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# Change in luminescence properties of porous Si by F<sub>2</sub> and D<sub>2</sub>O exposure: *In situ* photoluminescence, Raman, and Fourier-transform infrared spectral study

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*In situ* photoluminescence (PL), Raman, and infrared (IR) spectra of porous Si (PS) during F<sub>2</sub>/D<sub>2</sub>O exposures were investigated. F<sub>2</sub> exposure at 298 K resulted in a peak shift of PL band from 750 nm to 670 nm with an intensity reduction. IR spectra revealed that the surface hydrogenated Si of the PS was displaced by fluorinated one. By subsequent D<sub>2</sub>O exposure, the PL band further shifted to a shorter wavelength with a significant intensity increase: IR bands due to surface oxides as well as SiD and SiOD bonds were observed after the exposure. On the contrary, the average size of the Si crystallites in the PS evaluated from Raman spectra remained almost unchanged throughout the exposures. These results suggest that surface chemistry plays a crucial role in the PL of the PS.

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Since the efficient room-temperature visible photoluminescence (PL) from electrochemically generated porous Si (PS) was reported by Canham,<sup>1</sup> a number of studies of PS has been carried out. The origin of the strong “red” PL of PS is still controversial; to date, PL from PS has been explained on the basis of “pure” quantum confinement of Si nanocrystallites in PS<sup>1,2</sup> or contributions of surface/interface-related chemical structures of the crystallites.<sup>3–11</sup>

It is widely accepted that the surface Si atoms of anodized PS are terminated by H and/or O atoms.<sup>12–15</sup> Although chemical reactions of the PS surface have been investigated with infrared (IR) spectroscopy,<sup>16,17</sup> the correlation between the PL properties and the surface chemical structure of the PS has been still unclear. F<sub>2</sub> is one of the effective dry etchants for Si,<sup>18</sup> which may modify the chemical structure of the PS surface through bond breaking reactions of Si–H and/or Si–O bonds as well as etching reactions of Si atoms. Further, the PS surface after F<sub>2</sub> exposure should be highly reactive because of formations of SiF<sub>x</sub> bonds and/or Si dangling bonds. Therefore, a subsequent exposure to water vapor may also yield a chemically modified structure on the PS surface.

In this letter, we report *in situ* PL, Raman, and IR spectral changes of the PS during F<sub>2</sub> and a subsequent D<sub>2</sub>O exposure. During these exposures, PL spectral features significantly changed accompanying IR spectral changes, while the average diameter of the Si nanocrystallites evaluated from Raman measurements remained almost unchanged. These results cannot be explained by quantum confinement alone. Modification of the surface chemical structure does account for the PL changes in the present work.

The PS samples were prepared by the electrochemical etching of *p*-type Si(100) (8.5 Ω cm) wafers at a current density of 10 mA/cm<sup>2</sup> for 30 min in HF:H<sub>2</sub>O = 1:1 solution under a high-pressure Hg lamp (100 W) illumination. The spectrophotometer used for the PL and Raman measurements

has been described elsewhere.<sup>19</sup> The base pressure of the stainless-steel made vacuum cell was about  $1 \times 10^{-8}$  Torr. After evacuation of the cell, the PS was exposed to F<sub>2</sub> (diluted to 5% by He; 0.05 Torr) and then exposed to freeze-pump-thaw degassed D<sub>2</sub>O (99.75%; 0.3 Torr) at 298 K. The PS could be transferred vertically in the cell. In the *in situ* PL and Raman spectral measurements, the PS was located at a lower part of the cell. The PL and Raman scattered lights generated by Ar<sup>+</sup> laser 488 nm excitation were dispersed by a polychromator (JASCO;CT25TP) and detected with a liquid-nitrogen-cooled CCD detector (Princeton;ST130). *In situ* IR transmission measurements of the PS were carried out at an upper part of the cell through NaCl windows; a Fourier-transform IR spectrophotometer (Bomem;MB100) equipped with a pyroelectric (DTGS) detector was used and all the spectra were obtained as the average of 64 scans with a resolution of 4 cm<sup>-1</sup>. It took about 180 s for obtaining each spectrum.

*In situ* PL spectral changes of the PS at 298 K during F<sub>2</sub> and D<sub>2</sub>O exposures are shown in Fig. 1. Spectra (a), (b), and (c) were respectively measured before and after 10 min of F<sub>2</sub> and subsequent D<sub>2</sub>O exposure. Upon F<sub>2</sub> exposure the PL band of the PS in vacuum at 750 nm shifted its band peak to 670 nm accompanied by a reduction of the band intensity

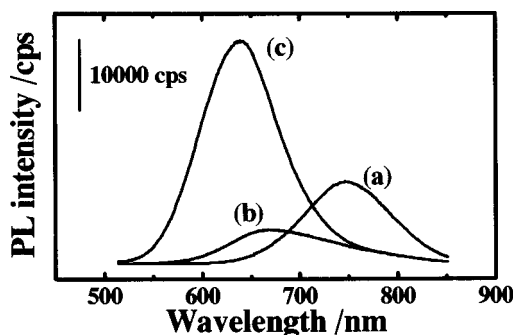


FIG. 1. PL spectra of the PS at 298 K. Spectra (a), (b), and (c) were recorded before and after 10 min of F<sub>2</sub> and subsequent 10 min of D<sub>2</sub>O exposure, respectively. The acquisition time for each spectrum was 1 s.

