Density-functional-theory calculations for the silicon vacancy

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The atomic configurations and formation energies of a silicon vacancy in the +2, +1, 0, −1, and −2 charge states have been computed using density-functional theory with norm-conserving pseudopotentials and a plane wave basis. Calculations were performed in simple cubic supercells using two different forms of exchange and correlation: the local-density approximation (LDA) and the Perdew, Burke, Ernzerhof formulation of the generalized-gradient approximation (GGA). Convergence with respect to Brillouin zone sampling was tested for all charge states, and effects due to electrostatic interactions between the periodically repeated vacancies were removed by extrapolating the formation energies obtained in 215-, 511-, and 999-atom supercells to an infinite sized supercell. In agreement with experimental results, the GGA yielded a configuration with C_{2v} symmetry in the −1 charge state, whereas the LDA yielded D_{3d} symmetry. Transition energies between the charge states were also computed. The experimentally observed negative-U behavior of the donor states was reproduced in the GGA results, but not in the LDA results. Both the LDA and GGA predict negative-U behavior for the acceptor states.

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I. INTRODUCTION

Density-functional-theory (DFT) (Ref. 1) calculations in supercells are widely used to obtain information about point defects in semiconductors. In these calculations, periodic boundary conditions are applied to a parallelpiped containing a defect surrounded by bulk material, effectively producing an infinite, periodic array of defects. The use of periodic boundary conditions yields an efficient computational scheme, however it also introduces spurious electrostatic and strain interactions between the defect and its periodic replicas. The computed atomic configuration and formation energy of a defect are influenced by these interactions, which are difficult to quantify and may vary significantly with the shape and size of the supercell. This has led to disparities between results published by different groups for defects such as the Si vacancy (V_{Si}), in addition to the disparities that can arise from the use of different technical approximations such as the size of the basis set and the number of sampling points in the Brillouin zone.

One way to remove the effects of spurious interactions is to perform calculations in different sized supercells and then extrapolate the results to an infinite sized supercell corresponding to an isolated defect. This technique was used by Lento *et al.*[2] in DFT calculations for an unrelaxed +2 Si self-interstitial, and was recently studied in detail by Castleton *et al.*[3] for a variety of defects in InP. In the present study, we used this technique to obtain the atomic configurations, formation energies, and transition energies of V_{Si}. DFT calculations were performed in simple cubic supercells containing 215, 511, and 999 atoms (standard 216-, 512-, and 1000-atom supercells minus one atom), and the formation energies were extrapolated via a maximum likelihood fit to the Makov-Payne formula.[4] In addition to quantifying the dependence of V_{Si} results on supercell size, we also examined how the results differ for two different forms of exchange and correlation: the local-density approximation (LDA) (Ref. 5) and the Perdew, Burke, Ernzerhof formulation[6] of the generalized-gradient approximation (GGA). We note that this study is part of a broader effort underway at Sandia National Laboratories to advance the understanding of radiation damage in Si bipolar junction transistors. This effort includes DFT studies of the vacancy,[7] divacancy,[7,8] and self-interstitial,[7,9] and finite-element modeling of gain degradation and recovery following irradiation.

The computational methods used in this study are described in Sec. II and the results from each supercell and V_{Si} charge state are given in Sec. III along with the extrapolation of the formation energies to an infinite sized supercell. Earlier DFT studies indicated that V_{Si} results can vary substantially with the number of sampling points in the Brillouin zone, and there are further indications that the formation energies are sensitive to the number of basis functions when using a plane wave basis. With this in mind, we performed extensive tests to check the convergence of bulk properties with respect to the plane wave basis, and the convergence of V_{Si} results with respect to both the plane wave basis and Brillouin-zone sampling. These tests are described at the end of Sec. II. In Sec. III, the LDA and GGA results are presented and compared with results from experiments and previous DFT studies. In Sec. IV, the findings from this study are summarized.

II. METHODOLOGY AND TESTS

A. Computational methods

DFT calculations for V_{Si} were performed using the Socorro code[10] with norm-conserving pseudopotentials and a plane wave basis. Hamann's GNCPP program[11] was used to construct LDA pseudopotentials and the FHI-98PP program[12] was used to construct GGA pseudopotentials. Sampling points in the Brillouin zone were generated using the Monkhorst-Pack technique,[13] and a Fermi function with kT=25.7 meV (corresponding to room temperature) was used to compute the occupations of the Kohn-Sham

functions.[14] For verification purposes, a limited number of LDA calculations were repeated using the Vienna *ab initio* simulation program (VASP) (Ref. 15) with ultrasoft pseudopotentials from the VASP database. As detailed below, the agreement between the Socorro and VASP results was excellent.

