Formation and migration energies of the vacancy in Si calculated using the HSE06 range-separated hybrid functional

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To overcome deficiencies of conventional density functional theory (DFT) utilizing the standard approximation for the exchange-correlation, the revised Heyd-Scuseria-Ernzerhof screened hybrid functional (HSE06) has been used for calculating the formation and migration energies of the vacancy in Si. It is demonstrated that the hybrid approach gives a much more accurate electronic description of the bulk and the vacancy. The correct description of the band gap and the donor transition levels obtained with the HSE06 functional builds confidence in predictions of the vacancy acceptor states. The calculated migration energies of the vacancy with different charge states agree well with low-temperature annealing measurements and, together with formation energies, provide an excellent estimate of the activation energy of vacancy-mediated self-diffusion in silicon.

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I. INTRODUCTION

Vacancies (V) in a crystalline materials are not only one of the most basic defects, but they are also extremely important technologically. Detailed knowledge of their properties has fundamental meaning in the case of semiconductors such as silicon and germanium, in which vacancies control, among other processes, self- and impurity (dopant) diffusion, annealing of implantation damage, and formation of extended defects. In silicon even small concentrations of donor or acceptor impurities cause huge changes in conductance, enabling the functionality of electronic and/or optoelectronic devices. As a result, the need for understanding silicon vacancy properties has been stimulating research on this native point defect over the past decades. Under these circumstances one might expect that all open questions on defect properties in Si have already been answered. However, in reality understanding of the defect properties and kinetics is still far from being satisfactory. For instance, different experimental1–5 and computational6–10 techniques have shown a large scatter in the estimates of V formation and migration energies. Consequently, diffusion properties of silicon vacancies are still a matter of controversy.11,12 In particular, the value of the activation energy of V-mediated self-diffusion has been the subject of unresolved debate, with some studies5,11 indicating 3.6 eV, while others12 4.5–4.6 eV. The experimental problems have been related to the temperature region for which self-diffusion has been accessible5 and to relative contributions of the native point defects to self-diffusion.4 This discrepancy cannot be solved theoretically because of an important shortcoming of the conventional implementations of density functional theory (DFT) related to the “band-gap problem”13 and supercell finite-size effects.14

An isolated vacancy in bulk silicon has been modeled by Puska et al.6 Probert and Payne,7 Wright,8 Ganchenkova et al.9 and Corsetti and Mostofi10 mainly to address finite-size effects. However, because of the band-gap problem, interpretation of the electronic properties of a vacancy in Si has been problematic.15–17 Since the band gap’s edges define the energy scale for defects, it has a fundamental meaning to quantitative predictions of defect levels15 and in certain cases (e.g., filled defect states in the band gap18) also to formation and migration energies.

In order to overcome deficiencies of conventional DFT based on the standard approximation for the exchange-correlation (xc) functional, i.e., the local density or generalized gradient approximation (LDA or GGA), we used one of the higher level electronic structure methods: the revised Heyd-Scuseria-Ernzerhof range-separated hybrid functional (HSE06).19 This functional, already proven useful in the study of the electronic and structural properties of defects in semiconductors,18,20–23 in this work has been employed to calculate the formation and migration energies of the neutral and charged vacancies in Si adopting, as for hybrid calculations, a relatively large 512 atom supercell. The results are compared with those obtained using the common GGA approach in the Pedrew-Burke-Ernzerhof (PBE) form24 and with literature data. It will be shown that by using the HSE06 functional it is possible to obtain a more accurate electronic description of vacancies and a good estimate for the activation energy of self-diffusion in Si, which is consistent with the experimental data.4 The defect levels calculated with this hybrid approach also agree well with electron paramagnetic resonance (EPR) and deep level transient spectroscopy (DLTS) measurements reported by Watkins.1

