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Multivalley Effective-Mass Approximation for Donor States in Silicon. II. Deep-Level Group-VI Double-Donor Impurities*

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It is suggested that the recently proposed two-parameter model impurity potentials of the shallow-level group-V donors in silicon may be scaled to give the model impurity potentials of the deep-level group-VI donors of the same row in the Periodic Table. It is shown that in the case of sulfur this suggestion follows naturally from examining the behavior of the true impurity potential in the central-cell region. By extending the multivalley effective-mass approximation (EMA) to singly ionized sulfur donors in silicon, using recently available optical data, it is found that indeed the potential parameters of sulfur are essentially identical to those of phosphorus, as expected from this model. A heliumlike model in the multivalley EMA is also developed and applied to the two-electron neutral group-VI donors in silicon. The calculated energy of neutral sulfur agrees well with observed thermal activation energy. Using the scaled model impurity potentials of As, Sb, and Bi, the energies of substitutional Se, Te, and Po in Si are predicted. It is also suggested that the same procedure may be applied to acceptor states. Holes bound to deep-level acceptors may be described simply by scaling the impurity potentials of the shallow-level group-III acceptors. The effects of the Δ_5 valence band and the Δ_2' conduction band on the deep-level donors are discussed. These effects are found to be small for singly ionized sulfur in silicon.

I. INTRODUCTION

The effective-mass approximation (EMA) of Kohn and Luttinger[1-3] has been highly successful in describing the electronic structure of the excited states of shallow-level impurities in semiconductors. In the case of group-V donors in silicon, good agreement with experiment is obtained even for the 1*s* states when the EMA is modified to take into account the multivalley nature of the conduction band.[4-7] However, the simple EMA has not been successfully applied to deep levels. As a result, several distinctly different theoretical approaches to the problem of deep-level defects have been adopted, with varying degree of success. We shall briefly discuss some of these efforts below.

To a certain extent these approaches can be grouped into three categories: (i) the free-atom approximation, (ii) the modified effective-mass approximation, and (iii) the intermediate approaches.[8] In the free-atom approximation, the impurity electron is considered so tightly bound that it sees essentially the potential of a free atom perturbed by the crystalline fields. The wave function is described in terms of the free-impurity-atom functions. This method has been applied to transition-metal impurities[9] and interstitial impurities.[10] However, only qualitative results were obtained because of the large number of uncertain parameters involved.

The modified effective-mass approximation differs from the Kohn-Luttinger EMA in that a more realistic impurity potential is used in the central-cell region.[11-13] Usually, to account for the central-cell correction, the potential is partitioned into two parts. For $r > R$, a simple screened Coulomb potential is assumed, while for $r < R$, various models have been used to approximate the potential. A review of these models has been given by Müller.[13] The calculated energy is a function of R, and in general there is some critical range of R in which the energy changes rapidly.[11,13] In the case of phosphorus and singly ionized sulfur in silicon, Müller found by fitting the experimental energies that $R(\mathrm{P}) = 3.8$ a.u. and $R(\mathrm{S}^+) = 2.6$ a.u., which is inconsistent with the fact that both phosphorus and sulfur have the same core configuration. One intrinsic difficulty of these EMA approaches, when applied to silicon and germanium, is that the valley-orbit interaction is neglected, which has been shown to be important even for the shallow impurities.[4-7]

Of the intermediate approaches, only a few will be discussed here. The Wannier representation in the pseudopotential formalism has been applied by Hermanson[14,15] to exciton and impurity states in rare-gas solids with good agreement with experiment, using a simple interpolation model for the band structure. However, the method may not be practical for germanium and silicon where the band structure is much more complicated. The two-band approximation has also been applied to the deep levels.[16-18] Analysis of the equations in the two-band approximation indicates that, depending on the details of the impurity potential, some impurity centers can capture both electrons and

