

## Photoluminescence properties of surface-oxidized Ge nanocrystals: Surface localization of excitons

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We have studied photoluminescence (PL) properties of surface-oxidized Ge nanocrystals with a 3.7 nm diameter. A difference between the absorption and PL excitation spectra and time-resolved PL measurements show that the site for the radiative recombination of excitons is different from that for the photogeneration of excitons. From fine structures in resonantly excited PL spectra at low temperatures, we concluded that excitons are localized on the surface of Ge nanocrystals and that the strong coupling of excitons with local vibrations of germanium oxides at the surface cause these fine structures. [S0163-1829(96)02347-8]

Recently, the discovery of efficient photoluminescence (PL) from Si (Ref. 1 and 2) and Ge nanocrystals (Ref. 3) at room temperature has stimulated considerable efforts in understanding optical properties of indirect-gap group-IV semiconductor nanocrystals.<sup>4</sup> In semiconductor nanocrystals (or zero-dimensional quantum dots), the band gap increases with decreasing diameter of nanocrystals, and electronic states become discrete with high oscillator strength.<sup>5</sup> Quantum confinement effects play an essential role in optical absorption and luminescence processes in nanocrystals. However, the emission wavelength in Si nanocrystals does not show the dependence on size expected from simple quantum confinement models.<sup>6</sup> With large surface-to-volume ratios, surface electronic states affect luminescence properties of Si nanocrystals.<sup>7,8</sup> The luminescence mechanism of Si nanocrystals is not clear.

The bulk Ge has a larger dielectric constant and smaller carrier masses compared to the bulk Si. Moreover, in Ge, the direct gap ( $E_0 \sim 0.88$  eV) is close to the indirect gap ( $E_g \sim 0.75$  eV).<sup>9</sup> Then, it is considered that quantum confinement effects would appear more pronounced in Ge than in Si, and Ge nanocrystals would exhibit a direct-gap semiconductor nature.<sup>10,11</sup> In this paper, we discuss visible luminescence properties of surface-oxidized Ge nanocrystals. Excitons are localized near the surface region and the strong coupling of localized excitons and local stretch vibrations of surface species cause fine structures in the PL spectrum. To our knowledge, PL spectra modified by local vibrations at the surface have never been reported in nanocrystals.

Light-emitting Ge nanocrystal samples were prepared by rf-magnetron cosputtering of Ge and SiO<sub>2</sub>, as described in Ref. 3. Thin films of the mixture of Ge and SiO<sub>2</sub> were deposited onto Si or fused silica glass substrates, and then annealed in an Ar gas atmosphere for 30 min at 300 °C in order to grow Ge nanocrystals in glassy matrices and to control the size of Ge nanocrystals. The size of Ge nanocrystals in glassy matrices was studied using a high-resolution electron microscopy using a JELO 2010 system operated at 200 keV. The average diameter of Ge nanocrystals in samples was 3.7 nm. To confirm the composition of the interface between Ge nanocrystals and glassy matrices, we analyzed samples by x-ray photoemission spectroscopy (XPS) at a base pressure of  $2 \times 10^{-8}$  Torr, using a Perkin-Elmer 5500 system. A scan

of the germanium  $2p_{3/2}$  region in the sample is shown in Fig. 1. This spectrum can be fitted by three bands of Ge, GeO<sub>2</sub>, and GeO.<sup>12</sup> Germanium suboxides, GeO<sub>x</sub> are formed at the interface between Ge nanocrystals and glassy matrices: Surface-oxidized Ge nanocrystals (Ge nanocrystals with germanium oxides surface layer) are prepared.

