Electronic structure of deep *sp*-bonded substitutional impurities in silicon

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The recently-developed Green's-function method for defects in semiconductors is used to investigate the electronic properties of deep substitutional *sp*-bonded impurities in Si. These impurities are grouped according to the value $\Delta_z = z_{imp} - z_{host}$ where z is the chemical valence. We choose a typical representative impurity from each group: sulfur with $\Delta z = 2$ (double donor), zinc with $\Delta z = -2$ (double acceptor), and hydrogen with $\Delta z = -3$ (triple acceptor). In each case we obtain the impurity-induced state-density changes in the valence bands, and the energy positions and wave functions of the bound states in the forbidden gaps. These results are compared with earlier results for the vacancy, which may be viewed as a $\Delta z = -4$ nominal quadruple acceptor. We describe a simple physical model which explains the chemical trends as a function of Δz and compare with available experimental data.

I. INTRODUCTION

Silicon and most tetrahedral semiconductors are known to be covalent materials whose electronic properties are determined primarily by the 3*s* and 3*p* atomic states. The valence bands of these materials consist primarily of bonding states formed from tetrahedrally directed sp^3 hybrid orbitals centered on each atom. Similarly, the lowest conduction bands consist primarily of the corresponding antibonding states. The fundamental gap is a manifestation of the bonding-antibonding splitting. From among the substitutional impurities in these materials, a special class consists of those elements which have only *s* or *s* and *p* valence electrons. Bonding of these impurities to the surrounding host atoms is primarily through *s* and *p* orbitals, and we therefore refer to them as *sp*-bonded impurities. They can be conveniently classified in terms of Δz, the difference between the valence of the impurity and the valence of the host atom they replace, namely,

$$\Delta z = z_{imp} - z_{host} \ . \qquad (1)$$

Impurities for which $\Delta z > 0$ are often referred to as *donor impurities* or nominal donors since they introduce excess electrons in the crystal.[1] Impurities for which $\Delta z < 0$ are often referred to as *acceptor impurities* or nominal acceptors.[1]

Impurities for which $|\Delta z| = 1$ form a special class because, except for first-row elements, they usually introduce bound states in the energy gap which are either very near the conduction-band edge ($\Delta z = +1$) or very near the valence-band edge ($\Delta z = -1$). They are, therefore, known as shallow impurities. The perturbation potential of these impurities is dominated by a screened Coulombic tail of the form $(\Delta z)e^2/\epsilon r$, where ϵ is the dielectric constant of the host crystal. Effective-mass theory[2–4] provides an adequate description of these states. Because of the similarities of the solutions to those of the hydrogen atom, shallow impurities are usually also referred to as hydrogenic.

Impurities for which $|\Delta z| > 1$ usually introduce bound states in the energy gap which are far from the valence- and conduction-band edges by energies that are a substantial fraction of the total gap. They are known as deep. The electronic structure of these impurities has not been well understood in the past because of general difficulties associated with obtaining accurate solutions of the appropriate Schrödinger equations.[3] Recently, these difficulties were removed by the development of Green's-function methods, which provide solutions that are as accurate as the corresponding solutions of the perfect bulk host crystal.[5,6] We have since used the Green's-function method of Ref. 5 to investigate the electronic properties of deep *sp*-bonded impurities in Si. A brief account of some of the results of this investigation was reported in Refs. 7 and 8. In this paper we give a detailed account of our investigation. In Sec. II we give a brief description of the Green's-function method. In Sec. III we describe our choice of representative impurities, present the results, and analyze them in terms of simple physical models.

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II. THE GREEN'S-FUNCTION METHOD

If the Hamiltonian of the perfect host crystal is H^0, the corresponding Green's function is formally defined by

$$G^0(E)=\lim_{\epsilon\to 0+}(E+i\epsilon-H^0)^{-1}\ . \tag{2}$$

According to this definition, the eigenvalues of H^0 correspond to poles in $G^0(E)$, and the purpose of the limiting procedure is to make $G^0(E)$ well-defined at all energies. Similarly, if H is the Hamiltonian of a crystal containing an impurity, the corresponding Green's function is defined by

$$G(E)=\lim_{\epsilon\to 0+}(E+i\epsilon-H)^{-1}\ . \tag{3}$$

If we write

$$H=H^0+U\ , \tag{4}$$

Dyson's equation, namely,

$$G=G^0+G^0UG\ , \tag{5}$$

follows immediately from (2) and (3). This equation can be solved formally to get

$$G=(1-G^0U)^{-1}G^0\ . \tag{6}$$

Thus, H has eigenvalues at all energies at which H^0 has eigenvalues, corresponding to poles of G^0, i.e., in the regions of the band coninua. In addition, it has eigenvalues whenever $(1-G^0U)^{-1}$ has poles in the energy gaps. In general, for a single impurity, the bandwidths and band edges remain unaltered, the densities of states within the band continua change, and bound states appear in the gap. One can derive the following results[5]:

(1) The bound-state energies are given by the condition

$$D(E)=\det||1-G^0U||=0\ . \tag{7}$$

(2) The state-density changes in the band continua are given by

$$\Delta N(E)=-\frac{2}{\pi}\frac{d}{dE}\arctan\frac{\mathrm{Im}D(E)}{\mathrm{Re}D(E)}\ . \tag{8}$$

(3) The charge-density changes in the valence bands (VB) are given by

$$\Delta\rho=\frac{2}{\pi}\mathrm{Im}\int_{\mathrm{VB}}dE\{1-[1-G^0(E)U]^{-1}\}G^0(E)\ . \tag{9}$$

As in Ref. 5, we choose a basis set of localized orbitals at the site of each atom in the perfect crystal to represent both $G^0(E)$ and U.

