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Size-dependent near-infrared photoluminescence from Ge nanocrystals embedded in SiO_2 matrices

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We have succeeded in observing the size dependent photoluminescence (PL) from Ge nanocrystals (nc-Ge) with 0.9–5.3 nm in average diameter (d_{ave}) in the near-infrared region. The nc-Ge were fabricated by rf cosputtering of Ge and SiO_2 and post annealing at 800 °C. It was found that the sample with $d_{ave}=5.3$ nm shows a PL peak at about 0.88 eV. With decreasing the size, the PL peak shifted to higher energies and reached 1.54 eV for the sample with $d_{ave}=0.9$ nm. It was also found that the PL intensity increases drastically with decreasing the size. The observed strong size dependence of the PL spectra indicates that the observed PL originates from the recombination of electron-hole pairs confined in nc-Ge. [S0163-1829(98)09535-6]

I. INTRODUCTION

Since the observation of the efficient visible photoluminescence (PL) from porous Si,[1] nanometer size Si and Ge structures have extensively been studied because it would open a new possibility for indirect-gap semiconductors as new materials for photoelectric applications. In particular, PL properties of Si nanocrystals (nc-Si) have widely been studied and the relationship between the size of nc-Si and the PL peak energy has been revealed experimentally for at least red and near-infrared PL.[2–4] According to these reports, the nc-Si with about 4 nm in diameter exhibits a PL peak at about 1.4 eV. As the size decreases further, the PL peak shifts to higher energies and reaches the visible region for nc-Si smaller than 2 nm. It has also been reported that the PL intensity increases drastically as the size decreases. In general, the red and near-infrared PL previously observed are considered to originate from the recombination of electron-hole pairs between the widened band gap of nc-Si (quantum size effects).

In contrast to nc-Si, clear size dependence of the PL spectra has not been reported so far for Ge nanocrystals (nc-Ge). Until now, nc-Ge has been prepared by several methods such as cosputtering of Ge and SiO_2 and post thermal annealing,[5–8] H_2 reduction of $Si_{1-x}Ge_xO_2$ alloy,[9] chemical vapor deposition of the tetra ethoxy silicate and the trimethylgerminate and post thermal annealing,[10] sol-gel method[11,12] and oxidation of SiGe alloy.[13] These samples are reported to exhibit strong visible PL at about 2.2 eV independent of the size of nc-Ge (2–15 nm) and the preparation methods. Although some authors[5–8] claimed that the 2.2 eV PL is caused by the quantum size effects, the nearly size-independent PL could not be explained by a simple quantum confinement model.

The exciton Bohr radius of bulk Ge crystal (17.7 nm) is much larger than that of bulk Si crystal (4.9 nm).[14] The quantum size effects will thus appear more conspicuously for nc-Ge than for nc-Si. Since the band gap of bulk Ge crystal is in the near-infrared (NIR) region (0.66 eV), we can expect to observe a PL peak in the NIR region for relatively large nc-Ge, and the high-energy shift of the peak from the NIR to visible region as the size decreases. The information on the size dependence of the PL spectra is indispensable for further understanding the quantum size effects of nc-Ge.

The purpose of this work is to experimentally reveal the size dependence of the PL spectra for nc-Ge. We have prepared nc-Ge by cosputtering of Ge and SiO_2 and post annealing, and studied the PL properties as a function of the size (0.9–5.3 nm) in the NIR and visible region. We will demonstrate that the PL spectra strongly depending on the size can be observed in the NIR region.

