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VI-4. Sulfur Donors in Silicon: Infrared Transitions and Effects of Calibrated Uniaxial Stress

W. E. KRAG, W. H. KLEINER, H. J. ZEIGER and S. FISCHLER

Lincoln Laboratory, Massachusetts Institute of Technology*
Lexington, Massachusetts, U. S. A.

We have found four distinct types of impurity centers arising from sulfur in silicon. For each of the four types we see a series of absorption lines due to transitions from the ground state to the effective mass p-like levels. In addition to these p-like transitions we see transitions to the excited $1s$-like states of the effective mass approximation. In applying a calibrated uniaxial stress to these samples, we have found that at least three of the four centers do not have the tetrahedral symmetry expected of a substitutional impurity atom.

It has been shown that the effective mass hydrogenic p-like energy levels for deep donors in Si[1] as well as shallow donors[2] in Ge and Si are fairly well described by effective mass theory.[2] Using the effective mass picture to identify the transitions observed for sulfur impurities in silicon, we can identify four different sulfur impurity centers, two neutral and two singly ionized. If we assume that the $2p_{\pm}$ level is 0.0059 eV below the conduction band edge, as calculated from theory,[2] the positions of all the other observed levels can be located with respect to the conduction band edge. These observed levels are shown in Fig. 1. For identification the effective mass levels have been plotted in the left hand column. The ground state energy for each type of center is circled at the bottom of the figure. For the two singly ionized centers (C and D), where the effective nuclear charge Z for the hydrogenic levels is 2, the spacings between the various levels have been divided by four. Some of the unlabeled levels in the energy region between -0.02 and -0.05 eV correspond to transitions from the

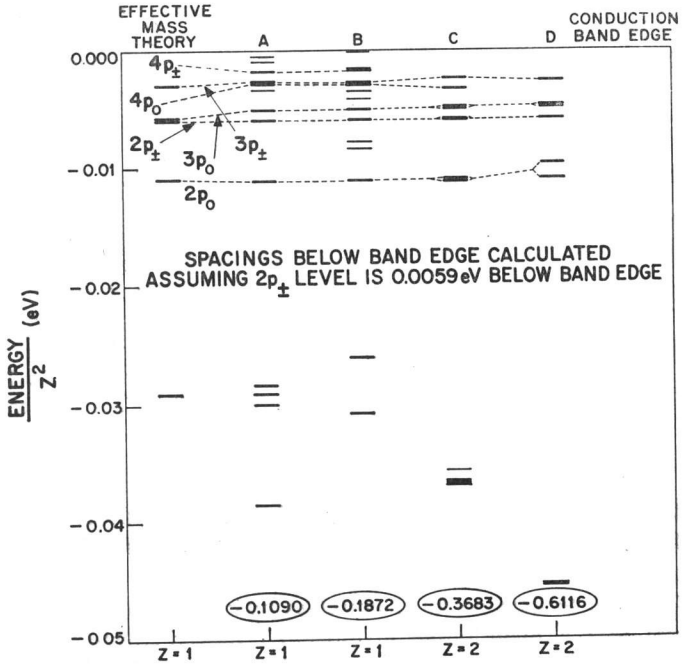

Fig. 1. Energy levels relative to conduction band edge for sulfur in silicon.

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ground state to excited 1*s*-like states of the effective mass approximation. That more than one *s*-like level is observed for each center can be accounted for by spin-orbit coupling and a lower than tetrahedral site symmetry for the center.

We use effective mass and deformation potential theory to describe the strain shifts of the *p*-like levels. Deformation potential theory gives for the energy shift with stress of the *j*-th ⟨001⟩ conduction band valley minimum in Si

$$\delta\varepsilon = E_1(s_{11}+2s_{12})T + E_2(m_{|j|}^2 - \tfrac{1}{3})(s_{11}-s_{12})T. \quad (1)$$

Effective mass theory predicts that under strain the impurity levels of each valley move rigidly with the valley minimum. In eq. (1), E_1 and E_2 are the dilatational and pure shear deformation potential coefficients,[3] s_{11} and s_{12} are the standard elastic compliance coefficients, T is the magnitude of the uniaxial stress, and $m_{|j|}$ is the component of a unit vector parallel to the stress axis along the principal axis of the *j*-th minimum of the conduction band. Using eq. (1), with an [001] stress we get $E_2 = \Delta(\delta\varepsilon)/(s_{11}-s_{12})T$, where $\Delta(\delta\varepsilon) = \delta\varepsilon^{(x,\bar{x})} - \delta\varepsilon^{(x,\bar{x},y,\bar{y})}$ is the splitting. Such a splitting has been observed for three of the four sulfur impurity centers, and we have obtained[4] the value $E_2 = 7.9 \pm 0.2$ eV.

