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Multivalley spin splitting of 1s states for sulfur, selenium, and tellurium donors in silicon

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Spin-valley splitting of the 1$s(T_2)$ states of the ionized chalcogen donors S^+, Se^+, and Te^+ in silicon is reported. The magnitude of the splitting is shown to be related to the impurity atomic spin-orbit splitting. The data are compared with the corresponding splittings of Sb^0 and Bi^0 donor impurities in silicon. Predictions of the magnitudes of the hitherto unobserved splittings of the neutral chalcogen donors and other group-V donors are made. In addition, the binding energies of the 1$s(T_2)$ states are compared with recent calculations by Altarelli. The available data on 1s states of group-V and -VI donor impurities in silicon are discussed.

The existence of six equivalent conduction-band minima along the [100] directions in silicon has a profound influence on the energy states of donors.[1] The central-cell potentials of donor atoms occupying tetrahedral lattice sites, either substitutional or interstitial, will split a sixfold-degenerate s state into a singlet (A_1), a triplet (T_2), and a doublet (E) state (see Fig. 1). This splitting is usually referred to as valley-orbit splitting. Since the central-cell potential is very localized, the splitting is much less for excited s states than for the 1s state and negligible for $p,d,\ldots$ states. These latter states are well described by effective-mass theory (EMT).[2]

Previous investigations have shown that the ground states of all group-V and -VI donors in silicon are 1$s(A_1)$ states,[3–5] in agreement with the fact that the E and T_2 wave functions (unlike the A_1 wave function) have nodes at the impurity atom and are therefore less affected by the strong central-cell potential.

If spin is included, the symmetry representations will be changed as follows: $A_1 \rightarrow \Gamma_6$, $E \rightarrow \Gamma_8$, and $T_2 \rightarrow \Gamma_7 + \Gamma_8$. The splitting of the T_2 level is due to its "valley-induced" p character which makes an interaction with the spin possible. This spin-"pseudo-orbit" splitting is sometimes referred to as spin-valley splitting[6,7] (see Fig. 1). Owing to their different degeneracies, the Γ_8 state will be shifted less than the Γ_7 state. If spin-valley interactions were absent, the unsplit 1$s(T_2)$ state would lie at an energy of $E(T_2) = \frac{1}{3}E(\Gamma_7) + \frac{2}{3}E(\Gamma_8)$.[8] Although the 1$s(E)$ state cannot split, the 1$s\Gamma_8(E)$ state may contain admixtures of T_2 states. However, to a first approximation, spin-valley interaction does not mix 1$s\Gamma_8(E)$ states with 1$s\Gamma_8(T_2)$ states, especially when the energy separation 1$s(T_2) -$ 1$s(E)$ is large.[9]

In this paper we report on the energy position of the 1$s(A_1)$ and 1$s(T_2)$ levels for some chalcogen donors in silicon. It has been shown earlier that after certain doping procedures, sulfur, selenium, and tellurium may give rise to two dominant donors in silicon, the A and B centers.[3,10–13] Although no definite proof has yet been given, the properties of these centers are best understood in terms of isolated substitutional donors. Filled A and B centers then correspond to singly ionized (D^+) and neutral (D^0) impurity centers, respectively. The energy positions of the 1$s(A_1)$ and 1$s(T_2)$ levels in this paper are compared with both the effective mass theory[2] and recent calculations by Altarelli.[14] Furthermore, the observed doublet in infrared-absorption spectra for D^+, earlier ascribed[3,15] to the transitions 1$s(A_1) \rightarrow$ 1$s(T_2)$ and

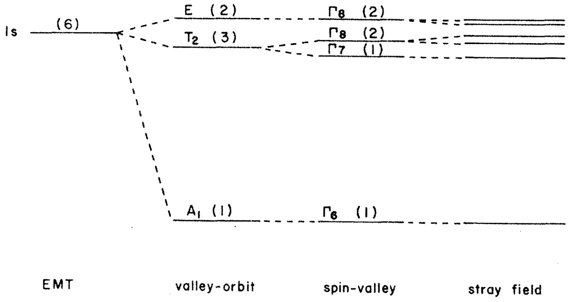

FIG. 1. Multivalley splitting of 1s donor states in silicon. The numbers in brackets are the degeneracies (excluding spin) of the states. For details, see text.

