Room temperature coherent spin-alignment of silicon vacancies in 4H- and 6H-SiC

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Optically induced inverse population of the ground state spin sublevels of the silicon vacancies in silicon carbide (SiC) at room temperature was observed for the first time, making them a very favorable defect for spintronics and quantum information processing. Room temperature transient nutations of the silicon vacancy spin in SiC after optical flash clearly demonstrate that the probed silicon vacancy spin ensemble can be prepared in a coherent superposition of the spin states. Very long coherence times of \( \gtrsim 80 \) \( \mu s \) were obtained at room temperature in our experiments even in crystals with high concentrations of the silicon vacancies. Two opposite schemes of the optical alignment of the populations between the ground state spin sublevels of the silicon vacancy are revealed in 4H- and 6H-SiC at room temperature upon illumination with unpolarized light.

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Detection and manipulation of the spin states in solids at room temperature is a basis of the emerging fields of quantum information processing and spintronics. The first system on which such manipulations were realized at room temperature was the nitrogen-vacancy (NV) center in diamond. Owing to its unique optical excitation cycle that leads to the optical alignment of triplet sublevels of the defect ground state, single NV center can be easily initialized, manipulated and readout by means of optically detected magnetic resonance (ODMR)\(^{1, 2}\). A search for systems possessing unique quantum properties of the NV defect in diamond that can extend the functionality of such systems seems to be a very promising objective.

On the basis of theoretical predictions and experimental data several other centers were proposed as the candidates comparable with the NV center in diamond. Among them such centers as nitrogen-vacancy center\(^{3, 4}\), silicon-carbon divacancy\(^{5, 6}\) and silicon vacancy (\(V_{\text{Si}}\))\(^{7, 8}\) in silicon carbide were proposed. Recently it was experimentally shown that several defect spin states in 4H-SiC can be optically addressed and coherently control at temperatures from 20 to 300 K\(^{9}\).

Silicon carbide is a wide-band-gap semiconductor with a well developed growth and doping technology that opens wide possibilities for scalable applications. The isotopic engineering of SiC crystals can be performed through the sublimation crystal growth\(^{10}\), which allows to reduce the natural abundance of \(^{29}\)Si (4.7%) and \(^{13}\)C (1.1%) nuclear spins. SiC can be crystallized in many different polytypes that arise from differences in the stacking sequence of the Si and C layers. The most common polytypes are 4H- and 6H-SiC. In 4H-SiC two nonequivalent crystallographic positions exist, one hexagonal and one quasicubic called \(h\) and \(k\), respectively. In 6H-SiC three nonequivalent positions are formed, one hexagonal (\(h\)) and two quasicubic ones (\(k1\) and \(k2\)) (see Fig. 1(a) and 3(a)). Due to the difference in the surrounding environments, a defect located at the \(h\) and \(k\) site often has different properties.

Vacancies are the primary defects in SiC incorporated at various sites in different polytypes. Both photoluminescence (PL) and electron paramagnetic resonance (EPR) spectra of these centers vary depending on their position in the crystal lattice. Unusual polarization properties of various vacancy defects in SiC were observed by means of EPR under optical excitation and reported for the first time in the work of Vainer and Il’in\(^{11}\). Observation of the low temperature optical spin alignment of the \(V_{\text{Si}}\) ground state and zero-field ODMR studies at 1.4 K were reported in Ref. \(^{12}\). Here we show that two opposite schemes for the optical alignment of the spin sublevels in the ground state of a silicon vacancies in 4H- and 6H-SiC can be realized even at room temperatures and that spin ensemble can be prepared in a coherent superposition of the spin states.

Crystals of two main SiC polytypes were studied in the present work: 4H-SiC and 6H-SiC. Silicon vacancies were introduced by irradiation with fast neutrons at room temperature with a dose of \(10^{15}\) \(\text{cm}^{-2}\). The samples, in the shape of platelets, had dimensions of about \(3 \times 4 \times 0.4\) mm\(^3\) and were oriented for rotation in the \(\{11\bar{2}0\}\) plane. The concentration of vacancies under the study in both samples is \(\sim 10^{15}\) \(\text{cm}^{-3}\). The precise concentrations are not required for the following analysis.

