Photoluminescent spectrum and dynamics of Si$^+$-ion-implanted and thermally annealed SiO$_2$ glasses

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We have experimentally studied the photoluminescent (PL) properties of Si clusters in fused silica matrices. Si clusters in the SiO$_2$ matrices were fabricated by Si$^+$-ion implantation (200 keV, 2×10^{17} cm^{-2}) into silica and then thermally annealed in forming gas. A broad PL peak is observed in the visible spectral region at room temperature. The temperature dependence of the luminescent spectrum and the PL decay dynamics are controlled by nonradiative recombination processes due to phonon-assisted tunneling between localized radiative and nonradiative centers. Resonantly excited PL spectra indicate that the strong coupling of excitons and stretching vibrations of the Si-O bonds cause fine structures in the luminescent spectra. It is concluded that the interaction between electronic and vibrational excitations control the luminescent emission and the observed dynamics. [S0163-1829(96)50244-4]

The goal of achieving efficient visible luminescence from Si nanocrystals has stimulated considerable research in understanding the optical properties of group-IV semiconductor nanocrystals with possible applications being the production of novel nanocrystal devices.[1–4] A size reduction to a few nanometers is required for the observation of visible light emission from Si nanocrystals when the band structure is modified from that of bulk Si, which has an indirect gap of 1.1 eV. It has been suggested that in semiconductor nanocrystals, quantum confinement effects play an essential role in controlling the optical absorption and luminescent processes. However, experimental observation of the photoluminescence (PL) wavelengths from oxidized Si nanocrystals and porous Si do not show the dependence on size which is expected from simple quantum confinement.[5,6]

The large surface-to-volume ratios of Si nanocrystals are expected to enhance surface effects to the extent that the PL peak wavelength (Ref. 7), the PL intensity (Ref. 8) and the fine structures in the PL spectrum at low temperatures (Ref. 9) will be modified by the surface chemistry of the Si nanocrystals, particularly with regard to the amounts of oxygen and hydrogen on the surfaces. Although there are many extensive studies concerning the origin of visible light emission, the mechanism of visible luminescence in Si nanocrystals and porous Si is still not clear.

In order to investigate the luminescence from of Si nanostructures, we need to fabricate Si nanostructures with near identical and stable surfaces. Silicon nanocrystals and clusters embedded in a SiO$_2$ matrix offer 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. Silicon nanocrystals in the SiO$_2$ system have been produced by ion-implantation and thermal annealing techniques.[10,11] Ion implantation can be used to create supersaturated Si solid solutions whilst the thermal annealing provides energy that drives the system to a two phase (Si/SiO$_2$) state. Very recently, continuously tunable PL from ultraviolet to infrared wavelengths has been reported from Si clusters in SiO$_2$ fabricated by ion implantation and thermal annealing.[12] These films exhibit size related and tunable PL spectra and detailed optical studies provide ongoing discussion for the understanding of the complicated mechanisms responsible for the luminescence both from Si nanocrystals and porous Si.

In this paper we discuss the PL properties of Si$^+$-implanted and annealed commercially available fused silica substrates. The sample temperature and excitation energy dependence of the PL spectra are presented and the data is interpreted in terms of phonon-assisted tunnelling between localized defect sites or coupling of excitons and Si/SiO$_2$ interfacial vibrations.

The substrates used in this work were commercially available fused silica glass of 1 mm thickness. All the samples used in these experiments were prepared by implanting at room temperature a dose of 2×10^{17}-cm^{-2}, 200-keV ^{28}Si$^+$ ions followed by lamp annealing [900 °C in forming gas (10% H$_2$+90% N$_2$) for 3 min].[13] The PL intensities in samples in forming gas were much higher than those annealed in N$_2$ gas. The thermal annealing in forming gas reduces the number of nonradiative recombination centers.[12,13]

