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Electronic energy levels of substitutional defect pairs in Si

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The major chemical trends are predicted for the deep-trap energies of 400 unrelaxed, nearest-neighbor, substitutional, sp^3-bonded defect pairs in Si. The theory predicts that (As,As) and (P,P) pairs form deep levels, but that (Sb,Sb) pairs do not. The energy of an isolated vacancy level in the band gap is found to be altered very little by pairing with a second point defect.

In this paper we show how the electronic energy levels of an isolated substitutional impurity in Si are changed by complexing with a second "spectator" impurity on a nearest-neighbor site. Such a spectator can push a shallow effective-mass-like level deep into the band gap or alter a deep level in a predictable manner—possibly even driving it shallow. Our theory focuses on the major chemical trends in the impurity-complex deep levels, and is simple and global enough that a large number of paired defects can be considered. The resulting level predictions should serve as a useful guide in interpreting experimental data.

We consider sp^3-bonded, nearest-neighbor substitutional pairs of defects and treat them according to the Hjalmarson *et al.*[1] theory of deep levels, which we have generalized for the treatment of paired defects.[2,3] The deep-level energies E are obtained using the Green's-function method,[4] by solving the secular equation

$$\det[1-(E-H_0)^{-1}V]=0 .$$

The host Hamiltonian H_0 for Si is taken to be the empirical sp^3s^* nearest-neighbor tight-binding model of Vogl *et al.*[5] with the excited s^* basis orbital necessary to produce an indirect-gap conduction band. The defect potential V is taken to be localized and is constructed using the rules of Hjalmarson *et al.*[1] The combination of the Vogl *et al.* theory of band structures with the Hjalmarson *et al.* theory of defects has been very successful in predicting the electronic structure of localized and quasilocalized states in semiconductors. These theories and their modifications have successfully treated (i) isolated impurity levels in IV and III-V semiconductors[1]; (ii) energy levels of pairs of impurities in $GaAs_{1-x}P_x$ and InP (Refs. 2 and 3); (iii) core excitons in the bulk[6] and at surfaces of III-V semiconductors[7]; (iv) energy levels of defects in CuCl (Ref. 8) and $Hg_{1-x}Cd_xTe$ (Ref. 9); (v) intrinsic surface-state energies and surface-lattice reconstruction of GaP and $GaAs_{1-x}P_x$ (Ref. 10); (vi) a mechanism of laser degradation in III-V quaternary alloy lasers and deep-defect energy levels in $In_{1-y}Ga_yAs_{1-x}P_x$ (Ref. 11); (vii) doping profiles in amorphous Si (Ref. 12); (viii) surface-defect levels and Schottky-barrier heights of GaAs, InP, AlAs, and GaSb (Ref. 13); (ix) energy levels of impurities at semiconductor-semiconductor interfaces[14]; (x) pressure dependences of deep levels,[15] and (xi) electron-nuclear double-resonance and electron-spin-resonance (EPR) spectra of deep impurities in Si.[16] The theoretical uncertainty is typically a few tenths of an eV. For instance, the chemical trends for the isolated acceptors in Si are correctly reproduced in the present theory[1] but the actual experimental binding energy for the deep acceptor In in Si is not accurately predicted (the present theory predicts a valence-band resonance for In). We are aware of only one experiment in significant disagreement with the theory[1]: Kennedy and Wilsey[17] place the A_1 level of the Ga vacancy in GaP above the T_2 level on the basis of their EPR experiment. The present theory[1] places it below (as do other theories[18–20]). The predictions of the theory[1] are in good agreement with extensive calculations (which have comparable theoretical uncertainties) with a major exception: The As vacancy level of Hjalmarson *et al.*[1] agrees with that given by some theories,[21,22] but disagrees with others.[19,23] Thus we have every reason to believe that, with allowances of a few tenths of an eV, the theory can describe the energy levels and their major chemical trends for the paired defects in Si.

