

Site Symmetry and Ground-State Characteristics for the Oxygen Donor in Silicon

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We have investigated the effect of stress upon the Rydberg series of infrared absorption bands due to oxygen donors in silicon. Our results establish that the donor has an effective-mass-like $1s$ ground state that is constructed from conduction-band valleys selected by the C_{2v} distortions associated with an extended "central cell."

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The electrically active, oxygen donor complex that forms in Czochralski-grown silicon during heat treatment at 450°C has been studied for thirty years.¹⁻³ Early work focused upon the $[\text{O}]^4$ dependence of the initial formation rate which led to an SiO_4 model.⁴ A specific structure was not proposed, nor was an explanation of the electrical activity suggested.

Recently, effective-mass-like infrared absorption bands have been identified for nine distinct oxygen donor species that appear sequentially during heat treatment, each with a different ground-state energy.⁵⁻⁷ The center has been shown to be a double donor.⁵⁻⁸ In compensated samples (initially p type, converted to n type by an oxygen-donor-formation heat treatment) two spectra due to the doubly and singly occupied charge states of the thermal donor, TD^0 and TD^+ , can be observed. Recent work has identified the EPR spectrum NL8 as the oxygen donor.⁹ This spectrum has a g -tensor anisotropy consistent with C_{2v} symmetry. In deep-level transient spectroscopy (DLTS), the stress- and electric-field-induced splittings of a feature assigned to TD^+ led to the proposal of complexes with D_{2d} and C_{2v} symmetry.^{10,11}

In spite of intense study, the structure of the oxygen donor is not understood. The infrared spectrum supports the notion that the oxygen donor can be described in terms of the effective-mass theory with wave functions constructed from conduction-band minima. However, the stress coupling coefficients observed in the DLTS studies^{10,11} are large compared to those reported for the lifting of orientational degeneracy of the shallow donor complex Li-O.¹² Hyperfine splitting has not been observed in the EPR spectrum.^{9,13} This negative result has not been explained and has prevented the identification of the oxygen donor's constituents.

In this paper we report the effect of uniaxial stress upon the low-temperature infrared (IR) absorption spectrum of oxygen donors. These results give important new insights into the electronic and atomic structure of the oxygen donor and establish for the first time that effective-mass theory^{14,15} provides a good description of the electronic structure when the anisotropic nature of the extended "central cell" is included.

Our experiments employ bulk, $10\ \Omega\text{-cm}$, boron-doped Czochralski silicon with $[\text{O}] \approx 10^{18}\ \text{cm}^{-3}$. This material received an oxygen-dissolution heat treatment of 8 h at 1350°C to place the oxygen in a well-defined initial state and a subsequent oxygen-donor-formation heat treatment of 8 h at 450°C . The final silicon resistivity was $\sim 10\ \Omega\text{-cm}$ n type. Our stress apparatus consists of a push-rod system (driven by a pneumatic piston) bolted to the cold finger of an Air Products Helitran dewar. A calibrated stress could be applied to samples at temperatures as low as 20 K. IR absorption measurements were made with a Nicolet 60SX Fourier transform spectrometer at a resolution of $2\ \text{cm}^{-1}$.

Spectra are shown in Fig. 1(a) for several stress orientations for the TD^0 transitions. Absorption bands are labeled by their final state,^{14,15} $2p_0$ or $2p_\pm$, and by donor-complex numbers which denote their sequence of appearance with annealing. We have used the assignments and notation of Oeder and Wagner.⁵ Spectra shown in Fig. 1(b) were taken with polarized light and a [001] stress axis. We have found no stress-induced splitting of the IR bands for the [001] stress orientation and small ($\sim 10\times$ less than the splitting of the conduction band) splittings for both [111] and [110] stress directions. The dependence of the splittings upon stress is shown in Fig. 2. As will be shown below, our results are explained well by a model in which the splittings of the states are given primarily by effective-mass theory (EMT). The fact that conduction-band-like splittings characteristic of EMT donors are not observed directly as splittings of the spectral features reveals a unique electronic structure for the ground state of this center. The small stress splittings that are shown in Fig. 1(a) are not effective-mass-like, but are due to the anisotropic atomic structure of the extended "central cell."

