

## EPR Identification of the Triplet Ground State and Photoinduced Population Inversion for a Si–C Divacancy in Silicon Carbide

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Received August 17, 2005

It is shown that intrinsic defects responsible for the semi-insulating properties of SiC represent Si–C divacancies in a neutral state ( $V_{\text{Si}}-V_{\text{C}}^0$ ), which have the triplet ground state. The energy level scheme and the mechanism of creating the photoinduced population inversion of the triplet sublevels of the divacancy ground state are determined. It is concluded that there is a singlet excited state through which spin polarization is accomplished, and this fact opens the possibility of detecting magnetic resonance on single divacancies. © 2005 Pleiades Publishing, Inc.

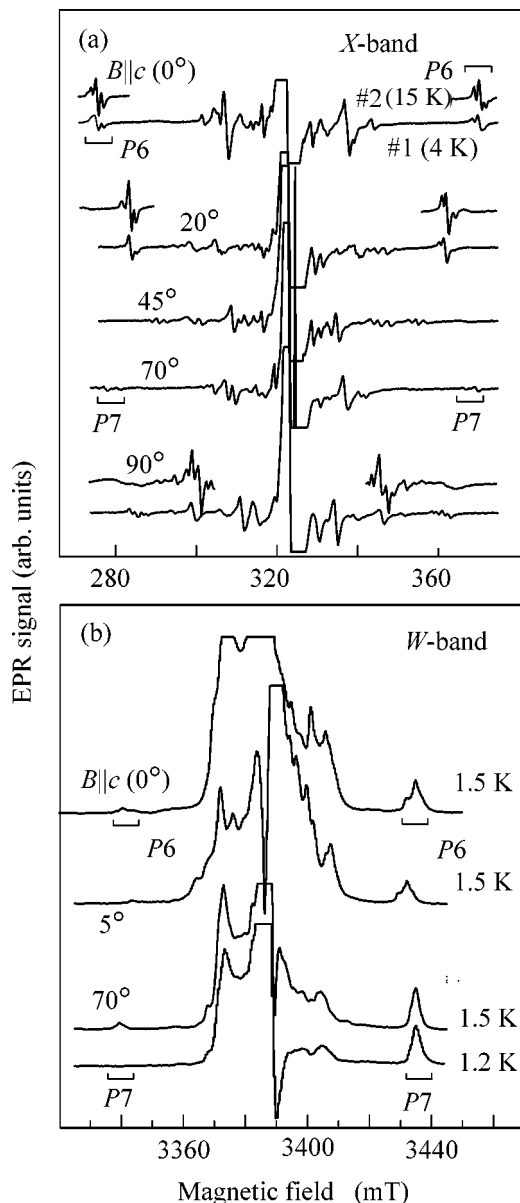
PACS numbers: 61.72.Ji, 61.72.Bb, 76.30.–v

There is a demand for replacing vanadium impurities responsible for the semi-insulating properties of silicon carbide (SiC) with intrinsic defects to create semi-insulating substrates required for manufacturing device structures. A similar problem was solved when the semi-insulating properties of GaAs were optimized by means of replacing chromium impurities by intrinsic EL2 defects. So-called *P6* and *P7* defects were detected in semi-insulating SiC crystals by the electron paramagnetic resonance (EPR) technique (these defects were observed in SiC crystals in [1]), and the suggestion was made that these defects are responsible for the semi-insulating properties of SiC [2]. The EPR spectra of *P6* and *P7* centers were observed in [1] only upon optical illumination; therefore, it was suggested that these centers belong to a triplet excited state of a Si–C divacancy ( $V_{\text{Si}}-V_{\text{C}}$ ). Recently, based on optically detected EPR studies, the structure of *P6* and *P7* centers has been reinterpreted and a model has been proposed in the form of a  $C_{\text{Si}}-V_{\text{C}}$  pair in which  $C_{\text{Si}}$  represents a carbon atom at a silicon position, that is, an anti-site defect, and the EPR spectra correspond to a triplet excited state of the defect [3]. In fact, the latter interpretation implies a triplet excited state of a silicon vacancy that encompasses one of four carbon atoms located in the nearest environment of the vacancy with a carbon vacancy remaining nearby. The main point of this interpretation was the statement that the EPR spectrum belongs to a triplet excited state, because it is difficult to imagine that this structure could form directly in the crystal after annealing at 700–1000°C and would not exist immediately after irradiation with neutrons.

Before our work, the EPR spectra of *P6* and *P7* centers had been observed only upon optical illumination, which has led to a wrong interpretation of their ground state and, as a consequence, to an erroneous model of their structure. A similar mistake was made in the interpretation of the triplet state of the known N–V defect in diamond [4] and the neutral  $V_{\text{Si}}^0$  vacancy in SiC [5]. It was considered that EPR spectra belong to the triplet excited states of the corresponding defects, because these spectra were observed only upon optical illumination. In fact, the reason for the observation of EPR spectra was optical alignment in the triplet ground state through a metastable singlet state and deviation of the population of triplet levels from the Boltzmann distribution, as a result of which the EPR signal was sharply enhanced. This problem was solved when the concentration of defects was increased and it became possible to observe the EPR spectra of the N–V defect in diamond [6] and  $V_{\text{Si}}^0$  in SiC [7] without optical illumination at low temperatures, which unambiguously pointed to the existence of the triplet ground state.