The main virtue of the above method is that it exploits the underlying periodicity of the host crystal *and* the localization of the perturbation potential U describing a deep defect or impurity. Its efficiency, compared with that of cluster methods, lies in the fact that even though individual wave functions can be much more delocalized than U, the size of the matrices that need to be calculated and manipulated is determined by the extent of U. In the actual calculations, as those of Ref. 5 and the ones reported here, the crystal containing a single defect is treated with precisely the same accuracy as the perfect host crystal without any new approximations.

The calculations proceed as follows: The host-crystal Hamiltonian H^0 is written as

$$H^0=-\nabla^2+\sum_{\vec{R}}v^0_{\mathrm{ion}}(\vec{r}-\vec{R})+V_{\mathrm{val}}\{\rho^0(\vec{r})\}\ , \tag{10}$$

where $\vec{R}$ are the atomic sites, $v^0_{\mathrm{ion}}(r)$ is an ionic pseudopotential describing the host ions, $\rho^0(\vec{r})$ is the valence-electron charge density, and V_{val} is the valence-electron effective one-electron potential consisting of an electrostatic term and an exchange-correlation term in the local-density approximation.[5] The band-structure calculation is carried out using the chosen basis set of localized orbitals, and the potential V_{val} is determined self-consistently.

In order to describe a crystal containing a substitutional impurity at $\vec{R}=0$, the one-electron Hamiltonian H is given by an expression analogous to (10) and the defect potential U is given by

$$U=v^{\mathrm{imp}}_{\mathrm{ion}}(r)-v^0_{\mathrm{ion}}(r)+\Delta V_{\mathrm{val}}(\vec{r})\ , \tag{11}$$

where $v^{\mathrm{imp}}_{\mathrm{ion}}(r)$ is an ionic pseudopotential for the impurity, and

$$\Delta V_{\mathrm{val}}(\vec{r})=V_{\mathrm{val}}\{\rho(\vec{r})\}-V_{\mathrm{val}}\{\rho^0(\vec{r})\}\ . \tag{12}$$

Here

$$\rho(\vec{r})=\rho^0(\vec{r})+\Delta\rho(\vec{r})\ , \tag{13}$$

and $\Delta\rho(\vec{r})$ is related to U via Eq. (9) so that the calculation must be done self-consistently.

The details of the calculation are described in Ref. 5 in the case of the vacancy in Si which is a special case of the above equations with $v^{\mathrm{imp}}_{\mathrm{ion}}(r)=0$. In order to describe *sp*-bonded substitutional impurities, the same procedure has been followed. The only new input is the impurity ionic pseudopotentials which are described in Sec. III. In each case all appropriate convergence studies were carried out as described for the vacancy in Ref. 5.

III. RESULTS

A. The choice of impurities

In general, impurities with the same Δz have similar behavior, differing only in details.[9] Thus, since our aim was to describe the general aspects of the electronic structure of deep *sp*-bonded impurities, we performed the calculations for a representative impurity for each value of Δz. For $\Delta z = 2$ (double donor) we chose sulfur as a representative of S, Se, and Te. For $\Delta z = -2$ (double acceptor) we chose zinc, which is the only double acceptor in Si that has been investigated experimentally. Ionic pseudopotentials for these elements were constructed.[10] For $\Delta z = -3$ (triple acceptor), none of the monovalent elements is known to occupy a substitutional site. We therefore chose hydrogen, for which an ionic pseudopotential was readily available.[11] The results, therefore, are to be viewed with a proper perspective. They should not be construed to imply that hydrogen occupies a substitutional site in Si. Instead, they should be viewed as describing the properties of a typical monovalent impurity if it were to occupy a substitutional site. The calculations were performed in order to study the chemical trends as one goes from $\Delta z = -2$ (double acceptor) to $\Delta z = -3$ (triple acceptor) and finally to $\Delta z = -4$ (nominally quadruple acceptor), which is simply the vacancy. Thus the study of monovalent substitutional impurities in Si constitutes a link to understand how the properties of the vacancy relate to those of substitutional impurities.

In the remainder of this section we first present separately the results for acceptors and for donors, and then give simple physical pictures in terms of which the origins and orbital content of the localized states can be understood.

