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Central-cell and screening effects on the binding energies of neutral chalcogen impurities in silicon

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The binding energies of D^0 states in S-, Se-, and Te-doped silicon crystals are calculated within a variational scheme in the effective-mass approximation and with a Chandrasekhar-type variational function for the two-electron envelopes. Central cells are modeled with a constant core potential within the impurity sphere. Screening effects for the potential and the electron-electron interaction are taken into account by means of a position-dependent dielectric function. Results are compared with recent theoretical and experimental work. It is found that central-cell effects and position-dependent screening are essential to account for the experimental data.

Recent photoconductivity spectra and high-resolution absorption experiments on chalcogen double donors (S, Se, and Te) in silicon[1,2] have provided very detailed information on the energy structure of these deep centers. This note is concerned essentially with the D^0 and D^+ centers, i.e., neutral and singly ionized states of an isolated chalcogen in a substitutional tetrahedral position in silicon. Because the silicon conduction band has six minima along the $\langle 100 \rangle$ directions and the symmetry of the impurity is tetrahedral (T_d point-group symmetry) the ground-state manifold splits into a ground-state singlet $1s(A_1)$ and excited triplet $1s(T_2)$ and doublet $1s(E)$ components. The central-cell potential responsible for this splitting is important only for the ground-state $1s$ multiplet; the excited states, in particular the optically accessible p states, are well described by the effective-mass (hydrogenic) model.[3]

Because of the ever-improving experimental techniques there is considerable information available on the ground-state energies of deep states in semiconductors. Theoretical progress, on the other hand, has been rather slow: Full many-body calculations of the ground-state binding energy remain a formidable numerical task,[4,5] even for single shallow donors and acceptors. For the chalcogens in silicon several approximation and model calculations have been published in the last few years.[6–10] The accuracy and reliability of the various approximations have been repeatedly challenged and are not yet unambiguously established. Physically simple models still retain their fundamental importance in clarifying the various aspects of deep-level spectroscopy in semiconductors.

Recently, Lee, Dow, and Sankey[10] employed a Green's-function method and an empirical tight-binding basis to determine self-consistently the energies of the deep-level chalcogens. They obtained values of 0.24 eV (S), 0.23 eV (Se), and 0.20 eV (Te) for the binding energy of the first electron (the A_1-symmetry states of the D^+ center) compared with the experimental values of 0.61 eV (S), 0.59 eV (Se), and 0.41 eV (Te). The binding energy of D^0, i.e., the energy obtained in binding the second electron, was found to be 0.01 eV in the calculation for all three chalcogens, whereas the experimental values[2] are 0.32 eV (S), 0.31 eV (Se), and 0.20 eV (Te). It should be noted that the *differences* in binding energies between D^+ and D^0 in all three cases are in reasonable agreement with experiment.

In this Brief Report a model calculation of the binding energies of all three D^0 states in Si is presented. A variational scheme within the effective-mass approximation is employed. The two-electron model Hamiltonian for the envelope function is given by

$$H=\sum_i [(-\hbar^2/2m^*)\nabla_i^2+V(r_i)]+e^2/[r_{12}\epsilon(r_{12})] \ , \quad (1)$$

with an Abarenkov-Heine–type[11] impurity potential

$$V(r)=\begin{cases} A, & r<R_c \ , \\ -2e^2/[r\epsilon(r)], & r>R_c \ , \end{cases} \quad (2)$$

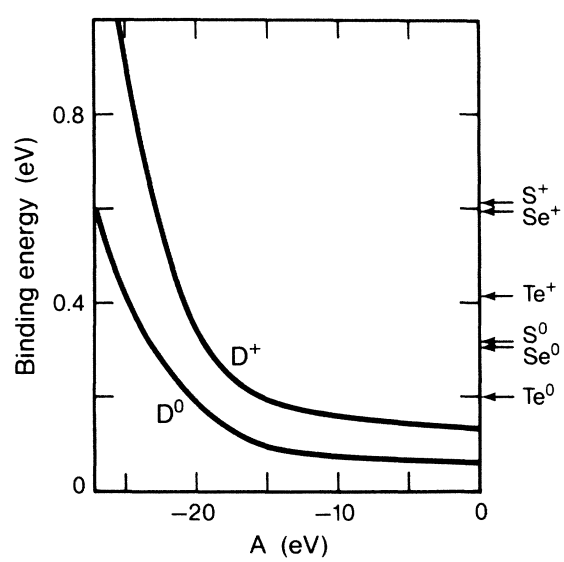

FIG. 1. Calculated binding energies of D^+ and D^0 states in chalcogen-doped silicon as functions of the depth of the central-cell impurity potential. The results were obtained with a position-dependent dielectric function and a screening parameter which fits the dielectric function of Wang and Kittel (Ref. 12), and Walter and Cohen (Ref. 13). Arrows on the right side of the diagram indicate the experimental values of Ref. 2.

