PHYSICAL REVIEW B VOLUME 49, NUMBER 20 15 MAY 1994-II

Origin of the blue and red photoluminescence from oxidized porous silicon

Yoshihiko Kanemitsu
Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Toshiro Futagi, Takahiro Matsumoto, and Hidenori Mimura
Electronics Research Laboratory, Nippon Steel Corporation, Kanagawa 229, Japan
(Received 13 December 1993)

We have studied the origin of the visible photoluminescence (PL) from oxidized porous Si fabricated by rapid-thermal-oxidization processes. At low oxidation temperature (T_{ox}), the PL spectrum with a peak near 750 nm is observed, and silicon oxyhydrides and silicon oxides are formed at the surface of nanocrystallites. At high T_{ox} above 800 °C, strong blue PL is observed around 400 nm and the surface of crystallites is covered by SiO_2. The electronic state of porous Si is very sensitive to the surface structure of crystallites. Spectroscopic data indicate that the red PL originates from the near-surface region in the crystallite, while the blue PL originates from the core region in the crystallite.

Very recently, a great deal of research effort has been focused on nanometer-size crystallites or quantum dots made from indirect-gap semiconductors such as Si (Refs. 1–3) and Ge.[4,5] In particular, strong visible photoluminescence (PL) from Si nanocrystallites fabricated by electrochemical etching, often called porous Si, is a phenomenon of considerable current interest from viewpoints of both fundamental physics and optical-device applications. However, the mechanism of the strong visible PL from porous Si still remains unclear.[6–8] The difficulty of this problem arises mainly from a large surface-to-volume ratio in nanostructures: The surface effects become more enhanced on decreasing the size of nanocrystallites. The surface of Si nanocrystallites in luminescent porous Si is usually covered by silicon oxyhydrides[9–11] or silicon dioxide,[12,13] which cause the electronic properties of the near-surface region to differ from those of the crystalline Si (*c*-Si) core. Therefore, recently proposed models are classed into two groups: quantum confinement effects in Si nanocrystallites cause efficient light emission from porous Si or the surface region in Si crystallites is responsible for the origin of visible PL from porous Si.[6–8]

To clarify the mechanism of strong visible PL from porous Si, we need to control the surface structure of the Si crystallites and to study the effects of the surface structure on optical properties of porous Si. In this paper, we have studied stable visible PL from oxidized porous Si fabricated by rapid-thermal-oxidization (RTO) processes, because short-time and low-temperature RTO processes preserve the Si crystalline core, and the RTO temperature can change the surface chemical structure of the *c*-Si core.[13] When the size of the Si crystallites decreases and the surface structure of the crystallites is covered by silicon dioxides, the PL spectrum changes from red to blue regions. Spectroscopic analyses indicate that the red PL originates from the near-surface region in the crystallite, while the blue PL originates from the *c*-Si core in the crystallite.

Porous Si layers were formed on *p*-type (100) Si wafers with ~4-Ω cm resistivity. 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 ($HF{:}H_2O{:}C_2H_5OH = 1{:}1{:}2$) at a constant current density of 10 mA/cm^2 for 5 min. Raman-spectroscopy and transmission-electron-microscopy (TEM) examinations show that the average diameter of the Si crystallites is about 3 nm. The as-etched porous Si samples were processed in a RTO apparatus. The heating rate was 200 °C/s, and the samples were kept for 35 s at an oxidation temperature T_{ox} ranging from 480 to 1200 °C under 1-atm O_2 pressure. The cooling rate was 100 °C/s. By controlling T_{ox}, we fabricated the strongly red- and blue-luminescent porous Si, as shown in Fig. 1.

