

Phonon structures and Stokes shift in resonantly excited luminescence of silicon nanocrystals

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We have studied luminescence Stokes shift and phonon-assisted luminescence in H-terminated and surface-oxidized Si nanocrystals by means of resonant excitation spectroscopy. For resonant excitation at energies within a broad luminescence band, TO- and TA-phonon related structures in luminescence spectra are observed in both H-terminated and surface-oxidized Si nanocrystals. In oxidized Si nanocrystals, the luminescence Stokes shift is large and the phonon-related structures are unclear compared to the case of H-terminated Si nanocrystals. The origin of the luminescence Stokes shift and surface localized states in surface-oxidized Si nanocrystals are discussed. [S0163-1829(98)05439-3]

Semiconductor nanocrystals of sizes comparable to or smaller than the exciton Bohr radius in bulk materials are attracting much attention from the fundamental physics viewpoint and from the interest in the application to functional devices.¹ Si nanocrystals and porous Si are receiving widespread interest because of their high quantum efficiency of light emission.² Porous Si is an inhomogeneous system in the sense that it has broad distributions of nanocrystal size and shape and variations of surface structures. Under blue or violet light excitation, porous Si shows broad photoluminescence (PL) at room temperature.² This “full” luminescence or nonresonantly excited luminescence contains contributions from all nanocrystals in the sample and the spectrum is inhomogeneously broadened. In these inhomogeneously broadened systems, resonant (or site-selective) excitation spectroscopy is a powerful method to obtain intrinsic information from inhomogeneously broadened spectra.^{3–6} Resonant excitation at energies within the luminescence band results in a well-resolved phonon progression in PL spectra at low temperatures since we suppress the inhomogeneously broadening of the luminescence by selectively exciting a narrow subset of nanocrystals.⁶ Porous Si shows TO phonon-related fine structures under resonant excitation at low temperatures.^{3,5,7,8} The phonon-related structures in the luminescence spectrum and the excitonic exchange splitting in Si nanocrystals have been discussed in conjunction with the origin of the efficient visible luminescence at room temperature.^{3,9,10}

In this paper we discuss the origin of the luminescence Stokes shift in H-terminated porous Si and surface-oxidized Si nanocrystals by means of resonant excitation spectroscopy. TO- and TA-phonon related structures in resonantly excited luminescence are observed in both H-terminated and surface-oxidized Si nanocrystals. However, in oxidized Si nanocrystals, the luminescence Stokes shift is large and phonon structures in the luminescence spectrum are unclear compared to the case of H-terminated porous Si. The shallow band-edge surface states in oxidized Si nanocrystals are discussed.

The porous silicon samples were prepared as follows. The substrates were (100)-oriented *p*-type crystalline Si (*c*-Si) wafers with resistivities of 0.9–5 Ω cm. The anodization in dark was carried out in HF-ethanol solution

(HF:H₂O:C₂H₅OH=1:1:2) at a constant current density of 10 mA/cm². By changing wafer resistivity or anodization time, we can obtain porous Si samples showing different color luminescence. Surface structure of porous Si samples has been studied by Fourier transform infrared absorption spectroscopy. In the as-prepared porous Si sample, the strong absorption peaks due to the Si-H_n bending mode, Si-H_n deformation modes, Si-H₂ scissors mode, and Si-H_n stretching modes were observed.⁷ The surface of nanocrystals in the as-prepared porous Si layer was covered by silicon hydrides (SiH, SiH₂, and SiH₃). The as-prepared porous Si sample is used as H-terminated Si nanocrystals.

SiO₂-capped Si nanocrystals were prepared by plasma decomposition of SiH₄ followed by thermal oxidation.¹¹ Si nanocrystals were formed in the plasma gas phase of SiH₄ diluted by H₂ and were collected on quartz substrates. The average size of Si nanocrystals was controlled by changing the partial pressure of SiH₄ and H₂. The SiO₂ surface layer was formed after thermal oxidation at 800 °C and at 10 min. The average size of the spherical *c*-Si core was ~2.5 nm, where the nanocrystal size was determined by transmission electron microscopy observations. Under 2.540-eV laser excitation, the luminescence efficiency of the SiO₂-capped Si nanocrystal sample is nearly equal to that of the as-prepared porous Si sample.