In the effective-mass approximation,^{14,15} shallow donors in silicon have wave functions that are symmetry-adapted linear combinations of the wave functions for each of the six degenerate conduction-band valleys. Each valley wave function is a product of a hydrogenic envelope function, $F_j(r)$, that reflects the Coulomb potential between the positive central cell and the bound electron, and a Bloch wave, $\psi_j(r)$, for the j th conduction-band valley. The $1s$ states of donors are split by the chemical interaction of the

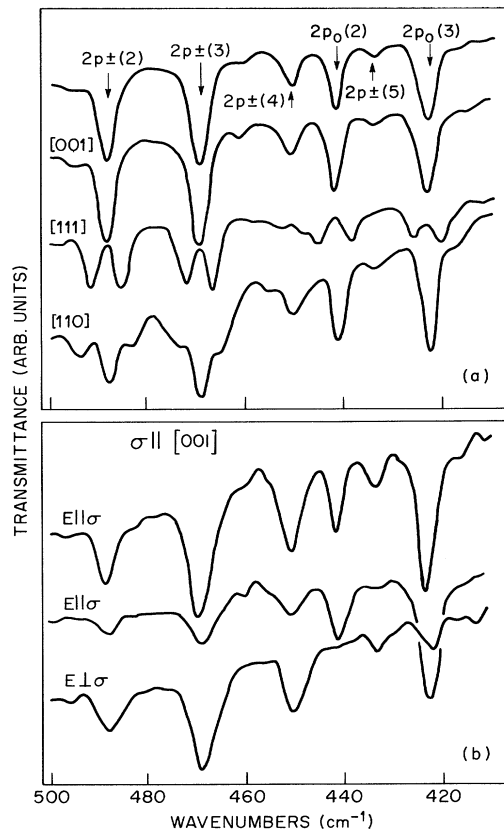


FIG. 1. (a) IR absorption features for TD^0 . Top, no stress; others, ~ 20 kgf/mm 2 for the stress orientation indicated. Transitions are labeled by their final state. The donor-complex number is indicated in parentheses. (b) IR absorption features for TD^0 for a [001] stress of 20 kgf/mm 2 . Top spectrum, $T=20$ K; lower two spectra, $T=60$ K. Spectra are labeled for polarization directions parallel and perpendicular to the stress axis.

bound electron and the central cell. The lowest component of the $1s$ manifold is the ground state.

Under uniaxial stress, the six conduction-band valleys are no longer degenerate. The components of the $1s$ manifold will split with stress in a fashion that depends on their zero-stress, energy separations and ordering. The very shallow excited states, np_0 or np_{\pm} , always split into components that shift like the conduction-band valleys with which they are associated. From group-theoretical considerations and EMT matrix-element selection rules, Ramdas and Rodriguez¹⁴ have determined the energy levels and polarization selection rules for a donor with T_d symmetry under stress.

All of the splittings shown in Fig. 1(a) are much smaller in magnitude and have a different dependence on stress orientation than the conduction-band-like splittings that are characteristic of EMT levels. [The

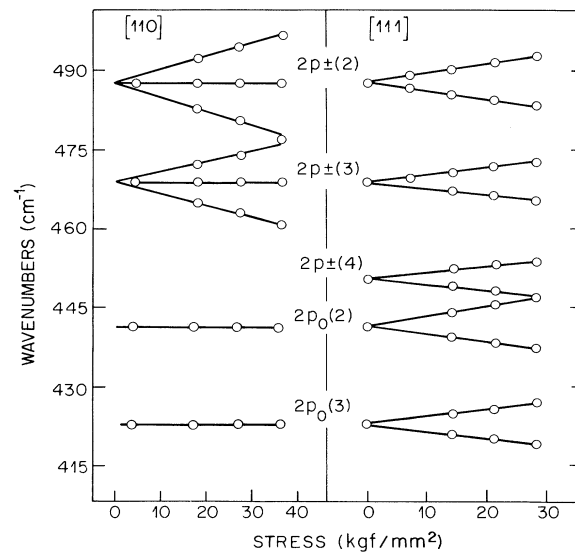


FIG. 2. Dependence of splitting upon stress for IR absorption features. Left, a [110] stress axis and [001] viewing axis. Right, a [111] stress axis and a $[1\bar{1}0]$ viewing axis.