As noted in the Introduction, careful convergence tests were performed for bulk Si and V_{Si}. Bulk properties were first determined as a function of the energy cutoff used to define the plane wave basis set. For each cutoff, total energy calculations were performed for a set of primitive cell volumes and the results were then fit to the Murnaghan equation[16] to extract the equilibrium lattice constant and bulk modulus. Converged LDA values (5.384 Å=10.175 Bohr and 0.944 Mbar) were obtained using energy cutoffs of 17 Ryd (231 eV) for the Kohn-Sham functions and 60 Ryd (816 eV) for the electron density. Converged GGA values (5.469 Å=10.335 Bohr and 0.856 Mbar) were obtained using a 20 Ryd (272 eV) cutoff for the Kohn-Sham functions and an 80 Ryd (1088 eV) cutoff for the electron density. The differences between these results and measured ones (5.431 Å=10.263 Bohr and 0.979 Mbar at room temperature)[17] are consistent with those found in earlier DFT studies. For comparison, we note that our VASP LDA results for bulk Si (5.389 Å=10.184 Bohr and 0.941 Mbar) are within 0.1% and 0.3% of the corresponding Socorro results.

Calculations for V_{Si} were performed in simple cubic supercells containing 215, 511, and 999 Si atoms (standard 216-, 512-, and 1000-atom supercells minus one atom). These supercells were generated using the LDA and GGA lattice constants noted above. The lengths along the x, y, and z axes were then $L=16.153$, 21.538, and 26.922 Å (30.525, 40.700, and 50.875 Bohr) in the LDA calculations and $L=16.407$, 21.876, and 27.345 Å (31.005, 41.340, and 51.675 Bohr) in the GGA calculations. Relaxed V_{Si} structures were determined as follows: (1) A starting structure was made by removing one atom from a bulk supercell and displacing a few of the remaining atoms in random directions to produce a structure with C_1 point-group symmetry. (2) A DFT calculation was performed in which all of the atoms were allowed to move until their forces were less than 2×10^{-4} eV/Å. (3) The point group of the relaxed structure was identified. Further refinement of the structure using larger Brillouin zone sampling meshes were typically performed using a symmetrized version of the structure obtained from the C_1 relaxation.

Once the relaxed structures were found, their zero temperature formation energies were computed using the expression[18]

$$E^f[V_{Si}^q;L,n_{MP},E_F] = E_T[V_{Si}^q;L,n_{MP}] - \left(\frac{N-1}{N}\right)E_T[\text{bulk};L,n_{MP}] + q(\varepsilon_{VBE}[\text{bulk};L,n_{MP}] + \Delta_{VBE} + E_F), \quad (1)$$

where $E_T[V_{Si}^q;L,n_{MP},E_F]$ is the total energy of a relaxed V_{Si} structure in charge state q computed in a supercell with length L using Monkhorst-Pack parameters $\{n_{MP},n_{MP},n_{MP}\}$ to generate sampling points in the Brillouin zone, $E_T[\text{bulk};L,n_{MP}]$ is the total energy of bulk Si computed in the same supercell using the same Monkhorst-Pack parameters, N is the number of Si atoms in the bulk supercell, $\varepsilon_{VBE}[\text{bulk};L,n_{MP}]$ is the Kohn-Sham eigenvalue at the valence band edge (VBE) in the bulk calculation, and E_F is the Fermi level defined to be zero at the bulk VBE. We note that among the supercells and Brillouin zone samplings used in this study, the values of $\varepsilon_{VBE}[\text{bulk};L,n_{MP}]$ differed by less than 3×10^{-5} eV for each exchange-correlation formulation. As such, we neglect the supercell and sampling dependences in $\varepsilon_{VBE}[\text{bulk};L,n_{MP}]$ and denote it simply as $\varepsilon_{VBE}[\text{bulk}]$.

Δ_{VBE} is defined so that $\varepsilon_{VBE}[\text{bulk}]+\Delta_{VBE}$ is equal to the measured VBE energy. As such, it has one value for all $V_{Si}^{q\neq0}$ states treated in this study (one value for the LDA and one value for the GGA).[7] We note that this definition differs from the standard one in which Δ_{VBE} is a shift that aligns the VBE eigenvalue in the defect supercell with $\varepsilon_{VBE}[\text{bulk}]$.[18,19] In practice, this shift is difficult to determine and is generally taken to be different for each defect state and supercell. The need for a shift is thought to arise from the lack of an absolute energy reference when using periodic boundary conditions. The definition employed in this study likewise recognizes the lack of an absolute energy reference, but assumes that this leads to a common shift in all bulk and defect supercells for a given exchange-correlation functional and a given set of pseudopotentials. This seems reasonable as long as spatially invariant components of potentials appearing in the Kohn-Sham equations (which shift the Kohn-Sham eigenvalues) are treated consistently in all bulk and defect calculations. We further note that the definition of Δ_{VBE} used in this study can, in principle, correct inaccuracies in $\varepsilon_{VBE}[\text{bulk}]$ due to the use of approximate exchange-correlation functionals. At present, we are not aware of a definitive procedure for computing Δ_{VBE} so we estimated its value as the difference in computed and measured energies for a transition between two particular charge states. Further details are given below where we discuss transition energies.