Flash-induced continuous wave (cw) direct-detection EPR (DD-EPR) technique was used\(^{13}\) at the X-band. The EPR signal obtained after the microwave mixer was amplified by wide-band amplifiers and sampled by a boxcar integrator (SR 250, Stanford Research Systems) triggered by the flashes. The sample was excited with 6 ns flashes (ca. 1.5 mJ per flash) from a parametric oscillator LP603 pumped by a Nd-YAG laser LQ 529B (Solar Laser Systems, Byelorussia), which was operated at a repetition rate of 11 Hz and 0.8 nm FWHM. The high-time resolution (ca. 50 ns) allowed signal detection shortly after the
4H-SiC n-irradiated X-band 300 K

DD EPR intensity (arb. units)

Energy (arb. units)

B||c

B⊥c

Magnetic field (mT)

318 320 322 324 326 328

V₃(h)

V₃(h)

V₃(h)

V₃(h)

Flash-induced cw DD-EPR spectra recorded at room temperature in the 4H-SiC crystal under excitation at the wavelength of 890 nm for B∥c and B⊥c orientations; (bottom) cw X-band EPR spectra detected under continuous optical illumination and in dark with B∥c at T = 100 K; (a) Structure of the 4H-SiC polytype; (b) Zeeman levels diagram for the V₃⁺ ground state (S=1) with the Mₛ = 0 sublevel predominantly populated due to the optical alignment; (c) Seven-level model interpreting the optical alignment of the ground-state sublevels in zero magnetic field.

FIG. 1. Flash-induced cw DD-EPR spectra recorded at room temperature in the 4H-SiC crystal under excitation at the wavelength of 890 nm for B∥c and B⊥c orientations; (bottom) cw X-band EPR spectra detected under continuous optical illumination and in dark with B∥c at T = 100 K; (a) Structure of the 4H-SiC polytype; (b) Zeeman levels diagram for the V₃⁺ ground state (S=1) with the Mₛ = 0 sublevel predominantly populated due to the optical alignment; (c) Seven-level model interpreting the optical alignment of the ground-state sublevels in zero magnetic field.

Conventional cw X-band EPR spectra of the silicon vacancies detected under continuous optical illumination and in dark for B∥c orientation at 100 K is shown in Fig. 1 (bottom). The central signal, marked by arrow is attributed to the negatively charged Si vacancy with S = 3/2, and zero-field splitting parameter D close to zero. This signal is optically silent and discussed somewhere else. Lines with the zero-field splitting parameter of 22×10⁻⁴ cm⁻¹ (65.9 MHz) labeled as V₃⁺ are observed under optical illumination and belong to the silicon vacancy. To date the spin state of the V₃⁺ giving rise to this splitting is under debate. While we support the model of the neutral V₃⁺ with S=1, in Ref. 13 it was suggested that such type of EPR spectra belong to the low-symmetry modification of the well-studied negatively charged Si vacancy in the regular environment with S=3/2. In our opinion, the authors have not presented sufficiently convincing arguments in favor of the revision of the model. We will further concern that these signals belong to the neutral V₃⁺ with S=1. The lines are accompanied by the pair of the hyperfine (HF) lines with a splitting of 0.29 mT due to the HF interaction with twelve equivalent Si atoms of the second shell of the Si vacancy. As expected, under optical pumping at 100 K, the intensity of the EPR spectra grew substantially and a phase reversal was observed for one of the two transitions.

Flash-induced cw DD-EPR signals of the V₃⁺ recorded at room temperature in the 4H-SiC crystal for two orientations of magnetic field: parallel (B∥c) and perpendicular (B⊥c) to the c axis are shown in the upper part of the Fig.1. The sample was selectively excited into the absorption band of the V₃⁺ at 890 nm. The same type of the EPR signal was also observed with the excitation light at wavelengths of 865, 900 and 917 nm. Vertical bars indicate the positions of the lines for the V₃⁺ vacancy in the h site for the parallel and perpendicular orientations.