II. EXPERIMENTAL

Ge nanocrystals embedded in SiO_2 matrices were prepared by an rf cosputtering method similar to those used in our previous studies on Ge (Refs. 15 and 16) and Si (Refs. 4 and 17) nanocrystals embedded in SiO_2 matrices. Small pieces of Ge chips ($2\times2\times0.5$ mm^3, purity 99.9999%) 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 (background pressure of 3×10^{-5} Pa) with an rf power of 200 W, using an SPF-210H(ANELVA) magnetron sputtering apparatus. The substrates were fused quartz plates. The substrates were not intentionally heated during the sputtering and kept lower than 100 °C by circulating cool water. The thickness of the films was about 3.6 μm. After the cosputtering, in order to grow nc-Ge in SiO_2 matrices, the films were thermally annealed in N_2 gas ambient for 30 min at 800 °C.[15,16]

In this method, the size of nc-Ge can be controlled by changing the concentration of Ge in the films.[15,16] The concentration was controlled by changing the number of Ge chips during the cosputtering. The atomic ratio of Ge to Si in films was determined by electron probe microanalyses

TABLE I. List of the samples studied. f_{Ge} is the volume fraction of nc-Ge, and d_{ave} is the average diameter.

f_{Ge} (%)	d_{ave} (nm)
0.2	0.9[a]
0.4	1.2[a]
0.9	1.7[a]
1.6	2.3[a]
3.6	3.2
4.4	3.8
5.2	4.3
5.7	4.7
7.2	5.3

[a] Estimated from f_{Ge}.

(EPMA) (JXA-8900 (JEOL)) for all the samples. The volume fraction of nc-Ge (f_{Ge}) was calculated from the atomic ratio using the densities of bulk Ge crystal ($5.33\ \mathrm{g/cm^3}$) and fused quartz ($2.20\ \mathrm{g/cm^3}$).[18] The estimated f_{Ge} are listed in Table I. After optical measurements, all the samples were studied by cross-sectional high-resolution transmission electron microscope (HRTEM) [JEM-2010 (JEOL) and H-8100 (HITACHI)]. The samples for the HRTEM observation were prepared by standard procedures including mechanical and Ar-ion thinning techniques.

The PL spectra were measured at room temperature in a photon energy region from 0.75 to 2.65 eV using two different systems. In the NIR region lower than 1.6 eV, a HR-320 monochromator (Jobin Yvon) equipped with an EO-817L Ge diode (North Coast) was used, while in the visible region higher than 1.6 eV, a U1000 monochromator (Jobin Yvon) equipped with a R943-02 photomultiplier (Hamamatsu Photonics) and a photon counting system was used. The excitation source was the 457.9-nm line of an Ar-ion laser. The beam power density was about $1\ \mathrm{W/cm^2}$. The spectral response of the measuring system was calibrated with the aid of a reference spectrum of a standard tungsten lamp. The absorption spectra of the samples from the ultraviolet to visible region were measured by a UV-3101PC (Shimadzu) spectrometer.

III. RESULTS AND DISCUSSION

A. HRTEM observation and size estimation

Figure 1 shows a typical cross-sectional HRTEM image of the sample with $f_{\mathrm{Ge}}=3.6\%$. We can observe lattice fringes corresponding to {111} planes of Ge with the diamond structure (0.33 nm). In Fig. 1, we can clearly see that spherical nc-Ge with the diamond structure are dispersed in $\mathrm{SiO_2}$ matrices. The average diameter (d_{ave}) of this sample determined from several HRTEM images was 3.2 nm. For all the samples with $f_{\mathrm{Ge}} \geqslant 3.6\%$, we could clearly observe lattice fringes of nc-Ge by HRTEM observations. Figure 2 shows d_{ave} obtained from HRTEM observations as a function of f_{Ge} (solid circles). The solid curve is the result of the least-squares fitting explained later. We can see that as f_{Ge} decreases from 7.2% to 3.6%, d_{ave} decreases from 5.3 to 3.2 nm.