Figure 2 shows optical absorption, PL, and PL excitation spectra from oxidized Ge nanocrystals at room temperature. The PL spectrum was measured under 2.540-eV laser excitation. The calibration for the spectral sensitivity of the measuring system was performed by using a tungsten standard lamp. Excitation spectra of luminescence at the PL peak energy were measured by using a Xe lamp and a monochromator. Peaks in the PL and PL excitation spectra appear around 2.25 and 2.35 eV, respectively. The peak energy of the PL excitation spectrum is close to the PL peak energy. Moreover, the onset of the absorption spectrum is observed near 2.4 eV, and it corresponds to the peak energy of the PL excitation spectrum.

A theoretical calculation<sup>10</sup> shows that the indirect band-gap energy of Ge nanocrystals is very sensitive to the size of nanocrystals. The calculated band-gap energy of 4-nm Ge nanocrystals is  $\sim 2.3$  eV,<sup>10</sup> which approximately corresponds to the peak energy of the PL excitation spectrum and the

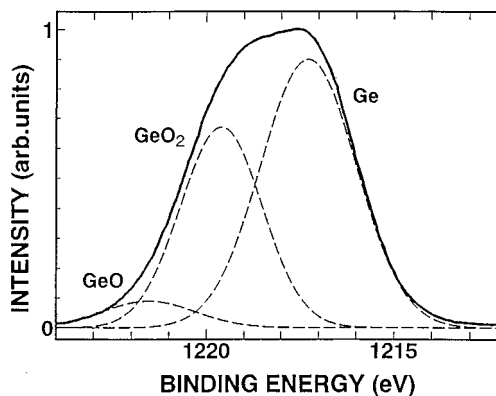


FIG. 1. X-ray photoemission spectrum of the germanium  $2p_{3/2}$  region in surface-oxidized 3.7-nm Ge nanocrystal. Germanium oxides, GeO<sub>2</sub>, or GeO are formed at the surface of Ge nanocrystals.

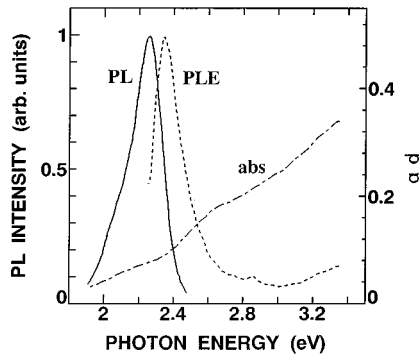


FIG. 2. Optical absorption (abs, dash-dotted line), photoluminescence (PL, solid line), and photoluminescence excitation (PLE, broken line) spectra in Ge nanocrystals at room temperature. The luminescence peak energy is close to the peak energy of luminescence excitation spectrum. The onset of the absorption spectrum is observed near the peak of the luminescence excitation spectrum. Peaks of the PL and PL excitation spectra in Ge nanocrystals appear around direct transitions in the bulk Ge.

onset of absorption spectrum. However, the peak energy of PL excitation spectrum does not depend on the size of nanocrystals.<sup>3</sup> The observed size dependence of PL and PL excitation spectra is not consistent with the calculated size dependence of the indirect band-gap energy. Moreover, in indirect semiconductor Si nanocrystals, featureless absorption and PL excitation spectra were observed in the near-infrared and visible regions,<sup>13,14</sup> because the indirect-gap energy ( $E_g \sim 1.1$  eV) is quite far from the direct-gap transition ( $E'_0 \sim 3.2$  eV) and phonon-assisted optical transitions cause the overlapping of optical transitions in Si nanocrystals.<sup>14,15</sup> Instead, the clear peak of the PL excitation spectrum and a relationship between the PL spectrum and the PL excitation spectrum in Ge nanocrystals are similar to those in direct-gap-semiconductor CdSe nanocrystals (Ref. 16) rather than indirect-gap semiconductor Si nanocrystals. In bulk Ge, the direct transitions of  $E_1$  and  $E_1 + \Delta_1$  are 2.25 and 2.43 eV, respectively, at 10 K.<sup>17</sup> The peaks of the PL and PL excitation spectra in Fig. 2 appear near the direct transitions of  $E_1$  and  $E_1 + \Delta_1$ . The peak energies of these direct transitions are not sensitive to the size of nanocrystals, because the electron and hole have the same mass and the valence and conduction bands are parallel in the band structure. In larger Ge nanocrystals (6 and 11 nm), similar structures in the absorption spectra were observed near 2 eV.<sup>11</sup> Then, it is considered that the direct optical transition plays a dominant role in determining the absorption and PL excitation spectra near the blueshifted band edge in Ge nanocrystals, although the direct-transition gaps are close to the indirect band gap in 3.7-nm nanocrystals. The onset of the absorption spectrum and the peak of the PL excitation spectrum in Ge nanocrystals can be explained by direct transitions in the bulk Ge.

