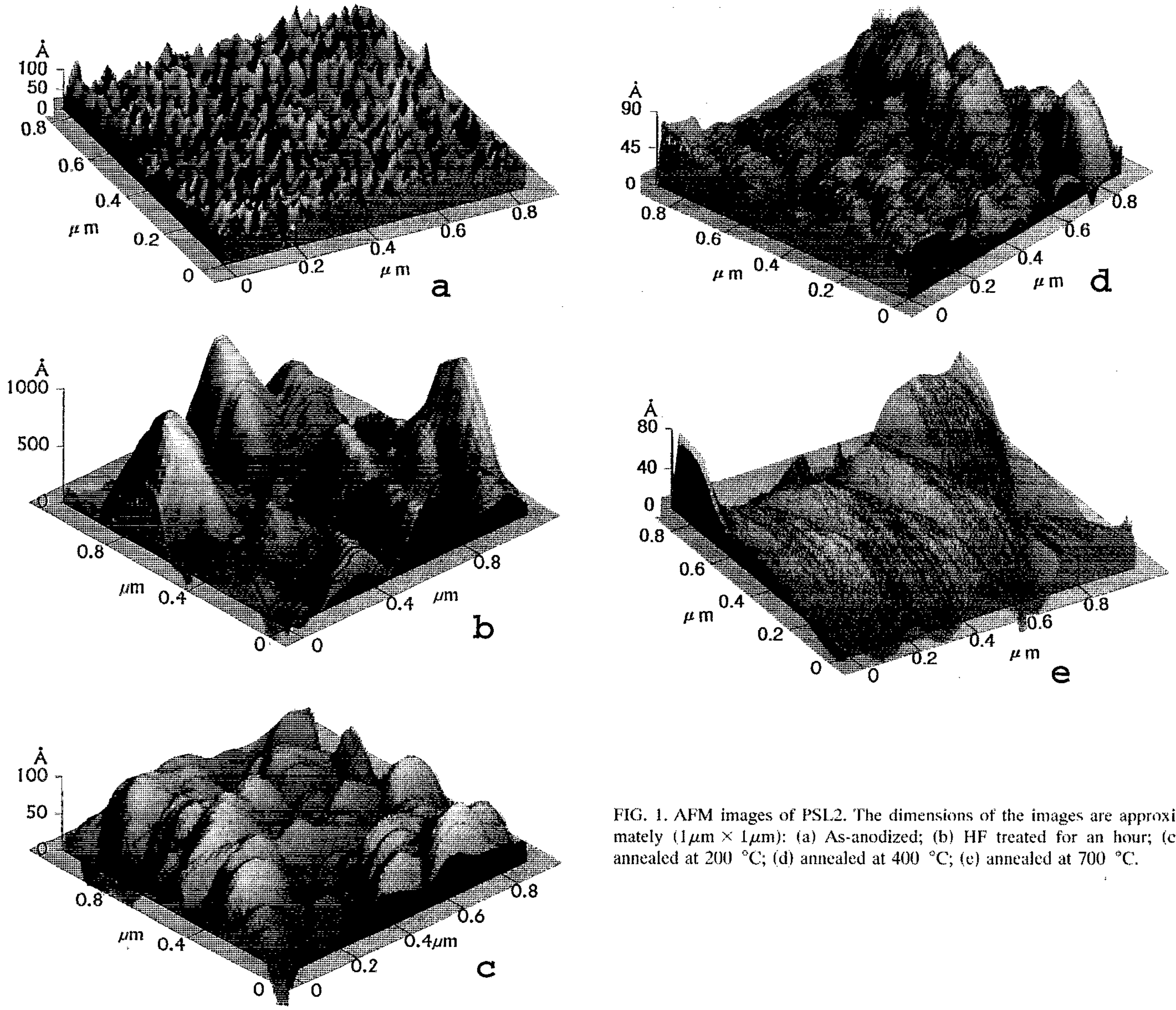

FIG. 1. AFM images of PSL2. The dimensions of the images are approximately (1μm × 1μm): (a) As-anodized; (b) HF treated for an hour; (c) annealed at 200 °C; (d) annealed at 400 °C; (e) annealed at 700 °C.

