

VI-5. Chemical Shifts of Shallow Donor Levels in Silicon

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The ground state energies of P, As and Sb donors in Si have been investigated theoretically by taking account of the dielectric screening of the impurity potential, the detailed behaviors of the wave functions at the conduction band minima, and the local distortion of the conduction band produced by the donor. It is shown that the doublet $1s(E)$ and the triplet $1s(T_1)$ are not degenerate, the former being above the latter for all donors. Agreements between the calculated energy levels and the recent observations are fairly good except for the $1s(A_1)$ states of P and Sb donors.

§ 1. Introduction

Energies of the ground states of shallow impurity levels in Si and Ge depend on the kind of the impurity atom.¹⁻³⁾ These chemical shifts cannot be explained by the effective mass theory (EMT)¹⁾ which predicts the same ground state energy irrespective of the kind of the impurity atom. Many attempts have been made to explain the chemical shifts by improving EMT without satisfying success so far.⁴⁻⁹⁾ It is the purpose of the present paper to explain the chemical shifts of the ground states of P, As and Sb donors in Si by taking account of the k -dependent dielectric screening of the donor potential, the detailed behaviors of the wave functions at the conduction band minima, and strain field produced by the donor.

§ 2. Basic Formulation

When one of the atoms in an otherwise perfect silicon crystal is replaced by a singly ionized impurity atom of Group V, the Hamiltonian for an excess electron is given by

$$H = (p^2/2m) + U(r) + \mathcal{V}_d(r), \quad (1)$$

where $U(r)$ is the periodic potential of the perfect silicon crystal and $\mathcal{V}_d(r)$ is the effective impurity potential which was introduced in a previous paper¹⁰⁾ on the basis of the many electron treatment. Here $\mathcal{V}_d(r)$ has the following properties:

$$\mathcal{V}_d(r) \equiv \int \frac{dk}{(2\pi)^3} \frac{v_d(k)}{\epsilon(k)} e^{ik \cdot r} \rightarrow \begin{cases} (Z_d - Z_{Si})(-e^2/r), & (r \rightarrow 0), \\ (1/\epsilon^{(0)})(-e^2/r), & (r \rightarrow \infty), \end{cases} \quad (2)$$

$$(2')$$

where $v_d(k)$ is the Fourier transform of the unscreened impurity potential, $\epsilon(k)$ is the wave-number-dependent dielectric function of Si,¹¹⁾ $\epsilon^{(0)}$ is the macroscopic dielectric constant, and Z_d and Z_{Si} are the atomic numbers of the donor and silicon atoms, respectively. Detailed investigation shows that¹²⁾ $\mathcal{V}_d(r)$ can be replaced by the asymptotic form (2') for $r > r_0$, where r_0 is of the order of the nearest neighbor distance. Thus our Schrödinger equation may be reduced to

$$[-(\hbar^2/2m)\nabla^2 + U(r) - (e^2/\epsilon^{(0)}r)]\phi = E\phi, \quad r \geq r_0, \quad (3)$$

$$[-(\hbar^2/2m)\nabla^2 + U(r) + \mathcal{V}_d(r)]\phi = E\phi, \quad r < r_0. \quad (4)$$

Let us consider one of the ground states of the system (3) and (4) with α -symmetry, where α is A_1 or T_1 and or E . It can be shown from EMT¹⁾ that the solution of eq. (3) with α -symmetry is given by

$$\phi^\alpha(r) = \sum_{i=1}^6 C_i^\alpha F^{(i)}(r) \phi_{k_i}(r), \quad r \geq r_0, \quad (5)$$

where $\phi_{k_i}(r)$ is the Bloch function at the i th of the six equivalent conduction band minima. Here $F^{(i)}(r)$ is the solution of the effective mass equation (EME) at the i th minimum which satisfies the boundary condition at infinity and has the energy parameter $\mathcal{E} = E - E_0$ relative to the bottom of the conduction band E_0 . In eq. (5) C 's are the numerical constants depending on the symmetry character α . In what follows, we approximate $F^{(i)}(r)$ by a spherically symmetric function. Then we may write eq. (5) as