B. Acceptors

As in the case of the vacancy[5] ($\Delta z = -4$), we find that Si:H ($\Delta z = -3$) and Si:Zn ($\Delta z = -2$) have a sixfold-degenerate bound state of T_2 symmetry. As is well known, the group-III shallow acceptors ($\Delta z = -1$) also have a T_2 bound state in the gap.[2–4] We display these energy levels in Fig. 1. In the neutral configurations of the centers, the T_2 bound state contains $6 - \Delta z$ electrons since it is sixfold degenerate and is pushed out of the valence bands.[5] Thus, in the one extreme, the vacancy level contains two electrons. In the other extreme, the shallow-acceptor level contains five electrons. Normally, one views the shallow-acceptor level as containing one hole, namely the hole described by effective-mass theory. In a similar spirit, the zinc level can be viewed as containing two holes (nominally double acceptor) and the hydrogen level as containing three holes (nominally triple acceptor). Finally, the vacancy level contains four holes.

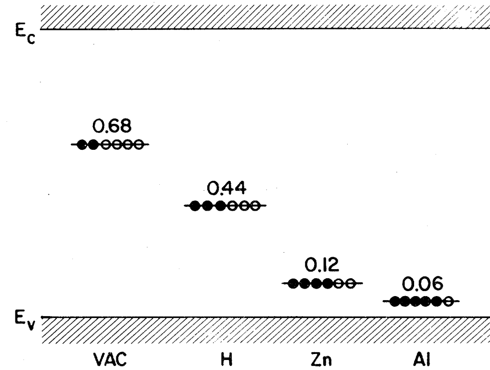

FIG. 1. T_2 energy level in the gap of a vacancy in Si, Si:H, Si:Zn, and Si:Al. In each case, the occupation of the level is shown when the defect is neutral.

The wave functions of the vacancy, hydrogen, and zinc T_2 levels are shown in Fig. 2. These wave functions are strikingly similar, suggesting that the dangling bonds created by the introduction of a vacancy remain unaltered even after the introduction of those impurities. The origin of this effect will be discussed in Sec. III D.

In Fig. 3 we show the valence-band density of states of a perfect Si crystal (top panel) and the changes in the density of A_1 and T_2 states induced by the vacancy and deep substitutional acceptor impurities. We find that the changes in the T_2 states are virtually identical in the three cases (Fig. 3), whereas the changes in the A_1 states are substantially different. In contrast to the vacancy, which introduces a sharp A_1 resonance just below the valence-band edge, hydrogen and zinc have only a broad resonance. The charge densities corresponding to these resonances are shown in Fig. 4. We see that the vacancy A_1 resonance is a dangling-bond-like state, just like the T_2 bound state in the gap (Fig. 2). The A_1 resonance of hydrogen and zinc, on the other hand, corresponds to spherical, *s*-like charge about the impurity atom.

In summary, the vacancy has both a T_2 and an A_1 localized dangling-bond-like state, whereas the deep-acceptor substitutional impurities have only a T_2 localized dangling-bond-like state. These results

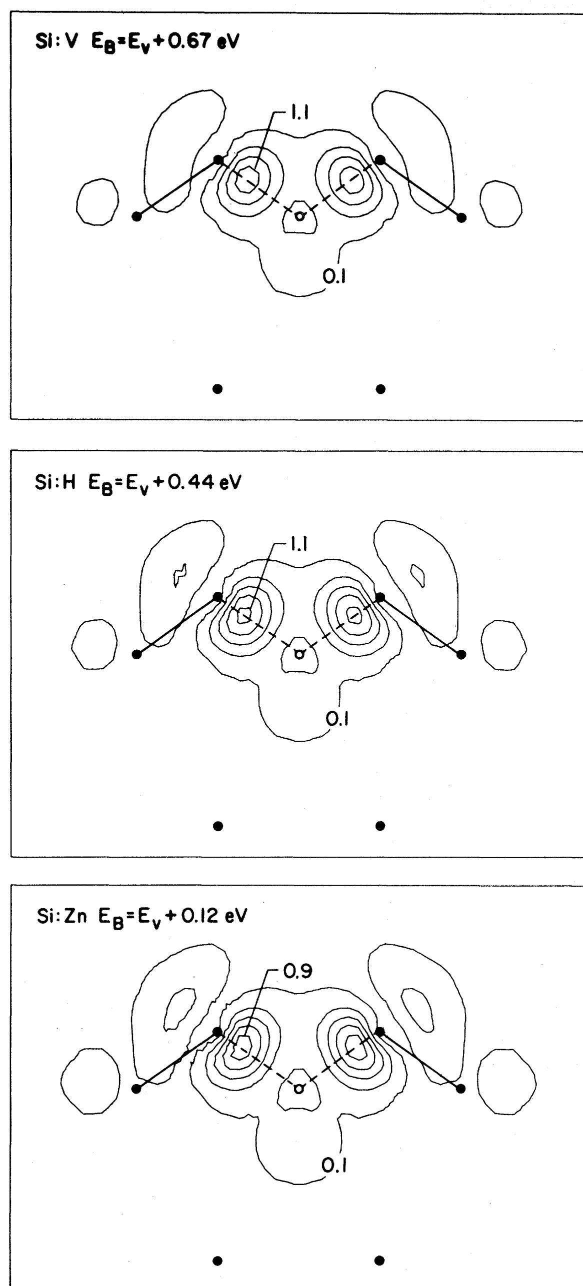

FIG. 2. Contour plot of the charge density associated with the T_2 bound state in the gap of the vacancy, Si:H, and Si:Zn. Units are electrons per unit cell.

