Shallow P donors in 3*C*-, 4*H*-, and 6*H*-SiC

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Abstract. EPR spectra originating from phosphorus shallow donors occupying silicon sites in 3*C*-, 4*H*-, and 6*H*-SiC are identified by using CVD grown films in which the interference from the signals from the nitrogen shallow donors is practically absent. Phosphorus donors occupying both silicon and carbon sites are observed in high-energy phosphorus ion implanted semi-insulating 6*H*-SiC which was also free from the interference from the signals from the nitrogen shallow donors.

Introduction

Incorporation of shallow donors or acceptors which controls the type and the magnitude of conductivity is essential for the fabrication of semiconductor devices. In silicon carbide (SiC), nitrogen (N) which is easily, even often unintentionally, incorporated during the crystal growth is used for controlling *n*-type conductivity. Phosphorous (P) which is an alternative shallow donor to N in SiC is expected to have advantages over N in the high doping range where the electrical conductivity in N-doping saturates [1]. Ion implantation which provides the means of selective area doping is required in the device fabrication process. For the electric activation of implanted ions, post-implantation annealing which removes implantation-induced defects and drives the implanted ions into the desired lattice sites is required. For improving the doping efficiency, characterization of the microscopic structure of implanted P ions is important. Electron paramagnetic resonance (EPR) is useful to identify impurities and defects at the microscopic level. In applying EPR techniques to elucidate the thermal behavior of implanted ions, it is crucially important to establish the assignment of the EPR spectra arising from the P shallow donors. The EPR spectra of isolated P shallow donors are observed in the neutral charge state when the donor electron is bound in the impurity phosphorus atom. Most of EPR studies of P in SiC used 6*H*-SiC doped by neutron transmutation of ^{30}Si in the host crystal to ^{31}P [2-6]. The phosphorus related centers reported are P_a, P_b [2,3] (labeled P_1, P_2 in Ref.2 and sP_{c1}, sP_{c2} in Ref.6) and P+V [2] (labeled sP_h in Ref. 6) observed at 77 K, P_1, P_2 [3-5] (labeled I_1, I_2 in Ref.3 and dP_h, dP_{c1}/dP_{c2} in Ref. 6) observed at $T < 10$ K. The P_a, P_b, and P+V spectra are observable down to 4 K [6, 7]. The P_a, P_b spectra were also observed in P-ion (9-21 MeV, and 340 keV) implanted 6*H*-SiC [8]. In these neutron-transmutation or ion-implantation doping studies, strong signals from N donors in the substrate had prevented detailed studies. It is natural to assume that P should substitute for silicon. However, for the case of doping by neutron transmutation, it was pointed out that a considerable fraction of P might end up in occupying the carbon sites after high-temperature (~1900 °C) annealing required in the doping method [7]. The P_a, P_b spectra are attributed to P at hexagonal carbon sites and P at quasi-cubic carbon sites (and P_C-C_{Si}), respectively [7]. The recoil process of the neutron transmutation creates the radiation

damages (vacancies) and interstitial P atoms [7]. It is likely that a similar, probably less severe, situation is encountered in the case of P incorporation by ion implantation.

In our present work, we have obtained EPR spectra from shallow P donors at silicon site in 6*H*-SiC as well as in 3*C*-SiC, and 4*H*-SiC by using the samples in which P is introduced during the chemical vapor deposition (CVD) growth and which are free from the interference by the N donor signals. After identifying the EPR spectra of the P donors at silicon sites, we have applied to determine the site of P after high-energy P ion implantation and the subsequent high-temperature annealing by using a high-purity semi-insulating (HPSI) 6*H*-SiC substrate which is also free from the interference by the N donor signals.

Experiment

3*C*-SiC, 4*H*-SiC, and 6*H*-SiC epitaxial layers doped with P during the CVD growth [9] were used. High-energy P ion implantation to *n*-6*H*-SiC crystals $(N_A - N_D \approx 10^{17}\,\mathrm{cm^{-3}})$ and HPSI 6*H*-SiC substrates was carried out at 800 °C with nine energies in the range from 9 to 21 MeV. The fluence of 5×10^{13} cm^{-2} was used for each stage. Post-implantation annealing was performed at 1650 °C for 30 min in Ar atmosphere.

EPR measurements were carried out using a Bruker E500 X-band spectrometer, a Bruker Elexsys E580 spectrometer, and a home-built W-band (95 GHz) spectrometer.