It is noted that there is a difference between the absorption and PL excitation spectra and the PL efficiency is very low under excitation higher than  $\sim 2.8$  eV. This result implies that the electronic processes from the photoabsorption to light emission are complicated. Here, we consider the sample inhomogeneity such as the nanocrystal size distribution. The visible PL comes from small nanocrystals whose

band-gap energies are larger than the PL peak energy. However, optical absorption occurs even in nanocrystals with large dimensions. Furthermore, in our samples, surface-oxidized Ge nanocrystals are embedded in  $\text{SiO}_2$  glassy matrices. The optical absorption and the light scattering in  $\alpha\text{-SiO}_2$  matrices affect the transmission spectrum at a higher-energy region. Then, the sample inhomogeneity and composite are a possible origin of the difference between the absorption and PL excitation spectra. However, the large decrease in the PL excitation spectrum at an energy above 2.8 eV cannot be explained by the sample inhomogeneity only, because inhomogeneous samples such as porous Si and surface-oxidized Si nanocrystals did not show a drastic difference between the absorption and PL excitation spectra. This difference between the absorption and PL excitation spectra suggests that the site for the radiative recombination of excitons is different from that for the photogeneration of excitons, as will be discussed later. We measured PL dynamics in Ge nanocrystals to understand electronic processes from absorption to light emission.

Figure 3 shows temperature and wavelength dependence of picosecond PL decay profiles. Picosecond luminescence decay under a 200-ps and 2.409-eV laser excitation was measured using a monochromator of subtractive dispersion and a synchroscan streak camera. The luminescence decay was approximately described as a single exponential having a time constant of  $\sim 850$  ps at room temperature and  $\sim 1$  ns at 4.2 K. Although the PL lifetime slightly decreases with increasing temperature and wavelength, PL decay profiles are not sensitive to the measurement temperature and monitored wavelength, compared to Si nanocrystals. The PL quantum efficiency is 0.5% at room temperature and 0.9% at 4.2 K, where the PL quantum efficiency is estimated by direct comparison with dye luminescence. From the PL lifetime ( $\tau_{\text{PL}}$ ) and the PL efficiency ( $\eta$ ), we can estimate that the radiative decay rate ( $\eta/\tau_{\text{PL}}$ ) is  $\sim 10^7$  s<sup>-1</sup> and is independent of temperature. The estimated radiative decay rate is much larger than the calculated rate in the indirect transition in Ge nanocrystals<sup>10</sup> and observed PL lifetime in porous Si.<sup>6</sup>

If the PL processes are determined by the indirect-gap nature of Ge nanocrystals, the PL decay time depends strongly on the nanocrystals size (i.e., the monitored PL wavelength) and the measurement temperature. However, no significant wavelength and temperature dependence of the PL decay profiles are observed. Picosecond PL decay measurements suggest that PL properties reflect nonradiative recombination processes rather than the radiative recombination process in the interior state of Ge nanocrystals. In semiconductor nanocrystals, a considerable modification of the electron relaxation process occurs. Phonon bottleneck phenomena affect the thermalization and relaxation of electrons excited at the upper quantized states in zero-dimensional quantum dots.<sup>18</sup> Slow relaxation mechanism from the upper states to the lowest excited state would decrease the luminescence efficiency in nanocrystals, because the nonradiative channels are efficient on a picosecond time scale. Moreover, with large surface-to-volume ratios, surface nonradiative recombination centers strongly affect the luminescence processes in nanocrystals. Under excitation of higher states (e.g., UV laser excitation), there are many different paths for the nonradiative recombination processes

