Experimental evidence for luminescence from silicon oxide layers in oxidized porous silicon

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A systematic study of the dependence of photoluminescence from porous silicon (PS) on oxidation extent and measurement temperature is given. Oxidation of PS samples at room temperature up to 200 °C results in photoluminescence spectra with maxima centered around 1.7 eV. The photoluminescence maxima shift with temperature 10–300 K always toward the 1.7-eV position. These results conflict with predictions of the quantum confinement model for PS luminescence, but can be explained by assuming that several types of luminescence center outside nanoscale Si units in PS are responsible for the luminescence, and that their relative contributions to luminescence change with oxidation extent and measurement temperature. The luminescence centers with luminescence wavelength around 700 nm in SiO_x layers, covering the nanoscale silicon particles or on the interfaces of nanoscale Si/SiO_x in PS, dominate after sufficient oxidation and their luminescence depends on measurement temperature to a lesser extent than other types of luminescence center do. [S0163-1829(96)08127-1]

I. INTRODUCTION

Porous silicon (PS) has been widely studied as a potential optoelectronic material, since its visible emission at room temperature was found.[1] However, the luminescence mechanism of PS is still a controversial problem. Several types of models have been suggested for PS luminescence. In one type of model the quantum confinement effect is considered necessary, while luminescence materials other than pure Si are not necessary;[1,2] in another type of model, on the contrary, luminescence materials other than pure Si are necessary, while the quantum confinement in nanoscale silicon is not necessary.[3–8] A third type of model, called the quantum confinement/luminescence center (QCLC) model,[9] postulates that electron-hole pairs are mainly excited inside the nanoscale Si and then recombine at luminescence centers (LCs) outside the nanoscale Si; for as-prepared PS, LCs are adsorbates at the surfaces of nanoscale Si, and for oxidized PS, LCs are impurities, defects, or self-trapped excitons in SiO_x layers covering the nanoscale Si.

When PS is oxidized by different methods—for example, native oxidation,[10,11] oxidation at high temperature,[12–14] rapid thermal oxidation,[15–18] laser,[19–21] and γ-ray-irradiation-enhanced oxidation[22]—photoluminescence (PL) energies show a complicated evolution, and results from different authors sometimes seem contradictory. Qin and Jia[9] and Prokes and co-workers[13,23] have independently suggested that nonbridge oxygen hole centers in SiO_x layers or on the interfaces of nanoscale Si particles and SiO_x layers are a possible source of PS luminescence. The distinction between their explanations is that Prokes and Glembocki[23] think PS luminescence does not need any nanoscale Si, and

that nonbridge oxygen hole centers are the only type of LCs contributing to red light emission before and after oxidation,[23] while Qin and Jia believe nanoscale Si is very important for PS luminescence, and that nonbridge oxygen hole centers are just one of several types of LCs in oxidized PS.

The investigations of Cullis *et al.*[10] show that crystalline Si nanostructures remain in heavily oxidized PS, and they believe this accounts for the $\sim$750-nm red luminescence, and that the luminescence properties of silicon oxides are of paramount importance in interpreting the many additional (shorter wavelength) emission bands observed. Lin *et al.*[24] reported that after oxidation promoted by γ-ray irradiation, there were three sharp peaks in PL spectra of Sm-doped PS, with wavelengths near to those of Sm-doped SiO_2; they believe this indicates that luminescence takes place in the SiO_2 layers in oxidized PS. The origin of blue light emission from oxidized PS has been attributed to SiO_x layers in PS by a number of researchers.[9,25–28]

On the other hand, the temperature dependence measurement of the photoluminescence is generally considered as an important method to reveal the luminescence mechanism of PS. A number of researchers have investigated the behavior of PL from PS as a function of measurement temperature.[8,29–34] Zheng, Wang, and Chen[29] found an anomalous temperature dependence of PL characteristics of PS: the emission intensity increases with decreasing temperature until reaching an intensity maximum at about 100–200 K, and then decreases at lower temperatures; the emission energy shift with temperature has no fixed trend, and varies with sampling point. Xu, Gal, and Gross[8] also found that different PS samples show dissimilar PL temperature

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dependences. Neither of these results supports the quantum confinement (QC) model[1] for PS luminescence. Fang, Li, and Ma[34] pointed out first that, from liquid-nitrogen temperature to room temperature, the PS photoluminescence spectra blueshift when their peak wavelength is longer, and redshift when their peak wavelength is shorter; however, they provided no demarcation lines for the peak wavelength and no definite explanation for this result. As far as we know, a systematic knowledge about the temperature dependence of PS luminescence is still lacking up to now, and few have investigated the oxidation effect on the temperature dependence of luminescence from PS.

