Jetlike photoelectromotive force in semiconductors

V. I. Belinicher

A. F. Ioffe Physicotechnical Institute, USSR Academy of Sciences

S. M. Ryvkin

Institute of Automation and Electrometry, Siberian Division, USSR Academy of Sciences

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The kinetics of the photo-emf in semiconductors is investigated and it is shown that at the initial instant of time the photo-emf is determined by the free separation of the photo-produced electrons and holes. When the particles are reflected from the boundary of the crystal, a directed motion of the carrier sets in, similar to the motion of a gas from the nozzle of a rocket.

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1. Several new types of photoelectromotive forces have been observed in recent years and are diligently studied. These, in contrast to the photo-emf of "diffusion" origin, are due directly to the light-induced asymmetry in the carrier momentum distribution.

This asymmetry is the result of momentum transfer from the directed photons to the electrons and holes during the light-absorption act (the effect of electron dragging by photons[1,2]) or of the asymmetry of the impurity – band and band – band phototransitions, as well as of scattering within the same band (the photovoltaic effect[3,4]). In the latter case the motion of the absorbed photons need not be directed, but effects of this type can take place only in crystals without inversion center.

A recently observed phenomenon[5,6] is the so-called surface photo-emf, which is due to the asymmetry of the momentum scattering in the bulk and on the surface of the crystal and is directed along the surface. In order for this asymmetry to manifest itself, the crystal must be anisotropic, for otherwise an emf is produced only under oblique incidence and depends substantially on the polarization of the light.

In this communication we call attention also to the possible onset of a photo-emf that is connected with the asymmetry of the momentum scattering but is possible in isotropic crystals at any angle of light incidence on the crystal surface.

The mechanism of producing this photo-emf (which we shall call "jetlike") reduces to the following.

Consider a homogeneous isotropic semiconductor crystal, one of the boundaries of which is an impenetrable reflecting "wall" for the carriers (the interface with vacuum, a dielectric, another wider-band semiconductor, or finally a suitable sufficiently high and steep bending of the bands inside the given semiconductor).

Figure 1 shows the corresponding energy diagram. When light is absorbed, e.g., by free electrons, their kinetic energy increases and during the time between collisions the electrons disperse in various directions. For carriers whose distance from the reflecting boundary exceeds the mean free path l_n, this dispersal is isotropic and does not lead on the average to a displacement of the electric charge and to onset of a photo-emf.

The carriers near the reflecting wall, however, at distances less than l_n, disperse asymmetrically; their reflection from the wall A causes their velocity to be directed mainly away from the wall into the interior of the sample, and this leads to a displacement of the charge relative to the crystal and to onset of a photo-emf.

The picture is perfectly analogous to that occurring when powder explodes in a rocket; the carriers (powders), which acquire upon absorption of the photons an excess kinetic energy (explosion), are dispersed isotropically but, encountering on one side an energy obstacle (the dead-end wall of the rocket), they shift relative to the crystal lattice (the shell of the rocket).

We shall therefore call the photo-emf produced under the described conditions "jetlike."

We consider now the feasibility and the conditions of observing a jetlike photo-emf.

Since the contribution to the onset of the photo-emf can be made only by carriers located in a region of the order of the mean free path l_n from the reflecting wall, it is obvious that it is desirable to use rather thin semiconductor layers and radiation that is sufficiently strongly absorbed. The latter circumstance points to the promise of using light from the intrinsic band with energy $\hbar\omega$ exceeding the width E_g of the band gap. To be sure, both hot electrons and hole are simultaneously produced thereby, so that the electron and hole jets cancel eath other. It is easily seen, however, that in the case, e.g., of direct optical transitions in semiconductors with overlapping band extrema the initial ratio of these currents is equal to the inverse ratio of the ef-

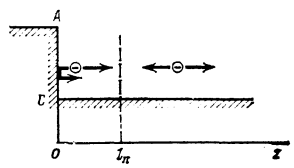

FIG. 1. Diagram illustrating the onset of a jetlike photo-emf when light is absorbed by free electrons; C—edge of conduction band; z—coordinate.

