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Vacancies and E-centers in silicon as multi-symmetry defects

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ABSTRACT

In this paper, using first-principles calculations, we demonstrate that vacancies and E-centers (AsV, SbV) in silicon can co-exist in several metastable configurations with notably different relaxation patterns, which have very similar formation energies. Thus these vacancy-type defects can be considered as multi-symmetry defects in the sense that, at elevated temperatures, the probabilities to find vacancies in different stable configurations are comparable. From an experimental point of view, the co-existence of various symmetries can complicate the identification of the defect.

1. Introduction

Silicon is the most widely used semiconductor among those applied for microelectronics. Even after many years of active search for alternative materials, silicon still dominates the market and is incorporated in over 90% of electronic devices [1]. Along with its other advantages, such as good material availability and suitable band gap, one of silicon's major assets is the high sensitivity of its electrical properties to relatively small amounts of doping impurities such as boron (B), phosphorus (P), or arsenic (As).

Because the reliable control of microelectronic device material performance is impossible without a detailed knowledge of the properties of defects it contains, the research on defects in silicon is an active field of microelectronics-related materials science. This research field has been faced with a broad spectrum of experimental approaches, largely supported by numerical simulations using such atomistic computational techniques as first-principles calculations, molecular dynamics, and kinetic Monte-Carlo [2–9]. One might expect that everything worth knowing on defect properties in Si has already been discovered, but in reality our understanding of the defect properties and kinetics remains far from complete.

Indeed, defect parameters and properties have broad uncertainty ranges even for the most basic defects in Si, such as vacancies, small vacancy clusters and vacancy-donor pairs (E-centers). For instance, the estimates of the monovacancy formation energy by different experimental and computational techniques fluctuate by more than 1 eV [2–7,10–16]. The same uncertainty is typical for defect migration energies [10–12,17,18].

From the experimental side, the scatter in the defect energy parameters is largely due to the difficulty of their direct determination. Very sophisticated measurements are used to obtain the data on the defect properties, and even then the extraction of defect parameters from the data remains largely interpretation dependent. For example, the most recent estimate of the vacancy formation energy, 3.15 eV, is derived [16] from a combination of the self-diffusion measurements of Shimizu et al. [19] and the neutral vacancy migration value deduced from [20,21]. To make things worse, the results of different techniques are often not compatible with each other. One of the reasons for this is the sensitivity of the defect formation energy to the Fermi level position in the crystal, so that the experimental results can vary depending on the sample doping level. Computational studies, on the other hand, are limited by the amount of computer resources required by the most reliable simulation techniques, which are often the only applicable ones. As a result, even for the simplest defect – monovacancy in silicon – numerical studies have been restricted for a long time only to the neutral charge state [4–7] and to small simulation cells and *k*-point sets [2,3,22,23].

Another issue that has been studied extensively without reaching a final agreement is the elastic relaxation pattern of vacancies and E-centers. The first model of anisotropic distortion for the silicon vacancy has been proposed by Watkins in Ref. [24]. It has been demonstrated that the relaxation pattern of the four silicon atoms constituting the first nearest-neighbor shell of a vacant lattice site should vary as a function of the defect charge. According to this model, the distortion for V^+ and V^0 is tetragonal, resulting in D_{2d}

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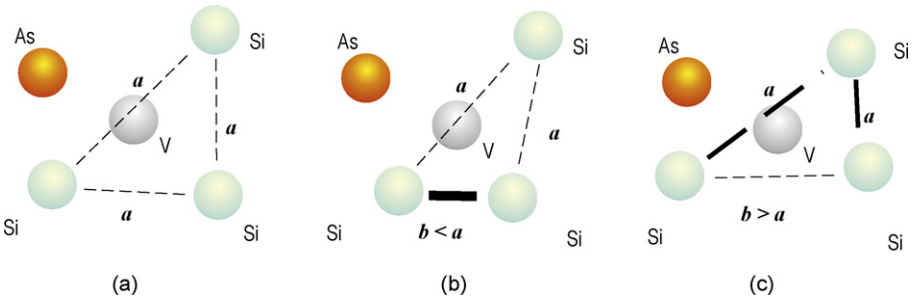

Fig. 1. Schematic representation of the vacancy nearest-neighbor distortion modes: breathing (a), pairing (b) or resonant (c).

symmetry of the relaxation pattern, whereas for V^- and V^{2-}, the symmetry is further lowered down to C_{2v}. Later on, it has been demonstrated [25] that purely symmetry-based arguments are not sufficient to guarantee either the predicted relaxation pattern, or its energetic proficiency. Accounting for the effects related to the elastic relaxation around the defect is at least equally important. For example, too strong elastic distortions around the vacancy in silicon were demonstrated to forbid the V^+ charge state [25,26]. More recent *ab initio* calculations [2–4,22,23,27] confirm a noticeable inward relaxation of the vacancy environment accompanied with the symmetry lowering. However, the predicted vacancy symmetries vary from one calculation to another.