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TABLE I. Binding energies of neutral D^0 states in silicon (all energies in eV).

	S^0	Se^0	Te^0
Pantelides[a]	0.41	0.27	0.11
Pantelides and Sah[b]	0.33	0.36	0.07
Bernholc, Lipari, Pantelides, and Scheffer[c]	0.25	. . .	. . .
Singh, Lindelfelt, and Zunger[d]	0.29	0.26	. . .
Lee, Dow, and Sankey[e]	0.01	0.01	0.01
Oliveira and Falicov (this work)	0.29	0.28	0.21
Experiment[f]	0.32	0.31	0.20

[a]Reference 6.
[b]Reference 7.
[c]Reference 8.
[d]Reference 9.
[e]Reference 10.
[f]Reference 2.

and a position-dependent dielectric function[12]

$$1/\epsilon(r) = (1/\epsilon_0) + [1-(1/\epsilon_0)]\exp(-r/a) \quad . \tag{3}$$

The average effective mass $m^* = 0.2987$ and the silicon dielectric constant $\epsilon_0 = 11.4$ yield[3] an effective Rydberg constant $R_H^* = m^* e^4/2\epsilon_0^2\hbar^2 = 31.27$ meV. The radius $R_c = 2.22$ a.u., taken to be half the nearest-neighbor Si distance, defines a "central-cell region." The screening parameter $a = 1.09$ a.u. is chosen, following Wang and Kittel,[12] so that the Fourier transform of (3) fits the dielectric function of Walter and Cohen.[13]

The trial envelope function for D^0 is assumed to be of the Chandrasekhar type,[14]

$$\Psi(D^0) = [\exp(-\xi_1 r_1 - \xi_2 r_2) + \exp(-\xi_1 r_2 - \xi_2 r_1)](1+\lambda r_{12}) \quad , \tag{4}$$

where the variational parameter λ takes electron-electron correlation into account. The parameters ξ_1, ξ_2, and λ are chosen optimally so that the total energy $E(D^0) = \langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$ is minimized.

For the singly ionized D^+ state, a single-electron problem, the Hamiltonian is

$$H = (-\hbar^2/2m^*)\nabla^2 + V(r) \quad , \tag{5}$$

and the envelope trial function is $\phi = (\xi^3/\pi)^{1/2}\exp(-\xi r)$.

Figure 1 shows the results for the binding energies as functions of the central-cell parameter A of Eq. (2). Qualitative agreement with the experimental values is obtained for 20 eV $\leq |A| \leq$ 24 eV. If the values of A are chosen so as to fit the binding energies of the singly ionized D^+ states—0.61 eV, $A = -23.03$ eV for S^+; 0.59 eV, $A = -22.87$ eV for Se^+; and 0.41 eV, $A = -21.09$ eV for Te^+—the results for the binding energies of the two-electron D^0 states are 0.29 eV for S^0, 0.28 eV for Se^0, and 0.21 eV for Te^0, in good agreement with the experimental values of 0.32, 0.31, and 0.20 eV, respectively. Results of various model calculations of the D^0 binding energies are shown in Table I.

TABLE II. Influence of the position-dependent dielectric function in the binding energies of the D^0 centers (all energies in eV).

	Constant $\epsilon = \epsilon_0$	Position-dependent $\epsilon = \epsilon(r)$
S^0	0.40	0.29
Se^0	0.39	0.28
Te^0	0.28	0.21

Table II clearly shows the importance of using a position-dependent dielectric function, as opposed to the pure silicon dielectric constant. The correction is of the order of 30%, a substantial change.

The value of the impurity core R_c, on the other hand, is not so crucial. Calculations were carried out with values of R_c between ≈ 2.0 a.u. and ≈ 2.5 a.u., with only small changes resulting in the binding energies of D^0. For S^0, for example, the binding energy varied between 0.29 and 0.30 eV.

In conclusion, a simple model calculation (i) within the effective-mass approximation, with (ii) a central-cell constant potential, and (iii) a position-dependent dielectric constant, and by means of (iv) a Chandrasekhar-type variational function produces results in good agreement with experiment. In order to account for the experimental values it is important that all first-principles calculations include, in addition to good silicon basis functions, a good impurity potential and, above all, a realistic nontrivial screening of both the impurity potential and the electron-electron interaction.

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