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[Figs. 1(a) and 1(b)]. Subsequent 10 min exposure to  $D_2O$  leads to a 30 nm blue shift of the PL band peak with a great intensity increment [Fig. 1(c)]. The PL peak intensity obtained after 10 min  $D_2O$  exposure is about three times more intense than that observed before  $F_2$  exposure.

The appearance of a much more intensified PL after  $F_2/H_2O^{20}$  and  $F_2/D_2O$  exposures can be explained by assuming an effective termination of the PS surface. In general, Si dangling bonds present at the nanocrystallites surface are considered to act as a nonradiative recombination center of the generated electron-hole pair.<sup>21</sup>  $F_2$  exposure to the PS might lead to the formation of Si dangling bonds, causing the PL intensity quenching: the subsequent  $D_2O$  exposure would result in the effective termination of the dangling bonds through some reactions, e.g., the dissociative adsorption of water vapor,<sup>16</sup> resulting in the recovery of the PL intensity.

$F_2$  exposure to the PS may lead not only to a change in the termination of the Si nanocrystallites surface but also to a size reduction of the crystallites through the evolution of silicon fluorides.<sup>18</sup> On the basis of the explanation in terms of quantum confinement, the size reduction of the nanosize crystallites would bring about the blue shift of the PL energy with a noticeable increase in oscillator strength.<sup>22</sup> Thus, we have measured the phonon band of the Si crystallites using Raman spectroscopy. The result showed that the peak position as well as the band width remained almost unchanged through  $F_2/D_2O$  exposures. This result is in good agreement with our previous  $F_2/H_2O$  exposure experiments on the PS,<sup>20</sup> confirming that the average size of the Si nanocrystallites is almost unchanged under the conditions employed.

As can be seen from Fig. 1(c), the PL band after 10 min  $D_2O$  exposure is located at 640 nm. This peak wavelength is about 100 nm shorter than that observed after subsequent  $H_2O$  exposure.<sup>20</sup> Matsumoto *et al.*<sup>4</sup> have reported that the PL band position is sensitive to the isotopic exchange of the PS surface termination from H to D. This isotopic shift is at present hard to explain on the basis of pure quantum confinement.

Changes in the chemical structure of the PS surface during  $F_2/D_2O$  exposures were investigated using IR transmission spectroscopy. Figure 2 shows the *in situ* IR spectral changes of the PS at 298 K in the regions of 2200–2000 and 1300–700  $cm^{-1}$ . Spectrum (a) was recorded before exposure to  $F_2$ . Spectra (b) and (c) were obtained after 10–13 min of  $F_2$  exposure and subsequent 5–8 min  $D_2O$  exposure, respectively. There are several distinct bands in spectrum (a). From the literature,<sup>12–15,17</sup> these bands can safely be assigned to  $SiH_3$  (2145),  $SiH_2$  (2110), and  $SiH$  (2080) stretching vibrations, and  $SiH_2$  (905 and 810) bending vibrations, respectively. Bands located around 1100  $cm^{-1}$  should be ascribed to the Si oxides,<sup>17</sup> indicating that the PS and/or substrate Si used have already been oxidized before  $F_2$  exposure.

$F_2$  exposure results in the intensity reduction of the bands due to the hydrogenated Si ( $Si-H_x$ ) bonds with emergence of strong absorptions at 960 and 850  $cm^{-1}$  [Fig. 2(b)]. The latter two bands can be ascribed to the antisymmetric and symmetric vibrations of  $SiF_2$ .<sup>23</sup> Although the detailed assignments are still controversial,<sup>10,17</sup> an evident feature around 1150  $cm^{-1}$  can be assigned to the Si surface oxides, revealing that  $F_2$  exposure brings about the oxidation of the