The bulk and V_{Si} total energies in Eq. (1) depend strongly on the Monkhorst-Pack parameters used to generate sampling points in the Brillouin zone. For this reason, we performed systematic tests for each supercell and charge state to explicitly determine the value of n_{MP} needed to obtain converged formation energies. As detailed near the end of this section, the results from these tests prompted us to use $n_{MP}=5$ for calculations in the 215-atom supercells, $n_{MP}=4$ for calculations in 511-atom supercells, and $n_{MP}=3$ for calculations in 999-atom supercells. We also estimated uncertainties in the V_{Si} formation energies as the difference in results obtained using the two highest sampling levels ($n_{MP}=2$ and $n_{MP}=3$ in the 999-atom supercell, for example). These uncertainties were used in the maximum likelihood fits of the supercell formation energies.

Consistent with earlier DFT results, q was found to range from +2 to −2. This range was determined by comparing the defect state eigenvalues with the eigenvalues of band-edge states. In particular, $q<-2$ produced defect states with eigenvalues above the conduction-band edge (CBE) and

$q>+2$ produced defect states with eigenvalues below the VBE. In calculations with $q\neq 0$, a uniform background charge (UBC) was used to remove the infinite electrostatic interaction energy between V_{Si}^{q} and its periodic replicas.[20] In a separate study by this author, the formation energies of unrelaxed V_{Si}^{+2} were computed in simple cubic 63-, 215-, 511-, 999-, and 1727-atom supercells using two different methods to remove the infinite electrostatic interaction energy: (1) the UBC method and (2) the local-moment countercharge (LMCC) method recently developed by Schultz.[7,21] When the formation energies from these two methods were extrapolated to an infinite sized supercell, they agreed to within 2 meV, demonstrating the consistency of the two methods.[22] A similar level of agreement was also found by Lento *et al.*[2] in UBC and LMCC calculations for an unrelaxed +2 Si self-interstitial.

The extrapolation of the formation energies from the three supercells to an infinite sized supercell was obtained from a maximum likelihood fit to the Makov-Payne formula truncated at the $1/L^3$ term[4]

$$E^{f}[V_{\mathrm{Si}}^{q};L,n_{\mathrm{MP}},E_{\mathrm{F}}]=E^{f}[V_{\mathrm{Si}}^{q};L\rightarrow\infty,E_{\mathrm{F}}]-\frac{\alpha q^{2}}{\varepsilon L}+\frac{A_{3}}{L^{3}}. \quad (2)$$

In this formula, $E^{f}[V_{\mathrm{Si}}^{q};L,n_{\mathrm{MP}},E_{\mathrm{F}}]$ is the formation energy of V_{Si}^{q} in a supercell of length L obtained using the n_{MP} values noted above, $E^{f}[V_{\mathrm{Si}}^{q};L\rightarrow\infty,E_{\mathrm{F}}]$ is the formation energy in an infinite sized supercell (determined from the fit), $\alpha=2.8373$ is the Madelung constant for a simple cubic lattice of point charges embedded in a uniform compensating background, ε is the static dielectric constant of Si, and A_3 is the coefficient of the $1/L^3$ term (determined from the fit). For consistency, DFT values of ε were used in the fits: 12.9 for the LDA and 12.6 for the GGA.[23] Further discussion about the fits can be found in Sec. III.

The main points of comparison with experiments discussed in Sec. III will be the V_{Si}^{+1} and V_{Si}^{-1} point groups, and the transition energies between V_{Si} charge states differing by $\Delta q=1$. The transition energy between two charge states is the value of E_{F} at which their formation energies become equal. For example, the transition between the q and $q+1$ states occurs at an energy

$$E^{q/q+1}=E^{f}[V_{\mathrm{Si}}^{q};L\rightarrow\infty,E_{\mathrm{F}}=0]-E^{f}[V_{\mathrm{Si}}^{q+1};L\rightarrow\infty,E_{\mathrm{F}}=0] \quad (3)$$

relative to the VBE. We note that E_{F} is set to zero when evaluating the extrapolated formation energies on the right-hand side of this expression. Furthermore, this expression cannot be fully evaluated until a value for Δ_{VBE} is obtained. In this study, Δ_{VBE} was selected to bring a computed transition energy into agreement with a measured value; specifically the $E^{1+/2+}$ level which occurs 0.13 eV above the VBE.[24] This procedure yielded $\Delta_{\mathrm{VBE}}=0.328$ eV for the LDA results and 0.159 eV for the GGA results. We emphasize that an optimal procedure for determining Δ_{VBE} has not yet been determined and, as such, the present approach should be viewed as provisional.

TABLE I. LDA formation energies (in eV) obtained in a 215-atom supercell using various Monkhorst-Pack parameters (n_{MP}) to generate sampling points in the Brillouin zone. The results are given at $E_{\mathrm{F}}=0$.

n_{MP}	$E^{f}[V_{\mathrm{Si}}^{+2}]$	$E^{f}[V_{\mathrm{Si}}^{+1}]$	$E^{f}[V_{\mathrm{Si}}^{0}]$	$E^{f}[V_{\mathrm{Si}}^{-1}]$	$E^{f}[V_{\mathrm{Si}}^{-2}]$
1	2.380	2.874	3.270	4.066	4.652
2	3.018	3.334	3.517	4.150	4.639
3	3.004	3.296	3.529	4.133	4.635
4	3.002	3.295	3.529	4.140	4.635
5	3.002	3.294	3.529	4.140	4.635

