Photoluminescence from Si/SiO$_2$ single quantum wells by selective excitation

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We have studied the photoluminescence (PL) mechanism of crystalline Si single quantum wells sandwiched between SiO$_2$ layers by site-selective excitation spectroscopy. The asymmetric PL spectrum is observed in the red spectral region at low temperatures and can be divided into two PL bands. The peak energy of the strong PL band is almost independent of the well thickness and appears near ~ 1.65 eV. Under selective excitation at energies within the weak PL band, TO-phonon structures are observed in both PL and PL polarization spectra. Steplike TO-phonon structure in the PL spectrum of two-dimensional Si quantum wells is similar to that of zero-dimensional Si nanocrystals. The PL properties of very thin Si quantum wells are discussed. [S0163-1829(97)51448-2]

The goal of achieving efficient visible luminescence from Si-based materials has stimulated considerable effort in understanding optical properties of Si nanostructures and producing nanostructure devices.[1] In particular, porous Si and Si nanocrystals, often called zero-dimensional (0D) Si quantum dots, are receiving widespread interest because of their high quantum efficiency of light emission. There are many extensive studies concerning the origin of visible light emission in porous Si and Si nanocrystals.[2] However, the mechanism of visible luminescence is still controversial, because porous Si and Si nanocrystals show various optical characteristics and their optical properties are sensitive to the surface chemistry of Si nanocrystals.[1,2] Therefore, well-characterized Si nanostructures are desirable for an understanding of photoluminescence (PL) mechanisms of porous Si and Si nanocrystals. Si nanostructures with SiO$_2$ surface layers 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. One approach to control Si/SiO$_2$ nanostructures is the fabrication of 2D quantum-well structures.

Very recently, an interesting type of Si-based quantum wells and superlattices, crystalline Si (c-Si)/SiO$_2$ and amorphous Si (a-Si)/SiO$_2$ systems, has been proposed (Ref. 3) and demonstrated.[4–7] These quantum wells show broad PL in the red spectral region at room temperature, similar to the case of SiO$_2$-capped Si nanocrystals.[8–10] These broad PL spectra suggest that 2D Si/SiO$_2$ quantum wells and superlattices are inhomogeneous systems and the inhomogeneously broaden PL spectrum will be due to the fluctuation of the 2D well thickness, strains in the wells, and structural variations of the interface between the Si well and SiO$_2$ barrier layers. In studying inhomogeneous materials, site-selective excitation spectroscopy is a powerful method to extract intrinsic properties from inhomogeneously broadened spectra.[11–13] Selectively excited luminescence spectra (or resonantly excited luminescence spectra) provide detailed information on the luminescence mechanism and exciton dynamics. It is expected that selective (or resonant) excitation may result in

fine structures in the PL spectrum of 2D c-Si systems, as in inhomogeneously broadened systems such as porous Si and Si nanocrystals.[10,13,14] In this work, we have studied luminescence properties of c-Si/SiO$_2$ single quantum wells by selective excitation spectroscopy. The experimental results indicate that the strong PL is ascribed to the radiative recombination in the Si-SiO$_2$ interface region, while the weak PL to the radiative recombination in the 2D Si quantum well.

The Si single quantum wells investigated here were formed on SIMOX (separation by implanted oxygen) wafers. SIMOX wafers were formed by implanting $^{16}O^+$ with a dose of 1.8×10^{18} cm^{-2} at 200 keV following by sintering at 1310 °C for 5 h and at 1350 °C for 40 h. High-dose implantation and long-period sintering in the high temperature of 1350 °C produce the very flat superficial Si layer on the SIMOX wafer, and these experimental conditions are essential for the production of the very flat Si layers.[4,15] The initial 140-nm superficial Si thickness was reduced to 3 nm or less by thermal oxidation at 900–1100 °C in dry oxygen ambient and etching with dilute HF solution. The 2D thin Si layers were formed between thin surface SiO$_2$ (~ 30 nm) and thick buried SiO$_2$ layers (~ 400 nm). Good crystalline quality in the Si layers was confirmed by the lattice image of transmission electron microscopy (TEM) and the reflectivity measurement. A typical TEM image of a 2.7 nm c-Si/SiO$_2$ single-quantum-well sample is shown in Fig. 1. The fluctuation of the Si layers was about 0.5 nm. In our samples used in this work, the c-Si well region is a single crystalline sheet (or sheetlike crystallite).

