PIEZOSPECTROSCOPY OF LITHIUM DONORS IN SILICON

C. Jagannath and A. K. Ramdas

Department of Physics Purdue University West Lafayette, Indiana 47907 USA

The effect of uniaxial stress on the excitation spectrum of isolated, interstitial lithium and lithium-oxygen donor complexes in silicon are studied with a quantitative stress cryostat. The results are discussed in terms of the ground state multiplet, the site symmetry of the donor and the deformation potential theory.

I. Introduction

On the basis of the Lyman spectrum of isolated interstitial lithium donors in silicon (Si(Li)) [1] its ground state was deduced to be a five fold degenerate $ls(E+T_2)$ state, the site symmetry of Li being T_d ; the $ls(A_1)$ state lies 1.76 meV above it. The ionization energy of Si(Li) is 33.02 meV, very close to the theoretical value of Faulkner [2], i.e., 31.27 meV. In contrast, Li-O donors have a "conventional" group V like ground state multiplet with $ls(A_1)$ below $ls(T_2)$ and ls(E) sub-levels which occur close to the effective mass position. The symmetry assignments for the transitions observed in the excitation spectra of Si(Li) and Si(Li-O) were deduced on the basis of the stress induced splittings and the polarization features of the components [1]. Here we report the results of a piezospectroscopic study of the excitation spectra of Si(Li) and Si(Li-O) obtained with a quantitative stress cryostat [3] and a high resolution Fourier Transform spectrometer equipped with a Ge-bolometer.

II. Isolated Li Donors

In Fig. (1) we show the excitation spectrum of lithium diffused into a floating zone silicon, nominally free of dispersed oxygen. The spectrum shows two series of





lines which are identified with Si(Li) and a species of Li-O donor complex, labeled A by Gilmer, Franks, and Bell [4]. In Fig. (2) the excitation spectrum of Si(Li)



is shown for compressive force, \vec{F} , along [001], the magnitude of the stress, T, being 1.9×10^8 dyne/cm²; the intensity of the incident radiation for the electric vector E along F and perpendicular to \vec{F} have been equalized by a polarization rotator thus simulating "unpolarized" light for these experiments. Each 1s \rightarrow np transition splits into three components, one at the zero stress position and one each above and below it; the lines have been labeled 0, +, and - in paren-

Figure 2 Excitation spectrum of Si(Li) with $\vec{F} \parallel [001]$

theses, respectively. In the inset, $2p_0(-)$, $2p_0(0)$, and $2p_0(+)$ lines for T = 1.12 $\times 10^8$ dyne/cm² are shown; a striking feature in this figure is the disappearance of $2p_0(+)$ and the large decrease in the intensity of $2p_{\pm}(+)$ at the larger stress. At extremely high stress the np(+) component ultimately vanishes and only np(0) and np(-) components survive. The np(+) and np(-) lines shift to higher and lower energies as a function of stress. The rate of shift of np(-) decreases with increasing stress, finally approaching asymptotically a limiting position.

For compressive force $\vec{F} \| \begin{bmatrix} 001 \end{bmatrix}$, the site symmetry of the lithium donor reduces to D_{2d} and $1s(E+T_2)$ splits into $1s(E+B_1)$, $1s(A_1^4)$, and $1s(B_2)$ in the order of decreasing energy given by $\varepsilon - \Delta_c$, $\frac{1}{2} \begin{bmatrix} (4\Delta_c - \varepsilon) - (9\varepsilon^2 + 12\varepsilon\Delta_c + 36\Delta_c^2)^{1/2} \end{bmatrix}$, and $-2\varepsilon - \Delta_c$, respectively. Here $6\Delta_c$ is the energy separation between $1s(A_1)$ and $1s(E+T_2)$, $\varepsilon = \frac{1}{3} \Xi_u(s_{11}-s_{12})T$, Ξ_u being the shear deformation potential constant and $s_{11} \& s_{12}$ the elastic compliance constants. The central component in Fig. (2) arises from $1s(B_2) \rightarrow p(-)$ and $1s(E+B_1) \rightarrow p(+)$ where the + and - signs refer to the conduction band valleys having energies above and below their center of gravity, respectively. The $1s(A_1^{\ell}) \rightarrow p(+)$ and p(-) transitions give rise to the outer components. In the effective mass approximation the impurity wavefunctions are

