

Phosphorus ion implantation in silicon nanocrystals embedded in SiO₂

Kouichi Murakami,^{1,a)} Ryota Shirakawa,¹ Masatoshi Tsujimura,¹ Noriyuki Uchida,² Naoki Fukata,³ and Shun-ichi Hishita⁴

¹*Institute of Applied Physics, University of Tsukuba, Tennodai 1-1-1, Tsukuba 305-8577, Japan*

²*Nanodevice Innovation Research Center, Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, Ibaraki 305-8562, Japan*

³*International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS) and JST PRESTO, 1-1 Namiki, Tsukuba 305-0044, Japan*

⁴*Sensor Materials Center, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

(Received 29 May 2008; accepted 23 January 2009; published online 10 March 2009)

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_b 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.

© 2009 American Institute of Physics. [DOI: [10.1063/1.3088871](https://doi.org/10.1063/1.3088871)]

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 the blue shift photoemission from Si nanostructures, and that shallow level impurities such as phosphorus (P) donor and boron (B) acceptor in bulk crystal Si have slightly deeper, but still shallow levels even in SiNCs less than approximately 10 nm.^{3,4} For nanoelectronics using semiconductors, impurity doping will continue to be very important for control of carrier concentration leading to control of the electrical conductivity and for control of the efficiency of light emission such as photoluminescence (PL) and electroluminescence.^{1,2,5} 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 SiO₂,¹⁻³ defect production,⁶ and impurity doping¹ in SiNCs.

Fujii and co-workers^{3,7} 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-

^{a)}Electronic mail: murakami@bk.tsukuba.ac.jp.

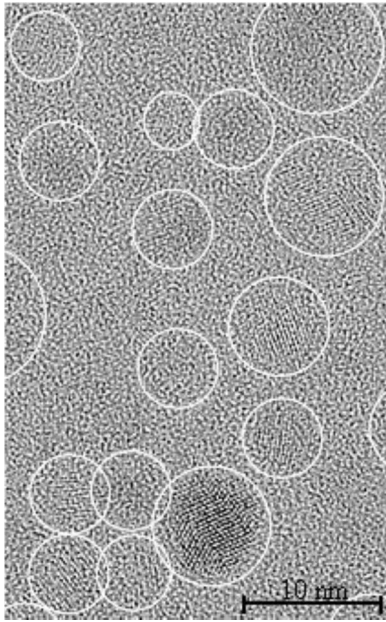


FIG. 1. Typical TEM image for a sample formed at 1200 °C, showing SiNCs embedded in SiO₂ by the dotted circulars.

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 SiO_x 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

SiO_x 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 P_b 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.

TABLE I. Samples prepared for P ion-implanted SiNCs.

Sample No.	Formation temperature of SiNCs (°C)	P ⁺ dose(1/cm ²)		Annealing temperature after ion implantation
		100 keV	200 keV	
1	1000			No anneal
2	1200	0	0	
3	1000			
4	1200	4.0 × 10 ¹³	1.0 × 10 ¹⁴	
5	1000			1000 °C
6	1200	2.0 × 10 ¹⁴	5.0 × 10 ¹⁴	
7	1000			
8	1200	4.0 × 10 ¹⁴	1.0 × 10 ¹⁵	
9	1000			1000 °C
10	1200	4.0 × 10 ¹⁵	1.0 × 10 ¹⁶	
11	1000			
12	1200	4.0 × 10 ¹⁶	1.0 × 10 ¹⁷	

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 SiO_x 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 (P_b 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 10⁴ times larger than those (~0.15 μm × 0.5 cm²) of the present samples.

Even for unimplanted samples, PL intensity increased by

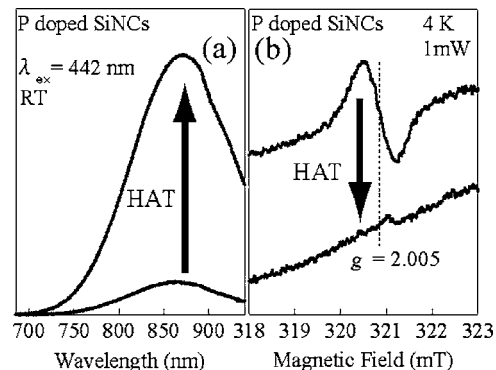


FIG. 2. HAT effects of (a) PL spectra observed at RT for sample 9 and (b) ESR spectra taken at 4.2 K for sample 3.

