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Hyperfine Structure of the Electron Spin Resonance of Phosphorus-Doped Si Nanocrystals

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Electronic states of P donors in Si nanocrystals (nc-Si) embedded in insulating glass matrices have been studied by electron spin resonance. Doping of P donors into nc-Si was demonstrated by the observation of optical absorption in the infrared region due to intraconduction band transitions. P hyperfine structure (hfs) was successfully observed at low temperatures. The observed splitting of the hfs was found to be much larger than that of the bulk Si:P and depended strongly on the size of nc-Si. The observed strong size dependence indicates that the enhancement of the hyperfine splitting is caused by the quantum confinement of P donors in nc-Si.

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The electronic states of shallow impurities in nanometer-size semiconductor crystals (nanocrystals) are expected to be strongly modified from those of bulk ones if the size is close to the effective Bohr radius of impurities. In particular, the binding (ionization) energy should be significantly enhanced because donors (acceptors) are squeezed three-dimensionally [1–3]. However, experimental studies concerning the doped shallow impurities in nanocrystals are still quite few [4,5], mainly due to the difficulties in preparing nanocrystalline samples that contain electrically active shallow impurities in a controlled manner. Since impurity doping is expected to change the electronic band structure of nanocrystals significantly, detailed knowledge on the electronic states is crucial to fully understand their optical and electrical transport properties.

The hyperfine structure (hfs) of electron spin resonance (ESR) of shallow donors is a sensitive sensor of the modification of their electronic states, because the strength of the hyperfine interactions is directly related to the localization of the dopant state electrons [6,7]. If donor wave functions are squeezed by spatial confinement, the hyperfine splitting should be enhanced. However, the size dependence of the hfs has not been successfully observed.

To observe the size dependent changes of the hfs, nanocrystalline samples should satisfy the following conditions. First, the size of nanocrystals must be close to the effective Bohr radius of shallow donors in bulk crystals. Second, the number of deep dangling-bond defects should be very small or ideally zero; otherwise, carriers are trapped at the defects, and electrons are not localized at donor nuclei [3]. Third, the average number of donors per nanocrystal should be nearly one. If more than two donors exist in a nanocrystal, the wave functions of these donors are overlapped, resulting in the delocalization of electrons and smearing the hfs. Furthermore, it is very im-

portant to develop a method to know (at least roughly) the average number of donors per nanocrystal. This cannot be made by simple element analysis, because impurity atoms are not necessarily in substitutional sites of nanocrystals and part of them are expected to be in matrices or interface regions. Hall effect is also not applicable, because carrier transport between nanocrystals is in many cases prohibited.

Recently, we have developed a method to grow P-doped Si nanocrystals (nc-Si) around 5 nm in diameter dispersed in phosphosilicate glass (PSG) thin films [8–10]. In these samples, nc-Si are isolated from the others by PSG barriers, and carrier transport between them is prohibited. Doping of P donors into nc-Si could be demonstrated by the observation of optical absorption in the infrared region due to intraconduction band electron excitation [10]. We also found that P doping results in the quenching of exciton photoluminescence (PL) due to the Auger interaction between electrons supplied by P donors and photoexcited excitons [8,9]. From the degree of PL quenching, we could roughly estimate the average number of electrically active P atoms in a nanocrystal.

These samples satisfy the condition mentioned in the above and provide an almost ideal system to study the hfs of doped nc-Si. In this work, we have performed ESR measurements of these samples. We demonstrate that P hfs can successfully be observed at low temperatures revealing a splitting much larger than that observed in bulk Si:P. We also show that the splitting depends strongly on the size of nc-Si and becomes larger with decreasing the size.