Results and discussion

It should be noted that the EPR signals of the N shallow donors were not observed in our CVD grown epitaxial layers. In Fig. 1, X-band echo-detected EPR spectra of 3*C*-SiC and 4*H*-SiC are shown. In Fig. 2(d), an X-band cw-EPR spectrum of 6*H*-SiC is shown. The EPR spectra from the P shallow donors are
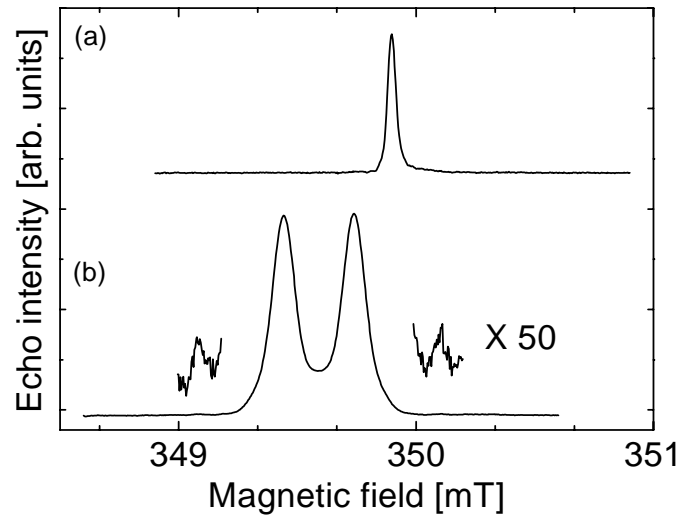
Fig. 1. Echo-detected EPR spectra of P-doped CVD grown epitaxial layers: (a) 3*C*-SiC:P (5 K, **B**//[111]) and (b) 4*H*-SiC (6 K, **B**//[0001]).
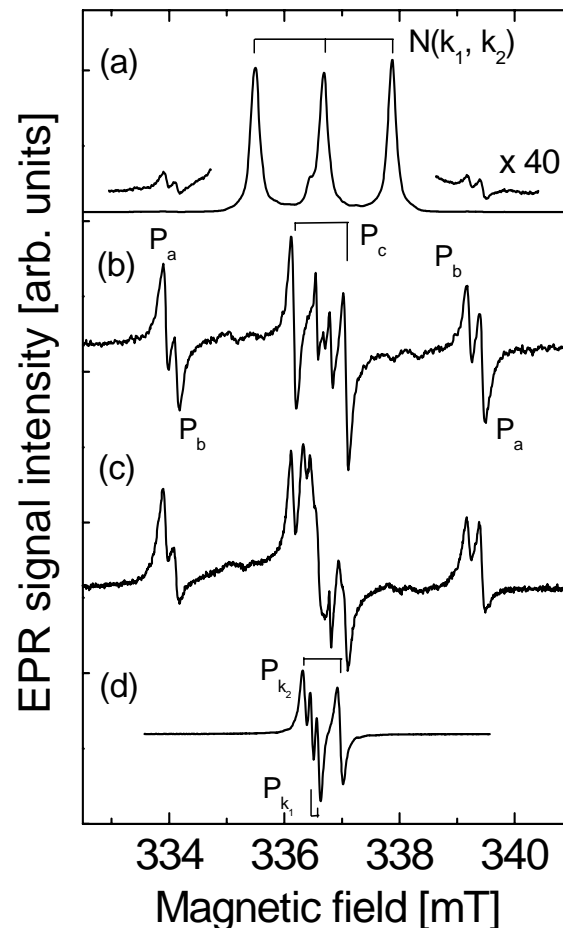
Fig. 2. EPR spectra (**B**//[0001]): (a) P-ion implanted and annealed *n*-6*H*-SiC, (b) P-ion implanted and annealed HPSI-6*H*-SiC (60 K), (c) P-ion implanted and annealed HPSI-6*H*-SiC (6 K), (d) P-doped CVD grown epitaxial layers of 6*H*-SiC (6 K).

Table 1. EPR parameters (the g and ^{31}P hf tensors) of the P centers.

Center	Site	Symmetry	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (mT)	$A_{\perp}$ (mT)
3C-SiC:P (5 K)	Si	D_{2d}	2.0051	2.0046	1.9×10^{-2}	-4.6×10^{-3}
4H-SiC:P$_k$ (6 K)	Si(k)	C_{3v}	2.0065	2.0006	0.294	0.21
6H-SiC:P$_{k1}$ (5 K)	Si($k_{1,2}$)	C_{3v}	2.0046	2.0028	0.113	0.023
6H-SiC:P$_{k2}$ (5 K)	Si($k_{1,2}$)	C_{3v}	2.0039	2.0025	0.607	0.220
6H-SiC:P$_a$ (60 K)	C(h) [7]	C_{3v}	2.0039	2.0029	5.51	5.43
6H-SiC:P$_b$ (60 K)	C($k_{1,2}$) [7]	C_{3v}	2.0040	2.0027	5.09	5.09
6H-SiC:P$_c$ (60 K)	?	C_{3v}	2.0044	2.0026	0.91	0.66

labeled P in 3C-SiC, P$_k$ in 4H-SiC, and P$_{k1}$ and P$_{k2}$ in 6H-SiC, respectively, based on their assignment of the silicon sites to be described later. P$_{k1}$ and P$_{k2}$ correspond to P$_1$ and P$_2$, respectively.