In this paper, we report experimental results in two respects: (1) The peak energy evolution rule of PL spectra from PS as a function of the oxidation extent is studied, and statistical results from numerous PS samples are reported which clearly show a focusing of PL peak energies on a small range centered around 1.7 eV during oxidation. (2) The peak energy evolution of PL spectra from PS samples with various PL peak positions at 10 K as functions of measurement temperatures, and the oxidation effect on the temperature-dependence relation, are studied. We will explain all the experimental results based on the QCLC model.[9]

II. EXPERIMENT

A. Sample preparation

PS samples were prepared by the electrochemical anodization method. Czochralski-grown c-Si wafers, with a resistivity of $\sim$10 Ω cm and (111) oriented, were used as host crystals. The front sides of the Si wafers were polished surfaces. Ohmic contacts were made on the back side by evaporating thin aluminum films and subsequently alloying in a N_2 environment at 530 °C for 5 min. In order to obtain PS samples with PL peak positions in a wide range of 1.4–2.3 eV, anodization processes were carried out with a current density in the range of 40–200 mA/cm^2, for 0.5–10 min in hydrofluoric-acid solutions with deionized water, ethanol, or methanol as solvents. Most samples are formed in natural light, some are anodized under illumination of a 500-W infrared lamp. Three groups of PS samples, A (45 pieces), B (102 pieces), and C, with PL peak positions in a wide range of 1.4–2.0, 1.4–1.9, and 1.4–2.3 eV, respectively, were fabricated. The samples in group A were stored in air at room temperature for half a year or one year, and those in group B were oxidized in air at 200 °C for 40 or 200 h accumulatively.

B. Measuring technique

All the PL spectra reported have not been corrected for spectral response of the instrument. The Fourier transform infrared (FTIR) spectra were measured on a Nicolet 7199B, in order to monitor the oxidation extent of the PS samples. During the measurement of the PL against the temperature, the PS sample was enclosed in the vacuum chamber ($<10^{-3}$ Torr) of a closed-cycle He cryostat.

III. RESULTS

The FTIR absorption spectra for one typical sample in group A, for an as-prepared sample, after half a year of stor-
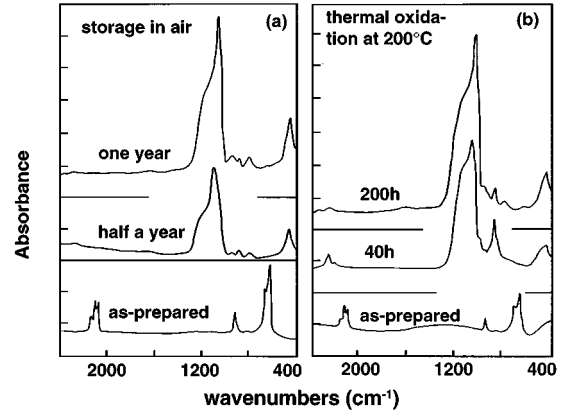

FIG. 1. FTIR absorption spectra evolution for (a) one sample in group A stored in air at room temperature and (b) one sample in group B oxidized in air at 200 °C.

age in air and after one year of storage in air, and for one in group B, for an as-prepared sample after 40 h of oxidation and after 200 h of oxidation at 200 °C, are shown in Figs. 1(a) and 1(b), respectively. No oxygen-related vibration absorption can be found within the detection limit of the instrument for the as-prepared samples in both groups A and B, which is consistent with our previous report.[35] However, a great increase of absorbance for the Si-O-Si asymmetry stretching mode located at 1068 cm^{-1} occurs after the PS samples were stored in air at room temperature for half a year [Fig. 1(a)], or thermally oxidized at 200 °C for 40 h [Fig. 1(b)]. After thermal oxidation at 200 °C for 200 h, the Si-O-Si vibration absorbance exceeds that for one year of storage in air. Therefore, thermal oxidation at 200 °C is an effective and convenient oxidation method. According to the measured FTIR spectra, we conclude that PS oxidation proceeds continuously during at least one year of storage in air or 200 h of thermal oxidation at 200 °C.

Several typical PL spectra for as-prepared PS samples in group B, and for these PS samples after being thermally oxidized at 200 °C for 200 h, are shown in Figs. 2(a) and 2(b), respectively. We see that, after thermal oxidation, as-prepared samples with PL energies of 1.42, 1.58, and 1.68 eV blueshift, and an as-prepared sample with PL energy of 1.82 eV redshifts. Finally, most of these PL peaks tend to be in a small range centered around 1.70 eV, as can be seen in Fig. 2(b).