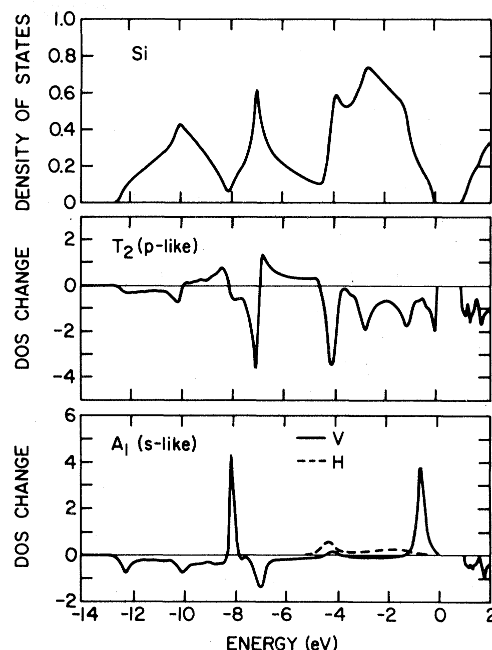

FIG. 3. Top panel: The density of states of a perfect Si crystal. Middle panel: Changes in the density of T_2 states, the same for the vacancy, Si:H, and Si:Zn. Bottom panel: Changes in the density of A_1 states, solid curve for the vacancy, dashed curve for Si:H.

will be explained in terms of simple physical models in Sec. III D, after we first present the results for deep donor impurities.

C. Donors

The nominal acceptors described in Sec. III B have fewer valence electrons than a Si atom. As a result, their ionic potentials are weaker than that of Si, so that the perturbation potentials U have an overall electron-repulsive character. As we saw, they push states up in energy. In particular, they push a T_2 state out of the valence bands into the band gap. Nominal donors, on the other hand, have more valence electrons than a Si atom so that their ionic potentials are stronger than that of Si. The corresponding perturbation potentials U, therefore, have an overall electron-attractive character. As a result, they pull states down in energy. In Fig. 5 we show the state-density changes produced by Si:S. We note that an A_1 state is pulled below the valence band, and another A_1 state is pulled from the conduction bands into the band gap. An A_1 resonance appears at about -8 eV, precisely where the host-crystal density of states has a cusp, as was the case in the acceptors. There are also a series of T_2 and E resonances.

In Fig. 6 we show the charge density associated with the A_1 localized states. We note that the state below the valence bands is almost completely localized on the sulfur atom and consists primarily of the sulfur s-like orbital. The sharp resonance at about -8 eV is an antibonding combination of s orbitals on the sulfur site and s orbitals on the nearest

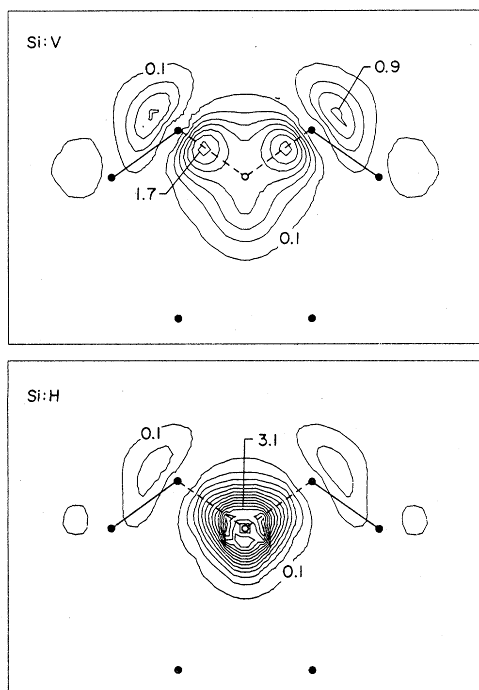

FIG. 4. Contour plot of the charge density associated with the vacancy A_1 resonance at $E_v-0.7$ eV (top panel) and of the corresponding broad resonance of Si:H (lower panel). Units are electrons per unit cell.