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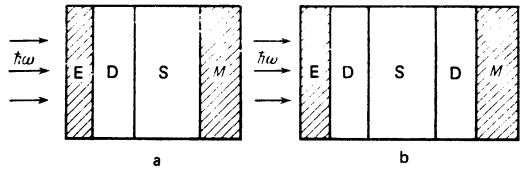

FIG. 2. Method of measuring the photo-emf in films: a) dielectric–semiconductor–metal structure; b) dielectric–semiconductor–dielectric structure; $\hbar\omega$–incident light; E–semitrasnparent electrode; D–dielectric; S–semiconductor; M–metal.

fective masses, and if the latter is large, then the cancellation of the currents in negligible and the effect is determined mainly by the lighter carriers.

The time of establishment of the jetlike photo-emf is determined by the momentum relaxation time, and is consequently very short. For sufficiently thick samples ($L \gg l_n$) the establishment of the jetlike photo-emf is followed by diffusion and thermalization processes, and consequently the onset of the jetlike photo-emf is only the initial stage of the process of diffusion of the hot carriers. Under stationary conditions it is difficult to separate it from the hot-carrier photo-emf. In principle, this separation is possible only by studying the kinetics of the process, but this calls for an ability to register very fast processes. In thin samples ($L \ll l_n$) the jetlike photo-emf can be the principal process, not encumbered by the onset of a photo-emf of different origin. It depends substantially in this case on the features of the momentum loss on the two faces of the film.

To observe the effect, we can use the capacitor method,[7-10] i.e., the structure shown in Fig. 2. A thin semiconductor with $L \lesssim l_n$ is bounded on the left side by a dielectric (reflecting wall) and on the right side by a metal (Fig. 2a) or else likewise by a dielectric (Fig. 2b). When the carriers generated by the light are incident on the metal, they interact with the electrons of the metal and therefore lose energy and momentum (thermalizing wall). The interaction of the electrons with the dielectric walls will be assumed to be specular. Several versions of real structures that are in principle suitable for the observation of the effect can be proposed. By way of example, we consider briefly one of them (Fig. 3).[1)]

An abrupt heterojunction is equipped with two metallic electrodes, between which the emf is measured. The one (E) on the wide-band part is semitransparent. The photons with energy lower than the band gap of the wide-band semiconductor but higher than that of the narrow-band one, after passing throught the semitransparent electrode and the wide-band semiconductor, are absorbed in the narrow-band semiconductor near the heterojunction, and generate electrons and holes.

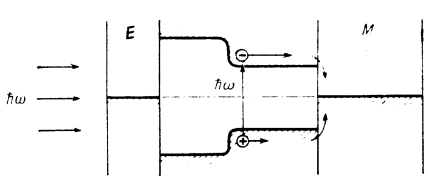

FIG. 3. Energy level scheme of structure with semiconductor heterojunction between two metals. E–semitransparent metallic electrode; M–metallic electrode.

The jetlike photo-emf is produced on account of the motion (with different velocity) of the electrons and holes reflected from the interface with the wide-band semiconductor towards the metal M, where they become thermalized (i.e., where in fact the carriers vanish or recombine). The thickness L of the narrow-band part of the heterojunction should be small compared with the mean free path of at least one type of carrier, for example l_n of the electrons.

Let us estimate the necessary thickness, with allowance for the limitation imposed by this inequality. If the initial energy of the electrons generated by the light is high, then, after emitting optical phonons, they "dump" the energy rapidly (within a time 10^{-12}–10^{-13} sec), without moving significantly from a generation region of thickness $1/k \sim 10^{-4}$–10^{-5} cm (k is the light absorption coefficient). This is followed by the above-described onset of the jetlike photo-emf under conditions when the electron mean free path is determined by the scattering by the acoustic phonons and, consequently is large enough at low temperatures: $l_n \sim 10^{-3}$ cm.[2)] Thus, as a condition for L we have $L \lesssim 10^{-3}$ cm.

