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Interaction of silicon vacancies in silicon carbide

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The density functional theory is used to show that negatively charged silicon vacancies in silicon carbide produced from silicon by the vacancy mechanism of coordinated substitution of atoms (VMCSA) are attracted to each other in the $\langle 1\bar{1}0\rangle$ direction. The nature of the attraction is that the carbon atoms with broken bonds repulse from the vacancies and come closer to each other, forming new C−C bonds. As a result, silicon vacancies line up in vacancy strings in the $\langle 1\bar{1}0\rangle$ direction, which significantly decreases the total energy. It is also found that the decrease in the length of stretched C−C bonds during electron localization leads to the effect of negative correlation energy of electrons localized on vacancies.

Keywords: silicon carbide, silicon vacancies, negative-U properties, magnetic moment.

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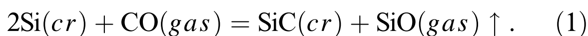
Silicon carbide (SiC) is a wide-gap semiconductor with a number of unique physical and mechanical properties, such as high hardness, high thermal, radiation, and chemical resistance, etc. [1,2]. Silicon vacancies in SiC have unique electrical, magnetic, spintronic, and qubit properties [3]. This makes SiC a promising material for the construction of high-current and high-frequency electronic devices [4]. The current substantial interest in SiC stems also from its use as a substrate for the growth of other wide-gap semiconductors [5]. The authors of [6,7] devised a fundamentally new mechanism for the growth of silicon carbide from silicon by means of coordinated substitution of silicon atoms by carbon atoms in chemical reaction



$$2\mathrm{Si}(cr) + \mathrm{CO}(gas) = \mathrm{SiC}(cr) + \mathrm{SiO}(gas)\uparrow . \quad (1)$$

The dependence of thickness of the grown SiC layer on the pressure of carbon monoxide (CO) turned out to be unusual [8]. It was found to be dome-shaped [8]; i.e., it first rises to a certain maximum level and then falls almost to zero. A theoretical drift model attributing this dependence to the influence of product gas SiO, which reduces the hydraulic diameter of channels in the crystal lattice and interferes with the flow of reactant gas CO within these channels, was developed in [8]. Dependences of the film thickness on both the gas pressure and time were calculated within this drift model. It was found later that the key role in the transfer of CO molecules to the reaction zone and SiO molecules from the reaction zone is played by silicon vacancies V_{Si} in SiC, which form from silicon vacancies in the Si substrate during chemical transformation (1). Specifically, a vacancy mechanism of coordinated substitution of atoms (VMCSA), wherein the Si substrate is kept for 1−5 min in vacuum at a temperature of 1200−1300°C prior to the initiation of reaction (1), was proposed in [9,10]. A certain number of vacancies form near its surface in this case, and some of them are converted in reaction (1) into silicon vacancies in SiC, which is produced from Si. This mechanism of formation of V_{Si} vacancies in SiC is very efficient and provides a V_{Si} density on the order of $10^{-3}-10^{-2}$ [9,10], which is many orders of magnitude higher than the density of V_{Si} obtained by irradiating SiC with high-energy electron beams [11]. A question then arises as to the interaction of silicon vacancies in SiC with each other and as to how exactly this interaction affects the optical, electrical, and magnetic properties of SiC containing silicon vacancies. The present study is focused on this issue. Vacancies may acquire different electric charges ranging from $-2e$ to $+2e$ in different scenarios [12,13], which leads to a very large number of options. Therefore, we examine only the simplest and most relevant scenario with initial silicon doped slightly with phosphorus, which gives rise to equal charges of $-e$ for all vacancies [12].