The observation of the resolved ^{31}P (I=1/2, 100%) hyperfine (hf) structure in the case of P$_{k1}$, P$_{k2}$ in 6H-SiC and P$_k$ in 4H-SiC and the observation of ^{31}P ENDOR in the case of P in 3C-SiC by using pulsed ENDOR technique confirm that the centers are related to P. The symmetry of the P donors was determined by the angular dependence of the EPR line positions.

While each silicon and carbon has two inequivalent lattice sites called hexagonal (h) and quasi-cubic (k) sites in 4H-SiC, only one kind of EPR spectrum was observed, which we assign to be arising from P shallow donors at Si(k) site (P$_k$). An *ab initio* calculation using a 576-atom supercell has predicted that A_1 is lower than E for P$_k$, while E is lower than A_1 for P at the Si(h) site (P$_h$). 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 P$_k$, 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 P$_h$. The observation of one set of ^{13}C hf satellite arising from one nearest-neighbor carbon atom as shown in Fig. 1(b) supports the assignment that the observed EPR spectrum is arising from P$_k$. The absence of the EPR spectrum from P$_h$ is ascribed to the degenerate ground state E which is likely to be broadened by local strains.

As shown in Fig. 2(d), two doublets, P$_{k1}$ and P$_{k2}$ (P$_{k2a}$) are observed in 6H-SiC for B//[0001]. With rotating the magnetic field away from [0001], the intensity of the With rotating from [0001], the intensity of the P$_{k2a}$ doublet decreases and the P$_{k2b}$ doublet appears. The intensity of the P$_{k2a}$/P$_{k2b}$ doublets strongly depends on the direction of the magnetic field. The ESEEM (electron spin echo envelope modulation) which is arising from the interference between the allowed ($\Delta M_S = \pm 1$, $\Delta m_I = 0$) and forbidden ($\Delta M_S = \pm 1$, $\Delta m_I = \pm 1$) transitions confirmed that the P$_{k2a}$/P$_{k2b}$ doublets in 6H-SiC (i.e. sP$_{c1}$/sP$_{c2}$ [6], which were previously assigned to two P centers at the two quasi-cubic sites [8]) belong to the allowed and forbidden transition of the same P center (P$_{k2}$). The analysis including the nuclear Zeeman interaction provides a satisfactory explanation for the angular dependence of the intensity of the P$_{k2a}$/P$_{k2b}$ doublets. The observation of ^{13}C satellites in P$_{k1}$, P$_{k2}$ suggests that P occupies silicon site. From the analogy to P$_k$ in 4H-SiC, the P$_{k1}$ and P$_{k2}$ doublets are assigned to the P shallow donors at Si(k_1, k_2) sites.

The assignment of P in 3C-SiC to be arising from P at Si site is based on the similarity of the temperature dependence of the EPR signals to that of P$_k$ in 4H-SiC and P$_{k1}$, P$_{k2}$ in 6H-SiC. The EPR parameters obtained in the present work are listed in Table I. The ^{31}P hf-tensors of P in 3C-SiC and P$_{k1}$ in 6H-SiC were determined by pulsed-ENDOR and that of P$_{k2}$ in 6H-SiC by ESEEM.

In Figs. 2(b) and 2(c), EPR spectra of HPSI 6H-SiC implanted with high-energy P ions and subsequently annealed are shown. In contrast to the case of n-6H-SiC substrate shown in Fig. 2(a), the absence of the signals from the N shallow donors allows us to examine the presence of the bound P donors at silicon sites. In the spectrum taken at 60 K, the P$_a$, P$_b$, and P+V (here, we tentatively label the spectrum P$_c$ in Figs. 2(b) and 2(c) since the microscopic origin has not been established). In the spectrum taken at 6 K, the signals P$_{k1}$ and P$_{k2}$ arising from the P shallow donors at the silicon sites are

noticed overlapped with a broad signal in the central part of the spectrum. The intensity of the signals from P shallow donors substituting C (P_a, P_b) is much stronger than that of the P shallow donors substituting Si (P_{k1}, P_{k2}). The observable temperature range of the EPR signals suggests that P_{k1}, P_{k2} are shallower than P_a, P_b. It should be noted that the predominant intensity of P_a, P_b over P_{k1}, P_{k2} might be either due to the much preferable incorporation into the carbon sites in the doping process or due to the relative position between the Fermi level and ($+|0$) causes most of the P donors at silicon sites take the charge state of EPR-inactive. Our results indicate that ion implantation and subsequent high-temperature annealing (1650 °C) also drive a considerable fraction of P into the carbon sites.

Summary

The use of P-doped CVD grown epitaxial layers which were practically free from N impurities allowed us to identify the EPR spectra originating from P shallow donors at silicon sites, P in 3*C*-SiC, P_k in 4*H*-SiC, and P_{k1} and P_{k2} in 6*H*-SiC. In the high-energy P-ion implanted HPSI 6*H*-SiC which was also free from the interference of the signals of the N shallow donors, EPR signals of P shallow donors both at carbon and silicon sites were observed, with the former with much stronger intensity.

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