At the present time, perfect crystalline semiconducting heterostructures with component thicknesses $\sim 10^{-3}$ cm are relatively easy to produce. To obtain the maximum values of the sensitivity, it is desirable to use a narrow-band layer with low conductivity – an insulator in the limit. Under conditions when the screening length is substantially larger than the thickness of the heterostructure, the carrier density in the latter is determined by the contact potential of the metal used for the electrodes, so that this metal must be specially chosen.

We note also that it is precisely the use of identical metals for the left and right contacts which ensures the absence of an electrode contact field from the semiconducting part of the structure. It ensures also the horizontality, needed to observe the undistorted jetlike photo-emf, of the edges of the bands in the two regions of the heterojunction.

To estimate the order of magnitude of the jetlike photo-emf signal, we assume that in the structure of Fig. 3 the conductivity of the narrow-band region is zero, and that the electron jet that increases the potential difference in this region is compensated in the stationary state only by the jet of the substantially slower holes. Thus, the time constant is determined by the time of flight $t_0^h = L/v_h$ of the holes.

Under these conditions, the stationary value V_{st} of the emf in the narrow-band region, referred to the intensity of the light, is

$$V_{st}/I = 4\pi e L^2/\varepsilon \hbar\omega v_h.$$

Here ε is the dielectric constant and $\hbar\omega$ is the photon energy.

Thus, at $\varepsilon \approx 4\pi$, $\hbar\omega \approx 1$ eV, $L = 10^{-3}$ cm, and $v_h = 10^7$ cm/sec we have

$V_{st}/I \approx 0.1\ \mathrm{V \cdot cm^2/W}$,

i.e., higher by approximately 5–6 orders than in other forms of the photovoltaic effect and the effect of dragging in semiconductors. It must be emphasized, however, that the maximum value of the jetlike photo-emf is limited and is determined by the kinetic energy of the carriers.

In the general case, the photo-emf for the structure shown in Fig. 2a has the characteristic time dependence shown in Fig. 4a. The growth of the photovoltage at the initial instant of time is due to the charge separation on account of the different velocities of the electrons and holes, and the decrease of the photovoltage is connected with the mutual cancellation of the electron and hole fluxes under stationary conditions and with the relaxation of the emf on account of the finite conductivity. The photo-emf for the structure shown in Fig. 2b has a characteristic oscillatory dependence which attenuates with time, as shown in Fig. 4b. These oscillations are due to the interference of the electron and hole fluxes incident and reflected from the dielectric walls.

The value of the stationary photo-emf is determined by the ratio of the lifetimes of the electrons and holes in the bands, i.e., by the distances over which the electrons and holes managed respectively to travel and diffuse during the lifetime in the absence of an electric field.[3)] If the lifetimes of the electrons and holes are equal, the stationary photo-emf is zero. A more detailed theoretical treatment of the jetlike photo-emf is given below.

2. We construct a theory of the jetlike photo-emf under the assumption that the depth of penetration of the light into the crystal is less than the characteristic lengths l_n and L of the problem. We shall neglect also the influence of the electric field on the motion of the electrons and holes; this is justified if the potential energies eV of the particles in the field are much less than their kinetic energy E_0.

The photo-emf $V(t)$ is determined by the field $E(t,z)$ in the sample:

$$V(t)=\int_0^L E(t,z)\,dz.$$

The field $E(t,z)$ can be determined from Maxwell's equation[4)]

$$\varepsilon\frac{\partial E(t,z)}{\partial t}=-4\pi\sigma E(t,z)-4\pi j(t,z). \tag{1}$$

Here σ is the total conductivity; $j(t,z)$ is that part of the electric current which is not connected with the drift of the electrons and holes in the electric field. The electric current is determined from the standard kinetic-theory expression for the current:

$$j(t,z)=e\int k_z(f_e(\mathbf{k},t,z)/m_e-f_h(\mathbf{k},t,z)/m_h)\,d\mathbf{k}.$$