B. Test calculations

Test calculations were performed: (1) to determine the plane wave energy cutoff needed to produce converged results for the relaxed structure of a neutral vacancy (V_{Si}^{0}), (2) to determine the Brillouin-zone sampling needed to produce converged results, and (3) to verify Socorro results by comparing them with results obtained using VASP. The tests for the plane wave energy cutoff were distinct from the aforementioned tests for bulk properties in that the vacancy tests checked the convergence of the forces used to optimize atom positions. In these tests, the formation energy of V_{Si}^{0} was obtained in a 215-atom supercell using a range of cutoffs for the plane wave basis set. A cutoff of 17 Ryd (231 eV) yielded a formation energy converged to within 10 meV using the LDA and a cutoff of 20 Ryd (272 eV) yielded the same level of convergence using the GGA. The resulting basis sets were then used in the calculations described below.

Tests for Brillouin-zone sampling focused initially on the LDA calculations in a 215-atom supercell for all of the V_{Si} charge states. The formation energies listed in Table I demonstrate that convergence to within 1 meV was achieved using $n_{\mathrm{MP}}=5$ to generate sampling points. We note that the Monkhorst-Pack grids generated using odd values of n_{MP} did not include a shift as has sometimes been used to gain efficiency. In this study, we simply increased n_{MP} systematically as shown in Table I until the formation energies converged. As noted in previous studies, we found that $n_{\mathrm{MP}}=1$ did not yield converged formation energies and that the lack of convergence was especially severe in the +2 and +1 charge states. Similar convergence tests were conducted in the 511- and 999-atom supercells using the LDA, and in 215-, 511-, and 999-atom supercells using the GGA. Based on these tests, the formation energies utilized in the extrapolation procedure were obtained using $n_{\mathrm{MP}}=5$, 4, and 3 to generate sampling points in the 215-, 511, and 999-atom supercells. These samplings generally yielded formation energies converged to within 1 meV. The exception was the V_{Si}^{+1} formation energy, which was converged to within 17 meV in the 999-atom supercell using the LDA and 10 meV in the 999-atom supercell using the GGA.

In a further effort to verify the Socorro results, VASP was used to compute the formation energies of relaxed V_{Si}^{0}, V_{Si}^{+1}, and V_{Si}^{+2} in 215- and 511-atom supercells using the LDA and $n_{\mathrm{MP}}=2$. VASP results in the 215-atom supercell differed from the corresponding Socorro results by: −10 meV for V_{Si}^{0},

TABLE II. Information about the relaxed LDA V_{Si}^{q} structures in 215-, 511-, and 999-atom supercells. Columns labeled "pg" give the point groups in Schoenflies notation. Columns labeled "fd" give the fractional distances (relative to the equilibrium bulk distance, 3.807 Å) between the four atoms surrounding the vacancy and their multiplicities in parentheses.

	V_{Si}^{+2}		V_{Si}^{+1}		V_{Si}^{0}		V_{Si}^{-1}		V_{Si}^{-2}	
Supercell	pg	fd	pg	fd	pg	fd	pg	fd	pg	fd
215-atom	T_d	0.95 (6)	D_{2d}	0.90 (4) 0.79 (2)	D_{2d}	0.89 (4) 0.76 (2)	D_{3d}	0.92 (3) 0.69 (3)	D_{3d}	0.91 (3) 0.68 (3)
511-atom	T_d	0.93 (6)	D_{2d}	0.89 (4) 0.76 (2)	D_{2d}	0.89 (4) 0.75 (2)	D_{3d}	0.92 (3) 0.69 (3)	D_{3d}	0.91 (3) 0.68 (3)
999-atom	T_d	0.91 (6)	D_{2d}	0.89 (4) 0.76 (2)	D_{2d}	0.89 (4) 0.75 (2)	D_{3d}	0.91 (3) 0.69 (3)	D_{3d}	0.91 (3) 0.68 (3)

−11 meV for V_{Si}^{+1}, and +1 meV for V_{Si}^{+2}. VASP results in the 511-atom supercell showed similar differences: −9 meV for V_{Si}^{0}, −8 meV for V_{Si}^{+1}, and +2 meV for V_{Si}^{+2}. We consider this to be excellent agreement in view of the different pseudopotentials used by the two codes. As additional verification, we note that our V_{Si}^{0} formation energy in a 215-atom supercell using the LDA and $n_{MP}=1$ (3.27 eV) is the same as the value obtained by Puska *et al.* also using a plane wave basis.[25] However, using $n_{MP}=2$ we obtained a formation energy 0.21 eV higher than their corresponding value (3.31 eV).