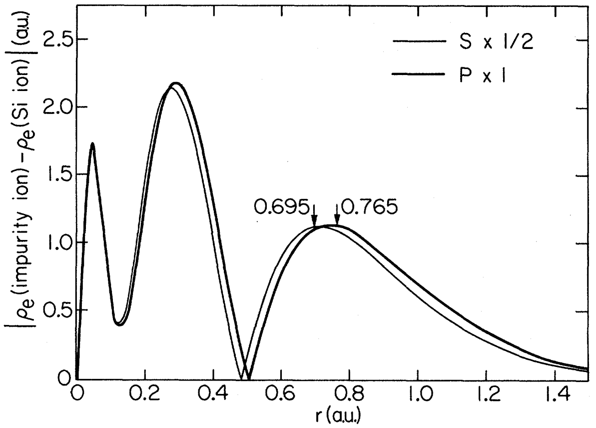

FIG. 1. Comparison of the effective electronic radial charge densities of sulfur and phosphorus ion cores in silicon. Arrows indicate positions of outermost maxima.

holes simultaneously.[16,17] However, because of the complexity of a two-band approximation, only semiquantitative results have been obtained even in the simplest band-structure model.[17] Another approach is the near first-principles treatment by the so-called LCAO-MO technique.[19,20] In this method, a defect level is simulated by a large cluster of host atoms surrounding the defect. The electronic states of this defect "crystal" are then computed by using the LCAO-MO method. In order to determine the energy levels with respect to the band edges of the crystal, a very large cluster, up to 100 atoms or more, may be needed. There are also the quantum defect[21] and the δ-function-potential[22] methods which have been used to calculate photo-ionization cross sections.

Recently we proposed a two-parameter model impurity potential of the form $U(\vec{r}) = -(e^2/\epsilon r) \times Z_{eff}(\vec{r})$, where ϵ is the dielectric constant of the crystal, and $Z_{eff}(\vec{r}) = (1 - e^{-br} + Br\,e^{-br})$, to describe the shallow-level group-V donors in silicon.[6,7] Using the multivalley EMA and the variation method, the potential parameters B and b were obtained by fitting the experimental $1s(A_1) \rightarrow 2p\pm$ and $1s(T_2) \rightarrow 2p\pm$ transition energies. Also, we suggested that the impurity potentials of the group-V donors may be scaled to account for the deep-level group-VI donors of the same row in the Periodic Table.[23] In this paper, we shall test this idea by extending the multivalley EMA to sulfur donor centers in silicon, using the recently available $1s$-state energies of the singly ionized sulfur in silicon.[24-27] Testing of this idea in other group-VI donors cannot be done at present because of the lack of experimental data.

The outline of this paper is as follows. In Sec. II the impurity potential of sulfur is discussed and compared with that of phosphorus. We shall show that the comparison leads to the natural suggestion of scaling the group-V impurity potentials to describe the group-VI impurities. In Sec. III the multivalley EMA will be extended to obtain the electronic structure of sulfur and other group-VI impurities in silicon. A heliumlike model in the multivalley EMA is also developed to describe the two-electron neutral donors. In Sec. IV the electric-dipole transition matrix elements of the singly ionized sulfur centers are calculated and compared with available experiments. Finally, in Sec. V, some corrections to the multivalley EMA for deep levels are discussed.

II. IMPURITY POTENTIAL OF SULFUR IN SILICON

It was shown[7] that the true impurity potential in the central-cell region is given qualitatively by a point charge of $e\Delta Z$ at the nucleus plus an effective electronic radial charge density of $-e\Delta\rho_e(r)$ distributed inside the central cell, where ΔZ is the difference between the atomic numbers of the impurity and the silicon atoms, and $\Delta\rho_e(r)$ is the difference between the radial electronic charge distribution functions of the impurity ion and the Si^{+4} ion. In Fig. 1 we have plotted $|\Delta\rho_e|$ of both sulfur and phosphorus in silicon for comparison, using the Herman-Skillman table of atomic functions.[28] Figure 1 clearly indicates that the radii of the distribution of $\Delta\rho_e(P)$ and $\Delta\rho_e(S)$ are about the same, which is consistent with the fact that both sulfur and phosphorus have the same ion core configuration $(1s^2 2s^2 2p^6)$, and that $\Delta\rho_e(S)$ is almost exactly twice $\Delta\rho_e(P)$. This, together with the fact that $\Delta Z(S) = 2\Delta Z(P)$, means that the impurity potential of sulfur should be essentially twice that of phosphorus, yet the radii of the central-cell correction to the two potentials should be essentially the same.