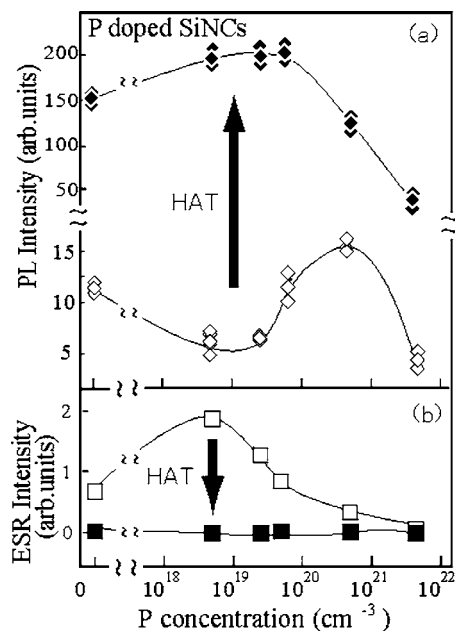


FIG. 3. Phosphorus concentration dependence of (a) the intensity of PL originated from SiNCs and (b) ESR intensity of interface defects before and after HAT.

12 times and ESR intensity decreased significantly by HAT. Similar effects were also observed for the other samples with other P concentrations. This strongly suggests that P donor concentration dependence should be investigated using SiNCs/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 about 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 $N_{\text{Si}}/N_{\text{SiO}_2}$ 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-

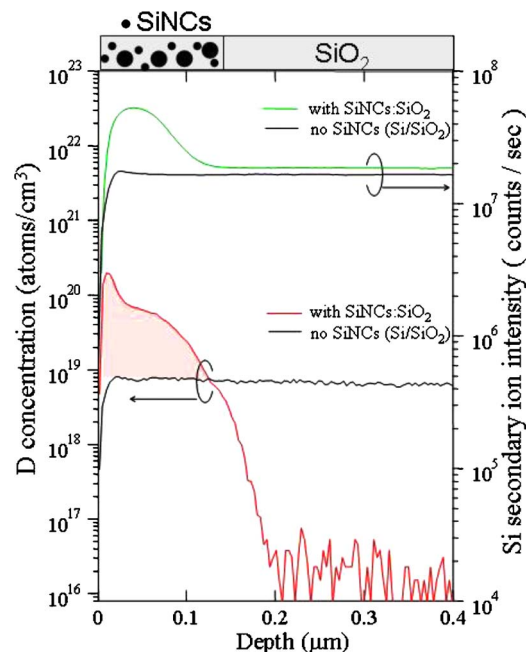


FIG. 4. (Color online) Deuterium atom profile after DAT of SiO₂ layer including SiNCs obtained by SIMS measurement.

duced by the multiple knock-on phenomena. Above a critical dose (approximately 100 keV P⁺ $4.0 \times 10^{15}/\text{cm}^2$ + 200 keV P⁺ $1.0 \times 10^{16}/\text{cm}^2$), complete mixing among SiNCs and SiO₂ matrix will take place, leading again to a state of SiO_x.

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 annealing,^{12,16} although the passivation effect of HAT is stronger than that of H₂ gas annealing.¹² Through hydrogen passivation of defects by HAT, P_b 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 ($1 \times 10^{17}/\text{cm}^2$) 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 averaged 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.

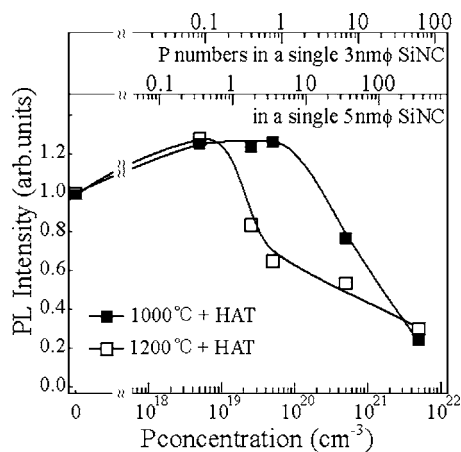


FIG. 5. PL intensity as a function of P peak concentration for 1000 °C-annealed and 1200 °C-annealed samples, followed by HAT at 500 °C. The calculated, average number of P donors included in each SiNC with averaged diameters of 3 nm and 5 nm are shown in horizontal axes at the top, respectively.

