# Photoconductivity of randomly-inhomogeneous semiconductors

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The photoconductivity of an inhomogeneous semiconductor whose energy bands are modulated by a random potential is considered. The presence of such a potential causes spatial separation of the light-produced electron-hole pairs and this results in a sharp increase of the lifetime of the nonequilibrium carriers. This model can be used to explain the major features of long-duration relaxation and residual conductivity phenomena observed in compensated and amorphous semiconductors.

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One of the most interesting photoelectric phenomena in semiconductors is the residual (quenched) conductivity (RC), which is observed in a large number of various semiconductor compounds (see the bibliographies in [1–3]). An opinion has been gained recently that the cause of the RC is the presence in the sample of potential barriers connected with some kind of inhomogeneities. Several particular models were proposed for these barriers and have resulted in considerable progress in the understanding of the physical principles of RC. For example, Sheĭnkman, Markevich, and Khvostov[4] were the first to show that the high multiplicity of the RC is due to the changes in the overlaps of the space-charge region. This idea was further developed in the concepts of drift and recombination barriers, introduced by Sandomirskiĭ et al.[4] Nevertheless, there is still no consistent quantitative theory that explain all the observed features of RC.

Ryvkin and Shlimak[5] were the first to point out the possibility of explaining the RC in a very general semiconductor model, in which the energy bands are modulated by a random potential. This model can describe doped,[6] amorphous,[5,7] and in some cases also arriadiated semiconductors. Tkach[9] has made the first attempt to construct a quantitative theory within the framework of this model. The present paper is devoted to further development of this idea. We consider the photoconductivity of a randomly-inhomogeneous semiconductor and show that the proposed model makes it possible to explain both the main experimental regularities of the RC, and many other features of the photoconductivity of compensated and amorphous semiconductors.

Consider a semiconductor with a random potential relief $V(\mathbf{r})$. It is known that such a relief can be characterized by "percolation levels" $E_p^e$ in the conduction band and $E_p^h$ in the valence band. We assume that the level of the chemical potential $\zeta$ satisfies the condition $E_p^h < \zeta < E_p^e$ (in doped semiconductors this takes place in the case of strong compensation[10]). In this case both the electrons and the holes are localized: the former at the minima and the latter at the maxima of $V(\mathbf{r})$, and to take part in the conductivity they must be activated to the percolation level.

When the semiconductor is illuminated with light of frequency $\omega$ and intensity J there are generated $\alpha\beta J$ electron-hole pairs per cm$^3$ and per second ($\alpha$ is interband absorption coefficient and $\beta$ is the quantum yield). The pairs will be separated by the internal electric field $E = \nabla V/e$. It can be shown[9] that the characteristic time of this process, $\tau_0$, is practically always shorter than the time $\tau_r$ of recombination in the absence of spatial separation of the electrons and holes. Then all the equilibrium carriers will become localized in the extrema of $V(\mathbf{r})$ that are closest to the point of pair production. We shall show that the localized carriers go over with large probability into another more energywise favored extremum, rather than recombine. Tkach[9] has postulated this statement without proof.

Since $\tau_r > \tau_0$, to prove this statement it suffices to verify that for electrons from a certain minimum with energy $E' > \zeta$ the process of transition to a lower-lying minimum is connected with overcoming a smaller potential barrier than the recombination process.

Recombination can take place either with equilibrium holes or with nonequilibrium holes from maxima of energy $E'' < \zeta$. In the former case if the electrons are to recombine they must be activated to $\zeta + E_g - E'$ in order to fall into hole-containing regions. By virtue of the condition $E_p^h < \zeta$, these regions are not connected with one another. Therefore a path joining two minima of $V(\mathbf{r})$ can always be drawn through regions with a potential energy lower than $\zeta + E_g$, q.e.d.

In the second case, if the electrons are to recombine they need no longer reach the highest maxima of $V(\mathbf{r})$, so that a situation is possible wherein the minimum $E'$ and the maximum $E''$ are separated from all the low-lying minima by a barrier that is higher than $E''$. It might seem that here the electrons should recombine without having time to go over to another minimum. There will be no recombination, however, because the holes go off from the maximum $E''$ to the vertices of the aforementioned barrier. This path, circumventing the minimum $E'$, is connected with activation by an energy smaller than the $E_g - E' + E''$ needed for the recombination.

