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Slow decay dynamics of visible luminescence in porous silicon: Hopping of carriers confined on a shell region in nanometer-size Si crystallites

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We have studied the decay dynamics of visible photoluminescence (PL) from nanometer-sized Si crystallites fabricated by electrochemical etching of single-crystalline Si and laser breakdown of SiH₄ gas. In the two types of Si crystallites, the slow-decay behavior of red PL in the time range $10^{-6}-10^{-2}$ s is characterized by a stretched exponential function and the PL decay time scarcely depends on the size and the surface structure. The temperature dependence of the PL decay rate is identical with that of variable-range hopping of carriers in two-dimensional systems. It is concluded that the slow-decay PL is caused by the hopping-limited recombination in a quasi-two-dimensional interface region between the crystalline Si core and the surface layer.

Very recently, a great deal of research effort¹⁻⁶ has been focused on nanometer-sized semiconductor crystallites made from Si or Ge. The strong photoluminescence (PL) from Si nanostructures fabricated by electrochemical etching, often called porous Si, has attracted much attention both from the fundamental physics viewpoint and due to the potential application to optical devices.⁴⁻⁶ However, despite many attempts to clarify the mechanism of the strong PL in porous Si, it still remains unclear.

With a large surface-to-volume ratio in porous Si, the surface effects become more enhanced on decreasing the size of nanometer-sized crystallites. The surface of luminescent Si nanometer-sized crystallites is usually terminated by H or O atoms,⁷⁻⁹ which cause the electronic properties of the near-surface region in the crystallite to differ from those of the c-Si core in the crystallite. The surface effects as well as the quantum confinement effects in the c-Si core influence and complicate the mechanism of the visible PL.¹⁰ In fact, time-resolved PL studies^{9,11-13} in porous Si indicate that the recombination processes are complex and the PL decay exhibits nonexponential behavior. A wide range of PL decay times has been reported in picosecond to microsecond time regimes.^{9,11-13} Since the slow-decay component observed on a time scale of 10^{-7} s or more determines the time-integrated PL intensity, the experimental and theoretical analyses of the slow PL decay are expected to clarify the origin of the strong visible PL and carrier recombination processes in porous Si.

In this paper, we have studied the PL decay dynamics in the range $10^{-7}-10^{-2}$ s in nanometer-sized Si crystallites with different surface structures, electrochemically etched porous Si and oxidized Si crystallites. Spectroscopic analysis of these samples leads us to propose a model in which the slow PL decay is caused by the hopping-limited recombination in a middle, quasi-twodimensional region between the c-Si core and the surface compounds.

The free-standing porous silicon films were prepared as follows.¹⁰ The substrates were (100)-oriented p-type sil-

icon wafers with various resistivities of $0.2-230 \ \Omega \text{ cm}$. Thin Al films were evaporated on the back of the wafers to form a good Ohmic contact. The anodization was carried out in HF-ethanol solution (HF:H₂O:C₂H₅OH=1:1:2) at a constant current density of $10-30 \text{ mA/cm}^2$ for 15-60 min. After the anodization, we abruptly increased the current density up to about 700 mA/cm² and electrochemically removed a porous Si layer from the Si substrate. The thickness of porous Si films was 20-40 μ m. Microstructures of these porous Si films were studied using both transmission electron microscopy (TEM, a JEOL 2010 system operated at 200 keV) and Raman spectroscopy (a backscattering configuration using 514.5-nm laser light and a Japan Spectroscopic R-MPS-11 system). In the porous Si films, the crystalline Si (c-Si) spheres with diameters of nanometer order are dispersed in the amorphous Si-based material (Si:O:H compounds $^{7-9}$). We prepared the sample films with different average diameters of c-Si spheres.

The nanometer-sized Si crystallites were also produced by laser breakdown of SiH₄ gas.¹⁴ Pure SiH₄ gas was introduced into a vacuum chamber (a background pressure of $< 10^{-6}$ Torr) and the pressure of SiH₄ gas was held at 10 Torr. Laser pulses (~200 mJ per pulse at 1.06 μ m, 10-ns pulse duration) from a Nd³⁺:YAG (yttrium aluminum garnet) laser system were focused. The c-Si crystallites deposited on quartz substrates were oxidized at room temperature. TEM, Fourier-transform infrared spectroscopy, and x-ray photoemission spectroscopy examinations clearly indicate that the oxidized Si crystallites consist of a c-Si sphere of the 3.7-nm average diameter and a 1.6-nm-thick amorphous SiO₂ (a-SiO₂) surface layer.¹⁴ By comparing the PL properties of this welldeveloped sample and porous Si, we tried to clarify the mechanism of the strong visible PL from porous Si.

