

Identification of Chalcogen Point-Defect Sites in Silicon by Total-Energy Calculations

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We report parameter-free, self-consistent, electronic-structure and total-energy calculations for chalcogen point defects in crystalline silicon. Both possible defect sites of tetrahedral symmetry are investigated. The calculated total energies are discussed in terms of dissolution and reaction energies. From these, the stable defect position is identified as substitutional. The comparison of our theoretical results (spin and ground-state wave function) with experimental data such as infrared-absorption, EPR, and ENDOR spectra further supports this identification.

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Impurities in semiconductors generally exist in several different configurations, such as interstitials, substitutional sites, and complexes.¹ Their stabilities and relative concentrations are primarily determined by the different dissolution energies. So far, little is known about these energies for different impurities and even for a particular impurity on different sites. Therefore, previous identifications of the geometrical configurations of defects were based on a comparison of theoretical electronic-structure calculations with experimentally observed quantities, such as defect wave-function symmetries (e.g., Ludwig,² and Meyer, Spaeth, and Scheffler³). In this paper we show that *total-energy* calculations can be used to determine the impurity site.

The stable configuration of chalcogen point-defect impurities in silicon has for a long time been unclear. Extensive experimental investigations have been performed on these centers,⁴⁻¹⁴ partly out of technological interest (e.g., infrared detectors and solar cells).^{4,10} Much experimental work was devoted to infrared absorption studies (see Refs. 4, 5, and references therein) which allow the determination of the energetic positions and symmetries of the ground state and various (effective-mass-like) excited states. The spectra could be interpreted in a one-electron picture. From an analysis of dipole selection rules, the symmetry of the deep-level wave function was determined to belong to the A_1 representation of the T_d point group. This result was confirmed by electron paramagnetic resonance (EPR) and electron-nuclear double-resonance (ENDOR) experiments.^{2,6,9} Furthermore, deep-level energies were determined by deep-level

transient spectroscopy^{7,8} and Hall-effect measurements.^{11,12} Despite this extensive experimental work it has not been possible to identify whether isolated chalcogen impurities in Si occupy substitutional or T_d interstitial sites. Many authors suggested that S, Se, and Te atoms are incorporated substitutionally,^{2,4,9} but the possibility of the interstitial site was also mentioned frequently.^{2,4,6,14} Recently, Niklas and Spaeth⁶ performed detailed ENDOR experiments on Si:Te and Si:Se. Their analysis of the spin densities at many shells of Si neighbors led them to suggest that the interstitial position appears to be the more likely site. In this paper we report self-consistent total-energy calculations for S, Se, and Te impurities in silicon. We show that total-energy calculations can clearly distinguish between the above-mentioned alternative sites. The theoretical results identify the stable site of S, Se, and Te point defects in silicon as substitutional.

Green's-function methods have been shown to be powerful for electron-structure calculations of localized defects.^{15,16} Recently these methods have been developed to a state which also allows one to evaluate the total energy of the many-electron system¹⁷⁻²⁰ and its gradient, i.e., the forces.²¹ Here we use the linear-muffin-tin-orbital (LMTO) Green's-function method in the atomic-spheres approximation.¹⁷ We use a variational expression (within the atomic-spheres approximation) for the total energy, which therefore converges faster than the eigenvalue spectrum. Further details will be discussed in a subsequent paper.²² The exchange-correlation energy is treated in the local-density approximation (LDA). It is well-known that as a result of this approximation and the neglect of the

discontinuity of the exchange-correlation functional derivative,^{23,24} the band gap in Si is about half of the experimental value. The results presented here were calculated with this too-small gap. In order to check the sensitivity of the results to the gap size we have performed the following tests: (1) The perfect-crystal Green's function was calculated from a band structure with the conduction band shifted rigidly to give the experimental gap, i.e., using the so-called "scissor" operator.²⁵ (2) The potential was modified so that the band-structure calculation gave a virtually unchanged valence band but the correct band gap. The three approaches—i.e., the pure LDA and methods (1) and (2)—gave different total energies which in the worst case differed by as much as 3.6 eV.²⁶ Thus, the uncertainty of total energies due to the band-gap problem can indeed be significant. This is a general problem of the LDA and not due to a Green's-function method. Since it is not clear which treatment of the problem is preferable we show in this paper only the pure (not modified) LDA results. We emphasize that the conclusions presented below are exactly the same for all three methods despite the above-mentioned uncertainty.

