

CHALCOGEN AND VACANCY PAIRS IN SILICON: ELECTRONIC STRUCTURE AND STABILITIES

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ABSTRACT

The electronic structure and total energies of chalcogen pairs in Si have been calculated for three different nearest neighbor sites using the self-consistent Green-function technique. The different electronic structures, bonding properties and pair binding energies for each pair are discussed with respect to stabilities of the chalcogen pairs in Si. We predict the concentration of chalcogen pairs where both atoms occupy substitutional sites to be highest.

INTRODUCTION

Investigations of impurity pairs with total-energy Green-function calculations reveal the electronic structure, the stability and the site preference of the pair. Thus, the method allows to study defect reactions as well as stabilities of impurity pairs in solids. If there were no interactions between impurity atoms they were randomly distributed in the crystal. In the presence of attractive forces between impurities there will be complex formation. For a given impurity concentration $[A_i]$ and $[B_j]$ of impurities A and B at sites i and j respectively, the number of pairs $[A_k B_l]$ is given by the law of mass action

$$[A_k B_l] = C * [A_i][B_j] * \exp(-\Delta E/kT) \quad (1)$$

The quantity ΔE is called the pair binding energy and determines whether pair formation is exothermic ($\Delta E < 0$) or endothermic ($\Delta E > 0$). C contains the entropy contribution ΔS which will be neglected here.

Interaction forces between two impurities in a crystal can have different character. Donor-donor interactions are often assumed to be repulsive and for donor-acceptor pairs bonding is assumed to be coulombic due to the different effective charges. We show in this paper that also donor-donor interactions can be attractive and that two chemically identical impurities can have covalent or ionic binding depending on where they are placed in the crystal.

CHALCOGEN PAIRS IN SILICON

Sulfur related centers with axial symmetry have been reported by Kleiner, Zeiger and Fischler [1]. Ludwig [2] identified sulfur pairs in silicon using spin resonance. Wörner and Schirmer [3] investigated the ESR signal and hyperfine interaction of selenium in silicon and found the axial (D_{3d}) symmetry of selenium pairs. Janzen, Stedman, Grossmann and Grimmeiss [4] found evidence of sulfur and selenium pairs from IR-absorption spectra from the ground state into bound excited states and resonances in the conduction band. Using a similar technique, Wagner, Holm, Sirtl, Oeder and Zulehner [5] proposed the existence of tellurium pairs and mixed chalcogen pairs.

In this paper we report density-functional theory (DFT) calculations in the local-density approximation (LDA) using the LMTO Green-function method [6]. Calculations are done neglecting lattice distortions. Because our concern here is to study ground state total energies and defect reactions, we stay within the pure DFT-LDA theory. Thus we have not manipulated the DFT-LDA band gap. For isolated chalcogen impurities in silicon the electronic structure and dissolution energies have been calculated by Beeler, Scheffler, Jepsen and Gunnarsson [7] using the same method.

For nearest neighbor pairs in elemental semiconductors we consider the following equidistant sites: both atoms at substitutional (sub-sub), at interstitial (int-int) sites and the mixed substitutional-interstitial (sub-int) geometry. In all three cases the pair axis is in the (111) direction. The point symmetry of the defect pair is C_{3v} . Identical impurities for the sub-sub or int-int geometry have an additional inversion center yielding D_{3d} symmetry.

