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Evidence for quantum confinement in porous silicon from photoluminescence measurements

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We have investigated the correlation of photoluminescence (PL) properties with certain etching conditions, thermal annealing, and powdering of porous silicon. A blueshift of the PL main peak was observed with a decrease of the PL intensity. PL quenching in *p*-Si corresponds to a relaxation or desorption process with the activation energy of 0.37 ± 0.13 eV. The decrease of the PL efficiency and the shift of the PL main peak to the blue region were investigated as a function of excitation intensity. On the basis of our results we verified some physical models of porous silicon PL. It is shown that the features of porous silicon PL are associated with a quantum confinement effect in silicon nanocrystallites. A model for competing nonradiative and radiative recombination channels is proposed to explain the observed phenomena.

I. INTRODUCTION

The mechanisms of luminescence of porous silicon have been extensively studied by many groups.[1–5] Nevertheless, existing experimental data are still insufficient to select any specific model for the phenomenon of strong luminescence of porous Si.

We have shown the correlation between photoluminescence (PL) peculiarities and certain etching conditions, and annealing and powdering of porous Si (*p*-Si). We have investigated the dependence of the PL intensity on the PL peak position for the annealed and as-etched samples, and also the dependence of the *p*-Si PL efficiency on the excitation intensity, and have compared it with that of silicon clusters synthesized by spark ablation in Ar.[6] The activation energy for *p*-Si photoluminescence degradation is estimated. The results are used for verification of physical models of *p*-Si photoluminescence. The model of competing nonradiative and radiative recombination channels, developed on the basis of the Delerue-Allan-Lannoo theory[5] of the optical properties of silicon nanocrystallites, is employed to explain the observed experimental results.

II. EXPERIMENT

Porous silicon layers were prepared from boron-doped *p*-type (100) silicon of 12 Ω cm resistivity by electrochemical etching in the electrolyte H_2O:HF:$C_2H_5OH = 1:1:2$. We used two etching regimes with average current density of 70 and 14 mA/cm^2, respectively, and etching time of 20 min. It should be mentioned that a minor spread in optical properties was observed for samples obtained under apparently the same conditions.

As-etched porous silicon samples were cut into pieces to carry out PL measurements, annealing, and powdering treatments. For PL excitation we used either a pulsed nitrogen laser with wavelength 337 nm, pulse duration 15 ns, and pulse energy 2×10^{-3} J, or the 365.5 nm spectral line of a 100 W mercury lamp. We studied the PL efficiency dependence on the excitation intensity in the range from 1 to 100 mW/cm^2. PL spectra of the *p*-Si samples were acquired in the photon-counting mode. The observed PL intensity of *p*-Si layers was normalized to the PL intensity of a reference sample detected under the same conditions.

Thermal treatments of the *p*-Si samples were performed in a furnace with an automatic temperature control using a platinum thermoresistor in contact with the sample block as a temperature sensor. Annealing of the porous Si was carried out in a nitrogen atmosphere in the temperature range of 100–500 °C for 2, 10, and 20 min. After each thermal treatment the PL peak position and PL intensity were determined in accordance with the technique described above.

III. RESULTS AND DISCUSSION

Figure 1 (solid lines) shows the correlation between the PL peak position and the PL intensity of the porous Si layers. The *p*-Si PL intensity decreases when the PL peak shifts to higher energy. In addition, the samples anodized with higher current density ($J = 70$ mA/cm^2) have a weaker PL intensity and a higher PL peak energy than the samples anodized with 14 mA/cm^2. The experimental dependence of the PL intensity on the PL peak position is plotted in Fig. 2 (series A). We have also found that, in addition to the main band, a low-energy band at

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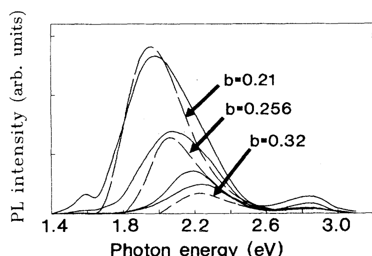

FIG. 1. PL spectra of different porous silicon layers obtained at fixed excitation intensity (solid lines) showing a correlation between the PL peak position and PL intensity. Dashed lines are theoretically calculated spectra for different relative dangling-bond density in a nanocrystallite, b, using Eq. (5) and radiative recombination rates corresponding to Eq. (6).