This observation naturally suggests that the phenomenological model impurity potential[6,7] of phosphorus in silicon may be scaled to describe that of sulfur in silicon. That is, we take the model impurity potential of singly ionized sulfur to be

$$U(\mathrm{S}^{++}) = -(e^2/\epsilon r) Z_{eff}(\mathrm{S}^{++}) , \tag{2.1}$$

where

$$Z_{eff}(\mathrm{S}^{++}) = 2[1 - e^{-br} + Br\,e^{-br}] , \tag{2.2}$$

and ϵ is the dielectric constant of silicon. The factor of 2 in $Z_{eff}(\mathrm{S}^{++})$ comes from the fact that an electron in a singly ionized center sees an effective nuclear charge of $+2e$. We expect the potential parameters B and b to be essentially identical to those of phosphorus.

We also note that the radius of maximum Z_{eff}, which measures the radius of the central-cell correction, is given by $R_Z = (B + b)/Bb$, which is independent of the scaling. Thus, in our model, R_Z

TABLE I. Comparison of the peak position R_Z of the effective impurity charge with the effective radius R_{ion} of the impurity ion core for sulfur and phosphorus in silicon.

	b (a.u.)	B (a.u.)	R_Z (a.u.)	R_{ion} (a.u.)	$\frac{R_Z}{R_{\text{ion}}}$
P	0.8724	7.310	1.283	0.765	1.68
S	0.8783	7.316	1.275	0.695	1.83

is essentially the same for both phosphorus and sulfur, as it should be according to the discussion of $\Delta\rho_e$ above. Hence, our model impurity potential does not have the inconsistency between sulphur and phosphorus as does the cavity model used by Müller,[13] who found that the cavity radius of sulfur is much smaller than that of phosphorus.

III. MULTIVALLEY EMA

A. Singly Ionized Sulfur Centers in Silicon

The multivalley EMA previously used for the group-V donors[6,7] can easily be extended to include singly ionized sulfur in silicon. The sulfur model impurity potential is taken from (2.1) and (2.2). The potential parameters b and B are determined by fitting the calculated $1s(A_1) \rightarrow 2p\pm$ and $1s(T_2) \rightarrow 2p\pm$ energies to experiment, as was done for the group-V impurities, using the recent optical data of $1s(A_1) \rightarrow 2p\pm = 587.95$ meV [26] and $1s(A_1) \rightarrow 1s(T_2) = 425$ meV.[27]

In Table I the potential parameters b and B for singly ionized sulfur are compared with those of phosphorus. Here R_Z is the peak position of Z_{eff}, and R_{ion} is the position of the outermost maximum of $|\Delta\rho_e|$. The results in Table I clearly indicate that the potential parameters are indeed essentially identical for phosphorus and sulfur in silicon. This close agreement gives further confidence to the proposed model potential, for describing not only shallow donor impurities, but also deep donor impurities.

The energies calculated with $b = 0.8783$ a.u. and $B = 7.316$ a.u. are given in Table II together with the experimental values. The agreement between theory and experiment is good, except for the $2s(T_2)$ state. In the calculation we have neglected the coupling between states of the same symmetry.[29] Since the $2s(T_2)$ state lies between the $2p_0$ state and the $2p\pm$ states, and since there are twice as many $2p\pm$ states as $2p_0$ states, the coupling with the $2p_0(T_2)$ and the $2p\pm(T_2)$ states would have the net effect of depressing the energy of the $2s(T_2)$ state.

In extending the multivalley EMA to include singly ionized sulfur in silicon, we have implicitly assumed that the donor electron has components only from the six Δ_1 valleys of the conduction band, and that the central-cell correction is not strong enough to appreciably couple in the valence bands. This is consistent with the observation that the emission and capture rates of holes are negligible compared with those of electrons.[31] We shall give a semiquantitative estimate of the effects of the valence and higher-energy conduction bands in Sec. V.

