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AN EXPLANATION OF ELECTRONIC STRUCTURE FOR THERMAL  
DOUBLE DONORS IN SILICON

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A model of two donor centers is suggested to explain electronic structure of thermal double donors in silicon. The model consistently explains the two valley structure of the ground state, the splitting of the  $2p_{\pm}$ -levels and other data obtained from infra-red absorption investigations of these defects.

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THERMAL double donors (TDDs) are oxygen complexes consequently formed in Czochralski-grown silicon crystals during heat-treatments at 350–500°C. They have been known for over 40 years and have been investigated with different magnetic resonance and infra-red (IR) absorption techniques, using Hall-effect and DLTS measurements (see [1, 2] and references therein). However their atomic and electronic structure is not understood yet.

Electronic structure of TDDs has been well explored by IR absorption techniques [2–4]. It may be described in the framework of the effective mass approximation (EMA) but reveals distinct deviations from the standard EMA. As it has been found in [2–4], the main deviations are: (a) the two valley structure of the ground state, (b) the splitting of the  $2p_{\pm}$ -states, (c) the lowering of the  $2p_{\pm 1}$ -level with increasing TDD number, while the other levels become higher (energy levels are labelled as in [2]). Although atomic structure of TDDs is not known, it is possible to explain their electronic structure in a consistent way. This is the aim of this work.

**A model of atomic structure and valley selection.** The explanation is based on the following suggestion: *Electrical activity of TDD is due to two donor active atoms and its atomic structure may be modeled by a pair of donors ( $D_2$ ).*

The nature of these atoms is still unclear. It is not necessary, however, that when separated they should act as single donors. These atoms can become donor

active when they form a complex and this suggestion does not require that TDD would be created by pairing of two single donors. There is another method of formation, when it is formed by reaction of several neutral components. The neutral complex formed can rearrange to the configuration with shallow donor levels, such as has been experimentally observed for the TDD1–TDD2 [2].

In this model, the single-pair valley structure of TDDs is explained as a result of a specific direction of the donor pair axis. In the standard EMA developed for substitutional shallow donors in Si [5], wave function of bound states is

$$\phi(\mathbf{r}) = N \sum_{i=1}^{\nu} c_i F_i(\mathbf{r}) U(\mathbf{k}_{0i}, \mathbf{r}), \quad (1)$$

where  $N$  is a normalizing factor,  $\nu$  is the number of valleys,  $U(\mathbf{k}_{0i}, \mathbf{r})$  is the Bloch function of the  $i$ th valley,  $F_i(\mathbf{r})$  its envelope function and all  $c_i$  are equal to unity [5]. However for the TDDs in Si and Ge only two of all  $c_i$  are equal to unity [3, 4, 6]. To explain this fact, let us consider the dependence of  $D_2^+$  ionization energy on mutual orientations of the pair axis (the  $OZ$  axis in Fig. 1) and of the longer axis of constant energy ellipsoid for one of the conduction band valleys (the  $OK_3$ -axis in Fig. 1).

When  $OZ \parallel OK_3$  the EMA-equation is

$$\left[ -\Delta + (1 - \gamma) \frac{\partial^2}{\partial z^2} - \frac{2}{r_a} - \frac{2}{r_b} \right] F(\mathbf{r}) = EF(\mathbf{r}) \quad (2a)$$

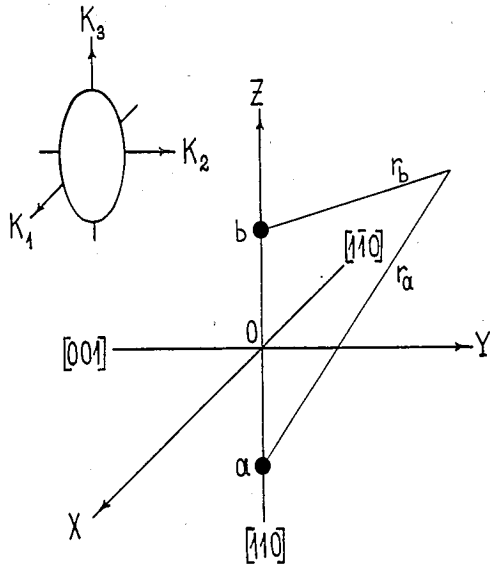


Fig. 1. (a) A conduction-band valley of silicon. The values of effective masses are  $m_1^*$ ,  $m_2^*$  and  $m_3^*$  along the  $OK_1$ ,  $OK_2$  and  $OK_3$  axes, respectively. (b) The coordinate system used for calculations of energy levels of a donor pair in anisotropic semiconductors. The internuclear distance between the donors a and b is  $R$  with their coordinates  $z_a = R/2$  and  $z_b = -R/2$ . The crystallographic axes indicated correspond to the case of thermal double donors.