The PL spectra were detected by using a 50 cm double monochromator and a photomultiplier (Hamamatsu, R1477). The spectral sensitivity of our system was calibrated by using a tungsten standard lamp and the good spectral response was up to 880 nm. For the excitation sources, a 532-nm pumped Ti:sapphire laser (Spectra Physics, Millennia and 3900S) was used for the measurement of selectively excited PL spectra. Two experimental geometries were used. In the normal excitation geometry for the PL measurements, the
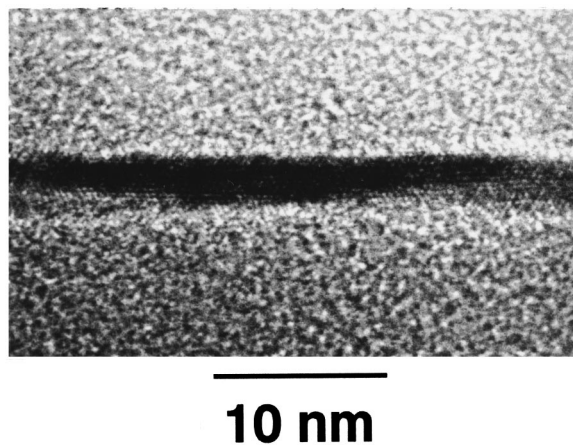
FIG. 1. Cross-section TEM image of a c-Si/SiO$_2$ single quantum well.

excitation light was normally incident on the sample surface. In the edge excitation geometry for the PL polarization measurements, the polarized excitation light was incident on a cleaved edge of the sample. The polarization of luminescence was determined by a polarizer and polarized luminescence was focused onto the entrance slit of a monochromator through a depolarizer. The samples were immersed in superfluid liquid helium or mounted on a cold finger in a closed-cycle helium gas cryostat during the measurements.

Figure 2 shows thickness dependence of PL spectra in 2D c-Si/SiO$_2$ systems under 488-nm laser excitation at 2 K. Efficient PL in the visible spectral region was observed in very thin well samples (<2 nm). The asymmetric PL spectra in the red and infrared spectral region can be fitted by two Gaussian bands, the weak PL band (denoted as **Q**) and the strong PL band (denoted as **I**), as shown in Fig. 2. The PL peak energy of the **I** band is almost independent of the well thickness and appears at $\sim$1.65 eV. Efficient 1.65 eV PL has been reported in 0D c-Si/SiO$_2$ nanocrystals.[8] In contrast, the peak energy of the **Q** band depends on the thickness of the c-Si well, and shifts to higher energy with a decrease of the
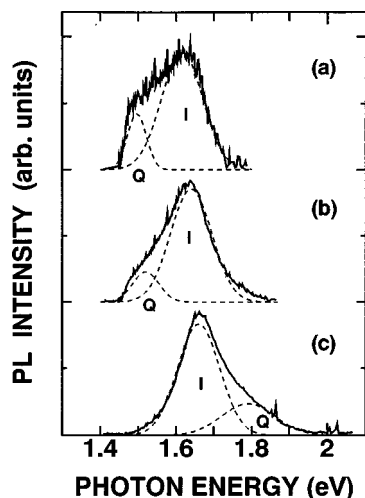

FIG. 2. Photoluminescence spectra of c-Si/SiO$_2$ single quantum wells under 488 nm laser excitation at 2 K: (a) 1.7, (b) 1.3, and (c) 0.6 nm thickness. The asymmetric PL spectra can be fitted by two Gaussian bands, the weak **Q** band and the strong **I** band.
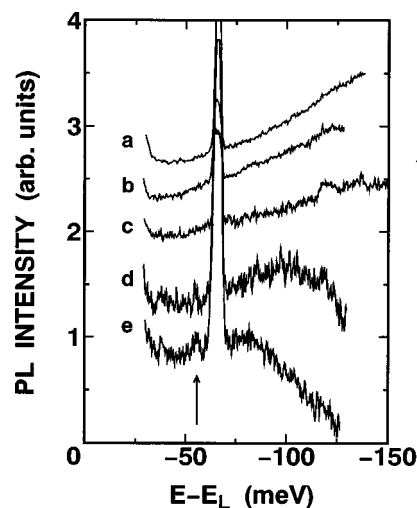