B. Neutral Sulfur Centers in Silicon

It was recognized by Breitenecker *et al.*[12] and Glodeanu[32] that double-donor or double-acceptor impurities in semiconductors may be described by a heliumlike model. Glodeanu started with the equation

$$\left(-\frac{\hbar^2}{2m_0}(\nabla_1^2+\nabla_2^2)-\frac{Ze^2}{\epsilon r_1}-\frac{Ze^2}{\epsilon r_2}+\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}\right)F_n(\vec{r}_1,\vec{r}_2) = EF_n(\vec{r}_1,\vec{r}_2)\,, \qquad (3.1)$$

which is just the extension of the hydrogenlike one-valley EMA to a heliumlike donor, but with the free-electron mass m_0 for the donor electrons instead of the effective mass m^*. The use of m_0 instead of m^* in (3.1) amounts to neglecting the periodic potential and band structure of the host crystal.[33] Nevertheless, Glodeanu's result does not compare satisfactorily with experiment.

The multivalley EMA can be extended to describe a heliumlike double-donor impurity in silicon. We shall take neutral sulfur as a specific example.

TABLE II. Binding energies of singly ionized sulfur centers in silicon.

	Variation parameters (a.u.)		Energy $(E_c - E)$ (meV)	
State	a_t	a_l	Theory	Experiment
$3p_\pm$	25.3	15.5	11.25[a]	11.88[b]
$2p_\pm$	25.3	15.5	25.31[a]	25.31[b]
$2s(E)$	17.2	17.2	33.16	···
$2s(T_2)$	15.8	15.8	35.73	40.27[b]
$2p_0$	16.9	10.2	45.51[a]	45.29[b]
$2s(A_1)$	10.3	10.3	62.29	···
$1s(E)$	14.2	14.2	147.48	···
$1s(T_2)$	10.2	10.2	188.26	188.26[c]
$1s(A_1)$	7.3	7.3	613.26	613.26[b,c]

[a] Obtained in the one-valley parabolic-band EMA. Central-cell correction is 0.01 meV for $2p\pm$ and $3p\pm$, and 0.13 meV for $2p_0$.

[b] From Refs. 24 and 25. The $2p\pm$ level has been matched to the present theory (25.31 meV) instead of 4 times Faulkner's value in Ref. 30 (25.60 meV). 0.28 meV of this difference comes from the difference in the low-temperature dielectric constants used, $[(\text{here})/(\text{Faulkner})]^2 = (11.46/11.40)^2$, and 0.01 meV from the central-cell correction included here.

[c] From Ref. 27.

In this case the two-electron Hamiltonian is

$$H=H(1)+H(2)+U_{ee}(\vec{r}_1,\vec{r}_2)\ , \tag{3.2}$$

where $H(1)$ and $H(2)$ are just the one-electron model Hamiltonians of the singly ionized sulfur center and $U_{ee}(\vec{r}_1,\vec{r}_2)$ is the electron-electron interaction which includes the effect of screening by the dielectric function of the host crystal. In terms of the model impurity potential, $H(1)$ is given by

$$H(1)=H^0+U(\mathrm{S}^{++})\ , \tag{3.3}$$

where H^0 is the one-electron Hamiltonian of the pure crystal, and $U(\mathrm{S}^{++})$ is the model impurity potential of sulfur which has been determined in Sec. II. Now, since the bare electron-electron interaction is

$$\frac{e^2}{|\vec{r}_1-\vec{r}_2|}=\frac{e^2}{2\pi^2}\int d^3k\,\frac{e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_2)}}{k^2}\ , \tag{3.4}$$

the screened electron-electron interaction, in the linear response theory, can be written as

$$U_{ee}(\vec{r}_1,\vec{r}_2)=\frac{e^2}{2\pi^2}\int d^3k\ \frac{e^{i\vec{k}\cdot(\vec{r}_1\vec{r})}}{k^2}\ , \tag{3.5}$$

where $\epsilon(\vec{k})$ is the k-dependent dielectric function of silicon. We use

$$1/\epsilon(k)=\frac{Ak^2}{k^2+\alpha^2}+\frac{Bk^2}{k^2+\beta^2}+\frac{C\gamma^2}{k^2+\gamma^2}\ ,$$

with $\alpha=0.7572$ a.u., $A=1.175$, $\beta=0.3123$ a.u., $B=-0.175$, $\gamma=2.044$ a.u., and $C=\frac{1}{11.46}$, as given by Nara and Morita.[34] The two-electron wave function, assuming both electrons in the $1s(A_1)$ state, is