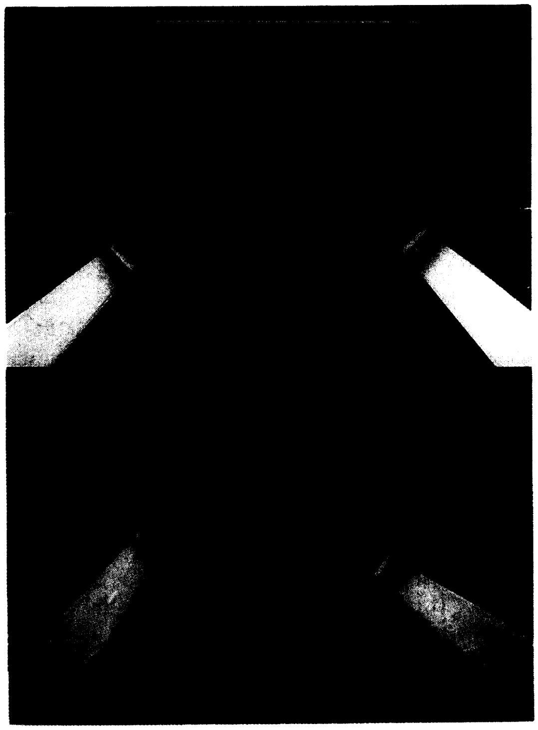

FIG. 1. Photographs of the red and blue PL from oxidized porous silicon ($T_{ox} = 680$ and 880 °C).

PL spectra from oxidized porous Si were measured using 325-nm excitation light from a He-Cd laser. 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 was calibrated by using a tungsten standard lamp. The initial decay of PL in the picosecond time region was measured using a streak camera and a 240-nm, 200-fs pulse from the fourth harmonic of a cw-mode-locked Ti:Al_2O_3 laser.

Figure 2 shows PL spectra from oxidized porous Si under 325-nm excitation at room temperature as a function of T_{ox}. In porous Si oxidized at low T_{ox} ($<800\,°C$), the PL peak is around 750 nm. The spectral width of the broad PL is about 0.3 eV full width at half maximum (FWHM). Both the PL peak and the PL width in oxidized porous Si are nearly equal to those in the as-etched porous Si. At higher T_{ox} above 800 °C, the strong blue PL near 400 nm appears, while the red PL near 750 nm disappears. TEM studies indicated that the number of nanocrystallites decreases rapidly with increasing T_{ox} ($T_{ox} > 800\,°C$), as reported in Ref. 14. When the number of Si crystallites decreases, the blue PL intensity decreases. These imply that Si nanocrystallites participate in the blue PL process in oxidized porous Si.

Fourier-transform infrared (FTIR) spectroscopy provides information about the internal surface of porous Si. In the as-etched porous Si samples (before RTO processes), absorption peaks due to Si-H and Si-H_2 were observed near 900 and 2100 cm^{-1}. After oxidization, these two peaks disappeared. Figure 3 shows the dependence of FTIR spectra on T_{ox}. At low T_{ox} below 800 °C, an absorption band due to silicon oxyhydride (Si:O:H) is observed near 3400 cm^{-1}. At T_{ox} higher than 800 °C, this broad absorption band disappears. With rising T_{ox}, the amount of silicon oxides increases monotonically. These FTIR spectra strongly suggest that at low T_{ox}, the surface of Si crystallites is covered by Si:O:H compounds and silicon oxides, while at high T_{ox} above about 800 °C, the surface of Si crystallites is covered by silicon oxides. X-ray photoemission spectroscopy examinations suggest that a large part of silicon oxides at high T_{ox} is amorphous SiO_2 (a-SiO_2). It is found that there is a good relationship between the PL spectrum and the surface-termination condition.

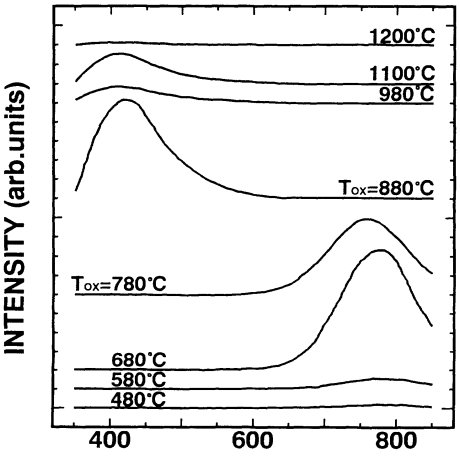

FIG. 2. PL spectra from oxidized porous Si under 325-nm excitation as a function of T_{ox}.