Considering now the neutral B center (Fig. 1) we have observed extra splittings with stress which are not expected on the basis of eq. (1). Figure 2 shows the shifts and splitting we observed for transitions to the *p*-like states for the B center, for stresses in the three principal directions. It will be noted that we observe a splitting with an [001] stress, which is expected, but that we also see a splitting for a [111] stress, which is not expected. We explain this extra splitting on the basis of impurity centers each having a trigonal axis lying along one or another of the four ⟨111⟩ crystal axes. With such centers, for an [001] stress, only the splitting of the band edges is expected since all ⟨111⟩ axes are symmetrically oriented with respect to the [001] stress axis. For a [111] stress only the separation of the ground states is expected since the axes of the conduction band minima are symmetrically oriented with respect to the stress axis, but only one of the ⟨111⟩ axes is parallel to the stress axis. For a [110] stress both effects are expected, and the transitions to the *p*-like levels should split into four components. As shown in Fig. 2 all these predictions are in agreement with the data.

We now discuss how we associate the B center levels at -0.026 eV and -0.031 eV in Fig. 1 with the 1*s*-like levels of effective mass theory. The 6-fold degenerate 1*s*-like ground level of effective mass theory is split, for a center of tetrahedral (T_d) symmetry in the silicon lattice, into 1-, 2- and 3-fold degenerate levels with A_1, E and T_2 symmetry, respectively. The A_1 level is expected to have the lowest energy.[2] The transitions to the *p*-like states are, in fact, in agreement with the assumption of a non-degenerate ground state. If the impurity center has a trigonal axis, consistent with the transitions to the *p*-like states, the site symmetry of the center is C_{3v} or D_{3d}. We discuss here only C_{3v} symmetry: our conclusions are, however, essentially unchanged for D_{3d} symmetry. In general,

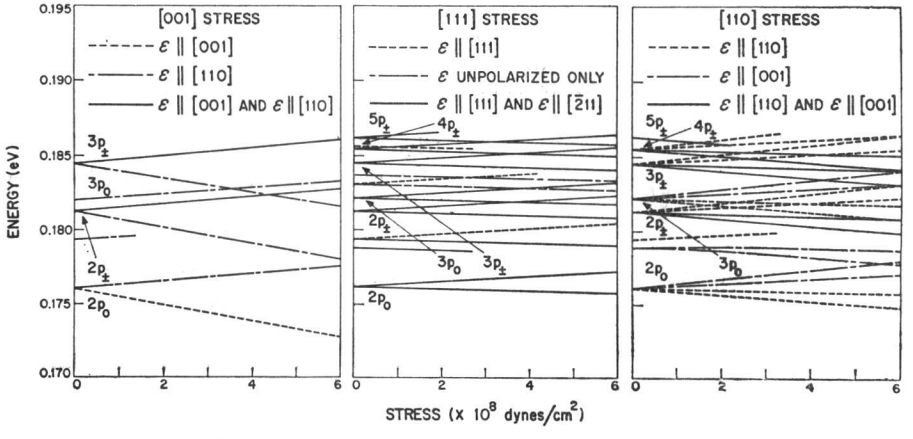

Fig. 2. Effect of uniaxial stress on *p*-like absorption spectrum of silicon containing B center impurity.

in going from T_d to C_{3v} symmetry, the A_1 and the E levels do not split, but the T_2 level splits into a non-degenerate A_1 level and a doubly degenerate E level.