Since we are interested primarily in the deep levels and their chemical trends, we focus our attention exclusively on the two central-cell parts of the defect potential of the paired complex. We follow previous work and neglect lattice relaxation; this greatly simplifies the calculation without significantly altering the levels or their chemical trends.[1] As a result, in the site representation, the defect potential V is diagonal, because the off-diagonal matrix elements of the empirical tight-binding Hamiltonian depend only on the bond length (Harrison's d^{-2} rule[24]) which does not change if there is no lattice relaxation. According to the prescription of Hjalmarson *et al.*,[1] the diagonal elements of V are taken to be proportional to the differences between the impurity and host atomic energies, and the s^* diagonal element is neglected. As a result, the secular determinant in the tight-binding representation is 8×8. A complete derivation of this 8×8 secular determinant has been published.[3]

The tetrahedral (T_d) point-group symmetry[25] about a diamond-lattice site leads to further reductions of the size of the secular matrix. An *isolated* single defect senses the T_d symmetry and produces four states from the sp^3-orbital manifold, one orbitally nondegenerate A_1 (or s-like) level and one triply degenerate T_2 (p-like) level. Neither, either, or both of these levels may fall in the band gap producing a deep trap, depending on quantitative considerations. (In addition, any defect with a long-range Coulomb potential produces an infinite number of shallow hydrogenic effective-mass levels near the relevant band edge. This long-range potential is neglected in the present theory, following the established custom[1] for theories of deep levels.)

For nearest-neighbor *paired* defects, the point-group symmetry of the pair "molecule" is reduced to C_{3v}; the two triply degenerate isolated-impurity T_2 levels split, and produce two sets of doubly degenerate e-symmetric (π-like) "molecular" orbitals and two (of four) nondegenerate a_1 (σ-like) orbitals, for a total of six distinct energy levels in or near the gap. The π-like orbitals correspond to linear combinations of the defects' p orbitals polarized perpendicular to the molecular axis. Because the π orbitals are oriented perpendicular to the spine of the molecule, their overlap is small, and the energies of the π-like e states differ little from the T_2 energies of the isolated defects. Thus a threefold-degenerate T_2 isolated-impurity level cannot be completely removed from the gap by pairing with an impurity; a residual, twofold-degenerate, e-symmetric molecular level of essentially the same energy as the isolated defect T_2 state must remain.

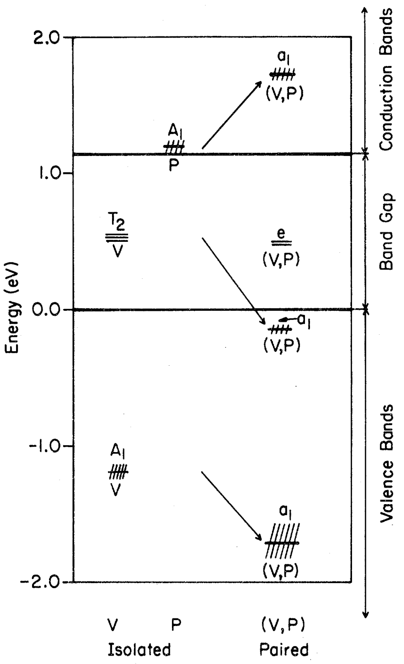


FIG. 1. Central-cell-induced (i.e., "deep") A_1 and T_2 energy levels of the isolated vacancy (V) and phosphorous (P) defects (after Ref. 1) and of the a_1 and e levels of the paired defect (V,P). Isolated A_1 level of P is a conduction-band resonance (thus producing a shallow donor level when the long-range Coulomb potential is included) and is driven upward in the conduction band by the vacancy. Similarly, the A_1 valence-band resonance level of the isolated vacancy is driven deeper in the valence band when paired with P and is considerably broadened (as suggested by the hashed line). The T_2 gap level of the isolated vacancy, when paired with P, splits into a_1 and e pair levels—the e levels remain nearly unchanged from its parent T_2 level while the a_1 level is driven into the valence band.