ELECTRONIC STRUCTURE OF CHALCOGEN PAIRS

The results for the electronic structure are displayed in the plots of the induced density of states (DOS) (figure 1). The sulfur pair at substitutional sites is best understood as a S_2 molecule placed into a divacancy (figure 2). The divacancy has two levels of e_u and e_g symmetry in the gap and resonances of symmetry a_{1g} and a_{2u} just below the valence band maximum. These states couple to the σ and π states stemming from both the s and p electrons of the diatomic molecule. The resulting levels shown in figure 2 can be identified in the plot of the induced DOS of substitutional S_2 (figure 1a). Below the valence band we see the $\sigma_g(s)$ and $\sigma_u(s)$ states of S_2 as an energetically lower a_{1g} and a higher lying a_{2u} state. The three uppermost a_{2u} , a_{1g} , a_{2u} levels in figure 2 correspond to the peak just below the valence band maximum, and the two peaks at 0.6 eV and 1.4 eV respectively. The a_{1g} level in the middle of the spectrum is smeared out in the valence band. It corresponds to the sulfur-sulfur bond which refills the missing Si-Si bond of the divacancy and therefore appears as a broad resonance. Our calculations show that all substitutional chalcogens have the level ordering shown in figure 2 in agreement with Sankey and Dow [8]. This level ordering means that for neutral pairs the highest occupied level has a_{1g} symmetry and is filled with two electrons. The pair level of Se_2^+ identified by ESR [3] therefore is of a_{1g} and not of a_{2u} symmetry as was deduced by Wörner and Schirmer from the analysis of their hyperfine data. Both our calculations and experiment agree that the uppermost state of Se_2^+ is mainly divacancy like, i. e. that the main weight of the wavefunction is at the silicon neighbors nearest to the pair. Therefore an additional node of the wavefunction between the two sulfur atoms which distinguishes the a_{1g} from the a_{2u} symmetry does not markedly alter the electron density near the Se atoms which is responsible for the Fermi contact term of the hyperfine interaction. For this reason it is difficult to

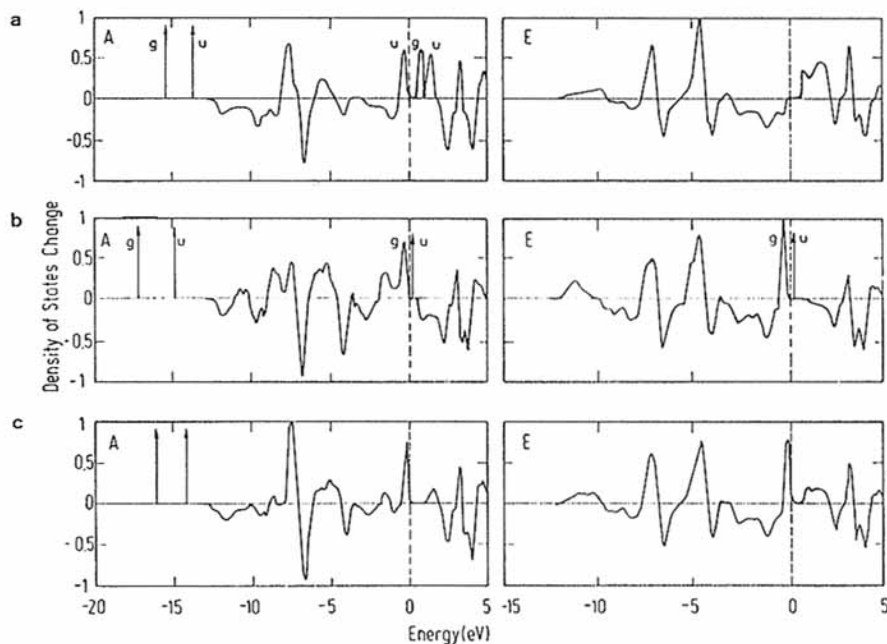


Figure. 1. The changes in the density of states of A and E symmetries induced by nearest neighbor sulfur pairs for a) sub-sub sites, b) int-int sites and c) sub-int sites. Even and odd states are denoted by g and u respectively.

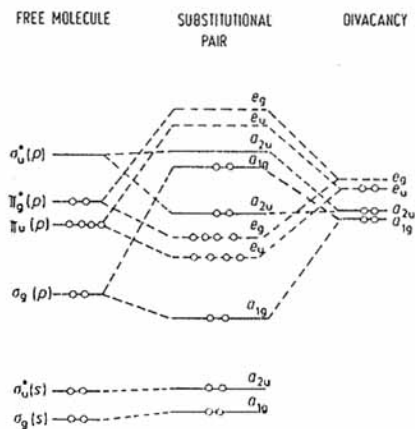


Figure. 2. Schematic summary of figure 1a. It explains the interaction of a free chalcogen molecule with the dangling bonds of the divacancy. The marked occupancies correspond to the neutral centers.

distinguish the a_{1g} from the a_{2u} level from the hyperfine data as has been attempted by Wörner and Schirmer [3] for Se pairs. They concluded from their data that the a_{2u} level is highest but their experimental results agree equally well with the wavefunctions found by our calculation which show the reversed ordering. If the a_{1g} wavefunction is analysed with respect to its s and p character at the Se atoms, the ratio of the square of the s to p expansion coefficients is calculated as 2.5. This value is significantly smaller than that reported in Ref. 3. However, we were recently informed, that a reanalysis [9] of the experimental data gave a value of 3, which then is in reasonable agreement with our calculated result.