$$\Phi(1,2)=\Phi(1)\Phi(2)\ , \tag{3.6}$$

where $\Phi(1)$ and $\Phi(2)$ are just the one-electron wave functions of the $1s(A_1)$ state given by[6,7]

$$\Phi(1)=\sum_{i=1}^{6}\ \alpha_i\sum_{\vec{k}}F_i(\vec{k})\psi_k^0(\vec{r}) \tag{3.7}$$

and

$$\alpha_i=(1,1,1,1,1,1)/\sqrt{6}\ . \tag{3.8}$$

The Fourier transform of $F_i(\vec{k})$ is $F_i(\vec{r})$, which is taken to be of the form

$$F_i(\vec{r})=(\pi a^3)^{-1/2}e^{-r/a}\ , \tag{3.9}$$

where a is the variation parameter.

The energy $E(\mathrm{S}^+)$ of the neutral sulfur is given by

$$E(\mathrm{S}^+)=\frac{\langle\Phi(1,2)|H|\Phi(1,2)\rangle}{\langle\Phi(1,2)|\Phi(1,2)\rangle}$$

$$=2\frac{\langle\Phi(1)|H(1)|\Phi(1)\rangle}{\langle\Phi(1)|\Phi(1)\rangle}+\frac{\langle\Phi(1,2)|U_{ee}(\vec{r}_1,\vec{r}_2)|\Phi(1,2)\rangle}{\langle\Phi(1,2)|\Phi(1,2)\rangle}\ . \tag{3.10}$$

The first term is just twice the $1s(A_1)$-state energy of a singly ionized sulfur center. The second term is the electron-electron interaction energy, which has been evaluated in terms of the variational parameter in Ref. 35 using a spherical approximation for terms that involve more than one valley. Minimizing the energy with respect to the variational parameter, we obtain

a = variational parameter (effective Bohr radius)

= 8.1 a.u.

and

$$E(\mathrm{S}^+)=-928.2\ \mathrm{meV}\ . \tag{3.11}$$

Now, from Secs. II and III A, the ground-state energy of singly ionized sulfur in silicon is $E(\mathrm{S}^{++})=-613.3$ meV. Therefore, the first ionization energy of neutral sulfur in silicon is

$$E(\mathrm{S}^{++})-E(\mathrm{S}^+)=(928.2-613.3)\ \mathrm{meV}=314.9\ \mathrm{meV}. \tag{3.12}$$

Using dark capacitance transient techniques, Rosier and Sah[31] observed a thermal activation energy of 302 ± 1.1 meV due to neutral sulfur centers in silicon. This value is slightly smaller than the calculated first ionization energy. The difference of 315 – 302 = 13 meV can be accounted for by a thermal (phonon) excitation process via excited states.

It is known from the study of helium and heliumlike ions[36] that for these systems the usual excited states are such that one of the two electrons is in the ground state. If the excited electron is in a state of large n and $l\neq 0$, then its wave function does not overlap appreciably with that of the inner (ground-state) electron. In that case, the inner electron sees essentially no screening by the outer electron, while the outer electron sees total screening by the inner electron. Thus, for these states, the energies of He are approximately equal to those of H plus the ground-state energy of He$^+$. And the ionization energy of a helium atom with an electron in an excited $(n, l\neq 0)$ state is approximately given by the ionization energy of a hydrogen atom in the corresponding (n, l) state.

Thus, in our heliumlike model for neutral sulfur centers in silicon, an excited state of neutral sulfur would consist of one electron in the ground state $1s(A_1)$, whose energy is just the ground-state energy of the singly ionized sulfur, and another electron in an (n, l, m) state, whose energy is just the corresponding (n, l, m)-state energy of a group-V donor electron. In other words, the first ionization energy of a neutral sulfur center in the $[1s(A_1)][n, l, m]$ state is given approximately by the ionization energy of a group-V donor center in the corresponding (n, l, m) state. For $n=2$, this energy is about 10 meV.[7]

The same argument also applies to the excited $1s$

TABLE III. Predicted first ionization energy, E (impurity$^+$) $-$ E (impurity^{++}), of the neutral centers and the ground-state energy, E (impurity^{++}), of the singly ionized centers of Se, Te, and Po in silicon.

