Mechanisms of Visible Photoluminescence from Size-Controlled Silicon Nanoparticles

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ABSTRACT

We have observed visible photoluminescence (PL) spectra (peak energy: 3.1 eV) of size-controlled silicon (Si) nanoparticles annealed in oxygen gas. The PL peak energy did not depend on the temperature, and the PL lifetime was relatively fast (on the order of nanoseconds). It was inferred that the visible PL was attributed to localized states in the oxidized surfaces of size-controlled Si nanoparticles. We also observed the PL excitation spectra and studied the excitation process. In order to elucidate mechanisms of the visible PL, excitation and recombination processes are discussed.

INTRODUCTION

It is well known that group IV elements (Si, Ge) are capable of emitting strong visible light at room temperature when the size reduces to the nanometer region [1]. Recently, various methods to form nanostructured Si have been studied. However, it has been difficult to develop nanoparticles into advanced functional devices because they have a large surface to volume ratio, and are extremely sensitive to impurities and/or damage. Light-emitting properties of the nanoparticles, particularly light-emitting wavelength and efficiency, strongly depend on their mean sizes, size distributions [2], and surface conditions [3].

Pulsed laser ablation (PLA) in inert background gas (PLA-IBG) is one of the promising methods to form nanoparticles [4,5], because cold-walled clean processing which excites only beam-focused areas. Size-controlling of nanoparticles can be precisely performed by low-pressure-operated differential mobility analyzers (LP-DMA) which can be combined into the PLA-IBG formation units [6,7]. Surface conditions of nanoparticles can be controlled by annealing in ambient gas after deposition of nanoparticles on a substrate [3,8].

In this paper, we report the light-emitting properties of visible PL of size-controlled Si nanoparticles (np-Si). After controlling surface conditions of the np-Si by annealing in oxygen (O2) gas, broad visible PL spectra were observed at room temperature. In order to elucidate mechanisms of the visible PL, excitation and recombination processes are discussed from observations of time-resolved and steady-state spectra, and PL excitation spectra.
EXPERIMENTS

We designed an integrated process system to synthesize size-controlled np-Si. The process system can carry out sequential formation of nanoparticles by PLA-IBG, size-classification using LP-DMA, and deposition by nozzle jet on a substrate in a deposition chamber. The details were described in Refs. [6] and [7]. By using the system, we can control the nanoparticle sizes of nominal diameters of less than 10 nm with the geometrical standard deviation of 1.2.

In this study, np-Si were formed using PLA in helium gas of 7.0 Torr. We adopted a second-harmonic pulsed Nd:YAG laser (wavelength: 532 nm, pulse width: 6.3 ns, pulse energy: 100 mJ, and repetition rate: 10 Hz) as an excitation light source for Si ablation. Size-controlled np-Si with the nominal diameter of 5 nm were deposited on single-crystalline Si substrates.

After deposition of the np-Si on the substrates, they were annealed under two sets of conditions using a rapid thermal annealing process. One was annealing at 1000 °C for 10 s in O₂ gas (sample-A). The other was annealing subsequently at 1100 °C for 500 s in O₂ gas after annealing at 1000 °C for 10 s in O₂ gas (sample-B). For both samples, the annealing chamber was evacuated to a pressure lower than 5.0×10⁻⁵ Torr before annealing, and the purity of O₂ gas during the annealing was 99.9999%.

The PL spectra were measured with a single polychromater system (SpectraPro-308) equipped with a gated ICCD (Princeton PI-MAX-1024RB) detector under various temperature. A third-harmonic pulsed Nd:YAG laser line (wavelength: 355.0 nm, pulse width: 4.0 nm, energy density: 6.4 mJ/cm², and repetition rate: 10 Hz) was employed for the time-resolved PL excitation. The time resolution of the experimental setup was 4 ns. The continuous wave (CW)-laser line (325.0 nm of HeCd, 457.9, 488.0, 514.5 nm of Ar, 632.8 nm of HeNe) was also employed for the PL and photoluminescence excitation (PLE) measurements.