By virtue of the foregoing proof, the carriers in an illuminated inhomogeneous semiconductor can be regarded as quasi-equilibrium and characterized by electron and hole Fermi quasilevels $\zeta_e$ and $\zeta_h$, respectively. For the electron to find itself at one point of space with a hole and to recombine, it is necessary to overcome a potential barrier of height $E_\tau = E_g - \zeta_e + \zeta_h$. The lifetime of the nonequilibrium carriers is then $\tau_r \exp(E_\tau/T)$, and their stationary concentration is

$$\Delta n = \alpha\beta J\tau_r \exp\left(\frac{E_g - \zeta_e + \zeta_h}{T}\right). \tag{1}$$

It was assumed above that the recombination barrier $E_\tau$ is surmounted by thermal activation, and tunneling effects were neglected. This calls for not too low a temperature; for example, for strongly doped compensated semiconductors $T > E_B(na^3)^{1/2}$, where $E_B$ and a are the Bohr energy and radius, and n is the electron density.[11] At low temperatures expression (1) does not hold, but the conclusion that quasi-equilibrium sets in remains in force. The point is that the radius and amplitude of the fluctuations of the electrostatic potential $V(\mathbf{r})$ are connected with each other by the Poisson equation. Because of this, higher maxima of V(r) also have a lower tunnel penetrability, and allowance for tunneling will not change our arguments.

Since the Fermi quasilevels are determined by the carrier density, expression (1) determines the function $\Delta n(J)$ in implicit form. Since

$$d(\zeta_e-\zeta_h)/d(\Delta n)>0,$$

it can be stated that this dependence is sublinear. To determine it exactly it is necessary to know the concentration dependence of the quasilevels. We shall solve this problem for a strongly-doped compensated semiconductor.

The form of $\Delta n(J)$ is different at different light intensities. In the case of high intensities, such that $\Delta n > n_0$ ($n_0$ is the electron density in darkness), the electron and hole densities can be made the same and equal to $\Delta n$. If at the same time we have

$$\alpha\beta J\tau_r \gg e^6N^2/\varkappa^3T^3$$

(N is the impurity density and $\kappa$ is the dielectric constant), then the screening by the nonequilibrium carriers lowers the amplitude V(r) to a value ~T, and $\Delta n$ takes the same form as in a homogeneous sample:

$$\Delta n=\alpha\beta J\tau_r. \tag{2}$$

At lower intensity we have $-\zeta_e \sim \zeta_h + E_g \sim e^2N^{2/3}/\kappa(\Delta n)^{1/3}$,[10] so that (1) takes the form

$$\Delta n=\alpha\beta J\tau_r \exp\{\gamma_1 e^2N^{2/3}/\varkappa(\Delta n)^{1/3}T\}, \tag{3}$$

and $\gamma_1$, like $\gamma_2$ and $\gamma_3$ in the succeeding formulas is a numerical factor on the order of unity. Solving (3), we obtain

$$\Delta n\approx N^2\{\gamma_1 e^2[\varkappa T \ln (e^6N^2/\varkappa^3T^3\alpha\beta J\tau_r)]^{-1}\}^3. \tag{4}$$

The region of applicability of (4) is determined by the inequalities

$$\frac{e^6N^2}{\varkappa^3T^3}\exp\left(-\gamma_1\frac{E_0}{T}\right)\ll\alpha\beta J\tau_r\ll\frac{e^6N^2}{\varkappa^3T^3} \tag{5}$$

($E_0 = e^2N^{2/3}/\kappa n_0^{1/3}$ is the characteristic amplitude of $V(\mathbf{r})$ in the absence of illumination). At $N \sim 10^{18}$ cm$^{-3}$, $n_0 \sim 10^{16}$ cm$^{-3}$, $\kappa \sim 10$, and $T \sim 10^{-14}$ erg, expression (5) is satisfied if the intensity of the light is such as to produce in a homogeneous sample with the same $\tau_r$ a stationary carrier density from $10^{14}$ to $10^{18}$ cm$^{-3}$.