II. COMPUTATION DETAILS

The calculations were performed using the pseudopotential method with projector augmented wave (PAW) potentials as implemented in the VASP code.25 Convergence of the total energy was assured by setting the plane-wave cutoff energy to 320 eV. For the structural properties and bulk modulus a primitive cell with a 12 × 12 × 12 Monkhorst-Pack (kMP = 123) Brillouin zone (BZ) sampling26 was used, reduced by a factor of 2 in the HSE Fock-exchange part.27 For evaluating the theoretical lattice constant a0 and the bulk modulus B0, the volume dependence of the static energy was fitted to a Murnaghan equation of state.28

The results of calculations of the structural, elastic and electronic properties are summarized and compared to experimental findings in Table I. It can be noted that, compared
TABLE I. The optimized theoretical lattice constants $a_0$, bulk moduli $B_0$, and Kohn-Sham band-gap $E_g$ in Si, calculated using different xc functionals are compared to the experimental findings. The relative errors compared to experiment for the calculated lattice constants and band gaps are given in parentheses.

<table>
<thead>
<tr>
<th>xc functionals</th>
<th>$a_0$ (Å)</th>
<th>$B_0$ (GPa)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>5.469(+0.7%)</td>
<td>88</td>
<td>0.65(−44.4%)</td>
</tr>
<tr>
<td>HSE06</td>
<td>5.435(+0.1%)</td>
<td>98</td>
<td>1.19(+1.7%)</td>
</tr>
<tr>
<td>Expt.</td>
<td>5.431</td>
<td>94.8−99</td>
<td>1.17</td>
</tr>
</tbody>
</table>

*aExperimental values from Ref. 29.

The relative errors compared to experiment for the calculated lattice constants and band gaps are given in parentheses.

to PBE, the HSE06 functional yields a lower value of the lattice constant, which agrees in an excellent way with the experimental one. The fact that PBE overestimates the lattice constant results in an underestimation of the bulk modulus. As expected, PBE severely underestimates also the band gap due to a spurious electron self-interaction and the complete absence of the discontinuity of the derivative of the xc potential with respect to the number of electrons.13 The hybrid functional does not overcome all these limitations; however, due to the nonlocal screened exchange operator the HSE one-electron gap compares well with the experimental one.

Calculations of the properties of vacancy were carried out using $\Gamma$ point sampling, which has been proven reliable for different defects analyzed with the HSE functional.21,22 To reduce finite-size effects, a periodic supercell of $N = 512$ atoms was used with computed equilibrium lattice constants listed in Table I. In order to maximize the accuracy of defect calculations, the symmetry constraints were switched off, and the potential-alignment technique together with an image charge correction were applied as proposed in Ref 14. The spin polarization has not been taken into account.

In order to estimate an influence of the spin degree of freedom, spin-polarized HSE06 calculations on a smaller cell (216 atoms, $\Gamma$ point BZ sampling, with a force convergence criterion of 1 meV/Å) were performed. These calculations provide results similar to those recently reported by Weber et al.30 The observed underestimation of the Jahn-Teller distortion in these results can be explained by the fact that spin-polarized atoms are much more stable for hybrid functionals than for semilocal exchange correlation functionals.27,31–33 However, neglecting spin-polarization effects, hybrid functionals do behave reasonably similar to semilocal functionals.32 In further study we have thus focused attention on non-spin-polarized calculations in a 512 atom supercell.

III. RESULTS AND DISCUSSION

It can be noted that HSE vacancy shows symmetries which are the same as obtained with PBE. Our results are also in agreement with the EPR experiments and Watkins’ LCAO model1 for positive and neutral charge states. The point groups are $T_d$ for $V^{2+}$ and $D_{2h}$ for $V^{1+}$ and $V^0$. As previously reported6–10 $C_{2v}$, symmetry of $V^{1–}$ obtained from DFT is not stable, and in our calculations relaxes to another orthorhombic structure, $D_2$. Lento and Nieminen8,10 also found this symmetry for $V^{1–}$ in LDA calculations using a 256-atom supercell, and one $k$ point in the BZ. In fact, almost all previous papers describing conventional DFT calculations of the Si vacancy6–10,34 report that the relaxation of $V^{1–}$ is the most problematic and in many cases fails to reproduce an experimentally confirmed $C_{2v}$ symmetry.35,36 In the doubly negative vacancy, our and recent theoretical studies6–10 show that one of the nearest-neighbor ions of the vacancy is relaxed towards the vacancy site, forming a split vacancy configuration, with a point group symmetry of $D_{sd}$.