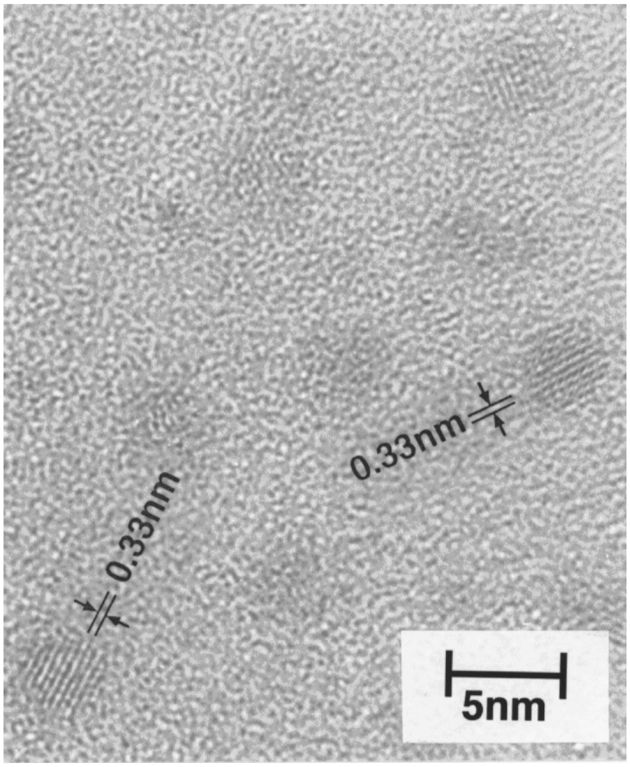

FIG. 1. Cross-sectional HRTEM image of the sample with $f_{\mathrm{Ge}}=3.6\%$. Lattice fringes corresponding to {111} planes of Ge with the diamond structure can clearly be seen.

For the samples with $f_{\mathrm{Ge}} \leqslant 1.6\%$, we could not observe nc-Ge in HRTEM images due probably to the intense background image of $\mathrm{SiO_2}$ matrices. Although d_{ave} could not be determined directly from HRTEM observations, it is possible to roughly estimate d_{ave} from f_{Ge}, because d_{ave} depends on f_{Ge} as can be seen in Fig. 2. For the estimation, we consider a simple model in which spherical nc-Ge with d_{ave} in diameter are arranged in a simple cubic lattice with a lattice constant of $(s+d_{ave})$, where s is the distance between the surfaces of two neighboring nc-Ge. The definition of s is shown in the inset of Fig. 2. We also assume that, if the annealing condition is the same, s is the same for all the samples and is independent of f_{Ge}, and only d_{ave} changes as f_{Ge} changes. The assumption is based on the following consideration. In

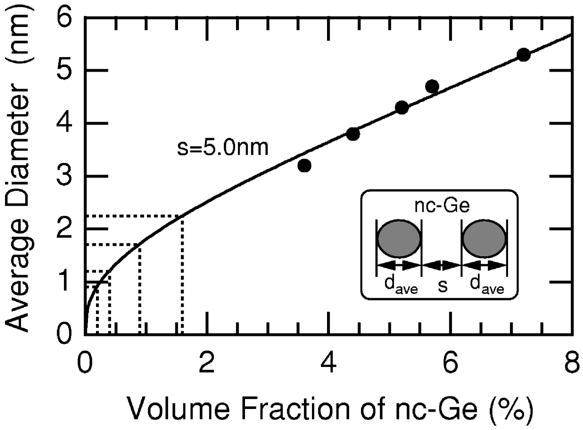

FIG. 2. Average diameter of nc-Ge as a function of f_{Ge} (solid circles). Solid curve is the result of the least-squares fitting assuming that nc-Ge are arranged in a simple cubic lattice. The average separation of nc-Ge obtained from the fitting was 5.0 nm.

the present method, nc-Ge are grown by annealing the mixture of Ge and SiO_2. During the thermal annealing Ge atoms diffuse in the SiO_2 matrices and grow to nc-Ge. The separation between the resulting nc-Ge is considered to be determined by the diffusion length of Ge atoms during the annealing. Since the diffusion length depends only on the annealing condition (time, temperature, and atmosphere) provided that $f_{\rm Ge}$ is small, s is considered to be nearly the same for all the samples.