$$\psi_{i}(\vec{r}) = \sum_{j=1}^{o} \alpha_{ij} F_{j}(\vec{r}) \phi_{j}(\vec{r}) , \qquad (1)$$

where $\phi_j(\vec{r})$ is the Bloch wavefunction of the $j^{\underline{th}}$ conduction band minimum, α_{ij} are the numerical coefficients which describe the relative contributions from each of the six $\langle 100 \rangle$ conduction band minima of Si, and $F_j(\vec{r})$ are the "hydrogen-like" envelope functions satisfying the effective mass equation. The coefficients α_{ij} which correspond to $1s(A_1^{\ell})$ for $\vec{F} \parallel \begin{bmatrix} 001 \end{bmatrix}$ are: (b,b,b,b,a,a) where $a^2 = (1/4)(1+\beta)$, $b^2 = (1/8)(1-\beta)$ and $\beta = (3\varepsilon + 2\Delta_c) (9\varepsilon^2 + 12\varepsilon\Delta_c + 36\Delta_c^2)^{-1/2}$.

In order to understand the stress dependence of the intensity of the excitation lines we now consider the transition probability from the $ls(A_1^{\ell})$ to the excited states. It can be shown that the stress dependence of the intensity ratios of the higher and lower energy components for $2p_0$ and $2p_{\pm}$ using "unpolarized" incident light are given by

$$\frac{I[2p_{o}(+)]}{I[2p_{o}(-)]} = \frac{\omega_{1}(+)}{\omega_{1}(-)} \frac{b^{2}}{a^{2}} \text{ and } \frac{I[2p_{\pm}(+)]}{I[2p_{\pm}(-)]} = \frac{\omega_{2}(+)}{\omega_{2}(-)} 3 \times \frac{b^{2}}{a^{2}} , \qquad (2)$$

where $w_1(+)$, $w_1(-)$, $w_2(+)$ and $w_2(-)$ are the energies corresponding to the transitions from $1s(A_1^{\ell})$ to $2p_0(+)$, $2p_0(-)$, $2p_{\pm}(+)$, and $2p_{\pm}(-)$, respectively. The ratios $w_1(+)/w_1(-)$ and $w_2(+)/w_2(-)$ can be taken to be 1 for low stresses. We note that even for small stresses, the intensity of $2p_0(+)$ is at least a factor four smaller than that of $2p_0(-)$. In addition it is noteworthy that even for T as small as 1×10^8 dyne/cm² corresponding to $\varepsilon' = (\varepsilon/\Delta_c) = 0.95$ the intensity ratio $2p_0(-)$: $2p_0(+)$ is ~ 10 , representing a dramatic decrease in the intensity of $2p_0(+)$; when $\varepsilon' = 3$ corresponding to $T \sim 3 \times 10^8$ dyne/cm², $2p_0(+)$ is below the level of detection. The disappearance of $2p_0(+)$ as the stress is increased, is thus explained by the inverted ground state combined with a small Δ_c . Although $2p_{\pm}(+)$ also shows the expected decrease in going to higher stresses, the agreement with the theoretical calculation is only qualitative in that it is observed in Fig. (2) with an intensity significantly larger than expected.

We note that the $2p_0(0)$, $2p_{\pm}(0)$, $3p_0(0)$ and $3p_{\pm}(0)$ lines occur at 21.47, 26.54, 27.48, and 29.82 meV, respectively, even at stresses as high as 1.8×10^9 dyne/cm²; this is in excellent agreement with the zero stress values of these excitation lines. We therefore deduce that Ξ_u of $1s(B_2)$ and $1s(E+B_1)$ is identical to that of the excited states and hence that of the conduction band minima, i.e., $\Xi_u = 8.77 \pm 0.07$ determined by Tekippe <u>et al</u>. [3].