conditions. However, the holes accumulated on the silicon surface are apparently essential to both reactions[18–20]

$$\mathrm{Si}+4\mathrm{OH}^-_{(ad)}+\lambda h^+\rightarrow \mathrm{Si(OH)}_4+(4-\lambda)e^- \rightarrow \mathrm{SiO}_2\xrightarrow{\mathrm{HF}}\mathrm{H}_2\mathrm{SiF}_{6\,(aq)}(\lambda\leq 4), \quad (3.1)$$

$$\mathrm{Si}+2\mathrm{F}^-_{(ad)}+\lambda h^+\rightarrow \mathrm{SiF}_2+(2-\lambda)e^-\xrightarrow{\mathrm{HF}}\mathrm{SiF}_4+\mathrm{H}_{2\,(g)} \rightarrow \mathrm{H}_2\mathrm{SiF}_{6\,(aq)}(\lambda\leq 2), \quad (3.2)$$

where *ad* and *aq* indicate adsorbed and aqueous ones, and h^+ and e^- are hole and electron, respectively. Several works[4,21,22] reported that prior to the formation of H_2SiF_6 in the last stage of the above reactions, an intermediate species SiF_6^{-2} was formed on the silicon surface, and the overall limiting process might be the transport of these species from the surface to the bulk solution. This adsorbed SiF_6^{-2} is dissolved in HF solution in a form of H_2SiF_6. However, if the hole concentration on the silicon surface is high enough, the production rate of SiF_6^{-2} becomes greater than that of the removal rate of SiF_6^{-2} from the surface by HF. The adsorbed SiF_6^- then reacts with ions in the solution to form layers of various complexes which are less soluble than SiF_6^{-2} in HF.[23,24] The amount of deposited compounds will also increase with anodization time, i.e., PSL1 shows much less corrugations than PSL2. Since the deposited layers are removed by the HF treatment, the morphology is quite different, as shown in Fig. 1(b). It should be noted from the above reactions that Si and SiF_6^{-2} can form various complexes with OHs which are dissolved in HF solutions. This will be discussed later by correlating with PL spectra. The above assertion is further supported from our experiment that the size and height of the pitches in AFM picture became larger with anodization time and also enhanced the PL intensity.

With annealing at 200 °C, more oxygens will be incorporated into the sample and form O-Si-H compounds. The surface became less mountainous than that of HF treated sample as shown in Fig. 1(c). Note that the height scale in Fig. 1(c) is 100 Å. With further annealing at 400 °C, more oxygen is introduced onto the sample, giving more corruga-

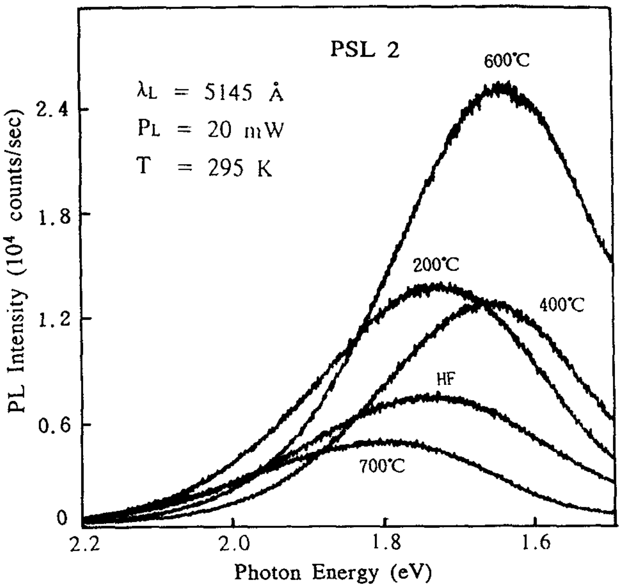

FIG. 2. PL spectra of PSL2: (a) HF treated for an hour; (b) annealed at 200 °C; (c) annealed at 400 °C; (d) annealed at 600 °C; (e) annealed at 700 °C.

