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Mechanism of Visible Photoluminescence from μc-Ge Embedded in SiO_2 Glassy Matrices

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The origin of visible photoluminescence of Ge microcrystals (μc-Ge) in SiO_2 glassy matrices was examined. The spectroscopic analyses and formation mechanism show that the origin of strong light emission with nanosecond decay time is attributed to the effective surface termination and the new nanostructure of μc-Ge with diameter less than 4 nm which forms from reduction reaction of germanium oxides at low annealing temperature.

1. Introduction

Room temperature visible light emission from nanometer size structure of Si or Ge such as porous silicon (p-Si)[1,2] or microcrystals[3-5] has been reported. Recently, many researchers are interested in this visible light emission from nanostructure of indirect band gap semiconductors and propose some mechanisms such as a quantum dot or wire theory.

We have observed visible photoluminescence (PL) at room temperature from Ge microcrystals (μc-Ge) of the average size of about 6 nm which was made by a radio frequency (rf) magnetron co-sputtering method and annealing.[4] The PL spectrum showed very broad and had the peak at 570 nm. In our preliminary study, this visible light emission and large blue shift of the band gap were explained by simple three dimensional quantum confinement theory. However, recently we confirmed that the PL spectrum does not show a simple shift depending on the microcrystal size which can be estimated by three-dimensional confinement theory [6]

In this study, in order to make the mechanism of light emission from the μc-Ge system clear, we examine a formation mechanism and crystallographic properties of the μc-Ge system, PL spectrum, PL decay time, and the excitation spectrum as a function of the size. On the basis of these data, the mechanism of PL from μc-Ge system will be discussed.

2. Experimental

The samples were prepared onto a silicon wafer or a polished quartz glass by an rf-magnetron co-sputtering method. The sputtering target used was 4n's pure SiO_2 (100mm in diameter) with 6-9 chips of 6 n'sGe. The sputtering conditions were an Ar partial pressure of 0.26Pa and an applied rf-power of 1.25 kW. The deposition chamber was evacuated to be 10^{-6} Pa with a cryovacuum pump. The Ge content in the deposited film analyzed by an inductively coupled plasma spectrometry (ICPS) was 40-45 mol% Ge. The major impurities such as Fe etc. were less than 0.1 ppm. The film thickness was 0.8-1.0 μm. All samples were annealed in Ar atmosphere at 300-800 °C. The crystallographic observation and size of the μc-Ge formed in SiO_2 matrices was examined by using a high resolution transmittance electron microscope (HREM) and a high resolution scanning electron microscope (HRSEM). The photoluminescence spectrum was excited by 488-514.5 nm Ar ion laser. Picosecond PL decay under a 200-ps and 5145-nm laser excitation was measured using a monochromator of subtractive dispersion and a synchroscan streak camera.

3. Results and Discussion

3.1 *Formation mechanism of μc-Ge*

The states of as-deposited and annealed films were examined by X-ray photoemission spectroscopy (XPS). The spectrum of Ge $2p_{3/2}$ revealed that the as-deposited film includes much amount of germanium oxides (GeO_2 and GeO) and element Ge in a SiO_2 matrix including elemental Si, and that after annealing the sample their oxide rapidly decreased. Figure 1 shows that their oxides decrease and elemental Ge increases with increasing the annealing temperature and time. This fact shows that almost of the elemental Ge is supplied from their oxides by the reduction reaction; $GeO_2+Si=Ge+SiO_2$. The standard Gibbs free energy ΔG^0_T for the displacement

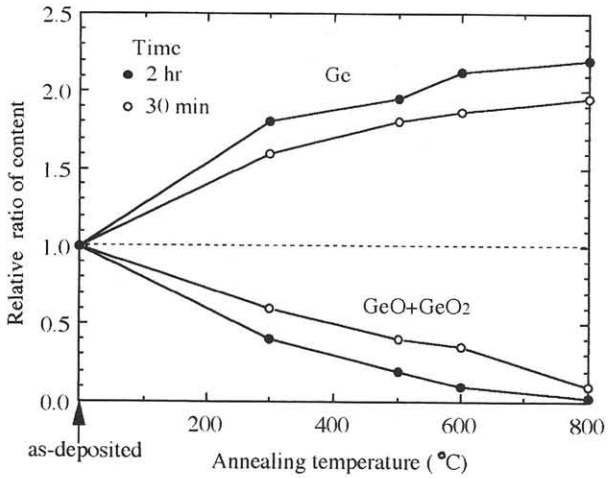

Fig.1 Relative ratio of each content obtained from XPS data. The ratio is normalized by the content of the as-deposited sample.