In fact, the above phenomena hold for all PS samples in groups A and B. The statistical results of PL energy evolution for samples in groups A and B are shown in Figs. 3 and 4, respectively. Using 1.0 eV as the energy interval, Fig. 3(a) shows a distribution of PL peak energies in a range of 1.4–2.0 eV for group-A samples in the as-prepared state. However, storage in air for one year results in a narrower distribution centered around 1.70 eV, as shown in Fig. 3(b) (an interval of 0.5 eV is used). We use a PL energy focus to describe this phenomenon, which can be more obviously seen for the samples in group B as shown in Fig. 4. In Fig. 4, using an interval of 0.5 eV, because of the greater number of samples in group B, the PL peak energies of the as-prepared samples are seen to be distributed in the range 1.4–1.9 eV; during 200 °C oxidation for at least 200 h, the PL peak en-
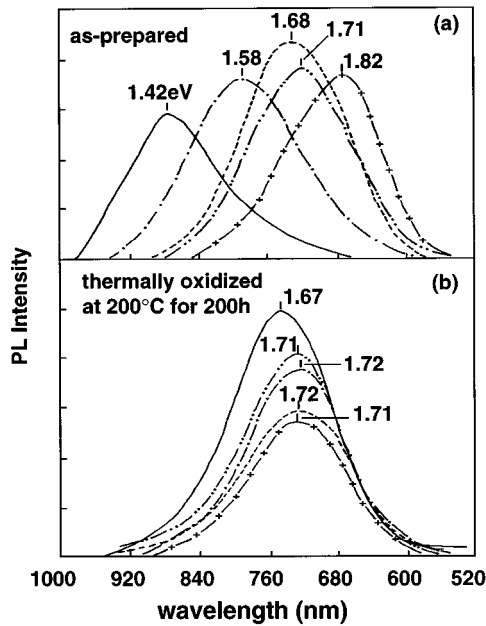
FIG. 2. PL spectra of five typical PS samples in group B thermally oxidized in air at 200 °C (a) as-prepared and (b) after oxidation at 200 °C for 200 h.

ergies for the samples in group B continuously focus toward 1.70–1.75 eV. Even after 40 h of thermal oxidation, the PL peak energy distribution shows a focus toward 1.70–1.75 eV, as shown in Fig. 4(b); this is a more concentrated distribution than that shown in Fig. 3(b) for group-A samples which had been stored in air for one year. An even sharper distribution is obtained for group-B samples which have been oxidized at 200 °C for 200 h, and, from Fig. 4(c), 77% of the samples have PL energies in a range of 1.70–1.75 eV and there are no samples with PL peak energies lower than 1.65 eV or higher than 1.8 eV.

PL spectra of PS usually shifts in peak position and changes in intensity with increasing temperature. Typical PL
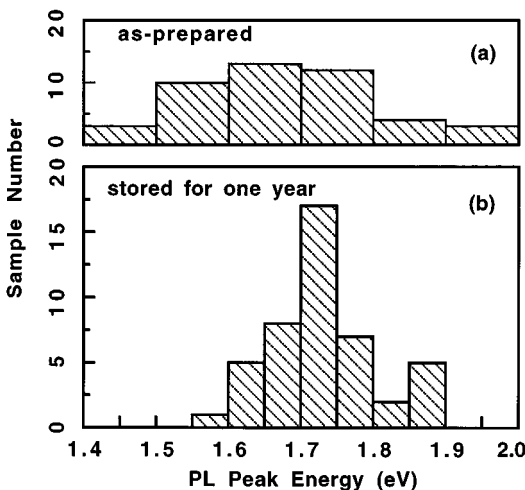

FIG. 3. The statistical distribution of PL peak energies for PS samples in group A stored in air at room temperature: (a) as-prepared and (b) after storing in air for one year.
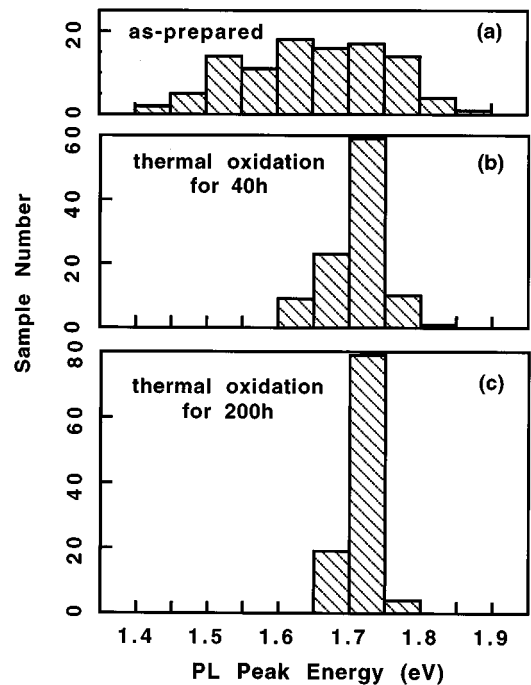