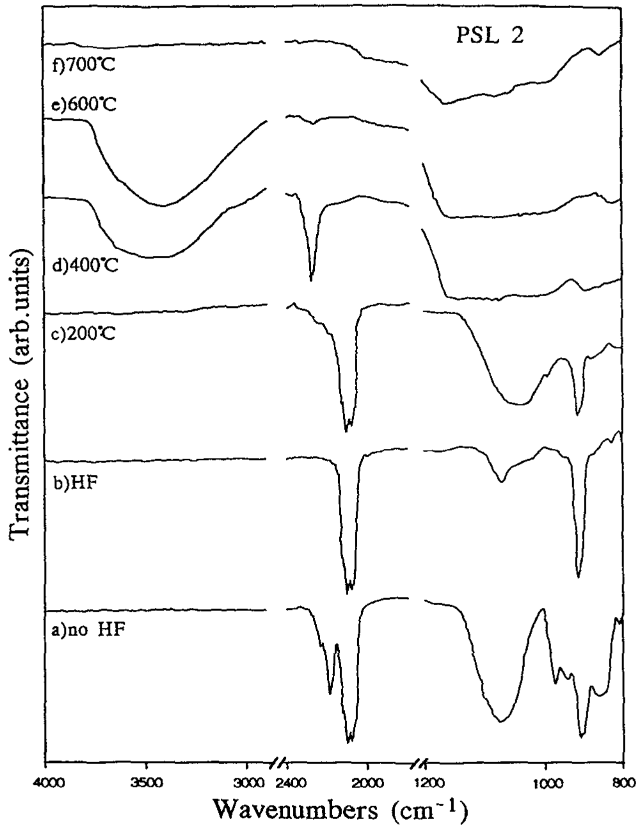

FIG. 3. IR transmission spectra of PSL2: (a) as-anodized; (b) HF treated for an hour; (c) annealed at 200 °C; (d) annealed at 400 °C; (e) annealed at 600 °C C; (f) annealed at 700 °C.

tions. Contrary to these trends, the small pitches disappear in the sample annealed at 700 °C, indicating that the light emission under this condition may be different from the previous ones. In fact, one can expect that all the hydrogen and oxygen atoms should be desorbed from the surface at this annealing temperature. This will be discussed later with IR transmission results.

Figure 2 shows the PL spectra for different annealing temperatures. The PL intensity increases, in general, with annealing temperature up to 600 °C. Since oxygen atoms are adsorbed onto the sample with annealing in air, one can expect that the increase of the PL intensity is mainly due to the O-Si-H compounds. At 700 °C, hydrogen and oxygen atoms are desorbed and therefore the PL intensity should decrease. The PL energy shows red shift with annealing temperature up to 600 °C. At 700 °C, the energy suddenly increases. It is also noted that the PL spectra have shoulders at high energy sides, indicating the existence of more than one origin for the light emission.

Figure 3 illustrates IR transmission spectra of PSL2 in terms of annealing temperatures. The as-anodized sample [Fig. (3a)] clearly shows Si-H_n stretching modes around 2100 cm^{-1}, Si-H_n bending modes in the range of 860–980 cm^{-1}, and the Si-O-Si asymmetric stretching mode around 1100 cm^{-1}. Furthermore, distinct peaks appear near 2200 and 2250 cm^{-1}, slightly higher than the Si-H_n stretching modes. These are attributed to oxygen atoms incorporated into the backbonds of Si-H bonds on the surface. Strong electronegative oxygen atoms change the charge distribution of Si-H bondings, making Si-H bondings stronger.[25] The Si-O-Si asymmetric mode around 1100 cm^{-1} became weaker and the stretching modes of oxidized Si-H_n bonds disappeared completely with the HF treatment. This means that most of the oxygen atoms incorporated into the backbonds of Si-H_n are removed. Therefore the light emission from siloxene derivatives which have hydrogen and oxygen atoms is very unlikely in the HF treated sample, which suggests that another light emission mechanism exists. Annealing at 200 °C introduces the oxygen atoms onto the surfaces or backbonds of SiH_n bonds which are evidenced by the growing peaks near 2200 cm^{-1} and broad peaks around 1100 cm^{-1}. With annealing at 400 °C hydrogen peaks near 2100 cm^{-1} (stretching) disappeared completely, whereas the peaks near 2250 cm^{-1} (O-Si-H modes) are sharply developed. It is also noted that a broad peak centered at 3500 cm^{-1} appeared at this temperature. This can be identified as O-H stretching modes. Thus all the hydrogen atoms except those backbonded with oxygen atoms are desorbed at this temperature. The oxygens are incorporated not only into the backbonds of Si-H but also on the surface in a form of O-H bonding. The oxygens backbonded to Si-H_n are desorbed with annealing at 600 °C as shown in Fig. 3(e) whereas O-H stretching peaks show no change.

With annealing at 700 °C, both the O-H and O-Si-H bonds disappeared. There is a broad background around 1000–1200 cm^{-1}, which may be due to completely bonded SiO_2 by the annealing effect. In general, one expects that