At still lower intensity, we arrive at the case $\Delta n < n_0$, where we can assume that $\zeta_e = \mathrm{const}(\Delta n) = \gamma_2 E_0$. No such formula, however, holds for $\zeta_h$. The concentration dependence of the Fermi level, described by this formula, reflects the n-dependence of the characteristic dimensions of the fluctuations of $V(\mathbf{r})$. In our case the latter are determined by a constant value $n_0$ greatly exceeding $\Delta n$, and the $\zeta_h(\Delta N)$ dependence is connected only with the change of the filling of these fluctuations. With the aid of the distribution function of $V(\mathbf{r})$, obtained by Shklovskiĭ and Éfros[12] in the region of high energies:

$$F(V)\sim\frac{1}{E_0}\exp\left\{-\frac{1}{3}\sqrt{\frac{2}{\pi}}\left(\frac{V}{E_0}\right)^{3/2}\right\},$$

we easily obtain

$$\zeta_h+E_g=\gamma_3E_0\left[\ln\frac{(mE_0)^{3/2}}{\hbar^3\Delta n}\right]^{2/3}. \tag{6}$$

Expression (1) then reduces to the cubic equation

$$x^3+\gamma_3\frac{E_0}{T}x^2+\gamma_2\frac{E_0}{T}-\ln\frac{(mE_0)^{3/2}}{\alpha\beta J\tau_r\hbar^3}=0,$$

$$x=\left[\ln\frac{(mE_0)^{3/2}}{\hbar^3\Delta n}\right]^{1/3} \tag{7}$$

the solution of which yields $\Delta n$.

In the derivation of (6) and (7) it was assumed that in spite of the strong compensation, the concentration $p_0$ of the equilibrium holes is negligibly small in comparison with $n_0$ and $\Delta n$. In compensated semiconductors this is as a rule satisfied. In amorphous substances, however, which in a number of cases can be regarded as fully compensated, $n_0 = p_0 \sim N^2e^6/\kappa^3E_g^3$,[17] and the indicated formulas do not hold. For these, in the region

$$\alpha\beta J\tau_r \gg \frac{e^6N^2}{\varkappa^3T^3}\exp\left(-\frac{E_g}{T}\right)$$

$\Delta n$ is described by (4), and at lower intensities the inequality $\Delta n < n_0$ is satisfied, the change of the quasilevels upon illumination is small, and

$$\Delta n=\alpha\beta J\tau_r \exp(E_g/T). \tag{8}$$

We turn now to a directly measurable quantity, the conductivity of the sample. At $\zeta_e < E_p^e$ it has an activation character:

$$\sigma=n^*e\mu\exp(-E_\sigma/T), \quad E_\sigma=E_p{}^e-\zeta_e, \tag{9}$$

where $\mu$ is the mobility and $n^*$ is the effective density of states. It is of interest to compare the activation energies $E_\sigma$ and $E_\tau$, which determine the temperature dependences of the conductivity and of the lifetime.1) For n-type semiconductors

$$E_\sigma<(E_p{}^e-E_p{}^h-\zeta_e+\zeta_h)/2.$$

Using the inequality[13] $E_g > E_p^e - E_p^h$, we ultimately have

$$E_\tau>2E_\sigma. \tag{10}$$

The foregoing arguments prove the statement made by Smorodinskiĭ et al.[13] that the drift barriers are lower than the recombination barriers. A qualitative explanation of this effect was proposed by Ryvkin and Shlimak.[5]

To calculate the explicit form of the lux-ampere characteristics $\sigma(J)$ it is necessary to know, besides the expressions derived above for $\Delta n(J)$, the function $E_\sigma(\Delta n)$. In compensated and amorphous semiconductors we have

$$E_\sigma\sim e^2N^{2/3}/\varkappa n^{1/3}.$$

The indeterminate factor can be set equal here, by virtue of (10), to $\gamma_1/\eta$, where $\eta > 2$. For high intensities we then obtain directly from (4)

$$\Delta\sigma=\sigma-\sigma_d\approx\sigma=n^*e\mu(\varkappa^3T^3\alpha\beta\tau_rJ/e^6N^2)^{1/\eta} \tag{11}$$

($\sigma_d$ is the dark value of the conductivity). Thus, the function $\Delta\sigma(J)$ in the indicated intensity band varies somewhat more slowly than in proportion to the square root.