The spectra were corrected by means of the spectral sensitivity of the measurement system achieved through the use of a standard tungsten lamp.

RESULTS AND DISCUSSION

After controlling surface conditions of np-Si by annealing in O₂ gas, broad visible PL spectra (peak energy: 3.1 eV) were observed. Figure 1 shows the influence of the annealing conditions on PL spectra of the np-Si excited by CW-HeCd laser at room temperature. As shown in Fig. 1, the PL intensity of the sample-B was 18 times as strong as that of the sample-A. This increase of PL intensity indicates that the visible PL was oxygen related emission. The peak energy did not shift within the temperature region below 275 K. Then, it is considered that the visible PL originates from the recombination of carriers in localized states.

Figure 2 shows the PL decay profiles of the
np-Si at the emission photon energy of 3.1 eV at 14 K. The PL intensity rapidly decreased within the nanosecond time region. The PL decay profiles, $I(t)$, are approximately fitted by two exponential components (solid curves in Fig. 2),

$$I(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) \quad (1)$$

where $I_1 + I_2$ are the PL intensities just after pulsed laser excitation and $\tau_1$ and $\tau_2$ are time constants. We defined the mean PL lifetime, $\tau_{PL}$, as,

$$\tau_{PL} = \frac{1}{I(0)} \int I(t)dt \quad (2)$$

where $I(0) = I_1 + I_2$ is the initial PL intensity just after pulsed laser excitation. The mean PL lifetimes, $\tau_{PL}$, of the sample-A and that of the sample-B were 6.8 and 5.8 ns at 14 K, respectively. There are some previous reports concerning time-resolved visible PL from defects in amorphous-Si dioxide (a-SiO$_2$). For example, lifetimes of a Si lone-pair centers (peak energy: 3.1 eV) [9] and neutral oxygen vacancies (2.7 eV) [10] are 110 $\mu$s, 9-10 ms, respectively. The lifetimes of our samples observed at 14 K are much faster than those reported previously. Therefore, the mechanisms of the PL are different from defects in a-SiO$_2$ previously reported. It was inferred that the visible PL was attributed to unique localized states in the oxidized surfaces (a-SiO$_2$) of the np-Si.

Figure 3 shows the mean PL lifetime, $\tau_{PL}$, of the np-Si at 3.1 eV as a function of temperature. The PL lifetime of both samples did not depend sensitively on the temperature below 275 K. Figure 4 shows the mean PL lifetime, $\tau_{PL}$, in the np-Si as a function of the emission photon energy at 14 K. In the low energy region, the PL lifetime of the sample-B was longer than that of the sample-A.

In order to discuss recombination processes of carriers as shown in Figs. 3 and 4, the temperature dependence of the PL intensity was measured. Figure 5 shows the PL intensity at

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**Figure 2.** PL decay profiles of Si nanoparticles (photon energy: 3.1 eV) at 14 K.

**Figure 3.** PL lifetime of Si nanoparticles as a function of temperature at 3.1 eV.

**Figure 4.** PL lifetime of Si nanoparticles as a function of photon energy at 14 K.
the peak energy as a function of temperature.
The decrease in the PL intensity at a higher temperature region for the sample-B was much smaller than that for the sample-A.

A simple model of PL efficiency as a function of temperature is obtained by assuming a temperature-independent radiative recombination probability, $P_r$, and a thermal activation type of nonradiative recombination probability, $P_{nr}(T)$, written as follows,

$$P_{nr}(T) = P_{nr0} \exp\left(\frac{E^*}{kT}\right)$$  \hspace{1cm} (3)

where, $P_{nr0}$, $E^*$, $k$, and $T$ are a pre-exponential factor, an activation energy for nonradiative transition, Boltzman constant, and temperature, respectively. Then, the temperature dependence of PL efficiency, $\eta(T)$, is described as follows,

$$\eta(T) = 1/(1 + (P_{nr0}/P_r)\exp(-E^*/kT)) \hspace{1cm} (4)$$

We estimate the order of $E^*$ and $P_{nr0}/P_r$ values by curve fitting of eq. (4) to Fig. 5. The value of $P_{nr0}/P_r$ of the sample-A and sample-B was on the order of $10^3$ and 1, respectively. On the other hand, $E^*$ was on the same order, $10^{-1}$-$10^{-2}$ eV, for our samples. Therefore, the difference of the temperature dependence between our samples in Fig. 5 is due to the difference of the value of $P_{nr0}/P_r$.