$1s(A_1)\rightarrow 1s(E)$, respectively, is interpreted as arising from transitions from the ground state to the spin-valley split $1s(T_2)$ states. The magnitude of these splittings is compared with theory and with earlier experimental results on group-V donors. Predictions for the magnitudes of the hitherto unobserved spin-valley splittings of the shallower chalcogen centers (D^0) are also made.

EXPERIMENTAL

The excited states of chalcogens in silicon have been investigated at low temperatures (~ 6 K) using a Fourier spectrometer for infrared absorption. The preparation of the samples is described in Refs. 3, 10, and 11. From the Rydberg series close to the conduction-band edge, the binding energies of the $1s(A_1)$ ground states could be determined accurately by adding the EMT value of 6.40 meV (Ref. 2) to the energies of the transitions $1s(A_1)\rightarrow 2p_{\pm}$ for the D^0 centers and 4×6.40 meV for the D^+ centers, respectively (see Figs. 2 and 3). The values obtained are in good agreement with earlier published data[3,13,15,16] except in the case of Se^+ for which our binding energy is 4 meV larger than that in Ref. 15 although the excitation energy for the $1s(A_1)\rightarrow 1s(T_2)$ transition is the same. The S^0 data have been taken from Ref. 17 and are in good agreement with values given in Refs. 11 and 13. The positions of the $1s(T_2)$ states deduced from absorption spectra are also shown in Figs. 2 and 3. The $1s(T_2)$ states of the D^+ centers in Fig. 2 are all split, the splitting increasing with increasing mass of the impurity atom (see Fig. 4). The absorption doublet of S^+ has not been reported previously.

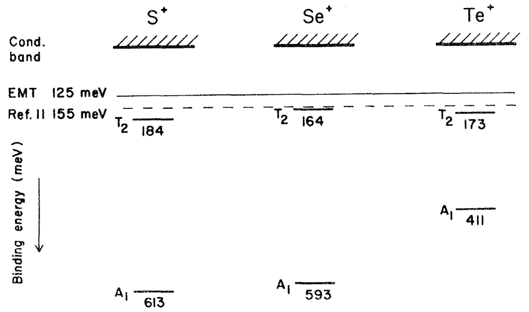

FIG. 2. Experimentally determined multivalley split $1s$ states for the A levels (D^+) in silicon doped with S, Se, or Te. The thin solid line corresponds to the $1s$ level calculated from EMT (see Ref. 2). The dashed line indicates the position of the $1s(T_2)$ level as calculated by Altarelli (see Ref. 14). The numbers give the energy distance in meV from the conduction band. The values of the $1s(T_2)$ states are the mean values of the split states Γ_7 and Γ_8: $E(T_2)=\frac{1}{3}E(\Gamma_7)+\frac{2}{3}E(\Gamma_8)$.

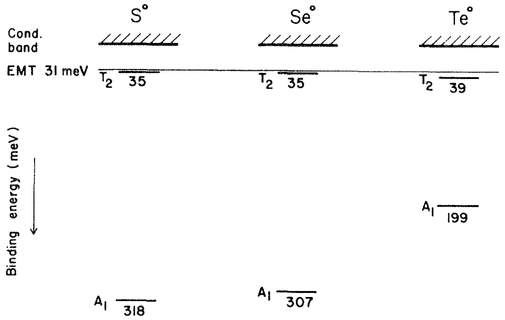

FIG. 3. Experimentally determined multivalley split $1s$ states for the B levels (D^0) in silicon doped with S, Se, or Te. The same notations as in Fig. 2 are used.