1.6 eV and a high-energy band at 2.85 eV are present in the PL spectra of our samples (Fig. 1, solid lines). The spectral positions of these bands do not change considerably but these peaks appear only in PL spectra of samples with an intense main peak and under high excitation intensity.

It is well known that the PL intensity of p-Si is quenched by thermal annealing in the temperature range of 400–450 °C.[7] We investigated the temperature-induced degradation of the main PL peak in a nitrogen atmosphere in the temperature range of 100–500 °C for 2, 10, and 20 min. Since the quenching of the PL intensity in p-Si is related to some desorption or dissociation process described by an Arrhenus law,[8] the temperature dependence of the PL intensity in p-Si is given by the

$$I=I_0[1-\exp(-\Delta/kT)K(t)] \ . \tag{1}$$

where I_0 is the PL intensity before thermal treatment, I is the PL intensity after thermal treatment, Δ is the activation energy of the desorption or of the dissociative process (we will refer to it as the threshold energy of PL degradation), and $K(t)$ is a function of time. As a first approximation, we accept $K(t)=\exp(-t/\tau)$, where τ is the characteristic degradation time which is independent of T. In Fig. 3 we plotted $f=1-(I/I_0)$ as a function of $1/T$ for the different annealing times (2, 10, and 20 min) (on a semilogarithmic scale). On the base of the experimental results shown in Fig. 3 we calculated the threshold energy of degradation of the PL of porous silicon:

$$\Delta=(0.37\pm0.13) \text{ eV} \ .$$

The correlation between the PL intensity and the PL peak position of the annealed samples is plotted in Fig. 2 (series B).

Such a low threshold energy of PL degradation indicates that the temperature-induced degradation of p-Si photoluminescence is the result of thermodesorption from the surface or of some relaxation process in porous silicon. Chemical reactions usually have much higher activation energies and can hardly be responsible for the PL degradation.

We have shown that the decrease of PL intensity depends on the annealing duration (Fig. 3). This dependence should be taken into consideration for the verification of what particular surface species desorption leads to p-Si PL degradation. Our quadrupole mass-spectroscopy studies of the thermal desorption from etched silicon have shown that temperature-induced degradation of p-Si photoluminescence can be correlated not only with the release of SiH_3 and SiF_3 surface species (as suggested in Ref. 7) but also with dissociation of SiH_n and SiO_n species, as well as with oxygen and hydrogen removal in the form of different compounds, for example, as carbon compounds.

To clarify the role of porous Si layer morphology and chemical compounds in the PL properties of the layers the following experiment was conducted. We scraped the upper part of the as-etched porous Si layer and powdered it. Then we investigated the PL spectra of the powdered part and the remaining part of the porous layer to com-

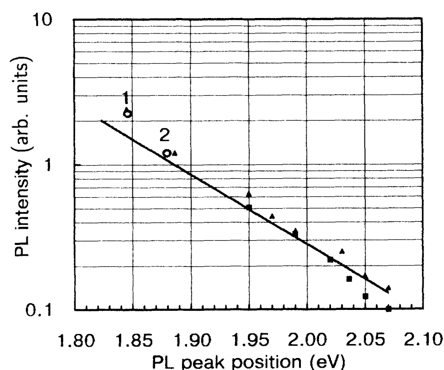

FIG. 2. The experimental dependence of the PL intensity on the spectral position of PL main peak. Triangles (series A): as-etched porous silicon samples (electrochemical etching in electrolyte H_2O:HF:C_2H_5OH=1:1:2 with average current density $J_1=70$ mA/cm^2 and $J_2=14$ mA/cm^2): squares (series B): annealed samples: open circles (series C): porous silicon samples before powdering (circle 1) and after powdering (circle 2); solid line: theoretical curve.

