Molecular-Dynamics Calculation of the Recombination Cross Section at Ionized Impurities in Semiconductors

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(Received 27 February 1989)

We present a novel first-principles calculation of the microscopic and macroscopic capture cross sections due to acoustic-phonon processes. The role of excited levels in determining the recombination is naturally included and found to be of main importance at increasing lattice temperatures. Numerical results compare favorably with available experiments.

PACS numbers: 72.20.Jv, 72.10.−d, 72.80.Cw

The recombination cross section at shallow impurity centers assisted by acoustic phonons is one of the most important physical quantities in determining the extrinsic transport properties in semiconductors at low temperatures. The cascade-capture model, originally introduced by Lax[1] and further elaborated by the Leningrad group,[2,3] is at the basis of the theoretical investigation of existing experimental results. (Attempts to improve the cascade model allowing for the quantum nature of transitions between energy levels have also been reported in Ref. 4. However, the calculated cross section was in large disagreement with experiments.) Despite significant success in interpreting experiments, the analytical approaches used so far are, however, subject to the following limitations. Within Lax's approach[1] one has to resort to the sticking function. This function accounts, at a kinetic level, for the probability a carrier has to finally reach the ground state of the impurity without returning to the conducting band, and its determination remains a complicated affair.[5-9] As a result, the effect of excited impurity levels during recombination remains hidden in spite of its recognized importance in determining the dynamics of recombination[10] and low-temperature breakdown phenomena.[11] The Leningrad group[2,3] has made use of a phenomenological energy-relaxation time to solve the appropriate kinetic equation. They succeeded in providing analytical results of the average capture cross section, but only in the two asymptotic regions $kT \ll ms^2$ and $kT \gg ms^2$ (m and s being the effective mass and the sound velocity, respectively). As a consequence, in the intermediate region $kT \simeq ms^2$, which for the case of p-Si treated here corresponds to the interesting temperature region centered around 2 K, a simple interpolation formula for the average capture cross section has been provided.

The aim of this Letter is to present a new approach which is free from the above limitations and, as will be shown later, opens new possibilities of investigation. It consists of a simulation of the carrier motion in the energy-configuration space of an impurity center, thus resembling a molecular-dynamics calculation. Looking for a first-principles determination of the recombination cross section, we have devised the following Monte Carlo procedure which extends previous results.[12] The main feature is that the semiclassical Boltzmann equation, ordinarily used for the carriers in conducting bands, can be easily extended to treat recombination and generation processes at impurity centers.

Figure 1, together with the ladder of excited levels, shows the potential energy of the single charged Coulomb center, $U(r)$, given by

$$U(r) = -\frac{e^2}{4\pi\kappa\kappa_0 r}, \qquad (1)$$

where e is the electron charge with its sign, κ the relative state dielectric constant of the material, and κ_0 the vacuum permittivity.

As long as the distance between the excited levels around kT is negligible with respect to both the ionization energy $E_I^{(0)}$ and the thermal energy kT, the energy region from the bottom of the conducting band to, let us say, the first ionized level $E_I^{(1)}$ can be considered as a continuum spectrum. Therefore, within the temperature range $kT < E_I^{(1)}$, the Boltzmann equation can be applied in the whole energy region covering the conducting and the bound states.[3]

Here we consider our system at equilibrium (but an extension to the presence of an external electric field gives, in principle, no difficulties) and we use a total-energy scheme. This scheme accounts for both the kinetic energy of the carrier and the potential energy of the impurities (here for convenience the case of acceptors has been considered) as shown in Fig. 1. Accordingly, the carrier kinetic energy, ϵ, can be written as