and when  $OZ \perp OK_3$  we have

$$\left[ -\Delta + (1 - \gamma) \frac{\partial^2}{\partial y^2} - \frac{2}{r_a} - \frac{2}{r_b} \right] F(\mathbf{r}) = EF(\mathbf{r}). \quad (2b)$$

Both these equations are written using  $a^* = 4\pi\epsilon_0/\hbar^2/(m_1e^2)$  as the length unit and  $Ry^* = m_1e^4/(2\hbar^2(4\pi\epsilon_0)^2)$  as the energy unit. According to [5, 7] let us introduce systems of deformed coordinates (a)  $\tilde{x} = x$ ,  $\tilde{y} = y$  and  $\tilde{z} = \beta z$  when  $OZ \parallel OK_3$  and (b)  $\tilde{x} = x$ ,  $\tilde{y} = \beta y$  and  $\tilde{z} = z$  when  $OZ \perp OK_3$ , where  $\beta$  is a variational parameter which is chosen so that the function

$$F_0(\mathbf{r} = N \exp(-\alpha \tilde{r}) \quad (3)$$

would be the best approximation for the  $F(\mathbf{r})$  of the ground state for point-charge donor.

For small internuclear distances between the donors ( $R \ll 1$ ) the value of  $\beta$  will be practically the same for both the donor pair orientations. Because of  $\beta > 1$  for Si and Ge (for example for Si  $\beta \cong 1.7$  [5, 7]), we have

$$\tilde{R}_{\parallel} = \beta R > R = \tilde{R}_{\perp}. \quad (4)$$

That is in the system of deformed coordinates for  $OZ \parallel OK_3$  the internuclear distance ( $\tilde{R}_{\parallel}$ ) is greater than that one ( $\tilde{R}_{\perp}$ ) for  $OZ \perp OK_3$ . Then using the standard theory of hydrogen molecular ion  $H_2^+$  [8],

a conclusion may be drawn that the ground state of  $D_2^+$  is higher in the case  $OZ \parallel OK_3$  as compared to the case  $OZ \perp OK_3$  at the same interdonor distances. This conclusion is confirmed by more detailed calculations [9].

Hence, choosing the axis of the pair orientation along one of the  $[110]$  directions in Si crystal we have lower energies for those  $1s\sigma$  states which are constructed from the Bloch functions of the two valleys elongated in the  $[001]$  direction. This is because this direction is of the greatest angle with the  $OZ$  axis. Consequently, the wave function of the TDD ground state will be constructed from the Bloch functions of these two valleys only. Without any additional assumption this  $OZ$ -axis orientation predicts electronic structure for TDD's in Ge experimentally observed in [6].

**Energy levels of  $2p$ -states.** To explain the splitting of  $2p_{\pm}$ -levels of TDDs, no additional assumption is necessary. For the chosen axis of the donors location, the  $2p_{\pm}$ -level of TDDs is split because in the two center potential the  $|p_x\rangle$  and  $|p_z\rangle$  orbitals become inequivalent and are converted in the molecular  $2p\pi_x$  and  $2p\sigma_z$  orbitals, respectively. The  $|p_y\rangle$  orbital which corresponds to the  $2p_0$ -state of point-charge donor [5] is converted in the molecular  $2p\pi_y$  orbital. Using the system of deformed coordinates introduced for the case  $OZ \perp OK_3$  and approximate molecular orbitals for  $2p$ -states of  $H_2^+$  suggested in [10, 11], variational calculations of  $2p$ -levels of  $D_2^+$  in Si have been performed. The calculation results are presented in Fig. 2.

