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# In situ photoluminescence spectral study of porous Si in HF aqueous solution

T. Wadayama, S. Yamamoto, and A. Hatta

Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980, Japan

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Time-dependent change in the visible luminescence of porous Si immersed in HF aqueous solution was measured in a short acquisition time (5 s) with a charge coupled device detector. Under Ar<sup>+</sup> laser light (514.5 nm) irradiation, the photoluminescence band of the porous Si shifted to shorter wavelength accompanying a reduction of the peak intensity. The result suggests that the size of the Si nanostructure is closely related to the gap energy of the porous Si.

Since the first reported observation<sup>1</sup> of room-temperature visible photoluminescence (PL) from porous silicon (PS), a large number of investigations<sup>2,3</sup> have been reported on the mechanisms responsible for the visible PL as well as on its application to optoelectronic devices. To date, the visible PL from PS samples has been explained on the basis of quantum confinement effects<sup>1,4-7</sup> in Si nanostructures or the formation of wide-gap materials such as hydrogenated species at the PS surface,<sup>8-11</sup> silicon oxide,<sup>12</sup> siloxene,<sup>13</sup> and amorphous silicon including Si—H and Si—O bonds.<sup>14</sup>

It is well known that PL spectra of PS samples depend strongly upon both anodization conditions and post-treatments including, for example, oxidation in air,<sup>11</sup> anodic oxidation,<sup>9</sup> boiling in tap water<sup>15</sup> and further immersion in dilute KOH solution,<sup>16</sup> etc. However, most of the PL spectra thus far reported were recorded in air after anodization. Such *ex situ* measurements present a problem as atmospheric oxygen and water both probably affect the characteristics of the sample. Thus, dynamic changes in the PL spectra of PS in electrolytes are yet to be further elucidated: *in situ* PL analysis of the samples in electrolytes would provide us with an important clue to understand the mechanisms of the visible PL.

In the present work, we investigated the time-dependent PL spectral change of PS in HF:H<sub>2</sub>O=1:1 solution with a charge coupled device (CCD) detector. The results show that the peak position of the PL band of the PS immersed in the electrolyte shifts to shorter wavelength during the PL measurements. The quantum confinement effect in Si nanostructures is proposed to account for the blue shift.

We used *p*-type Si (100) (8.5 Ω cm) wafers with optically polished faces. Aluminum was evaporated in vacuum on the back side of the wafer to form a good Ohmic contact. The wafers were anodized in HF:H<sub>2</sub>O=1:1 solution for 30 min using a power supply. A current density was kept constant at 10 mA/cm<sup>2</sup> during the anodization. A schematic experimental setup for *in situ* PL measurements is depicted in Fig. 1. The PS was excited by 514.5 nm light from an Ar<sup>+</sup> laser (50 mW). Luminescence from the sample was dispersed by a polychromator (JASCO CT25TP) and detected with a liquid N<sub>2</sub> cooled CCD detector (Princeton ST130). The detection system was interfaced to a personal computer (NEC PC-9801) for data acquisition and storage. The cylindrical cell for the *in situ* PS measurements was made of polyvinyl chloride resin.

Figure 2 shows the PL spectra of two PS on the Si wafers subjected to 30 min anodization. In this figure, (A) and (B) were measured *in situ* and *ex situ* (i.e., in air), respectively. The PS samples displayed a translucent dark brown hue. Because of the limited use of our grating (600 gr/mm), the wavelength of radiation projected at the CCD detector was restricted within about 80 nm. Thus, the whole spectrum for each shown in Fig. 2 was obtained as the composition of seven divided measurements. The data acquisitions were carried out from longer to shorter wavelength region and the total time for obtaining the whole spectrum was about 210 s.