For PL measurements, Ar⁺, He-Ne or Ti:Al₂O₃ lasers were used as excitation sources. The typical excitation energy density was ~1 W/cm² and the modulated frequency was ~20 Hz. The PL spectra were dispersed by a 50-cm double-grating monochromator and detected by a photomultiplier. The samples were immersed in superfluid liquid He or mounted on the cold finger of a temperature-variable closed-cycle He gas cryostat during the measurements. The spectral sensitivity of the measuring system was calibrated by using a tungsten standard lamp.

Figure 1 shows typical PL spectra of H-terminated porous Si recorded at 7 K using excitation photon energies of (a) 1.785, (b) 1.587, (c) 1.564, and (d) 1.503 eV. Under 1.785-eV excitation, a broad PL band (full PL) is observed in the red and infrared spectral region and the peak energy is located near 1.5 eV. Resonant excitation at energies within the broad PL band results in fine structures in the spectrum.

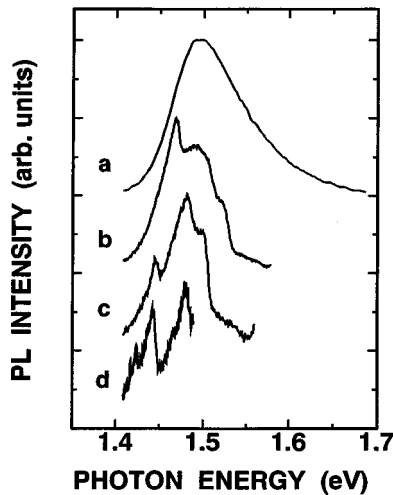


FIG. 1. Resonantly excited PL spectra of H-terminated porous Si at 7 K. The excitation photon energy is (a) 1.785, (b) 1.587, (c) 1.564, and (d) 1.503 eV.

Steplike structures are observed under resonant excitation of the high-energy side in the PL spectrum. With a decrease of excitation photon energy, the peak structure appears.

Figure 2 shows, in more detail, resonantly excited PL spectra of H-terminated porous Si using excitation photon energies of (a) 1.587, (b) 1.564, (c) 1.543, (d) 1.523, (e) 1.503, and (f) 1.489 eV, where the zero on the abscissa scale corresponds to the excitation energy. The arrows show the TA(Δ) and TO(Δ) phonon energies in bulk *c*-Si, where TA(Δ) and TO(Δ) are transverse acoustic and transverse optical phonons, respectively, at the conduction-band-minimum Δ point and the phonon energies of TA(Δ) and TO(Δ) are 18.5 and 57.5 meV, respectively.¹² The energies of peak and steplike structures are almost consistent with those of one phonon [TA(Δ) or TO(Δ)] and two phonons [TA(Δ +TO(Δ))

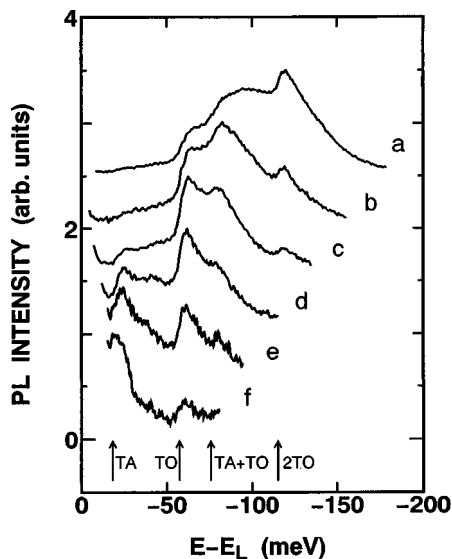


FIG. 2. PL spectra of H-terminated porous Si at the low-energy side of the excitation energies at 7 K: (a) 1.587, (b) 1.564, (c) 1.543, (d) 1.523, (e) 1.503, and (f) 1.489 eV. The TA(Δ) and TO(Δ) phonon energies of bulk crystalline Si are indicated by the vertical arrows.

