

Pulsed EPR studies of Phosphorus shallow donors in diamond and SiC

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Abstract

Phosphorus shallow donors having the symmetry lower than T_d are studied by pulsed EPR. In diamond:P and 3C–SiC:P, the symmetry is lowered to D_{2d} and the density of the donor wave function on the phosphorus atom exhibits a predominant p -character. In 4H–SiC:P with the site symmetry of C_{3v} , the A_1 ground state of the phosphorus donors substituting at the quasi-cubic site of silicon shows an axial character of the distribution of the donor wave function in the vicinity of the phosphorus atom.

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1. Introduction

Controlling the conductivity by doping shallow donor or acceptor impurities is essential in fabrication of semiconductor electronic devices. In the effective mass theory (EMT), the dopant atoms binding one electron or hole are described as solid state analogues of hydrogen atom with the Coulomb potential reduced by $1/\epsilon_s$ (ϵ_s , the static dielectric constant) and the effective mass of the relevant conduction band of the host crystal [1]. The bound electron has a $1s$ like ground state and $2s, 2p, 3s, 3p, \dots$ like excited states. Among the differences of shallow impurity states from the hydrogen atom is $1s$ ground state degeneracy originating from the presence of the equivalent minima in the conduction band which occurs in semiconductor crystals with the conduction band minima located not at the center of the Brillouin zone ($\mathbf{k} = 0$).

The degeneracy of the $1s$ ground state is partly lifted by the site symmetry of the impurity atom (valley–orbit

splitting). In the case of group-V impurity in silicon, the sixfold degeneracy due to six conduction band minima is split by T_d symmetry to a singlet $1s(A_1)$, a doublet $1s(E)$ and a triplet $1s(T_2)$ with the ground state $1s(A_1)$. The singlet state which is a symmetric superposition of all six valleys has a non-vanishing value for $|\psi(0)|^2$ and gives rise to an isotropic hyperfine splitting. For the doublet and triplet states which have a node at the donor nucleus ($|\psi(0)|^2 = 0$), no isotropic hyperfine interaction is expected. The phosphorus donor in silicon exhibits the T_d symmetry with the isotropic ^{31}P hyperfine splitting of 4.2 mT and the isotropic g -value of 1.99850 [2]. In the case of group-V impurity in germanium, the fourfold degeneracy is split by T_d symmetry to a singlet $1s(A_1)$ and a triplet $1s(T_2)$ with the ground state $1s(A_1)$. The phosphorus donor in germanium exhibits the T_d symmetry with the isotropic ^{31}P hyperfine splitting of 2.1 mT and the isotropic g -value of 1.5631 [3].

The valley–orbit splitting is due to the interaction of the localized donor electron and the donor core (called the central cell correction) and is dependent on the donor species (chemical effect). While the other hydrogen-like

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excited states ($2p_0, 2s, 2p_{\pm}, \dots$) lie well above these $1s$ states, the separation between/among the $1s$ states (valley-orbit splitting) is rather small.

We have studied the phosphorus shallow donors in diamond, $3C\text{-SiC}$, and $4H\text{-SiC}$ in which phosphorus impurities are introduced during the CVD growth. The present work concerns with the effect of a lower symmetry brought either by the hexagonal symmetry of the host crystal ($4H\text{-SiC:P}$) or by local distortion in the case of cubic symmetry of host crystal (diamond:P, $3C\text{-SiC:P}$).

2. Experiment

Electron paramagnetic resonance (EPR) has been proved powerful in providing detailed information about the structure of the shallow donor impurities in silicon and germanium. Here, we have applied pulsed EPR techniques. Echo-detected EPR, in which the intensity of Hahn echo ($90^\circ - \tau - 180^\circ - \tau - \text{echo}$) is measured as a function of the external magnetic field, has been utilized to eliminate unwanted, disturbing signals by choosing the value of τ and the repetition rate of the pulse sequence in accumulation and to obtain spectra free from distortion due to passage effects encountered in continuous wave EPR for a system with a relatively long relaxation time. Pulsed electron nuclear double resonance (ENDOR) was used to extract weak hyperfine interaction hidden underneath the line broadening ($3C\text{-SiC:P}$) or to identify the origin of the doublet (diamond:P). The valley-orbit splitting is estimated from the temperature dependence of the spin-lattice relaxation time when the spin-lattice relaxation is dominated by the Orbach process which is resonant two-phonon process with the phonons of energy comparable to the transition between the ground state and the excited state [4]. The three-pulse inversion recovery ($180^\circ - t - 90^\circ - \tau - 180^\circ - \tau - \text{echo}$) was used to measure the spin-lattice relaxation time. Pulsed experiments were carried out using a Bruker Elexys E580 spectrometer, and samples were kept in an Oxford ER4118CF cryostat. Temperature was controlled with an Oxford ITC503 temperature controller.