As demonstrated in our previous papers [10], PL intensity of P-doped nc-Si increases with increasing P concentration at low P concentration range and then decreases. In the present samples, this behavior is also observed. Figure 1 shows P concentration dependence of PL spectra. The PL peak observed at about 1.26 eV arises

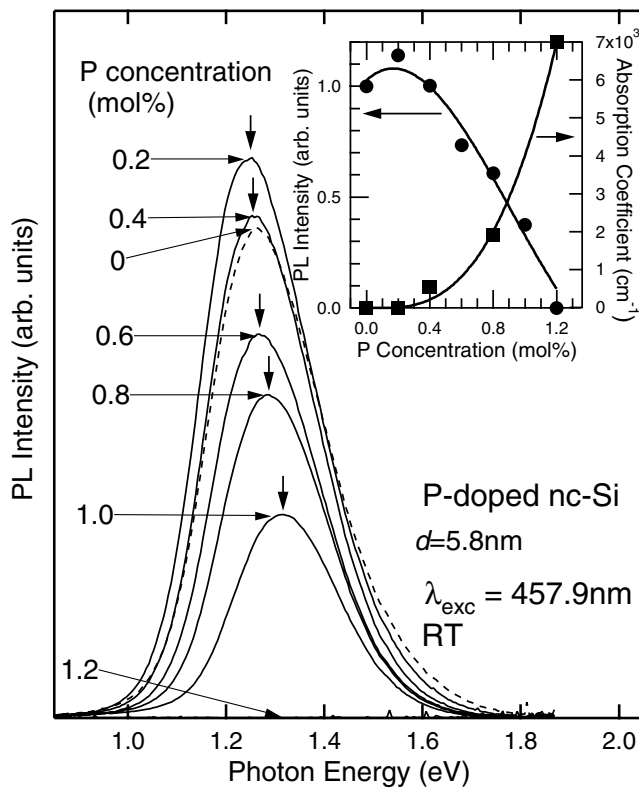


FIG. 1. PL spectra of nc-Si dispersed in PSG matrices. Arrows indicate the position of maximum intensity. In the inset, PL intensity and absorption coefficient at $4 \mu\text{m}$ are shown as a function of P concentration.

from the recombination of excitons confined in nc-Si [11]. The increase in the PL intensity was found to be due to the termination of dangling-bond defects at Si-SiO₂ interfaces by P doping [8,9].

The PL quenching at high P concentration range is always accompanied by the appearance of featureless optical absorption in the infrared region, which increases monotonously to a longer wavelength region. This absorption can be assigned to the electron excitation within conduction band valleys [10]. The observation of the absorption is the direct evidence that P atoms are doped into substitutional sites of nc-Si and electrons are supplied to conduction bands. In the inset in Fig. 1, the PL intensity and the absorption coefficient at $4 \mu\text{m}$ are plotted as a function of P concentration. For the sample without P doping, the absorption coefficient is nearly zero, because the detecting energy is far below the band gap of nc-Si. On the other hand, at the P concentration where the PL intensity just exceeds the maximum (0.4 mol%), the infrared absorption starts to appear. With increasing P concentration, i.e., with decreasing PL intensity, the absorption becomes stronger. If an electron is supplied in a nanocrystal, a three-body Auger recombination process among the electron and a photo-excited exciton becomes possible. Since the Auger recombination time is several orders of magnitude shorter than

the exciton radiative recombination time [3], PL efficiency of the nanocrystal is significantly reduced.

In actual samples, both doped and undoped nc-Si coexist and the ratio depends on P concentration. For example, for the sample with the P concentration of 0.8 mol%, the PL intensity is about half of the maximum intensity, suggesting that half of nc-Si are still intrinsic, and others are P doped. With further increasing P concentration, PL is almost completely quenched (e.g., 1.2 mol%), indicating that almost all nc-Si have P donors.

Figure 2 shows X-band ESR spectra obtained at 40 K. Two sharp ESR signals with $g = 2.006$ and 2.002 are due to dangling-bond defects at Si-SiO₂ interfaces [9]. By P doping, these signals become weaker. The behavior of these signals has been discussed in detail in our previous papers [9,10]. At the P concentration of 0.4 mol%, broad features appear at the magnetic fields of 3180, 3225, and 3270 G. The broad features are observed at temperatures lower than about 100 K. The g value of the central signal