$$\phi^\alpha(\mathbf{r}) \simeq F(r) \sum_i C_i^\alpha \phi_{k_i}(\mathbf{r}) \equiv F(r) \phi_0^\alpha(\mathbf{r}), \quad r \geq r_0, \quad (6)$$

where $F(r)$ satisfies the simple hydrogenic equation with an appropriate average mass m^* :

$$[-(\hbar^2/2m^*)\nabla^2 - (e^2/\epsilon^{(0)}r)]F(r) = \mathcal{E} F(r), \quad r \geq r_0. \quad (7)$$

Here ϕ_0^α satisfies the unperturbed Schrödinger equation of the silicon crystal:

$$[-(\hbar^2/2m)\nabla^2 + U(r)]\phi_0^\alpha = E_0 \phi_0^\alpha. \quad (8)$$

From eqs. (4) and (8) we obtain

$$\phi_0^\alpha \nabla^2 \phi^\alpha - \phi^\alpha \nabla^2 \phi_0^\alpha = (2m/\hbar^2)[\mathcal{V}_d - \mathcal{E}]\phi_0^\alpha \phi^\alpha. \quad (9)$$

Let us expand ϕ_0^α and ϕ_0 as

$$\left. \begin{aligned} \phi_0^\alpha &= \sum_l (R_l^\alpha(r)/r) K_l^\alpha(\theta, \phi), \\ \phi^\alpha &= \sum_l (\tilde{R}_l^\alpha(r)/r) K_l^\alpha(\theta, \phi), \end{aligned} \right\} \quad (10)$$

where $K_l^\alpha(\theta, \phi)$ is the l th cubic harmonics¹³⁾ with α -symmetry. Since we have assumed that $F(r)$ is spherically symmetric, it follows from eqs. (6) and (10) that

$$d \ln F(r)/dr = d \ln \tilde{R}_l^\alpha/dr - d \ln R_l^\alpha/dr, \quad (11)$$

for arbitrary l and α . Accordingly, we can show that, from eqs. (9), (10) and (11),

$$\left\{ \frac{d \ln F(r)}{dr} \sum_l R_l^\alpha \tilde{R}_l^\alpha \right\}_{r=r_0} = \frac{2m}{\hbar^2} \int_0^{r_0} [\mathcal{V}_d - \mathcal{E}] \sum_l R_l^\alpha \tilde{R}_l^\alpha dr, \quad (12)$$

where we have assumed that $\mathcal{V}_d(r)$ is well approximated by a spherical potential.¹²⁾

The solution of eq. (4) in the interior region should be orthogonal to the core states of the donor which replaces a silicon atom. Therefore we assume that the correct solution in this region has the form of

$$\phi^\alpha(\mathbf{r}) = f(r) \phi_0^{\alpha'}(\mathbf{r}),$$

where $f(r)$ is some envelope function and

$$\begin{aligned} \phi_0^{\alpha'}(\mathbf{r}) &= \sum_i C_i^{\alpha'} \phi_{k_i}'(\mathbf{r}), \\ \phi_{k_i}' &= \phi_{k_i} + \sum_\lambda (\phi_\lambda, \phi_{k_i}) \phi_\lambda - \sum_\nu (\phi_\nu, \phi_{k_i}) \phi_\nu, \end{aligned} \quad (13)$$

where ϕ_λ and ϕ_ν are the core states of the silicon and the donor at the donor site, respectively. Since we may reasonably assume that $f(r)$ is a spherical and gentle function over the interior region, we get finally

$$\begin{aligned} &\left[\frac{d \ln F(r)}{dr} \right]_{r=r_0} \\ &= \frac{2m}{\hbar^2} \int_0^{r_0} [\mathcal{V}_d - \mathcal{E}] \sum_l R_l^\alpha R_l^{\alpha'} dr / \left[\sum_l R_l^\alpha R_l^{\alpha'} \right]_{r=r_0}, \end{aligned} \quad (14)$$

where $R_l^{\alpha'}$ is defined by

$$\phi_0^{\alpha'}(\mathbf{r}) = \sum (R_l^{\alpha'}/r) K_l^\alpha(\theta, \phi).$$