3. Results and discussion

In Fig. 1, echo-detected EPR spectra of diamond:P, $3C\text{-SiC:P}$, and $4H\text{-SiC:P}$ are shown. In diamond:P and $4H\text{-SiC:P}$, the ^{31}P ($I = 1/2, 100\%$) hyperfine splitting was resolved. From the number of distinguishable sites when the magnetic field (\mathbf{B}) is along a high symmetry direction (2 sites in both $\mathbf{B} // [100]$ and in $\mathbf{B} // [011]$ and one site in $\mathbf{B} // [111]$ for both diamond:P and $3C\text{-SiC:P}$, one site both in $\mathbf{B} // \mathbf{c}$ and in $\mathbf{B} \perp \mathbf{c}$ for $4H\text{-SiC:P}$) and from the pattern of the rotational plots, it is determined that the symmetry of the phosphorus donors is D_{2d} for diamond:P and $3C\text{-SiC:P}$ and C_{3v} for $4H\text{-SiC:P}$. By using pulsed ENDOR, it is confirmed that the doublet structure in diamond:P (Fig. 1(a)) is arising from the ^{31}P hyperfine interaction. The two-line structure at $\mathbf{B} // [100]$ of

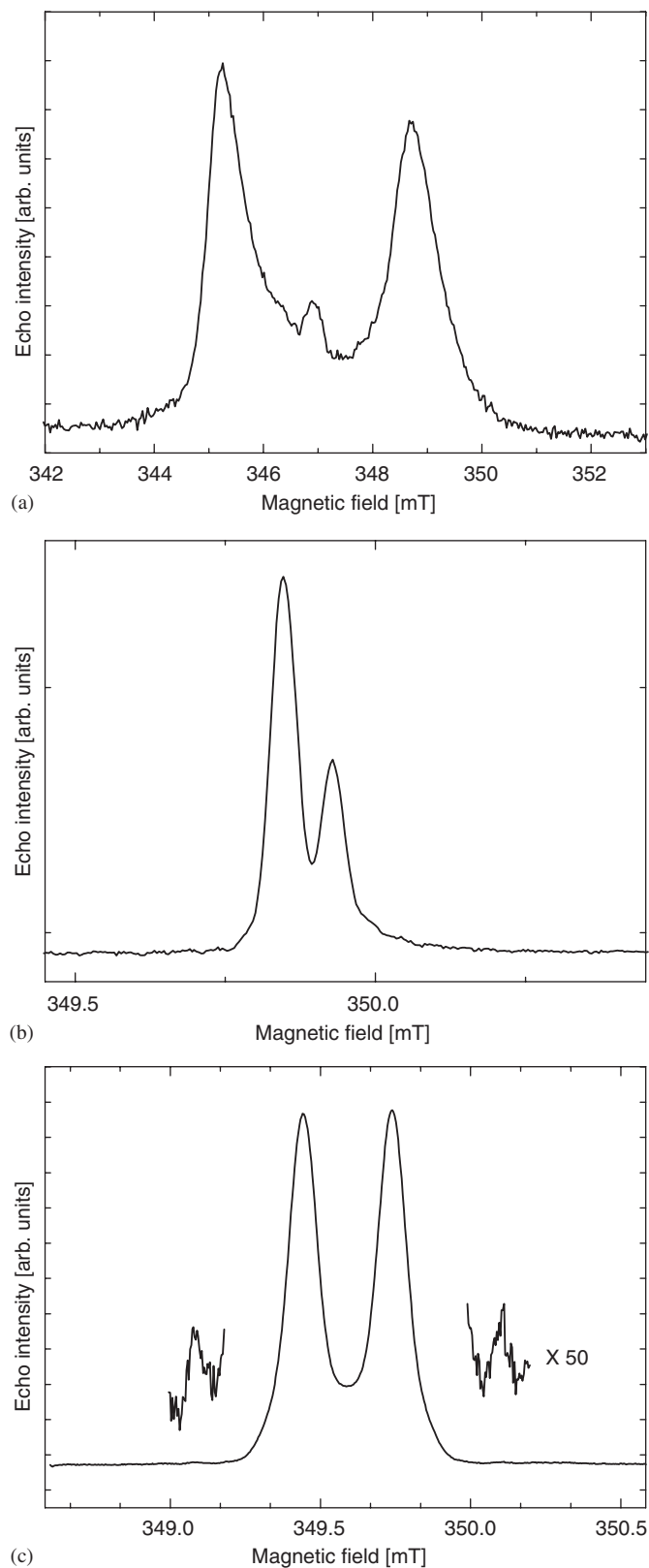


Fig. 1. Echo-detected EPR spectra of phosphorus donors: (a) diamond:P (10 K, $\mathbf{B} // [111]$, 9.7246 GHz), (b) $3C\text{-SiC:P}$ (5 K, $\mathbf{B} // [001]$, 9.8181 GHz), (c) $4H\text{-SiC:P}$ (6 K, $\mathbf{B} // [0001]$, 9.8177 GHz).

Table 1
EPR parameters

	Symmetry	g_{\parallel}	g_{\perp}	A_{\parallel} (mT)	A_{\perp} (mT)
Diamond:P(10 K)	D_{2d}	1.99051	2.00573	5.68	1.14
3C–SiC:P (5 K)	D_{2d}	2.0051	2.0046	1.9×10^{-2}	-4.6×10^{-3}
4H–SiC:P (6 K)	C_{3v}	2.0065	2.0006	0.294	0.21
Si:P (Ref. [2])	T_d	1.99850(isotropic)		4.2 (isotropic)	

Table 2
 ^{31}P hyperfine and orbital parameters