The PL spectra were excited by using Cd-He, He-Ne, Ar, and Ti:Al$_2$O$_3$ lasers. The measurement temperature was varied from 2 to 300 K in a cryostat. Time-resolved PL spectra, where the emission was stimulated by 2-ps pulses from a 380-nm laser line (Spectra Physics, Tsunami 3960C-L25), were measured using a synchroscan streak camera (Hamamatsu, C1587). The spectral sensitivity was calibrated by using a tungsten standard lamp and the time resolution was 20 ps.
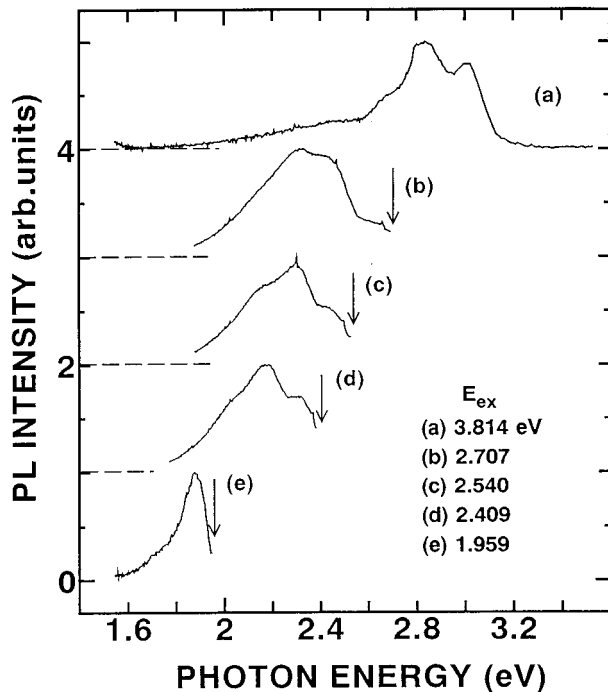
FIG. 1. Photoluminescent spectra from Si^+-implanted and thermally annealed silica films stimulated by photon energies of (a) 3.814 eV at 18 K, (b) 2.707 eV at 18 K, (c) 2.540 eV at 18 K, (d) 2.409 eV at 18 K, and (e) 1.959 eV at 2 K. The vertical arrows indicate the photon energies of the excitation radiation.

Figure 1 shows typical PL spectra recorded at 18 and 2 K using excitation photon energies of 3.814 (a), 2.707 (b), 2.540 (c), 2.409 (d), and 1.959 eV (e). A broad PL peak, which shifts to higher energy with increasing excitation energy, is evident in each case. The energy interval (Stokes shift) between the energy of excitation and peak emission also increases monotonically. In each case, the spectra show fine structure that is in contrast to the featureless, Gaussian-like peaks recorded from these samples at room temperature.[11,13]

Figure 2 shows, in more detail, spectra recorded at 18 K using excitation photon energies of 2.540 (curve a), 2.409 (curve b), and 2.330 eV (curve c) where the zero on the abscissa scale corresponds to the excitation energy. A curve fitting program has been used to generate the Gaussian components, which are shown as dashed curves. The energy interval (Stokes shift, E_s) between the excitation energy and the highest calculated energy PL peak is indicated in the figure. It is evident that the Stokes shift depends on the excitation energy and is appreciably larger than the exciton splitting energy.[14–17] We conclude that the large Stokes shift is mainly caused by exciton-phonon interactions.[16,17] The experimental values of the spacing between the Gaussian peaks (horizontal arrows in the figure) are approximately 135–140 meV, which is much larger than the reported energy of 57 meV of TO phonons in crystalline silicon.[14,15] This large difference cannot be explained simply by the exciton-phonon coupling in the Si crystallites as excitons are highly delocalized within the nanocrystals, and fine structures do not correspond to phonon spectra in bulk Si. Instead, this energy is almost equal to the local vibration energy of the Si-O stretch mode ($\sim 1100 \text{ cm}^{-1}$).[18] The coupling of excitons and surface
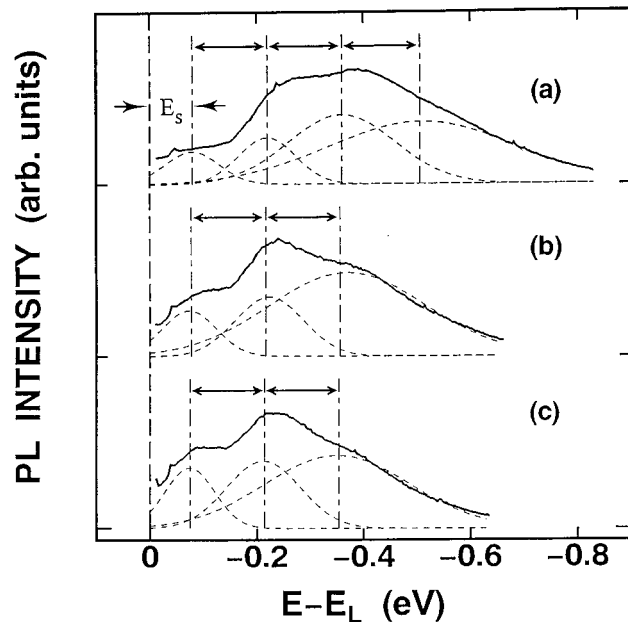

