Excitation Properties of Silicon Vacancy in Silicon Carbide

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Abstract. Isolated point defects possessing a high spin ground state and below-band-gap excitation may play a key role in realizing solid state quantum bits in semiconductors which are the basic building blocks of quantum computers. The silicon vacancy in silicon carbide provides these features, making it a feasible candidate in this special and emerging field of science. However, the exact nature of the luminescence of silicon vacancies detected in hexagonal polytypes has not been clarified. This is the first crucial step needed to understand this basic defect in silicon carbide. We report density functional theory based calculations on the silicon vacancy defect. Based on the obtained results we identify the silicon vacancy related photoluminescence signals with the negatively charged defect.

Introduction

The silicon vacancy in silicon carbide (SiC) is a subject of great interest due to its peculiar properties: in the ground state it exhibits a high-spin electronic state and shows luminescence in the near infrared range at around 1.4 eV [1,2]. Photo-electron paramagnetic resonance (EPR) studies indicate that an effective electron spin polarization can occur for the silicon vacancy in SiC [3,4] and its photoluminescence (PL) signal can be detected even at room temperature [5]. Despite recent efforts towards understanding the nature of the silicon vacancy centers [2,6] there is still a debate about the nature of the luminescence. The detailed understanding of the excitation of the silicon vacancy is necessary toward its application in quantum optics and quantum information processes. Recent developments in simulation methods have made it possible to investigate the excited states by ab initio calculations where no a priori assumptions have to be applied for the defect states. For instance, we have recently shown that the excitation property of the neutral divacancy in SiC or the negatively charged nitrogen-vacancy defect in diamond can be well calculated by time-dependent density functional theory (TD-DFT) [7]. We applied this methodology to the calculation of the excitation spectrum of the silicon vacancy defect in SiC.

Methodology

We investigated the silicon vacancy in a 576-atom hexagonal 4H-SiC clustger by a screened hybrid density functional theory (HSE06) which provided quantitatively accurate results for the thermal ionization energies of point defects in group IV semiconductors (see Refs. [8,9] and references therein). In addition, we applied the TD-DFT method with PBE0 hybrid density functional in the kernel for a nano cubic 3C-SiC cluster with a diameter of about 1.4 nm (see Ref. [7] and references therein). This particular SiC nanocrystal is centered at the interstitial site; thus a silicon vacancy will possess a very slightly distorted T_d symmetry to C_3v symmetry due to the crystal field of the nanocrystal, which mimics the hexagonal environment in bulk SiC regarding the symmetry. The relaxation energy due to electronic excitation was calculated by the constrained DFT method [7].
Results and Discussion

First, we studied the silicon vacancy in bulk 4H-SiC. We found that the spin-polarized local density approximation of DFT (DFT-LDA) provided only a single $a_1$ and a single $e$ level in the fundamental gap, which are occupied by two or three electrons in the neutral and negatively charged state, possessing high spin $S=1$ and $S=3/2$ states, respectively. These $a_1$ and $e$ states are the split $t_2$ states of the vacancy in the low-symmetry crystal field of the hexagonal crystal. According to our previous group theory analysis [6], another fully occupied $a_1$ level should exist in this defect which falls in the valance band in DFT-LDA. In the negatively charged state of the silicon vacancy, a generalized gradient approximation of DFT (DFT-PBE) showed the appearance of this low-lying $a_1$ state just above the valence band in the minority spin channel. The HSE06 functional mimics the quasi-particle correction of DFT levels, which opens the gap by lowering the energy of the valance band edge and increasing the energy of the conduction band edge. In the HSE06 calculation the appearance of the low-lying $a_1$ state in the gap in the minority spin channel is very clear and is even visible in the spin majority channel just above the valence band edge. In addition, the order of the empty single particle levels is $a_1$ and $e$ for the split $t_2$ level in the minority spin channel. The corresponding single particle energies at the cubic and hexagonal sites are equal within 0.05 eV, so the site dependence on the electronic structure of the negatively charged Si-vacancy is not very significant. However, the different amount of splitting of the empty $a_1$ and $e$ levels may cause different PL spectra at low and elevated temperatures. The situation for the neutral silicon vacancy is not so clear. The low-lying $a_1$ state falls in the valence band in the HSE06 calculation. In the spin majority channel the $e$ state is fully occupied while the upper $a_1$ level is empty (see Fig. 1). This gives a $^3A_2$ ground state. (Interestingly, the order of single particle states was reversed in the LDA calculation, which would imply a $^3E$ ground state.) This is also a high spin $S=1$ configuration; nevertheless, it cannot be excluded that the many-body singlet state may be the ground state. In 3C-SiC (where the symmetry is $T_d$) theory proposed that the singlet state of the neutral Si-vacancy may be the true ground state where the multi-determinant nature of the many-body wave function could be directly calculated, although, in a relatively small nanocrystal model [10]. A very recent photo-EPR study [11] indicates that the neutral silicon vacancy has a singlet ground state in 3C-SiC. The corresponding EPR signal could be measured only after photo-excitation with quenching of the $S=1$ metastable state after system intercrossing in the excitation process. Nevertheless, the crystal field splitting in hexagonal SiC may stabilize the $S=1$ state as the ground state. Here, we assume that the $S=1$ state is the ground state in hexagonal SiC and we apply this model in nano SiC studies.