$$\epsilon = E_0 - U(r) = E_0 + E_0^f/x, \qquad (2)$$

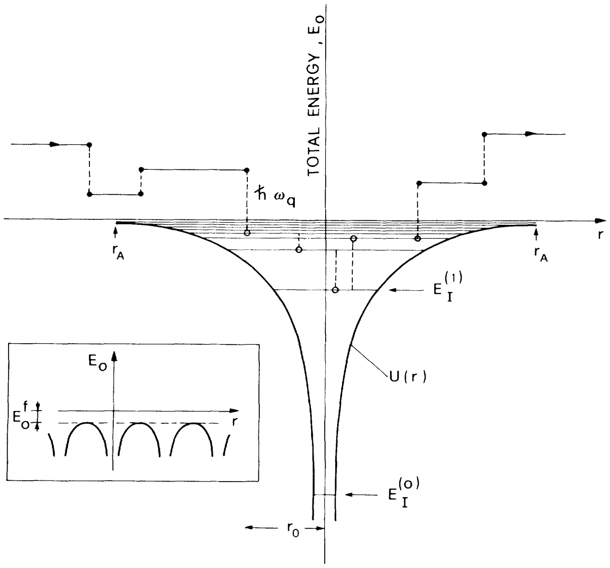

FIG. 1. Schematic representation of a trajectory of an electron in the (total) energy space at equilibrium. The full dots mark a scattering process via phonons with energy $\hbar\omega_q$ that an electron undergoes in the positive-energy region where it moves freely. In the attractive Coulomb field $U(r)$ it is accelerated and at a distance r_0 (measured from the charged center) the electron enters the negative-energy region. The open dots mark transitions between the energy levels of the impurity center in the negative-energy region where the electron is considered as trapped. All transitions are assumed to occur instantaneously in space and time (transitions in the negative-energy region supposedly are to occur at the impurity site). Inset: The energy level E_0^f associated with the fluctuational Coulomb potential of the impurity.

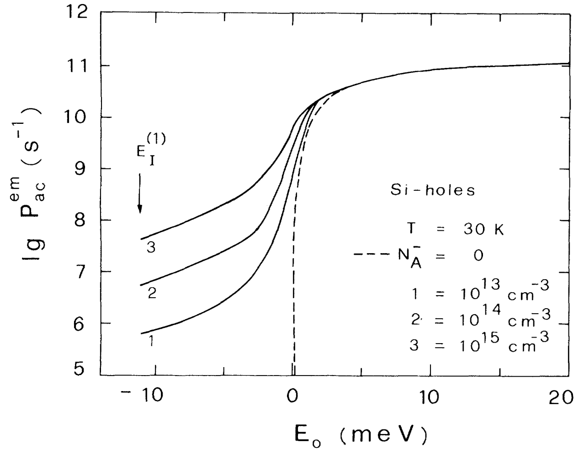

FIG. 2. Scattering rate for the process of acoustic-phonon emission as a function of the (total) carrier energy for p-type Si at 30 K and for the given ionized acceptor concentration.

where E_0 is the carrier total energy (or simply the energy), $E_0^f=(e^2/4\pi\kappa_0\kappa)(N_A^-)^{1/3}$ is the Coulomb energy at $r=r_A$, with $r_A=(N_A^-)^{-1/3}$ the mean radius of one impurity, due to the randomly distributed impurities, N_A^- is the ionized acceptor concentration, and $x=r/r_A$ is a dimensionless distance.

In this scheme, we assume that the positive-energy region corresponds to conducting states while the negative-energy region corresponds to trapped states. We remark that this is an operative definition for a trapped state; indeed, because of the role of excited levels, a rigorous definition of recombination remains an open problem, as will be discussed later. To this end, we should make a space average of the energy density of states and of the scattering rates. For a single Coulomb center of space average of a given function $A(\epsilon)$ is[3]

$$A(E_0)=\langle A(\epsilon)\rangle_{\text{space}}=\frac{\int_0^{r_{\max}}A(\epsilon)r^2dr}{\int_0^{r_A}r^2dr}$$

$$=3\int_0^{x_{\max}}A(E_0+E_0^f/x)x^2dx\,, \tag{3}$$

where the integration domain is the volume belonging to one impurity and $x_{\max}$ is determined by the constraint $\epsilon\geq 0$, i.e., $x_{\max}=1$ for $E_0\geq -E_0^f$ and $x_{\max}=-E_0^f/E_0$ for $-E_I^{(1)}\leq E_0<-E_0^f$. (Here the Coulomb potential for a single impurity has been cut off at $-E_0^f$. However, more generally, the Coulomb potential for a single impurity should be cut off at the percolation energy value,[9] which leads to a somewhat larger volume average than in our case.)

The above scheme is applied to the case of p-type silicon at temperatures below 77 K. A single spherical band model, the heavy holes, with a temperature-dependent effective mass which accounts for nonparabolic effects is used.[13] Because of the low temperature considered, the nonpolar optical-phonon interaction is neglected. Furthermore, being at equilibrium we do not need to follow the momentum of carriers, so that only changes of E_0 due to scatterings are important. Therefore, elastic scattering mechanisms, such as ionized impurities, can be neglected in the simulation.