The value of $P_{nr0}/P_r$ for our samples decreased $10^{-3}$ times by the subsequent annealing at 1100 °C. This means the decrease of the pre-factor of transition probability of carriers to nonradiative recombination center, $P_{nr0}$, and/or the increase of the radiative recombination probability, $P_r$. This result is consistent with an increase in the visible PL intensity of the sample-B at room temperature as shown in Fig. 1.

In general, the PL lifetime, $\tau_{PL}$, is expressed as $\tau_{PL} = \tau_r \tau_{nr} / (\tau_r + \tau_{nr})$, where $\tau_r$ and $\tau_{nr}$ are the radiative and nonradiative lifetime, respectively. The PL lifetime of the sample-A was insensitive to temperature and photon energy as shown in Figs. 3 and 4. This result suggests that the lifetime, $\tau_{PL}$, is affected by the nonradiative recombination centers, which have a shorter $\tau_{nr}$ than few nanoseconds and are spread over the photon energy region observed.

On the other hand, the small value of $P_{nr0}/P_r$ of the sample-B indicates that much carriers should transfer to the radiative centers. Thus, it is considered that the variation of $\tau_{PL}$ in photon energy in Fig. 4 reflects the variation of $\tau_r$ in photon energy. This means that the radiative recombination centers with various lifetimes are spread over the photon energy region observed.

In order to elucidate mechanisms of the visible PL, we also discuss the excitation process of carriers. Figure 6 shows the PLE spectrum of sample-B monitored at 1.9 eV. The PLE intensity increased gradually in the excited photon energy region higher than 2.3 eV. We expected that the optical absorption of localized defects in a-SiO$_2$ is much weaker than the band-to-band absorption of the np-Si. Therefore, it is inferred that the PLE spectrum was attributed not to the absorption of the localized states in the oxidized surface (a-SiO$_2$) of np-Si but to the absorption
of Si nanoparticle core. The mean diameter of the np-Si should decrease to the diameter of less than 5 nm by annealing in O_2 gas, then the absorption edge should be wider by quantum confinement effects. When we assume that the absorption edge of np-Si is wider than 2.3 eV, the diameter of np-Si is estimated to be smaller than 2 nm [11]. If we do not control the nanoparticle size by the integrated process system, the size distribution is wider and the PLE spectrum would have a tail in the lower energy region than 2.3 eV. The energy region at which carriers are absorbed in the np-Si core corresponds to the energy region at which the visible PL was observed in Fig. 1. We inferred the mechanism of the visible PL as follows, at first the excited light was absorbed effectively in the Si nanoparticle core, next the excited carriers in the core transferred to the localized defect states in the oxidized surface of the nanoparticles, and recombined. Thus, both excitation and recombination processes play an important role for the visible PL of size-controlled np-Si annealed in O_2 gas.

CONCLUSIONS

We reported the visible emission properties of size-controlled np-Si annealed in O_2 gas. The peak energy was insensitive to the measurement temperature and the lifetime was on the order of nanoseconds. These results suggest that the visible PL was attributed to localized states in the oxidized surfaces of size-controlled np-Si. We found that the ratio of the nonradiative recombination probability to the radiative one decreased by the subsequent annealing in O_2 gas at 1100 °C for 500 s. The absorption of size-controlled np-Si core was found in the same energy region as the visible PL. The mechanism of the visible PL was inferred as follows, at first the excited light was absorbed effectively in the Si nanoparticle core whose absorption edge is wider by quantum confinement effects, next the excited carriers in the core transferred to the localized defect states in the oxidized surface of the nanoparticles, and recombined.

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REFERENCES


