

Polarization retention in the visible photoluminescence of porous silicon

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The polarization state of the visible photoluminescence of porous silicon excited with linearly polarized light has been examined. The photoluminescence was linearly polarized in the same direction as the excitation light, independent of the crystallographic orientation of the sample. The degree of linear polarization decreased significantly with increasing emission wavelength. However, no definite trend of its excitation-wavelength dependence was observed. An interesting correlation was found to exist between the photoluminescence efficiency and the degree of linear polarization, where polarized photoluminescence was more prominent in photoluminescence-inefficient samples. Furthermore, the polarization retention phenomenon was found to be independent of temperature. These experimental results can be explained by the radiative recombination of excitons localized within optically anisotropic and randomly distributed Si nanocrystallites.

I. INTRODUCTION

The observations¹⁻³ of efficient visible photoluminescence (PL) of porous silicon (PS) at room temperature motivated a great deal of experimental and theoretical research effort on this material. The quantum confinement effect of photoexcited carriers within nanometer-sized silicon structures was proposed as the origin of this interesting optoelectronic property.^{4,5} Other mechanisms have also been suggested, which relate to surface/interface luminous compounds⁶⁻⁸ and an amorphous structure.^{9,10} Although it is still under debate whether quantum confinement actually prevails in PS, many experimental results supporting this hypothesis have been reported to date: band-gap widening verified by optical transmission^{4,11,12} and ultraviolet photoelectron^{13,14} spectra; continuous and controllable blueshift of PL throughout the visible range, as a result of photochemical etching;¹⁵⁻¹⁷ preservation of substrate crystallinity confirmed by x-ray-diffraction,^{12,18} transmission electron microscopy,^{5,19,20} and electron-spin-resonance measurements.^{21,22} Some experimental results showing the existence of an important correlation between characteristic dimension of the nanostructure and its PL peak energy have been reported also.²³⁻²⁵

When we attempt to describe the visible PL of PS on the basis of the quantum confinement hypothesis, there appears a question regarding how photoexcited electronic carriers recombine radiatively in such a system. Possible mechanisms suggested to date include those based on a relaxed momentum-conservation rule,^{26,27} phonon-assisted indirect transitions,²⁸⁻³⁰ carrier transfer to luminescent regions,³¹ and the effect of strong carrier localization.^{16,32-35} A large separation between optical absorption and emission spectra (Stokes shift)^{16,19,34} and the broad Gaussian-shaped PL spectra, which can hardly be attributed to sample inhomogeneity,^{15,16,36,37} seem to be strong supports to the last mechanism. A detailed picture of the localization is required to be clarified in order

to confirm this model.

Recently, it was reported by Starukhin *et al.*³⁸ and by Andrianov *et al.*³⁹ that the visible PL of PS has a property to retain the linear polarization of the excitation light. When a PS sample is irradiated with linearly polarized excitation light, the PL is also linearly polarized and its polarization direction coincides with that of the excitation light. It was suggested that microstructural anisotropy in the material was responsible for this phenomenon. However, the physical origin has not been fully explored yet. Understanding this phenomenon should provide an important insight into the luminescence of PS from a microscopic point of view.

In this paper, we present detailed and systematic information about the polarization retention phenomenon of the visible PL of PS. Besides the simple polarization memory similar to that reported in the literature,^{38,39} we report that the degree of linear polarization has a definite correlation with PL intensity. Furthermore, some characteristic phenomena are presented regarding the dependences of the polarization retention degree on excitation wavelength and temperature. These experimental results are discussed on the basis of the localized exciton luminescence in a quantum-sized Si structure.