The interaction of negatively charged V_{Si}^{-e} vacancies in cubic silicon carbide (3*C*-SiC), which is almost always obtained by VMCSA, was studied by the density functional theory method in the generalized gradient approximation with pseudopotentials utilizing the Blöchl projector augmented-wave (PAW) method [14]. The PBE [15] functional was used to calculate the exchange-correlation energy. Calculations were performed in the MedeA-VASP package [16] in the plane wave basis and in the spin-polarized approximation [15]. The plane-wave cutoff was 400 eV in all calculations. A $2\times2\times2$ Monkhorst−Pack grid of k-points with a distance shorter than 0.24 Å^{-1} between them was used for integration over the Brillouin zone [15]. The PBE functional was chosen for the fact that it makes due allowance for exchange-correlation effects, optimizes geometry very efficiently, and is the best at calculating the magnetic moments in crystals, which are very important in this case. Temperature effects were neglected. A supercell of 300 atoms (150 Si atoms and 150 C atoms) with a size of $15.41\times15.41\times15.10$ Åand the

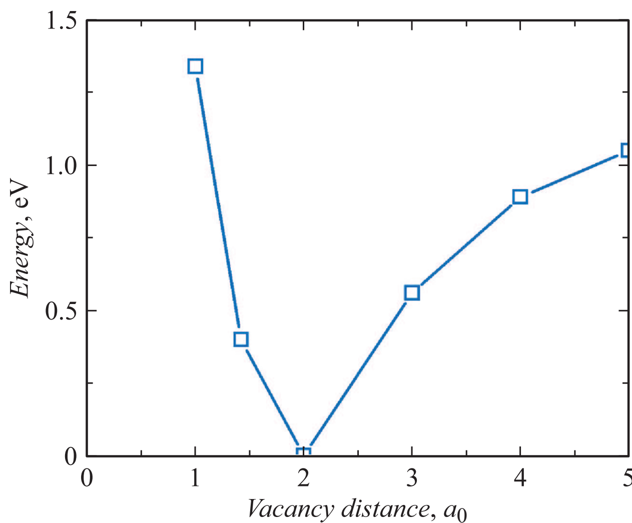


Figure 1. Dependence of the interaction energy of two silicon vacancies V_{Si}^{-e} in silicon carbide on the distance between them in any direction of the $\langle 1\bar{1}0\rangle$ family. $a_0 = 3.08$ Å is the size of a primitive SiC cell.

cubic polytype structure was chosen as the initial system to be studied. The z axis was aligned with the $\langle 111\rangle$ direction, and periodic boundary conditions were imposed in all three dimensions. Two Si atoms were then removed from the supercell in every possible way. Group-theoretical analysis of the resulting system revealed that it may feature one of the following symmetry groups: $P3m1$, Cm, Cc, and $P1$. The main symmetry-independent systems were optimized; in other words, we identified the geometry corresponding to the minimum energy with account for the magnetic moment in the spin-polarized approximation (a charge of $-2e$ was introduced into the system). The aim of these calculations was to find the mutual arrangement of V_{Si}^{-e} vacancies corresponding to the minimum energy.

The results of calculations demonstrated that V_{Si}^{-e} vacancies repel each other in most cases; i.e., the energy decreases as the distance between them increases. This is evidently attributable to the Coulomb repulsion of like-charged vacancies. The entire $\langle 1\bar{1}0\rangle$ direction family was the exception. If two V_{Si}^{-e} vacancies in a 3C-SiC crystal lie on any of the three equivalent $\langle 1\bar{1}0\rangle$ lines, they are strongly attracted to each other (despite the Coulomb repulsion). A different supercell ($10.8 \times 12.4 \times 40.5$ Åin size) with 510 atoms (254 Si atoms and 256 C atoms) elongated along one of the directions of the $\langle 1\bar{1}0\rangle$ family was used to study this attraction in more detail. The distance between k-points in the Monkhorst–Pack grid in reciprocal space was always set to less than 0.24 Å^{-1}, which ensured the accuracy of calculations. Figure 1 presents the energy of a system with two V_{Si}^{-e} vacancies as a function of distance between them in the $\langle 1\bar{1}0\rangle$ direction. The distance is measured in units of primitive SiC cell size $a_0 = 3.08$ Å (and is equal to the distance between Si atoms in the $\langle 1\bar{1}0\rangle$ direction); the energy is measured from the lowest possible level. A point with distance $1.4a_0$ (second from the left), which corresponds to the sole case of vacancy attraction outside of the $\langle 1\bar{1}0\rangle$ direction family (namely, direction $\langle 2\bar{1}2\rangle$), is also shown in Fig. 1 for completeness.

