Electronic structure calculations for substitutional copper and monovacancies in silicon

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Abstract

Two different computer program packages based on the self-consistent local-spin-density approximation—*AIMPRO* and *VASP*—are employed in this study of substitutional copper Cu_{Si} and monovacancies V_{Si} in silicon, including the effects of their charge state. The programs differ in the types of basis sets and pseudopotentials they use, each with their own relative merits, while being similar in overall quality. This approach aims to reduce uncertainty in the results, particularly for small or subtle effects, where the risk is greatest that the conclusions are affected by artifacts specific to a particular implementation. The electronic structures of the two defects are closely related, hence they are expected to behave in a similar manner. For both defects structural distortions resulting in lower point group symmetries than T_d (the highest possible) are found. This is in good agreement with the results of previous studies of V_{Si} . Much less is known about symmetry-lowering effects for Cu_{Si} ; however, the electronic levels of Cu_{Si} have been measured accurately, while those for V_{Si} are less accessible. Calculating them is a challenging task for theory. The strategy we adopt, based purely on comparing total energies of supercells in different charge states, with and without model defects, reproduces the three known levels for Cu_{Si} reasonably well. Satisfactory results are also obtained for V_{Si} , so far as can be judged for this more complex case.

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1 Introduction

The silicon monovacancy V_{Si} and substitutional transition metal atoms TM_{Si} with full or nearly full d -shells possess closely related electronic structures. They are described well in terms of one-electron models developed by Watkins [1, 2]. As a consequence of the Jahn-Teller effect, structural distortions occur that lower the symmetry of the defects from the T_d point group. In an undistorted configuration, with T_d symmetry, V_{Si} and TM_{Si} have a degenerate triplet t_2 state in the forbidden

band. Therefore, depending on how this is affected by structural relaxation, they may have up to six possible charge states. For TM_{Si} there is also an interaction between the t_2 state in the bandgap and the d -electrons which lie in the valence band.

In the case of V_{Si} , five charge states (+2, +1, 0, -1, -2) and their corresponding four levels apparently exist. However, the Jahn-Teller effect is sufficiently strong in the neutral state to reverse the energetic ordering of the (0/ +1) and (+1/ +2) transitions [3, 4]. In other words, it has ‘negative- U ’ and V_{Si}^{+1}

is energetically unstable. Only three levels are observed for substitutional copper Cu_{Si} , corresponding to charge states +1, 0, -1, and -2 [5–10]. There is no experimental information about the defect’s symmetry at present.

The Jahn-Teller distortions for V_{Si} and TM_{Si} possess two components. The main one is tetragonal in character: alone, it gives the defects D_{2d} symmetry. The tetragonal distortion may occur in two opposite senses. This determines the relative energetic ordering of the resulting electronic states [11]. We will label these two senses *A* and *B*. They correspond to different relative lengths for the six Si-Si distances surrounding the centre. For the D_{2d} point group, four of them belong to one set of equivalent Si-Si lengths, and two belong to a second set of equivalent lengths. Type-*A* distortion has the pair longer than the fourfold set; type-*B* is the other way around. Type-*A* distortion splits the t_2 state into a singlet a_1 state above a doublet e state, while type-*B* does the opposite. TM_{Si} defects relax in the *A*-direction [12]. Silicon monovacancies relax in the opposite sense, *B* [1].

When the system contains sufficient electrons to occupy the e state, a weaker trigonal distortion is expected: it lowers the symmetry to C_{2v} . The twofold equivalent Si-Si lengths in the D_{2d} case become unequal. This splits the e state into orbitals of b_1 and b_2 character. Spin-orbit coupling may also affect the splitting of these states for TM_{Si} defects [12].

2 Methods

The underlying theory used here is the local-density approximation (LDA) or local-spin-density approximation (LSDA) of density functional theory (DFT), depending on the net electronic spin. Existing theoretical methods appear to perform poorly at estimating the energies of electrical levels in semiconductors. The sources of errors responsible for this may be divided into three main parts: the underlying theory, the approximations required to construct each specific implementation, and the model used to represent the particular system of interest. In this study we compare the results of two different computer program packages based on the same underlying theory, applied to V_{Si} and Cu_{Si} . By doing this we aim to reduce the uncertainties in the results, and possibly identify particular strengths or weaknesses of each program package. Moreover, being less constrained by finite computer resources than in the past, we can also make a better assessment of how well electrical levels may be calculated.