To calculate the effect of strain, or stress, on these levels we use first order perturbation theory, taking account of the symmetry. Using an approach similar to Kaplyanski's,[5] we write the perturbation operator as $V=\sum_{ik} V_{ik}S_{ik}$ where the V_{ik} are symmetric in i and k, and the S_{ik} are the components of the strain tensor. The matrix elements of the perturbation can then be written as

$$\langle\phi_l|V|\phi_m\rangle=\sum_{ik}\langle\phi_l|V_{ik}|\phi_m\rangle S_{ik}\,, \qquad (2)$$

where the $|\phi_l\rangle$'s are the energy eigenstates for the level in the absence of strain. Relations between the matrix elements are determined by symmetry. The solutions of the secular equation yield the energy shifts with strain. The corresponding eigenstates ($|\psi\rangle$'s) are used to calculate the electric dipole transition intensities. The intensity of a transition between $|\psi_i\rangle$ and $|\psi_f\rangle$ is proportional to

$$I=|\langle\psi_f|\boldsymbol{\varepsilon}\cdot\boldsymbol{r}|\psi_i\rangle|^2\,, \qquad (3)$$

where $\boldsymbol{r}$ is the position operator and $\boldsymbol{\varepsilon}$ is the unit polarization vector. Symmetry is used again to relate the position matrix elements $\langle\phi_l'|x_\rho|\phi_m\rangle$ involved.

The energy shift expressions developed using eq. (2), and the intensities evaluated using eq. (3), are applied to fit the spectral data, the independent matrix elements being taken as adjustable parameters. Centers differing in the orientation of their trigonal axes are treated separately, with the number of centers with trigonal axes along each $\langle 111\rangle$ axis assumed to be the same. Then contributions to the intensity from all transitions with the same energy are added. In this way the transitions which occur at approximately 0.156 eV and 0.161 eV (Fig. 3) are identified as transitions from the ground A_1 level to the E level and to the excited A_1 level, respectively. (In Fig. 1 the ground A_1 level is at -0.1872 eV, the E level is at -0.031 eV, and the excited A_1 level is at -0.026 eV).

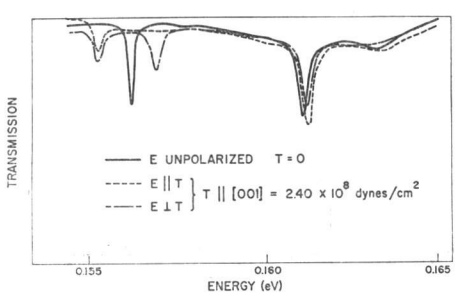

Fig. 3. Effect of stress on B center spectrum in silicon.

In addition to identifying these levels, with a calibrated stress we are also able to evaluate the strain shift parameters using the following expressions developed from eq. (2). In these formulas the Greek symbols are abbreviations for certain linear combinations of the matrix elements. For a [110] stress, the ground and excited A_1 levels shift respectively according to $\delta\varepsilon=\alpha_1(s_{11}+2s_{12})T\pm\frac{1}{2}\beta_1 s_{44}T$ and $\delta\varepsilon=\alpha_3(s_{11}+2s_{12})T\pm\frac{1}{2}\beta_3 s_{44}T$, the shift for half the centers being described by the plus sign and the shift for the other half by the minus sign. For a [110] stress, the observed E level of each center shifts and splits according to $\delta\varepsilon=\alpha_2(s_{11}+2s_{12})T\pm\frac{1}{2}\beta_2(s_{11}-s_{12})T\pm(1/6)\gamma_2 s_{44}T\pm(1/12)\delta_2 s_{44}T$, the plus-minus signs appearing in the four combinations $+++$, $+--$, $-+-$ and $--+$.

Preliminary evaluation of the parameters indicates that the differences $\alpha_2-\alpha_1$ and $\alpha_3-\alpha_1$ are small, as is the mean shift of the transitions to the p-like levels. For the excited A_1 level the same shift occurs for all centers ($\beta_3=0$), but for the ground A_1 level there is an apparent splitting ($\beta_1\approx 1.32$ eV). Satisfactory values for the E level parameters have not yet been obtained.

In summary, using infrared absorption techniques at low temperatures we have identified four different impurity centers due to sulfur in silicon. We have, using calibrated uniaxial stress measurements, obtained a value for the pure shear deformation potential coefficient of the conduction band edge, and have measured parameters which describe the shifts and splittings of the s-like levels. We have also shown that at least one of the impurity centers has trigonal symmetry, and not the site symmetry of a monatomic substitutional impurity.

References

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DISCUSSION

Fan, H. Y.: Do you have tentative models for any of the four centers, particularly center B?

Krag, W. E.: We do have tentative models for three of the four centers, but we regard them as strictly speculative and would rather not comment.