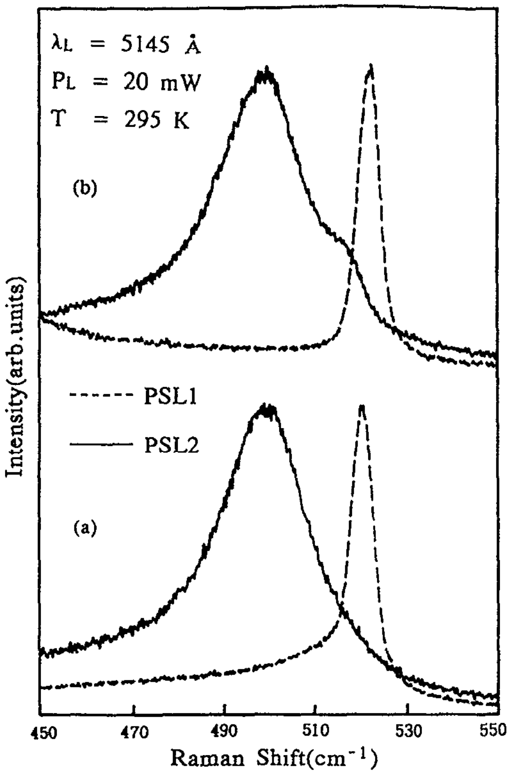

FIG. 4. Raman spectra of PSL1 and PSL2: (a) HF treated for an hour; (b) annealed at 600 °C.

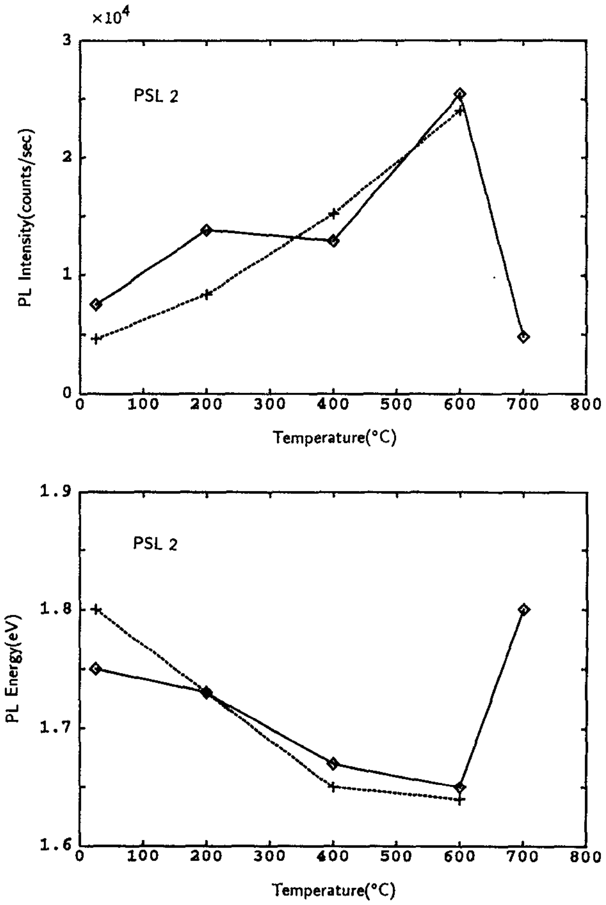

FIG. 5. PL intensity and energy extracted from Fig. 2 in terms of annealing temperature.

SiO_x bondings where x is less than 2 should be desorbed at 600 °C. However, Si-O-Si bonds still remain at this temperature as shown in Figs. 3(e) and 3(f), indicating that some of Si-O configurations are completely bonded. Raman spectra also reveal the annealing effect at this temperature.

Figure 4 shows Raman spectra of PSL1 and PSL2 with different conditions. After the HF treatment, PSL1 exhibits a Raman peak at 520 cm^{-1} with a weak shoulder at the low energy side while PSL2 shows a broad peak near 500 cm^{-1} with a FWHM 24 cm^{-1} as can be seen in Fig. 4(a). The difference of those two types of Raman spectra has been attributed to the structural difference between two types of samples.[17] After annealing at 600 °C, both samples show better crystallinity as can be conjectured from Fig. 4(b); the low energy shoulder has disappeared in PSL1 and a new peak arose near 520 cm^{-1} in PSL2.

Figure 5 shows the data of the PL intensity and PL energy extracted from Fig. 2. The PL intensity increases with annealing temperature up to 600 °C and decreases sharply at 700 °C, whereas the PL energy changes in the opposite way. In order to explain these changes for the light emission from porous silicon, the results from pseudopotential calculations by van der Walle and Northrup[13] are adopted. They chose two silicon slabs along the [111] direction where the dangling bonds of the top and bottom layers are saturated by either H or OH groups. We regard the slabs saturated by purely H as two dimensional quantum planar structures or quantum wires in a form of slab which gives the quantum size effect, and the slabs saturated by OH groups as siloxene derivatives which also give strong luminescence. Various siloxene derivatives which are simply compositional changes of Si-O-H bonds, have been suggested by Brandt *et al.*[10] Both structures give strong direct transition from matrix elements calculations whose direct band gaps are 2.75 eV for H termination, and 1.7 eV for OH termination. Although both structures show strong transition probabilities, it is not clear which one reveals stronger transition. We assume, therefore, that their transition rates are approximately equal. In such a case, the PL intensity is solely determined by the amount of each composition. The size of the slab may vary with various etching conditions, inducing the change of the band gap of quantum size effect.

