Self-compensation induced in semiconductors by centers with a negative correlation energy

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(Submitted 26 December 1986)
Pis'ma Zh. Eksp. Teor. Fiz. **45**, No. 5, 231–234 (10 March 1987)

Self-compensation processes which depend on an external electric field have been observed during optical pumping of GaAs containing antisite defects of the type As_{Ga}. A new model is proposed for an antisite defect on the basis of the concept of a negative correlation energy. This model incorporates two-electron capture, metastability, and self-compensation.

The deep levels of the group EL2, which are responsible for the semi-insulating properties of single crystals and epitaxial films of GaAs, have recently attracted research interest.[1,2] It has been shown by an ESR method that EL2 belongs to a neutral charge state of a donor antisite defect[3–5] As_{Ga}. A study of this topic is very important to the development of technology for a new generation of integrated circuits.[2,5] One purpose of the present study was to learn how an electric field affects those photoconduction and electrical properties of GaAs which stem from the interrelation between the metastability and self-compensation of As_{Ga} defects. Another purpose was to construct a model for an antisite defect incorporating the concept of a field-dependent negative correlation energy (negative U).

We measure the photoconductivity spectrum (Fig. 1) in semi-insulating, chromium-doped n-type GaAs crystals grown by the Czochralski method. The dark density of conduction electrons at $T = 300$ K is 2×10^{10} cm^{-3}. Experiments are carried out at various temperatures (Fig. 1a) and at various electric field strengths (a forward bias voltage) in pin structures, where the given material is used as the i layer (Fig. 1b). At $h\nu > 0.75$ eV we observe an increase in the photoconductivity (Fig. 1a). At a higher energy, however, at $h\nu > 0.9$ eV, the photoconductivity decays (Fig. 1a), to an extent which depends on the temperature in an activation fashion [$h\nu = 1.06$ eV, $I_{ph} \propto \exp(-0.042\ \text{eV/kT})$]. In several of the samples studied, the decrease in the photoconductivity at $h\nu > 0.9$ eV is accompanied by an n–p conversion. At $h\nu > 1.1$ eV the photoconductivity increases again (Fig. 1a). When an electric field is applied in the forward direction to the pin diode ($\mathscr{E}$ does not exceed 4×10^3 V/cm), the photocurrent increases sharply at $h\nu < E_g$ both at $T = 300$ K (Fig. 1b) and at lower temperatures. The field dependence of the photocurrent in this spectral region is described by the exponential law $I_{ph} \propto \exp(\mathscr{E}/\mathscr{E}_0)^{\alpha}$, where the exponent $\alpha = 2$ differs substantially from that of the Frenkel-Poole law for the electroabsorption in semiconductors with shallow Coulomb centers.

The results of these experiments can be explained in the model of a two-electron center (Fig. 2), whose charge states correspond to different equilibrium positions in the lattice, which differ in the magnitude and sign of the effective electron-electron interaction U. The center As_{Ga} is represented as a site-(interstitial position) tunneling

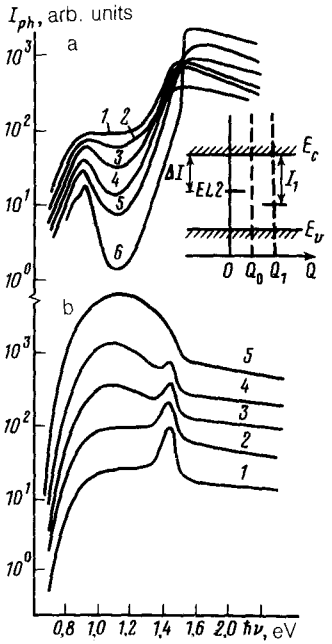

FIG. 1. Photocurrent spectrum. a: In semi-insulating GaAs. 1—$T = 340$ K; 2—297 K; 3—240 K; 4—185 K; 5—148 K; 6—96 K. b: In a pin structure based on semi-insulating GaAs. 1—2 V; 2—4 V; 3—6 V; 4—8 V; 5—10 V. The inset in part a is the one-electron band diagram of GaAs containing antisite defects. The different charge states correspond to the levels $E_c - I_1 = E_V + 0.52$ eV $[(D_i V)^+]$ and EL2 $- E_c - \Delta I = E_c - 0.75$ eV (a correlated electron at a D_s^0 center).