The time-resolved PL spectra of porous Si and oxidized Si crystallites were measured in a vacuum under 5-ns, 355-nm excitation (30 Hz repetition rate) using a boxcar signal averager. The temperature was varied from 10 to 300 K by controlling the flow rate of cold He gas in a cryostat. The spectral sensitivity of the measuring system

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was calibrated by using a tungsten standard lamp.

Figure 1 shows PL spectra in two samples of (a) porous Si of $\langle D_s \rangle \sim 3.5$ nm and (b) oxidized Si crystallites of $\langle D_s \rangle \sim 3.7$ nm at room temperature under 325-nm laser excitation, where $\langle D_s \rangle$ is the average diameter of the c-Si spheres. In both samples, the PL peak is around 750 nm and the PL spectra are very broad (~0.3 eV full width at half maximum) with Gaussian-like shape. The PL spectrum of oxidized Si crystallites is very similar to that in porous Si. This implies that the outer surface materials surrounding the Si crystallites, a-SiO₂ or Si:O:H compounds, do not contribute themselves to the strong visible PL.

Figure 2 shows PL decay profiles at 750 nm in a porous Si film of $\langle D_s \rangle \sim 3.5$ nm at 20, 78, and 290 K. The PL decay profiles are nonexponential, and they are well described by a stretched exponential function:^{15,16}

$$I(t) = I_0 (\tau/t)^{1-\beta} \exp[-(t/\tau)^{\beta}], \qquad (1)$$

where τ is an effective decay time, β is a constant between 0 and 1, and I_0 is a constant. The solid lines in this figure are given by the above function. The least-squares fitting of the data gives values of τ and β . This stretched exponential decay is usually observed in the PL decay and transport properties of disordered systems such as amorphous semiconductors and glasses.^{15,16}

The value of β does not strongly depend on the temperature and is almost a constant of 0.8 ± 0.05 in all samples over 10-300 K. On the other hand, the decay time τ strongly depends on the temperature as shown in Fig. 3(a). However, the PL decay dynamics scarcely depends on the average size of *c*-Si spheres in porous Si films. The above results (no average-diameter dependence of the PL spectrum and the PL decay time τ) imply that only small crystallites with sizes less than a certain diameter in porous Si contribute to the strong visible PL, as discussed in oxidized Ge and Si crystallites.^{3,14}

Figure 3(b) shows the temperature dependence of τ in oxidized Si crystallites. The temperature dependence of τ in oxidized Si crystallites is very similar to that in porous Si. This also indicates that the slow-decay dynamics of red PL is not sensitive to the materials surrounding the *c*-Si spheres (either *a*-SiO₂ or Si:O:H compounds). In oxi-



FIG. 1. Photoluminescence spectra of (a) a porous Si film of $\langle D_s \rangle \sim 3.5$ nm and (b) an oxidized Si crystallite sample of $\langle D_s \rangle \sim 3.7$ nm.



FIG. 2. Double logarithmic plot of photoluminescence decay curves in a porous Si film of $\langle D_s \rangle \sim 3.5$ nm at 20, 78, and 290 K. The solid lines are theoretical curves given by stretched exponential functions.

dized Si crystallite samples, the c-Si spheres are isolated from each other.¹⁴ Consequently, the carriers can hardly move out of the c-Si spheres and are confined in the Si crystalline spheres due to the large band gap of a-SiO₂ surface layer. Based on the agreement of these two types of samples, it is concluded that a large number of the photogenerated carriers are confined in the c-Si spheres even in porous Si.

Let us now consider why the confined carriers recombine very slowly in nanometer-sized crystallites in porous Si. In porous Si, the surface of the c-Si spheres is terminated by H or O atoms (including OH groups). Then, it is considered that the electronic properties of the nearsurface region in the c-Si sphere are different from those of the c-Si core in the c-Si sphere: From the viewpoint of electronic structures, there are two states of a c-Si core and an interface region in a c-Si sphere. We propose a three-region model for porous Si composed of (a) a c-Si core with diameter D_c , (b) a surface compound (amorphous Si:O:H compound), and (c) an interface region between the c-Si core and the surface compound. In this model, H and O atoms or OH groups in the surface



FIG. 3. (a) Decay time τ as a function of temperature in different porous silicon films of $\langle D_s \rangle \sim 2$, 3.5, and 13 nm. (b) The temperature dependence of the decay time τ in oxidized Si crystallites.

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amorphous compound create a novel electronic state in an interface region (this state is mainly due to oxygen atoms interconnecting the c-Si sphere with the surface compound). Here, we stress the importance of the interfacial region between the c-Si core and the outer surface compound.