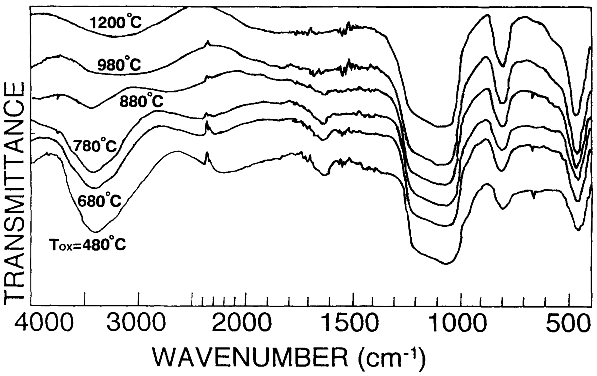

FIG. 3. FTIR spectra of oxidized porous Si as a function of T_{ox}.

Figure 4 shows the temperature dependence of the red PL intensity in a sample of $T_{ox}=680\,°C$, and of the blue PL intensity in a sample of $T_{ox}=880\,°C$. The red PL increases with temperature up to about 100 K, and then gradually decreases. Similar temperature dependence is also observed in CdSe crystallites[15] and c-Si spheres.[16] This behavior is explained by a picture[15,16] in which carriers are confined or localized into the lower-energy state, and PL originates from the lower-energy state (the near surface region) rather than the band-edge state (the c-Si core). On the other hand, the blue PL intensity does not decrease at low temperatures.

Figure 5 shows the initial decay of PL in the picosecond time region. The rapid decrease in the PL intensity is observed at 750 nm: There are two components of fast and slow decay in the picosecond time region. In the red PL from porous Si oxidized at low T_{ox}, we observed the redshift of the PL peak in the initial decay stage. Moreover, as shown in the inset of Fig. 5, the long and nonexponential components of the red PL are clearly observed in the microsecond time region. These rapid red-

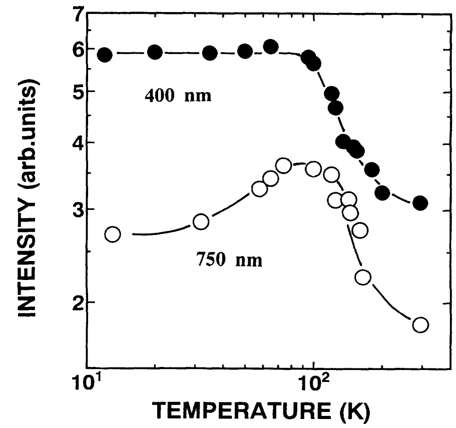

FIG. 4. Temperature dependence of the PL intensity at 400 nm ($T_{ox}=880\,°C$) and 750 nm ($T_{ox}=680\,°C$).

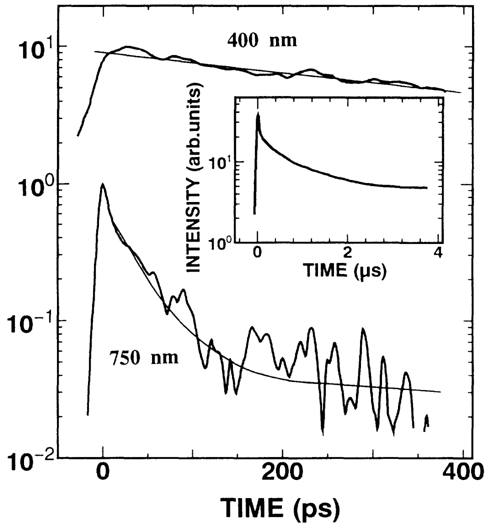

FIG. 5. Picosecond PL decay at 400 nm ($T_{ox}=880\,^\circ\mathrm{C}$) and 750 nm ($T_{ox}=680\,^\circ\mathrm{C}$). The solid line at 400 nm indicates a single exponential decay, and the solid line at 750 nm is a guide to the eye. The inset shows the slow decay components of the red PL in the microsecond time region.