II. EXPERIMENT

PS samples were prepared by the conventional anodization method in a solution of 55% HF: ethanol = 1:1. A variety of Si substrates [*p*- and *n*-type, (111)- and (100)-oriented, and 0.01–100 Ω cm in resistivity] were used. Anodization current density and time were 10–100 mA/cm² and 5–70 min, respectively. Some samples were illuminated in the HF solution during or after the anodization in order to intensify and to cause a blueshift of their PL.^{2,3,11,16,17} Data presented in this paper were taken mainly from the following two samples: Sample A, which apparently exhibited the polarization retention phenomenon, was prepared by the anodization of a *p*

type, (111), 1–2 Ω cm wafer at 100 mA/cm² for 5 min in the dark. Sample *B*, which showed little sign of the phenomenon, was fabricated by the anodization of an *n*-type, (111), ~ 0.018 Ω cm wafer at 100 mA/cm² for 5 min under illumination by a 500-W tungsten lamp from a distance of 20 cm. The appearance of the polarization retention in PL was independent of whether the sample was *n* or *p* type. The different behavior in the polarization retention between samples *A* and *B* is related to the difference in their PL efficiencies as described below.

During PL measurements, PS samples were kept in an N₂ atmosphere or in a vacuum ($\sim 10^{-2}$ Pa) to avoid significant sample degradation due to laser irradiation.⁴⁰ A linearly polarized 325-nm (He-Cd) or 514-nm (Ar⁺) laser beam was introduced normally to the sample surface. The emission was collected at an angle of $\sim 30^\circ$ from the excitation direction through a polarizer and measured by a 25-cm monochromator and a photomultiplier. The polarization direction of the excitation light was changed by rotating a half-wavelength plate placed in front of the sample holder. In order to avoid the effect of the polarization-dependent response of the measurement system, the degree of linear polarization in PL was measured by rotating the polarization direction of the excitation beam, while the angle of the polarizer was fixed at a constant value. Special attention was paid to prevent the scattered excitation light from entering the detection system. All the measured PL spectra were corrected for apparatus response.

III. RESULTS

Figure 1(a) shows PL intensity of Sample *A* as a function of the rotation angle of the half-wavelength plate (θ_{HWP}). For a fixed rotation angle of the polarizer (θ_{POL}), the PL intensity shows a sinusoidal behavior with a period of 90° . This means that the PL intensity changes in accordance with the polarization direction of the excitation light with a period of 180° . The peak positions of the sinusoidal variation show a shift of 45° when we ro-

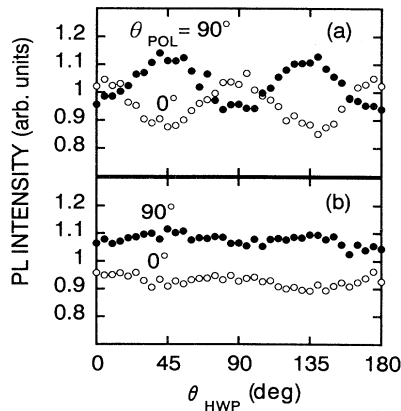


FIG. 1. PL intensity of (a) sample *A* and (b) sample *B* as a function of the rotation angle of the half-wavelength plate (θ_{HWP}). θ_{POL} is the rotation angle of the polarizer. The PL was excited at 514 nm and detected at 760 nm in both cases.

tate the polarizer by 90° . These facts explicitly indicate that the PL is linearly polarized and that the polarization direction coincides with that of the excitation light. The slight difference between the two average PL intensities is due to polarization-dependent response of the measurement system. We observed little variation for some samples including sample *B* shown in Fig. 1(b). As mentioned above, this difference correlates with the difference in their PL efficiencies.

We define the degree of linear polarization *P* as follows:^{38,39,41}

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}, \quad (1)$$

where I_{\parallel} and I_{\perp} are the intensity components of PL polarized parallel and perpendicular to the plane of polarization of the excitation light, respectively. In Fig. 2 we plot the *P* value of Sample *A* as a function of emission wavelength. Three sets of data are compared taken for three different orientations of the sample (θ_{SAMPLE}) with respect to the direction of linear polarization of the excitation beam. Also shown in the figure by a solid curve is its PL spectrum measured without the polarizer. It can be seen that the *P* value is independent of the crystallographic orientation of the sample. Thus, the polarization direction of PL proved to be determined exclusively by the polarization direction of excitation light. It was also found in a separate experiment that the polarization degree does not depend on the intensity of excitation light.