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 5×10^{19} P/cm³ for 1000 °C-annealed sample and 5×10^{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 1×10^{19} P/cm³ is not caused by P-atom effects^{7,15} 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 5×10^{19} and 1×10^{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

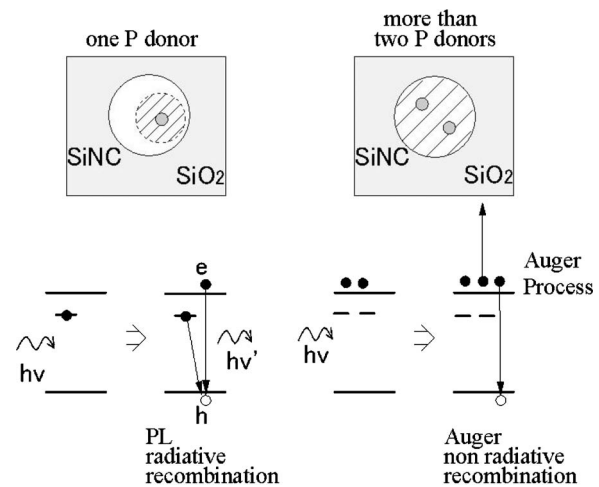


FIG. 6. A possible idea of the recombination of excited electron and hole in each SiNC including a single P donor and P donors more than two, corresponding to enhancement and quenching of PL.

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-

mately 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 P_b 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.

ACKNOWLEDGMENTS

We would like to thank Professor N. Kishimoto for preparation of the Si⁺ ion-implanted SiO₂ samples for comparison. This work was supported in part by the “Nanoscience Research Project” of University of Tsukuba in 2002–2006, by METI’s Innovation Research Project on Nanoelectronics Materials and Structures (2007–2010), and by MST (Foundation for Promotion of Material Science and Technology of Japan) Collaboration-Research Fund (2007–2008).

- ¹P. G. Kik and A. Polman, *Appl. Phys. Lett.* **91**, 534 (2002).
- ²M. Carrada, A. Wellner, V. Paillard, C. Bonafos, H. Coffin, and A. Claverie, *Appl. Phys. Lett.* **87**, 251911 (2005).
- ³M. Fujii, A. Mimura, S. Hayashi, Y. Yamamoto, and K. Murakami, *Phys. Rev. Lett.* **89**, 206805 (2002).
- ⁴D. V. Melnikov and J. R. Chelikowsky, *Phys. Rev. Lett.* **92**, 046802 (2004).
- ⁵Y. Liu, T. P. Chen, L. Ding, M. Yang, J. I. Wong, C. Y. Ng, S. F. Tu, Z. X. Li, C. Yen, F. R. Zhu, M. C. Tan, and S. Fung, *J. Appl. Phys.* **101**, 104306 (2007).
- ⁶D. Pacifici, E. C. Moreira, G. Franzo, V. Martorino, F. Priolo, and F. Iacona, *Phys. Rev. B* **65**, 144109 (2002).
- ⁷A. Mimura, M. Fujii, S. Hayashi, D. Kovalev, and F. Koch, *Phys. Rev. B* **62**, 12625 (2000).
- ⁸See, for example, *Hydrogen in Semiconductors*, edited by J. I. Pankove and N. M. Johnson, *Semiconductors and Semimetals Vol. 34* (Academic, New York, 1991).
- ⁹A. Stesmans, *Phys. Rev. B* **61**, 8393 (2000).
- ¹⁰N. Fukata, J. Chen, T. Sekiguchi, N. Okada, K. Murakami, T. Tsurui, and S. Ito, *Appl. Phys. Lett.* **89**, 203109 (2006).
- ¹¹N. Fukata, J. Chen, T. Sekiguchi, S. Matsushita, T. Oshima, N. Uchida, K. Murakami, T. Tsurui, and S. Ito, *Appl. Phys. Lett.* **90**, 153117 (2007).
- ¹²N. Fukata, C. Li, H. Morihiro, K. Murakami, M. Mitome, and Y. Bando, *Appl. Phys. A: Mater. Sci. Process.* **84**, 395 (2006); N. Fukata, S. Sasaki, S. Fujimura, H. Haneda, and K. Murakami, *Jpn. J. Appl. Phys., Part 1* **35**, 3937 (1996).
- ¹³H. F. Wolf, *Silicon Semiconductor Data* (Pergamon, New York, 1969), p. 571.
- ¹⁴K. Inoue, F. Yano, A. Nishida, T. Tsunomura, T. Toyama, Y. Nagai, and M. Hasegawa, *Appl. Phys. Lett.* **92**, 103506 (2008).
- ¹⁵X. D. Pi, G. Gresback, R. W. Liptak, S. A. Campbell, and U. Kortshagen, *Appl. Phys. Lett.* **92**, 123102 (2008).
- ¹⁶A. R. Wilkinson and R. G. Elliman, *Appl. Phys. Lett.* **83**, 5512 (2003).