system, where the two-electron state $(As_{Ga})_s^0 = D_s^0$ $(n = 2)$ with $U < 0$ is stable at a lattice site $(Q = 0)$, while the states $(As_{Ga})_i^+ = (D_i V)^+$ $(n = 1)$ and $(As_{Ga})_i^{2+} = (D_i V)^{2+}$ $(n = 0)$ with $U > 0$ exist only in a noncentral interstitial position (Fig. 2). The corresponding Hamiltonian is

$$H = \frac{P^2}{2M} + \frac{\kappa}{2}Q^2 + E_0(n_\uparrow + n_\downarrow) + Un_\uparrow n_\downarrow - F_0 Q - (F_1 - F_0)Q(n_\uparrow + n_\downarrow)$$

$$+ (F_0 - 2F_1)Qn_\uparrow n_\downarrow$$

$$- \delta FQ(2 - n_\uparrow - n_\downarrow), \qquad (1)$$

where P and Q are the canonical momentum and coordinate of the center; M and κ are the mass and the corresponding force constant of the center, E_0 and F are the one-electron energy and the constant of the electron-vibrational interaction (which depends in a nonmonotonic way on the number of electrons at the center; $F_0 \neq F_1$); n_σ are the occupation numbers of the center describing the occupation by electrons with spins $\sigma = \uparrow, \downarrow$; the last term in (1) is the perturbation of the charge states of the center when it is immersed in an electric field $\mathscr{E}$; $Q_0 = F_0/\kappa$, $Q_1 = F_1/\kappa$ is the shift of the center in the absence of an electric field (Fig. 2); $\delta F = e\mathscr{E}\cos\theta$; θ is the angle between the direction of the field $\mathscr{E}$ and the coordinate Q; and $\delta Q = \delta F/\kappa$ is the shift of a single-charge center in an electric field (Fig. 2b). The two-charge state shifts by $2\delta Q$ (Fig. 2b). Our model incorporates the linear and quadratic Stark effects at the deep center and also its interrelation with the electron-vibrational interaction. Using (1),

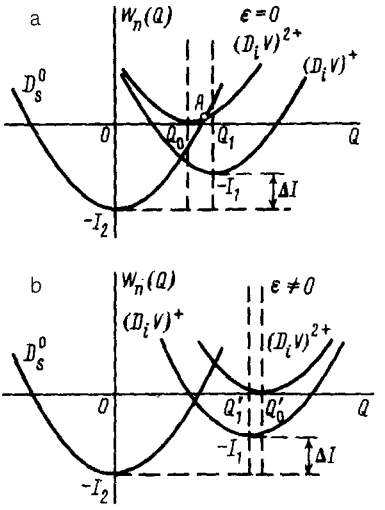

FIG. 2. Adiabatic potentials of the charge states of the antisite defect As_{Ga}. a—$\mathscr{E} = 0$; b—$\mathscr{E} \neq 0$; $Q_0' = Q_0 + 2\delta Q$; $Q_1' = Q_1 + \delta Q$.

we found explicit expressions for the adiabatic potentials for various values $n = n_1 + n_1 = 0, 1, 2$ (Fig. 2, a and b), where the value I_1 corresponds to one-electron transitions $(D_i V)^+ \leftrightarrow (D_i V)^{2+}$ and I_2 corresponds to two-electron transitions $(D_i V)^{2+} \leftrightarrow D_s^0$. The two-electron state D_s^0 is taken into account in the one-electron band diagram (see the inset in Fig. 1a) by introducing a level of a correlated electron, $E_L 2 - \Delta I = I_1 - I_1$ (Fig. 2a).