Our visible spectrophotometer used in the *in situ* PL measurement is of course useful for Raman spectroscopy and, thus, Raman light scattered from the electrolyte as well as the Si wafer can simultaneously be detected in principle. Actually, however, the Raman bands of both H<sub>2</sub>O (Ref. 17) in the electrolyte and Si,<sup>11</sup> which might be expected to appear at about 3400 cm<sup>-1</sup> (625 nm in wavelength) and 520 cm<sup>-1</sup> (528 nm), are not located in the PL spectra shown in Fig. 2. In general, Raman bands are extremely weak in comparison to luminescence bands and hence the Raman bands from the solution and the Si wafer are probably buried in the strong PL band.

As shown in Fig. 2(B), the PL band of the PS measured in air peaks at 660 nm. On the contrary, the PL band recorded in the solution [Fig. 2(A)] shows its peak at 630 nm. It is most likely that the PL peak of the sample in the solution just after beginning the PL measurement was located at a

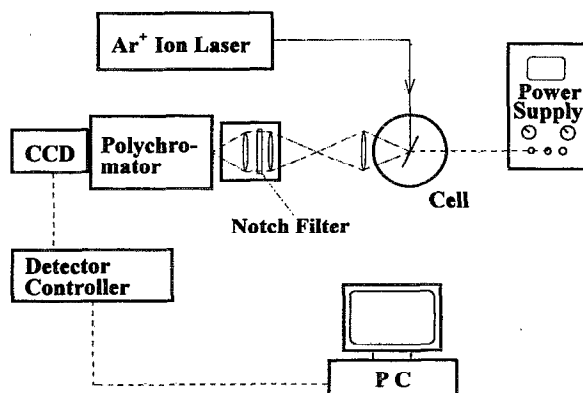


FIG. 1. Experimental set up for the *in situ* photoluminescence measurement.

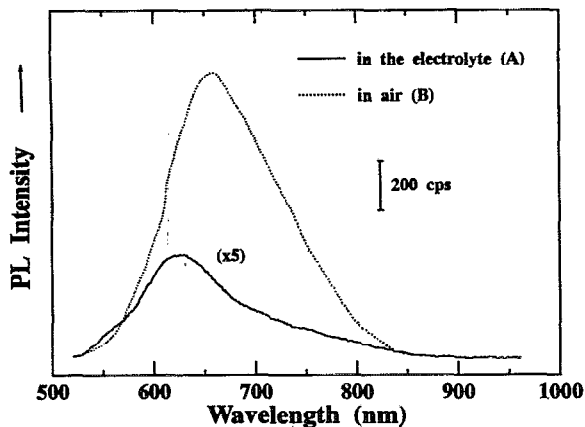


FIG. 2. Photoluminescence spectra of the porous Si recorded (A) in the electrolyte solution ( $\times 5$ ) and (B) in air. Excitation:  $\text{Ar}^+$  laser 514.5 nm, power 50 mW.

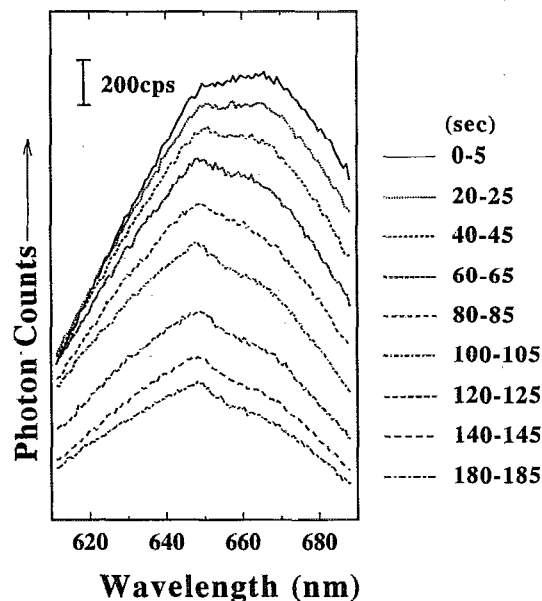


FIG. 3. Time-dependent change of the *in situ* photoluminescence spectrum for the porous Si in the electrolyte solution ( $\text{HF}:\text{H}_2\text{O}=1:1$ ). The data acquisition time for each spectrum was 5 s.