III. RESULTS

Structural information about the relaxed LDA and GGA configurations is given in Tables II and III. The point groups of the GGA structures were T_d for V_{Si}^{+2}, D_{2d} for V_{Si}^{+1} and V_{Si}^{0}, C_{2v} for V_{Si}^{-1}, and D_{3d} for V_{Si}^{-2}. In the T_d, C_{2v}, and D_{2d} structures, the four atoms surrounding the vacancy remained relatively near their bulk sites. In the D_{3d} structure (often referred to as a split vacancy) one of these atoms shifted halfway toward the vacancy site, thereby placing it equidistant from six atoms. The LDA point groups were the same as the GGA point groups except for that of V_{Si}^{-1} which had D_{3d} symmetry. We note that additional calculations were performed for structures having different point groups than those noted above. For $q=-2$ and -1, the D_{2d} structure was considered in addition to C_1, C_{2v}, and D_{3d}. For $q=0$ and $+1$, D_{3d} and T_d structures were considered in addition to C_1 and D_{2d}. For $q=+2$, the D_{2d} structure was considered in addition to C_1 and T_d. In each case, the structure found when starting with C_1 symmetry had the lowest energy. It should be noted, however, that the LDA and GGA formation energies of the V_{Si}^{-1}, C_{2v}, and D_{3d} structures were similar. Their extrapolated GGA formation energies differed by 14 meV and their extrapolated LDA values differed by the same amount.

Experimental information about the V_{Si}^{+1} and V_{Si}^{-1} structures has been gleaned from electron paramagnetic resonance (EPR) data taken under illumination.[24] These studies found D_{2d} symmetry for V_{Si}^{+1} and C_{2v} symmetry for V_{Si}^{-1}. Both the LDA and GGA yielded D_{2d} symmetry for V_{Si}^{+1}. The GGA yielded C_{2v} symmetry for V_{Si}^{-1}, but as noted above the LDA found D_{3d} symmetry. There is no direct experimental information about the point groups of the other charge states. A simple model utilizing a linear combination of atomic orbitals on the four atoms surrounding a vacancy has yielded the point groups T_d, D_{2d}, D_{2d}, and C_{2v} respectively for V_{Si}^{+2}, V_{Si}^{+1}, V_{Si}^{0}, and V_{Si}^{-1}.[24] The GGA point groups agree with the model results and the LDA point groups agree except for V_{Si}^{-1}. Our

TABLE III. Information about the relaxed GGA V_{Si}^{q} structures in 215-, 511-, and 999-atom supercells. Columns labeled "pg" give the point groups in Schoenflies notation. Columns labeled "fd" give the fractional distances (relative to the equilibrium bulk distance, 3.867 Å) between the four atoms surrounding the vacancy and their multiplicities in parentheses.

	V_{Si}^{+2}		V_{Si}^{+1}		V_{Si}^{0}		V_{Si}^{-1}		V_{Si}^{-2}	
	pg	fd	pg	fd	pg	fd	pg	fd	pg	fd
215-atom supercell	T_d	1.00 (6)	D_{2d}	0.96 (4) 0.91 (2)	D_{2d}	0.92 (4) 0.79 (2)	C_{2v}	0.89 (4) 0.85 (1) 0.74 (1)	D_{3d}	0.92 (3) 0.69 (3)
511-atom supercell	T_d	0.98 (6)	D_{2d}	0.93 (4) 0.84 (2)	D_{2d}	0.91 (4) 0.78 (2)	C_{2v}	0.89 (4) 0.85 (1) 0.73 (1)	D_{3d}	0.92 (3) 0.69 (3)
999-atom supercell	T_d	0.97 (6)	D_{2d}	0.92 (4) 0.81 (2)	D_{2d}	0.91 (4) 0.78 (2)	C_{2v}	0.89 (4) 0.84 (1) 0.73 (1)	D_{3d}	0.92 (3) 0.69 (3)

TABLE IV. Formation energies of the relaxed LDA V_{Si}^{q} structures in 215-, 511-, and 999-atom supercells, and parameters obtained from maximum likelihood fits to these results. The rows labeled "215-, 511-, and 999-atom supercell" list the formation energies at $E_F=0$ with uncertainties taken to be ± the absolute difference in the formation energies from the two highest levels of Brillouin-zone sampling, with a limiting value of ±0.001 eV. The row labeled "fit" lists the two parameters obtained from maximum likelihood fits of the supercell data: $E^f[V_{Si}^q; L\rightarrow\infty, E_F=0]$ (in eV) and A_3 (in eV Å^3). To convert the A_3 values from eV Å^3 to eV Bohr^3, multiply by 6.748 333 037 Bohr^3/Å^3).

	V_{Si}^{+2}	V_{Si}^{+1}	V_{Si}^{0}	V_{Si}^{-1}	V_{Si}^{-2}
215-atom supercell	3.002±0.001	3.294±0.001	3.529±0.001	4.140±0.001	4.634±0.001
511-atom supercell	2.924±0.001	3.219±0.001	3.486±0.001	4.202±0.001	4.729±0.001
999-atom supercell	2.921±0.001	3.190±0.017	3.473±0.001	4.229±0.002	4.792±0.002
fit: E^f	3.090±0.001	3.220±0.002	3.457±0.001	4.302±0.002	5.023±0.002
A_3	1280±7	726±10	304±7	−271±9	11±9

LDA point groups are the same as those found by Puska *et al.*[25] in LDA calculations using a plane wave basis, a 215-atom supercell, and $n_{MP}=1$. Our LDA point groups for V_{Si}^{+2}, V_{Si}^{+1}, V_{Si}^{0} are the same as those obtained by Lento and Nieminen (Ref. 28) in recent LDA calculations using a plane wave basis, a 255-atom (body-centered cubic) supercell, and the (1/4, 1/4, 1/4) point to sample the Brillouin zone. However, they found D_2 symmetry for V_{Si}^{-1} and D_{2d} symmetry for V_{Si}^{-2} whereas we found D_{3d} for both of these charge states. Our V_{Si}^{0} point group is the same as that found by Zywietz *et al.*[26] in LDA calculations using a plane wave basis, a 215-atom supercell, and $n_{MP}=4$; and by Probert and Payne (Ref. 27) in GGA calculations using a plane wave basis, a 255-atom supercell, and $n_{MP}=2$.

