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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.

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 important 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
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-SiO$_2$ 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 $\mu$m are plotted as a function of P concentration.

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-SiO$_2$ 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...
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 in-
frared 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 \( P_{\delta} \) 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 pro-
nounced 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 pur-
pose 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 nano-
crystal, 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 in-
creasing 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 concentra-
tion, 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, suggest-
ing 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 hyper-
fine 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 \( ± \sigma \) of nc-Si estimated from high-
resolution transmission electron microscopic (TEM) ob-
servations; 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 probabil-
ity 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 con-
tribute to the hfs. On the other hand, at high P concentra-
tion, 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 contain-
ing 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 (\( \triangle \) 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 (\( a^*_B \)).
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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