Using this model, the relationship between $f_{\rm Ge}$ and d_{ave} is expressed as

$$\frac{f_{\rm Ge}}{100}=\frac{\frac{4}{3}\pi\left(\frac{d_{ave}}{2}\right)^{3}}{(s+d_{ave})^{3}}. \tag{1}$$

In actual estimation, we first fitted the data in Fig. 2 with Eq. (1) using s as a fitting parameter. The solid line in Fig. 2 shows the result of the least squares-fitting. We can see that the experimental data could be well fitted by the model. The average separation obtained from the fitting was 5.0 nm. By assuming that the model is also applicable to $f_{\rm Ge} \leqslant 1.6\%$, we estimated d_{ave} using $f_{\rm Ge}$ obtained from EPMA. The broken lines in Fig. 2 represent the relation between the estimated size and $f_{\rm Ge}$. The results of the estimation are summarized in Table I. We can see that d_{ave} decreases from 5.3 to 0.9 nm as $f_{\rm Ge}$ decreases from 7.2% to 0.2%. In the following, we will use the size estimated by this method to discuss the photoluminescence (PL) properties of the samples with $f_{\rm Ge} \leqslant 1.6\%$.

It is noted here that, although we assumed a simple cubic lattice to estimate d_{ave}, the choice of the arrangement of the particles is not crucial. We also estimated d_{ave} assuming face-centered and body-centered cubic lattices. It was found that the variation of d_{ave} resulting from the different choice of the particle arrangement was at most 20% of the value in Table I.

B. Photoluminescence spectra

Figure 3 shows the PL spectra for the samples with various d_{ave} and a pure SiO_2 film prepared by sputtering only the SiO_2 target. The PL spectra are normalized at their maximum intensities and the scaling factors for the normalization are shown in the figure (a larger factor corresponds to a smaller PL intensity). We can see that the sample with $d_{ave} = 5.3$ nm shows a PL peak at about 0.88 eV, which is slightly larger than the band gap of bulk Ge crystal. As d_{ave} decreases, the PL peak shifts monotonously to higher energies and reaches about 1.54 eV as d_{ave} decreases to 0.9 nm. The PL spectra were highly reproducible and stable under the laser irradiation.

In Fig. 3, we see that the sample not containing nc-Ge (pure SiO_2 film) shows a PL peak at about 2.2 eV. The origin of the peak is considered to be the oxygen deficient defect center in the SiO_2 film.[19] The 2.2-eV peak from the SiO_2 matrix is also observed for the samples with small d_{ave} ($d_{ave} \leqslant 1.7$ nm). In the present samples, the size of nc-Ge is controlled by changing $f_{\rm Ge}$. For the samples with small d_{ave}, $f_{\rm Ge}$ is also very small (Table I) and the fraction of SiO_2 is large. The large fraction of SiO_2 causes the appearance of the 2.2-eV PL. Furthermore, the onset of optical absorption shifts to higher energies as d_{ave} decreases, and for the samples with $d_{ave} \leqslant 1.7$ nm, absorbance at around 2.2 eV is very small. The absorbance of the sample with $d_{ave} = 0.9$ nm is about one hundredth of that with $d_{ave} = 5.3$ nm. The small absorbance also causes the appearance of the 2.2-eV peak for these samples.