This figure also presents experimental data for the TDD $_n$  with  $n = 1-7$  obtained in [2, 12]. Findings for TDDs with the greater numbers are uncertain because IR-absorption bands of different TDD species are superimposed. Internuclear distances between the donor atoms were determined by comparing the calculated and experimental values of  $\delta_{Rn}^{theor} = E_{Rn}(2p\pi_x) - E_{Rn}(2p\sigma_z)$  and  $\delta_n^{exp} = E_n(2p_{\pm h}) - E_n(2p_{\pm l})$  suggesting that  $\delta_{Rn}^{theor} = \delta_n^{exp}$  (Fig. 3). As seen in Fig. 2 the changes of  $2p$ -levels with growing TDD number are adequately described by the calculated dependences though the magnitudes of their binding energies are different.

To explain this difference, interstitial positions of the donor atoms of TDDs should be taken into account [1]. From the data on Al $_i$  [12] and Mg $_i$  [13] it is evident that energy levels of the  $2p$ -states of interstitial donors are deeper than those predicted in the EMA. This is due to local field corrections which are dependent on donor atom position in the unit cell [13, 14]. The corrections are most essential for the  $2p_0$ -state [13]. Because of this should be expected the

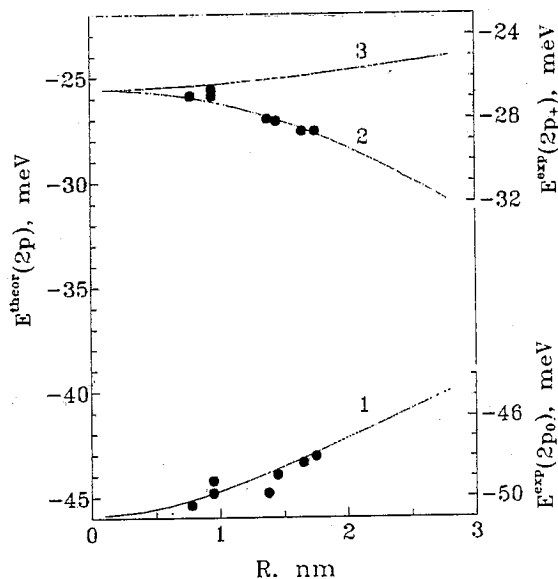


Fig. 2. Energy levels (solid lines) for the  $2p\pi_y$  (1),  $2p\sigma_z$  (2) and  $2p\pi_x$  (3) states of  $D_2^+$  calculated in the framework of the effective mass approximation for Si. The coordinate system is shown in Fig. 1. The  $OK_3$ -axis is parallel to the  $OY$  axis. Experimental data for different thermal double donor species (circles) are from [2].

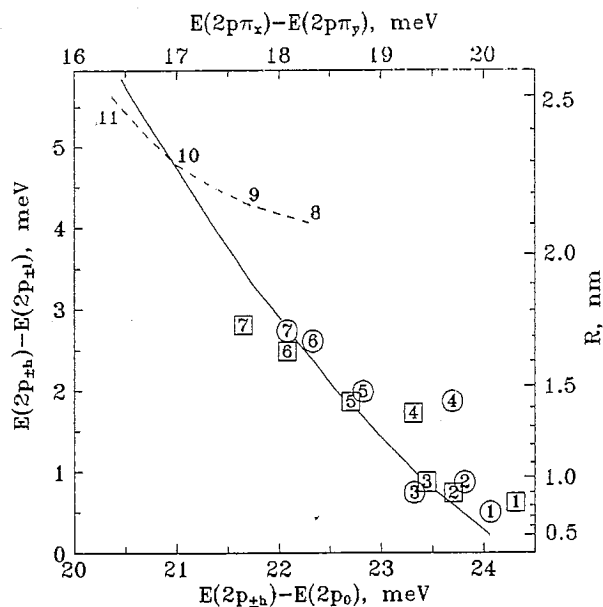


Fig. 3. Experimental values of  $\delta_{exp} = E(2p_{\pm h}) - E(2p_{\pm 1})$  and  $\Delta_{exp} = E(2p_{\pm h}) - E(2p_0)$  for the different TDD species (their numbers are indicated inside the symbols) and calculated  $\delta_{theor} = E(2p_{\pi_x}) - E(2p_{\sigma_z})$  and  $\Delta_{theor} = E(2p_{\pi_x}) - E(2p_{\pi_y})$  (solid line). The experimental data are from [2] (circles) and [12] (squares). Possible positions of the points for TDD8-TDD11 are shown by dashed line.

greater deviations of  $\Delta_n^{exp} = E_n(2p_{\pm h}) - E_n(2p_0)$  from  $\Delta_{Rn}^{theor} = E_{Rn}(2p_{\pi_x}) - E_{Rn}(2p_{\pi_y})$ . The difference between them  $\Delta_{LFC,n} = \Delta_n^{exp} - \Delta_{Rn}^{theor}$  depends on the TDD numbers. This is seen from Fig. 3.