Observed DD-EPR spectra can be described with standard spin Hamiltonian

\[ \hat{H} = g \mu_B B \hat{S} + D (\hat{S}_z^2 + 1/3 S(S+1)) \]  

where \( \mu_B \) is the Bohr magneton, g - is the isotropic g-factor (g=2.0032), S=1. For 4H-SiC the zero-field splitting parameter D of the V₃⁺ was found to be 22×10⁻⁴ cm⁻¹ (65.9 MHz) for the h site.

For the high-field transitions the emission instead of absorption is detected, thus we can conclude that optical excitation at room temperature results in establishment of the inverse population between certain sublevels, i.e. optical alignment of the ground spin sublevels. Zeeman levels diagram for the V₃⁺ ground state is shown in Fig. 1(b). The populations of the ground state energy sublevels under optical pumping are indicated by different numbers of filled circles. The emission observed for the high-field component of the EPR spectra is due to predominant population of the Mₛ=0 sublevel.

To explain the photokinetic process leading to the spin alignment under optical pumping, we adopt the seven-level model proposed in Ref. 12 for the NV centers in diamond and adopted in Ref. 10 to explain observed DD-EPR spectra of V₃⁺ under optical pumping, which suggests the existence of the non-radiative recombination channel. Level diagram shown in Fig. 1(c) comprises ³A ground state, ⁴E excited state for which only three lower sublevels are depicted, and one singlet ¹A state. Optical transition between the ³A and ⁴E states is spin conserving (solid lines in Fig. 1(c)). In addition, triplet-singlet intersystem crossing (ISC) due to the spin-orbit coupling between ³E and ¹A levels occurs. The centers in the Mₛ=±1 sublevels have significantly higher probability to undergo the ISC, thus, the rate r₂₃ of the non-radiative transition from the Mₛ=±1 sublevels of the excited ³E state to the metastable singlet ¹A state is much larger than the rates of the transition from the Mₛ=0 sublevel. Subsequent decay from the ¹A to the Mₛ=0 sublevel of the ³A ground state also occurs with
the photoluminescence intensity observed in the ODMR temperature and is similar to the NV defects in diamond.

The transition nutation decays due to inhomogenity of a function of the time duration \( t \) after optical flash.

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The population differences between sublevels are indicated by the different numbers of circles. Such population differences between sublevels are indicated by the different numbers of circles.

the higher rate \( r_{31} \) than that between \( ^1A \) and \( M_S = \pm 1 \). As a result the \( M_S = 0 \) sublevel becomes predominantly populated. As the \( M_S = 0 \) sublevel has a higher probability of fluorescence due to the non-radiative nature of the ISC, the fluorescence intensity between \( ^1S \) and \( ^3A \) is spin-dependent. The discussed scheme is true for the \( ^1S \) center in the h-site of the 4H-SiC at room temperature and is similar to the NV defects in diamond.

This type of polarization results in a giant decrease of the photoluminescence intensity observed in the ODMR experiments in zero magnetic field.

In Fig. 2, the transient nutations for the \( V_{\text{Si}}^0 \) center in 4H-SiC at room temperature are shown for three values of microwave power, the positive traces for absorption \( B_0 = 321.5 \text{ mT} \), and the negative traces for emission \( B_0 = 323.8 \text{ mT} \) of microwaves. Absolute mw power value is estimated as ca. 5 mW at 10 dB attenuation; (inserts) Corresponding Fourier transform.

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FIG. 2. Transient nutations for the \( V_{\text{Si}}^0 \) center in 4H-SiC at room temperature are shown for three values of microwave power: the positive traces for absorption \( B_0 = 321.5 \text{ mT} \), and the negative traces for emission \( B_0 = 323.8 \text{ mT} \) of microwaves. Absolute mw power value is estimated as ca. 5 mW at 10 dB attenuation; (inserts) Corresponding Fourier transform.