Similar uncertainties are met where the relaxation pattern of E-centers in silicon is concerned. Three main modes of vacancy environment relaxation in E-center have been suggested by now, namely—breathing, pairing and resonant distortion patterns (see Fig. 1). The breathing distortion keeps equal bond lengths between the silicon atoms nearest to a vacant site. In contrast, resonant and pairing distortions break the initial symmetry. In pairing mode, weak covalent bonds are formed between the vacancy neighbours in such a way that one of the three bonds is noticeably shorter than the other two. In resonant bonding, no bond is formed between two vacancy neighbours and the corresponding interatomic distance turns out to be longer than between the bound atoms. Pairing is claimed to be observed in the case of a neutral E-center in EPR studies [14,28], whereas stress measurements [29] indicate resonant bonding in the negatively charged state. Density-functional theory (DFT) cluster calculations for AsV by Öğüt and Chelikowsky [30] are in favour of these interpretations. However, for the PV complex the resonant bonding configuration has been proposed to be the ground state in all possible charge states [31].

In this paper, using first-principles calculations, we demonstrate that vacancies and E-centers (AsV, SbV) in silicon do not exhibit one dominant relaxation pattern. Instead, these vacancy-type defects can be considered as multi-symmetry defects since, at each charge state, there exist several metastable defect configurations with notably different relaxation patterns, but with very similar formation energies.

2. Computational details

The vacancy configurations with different relaxation patterns, even if exist, correspond to some local total energy minima and it is not easy to scan all the desired symmetries starting from completely arbitrary initial configurations, as it has been done, e.g. in [32]. Hence, we have adopted a "predefined initial symmetry" strategy, where the initial shifts of the atoms in the 1NN shells of the defects were constrained to different point symmetry groups. The considered initial symmetries included T_d, D_{2d}, C_{2v}, and C_{3v}, as well as the 'split' configuration of D_{3d} symmetry. However, no further symmetry restrictions were imposed during the atomic relaxation to the nearest elastically stable configurations. The approach is very similar in its spirit to that adopted in [32], where, however, only T_d, D_{2d} and C_{3v} starting patterns were considered and somewhat different calculation conditions were employed.

The results reported here have been obtained using the spin-polarized generalized gradient approximation (GGA) [33] for the exchange-correlation description as implemented in the DFT-based program VASP [34,35]. GGA-s is usually assumed to better reproduce the vacancy properties than the other broadly used local density approximation (LDA or, where spin polarization is treated explicitly, LSDA) [36]. In fact, we have checked that the use of LSDA does not affect the elastic stability of any considered configuration, even though the relaxation patterns are slightly different. Therefore, we focus on discussing the GGA results. The ultrasoft Vanderbilt-type pseudopotential [37] was used for all calculations. We used a supercell of 216 atoms, with the silicon lattice parameter of 5.46 Å. The Brillouin zone (BZ) sampling was done using the $(2 \times 2 \times 2)$ k-point mesh of Monkhorst and Pack [38] and the cutoff energy was 250 eV. A relaxation run was terminated when the Hellmann–Feynman forces on all atoms fell below 0.01 eV/Å, or the total energy variation within one electronic relaxation step fell below 10^{-4} eV.

3. Results and discussion

The monovacancy in silicon was studied starting from five above-mentioned symmetries in five charge states, as listed in Table 1. In order to permit comparison of different configurations from the energy proficiency point of view, Table 1 presents for different stable vacancy configurations only the formation energy excess over the lowest formation energy in each charge state, while the lowest formation energies themselves are given in Table 2. As can be immediately seen, starting from V^+, the monovacancy can exist in several metastable configurations with different symmetries. The maximum difference in energy with the lowest energy configuration is only 0.2 eV, which makes all configurations feasible.

In full agreement with all earlier studies, the vacancy in charge state 2+ is uniquely characterized by T_d symmetry of its relaxation pattern. In the V^+ charge state, the same ground-state energy was

Table 1
Formation energies with respect to the lowest formation energy of each charge state.

Vacancy symmetry	V^{2+}	V^+	V^0	V^-	V^{2-}
T_d	0.00	–	–	0.07	0.20
D_{2d}(A)	–	0.00	0.00	0.01	0.19
D_{2d}(B)	–	0.00	0.17	0.06	0.10
C_{2v}	–	–	0.00	0.00	0.20
C_{3v}	–	–	0.18	–	–
C_{2h}	–	–	–	0.00	–
D_{3d} ('split')	–	0.20	0.20	0.04	0.00