

Large and irregular shift of photoluminescence excitation spectra observed in photochemically etched porous silicon

Hideki Koyama, Noriko Shima, and Nobuyoshi Koshida

*Division of Electronic and Information Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology,
Koganei, Tokyo 184, Japan*

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Photoluminescence excitation (PLE) spectra of porous silicon have been studied for samples subjected to postanodization photochemical etching in a HF solution. It is shown that the peak energies of the PLE spectra show a large shift of about 1 eV with increasing etching time. Furthermore, the manner in which the PLE spectra shift is irregular; they first move toward lower energies, and then back to higher energies with increasing etching time. This behavior is interpreted by assuming two independent excitation mechanisms competing with each other in luminescent Si nanocrystallites: a direct-gap absorption process similar to the ~ 4 -eV absorption in bulk crystalline Si and the direct excitation of localized states in the crystallites. The latter excitation mechanism is more important in efficiently luminescent samples. [S0163-1829(96)52420-3]

The discovery of efficient, room-temperature visible photoluminescence (PL) in porous silicon (PS) has stimulated an enormous research interest in this material.¹ Various models have been proposed to account for the observed phenomena, including those based on quantum size effects in Si nanostructures,¹⁻⁶ hydrides,^{7,8} oxides,⁹ Si-O-H compounds,^{10,11} and disordered structures.¹²⁻¹⁴ Although the quantum confinement model is not yet supported by general consent, some important evidences for it have been provided: observation of a great number of Si nanocrystallites which are small enough to cause an energy-gap upshift into the visible region;^{15,16} band-gap widening observed with optical transmission spectra,^{2,17} and ultraviolet photoelectron spectroscopy;^{18,19} and blueshifting of PL spectra as a result of photochemical etching.^{20,21} Recently, several research groups have reported experimental results which show that the PL peak position shifts as a function of crystallite size in a manner consistent with the quantum confinement hypothesis.²²⁻²⁴

While most of the studies have concerned the behavior of the emission spectrum, a moderate number of studies have been interested in the optical absorption process in PS. A special concern is the origin of the characteristic peak which appears in the absorption spectrum.²⁵⁻²⁸ A similar peak is found also in the PL excitation^{15,29-40} (PLE) and the photoconduction^{17,33,35,41} spectra of the material. Such a peak is also predicted in the imaginary part of the dielectric constant by a theoretical study on Si quantum dots.⁴² The theoretical result states that the prominent peak is bulk related (i.e., corresponds to the direct-gap absorption band in bulk crystalline Si) and does not shift by changing the Si nanostructure size, although the absorption edge does shift due to quantum confinement. An experimental result has been reported⁴⁰ for samples subjected to anodic oxidation just after the anodization. With increasing the oxidation time, the PL spectra of the samples apparently shifted toward higher energies. The prominent peak in their PLE spectra, however, did not show a significant shift and remained at the E_2 peak position (4.3 eV) of bulk crystalline Si. This seems to be consistent with the theoretical result. Several researchers also reported similar PLE spectra.³⁶⁻³⁹

On the other hand, PLE spectra whose peak energies are far from the E_2 peak position are presented in some papers.^{15,29-37} These experimental data make a remarkable contrast to both the theoretical and experimental results mentioned above. In particular, it is noteworthy that a practically important PL-efficient sample has its PLE peak at ~ 3.2 eV, which is about 1 eV lower than the E_2 peak.^{33,35} Because of its Gaussian-like spectral shape similar to the PL spectra, the absorption band of this type of samples is attributed to a Franck-Condon shift due to strong electron-phonon coupling.^{31,33-35} Thus the interpretation for the absorption process in PS has not been unified yet. More systematic studies are required to explore the origin of the absorption peak.