The value of *P* tends to decrease significantly with increasing the wavelength of detected emission. In the earlier papers,^{38,39} this is attributed to the relaxation process which becomes more apparent as the difference between PL excitation and emission energies increases. If this is the case, an increase in the excitation energy should also result in a decrease in the polarization degree at a fixed emission wavelength. In our experiment, however, excitation at shorter wavelengths did not necessarily lead to decrease in the polarization degree, as shown in Fig. 3. This is in a marked contrast to the result in the previous

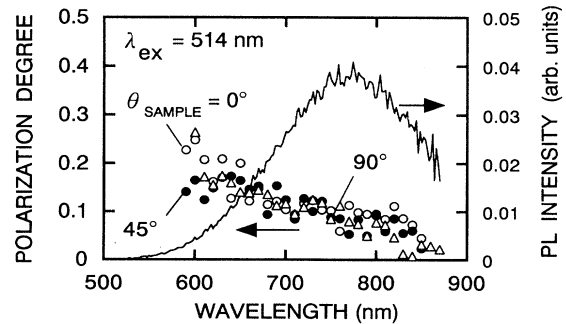


FIG. 2. The degree of linear polarization of PL for sample *A* as a function of emission wavelength. Three sets of data are shown taken for three different rotation angles of the sample (θ_{SAMPLE}) around the axis normal to the sample surface. The solid curve is the unpolarized PL spectrum of the sample. The PL was excited at 514 nm.

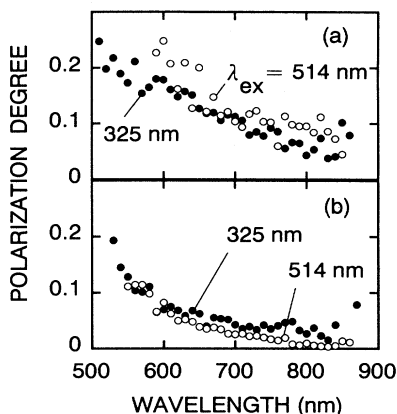


FIG. 3. Excitation-wavelength dependences of the polarization degree for (a) sample *A* and (b) sample *B*.

paper,³⁹ where an apparent tendency of *P* to decrease with decreasing excitation wavelength is reported.

The polarization retention in PL was found to have a negative correlation with PL efficiency. In Fig. 4, we show a typical example of this property. Sample *B*, which showed no appreciable signs of polarized PL as shown in Fig. 1(b), had a PL efficiency two orders of magnitude higher than sample *A*. Note that the two spectra are similar in shape except for intensity. To confirm this interesting relationship, the PL polarization has been measured for a variety of samples made on different substrates and under different anodization conditions. The result is shown in Fig. 5 by plotting the polarization degree of PL as a function of relative PL efficiency.

Some experimental results have shown that the visible PL of PS has an ultimate spectral bandwidth (homogeneous bandwidth) of ~ 0.3 eV in full width at half maximum, which can never be reduced further by eliminating sample inhomogeneity.^{15,16,36,37} Actual PL spectra are made up by the superposition of these broad homogeneous spectra with their peaks being slightly different from one another. Thus, care should be taken in evaluating *P* at wavelengths far from the PL peak, since the polariza-

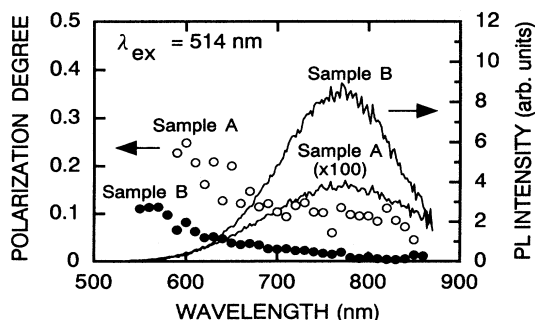


FIG. 4. Comparison of samples exhibiting a relatively high polarization degree with low PL intensity (sample *A*) and a relatively low polarization degree with high PL intensity (sample *B*). The excitation wavelength is 514 nm.