In nano cubic 3C-SiC the gap opens due to quantum confinement; therefore, the vacancy-related states are apparent even in DFT-PBE calculations. The order of single particle states closely follows that obtained in HSE06 calculations in bulk 4H-SiC. The PBE0 hybrid density functional also provided qualitatively the same single particle picture as DFT-PBE did. Next, we calculated the excitation energies by the TD-DFT method based within PBE0 functional both for the neutral and negatively charged silicon vacancy.

In the case of the neutral silicon vacancy, the lowest excitation energy is at about 2.0 eV. This excitation occurs predominantly in the spin majority channel between the occupied $e$ state and the empty $a_1$ state. In the other excitations the “valence” states mix into the many-body exciton state resulting in higher excitation energies and will not be considered further in the discussion. In the lowest excitation the resulting excited state is $^3E$ and there is no other feasible spin-conserving excitation route between the localized defect states (see Fig. 1). The ground state was $^3A_2$, so only such photons may be absorbed (infrared absorption) or emitted (PL) in this process that are polarized perpendicular to the symmetry axis (see detailed group theory description in Ref. [6]).

The situation for the negatively charged silicon vacancy is very different. In that case the excitation occurs in the spin minority channel between the occupied lower $a_1$ level and the empty upper $a_1$ and $e$ levels (see Fig. 1). The ground state is $^4A_2$ while the symmetries of the corresponding excited states are $^4A_2$ and $^4E$, respectively, with calculated excitation energies of 1.568 eV and 1.572 eV. In these processes the selection rules may be applied and it can be shown that the light would be...
only absorbed with polarization parallel \((E_{\parallel}c)\) and perpendicular \((E_{\perp}c)\) to the symmetry axis, respectively. The calculated relaxation energy due to excitation is about 0.1 eV, which puts the calculated zero-phonon line at about 1.47 eV.

![Diagram showing single particle levels of the neutrally and negatively charged silicon vacancy in 4H SiC. CBM (VBM) indicates the conduction (valence) band edge. Beside the ground states (GS) the lowest excited states (ES) are shown. The arrows indicate the photon emission processes; the selection rules can be seen above or below the arrows. See text for more explanation.]

In 4H-SiC the V1, V1’ and V2 zero-phonon lines (ZPL) are associated with the Si-vacancy where the corresponding optically detected magnetic resonance centers (ODMR) of TV1a, etc. can also be detected. The transition energy of V1 and V1’ is at around 1.44 eV while it is at 1.35 eV for V2, where these ZPL signals may be associated with the inequivalent sites of the Si-vacancy in 4H-SiC. According to detailed analysis V1 (and V1’) may be associated with the cubic site [6]. The emitted photons of the V1 ZPL are polarized parallel to the symmetry axis while perpendicular to that for the V1’ ZPL with about 4.5 meV of energy difference where the V1 ZPL is lower in energy than that of the V1’ ZPL. The neutral \(S=1\) Si-vacancy does not show these features because no parallel polarization of the emitted light is expected from that defect, and the calculated excitation energy is significantly larger than the measured one. In contrast, the calculated properties of the negatively charged vacancy can all explain the experimental data, particularly, at the \(k\)-site which we model in nano 3C-SiC. The estimated ZPL is very close to the measured one, and the V1, V1’ ZPLs with the corresponding polarizations can be well explained by the selection rules of optical emission from the \(^4A_2\) and \(^4E\) excited states, respectively.

Based on these results we claim that V1 and the closely related other PL centers at different sites are associated with the negatively charged Si-vacancy. The negatively charged Si-vacancy has \(S=3/2\) spin which may be useful in magnetometer applications and the sensitivity might be larger than for the negatively charged nitrogen-vacancy center (NV) in diamond. Since the Si-vacancy has a very localized defect state and spin polarization occurs in photo-excitation [2], it can be a suitable spin for quantum optics and quantum information applications with close-to-telekom wavelength of luminescence, in contrast to the NV-center in diamond which emits at higher wavelengths (see Ref. [7] and references therein). Silicon carbide can be easily doped and may be easily integrated with existing electro- and optoelectronic devices, and may simultaneously host quantum bits for quantum computing. Progress is needed in controlling of point defects in SiC in order to reduce those defects.
that may quench the luminescence signals from the Si-vacancy and could provide additional electron spins that may decohere the electron spin of the Si-vacancy. Another important issue is to isotope engineer SiC in order to reduce the hyperfine active $^{29}\text{Si}$ and $^{13}\text{C}$ isotopes around the defect, in order to enhance the coherence time of Si-vacancy spins. Besides, the ultimate control of excitation of the Si-vacancy is needed. For this purpose, the optimization of excitation wave lengths is necessary as well as an investigation of the effects of strain and other perturbations on this defect that may change its luminescence and hyperfine interactions.

Summary

The isolated Si-vacancy was studied in bulk 4H-SiC and nano 3C-SiC. We explored its single particle spectrum in the neutral and negatively charged states. We found that the PL and ODMR lines associated with the Si-vacancy originate from the negative charge state which has a $S=3/2$ high spin ground state. The PL signal of the negatively charged Si-vacancy is detectable at room temperature, which makes this defect a promising candidate for quantum optics and sensitive magnetometer applications.

References