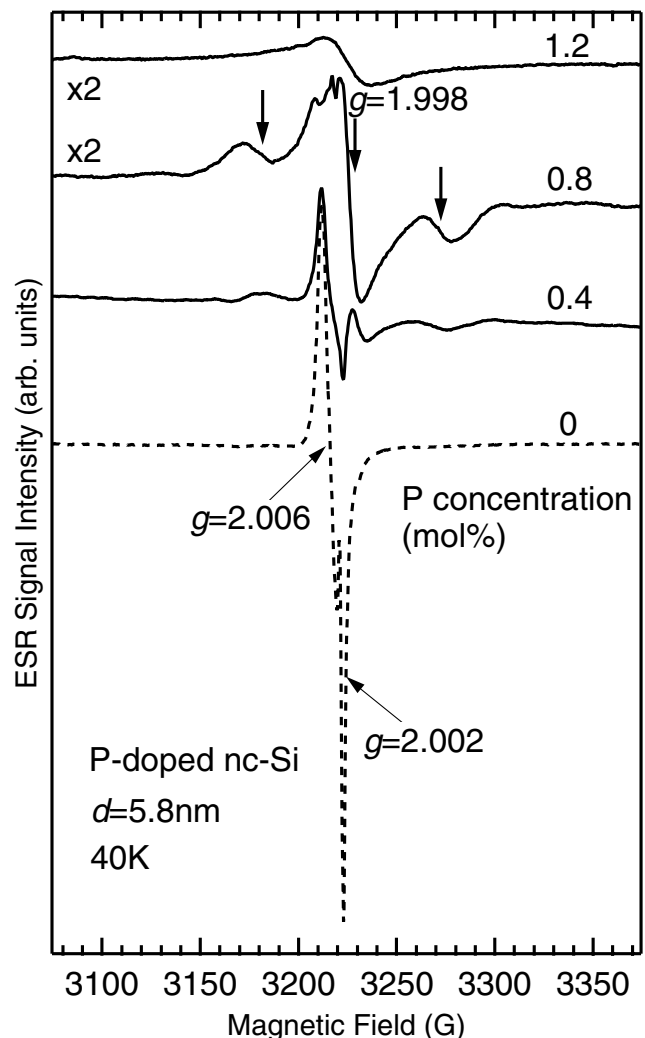


FIG. 2. ESR derivative spectra of nc-Si dispersed in PSG matrices. Arrows indicate the position of the features at 3180, 3225, and 3270 G.

at 3225 G is approximately 1.998, which is very close to that of the conduction-electron signal of bulk Si crystals [6,12,13]. This signal is thus assigned to the conduction electrons in nc-Si. This assignment is supported by infrared absorption data in the inset in Fig. 1, because the absorption starts to appear at the P concentration of 0.4 mol %.

On both sides of the conduction-electron signal with $g = 1.988$, two broad bands are observed at 3180 and 3270 G. These features are seen only at a moderate P concentration range. At the highest P concentration (1.2 mol %), the features completely disappear and only the smooth conduction-electron signal remains. The most probable origin of these features is the P donor hfs; a donor electron localizes at P nucleus and interacts with the nuclear spin leading to the split of a single resonance line into a line doublet [6]. Another possible origin of the doublet signal is defect centers such as P_4 centers in PSG matrices [14]. However, this possibility can be ruled out by the following experimental results.

We have studied in detail the ESR as a function of temperature, microwave power, P concentration, and the size of nc-Si. The hfs is observed at temperatures lower than 77 K and the signal saturates below 20 K. The saturation is due to very long spin-lattice relaxation time at low temperatures. The splitting depends on the temperature and becomes smaller with decreasing the temperature. The intensity and the splitting of the hfs also depend on microwave power. The hfs is more pronounced and the splitting becomes larger for smaller microwave power. These dependences may arise from size distribution of nanocrystals and size dependent spin-lattice relaxation time. The spin-lattice relaxation time is considered to be longer for smaller nanocrystals because of the stronger localization of donors. The longer spin-lattice relaxation time results in the saturation of signals from smaller particles at low temperatures and high microwave power. Therefore, under these measurement conditions, signals originate mainly from nanocrystals in the larger-side tail of size distribution. To avoid this effect, we measured ESR at temperatures as high as possible (40 K) with the lowest microwave power. Detailed discussion on these effects are beyond the purpose of this Letter and will be made elsewhere.