As was noted the spin state of the silicon vacancy is explained if we suggest the existence of spin-dependent non-radiative decay path via \( ^1E \) level in the optical cycle. The decay rate \( r_{23} \) from the \( M_S = \pm 1 \) sublevels of the excited \( ^3E \) state to the metastable \( ^1E \) state is again much larger than the rates of transition from the \( M_S = 0 \) sublevel, but, on contrast to the \( ^3S_1 \) in 4H-SiC, the rates of the transitions \( r_{31} \) between the \( ^1E \) state and \( M_S = 0 \) sublevel of the ground state are much smaller than the rates of the transitions from the \( ^1E \) to the \( M_S = \pm 1 \) sublevels of the ground \( ^3A \) state. Thus, the spin sublevels with \( M_S = \pm 1 \) of the \( ^3A \) ground state are predominantly populated. This type of polarization results in a giant increase of the photoluminescence intensity observed in the ODMR experiments in zero magnetic field.

As was noted the spin state of the silicon vacancy is described with standard spin Hamiltonian (eq. (1)) with \( D = 42.8 \times 10^{-4} \text{ cm}^{-1} \) (128.3 MHz) and \( 9 \times 10^{-3} \text{ cm}^{-1} \) (26.9 MHz) for \( h \) and \( k \) sites in 6H-SiC, respectively.

As can be seen from Fig. 3 another type of the optical alignment is realized for the \( V_{\text{Si}}^0 \) in the h-site in the 6H-SiC at room temperature. To explain the emissive nature of the low-field transition, Zeeman levels diagram for the \( V_{\text{Si}}^0 \) ground state is shown in the inset (Fig. 3). The population differences between sublevels are indicated by the different numbers of circles. Such population differences induced by the optical pumping can be explained if we suggest the existence of spin-dependent non-radiative decay path via \( ^1E \) level in the optical cycle. The decay rate \( r_{23} \) from the \( M_S = \pm 1 \) sublevels of the excited \( ^3E \) state to the metastable \( ^1E \) state is again much larger than the rates of transition from the \( M_S = 0 \) sublevel, but, on contrast to the \( V_{\text{Si}}^0 \) in 4H-SiC, the rates of the transitions \( r_{31} \) between the \( ^1E \) state and \( M_S = 0 \) sublevel of the ground state are much smaller than the rates of the transitions from the \( ^1E \) to the \( M_S = \pm 1 \) sublevels of the ground \( ^3A \) state. Thus, the spin sublevels with \( M_S = \pm 1 \) of the \( ^3A \) ground state are predominantly populated. This type of polarization results in a giant increase of the photoluminescence intensity observed in the ODMR experiments in zero magnetic field.
still under debate. However, there is no doubt that the high-spin state is the ground state of the silicon vacancy thus the similar alignment processes can be valid for the $S=3/2$ system. In principle the mechanism of spin alignment should remain almost the same with the only difference that the $M_S=\pm 1$ and $M_S=0$ sublevels should be replaced by $M_S=\pm 3/2$ and $M_S=\pm 1/2$, respectively. For this model $M_S=\pm 1/2$ sublevels should be equally populated and the existence of a metastable doublet state instead of singlet state should be assumed.

To conclude, optically induced inverse population of the ground state spin sublevels of the simplest intrinsic defect that can be designed in the nuclear magnetic moment free surrounding, Si vacancy in 4H- and 6H-SiC, was observed for the first time at room temperature. In distinction from the known NV defect in diamond$^{13}$, and recently observed defects in SiC$^{2}$, two opposite schemes for the optical alignment of the populations of the spin sublevels in the ground state of $V_S^0$ in 4H- and 6H-SiC were observed at room temperature upon illumination with unpolarized light. Based on the measured transient mutations of the EPR signal intensity estimated coherence time is expected to be longer than 80 $\mu$s at room temperature. Zero-field splitting parameters for $V_S^0$ in 4H- and 6H-SiC are much lower than that of the NV center in diamond ($D=2.87$ GHz for NV center) and recently observed defects in SiC. Thus the $V_S^0$ can be manipulated by the low-energy radiowave quanta in the range of 20-150 MHz, depending on the position of the silicon vacancy in the crystal lattice, which is one-two orders of magnitude lower than the energy required to manipulate the NV defect in diamond and neutral carbon-silicon divacancy in SiC.

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