For the specific case of the Si vacancy,[26] this means that pairing with a nearest-neighbor impurity cannot alter the vacancy deep-trap energy very much—because it is derived from a T_2 level.[27–29] These considerations are illustrated in Fig. 1 where we show, as an example, the evolution (from their parent A_1 and T_2 levels) of the a_1 and e (V,P) pair levels of a vacancy (V) with a nearest-neighbor substitutional phosphorous (P) impurity. This insensitivity of the e levels to a neighboring defect has been observed for the (V,P), (V,As), (V,Sb), and (V,Bi) complexes in Si, where experimentally they all lie very near the predicted energy of $\simeq 0.5$ eV (i.e., relative to the conduction-band minimum E_c, at $\simeq E_c - 0.65$ eV) at nearly the same energy: 0.68 eV ($E_c - 0.47$ eV),[30] 0.69 eV ($E_c - 0.46$ eV),[30] 0.72 eV ($E_c - 0.43$ eV),[30] and $\simeq 0.75$ eV ($\simeq E_c - 0.4$ eV),[31] respectively. (Experiments show, however, that these levels are not entirely *e* symmetric, since lattice distortion is observed.[32,33]) The divacancy, since its occupied levels in the band gap are *e* symmetric, should have an energy close to that of the (*V*,donor) complexes, and is experimentally observed to lie nearby at 0.75 eV ($E_c - 0.4$ eV) to 0.25 eV ($E_c - 0.9$ eV), depending on the charge state.[34] The recent calculations of Kauffer *et al.*[35] have also shown, for the special case of the unrelaxed divacancy in Si, that the *e*-symmetric pair levels remain very close to their parent T_2 isolated levels, in agreement with our results, but contrary to the results of earlier cluster calculations.[36] An a_1 divacancy level is also formed from the T_2 levels of the isolated vacancies and lies *below* the valence-band maximum. This a_1 level can hold two electrons and thus may be the driving force in binding the divacancy, since these two electrons have been removed from the higher-energy isolated-vacancy levels in the band gap.

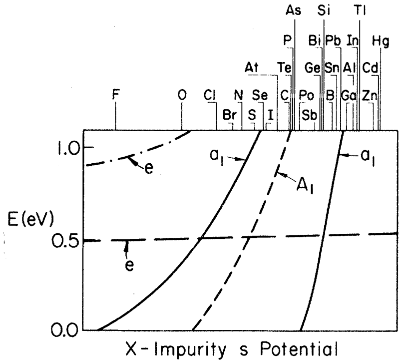


FIG. 2. Predicted a_1 pair levels of a vacancy and a nearest-neighbor substitutional defect (denoted generically as *X*) as first discussed in Ref. 12. A_1 level of the isolated impurity *X* (Ref. 1) (short dashed line) is shown for comparison. Ordinate is the energy in the band gap ($E = 0.0$ eV is the top of the valence band) and the abscissa is the *s*-impurity central-cell potential of the impurity *X*, with the impurities shown at the top of the figure at their corresponding central-cell potentials. The rightmost a_1 curve may be considered to be a perturbation of one member of the triply degenerate manifold of T_2 gap levels of the isolated vacancy. This member is driven downward in energy for electronegative impurities (those to the left of Si at the top of the figure) and driven upward in energy by electropositive impurities (those to the right of Si). The leftmost a_1 curve may be considered a perturbation of the isolated A_1 level of the *X* impurity by the vacancy which, for a given impurity, is driven to higher energy by the vacancy. The chained (long dashed) line indicates the *e* levels of the pair which are nearly identical to the T_2 levels of the isolated *X* impurity (vacancy). Since the *s* and *p* orbitals couple for paired complexes, the approximation is made that the *p*-defect potential is half the *s*-defect potential (H. P. Hjalmarson, private communication). This approximation, although not difficult to relax, greatly simplifies the presentation of the results and is also used in the construction of Figs. 3 and 4.

In general, the σ-bonded a_1 molecular levels are significantly different from their parent isolated-defect levels. For instance, an A_1 (*s*-like) isolated deep-trap level can be driven upward in energy by pairing with a nearest-neighbor vacancy (Fig. 2).