FIG. 2. Photoluminescent spectra from Si^+-implanted and thermally annealed silica samples at the low-energy side of the excitation energies at 18 K: (a) 2.540, (b) 2.409, and (c) 2.330 eV. The dotted lines show the Gaussian components of the experimental data. The peak energies are identified by the vertical broken lines.

silicon oxide vibrations are expected to increase with localization of excitons in smaller dimensions. These fine structures were clearly observed at high temperatures up to 250 K, although the phonon-related structures in porous Si are only observed at low temperatures below ~ 100 K.[15,19] Luminescent properties of the nanocrystals in these Si^+-implanted silica samples resemble, more closely, the emissions from molecules rather than a solid, which we propose is due to the strong coupling of excitons and local vibrations, which are usually observed in isolated small molecules at room temperature.[20]

Figure 3 shows the temperature dependence of the integrated PL intensity which is recorded from a sample under 2.707 eV excitation, see curve (b) in Fig. 1. The PL intensity gradually decreases with increasing temperature. The temperature dependence of the lattice-relaxed luminescence has usually been understood in terms of the adiabatic potential model where excitons first relax to the local minimum of the potential for the excited states and then drop back to the ground state by radiative or nonradiative recombination processes.[21] Under these conditions, the temperature dependence of the luminescent intensity $I(T)$ is described by the relation

$$I(T) \propto R_r / [R_r + R_{nr} \exp(-W/kT)], \qquad (1)$$

where R_r is the radiative recombination rate, R_{nr} the nonradiative recombination rate, and W is the height of the potential for the nonradiative process. This conventional relation is not applicable to the explanation of our observation. On the other hand, Street[22] proposed a phonon-assisted tunnelling model for a-Si:H in which the luminescent intensity is controlled by nonradiative processes when the following simple relation is obtained:

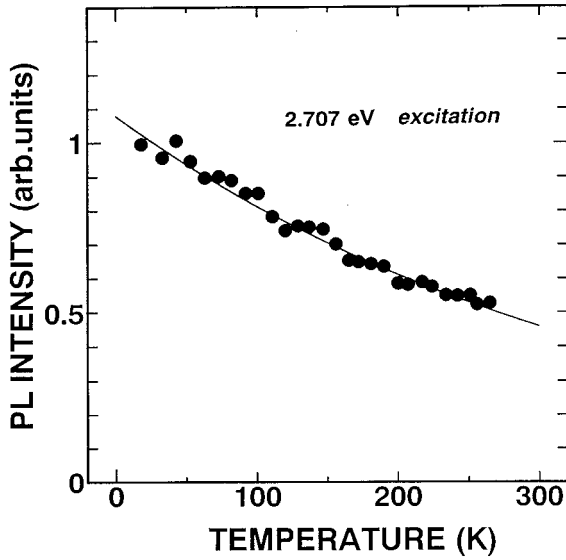FIG. 3. Temperature dependence of the photoluminescent intensity from a Si$^+$-implanted and thermally annealed silica film under 2.707 eV laser excitation. The solid line shows the theoretical dependence based on the street model.
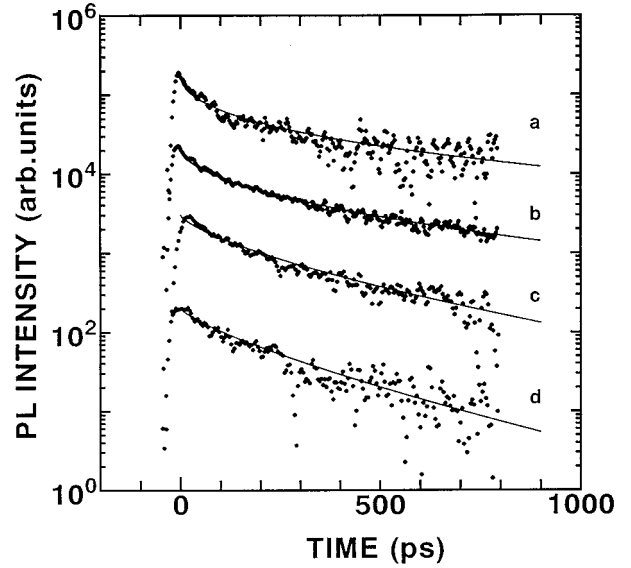