FIG. 3. Selectively excited luminescence spectra for the 1.7-nm Si well thickness of the Si/SiO$_2$ quantum well under various excitation photon energies at 7 K: (a) 1.769, (b) 1.697, (c) 1.630, (d) 1.588, and (e) 1.568 eV. The zero on the abscissa scale corresponds to the laser excitation energies. The arrow indicates a peak structure within the broad PL spectrum.

Si well thickness [from Fig. 2(a) to 2(c)]. This implies that the quantum confinement state in c-Si wells (Refs. 16 and 17) plays a key role in the **Q** band luminescence. In order to clarify the PL origin of the weak **Q** and strong **I** bands, we measured PL spectra under selective excitation at energies within the **Q** or **I** band.

Figure 3 shows selectively excited PL spectra for the 1.7-nm Si well thickness of Si/SiO$_2$ quantum well under the various excitation photon energies at 7 K: (a) 1.769 eV, (b) 1.697 eV, (c) 1.630 eV, (d) 1.588 eV, and (e) 1.568 eV. The zero on the abscissa scale corresponds to the laser excitation energies. In this sample, the weak **Q** band appears at $\sim$1.5 eV and the main PL peak is located at $\sim$1.65 eV, as shown in Fig. 2(a). Under laser excitation above $\sim$1.65 eV (the higher-energy side of the main PL peak), there is no fine structure in the PL spectrum and the PL spectrum is broad. On the other hand, under resonant excitation at the lower-energy side of the PL peak (curves d and e), there appears a peak in the broad PL spectrum, as indicated by the arrow in the figure. The peak position of $\sim$56 meV is almost equal to the 57.4-meV TO(Δ)-phonon energy at the conduction-band minimum, close to the X points, in bulk c-Si.[18,19] Then, we speculate that this peak is related to the momentum-conversing TO-phonon-assisted luminescence in c-Si wells. The intensity of TO-phonon-related luminescence is so weak compared with that of the LO(Γ)-phonon Raman signal from c-Si substrate ($\sim$64.5 meV), since the number of the absorbed photons in 2D c-Si wells is much smaller than that in the c-Si substrate.

In thick well samples, the PL efficiency of the **Q** band is quite low under the laser excitation lower than $\sim$1.65 eV (the lower-energy side of the **I** band) and the **Q** and **I** bands are overlapped in the spectral region. Then, it is difficult to observe the TO-phonon-related structure clearly under selective excitation of the **Q** band in thick well samples. We need to study fine structures in the **Q** band in very thin well samples, since the PL intensity increases with a decrease of
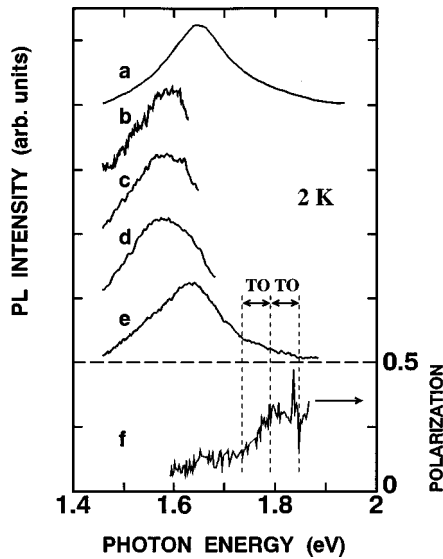
FIG. 4. Selectively excited photoluminescence and photoluminescence polarization spectra for the 0.6-nm Si well thickness of the Si/SiO$_2$ quantum well under the various excitation photon energies at 2 K: (a) 2.540 eV (full luminescence), (b) 1.658, (c) 1.687, (d) 1.724, and (e) and (f) 1.959 eV. Under selective excitation at energy within the **Q** band, TO-phonon-related structure is observed in both luminescence and luminescence polarization spectra.

the well thickness and the **Q** band is apart from the 1.65-eV peak of the **I** band.