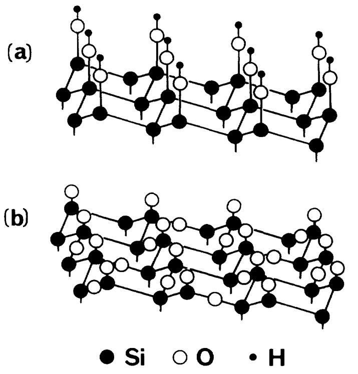

FIG. 6. Models of the surface structure of oxidized Si nanocrystallites at (a) low T_{ox} and (b) high T_{ox}.

shifts in the picosecond time region and the long nonexponential PL decay suggest that carriers are localized into the long-lived lower-energy state.[11,15] On the other hand, the blue PL decay is approximately exponential (in Fig. 5, the time constant is about 650 ps), and the redshift of the PL peak is not observed, where we measured the PL decay up to 5 ns and the PL decay is single exponential over 5 ns. There is no long component of the blue PL. Both the PL dynamics and the temperature dependence of the PL intensity indicate that the mechanism of blue PL is different from that of red PL.

To discuss the mechanism of the strong blue and red PL from oxidized porous Si, we first consider the effect of oxygen atoms on electronic properties of Si nanocrystallites, because there is a relationship between the PL spectrum and the surface chemical structure. During RTO processes, the composition of the internal surface changes from silicon hydrides to silicon oxyhydrides (Si:O:H) and silicon oxides (Si:O) for $T_{ox} < 800\,^\circ\mathrm{C}$, or to a-SiO$_2$ for $T_{ox} > 800\,^\circ\mathrm{C}$. The PL peak energy changes from about 1.65 eV ($T_{ox} < 800\,^\circ\mathrm{C}$) to 3 eV ($T_{ox} > 800\,^\circ\mathrm{C}$). Here we stress the importance of the structure of the oxidized surface layer in visible PL processes.

It is known that oxygen-terminated Si sheets (like siloxene) exhibit visible PL,[17] and the oxygen atoms strongly affect the electronic structures of two-dimensional Si sheets.[18,19] We employ the results of *ab initio* electronic structure calculations reported in Ref. 18 in order to discuss the band of the oxidized surface monolayer. In the oxidized Si monolayer, the position of oxygen atoms critically affects the electronic structures. Here we consider two types of Si:O compounds as the model of the surface structure of the c-Si core, and these compound structures are illustrated in Fig. 6.

At low T_{ox} ($T_{ox} < 800\,^\circ\mathrm{C}$), the surface of the c-Si core is covered by silicon oxyhydrides and silicon oxides: H atoms at the surface in the as-etched porous Si are replaced by OH groups or O atoms, and O atoms cannot migrate into the Si network, as shown in Fig. 6(a). In this layer, the oxygen atoms are located out of plane in the Si monolayer. The most characteristic feature of this layer is a direct-gap structure of 1.7 eV at the Γ point.[18] Therefore, we can propose the O-terminated Si surface layer as a possible origin of the strong red PL in oxidized Si nanocrystallites.

TEM and Raman-spectroscopy examinations indicate that the RTO process at low T_{ox} preserves the Si crystallite with about 3-nm diameter. According to the optical-absorption spectrum measurements[20] and effective-mass approximation calculations,[21] the band gap of the 3-nm Si core is evaluated to be about 2.4 eV. The band-gap energy of the c-Si core (>2 eV) is larger than that of the near-surface layer in the crystallite (1.7 eV) [Fig. 6(a)]. The spectroscopic characteristics of the red PL (the picosecond PL dynamics, the long nonexponential PL decay, and the temperature dependence of the PL intensity) suggest that the photogenerated carriers in the c-Si core are rapidly localized into the lower-energy state (the near-surface layer) with a small overlap between the electron and hole wave functions. The above theoretical considerations and the spectroscopic data lead us to conclude that the photogeneration of carriers occurs in the c-Si core whose band gap is modified by the quantum confinement effect, and that radiative recombination occurs at the near-surface layer. The red PL is caused by the radiative recombination of excitons that are confined in the luminescent surface layer.