Fractional distances between the four atoms surrounding the vacancy are listed in Tables II and III. The LDA values are smaller than the GGA values with the differences being greatest in the +2 and +1 charge states. This suggests that the binding among these four atoms is stronger when using the LDA. We also note that the fractional distances are converged to within 0.01 in the 215-atom supercell for all charge states except +2 and +1 in the GGA results. The LDA fractional distances from the 215-atom supercell are within 0.01 of the values obtained by Puska *et al.*[25] using the same supercell and $n_{MP}=1$, except for the +2 charge state where their value is 0.04 lower than ours. This disparity is likely due to the different Brillouin zone sampling utilized in the two calculations. Using $n_{MP}=1$ instead of $n_{MP}=5$ in the 215-atom supercell, we found a fractional distance within 0.01 of the value obtained by Puska *et al.*[25] We note that the fractional distances found in our study are all <1 indicating an inward breathing mode relaxation. In contrast, Lento and Nieminen (Ref. 28) found outward breathing mode relaxations for all V_{Si} charge states in recent screened exchange, LDA calculations in a 31-atom (body-centered cubic) supercell. They obtained qualitatively similar results in a 255-atom supercell, although they were unable to fully relax the V_{Si} structures because of the increased computational costs of the screened-exchange calculations which employ a nonlocal formulation of exchange.

The formation energies from each supercell and for each charge state are listed in Tables IV (LDA) and V (GGA). We note that quantative comparisons with earlier DFT results for $q\neq 0$ are complicated by our use of a different definition for Δ_{VBE}. Because of this, we make comparisons only for the neutral charge state. Moreover, we restrict our comparisons to earlier results that were obtained in supercells containing at least 215 atoms. Our LDA V_{Si}^{0} formation energy from the 215-atom supercell is 0.026 eV higher than the 3.503 eV obtained by Zywietz *et al.*[26] in the same supercell using a plane wave basis and $n_{MP}=4$. Puska *et al.*[25] performed LDA calculations in a 215-atom supercell with a plane wave basis and obtained V_{Si}^{0} formation energies of 3.27 eV using $n_{MP}=1$ and 3.31 eV using $n_{MP}=2$. We also found 3.27 eV using $n_{MP}=1$, but with $n_{MP}=2$ we obtained a formation energy 0.21 eV higher than their value. At this time, we do not understand the origin of this difference. More recently, Schultz obtained a V_{Si}^{0} formation energy of 3.58 eV in a 249-atom (face-centered cubic) supercell using the LDA, a Gaussian basis, and $n_{MP}=2$.[7] Using the same supercell and sampling, we found a formation energy only 0.040 eV lower. Lento and Nieminen (Ref. 28) found a V_{Si}^{0} formation energy of 3.6 eV in a 255-atom supercell using the LDA, a plane wave basis and the (1/4, 1/4, 1/4) point to sample the Brillouin zone. Using the same supercell and $n_{MP}=2$ with the Monkhorst-Pack grid shifted to place a sampling point at the Brillouin zone origin, we obtained an LDA V_{Si}^{0} formation energy 0.1 eV smaller than their value. Probert and Payne (Ref. 27) found a formation energy of 3.17 eV for V_{Si}^{0} in plane wave calculations using a 255-atom supercell, $n_{MP}=2$, and the PW91 form[29] of the GGA. We found a substantially higher value (3.65 eV) using the same supercell, exchange-correlation functional, and n_{MP} value. After several test calculations, we concluded that the disparity is mainly due to the different lattice constants used to generate the supercells and the different cutoff energies used to define the plane wave basis sets. When we used the same lattice constant (5.429 Å) and energy cutoff (12 Ryd=163 eV) as they did we obtained a formation energy (3.22 eV) within 0.050 eV of their value.

TABLE V. Formation energies of the relaxed GGA V_{Si}^q structures in 215-, 511-, and 999-atom supercells, and parameters obtained from maximum likelihood fits to these results. The rows labeled "215-, 511-, and 999-atom supercell" list the formation energies at $E_F=0$ with uncertainties taken to be ± the absolute difference in the formation energies from the two highest levels of Brillouin-zone sampling, with a limiting value of ±0.001 eV. The row labeled "fit" lists the two parameters obtained from maximum likelihood fits of the supercell data: $E^f[V_{Si}^q; L\to\infty, E_F=0]$ (in eV) and A_3 (in eV Å^3). To convert the A_3 values from eV Å^3 to eV Bohr^3, multiply by 6.748 333 037 Bohr^3/Å^3).