	A_{iso} (mT)	b (mT)	η^2	β^2/α^2
Diamond:P(10 K)	2.66	1.51	0.121	19
3C–SiC:P (5 K)	3.2×10^{-3}	7.9×10^{-2}	6.1×10^{-4}	89
4H–SiC:P (6 K)	2.38×10^{-1}	2.8×10^{-2}	2.6×10^{-3}	4.3
Si:P (Ref. [2])	4.2	0	8.8×10^{-3}	0

3C–SiC:P (Fig. 1(b)) is arising from the difference in the g -value (site splitting). And the weak ^{31}P hyperfine interaction hidden underneath the line broadening was extracted by pulsed ENDOR technique. The spin-Hamiltonian parameters were determined by fitting the line positions (\mathbf{g}, \mathbf{A} of diamond:P, 4H–SiC:P, \mathbf{g} of 3C–SiC:P) and the ENDOR frequencies (\mathbf{A} of 3C–SiC:P) to the spin-Hamiltonian:

$$\mathcal{H} = \beta_e \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} - g_n \beta_n \mathbf{B} \cdot \mathbf{I}. \quad (1)$$

Here $S = 1/2$ and $I = 1/2$, and $g_n = 2.2632$ for ^{31}P . The principal values of \mathbf{g}, \mathbf{A} and the hyperfine and orbital parameters are listed in Tables 1 and 2. The ^{31}P hyperfine interaction is divided into the isotropic part A_{iso} and the anisotropic part ($A_{\parallel} = A_{\text{iso}} + 2b, A_{\perp} = A_{\text{iso}} - b$). To discuss the distribution of the donor wave function, we use the fractional unpaired population (η^2) on the phosphorus atom and the sp hybrid ratio (β^2/α^2 , where $\alpha^2 + \beta^2 = 1$) obtained by assuming that the one-electron linear combination of atomic orbital (LCAO) approximation should be applicable for interpreting the hyperfine parameters. In the estimation ($\eta^2 \alpha^2 a_0 = A_{\text{iso}}, \eta^2 \beta^2 b_0 = b$), we used $a_0 = 474.79$ mT and $b_0 = 13.088$ mT.

