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On the origin of visible photoluminescence in nanometer-size Ge crystallites

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We have studied the origin of visible photoluminescence of Ge nanocrystals in SiO_2 glassy matrix. Spectroscopic analyses of Ge nanocrystals indicate that the room-temperature photoluminescence comes from Ge nanocrystals of diameter of 4 nm or less. High-resolution electron microscopic studies imply that the structure of Ge nanocrystals of diameter ≤ 4 nm differs from the diamond structure. These data suggest that new nanostructure crystalline Ge having a character of direct optical transition exhibits the visible photoluminescence.

Optical and electronic properties of semiconductor nanocrystallites, often called quantum dots, have attracted much attention, because they exhibit new quantum phenomena and have potentials for becoming novel and future photonic devices.¹ Most of the previous works have been studied on nanocrystals or quantum dots made from direct-gap semiconductors such as CdS, CdSe, CuCl, etc., experimentally¹ and theoretically.² Very recently, optical properties of nanostructures made from indirect-gap semiconductors such as Si,^{3,4} Ge,⁵ etc. have been reported. The discovery of luminescence in nanocrystals of Si and Ge is an extremely important scientific breakthrough with enormous technological implications, since it opens a new possibility for group IV semiconductors as new materials for optoelectronic applications. The origin and mechanism of strong visible luminescence in Si and Ge nanocrystals at room temperature are currently under discussion.⁶ In this letter, we present an origin of strong visible photoluminescence of Ge nanocrystals in SiO_2 glassy matrix. Spectroscopic and electron microscopic studies show that a new Ge nanostructure of diameter ≤ 4 nm in SiO_2 glassy matrix exhibits the strong room-temperature photoluminescence.

The samples were prepared by a method of rf-magnetron cosputtering of Ge and SiO_2 , as previously reported.⁵ The Ar pressure and the rf power were 3×10^{-3} Torr and 1.2 kW, respectively. Thin films of the mixture of Ge and SiO_2 were deposited onto Si substrates, and then annealed in an Ar gas atmosphere for 30 min at 300, 600, or 800 °C in order to grow Ge nanocrystals in SiO_2 glassy matrix and to control the size of Ge nanocrystals. The concentration of chemical elements except Ge, Si, and O were less than 0.1 ppm, which were measured by an inductively coupled plasma emission spectroscopy. The crystallinity and size of Ge nanocrystals in SiO_2 matrix were studied by using a high-resolution electron microscopy (HREM).

The photoluminescence (PL) spectra of Ge nanocrystallites were measured by using 454.5–514.5 nm excitation light from an Ar ion laser. The calibration for the spectral sensitivity of the measuring system was performed by using a tungsten standard lamp. The temperature was varied from 10 to 300 K by controlling the flow rate of cold gas of

He in a cryostat. Excitation spectra of PL at the peak photon energy were measured by using a Xe lamp and a monochromator. Picosecond PL decay under a 200 ps and 514.5 nm laser excitation was measured using a monochromator of subtractive dispersion and a synchroscan streak camera.

The size distribution of Ge nanocrystals in samples used in this work are shown in Fig. 1. The size distribution of Ge nanocrystals in two samples (solid lines in Nos. 2 and 3) is characterized by a log-normal function given in Ref. 7. In samples (Nos. 2 and 3), the volume-average diameter d_v is calculated using the log-normal function. However, in the sample No. 1, the size distribution of Ge nanocrystals is highly asymmetric and d_v is directly evaluated from the size distribution of Ge nanocrystals in Fig. 1. Sample parameters are summarized in Table I.

Figure 2 shows typical HREM images of Ge nanocrystals in SiO_2 glassy matrix. In Ge nanocrystals larger than 5 nm in diameter, the interplane spacing is 0.326 nm and the surface of the Ge crystals consists of the (111) planes of the diamond structure. However, in Ge nanocrystals of diameter ≤ 4 nm, the spacing is 0.298 nm and this spacing cannot be derived from the diamond structure

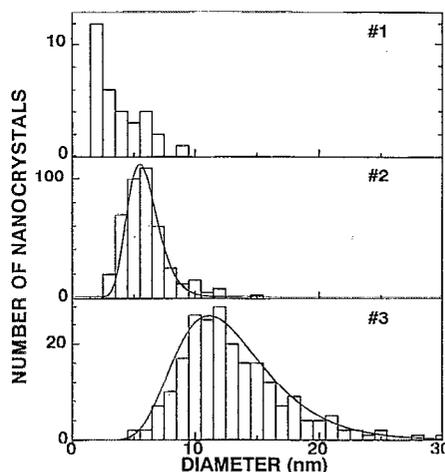


FIG. 1. The size distribution of Ge nanocrystals in SiO_2 matrix. The solid lines are log-normal functions.

TABLE I. Sample parameters including the annealing temperature T_A , the volume-average diameter d_v , the PL peak energy E_p , the volume fraction of Ge nanocrystals with diameter <4 nm V_4 , the PL intensity I_{PL} , and the time constant of the PL decay τ .