FIG. 4. The statistical distribution of PL peak energies for PS samples in group B oxidized in air at 200 °C: (a) as-prepared, (b) after oxidation for 40 h, and (c) after oxidation for 200 h.

spectra for the as-prepared samples $C3$-2 and $C3$-5 at different temperatures are shown in Fig. 5. Sample $C3$-2 was fabricated in a solution of $HF:H_2O=1:2$ with a current density of 30 mA/cm^2 for 4 min, and sample $C3$-5 was fabricated in the same solution with a current density of 150 mA/cm^2 for 0.5 min. At 10, 200, and 300 K, the PL peak for sample $C3$-2 is located at 840, 800, and 770 nm [Fig. 5(a)], and that for sample $C3$-5 is at 570, 600, and 630 nm [Fig. 5(b)], respectively. Figure 6 shows the temperature dependence of PL peak wavelengths for the as-prepared PS samples with PL peak wavelengths distributed in a range from 540 to 860 nm at 10 K. As can be seen, if the PL peak wavelength is longer (>720 nm) at 10 K, it will blueshift with increasing
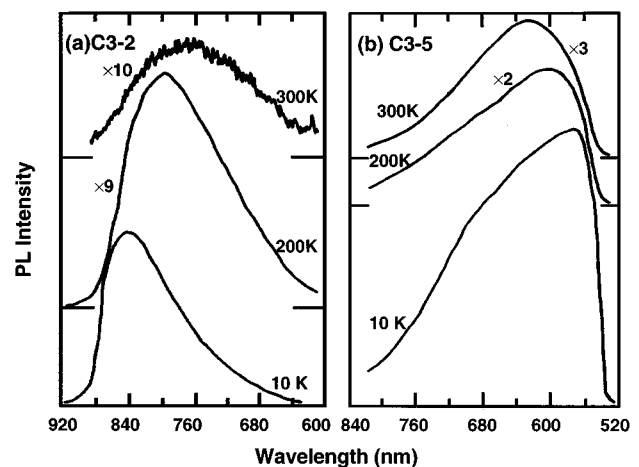

FIG. 5. PL spectra at 10, 200, and 300 K for two as-prepared PS samples (a) $C3$-2 and (b) $C3$-5.
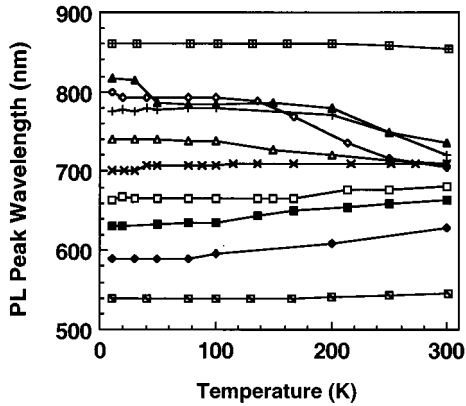
FIG. 6. Temperature dependence of the PL peak wavelength of as-prepared PS samples in the temperature range of 10–300 K.

FIG. 8. The temperature dependence of PL peak positions of two PS samples C2-9 and C5-4 when as prepared and after stored in air for three months.

measurement temperature; if the PL peak wavelength is shorter (<680 nm) at 10 K, it will redshift with increasing temperature. When the peak wavelength is around 700 nm, or much longer or shorter than 700 nm, such as 860 and 540 nm, the PL peak shift with temperature increasing is quite small.