**Essential distinction between TDD3 and TDD4.** A gap between experimental points for the TDD3 and TDD4 in Fig. 3 is worth taking note of. A distinct change in properties of these TDD species was pointed out in [2]. This fact allows us to divide all the considered species into two groups. The first group consists of TDD1-TDD3 and optically undetected TDD0 [15]. The next group is TDD4-TDD7.

Intermolecular distances between the donor atoms are around  $R_1 = \sqrt{2}a_0 \cong 0.77$  nm for the first group species and around  $R_2 = 2\sqrt{2}a_0 \cong 1.54$  nm for the second group ones where  $a_0$  is the lattice constant of Si. These distances correspond to the location of the donor active atoms around the central tetrahedral interstitial sites of the two unit cells. For TDD0-TDD3 these unit cells are nearest-neighbor in the  $[110]$  direction and for TDD4-TDD7 they are next nearest in the  $[110]$  direction (Fig. 4). That is, while the transformation of TDD3 in TDD4 one of the donor atoms is transferred into the next unit cell. As this takes place, not only the internuclear distance markedly grows but the locations of the donor atoms in their unit cells are changed dramatically (see Fig. 4). Such changes result in different local field corrections  $\Delta_{LFC}$  for the TDD3 and TDD4.

If one takes into account that both the groups consist of the four TDD species, then the third group may be suggested (a) to consist of TDD8-TDD11 (b) to be located with internuclear distances around  $R_3 = 2.3$  nm and (c) to have local field corrections of  $\Delta_{LFC,n+4} = \Delta_{LFC,n}$ . Then using Figs 2 and 3, one can predict the positions of absorption bands related to the transitions into  $2p_{\pm}$ -states of TDD8-TDD11. Experimental data on these bands could be used to verify the model suggested.

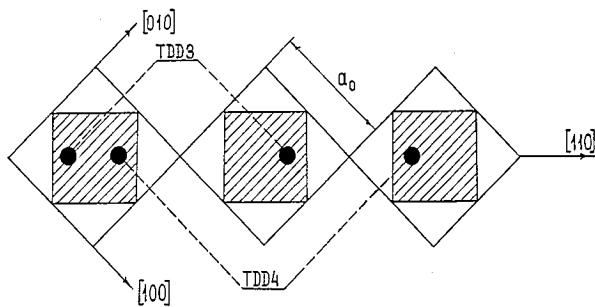


Fig. 4. A schematic sketch to explain the distinct change between spectroscopic features of the TDD3 and TDD4 with possible regions (crosshatched) of the unit cells of Si where electrically active atoms (black circles) of TDDs may be located.

**Configurational bistability of thermal donors.** In the framework of the present model configurational bistability of early TDDs can be explained also. As is well known (see [2, 15]) TDD0, TDD1 and TDD2 may be in two configurations. In the first one (the *H*-configuration) the complex has shallow levels  $E(0/+) = E_c - 0.05 \text{ eV}$  and  $E(+/++) = E_c - 0.15 \text{ eV}$ . In the second one (*B*-configuration) localized electrons are strongly bound to the complex. During the transition from the *H*- to *B*-configuration the degree of electron localization at paired donors may be increased drastically when the internuclear distance becomes less than a critical value. The increase of electron density between paired ions results in their coming closer which in turn brings about the increase of bound electrons localization at the complex site. This is similar to the extrinsic self-trapping [16].

In conclusion, the suggested model of thermal double donor structure gives a consistent explanation of the main features of their electronic structure: the valley selection for the ground state, the splitting of the  $2p_{\pm}$ -levels, the lowering of the  $2p_{\pm 1}$ -level and rise of the other levels with growing of TDD number. Evaluating the separation between donor-active atoms it is possible to explain the distinct change in properties of TDD3 and TDD4.

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