PHYSICAL REVIEW B VOLUME 31, NUMBER 6 15 MARCH 1985

Electron-hole exchange transitions at defects in semiconductors

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(Received 29 November 1984)

We predict a new effect, electron-hole exchange transitions, which occur at all amphoteric defects. We show that these transitions play a dominant role in electron-hole recombination at deep centers. In particular, our results demonstrate that recent conflicting data on gold-doped silicon are all consistent with the observed donor and acceptor levels belonging to the same center.

Many important deep centers in semiconductors are *amphoteric,* in the sense that they have both a donor and an acceptor level in the band gap, as shown in Fig. 1(a). Such centers are also known as three-charge-state defects because they can exist in three different charge states. The assignment of observed donor and acceptor levels to the *same* center is, in general, a difficult task. A necessary, though not sufficient, condition is that the two levels belong to centers with the same concentration. During the past ten years, deep-center concentrations have been routinely extracted from deep-level-transient-spectroscopy (DLTS) measurements. For amphoteric centers, the relevant analysis was developed in 1973 by Henry, Kukimoto, Miller, and Merritt[1] on the basis of rather straightforward assumptions regarding the energy-level structure and carrier capture and emission processes at such centers. Using that analysis, Lang, Grimmeiss, Meijer, and Jaros[2] carried out a detailed investigation of the widely studied donor and acceptor levels in gold-doped Si, which were at that time almost universally attributed to the same gold center. They concluded that the two levels do *not* belong to the same gold center, and postulated a family of gold-related centers in order to account for the observations. Recently, Ledebo and Wang[3] performed independent tests and concluded that the two levels do belong to the same center, but they could not account for the conflict with the data of Ref. 2.

In this paper we demonstrate that a hitherto unrecognized phenomenon plays a dominant role in the carrier capture and emission processes at deep amphoteric centers in semiconductors. This phenomenon is a two-body internal transition which is akin to Auger transitions,[4] but differs from them in fundamental ways. As a consequence of this internal transition, the relevant equations used in the analysis of DLTS data are altered. In particular, from a quantitative analysis of the rate equations, we find that the data of Lang *et al.*[2] are indeed consistent with the observed donor and acceptor levels belonging to the same gold center.

The conventional energy-level diagram for an amphoteric center is shown in Fig. 1(a). We use the letter C to denote such a center. Electron capture at the positive donor C^+ usually occurs in two steps:[5] capture of an electron into a shallow Rydberg level located an energy E_e below the conduction-band minimum, followed by a transition to the ground state C^0. The energy dissipated in this latter transition, E_1-E_e, is emitted in the form of photons or phonons. The neutral defect may then capture a second electron to form C^-. Similarly, the acceptor C^- can capture a hole in a Rydberg level located E_h above the valence-band maximum, followed by a transition to the state C^0, dissipating an energy E_2-E_h. A second hole may then be captured to form C^+. All of these processes are indicated by arrows in Fig. 1(a). We note that, in this conventional description of amphoteric centers, electron and hole processes are viewed as independent, so that no significance is attached to the possibility that E_1-E_e may be equal to or nearly equal to E_2-E_h.

Now let us look at an amphoteric defect by examining the total energies of the various states. We start with a neutral center C^0 in an otherwise perfect crystal, such that there is one electron in a doubly degenerate bound state in the gap. We take the total energy of this state as the zero of our energy scale. We then focus on two possible excited states of this system. (a) The single electron occupying the bound state in the gap can be excited into the shallow Rydberg state just below the conduction band. We label this state $(C^+e^-)^*$; its total energy is E_1-E_e. (b) The single hole in the bound state in the gap can be excited into the shallow Rydberg state just above the valence band. We label this state $(C^-h^+)^*$; its total energy is E_2-E_h. Other excited states of the system can be defined in a similar way. Thus, instead of the conventional level diagram of Fig. 1(a), we arrive at a diagram of *total* energies as shown in Fig. 1(b). The significance of this approach is that it allows us to

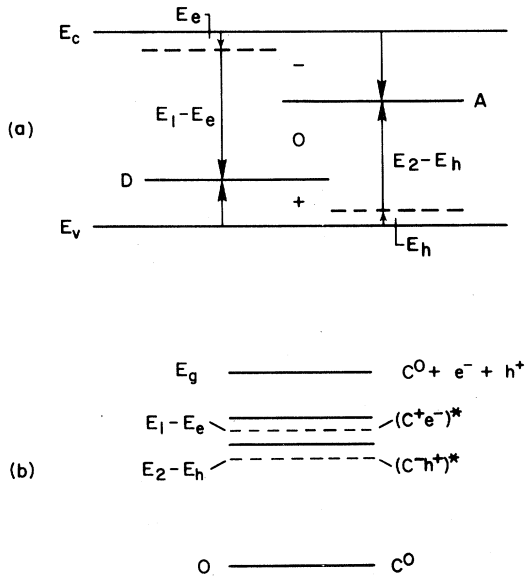

FIG. 1. (a) Conventional energy-level diagram for an amphoteric defect, showing the donor (D) and acceptor (A) levels. (b) Total electronic energies for the states of the same defect.