The aim of this work is to prove the existence of the triplet ground state for *P6* (*P7*) centers, to elucidate the mechanism of creating the population inversion of spin sublevels in the ground state and, as a result, to argue that the structure of the center represents a  $V_{\text{Si}}-V_{\text{C}}$  divacancy in the neutral state.

The EPR experiments were performed at low temperatures (1.2–4 K) in total darkness, which excluded the possibility of thermal or optical population of the excited state. The EPR spectra were detected in the



**Fig. 1.** EPR spectra of the  $P6$  and  $P7$  centers in a 6H-SiC crystal measured in samples 1 and 2 for several orientations in darkness (a) in the X range at 4 K (sample 1) and 15 K (sample 2) and (b) by the ESE technique in the W range at 1.2 and 1.5 K in sample 1.

X range (9.3 GHz) on a cw radiospectrometer in the temperature range 3.5–300 K and also in the W range (95 GHz) on a pulse electron spin echo (ESE) spectrometer at temperatures 1.2–2 K. The results of studying four 6H-SiC samples exposed to various doses of irradiation with fast neutrons. Samples 1 and 2 were irradiated with neutrons with a dose of  $10^{20} \text{ cm}^{-2}$ , and samples 3 and 4 were irradiated with neutrons with a dose of  $10^{18} \text{ cm}^{-2}$ . Sample 4 was grown with a changed isotope composition of  $^{13}\text{C}$  (13%  $^{13}\text{C}$  at the natural concentration of 1.1%, the exact concentration of  $^{13}\text{C}$  was determined by the hyperfine (HF) structure observed in

the EPR spectrum of a silicon vacancy). After neutron irradiation, all samples were subjected to annealing at a temperature of 700°C for 20 min.

Figure 1a presents EPR spectra measured for samples 1 (4 K) and 2 (15 K) (particular lines for  $P6$  centers are given, the relative intensities of EPR lines for  $P7$  centers in this sample are considerably lower) in the X range in darkness for several crystal orientations in the magnetic field. The EPR spectra are described by the standard spin Hamiltonian for the electronic spin  $S = 1$  with parameters coinciding within the experimental error with the corresponding values reported in [1] for  $P6$  and  $P7$  centers. The orientations  $B \parallel c$  ( $\theta = 0^\circ$ ) and  $\theta = 70^\circ$  correspond to the symmetry axes of  $P6$  and  $P7$  centers, respectively, and the EPR spectra of  $P6$  and  $P7$  centers marked with brackets exhibit a maximum hyperfine structure splitting in these orientations. The signals for each center consist of three pairs of lines corresponding to different positions in the lattice of the 6H-SiC polytype. Figure 1b demonstrates ESE signals measured in sample 1 at a high frequency (95 GHz) and at very low temperatures (1.2–1.5 K) in total darkness.

The intensities of the low- and high-field fine-structure components measured in the EPR spectra by ESE at temperatures of 1.2 and 1.5 K sharply differ from each other because of a strong difference in the populations of triplet sublevels at low temperatures and large Zeeman splittings. The ratio of intensities of these components gives direct information on the temperature of the sample and allows the sign of the fine-structure splitting  $D$  to be determined ( $D > 0$ ).

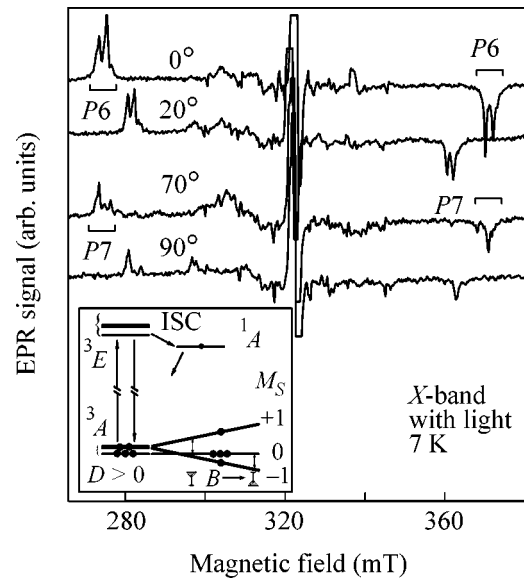
Figure 2 presents the EPR spectra of  $P6$  and  $P7$  centers measured in sample 3 under continuous optical illumination in the visible range. In this case, the distribution of populations of the triplet sublevels deviates from the Boltzmann distribution. As a result, emission rather than absorption was detected for the high-field transition because of the creation of the population inversion for the triplet sublevels. In crystals exposed to high doses of neutron irradiation, the EPR signal of  $P6$  ( $P7$ ) centers is observed directly without photoexcitation, because the concentration of defects is high and the spin-lattice relaxation time  $T_1$  is shorter. For low concentrations of defects, the EPR signal is saturated because of long  $T_1$  [1], which also hinders its observation.

