# Photoluminescence mechanism in surface-oxidized silicon nanocrystals

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We have studied photoluminescence (PL) properties of surface-oxidized Si nanocrystals fabricated with a $SiH_4$ plasma cell. The size dependence of the PL spectrum, the PL decay dynamics, and site-selective excitation spectroscopy show that the efficient and broad PL band around $\sim$1.65 eV originates from excitons localized at the interface between crystalline Si and the $SiO_2$ surface layer. The PL from the crystalline Si core state in large nanocrystals appears in the infrared spectral region. By comparison between surface-oxidized Si nanocrystals and as-prepared porous Si, the size and surface dependence of the coupling between electronic and vibrational excitations are discussed. [S0163-1829(97)52212-0]

Efficient visible luminescence from Si nanostructures has stimulated considerable efforts in understanding optical properties of group-IV semiconductor nanostructures and producing nanostructure devices.[1] In particular, porous silicon and Si nanocrystals are receiving widespread interest because of their high quantum efficiency of light emission and potential applications as light-emitting devices compatible with silicon-based optoelectronic integrated circuits. There are many extensive studies concerning the origin of visible light emission in porous Si (Refs. 2–10) and surface-oxidized Si nanocrystals.[11–13] However, the mechanism of visible luminescence is not clear and is still controversial, because porous silicon and Si nanocrystals show various optical characteristics.[1,14]

A drastic size reduction to a few nanometers is required for the observation of efficient visible light emission. With large surface-to-volume ratios in Si nanocrystals, surface effects become more enhanced on decreasing the size of nanometer-sized crystallites. The photoluminescence (PL) intensity and the PL spectrum are sensitive to the surface chemistry of Si nanocrystals, particularly with regard to the amounts of oxygen and hydrogen on the surface.[5,6,8] The PL peak energy in H-terminated Si nanocrystals is very sensitive to the nanocrystal size,[9] compared with surface-oxidized Si nanocrystals.[12] Luminescence properties of H-terminated Si nanocrystals are considered to be different from those of surface-oxidized Si nanocrystals.[14] The influence of surface states and passivation on optical and electronic properties is a long-standing issue of the physics of semiconductor clusters and nanocrystals.[15] Therefore, in order to understand luminescence properties of Si nanocrystals, we need to study the optical properties of Si nanocrystals with near identical and stable surfaces. Si nanocrystals with a $SiO_2$ surface layer have some advantages because $SiO_2$ is a well-characterized material known to passivate Si surfaces where the $Si/SiO_2$ system is fully compatible with Si technology. In this work, we have studied PL spectra and dynamics in Si nanocrystals capped by a $SiO_2$ thin layer. The visible and broad PL in surface-oxidized Si nanocrystals is explained in terms of exciton localization at the interface between crystalline Si and ($c$-Si) core and a surface $SiO_2$ layer, while the infrared PL originates from the $c$-Si core state in large nanocrystals. By comparison between surface-oxidized Si nanocrystals and as-prepared porous Si, the size and surface dependence of the coupling between electronic and vibrational excitations are also discussed.

The nanometer-sized Si crystallites were prepared with $SiH_4$ plasma cell attached to the ultrahigh-vacuum (UHV) chamber. Details of the preparation of nanocrystal samples are given in Refs. 16 and 17. Here we briefly describe the sample preparation procedure. Si nanocrystals were formed in the plasma gas phase of $SiH_4$ diluted by $H_2$ by coalescence of radicals produced from $SiH_4$. Si nanocrystals were extracted out of the plasma cell through the orifice to the UHV chamber. Si nanocrystals were collected on quartz substrates. The average size of Si nanocrystals was controlled by changing the partial pressure of $SiH_4$ and $H_2$. The surface of the as-prepared Si nanocrystals was terminated by hydrogen atoms. Si nanocrystals with $SiO_2$ surface layer were formed after thermal oxidation at 800 °C. The average size of crystalline Si core was varied from 2.5 to 6 nm, by changing the oxidation time from 0 to 30 min, where the nanocrystal size was determined by transmission electron microscopy (TEM) observations.[16] TEM observations showed that the shape of the nanocrystal is spherical. This fact was also confirmed by the PL polarization memory, where the polarized PL was not observed in our samples.

The luminescence spectra were obtained by using He-Cd, He-Ne, and $Ti:Al_2O_3$ lasers. The time-resolved PL spectra of oxidized Si nanocrystals were measured under 5 ns, 532 nm excitation (30 Hz repetition rate) using a digital oscilloscope. The spectral sensitivity of the measuring system was calibrated by using a tungsten standard lamp. The samples were immersed in superfluid liquid helium at 2 K.