At higher T_{ox}, the surface of the c-Si core is covered by an a-SiO$_2$ layer. The a-SiO$_2$ layer does not itself contribute to the visible PL, because the band-gap energy is out of the visible range (>8 eV).[22] However, this layer creates an electronic state in an interfacial region between the c-Si core and the a-SiO$_2$ layer. Since the diameter of the c-Si core decreases at high T_{ox}, oxygen atoms migrate into the Si-skeleton layer and oxygen atoms form the bridges or interconnect Si atoms. A possible surface structure is illustrated in Fig. 6(b). This structure has a direct gap of 3–4 eV.[18] On the other hand, at a high T_{ox} of 880 °C, a decrease of the c-Si core size occurs. The band-gap energy of the c-Si core at about 2 nm is estimated to be about 3 eV,[21,23] which is nearly equal to or less than that of the interfacial region. Consequently, it is considered that carriers are confined in the *c*-Si core due to the large band gaps of the interface region and the outer surface *a*-SiO_2 layer.

In the experiments, both the temperature dependence of the blue PL intensity and the decay dynamics of the blue PL are entirely different from those of the red PL. The blue PL intensity decreases monotonically with increasing temperature, while an unusual temperature dependence of the red PL intensity is observed. The initial decay of the blue PL is given approximately by a single exponential function. The long nonexponential decay of the blue PL is not observed, but that of the red PL is clearly observed. These results suggest that the mechanism of the blue PL is different from that of the red PL originating from the long-lived near-surface state. A theoretical calculation also suggests that both the band-gap energy E_g and the exciton binding energy E_x increase with decreasing crystallite size: The optical gap energy $E_g - E_x$ does not strongly depend on the size of very small crystallites.[24] Moreover, the PL efficiently strongly depends on the size of the Si crystallites.[16] Therefore, it is difficult to experimentally observe the size dependence of the blue PL peak energy in an oxidized porous silicon sample having a broad size distribution. However, the above theoretical consideration (carriers are confined in the *c*-Si core due to the large band-gap energy of the surrounding materials) and spectroscopic data (rapid single-exponential decay and the usual temperature dependence of the blue PL) indicate that a possible origin of the broad blue PL is the radiative recombination of excitons confined in the small *c*-Si core.

In conclusion, we have studied the mechanism of the strong blue and red PL from oxidized porous Si. The oxidized surface layer plays an essential role in strong blue and red PL processes: The surface structure changes the origin of visible PL. Our studies show that the red PL originates from the radiative recombination of excitons in the near-surface region in the crystallite, while the blue PL originates from the radiative recombination of excitons confined in the *c*-Si core in the crystallite.

The authors would like to thank Professor F. Koch of Technischen Universität München for discussions and Dr. T. Ogawa, Dr. K. Takeda, and Dr. K. Shiraishi of NTT Basic Research Laboratory for discussions of the electronic structure of oxidized silicon sheets. One of the authors (Y.K.) thanks the Sumitomo Foundation for financial support.

---

[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[2] A. G. Cullis and L. T. Canham, Nature **353**, 335 (1991).

[3] V. Lehman and U. Gosele, Appl. Phys. Lett. **58**, 856 (1991).

[4] Y. Maeda *et al.*, Appl. Phys. Lett. **59**, 3168 (1991).

[5] Y. Kanemitsu *et al.*, Appl. Phys. Lett. **61**, 2187 (1992).

[6] *Light Emission from Silicon,* edited by S. S. Iyer, R. T. Collins, and L. T. Canham, MRS Symposia Proceedings No. 256 (Materials Research Society, Pittsburgh, 1992).

[7] *Microcrystalline Semiconductors: Materials Science and Devices,* edited by P. M. Fauchet, C. C. Tsai, L. T. Canham, I. Shimizu, and Y. Aoyagi, MRS Symposia Proceedings No. 283 (Materials Research Society, Pittsburgh, 1993).

[8] *Silicon-Based Optoelectronic Materials,* edited by R. T. Collins, M. L. Thewalt, M. A. Tischler, and G. Abstreiter, MRS Symposia Proceedings No. 298 (Materials Research Society, Pittsburgh, 1993).

[9] M. A. Tischler, R. T. Collins, J. H. Stathis, and J. C. Tsang, Appl. Phys. Lett. **60**, 639 (1992).

[10] C. Tsai *et al.*, Appl. Phys. Lett. **60**, 1700 (1992).