To discuss the stability of the two possible impurity configurations of T_d symmetry, we first calculated the total energies of the processes in which chalcogens diffuse from the gas phase into a Si crystal and occupy a substitutional (sub) or T_d -interstitial (int) site. In both cases the initial state is an isolated chalcogen atom and a perfect Si crystal. The final state for the reaction "sub" is a Si crystal where a chalcogen atom replaces a Si atom, which has been moved to the surface. The differences between the calculated total energies of the final and initial states (dissolution energies) are given in Table I. In this paper we assume that the Si crystal is undoped. A discussion of the dissolution- and reaction-energy dependences on the Fermi-level position is given elsewhere. The energies in Table I refer to the neutral situation. For the substitutional centers these energies are obtained by calculation of the double-positive charge state and addition of two electrons to the conduction band. As men-

tioned above, we use the pure LDA results, i.e., a theoretical band gap of 0.5 eV. The results in Table I show that the substitutional incorporation is exothermic for all chalcogens, and that this process is energetically clearly favored compared to the interstitial incorporation. Further evidence for the stability of the substitutional lattice site comes from considering the process where a substitutional chalcogen and a Si T_d self-interstitial change places. This process is called the interstitial-interchange reaction (labeled iic in Table I). The results show that at nonzero temperature the relative occupancy of interstitial and substitutional sites depends sensitively on the atomic number. The stability of the substitutional site relative to the interstitial site increases from S to Se to Te. From the last line of Table I it follows that at nonzero temperature a certain amount of S atoms may exist as interstitials if Si self-interstitials are present. The accuracy of the calculation, in particular the uncertainty due to the band-gap problem, does not allow us to decide if the iic process for S is really slightly endothermic, or if it is slightly exothermic. Either way, the theoretical results suggest that the diffusion of sulfur is partly determined by an interstitial component, whereas this is significantly less important for Se and Te. It is interesting to notice that interstitials (as for example Au or Fe) usually diffuse extremely rapidly. Therefore, in analogy to arguments given by Janzen *et al.*,¹⁴ our results, that a certain fraction of interstitials is possible for S, can be interpreted to mean that S diffuses faster than Se and Te. This interpretation is consistent with measurements which show that the diffusion coefficient decreases significantly from S to Te, i.e., from $\sim 10^{-8}$ cm²/s for S, to $\sim 10^{-9}$ cm²/s for Se to $\sim 5 \times 10^{-12}$ cm²/s for Te (see Ref. 14, Fig. 3, at 1200 °C and references therein, or Table 1 in Ref. 4).

In the total-energy calculations in Table I the distortions of the Si lattice were not taken into account. This effect was calculated independently by the self-consistent pseudopotential method.²¹ We find that lattice relaxation would lower the energies by less than 0.3 eV for the substitutional defects (see for example Fig. 5 in Ref. 20). For the T_d interstitials the effect of lattice distortions is estimated to lower the total energy by less than 0.8 eV. As a consequence, the effect of lattice distortions is not important for the above arguments.

Additional support for the identification of the substitutional site is obtained by comparison of the theoretical electronic-structure results with available experimental data. In Fig. 1 we show the defect-induced changes in the density of states due to an interstitial and a substitutional Se impurity atom in Si. For reasons of clarity only states of A_1 (s -like at the impurity) and T_2 (p -like at the impurity) symmetries are displayed. As might be expected from the elec-

TABLE I. Calculated total energies in electronvolts (Ref. 27) for various processes of neutral chalcogens in silicon (see text).