reaction is given by ΔG^0_T =-202.4-0.008T (kJ/mol). We can get ΔG^0_{573} =-207.2 kJ/mol at 300°C (T=573 K) which is large energy, so that this reaction can proceed at 300°C. When elemental Si is supplied smoothly at that reaction interface, with proceeding this reaction the concentration fluctuation of Ge in a SiO_2 matrix increases. Paine et al.[7] reported that nanocrystalline Ge precipitates in SiO_2 through this reaction by different synthesis method. We were able to observe that very small size (<3nm) μc-Ge precipitates in the high density portion of Ge atoms in HREM image of Fig. 2, probably nucleation of the microcrystal or clustering of Ge atoms take place frequently in such Ge dense portion because the nucleation is driven only by the supersaturation except of spinodal decomposition. In fact, in the sample without any germanium oxides at such low annealing temperature we did not observe any nucleation and growth of microcrystals. This fact shows that nucleation and growth though the reduction of germanium oxides have great roles in formation of very small size μc-Ge at low annealing temperature. At such low temperature Ge atom diffusion is limited, so that only small size μc-Ge can precipitate in the Ge dense portion. The formation process described above can contribute to termination of the surface between μc-Ge and a SiO_2 matrix. The displacement reaction can make the surface termination by oxygen atoms easier. The surface termination affects radiative efficiency. Therefore, we think the μc-Ge terminated with a SiO_2 matrix by oxygen atoms, which is formed by the displacement reaction, can emit effectively. From above discussion, we believe that the essential condition for visible light emission: small size and radiative efficiency can be achieved in μc-Ge formed at low annealing temperature.

3.2 *Size distribution and morphology*

Using the image of HREM and HRSEM, we examined the actual size distribution. From these

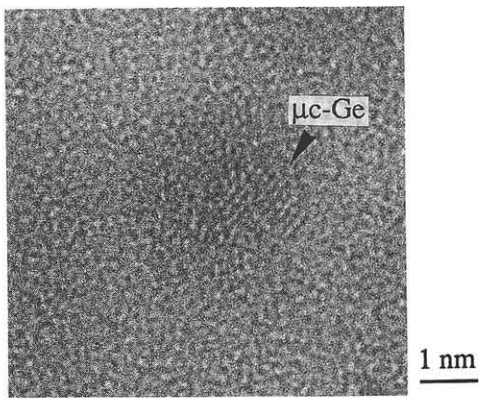

Fig.2 Very small μc-Ge formed in Ge dense portion (dark portion) at 300°C annealing.

obsevation, the size distribution was found to depend strongly on the annealing temperature, but weakly on the annealing time. In the annealing at 300°C, small μc-Ge of the average diameter of 4.2 nm is obtained. The size distribution does not obey well-known Lifshitz-Sleyzov function, but modified log-normal function which is found widely in semiconductor doped glassy materials.

Figure 3 shows the HREM image of the μc-Ge formed in a SiO_2 glassy matrix. It was observed that the morphology of μc-Ge changes remarkably, when the size is less than 4 nm. In almost μc-Ge of the size more than 6nm in Fig.3 (b)-(d), their planes with the symmetry of (111) of diamond structure are observed. However, when the size is less than 4nm in Fig3 (a), the plane which may be other crystalline structure was observed. With decreasing the size, diamond structure becomes thermodynamically unstable and transforms into other closer packing structure. At the present stage, we have not yet

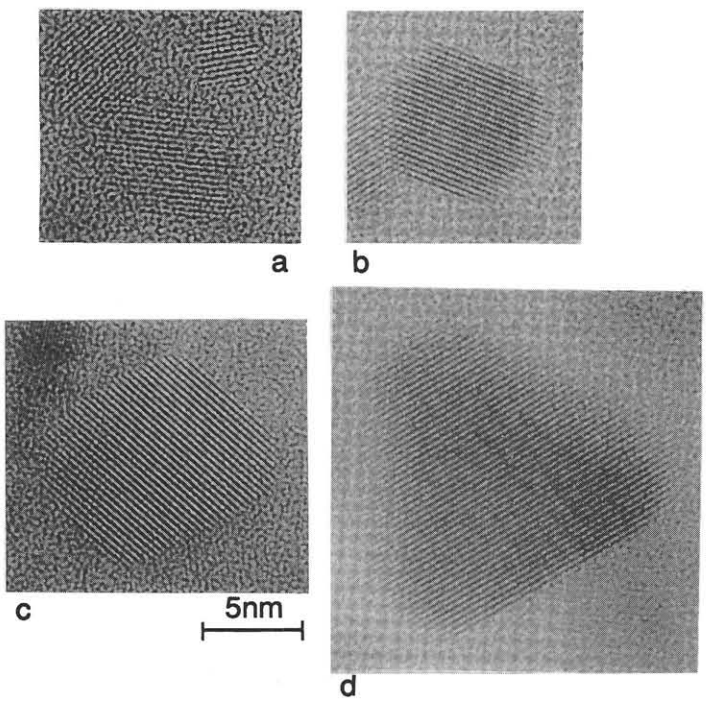

Fig.3 Morphology of μc-Ge formed in a SiO2 glassy matrix.