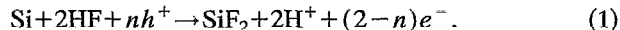
somewhat longer wavelength with a stronger intensity. These changes in peak position and intensity arises from the rather long data acquisition time (210 s). In fact, at the second data acquisition of the sample in the solution, the PL band intensity decreased more significantly. Thus, we attempted to measure the PL change with another PS sample immersed in the solution in a shorter acquisition time.

Figure 3 shows the resultant PL spectra. The data acquisition was started just after 30 min anodization in the solution. The acquisition time required for each spectrum was 5 s. Since the wavelength range of radiation that can be detected at a time was limited within 80 nm as described previously, our measurements were limited in the range from 610 to 690 nm, as indicated in Fig. 3. Nevertheless, the results clearly demonstrate distinct changes in the peak shift and intensity of the PL band with passing time.

As can be seen in Fig. 3, the PL peak just after starting  $\text{Ar}^+$  laser irradiation is positioned at around 650–670 nm. However, after repeated measurements, i.e., with increasing laser irradiation time, the peak position of the PL band shifts to shorter wavelengths accompanying a decrease of the intensity; after 180 s, for instance, the peak position is 650 nm. After the *in situ* PL measurements, we could see a spot (about 3 mm in diameter) on the PS surface at the very place where the laser was irradiated, suggesting that Si atoms or clusters of the PS were dissolved into the solution under  $\text{Ar}^+$  ion laser irradiation.

Lehmann and Gosele<sup>6</sup> proposed the dissolution mechanism of silicon electrodes in HF solution. According to their mechanism, a Si surface saturated by bonded hydrogen is virtually inert against attack of  $\text{F}^-$ , as long as no electric holes ( $h^+$ ) are available at the Si electrode. If a  $h^+$  reaches the surface of the PS with a nanostructure,  $\text{F}^-$  in the electrolyte can react with surface Si—H bonds. Through this reaction, Si—F bonds can be formed on the PS surface. The electron density inside the nanostructure should be lowered because of the polarization induced by the Si—F bonds, resulting in weakened Si—Si bonds. In the present experimental condition,  $\text{Ar}^+$  laser irradiation to the sample should gen-

erate carriers ( $h^+$ ) at the interface between the PS and the electrolyte solution. If the generated  $h^+$  reaches the interface, the bond weakening mentioned above probably occurs. As a result, dissolution of the Si would occur through the electrochemical reaction,<sup>17</sup>



If Si atoms in the Si nanostructure responsible for the visible PL light are dissolved into the electrolyte through reaction (1), the size of the nanostructure should be reduced. The quantum confinement effects result in an increase in the effective band-gap energy<sup>1,4-7</sup> and, thus, the dissolution of the Si atoms under the laser irradiation probably cause the peak shift of the PL band during the PL measurements, as shown in Fig. 3. Furthermore, the dissolution also decreases the total amount of the Si atoms or clusters constituting the nanostructure, resulting in the reduction of the PL band intensity.

Li *et al.*<sup>18</sup> showed that the PL behavior of anodized samples in electrolyte solutions depends upon the composition of the electrolytes in which the samples were immersed. They also deduced that PL band shifts observed can be attributed to electrolytically induced changes in the energy of the surface states. However, there is a possibility in our case that changes in energy of the surface states contributed to the blue shift of the PL energy, since the dissolution of the Si atoms may also lead to a change in the chemical structure of the PS surface. Because it was difficult to observe dynamic changes in chemical species at the PS surface in the electrolyte,<sup>19</sup> we cannot draw a line definitely, at present, between the contribution of the quantum confinement effect and that of the changes in the surface states.

