

Mechanisms of Defect Pairing in Semiconductors: A Study for Chalcogens in Silicon

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Electronic-structure and total-energy calculations are reported for the vacancy and the substitutional and interstitial S, Se, and Te impurities in Si. We identify several mechanisms of impurity-impurity interactions. This theoretical study also serves to determine the dominant defect site of chalcogen pairs as two substitutionals.

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Experimentally it is well known that for impurities or intrinsic defects in semiconductors the formation of complexes *can* be favored compared to single-atom defects.¹ For example, for sulfur in Si defect pairs may be clearly dominant.²⁻⁸ Nevertheless, the theoretical understanding of defect-complex formation of localized (so-called deep) impurities in semiconductors is quite shallow. As far as we know, a detailed theoretical study of impurity-impurity or impurity-intrinsic-defect interactions has not been performed so far. Below we report parameter-free total-energy calculations within the density-functional theory. The electronic charge density of the macroscopic Si crystal with single-atom defects as well as

with defect pairs is calculated by means of the self-consistent linear muffin-tin orbital Green's-function method.^{9,10} We use the local-density approximation for the exchange-correlation functional and the atomic-spheres approximation for the effective potential.⁹ The range of the defect-induced change in the potential is restricted to a volume of sixteen atomic spheres, i.e., 160 Å³, but no restriction is placed on the extent of wave functions. Lattice distortions are neglected.¹¹

We consider three different pair geometries: Both constituents occupying substitutional sites (sub-sub), both occupying interstitial sites (int-int), and the mixed substitutional-interstitial (sub-int) geometry. In all

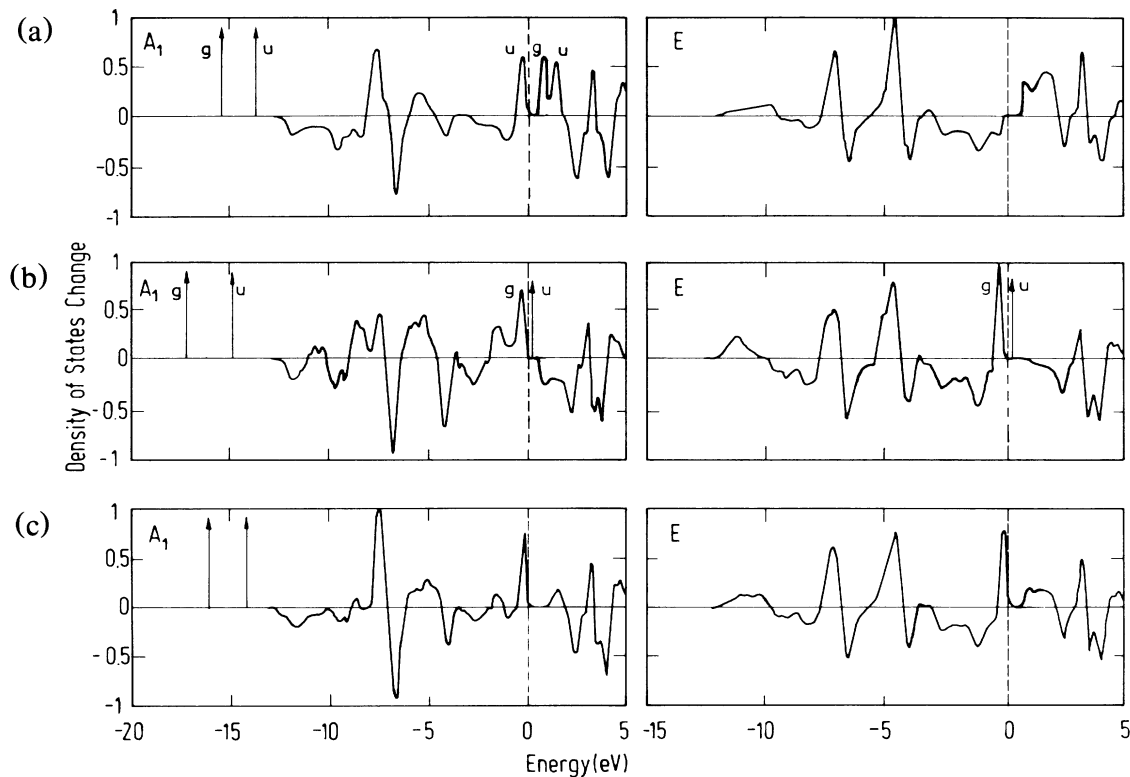


FIG. 1. The changes in the density of states of A_1 and E symmetries (designation according to the C_{3v} point group) induced by nearest-neighbor sulfur pairs for (a) sub-sub, (b) int-int, and (c) sub-int geometries. Even and odd states in rows (a) and (b) are denoted by g and u (Ref. 12).

three cases the principal axis of the complex is the threefold-symmetric (111) axis and the symmetry is C_{3v} . If the two constituents are identical, the sub-sub and int-int geometries have, in addition, an inversion center yielding D_{3d} symmetry. Because the stable site of isolated chalcogens is substitutional¹⁰ we will discuss chemical reactions starting from isolated substitutional chalcogens. We note that the actual reaction may pass through various configurations, but for reaction energies only the total energies of the initial and the final configurations enter.