Figure 2 shows the energy dependence of the scattering rate for acoustic-phonon emission $P_{\text{ac}}^{\text{em}}(E_0)$. As seen, the presence of the impurities is responsible for a tail of the scattering rate in the negative-energy region (the same happens for the case of acoustic-phonon absorption). This tail is more pronounced at increasing impurity concentrations.

The determination of the (velocity) average capture cross section $\bar{\sigma}_{\text{ac}}$ follows from its definition in terms of the recombination time, τ_r, through the standard relationship

$$\bar{\sigma}_{\text{ac}}=(\tau_r N_A^-\langle v\rangle)^{-1}\,, \tag{4}$$

where $\langle v\rangle$ is the equilibrium average velocity of carriers.

Thus, the main task of the present approach is to define τ_r. The most natural way of doing so is to calculate τ_r from the ratio between the time the carrier spends in the valence band and the number of transitions which

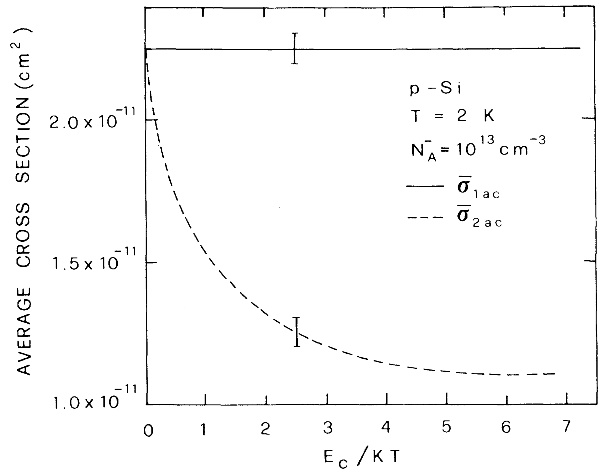

FIG. 3. Average capture cross sections in p-type Si as a function of the cutoff energy in the negative-energy region. Bars indicate the uncertainty of the calculations.

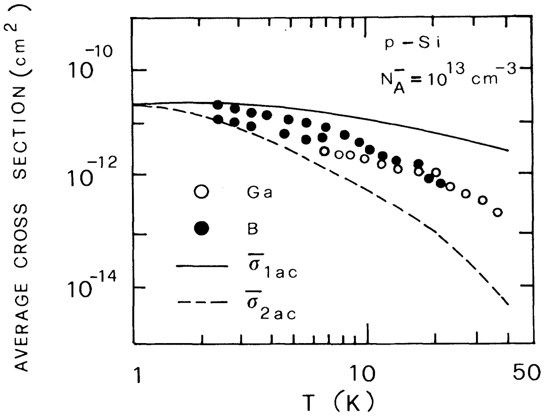

FIG. 4. Average capture cross section of p-type Si at equilibrium as a function of temperature. Curves report the present calculations performed for $N_A^- = 10^{13}$ cm^{-3} and symbols the experiments with various acceptors (Ref. 3). The continuous and dashed lines refer to $\bar{\sigma}_{1ac}$ and $\bar{\sigma}_{2ac}$ obtained for $E_c = -kT$, respectively (see text).

the carrier undergoes in the negative-energy region. However, in the negative-energy region the carrier has two possibilities: (i) to spend some time in the upper excited levels and then come back to the conducting band; and (ii) to penetrate far into the negative-energy region, that is where $E_0 \leq -kT$. The case (ii) corresponds to the concept of a real capture, and when this occurs we stop the simulation of the given particle and generate a new one in the conducting band with a velocity determined from detailed balance. In accordance with the above two possibilities we introduce two different times of recombination, τ_{r1} and τ_{r2} which, from Eq. (4), define two different cross sections $\bar{\sigma}_{1ac}$ and $\bar{\sigma}_{2ac}$. While the former accounts for all the transitions to $E_0 \leq 0$, the latter accounts only for those transitions, among the former ones, which lead the carrier along the ladder of excited levels to $E_0 \leq -E_c$, where E_c is a cutoff energy of the order of kT. Of course $\bar{\sigma}_{2ac}$ depends on the value of E_c; in any case it tends to saturate at increasing values of E_c.

Figure 3 shows the dependence of $\bar{\sigma}_{2ac}$ on E_c as obtained from calculations. It demonstrates that in most cases the high excited states exchange carriers in practice only with the conducting band. We believe that the saturation value of $\bar{\sigma}_{2ac}$ should be taken as the recombination average cross section associated with the true capture.