A particularly interesting set of paired defects are nearest-neighbor pairs of identical impurities—which can occur naturally at high impurity concentrations (Fig. 3). Concentrating on the branch of the theory labeled by the (P,P) and (As,As) pairs, we see that these defects are predicted to produce deep levels in the gap, in contrast with (Sb,Sb) pairs. The (Sb,Sb) "deep" pair level is

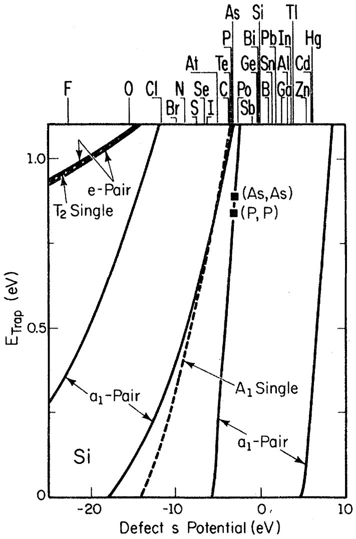


FIG. 3. A_1 and T_2 levels of the isolated or single impurities after Ref. 1 (dashed lines), and the a_1 and *e* levels of a nearest-neighbor pair of identical impurities (solid lines) in Si. The ordinate is the energy in the band gap and the abscissa is the *s*-impurity potential of the impurities. There are four branches of the theory which determine the a_1 levels of the pair corresponding to the *s* (A_1) and p_z (T_2) orbitals (*z* being the axis of the "molecule") of each impurity. *e*-symmetric pair levels are very nearly the same as the T_2 levels of the isolated impurity. Predicted (As,As) and (P,P) pair energies are denoted by solid squares.

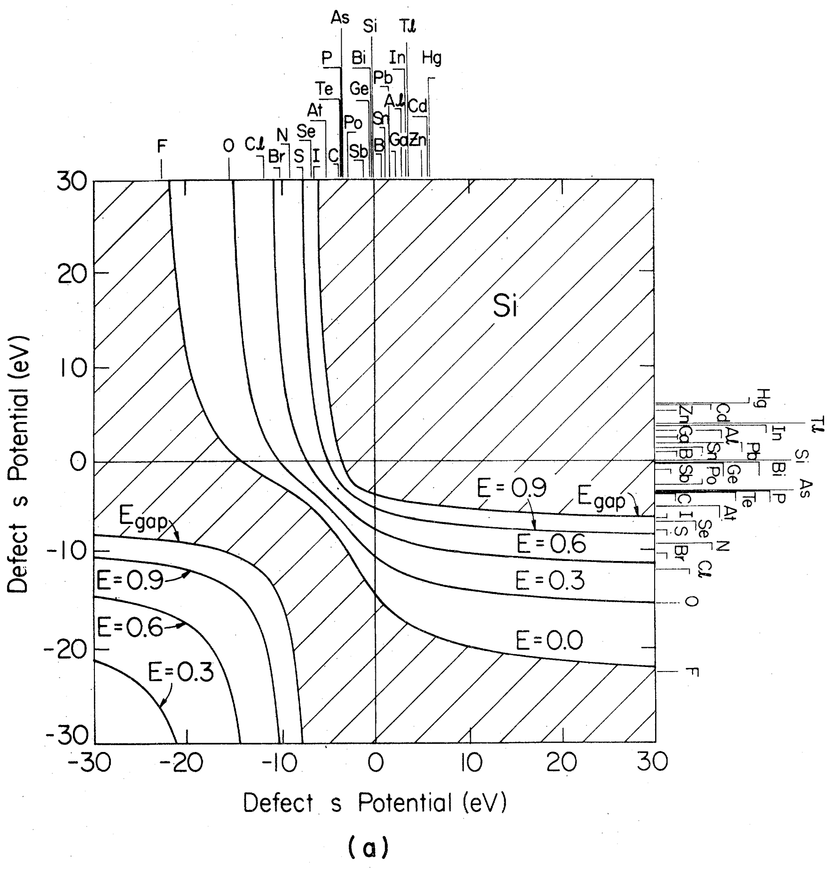
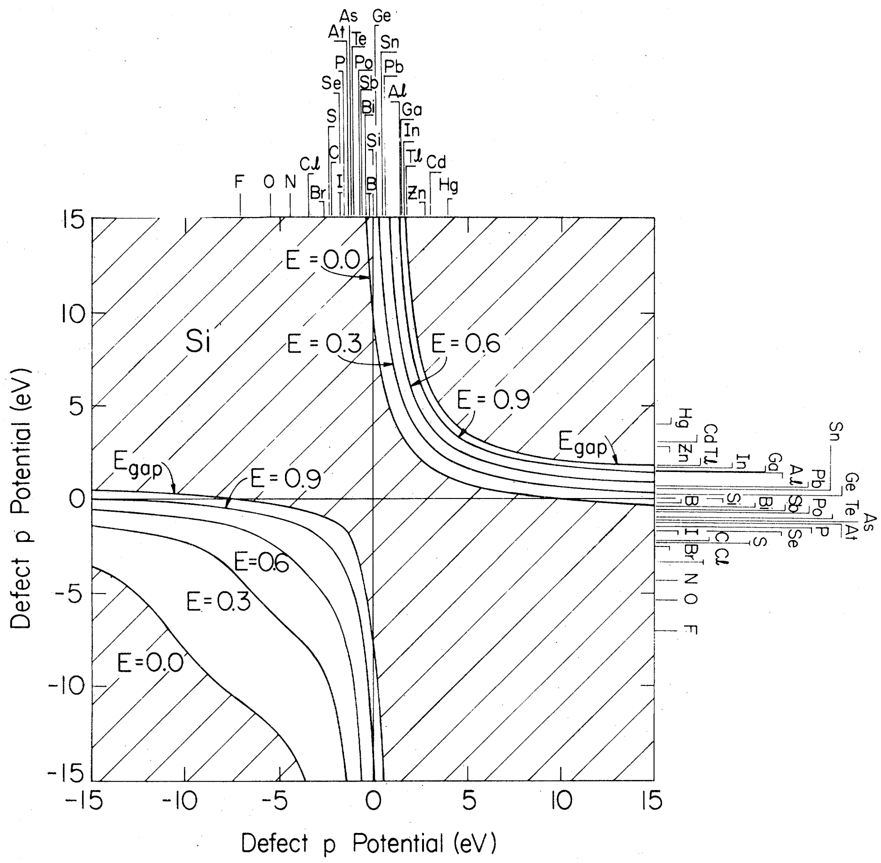