The detection of the EPR spectra of  $P6$  ( $P7$ ) centers at low temperatures in darkness proves that the ground state of these centers is triplet ( $S = 1$ ) rather than singlet as was argued in [1, 3]. One of the arguments presented in [3] in favor of the presence of  $\text{C}_{\text{Si}}$  in the structure of  $P6$  centers was an observation of the HF interaction with one carbon atom of 48 MHz. We do not consider this result a weighty argument. Firstly, the EPR spectra in [3] were measured only for one orientation,  $B \parallel c$ , and a small inaccuracy in the orientation would lead to a change in the ratio of intensities of EPR signals. Thus, it seems that the observed structure corresponds to

interaction with three C atoms, which corresponds to the value of HF interaction with three C atoms for a neutral silicon vacancy [8]. Secondly, the value 48 MHz seems to be very small for the HF interaction in  $C_{Si}$  (approximately 1% spin density on C under the suggestion that this is an isotropic HF interaction constant). In 6H-SiC crystals containing 13%  $^{13}C$  (sample 3), we detected centers with  $S = 1/2$  for which we observed HF interaction with one C atom with constants  $A_{\parallel} = 230$  MHz and  $A_{\perp} = 87$  MHz. This approximately corresponds to the spin-density distribution 44% on the carbon 2p orbital and 3.6% on the carbon 2s orbital. Such values, being the maximum observed HF interaction with carbon in SiC, are evidently typical for a single C atom in an antisite defect or for an interstitial C atom. The results of studying this center will be presented in a subsequent publication. It should be added that the energies and structure of the phononless lines, whose relation to  $P6$  ( $P7$ ) centers was proved in [3], are close to the corresponding characteristics for a neutral silicon vacancy. This also gives evidence in favor of the presence of a neutral silicon vacancy in the structure of  $P6$  ( $P7$ ) centers. Thus, the model suggested by the authors of [3] as a  $C_{Si}-V_C$  pair, which is currently used in numerous publications (see, for example, [2]) does not comply with new experimental data and should be reconsidered.

We believe that the  $P6$  ( $P7$ ) centers represent the most natural defect in the form of a silicon-carbon divacancy in the neutral state  $(V_{Si}-V_C)^0$ . The divacancy axis in the  $P6$  center is oriented along a bond parallel to crystal axis  $c$ , and the divacancy axis in the  $P7$  center is oriented along a bond that is not aligned with axis  $c$ .

To explain photokinetic processes in a  $(V_{Si}-V_C)^0$  divacancy in silicon carbide based on the available experimental data, an energy level scheme is proposed that includes the levels of the  $^3A$  ground state,  $^3E$  excited state, and the metastable  $^1A$  singlet state (inset in Fig. 2); that is, the conclusion is drawn that there exists a singlet excited state through which spin polarization is accomplished. Luminescence and optical absorption are due to transitions between spin sublevels of the  $^3E$  and  $^3A$  states. Here, it may be suggested (as well as in the N-V defect in diamond [9]) that nonradiative transitions between the  $^3E$  and  $^1A$  states (so-called intersystem crossing, ISC) are strictly spin-dependent and that the rate of the transition between the sublevel  $M_S = 0$  of the  $^3E$  state and the  $^1A$  state is much lower as compared with transitions from sublevels with  $M_S = \pm 1$ . On the contrary, the rates of nonradiative transitions  $^1A \rightarrow ^3A$  are approximately similar for all sublevels. As a result, the level with  $M_S = 0$  in the  $^3A$  ground state is filled predominantly; that is, population inversion is created and only transitions between the levels with  $M_S = 0$  in the ground and  $^3E$  excited states contribute to photoluminescence and photoabsorption. The existence of a deep analogy in the properties of the  $(V_{Si}-V_C)^0$  divacancy in silicon carbide and the N-V defect in dia-



**Fig. 2.** EPR spectra of the  $P6$  and  $P7$  centers in a 6H-SiC crystal measured in sample 3 for several orientations under optical illumination. The inset presents the energy level scheme and the optical alignment process for the triplet sublevels of the ground state of a neutral  $(V_{Si}-V_C)^0$  divacancy.

mond, for which magnetic resonance on a single defect was first detected [9], allows the divacancy in silicon carbide to be considered a potential defect for the spectroscopy of individual quantum objects.

This work was supported by the Russian Foundation for Basic Research, project nos. 03-02-17645 and 04-02-17632, and by the Russian Academy of Sciences, under the program "Spin-Dependent Effects in Solid State and Spintronics."

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*Translated by A. Bagatur'yants*