The formation energy of the vacancy in charge state $q$ as a function of the Fermi level is given by

$$\Delta H_{\text{V},q}^f(E_F) = E_{q}^{N-1} - \frac{N-1}{N} E^N + q(E_F + E_V + \Delta E_{\text{pa}}),$$

where $E_{q}^{N-1}$ is the total energy of a relaxed supercell containing $N - 1$ atoms and one vacancy with charge state $q$, $E^N$ is the total energy of the perfect neutral cell containing $N$ atoms, and $E_F$ is the Fermi level in the band gap, with respect to the valence band maximum $E_V$. The presence of a vacancy in the supercell strongly affects the band structure, therefore we used a potential-alignment technique37 and a correction term $\Delta E_{\text{pa}}$ was added to the bulk $E_V$. To solve the problem of spurious electrostatic interactions of charged defects due to periodicity and finite supercell size, an image charge correction was applied. According to Ref. 14, the total energy was corrected by 63% of the monopole-monopole interaction, scaled down by the experimental dielectric constant $\varepsilon = 12$.39

The value of the electrostatic potential correction term $\Delta E_{\text{pa}}$ varies from $−0.02$ to $−0.11$ eV, depending on the functional used in the calculations and the charge state of the vacancy. The value of the charge correction term which is added to total energy of the defect supercell, $E_{q}^{N-1}$, is about 0.05 and 0.20 eV for a single and double charged vacancy, respectively. Based on Kohn-Sham eigenvalues the band dispersion error for the neutral vacancy was estimated at 0.06 eV.

The formation energies of the Si vacancy in $2^+, 1^+, 0$, $1−$ and $2−$ charged states, i.e., $V^{2+}$, $V^{1+}$, $V^0$, $V^{1−}$, and $V^{2−}$, obtained with the PBE and HSE06 functionals are shown in Fig. 1 as a function of the position of the Fermi level in the band gap. The values of formation energy at $E_F$ for the neutral and charged vacancies obtained within the present work are listed in Table II together with other published results. In the

![FIG. 1. (Color online) The formation energy of the vacancy in Si as a function of the Fermi level and the charge state calculated using the PBE and hybrid functional HSE06.](image-url)
previous DFT studies\textsuperscript{6,8–10} different schemes and procedures for correcting of finite-size effects have led to strongly varying predictions, therefore we will compare only neutral vacancy results.

Analyzing the results in Table II one can notice that the V-formation energy in Si obtained with LDA and GGA seems to converge to values of 3.45 and 3.60 eV, respectively, while hybrid calculations yield a value of around 4 eV. The HSE functional and the quantum Monte Carlo method lead to a similar increase in the predicted formation energies for silicon self-interstitials.\textsuperscript{20} Thereby it can be concluded that both LDA and GGA considerably underestimate the formation energy, mainly due to an underestimation of the band gap.

The charge state transition level $\epsilon(q/q')$, describing the $E_F$ at which the formation energies of two different charge states $q$ and $q'$ become equal, is given by\textsuperscript{14}

\[
\epsilon(q/q') = \frac{\Delta H_{\nu,q}^f (E_F = 0) - \Delta H_{\nu,q}^f (E_F = 0)}{q - q'}.
\]