FIG. 4. (a) Contour plot of constant energy in the band gap of Si for deep a_1 levels derived chiefly from the A_1 levels of the isolated defects for a nearest-neighbor substitutional pair. Impurity s potential of one member of the pair labels the ordinate and the impurity s potential of the second member of the pair labels the abscissa. Defects corresponding to their impurity potentials are also shown. The contour labeled zero energy corresponds to the valence-band maximum. Resonance levels in the valence or conduction band lie in the cross-hatched regions. Singularities and asymptotes correspond to vacancies (infinite potential). (b) Contour plots of constant energy in the band gap for a_1 pair levels derived chiefly from the T_2 levels of the isolated defects. Interpretation is similar to that of (a). The e-symmetric levels of the pair can approximately be obtained from the T_2 levels of each of the isolated impurities [obtained from the figure by considering the (Si,X) pair].

predicted to lie above the band edge and is thus resonant with the conduction band—hence in this model, which neglects the long-range donor Coulomb potential, (Sb,Sb) pairs do not produce deep levels in the gap.[37] This disturbing prediction, that common Si n dopants yield deep traps when paired, implies that *Sb doping may be necessary to produce shallow donors rather than deep traps in submicrometer Si device fabrication*: Doping densities must be sufficiently high that the screening length is shorter than the device size; at these densities significant numbers of pairs may be present. Experiments suggest that (As,As) (Refs. 38 and 39) and (P,P) (Ref. 40) complexes do indeed form deep levels in Si. This agreement between the predictions and the data should be regarded as tentative however: At present there is no direct evidence that the observed defect complexes are simple nearest-neighbor pairs, and the predicted energy levels of the defects (which may be uncertain by a few tenths of an eV) must be observed before the theory can be claimed to have been verified.

Finally we present our predictions of a_1 molecular levels for all nearest-neighbor paired substitutional sp^3-bonded defects in Figs. 4(a) and 4(b). The levels in Fig. 4(b) are derived from the T_2 levels of the isolated impurities. Thus the e-sym-



(b)

FIG. 4. *(Continued.)*

metric levels of the (X,Y) defect molecule in Si, which are virtually unchanged from the isolated defect T_2 levels, can also be determined from Fig. 4(b): They are approximately the (Si,X) and (Y,Si) levels. We hope that these contour plots will be useful in interpreting data and in suggesting new experiments.

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