In Fig. 1 we show as a prototype example the calculated results for the electronic structures of the three considered sulfur pairs in Si. This figure displays the results for the a_1 and e states of the C_{3v} point group. For sub-sub and int-int pairs, which consist of identical species, the states can be labeled with respect to their behavior upon inversion at the center of the molecule as even (*gerade*) and odd (*ungerade*).¹² Figure 1 shows that in the region of the band gap the electronic structures of the three types of pairs differ significantly. An analysis of these results yields that the impurity-impurity interactions in these three examples can be described as follows.

Both atoms substitutional.—The results of Fig. 1(a) are summarized (and simplified) in the energy-level diagram of Fig. 2. Whereas a distant sub-sub pair can be understood in terms of the bonding and antibonding states which are derived from isolated-impurity deep-level wave functions, this concept is not appropriate for nearest-neighbor sub-sub pairs. Here the electronic structure can be described in terms of a sulfur molecule which is placed into a divacancy.¹⁴ The divacancy dangling orbitals couple to the σ and π states of the diatomic

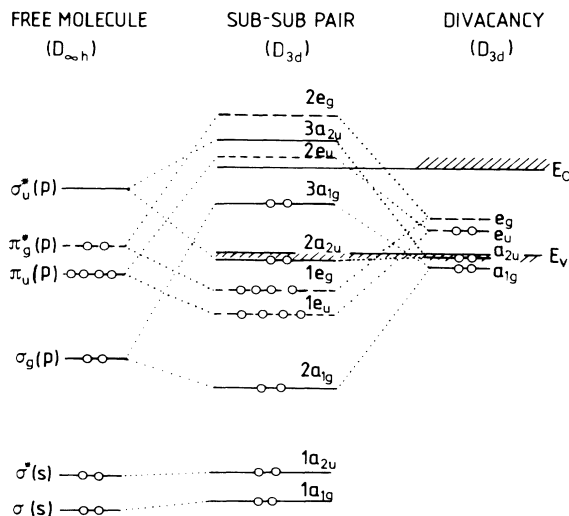


FIG. 2. Schematic summary (Ref. 13) of Fig. 1(a). It explains the interaction of a free chalcogen molecule with the dangling bonds of the divacancy (Ref. 14). The marked occupancies correspond to the neutral centers.

molecule. Filling these levels with the number of electrons available for a neutral center shows that the highest occupied level is $3a_{1g}$,¹⁵ which corresponds to the peak at 0.6 eV above the valence band in Fig. 1(a). Our calculations reveal that all nearest-neighbor sub-sub chalcogen pairs have the level ordering of Fig. 2. The reaction energy of the process where two distant S_{Si} impurities form a nearest-neighbor pair is shown in Fig. 3 as a function of the Fermi level.

For *n*-type material both the isolated impurities and the pair are neutral. Because the highest occupied impurity-induced level is completely filled, the interaction between distant isolated impurities is practically absent. The stability of the nearest-neighbor sulfur pair is due to the fact that the bonding sulfur pair σ_g -derived levels ($2a_{1g}, 3a_{1g}$) are filled, whereas the upper antibonding σ_u -derived ($3a_{2u}$) level is empty. Because of the interaction with the six divacancy dangling orbitals, which supply six electrons, the antibonding π_g -derived level ($1e_g$), which is filled with two electrons in the neutral free molecule, is filled with four electrons in the impurity pair. Because of this and because of the larger extent of the wave functions the interaction becomes very weak, compared to the gas phase. The Fermi level is not involved in the reaction and therefore the reaction energy is a constant.

If the Fermi level is around $E_v + 0.7$ eV the distant sulfur pair has a charge $2+$ and the nearest-neighbor pair has a charge $1+$. Because the difference between the charges of final and initial configurations is -1 the reaction energy changes as $-E_F$. Because two distant S_{Si}^+ centers repel each other, pair formation (as well as pair dissociation) is hindered by a barrier.

If the Fermi level is in the lower half of the gap the difference between the charges of final and initial systems is -2 and the reaction energy therefore changes as $-2E_F$. The reaction becomes endothermic at low Fermi, or if both systems (the isolated impurities and the nearest-neighbor pair) are doubly ionized.