At smaller J, when $p_- < \Delta n < n_0$, we have for compensated semiconductors

$$\Delta\sigma \approx n^* e\mu \exp\left(-\frac{\gamma_1}{\eta}\frac{E_0}{T}\right)\left[\exp\left(\frac{\gamma_1}{3\eta}\frac{E_0}{T}\frac{\Delta n}{n_0}\right)-1\right], \tag{12}$$

where $\Delta n$ is determined from (7). The lux-ampere characteristic described by these formulas is shown in the figure. It is seen that at $\gamma_2 E_0/T = 3$ it is close to a square-root curve, and becomes steeper with increasing temperature. This is physically understandable, for with increasing T the inhomogeneities become less influential and we approach the case of a homogeneous sample, where $\Delta\sigma \sim J$. It should be noted that at low intensities, when $\Delta\sigma \sim \Delta n$, the form of $\Delta\sigma(J)$, as is easily seen from (12), does not depend on the parameters $\eta$ and $n_0\hbar^3(mE_0)^{-3/2}$ which characterize the properties of the random potential V(r). When plotting the curves in the figure we have assumed for the sake of argument $\eta = 3$ and $n_0\hbar^3(mE_0)^{-3/2} = 1/3$.

As to amorphous semiconductors, their lux-ampere characteristic comes close to linear already at $\Delta n < n_0$:

$$\Delta\sigma \approx n^* e\mu \exp\left[\frac{E_g}{T}\left(1-\frac{1}{\eta}\right)\right] \tag{13}$$

$$\cdot\left\{\exp\left(\frac{E_g{}^4\varkappa^3\alpha\beta J\tau_r}{TN^2e^6}\right)-1\right\}.$$

The foregoing formulas are valid for the case of linear recombination, when $\tau_r = \text{const}(\Delta n)$. At high intensities, however, quadratic recombination can also take place. Then

$$\gamma(\Delta n)^2 = \alpha\beta J \exp\left(\frac{E_g-\zeta_e+\zeta_h}{T}\right) \tag{14}$$

($\gamma$ is the recombination coefficient), and in place of (11) we obtain a somewhat different formula:

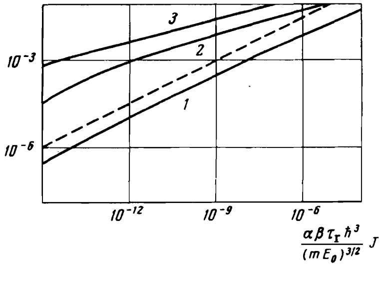
$$\Delta\sigma \approx n^* e\mu(\varkappa^6 T^6\alpha\beta J/\gamma e^{12}N^4)^{1/\eta}. \tag{15}$$

The foregoing formulas allow us also to calculate the temperature dependence of the photoconductivity. With increasing temperature, at a given light intensity, a strong decrease takes place in the lifetime and concentration of the free carriers (see (1) and (14)). We then go over from the region $\Delta n > n_0$, where expression (11) or (15) is valid and $\Delta\sigma(T)$ is an increasing function, into the region $\Delta n < n_0$ where this function, according to (7), (12), and (13), is decreasing. As a result, $\Delta\sigma(T)$ should have a maximum that shifts towards higher temperatures with increasing J (the temperature dependence of $\sigma_d$ has then the usual activation character).

We have calculated above the stationary values of the conductivity and the concentration of the nonequilibrium carriers. When photoactive illumination is turned on, these values reach steady-state within a time

$$\tau_c \sim \Delta n/\alpha\beta J.$$

Since (with the exception of the case of extremely large J) $\alpha\beta J\tau_r \ll \Delta n$ and the function $\Delta n(J)$ is sublinear, it follows that $\tau_c$ greatly exceeds $\tau_r$ and decreases with increasing intensity of the light more slowly than $J^{-1}$, for extremely low intensities we have $\tau_c = \tau_r \exp(E_g/T)$.