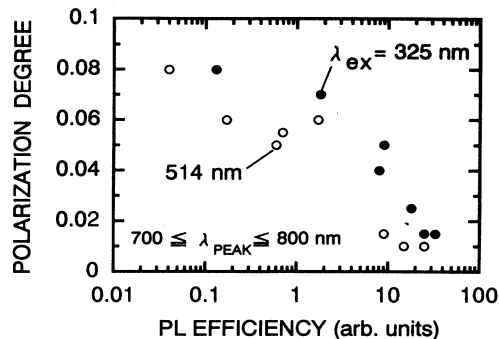


FIG. 5. The degree of linear polarization at the PL peak vs PL efficiency plotted over various PS samples with their PL peaks in the range between 700 and 800 nm. Data for two different excitation wavelengths are shown. The PL efficiency values cannot be compared directly between the two different excitation beams, because of the difference in their beam spot size and their different absorption coefficients.

tion degree at these points is greatly determined by the PL components near the peak, which are supposed to have a significant amount of intensity at these points. The emission at the PL peak is the purest emission in the sense that it suffers little influence from the components with fairly different peak wavelengths, i.e., with fairly different values of *P*. In Fig. 5, therefore, we plotted the *P* values at PL peak wavelengths. Furthermore, the data of the samples whose PL spectra peak in the range between 700 and 800 nm are shown here in order to avoid possible effects of the peak wavelength dependence of *P*. A negative correlation between the degree of linear polarization at the PL peak and the PL efficiency of the sample can clearly be seen for two different excitation wavelengths.

Temperature dependence of the PL polarization retention is also a matter of interest. The experimental result for sample *A* is shown in Fig. 6. The PL intensity of PS, in general, increases to a large extent with decreasing temperature. In contrast, no appreciable change in the degree of linear polarization was observed in all samples examined. This is in disagreement with the earlier report.³⁸

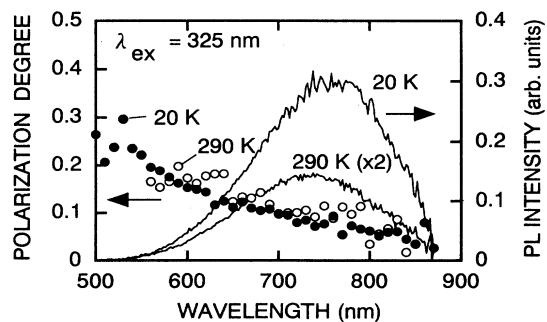


FIG. 6. Temperature dependence of the polarization degree and corresponding PL spectra of sample *A*. PL was excited at 325 nm.

IV. DISCUSSION

It was thoroughly discussed in the literature^{38,39} that the retention of linear polarization in the visible PL of PS is not due to the momentum alignment of photoexcited carriers, which has been proposed to explain similar phenomena observed in the hot PL of direct-gap semiconductors.⁴² This conclusion was derived based on the following experimental results: absence of polarization preservation in the case of the excitation by circularly polarized light; no effects of an applied magnetic field on the polarization properties; the depolarization time of the linearly polarized PL ($\sim 10 \mu\text{s}$), which is much longer than the relaxation time of the momentum alignment.

Polarization retention may also occur if some of the six equivalent conduction-band minima are populated selectively by the excitation with linearly polarized light.⁴²⁻⁴⁴ In fact, a selective population of conduction-band valleys has been demonstrated for the (111)-surface of single-crystal Si and the (100) surface of Ge at 1.8 K.⁴⁴ If this is the case, the degree of linear polarization should depend on the sample orientation to some extent for single-crystal materials such as PS. This is because electrons simultaneously photoexcited into different valleys due to a halfway angle of the polarization direction with respect to the crystallographic axes recombine incoherently, which reduces the degree of polarization retention more than in the case that the polarization direction is properly aligned to the axes. In the present case, however, no significant change was observed when the sample was rotated around its surface normal in both (100) and (111) samples. Furthermore, intervalley scattering of electrons is expected to predominate over radiative recombination of them at room temperature, since the former process is reported to compete well with the latter even at 1.8 K.⁴⁴ This may also oppose the possibility of selective-valley population as an origin of the polarization retaining PL of PS.