Sample No.	T_A °C	d_v (nm)	E_p (eV)	V_4^a	I_{PL}^a	τ (ns)
1	300	4.2	2.3	100	100	0.85
2	600	6.0	2.2	9.8	7.6	0.90
3	800	14.4	2.3	<0.1	0.8^b	0.86

^aNormalized values.

^bThe PL intensity of the sample No. 3 is comparable to that of the as-deposited sample.

of bulk Ge. This fact implies that the structure of nanocrystalline Ge changes critically at the size of about 4 nm. The volume fraction of Ge crystals of diameter ≤ 4 nm to total Ge crystals, V_4 are shown in Table I. This volume fraction, V_4 , is a very important parameter in the understanding of the origin of the visible photoluminescence from Ge nanocrystals.

Figure 3 shows the PL spectra from Ge nanocrystals at room temperature under 488 nm laser excitation and the excitation spectra of the PL peak. Broad PL spectra exhibiting the peak of 2.2–2.3 eV were observed in all samples. The quantum efficiency as high as about 0.5% was obtained in the sample No. 1 and the relative PL intensity in three samples are summarized in Table I. The peak energy of the PL spectrum scarcely depends on the average diameter of Ge nanocrystals in the sample, d_v . The peak energy of the excitation spectrum near 530 nm also does not depend on the sample and the excitation spectrum differs from the absorption spectrum of bulk Ge of the diamond structure. However, it was found that the PL intensity of the sample is proportional to the volume fraction V_4 . Therefore, it is concluded that Ge nanocrystals in the ≤ 4 nm size regime exhibit the strong visible photoluminescence.

The PL decay at the peak photon energy was approximately described as a single exponential having a time

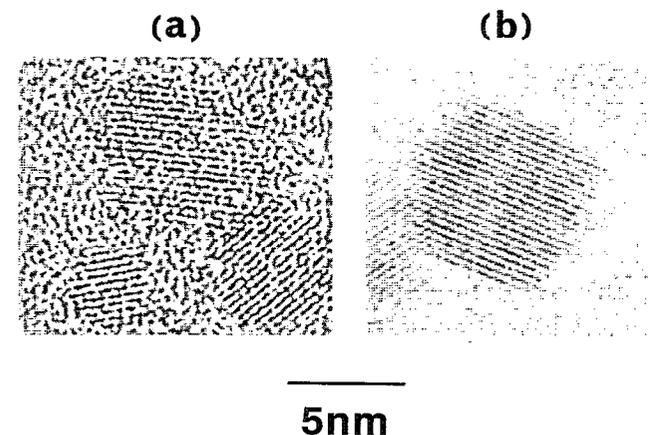


FIG. 2. HREM images of Ge nanocrystals with the diameter of (a) <4 nm and (b) 6.7 nm. The spacing in Ge nanocrystals of diameter <4 nm is 0.298 nm. The spacing of the larger nanocrystals is 0.326 nm.

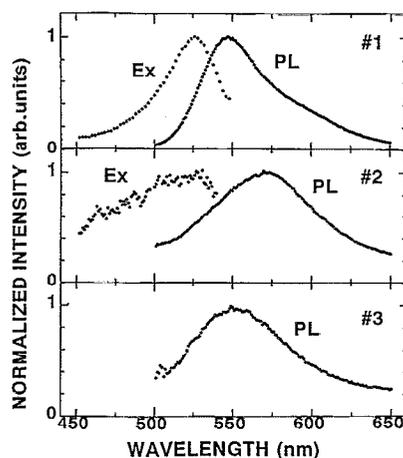


FIG. 3. PL spectra under 488 nm laser excitation and excitation spectra at the peak of the PL spectrum in three different samples.

constant τ and τ is summarized in Table I. The PL lifetime τ does not depend on the photon energy in the broad PL band. No temperature dependence of τ was observed between 10 and 300 K. Since τ is about 40 μ s near 4 K in bulk Ge,⁸ the PL decay rate is enhanced in Ge nanocrystals. Table I shows that τ does not depend on the average diameter of Ge nanocrystals. The fast PL decay implies that the indirect-gap semiconductor Ge begins to have a character of direct optical transition as size decreases.

Figure 4 shows the temperature dependence of PL intensity and spectrum in the sample No. 1. The PL spectrum does not depend on the temperature, but the PL intensity, I_{PL} , slightly depends on the temperature in all samples. If the radiative transition is excitonic and controls τ and I_{PL} , the temperature dependence of I_{PL} in the $\ln I_{PL} - 1/T$ plot gives the dissociation energy (or binding en-