To conduct our study, we employ the AIMPRO [13–15] and VASP [16–19] program packages. The model defects are constructed in supercells based on $3 \times 3 \times 3$ conventional cubic unit cells in the diamond structure stacked together (216 atoms). The volume of the supercells is held fixed at the size corresponding to the equilibrium lattice parameter a calculated by the respective methods, while the atoms are moved to minimise their total energy and forces on them. This aims to simulate more nearly an infinite crystal where a would not change in response to the presence of a single defect. During the energy minimisation procedure, the atomic coordinates may optionally be constrained to a particular point group symmetry, or allowed to relax freely.

Within the AIMPRO formalism, the core electrons of atoms

Table 1: Calculated and measured values for the lattice parameter a and bulk modulus B_0 of Si.

method	a (Å)	B_0 (GPa)
AIMPRO	5.3948	97.0
VASP + VUS	5.390	87.7
VASP + PAW	5.403	72.8
<i>measured</i>	5.431021	97.9

are represented by pseudopotentials constructed according to the norm-conserving Hartwigsen-Goedecker-Hutter (HGH) scheme [20]. The exchange-correlation energy contribution is evaluated according to the formula described by Perdew and Wang [21]. The VASP package includes pseudopotentials based on the Vanderbilt ultrasoft construction [22, 23] (VUS), and the projector augmented wave method [24, 25] (PAW). The Cu-3d electrons are included explicitly with the HGH and PAW schemes, while they are not for the VUS pseudopotential. In both AIMPRO and VASP, the bandstructure is sampled according to the Monkhorst-Pack (MP) scheme [26]. The convergence criterion for total energies is $\epsilon \lesssim 10^{-4}$ eV. To achieve this requires MP-2³ **k** points. These are folded according to the symmetry of the system, and shifted to avoid the Γ point. Both packages represent the charge density using a plane-wave basis. The kinetic energy cutoff needed to meet the convergence criterion depends on the types of atoms present, and the pseudopotentials used. Trial calculations are performed to determine the appropriate settings. The wavefunction is also described by a plane-wave basis in the VASP package, while AIMPRO uses a Gaussian basis. To obtain satisfactory results it is necessary to have four exponents per atom. Suitable prefactors provide orbital symmetries with maximum angular momentum $l_{\text{max}} = 2$ for all four on Cu atoms, while on Si atoms the two largest exponents have $l_{\text{max}} = 1$ and the two smallest have $l_{\text{max}} = 2$.

Electrical levels are calculated from the change in total energy when electrons are added to or removed from the system. When supercells are charged, a compensating background charge of equal and opposite magnitude is added to prevent the total energy from becoming divergent. However, the potential is undefined. There are several methods to obtain a reference. The one that we use is to compare the change in energy when electrons are added or removed, with that for a pure, ideal silicon supercell of equivalent size. The potential of the top of the valence band E_v is determined by calculating the difference in energy between a neutral, perfect supercell and one with charge $q = +1$, while the bottom of the conduction band E_c is equal to the electron affinity of a perfect supercell. The bandgap $E_g = E_c - E_v$ depends on the size of the supercell: the greater its volume V , the smaller the gap, converging ultimately at the LDA value. The main factor responsible for this effect is simply that the electron or hole concentration varies as $1/V$. We may also calculate the energies of defects with respect to one another. This is the so-called ‘marker method’. Full details of the procedures for calculating electrical levels are given in Ref. [27].

Table 2: Calculated and measured electrical levels for V_{Si} and Cu_{Si} . The AIMPRO results include the use of different symmetry constraints. For V_{Si} , where two point groups are given, the first is the symmetry in positive and neutral states, and the second is the symmetry in negative charge states. The VASP calculations do not have any symmetry constraints.

