Negative-U tunnelling centers and photostimulated reactions in semiconductors

N. T. Bagraev and V. A. Mashkov
A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR

(Submitted 9 January 1984)
Pis'ma Zh. Eksp. Teor. Fiz. **39**, No. 5, 211–213 (10 March 1984)

Tunneling systems formed by centers in semiconductors with negative U are observed because of the dependence of the electron-vibrational interaction constant on the charge state, whose presence leads to an experimentally observable reversible restructuring in the system of lattice defects under the action of optical pumping.

Centers with deep levels in semiconductors are generally characterized by low-symmetry Jahn-Teller distortions and interelectronic correlations. Anderson[1] showed that these effects could be interrelated, and he proposed a model of a deep center in which a bound state of two electrons arises at the center due to electron-vibrational interaction (EVI) (model with effective negative U). A peculiarity of the model[1] is that the EVI constant is independent of the number of electrons at the center, which is similar to the band-theory concept. In this connection, this model can only be used to describe so-called elastic systems, for which strong deformation of wave functions with a change in the number of electrons at the center is observed. An example of such centers is a vacancy in silicon, which has inverted levels in the forbidden band due to $U<0$,[2] which was confirmed experimentally in recent studies by Watkins *et al.*[3] It

 0021-3640/84/050251-05$01.00 © 1984 American Institute of Physics

should be noted that other mechanisms for producing $U<0$ have been discussed in the literature.[4]

In this paper we examine an alternative situation for the appearance of $U<0$, characterized by the absence of a Jahn-Teller effect and large deformations of wave functions of the deep center accompanying a change in its charge state. As a result, such a center can be called a rigid center. The equivalent of the Jahn-Teller distortions in the proposed model is a transition of the center to a new equilibrium position as a result of changing its charge state. The physical reason for the appearance of two positions of equilibrium is the nonmonotonic dependence of the EVI constant on the number of electrons at the center, in contrast to Ref. 2, which is characteristic for deep centers with a small localization length.[5] In this case, there is a tunneling system with an interaction U of different sign and magnitude in different positions of the center in the lattice, for example, a lattice site-interstice system. We shall examine a model tunneling system with three charge states: two-electron state A_- ($n=2$), single-electron state A_0 ($n=1$), and empty state A_+ ($n=0$), whose adiabatic potentials are plotted in Fig. 1 as a function of the configurational coordinate Q. The A_+ and A_- states of the system are stable at the lattice site, and the states A_0 exists only at an interstice and correponds to the absolute minimum of the energy of the system. The corresponding Hamiltonian has the form

$$H=\frac{P^2}{2M}+\frac{\kappa}{2}Q^2+E_0(n_\uparrow+n_\downarrow)+Un_\uparrow n_\downarrow-FQ(n_\uparrow+n_\downarrow-2n_\uparrow n_\downarrow), \tag{1}$$

where P and Q are the canonical momentum and the coordinate of the center, M and κ are its mass and the corresponding force constant, E_0 and U are the single-electron energy and the interelectronic interaction at the center, F is the EVI constant, and n_σ is the occupancy number of the center for electrons with spin $\sigma=\uparrow,\downarrow$. As a result of diagonalizing (1) with respect to the charge states of the tunneling system, we find the explicit form of the adiabatic potentials for different values of $n=n_\uparrow+n_\downarrow$ (see Fig. 1, where the energy is measured with respect to the bottom of the conduction band):

$$E_n(Q)=\{\frac{\kappa}{2}Q^2,\ n=0;\ -I_1+\frac{\kappa}{2}(Q-Q_0)^2,\ n=1;\ -I_2+\frac{\kappa}{2}Q^2,\ n=2\}, \tag{2}$$

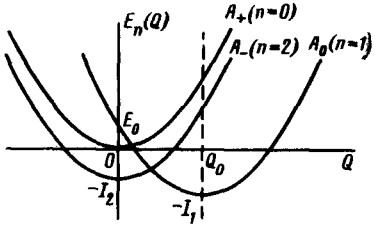

FIG. 1. Adiabatic potentials of different charge states of the tunneling system of centers with an interaction U differing in sign and magnitude, as a function of the configurational coordinate.