Lux-ampere characteristic of a compensated semiconductor at low light intensities. For curves 1, 2, and 3 the values of the parameter $\gamma_2E_0/T$ are respectively 3, 5, and 7. The dashed line shows, for comparison, a plot of $\Delta\sigma \sim J^{1/2}$, In the calculations it was assumed that $\gamma_2 = \gamma_3$ and $\gamma_1 = 2\gamma_2$ (the latter is valid for a symmetrical potential V(r).

When the light is turned off, the conductivity relaxes slowly to its dark value. The instantaneous relaxation time $\tau_r \exp(E_\tau/T$ increases continuously during the course of the process (owing to the increase of $E_\tau$), from an initial value $\tau_c$ to a value $\tau_r \exp(E_g/T)$ at the end of the relaxation. In broadband semiconductors, even near room temperature, the relaxation time can become so long that during the observation time $t_0$ the conductivity remains practically unchanged, a fact that the experiment will record as residual conductivity (RC). This calls for the condition $t_0 \ll \tau_r \exp(E_g/T)$. The value of the RC should not depend on the light intensity, provided only that the latter exceeds the value at which $E_\tau/T = \ln(t_0/\tau_r)$.

In some cases it is easy to obtain also exact analytic expressions that describe the kinetics of the photoresponse. For example, the decrease of the photoconductivity in the region $\Delta n \gg n_0$ is described by the equation

$$\frac{d\sigma}{dt} = \frac{d\sigma}{dn}\frac{dn}{dt} = -\frac{\Delta n}{\tau_r}\frac{d\sigma}{dn}\exp\left(-\gamma_1\frac{e^2N^{2/3}}{\varkappa(\Delta n)^{1/3}}\right) \tag{16}$$

Since

$$\sigma = n^* e\mu \exp(-\gamma_1 e^2N^{2/3}/\eta\varkappa(\Delta n)^{1/3}),$$

Eq. (16) can be reduced to the form

$$\frac{d\sigma}{dt} = -\frac{1}{3}\frac{\sigma}{\tau_r}\left(\frac{\sigma}{n^*e\mu}\right)^\eta \ln\frac{n^*e\mu}{\sigma}. \tag{17}$$

Hence

$$\sigma(t) \approx n^* e\mu\left[\left(\frac{n^*e\mu}{\Delta\sigma}\right)^\eta + \frac{t}{\tau_r}\ln\frac{n^*e\mu}{\Delta\sigma}\right]^{-1/\eta}, \tag{18}$$

where $\Delta\sigma$ is the stationary value of the photoconductivity (11). It is easily seen that in this case the instantaneous relaxation time

$$\tau_{\text{inst}} = \sigma(d\sigma/dt)^{-1}$$

increases linearly with time. A similar result is obtained also for the case of quadratic recombination.

We note that owing to the dependence of $E_\tau$ on the carrier density, the photoconductivity of inhomogeneous semiconductors, even in the case of linear recombination, has features similar to those of photoconductivity under conditions of quadratic recombination, namely, a sublinear lux-ampere characteristic, a short rise time in comparison with fall-off time of the photoresponse, and a rise of the latter during the curse of the relaxation.

All the foregoing features of the photoconductivity of inhomogeneous semiconductors are observed experimentally in compensated, irradiated, and amorphous semiconductors. Let us list briefly again these features and let us compare them with the corresponding experimental results.

1. The heights of the drift and recombination barriers are connected by the inequality (10). In all the experiments where both quantities are determined, this inequality holds. For example, Markevich and Sheĭnkman obtain $E_\sigma = 0.05$ eV and $E_\tau = 0.6$ eV; Sandomirskiĭ et al. have $E_\sigma = 0.05$ eV and $E_\tau = -0.2$ eV; in [14] $E_\sigma = 0.06$ eV and $E_\tau = 0.15-0.26$ eV.

2. In amorphous semiconductors the lux-ampere characteristic is linear at $\Delta n < n_0$ and sublinear at $\Delta n$

$> n_0$. A similar regularity is observed in most chalcogenide glasses, and at $\Delta n > n_0$ the $\Delta\sigma(J)$ dependence is close to a square-root one (see, e.g., [15], where a detailed bibliography can be found).

3. In compensated semiconductors, the lux-ampere characteristic is sublinear down to very low light intensities. This is confirmed by experiments on compensated Ge[16] and GaAs[17].