In the present samples, the size of nc-Si is close to the effective Bohr radius of P donors in bulk Si crystal. This means that if more than two P donors exist in one nanocrystal, their wave functions are overlapped, resulting in the delocalization of electrons even at low temperatures. Therefore, nc-Si containing more than two P donors will show only a conduction-electron signal. With this simple model, P concentration dependence of the ESR signal in Fig. 2 can be well explained. For the sample with the P concentration of 0.4 mol %, PL intensity starts to decline and infrared absorption starts to appear (see the inset in Fig. 1), suggesting that a fraction of nc-Si have P donors and others are still intrinsic. As a result, we can see weak

hfs and the conduction-electron signal. With further increasing P concentration (0.8 mol %), the ratio of doped nc-Si increases, resulting in the increase in both the hfs and the conduction-electron signal. In this P concentration, the conduction-electron signal is much stronger than the hfs, indicating that the number of nc-Si having more than two P donors is rather large. At the P concentration of 1.2 mol %, PL is completely quenched and only the conduction-electron signal is observed in ESR, suggesting that almost all nanocrystals contain more than two P donors.

In Fig. 2, the separation of the hyperfine splitting [$\Delta H(\text{hfs})$] is about 90 G, which is twice larger than that of the bulk value (42 G). This enhancement of the hyperfine splitting can be caused by the quantum confinement of P donors, because P donors are confined in a space close to the effective Bohr radius of P donors in bulk Si crystals (1.67 nm). This model can directly be proved by studying the size dependence of $\Delta H(\text{hfs})$.

In Fig. 3(a), the size dependence of $\Delta H(\text{hfs})$ is plotted and that of the ESR signal is shown in the inset. The symbol \times and the error bars represent average sizes and size distributions ($\pm \sigma$) of nc-Si estimated from high-resolution transmission electron microscopic (TEM) observations; about 70% of nc-Si in size distribution is in this range. It should be noted here that average sizes estimated from TEM observations are not directly related to the size of nc-Si responsible for the hfs, because only nc-Si having one P donor can contribute to the hfs. If P atoms are uniformly dispersed in a sample, the probability of having P atoms in a nanocrystal is larger for larger nc-Si. Therefore, at low P concentration, only nc-Si in the larger-side tail of size distribution is P doped and contribute to the hfs. On the other hand, at high P concentration, larger nc-Si have more than two P donors, and the average size of nc-Si responsible for the hfs becomes smaller even if the size distribution is the same.

This effect results in the high energy shift of PL with increasing P concentration (see Fig. 1), because PL quenching starts from larger nc-Si. In other words, in P-doped samples, PL spectra arise only from undoped nc-Si. Therefore, from the relation between PL peak energy and the average size of nc-Si obtained for undoped samples [11], we can roughly know the average size of nc-Si remaining undoped. The average size estimated by this method is slightly smaller than that of nc-Si containing one P donor. However, considering the small shift of PL peak energy by P doping, the difference may be very small ($\sim 10\%$ of average diameter) [11]. Therefore, we adopt the size estimated by this method to index the samples in Fig. 3 (\blacktriangle and \bullet).

In Fig. 3, we can clearly see that with decreasing the size of nc-Si, $\Delta H(\text{hfs})$ increases drastically. This is the direct evidence that the observed large hyperfine splitting arises from quantum confinement of P donors in nc-Si. From the observed size dependence of the hfs, we can roughly estimate the effective Bohr radius of donors (a_B^*).