where

$$Q_0 = F/\kappa\,;\; I_1 = -E_0 + \frac{F^2}{2\kappa} > 0;\; I_2 = -(2E_0 + U) > 0\,. \tag{3}$$

The condition for stability of the equilibrium position at an interstice is $I_1 > I_2$, i.e., $E_0 + U + F^2/2\kappa > 0$. The instability of the state A_0 at a lattice site is described by the inequality $E_0 > 0$, while a condition of stability of A_- at a lattice site is equivalent to the last relation in (3), i.e., the inequalities $U < -2E_0 < 0$ are satisfied. Thus, when a center makes a transition from an unstable state at a lattice site ($Q = 0$, $U < 0$) to an interstice ($Q = Q_0$), the single-electron energy decreases, and the interelectronic interaction increases and changes sign. Therefore, an Anderson system with $U < 0$ exists at the lattice site (A_- is the ground state, A_+ and A_0 are the excited states), while at an interstice the system has the usual order of levels (A_- is the ground state, A_- and A_+ are the excited states). The proposed scheme, which takes into account the rigidity of the electronic wave functions, predicts low tunneling transition probabilities with a change in the charge state of the system $\Delta n = \pm 1$. For this reason, the times τ of photostimulated and spontaneous transitions of the centers between stable configurations A_- at a lattice site and A_0 at an interstice differ by the factor K from the corresponding values characterizing the excitation and trapping of carriers, in which the structural changes are ignored: $\tau^{-1} = \tau_0^{-1} K$. The cross sections for trapping and photoionization of carriers ($\sigma = \sigma_0 K$) change analogously. A quantum-mechanical calculation of the probabilities of tunneling transitions between equilibrium positions of the system, accompanying photostimulated and spontaneous "level-band" transitions of the electron or hole at the center, gives the following upper limit for the tunneling factor K:

$$K_{max} = (2\pi N_m)^{-1/2} (\bar{N}/N_m)^{N_m} e^{(\bar{N} - N_m)};\; \bar{N} = (Q_0/2 < \delta Q >)^2; \tag{4a}$$

$$N_m = \{ \frac{\Delta\Omega}{\omega_0};\; \frac{\Delta E}{\hbar\omega_0} \} \ll \bar{N};\; \omega_0^2 = \kappa/M;\; < \delta Q > = (\hbar/2M\omega_0)^{1/2}, \tag{4b}$$

where $\Delta\Omega$ is the width of the spectrum of the pumping light, ΔE is the difference between the energies of the electronic subsystem with a spontaneous transition, and ω_0 is the frequency of localized vibrations. The inequality corresponding to maximum quantum nature of the process $N_m \ll \bar{N}$ is a result of the rigidity of the tunneling system $\Delta E > \omega_0 > \omega_D$, where ω_D is the Debye frequency. An example of the tunneling systems examined with sign-alternating U are gold impurity centers in silicon, which create two levels in the forbidden band (see Fig. 2): an acceptor level (E_c—0.49–0.54 eV),[6] which correponds to a center Au^- at a lattice site, and a donor center ($E_v + 0.35$ eV), which belongs to a noncentral, interstitial, neutral gold atom.[7] The independence of the donor and acceptor gold levels has been proved with the help of different techniques.[6–9] In addition, it has been shown that in Si⟨Au⟩ central gold centers are not observed at the lattice sites.[9]

It is well known[6–9] that Si⟨Au⟩ is characterized by rapid recombination processes. However, the existence of an extremely slow process $Au^0 + e \rightarrow Au^-$, which is related to the low tunneling probability of the given transition, was reported in Ref. 10. The data on Ref. 10 agree well with the computed values of K_{max}, obtained with the

