Visible photoluminescence of Ge microcrystals embedded in SiO_2 glassy matrices

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Ge microcrystals embedded in SiO_2 glassy matrices were formed by a radio-frequency magnetron cosputtering technique and then annealed at 800 °C for 30 min. The average radius of the Ge microcrystals in SiO_2 was determined to be about 3 nm by means of Raman spectroscopy and high resolution electron microscope. The annealed sample showed a strong room temperature luminescence with a peak at 2.18 eV. This is consistent with quantum confinement of electrons and holes.

Semiconductor-doped glasses show interesting optical properties as a result of quantum confinement of electron and hole wave functions into the semiconductor microcrystals.[1–3] Recently, visible photoluminescence in Si microcrystal powder[4] and silicon quantum wire array[5] fabricated by electrochemical and chemical dissolution of wafers have been reported. Their visible emission are attributed to three- or two-dimensional quantum size effects.

The quantum size effect due to three-dimensional confinement is obvious when the microcrystal size is less than the exciton effective Bohr radius. Since Ge has smaller electron and hole effective masses and a larger dielectric constant than Si, the effective Bohr radius of the excitons in Ge is larger than that in Si. This implies that the Ge microcrystals show a larger shift of an optical band gap (blue shift) than the Si microcrystals. In fact, Hayashi *et al.*[6] examined the optical absorption spectra of Ge microcrystals embedded in SiO_2 glass films deposited by a radio-frequency (rf)-magnetron cosputtering method and reported the large blue shift to visible wavelength region due to a quantum size effect. However, visible wavelength luminescence has not yet been observed in the Ge microcrystals.

In this letter, we report the first observation of visible photoluminescence of Ge microcrystals embedded in SiO_2 glassy matrices prepared by an rf-magnetron cosputtering method.

The samples were prepared by the rf-magnetron cosputtering method. Some chips of 99.999% purity Ge were set onto a 99.99% purity SiO_2 target of 100 mm in diameter. The cosputtering was performed with an Ar partial pressure of 3 mTorr and rf power of 1.2 kW. The sample was deposited on Si wafers cooled by water, and then annealed in an Ar gas atmosphere at 800 °C for 30 min in order to grow Ge microcrystals in SiO_2 glass matrices. The Ge content of the sample was determined to be 42.7 at. % by an inductively coupled plasma optical emission spectroscopy (ICPS).

Figure 1 shows x-ray photoelectron spectra (XPS) of (a) the as-deposited and (b) annealed samples. The XPS data show that both GeO_2 and Ge exist in SiO_2 in the as-deposited state and that most GeO_2 decomposes into Ge after annealing. We found that in the sputter-deposited sample the formation and growth processes of Ge microcrystals involve the decomposition of GeO_2 into Ge and O_2 and the diffusion process of Ge atoms.[7]

Figure 2 shows Raman spectra for (a) as-deposited and (b) annealed samples obtained using 200 mW of the 514.5 nm Ar ion laser. The as-deposited sample shows a very broad spectrum out to 300 cm^{-1} which is similar to the spectrum of amorphous Ge. The annealed sample showed a sharp Raman peak at 297.5 cm^{-1} with a full width at half-maximum (FWHM) of 6.2 cm^{-1}, indicating the growth of Ge microcrystals with good crystallinity after annealing. Fujii *et al.*[8] reported the relationship between FWHN of Raman peak and average size of the Ge microcrystals. According to their data, the average diameter of our sample is estimated to be about 6 nm.

Figures 3(a) and 3(b) show high-resolution electron microscopic (HREM) images of the as-deposited and annealed samples. In the as-deposited sample, we were able to

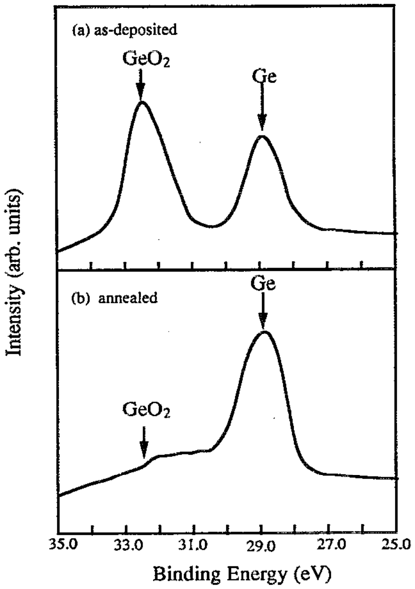


FIG. 1. X-ray photoelectron spectra of (a) as-deposited and (b) annealed samples. We found decomposition of GeO_2 after annealing.

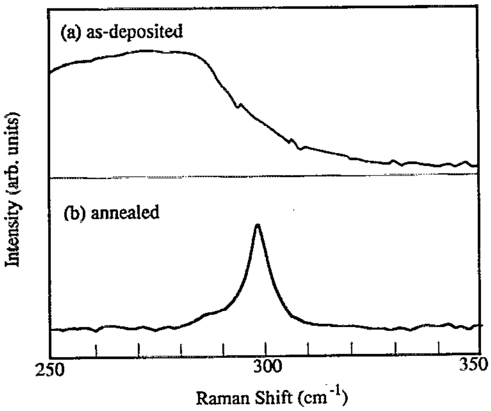


FIG. 2. Raman spectra of (a) as-deposited and (b) annealed samples at room temperature (300 K). The spectra were obtained using a 514.5 nm Ar ion laser, a double monochromator and a photon counter unit through a GaAs(Cs) photomultiplier. We observed Ge microcrystals with good crystallinity.