The temperature dependence of the two average capture cross sections defined above is shown in Fig. 4 and compared with available results in the literature referring to the shallow acceptors boron and gallium. Theoretical calculations, which have been performed for an ionized acceptor concentration $N_A^- = 10^{13}$ cm^{-3}, show that $\bar{\sigma}_{2ac}$ is systematically smaller than $\bar{\sigma}_{1ac}$. Furthermore, the dependence on temperature of the former exhibits a more steeply decreasing behavior. Consistent with our model, these results reflect the different role we have attributed to the excited states in defining the average capture cross sections. We noticed that the experimental results lie between the two theoretical curves. However, the fundamental question arises: What do experiments really measure? It can easily be argued that, as a general trend, the experiments should measure something intermediate between $\bar{\sigma}_{1ac}$ and $\bar{\sigma}_{2ac}$, this latter quantity representing a smallest asymptotic limit. Indeed, a more critical use of Eq. (4), in what concerns the physical meaning of the characteristic time the experimentalists substitute for τ_r, should lead to a reinterpretation of most of the data that have appeared in the literature. Thus, we conclude that our calculations provide a physically well-founded scheme for the interpretation of the recombination cross section at shallow impurity levels. In particular, we do not need to exploit the sticking function (which has been an open source of controversy in the literature[1-9]), *since sticking processes are self-consistently accounted for in our simulation.*

Our preliminary results for $10^{12} \leq N_A^- \leq 10^{14}$ cm^{-3} show that both cross sections slightly decrease for increasing ionized impurity concentrations. Finally, by keeping track of the initial carrier energy and constructing the histogram of the number of transitions to the negative-energy region, the simulation enables us to determine the differential capture cross section $\sigma(E_0)$ [which enters the definition of $\bar{\sigma}$ through $\bar{\sigma} = \langle\sigma(E_0)v\rangle/\langle v\rangle$] as a function of the carrier energy. A typical result is reported in Fig. 5. According to the results for the average cross sections, $\sigma_{1ac}(E_0)$ is systematically larger than $\sigma_{2ac}(E_0)$. Furthermore, both $\sigma_{1ac}(E_0)$ and $\sigma_{2ac}(E_0)$ exhibit a steeply decreasing dependence

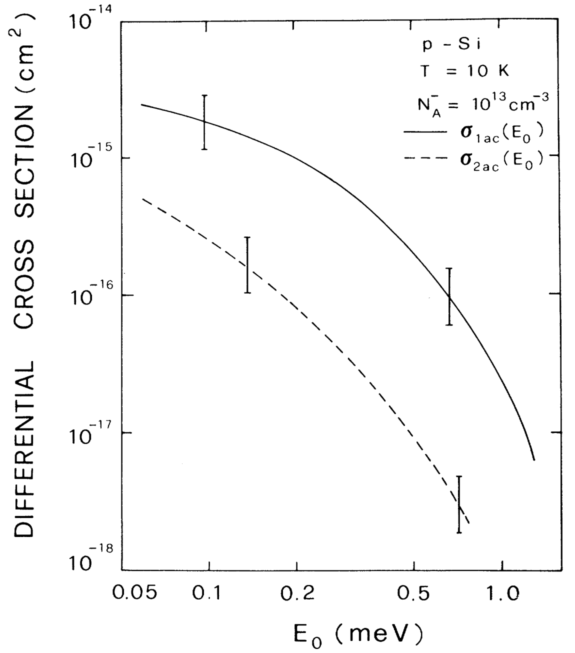

FIG. 5. Energy dependence of the differential capture cross sections as obtained by the Monte Carlo simulation. Bars indicate the uncertainty of the calculations.

with increasing energy, which reflects the dominant importance of low-energy carriers in the process of recombination, in general agreement with previous analytical calculations.[14]

In conclusion, a molecular-dynamics calculation is presented here as a novel numerical method to study the recombination cross section of free carriers at ionized shallow centers. The essence of the method enables us to avoid any approximate solution of the kinetic equation and to clarify the fundamental importance of excited levels in the determination of the capture cross section for temperatures as low as a few kelvin. The satisfactory agreement obtained with available experiments and the clarity of the physics underlying the calculations gives us confidence in predicting that this technique will be further developed to account for refinements in the theory.

This work has been performed on the basis of a Scientific Cooperation Agreement between the Academy of Sciences of the U.S.S.R. and the National Research Council of Italy. Partial support is provided by Ministero della Pubblica Istruzione and the Centro di Calcolo of the Modena University.

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