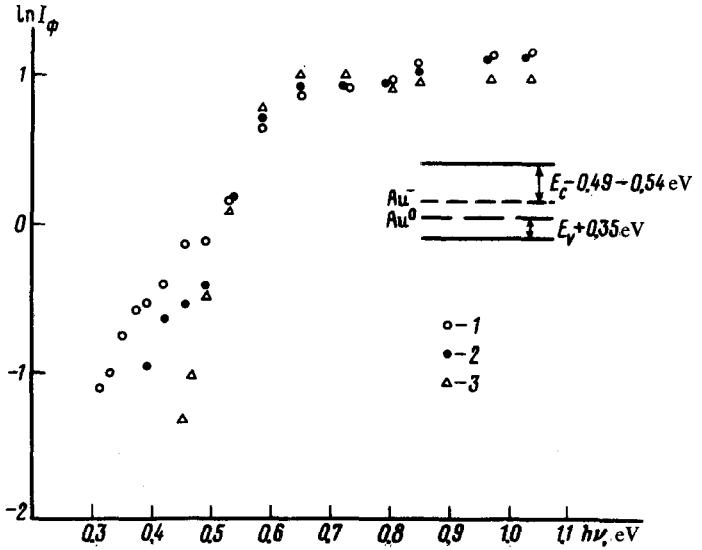

FIG. 2. Spectral dependence of the impurity photoconductivity of n-type silicon doped with gold. 1) Initial state, 2) after optical pumping with light from a 1–kW incandescent lamp for 3.5 h 3) after optical pumping with light from an incandescent lamp (1 kW) for 5.5 h.

help of (4): $1.4\times10^{-11}<K_{\max}<2\times10^{-5}$, depending on N_m. Thus, under prolonged optical pumping in the tunneling gold system in silicon, there should be a gradual disappearance of Au^0 centers, with a corresponding increase in the concentration of Au^-, which we obtained while investigating the spectra of impurity photoconductivity of n-type Si⟨Au⟩ (see Fig. 2). The starting state correponds to the presence of Au^0 centers (see the increase of I_p at $h\nu\simeq0.31$ eV) and Au^- centers (see the increase of I_p with $h\nu\simeq0.49$–0.54 eV on curve 1 in Fig. 2), which appeared due to cancellation of the phosphorus donor centers. To record the transitions v-band–($E_v+0.35$ eV), the photoconduction spectra were recorded in daylight. As a result of prolonged optical pumping by light from an incandescent lamp, with intensity 1 kW, a gradual disappearance of Au^0 centers and simultaneous increase in the concentration of Au^- centers were observed (see Fig. 2). In addition, the times of the transitions of the Au^0 center from the state with $U>0$ to the state with $U<0$ are in quantitative agreement with the model discussed above (see Fig. 2). The relaxation of the tunneling gold system in silicon to the initial state after the pump light was switched off occurred over a time of the same order of magnitude, consistent with the proposed model.

The authors thank E. V. Astrov for help in performing the experiments.

[1]P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).
[2]G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B **21**, 5662 (1980).
[3]J. L. Newton, A. P. Chatterjee, R. D. Harris, and G. D. Watkins, Physica B **116**, 219 (1983).
[4]V. G. Karpov and M. I. Klinger, Fiz. Tekh. Poluprovodn. **12**, 1887 (1978) [Sov. Phys. Semicond. **12**, 1122 (1978)], I. A. Drabkin and B. Ya. Moĭzhes, Fiz. Tekh. Poluprovodn. **17**, 969 (1983) [Sov. Phys. Semicond. **17**, 611 (1983)].

[5]V. S. Vikhnin, I. M. Zaritskiĭ, A. A. Konchits, and B. K. Krulikovskiĭ, Fiz. Tverd. Tela **17**, 3609 (1975) [Sov. Phys. Solid State **17**, 2348 (1975)].
[6]D. V. Lang, H. G. Drimmeis, E. Meijer, and M. Jaros, Phys. Rev. B **22**, 3917 (1980).
[7]V. S. Postnikov, V. I. Kapustin, V. I. Kirillov, S. A. Ammer, and Yu. I. Kozlov, Fiz. Tverd. Tela **20**, 3509 (1978) [Sov. Phys. Solid State **20**, 2032 (1978)].
[8]S. J. Pearton and A. J. Tavendale, Phys. Rev. B **26**, 7105 (1982).
[9]N. T. Bagraev, Physica B **116**, 236 (1983).
[10]W. D. Bickley and D. V. Eddolls, Solid State Electronics **21**, 1616 (1978).

Translated by M. E. Alferieff
Edited by S. J. Amoretty