In this study, we measured PLE spectra for PS samples subjected to the postanodization photochemical etching using filtered light.^{20,21} This technique provides a relatively large blueshift of PL spectra without affecting the PL efficiency, presumably due to suppression of deteriorative sample oxidation. This treatment is, therefore, useful in preparing PS samples with a large difference in PL energy. Our important result is that, for these samples, a large peak shift in PLE spectra (~ 1 eV) was observed as a function of illumination time. In addition, the manner in which the PLE peak shifts with increasing illumination time is irregular: it first shifts to lower energies and then back to higher energies, while the PL peak show a monotonous blueshift. The extent to which the PLE peak position changes almost covers the range of reported values. Thus the inconsistency in previously reported PLE spectra may be resolved by investigating the origin of this interesting phenomenon. We suggest a model in which the existence of two independent absorption bands in PS is assumed.

PS samples were prepared from p -type (100) 5–6- Ω cm Si wafers. The wafers were anodized in an ethanoic HF solution (55% aqueous HF: ethanol=1:1 by volume) at a current density of 10 mA/cm² for 5 min. Samples were placed in the dark during anodization. Immediately after the anodization, they were illuminated therein with a 150-W halogen lamp through long-wavelength-pass glass filters. We employed three kinds of filters having different cutoff wavelengths (480, 540, and 600 nm).

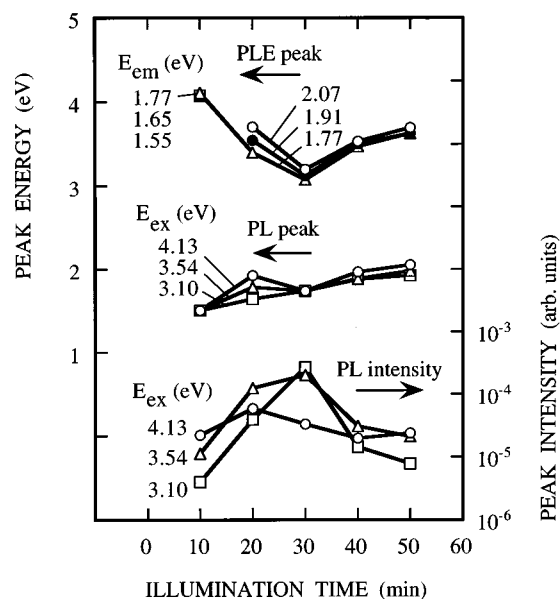


FIG. 1. Peak positions of PLE and PL spectra for different emission (E_{em}) and excitation (E_{ex}) photon energies, respectively, plotted as a function of illumination time. Corresponding changes in PL intensity at different excitation photon energies are also shown.

During measurements of PL and PLE spectra, PS samples were kept in a N_2 atmosphere in order to avoid significant degradation of their PL properties. Samples were excited by a 150-W Xe lamp through a 10-cm monochromator (Jobin-Yvon, H-10). Emission was dispersed by a 25-cm monochromator (Nikon, G-250) and detected by a photomultiplier tube (Hamamatsu, R928). The spectral resolution was less than 5 nm in both excitation and emission spectra. All measured spectra were corrected for apparatus response.

Figure 1 shows the peak energies of PL and PLE spectra for different excitation and emission photon energies, respectively, as a function of the illumination time in the HF solution. Corresponding changes in PL peak intensity are also shown. Although the cutoff wavelength of the filter is 540 nm in this case, essentially the same behavior was observed for the other two filters. As in the previous studies,^{20,21} the PL peak shifts almost monotonously to higher energies with increasing the illumination time. The PLE peak, on the other hand, initially moves toward lower energies and then back to higher energies. The overall PLE peak shift extends to about 1 eV. The PL intensity increases at the initial stage of illumination and then decreases. No detectable PL was observed without illumination.

Changes in PL and PLE spectra are shown in Fig. 2. In the sample subjected to relatively short-time illumination [Fig. 2(a)], PLE spectra have a peak at about 4 eV and a broad bandwidth of more than 1.5 eV. With increasing illumination time, the PLE spectra first show a redshift [Fig. 2(b)] and then a blueshift [Fig. 2(c)] as mentioned above. In the sample subjected to a long-time illumination [Fig. 2(c)], PLE spectra are more Gaussian and have a narrower bandwidth. The bandwidth of PL spectra, on the other hand, monotonously increases with increasing the illumination time and becomes also more Gaussian.