$d \setminus q/q'$	0/ + 2	+1/ + 2	0/ + 1	-1/0	-2/ - 1	-2/0	method
$V_{Si}(T_d)$		$E_v + 0.07$	$E_v + 0.18$	$E_c - 0.34$	$E_c - 0.24$		AIMPRO
$V_{Si}(D_{2d}/C_{3v})$	$E_v + 0.00$	$E_v + 0.05$	$E_v - 0.04$	$E_c - 0.31$	$E_c - 0.43$	$E_c - 0.37$	AIMPRO
$V_{Si}(D_{2d}/C_{2v})$	$E_v + 0.00$	$E_v + 0.05$	$E_v - 0.04$	$E_c - 0.29$	$E_c - 0.24$		AIMPRO
V_{Si}	$E_v + 0.09$	$E_v + 0.13$	$E_v + 0.05$	<i>exists</i>	<i>exists</i>		Ref. [1]
$Cu_{Si}(D_{2d})$			$E_v + 0.17$	$E_c - 0.50$	$E_c - 0.24$		AIMPRO
$Cu_{Si}(T_d)$			$E_v + 0.21$	$E_c - 0.40$	$E_c - 0.35$		AIMPRO
$Cu_{Si}(\approx D_{2d})$			$E_v + 0.07$	$E_c - 0.45$	$E_c - 0.18$		VASP + VUS
$Cu_{Si}(\approx T_d)$			$E_v + 0.17$	$E_c - 0.34$	$E_c - 0.26$		VASP + PAW
Cu_{Si}			$E_v + 0.21$	$E_c - 0.69$	$E_c - 0.17$		Refs. [8–10]

3 Results and discussion

This report represents work in progress, and as such some of the results should be regarded as preliminary. This applies especially to the results obtained with the VASP code, where some technical issues remain unresolved at present. In particular, structural optimisation of both defects has proved problematic for VASP, possibly due to them having fairly flat energy surfaces in the region of their minima. At present we are not yet confident that our results obtained with the VASP code for V_{Si} are sufficiently reliable to report in full.

Both methods are able to reproduce the lattice parameter a and bulk modulus B_0 of Si well. The results, compared with the measured values are shown in Table 1. Note that B_0 calculated by the AIMPRO method uses the Birch equation of state, while the VASP calculations use the harmonic approximation. If anharmonic terms are taken into account, then B_0 is expected to be $\sim 5\%$ larger than without them.

The bandgap E_g represents the least well defined, and least accurate quantity that we calculate. This is a well-known deficiency of the underlying formalism, however, it will be seen that using our strategy for calculating electrical levels means it does not lead to any further difficulties. Both AIMPRO and VASP give similar results: $E_g(\text{AIMPRO}) \approx 0.71$ eV, while $E_g(\text{VASP}) \approx 0.60$ eV. The VASP result does not depend on whether the pseudopotential type is VUS or PAW.

All of the defect levels calculated here are sufficiently deep that the energies of donors can be given with respect to E_v and acceptors with respect to E_c . This is the preferred situation. Then the sign of the charged ideal supercell used to calculate the reference potential is the same as the defect supercell, hopefully giving better cancellation of systematic errors. None are so shallow that their energy is between the theoretical and true bandgap. If this were the case, then it would be necessary to use the opposite ideal-crystal band for the reference potential. The nearest case to this occurring is the midgap level of Cu_{Si} . Calculated and measured electrical levels for both defects are presented in Table 2. The results obtained with the AIMPRO package include different symmetry constraints to show their effect.

While both program packages are set to use similar thresholds in terms of energies and forces for deciding when structural optimisation is complete, the outcome shows some

differences. When no symmetry constraints are applied, both methods typically have residual, random differences for equivalent lengths between atoms, related by symmetry, that are $\lesssim 0.01$ Å. The differences between inequivalent lengths for the six Si-Si distances surrounding the central Cu atom or the vacancy are typically ~ 0.1 Å, making it quite apparent what the symmetry is.

It is found with the AIMPRO package that the direction of the main tetragonal distortion, giving D_{2d} symmetry, is in the expected direction for each defect: type-*B* for V_{Si} , and type-*A* for Cu_{Si} . The VASP package also finds that V_{Si}^0 exhibits a type-*B* D_{2d} distortion (results for other charge states are inconclusive at present). VASP yields approximately a type-*A* D_{2d} distortion for Cu_{Si} when the VUS pseudopotential is used, but there is no significant distortion from T_d symmetry with the PAW method. To demonstrate the effect of constraining the symmetry of the defect to be T_d , the levels calculated using AIMPRO for this configuration are also given in Table 2.