When the as-anodized sample is etched in HF solution, most oxygen atoms are removed whereas the H atoms still remain on the surface of the sample as shown in Fig. 3. Therefore, the PL spectrum from the HF treated sample is most likely due to the quantum size effect. As we observed from the AFM images (Fig. 1) the deposited oxygen compounds are removed by the HF treatment, leaving deep crests, i.e., quantum dots or silicon particles. With increasing annealing temperatures up to 600 °C, oxygen atoms are incorporated onto the sample, resulting in the formation of siloxene derivatives; the siloxene effect becomes dominant and enhances the PL intensity. However, the PL energy de-

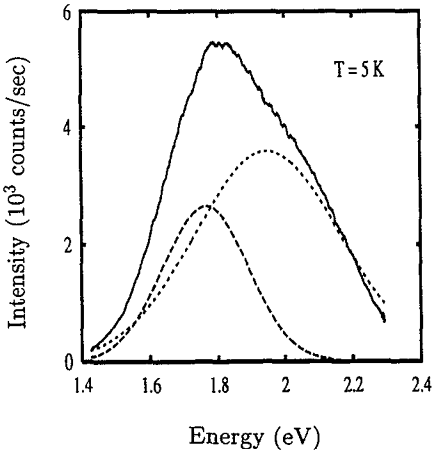

FIG. 6. The PL spectrum at 5 K. The PL curves are fitted to two separate curves with Gaussian shape.

creases with an increase in the amount of siloxene derivatives since the siloxene derivatives give lower band energy than the quantum slabs as suggested in the pseudopotential calculation.[13] The surface becomes uniform as more oxygen is deposited at 400 °C. Both Kautsky siloxene (or Wöhler compound) and OH terminated compounds[9] coexist at 400 °C but Kautsky siloxene disappears at 600 °C, as seen in Fig. 3(e).

With annealing at 700 °C, IR spectra showed that most of the hydrogen and oxygen atoms are desorbed from the sample. We expect, therefore, that the effect from siloxene compounds should disappear and the quantum size effect takes over the luminescent phenomena. As a result, the PL intensity decreased since the total amount of constituents contributing to the PL intensity decreased, while the PL energy due to the quantum size effect gives higher energy than the siloxene compounds. It is noted that although the surface constituents are different from each other, the PL energy at 700 °C is approximately equal to that of the HF treated sample. The intensity may be lower at 700 °C compared to that of the HF treated sample because of the nonradiative recombination process due to dangling bonds created by the hydrogen desorptions. This observation is against the previous assertion that SiH_n excitation is the origin of luminescence in porous silicon.[12] It should be noted that some oxygen atoms still remain on the surface at 700 °C in a form of complete SiO_2 bondings. PSL1 also exhibits similar behavior.

The low temperature measurement of PL also suggests that there may be two different origins of the visible luminescence. Figure 6 shows the PL spectrum of PSL1 at 5 K. The spectrum shows noticeable asymmetry with shoulder at high energy side. We tried to fit the PL curve with many Gaussians but two peaks near 1.77 and 1.95 eV gave the best fit. The energies of both peaks do not show monotonous changes with increasing temperatures. They seem to be nearly constant around 1.80 eV and 1.95 eV with fluctuations of about 0.05 eV. Peak intensities increase in the low temperature region and decrease in the high temperature region, showing maxima around 150 K. Details of the temperature dependence will be discussed elsewhere.[26] The low temperature PL spectra show that more than one origin of the luminescence coexists in PSLs.

IV. CONCLUSION

We performed a comprehensive study of porous silicon by AFM, IR, PL, and Raman scattering measurements with varying annealing temperatures. The PL energy decreases with increasing annealing temperatures up to 600 °C and increases suddenly after annealing at 700 °C, whereas the PL intensity changes in the opposite way. Annealing up to 600 °C in air introduces more oxygen onto the sample. The siloxene compounds seems to be formed on the surface during the anodization and removed by the HF treatment or annealing above 100 °C. Low temperature PL data also suggests that two kinds of origin for the visible luminescence exist. We conclude that these phenomena can be understood by the assertion that the origins for the visible light emission of porous silicon are both the siloxene compounds and the quantum size effect.

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