To understand the most essential feature of the electronic properties of the thin interface region, we consider a monolayer Si sheet terminated by H and O atoms as the interface region, and use the result of the ab initio calculations for the one-sided oxidized Si sheets.¹⁷⁻¹⁹ The H and O atoms are located out of plane in the Si sheet and oxygen atoms critically affect electronic structures of the two-dimensional Si sheet. These oxidized Si sheets have *direct* band gaps at the Γ point.^{17,19} The band-gap energy in one-sided oxidized Si sheets decreases with increasing the O-covering ratio (the ratio of O atoms bonding Si atoms to H atoms bonding Si atoms), however, the bandgap energy weakly depends on the O-covering ratio: e.g., 2.0 eV in an incompletely oxidized sheet (Si:O:H =5:1:4, 20% O-covering ratio) to 1.7 eV in fully oxidized Si sheets (Si:O:H=1:1:0, 100% O-covering ratio) like a planar siloxene.^{18,20} Therefore, it is concluded that this one-sidedly oxidized interface layer becomes the possible origin of visible PL. The weak dependence of the bandgap energy of the Si sheets on the O-covering ratio causes the similar PL properties between the porous Si and the oxidized Si spheres. The O-covering ratio dependence of the band-gap energy in the Si sheets can also explain an experimental fact^{8,9} that the PL peak energy shifts to the higher energy on increasing the H concentration in porous Si films.

Theoretical calculations^{19,21} show that for sizes of nanometer order, the band-gap energy of the c-Si core depends sensitively on the core size D_c . The band-gap energy of the c-Si core of $D_c \leq 4-7$ nm is higher than that of 1.7-2.0 eV of the interface layer. When the band-gap energy of the interface layer is lower than that of the c-Si core, the carrier is confined on the interfacial sphericalshell region. It is possible that only small crystallites with sizes of less than a certain diameter contribute to the strong visible PL. This causes the size-independent PL spectrum and PL decay time. On the other hand, in larger crystallites, the band-gap energy of the c-Si core is lower than that of the interface region. The radiative recombination rate in the c-Si core is very small compared with that in the interface layer, because of the indirect character of the c-Si core with large diameters, and we would expect no strong PL.¹⁴ Therefore, we believe that the c-Si spheres exhibiting visible PL in porous Si have the energy-gap diagram as drawn in Fig. 4.

Next, to explain the slow-decay dynamics of red PL from porous Si, we consider that the hopping of confined carriers²² occurs in a quasi-two-dimensional interface region as shown in Fig. 4. The variable-range hopping rate in two-dimensional systems τ_h^{-1} is given by^{23,24}

$$\tau_h^{-1} \propto \exp[-C/T^{1/3}] , \qquad (2)$$

where the factor C is a constant determined by the localization length of carriers and the two-dimensional density of states. Figure 5 shows the $\log_{10}\tau^{-1}$ versus $T^{-1/3}$ plots.



FIG. 4. Energy-gap diagram for porous Si exhibiting the strong visible PL. The c-Si sphere consists of the c-Si core and the interface region. D_s is the diameter of the c-Si spheres. The band-gap energy of the interface layer E_{core}^{gap} is $\sim 1.7-2.0$ eV. The energy gap of the c-Si core E_{core}^{gap} increases with decreasing diameter of the c-Si core D_c . In the case of $D_c \leq 4-7$ nm, the carrier is confined in (c) the interface region surrounded by (a) the c-Si core and (b) the surface Si:O:H compound.

A good linear relationship is observed in the $\log_{10}\tau^{-1}$ versus $T^{-1/3}$ plots in porous Si and oxidized Si crystallites. This supports a model in which the carrier is confined in the interface region and the hopping motion occurs in this quasi-two-dimensional region. As mentioned above, the band-gap energy of the interface layer depends on the O-covering ratio and ranges from 2.0 (20% O-covering ratio) to 1.7 eV (100% O-covering ratio). The random O termination and the spatial fluctuation of the O-covering ratio cause the fluctuation of the band-gap energy of the interfacial region. The random potential fluctuation in the interface region induces the localization of carriers such as the Anderson localization due to its low dimensionality. The bandwidth of the PL spectrum roughly agrees with the calculated band-gap energy fluctuation of the interface region. Therefore, it is concluded that the radiative recombination rate of carriers is limited by the variable-range hopping in the quasi-two-dimensional interfacial region.²⁵ The interface region in nanometer-sized Si crystallites serves as a two-



FIG. 5. PL decay rate τ^{-1} vs $T^{-1/3}$ (open circles, oxidized Si crystallites; the others, porous Si). The straight line indicates that the PL decay is determined by the variable-range hopping of carriers in a quasi-two-dimensional interface region.

dimensional random system that has unique optical and electronic properties.

In conclusion, we have studied the decay dynamics of visible luminescence from free-standing porous Si thin films fabricated by electrochemical etching and oxidized Si crystallites produced by laser breakdown of SiH₄ gas. The slow-decay behavior of luminescence in the time range $10^{-7}-10^{-2}$ s is the same and is well described by a stretched exponential function. Temperature dependence of the PL decay dynamics shows that the decay rate is determined by the variable-range-hopping-limited recom-

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