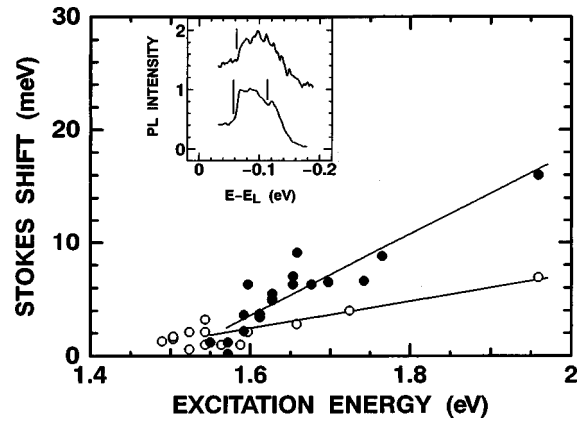


FIG. 3. Luminescence Stokes shift derived from resonantly excited PL spectra in H-terminated porous Si (\circ) and surface-oxidized Si nanocrystals (\bullet) as a function of excitation laser energy. The inset shows luminescence spectra of H-terminated porous Si (lower) and SiO₂-capped Si nanocrystals (upper) under 1.597-eV excitation.

or 2TO(Δ)]. This figure shows that the PL fine structures of H-terminated porous Si are related to TA- and TO-phonon-assisted luminescence, such as bulk *c*-Si. The Si nanocrystal is an indirect gap semiconductor and then the absorption and emission of momentum-conserving phonons are needed during the light absorption and emission processes.

With an increase of excitation energy, the TA and TO phonon structures shift to the lower energy and become unclear. There is small energy difference in TO-phonon-assisted luminescence between porous Si and bulk *c*-Si, as discussed in Ref. 3. The phonon peak and step structures at the lower-energy side of the excitation energy appear at ΔE_{PL} ,

$$\Delta E_{PL} = \Delta_S + nE_{TO}, \quad (1)$$

where E_{TO} is the TO-phonon energy in Si nanocrystals [$n = 1$ (one TO phonon) or $n = 2$ (two TO phonons)] and Δ_S is defined as the luminescence Stokes shift under resonant excitation. The energy position of TO-phonon assisted luminescence ΔE_{PL} depends on the excitation photon energy. It is considered that the excitation energy dependence of ΔE_{PL} reflects that of the luminescence Stokes shift Δ_S because the TO(Δ) phonon energy near the Brillouin zone edge is not sensitive to the nanocrystal size. Based on the above assumption, we estimated the excitation energy dependence of the luminescence Stokes shift Δ_S from that of TO-phonon-related structures in resonantly excited PL spectra. The luminescence Stokes shift Δ_S in H-terminated porous Si is summarized in Fig. 3. The luminescence Stokes shift of H-terminated porous Si is consistent with the onset energy or the forbidden gap in the previous experiment.³

The origin of the luminescence Stokes shift Δ_S has been discussed in terms of the exciton exchange splitting.^{3,9,10} With a decrease of the nanocrystals size, the exciton exchange energy increases and the triplet exciton becomes stable: The lowest excitonic state is split into the singlet ($S = 0$) and triplet ($S = 1$) states due to the exchange interaction between electrons and holes. At low temperatures, the light absorption occurs between the ground state and the upper singlet-exciton state and light emission occurs from the

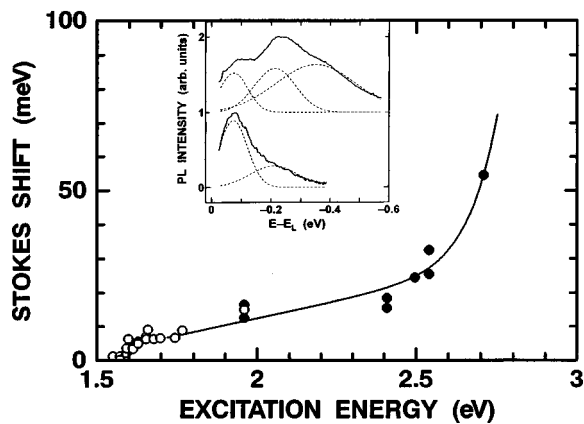


FIG. 4. Luminescence Stokes shift derived from resonantly excited PL spectra in oxidized Si nanocrystals as a function of excitation laser energy. The inset shows luminescence spectra of surface-oxidized Si nanocrystals under 1.959-eV (lower) and 2.409-eV (upper) excitation at 7 K.

lower triplet-exciton state. The exciton exchange splitting contributes to the luminescence Stokes shift. The calculated size dependence of the exchange energy¹⁰ is in rough agreement with that of the luminescence Stokes shift of H-terminated porous Si. TO-phonon structures are attributed to the interior *c*-Si state in H-terminated porous Si.