In both, diamond:P and 3C–SiC:P, we note that the wave function of the donor electron on the phosphorus atom is almost purely p -like. Thus, the ground state is not likely to be A_1 . Diamond has Si-like conduction band structure with the minimum located at k_0 (~ 0.74) along the Δ -axis, near the X point [5]. Under the T_d symmetry of an unrelaxed substitutional site, the sixfold degeneracy of the $1s$ ground state due to six minima of the conduction band is split into a singlet $1s(A_1)$, a doublet $1s(E)$, and a triplet $1s(T_2)$. In 3C–SiC:P, the threefold degeneracy of the $1s$ ground state due to three minima of the conduction band with the conduction band minimum at the X point [6] is either remains threefold degenerate with a triplet state T_2

or splits into a singlet A_1 and a doublet E under the T_d symmetry. With lowering symmetry from T_d to D_{2d} , the doublet E is split into A_1 and B_1 and the triplet T_2 is split into a singlet B_2 and a doublet E . For both diamond:P and 3C–SiC:P, since the wave function on the phosphorus has predominant p -character, the ground state is likely to be B_2 (T_{2z} in T_d) which has a node at the donor nucleus.

In 4H–SiC:P, the p -character of the wave function of the donor electron on the phosphorus atom is large (the sp ratio ~ 4). In 4H–SiC:P, the threefold degeneracy of the $1s$ ground state arising from the three equivalent conduction band minima with the conduction band minimum located at M point is split into a singlet A_1 and a doublet E under the C_{3v} symmetry of the donor site [7]. While each silicon and carbon has two inequivalent lattice sites called hexagonal (h) and quasi-cubic (k) sites, only one kind of EPR spectrum was observed, which we assign to be arising from phosphorus shallow donors at Si(k) site. An *ab initio* calculation using a 576-atom supercell has predicted that A_1 is lower than E for phosphorus at the Si(k) site, while E is lower than A_1 for phosphorus at the Si(h) site. The calculation has predicted that the spin density on the axial carbon is much larger than that of the three basal carbon atoms for the ground state A_1 of the phosphorus at Si(k), while the spin density on the three basal carbon atoms is much larger than that on the axial carbon atom for the ground E state of the phosphorus at Si(h). The observation of one set of ^{13}C hyperfine satellite arising from one nearest-neighbor carbon atom (Fig. 1(c), isotropic within the resolution of echo-detected EPR with the fractional spin density $\eta^2 \sim 5 \times 10^{-3}$) supports the assignment that the observed EPR spectrum is arising from the phosphorus donor at Si(k). The absence of the EPR spectrum from the phosphorus at the Si(h) site is ascribed to the degenerate ground state E which is likely to be broadened by local strains. From the temperature dependence of the spin-lattice relaxation time, the valley-orbit splitting, i.e., the energy separation between the ground and excited states within the $1s$ manifold has been estimated to be 4.2 meV for 4H–SiC:P. This rather small valley-orbit splitting suggests that the relative energy positions of A_1 and E might be well affected by the difference in the arrangement of next-nearest neighbors between Si(k) and Si(h) sites. Thus, the experimental observation agrees qualitatively with the results of the *ab initio* calculation that the ordering of A_1 and E could be different between the two inequivalent silicon sites.

4. Summary

As a summary, phosphorus donors, diamond:P, 3C–SiC:P, and 4H–SiC:P are studied by pulsed EPR. In the cubic lattices of diamond and 3C–SiC, the predominant p-character of the wave function density on the phosphorus atom is ascribed to the B_2 ground state (which corresponds to T_{2z} of the T_d symmetry) under the symmetry of D_{2d} . In the hexagonal lattice of 4H–SiC, the observation of one set of ^{13}C satellites and the sp hybrid orbital of phosphorus pointing toward the carbon atom suggests that the extent of the donor wave function is quite non-spherical at least in the vicinity of the phosphorus atom for the A_1 ground state under the C_{3v} symmetry.

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