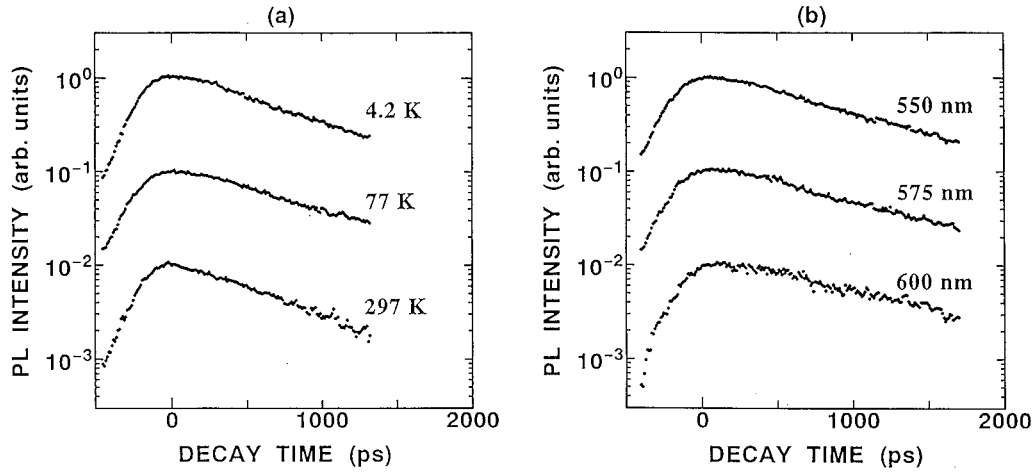


FIG. 3. (a) Picosecond luminescence decay at 530 nm in Ge nanocrystals at 4.2, 77, and 297 K. (b) Picosecond luminescence decay at room temperature in Ge nanocrystals at different wavelengths of 550, 575, and 600 nm. The temporal decay is approximately described by a single exponential. The luminescence decay profiles are not sensitive to the measurement temperature and monitored wavelength.

and the PL efficiency is low. The fast nonradiative recombination processes cause the difference between the absorption and PL excitation spectra. Only resonant excitation of the lowest excited states in Ge nanocrystals causes highly efficient PL. In surface-oxidized Ge nanocrystals, the nonradiative recombination processes determine the PL dynamics and PL excitation spectra.

In order to clarify the mechanism of visible luminescence in Ge nanocrystals, we applied site-selective excitation spectroscopy to Ge nanocrystals. Site-selective excitation spectroscopy is a powerful method to extract individual and intrinsic information from an inhomogeneously broadened spectrum and has successfully been applied to CuCl (Ref. 19), Si (Ref. 20), and CdSe (Ref. 21) nanocrystals. We observed well-resolved fine structures in luminescence spectra in our samples.

The excitation-energy dependence of the PL spectrum in Ge nanocrystals at 2 K is summarized in Fig. 4. Fine structures are observed at low temperatures only. When the excitation photon energy is above 2.4 eV, the PL peak energy stays almost constant and appears around 2.25 eV. The peak energies of fine structures are estimated by using Gaussian functions and the broken lines are Gaussian profiles. A spacing between the PL peaks of Gaussian profiles is  $\sim 110$  meV, and is much larger than the phonon energies of crystalline Ge. Instead, this energy is almost equal to the local vibration energy of the Ge-O-Ge stretch mode ( $\sim 900$   $\text{cm}^{-1}$ ).<sup>22</sup> This fact also confirms that the PL properties of surface-oxidized Ge nanocrystals reflect the intrinsic interior state of Ge nanocrystals. To our knowledge, this is the first observation of the PL spectrum modified by local vibrations of surface species.<sup>23</sup> The coupling of excitons and local vibrations of surface species, germanium oxides, is expected to increase with localization of excitons at the surface.

