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Phosphorus ion implantation in silicon nanocrystals embedded in SiO₂

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We have investigated phosphorus ion (P⁺) implantation in Si nanocrystals (SiNCs) embedded in SiO₂, in order to clarify the P donor doping effects for photoluminescence (PL) of SiNCs in wide P concentrations ranging in three orders. Some types of defects such as P⁺ centers were found to remain significantly at the interfaces between SiNCs and the surrounding SiO₂ even by high-temperature (1000 °C) annealing of all the samples. Hydrogen atom treatment (HAT) method can efficiently passivate remaining interface defects, leading to significant increase in the intensity of PL arising from the recombination of electron-hole pairs confined in SiNCs, in addition to significant decrease in interface defects with dangling bonds detected by electron spin resonance. From both the results of the P dose dependence before and after HAT, it is found that the amount of remaining defects is higher for samples with SiNCs damaged by implantation with relatively lower P⁺ doses and then annealed, and that through HAT the observed PL intensity increases surely as the P concentration increases up to a critical concentration. Then it begins to decrease due to Auger nonradiative recombination above the critical concentration which depends on the size of SiNCs. These results suggest an effect of relatively low concentration of P atoms for the enhancement of PL intensity of SiNCs and we present an unconventional idea for explaining it.

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I. INTRODUCTION

Light emitting silicon (Si) nanostructures such as porous Si and Si nanocrystals (SiNCs) or Si nanodots embedded in SiO₂ matrices have been attractive for the optoelectronics application¹ and nonvolatile memory devices,² while the present Si-LSI technology has advanced into the nanoscale sizes less than 100 nm for more than 10 years. It has been already understood that quantum confinement is an origin for emission such as photoluminescence (PL) and electroluminescence such as electroluminescence. While as an impurity doping technique, only ion implantation has been developed especially for Si-LSI processes since 1970s, it has been used also in formation of SiNCs in SiO₂,¹ ² defect production,⁶ and impurity doping⁴ in SiNCs.

Fujii and co-workers⁷ reported P doping effects for PL intensity that light doping produces enhancement of PL for SiNCs with relatively small sizes, but not for those for larger SiNCs, and heavy P doping leads to decrease in PL intensity. The latter is due to Auger nonradiative recombination.⁷ On the other hand, any clear explanations have been given for the former enhancement, although it has been reported that the decrease in the number of interface defects may be produced by light P doping.⁷

Since SiNCs embedded in SiO₂ have very large interface-to-bulk ratio, the large difference between the Si–Si atom bonding distance in the Si crystal cores and that of the surrounding SiO₂ induces high density of interface defects. Thus, we have to investigate P doping effects for SiNCs embedded in SiO₂ in which the interface defects are enough passivated. This is just the problem for Si nanostructures because Si surface is easily oxidized. Annihilation of deep levels caused by the interface defects, or passivation of the defects, is needed also for development of the future Si-nanostructure devices. One candidate of techniques for it is hydrogen passivation which has been intensively investigated for surface layers up to several microns of bulk Si,⁸ Si/SiO₂ interface,⁹ and Si surface.

In this study, we have used P⁺ ion implantation in SiNCs formed in SiO₂ matrices and a hydrogen passivation technique in order to clarify the P donor doping effects for PL of SiNCs with P concentrations ranging in three orders, much wider than those of the previous studies.³,⁷ For investigation of ion implantation effects in silicon (Si) nanostructures, we have measured PL and electron spin resonance (ESR) of un-

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doped SiNCs and P doped SiNCs embedded in SiO₂ before and after hydrogen passivation. We call hereafter these systems SiNCs/SiO₂, for simplicity. For these experiments, first the samples of SiNCs/SiO₂ systems were grown by high-temperature annealing at 1000 or 1200 °C of SiO₂ films deposited on a quartz glass. Second, for preparation of P-doped SiNCs, the SiNCs/SiO₂ were implanted with P⁺ ion and then annealed at 1000 °C, followed by an optimum hydrogen passivation to annihilate deep levels of defects at the Si/SiO₂ interfaces.

### II. EXPERIMENTAL PROCEDURE

SiO₂ films were deposited by thermal evaporation of SiO. The thickness was approximately 500 nm. Si⁺ ion implantation in thermally oxidized SiO₂ was also done to make another SiNCs/SiO₂ system. After the deposition or Si⁺ ion implantation, thermal annealing was performed at 1000 and 1200 °C, respectively, to attain SiNCs growth concomitantly with formation of SiO₂ phase. The averaged diameter was estimated to be about 3–4 and 5–6 nm for the films formed at 1000 and 1200 °C, respectively. These values were obtained from transmission electron microscopy (TEM) image measurements of some samples, as shown in Fig. 1 as a typical example (sample 2). Then phosphorus (P) ions were doubly implanted with the doses ranging from 10¹⁴ to 10¹⁷/cm² at energies of 100 and 200 keV to obtain nearly flat P impurity distribution in the depth direction, followed by thermal annealing of produced defects at 1000 °C. PL at room temperature (RT) and ESR measurements at 4.2 K were performed before and after hydrogen atom treatment (HAT),¹⁰–¹² i.e., hydrogen passivation of remaining defects such as P₇ centers induced at the interface between SiNCs and the surrounding SiO₂. HAT was done at 500 °C which was found to be an optimum temperature for efficient elimination of the interface defects.¹² The samples prepared in this systematical study are summarized in Table I.