In the above, we show only the temperature dependence of the PL peak position for the usual luminescence spectra of PS, which have no obvious structures but a Gaussian-like shape. It is well known that a small fraction of PS samples have PL spectra with multiband structures. In the following, let us check some of these spectra and see how they change with increasing temperature. In Fig. 7(a), there are several luminescence bands in the PL spectra of one PS sample, C4-3, fabricated in a solution of HF:CH$_3$CH$_2$ OH=1:1 with a current density of 60 mA/cm^2 for 4 min. At 10 K, band No. 1 peaked at 810 nm is visible, and band No. 2 at 780 nm is the strongest one; at 77 K, band No. 1 declines to be a shoulder, while band No. 3 at 720 nm arises relatively; at 300 K, band No. 3 becomes the strongest band and then makes the whole PL spectrum blueshift. The spectra at different temperatures for another PS sample, C3-6, formed in a solution of HF:H$_2$O=1:2 with a current density of 120
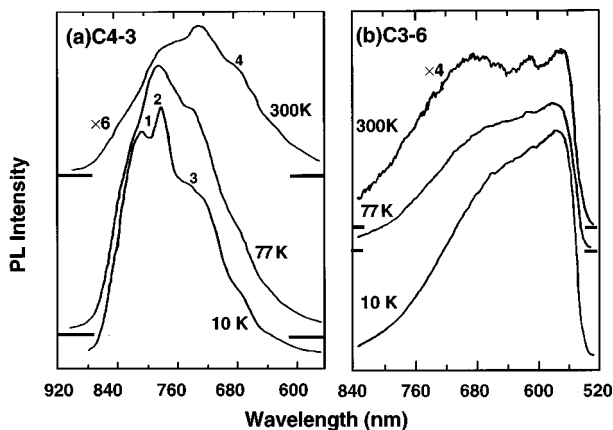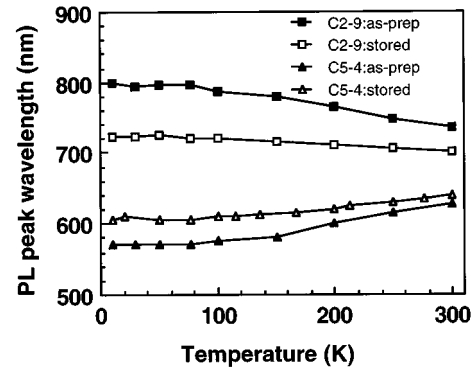
mA/cm^2 for 0.5 min, are shown in Fig. 7(b). At 10 K, there is a shoulder around 680 nm in addition to the strongest band peaking at a shorter wavelength of 580 nm. The shoulder peaked at 680 nm increases relatively at 77 K; at 300 K it has an intensity comparable to the band around 580 nm. Briefly, in a PL spectrum with a multiband structure, the luminescence band around $\sim$700 nm will become stronger and stronger with respect to other bands when the temperature increases from 10 K to room temperature.

The effects of native oxidation and low-temperature oxidation on the temperature dependence of PL spectra for PS have been studied. Figure 8 illustrates the temperature dependence of PL spectra for two samples, C2-9 and C5-4, in the as-prepared case and after storage in air for three months. Sample C2-9 was prepared in a solution of HF:H$_2$O=1:1 with a current density of 50 mA/cm^2 for 5 min, and sample C5-4 was formed in a solution of HF:CH$_3$COCH$_3$=1:1 with a current density of 200 mA/cm^2 for 0.5 min. It is clear that storage in air for three months brings about a weaker temperature dependence of PL spectra of PS as well as a shift of PL peaks toward medium wavelength. Figures 9(a) and 9(b) show the PL spectra at 10, 200, and 300 K for samples C3-2 and C3-5 oxidized in air at 200 °C for 200 h. Very different from the as-prepared cases shown in Fig. 5, these

FIG. 7. PL spectra with multiband structure measured at 10, 77, and 300 K for two as-prepared PS samples (a) C4-3 and (b) C3-6.
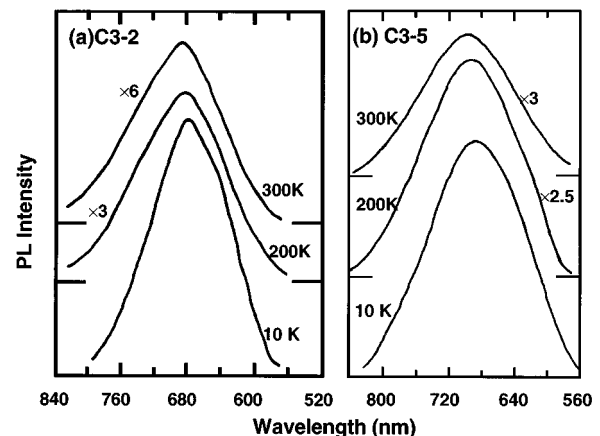

FIG. 9. PL spectra at 10, 200, and 300 K for two PS samples (a) C3-2 and (b) C3-5, mentioned in Fig. 5, after being oxidized at 200 °C in air for 200 h.
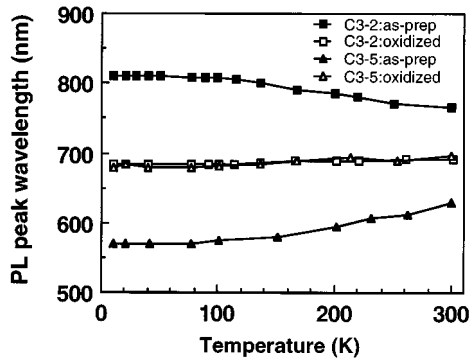
FIG. 10. The temperature dependence of PL peak positions of two PS samples (a) C3-2 and (b) C3-5, mentioned in Figs. 5 and 9, when they are as-prepared and oxidized in air at 200 °C for 200 h.