The calculated values of $\epsilon(q/q')$ are shown in Fig. I and compared with other published results in Table III. It can be noted that, in contrast to PBE, the HSE\textsubscript{06} functional quantitatively reproduces the measured\textsuperscript{1} values for $\epsilon(2 + /1+)$ and $\epsilon(1 + /0)$ at 0.14 and 0.02 eV above the valence band maximum, respectively. A negative-U effect,\textsuperscript{40,41} by which the stable charge state changes directly from $V^{2+}$ to $V^0$ is also observed in hybrid functional results at $E_V + 0.08$ eV. This effect was also observed by Weber \textit{et al.};\textsuperscript{30} however, the donor states in their work are located closer to the middle of the band gap. In our spin-polarized calculations in a 216 atom supercell, we found that application of the spin degree of freedom leads to smaller Jahn-Teller distortion and in turn to smaller formation energies. The charge transition levels calculated from these values do not agree with measured ones, e.g., the calculated $\epsilon(1 + /0)$ level at $E_V + 0.37$ eV is in disagreement with the measured one at 0.03–0.05 eV above the valence band maximum.\textsuperscript{1} Another very important observation is that the spin-polarized calculations do not reproduce measured symmetries of the charged vacancies even with forces well below 1 meV/Å. The reason for these discrepancies is that the inclusion of exact exchange in the hybrid functionals very likely causes an overestimation of the exchange splitting. The associated increase in the spin-polarization energy of the atomic system stabilizes spin-polarized solutions compared to non-spin-polarized solutions, and leads to slight and sizable underestimation of the atomization energies for $sp$ elements and $d$ metals, respectively.\textsuperscript{27,31–33} In our opinion spin-polarized HSE\textsubscript{06} calculations favour high-spin symmetric structures and smaller relative volume relaxation. This in turn explains why Weber \textit{et al.} report donor states in Ge vacancies, and higher values for donor levels (smaller values in the case of acceptor levels) compared to our non-spin-polarized Si vacancy results.

\[
\begin{array}{cccccccc}
\text{Charge} & \text{This work} & \text{Ref. 6} & \text{Ref. 8} & \text{Ref. 9} & \text{Ref. 10} & \text{Ref. 38} \\
 & \text{PBE} & \text{HSE\textsubscript{06}} & \text{LDA} & \text{LDA} & \text{LDA} & \text{Corr}\textsuperscript{a} \text{GGA} \\
 & N = 512 & k = \Gamma & N = 216 & L \rightarrow \infty & k_{\text{MP}} \text{ up to } 3^3 & N = 216 & k = \Gamma & k_{\text{MP}} = 3^3 \\
2 + & 3.49 & 3.92 & 3.01 & 3.090 & 3.415 & 3.48 & 2.85 & 3.66 \\
1 + & 3.49 & 4.06 & 3.20 & 3.220 & 3.545 & 3.61 & 3.00 & 3.55 \\
0 & 3.53 & 4.08 & 3.27 & 3.457 & 3.605 & 3.67 & 3.06 & 3.45 \\
2− & 4.69 & 5.91 & 4.29 & 5.023 & 4.909 & 4.40 & 3.57 & 3.72 \\
\end{array}
\]

\textsuperscript{a}A correction based on the hybrid B3LYP functional was applied to DFT/PW91 results.

\textsuperscript{b}The extrapolation of the formation energies from the three supercells ($N = 216, 512$, and 1000) to an infinite sized supercell using the Makov-Payne formula (Ref. 39).