FIG. 4. Picosecond luminescence decay profiles measured at 77 K: (a) 390, (b) 440, (c) 550, and (d) 600 nm. The overall shape of the decay curve is insensitive to temperature. The PL lifetime increases with increasing monitored wavelength.

$$I(T) \propto R_r/[R_r + R_{nr} \exp(T/T_0)], \qquad (2)$$

where T_0 is the characteristic temperature. Using the above equation, we can fit the temperature dependence of the luminescent intensity, where $R_{nr}/R_r = 21.8$ and $T_0 = 340$ K as shown by the solid line in Fig. 3. In this model the excitons undergo the phonon-assisted tunnelling from the radiative recombination centers to the nonradiative centers. The PL intensity is determined both by the localization of excitons and nonradiative processes.

Moreover, the PL decay profiles are nonexponential even at low temperatures, as shown in Fig. 4, and they are well described by a stretched exponential function,

$$I(t) = I_0 \exp[-(t/\tau)^\beta], \qquad (3)$$

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 Fig. 4 are given by the above function and the value of the decay time τ can be determined using a least-squares fitting of the data. The values of τ range from 80 to 170 ps. It is noted that the lifetime in these Si$^+$-implanted silica films is much shorter than the measured lifetime of porous Si and surface-oxidized Si nanocrystals.[5] The fast PL decay, in the picosecond time region, is determined by the nonradiative recombination decay rate. This stretched exponential decay is usually observed in the PL decay and transport properties of disordered systems.[5,22] The temperature dependence of the PL intensity and the nonexponential PL decay provide strong evidence for the localization of excitons in small dimensions which supports the proposal that phonon-assisted nonradiative processes are controlling the PL properties of these implanted silica.

In porous Si, steplike phonon structures, due to TO phonons, are clearly observed at low temperatures (<70 K), by reducing the excitation laser energy below 2 eV (resonant excitation).[9,14,15,19] The steplike structures suggest that the ~3-nm Si nanocrystal is an indirect-gap semiconductor. The

theoretical calculations suggest that the steplike structures reflect the phonon-assisted absorption process rather than the light emission process.[15] In porous silicon, the visible luminescence is observed after high-level vibration excitation in the Si-O-Si and/or SiH$_x$ vibration bands.[23,24] These experiments clearly show that the surface state and the phonon-assisted processes play an important role in the absorption and PL excitation processes. However, these c-Si phonon-related and steplike PL structures under resonance excitation are not observed in this work.[25] Instead, the peak structures in the PL spectrum are clearly observed in Si clusters in SiO$_2$ glass under resonance excitations, as shown in Fig. 2. These peak structures are clear evidence that the exciton and Si-O vibrational coupling dominate the luminescent process in smaller dimensions. Our results are in good agreement with how the peak structure would appear in the PL spectra if the phonon-assisted luminescent process determines the phonon structures.[14,15] Then, the peak structures in the PL spectrum show that the interaction between electronic and vibrational excitations is important in the luminescence processes in small Si clusters. Since the Si-O bond is polar, the coupling of excitons and stretch vibrations of surface species increase with localization of excitons in smaller dimensions. The relative strength between Fröhlich and deformation-potential contributions depends strongly on the size of nanocrystals and clusters.[26] In particular, in non-polar Si and Ge nanocrystals, the interaction strength between excitons and vibrations depends on either polar (Si-O bonding) or nonpolar (Si-H bonding) surface structures. The exciton-phonon interaction increases with decreases in the size of Si nanocrystals and clusters with polar bonding. Resonantly excited PL spectra of Si nanostructures would reveal visible luminescent mechanism of Si quantum structures and materials.

We have studied the dynamics and spectroscopy of Si$^+$-implanted SiO$_2$ and fused silica. Luminescent properties

are understood in terms of the localization of excitons in very small dimensions. The coupling of excitons and polar Si-O-Si vibrations cause fine structures in the luminescent spectra. This experiment is the first evidence that the interaction between excitons and Si-O vibrations in the cluster-matrix interface dominate the luminescent properties of Si clusters and nanocrystals.

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