It is evident from Fig. 1 that the most advantageous arrangement of V_{Si}^{-e} vacancies in 3C-SiC corresponds to one-dimensional „strings“ extending in any of the equivalent $\langle 1\bar{1}0\rangle$ directions. The optimal distance between two vacancies in a string is $2a_0$. The attraction of like-charged vacancies has the following physical explanation. Each V_{Si}^{-e} vacancy produces extended elastic, electric, and magnetic fields around itself. The magnetic field is associated with unpaired p electrons of carbon atoms with dangling bonds. These fields interact strongly with each other. If the vacancies are positioned on one of the lines of the $\langle 1\bar{1}0\rangle$ family, the interaction of elastic fields lowers the total energy due to the attraction of carbon atoms with dangling bonds that form when Si atoms are removed. A carbon atom is repelled by a V_{Si}^{-e} vacancy, and when vacancies approach each other, C atoms may get so close that they form a new C–C bond. The minimum energy corresponds to a distance of $2a_0$ between the vacancies. This new C–C bond leads to pairing of unpaired electrons in C atoms with different spins, the elastic field becomes significantly weaker, and the magnetic field vanishes completely (but remains present around other atoms with dangling bonds). When carbon bonds form, the magnetic moment decreases from $3\mu_{\mathrm{B}}$ to $1\,\mu_{\mathrm{B}}$ per vacancy, where μ_{B} is the Bohr magneton. Figure 2 presents different views of the 3C-SiC structure with a vacancy string in the $\langle 1\bar{1}0\rangle$ direction; V_{Si}^{-e} vacancies are represented by translucent spheres, and the resulting C–C bonds are marked with colored rings (see the online version of the paper). Figure 3 shows the distribution of electric charge and magnetic moment in vacancy strings. The inset in Fig. 3, *a* presents the projection of the electric potential distribution onto the (111) plane (approximately at the level of the vacancy center). The regions of positive potential and negative charge correspond roughly to vacancies.

It is evident that other vacancy structures formed by the $\langle 1\bar{1}0\rangle$ family of directions (e.g., a regular hexagon of six vacancies (0,0,0), (2,0,$\bar{2}$), (2,2,$\bar{4}$), (0,4,$\bar{4}$), ($\bar{2}$,4,$\bar{2}$), and ($\bar{2}$,2,0)) may emerge alongside with one-dimensional strings. The study of such structures will be the subject of a separate paper. Here, we just note that closely similar hexagons were revealed by photoelectron spectroscopy in 3C-SiC(111)-8° samples depleted in silicon [17]. It is entirely possible that terraces of the vicinal surface deviating by 8° from (111) promote the formation of such vacancy and carbon structures [17].

Another important property of vacancy strings in SiC that is worthy of mention is the Hubbard attraction, or negative correlation energy of electrons localized at the site of vacancies (negative-U) [18]. Calculations of the localization energy of electrons in a string demonstrate that while the charge per vacancy varies within the range from $-e$ to $-2e$, localization of the next electron is, in