### III. RESULTS AND DISCUSSION

The samples including SiNCs doped with peak P concentrations from 5 × 10¹⁸ to 5 × 10²¹/cm³ were systematically measured by PL at RT and ESR at 4.2 K. Figure 2 shows (a) PL spectra for SiNCs/SiO₂ system with a P concentration of 5 × 10²⁰/cm³ (sample 9) and (b) ESR spectra for that with 5 × 10¹⁸ P/cm³ (sample 3). As an example, sample 3 was formed by (1) 1000 °C annealing of SiO₂ films, (2) double P⁺ ion implantation at an energy of 100 keV with a dose of 4.0 × 10¹³ P⁺/cm² and at 200 keV with 1.0 × 10¹⁴/cm², (3) second annealing at 1000 °C, and (4) HAT at 500 °C. It can be seen in Fig. 2 that HAT enhances PL intensity by approximately ten times and decreases drastically ESR intensity of defects (P₇ centers) at the interface between Si core and SiO₂. These results indicate that the carrier compensation by the interface defects can be almost completely removed by hydrogen passivation at 500 °C. However, for these samples we were possible to detect no ESR signals of conduction electrons originated from P donors electrically activated in SiNCs because of very low spin numbers. For the samples used in our previous ESR work (Ref. 3), the volumes (~35 μm × 30 cm²) of the SiO₂ films with SiNCs were approximately 10² times larger than those (~0.15 μm × 0.5 cm²) of the present samples.

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SiNCs and SiO2 systems in which interface defects are enough

annihilated by a passivation technique such as HAT. In the

previous studies (for example, Refs. 3 and 7), no attention

has been paid to nearly perfect passivation of interface
defects.

Figure 3 shows the P concentration (or P dose) dependence of PL intensity for SiNCs samples (samples 1, 3, 5, 7, 9, and 11) with and without HAT, respectively. Here we assume the samples implanted with P ions have a homogeneous distribution of P between the Si cores and the SiO2 phase even after annealing, to describe averaged P concentrations instead of implanted P doses. These values are rough estimation because there will be competing processes, i.e., (1) the segregation coefficient Ns/Nsio2 of P impurity between Si and SiO2 is higher than 1.0 [1.1–1.5 for thermal oxidation of bulk Si at 1000 °C (Ref. 13)] and (2) there should be P segregation just at the Si/SiO2 interfaces for SiNCs embedded in SiO2.14,15 For the samples without HAT, we can divide the P concentration into three ranges. That is, (1) the PL intensity decreases compared to that of the unimplanted sample in the lower concentration range (samples 3 and 5), (2) it increases with increasing the concentration in the intermediate range (samples 7 and 9), and (3) it decreases again with increasing the P concentration in the higher range (sample 11). It is noted that large enhancement of PL can be seen after HAT in the three ranges.

An ion with a high energy of 100 or 200 keV penetrates into a SiO2 matrix including SiNCs, and then collides with atoms to be displaced by knock-on, resulting in high density of defects of SiNCs and SiO2. As the ion dose increases, the SiNCs become amorphous6 and then vague via mixing in-

duced by the multiple knock-on phenomena. Above a critical dose (approximately 100 keV P+ 4.0 × 1013/cm2 + 200 keV P+ 1.0 × 1016/cm2), complete mixing among SiNCs and SiO2 matrix will take place, leading again to a state of SiO2.

It is found from these results that some types of defects that act as nonradiative recombination centers remain even after high-temperature (1000 °C) annealing of implanted SiNCs/SiO2 system. Therefore, the defects should be passivated by an effective technique such as hydrogen passivation to obtain defect-free SiNCs in SiO2 for the study of ideal physical properties of SiNCs.

HAT is found to induce drastic changes in the intensities of PL and ESR spectra, as seen in Figs. 2 and 3. Similar results have been reported for hydrogen gas annealing12,16 although the passivation effect of HAT is stronger than that of H2 gas annealing.12 Through hydrogen passivation of defects by HAT, Pn centers can be nearly eliminated, as can be seen in Fig. 3(b). We measured furthermore deuterium (D) concentration depth profile instead of hydrogen by secondary ion mass spectrometry (SIMS) for a sample after deuterium atom treatment (DAT) of a thermally oxidized SiO2 layer. The SiO2 layer with 2.0 µm thickness includes high density of SiNCs formed by high dose (1 × 1017/cm2) Si+ ion implantation followed by high-temperature annealing. Figure 4 shows SIMS profile of D as a function of depth from the surface of SiO2 layer. D atoms are found to be trapped by the interfaces and SiO2 layer within the Si ion-implanted range (~150 nm), while D atoms penetrate easily into SiO2 without high density of SiNCs. If all the implanted Si atoms are assumed to form SiNCs with an average size of 5 nm, each SiNC can be estimated to get approximately 30 D atoms. This number suggests HAT and DAT passivate interface defects or annihilate defect levels in the band gap of SiNCs very efficiently.
Moreover, the PL intensity increases initially and then begins to decrease at a critical concentration as the P concentration increases, as can be seen in Fig. 3(a). This indicates that P doping in SiNCs induces small increase in PL intensity at the initial stage of lower P concentrations. Furthermore, it is clear that the PL intensity decreases monotonically with P doses higher than a critical one. This decrease is due to the Auger recombination process among excited electrons-holes, and the conduction electrons originated from donors doped in each SiNC, inducing nonradiative recombination.7