Broad luminescence was clearly observed in the red and infrared spectral region. Figure 1 shows the size dependence of the PL peak energy under $\sim$1-mW/cm$^2$, 325-nm excitation from a cw He-Cd laser. The blueshift of the PL peak energy is observed with a decrease of crystallite size. This
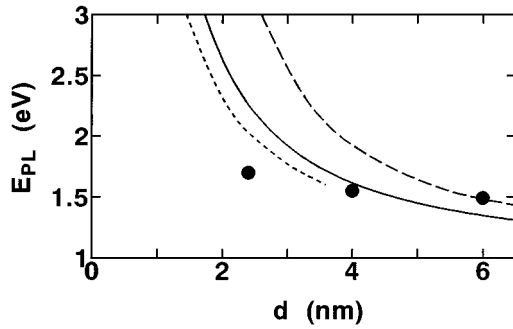
FIG. 1. Size dependence of the luminescence peak energy in surface-oxidized Si nanocrystals. Theoretical curves for the band-gap energy are reproduced from broken (Ref. 18), solid (Ref. 19), and dashed (Ref. 20) lines.

size dependence of the PL peak energy is very similar to the previously reported result in Ref. 12. However, the weak size dependence of the PL peak energy in surface-oxidized Si nanocrystals cannot be explained by the proposed simple quantum confinement theories.[18–21] In theoretical calculations, the authors assumed that the Si nanocrystals have hydrogen termination[19,20] or no surface effect.[18] The size dependence of as-prepared porous Si is consistent with the theoretical calculations,[9,22] where the surface of as-prepared porous Si is mainly terminated by hydrogen atoms.[6] The electronic structures of $SiO_2$-capped Si nanocrystals are very complicated, compared with those in H-terminated Si nanocrystals.[18–21]

In order to discuss the PL mechanism in detail, we measured PL decay profiles at 2 K under 532-nm, 5-ns laser pulse excitation. The PL decay profiles are nonexponential, and they are well described by a stretched exponential function.[1]

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

where $\tau$ is an effective decay time, $\beta$ is a constant between 0 and 1, and $I_0$ is a constant. The solid line in the inset of Fig. 2 is given by the above function. The least-squares fitting of the data gives the value of $\tau$ and $\beta$. This stretched exponential decay is usually observed in the PL decay and transport properties of disordered or inhomogeneous systems. Figure 2 shows the luminescence decay rate as a function of the PL wavelength in 4-nm Si nanocrystals. The PL decay time decreases with an increase in the PL wavelength in the visible spectral region ($\lambda_{PL} < 750$ nm). At PL wavelengths longer than ~750 nm (photon energies below ~1.65 eV), the decay time is not sensitive to the monitored wavelength. The PL decay dynamics measurements imply that the origin of PL above ~1.65 eV is different from that below ~1.65 eV, although the broad PL bands are overlapped in red and infrared spectral region.

Since the PL lifetime is very long at low temperatures the PL spectrum depends strongly on the excitation laser intensity. Figure 2 shows the power dependence of the PL spectra in 4-nm Si nanocrystals under 325 nm excitation from a cw He-Cd laser. With an increase in the laser intensity, the PL peak energy is blueshifted from ~800 to ~750 nm. The asymmetrical PL band can be fitted by two Gaussian bands with peaks of ~800 and ~750 nm. Then, the PL decay dy-
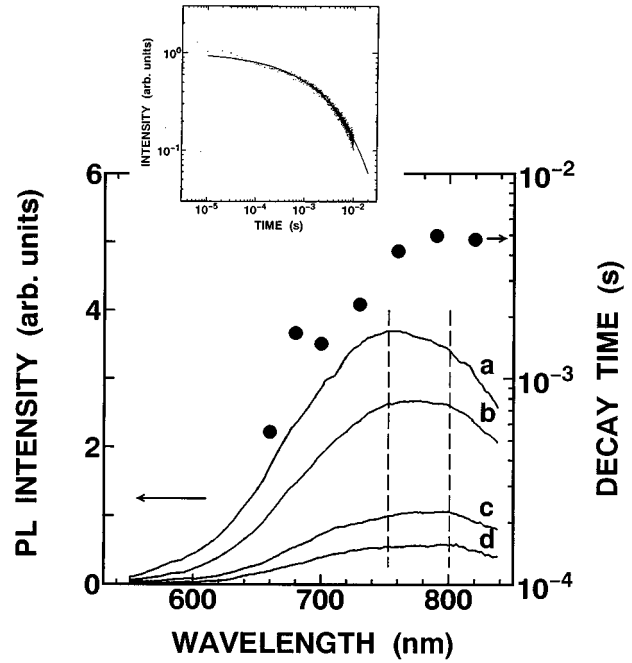