recognize the consequences of $E_1 - E_e$ being equal or nearly equal to $E_2 - E_h$. First, we note that the "excited states" described above are not necessarily true eigenstates of the many-electron system. Indeed, it is straightforward to show[5] that these two states are coupled by electron-electron interactions similar to those that give rise to excitons and to Auger transitions. This coupling produces transitions between the states, written as $(C^+e^-)^* \rightarrow (C^-h^+)^* + \Delta E$, where $\Delta E = (E_1 - E_e) - (E_2 - E_h)$ is the energy dissipated during the transition. We consider the case in which this energy is emitted in the form of localized phonons, as illustrated in the configurational-coordinate diagram of Fig. 2(a). We call this transition an "electron-hole exchange transition."

Using the Born-Oppenheimer and the unrestricted Hartree-Fock approximations, the rate of the electron-hole exchange transitions is given by

$$\frac{1}{\tau_{ex}} = \frac{2\pi}{\hbar}\left|\left\langle \phi_{Rc}\phi_{Rv}\left|\frac{1}{r_{12}}\right|\phi_{t1}\phi_{t2}\right\rangle\right|^2 \times \sum_{m,n} P_m |\langle \chi_m^f | \chi_n^i \rangle|^2 \delta(\epsilon_f - \epsilon_i - \Delta E) \quad . \tag{1}$$

The first term is the Coulomb interaction between electron and hole, where ϕ_{Rc} and ϕ_{Rv} are conduction- and valence-band Rydberg states, and ϕ_{t1} and ϕ_{t2} are trap states (spin up and spin down). The magnitude of this matrix element is determined primarily by the degree of localization of the wave functions, not by their particular shape (unless symmetry forces the matrix element to vanish). For trap wave functions with a radius in the range 3–6 Å, we estimate this matrix element to have an order of magnitude of 30 meV. The second term in Eq. (1) is an overlap of vibrational wave functions χ, summed over the sets of initial- and final-state occupation numbers m and n, and weighted by the thermal occupation P_m of initial states. The vibrational energies of the initial and final states are denoted by ϵ_i and ϵ_f. The functional form of this overlap term has been studied by many authors.[6] In the limit of low temperature, the overlap term can be approximated by

$$\sum_{m,n} P_m |\langle \chi_m^f | \chi_n^i \rangle|^2 \delta(\epsilon_f - \epsilon_i - \Delta E) \rightarrow \frac{1}{\hbar\omega} e^{-S} \frac{S^n}{\Gamma(n+1)} \quad , \tag{2}$$

where S is the Huang-Rhys coupling strength, $\hbar\omega$ the effective phonon energy, and $n = \Delta E/(\hbar\omega)$ the number of phonons emitted in the transition. In this formula we have broadened the phonon modes to form a continuum, in which case n can be regarded as a continuous variable. It is the dependence of Eq. (2) on n or equivalently, ΔE, which mainly determines the magnitude of the exchange rate; as ΔE increases and the number of phonons emitted becomes large, the probability for the process decreases very rapidly. Let us consider the specific case of gold in silicon, with $E_1 = 0.82$ eV and $E_2 = 0.61$ eV. From the optical spectra of Thebault *et al.*[7] we estimate an effective phonon energy of $\hbar\omega \approx 20$ meV with Huang-Rhys factor of $S \approx 1.3$ (these parameters apply between positive and neutral charge states; we assume the same coupling between neutral and negative charge states). Then, evaluating the vibrational overlap at an energy of $\Delta E = 0.21$ eV yields an exchange rate of about 10^{11} s^{-1}. Clearly this is a fast transition, and should play a significant role in electron-hole recombination.

We now describe one consequence of electron-hole exchange transitions which has significant ramifications on the interpretation of experimental data. Specifically, we consider the results of Lang *et al.*[2] that the saturated DLTS signals for the gold donor and acceptor are different, from which they concluded that the donor and acceptor levels are *not* associated with the same defect, in contradiction to the results

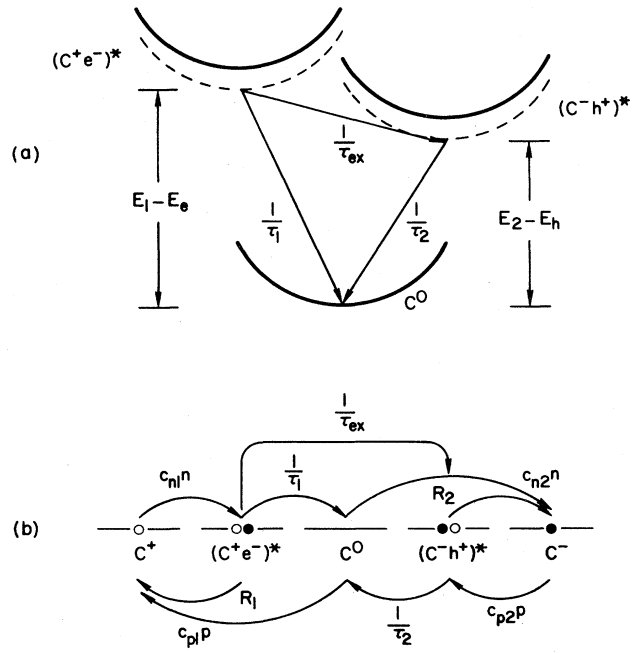

FIG. 2. (a) States of an amphoteric defect as seen on a configurational-coordinate diagram. Exchange transitions are labeled by $1/\tau_{ex}$. (b) Schematic view of the electron-hole kinetics.