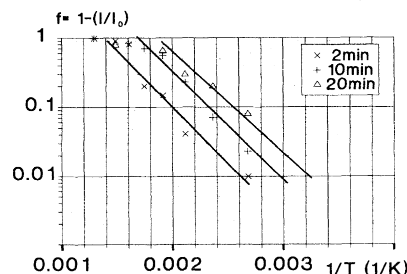

FIG. 3. The temperature-induced degradation of porous silicon photoluminescence $f=1-(I/I_0)$ as a function of $1/T$ with annealing time 2, 10, and 20 min. Solid lines are guides to the eye.

pare them with the PL spectrum of the initial layer (before scraping). For the main photoluminescence band of p-Si we found that the PL peak of the powdered part shifted to higher energy, while the peak position in the remaining part coincided with the peak position in the initial layer. In Fig. 2 the PL intensity and the PL peak position of the p-Si sample before powdering (circle 1) and after powdering (circle 2) are plotted. The curves in Fig. 2 prove that the dependence of the PL intensity on the PL peak position is universal for all the samples subjected to the annealing and the powdering as well as for the as-etched samples within the experimental accuracy ($\Delta E = \pm 0.02$ eV, $\Delta I = \pm 0.1$).

Also, the powdering experiment leads to the suggestion that the PL main peak in porous Si is unlikely to be related to the luminescence of a molecular compound as envisaged in Refs. 9 and 10. In the latter case, the shift of the PL peak will not occur in the powdered part of the layer as compared to the initial as-etched layer. In addition, the sum of the PL intensities of the powdered part and the remainder of the sample is considerably lower than that of the as-etched layer. This observation also contradicts the model of molecular compounds.

We have also investigated the peculiarities of the luminescence spectra as a function of the uv excitation power. We have found that with the decrease of the excitation intensity the PL efficiency increases, and the main PL peak shifts to lower energy. The dependence of the PL peak efficiency, defined as the luminescence peak intensity normalized to the excitation uv intensity or power (since the focusing conditions remained unchanged), on the excitation power is shown in Fig. 4 (curve a) on a logarithmic scale. The experimental curve is in close agreement with the equation

$$\frac{I}{W/W_m} = A(W/W_m)^{-1/3} , \tag{2}$$

where I is the PL peak intensity, W is the excitation power, W_m is the maximum excitation power, estimated to be 30 mW in the experiment, and A is the proportionality constant. Therefore the PL intensity of porous Si depends on the excitation power according to a power law with index $\alpha = \frac{2}{3}$ $[I = A(W/W_m)^{\alpha}]$. Taking into account the experimental accuracy $[\Delta E = \pm 0.02$ eV, $\Delta I = \pm 0.1$, $\Delta(W/W_m) = \pm 0.05]$ we can determine $\alpha = 0.7 \pm 0.1$.

In Fig. 5 the PL peak position is plotted as a function of the excitation power. The peak position shifts with excitation intensity to higher energies as described by the equation

$$E = E_0 + C(W/W_m)^{\beta} , \tag{3}$$

where $\beta = 0.6 \pm 0.18$, C is the proportionality constant estimated as 0.09 eV, and $E_0 = 1.92$ eV (obtained by extrapolation).

Our results are in close agreement with those of a similar experiment performed for silicon clusters synthesized by spark ablation in Ar.[6] In Fig. 4 (curve b) we plotted the dependence of the PL efficiency on the excitation power for the structure investigated in Ref. 6 to compare with our results. PL of the Si cluster sample showed a similar blueshift with increasing excitation intensity. By comparison of curve a with curve b we have found that they are described by the same phenomenological equation with good accuracy. Therefore we conclude that the photoluminescence of porous Si produced by anodizing and that of a cluster structure synthesized by spark ablation[6] have the same origin.

This result and the observation that annealing, powdering, and anodization-current-density variation have a similar effect on the photoluminescence of porous Si confirm that the PL of the p-Si layers cannot be related to that of molecular compounds (oligosilane, siloxen) or of hydrogenated amorphous silicon as suggested in Refs. 9–11.

It has been mentioned above that, in addition to the main peak, a 1.6 eV peak and 2.85 eV bands are present in the PL spectra of the porous Si samples. Figure 1 shows that with increase of the excitation intensity the PL intensities of the 1.6 and 2.85 eV peaks grow relative to the PL intensity of the main peak.