III. Li-O Donor Complexes

Figure (3) shows the spectrum of Li-O donor complexes in Si for $\vec{F} \parallel \begin{bmatrix} 001 \end{bmatrix}$ and



Figure 3 Excitation spectrum of Si(Li-O) for $\vec{F} \parallel \begin{bmatrix} 001 \end{bmatrix}$

ting is not seen for series D or for phosphorus donors. For $\vec{F} \parallel \begin{bmatrix} 110 \end{bmatrix}$ such additional splitting of each transition into two was observed only for T $\ge 13 \times 10^8$ dyne/cm².

ponents, (1) and (2). How-

ever, this additional split-

The splitting of each component np(+) and np(-) into two subcomponents each with $\vec{F} \parallel \begin{bmatrix} 001 \end{bmatrix}$ or $\vec{F} \parallel \begin{bmatrix} 110 \end{bmatrix}$ strongly suggests that the donor complex has a noncubic symmetry with a symmetry axis along $\begin{bmatrix} 001 \end{bmatrix}$; thus species with axes along $\begin{bmatrix} 001 \end{bmatrix}$, $\begin{bmatrix} 010 \end{bmatrix}$ or $\begin{bmatrix} 100 \end{bmatrix}$ will exhibit collectively "orientational degeneracy" $\begin{bmatrix} 5 \end{bmatrix}$ in their optical transitions. Assuming a random distribution of these complexes in the crystal one expects equal numbers of centers with their symmetry axes pointing along $\begin{bmatrix} 001 \end{bmatrix}$,

C. JAGANNATH and A. K. RAMDAS

[010] and [100]. In such a case, with $\vec{F} \parallel [001]$ the Li-O donor species having its axis of symmetry along [001] is affected differently from those along [010] and [100]. For $\vec{F} \parallel [110]$ the species along [100] and [010] should exhibit identical behavior whereas the species along [001] should behave differently. For either direction of \vec{F} one expects, at the most, each line to split into two. However, for $\vec{F} \parallel [111]$ the species along [100], [010] and [001] are expected to behave identically and no further splitting is expected due to the lifting of the orientational degeneracy. Our experimental results for $\vec{F} \parallel [111]$ agree with this prediction. If the symmetry axis of the complexes were to be along $\langle 110 \rangle$, $\vec{F} \parallel [001]$, [110] and [111] would result in 2, 3 and 2 subcomponents, respectively. For orientational degeneracy along $\langle 111 \rangle$ there would be no splitting for $\vec{F} \parallel [001]$ and 2 subcomponents would be present for $\vec{F} \parallel [110]$ or [111]. Our experimental results strongly indicate that the Li-O donor complexes have their symmetry axes along $\langle 100 \rangle$.

From the spacing of the excited states for the A and D series we find $\Xi_u = (8.58 \pm 0.12)$ eV for the excited states in excellent agreement with the values obtained by Tekippe <u>et al</u>. [3] for phosphorus, arsenic and antimony donors in silicon.

Acknowledgments

We are indebted to Professors S. Rodriguez, Z. W. Grabowski, and P. Fisher for stimulating discussions. This work has been supported by the National Science Foundation Grant No. DMR77-27248 and NSF-MRL Program No. DMR77-23798.

References

- R.L. Aggarwal, P. Fisher, V. Mourzine and A. K. Ramdas: Phys. Rev. 138 (1965) A882.
- 2) R.A. Faulkner: Phys. Rev. 184 (1969) 713.
- V.J. Tekippe, H.R. Chandrasekhar, P. Fisher and A.K. Ramdas: Phys. Rev. B6 (1972) 2348.
- 4) T.E. Gilmer, R.K. Franks and R.J. Bell: J. Phys. Chem. Solids 26 (1965) 1195.
- 5) A.A. Kaplyanskii: Optics and Spectroscopy 16 (1964) 329.