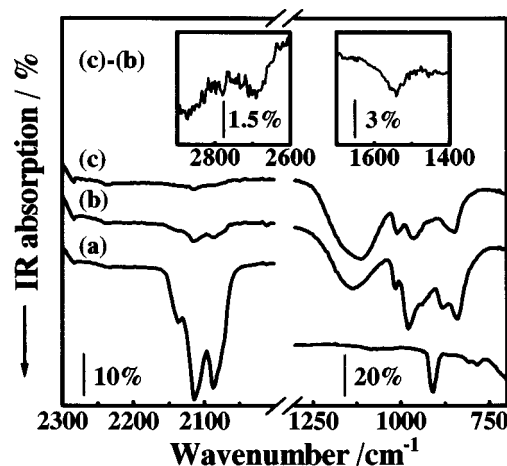


FIG. 2. IR transmission spectral changes of the PS by  $F_2/D_2O$  exposures at 298 K. (a) Before  $F_2$  exposure, (b) after 10–13 min of  $F_2$  exposure, and (c) 5–8 min of  $D_2O$  exposure after (b). Each spectrum is shifted vertically for clarity. The insets show the difference spectrum of (b) and (c) in the (Si)O–D (left) and Si–D (right) stretching regions. Downward peaks correspond to the increase in absorption intensity by the  $D_2O$  exposure.

PS. This oxidation may correspond to the reaction of neighboring Si–O bonds with the dangling bonds formed through the bond breaking reaction of the  $Si-H_x$  by  $F_2$ .

As shown in Fig. 2, the subsequent  $D_2O$  exposure leads to an intensity increase of the surface oxide band and a decrease of the  $SiF_2$  bands. The insets in Fig. 2 refer to the difference spectrum of (b) and (c) in the (Si)O–D (left) and Si–D (right) stretching regions. There are two bands at 2700 and 1540  $cm^{-1}$ : the positions are in good agreement with those reported for (Si)O–D and Si–D stretching vibrations, respectively.<sup>16</sup> The results clearly indicate that the PS was oxidized by the  $D_2O$  exposure with the concomitant formation of SiOD and SiD bonds.

Above-mentioned results suggest that changes in the chemical structure of the PS contribute to the observed PL spectral changes during the  $F_2/D_2O$  exposures. The correlation between the luminescent properties of layered polysilane ( $Si_6H_6$ ) and PS has been demonstrated by Dahn *et al.*<sup>8</sup> However, in spite of the fact that the IR absorption intensity of the Si–D band is quite weak (3%) in comparison to that of the Si–H band before the  $F_2$  exposure (30%), the PL band intensity increases more than three times by the  $F_2/D_2O$  exposures (Figs. 1 and 2). Thus, the layered polysilane is not responsible for the strong PL of the PS.

Recently, Gole and Dixon<sup>10</sup> showed that the PL spectrum of the PS corresponds well with the silanone-based Si oxyhydride [ $Si=O(OR)$  and/or  $Si=O(OHR)$ ;  $R=H$ ,  $SiH_3$ , or a hydrocarbon radical]. Independently, Dettlaff–Weglikowska *et al.*<sup>11</sup> investigated the effects of vacuum annealing on the structure and the optical properties of Wöler siloxene, and deduced that the annealed siloxene is responsible for the PL of PS. Actually, SiOD and surface oxide bonds are formed by exposure to  $D_2O$  as shown in Fig. 2. Thus, our present results suggest that such chemical species having silanone-based Si oxyhydride structures play an important role in the PL of the PS. It should be pointed out here that, in spite of the strong PL intensity [Fig. 1(a)], there was no band ascribable to (Si)O–H stretching (about 3700  $cm^{-1}$ ) in the IR spectrum before  $F_2$  exposure (not shown in the

figure). Further, the IR absorption intensity of the (Si)O–D stretching band occurred by the exposure of D<sub>2</sub>O is less than 2%. Thus, it seemed that the contribution of the Si–OH(D) to the enhanced PL is not dominant, remaining the possibility of the contribution of Si=O(OR) type species (R=SiH<sub>3</sub> or a hydrocarbon radical).

Nonbridging oxygen hole center (NBOHC) is another candidate for the strong PL of the PS. Prokes and Carlos<sup>5</sup> have first showed the presence of NBOHC in the PS and its direct connection with the red PL of the PS using electron spin resonance spectroscopy. Lowe–Webb *et al.*<sup>7</sup> also deduced from their results of *in situ* PL and *ex situ* FTIR measurements that the PL in the PS is associated with such oxide-related defects as NBOHC. The PL energy of NBOHC has been reported to be sensitive to the chemical environments.<sup>24</sup> In fact, IR spectra recorded *in situ* during F<sub>2</sub>/D<sub>2</sub>O exposures indicate the significant changes in the chemical structure of the PS surface, as shown in Fig. 2. Thus, our observed changes in the PL features during the exposures would also fit the NBOHC model, though the results are not quantitative enough to assess the direct contribution of NBOHC.

In summary, our results obtained through the *in situ* PL, Raman, and IR measurements during F<sub>2</sub>/D<sub>2</sub>O exposures cannot be explained by a pure quantum confinement picture. Although we are not able to specify the surface chemical structures of the PS responsible for the observed PL changes, the results clearly indicate that the surface chemistry of nanocrystallites of Si plays a crucial role in the PL process of PS.

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