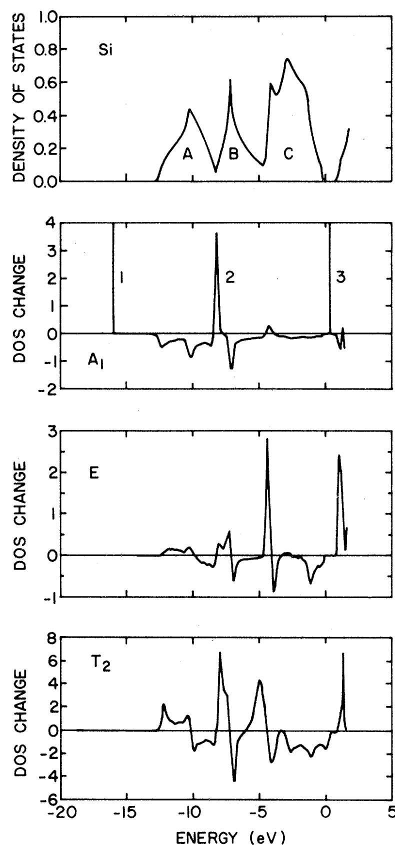

FIG. 5. The density of states of a perfect Si crystal (top panel) and the changes in the A_1, E, and T_2 states induced by Si:S.

neighbors. Finally, the A_1 state in the gap is an antibonding combination of s orbitals on the sulfur site and orbitals on the nearest neighbors which are primarily p-like with a small s-like admixture. In Fig. 7, we show the charge-density contours of the T_2 and E resonances which lie very near the conduction-band edge. We note that the T_2 state has p-like character on the sulfur atom and something similar to sp^3-like character on the neighbors. The origins and orbital content of all these localized states are described in terms of physical models in Sec. III D.

D. Discussion of results

The origin and character of the localized states introduced by a vacancy or a deep substitutional impurity can be understood in several complementary ways.

(1) The localized states can be viewed as being pulled out of the band continua by the perturbation potential. An attractive potential, e.g., the potential of donor impurities, pulls states down in energy, whereas a repulsive potential, e.g., the potential of the vacancy or an acceptor impurity, pushes states up in energy. Figures 3 and 5 are an illustration of this general trend. The case of the A_1 states of Si:S (Fig. 5) is particularly clear. Note first that the perfect-crystal valence-band density of states has three main "bands." The one lowest in energy (band A) consists mostly of s-like states, the middle one (band B) consists of a mixture of s-like and p-like states, and the third (band C) consists primarily of p-like states. In the presence of an attractive perturbation, states are pulled down in energy. It looks like the A_1 state at -16 eV is pulled down from band A (note the antiresonance in the energy range of band A) and the A_1 sharp resonance at -8 eV is pulled from band B (again note the antiresonance in the energy range of band B). There even is a weak resonance at -4 eV that appears to be pulled from band C (again note the antiresonance). Finally, the state in the gap is pulled down from the conduction bands. If we examine the T_2 and E states (Fig. 5), we see the same overall behavior.

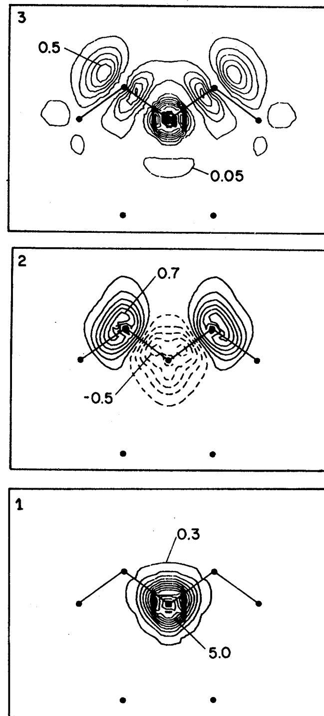

FIG. 6. Contour plots of the charge densities associated with the three localized A_1 states of Si:S numbered 1, 2, and 3 in Fig. 5. Units are electrons per unit cell.

In general, we see that localized states (bound states or resonances) appear in regions where the host-crystal state density is either zero (as in gaps) or goes through a minimum. Each localized state can be viewed as arising largely from the "band" of states immediately preceding or following it for repulsive and attractive perturbations, respectively. It would be inappropriate, however, to use this result to infer information about the orbital content of the wave functions of the localized states. For example, even though A_1 and T_2 localized states appear at approximately the same energies apparently deriving from the same "band," their wave functions are significantly different. In order to understand the character of the localized-state wave function, we must adopt an atomistic point of view as discussed below.

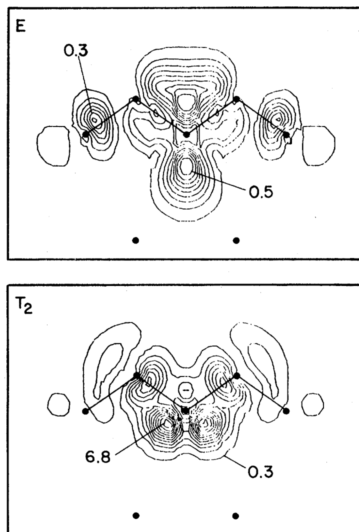

FIG. 7. Contour plots of the charge densities associated with the E and T_2 localized states near the conduction-band edge induced by Si:S. Units are electrons per unit cell.