On the other hand, the phonon-related structures are sensitive to the surface structure of Si nanocrystals.^{11,13} As an example, the inset of Fig. 3 shows PL spectra in SiO₂-capped Si nanocrystals and H-terminated porous Si under 1.597-eV excitation. The phonon-related fine structures in SiO₂-capped Si nanocrystals and oxidized porous Si are unclear compared to the case of H-terminated porous Si. The Stokes shift in SiO₂-capped Si nanocrystals is also summarized in Fig. 3. At excitation energies higher than ~ 1.6 eV, the Stokes shift in SiO₂-capped Si nanocrystals is larger than that in H-terminated porous Si. This observation shows that the surface states affect the luminescence properties in smaller nanocrystals. In large nanocrystals, however, the surface states do not critically affect the PL process exhibiting infra-red PL.

Very small oxidized Si nanocrystals show efficient luminescence in the blue-green spectral region.² Under resonant excitation, broad luminescence spectra with multiplexes appear and are divided by the Gaussian bands, as shown in the inset of Fig. 4. The energy intervals between the Gaussian peaks $E_{\text{Si-O}}$ ($=135\text{--}140$ meV) correspond to the 1100-cm^{-1} Si-O-Si stretching mode.^{7,14} In this case, the PL peak position at the lower-energy side of the excitation laser is described as $\Delta E_{\text{PL}} = \Delta_{\text{Si-O}} + nE_{\text{Si-O}}$, where $n=0,1,2,3$. These results indicate that excitons are strongly localized at the Si/SiO₂ interface since the coupling of electronic and vibrational excitations dramatically increases with localization of excitons in smaller dimensions.¹⁴ When the luminescence shift $\Delta_{\text{Si-O}}$ is much larger than the TO-phonon energy of *c*-Si, the momentum-conserving TO-phonon emission occurs in the light-absorption process. It is believed that the value of $\Delta_{\text{Si-O}} - E_{\text{TO}}$ gives the luminescence Stokes shift because the resonantly excited PL spectrum reflects the light absorption process.⁴ The Stokes shift in the higher energy region

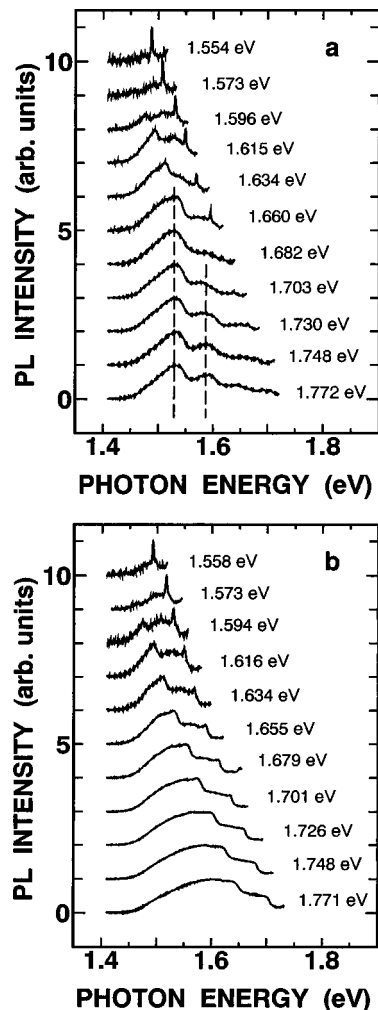


FIG. 5. Resonantly excited PL spectra of surface-oxidized porous Si (a) before and (b) after prolonged light illumination at 7 K.

($\Delta_{\text{Si-O}} - E_{\text{TO}}$) is summarized in Fig. 4. In oxidized Si nanocrystals, the luminescence Stokes shift estimated from the Si-O vibration structure (solid circles) is smoothly connected with that from the TO-phonon structure (open circles).