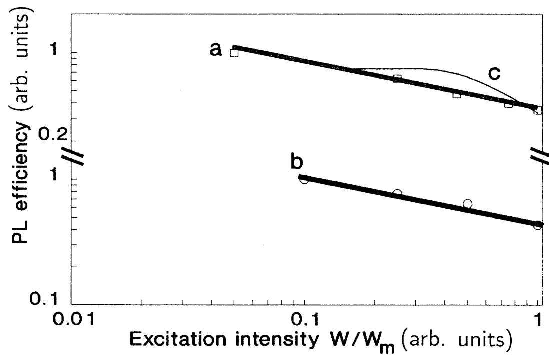

FIG. 4. The dependence of PL efficiency (luminescence peak intensity I normalized to the uv excitation intensity W/W_m) on the excitation intensity W/W_m. Curve a for porous silicon sample; curve b for Si structure consisting of silicon clusters synthesized by spark ablation in Ar (Ref. 61); curve c obtained from our theoretical model.

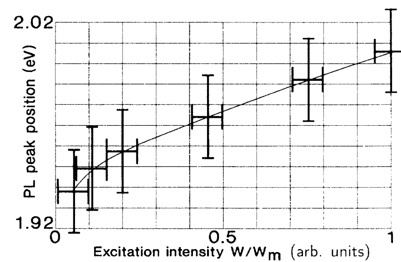

FIG. 5. The dependence of the main PL peak position on the excitation intensity W/W_m. Points represent experimental results; solid line is a guide to the eye.

To explain the experimental results we are using a quantum confinement model with two competing recombination processes: radiative recombination of the electron-hole pairs in silicon nanocrystallites, and nonradiative capture/recombination of carriers at the neutral silicon dangling bonds. In this model we assume the following.

(1) The PL of porous Si is related to the recombination of quantum confined electron-hole pairs in Si crystallites with dimensions of 1.6–5 nm.

(2) The distribution of sizes of Si crystallites is described by the Gauss function

$$G(D)=(\pi\sigma)^{-1/2}\exp[-(D-a)^2/\sigma] , \quad (4)$$

where $\sigma=27\pm0.5$ and $a=37.55\pm0.25$ Å. [In Eqs. (4)–(9) all sizes are given in angstroms. All numerical coefficients in Eqs. (4)–(6) are obtained by fitting of the calculated PL spectra to the experimental ones.]

(3) The PL properties of a crystallite of porous Si are independent of those of adjacent crystallites.

(4) The effective band-gap energy of a silicon crystallite as a function of its diameter is described by the Delerue, Allan, and Lannoo (DAL) theory.[5]

(5) According to the DAL theory, the presence of one silicon dangling bond on the surface of a crystallite of porous Si destroys its luminescence in the 1.4–2.2 eV range due to a high nonradiative capture/recombination rate.

(6) The radiative recombination rate of electron-hole pairs and the capture of carriers on a single neutral silicon dangling bond are calculated as functions of the excitonic gap energy using the DAL theory.

(7) The probability that a silicon crystallite with diameter D has dangling-bond traps on its surface is proportional to D^2. Then the density, S of silicon crystallites with diameter D which have dangling-bond traps on their surface is given by the equation

$$S=bG(D)D^2/B , \quad (5)$$

where $B=260$ and $b<1$ are coefficients characterizing the density of traps. The best-fit values of b were in the range of 0.06–0.4 for the samples studied (Fig. 1, dashed lines).

(8) In first-order approximation, we consider the capture rate q of photons with the energy of 3–4 eV (q equals the optical absorption coefficient for a silicon crystallite times the speed of light[12] to be higher than 10^8 s^{-1}. We also will regard q to be independent of the number of electron-hole pairs in the same crystallite. However, we believe that the probability of nonradiative recombination due to the Auger effect increases with the number of electron-hole pairs in the same crystallite. Therefore we consider that in the first-order approximation the radiative recombination intensity $I(\theta)$ from a crystallite of diameter D without dangling bonds on the surface is proportional to the number of uv photons $\theta(D)$ irradiating this cluster per second when $\theta(D)<\theta_c=1/\tau_r$, where τ_r is the radiative recombination lifetime for the same silicon crystallite. For $\theta>\theta_c$, we assume $I(\theta)=\text{const}=I(\theta_c)$.

