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The Nonlinear Effect of Uniaxial Stress for Shallow Donors in Silicon

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It is well known /1/ that the uniaxial deformations distorting the equivalency of the main minima in the conduction band of many-valley semiconductors lead to a considerable variation of the eigenstates of shallow donors. When the deformations are symmetric as regards the main minima (for example, in Si at $\vec{P} \parallel [111]$, where P is a mechanical stress), their equivalency is not disturbed and the conditions for such variations seem to be non-existent. Nevertheless, even in this case, we have revealed a considerable nonlinear change in the energy of the ground state of shallow donors in silicon.

The effect was studied experimentally by measuring the dependence of the Hall coefficient (R) on the uniaxial stress along [111] in the range of sufficiently low temperatures when only a small part of donors is ionized, similarly to the technique adopted in /2/. In this case, even slight variations of the ground state energy (E_i) of the shallow donor during deformation lead to a considerable variation of the free electron concentration. The latter may be determined precisely by measuring the Hall coefficient. As a result we have obtained the dependences $\delta E_i(P)$ for silicon doped by phosphorus and arsenic up to concentrations of 10^{14} to 10^{15} cm^{-3}. These dependences are shown in Fig. 1. Here, δE_i is the change in the position of the donor ground state with respect to the minimum of the conduction band.

For all the samples studied the dependences may be well approximated by the formula

$$\delta E_i(P) = A_1 P + A_2 P^2 \quad . \tag{1}$$

The linear part of (1) may depend on both the deformational variations of some parameters of the crystal and the possible desorientation of the applied

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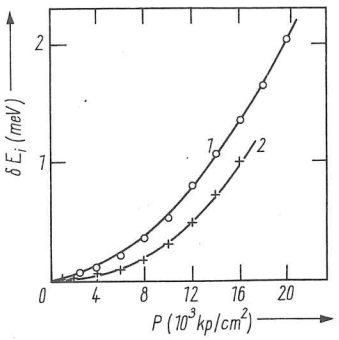

Fig. 1. Dependence of the shallow donor ionization energy on uniaxial compression $\vec{P} \parallel [111]$: (1) Si:P, T = 20.4 K; (2) Si:As, T = 63 K

pressure from the direction [111], giving rise to a tetragonal component, the pressure field. The existence of this component explains the significant variation of the A_1 values observed in different samples and interferes with a rigorous analysis of the linear part of the dependence (1).

The term containing the square of the pressure seems to be of special interest. Least-squares calculations of the coefficient A_2 gave identical values for all the samples containing both types of impurities: $A_2 = (5 \pm 1) \times 10^{-9}$ meV/(kp/cm^2)^2. The presence of such a strong quadratic effect, which becomes dominant at pressures as low as $P \geq 2 \times 10^3$ kp/cm^2, presents a non-trivial case which invites special consideration.

The observed quadratic increase in the energy gap between the impurity ground state and the conduction band cannot be explained by merely a reduction of the interatomic spacing in the crystal lattice at $\vec{P} \parallel [111]$. This is evident from the analysis of the data on the hydrostatic compression of silicon which also leads to a decrease in the lattice constant, but does not change the symmetry and form of the electron wave functions. It is shown in /3/ that in such a case, the reapprochment of atoms in the Si lattice is responsible for the decreasing of the effective mass of electrons and of the E_i values.

Since at $\vec{P} \parallel [111]$ the energies at the main minima of the conduction band do not vary, the observed square-law pressure effect may be caused by the following reasons: distortion of the one-valley states, variations of the valley-orbit interactions and effective mass of electrons. The latter effect is due, mainly, to variations of the interaction between the bands Δ_1 and Δ'_2 associated with the removal of their degeneracy at the point X /1/. This leads to the squared P dependence of the donor ground state energy changes δE_1. The calculations of these changes in terms of perturbation theory at $\vec{P} \parallel [111]$ give the expression $\delta E_1 \approx -E_i (C'/\Delta)^2 e^2$, where C' is the interband matrix element for the deformation, Δ is the splitting of the bands Δ_1 and Δ'_2 at the

point k_{min}; $e = e_{xy} = e_{yz} = e_{xz}$ is the component of the deformation tensor. The estimation of δE_1 with the use of the C' value determined experimentally /4, 5/ shows that in the case under consideration the deformational change of the effective mass amounts to $A_2 \approx 1 \times 10^{-9}$ meV/(kp/cm^2)^2 which is only 20% of the observed value. The significant nonlinear effect observed in this study cannot be explained by the change in valley-orbit interaction in the field of symmetric pressures, either.

As a probable mechanism, consider the mutual repulsion of the ground state (A_1) of the shallow donor and the excited state (T_2^*) of the deep center in the same donor impurity. The states of such deep center are represented by a linear combination of the ligand states of the first coordination sphere of the donor impurity.[2)] In the crystalline field, the initial fourfold degeneracy of these ligand states is withdrawn, the ground holosymmetric state appearing to be deep in the gap zone. The excited ligand state of the T_2 symmetry is located in the conduction band. On the basis of the initial triplet of the ligand states, at the expense of the Jahn-Teller effect, vibronic states originate. The lowest of these is also a T_2^* triplet (but already vibronic). In this case, because of the Jahn-Teller energy decrease, the T_2^* level may be located near the bottom of the conduction band. Here, the T_2^* state has a small natural width due to the low density of states in the electron band, the energy spacing δ between the T_2^* and A_1 levels of the shallow center being of the order of magnitude of the ionization energy for the shallow center. In the second-order approximation theory of perturbation, the value of the square-law effect of symmetric deformations

$$\delta E_A = -3h^2 e^2/\delta \qquad (2)$$

will, then, comply with the value found experimentally at $\delta = 0.04$ eV and $h = 0.6$ eV. Here, h is the non-diagonal matrix element of interaction between the trigonal deformations; this element is responsible for mixing the ligand state T_2^* with the ground state of the shallow center A_1.

Thus, the mixing of the ligand states with the electron wave functions explains the nonlinear effect observed in the field of symmetric stresses at reasonable values of the parameters.

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2) Here we actually used the imperfect molecule method /6, 7/, which was widely adopted in explaining the deep center properties both by EPR /8/ and by spin-lattice relaxation /9/.

We have also examined the $\delta E_i(P)$ dependences in antimony-doped germanium at $\vec{P} \parallel [100]$. It is worth noting that in the case of Ge, the aforesaid deformational variations of effective mass do not occur and, hence, one could expect that hybridization of the electron wave functions of the shallow center in the field of symmetric deformations would be manifested in a pure form. However, in this case, the effect observed experimentally is, at least, by one order of magnitude smaller than in silicon. Evidently, in Ge, the T_2^* state is deep in the conduction band as a result of a weaker vibronic interaction at the Jahn-Teller effect. Therefore, the contribution under consideration vanishes for two reasons. First, the energy spacing between A_1 and T_2^* may increase by more than one order of magnitude compared with a hypothetical case of strong vibronic interaction at the Jahn-Teller effect in Si. Second, the T_2^* level will simultaneously become considerably wider (with the allowance for interaction with the band states) due to increase of the electron density states with the conduction band depth.

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