The induced density of states of a sulfur pair where both atoms occupy interstitial positions are shown in figure 1b. Isolated chalcogens at interstitial sites have a t_2 level in the lower half of the gap [7]. Interaction between the two t_2 levels yields levels of which the a_{1g} and e_g level is pushed into the valence band. For the neutral complex there is a filled level of a_{2u} symmetry at 0.3 eV above the valence band. For two sulfur atoms at nearest neighbor substitutional and interstitial sites the interaction is between the a_1 level of the isolated substitutional atom and the t_2 level of the isolated T_d interstitial. The t_2 level is split into a_1 and e symmetry. Both levels are pushed into the valence band due to the presence of the nearest neighbor sulfur atom.

The electronic structure of substitutional Se and Te pairs is similar to that of substitutional sulfur pairs. The level ordering shown in figure 2 remains the same. The main difference is that the a_{2u} level at the top of the valence band is lifted to higher energies and emerges into the gap for Te_2 . The reason for this trend is the increased interaction of the p states with the low lying s states in going from S_2 to Te_2 . Due to this s-p mixing, the a_{2u} level at the top of the valence band is increasingly repelled to higher energies by the a_{2u} level below the valence band.

STABILITIES OF CHALCOGEN PAIRS

From the total-energy calculation we obtain the pair binding energy ΔE by subtracting the total energy calculated for the two isolated impurities from the total energy of the pair. ΔE is plotted as a function of the Fermi energy E_F . Because the charge state changes both for the isolated impurities and for the pair, various kinds of reactions are possible depending on the position of E_F . The different reactions are separated by vertical lines.

For substitutional S_2 , formation is exothermic if the Fermi energy is in the upper half of the gap, the pair binding energy for the neutral species being -0.3 eV. Pair binding energy for S_2 is smaller than for the divacancy for which we have calculated a pair binding energy of -1.6 eV for V_2 . The reason is that when the divacancy is formed, the number of dangling bonds changes from 8 dangling bonds for two isolated vacancies to 6 dangling bonds of V_2 which is equivalent to the creation of an additional bond compared to two isolated vacancies. On the other hand, 8 S-Si bonds are converted into 6 S-Si bonds and one S-S bond when a sulfur pair is formed out of two isolated S atoms. Thus, no new bond is formed upon sulfur pair formation.

Figure 3b shows the pair binding energy of two sulfur atoms at interstitial sites. For two adjacent neutral interstitials the energy gain by pairing is -0.55 eV. This time the Fermi energy must be in the lower half the fundamental gap for pairing to be exothermic. For interstitial impurities, bonds are not saturated by Si bonds and are therefore free to form sulfur-sulfur bonds screened by the silicon surrounding. As has been shown for the induced density of states in figure 1b, this is the case. The energy gain can be accounted