Center	State	Energy ($E_c - E$) (eV) Se	Te	Po
	$1s(E)$	0.132	0.137	no minimum $\langle H\rangle$
singly	$1s(T_2)$	0.158	0.161	0.147
ionized	$1s(A_1)$	1.123	0.539	1.937
neutral	1st ionization	0.585	0.265	1.003

states, since by symmetry, the excited-state wave function $\Phi_{1s(T_2)}$ or $\Phi_{1s(E)}$ has zero amplitude at the nucleus where the amplitude of the ground-state wave function $\Phi_{1s(A_1)}$ is maximum. Thus, the first ionization energy of a neutral sulfur center in the $[1s(A_1),\ 1s(T_2)]$ or $[1s(A_1),\ 1s(E)]$ state is about 32 meV.[7]

The above result indicates that in the indirect thermal ionization of neutral sulfur centers via excited states, an electron is first thermally excited to the $n = 2$ state, which is probably thermally broadened appreciably, and then thermally excited into the conduction band. During the transition process the other electron remains in the ground state.

C. Other Group-VI Donor Impurities in Silicon

The above results show that the two-parameter model impurity potential of sulfur in silicon is essentially identical to that of phosphorus in silicon, except for the scale factor which accounts for the difference in the valencies of the phosphorus and sulfur atoms. Also, it was suggested that the impurity potentials of the other group-V donors may be scaled accordingly to account for the group-VI deep-level donors of the same row in the Periodic Table.[23] That is, we expect that substitutional impurities of Se, Te, and Po in silicon may be described by the potentials

$$U(\mathrm{Se}^{++}) = 2U(\mathrm{As}^{+}) \ , \quad U(\mathrm{Te}^{++}) = 2U(\mathrm{Sb}^{+}) \ , \quad U(\mathrm{Po}^{++}) = 2U(\mathrm{Bi}^{+}) \ , \qquad (3.13)$$

where $U(\mathrm{As}^+)$, $U(\mathrm{Sb}^+)$, and $U(\mathrm{Bi}^+)$ are the model impurity potentials of As, Sb, and Bi in silicon.[7] This model may then be used to predict the energy levels of Se, Te, and Po in silicon, using the results of Secs. III A and III B.

In Table III, the predicted first ionization energies of the neutral centers and the $1s$-state energies of the singly ionized centers of Se, Te, and Po in silicon are given. The predicted results show that the $1s(A_1)$ donor states of Se and Po are in the valence band (energy band gap of silicon equal to 1.12 eV) and would always be occupied. They form resonance states in the valence band. No experimental data are available for comparison with the predicted results.

It is evident that this procedure can be extended to group-VII triple donors. A similar procedure may also be applied to holes bound to the deep-level acceptor impurities, such as group-II double acceptors Zn, Cd, and Hg and group-I triple acceptors such as Cu, Ag, and Au, by using the impurity potentials of the group-III shallow-level acceptor impurities Ga, In, and Tl, respectively.

IV. ELECTRIC-DIPOLE MATRIX ELEMENTS

With the trial wave functions obtained in the variation calculation of the energies, the electric-dipole matrix elements for singly ionized sulfur centers in silicon have been calculated. The results are given in Table IV. These values may be used to estimate the intensities of the absorption lines from the equation[37]

$$\int \sigma_{i\to f}(\hbar\omega)\,d\hbar\omega = \left[\left(\frac{E_{\mathrm{eff}}}{E_0}\right)^2 \frac{n}{\epsilon}\right]\frac{4\pi^2\alpha}{3} \times \hbar\omega_{if}\left|\langle f|r|i\rangle\right|^2 \ , \qquad (4.1)$$

where n is the optical index of refraction, ϵ is the optical dielectric constant, E_{eff}/E_0 is the effective electric-field ratio at the trap center, and $\alpha = e^2/\hbar c$ is the fine-structure constant. No experimental data are available for comparison. However, by using an effective field ratio of $(E_{\mathrm{eff}}/E_0) = 2$ for the $1s(A_1) \to 1s(T_2)$ transition and a ratio of $(E_{\mathrm{eff}}/E_0) = 0.5$ for the $1s(A_1) \to 2p$ and $1s(A_1) \to 3p$ transitions, we were able to match the observed photothermal ionization spectrum of electrons from singly ionized sulfur in silicon very well.[27] Such effective field ratios are not unreasonable in view of the many approximations involved in calculating the electric-dipole matrix elements.