	V_{Si}^{+2}	V_{Si}^{+1}	V_{Si}^{0}	V_{Si}^{-1}	V_{Si}^{-2}
215-atom supercell	3.275±0.001	3.534±0.001	3.658±0.001	4.170±0.001	4.507±0.001
511-atom supercell	3.227±0.001	3.508±0.001	3.627±0.001	4.226±0.001	4.607±0.001
999-atom supercell	3.233±0.001	3.498±0.010	3.617±0.001	4.248±0.001	4.672±0.001
fit: E^f	3.415±0.001	3.545±0.002	3.605±0.001	4.319±0.001	4.909±0.001
A_3	1130±8	388±11	232±8	−222±8	−32±8

Rows labeled "fit" in Tables IV and V list the parameters $E^f[V_{Si}^q; L\to\infty, E_F=0]$ and A_3 obtained from the maximum likelihood fits of the supercell formation energies to Eq. (2). Two points are worth noting: (1) The A_3 coefficients are consequential for all charge states except −2. For example, the values of A_3/L^3 in the LDA fit for the neutral charge state are 72, 30, and 16 meV at L values corresponding to the 215-, 511-, and 999-atom supercells. (2) For all charge states except 0 and +1, $E^f[V_{Si}^q; L\to\infty, E_F=0]$ differs substantially (of order 0.1 eV) from the formation energies computed in the 999-atom supercells. This indicates that the spurious interactions among the periodically repeated vacancies are consequential even in 999-atom supercells. This conclusion is consistent with the one reached by Castleton *et al.*[3] in their studies of defects in InP. In addition, we note that the fits of the supercell data (Fig. 1) appear to be good, suggesting that the Makov-Payne formula [Eq. (2)] provides a good representation of the DFT results. The formation energy of V_{Si}^0 has been found to be 3.6±0.2 eV in experimental studies.[30] Our extrapolated LDA and GGA V_{Si}^0 formation energies (3.457 and 3.605 eV) agree with the experimental result to within its uncertainty.

Transition energies derived from the $E^f[V_{Si}^q; L\to\infty, E_F=0]$ are listed in Table VI. In presenting these results, we reiterate that Δ_{VBE} in Eq. (1) was chosen to produce agreement with the measured $E^{1+/2+}$ level (0.13 eV). The GGA result for $E^{0/1+}$ (0.060 eV) is within 0.010 eV of the measured value (0.05 eV) and thus reproduces the observed negative-U behavior of the donor states.[24] The LDA result for $E^{0/1+}$ (0.237 eV) is 0.19 eV higher than the measured value and does not yield the observed negative-U behavior. There are currently no measurments of the $E^{1-/0}$ level, and the only available information on the $E^{2-/1-}$ level is that it lies at least 0.17 eV below the CBE.[24] The LDA and GGA $E^{2-/1-}$ levels both fall within this range, with the LDA level being 0.45 eV below the (measured) CBE and the GGA level being 0.58 eV below the CBE. In addition, we note that both the LDA and GGA results yield negative-U behavior for the acceptor states, meaning that the $E^{2-/1-}$ level falls below the $E^{1-/0}$ level. Negative-U behavior for the acceptor states was

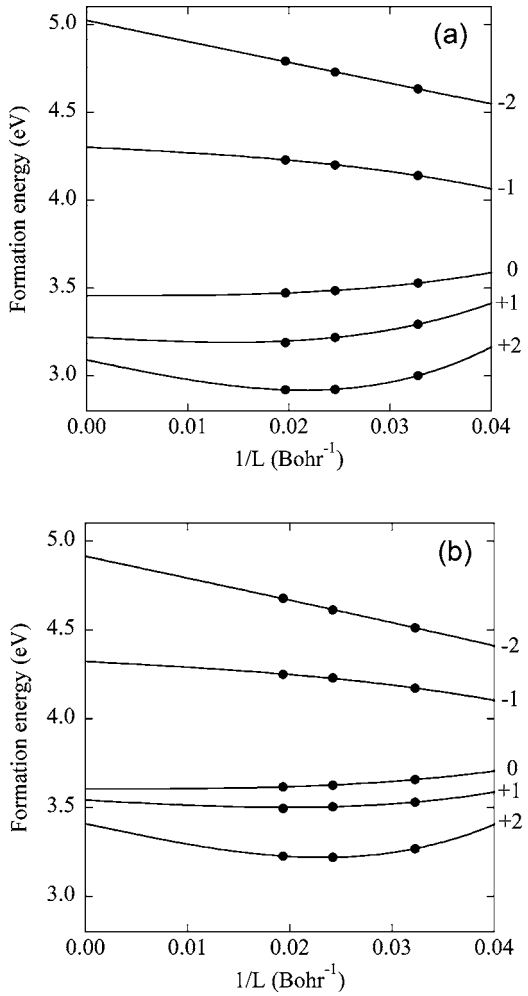

FIG. 1. Plots of V_{Si}^q formation energies (eV) versus $1/L$ (1/Bohr) and fits to Eq. (2). Filled circles indicate the formation energies computed in 215-, 511-, and 999-atom supercells. Lines show the fits of the supercell data to Eq. (2). The charge states, q, are given along the right side of the plot. (a) Results obtained using the LDA. (b) Results obtained using the GGA.