conduction band splits by ~ 140 cm $^{-1}$ for the [001] stress¹⁴ used in Fig. 1(a).] The absence of an observed [001] splitting requires that the ground and np excited states each split identically in accord with the stress-split conduction-band valleys with which they are associated. The optical transitions do not occur between the levels associated with the different sets of conduction-band valleys. An explanatory energy-level diagram is shown in Fig. 3(a). For T_d site symmetry, equal ground- and excited-state splittings under [001] stress occur for the T_2 wave functions that are constructed from the three antisymmetric pairs of conduction-band valleys.¹⁴ For lower site symmetries, $1s$ states will split like the np excited states if they are constructed from a pair or pairs of conduction-band valleys.¹⁶ The polarization selection rules shown in Fig. 3(a) are derived from the valley-pair makeup of the stress-split components of the states.

Spectra taken with polarized light allow transitions originating from the upper and lower components of the stress-split ground state, $1s(+)$ and $1s(-)$, respectively, to be examined separately. The following measurements reveal that the ground state is electronically nondegenerate and that the $1s(+)$ and $1s(-)$ components arise from different donor sites that are oriented differently with respect to the applied stress. The spectra shown in Fig. 1(b) were all taken with polarized light for a [001] stress of $\sigma = 20$ kgf/mm 2 (1 kgf ≈ 9.8 N). For the spectrum at the top of Fig. 1(b), the stress-splitting and thermal energies are $E_s = 17$ meV (estimated from the deformation potential constants¹⁴) and $kT = 1.7$ meV, respectively. If the ground state were degenerate in the absence of stress,

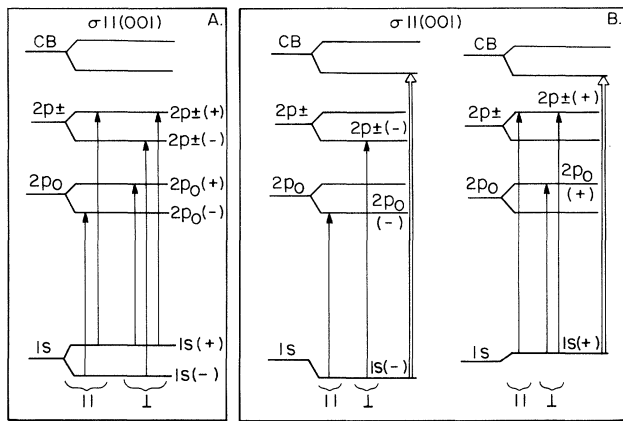


FIG. 3. (a) Energy-level diagram for the splitting of effective-mass-like shallow donor transitions for a [001] stress axis. Allowed transitions for each polarization direction are indicated. (b) Energy-level diagram in which the orientational degeneracy of the $1s$ ground state is shown explicitly. Double arrows denote thermal ionization transitions.

only the $1s(-)$ component of the ground state would be appreciably occupied because $E_s \gg kT$ and, for $E \parallel \sigma$, only $1s \rightarrow np_0$ transitions would be observed. This preferential occupation of $1s(-)$ at 20 K does not occur. However, such polarization selection rules are observed in the two lower spectra of Fig. 1(b) that were taken at $T=60$ K. This is not a kinetic effect due to a barrier to relaxation from $1s(+)$ to $1s(-)$. When the sample is cooled from 60 to 20 K with the stress maintained, the lower state, $1s(-)$, is no longer preferentially occupied and the uppermost spectrum is recovered, demonstrating that a preferred occupation of $1s(-)$ cannot be quenched in. The preferential occupation of $1s(-)$ at 60 K is due to the thermal ionization of the higher-energy $1s(+)$ state [i.e., the Fermi level moves to below the $1s(+)$ state] and not thermal relaxation from $1s(+)$ to $1s(-)$. Thus, while the EMT-like splitting of the ground state cannot be observed directly as a splitting of the spectral features, the occupation statistics of the ground state, as probed by polarized light, show that the state is indeed split. An energy-level diagram is shown in Fig. 3(b) with the *orientational degeneracy* of the $1s$ ground state shown explicitly. The polarization selection rules observed at 60 K that were derived for hydrogenic conduction-band-valley wave functions confirm the EMT character of the ground state and that it is constructed from conduction-band-valley pairs. That the ground state is nondegenerate establishes that it is constructed from a *single* pair of conduction-band valleys.