V. SOME POSSIBLE SOURCES OF CORRECTIONS FOR DEEP LEVELS

A. Effect of the Δ_5 Valence Band

It has long been recognized that for deep-level

TABLE IV. Matrix elements $|\langle f|\vec{r}|i\rangle|^2$ for singly ionized sulfur centers in silicon. The effective Bohr radii of the s states are from variational energy calculations, while those of the p states are assumed to be $(\epsilon/2)(m_0/m^*) = 19.5$ a.u.

Transition	$\lvert\langle f\lvert\vec{r}\rvert i\rangle\rvert^2$ (10^{-16} cm^2)
$1s(A_1) \to 1s(T_2)$	4.23×10^{-3}
$1s(A_1) \to 2s(T_2)$	1.23×10^{-4}
$1s(A_1) \to 2p_0(T_2)$	0.633
$1s(A_1) \to 2p\pm(T_2)$	1.26
$1s(A_1) \to 3p_0(T_2)$	0.199
$1s(A_1) \to 3p\pm(T_2)$	0.398

impurities the one-band effective-mass approximation breaks down. Several attempts have been made to take into consideration the effects of both the conduction band and the valence band.[16,17] Analysis of the equation in the two-band approximation indicates that, depending on the details of the impurity potential, some impurity centers can capture both electrons and holes simultaneously.[16,17] However, because of the complexity of a two-band approximation, no quantitative results have been obtained even in the simplest band-structure model. Nevertheless, we could give a rough estimate of the effect of the valence band on the energy and the wave function by following the analysis of Kohn.[1] Again, we shall take singly ionized sulfur as a specific example of a deep-level donor.

Let $F_c(\vec{k})$ and $F_v(\vec{k})$ be the wave-function components from the conduction band and the valence band, respectively. Then, $F_v(\vec{k})$ is given approximately by[38]

$$F_v(\vec{k}) = -\frac{1}{E_v(\vec{k})-E}\sum_{\vec{k}'}\langle v\vec{k}|U|c\vec{k}'\rangle F_c(\vec{k}') . \tag{5.1}$$

Now,

$$\langle v\vec{k}|U|c\vec{k}'\rangle = \int d^3r\, u^*_{vk}e^{-i\vec{k}\cdot\vec{r}}\,U u_{ck'}e^{i\vec{k}'\cdot\vec{r}} , \tag{5.2}$$

and the periodic function $u^*_{vk}u_{ck'}$ may be expanded in the form

$$u^*_{vk}u_{ck'} = \sum_{\vec{G}\neq 0} C(\vec{G})e^{i\vec{G}\cdot\vec{r}} , \tag{5.3}$$

where $\vec{G}$ is a reciprocal-lattice vector. There is no $\vec{G}=0$ component in Eq. (5.3) because of the orthogonality of the valence- and conduction-band states. Assuming that only one component of $\vec{G}$ is important, then (5.2) and (5.3) give

$$\langle v\vec{k}|U|c\vec{k}'\rangle \simeq C(\vec{G})\,U(\vec{G}+\vec{k}'-\vec{k}) , \tag{5.4}$$

where $U(\vec{k})$ is the Fourier transform of $U(\vec{r})$. Substituting (5.4) into (5.1) and making the substitution of $\vec{k}''=\vec{G}+\vec{k}'$, we obtain

$$F_v(\vec{k}) = -\frac{C(\vec{G})}{E_v(\vec{k})-E}\sum_{\vec{k}''}U(\vec{k}''-\vec{k})F_c(\vec{k}'')\frac{F_c(\vec{k}''-\vec{G})}{F_c(\vec{k}'')} . \tag{5.5}$$