Figure 4 shows selectively excited PL spectra for the 0.6-nm Si well thickness of the Si/SiO$_2$ quantum well at 2 K. Under blue laser excitation, the asymmetric PL consisting of the **Q** and **I** bands is observed in the red spectral region (curve *a*). No *c*-Si phonon-related structures are observed when selective excitation at energies within the **I** band, as shown in curves *b-d* in Fig. 4. It is concluded that the broad and size-insensitive **I** band PL (strong luminescence at ~1.65 eV) is caused by radiative recombination in the localized interface state between *c*-Si and SiO$_2$.

On the other hand, under selective excitation within the **Q** band, a steplike structure is observed (curve *e*). The energy positions of the steplike structure are shown by the vertical broken lines in the figure. We also measured the luminescence polarization spectrum of cleaved samples. The degree of linear polarization of luminescence is defined as, $\rho = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$, where $I_\parallel (I_\perp)$ is the intensity of the PL polarized parallel (perpendicular) to the polarization of the excitation laser light and the polarization of the excitation laser is parallel to the unconfinement direction in the cleavage plane. We show the polarization ρ spectrum in Fig. 4 (curve *f*). When the PL photon energy approaches the excitation laser energy, ρ becomes larger. It is considered that a high and positive value of ρ in the **Q** band is caused by dielectric effects and/or the anisotropy of luminescence state. On the other hand, when selective excitation within the **I** band, the polarization degree also shows a small positive value, but the TO–phonon-related structure is not observed. Then, the fine structure in the PL polarization memory spectrum (curve *f*) strongly suggests the **Q**-band PL originating from optically anisotropic 2D quantum wells, as will be discussed below.

There is a good correlation between the resonant PL and PL polarization spectra in the **Q** band. With an increase of

the energy difference between the PL energy and excitation laser energy, the polarization degree ρ decreases and the intensity of the featureless broad PL increases. The polarization ρ shows higher values in the **Q** band and decreases due to the carrier scattering in the **Q** band and the overlapping of the **Q** and **I** band. At the TO-phonon energies, the polarization degree ρ also changes. At low temperatures, the momentum-conserving TO phonons are emitted in both the light absorption and light emission processes. Therefore, the TO-phonon-related structure is observed in indirect-gap semiconductor quantum wells. TO-phonon-related fine structures in the resonant PL spectrum and the PL polarization spectrum show that the **Q**-band PL is related to the size-quantified states of 2D wells showing an indirect optical-transition nature.

The steplike TO-phonon structure in the selectively excited PL spectrum and the TO-phonon steps in the PL polarization spectrum in 2D *c*-Si wells are very similar to those in 0D Si nanocrystals and porous Si.[10,13] It has been reported that in 0D nanocrystals the steplike structure in the selectively excited PL spectrum reflects the phonon-assisted absorption process rather than the phonon-assisted light emission process.[20] The spectral dependence of the absorption coefficient in the vicinity of the band gap in 0D Si nanocrystals is given by the expression for bulk *c*-Si.[20] From similar phonon structures in 2D and 0D structures, we suppose that the absorption spectrum in 2D structures is similar to that in the bulk *c*-Si and 0D Si nanocrystals. In fact, in 2D Si/Ge superlattices, the observed spectral dependence of the absorption coefficient can be fitted by the expression for the indirect-gap semiconductors in the bulk.[21] In *c*-Si, the *p*-type conduction band near the Δ point has a large density of states and phonon-assisted optical transitions cause overlapping of the optical transitions. Then, the quantized optical spectrum will appear continuous and similar featureless absorption spectra are experimentally observed in low-dimensional Si materials. Further experimental and theoretical studied are needed for quantitative discussion regarding the origin of the phonon related structure in 2D and 0D Si quantum structures.

In conclusion, we have studied the PL mechanism of single-crystalline Si single quantum wells sandwiched between SiO$_2$ layers by site-selective excitation spectroscopy. From selectively excited PL and PL polarization spectra, we concluded that both the Si-SiO$_2$ interface states and the quantum confinement states play a role in the radiative recombination. We have demonstrated that site-selective excitation spectroscopy is a powerful method to clarify the PL mechanism of Si nanostructures.

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