According to this model, the initial increase in the photoconductivity (Fig. 1a) stems from a single ionization of a D_s^0 center ($h\nu > \Delta I$). The subsequent decay of the photoconductivity at $h\nu > 0.9$ eV results from the chain of reactions (I) $(D_i V)^+ + h\nu \rightarrow (D_i V)^{2+} + e$, (II) $(D_i V)^{2+} + 2e \rightarrow D_s^0$. The conduction electron produced in reaction (I) induces a rapid two-electron capture to the $(D_i V)^{2+}$ center. As a result, there is an effective "pumping" of electrons out of the conduction band. The mechanism for this nonradiative two-electron capture is an electron-electron interaction in the conduction band with simultaneous multiquantum excitation of a local mode of the defects. The lifetime of a conduction electron with respect to a capture of this type is

$$\frac{1}{\tau_n(\mathscr{E})} = \frac{2\pi}{\hbar} N_i a_0^3 \left(\frac{e^2}{a_0}\right)^2 \mathbf{N}(\mathscr{E}); \quad \mathbf{N}(\mathscr{E}) = n a_0^3 \frac{K(\mathscr{E})}{\hbar\omega_0};$$

$$K(\mathscr{E}) = (2\pi N)^{-1/2} (\bar{N}/N)^N \exp(N - \bar{N}); \quad \bar{N} = \frac{\kappa (Q_0 - 2\delta Q)^2}{2\hbar\omega_0}; \qquad (2)$$

$$N = 2\bar{N}_0 - \bar{N},$$

where the final-state density $\mathbf{N}$ is constant over an energy region of width $\bar{N}_0^{1/2}\hbar\omega > kT$ near the bottom of the conduction band, a_0 is the first Bohr radius of the electron state at the defect, n and N_i are the densities of conduction electrons and of

$(D_i V)^{2+}$ centers, respectively, $\omega_0 = (\kappa/M)^{1/2}$ is the frequency of a local mode, $K(\vec{\mathscr{E}})$ is a field-dependent tunneling factor for the reaction, which is related to a change in the structure of the center upon the capture of carriers,[6] and $\overline{N}$ and $\overline{N}_0$ are the optimum number of quanta for the process in the field $\vec{\mathscr{E}}$ and in the absence of a field ($\delta Q = 0$). According to (2), the field dependence of the photoconductivity is quadratic in logarithmic scale:

$$\frac{\Delta\sigma_{ph}}{\sigma_{ph}} = \frac{\Delta n}{n} \simeq \frac{K(0)}{K(\mathscr{E})} \simeq \exp\left(32\tilde{N}_0\left(\frac{\delta F}{F_0}\right)^2\right), \tag{3}$$

in good agreement with the data in Fig. 1b. The increase in the carrier lifetime with increasing field $\vec{\mathscr{E}}$ in (2) and (3) is therefore a consequence of a relative shift of the adiabatic potentials of the different charge states of the defect (Fig. 2b). This mechanism is distinct from the Frankel-Poole effect. The disappearance of the decay of the photoconductivity at $h\nu > 0.9$ eV (Fig. 1a) with increasing temperature, which can be attributed to a thermal excitation of a local mode of the $(D_i V)^+$ center, can be described by the thermal exponential function given above with an activation energy roughly equal to the energy of a local phonon. In this case, the contribution of reaction (1) to the photoconductivity begins to increase, since the final term $(D_i V)^{2+}$ is excited below a point A (Fig. 2a). At $h\nu > 1.15$ eV, the photoconductivity increases again (Fig. 1a) because of the finite width of the absorption band, $(D_i V)^+ \leftrightarrow (D_i V)^{2+}$ (Fig. 2a).

In summary, an electric field controls the interrelation between the metastability and the self-compensation under conditions such that there is a negative correlation energy, $U < 0$. This mechanism can apparently determine to a significant extent the operating conditions of III–V semiconductor devices.

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Translated by Dave Parsons