(2) The localized states of both deep donors and deep acceptors can be understood in a systematic way by starting with the localized states of the vacancy. As we saw in Ref. 5, the vacancy introduces a T_2 bound state in the fundamental gap. In addition, it introduces resonances and antiresonances in the band continua. Most of these tend to be broad and, therefore, strongly coupled with Bloch functions at the same energies. Two A_1 resonances, however, one at -0.7 eV and one at about -8 eV, are very sharp and hence quite localized in space. These three localized states can be understood as being primarily linear combinations of the s and p orbitals centered on the nearest neighbors of the vacant site. We note that one can form an A_1 combination from the s orbitals and another A_1 combination from the p orbitals. These two states interact via the crystal Hamiltonain giving rise to a low-energy, primarily s-like state (the resonance at about -8 eV) and a higher-energy state (the resonance at -0.7 eV, which is mostly p-like, close to sp^3). Similarly, one can form T_2 combinations from both the s and p orbitals on the nearest neighbors. After interaction via the crystal Hamiltonian, the state that is mostly p-like (close to sp^3) becomes the state in the fundamental gap, and is usually referred to as a dangling-bond-like state. The state that is mostly s-like is one of the broad resonances in the valence-band continuum.

Let us now imagine placing a Si atom back at the vacant site. Its orbitals interact primarily with the localized vacancy states. For example, its p state interacts with the dangling-bond-like state in the gap. The result is a bonding state that goes down and merges in the band continuum and an antibonding state that goes up and merges in the conduction-band continuum. Similarly, the s state interacts with the A_1 states of the vacancy. Bonding states merge in the valence-band continuum and antibonding states merge in the conduction-band continuum, thus recovering the perfect-crystal band structure.

If, however, instead of a Si atom, we fill the vacancy with an impurity atom, the same interactions will occur, but to a different extent. For *acceptors,* our results suggest that the following occurs: For A_1 states, the impurity s orbital lies in the vicinity of the vacancy A_1 dangling-bond-like state and interacts with it strongly. The resulting bonding orbital goes down in energy and merges in the valence-band continuum (equivalently, the sharp vacancy resonance goes down in energy and broadens considerably because it becomes degenerate with a higher density of A_1-like crystal states). Correspondingly, the resulting antibonding orbital goes up in energy and merges in the conduction-band continuum. In contrast, the impurity p orbital lies quite high in energy, and thus interacts weakly with the vacancy T_2 dangling-bond-like state. The resulting "bonding" orbitals go down in energy very slightly (see Fig. 1), and the wave function remains predominantly dangling-bond-like. (See Fig. 2.) The corresponding "antibonding" orbital must lie high in the conduction bands and is primarily impuritylike. The above analysis can be summarized by saying that, when a deep-acceptor impurity is inserted in a vacancy, the connectivity of the lattice is restored for the s part of crystal electrons, but not for the p part. This result can be traced to the fact that group-II and group-I elements have s electrons but do not have p electrons. Thus their s electrons behave in the same way as Si electrons and restore the s-like part of the broken bonds. These impurities, however, do not support p electrons in the atomic cell and continue to look like vacancies to crystal p-like electrons.

For *donors,* the impurity s and p states lie at lower energies than the corresponding Si states. As a result, interaction with the localized vacancy states produce bonding states which are lower in energy than crystal bonding states and antibonding states that may not quite make it into the conduction-band continuum. Indeed, our results show that the A_1 state at -16 eV may be viewed as a bonding state ("$s+s$") with amplitude primarily on the impurity. The sharp resonance at about -8 eV may be viewed as the corresponding antibonding orbital ("$s-s$") which remains at the same energy as in the case of the vacancy because of the cusp in the perfect-crystal density of states at that energy. Finally, the A_1 state in the fundamental gap may be viewed as an antibonding state consisting primarily of p state on the nearest neighbors and the s state of the impurity. For T_2 state, a similar picture applies. The primary effect is that the vacancy T_2 state is pushed up into the gap and is an antibonding state (Fig. 7). The corresponding bonding state is in the valence bands as a broad resonance.

In summary, the localized state of deep acceptors and deep donors can be viewed as arising from incomplete bonding between the impurity s and p orbitals with the vacancy dangling bonds. For acceptors, the impurity orbitals lie too high in energy, and the gap states are the *bonding orbitals* that did not make it all the way into the valence bands. Their amplitude is mostly on the neighboring atoms. For donors, the impurity atoms lie too low in energy, and the gap states are the *antibonding orbitals* which did not make it all the way into the conduction bands. Again, their amplitude is mostly on the neighboring atoms.[12]

(3) Finally, another complementary physical picture can be developed in terms of which to explain the number, energy positions, and orbital content of the impurity localized states. We consider the impurity atom surrounded by host atoms and assume that the most important localized states are primarily composed of s and p orbitals on the impurity atom and its four nearest neighbors. The orbitals on the neighbors can be symmetrized into orbitals of A_1 and T_2 symmetry. Thus, A_1 localized states can be formed from the following basis orbitals:

$$\phi_\alpha = s_I ,$$

$$\phi_\beta = N_s \sum_n s_n ,$$

$$\phi_\gamma = N_p \sum_n p_n ,$$

where s_I is the impurity s orbital, s_n is the s orbital on the nth nearest neighbor, p_n is the p orbital on the nth neighbor pointing in the direction of the impurity, and N_s and N_p are appropriate normalization constants. For donors, the ordering of energies of these orbitals is shown in Fig. 8 (left and right). When these basis orbitals are allowed to interact, the states shown in Fig. 8 (middle) follow. The lowest state is bondinglike, consisting primarily of impurity s orbitals, the middle state is the corresponding antibonding orbital, consisting primarily of s orbitals on the impurity and nearest neighbors. Finally, the highest state is also antibondinglike, consisting primarily of p orbitals on the nearest neighbors and a small admixture of s orbitals. These results are consistent with the actual wave functions shown in Fig. 6 and with the analysis given above in terms of impurity and vacancy states. A similar picture can be constructed for T_2 states. In general, however, such models are only

interpretive, not predictive, since one or more of the states resulting from these models may end up being degenerate with a high density of crystal states, becoming a broad resonance and thus not recognizable as a localized state.

In Fig. 8 we also included some higher atomic energy levels labeled with a question mark. These states are likely to contribute significantly to the perfect-crystal conduction bands and consequently to the donor gap states. We will not discuss these states further in this paper, however.[13]

E. The states in the gap region—Comparison with experimental data

1. Acceptors

As we already saw in Sec. III B, the deep-acceptor impurities have a partially occupied T_2 level in the gap (Fig. 1). We note that this result is consistent with what one would expect from effective-mass theory. We note, however, that the corresponding wave functions (Fig. 2) have a dangling-bond-like character, whereas effective-mass theory would *assume* that these wave functions have the same character as the Bloch function at $k=0$, i.e., a bonding character, being symmetric about the midpoints of the lines connecting the impurity atom and its four nearest neighbors. (For further discussion of this point, see Ref. 14.)

It would be desirable to compare our numerical results for the gap states with available experimental data. Unfortunately, unambiguous data are not available for any of the impurities of interest here with the possible exception of zinc. The most significant difficulty in obtaining reliable data lies in identifying the observed centers. The case of Au in Si, which, if substitutional, would be a $\Delta z=-3$ impurity, is the most striking example.[2] The data on Zn-doped Si, however, may correspond to substitutional Zn. Two charge states have been observed with ionization energies of 0.3 and 0.6 eV, respectively.[15] We have therefore repeated our calculations for Zn^- and Zn^{2-}. We also determined the first and second ionization energies using the transition-state approximation.[16] The effect of the Coulombic tail was included by using the formula obtained for acceptors in Si by Vigneron, Pantelides, and Lipari,[17] namely,

$$\Delta E_{\mathrm{Coul}} \cong 0.15Z$$

in units of eV, where Z is the charge on the impurity. We get 0.22 and 0.44 eV for the two ionization energies, which compare well with the experimental values of 0.3 and 0.6 eV. For a more precise determination of these ionization energies, other effects, which were left out for the purposes of the present study, would have to be included. Such effects include lattice relaxation,[18] spin-orbit interactions, and a self-consistent treatment of the Zn d electrons. None of these effects would change the general results discussed in this paper, but each could contribute corrections to the ionization energies of order 0.1 eV.

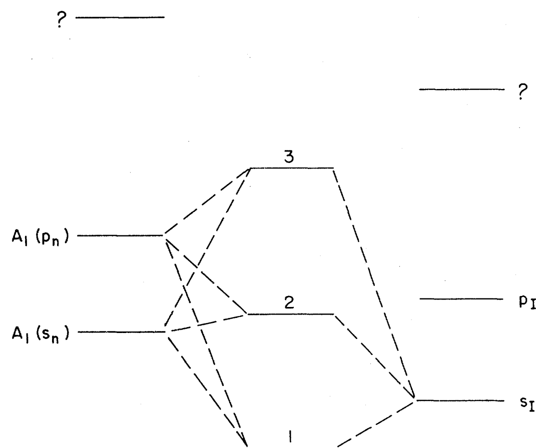

FIg. 8. Schematic of how the s orbital of the impurity atom (s_I) and the A_1 linear combinations of the s and p oribtals of the host nearest-neighbor atoms interact to give rise to the localized states associated with a substitutional deep-donor impurity.

2. Donors

The localized states induced by Si:S in the gap region are consistent with the usual effective-mass analysis. According to effective-mass theory, donor states derive from the six equivalent minima of the lowest conduction band. By making linear combinations of the Bloch functions of the six minima, one expects states of A_1, T_2, and E symmetries. Effective-mass calculations[19] show that the A_1 state is deep and sensitive to the central-cell part of the impurity potential, whereas the T_2 and E states have a binding energy which is almost completely determined by the screened Coulombic tail of the impurity potential. The present calculations for neutral sulfur (two electrons in the A_1 state) yield an A_1 state at $E_c-0.1$ eV and T_2 and E resonances

just above the band edge. The T_2 and E states are not true bound states because the impurity potential does not have a Coulombic tail. When we study charge states of the impurity, the A_1 state becomes deeper and the T_2 and E states become true bound states just below the band edge. We used the charged-state calculations to estimate[20] the first and second ionization energies of sulfur. We find 0.25 and 0.45 eV, respectively, in fair agreement with the experimental values[21] of 0.31 and 0.61 eV, respectively. As in the case of Zn, more refined calculations would be necessary to remove uncertainties of order 0.1 eV in the theoretical ionization energies. No such calculations have been attempted.