It has been suggested in several papers that lattice relax-

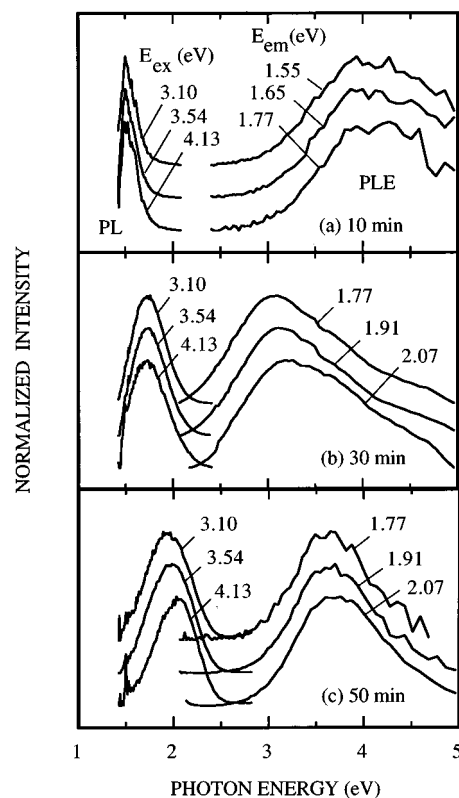


FIG. 2. Normalized PL and PLE spectra of the samples illuminated for (a) 10 min, (b) 30 min, and (c) 50 min.

ation due to strong electron-phonon coupling plays an important role in the PL process of PS.^{31,33–35,43} The hypothesis is based on (1) its broad (0.3–0.4 eV in full width at half maxima) and Gaussian-shaped PL band that cannot be ascribed to any structural inhomogeneities, and (2) a large Stokes shift between PL and PLE spectra which seems to reflect the Franck-Condon shift. These characteristics are clearly seen in the experimental data of the sufficiently illuminated sample [Fig. 2(c)]. It can be concluded, therefore, that the strongly localized states within Si nanocrystallites responsible for the lattice relaxation are directly excited in this type of sample.

On the other hand, an essentially different character is seen in the spectra of the slightly illuminated sample [Fig. 2(a)]: the bandwidth of PLE spectra (about 1.5 eV) is far wider than that of PL spectra (about 0.2 eV), and the separation between PL and PLE spectra is quite large as compared to its expected Franck-Condon shift. The position of the maximum of PLE spectra nearly coincides with the E_2 absorption peak of bulk crystalline Si. A similar absorption band is usually observed in PS by other optical measurements such as spectroscopic ellipsometry^{25–27} or photoreflectance spectroscopy.²⁸ The absence of the localized state absorption band in these PLE spectra may be due to a lower probability of electronic transitions via localized states within the crystallites. This is possibly due to a less confined configuration of excitons in relatively large size crystallites and/or to a less effective role of the localized states. The latter is also supported by the observed narrow PL bandwidth. Then the direct-gap absorption band that should pro-

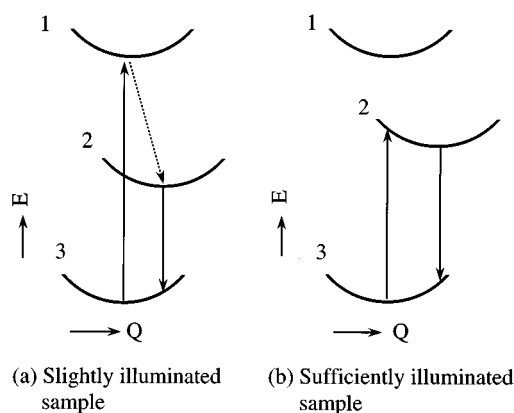


FIG. 3. Simplified configuration-coordinate diagrams (i.e., energy E vs configuration coordinate Q) proposed to explain the different excitation processes in (a) slightly and (b) sufficiently illuminated PS samples. The diagrams essentially consist of three states: (1) unexcited state, (2) state excited by a transition corresponding to the bulk crystalline Si direct-gap absorption, and (3) relaxed excited state just before radiative recombination.