These calculations suggest two possible ways to

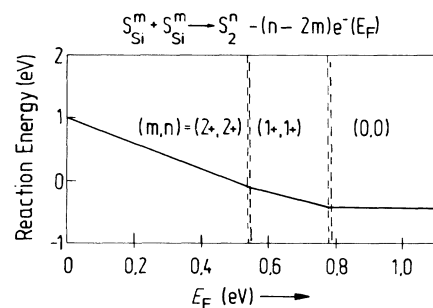


FIG. 3. Reaction energy for the formation of a nearest-neighbor impurity pair for sulfur in Si. Zero of E_F is the top of the valence band (Ref. 13). A negative reaction energy corresponds to an attractive interaction (exothermic process).

suppress the formation of pairs: (1) high temperature, so that the Fermi level is at mid gap, or (2) *p*-type material. In thermal equilibrium relative concentrations of different impurity configurations (isolated substitutionals, isolated interstitials, pairs, etc.) are determined by the law of mass action.¹ In reality thermal equilibrium is often not reached and the concentration of defects at low temperature may correspond to the equilibrium concentration at higher temperatures. Comparing the reaction energies for S, Se, and Te pairs, we find that in *n*-type material the reaction is still slightly exothermal for Se (-0.1 eV), but for Te it is strongly endothermal (4.0 eV). The neglect of lattice distortions¹¹ will be particularly important for Te pairs, but we believe that it cannot overcome a value of 4 eV. Thus, nearest-neighbor sub-sub pairs are possible for S and Se, but they should not form for Te. However, nearest-neighbor Te-S pairs cannot be ruled out to be stable from our calculations.

Both atoms at interstitial sites.—Isolated chalcogens at T_d interstitial positions have a t_2 level (chalcogen *p*-like) in the band gap.¹⁰ For the neutral centers this level is filled with four electrons. Therefore the interaction between two neutral interstitials is qualitatively similar to that of two chalcogen atoms in the gas phase [see Fig. 4(a)]. However, as noted above, the relevant process is the one where two isolated *substitutional* chalcogens go onto interstitial sites and form an impurity pair, and the remaining vacancies are filled by Si atoms from the surface. There is a small energy gain due to the pairing but the energy cost to bring two chalcogens from the substitutional to the interstitial position is larger by several electronvolts. Therefore, the energy of a crystal with two substitutional chalcogens is lower than that of a crystal with a nearest-neighbor interstitial pair. As a conse-

quence, chalcogen pairs where both atoms occupy interstitial sites should not exist in significant concentration.

One atom substitutional and one atom interstitial.—The electronic structure of these systems is summarized in Fig. 4(b). It results from the interaction between the a_1 level of the substitutional and the t_2 level of the interstitial.¹⁰ Because the interstitial t_2 level is below the substitutional a_1 level two electrons are transferred from the more substitutional-type to the more interstitial-type wave function. Thus, a chalcogen interstitial, which is usually believed to act as a donor, can also act as an acceptor and take two additional electrons. As a consequence, the binding of this system has some ionic character. However, a simple treatment in terms of purely Coulomb interactions, screened by a static dielectric constant, is not appropriate and overestimates the binding energy by about a factor of 2.¹⁶ The energy gain due to pairing is smaller than the cost to bring a chalcogen atom from its normal substitutional site to the interstitial position. Only for sulfur atoms and in *n*-type material are these two energies of similar size and we cannot exclude from the calculations that sub-int pairs may exist in low concentrations.

Chalcogen-vacancy pairs.—The electronic structure of these centers can be understood analogously to the discussion of sub-sub pairs: The divacancy dangling orbitals interact with the $3p$ orbitals of an *isolated* S atom. Total-energy calculations for the S-vacancy pair show that in intrinsic material these pairs will form under exothermal reaction of 2 eV. Nevertheless, the concentration of these centers will usually be low, because of the higher vacancy-formation energy.

In conclusion, if we compare the mechanisms which yield complex formation in semiconductors to those giving rise to molecule formation in normal chemistry we find that differences are mainly due to the following six reasons.

(i) Chemical reactions in solids do not require charge conservation, because the Fermi level can take or give electrons, if needed. Therefore it can depend on the position of the Fermi energy if complex formation is exothermal or endothermal.

(ii) The wave function of the highest occupied level for an isolated defect is usually *qualitatively* different (spatial distribution and degree of degeneracy) from that of the free atom. To give an example: The electronic structure of a neutral substitutional sulfur impurity in Si has a closed shell¹⁷ and therefore the interaction between distant centers may be better compared to argon than to sulfur atoms.

(iii) Impurities in semiconductors can generally exist at different sites (substitutional and interstitial). This can allow two atoms of the same kind to form a partly ionic bond.

(iv) The impurity-impurity equilibrium distance is largely influenced by the host crystal structure.