[11] T. Matsumoto, T. Futagi, H. Mimura, and Y. Kanemitsu, Phys. Rev. B **47**, 13 876 (1993).

[12] J. C. Vial *et al.*, Phys. Rev. B **45**, 14171 (1992).

[13] V. Petrova-Koch *et al.*, Appl. Phys. Lett. **61**, 943 (1992).

[14] V. Lehmann *et al.*, in *Microcrystalline Semiconductors: Materials Science and Devices* (Ref. 7), p. 247.

[15] M. G. Bawendi *et al.*, Phys. Rev. Lett. **65**, 1623 (1990); M. G. Bawendi, P. J. Carroll, W. L. Wilson, and L. E. Brus, J. Chem. Phys. **96**, 946 (1992).

[16] Y. Kanemitsu, T. Ogawa, K. Shiraishi, and K. Takeda, Phys. Rev. B **48**, 4883 (1993).

[17] M. S. Brandt *et al.*, Solid State Commun. **81**, 307 (1992).

[18] K. Takeda and K. Shiraishi, Solid State Commun. **85**, 301 (1993); Phys. Rev. B **39**, 11028 (1989).

[19] T. Ogawa, K. Takeda, K. Shiraishi, and Y. Kanemitsu (unpublished).

[20] Y. Kanemitsu *et al.*, Phys. Rev. B **48**, 2827 (1993).

[21] Y. Takagahara and K. Takeda, Phys. Rev. B **46**, 15 578 (1992).

[22] It is known that the point defects in SiO_2 such as nonbridging-oxygen hole centers ($\equiv$Si-Si$\equiv$) and neutral oxygen vacancies ($\equiv$Si-O.) play a role in the visible PL process (2.7 eV) in SiO_2 glass [as a review, see D. L. Griscom. J. Ceram. Soc. Jpn. **99**, 923 (1991)]. However, the temperature dependence of the 400-nm (3 eV) PL from oxidized porous Si is different from that of 2.7-eV PL from defects in SiO_2. The PL decay dynamics in oxidized porous Si is also different from that of defect in SiO_2. Moreover, the polarization memory of PL from porous Si is also reported [D. I. Kovalev, T. Muschik, V. Petrova-Koch, I. D. Yaroshetzkii, and F. Koch (unpublished)]. Thus we conclude that the blue PL from oxidized porous Si is different from the 2.7-eV PL from point defects in SiO_2 glass.

[23] S. Y. Ren and J. D. Dow, Phys. Rev. B **45**, 6492 (1992).

[24] T. Ohno, K. Shiraishi, and T. Ogawa, Phys. Rev. Lett. **69**, 2400 (1993).

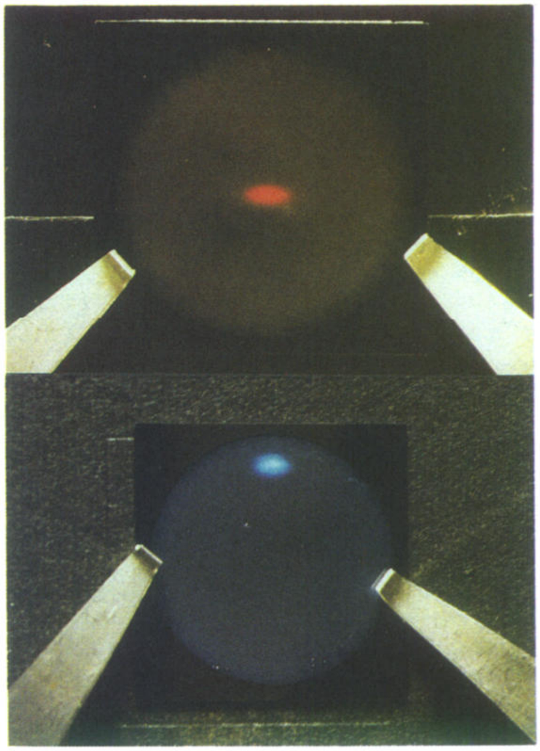

FIG. 1. Photographs of the red and blue PL from oxidized porous silicon ($T_{ox} = 680$ and 880 °C).