duce strong absorption essentially independent of crystallite size⁴² dominates the overall PLE spectrum. Since the overall absorption process is a result of competition between those in luminescent and nonluminescent regions, the weak PLE band corresponding to the excitation of localized states disappears against the strong absorption by nonluminescent regions at the same photon energy. Indeed, experimental studies on electric-field-induced PL quenching and photoconduction revealed a significant volume of nonluminescent regions in PL-inefficient samples.^{35,44}

A suggested simple configuration-coordinate diagram corresponding to this situation is shown in Fig. 3(a). The most effective excitation of crystallites in these slightly illuminated samples results from the transition from the unexcited state (state 1) to the state reached by the direct-gap absorption (state 2). Relaxation of photoexcited electron-hole pairs brings the crystallites into the third state (state 3), from which the radiative transition occurs. In the figure, it is assumed that either the electron or hole in state 3 is strongly localized,⁶ which results in a significant Franck-Condon shift in PL. The localization, however, can be weak or virtually negligible for only slightly illuminated samples, as suggested by the narrower PL bandwidth shown in Fig. 2(a). The direct excitation of the localized state (i.e., transition from state 1 to 3) is not effective in these samples due to its lower transition probability than that of the direct-gap excitation.

PLE spectra similar to that shown in Fig. 2(a) can be observed also if carriers are photoexcited in bulklike nonluminescent regions and then transfer to luminescent crystallites where they recombine radiatively.⁴⁵ This is not the case here, however, since it is observed that the PL of PS significantly retains the linear polarization of excitation light.^{33,46} This means that a major part of photoexcited electron-hole pairs do not dissociate before radiative recombination. In addition, the degree of the polarization memory is almost independent of temperature,⁴⁶ unlike any possible carrier transfer mechanisms within the material.^{35,41} Thus the observed PLE

spectra should be ascribed to absorption bands of luminescent Si crystallites rather than those of nonluminescent regions.

As the photochemical etching proceeds, the volume fraction of luminescent regions in PS should increase. At the same time, the radiative transition probability in luminescent crystallites also increases due to a strengthened confinement. In addition, the localized centers are supposed to become more effective as suggested by the increased PL bandwidth, which can also contribute to increase the radiative transition probability. Then the direct excitation of the localized states becomes significant. This situation can be represented by the configuration-coordinate diagram shown in Fig. 3(b), where the direct excitation from state 1 to 3 is dominant. In this way the localized-state absorption band appears in the PLE spectrum. Since its position is significantly lower in energy than that of the direct-gap absorption band, the overall PLE spectrum exhibits a redshift.

Further progress of the photochemical etching reduces the average size of the luminescent crystallites. This may cause an upshift of state 3 in the configuration-coordinate diagram and produce a blueshift of the localized-state PLE band. The compatibility between quantum confinement and strong lattice relaxation in luminescent Si nanocrystallites is discussed in our previous papers.^{6,33,34,46} The degradation of PL intensity at this stage is presumably due to sample corrosion, judging from mat surfaces of sufficiently illuminated samples.

The above model is still rather hypothetical at present and requires further support. Of particular interest is the comparison with the corresponding behavior of optical absorption spectra determined by other methods such as spectroscopic ellipsometry or reflectance measurements. Furthermore, the origin of the localized states is left unclarified. As suggested in our previous paper,⁶ these localized states are supposed to cause radiative recombination similar to donor-to-acceptor transitions in bulk materials. The increase in localization energy with increasing illumination time, which can be inferred from the increase in the PL bandwidth (Fig. 2), is an important point to be investigated.

In conclusion, we have studied the PLE spectra of PS samples subjected to postanodization filtered illumination treatments. It was found that PLE spectra show a large and irregular shift as a function of illumination time: the spectra first exhibit a redshift and then a blueshift as the illumination time increases. We interpret the phenomenon by introducing two different excitation mechanisms. In slightly illuminated samples, the direct-gap absorption band of luminescent crystallites dominates their PLE spectra. On the other hand, the localized-state absorption becomes predominant in sufficiently illuminated samples. The anomalous behavior of PLE spectra can be explained by the competition between these two absorption mechanisms in luminescent crystallites surrounded by significant nonluminescent regions.

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