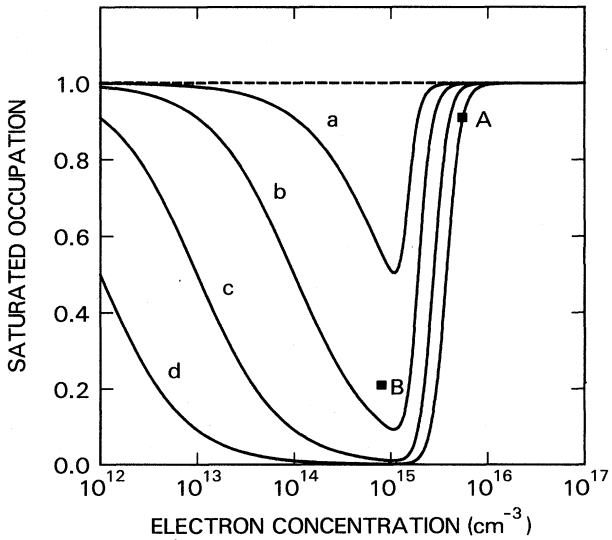

FIG. 3. Saturated fractional occupation of the gold donor as a function of the free-electron concentration. All previous theories have neglected exchange transitions, producing an occupation of unity, as shown by the dashed line. The solid lines give our theoretical results for various values of the kinetic parameter $\tilde{n}$: a, 10^{15} cm^{-3}; b, 10^{14} cm^{-3}; c, 10^{13} cm^{-3}; d, 10^{12} cm^{-3}. Experimental points *A* and *B* from Ref. 2.

of earlier and later studies.[3] We carefully examine their results in the light of our prediction of exchange transitions. In Fig. 2(b) we show a schematic view of the kinetics at amphoteric defects, including exchange transitions. The relevant experimental situation is saturation of the gold donor in n-type material. In that case, the hole concentration $p \rightarrow \infty$ and the electron concentration $n \neq 0$. Then, neglecting exchange transitions, it can be seen from Fig. 2(b) that since $c_{p1}p \rightarrow \infty$ and $c_{p2}p \rightarrow \infty$, all the defects eventually end up in either of the C^+ or $(C^+e^-)^*$ states. However, exchange transitions cause some of the defects to "leak" into the $(C^-h^+)^*$ state, and remain there until that state *slowly* decays to C^0 and then immediately captures a hole to form C^+. Thus, the saturated fractional occupation of the donor state, including both C^+ and $(C^+e^-)^*$ states, is less than unity. The saturated fractional occupation of the acceptor, on the other hand, *is* given by unity. Thus, exchange transitions can explain why the saturated donor and acceptor DLTS peaks are different.[2]

From a detailed analysis of the rate equations,[8] we find that the dependence of the fractional occupation f of the gold donor on the electron concentration n can be essentially described in terms of a single kinetic parameter. For low values of n, we find that

$$f = 1 - \frac{n}{n + \tilde{n}} \ , \tag{3}$$

where $\tilde{n}$ is a ratio of terms involving release out of the state $(C^-h^+)^*$ divided by terms involving capture into the state $(C^+e^-)^*$ and transitions to $(C^-h^+)^*$. This formula is valid up until an electron concentration of about 1×10^{15} cm^{-3} at which point the electric field in the junction becomes significant and tunneling of electrons and holes out of their Rydberg states becomes dominant.[9] This process produces a rapid quenching of any exchange transition effects, and f approaches unity. Using estimated values for this tunneling rate and for various other kinetic parameters, but maintaining $\tilde{n}$ as a free parameter, we have made theoretical predictions for f. In Fig. 3 we show our results, and compare them with the two data points of Lang *et al.*[2] Clearly the trend in the data is reproduced by the theory. For $\tilde{n} < 10^{15}$ cm^{-3} we achieve quantitative agreement between experiment and theory. This value of $\tilde{n}$ is completely consistent with our theoretical estimates,[8] although the uncertainties in the theory are sufficiently large so that it is probably best to regard $\tilde{n}$ as a free parameter. Additional data are required for a more definitive comparison between theory and experiment.

We thank T. N. Morgan for useful discussions. This work was supported in part by the Office of Naval Research under Contract No. N00014-80-C-0679.

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