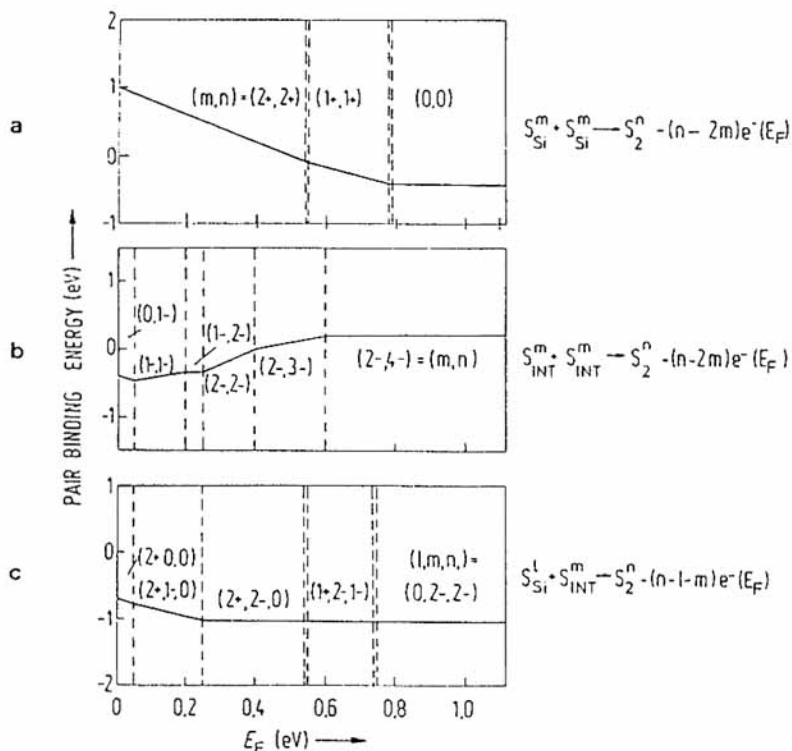


Figure 3. Pair binding energies for sulfur pairs as a function of the Fermi level position for a) sub-sub sites, b) int-int sites and c) sub-int sites. The numbers in brackets belong to the charge states of the partners of the reaction which is written on the right hand side of the diagram. A negative pair binding energy corresponds to an attractive interaction. The zero of E_F corresponds to the top of the valence band.

for by the lowering of the six electrons in the a_{1g} and e_g level into the valence band.

The pair binding energy of a substitutional-interstitial pair is shown in figure 3c. Due to the difference in surrounding of both defects, bonding becomes ionic. For the neutral charge state of the pair the charge of the substitutional sulfur is $2+$ whereas for the interstitial it is $2-$. The a_1 and e interstitial derived states are pushed into the valence band. The pair binding energy is calculated -1.1 eV for the neutral complex and remains almost constant with respect to the Fermi level position. Using a simple coulombic model of a screened donor-acceptor interaction, the binding energy would be -2.1 eV for a nearest neighbor distance of 4.44 a.u. and a dielectric constant of $\epsilon=12$. Our calculations show that this model is not appropriate to evaluate pair binding energies for nearest neighbor pairs since locally the electronic response is different from what the simple screening model suggests.

How do the above results compare with the experimental data? It is known from experiment that the tendency to form complexes reduces in going from S to Te [5]. This agrees with our calculations for neutral substitutional S_2 and

Se₂ with pair binding energies $\Delta E(S_2) = -0.3$ eV and $\Delta E(Se_2) = -0.1$ eV. Te pair formation, however, has been found to be endothermic by our calculation for the undistorted geometry which is in contradiction to Ref. 5 where Te₂ has been proposed [10]. However, thus far no ESR measurements have been performed for Te₂ which would prove the symmetry of the pair.

In order to understand which pairs dominate, the results of the pair binding energy must be looked at together with the results for the dissolution energy of single chalcogen atoms [7]. For all isolated chalcogens the substitutional site is by several eV more favourable than the interstitial site. Pair configurations containing interstitials have binding energies higher than -1.2 eV. Therefore the energy gain by pairing with an interstitial cannot overcome the preference of the substitutional sites. Thus, the concentration of substitutional pairs should be dominant.

CONCLUSION

Total-energy calculations for the three nearest neighbor chalcogen pair sites in Si have been performed. The main results are:

- 1) The character of bonding is covalent in the case of the sub-sub and int-int pairs. Ionic bonding is possible even for pairs of identical atoms at the sub-int geometry. The pair binding energy for chalcogens at sub-sub sites is greatest for n-type silicon whereas the int-int pairs have maximum pair binding energy for p-type material. Pairs at sub-int geometry have a pair binding energy which is almost independent of the Fermi level position.
- 2) The concentration of chalcogen pairs with both constituents at substitutional sites are predicted to be dominant.
- 3) The tendency of pair formation decreases from S to Se. For the undistorted geometry, pair formation of Te is found to be endothermic.

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