A possible origin which can explain all the experimental results is some kind of optically anisotropic elements randomly distributed in PS. In this case, the linearly polarized light preferentially excites the elements directed such that they can respond to the excitation light with a large electronic transition probability. Linearly polarized PL occurs if the photoexcited electronic carriers recombine just at the elements wherein they were generated. PL depolarization may occur if the carriers escape from one element to another and recombine there. In other words, the luminescence is due to localized excitons^{30,45} at these elements.

In a system of randomly distributed and optically anisotropic elements, the degree of linear polarization in PL is given by⁴¹

$$P = \frac{3(\Gamma_1^2 + \Gamma_2^2 + \Gamma_3^2) - (\Gamma_1 + \Gamma_2 + \Gamma_3)^2}{\Gamma_1^2 + \Gamma_2^2 + \Gamma_3^2 + 3(\Gamma_1 + \Gamma_2 + \Gamma_3)^2}, \quad (2)$$

where Γ_1 , Γ_2 , and Γ_3 denote the principal transition probabilities along three mutually perpendicular principal axes of the element. Possible values of P range from 0 (when the element has a spherical oscillator, i.e.,

$\Gamma_1 = \Gamma_2 = \Gamma_3 \neq 0$) to 0.5 (linear oscillator, i.e., for instance, $\Gamma_1 \neq 0$, $\Gamma_2 = \Gamma_3 = 0$). All our experimental data fall within this range.

Electron microscopic studies have revealed that many Si crystallites exist in luminescent PS.^{19,20} Appearance of quantum confinement effects in such a structure [crystallite-size-dependent PL (Refs. 23-25) in particular] implies that photoexcited excitons are localized in these crystallites with their wave functions extending significantly to respective surfaces.⁴⁶ In other words, the optically anisotropic element introduced above corresponds to the Si crystallite itself and not to any local site within it. Such local sites, however, are suggested to affect the polarization retention property significantly as described later.

We should note that polarization-retaining PL with a similar energy dependence of P has been observed also in both Gaussian-spectrum⁴⁷ and high-energy⁴⁸ PL bands of chalcogenide glasses. In these cases, the localization of excitons was attributed to a random structure existing in these materials. In case of PS, on the other hand, excitons should be located in Si crystallites in the manner described above if the quantum confinement is to be accepted, although the possibility of metastable states similar to chalcogenides has been suggested also in PS.⁴⁹ The fact that the PL of PS is still efficient at room temperature, which is in contrast to that of chalcogenide glasses (the Gaussian PL band of these chalcogenides disappears at room temperature in spite of its high efficiency at low temperatures^{47,48}), is likely to indicate that the exciton localization in PS is stronger than that in chalcogenides.

Some information about the origin for the appearance of optical anisotropy in the Si crystallite can be obtained from the experimental result on the relationship between the polarization degree and PL efficiency. We believe that the PL efficiency of a sample reflects its structural homogeneity. Relatively inhomogeneous samples have lower values of PL efficiency, because of the lower densities of luminous crystallites. This conclusion is based on the experimental results of the PL quenching by external electric fields.^{16,50,51} The quenching is explained by field-assisted separation of photoexcited electrons and holes before they recombine radiatively. We found that only efficiently luminous samples (e.g., sample *B*) exhibit this PL quenching phenomenon. This demonstrates that in efficiently luminous samples, the electric field applies to almost all the luminous crystallites in a sample, simply because of its electrical, and hence structural, homogeneity. In relatively inhomogeneous samples (e.g., sample *A*) there exist conductive nonluminescent regions and, therefore, the effect of the external field in the luminous regions is negligible. In fact, it was found that inefficiently luminous PS samples show PL excitation spectra different far from their respective photoconduction spectra. The two spectra almost coincide with each other in efficiently luminous samples.⁵¹