We can evaluate the left-hand side of eq. (14) by solving EME of eq. (7) with $\mathcal{E}$ as a parameter and the right-hand side by integrating numerically with the knowledges of $\mathcal{V}_d(r)$, $\phi_{k_i}(r)$ and the core states. The energy $\mathcal{E}$ is determined so as to equate the both sides of eq. (14)

§ 3. Effect of Strain Field^{5,7)}

Let us consider a spherical cavity with the radius $2r_{\text{cov}}(\text{Si})$ in the silicon lattice which is regarded as an elastically homogeneous medium, where $r_{\text{cov}}(\text{Si})$ is the tetrahedral covalent radius¹⁴⁾ of Si atom. Then we suppose that an impurity in an otherwise perfect silicon crystal is equivalent to a sphere of the same medium with the radius $(r_{\text{cov}}(\text{Si}) + r_{\text{cov}}(\text{donor}))$ squeezed into the cavity,* where $r_{\text{cov}}(\text{donor})$ is the covalent radius of the donor atom. In this model, the sphere is uniformly compressed or expanded to the radius $(1 + \delta)(2r_{\text{cov}}(\text{Si}))$ with

$$\delta = (3C_{11} - 4C_{44}/3C_{11}) \Delta r_{\text{cov}} / 2r_{\text{cov}}(\text{Si}),$$

where $\Delta r_{\text{cov}} = r_{\text{cov}}(\text{donor}) - r_{\text{cov}}(\text{Si})$ and C 's are the elastic constants of the medium. Using the values of C_{11} and C_{44} for Si,¹⁵⁾ one obtains a correction to $\mathcal{V}_d(r)$ from the uniformly deformed sphere:

$$\begin{aligned} \Delta \mathcal{V} &= E_1 \times 3 \times 0.63 \times [\Delta r_{\text{cov}} / 2r_{\text{cov}}(\text{Si})] \\ &\quad + O\{(\Delta r_{\text{cov}})^2\}, \end{aligned} \quad (15)$$

where E_1 is the band-edge shift per unit change of volume given by $E_1 = \mathcal{E}_d + (1/3)\mathcal{E}_u$.¹⁶⁾

§ 4. Numerical Calculation and Discussions

As for the core wave functions, we assume the orthonormalized set of the functions,

$$\phi_{ns}^0 = r^{n-1} \exp[-(Z - \sigma_n)/n]r,$$

where the screening constants are listed in Table I. The Bloch functions were calculated¹¹⁾ by the pseudo-potential method. The value of $\epsilon^{(0)}$ of Si is 11.7.¹⁷⁾ The effective mass m^* ($=0.292 m_0$)

* Strictly speaking, the elastic property of the sphere is somewhat different from that of the medium.

in eq. (7) was so determined that the calculated lowest eigenvalue of EME satisfied by $F^{(i)}(r)$ (-29 meV) should be equal to that of eq. (7) with $r_0=0$.

The screened impurity potentials $\mathcal{V}_d(r)$ for P, As and Sb donors are shown in Fig. 1.¹²⁾

Table I. Effective screening constants in atomic units so determined as to give the best fit to the Hartree-Fock calculation.

Element	1s	2s	3s	4s
Si	0.64	3.38		
P	0.64	3.38		
As	0.646	3.874	10.73	
Sb	0.64	4.0	10.8	20.74