PL peak positions remain almost the same at different temperature. Figure 10 compares the temperature dependence for as-prepared and thermally oxidized cases for these two samples. With increasing temperature, their PL peak positions exhibit blueshift and redshift when as-prepared, and fixed values around ∼690 nm after thermal oxidation in air at 200 °C for 200 h.

IV. DISCUSSION

There are a number of studies on individual PS samples.[10–13,15–17,19,22] A comparison of our statistical results with individual cases is meaningful but difficult. When we compare our results with others, we find consistency in most cases, but contradiction in a few cases. For example, Prokes[13] carried out a series of 1-min isochronal annealing from 600 to 1100 °C for PS samples, and found a blueshift of the PL peak between 600 and 800 °C, and then a pinning of the PL peak at about 1.7 eV above 800 °C. Fu et al.[22] reported that after γ-ray-irradiation-enhanced oxidation, the PL peak located at 820 nm for an as-grown PS sample shifts to 750 nm. Batstone, Tischler, and Collins[16] reported that a PL peak shifted from 820 to 720 nm after rapid thermal oxidation at 950 °C for 2 min. Cullis et al.[10] reported that the PL peak position of a PS sample fabricated from 0.01–0.04 Ω cm crystalline Si with its initial PL peak position at 1.36 eV shifts to 1.59 eV after one year storage in air. In all the above four cases, the PL peak position evolution tendencies are consistent with that described in this paper, and the final peak positions in Refs. 13, 16, and 22 are very near to our central PL peak position of 730 nm (∼1.7 eV) after oxidation. In the paper by Cullis et al.,[10] after one year storage in air, the final PL peak position was at 1.59 eV, which is in our range of 1.55–1.9 eV for statistical results for one year storage in air as shown in Fig. 3, though deviating from our statistical central PL peak position. Shih et al.[12] studied the PL peak position evolution as a function of oxidation time, and found a PL blueshift for a PS sample with its initial PL peak located at 740 nm, followed by a pinning at about 640 nm. Maruyama and Ohtani[11] found a pinning of the PL peak of PS samples with a water rinse at about 660 nm. In our experiments, we find many cases of PL peak position pinning at positions near the central position of 730 nm during the later stage of oxidation. However, the PL pinning posi-

tions of Shih et al.[12] and Maruyama and Ohtani[11] are different from those of Prokes[13] and us. Kumar, Kitoh, and Hara[17] carried out a 1-min isochronal annealing from 300 to 1000 °C; the initial peak position was at 878 nm, and shifted to 806 nm after 1000 °C annealing; the PL peak position evolution tendency is consistent with Prokes'[13] and ours, but the final peak position is not. To sum up, PL peak evolution tendencies for PS during oxidation reported in various papers including this one are consistent with each other; however, the final PL peak positions after oxidation vary. We consider that experimental factors such as the resistivity of crystalline Si, anodization conditions including the composition of the electrolyte, current density and anodization time, oxidation methods, and excitation wavelength in PL experiments have important effects on the PL peak energies for oxidized PS samples; thus it is not difficult to understand the differences in final PL peak energies. We will discuss the origin of these discrepancies further below.

It is well known that oxidation of PS will cause a nanoscale Si shrinkage.[16] Using either the quantum confinement model of Canham[1] or the Si surface-state model of Koch et al.,[2] who suggested an energy difference of about 0.3 eV or 0.3 eV×2=0.6 eV between light excitation in nanoscale Si and emission in the Si surface states, the PL peak energies should blueshift continuously during oxidation. Neither of these models can explain why the PL spectra focus on a definite and a small energy interval centered around 1.7 eV, but this can be explained by the QCLC model.[9]