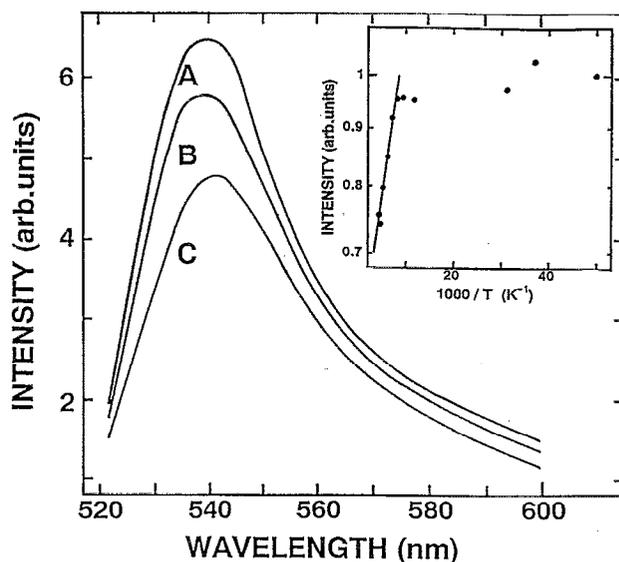


FIG. 4. Temperature dependence of the PL spectrum in the sample No. 1: A; 18 K, B; 85 K, and C; 230 K. The inset shows the temperature dependence of the PL intensity at the peak.

ergy) of excitons in Ge nanocrystals. This energy does not depend on the samples (Nos. 1, 2, and 3) and is about 7 meV. Since the binding energy of excitons is 4.7 meV in the bulk diamond structure Ge,⁸ the significant enhancement of the binding energy of excitons due to quantum confinement effects⁹ is not observed in Ge nanocrystals. On the other hand, if τ and I_{PL} are controlled by the nonradiative processes, the above experimental results mean that the nonradiative recombination rate scarcely depends on the temperature. Since the nonradiative recombination rate strongly depends on the temperature in bulk Ge, the nonradiative processes in Ge nanocrystals are entirely different from those in bulk Ge. Therefore, we consider that the radiative and nonradiative processes in Ge nanocrystals are very complicated. The insensitivity of the PL intensity and the PL spectrum to temperature suggests that Ge nanocrystals in the ≤ 4 nm size regime resemble isolated molecules rather than an indirect-gap semiconductor.¹⁰

Now we discuss the mechanism of the room-temperature photoluminescence from Ge nanocrystals. An important issue is the role of momentum conservation in optical transitions in the indirect-gap Ge. Bulk crystalline Ge has a conduction-band minimum at the L point and the valence-band maximum at the Γ point in the Brillouin zone. It is expected that the blue shift of the L - Γ indirect transition occurs as size decreases. Takagahara and Takeda⁹ calculated the quantum confinement effect on the L - Γ radiative transition using the effective mass approximation and the Luttinger Hamiltonian in Ge quantum dots. They showed that the blue shift of the peak of PL spectrum from infrared to visible region occurs as the diameter decreases: The Ge quantum dots of 14.4, 6.0, and 4.2 nm in diameter show the peaks of 0.9, 1.3, and 2.2 eV in PL spectra, respectively. The radiative lifetime varies from microseconds to nanoseconds. However, the peak energy of the PL spectrum, the PL lifetime, and the activation energy of the PL intensity do not depend on the average diameter of Ge nanocrystals. Therefore, our experimental results do not favor the model of the visible luminescence due to the confinement-induced blue shift of the L - Γ transition in diamond structure Ge.

On the other hand, our HREM studies show that the crystal structure of Ge having 4 nm or less in SiO₂ glassy matrix does not favor the diamond structure, as previously reported.^{11,12} Saito¹¹ pointed out that smaller Ge nanocrystals have a new structure of tetragonal system ($a=0.537$ nm and $c=0.904$ nm). The observed spacing of 0.298 nm as shown in Fig. 2 is nearly equal to 0.292 nm spacing

consisting of the (112) plane of the tetragonal unit. However, at the present stage, we cannot identify a new structure of Ge nanocrystals in SiO₂ glassy matrix, because we cannot obtain the electron diffraction pattern of Ge nanocrystals with diameter ≤ 4 nm only. We consider that the structure of crystalline Ge changes critically at about 4 nm in diameter and that the origin of the visible photoluminescence is Ge nanocrystals of ≤ 4 nm in diameter. In very small nanocrystals, the state mixing occurs for different k states.¹⁰ The transition acquires some allowed character from the k state admixture and k is not a good quantum number. Therefore, we consider that crystalline Ge of diameter ≤ 4 nm in SiO₂ glassy matrix has a new nanostructure exhibiting visible luminescence and has the character of direct optical transition due to hybrid electronic properties between the molecular and solid state limits.

In conclusion, we studied the origin and mechanism of visible photoluminescence in Ge nanocrystals in SiO₂ matrix. As the diameter of Ge crystals decreases below about 4 nm, the strong visible photoluminescence is observed and the nanocrystal structure seems to differ from the diamond structure Ge. We consider that visible photoluminescence of Ge nanocrystals in SiO₂ matrix arises from Ge nanocrystals of diameter ≤ 4 nm with a new structure and a molecularlike character. The small Ge quantum dot probably has a character of direct optical transition.

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