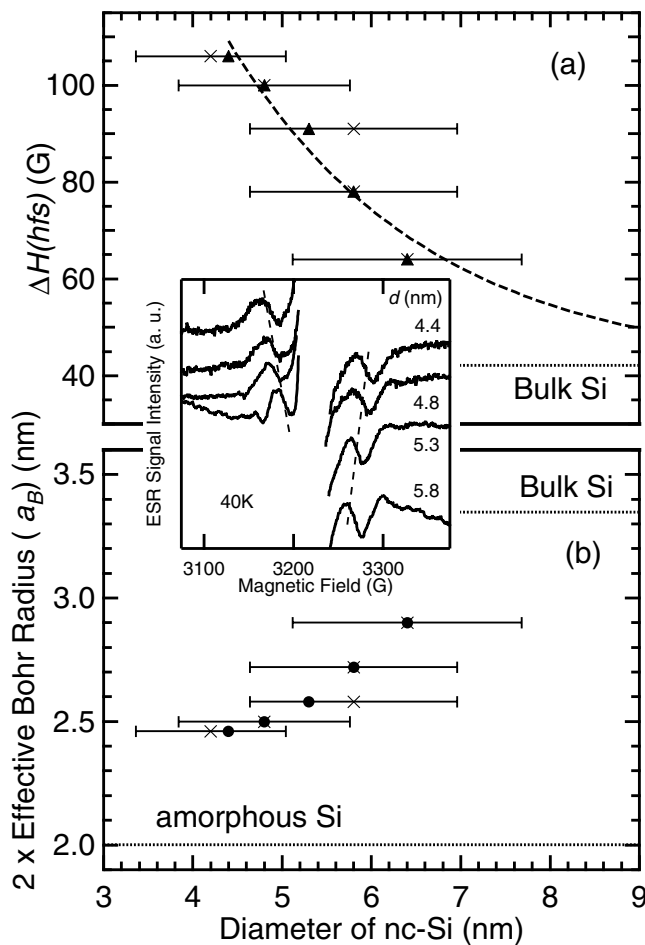


FIG. 3. (a) P hyperfine splitting and (b) twice the value of effective Bohr radius as a function of nc-Si diameter. P concentration is within the range between 0.2 and 0.8 mol %. The inset is the hfs of ESR derivative spectra for the samples with different sizes of nc-Si.

In a simple approximation that the ground-state donor wave function is spherically symmetric, $\Delta H(\text{hfs}) \propto |\Psi(0)|^2$, where $|\Psi(0)|$ is the value of the s -like electronic donor wave function at the position of the P nucleus [5,7]. Since the relation $|\Psi(0)|^2 \propto (a_B^*)^{-3}$ holds between $|\Psi(0)|$ and a_B^* , $\Delta H(\text{hfs}) \propto (a_B^*)^{-3}$ [5,7]. Using the value of $a_B^* = 1.67$ nm in bulk Si crystal, size dependence of a_B^* can be obtained. In Fig. 3(b), twice the value of a_B^* (i.e., the diameter) is plotted as a function of the size. We can clearly see that P donors are squeezed with decreasing the size. The estimated value is in between those of bulk Si crystals and amorphous Si [7] and is about the half of the size of nc-Si.

The enhancement of the P hyperfine splitting was also observed for hydrogenated microcrystalline silicon by Müller *et al.* [5]. They observed the splitting of about

110 G for the samples with the average nc-Si diameter of 20 nm, which is about 5 times larger than that of the present nc-Si. In their work, the observed hfs was quite small and the signal intensity in the doublet was less than 5% of the conduction-electron signal intensity. This seems to indicate that majority of nc-Si in size distribution contribute to the conduction-electron signal and nc-Si in the smaller tail of the distribution are responsible for the hfs.

Size dependence of hfs is also reported by Pawlak *et al.* [4] for nc-Si prepared by ball milling and oxidation. However, the range of the nc-Si size studied (around 100 nm in diameter) is much different from that of the present work. They observed slight narrowing of the hyperfine splitting with decreasing the size and explained the narrowing by anisotropic perturbation of the conduction band bottom due to the asymmetric shape of nc-Si (the ratio between the short and long axis is about 0.6). Since nc-Si in the present samples are nearly spherical, the effect they discussed is not expected.

In conclusion, we have succeeded in observing P hfs in P-doped nc-Si about 5 nm in diameter. The observed splitting was much larger than that of P-doped bulk Si, and the splitting increased with decreasing the size. This strong size dependence indicates that the observed enhancement of the hyperfine splitting is due to the quantum confinement of P donors in nc-Si. It was found that the size of donors estimated from the hfs is about the half of that of nc-Si.

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