Notice in Table 2 that the donor levels calculated by AIMPRO for V_{Si} exhibit negative- U (giving reversed order) when T_d symmetry is permitted to break. Both donor transitions are also slightly too deep, so the calculated (0/ + 1) level lies below the top of the valence band.

The calculated donor transition for Cu_{Si} is closer to the measured value than for V_{Si} . Both AIMPRO and VASP-PAW yield equal energies for the (0/ + 1) level of Cu_{Si} , in spite of having different structures for the defect.

Regardless of constraint choice, no clear evidence is seen for the expected trigonal component of the distortion for Cu_{Si} . A possible explanation for this discrepancy may be found in the way that the bandstructure is sampled: the degeneracy of the electronic system is lifted without a structural distortion. The lack of spin-orbit coupling in the theory, and finite size of the model are two other factors that may also be affecting the outcome.

The situation is more complicated for V_{Si} . While the optimised structure in positive and neutral charge states calculated by AIMPRO has D_{2d} symmetry as expected, it must be constrained to be C_{2v} in the negative charge states, otherwise the lowest energy structure is a C_{3v} symmetry split-vacancy configuration with nearly, but not exactly D_{3d} symmetry. The outcomes in both cases are shown in Table 2. Previously, Puska

et al. found that V_{Si} in negative charge states adopts a split-vacancy configuration as well [28]. They provide a review of earlier work; see also Ref. [29].

According to our calculations, the energy differences between the C_{2v} and C_{3v} configurations of V_{Si} in the -1 and -2 charge states are 0.02 eV and 0.20 eV, respectively. Thus, the high stability of the C_{3v} configuration in the -2 charge state means that V_{Si} also has negative- U for the acceptor levels, according to this model. Probably, but not certainly, this is incorrect, and the model constrained to have C_{2v} symmetry in negative charge state is the true situation. If the split-vacancy configuration does exist, then according to the Jahn-Teller theorem it should have lower symmetry than D_{3d} in the -1 charge state, while it may be D_{3d} symmetry in the -2 state. Little is known from experiment at present about the negative charge states of V_{Si} other than they apparently exist.

The calculated energy for the $(-1/0)$ acceptor level of Cu_{Si} near midgap is somewhat deeper than the measured value, while the second acceptor is shallower. The Jahn-Teller effect moves these levels apart, making the $(-1/0)$ level shallower and the $(-2/-1)$ level deeper, each by ~ 0.1 eV. Thus, our calculations appear to underestimate the size of the Jahn-Teller effect, and especially for the VASP-PAW calculation, where no significant distortion from T_d symmetry occurs. It is reasonable to suppose that a similar pattern will be found for the acceptor states of V_{Si} if they are measured, and the expected C_{2v} model without negative- U prevails.

If the measured electrical levels for Cu_{Si} are compared with the three corresponding electrical levels of V_{Si} instead of using ideal, pure supercells, and we use the C_{2v} model in negative charge states, then the first acceptor level is about 0.2 eV shallower, while the donor and double acceptor change much less. The three energies calculated with AIMPRO are: $E(0/+1) \approx E_v - 0.01$ eV, $E(-1/0) \approx E_c - 0.48$ eV, and $E(-2/-1) \approx E_c - 0.17$ eV.

4 Conclusions

The structures and electrical levels for V_{Si} and Cu_{Si} calculated using the AIMPRO method are mostly in good agreement with accepted models and experimental observations. The main exception is the negatively charged states of V_{Si} , where the calculations appear to disagree with the conventional model. The VASP program package is also able to reproduce reasonably well the three electrical levels of Cu_{Si} , although calculations based on the PAW scheme apparently underestimate the size of the Jahn-Teller effect. A more satisfactory result appears to be obtained using the VUS pseudopotential, in spite of neglecting the Cu-3d electrons.

Overall, these results give grounds for believing that electrical levels of defects in semiconductors—which are considered to be difficult to estimate accurately—can be calculated reliably using conventional DFT-based methods, provided it is done with appropriate care.

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