TABLE VI. Transition energies (in eV relative to the VBE) computed from the extrapolated LDA and GGA formation energies list in Tables IV and V. Note that the value of Δ_{VBE} in Eq. (1) was chosen to produce agreement with the experimental $E^{2+/1+}$ value.

	$E^{2+/1+}$	$E^{1+/0}$	$E^{0/1-}$	$E^{1-/2-}$
LDA	0.130	0.237	0.845	0.721
GGA	0.130	0.060	0.714	0.590
Experiment	0.13	0.05		<1.0

also obtained by Puska *et al.*[25] in LDA plane wave calculations using a 215-atom supercell and $n_{MP}=1$, but not by Schultz (Ref. 7) in his recent LDA calculations using a Gaussian basis, a 249-atom supercell, and $n_{MP}=2$. Puska *et al.*[25] also obtained negative-U behavior for the donor states, however this disagrees with our LDA results and the LDA results of Schultz.[7]

We note that although the Makov-Payne formula models electrostatic interactions among periodically repeated defects, it does not model strain interactions having a $1/L$ dependence because the coefficient of this term is fixed in Eq. (2). Castleton and Mirbt (Ref. 31) noted the possibility of such strain interactions in their calculations for defects in InP using nominal 8-, 64-, 216-, and 512-atom supercells. One way to determine if these interactions are consequential in Si is to fit to an unrestricted version of Eq. (2) including results from either a smaller (63-atom) or a larger (1727-atom) supercell. We attempted calculations for a 63-atom supercell, but found the results to be unreliable. For example, relaxation of V_{Si}^0 in a 63-atom supercell yielded T_d symmetry instead of the D_{2d} symmetry found in the 215-, 512-, and 999-atom supercells. Calculations in a 1727-atom supercell were not feasible given presently available computing resources.

To estimate the magnitude of possible $1/L$ strain interactions, we computed LDA formation energies for V_{Si}^0 in face-centered cubic supercells containing 249, 431, 685, and 1023 (face-centered cubic) atoms using $n_{MP}=4$ for the 249-, 431-, and 685-atom supercells and $n_{MP}=3$ for the 1023-atom supercell. The results were fit both to Eq. (2) and to an unrestricted version of Eq. (2)

$$E^f[V_{Si}^0;L,n_{MP}] = E^f[V_{Si}^0;L\rightarrow\infty] + \frac{B_1}{L} + \frac{B_3}{L^3}, \qquad (4)$$

with L defined to be the cube root of the supercell volume (16.960, 20.352, 23.744, and 27.136 Å=32.050, 38.460, 44.870, and 51.280 Bohr in the 249-, 431, 685, and 1023-atom supercells). We note, first of all, that the values of $E^f[V_{Si}^0;L\rightarrow\infty]$ from the fits to Eqs. (2) and (4) (3.456 and 3.459 eV) were nearly identical to the 3.457 eV obtained from the fit of the simple cubic supercell results to Eq. (2). The value of A_3 obtained from the fit to Eq. (2) was 396 eV Å^3, whereas the values of B_1 and B_3 from the fit to Eq. (4) were −0.085 eV Å and 407 eV Å^3. In the range of $1/L$ values noted above, the magnitude of B_3/L^3 is thus at least 6.5× the magnitude of B_1/L. This suggests that the $1/L$ dependence in the strain interactions is not significant for the range of supercell sizes treated in this study. We note that this conclusion is provisional pending further study. In particular, calculations with a 1727-atom supercell for all of the V_{Si} charge states, and unrestricted fits of those results and the present ones to Eq. (4) would be worthwhile to further refine the extrapolated formation energies reported herein.

IV. SUMMARY

The atomic configurations, formation energies, and transition energies of V_{Si} were obtained from DFT calculations using norm-conserving pseudopotentials, a plane wave basis, and the LDA and GGA for exchange and correlation. Calculations were performed in simple cubic supercells containing 215, 511, and 999 atoms, and formation energies from these supercells were extrapolated to an infinite sized supercell to remove spurious electrostatic interactions arising from the use of periodic boundary conditions. The GGA reproduces the observed symmetry (C_{2v}) of V_{Si}^{-1}, whereas the LDA does not. In addition, the GGA correctly yields negative-U behavior for the V_{Si} donor states, whereas the LDA does not. Overall, the GGA appears to give results in better agreement with available experimental results for V_{Si}. With regard to technical issues, the results from this study suggest that the spurious electrostatic interactions between V_{Si}^q and its periodic replicas are consequential even in 999-atom supercells. Finally, we reiterate that the results obtained in this study are for zero temperature. A recent study by Al-Mushadani and Needs (Ref. 32) has examined the finite temperature contributions to the free energy of V_{Si}^0 using the LDA in a 63-atom supercell. Their calculations suggest that these contributions become consequential when utilizing theoretical results to predict equilibrium vacancy contributions.

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