Several authors reported the relationship between the size of Si nanostructure and the energy gap on the basis of

the theoretical calculations.<sup>4,5,7</sup> Qualitatively, the results resemble each other: the gap energy becomes larger with decreasing the size of Si cluster. For example, Proot *et al.*<sup>5</sup> calculated optical band-gap energies for various Si crystallites with respect to their diameter  $d$ , the results of which revealed that the gap energy follows approximately a  $d^{-1.39}$  law. If we assume the blue shift of the PL band to be explained by the quantum confinement effect alone, a 20 nm blue shift observed after 180 s (Fig. 3) corresponds to a reduction less than 1 Å of the Si cluster.

In summary, *in situ* PL measurements of the PS in the HF:H<sub>2</sub>O=1:1 solution have been carried out in a short acquisition time (5 s) by using the CCD detector. The PL peak position shifted to shorter wavelength during the PL measurement. This shift was attributed to the quantum confinement effect in Si nanostructures, i.e., the reduction of the Si cluster size through electrochemical dissolution probably led to the blue shift of the PL energy.

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<sup>1</sup>L. T. Canham, Appl. Phys. Lett. 57, 1046 (1990).

<sup>2</sup>R. L. Smith and S. D. Collins, J. Appl. Phys. 71, R1 (1992).

<sup>3</sup>G. Bomchil, A. Halimaoui, I. Sagnes, P. A. Badoz, I. Berbezier, P. Perret,

B. Lambert, G. Vincent, L. Garchery, and J. L. Regolini, Appl. Surf. Sci. 65/66, 394 (1993).

<sup>4</sup>T. Takagahara and K. Takeda, Phys. Rev. B 46, 15578 (1992).

<sup>5</sup>J. P. Proot, C. Delerue, and G. Allan, Appl. Phys. Lett. 61, 1948 (1992).

<sup>6</sup>V. Lehmann and U. Gosele, Appl. Phys. Lett. 58, 856 (1991).

<sup>7</sup>S. Gardeils, J. S. Rimmer, P. Dawson, and B. Hamilton, Appl. Phys. Lett. 59, 2118 (1991).

<sup>8</sup>S. K. Banerjee, A. F. Tasch, J. C. Campbell, B. K. Hance, and J. M. White, Appl. Phys. Lett. 60, 1700 (1992).

<sup>9</sup>S. Shih, K. H. Jung, D. L. Kwong, M. Kovar, and J. M. White, Appl. Phys. Lett. 62, 1780 (1993).

<sup>10</sup>Y. M. Weng, Zh. N. Fan, and X. F. Zong, Appl. Phys. Lett. 63, 168 (1993).

<sup>11</sup>Y. H. Seo, H.-J. Lee, H. I. Jeon, D. H. Oh, K. S. Nahm, Y. H. Lee, E.-K. Suh, H. J. Lee, and Y. G. Kwang, Appl. Phys. Lett. 62, 1812 (1993).

<sup>12</sup>Y. Kanemitsu, Phys. Rev. B 48, 4883 (1993).

<sup>13</sup>M. S. Brandt, H. D. Fuchs, M. Stuzmann, J. Weber, and M. Cardona, Solid State Commun. 81, 307 (1992).

<sup>14</sup>S. M. Prokes, J. Appl. Phys. 73, 407 (1993).

<sup>15</sup>X. Wang, G. Shi, F. L. Zhang, H. J. Chen, W. Wang, P. H. Hao, and X. Y. Hou, Appl. Phys. Lett. 63, 2363 (1993).

<sup>16</sup>N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy* (Academic, London, 1964).

<sup>17</sup>P. C. Searson, J. M. Macaulay, and F. M. Ross, J. Appl. Phys. 72, 253 (1992).

<sup>18</sup>K.-H. Li, C. Tsai, J. Sarathy, and J. C. Campbell, Appl. Phys. Lett. 62, 3192 (1993).

<sup>19</sup>A. V. Rao, F. Ozanam, and J.-N. Chazalviel, J. Electrochem. Soc. 138, 153 (1991).