As follows from item (8), the number of crystallites $n(D)$ taking part in the uv photon absorption is constant for excitation intensity $\zeta=10^{13}-10^{18}$ photons/s cm^2, and we envisage that the saturation excitation intensity $\zeta(\theta_c)=n(D)\theta_c$. Following the DAL theory we consider that the crystallites taking part in the optical absorption at 365.5 nm have diameter sizes of about 1.6–5 nm.

These results explain the absence of normalization to the quantity of the desorbed or starting material, as the mean concentration of silicon crystallites is estimated to be about 10^{17} cm^{-3} with a mean size of about 2 nm.[13] Thus a 1 cm×1 cm×1 μm p-Si layer provides efficient absorption of an incident uv radiation flux with power up to 1 W/cm^2.

By approximating the DAL theory calculated points we take the dependence of decay rates R on crystallite diameter D in the form

$$R=r[\exp(-D\times0.3074)]\times10^6 . \quad (6)$$

The coefficient r (s^{-1}) for the saturation excitation intensity $\zeta(\theta_c)$ corresponding to the crystallite of diameter D is numerically equal to

$$r=\zeta_{30}(\theta_c)/n . \quad (7)$$

Here $\zeta_{30}(\theta_c)$ is the saturation excitation intensity $\zeta(\theta_c)$ for a 3 nm crystallite (exciton energy of 1.99 eV), and n is the total number of crystallites of the 1.6–5 nm size which participate in uv photon absorption.

According to the proposed model, the blueshift of the PL main band with PL quenching (Fig. 1) is associated with increase of the dangling-bond density. This increase is described by the D^2 law for trap distribution [Eq. (5)] during the sample treatments. From items (4), (5), and (7) the PL from crystallites with diameter D is defined by the equation

$$P(D)=[G(D)-S(D)]I(\theta)n . \quad (8)$$

Figure 2 shows the dependence of an intensity of the main PL band on the peak position calculated according to the proposed model (solid line). Points in Fig. 2 corresponding to the experimental results are well fitted to the theoretical curve. Therefore Fig. 2 strongly supports the conclusion that the PL degradation is related only to the density of silicon dangling bonds and their distribution function.

The decrease of the PL efficiency and blueshift of the PL main peak position with increase of excitation intensity have also an excellent explanation in terms of the proposed model. The calculated dependence of the PL peak efficiency on the excitation intensity is presented in Fig. 4 (curve c). We believe that the PL efficiency decrease with increasing excitation intensity is related to the saturation of the radiative recombination channel [item (8)].

In Fig. 6, the correlation between the PL intensity and the PL main peak position under different excitation intensities is plotted using the experimental results shown in Figs. 4 and 5 (crosses) and those obtained from our theoretical model (solid curve) which is described in items (2), (3), (7), and (8), and uses the proposed dependences of the radiative recombination rate on the crystallite size. The radiative recombination rate increases with increas-

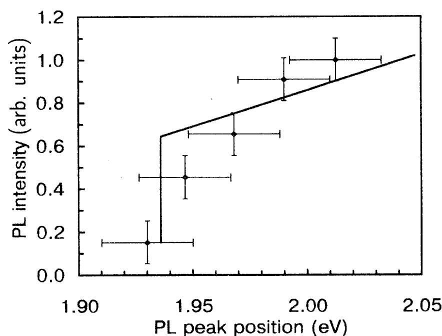

FIG. 6. Correlation between the PL intensity and the main PL peak position of the same p-Si sample under different excitation intensities. Crosses are plotted using experimental results presented in Figs. 4 and 5: solid line corresponds to the proposed theoretical model for $b=0.245$ [Eq. (5)].

ing exciton energy. Thus, when the excitation intensity is increased, the radiative recombination channel through low-energy excitons saturates first, resulting in the blue shift of the main PL peak.

The upper limit for the recombination rate can be estimated from the proposed model using the experimental dependence of PL efficiency dependence on the uv excitation intensity. The recombination rate is found to be lower than $10^4\ s^{-1}$ for 1.8 eV exciton energy, if the following parameters are assumed: thickness of an absorbing layer of p-Si about 1 μm, density of ≈ 2 nm clusters, $10^{17}\ cm^{-3}$,[13] and experimentally observed saturation excitation intensity $\zeta(\theta_c) < 10^{17}$ photons/s cm^2 at room temperature. This result is in good agreement with the DAL theory.