4. The temperature dependence of the photoconductivity has a maximum in the region where $\Delta n \sim n_0$. This behavior of the photoconductivity is typical of most amorphous semiconductors.[15,16] With increasing light intensity, the maximum shifts, as called for by the theory, towards higher temperatures.

5. The time of establishment of stationary photoconductivity increases with decreasing illumination intensity. This effect takes place in all samples having RC, both crystalline (see, e.g., [14]) and amorphous.[15]

6. In all samples with RC, the instantaneous fall-off time of the photoresponse increases in the course of the relaxation, and in many cases the decrease is like $\tau_{\mathrm{inst}} \sim t$.[17,19]

7. At high light intensities the value of the RC does not depend on the intensity.[15,20,21]

As shown above, in inhomogeneous semiconductors the photoconductivity relaxation process is extremely slow. It can be strongly accelerated (the RC can be quenched), for example, by raising the temperature. Another method of quenching the RC is to apply infrared light. Let us consider some features of this effect. We assume that the time needed for a nonequilibrium electron to cool down to an energy E is proportional to E and can be written in the form AE. Then the stationary concentration of the electrons excited by illumination of frequency $\omega'$ and intensity $J'$ is equal to $\delta n = nSJ'A\hbar\omega'$ (S is the cross section for photon absorption by the electron). A fraction of the electrons, namely

$$\delta n \frac{\hbar\omega' - E_\sigma}{\hbar\omega'},$$

lies above the percolation level and takes part in the conductivity. The number recombining in one second is

$$\frac{\delta n}{\tau_r} \frac{\hbar\omega' - E_\tau/2}{\hbar\omega'}$$

and electrons having an energy higher than $\zeta_e + E_\tau$ can recombine with equilibrium holes, while those having a lower energy can be recombined only with holes that have also absorbed photons. It follows from the foregoing that infrared illumination of a sample in the RC state gives rise to a rapid increase of the conductivity, by an amount $ne\mu SJ'A(\hbar\omega' - E_\sigma)$, followed by a fall-off having a characteristic time

$$\frac{\tau_r}{A(\hbar\omega' - E_\tau/2)SJ'}$$

to a value $\sigma_d + n_0 e\mu SJ'A(\hbar\omega' - E_{st})$. When the additional illumination is turned off, the dark value $\sigma_d$ is rapidly restored.

The foregoing arguments are valid at $\hbar\omega' > E_\tau/2$. If $\hbar\omega' < E_\tau/2$, then the excited electron and hole cannot be present at the same point of space, and recombination calls for additional tunneling or activation, and this greatly lowers the quenching effectiveness. Therefore in the case $E_\tau/2 < \hbar\omega' < E_g/2$ (in substances with large RC multiplicity, this spectral interval is quite wide), the additional illumination rapidly lowers the RC not to zero, but to a level at which $\zeta_e - \zeta_h = E_g/2 - \hbar\omega'$, after which the relaxation slows down abruptly. It is possible that this effect explains the incomplete infrared quenching of the RC in certain experiments.[22,23]

In conclusion, let us discuss the question of the influence of illumination on the carrier Hall mobility $\mu_H$. Numerous experiments show that in inhomogeneous (compensated, irradiated) semiconductors $\mu_H$ has an anomalously low value that cannot be explained by the classical kinetic theory. It was shown earlier[24] that this effect is not connected with the behavior of the true (drift) mobility, but is due to singularities of the Hall effect in an inhomogeneous sample. The measured value of $\mu_H$ is smaller the larger the amplitude of the inhomogeneities. Since the latter decreases with increasing carrier density, illumination of the sample will increase $\mu_H$. If CR takes place in the sample, then $\mu_H$ in the CR state should be smaller than in light, but larger than in a non-illuminated samples, as is indeed observed in experiment.[1,20,25-27] We emphasize once more that the foregoing pertains only to $\mu_H$. The drift mobility $\mu$, which enters in particular in the formulas for the photoconductivity, depends weakly on the illumination.

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[1)] Smorodinskiĭ et al. [3] called $E_\sigma$ and $E_\tau$ the drift and recombination barriers, respectively.

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