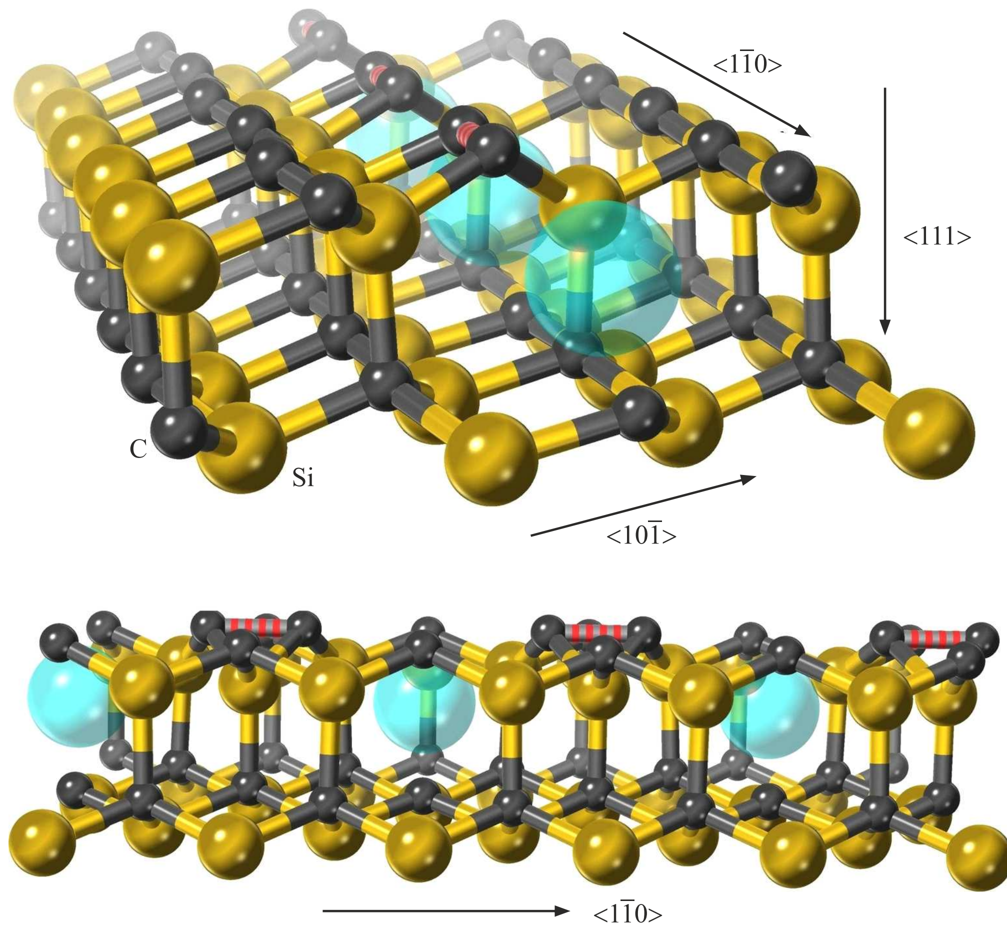


Figure 2. String of silicon vacancies V_{Si}^{-e} corresponding to the minimum energy. Vacancies are represented by translucent spheres, and the formed C−C bonds, which lower the energy, are marked with red rings. A color version of the figure is provided in the online version of the paper.

certain cases, more favorable (approximately by 0.1 eV) than that of the previous one. Since the magnetic moment of the system decreases by $1\,\mu_{\mathrm{B}}$ with the localization of an electron, a pair is formed by electrons with opposite spins. This happens because when an electron is localized, the total volume of the system increases and the C−C bond length decreases from approximately 1.72 to 1.71 Å (for comparison, the equilibrium C−C bond length in diamond is 1.54 Å), causing a significant reduction in the elastic energy of the crystal with a string. In addition, the energy of the magnetic field decreases in the event of electron localization. Thus, despite the Coulomb repulsion, the reduction in elastic and magnetic energies of the crystal in the process of formation of an electron pair lowers the total energy of the system. It is this effect that is likely to be behind the anomalous behavior of magnetic susceptibility of this material [19].

Thus, it was established that negatively charged silicon vacancies in SiC are attracted to each other in any of the three $\langle 1\bar{1}0\rangle$ directions (Fig. 1) and form vacancy strings that govern the optical, electrical, and magnetic properties of silicon carbide containing silicon vacancies. This attraction is attributable to the emergence of new stretched C−C bonds, which lower the elastic energy of SiC, in the process of formation of strings. It was also found that the reduction in length of stretched C−C bonds in the event of electron localization is responsible for the negative correlation energy of electrons localized at the site of vacancies.

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Conflict of interest

The authors declare that they have no conflict of interest.