DISCUSSION

From symmetry it can be seen that the transition $1s(A_1)\rightarrow 1s(T_2)$ is allowed whereas the transition $1s(A_1)\rightarrow 1s(E)$ is forbidden. In spite of this, both

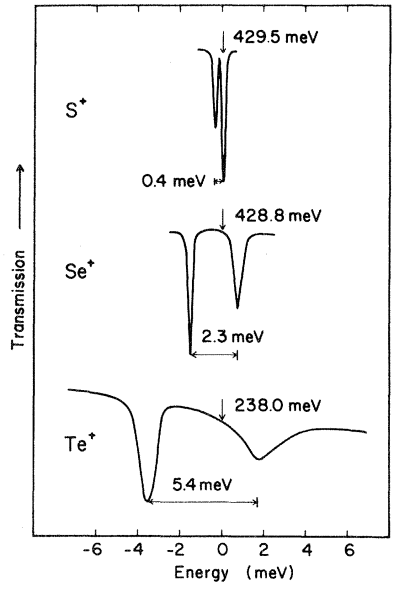

FIG. 4. Excitation spectra due to transitions from the ground states $1s(A_1)$ to the spin-valley split $1s(T_2)$ states for S^+, Se^+, and Te^+ donors in silicon. The component to the right corresponds to $1s\Gamma_8(T_2)$ and that to the left $1s\Gamma_7(T_2)$. The origin of the energy scale is the transition energy to the unsplit $1s(T_2)$ state into which the two components of the doublet would reduce if the spin-valley interaction were absent.

transitions are forbidden according to EMT since they are transitions between 1s states. For the transition $1s(A_1) \rightarrow 1s(T_2)$ to become an allowed transition, at least one of the states has to be mixed with other states, e.g., p states or states from higher-lying conduction bands or the valence band. It is found experimentally that this mixing increases with increasing binding energy of the ground state. For shallow donors[18] (43–54 meV), no transitions among 1s states have been observed in silicon. For Bi (Ref. 9) (70 meV), a very weak doublet has been detected and for some of the chalcogens[3,13] (200–610 meV) the forbidden 1s transitions are obviously as allowed as the transitions from the $1s(A_1)$ state to the p states.

For the transition $1s(A_1) \rightarrow 1s(E)$ to be allowed some random electric field or stress must exist in the crystal. However, it is unlikely that such disturbances would make the forbidden transition $1s(A_1) \rightarrow 1s(E)$ nearly as probable as the allowed transition $1s(A_1) \rightarrow 1s(T_2)$. In Refs. 3 and 15, the doublets observed for Se^+ and Te^+ in silicon (Fig. 4) were interpreted as arising from the transitions $1s(A_1) \rightarrow 1s(T_2)$ and $1s(A_1) \rightarrow 1s(E)$. Since the absorption peaks in Fig. 4 are of the same magnitude, we have strong reasons to believe that the observed doublets are due to transitions from the ground states to the spin-valley split $1s(T_2)$ states, i.e., $1s\Gamma_7(T_2)$ and $1s\Gamma_8(T_2)$. Similar splittings have earlier been reported for Bi (Ref. 9) and Sb (Ref. 18) in silicon, although in the case of Sb the split $1s(T_2)$ states could only be observed as photoexcited transitions from thermally populated initial states to p states.

It is not clear whether $1s\Gamma_7(T_2)$ or $1s\Gamma_8(T_2)$ should have the larger binding energy. However, Γ_8 corresponds to a "pseudo" $P_{3/2}$ state and Γ_7 is a "pseudo" $P_{1/2}$ state. Hund rules tell us that for a single electron the energy is lowest when the spin is antiparallel to the orbital angular momentum. If Hund rules are applicable for these kinds of "pseudo" states, Γ_8 should lie above Γ_7. It is found experimentally in Fig. 4 that the integrated absorption of the upper energy component is larger than the lower one suggesting that $1s\Gamma_8(T_2)$ with degeneracy 2 (excluding spin) has a smaller binding energy than $1s\Gamma_7(T_2)$ with degeneracy 1. If any random stress or electric field is present in the crystal, $1s\Gamma_8(T_2)$ will split (see Fig. 1) and the corresponding peak will become broader. This effect is clearly seen in Fig. 4 for Se^+ and Te^+. The upper component is considerably broader than the lower one, which indicates that $1s\Gamma_8(T_2)$ does lie above $1s\Gamma_7(T_2)$. The broadening, however, is large enough to imply some uncertainty in the magnitude of the splitting, since it cannot be taken for granted that the peak positions are not changed due to the presence of random stress or fields. By using uniaxial stress which splits the upper component into two peaks but leaves the lower component unsplit (see Fig. 1), Krag *et al.* have shown that the ordering mentioned above is correct for Bi (Ref. 9) in Si. Although the data for Sb (Ref. 18) can be interpreted in the same way, the splitting was not discussed in these terms in Ref. 18.