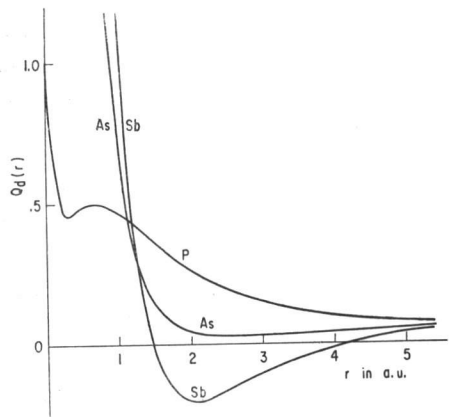


Fig. 1. The spatial dependence of the screened donor potential for P, As and Sb donors. Here $Q_d(r)$ is defined by

$$\mathcal{V}_d(r) = (-e^2/r)Q_d(r).^{12)}$$

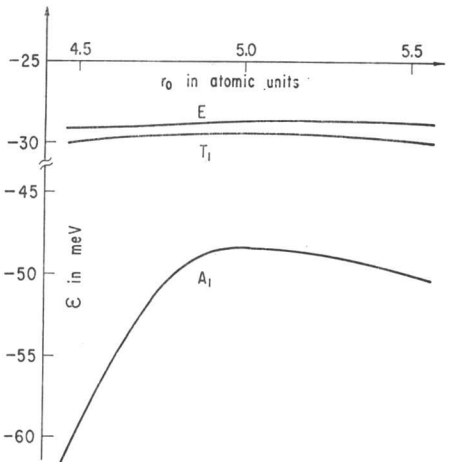


Fig. 2. The r_0 -dependence of the calculated energies of the ground states $1s(A_1)$, $1s(T_1)$ and $1s(E)$ of As donor taking account of the radial functions up to $l=6$.

Since the tetrahedral covalent radius of As is nearly equal to that of Si,¹⁴⁾ the effect of the strain field may be neglected in the case of As donor. The energies of the ground states $1s(A_1)$, $1s(T_1)$ and $1s(E)$ of As donor are calculated as functions of r_0 , by taking account of the radial functions up to $l=6$, and are shown in Fig. 2.

It is seen from Fig. 2 that the energy of the $1s(A_1)$ depends somewhat strongly on r_0 for r_0 much smaller than 5 a.u., while it becomes insensitive to r_0 near, and larger than, 5 a.u. This situation may be explained as follows. If we could treat the whole problem exactly, the calculated energies must be independent of a choice of the joining point r_0 . However, since we have assumed that the potential in the exterior region is given by $-e^2/\epsilon^{(0)}r$, a choice of a too small value of r_0 results in an appreciable change in the potential and the smaller r_0 becomes, the more such a change is pronounced. The weak r_0 -dependence of the energy of the $1s(A_1)$ for larger r_0 may be attributed to the neglect of higher harmonics. In what follows, we calculate the energy spectra by taking up to the sixth harmonics in the ex-

Table II. Calculated and optically observed⁸⁾ ionization energies of the ground states $1s(A_1)$, $1s(T_1)$ and $1s(E)$ of P, As and Sb donors in Si (in meV).

State	P		As		Sb	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$1s(A_1)$	38.	45.31	48.	53.51	50.	42.51
$1s(T_1)$	30.4	33.69	29.4	32.42	28.8	32.67
$1s(E)$	29.2	32.36	28.6	31.01	27.8	30.37

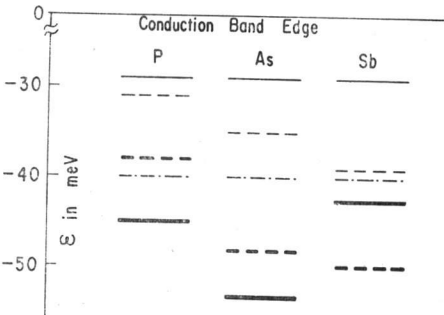


Fig. 3. The energies of the lowest ground state $1s(A_1)$ of P, As and Sb donors obtained by several authors. Experiment⁸⁾ (heavy solid line), Calculated (heavy dashed line), EMT (solid line), Csavinsky⁸⁾ (dashed line), and Müller⁹⁾ (chained line).

pansion of ϕ_0 and ϕ_0' and choosing $r_0=5$ a.u. as a joining point, which is somewhat larger than was hitherto considered.^{4,9)}

Kawamura *et al.*¹⁸⁾ have obtained the values of E_u and E_d from the anisotropy of carrier scattering in their cyclotron resonance experiment on Si ($E_u=8.50$ eV, $E_d=-5.2$ eV), which give $E_1=-2.37$ eV.