Our model shows that the high PL efficiency of p-Si is determined primarily by three factors: the distribution of sizes of Si crystallites, comparatively high uv absorption by the small-size nanocrystallites, and the low fraction of silicon crystallites of the 1.6–5 nm size containing dangling bonds. For instance, when the relative dangling-bond density in a nanocrystallite $b=0.21$ [Eq. (5)], the maximum PL integrated efficiency (calculated as the probability of existence of silicon clusters 1.6–5 nm in diameter without dangling bonds) is about 0.03 (Fig. 1, dashed lines). When $b=0.1$, the calculated maximum integrated efficiency is equal to 0.61, and the calculated PL peak position corresponds to 1.85 eV. These results are also in good agreement with the experimental observations.

As for the 1.6 and the 2.85 eV peaks, their positions do not change considerably but they are more pronounced in the PL spectra of samples which exhibit an intense main peak. The origin of the peak at 2.85 eV can be described if the dependence of the radiative recombination rate on exciton energy in the 2.6–3.0 eV region is calculated more accurately. The DAL theory gives a stronger dependence of the radiative recombination rate on exciton energy then Eq. (6) in the 2.6–3.0 eV region. This leads to the appearance of the 2.85 eV peak with increase of the excitation intensity, provided that the defect density is low ($b<0.22$).

We envisage that the origin of the peak at 1.6 eV can also be explained in the framework of the proposed model if the dependence of the radiative recombination rate on the exciton energy is nonmonotonic in the 1.5–1.8 eV region. This does not conflict with the DAL theory. Therefore it is reasonable that when the density of dangling bonds is lower the PL intensity of the main peak and of the two additional peaks is higher.

It was considered before [item (8)] that q is independent of crystallite size. In addition, we examined the case when

$$q(D)=0.34[E(16)-E(D)]^2 , \tag{9}$$

where $E(D)$ is the exciton energy of a crystallite with diameter D in angstroms. Equation (9) is derived using the DAL optical absorption calculation. Taking this dependence into account, we obtained different value of the coefficient $a=36.9\pm0.25$ Å in Eq. (4), although the theoretical curves in Figs. 1, 2, 4, and 6 fit the experimental points equally well.

Two interesting results of our model should be pointed out, and we will provide a more detailed analysis of them elsewhere. (i) The distribution of crystallite sizes is independent of the processing parameters used for p-Si preparation; and (ii) it is seen from Figs. 4 and 6 that the estimation of the Auger recombination rate given in item (8) requires refinement. θ_c should be less than $1/\tau_r$ because of the nonzero probability of the absorption of more than one photon by a single crystallite during the recombination time τ_r. In addition, for $\theta > \theta_c$, $\zeta(\theta)$ is not constant but grows slowly with excitation intensity. A detailed analysis of the Auger process will probably explain the difference (more than one order of magnitude) between the experimentally observed PL decay time[14] and that derived from the DAL theory. The experimental confirmation of this explanation may be obtained from PL decay-time measurements at excitation intensities below 10 mW/cm^2, while usually time-resolved PL measurements are performed at excitation intensities much higher than 100 mW/cm^2.

IV. CONCLUSION

To summarize, we have investigated the correlation between optical properties and etching conditions, annealing, and powdering of porous Si. We have found that the dependence of the PL intensity on the PL peak position is universal for all the annealed, as-etched, and powdered samples. The activation energy of degradation of porous silicon PL derived from our experimental results is found to be

$$\Delta=(0.37\pm0.13)\ \text{eV} .$$

The decrease of the PL efficiency and blueshift of the main PL peak with increase of the excitation intensity are investigated. We have shown that the dependence of the p-Si PL efficiency on the excitation intensity is in close agreement with a similar dependence for silicon nano-

clusters synthesized by spark ablation in Ar. These results reveal fundamental features of *p*-Si and should be taken into account for verification of physical models of *p*-Si photoluminescence. Our experimental results show that PL degradation in porous silicon is related to the formation of recombination centers associated with Si dangling bonds. A model of competing nonradiative and radiative recombination channels, developed on the basis of the Delerue-Allan-Lannoo theory of the optical properties of silicon nanocrystallites, is suggested to explain the observed experimental results.

ACKNOWLEDGMENT

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