In Table I we have summarized all available data on 1s states for group-V and -VI impurites in silicon. It is readily seen that, although the ground state $1s(A_1)$ binding energies vary widely, the energy positions of the $1s(T_2)$ states are very similar and close to the EMT value for all D^0 centers. Only for neutral tellurium is $1s(T_2)$ slightly deeper. The deviations are larger for the ionized (D^+) chalcogens. This is not surprising since the Bohr radii for D^+ states are only about 7 Å which should be compared with 20 Å for D^0 ones. Thus, the $1s(T_2)$ states for D^+ centers are more affected by the central-cell potential than those for D^0 centers.

Altarelli[14] has recently carried out more detailed calculations of the binding energies of the excited states of an electron bound to a substitutional $+2e$ point charge in Si. The Coulomb potential used was screened by a space-dependent dielectric function $\epsilon(\bar{r})$ [$\epsilon(r) \rightarrow 11.4$ when $r \rightarrow \infty$ and $\epsilon(r) \rightarrow 1$ when $r \rightarrow 0$]. Only the six lowest equivalent conduction-band minima were included but both direct and umklapp intervalley interactions were taken into account. The binding energies obtained for the $1s(T_2)$ and $1s(E)$ states were 155 and 130 meV, respectively (see Table I). It is interesting to compare these calculations with earlier calculations by Pantelides,[19] from which binding energies of 127 meV [$1s(T_2)$] and 117 meV [$1s(E)$], were obtained when umklapp interactions were neglected. The deviation between the calculations may, however, partly be due to differing treatments of the intervalley kinetic energy.[20]

A valley-orbit splitting, $1s(T_2) - 1s(E)$, of about 25 meV is expected from Altarelli's calculations. This is much larger than the doublet splitting discussed above, in agreement with our assignment. Altarelli's calculated $1s(T_2)$ value is in fair agreement with our experimental data. If different impurity pseudopotentials had been used, even the chemical shifts could perhaps have been repro-

TABLE I. Available data on the binding energies (in meV) of 1s donor states for group-V and -VI impurities in silicon. All unlabeled data are from the present work.

	$1s(A_1)$	$1s(T_2)$	$1s\Gamma_7(T_2)-1s\Gamma_8(T_2)$ expt.	calc.	$1s(E)$	$1s(T_2)-1s(E)$
P^0	45.58[a]	33.90[c]		0.015	32.6[b] 32.57[c]	1.33[c]
As^0	53.77[a]	32.65[d]		0.086	31.5[b] 31.24[d]	1.41[d]
Sb^0	42.77[a]	32.88[c] 33.17[c]	0.29[c]	0.34	30.6[b] 30.58[c]	2.40[c]
Bi^0	71.00[a]	31.92[e] 32.92[e]	1.00[e]	1.03		
S^0	318.4[f]	35.1[f]		0.017	31.6[f]	3.5[f]
Se^0	306.7	34.5		0.13		
Te^0	198.8	39.1		0.55	31.5[g]	7.6
D^0	31.27[h] 47.5[j]	31.27[h] 31.4[j]			31.27[h] 30.6[j]	0.8[j]
S^+	613.5	183.9 184.3	0.4	0.36		
Se^+	593.3	163.7 166.0	2.3	1.6		
Te^+	410.8	171.0 176.4	5.4	6.9		
D^+	125.08[h]	125.08[h] 155[i]			125.08[h] 130[i]	25[i]