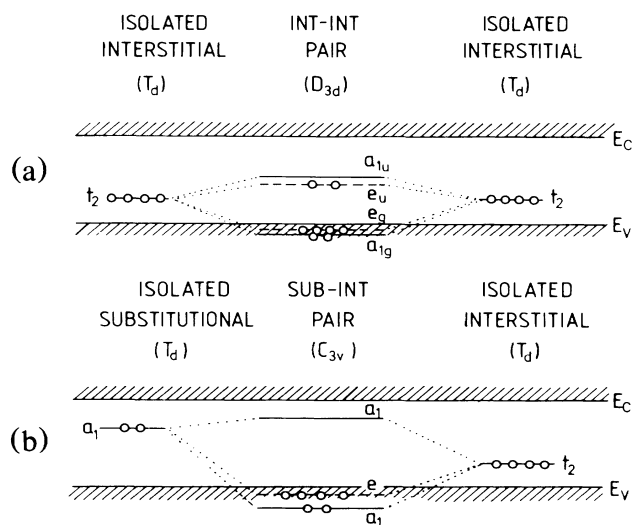


FIG. 4. Schematic summary of the calculations for the formation of (a) nearest-neighbor sub-int [compare Fig. 1(b)], and (b) nearest-neighbor int-int [compare Fig. 1(c)] pairs.

(v) Because of dielectric screening and the larger extent of wave functions the strengths of impurity-impurity ionic and covalent interactions are reduced compared to gas-phase ion-ion or atom-atom interactions. Furthermore, if a deep level shifts upon impurity-impurity interaction and approaches the conduction band (or the valence band) it simultaneously gets more delocalized because of increasing hybridization with the band states.

(vi) In addition to the electronic impurity-impurity interactions, also elastic interactions are possible, but these have not been discussed in this paper (see the work of Bourgoin and Lannoo¹⁸).

Concerning the experimental situation we note that sulfur and Se pairs have been convincingly identified by Ludwig³ and by Wörner and Schirmer⁸ by EPR. The dominant complexes have D_{3d} symmetry,^{2,3} which rules out the sub-int geometry as the stable one, but it did not allow distinction between sub-sub and int-int geometries.⁸ This missing identification step is provided by the above-described calculations which show that the sub-sub geometry should be clearly dominant. Pensl *et al.*⁷ recently determined an activation energy of 0.58 eV for the thermal dissociation of sulfur pairs. This result gives the reaction-energy *barrier* mentioned above but it has no direct relation to the reaction energy shown in Fig. 2. Wagner and Holm⁶ reported an infrared-absorption study which showed that the concentration of pairs depends on the speed of cooling of the sample from 1200°C down to room temperature. After slow cooling the ratio of sulfur pairs to isolated sulfur impurities was >100. For Se this ratio was 0.33 and for Te it was 0.07. If the Si crystal is cooled down rapidly, the ratios are 0.22, 0.04, and <0.01. These results find their explanation in the above-described calculations (see Fig. 3). With respect to Te pairs, however, there is a conflict with our theoretical results which suggest that Te-Te pairs should not form. We note, however, that the theoretical results for Te are not as reliable as those for S and Se, because of lattice distortions¹¹ and because we have not taken spin-orbit coupling into account. On the other hand, we note that also the experimental situation for the Te-Te pairs is not conclusive, because these pairs have not been identified by paramagnetic resonance. Thus the existence of Te-Te pairs is not yet established.

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¹¹For isolated substitutional S, Se, and Te impurities the lattice relaxation energies have been calculated to be between 0.1 and 0.8 eV [see M. Scheffler, in Proceedings of the Second International Conference on Shallow Impurity Centers, edited by A. Baldereschi (Elsevier, Amsterdam, to be published); C. M. Weinert and M. Scheffler, to be published]. For a defect pair we assume here (as a first approximation) that the lattice relaxation energy equals the sum of that of the isolated constituents. In particular for Te pairs this is likely an underestimate because of the strong short-distance repulsion between two Te atoms if forced at a 2.35-Å distance.

¹²If the designation in Figs. 1(a) and 1(b) were made according to the D_{3d} point group, the a_1 states labeled as u would be a_{2u} and those labeled by g would be a_{1g} states.

¹³The self-consistent calculations were performed within the pure density-functional, local-density-approximation theory. Thus, we have not modified the density-functional-theory, local-density-approximation band gap. As a consequence, the energy range $E_v < E_F \leq E_v + 0.5$ eV (Fig. 3) is truly calculated but the range $E_F > E_v + 0.5$ eV is an extrapolation.

¹⁴The divacancy has two levels of e_u and e_g symmetry in the gap and resonances of symmetry a_{1g} and a_{2u} at the top of the valence band [see also S. T. Pantelides *et al.*, Physica (Amsterdam) **116B**, 18 (1983)]. The pair-binding energy of two isolated vacancies forming a divacancy is calculated as -0.5, -1.6, and -1.7 eV in p -type, intrinsic, and n -type Si (Weinert and Scheffler, Ref. 11).

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