Decay dynamics of near-infrared photoluminescence from Ge nanocrystals

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Photoluminescence (PL) decay dynamics of Ge nanocrystals (*nc*-Ge) 1.2–3.2 nm in average diameter embedded in SiO_2 matrices was studied. The samples showed a PL peak in the near-infrared region with strong size dependence. A very fast component ($\ll 1\ \mu$s) was found in decay curves for all the samples. For the samples containing relatively large *nc*-Ge, a slow component of the order of microseconds was also observed. With decreasing the size, the slow component gradually faded out, and the PL intensity increased significantly. The transition from indirect to direct recombination of carriers with decreasing the size is considered to be responsible for the observed PL decay dynamics. © *1999 American Institute of Physics.* [S0003-6951(99)00711-1]

Optical properties of nanometer size Si and Ge crystals have been investigated in recent years.[1] The band gap widening and the increase in the oscillator strength caused by the quantum size effects would appear in such nanocrystals. In particular, for Si nanocrystals (*nc*-Si), the relationship between the size and the photoluminescence (PL) properties has been revealed.[2–4] With decreasing the size, the PL peak shifts from the band gap of bulk Si to the visible region[2–5] and the decay time becomes shorter from milliseconds to microseconds.[5–8]

In contrast to *nc*-Si, little is known on the PL properties of Ge nanocrystals (*nc*-Ge). Since the exciton Bohr radius of bulk Ge crystal (17.7 nm) is much larger than that of bulk Si crystal (4.9 nm),[1] quantum size effects will appear more conspicuously for *nc*-Ge than *nc*-Si. Recently, we have succeeded in observing size dependent PL from *nc*-Ge in the near-infrared (NIR) region.[9] A PL peak was observed at about 0.88 eV for *nc*-Ge 5.3 nm in average diameter (d_{ave}). With decreasing the size, the PL peak shifted to higher energies and reached 1.54 eV for $d_{ave}=0.9$ nm. The PL intensity increased about two orders of magnitude as the size decreased. From these results, we concluded that the observed PL comes from the radiative recombination of electron–hole pairs confined in *nc*-Ge. In this work, in order to clarify the recombination process of electron–hole pairs confined in *nc*-Ge, PL decay measurements were performed for the same samples as those studied in our previous work.[9] It will be demonstrated that the PL decay time is much shorter than that reported for *nc*-Si. The transition of carrier-recombination process from indirect to direct one will be discussed.

Ge nanocrystals embedded in SiO_2 matrices were prepared by a radio frequency cosputtering method similar to those used in our previous studies on *nc*-Ge embedded in SiO_2 matrices.[9–11] Small pieces of Ge chips ($2\times 2\times 0.5\ mm^3$, purity 99.999 9%) were placed on a SiO_2 target (10 cm in diameter, purity 99.99%) and they were cosputtered in Ar gas of 2.7 Pa. Substrates were fused quartz plates. After cosputtering, the films were thermally annealed in N_2 gas ambient for 30 min at 800 °C to grow *nc*-Ge in SiO_2 matrices.

In the present preparation method, the size of *nc*-Ge can be controlled by changing the volume fraction of Ge in films (f_{Ge}).[9–11] In our previous work, we prepared *nc*-Ge with $d_{ave}=0.9$–5.3 nm by changing f_{Ge} from 0.2–7.2 vol %.[9] The size of *nc*-Ge was determined by cross-sectional high-resolution transmission electron microscopic (HRTEM) observation [JEM-2010 (JEOL)]. For the samples with $d_{ave}\leqslant 2.3$ nm, *nc*-Ge were not observed in HRTEM images due probably to the intense background image of SiO_2 matrices. The size of *nc*-Ge for these samples was estimated by the relationship between the size of *nc*-Ge and f_{Ge}.[9] In this work, we used the same samples as those studied in our previous work.

The PL spectra were measured at room temperature using a HR-320 monochromator (Jobin Yvon), a R5509-72 photomultiplier (Hamamatsu Photonics) and a SR830 lock-in amplifier (Stanford Research). The excitation source was the 457.9 nm line of an Ar-ion laser. The beam power density was about 1 W/cm^2. The spectral response of the detection system was calibrated with the aid of a reference spectrum of a standard tungsten lamp. For the PL decay measurements, a SR430 multichannel scaler (Stanford Research) was used. Excitation pulses were obtained from the 488.0 nm line of an Ar-ion laser by using an acoustic-optic modulator. The pulse width and repetition frequency were 400 ns and 11 kHz, respectively. The time resolution of the system is about 40 ns.