Here we consider the mechanism of surface-oxidized Ge nanocrystals. The indirect band gap in Ge nanocrystal is shifted by quantum confinement effects, and the indirect band gap of the 3.7-nm Ge nanocrystal in this work is calculated to be about 2.3 eV.<sup>10</sup> The indirect band gap is nearly

equal to the direct band gap. The optically allowed direct-gap plays a dominant role in absorption and PL excitation processes. The absorption and photoexcitation of carriers occurs in the Ge nanocrystals exhibiting solidlike properties (mostly delocalized states in Ge nanocrystals). On the other hand, fine structures in the PL spectrum are observed at low temperatures. The phonon structures cannot be explained by the exciton-phonon coupling in the Ge solids: Excitons are not delocalized in Ge nanocrystals and fine structures do not correspond to phonon structures in bulk Ge. Since the Ge-O bond is polar, the coupling of excitons and stretch vibrations of surface species increases with localization of excitons near the surface, through the Fröhlich interaction.<sup>24</sup> Luminescence spectra in Ge nanocrystals are like those of molecules rather than solids, because the strong coupling of excitons and local vibrations are usually observed in isolated small molecules.<sup>25</sup>

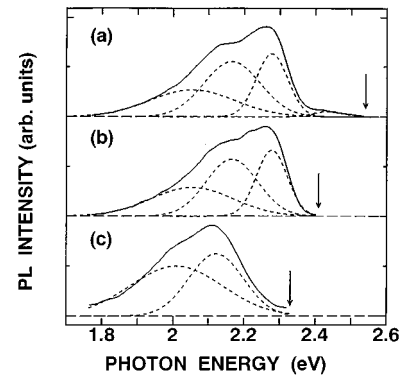


FIG. 4. Photoluminescence spectra of Ge nanocrystals under different excitation energies at 2 K: (a) 2.540 eV, (b) 2.409 eV, and (c) 2.330 eV. The peak energies of fine structures are estimated by using Gaussian functions and the broken lines are Gaussian profiles. The arrows mean the photon energy of the excitation laser. Fine structures in Ge nanocrystals cannot be explained by the phonon energies of crystalline Ge, but a spacing between peaks of the Gaussian profiles ( $\sim 110$  meV) can be explained by the stretch vibrations of germanium oxides.

Hybrid optical properties between the crystalline and molecular limits in nanocrystals are very interesting and an important issue in solid state and molecular science. Further theoretical studies are needed for the understanding of optical response of semiconductor nanocrystals.

In conclusion, we studied photoluminescence properties of Ge nanocrystals. The surface-oxidized 3.7-nm Ge nanocrystal has a character of direct-gap semiconductors but luminescence properties are similar to those of isolated small molecules. Excitons are localized near the surface of nanocrystals and the strong coupling of excitons and the stretch

vibrations of germanium oxides causes fine structures in the PL spectra. Since semiconductor nanocrystals have an unusually large surface-to-volume ratio, polar surface bond effects are clearly observed in optical properties in nonpolar group-IV semiconductor nanocrystals.

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<sup>23</sup>For example, in porous Si (Ref. 20) and CdSe nanocrystals (Ref. 21), fine structures are caused by the exciton-phonon coupling and phonon energies are nearly equal to that in the bulk Si and CdSe crystals.

<sup>24</sup>Excitons are not localized in the GeO<sub>2</sub> region, because fine structures have not been observed in SiO<sub>2</sub> and GeO<sub>2</sub> and broad and featureless PL spectra are only observed due to self-trapped excitons; see, for example, K. S. Song and R. T. Williams, *Self-Trapped Excitons* (Springer, Berlin, 1993).

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