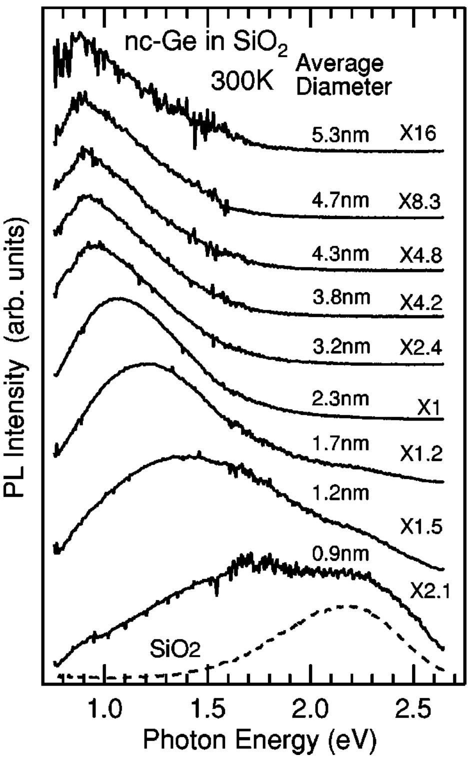

FIG. 3. Dependence of PL spectra on the average diameter of nc-Ge. A PL spectrum of a SiO_2 film is also shown.

In Fig. 4, the PL peak energies obtained from Fig. 3 are plotted as a function of d_{ave} (solid circle). For a comparison purpose, the data from the previous PL studies are also shown.[6–9] We can clearly see that the PL peak energy versus d_{ave} of the present samples is completely different from those reported in the previous studies. In the present samples, the PL peak shifts monotonously to higher energies as d_{ave} decreases, while that of the samples in the previous studies is almost independent of d_{ave}. To our knowledge, this is the first observation of the size dependent PL spectra for nc-Ge.

Figure 5 shows the PL intensity as a function of d_{ave}. The intensity is corrected by the amount of nc-Ge contained in the samples by dividing the raw integrated PL intensity by $f_{\rm Ge}$. The difference of the absorbance between the samples is also corrected.[20] In Fig. 5, we can see that the PL intensity depends strongly on the size. As the size decreases from 5.3 to 0.9 nm, the PL intensity increases about two orders of magnitude.

In the case of Si (Refs. 2–4) and other semiconductor[21] nanocrystals except for nc-Ge, the increase in the band gap with decreasing the size and the resulting high-energy shift of the PL peak has commonly been observed. The band-gap widening is considered to be due to the quantum confinement effects of electrons, holes, and excitons (quantum size effects). Furthermore, the increase in the PL intensity with de-

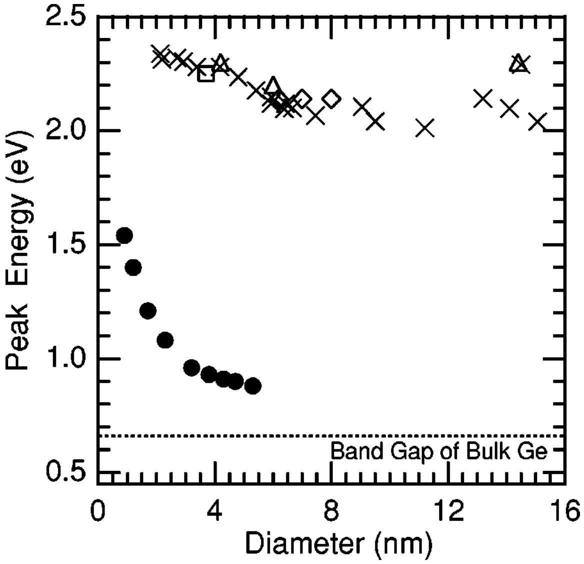

FIG. 4. PL peak energy versus average diameter of nc-Ge. Solid circles represent the present results. Previous experimental results for nc-Ge are taken from Ref. 6 (△), Ref. 7 (×), Ref. 8 (□), and Ref. 9 (◇).