FIG. 2. Effective luminescence decay rate $\tau^{-1}$ (●) as a function of the monitored luminescence wavelength at 2 K and the excitation power dependence of the luminescence spectra of 4 nm Si nanocrystals: (a) 80, (b) 40, (c) 16, and (d) 8 mW/cm². The luminescence spectra consist of the bands with the peaks around ~750 and ~800 nm. The inset shows the double logarithmic plot of photoluminescence decay curve at 730 nm. The decay time depends on the monitored luminescence wavelength shorter than ~750 nm, but is almost independent of the wavelength longer than ~750 nm.

namics measurements and the excitation power dependence of the PL spectrum suggest that there are different luminescence bands in Si nanocrystals.

In studying inhomogeneous systems, site-selective excitation spectroscopy is a powerful method to extract fine structures from a broadened spectrum.[2] Figure 3(a) shows resonantly excited PL spectra recorded at 2 K using excitation photon energies of 1.959, 1.724, 1.658, and 1.597 eV, where the zero on the abscissa scale corresponds to the excitation laser energy. The increase in the signal on the energy region below ~30 meV is caused by the scattering laser light and the tail of the excitation light from a tunable Ti:$Al_2O_3$ laser, because the PL efficiency is very low. Under laser excitations above ~1.65 eV, fine structures are not observed in surface-oxidized Si nanocrystals. The phonon-related structures are only observed under excitation lower than ~1.65 eV. At 1.597 eV excitation, for example, the step structure is observed near 60 meV, which is close to the TO phonon energy in crystalline Si. However, since the PL intensity is very low, we cannot exactly determine whether the energy interval in the step structures is equal to the TO-phonon energy in crystalline Si or not.

For a deeper understanding of the PL mechanism, we measured resonantly excited PL spectra of as-prepared porous Si. Under the same experimental condition, we can clearly observe TO phonon-related structures in the PL spectrum in as-prepared porous Si, as shown in Fig. 3(b). The porous layers were formed on p-type 3.5-$\Omega$ cm Si wafers using the conventional technique of Ref. 3. Porous Si is in-

**(a)**

PL INTENSITY (arb. units)

1.959 eV

1.724 eV

1.658 eV

1.597 eV

$E - E_L$ (eV)

**(b)**

TO    TO

PL INTENSITY (arb. units)

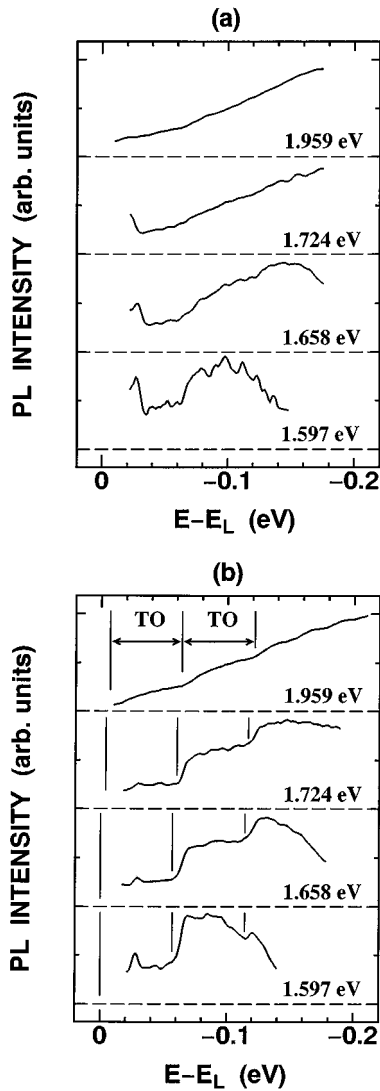1.959 eV

1.724 eV

1.658 eV

1.597 eV

$E - E_L$ (eV)

FIG. 3. Resonantly excited photoluminescence spectra of (a) surface-oxidized Si nanocrystals and (b) as-prepared porous Si at the lower-energy side of the laser line under the same experimental conditions. The zero on the abscissa scale corresponds to the excitation laser energy. The excitation laser energies are shown in the figure. The measurement temperature is 2 K. The TO phonon-related fine structures are clearly observed in as-prepared porous Si.

homogeneous in the sense that it has broad distributions of the crystallite size and shape, the surface roughness, and a fluctuation of surface stoichiometry. In particular, there exists the vertical inhomogeneity in the porous layer. This is a consequence of porous Si formation mechanism.[23] The top of the layer has been in the etching solution longer than the bottom. The crystalline silicon size is then smaller at the top of the layer. After air exposure, the top of the layer is easily oxidized, but the bottom of the layer is not easily oxidized. It is considered that the size and surface structure of nanocrystals in the top of the layer are completely different of those in the bottom of the layer. However, the phonon-related fine structures are clearly observed in highly inhomogeneous material porous Si.[24] In contrast to porous Si, the phonon-related fine structures in the PL spectrum are not observed in this work and the previous size-selected Si nanocrystals with

a $SiO_2$ surface layer.[13] These experimental observations are very important for understanding of the PL mechanism in Si nanocrystals.