Owing to the structural inhomogeneity, inefficiently luminous samples have a variety of crystallites with different shapes and different boundaries. Such a crystallite could induce an anisotropy in its electronic structure and, therefore, in its optical response, possibly through a

change in the positions and/or the extension degrees of the localized wave functions of carriers within it. A recent first-principles calculation on hydrogenated Si clusters⁵² suggests one possible way for this hypothesis, since it is shown that the wave function of the excited electron in a cluster is sensitive to its surface species while that of the hole, which is localized near the center of the cluster, is almost unaffected. On the contrary, many of the luminescent crystallites in efficiently luminous samples are thought to have significantly lower optical anisotropy due to their nearly isotropic shapes and/or boundaries. The degree of linear polarization is low in those samples because of the electronic oscillator which is far different from linear, i.e., for example, Γ_2 or Γ_3 being comparable to Γ_1 in Eq. (2). Further understanding of how such origins actually induce significant anisotropy in the crystallites, however, requires intensive studies in both experimental and theoretical methods.

The low polarization degree observed at efficiently luminous samples might also be explained by the depolarization due to radiative recombination of carriers having escaped from their original crystallites, because the electric-field induced PL quenching phenomenon observable in these samples^{6,50,51} can also be interpreted as a consequence of higher migration probability of carriers among crystallites. Indeed, it was found for all the PS samples examined in this study that the degree of linear polarization decreases as the emission wavelength increases. This can be easily explained by the introduction of the depolarization that should be enhanced for longer emission wavelengths. However, the result of experiments of changing excitation wavelength (Fig. 3) produced a doubt as to the significance of the depolarization due to carrier migration. In addition, the temperature-independent behavior of P is also incompatible with this depolarization process, since the carrier migration among crystallites is known to depend largely on temperature as suggested by temperature-dependent photoconductivity.^{51,53} Furthermore, the polarization degree of the efficiently luminous samples is still low even at wavelengths close to the excitation ones, as shown in Fig. 4. The different behavior of P between PL-efficient and PL-inefficient samples should be ascribed to the difference in the degree of optical anisotropy of Si crystallites.

The origin of the emission-wavelength dependence of P is still unclear at present. This might be accounted for if there is some distribution of luminous crystallites in which those emitting shorter-wavelength light have higher optical anisotropy. In general, however, excitation of higher-energy PL in such a distributed system requires higher-energy excitation light.¹⁹ In other words, shorter-wavelength excitation yields shorter-wavelength PL, which then should have a higher value of P in this assumption. This is inconsistent with the data shown in Fig. 3. Such a distribution of crystallites, on the other hand, may explain the small effect of the excitation wavelength on P . A shorter-wavelength beam may excite more polarized PL in some cases and less polarized PL in some other cases, although the peak emission wavelength is probably shorter in either case. The experimental results in Figs. 4 and 5, where a significant difference in P is

observed for samples with similar PL spectra, indicate that the polarization retention property does not necessarily follow the peak-wavelength shift of PL.

Several papers^{30,54,55} report that there are two different emission bands in the PL of PS: the fast band (decay time ~ 10 ns) and the slow band ($\sim 10 \mu\text{s}$). The emission wavelength of the fast band is significantly shorter than that of the slow band. Although the physical origin of the separate-band emission is still unclear, the observed emission-wavelength dependence of P might be explained if it is assumed that the fast band has a higher P value than the slow band. This assumption is reasonable because more processes, which may cause further depolarization, are supposed to precede the emission of the slow band. However, it seems difficult to explain the emission-wavelength dependence of P based on this fast band, especially in the wavelength range of the major PL emission, because the fast band is reported to comprise only several percent of the total PL intensity. This, on the other hand, may affect P and cause the excitation-wavelength effect at wavelengths very close to the excitation one where the fast band can compete well in intensity with the slow band. Some samples (e.g., sample *A*) exhibited this trend in this experiment, but we are not sure if this is the case for all samples.