\[
\begin{array}{cccccccc}
\text{Level} & \text{This work} & \text{Ref. 6} & \text{Ref. 8}\textsuperscript{a} & \text{Ref. 9}\textsuperscript{a} & \text{Ref. 10} & \text{Ref. 1} \\
 & \text{PBE} & \text{HSE\textsubscript{06}} & \text{LDA} & \text{LDA} & \text{GGA} & \text{GGA} & \text{LDA} \\
 & N = 512 & k = \Gamma & N = 216 & L \rightarrow \infty & k_{\text{MP}} \text{ up to } 3^3 & N = 216 & k = \Gamma & k_{\text{MP}} = 3^3 \\
\epsilon(2 + /1+) & 0.00 & 0.14 & 0.19 & 0.13 & 0.13 & 0.13 & 0.16 & -0.11 & 0.13 \\
\epsilon(2 + /0) & 0.02 & 0.08 & 0.13 & 0.18 & 0.10 & 0.10 & 0.11 & -0.11 & 0.09 \\
\epsilon(1 + /0) & 0.04 & 0.02 & 0.07 & 0.24 & 0.06 & 0.06 & 0.06 & -0.10 & 0.03–0.05 \\
\epsilon(0/1−) & 0.61 & 1.05 & 0.61 & 0.85 & 0.71 & 0.37 & 0.38 & 0.26 & <1.0 \\
\epsilon(0/2−) & 0.58 & 0.91 & 0.51 & 0.78 & 0.65 & 0.37 & 0.25 & 0.13 & <1.0 \\
\epsilon(1−/2−) & 0.55 & 0.77 & 0.41 & 0.72 & 0.59 & 0.36 & 0.13 & 0.00 & <1.0 \\
\end{array}
\]

\textsuperscript{a}The value of $\Delta E_{\text{pl}}$ in Eq. (1) was chosen to produce agreement with the experimental $\epsilon(2 + /1+)$ value.

TABLE II. Calculated charged vacancy formation energies in Si, obtained from Eq. (1) with $E_F = 0$ eV. All values are in eV.

TABLE III. Calculated transition levels (in eV relative to $E_V$) associated with the vacancy in Si. Bold numbers denote thermodynamically stable transitions.
In some previous LDA and GGA calculations\(^8,9\) a different potential-alignment technique was applied, so that \(\Delta E_{PZ}\) in Eq. (1) was chosen to ensure agreement with the measured \(\epsilon(2+/1+)\) level at 0.13 eV. This fitting, however, is of limited applicability.\(^{17,25}\) On the other hand, the well converged LDA results\(^5,0,15\) do not yield the observed negative-U behavior. Nevertheless, Puska \(\textit{et al.}\)\(^6\) and Corsetti \(\textit{et al.}\)\(^10\) obtained the negative-U effect using respectively 216 and 256 atom supercells and \(\Gamma\) point sampling. However, the absolute values of the defect formation energy (see Table II) in these calculations do not converge well, with respect to the dilute limit, when using this Brillouin zone integration.

It should be noted that no acceptor-like levels of the vacancy were identified by DLTS in \(n\)-type Si, and it was interpreted that they must be deeper than 0.17 eV below the conduction band edge (\(E_C\)).\(^1\) In addition, the evaluation of the relative contributions of charged native-point defects to silicon self-diffusion showed the existence of vacancy acceptor levels in the upper half of the Si band gap.\(^4\) The correct description of the band gap and the donor states obtained with the HSE06 functional builds confidence in the precision of calculations of the acceptor states.

In agreement with previous DFT studies\(^6,8,10\) the negative-U behavior for the acceptor states is also obtained in our calculations. The HSE06 acceptor levels, relative to the conduction band minimum, lie at \(E_C - 0.14\) eV, \(E_C - 0.28\) eV, and \(E_C - 0.42\) eV for \(\epsilon(0/1-), \epsilon(0/2-),\) and \(\epsilon(1/-2-)\), respectively. Similar levels were observed by DLTS in Czocharalski grown \(n\)-doped \(n\)-type Si.\(^{42}\) After a hole injection at 300 K followed by cool down under zero or reverse bias, the \(E_C - 0.13\) eV, \(E_C - 0.27\) eV, and \(E_C - 0.46\) eV peaks emerged. These peaks were found to form a bistable configuration: the presence or absence of the 0.13 eV DLTS peak depends on whether the diode is cooled under reverse (defect neutral) or zero bias (negatively charged). An additional hole injection at 140 K replaced the \(E_C - 0.13\) eV and \(E_C - 0.27\) eV peaks by a new one at \(E_C - 0.16\) eV. According to Watkins\(^43\) these levels come from multiconfigurational combination of interstitial carbon (\(C_i\)) substitutional-group V-donor (\(D_i\)) pairs. However, our HSE06 calculations suggest that these defects levels can be explained by negatively charged vacancies.