In SiO₂-capped Si nanocrystals, the phonon-related fine structures are unclear and the luminescence Stokes shift is large compared to the case of H-terminated porous Si. If the exciton is localized in the shallow localized states at the surface, the localization at the surface contributes to the Stokes shift. That is to say, the photogeneration occurs in the *c*-Si interior states (light-absorption process) and then the carriers are localized into the lower-energy tail states. The carriers localized in tail states can undergo radiative recombination through the formation of excitons (light-emission process). Moreover, in very small nanocrystals, the Si-O vibration structures are observed in resonant PL spectra. These observations suggest that shallow localized states are formed at the interface between the *c*-Si interior and the outer SiO₂ layer and the surface-localized states affect the luminescence properties in oxidized Si nanocrystals.

Surface-oxidized Si nanocrystals samples are obtained by oxidation of porous Si. Prolonged air exposure at room temperature converts the hydride surface of as-prepared samples to the native oxide surface of aged samples.^{7,15} After surface

oxidation, the surface of porous Si samples is covered by SiO₂ and oxyhydride SiO_xH_y compounds. The PL intensity increases (more than one order of magnitude) and the PL peak energy is blueshifted. Figure 5 shows resonantly excited PL spectra of oxidized porous Si. In this experiment, the porous Si samples of $\sim 1 \mu\text{m}$ thickness were chosen to provide a uniform optical excitation within the porous layer and a uniform native oxidation within the layer. Under lower photon energy excitation, the sharp peak is observed ~ 64 meV below the excitation laser energy, as shown in Figs. 5(a) and 5(b). This sharp peak is due to the LO(Γ) phonon Raman signal of the *c*-Si substrate.

Before PL measurements, the sample was kept in the dark at room temperature. Under resonant excitation, fine structures are clearly observed in a well-rested porous Si sample. At higher energy excitation above ~ 1.65 eV, a new structure appears near 1.6 eV and it does not depend on the excitation energy: The dashed-line peak structures in Fig. 5(a) are almost independent of the excitation energy. The energy interval between the peaks is equal to the TO-phonon energy. These features are similar to PL properties of defect-bound excitons in bulk *c*-Si.¹⁶ It has been pointed out theoretically that dehydrogenation creates midgap defect states due to dangling bonds.¹⁷ Therefore, it is considered that the size-independent luminescence near 1.6 eV is due to the defect luminescence in surface-oxidized porous Si.

After prolonged light illumination (in a light-soaked sample, 1-h illumination of ~ 5 W/cm², 1.772-eV laser light at 7 K), TO-phonon-related fine structures are clearly observed. With an increase of the excitation energy, the energy position of peak and step structures increases: In a light-soaked sample, all TO-phonon-related structures depend on the excitation energy. Since the radiative and nonradiative recombination lifetimes are so long at low temperatures,² the defect states are occupied by the photogenerated carriers and

the state filling in the deep and/or shallow defects occurs during prolonged light illumination at low temperatures. This experiment strongly suggests that the localized states with small state density are formed in oxidized porous Si.

Our experimental observations indicate that at higher energy above ~ 1.6 eV, the surface state affects luminescence properties in SiO₂-capped Si nanocrystals and surface-oxidized porous Si. Thus it is considered that oxygen-modified surface states provide the active states for efficient luminescence in the visible spectra region. Resonantly excited PL spectra suggest the coexistence of different PL processes in surface-oxidized porous Si samples. The PL mechanism of surface-oxidized porous Si is complicated, compared to the case of H-terminated porous Si. We believe that efficient luminescence comes from the oxygen-modified surface states, although other emission mechanisms are active in oxidized porous Si.

In conclusion, we have discussed luminescence Stokes shift and phonon-assisted luminescence in H-terminated and surface-oxidized Si nanocrystals by means of resonant excitation spectroscopy. In oxidized Si nanocrystals, the luminescence Stokes shift is large and the TO-phonon-related structures are unclear compared to the case of H-terminated Si nanocrystals. The oxygen-modified surface states affect luminescence properties in oxidized Si nanocrystals. Both the surface and interior *c*-Si states contribute to efficient PL in porous Si and Si nanocrystals.

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