The most probable origin for the emission-wavelength dependence of P in the main PL band seems to be correlated with carrier trapping within photoexcited crystallites. As mentioned earlier, there has been reported enough evidence for the existence of strong electron-phonon interaction in the PL process of PS.^{16,32-37} Experimentally obtained values for the Stokes shift range up to ~ 3 eV,³⁷ which is extremely large compared with those theoretically predicted for electronic transitions between delocalized states in ideally coordinated Si crystallites.^{56,57} This suggests the importance of carrier trapping by strongly localized states in the case of the crystallites in PS. If we accept the experimental results showing that the PL peak energy monotonically shifts in accordance with the crystallite size in the manner expected from the quantum-size effect,²³⁻²⁵ then it becomes difficult to suppose both the electron and the hole in a crystallite undergo strong localization. This is because in this situation, neither of the two carriers can have any information on the crystallite-size reduction, due to null wave function at the surface. Thus, one of the carriers should be either delocalized or trapped by a shallow state. Therefore, photoexcited excitons are supposed to exist in the crystallites in the form in which one of the electron and the hole is localized weakly and the other strongly.¹⁶

Carrier trapping, either by a shallow or by a deep state, is likely to cause significant depolarization of the PL. It may be possible to suppose that the more the electron and the hole are separated before recombination due to trapping, the less the P value becomes. If the trapping centers behave like donors and acceptors in bulk materials, then the emission wavelength decreases with increasing the electron-hole separation.⁵⁸ So the degree of linear polarization should decrease as the emission wavelength increases. Although at present this is still a speculation,

there are some important similarities in PL properties between PS and II-VI phosphors⁵⁹⁻⁶¹ (broad and Gaussian-shaped spectrum, redshift within a time period of the order of μs , and PL blueshift with increasing the band gap of the host material). The PL of the latter materials is attributed to the donor-acceptor pair recombination, where one of the centers is a deep trap which is responsible for strong electron-phonon interaction.^{59,60} It should be noted that an important role of shallow donors has been suggested for the PL of PS from electron-spin resonance experiments.⁶²

There is no reason to exclude the possibility of direct radiative recombination of photoexcited electron-hole pairs in our model. One possible way to introduce the direct recombination in our model is to ascribe the fast PL band to it, as suggested in an earlier paper.⁵⁵ In this case, we should plot P of the fast band in Fig. 5 rather than that at the PL peak, since it is the emission due to direct band-to-band transitions that reflects the optical anisotropy of Si crystallites best. However, this is difficult in the present study, because of the lower intensity of the fast band emission and the effect of the broad homogeneous bandwidth. Measurements on the dynamic behavior of P are required for further discussions.

V. CONCLUSION

The retention of linear polarization in the visible PL of PS has been investigated. The degree of linear polarization is independent of the crystallographic orientation of

the sample, indicating that randomly directed microscopic anisotropy in its structural property should be responsible for this phenomenon. A nanometer-sized Si crystallite having an anisotropic shape and/or a boundary is thought to be the origin of the microscopic anisotropy. This is consistent with the fact that the phenomenon is more prominent in PL-inefficient samples, where structural inhomogeneity may enhance such optical anisotropy in each of the crystallites. Since the polarization retention is independent of temperature, it is suggested that the radiative recombination of photoexcited carriers takes place without significant carrier migration among crystallites. The fact that no definite tendency was observed in the excitation-wavelength dependence of the polarization degree is likely to support this hypothesis. The polarization retention exhibits significant emission-wavelength dependence, on the other hand, where the degree of linear polarization monotonically decreases as the emission wavelength increases. A possible model is presented in which carrier trapping processes play an important role in depolarizing the PL.

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