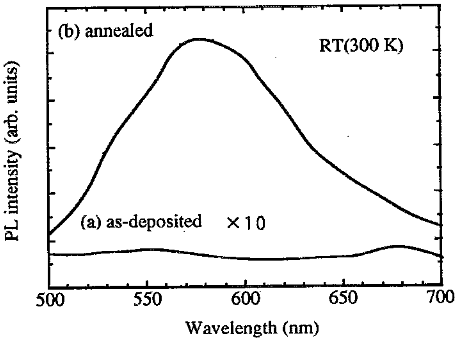
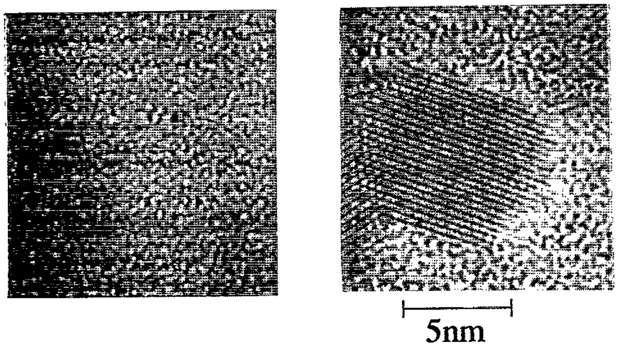


FIG. 4. Room temperature photoluminescence spectra at visible wavelength region of (a) as-deposited and (b) annealed samples. The spectra were obtained using a 488 nm Ar ion laser and a double monochromator.



(a) as-deposited (b) annealed

FIG. 3. High resolution electron microscopic images of (a) as-deposited and (b) annealed samples. We observed Ge microcrystals with good crystallinity.

observe only the glassy structure of SiO_2, while in the annealed sample we found spherical Ge microcrystals. There were less than 6–8 nm in diameter and of good crystallinity. Figure 3(b) shows {111} planes of diamond-structure Ge.

Figure 4 shows photoluminescence spectra excited by 10 mW Ar ion laser at 488 nm at room temperature (300 K). Only in the annealed sample, we observed very broad but pronounced photoluminescence ranging from 500 to 700 nm with the peak at about 570 nm.

We consider three-dimensional quantum confinement of an electron–hole pair in the Ge microcrystal as a possible mechanism for visible photoluminescence. Theoretical calculation of three-dimensional confinement in an infinite spherical potential was treated by Brus.[3] An effective Bohr radius a_B is given by

$$a_B = \kappa\hbar^2/\mu e^2, \tag{1}$$

where κ is a static dielectric constant, $\hbar$ is a reduced Planck constant, μ is reduced mass of an electron–hole pair, and e is electron charge. In the case of Ge bulk, κ is 15.8[9] and μ is reduced mass obtained from $1/\mu = 1/m_e + 1/m_h$. The lightest electron effective mass (m_e) and the lightest hole effective mass (m_h) at L and Γ points are $0.082m_0$ and $0.043m_0$, respectively. We can calculate $\mu = 0.028m_0$ and obtain $a_B = 24.3$ nm. This effective Bohr radius is very large due to the small reduced mass of an electron–hole pair and the large static dielectric constant. In our sample, the average radius of the Ge microcrystal is about 3 nm which is much smaller than the effective Bohr radius of 24.3 nm. Thus electrons and holes can be independently confined into the infinite spherical potential. In this case, the lowest energy of the electron–hole pair E_1 was given by[3]

$$E_1 = E_g + (\pi^2\hbar^2/2\mu R^2), \tag{2}$$

where E_g is an optical band gap of bulk crystalline Ge. This Eq. (2) is deduced for the isolated islands of microcrystals (Brus's model). In our case, the Ge microcrystals grow densely in the SiO_2 glassy matrix. The Brus's model is not appropriate to such dense condition. However, we employed the Brus's model in order to analyze our luminescence data.

Using values of $E_g = 0.66$ eV (at 300 K),[10] $R = 3$ nm and $\mu = 0.028\ m_0$, we can obtain $E_1 = 2.15$ eV. Our luminescence peak is located at 2.18 eV, in good agreement with the calculated electron–hole pair energy.[11] The broad spectrum may be associated with the size distribution of Ge microcrystals and complicated band structure of Ge. This result shows that the luminescence can be explained by the Brus's model. This implies that each Ge microcrystal is an isolated island in such dense condition. Furthermore, Rossetti *et al.*[12] suggested that an indirect gap semiconductor material should begin to resemble a direct gap material as the microcrystal size decreases. Visible photoluminescence of Ge microcrystals embedded in SiO_2 glassy matrices can be reasonably explained in this context.

Photoluminescence due to defects[13] in a-SiO_2 could also give rise to the observed spectrum. If such defects are indeed formed in SiO_2 during rf sputter deposition, we should observe luminescence in the as-deposited sample. However, we observed no significant luminescence as shown in Fig. 4(b). Furthermore, we should pursue the possibility of luminescence due to other defects in a-SiO_2 induced by annealing and decomposition of GeO_2.

In conclusion, we observed visible photoluminescence at room temperature in Ge microcrystals embedded in SiO_2 glassy matrices which were deposited by the rf magnetron cosputtering method. The formation and growth processes of the Ge microcrystals consisted of decomposition of GeO_2 and the diffusion of Ge atoms in SiO_2 glassy matrices. The broad luminescence spectrum with the peak at 570 nm (2.18 eV) was explained by three-dimensional confinement theory (Brus's model).

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[11] We can consider several combinations of electrons and holes, for example, electrons at Γ point, heavy and light holes at Γ point, split-off holes and electrons at L point. The observed broad luminescence can be associated with the complicated energy band and various combinations of electrons and holes. However, the blue shift of luminescence is dominated by the electron and hole pair with the lightest reduced mass. Therefore, the outline of our discussion can be considered to be appropriate.

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