Figure 1 shows the PL spectra for the samples with various d_{ave}. The PL spectra are normalized at their maximum intensities and the scaling factors for the normalization are

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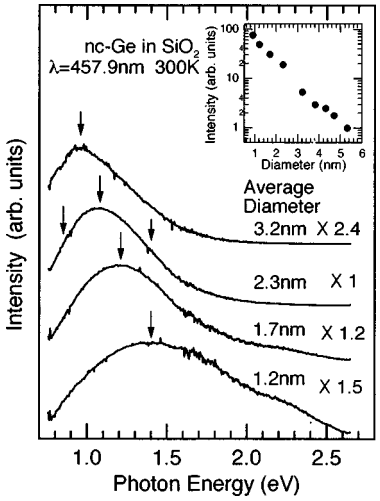

FIG. 1. Dependence of PL spectra on the average diameter of *nc*-Ge. The inset shows the size dependence of the PL intensity which was reported in our previous paper (in Ref. 9). The arrows show the energy at which decay dynamics was measured.

shown in Fig. 1 (a larger factor corresponds to a smaller PL intensity). The PL spectra have strong size dependence. For the sample with $d_{\mathrm{ave}}=3.2\,\mathrm{nm}$, the PL peak is located at about 0.96 eV. With decreasing d_{ave}, the PL peak shows blueshift and appears at 1.08, 1.21, and 1.40 eV for the samples with $d_{\mathrm{ave}}=2.3$, 1.7, and 1.2 nm, respectively. The PL intensity increases drastically as shown in the inset of Fig. 1. The PL intensity was corrected by the amount of *nc*-Ge in the films and the absorbance at the excitation wavelength.[9]

The PL decay curves monitored at the PL peak energy are shown in Fig. 2(a). We can see that the PL decay curves consist of fast and slow components for all the samples. The fast component has a decay time faster than 1 μs and the slow one of the order of microseconds. The decay time of fast component is shorter than the instrumental time resolution in this experiment ($\approx$40 ns). For the sample with $d_{\mathrm{ave}}=3.2\,\mathrm{nm}$, the contribution of the slow component to the PL decay curve is rather large, although the fast component dominates the PL decay curve. As the size of *nc*-Ge decreases, the slow component gradually fades out. The increase in the fast decay component and the drastic increase in the PL intensity shown in Fig. 1 with decreasing the size suggest that the oscillator strength of electron–hole recombination increases with decreasing the size.

Recently Ren calculated the electron and hole wave function distributions in the **k** space of some edge states in *nc*-Ge.[12] He showed that for *nc*-Ge 5.1 nm in diameter, the electron wave functions are located near *L* point and are well separated from the hole wave functions located near Γ point, while for *nc*-Ge 1.5 nm in diameter, the electron and hole wave functions spread in the **k** space and the overlaps of the wave functions become significant. This theoretical prediction indicates that the electron–hole pairs confined in *nc*-Ge about 5 nm in diameter recombine with the aid of phonon (indirect recombination). With decreasing the size, no-phonon process (direct recombination) begins to contribute to the recombination process, and for *nc*-Ge 1.5 nm in diameter, the direct recombination dominates the recombination process.

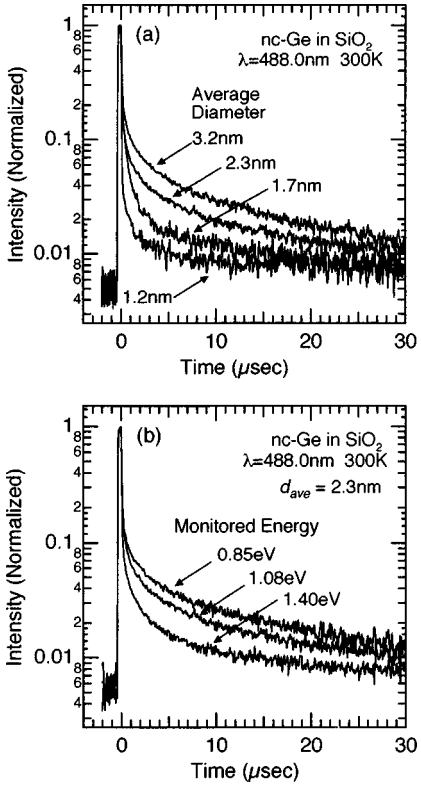

FIG. 2. PL decay curves monitored (a) at the PL peak energies for the samples shown in Fig. 1 and (b) at various PL energies for the sample with $d_{\mathrm{ave}}=2.3\,\mathrm{nm}$.