Since $F_c(\vec{k}) \sim [1+a^{*2}k^2]^{-2}$, where a^* is the effective Bohr radius of the ground state, the ratio $F_c(\vec{k}''-\vec{G})/F_c(\vec{k}'')$ is of the order of $[a^*G]^{-4}$. Therefore, in order of magnitude, Eq. (5.5) is given by

$$F_v(\vec{k}) \simeq -\frac{1}{E_v(\vec{k})-E}\,\frac{C(\vec{G})}{[a^*G]^4}\sum_{\vec{k}''}U(\vec{k}''-\vec{k})F_c(\vec{k}'') . \tag{5.6}$$

Since the potential energy is of the same order of magnitude as the ionization energy, we may further approximate the sum in (5.6) by

$$\textstyle\sum_{\vec{k}''}U(\vec{k}''-\vec{k})F_c(\vec{k}'') \simeq E_I F_c(\vec{k}) . \tag{5.7}$$

Finally, (5.6) and (5.7) give

$$\left|\frac{F_v(\vec{k})}{F_c(\vec{k})}\right| \simeq \frac{C(\vec{G})E_I}{[E_v(\vec{k})-E][a^*G]^4} . \tag{5.8}$$

Taking the values of $E_I = 0.61$ eV and $a^* = 7.3$ a.u. for singly ionized sulfur, $E_v(k)-E \simeq 4.0-0.61$ eV for $\vec{k}=(0.85, 0, 0)2\pi/a$,[39] where a is the lattice constant of silicon, and assuming $C(\vec{G}) \simeq 1.0$ and $G \simeq 2\pi/a$, we obtain $(F_v/F_c) = 4.5\times10^{-4}$. Therefore, for singly ionized sulfur in silicon, where the ground-state level lies about midway between the conduction-band and valence-band edges, the wave-function component from the valence band is small compared with that from the conduction band. This offers an explanation of the observation by Rosier and Sah[31] that the thermal emission rate of electrons is much larger than that of holes. The effect of the valence band on the ground-state energy is to shift it upward by $(F_v/F_c)^2 = (2\times10^{-5})\%$, which is very small.

B. Effect of the $\Delta_{2'}$ Conduction Band

In general, the inclusion of wave-function components from the higher-energy conduction bands has the effect of lowering the ground-state energy calculated using only wave-function components from the Δ_1 valleys. For silicon, $E(\Delta_1)-E(\Delta_{2'}) = 0.50\pm0.05$ eV at $\vec{k}=(0.85, 0, 0)2\pi/a$.[40] This is comparable to the ground-state energies of most deep-level impurities. Therefore, one would expect the coupling between the Δ_1 and the $\Delta_{2'}$ bands to be appreciable for the deep-level impurities. Using Eq. (5.8), with the subscript v replaced by $\Delta_{2'}$, we obtain $(F_{\Delta_{2'}}/F_{\Delta_1}) = 1.7\times10^{-4}$ for singly ionized sulfur in silicon, indicating that the effect of the $\Delta_{2'}$ band is also very small.

VI. SUMMARY

It was suggested that the impurity potentials of the shallow-level group-V donors may be scaled to give the model impurity potentials of the deep-level group-VI donors of the same row in the Periodic Table. By extending the multivalley EMA to include singly ionized sulfur centers in silicon, it was found that the model impurity potential of sulfur is indeed essentially identical to that obtained by scaling the model impurity potential of phosphorus.

It was also suggested that the same ideas may be applied to holes bound to deep-level acceptor impurities, by scaling the impurity potentials of the shallow-level group-III acceptors.

A heliumlike model in the multivalley EMA was also developed and applied to the two-electron neutral group-VI donors in silicon. Dielectric screening was included in the electron-electron interaction energy. The calculated energies of neutral sulfur agree well with the experimental thermal activation energies.

Using the scaled impurity potentials of As, Sb, and Bi, the energy levels of substitutional Se, Te, and Po in silicon were predicted.

The contribution from the Δ_5 valence band and the $\Delta_{2'}$ conduction band to the wave function and energy of the deep-level donors was discussed. For the case of singly ionized sulfur in silicon, the effects of the Δ_5 valence band and the $\Delta_{2'}$ conduction band were found to be small compared with the Δ_1 conduction band.

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