The QCLC model suggests that the luminescence of PS originates from the radiative recombination of electron-hole pairs, excited in nanocrystal Si particles and tunneling outwards, at the luminescence centers outside the nanocrystal Si units, as shown schematically in Fig. 11. The main LCs are some adsorbates on nanoscale Si particle surfaces in as-prepared PS, which change to some types of LCs in SiO_x layers in fully oxidized PS. We consider the reason that most photoexcited electron-hole pairs tunnel outside the nanoscale Si particles instead of recombining with themselves is the poor radiative efficiency in zero-dimensional nanostructures due to intrinsic effects, i.e., mainly the orthogonality of electron and hole states combined with slowed-down relaxation, as pointed out in Ref. 36. Our different fabrication conditions lead to different density distributions among various adsorbates, and result in different PL spectra, so that the PL peak energies of as-grown PS samples can be controlled by fabrication conditions. When oxide layers are fully grown outside nanoscale Si, the LCs in SiO_x layers become the main LCs. The focusing of PL peak energies into a range centered around 1.7 eV can be explained by the presence of one or more types of LCs in the SiO_x layers covering nanoscale Si that have light-emission energies around 1.7 eV, and these LCs dominate in luminescence. If more than one type of LCs is responsible for the red light emission from oxidized PS, then the differences in final PL peak positions of oxidized PS reported in the literature and stated above can be explained as follows: the type of LC in the SiO_x layers in PS samples which dominates in red light emission is determined by the fabrication conditions and oxidization methods, and can be different in different laboratories.

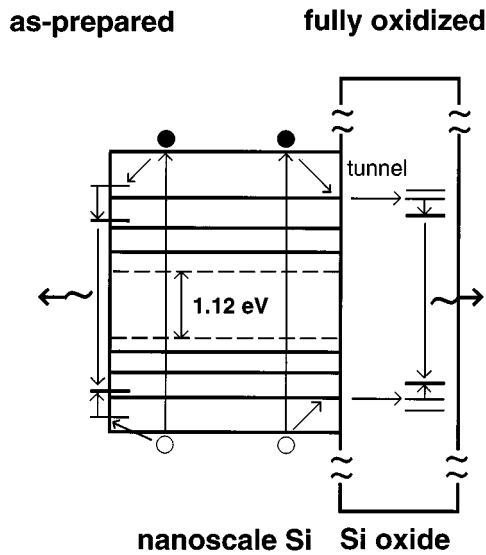A relationship between the variation of energy gap E_g

FIG. 11. Schematic illustration of the luminescence process that electron-hole pairs are excited in nanoscale silicon, and then recombine at luminescence centers to emit visible light. The left side denotes the main LCs are some adsorbates on nanoscale Si particles surfaces for as-prepared PS, while the right side denotes that the main LCs are some types of LC in SiO_x layers for fully oxidized PS.

with temperature T for semiconductors was proposed by Varshni:[37]

$$E_g = E_0 - \alpha T^2/(T+\beta). \qquad (1)$$

From Eq. (1),

$$dE_g/dT = -(\alpha T^2 + 2\alpha\beta T)/(T+\beta)^2. \qquad (2)$$

From (2), both the sign and value of dE_g/dT at a definite temperature are determined by α and β and should be definite. If the PL of PS is caused by the band-to-band transition in nanosilicon particles as claimed by the QC model, it is very difficult to explain the extremely different trends, redshift or blueshift or pinning, of PL peak energies against the increasing temperature observed for different PS samples.

In order to explain the observed blueshift of the PL peak with increasing temperature, Narasimhan et al.[31] pointed out that PL spectra of PS can be fitted as a sum of three Gaussians centered around 0.66, 0.74, and 0.82 μm with different temperature dependences of the intensity from each other, and the authors thought that different components dominate in different temperature ranges. We consider the reason that they did not observe a PL redshift with increasing temperature is that no PS with a luminescence peak wavelength shorter than 700 nm has been studied in their work. In fact, PL spectra of PS do not consist only of those Gaussians with peak wavelengths reported by Narasimhan et al.; for example, it is clear in Fig. 7(b), in which there is obviously a luminescence band with a shorter wavelength than 0.66 μm.

We think that the following two facts are connected to each other: with increasing temperature from 10 to 300 K, the redshift and blueshift of the PL peak toward ~700 nm, as shown in Fig. 6; and that there is a slower decrease in inten-

sity of the ~700 nm luminescence band from 10 to 300 K than those of other bands with shorter or longer wavelengths, as shown in Fig. 7. We agree with the point of view of Narasimhan et al.,[31] and extend their interpretation to the following form to explain the complicated evolution of PL peak energies vs temperature. There are usually several types of LCs in a PS sample, and one type of LC corresponds to one basic luminescence band. This implies that PL spectra of PS are multicomponent in nature. The energy position of a PL peak is determined by the relative intensities and peak energies of the various basic luminescence bands contained in the PL spectrum, and the temperature dependence of the PL peak energy is determined by the variation of intensities and peak energies of various basic luminescence bands vs temperature. Provided that the intensity of at least one basic luminescence band with light emission around 700 nm in Si oxide layers covering the nanoscale Si particles decreases to a lesser extent than those of all the other basic luminescence bands from 10 to 300 K, and that the peak positions of various basic luminescence bands depend weakly on temperature, experimental results for the ''as-prepared'' PS (in fact, the PS has already oxidized in a certain extent; see below) can be accounted for, in which the PL peak blueshifts if its wavelength is longer than ~720 nm, and redshifts if its wavelength is shorter than ~680 nm at 10 K, with increasing temperature from 10 to 300 K. The observed very weak PL peak shift with temperature for the as-prepared PS samples with PL peak wavelengths much shorter (e.g., ~540 nm) or much longer (e.g., ~860 nm) than 700 nm, as shown in Fig. 6, may be explained by the fact that LCs with light emission wavelengths around 700 nm are few in these samples.