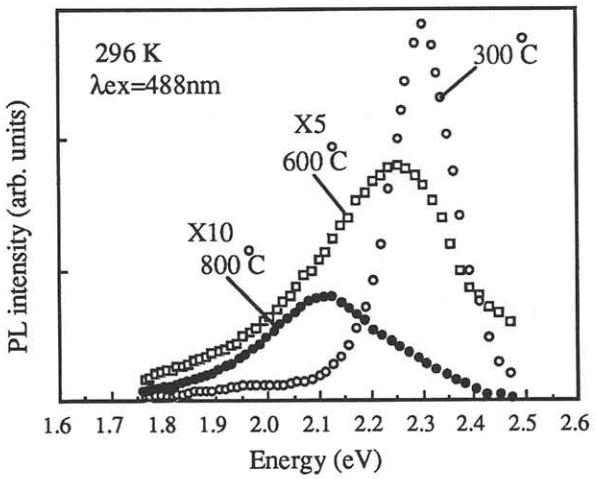

Fig.4 PL spectrum for the sample annealed at each temperature.

confirmed new structure of very small size μc-Ge because an electron diffraction only from 4 nm size μc-Ge is very difficult. However, there are several reports on instability of diamond structure of Si [8] and new phase of μc-Ge[9,10].

3.3 *Light emission properties of μc-Ge system*

Figure 4 shows the PL spectrum obtained from the samples annealed at 300, 600, 800°C for 30 min. These PL were excited by 488-nm Ar ion laser. The average sizes of[11] μc-Ge in those samples were 4.2, 6.0 and 6.5 nm, respectively. It is observed that the PL peak energy showed weak dependence on the average size of the distribution. On the other hand, the PL intensity increased remarkably with decreasing the average size. The PL properties for four different average sizes are given in Table I. The PL intensity for the average size of 4.2 nm is about 10 times than that for the average size of 6 nm. In the case of the average size of 14.4 nm, the intensity was very small and comparable to that of the as-deposited sample. The PL intensity was found to be proportinal to the volume fraction V_4 of μc-Ge with the diameter less than 4 nm. This shows that μc-Ge with the diameter less than 4 nm contributes to the strong PL.

The time constant of PL decay are also listed in Table I. The decay was found to show a single exponential process. The time constant was determined to be less than 1ns, which was not related to the average size of the μc-Ge system. This ns PL decay implies that the indirect-gap semiconductor Ge begins to have a character of direct optical transition as the size decreases. In the excitation spectrum, it was observed that the peak energy of the excitation spectrum for the PL peak is near the PL peak energy and the stokes shift was small (about 0.08eV).

The temperature dependence of PL intensity and spectrum of the average size of 4.2 nm was examined. The PL spectrum does not depend on the temperature, but the PL intensity slightly depends on the temperature. The Arrhenius plots of the intensity gives about 7 meV of the binding energy of excitons

Table I PL properties: the average size; d_v.,E_P; PL peak energy, I_{PL}; PL intensity , V_4; volume fraction of μc-Ge with diameter less than 4 nm, τ; time constant of PL decay.

d_v(nm)	E_P(eV)	I_{PL} [a]	τ (ns)	V_4 [a]
4.2	2.3	100	0.85	100
6.0	2.2	7.6	0.90	9.8
6.5	2.1	3.2	-----	2.1
14.4	2.3[b]	0.8[b]	0.86	<0.1

[a] Normalized values by that of dv=4.2 nm.

[b] This intensity is very weak and comparable to that of the as-deposited sample.

in μc-Ge. This shows that in μc-Ge the significant enhancement of the binding energy of excitons is not observed. Therefore, the radiative transition in Ge quantum dots is not due to excitonic process, rather resembles to isolated molecules.

4. Conclusions

The experimental findings obtained in this study show that the mechanism of visible light emission from μc-Ge is attributed to the effective surface termination and the new nonostructure of μc-Ge of diameter of less than 4 nm which is formed by the displacement reaction at low annealing temperature. The size regime of less than 4 nm can be considered to be a critical size from clusters to microcrystalline. We believe that the effective radiative μc-Ge has the critical size and new nanostructure which is different from diamond structure.

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11) The size distribution obeyed a log-normal distribution function F(u,σ) as described by
$F(u,\sigma)=\exp(\sigma^2)/(2\pi\sigma^2)^{1/2}\exp[-(\ln u+3/2\sigma^2)^2/2\sigma^2]$
where u is a size scaled by the average size dv and σ is dispersion factor. The average size dv is calculated by
$dv=(\Sigma n d^3/\Sigma n)^{1/3}$
where n is number of the size d.