The applied stress also lifts the orientational degeneracy associated with an anisotropic atomic structure of

the extended "central cell." This effect gives rise to the small stress splittings shown in Fig. 1(a) and can be used to determine that the symmetry of the anisotropic central cell is C_{2v} . The energy shift Δ of an individual C_{2v} anisotropic center¹⁷ is

$$\Delta = A_2\sigma_{xx} + A_2\sigma_{yy} + A_1\sigma_{zz} + 2A_3\sigma_{xy}. \quad (1)$$

The σ_{ik} are the components of the stress tensor and the A_i 's are the components of the piezospectroscopic tensor. The energy splittings displayed in Fig. 1(a) and Fig. 2 are consistent with C_{2v} symmetry with $A_1 = A_2 = 0$ and $A_3 = 3.2 \times 10^{-2} \text{ meV (kgf/mm}^2\text{)}^{-1}$ for donor 2 and $A_3 = 2.7 \times 10^{-2} \text{ meV (kgf/mm}^2\text{)}^{-1}$ for donor 3. Thus, Eq. (1) takes the simple form

$$\Delta = 2A_3\sigma_{xy}. \quad (2)$$

Equation (2) describes all of the splittings shown in Fig. 1(a) and Fig. 2. There is no [001] stress-induced splitting, equal-intensity components split about the zero-stress position by $\pm \frac{2}{3}A_3$ for a [111] stress axis, and three components split with intensity ratios 1:4:1 with energy shifts $+A_3, 0, -A_3$, respectively, for a [110] stress axis.

The simple form of the C_{2v} piezospectroscopic tensor provides an important clue to the donor's atomic structure. From Eq. (2) we see that only the shear components of the stress tensor in the x - y plane (i.e., only tension or compression along the [110] axis) contribute to the stress response of the IR spectra. This result is consistent with a structure elongated along a [110] axis. The species observed by transmission electron microscopy which evolve from the oxygen donor exhibit a macroscopic, linear [110] morphology.¹ An embryonic structure which incorporates a limited [110] chainlike cluster of Si-O-Si-O atoms^{1,2} would satisfy several of the requirements of the enlarged "central cell."

The single-valley-pair ground state is selected by the distortions associated with the anisotropic atomic structure of the oxygen donor. We have used group-theoretical techniques to construct the EMT wave functions that are consistent with the C_{2v} symmetry of the center. The only states that are consistent with the valley-pair ground state are constructed from the two k_z -axis conduction-band valleys (the z axis is the C_2 axis of the center). In Fig. 1(a) and Fig. 2 it is shown for the [110] stress axis and [001] viewing axis that $1s \rightarrow 2p_{\pm}$ transitions split into three components and that $1s \rightarrow 2p_0$ transitions do not split. The mutual constraints of the transition moment directions, the excitation geometry, and the different orientations of the centers also require that the $1s$ ground state is constructed from the pair of k_z -axis conduction-band valleys.

We have also investigated the effect of stress upon spectra due to the TD^+ charge state which is observed

in compensated samples.⁵⁻⁷ The same general features that have been discussed for TD⁰ characterize the TD⁺ results. There are no [001] stress-induced splittings so that both the ground and excited states must split identically. Small stress-induced splittings are present as a result of the anisotropy of the "central cell."

DLTS experiments^{11,12} have observed a splitting of the TD⁺ feature which conforms to the approximate magnitude and symmetry of the expected conduction-band splitting. We propose that the DLTS transitions are from a ground state, *split in accord with EMT*, to the energetically lower valleys of the stress-split conduction band as shown in Fig. 3(b). An energy splitting is observed for a [001] stress because the thermal ionization transitions measured by DLTS are not subject to the optical-selection rules that render the splittings of the $1s \rightarrow np$ transitions unobservable in IR absorption. In the context of our optical results, the DLTS measurements provide a complementary confirmation that the oxygen donor has a ground state that is constructed from $1s$ wave functions associated with a conduction-band-valley pair.

Our spectroscopic data clearly describe an effective-mass center with a $1s$ ground state that is constructed from a nondegenerate conduction-band-valley pair. The distortion associated with an *enlarged "central cell"* of C_{2v} symmetry acts to lift the electronic degeneracy of the ground state. The problem of how to augment EMT to explain the novel aspects of this center remains.

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