According to Figs. 8–10, oxidation will decrease the slope of the PL peak position vs temperature, and the higher the oxidation extent the lower the slope. These experimental facts can be explained by the fact that the type of LC in Si oxide layers with a luminescence energy around 1.7 eV (and a wavelength of ~700 nm) plays a more and more important role in the oxidation process.

There is experimental evidence that the peak positions of various basic luminescence bands depend weakly on temperature. Narasimhan et al.[31] reported that the position of every luminescence components in the PL spectrum of PS does not depend drastically on temperature. Joosen et al.[38] proved that the luminescence peak does not change with temperature for one type of LC, the self-trapped exciton, in SiO_2. Prokes and Glembocki[23] reported that there is no temperature dependence of the PL peak position in oxygen-stabilized PS. From Fig. 7(a), we can also see that various luminescence peak positions of the $C4$-3 sample do not change obviously with temperature in the range of 10–300 K.

There are contradictory reports as to whether as-prepared PS is oxidized or not: Buuren et al.[39] and Schuppler et al.[40] reported that there is no detectable oxygen in the as-grown PS samples. Murakoshi and Uosaki[41] found that an as-prepared PS layer, which is formed by anodic oxidation of silicon in an ethanolic HF solution, is covered with Si oxide. Tsybeskov and co-workers[42,43] observed obvious Si-O-Si infrared-absorption peak in as-prepared PS, and it was verified that anodization with light assistance leads to an accumulation of oxygen on the nanocrystallite surface. These

controversies can be realized if we consider that the oxidized speed of PS is very fast when the samples are taken out from the hydrofluoric-acid solutions, and that the time duration from then to the beginning of detection and the sensitivity of the devices to detect the oxidation are very different for different authors. In our case, we cannot avoid exposure of PS to air, although only for times shorter than 10 min; moreover, under illumination with a laser, our PS in a low vacuum system has to be oxidized further. Consequently, our as-prepared PS samples already have a thin oxide layer outside nanocrystalline Si during the PL measurement.

Cullis et al.[10] suggested that nanoscale crystalline Si can account for the ~750-nm (~1.65-eV) red luminescence from PS, and that luminescence in silicon oxides is very important in interpreting the shorter-wavelength emission bands. In fact, for sufficiently oxidized PS, the ~750-nm red luminescence also comes from the SiO_x layers according to what is reported in this paper. Together with reported results that blue luminescence from PS originates from SiO_2 layers,[9,25–27] we conclude that both blue and red luminescence from sufficiently oxidized PS originates from luminescence centers in SiO_x layers.

V. SUMMARY

To summarize, PL peak energies for as-prepared PS samples show a dependence on anodization conditions; furthermore, storage for one year or thermal oxidation at 200 °C for 200 h in air focuses the originally scattered PL peak energies in a small range centered around 1.7 eV. This focus of PL peak energies for oxidized PS samples can be explained by supposing that luminescence is carried out at luminescence centers in the SiO_x layers covering the nanoscale Si in oxidized porous Si, and that the energy focus range centered around 1.7 eV corresponds to light-emission energies of one or, most possibly, more types of luminescence centers in the SiO_x layers in porous Si. There is a lack of a common temperature dependence rule for PL peak energies of as-prepared PS samples. With increasing temperature from 10 to 300 K, the PL peak of PS will blueshift, redshift, or almost not shift, respectively, while its wavelength is longer than ~720 nm, shorter than ~680 nm, or around 700 nm at 10 K. After thermal oxidation in air at 200 °C for 200 h, no remarkable photoluminescence peak shift with temperature and pinning near ~700 nm is observed. These experimental facts can be explained in that the type of LC in Si oxide layers with a luminescence energy around 1.7 eV (wavelength ~700 nm) has a lower decrease of luminescence intensity with increasing temperature from 10 to 300 K than other types of LCs do, and that it dominates in luminescence in fully oxidized PS. We conclude that luminescence with various wavelengths including red and blue from sufficiently oxidized PS originates from luminescence centers in the SiO_x layers covering nanoscale silicon.

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