Let us now consider the PL mechanism of surface-oxidized Si nanocrystals. The PL peak energy in oxidized Si nanocrystals does not show the dependence on size that is expected from simple quantum confinement[18–21] and that is observed in as-prepared porous Si samples,[9,22] as mentioned above. Similar size-insensitive PL spectra are observed in oxidized porous Si after prolonged air exposure.[3,7] Moreover, in resonantly excited PL experiments, the TO-phonon-related fine structures are not observed in surface-oxidized Si nanocrystals, but are clearly observed in as-prepared porous Si. Broad and featureless PL is observed even in the present size-controlled and the previous size-selected samples.[13] Therefore, oxide termination may have several effects including the formation of the interface state between $c$-Si and $SiO_2$ layer and the modification of the electronic structures of the $c$-Si core state.[25] In $c$-Si/$SiO_2$ systems, the lattice mismatch between $c$-Si and $SiO_2$ in the plane form is very large (about 7% or more).[26] In addition, small spherical nanocrystals have large curvature. Thus, it is considered that the interface states are formed between $c$-Si and $SiO_2$ due to the lattice mismatch, surface roughness, and variations in surface stoichiometry ($SiO_x$).[12,25]

The nonpolar semiconductor $c$-Si has no long-range interaction with phonons and has electrons and holes with high mobility.[27] Then, the self-trapping and localization of excitons do not occur in bulk $c$-Si, because of the weak exciton-phonon coupling.[27] However, when the size of nanocrystals is smaller than the bulk exciton Bohr radius and the band-gap energy of the $c$-Si core is larger than that of interface state, excitons are localized near the disordered interface between $c$-Si and $SiO_2$. The coupling between excitons and vibrations increases with localization of excitons in smaller dimensions. The exciton localization in a disorder potential at the interface initiates the extrinsic self-trapping of excitons,[27,28] through the Fröhlich interaction between excitons and polar Si-O vibrations. In fact, self-tapped excitons with large lattice distortion are commonly observed in silica and ionic crystals.[28] Both the disorder potential at the interface and the extrinsic self-trapping of excitons with lattice distortion cause the size insensitive and broad PL in surface-oxidized Si nanocrystals. Small Si nanocrystals with $SiO_2$ surface layers do not show fine structures in the resonantly excited PL spectra. The interface localization of excitons with large lattice distortion causes a large difference between the observed PL peak energy and theoretical calculations in small nanocrystals, as shown in Fig. 1.

On the other hand, when the size of the $c$-Si core is very large and the surface S-O bonds do not critically affect the electronic properties in the $c$-Si core, the exciton energy of the $c$-Si core is the lowest optical transition even in surface-oxidized Si nanocrystals. Then, the radiative recombination of excitons could occur in the $c$-Si core state similar to the case in H-terminated Si nanocrystals. In fact, the phonon-related fine structures are observed in the infrared spectral region, similar to as-prepared porous Si [see, PL spectra under 1.597 eV excitation in Figs. 3(a) and 3(b)], where the laser light excites large size nanocrystals. In large nanocrystals, the intrinsic deformation potential coupling in nonpolar

Si is weak[27] and excitons are delocalized in the core state. The size and surface dependence of the coupling between electronic and vibrational excitations are very important issues of the physics of nanostructures.[29,30] In Si nanocrystals, both the interface and core states contribute to the red and infrared PL at low temperatures and the coupling strength of electronic and vibrational excitations is sensitive to the size and surface structure.

In conclusion, we have studied PL spectrum and dynamics of surface-oxidized Si nanocrystals. The exciton localization at the interface between $c$-Si and a $SiO_2$ surface layer plays an essential role in the visible PL process, while the $c$-Si core state in large-size nanocrystals contributes to the infrared PL process. The PL spectrum and dynamics are complicated by the overlapping of two different PL bands in the red and infrared spectral region. In nonpolar Si nanocrystals, the polar surface bonding affects critically optical properties, because of the weak deformation potential coupling between electronic and vibrational in the interior state.

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