	S ⁰	Se ⁰	Te ⁰
E^{sub}	-3.8	-3.2	-1.9
E^{int}	-0.1	+3.2	+9.1
E^{iic}	+0.3	+3.0	+7.6

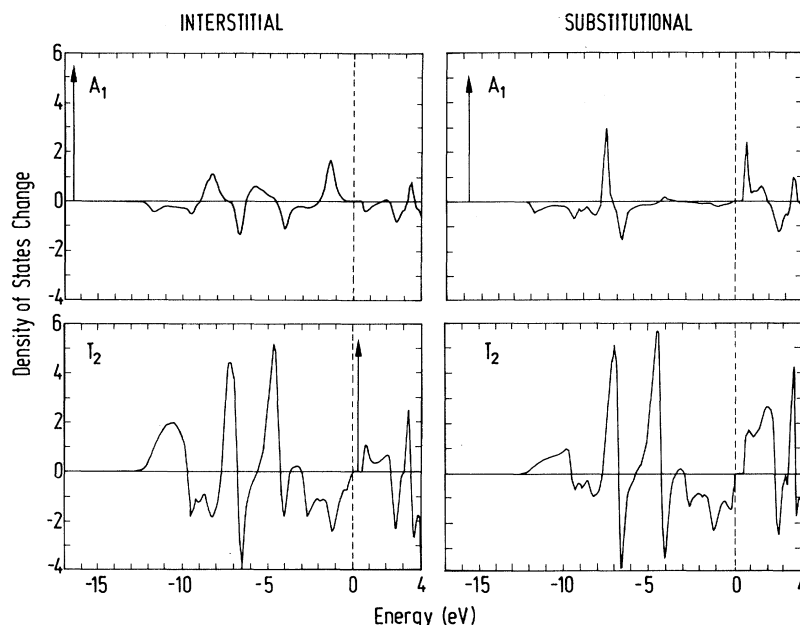


FIG. 1. The changes in the density of states of A_1 and T_2 symmetries induced by an interstitial (left) and a substitutional (right) Se atom in silicon. The energy zero is the top of the valence band.

tronic structure of the considered impurities (no d electrons), the effects on states of other symmetries are less important. Qualitatively similar results are obtained for S and Te. The general effect visible in Fig. 1 is that states are shifted to lower energies. For the interstitial this arises because the potentials of these defects are attractive compared to the slightly repulsive potential in the interstitial region of the defect-free Si crystal. All undistorted T_d interstitial chalcogens have a T_2 one-electron state in the gap, which in the neutral charge state is filled with four electrons. The site symmetry of paramagnetic chalcogen point defects was determined by infrared absorption experiments,^{4,5,9} EPR,⁹ and ENDOR^{2,6} as T_d and the spin of the paramagnetic state was found^{2,6,9} to be $\frac{1}{2}$. These experimental results are not consistent with the theoretical results for interstitial chalcogens: Here all many-electron states with spin $\frac{1}{2}$ are orbital degenerate and therefore unstable with respect to a symmetry-lowering Jahn-Teller distortion. Thus, the site symmetry of these interstitials must be lower than T_d . Furthermore, infrared absorption as well as EPR and ENDOR show that the deep-level wave function has no node at the chalcogen site, thus transforming according to the A_1 representation. Again, this experimental result is in contradiction to the theoretical results for interstitial centers (see Fig. 1). It therefore can be ruled out that the experimental data arise from interstitial chalcogens.

For substitutional chalcogens we find again that

states are shifted to lower energies (see Fig. 1). This can be explained by the higher electronegativity of chalcogens compared to that of a Si atom which is replaced. The unmodified LDA calculations do not give a level in the band gap, but there is a sharp A_1 resonance at the bottom of the conduction band. Since sulfur has two valence electrons more than Si, we are only able to calculate the double-positive charge state and to put two electrons into the conduction band. If we correct for the band-gap problem (see above), the A_1 resonance becomes a bound state in the gap, in agreement with earlier pseudopotential Green's-function calculations^{28,29} and with the experimental results.^{2,4-6,9}

In conclusion, we have shown that the calculation of dissolution and reaction energies allows one to identify the stable configuration of defects in semiconductors. For isolated S, Se, and Te impurities in Si the theoretical results imply that the stable position of these atoms is the substitutional site. This identification is supported by a comparison of the calculated electronic structure with EPR, ENDOR, and infrared-absorption data. Whereas for Te the substitutional site has significantly lower energy than the interstitial site, our results indicate that for S a certain amount of interstitials is possible if Si self-interstitials are present.

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- ²⁷The results of Table I for E^{sub} differ from those given in Ref. 20 because of a different treatment of the band-gap problem (see also Ref. 22).
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