[a] From absorption measurements at 10 K in Ref. 26.
[b] From electronic Raman scattering at about 20 K in Ref. 27.
[c] From absorption measurements at 30 K in Ref. 18.
[d] From absorption measurements at 59 K in Ref. 18.
[e] From absorption measurements at 10 K in Ref. 9.
[f] From photoconductivity measurements in Ref. 17.
in Ref. 22.

duced. Furthermore, considering the depth of the energy level, it is not unreasonable to assume that wave functions originating from other bands should be taken into account. If these bands are conduction bands the binding energies would increase.

Altarelli *et al.*,[21] have recently performed similar calculations on a substitutional $+1e$ point charge in Si. Although due to insufficient screening of the extra proton these results cannot be directly related to those for neutral chalcogen donors, the data are nevertheless presented in Table I for comparison.

Recently, the $1s(E)$ states for S^0 (Ref. 17) and Te^0 (Ref. 22) have been observed in photoconductivity measurements as dips in the photoconductivity above the ionization edge. The binding energies inferred were 31.6 meV for S^0 and 31.5 meV for Te^0 (Table I). The energy positions of the $1s(E)$ states for Bi^0, Se^0, and the ionized chalcogen donors have not as yet been reported. When the transition $1s(A_1) \rightarrow 1s(T_2)$ is observed the transition $1s(A_1) \rightarrow 1s(E)$ should also be seen if the admixture of T_2 states due to spin-valley interactions is sufficiently strong. Obviously the admixture is not very large for group-V and -VI donors in silicon since the $1s(A_1) \rightarrow 1s(E)$ transition has not been observed for any of them. Using the data presented in Table I, one may anticipate that the $1s(E)$ states for Bi^0 and Se^0 probably lie 2 – 5 meV above the $1s(T_2)$ states whereas, in the case of ionized chalcogen donors the energy difference, according to Altarelli's calculations, should be at least 25 meV.

The experimentally determined spin-valley splittings vary from 0.3 meV (Sb^0) to 5.4 meV (Te^+). The magnitude of this splitting should be approximately equal to the impurity atomic spin-orbit splitting reduced by the fraction of the donor envelope wave function in the central-core region.[6] By using spin-orbit parameters and atomic radii from Ref. 23 together with Bohr radii deduced from experimentally determined $1s(T_2)$ energy positions, the spin-valley splittings could be calculated. It turned out that the calculated values were 2 – 3 times smaller than those found experimentally. The best fit between the calculated and measured results was obtained by multiplying the calculated values by 2.4 (see Table I). Although the calculations are very crude they probably predict hitherto unobserved splittings within a factor of 2. In this context it is interesting to note that unpublished calculations by Roth,[24] suggest a splitting of 0.9 meV for Bi.

As for Sb^0, the $1s(T_2)$ [and $1s(E)$] states of P^0 and As^0 were observed in photoexcitation measurements as transitions from thermally populated initial states to p states.[18] However, due to the larger binding energy of As, the measurement temperature was so high that the broadening of the linewidth made it impossible to observe the spin-valley splitting. For Se^0 and in particular Te^0 spin-valley splittings should be observable if suitable samples can be fabricated. For P^0 and S^0, on the other hand, the spin-valley splittings will probably never be observed since the predicted splittings are comparable with the natural linewidth.[25]

To summarize, we have shown that the $1s(T_2)$ states of S^+, Se^+, and Te^+ exhibit spin-valley splitting related to the atomic spin-orbit splitting of the different impurities. The binding energies of the $1s(T_2)$ states are in reasonable agreement with recent calculations by Altarelli showing that the main part of the wave function of the electron in the bound $1s(T_2)$ state originates from the six lowest equivalent minima in the conduction band. From the data presented in Table I, similar conclusions can be drawn for the $1s(T_2)$ and $1s(E)$ states of S^0, Se^0, and Te^0.

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