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[1]The term donor (acceptor) is more generally used to describe a positively (negatively) charged state of an impurity since a positive (negative) charge corresponds to the impurity having donated (accepted) one of its electrons to (from) the crystal. Thus, in general, a given impurity may have both a donor and an acceptor state, in which case it is known as amphoteric.

[2]W. Kohn, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p.257; for more recent reviews, see Refs. 3 and 4.

[3]S. T. Pantelides, Rev. Mod. Phys. 50, 797 (1978).

[4]M. Altarelli, A. Baldereschi, and N. O. Lipari, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, in press).

[5]J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. Lett. 41, 895 (1978); Phys. Rev. B 21, 3545 (1980).

[6]G. A. Baraff and M. Schlüter, Phys. Rev. Lett. 41, 892 (1978); Phys. Rev. B 19, 4965 (1979).

[7]J. Bernholc, S. T. Pantelides, N. O. Lipari, and A. Baldereschi, Solid State Commun. 37, 705 (1981).

[8]S. T. Pantelides, J. Bernholc, and N. O. Lipari, J. Phys. Soc. Jpn. 49, Suppl. A, 235 (1980); J. Bernholc, N. O. Lipari, S. T. Pantelides, and M. Scheffler, in *Defects and Radiation Effects in Semiconductors,* edited by R. R. Hasiguti (IOP, London, 1981), p. 1.

[9]The first-row elements are the most notable exception to this rule. For example, P, As, Sb, and Bi have similar properties as substitutional impurities in Si, whereas N behaves very differently [K. H. Brower, Phys. Rev. Lett. 44, 1627 (1980)]. Similarly O in Si behaves very differently from S, Se, and Te.

[10]The ionic pseudopotentials of sulfur and zinc were expressed in the form

$$v(r)=-\frac{2Z}{r}\operatorname{erf}\left[\frac{r}{r_0}\right]+\frac{a}{r_0}e^{-(r/r_0)^2}+\frac{b}{r_0^3}r^2e^{-(r/r_0)^2}.$$

The coefficients r_0, a, and b were determined by requiring that the valence s and p energy levels and corresponding wave functions outside the radius r_0 are the same obtained from a standard atomic calculation. These pseudopotentials are local and therefore only an approximate fit was possible. The coefficients, in atomic units, were as follows. Zinc: $r_0=1.5$, $a=3.37$, $b=-2.96$, $Z=2$. Sulfur: $r_0=1.0$, $a=15.0$, $b=-7.5$, $Z=6$. We checked and found that our results are not very sensitive to the details of these pseudopotentials.

[11]S. G. Louie, Phys. Rev. Lett. 42, 476 (1979).

[12]In a recent study of deep impurities using empirical tight-binding Hamiltonians, H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow [Phys. Rev. Lett. 44, 810 (1980)] proposed that the A_1 localized states of deep donors can be understood simply in terms of the s orbital of the impurity and the s orbitals of the nearest neighbors. In that picture, one has a bonding $(s+s)$ state with amplitude mostly on the impurity (called *hyperdeep* and lying either in or below the valence bands) and an antibonding $(s-s)$ state in the gap. Our calculations show that there are actually *three* localized A_1 states, and that in order to understand their origins one must consider both s and p orbitals on the nearest neighbors since both can form an A_1 state about the impurity site. The result is $s+s$ and $s-s$ are both *hyperdeep* states and the state in the gap is actually $p-s$. Calculations using the tight-binding Hamiltonians of Hjalmarson *et al.* have been found to agree with the present results and analysis. Further details will be published elsewhere (Ref. 13).

[13]S. T. Pantelides and M. Scheffler (unpublished).

[14]S. T. Pantelides, N. O. Lipari, and J. Bernholc, Solid State Commun. 33, 1045 (1980).

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[16]J. C. Slater, Phys. Rev. B 1, 385 (1951); J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974). We also calculated higher-order corrections to the transition-state formula within the local density approximation and found them negligible.

[17]J. P. Vigneron, S. T. Pantelides, and N. O. Lipari, Phys. Rev. B (in press).
[18]A Jahn-Teller distortion similar to that of the vacancy [see, e.g., N. O. Lipari, J. Bernholc, and S. T. Pantelides, Phys. Rev. Lett. 43, 1354 (1979)] is likely to *increase* the ionization energies because holes to be emitted to the valence band are in the upper, fourfold-degenerate state.
[19]See, e.g., S. T. Pantelides and C. T. Sah, Phys. Rev. B 10, 638 (1974); also Ref. 3.
[20]The effect of the Coulombic tail is estimated by pertubation theory.
[21]L. L. Rosier and C. T. Sah, Solid State Electron 14, 41 (1971); W. E. Krag, W. H. Kleiner, H. J. Zeiger, and S. Fischler, J. Phys. Soc. Jpn. Suppl. 21, 230 (1966).