The energies obtained for the $1s(A_1)$, $1s(T_1)$ and $1s(E)$ states of P, As and Sb donors are listed in Table II together with the optically observed values.³⁾ The results for the lowest ground states $1s(A_1)$ are compared with the results obtained by other authors in Fig. 3.

The agreement between the calculated and observed energies is rather satisfactory, especially for all the states of As donor and for the excited states of P and Sb donors. The order of the $1s(A_1)$, $1s(T_1)$ and $1s(E)$ levels are consistent with the recent observation by Aggarwal and Ramdas.³⁾ The still remaining discrepancies, in particular for the $1s(A_1)$ states of P and Sb donors may come mainly from the following sources. (a) There is a little question on applying the deformation potential theory to such a short range strain field inside the donor sphere. (b) We have ignored the influence of the strain field outside the donor sphere. (c) The k -dependent dielectric function, $\epsilon(k)$, involved in the screened impurity potential $\mathcal{V}_d(r)$ (see eq. (2)) was obtained¹¹⁾ in the so-called bubble approximation. However, the unperturbed donor potential for Sb donor is rather strong. Therefore there is a little doubt on applying our dielectric function to the heavy donor such as Sb.

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DISCUSSION

Ramdas, A. K.: Can your theory account for the "inverted" ground state structure for the case of "isolated" interstitial lithium donors in silicon? Your calculations are the first successful attempt to predict the "species-dependent" chemical splittings of the $1s$ ground state of shallow donors. Hence an extension of these calculations to the case of lithium would be of great value.

Nara, H.: We have a plan to treat the interesting problem of the level structure of the ground state of lithium donor in silicon. We hope that we can account for the problem along the same lines as the present investigation.

Shimizu, T.: Dr. Weinreich calculated the effect of shear strain around the impurity on the chemical shift, and Dr. Narita and I improved their results and found that the effect is very little. Do you also think that the effect is very little?

Nara, H.: We have noticed your investigation⁷⁾ on the effect of the strain field outside the donor sphere, to find that the effect is very small. We have ignored the effect outside the donor sphere.

Tolpygo, K. B.: In what way have you obtained the repulsive potential for antimony

in silicon? Why is the factor $Q_d(r)$ for antimony negative at $2.8 < r < 5$ a.u.?

We (myself with T. Kutcher) have calculated the dielectric constant ϵ in Ge at the distances which are comparable with the lattice constant d . $\epsilon(r)$ tends to ϵ_0 at $r \gg d$ (but not to 1, if $r=d$), and is highly anisotropic at $r \sim d$, $2d$, and even $3d$. (The calculation was made for directions of $r || \langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$). The calculation is based on the lattice dynamic theory of Ge, and takes into account the polarization of each Ge atom under the influence of the field of two charges e_1 and e_2 (the distance of which is r) and the dipole-dipole interaction. This work was briefly reported at the Conference of the Theory of Semiconductors in Tartu, USSR, June 27—July 2, 1966 (Abstracts in Uspekhi fiz. Nauk).

Morita, A.: One of the present authors (H. Nara¹¹⁾) has calculated the k -dependent dielectric function, $\epsilon(k)$, of Si along the three directions of k , namely along $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$. This result shows that the anisotropy of $\epsilon(k)$ is not so serious. The detailed discussion of $Q_d(r)$ is given in ref. 12). $Q_d(r)$ consists of two parts. One of them comes from the nuclear charge of the donor atom and the other from the core charge cloud of the donor atom. The former contribution is always positive, while the latter is negative. If $\epsilon(k)$ were independent of k , $Q_d(r)$ will be always positive. However, if we take account of the k -dependence of the dielectric function, the latter contribution is enhanced compared with the former in the range of r which you mentioned. Such an effect becomes more significant for heavier donor atoms. So we obtained the behavior of $Q_d(r)$ shown in Fig. 1.