In general, the transition from the indirect to direct recombination process causes the increase in the oscillator strength, resulting in the faster decay time and the enhancement of the PL intensity. As the size of *nc*-Ge decreases and reaches the size which begins to show the direct recombination, the fast decay component due to the no-phonon transition will be superimposed on the slow component due to the phonon-assisted transition. With decreasing the size further, the ratio of the fast to slow components will increase. Therefore, a possible assignment of the observed fast and slow decay components is the no-phonon and phonon-assisted recombination, respectively. Our results demonstrate that, even for the largest *nc*-Ge studied in this work (3.2 nm in diameter), the direct transition is the dominant carrier recombination process, and as the size decreases further, the indirect transition becomes less probable. It is very plausible that as the size becomes larger than 3.2 nm, the slow component will play a significant role in the recombination process. Unfortunately, the PL signal of the samples containing *nc*-Ge larger than 3.2 nm was too weak to obtain PL decay curves.

Figure 2(b) shows the PL decay curves monitored at various PL energies for the sample with $d_{\mathrm{ave}}=2.3\,\mathrm{nm}$. The monitored PL energy is indicated by arrows in Fig. 1. The slow component gradually fades out with increasing the monitored PL energy. Similar results were observed for other samples. The increase in the fast decay component with increasing the monitored PL energy can be explained as follows. The PL spectra are broadened by inhomogeneous broadening caused by the size distribution. The PL decay curve obtained at higher energy side of the PL peak represents the signal from smaller *nc*-Ge in the size distribution, and at lower energy side from larger *nc*-Ge. Therefore, the

slow component of decay curve decreases with increasing the monitored PL energy.

It is noted here that the observed PL decay time is much faster than that of *nc*-Si previously reported.[5–8] The PL decay time of red and NIR PL for *nc*-Si is within the range of microseconds to milliseconds. No component faster than 1 μs has been reported. The slow PL decay indicates that the recombination of carriers in *nc*-Si is an indirect process. Hybertsen[13] and Ren[14] theoretically predicted that the direct recombination processes become important for *nc*-Si$\leqslant$1.5 nm in diameter. Recently, Kovalev *et al.* obtained the ratio of no-phonon transitions to phonon-assisted ones by resonant PL measurement.[15] They demonstrated that with increasing the confinement energy, the contribution of no-phonon transitions increases and becomes comparable with that of phonon-assisted transitions for confinement energy above 0.7 eV. Although the size of *nc*-Si has not been referred in their article,[15] the confinement energy of 0.7 eV corresponds to the size of about 1.5 nm from the size versus PL peak energy relation reported so far.[2–4] These theoretical and experimental results indicate that *nc*-Si which show the direct recombination of electron–hole pairs should be smaller than 1.5 nm. This may be the reason why the indirect character is preserved for *nc*-Si as small as a few nanometers in diameter. On the other hand, our results demonstrate that the direct recombination is the dominant process for *nc*-Ge as large as 3 nm in diameter. The large exciton Bohr radius of *nc*-Ge and the resulting strong confinement of carriers may be the cause of the indirect-to-direct transition at rather large sizes. Further studies including resonant excitation of PL spectra are required to fully understand the indirect-to-direct transition in *nc*-Ge.

In conclusion, we have studied the PL decay dynamics for *nc*-Ge embedded in SiO_2 matrices as a function of the size (d_{ave}=1.2–3.2 nm). A very fast component faster than 1 μs was observed in decay curves for all the samples. For the samples containing relatively large *nc*-Ge, a slow component of the order of microseconds was also observed. With decreasing the size, the slow component gradually faded out, and the PL intensity increased drastically. These results indicate that the direct recombination process is the dominant process for *nc*-Ge even for particles as large as 3 nm in diameter.

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