The calculated configuration coordinate (cc) diagram for \(V^0, V^{1-}\) and \(V^{2-}\), obtained by calculating the formation energy in the different charge states from Eq. (1) with \(E_F = E_C\), is shown in Fig. 2. The experimentally observed \(E_C - 0.46\) eV peak corresponds to an electron emission from split (\(D_{3d}\) symmetry) \(V^{2-}\) while the \(E_C - 0.13\) eV peak corresponds to the electron emission from a tetrahedral single negative vacancy. The cc diagram indicates a zero-phonon line transition from \(V^{2-}\) to \(V^0\) at 0.56 eV. This is the energy required to remove two electrons from the \(\epsilon(0/2-)\) level to the conduction band edge. Thus, the dependence of the \(E_C - 0.13\) eV peak intensity on the bias conditions under cooling can be explained as follows: (1) Under zero bias, emission from the thermodynamically stable \(\epsilon(0/2-)\) defect level mainly occurs; (2) application of the reverse bias sweeps electrons away from the junction, and also from the metastable \(\epsilon(0/1-)\) level, leading to 0.27 and 0.13 eV input in the observed DLTS spectra. The results in Fig. 2 also show that the observed \(E_C - 0.16\) eV peak after additional hole injection at 140 K is due to emission of two electrons from \(V^{2-}\) with tetrahedral symmetry. The HSE06 calculations indicate that the doubly negative vacancy with \(D_2\) symmetry induces two charge state transition levels with negative-U ordering at \(E_C - 0.16\) eV and \(E_C - 0.18\) eV for \(\epsilon(0/2-)\) and \(\epsilon(1/-2-)\), respectively.

The activation energy of \(V\)-mediated self-diffusion is given by \(\Delta H_{\text{f}}^\text{V} = \Delta H_{\text{f}}^\text{V} + \Delta H_{\text{m}}^\text{V}\), with \(\Delta H_{\text{f}}^\text{V}\) and \(\Delta H_{\text{m}}^\text{V}\) being the formation and migration energies of the vacancy, respectively. In order to calculate the migration energy, the climbing image nudged elastic band (CI-NEB) method\(^44\) was used. The migration of the vacancy occurs via motion of one of the four
formation and migration energies of the intrinsic point defects. The proposed hybrid approach applied here to the Si vacancy can also be used for other group-IV semiconductors, such as germanium which conventional DFT predicts to be metallic. In our opinion it may provide a quantitative description of doping, interactions of point defects, and of the properties of point defect clusters.

Acknowledgments

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References


TABLE IV. Comparison of theoretical and experimental values of the vacancy migration energy, $\Delta H^0_{V^q}$, and the activation energy of V-mediated self-diffusion, $\Delta H^0_{V} = \Delta H^0_{V^q} + \Delta H^0_{V}$, governed by neutral and charged vacancies in intrinsic Si. The values for $\Delta H^0_{V}$ were obtained from Eq. (1). All results are in eV.

<table>
<thead>
<tr>
<th>Charge</th>
<th>$\Delta H^0_{V^q}$</th>
<th>$\Delta H^0_{V}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HSE06</td>
<td>Expt.\textsuperscript{a}</td>
</tr>
<tr>
<td>2+</td>
<td>0.52</td>
<td>0.32 ± 0.02</td>
</tr>
<tr>
<td>1+</td>
<td>0.35</td>
<td>5.00</td>
</tr>
<tr>
<td>0</td>
<td>0.57</td>
<td>0.45 ± 0.04</td>
</tr>
<tr>
<td>1−</td>
<td>0.04</td>
<td>4.58</td>
</tr>
<tr>
<td>2−</td>
<td>0.24</td>
<td>0.18 ± 0.02</td>
</tr>
</tbody>
</table>

\textsuperscript{a}References 1 and 46.

\textsuperscript{b}Reference 4.