We have investigated the similar P concentration dependence and hydrogen passivation effects for SiNCs/SiO2 systems (samples 2, 4, 6, 8, 10, and 12) obtained by 1200 °C annealing as well. This higher annealing temperature produces SiNCs with larger averaged diameters (5–6 nm) in SiO2 (see Fig. 1). In Fig. 5 the P concentration dependence of PL intensity is shown for both the 1000 °C- and 1200 °C-annealed samples followed by HAT. The PL of SiNCs can be seen to increase first with increasing P concentration and reaches the maximum. The Auger recombination leading to the decrease in PL is clearly observed to take place above the critical P concentrations. The maximum can be seen at approximately $5 \times 10^{19}$ P/cm³ for 1000 °C-annealed sample and $5 \times 10^{18}$ P/cm³ for 1200 °C-annealed one. Thus the P concentrations for PL maximum depend on the averaged size of SiNCs.

These hydrogen passivation effects and P concentration dependence for the PL intensity of SiNCs suggest that the small increase in the PL intensity seen at relatively low P concentrations less than $1 \times 10^{19}$ P/cm³ is not caused by P-atom effects7,15 of decreasing nonradiative interface defects and also of changing significantly interface structures of SiNCs/SiO2. If we assume for simplicity that P impurities are distributed uniformly in the SiNCs/SiO2 films, as described already, almost all SiNCs contain one P donor at the critical concentrations of about $5 \times 10^{19}$ and $1 \times 10^{19}$ P/cm³ for the SiNCs formed by 1000 and 1200 °C annealing, respectively. Their averaged diameters are here estimated to be approximately 3.0 and 5.0 nm for each sample. Below these critical concentrations, P concentration is not so high (in $10^{18}$–$10^{19}$ P/cm³ range) for changing the interface structures.

This suggests a possibility that a single P donor doped in each SiNC enhances radiative recombination process via the donor level, relatively deeper than that in bulk Si, although this is in contrast to the conventional idea that the presence of one active donor doped in a SiNC gives Auger nonradiative recombination, leading to quenching of PL. The donor level in SiNCs has been known to be a little bit deeper (~60 meV) than that (~40 meV) of bulk crystal Si from larger ESR splitting of the hyperfine structure of P donors in SiNCs.3,4 Since the numbers of Si atoms contained in each SiNC with diameters of 3 and 5 nm are estimated to be approximately 680 and 3100, the number of allowed levels near the bottom of the discrete conduction band of each SiNC is much smaller compared to the states near the bottom of the continuum conduction band of bulk Si. Consequently a fraction of donor electrons is still bound by donor levels in SiNCs even at RT, which is entirely different from donors in bulk Si. Here we present one of possible ideas, as shown in Fig. 6, which indicates the radiative recombination process via the donor level after electron-hole excitation when only one P donor is doped in each SiNC. On the other hand, more than two donor electrons tend to be far each other due to the Coulomb repulsion and so extend in D⁺ level or the conduction band of a SiNC if two or more active P donors are doped in it without any compensating defects3 (see Fig. 6.) In this case, the Auger recombination process takes place more efficiently after the excitation, resulting in nonradiative recombination of excited electron-hole pair.7 It is noted that this possibility was first considered from the experimental results for the wide-range P-doped SiNCs/SiO2 systems obtained by optimum hydrogen passivation of the defects at the interfaces between SiNCs and the surrounding SiO2 layer.

IV. CONCLUSIONS

We have investigated (1) P⁺ implantation effects in the two types of SiNCs (with averaged diameters of approxi-
3–4 and 5–6 nm) embedded in SiO2, followed by annealing at 1000 °C, and (2) hydrogen passivation effects of the samples. Some types of defects such as Pb centers remain at the interfaces between SiNCs and the surrounding SiO2 even after high-temperature annealing of defects produced by ion implantation. It was clarified that hydrogen passivation using HAT induces significant changes in observed PL and ESR spectra since the interface defects are passivated with hydrogen. In wide-range P donor concentration dependence of PL for hydrogen passivated samples, PL intensity increases initially as the P concentration increases, and then begins to decrease at a critical concentration due to Auger nonradiative recombination. This suggests a possibility that a single P donor doped in each SiNC enhances radiative recombination process via a donor level.

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