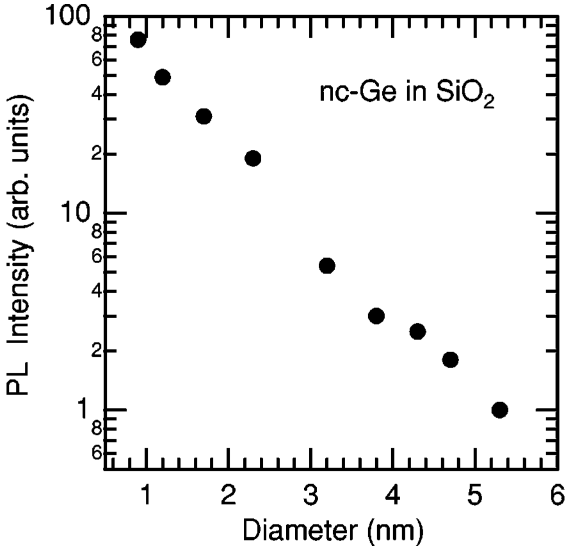

FIG. 5. PL intensity versus average diameter of nc-Ge. The PL intensity was corrected by the volume fraction and the absorbance of the excitation light of each sample.

creasing the size has also been observed for nc-Si.[4] The increase in the oscillator strength[22] and/or the decrease of the nonradiative Auger recombination processes[23] are considered as the origin of the enhancement of the PL intensity with decreasing the size. The observed size dependence of the PL spectra shown in Figs. 3–5 is very similar to those of Si and other semiconductor nanocrystals previously reported. This strongly suggests that the PL peak observed in this work originates from the recombination of electron-hole pairs between the widened band gap of nc-Ge.

In Fig. 4, the PL peak energy of the previous reports is almost independent of d_{ave}.[6–9] Some of the authors of the previous work insisted that quantum confinement of carriers in nc-Ge play a crucial role in the visible PL and the PL peak is due to the recombination of quantum confined electron-hole pairs between the widened band gap of nc-Ge. However, nearly size-independent PL peak energy shown in Fig. 4 cannot be explained by a simple quantum confinement model. One possible origin of the visible PL is the defects at the interface between nc-Ge and a surrounding matrix and/or in the matrix region. Although nc-Ge have been prepared by various methods,[7–13] the structure of all the samples exhibiting the visible PL at around 2.2 eV is very similar, i.e., nc-Ge are embedded in a SiO_2 matrix. As shown in Fig. 3, the SiO_2 film exhibits a defect related PL at about 2.2 eV. It is thus very plausible that the defects in the SiO_2 matrix region or the interface between the SiO_2 matrix and nc-Ge are responsible for the size-independent visible PL previously observed. Similar conclusion has been derived by Min *et al.*[24] They prepared nc-Ge by ion implantation of Ge in SiO_2 films and subsequent thermal annealing, and observed strong visible PL similar to those reported previously. However, they also demonstrated that very similar PL spectra can be observed for Xe doped samples. From the comparison between the PL spectra of Ge and Xe doped samples, they concluded that the visible PL is not caused by the radiative recombination of quantum confined carriers in nc-Ge but due to radiative defect centers in SiO_2 films.

In the case of Si, the band-gap energy of nanocrystals has intensively been studied theoretically as a function of the size.[25–27] On the other hand, only a few theoretical studies are made on nc-Ge. In the previous PL studies of nc-Ge, the band-gap energy calculated based on the effective-mass approximation (EMA) has been employed to discuss the observed PL properties.[7] However, EMA is known to highly overestimate the band-gap energy of the crystallites as small as a few nanometer[26,27] and is not appropriate in accounting for the optical properties of the present nc-Ge. To fully understand the observed PL properties of nc-Ge, further theoretical studies are required.

IV. CONCLUSION

We have studied the PL properties of nc-Ge as a function of the size ($d_{ave} = 5.3-0.9$ nm). We could observe the size dependent PL spectra in the near-infrared region. As the size of nc-Ge decreased from 5.3 to 0.9 nm, the PL peak energy shifted monotonously to higher energies from 0.88 to 1.54 eV and the PL intensity increased about two orders of magnitude. From the observed size dependence, the observed PL spectra are considered to be the radiative recombination of electron-hole pairs confined in nc-Ge.

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