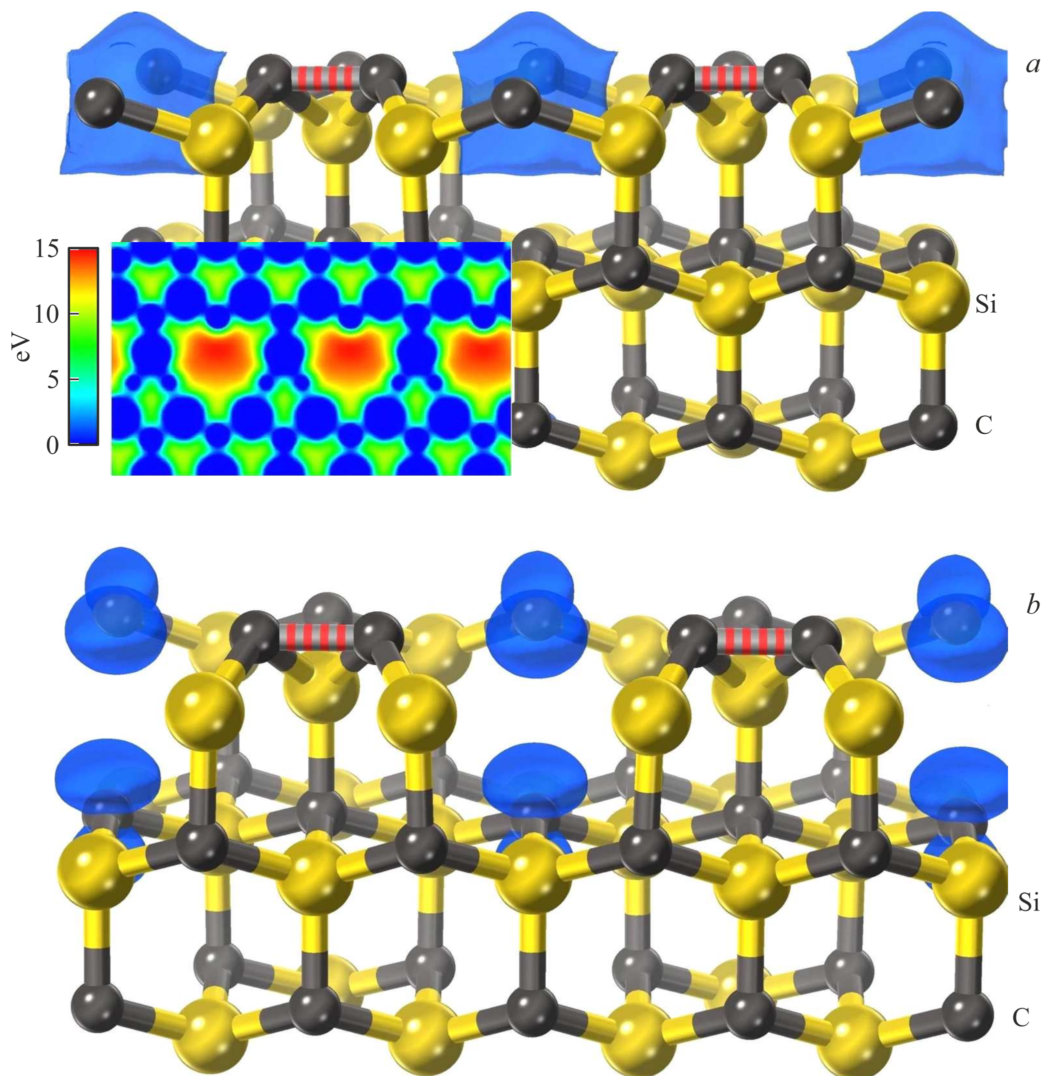

Figure 3. *a* — Regions of localization of the electric charge in a vacancy string. The boundaries of regions with a negative charge density of 0.05 $e/\text{Å}^3$ are highlighted in blue. The inset shows the projection of the electric potential distribution onto the (111) plane. Red regions correspond to vacancies. *b* — regions of localization of the magnetic moment in a vacancy string. The boundaries of regions with a magnetic moment density of 0.03 $e/\text{Å}^3$ are highlighted in blue. A color version of the figure is provided in the online version of the paper.

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