Deep levels in semiconductors

In semiconductors, there are two main types of impurities that give levels in the band gap: deep and shallow. The characteristic band gap is $E_g \approx 3$ eV, if the ionization energy is $E_i = E_x < E_g$; then these are shallow impurities. If $E_i = E_g$, then impurities giving deep levels. In any case, the characteristic size of the wave function of a localized charge carrier is $R = \frac{\hbar^2}{2mE_i}$.

For shallow levels $Ro >> a$, for deep levels $Ro ~ a$, where $a$ is the lattice constant. But there is an intermediate case $E_x < E_i$ and then $Ro~(2-5)a$.

In this case, the impurity atom + lattice atoms closest to it can be considered as a molecule and it can be assumed that the wave function of the charge carrier covers only the nearest neighbors. It is these impurities that will be considered in my report.

Photoluminescence spectrum of the $VaTe_{0.6}$ complex

Experimental data

Resonance polarization spectroscopy

$a =$ orthogonal scheme, $b =$ “reflection” scheme.

$\mathbf{E}_x$, $\mathbf{E}_y$, and $\mathbf{E}_r$ electrical vectors of the light wave of exciting and emitted light.

Demonstration of the anisotropy of the complex

Experimental dependences of the polarization ratio of photoluminescence in the band with a maximum at the photon energy $\sim 1.2$ eV on the value of uniaxial pressure. Direction of pressure: $a = [001], b = [111]$.

Excitation of photoluminescence by light from its own absorption band. T, K: 1 - 2, 2 - 77.

Model Charge states of a vacancy complex

The deepest level belongs to state of $a_1$ symmetry formed by the broken bond between the donor and the vacancy. The states with symmetry $a_1$ and $e$, formed by broken bonds of three As atoms surrounding the vacancy, and the level $a_1$ is located closer to the conduction band than the level $e$. The strong interaction with the donor causes a significant distortion of the original wave functions of the vacancy. In this case, the symmetry of the wave function of the upper $a_1$ state does not change. Interaction of electrons in the $a_1$ and $e$ states with non-totally symmetric phonons of E-type (Jahn-Teller pseudoeffect and Jahn-Teller effect) leads to further symmetry decreasing of the complex to monoclinic, to splitting of the electronic $e$-state, and a further change in the wave functions of electrons.

Model. Initial $C_3v$ symmetry

In this case one can be assumed that the state $a_1$ with the deepest energy does not change under the influence of the electron-phonon interaction. Considering the interaction of the original trigonal complex with E-vibrations in a cubic lattice, it is convenient to introduce a new rectangular coordinate system in which the axis $Z$ coincides with the volume diagonal of the cube containing the donor, and axis $X$ lies in the plane of symmetry of the monoclinic center. The generalized coordinates of the E-vibrations associated with this system will be denoted by $Q_x$ and $Q_y$. Then the Hamiltonian describing the donor influence and the interaction of one electron with E-vibrations in the basis of the original vacancy wave functions $X$, $Y$, $Z$ has the form

$$\hat{H} = \begin{pmatrix} -\Delta + F_2 Q_x & -F_2 Q_y & F_1 Q_x \\ -F_2 Q_y & -\Delta - F_2 Q_x & F_1 Q_y \\ F_1 Q_x & F_1 Q_y & 2\Delta \end{pmatrix}$$

For $Q_x, Q_y = 0 \lambda_1 = -\Delta, \lambda_2 = 2\Delta$. At $Q_x, Q_y$ are not equal to zero the expressions for $\lambda_i$ become cumbersome, and further, for a qualitative consideration, we will use more simple expressions obtained under the condition that $F_1 \gg F_2$:

$$\lambda_1 = \frac{\Delta}{2} + \sqrt{\frac{9}{4} \Delta^2 + F_1^2 q^2}$$

$$\lambda_2 = \frac{\Delta}{2} - \sqrt{\frac{9}{4} \Delta^2 + F_1^2 q^2} + \frac{F_1^2 q^2 \cos 3\beta}{2 \sqrt{2 \Delta^2 + F_1^2 q^2} \sqrt{\frac{9}{4} \Delta^2 + F_1^2 q^2}}$$

$$\lambda_3 = -\Delta - F_2 q \cos 3\beta$$

where the designations $Q_x = q \cos \beta$, $Q_y = q \sin \beta$ are introduced, and the angle $\beta$ is measured in the plane $XY$ from the axis $X$.\[\]
Model Charge states of a vacancy complex

In the absorbing state the vacancy complex binds 7 electrons, two of which are at the deepest level, their energy makes a constant contribution to the energy of both absorbing and emitting states, and will not be taken into account. The remaining states, in which 5 electrons are located, change under the influence of JTE, and this must be taken into account when calculating the adiabatic potential of the center. Since $\lambda_1 + \lambda_2 + \lambda_3 = 0$, the total energy of these 5 electrons, neglecting the interaction between them compared to the influence of the donor and JTE, can be equal to $-\lambda_1$, $-\lambda_2$, or $-\lambda_3$. The minimum value of the total energy will be equal to $-\lambda_1$, i.e., under equilibrium conditions at low temperatures, there is one electron in the weakest bound state $\lambda_1$. To determine the equilibrium configuration of the complex in the absorbing state, it is necessary to determine the position of the minimum of the adiabatic potential $W_1$, which is equal to the sum of the total electron energy of 5 localized electrons and the energy of elastic vibrations $W_1 = -\lambda_1 + K/2 q_0^2$

where $K/2 q_0^2$ is the elastic energy of E-vibrations of atoms, $K$ is the elasticity coefficient. At $F_2 = 0$ $W_1$ is independent of $\beta$ and is an annular trough with radius $q_0$. At $0 < |F_2| \ll F_1$, 3 minima of the adiabatic potential appear on this trough, which correspond to $\beta = 0$, 120 and 240° at $F_2 > 0$.

In the emitting state 6 electrons are bound to the complex, and therefore only 4 electrons are localized in the considered upper states, and the fifth electron is in the conduction band. The minimum total electron energy of 4 electrons will be equal to $-2\lambda_1 + E_c$, where $E_c$ is the electron energy in the c-band. In this case, the electronic state with energy $\lambda_1$ under equilibrium conditions at low temperatures is completely empty. In the emitting state, the adiabatic potential of the system complex + 5 electrons is $W_2 = -2\lambda_1 + K/2 q_0^2 + E_c$.

Since the electron in the conduction band does not interact with E-vibrations, $E_c$ does not depend on $q_0$ and the form $W_2$ in the space of generalized coordinates of E-vibrations differs from $W_1$ only by the coefficient 2 before $\lambda_1$. As can be seen from equations for $\lambda_i$, this is equivalent to replacing $F_1$, $F_2$ and $\Delta$ by $2F_1$, $2F_2$ and $2\Delta$, respectively. Thus, the efficiency of the JTE depends on the number of electrons localized on the complex, and in the emitting state the JTE is stronger than in the absorbing state. Accounting for this circumstance is a new result in the study of complex defects in semiconductors.

### Conclusion

The existence of an anisotropic trigonal Jahn-Teller defect in a cubic crystal is demonstrated. Such defects are V$_{Ga}$-TeAs and V$_{Ga}$-S$_{As}$ vacancy complexes in GaAs.

The presented model of the center makes it possible to explain the entire set of experimental data. According to the model, the barriers between equivalent states are higher in the emitting state, so that the reorientation occurs in the absorbing state, in which the height of the barriers is several meV. Due to the different efficiency of JTE in different charge states, the optical dipoles in them are oriented differently.

Thank you for your attention