Here $\mathbf{k}$ is the momentum of the electrons and holes. The distribution function $f_{e,h}(\mathbf{k},t,z)$ of the electrons or holes satisfies the kinetic equations

$$\frac{\partial f}{\partial t}+\frac{k_z}{m}\frac{\partial f}{\partial z}+eE\frac{\partial f}{\partial k_z}=-\Gamma(f-\bar f)+I_T(f)-\gamma f+b\delta(z). \tag{2}$$

Here $\bar f$ is the distribution function averaged over the angles; Γ are the frequencies of the momentum impacts; $I_T(f)$ is the thermalization term of the kinetic equation; γ^{-1} is the lifetime of the particles in the band; the last term of (2) describes the surface photogeneration of the particles. Assuming monoenergetic generation and rapid turning-on of the light, the coefficient b is given by

$$b=I\theta(t)\delta(k^2/2m-E_0)/2\pi\hbar\omega km,$$

where $\theta(x)$ is the step function; I and ω are respectively the intensity and frequency of the light.

The total distribution function f can be broken up into two parts: the low-energy function $f_{le}(\mathbf{k})$, which is responsible for the photoconductivity, and the high-energy function $\varphi(\mathbf{k},t,z)$, which describes the processes of flight and diffusion of the hot electrons. The equation for $\varphi(\mathbf{k},t,z)$ is obtained from (2) by omitting the drift term as well as the thermalization and recombination terms. The resultant equation can be solved in general form, but since the integrals involved are cumbersome, we consider this equation for times $t \leq \Gamma^{-1}$ and $t \geq \Gamma^{-1}$. At $t \leq \Gamma^{-1}$ we have the simple equation

$$\frac{\partial\varphi}{\partial t}+\frac{k_z}{m}\frac{\partial\varphi}{\partial z}=b\delta(z), \tag{3}$$

which we supplement with a boundary condition on the specular surface: $\varphi(\mathbf{k},t,0)=\varphi(\mathbf{k}^*,t,0)$ for $k_z>0$, where $\mathbf{k}^*$ differs from $\mathbf{k}$ in that the sign of k_z is reversed.

In the case $t \geq \Gamma^{-1}$ we have an equation of the diffusion type

$$\frac{\partial\Phi}{\partial t}-D\frac{\partial^2\Phi}{\partial z^2}=b\delta(z) \tag{4}$$

with boundary condition[11]

$$\frac{\partial\Phi(|\mathbf{k}|,t,z)}{\partial z}\Big|_{z=0}=0.$$

In this case

$$\varphi=\bar\varphi+\frac{k_z}{m\Gamma}\frac{\partial\bar\varphi}{\partial z},\quad j(t,z)=-4\pi D\int_0^\infty\frac{d\varphi}{dz}k^2\,dk.$$

We consider first the kinetics of the photo-emf in a sufficiently thick sample ($L \gg l_n$). At the initial instants of time we have the solution of Eq. (3) for $z > 0$:

$$\varphi=\frac{bm}{k_z}\theta(t-mz/k_z)\theta(k_z). \tag{5}$$

Calculating the electric current in solving Eq. (1), we obtain the following expression for the photovoltage $V(t)$:

$$V(t)=\lambda_I(v_e-v_h)\tau_M^2\left[\frac{t}{\tau_M}+\exp\left(-\frac{t}{\tau_M}\right)-1\right],\quad \lambda_I=\frac{2\pi eI}{\varepsilon\hbar\omega}. \tag{6}$$

Here v_e and v_h are the respective velocities of the elec-

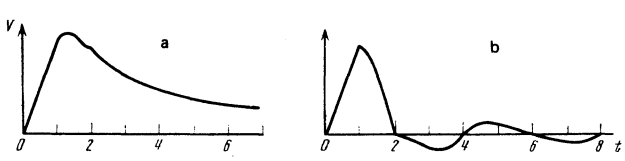

FIG. 4. Kinetics of photo-emf in dielectric–semicondutor–metal (a) and dielectric–semiconductor–dielectric (b) structures. Ordinates–V in relative units, abscissas–time in units of the electron time of flight t_0; the hole time of flight is chosen equal to $2t_0$.

tron and hole at the instant of photoproduction. At $t \ll \tau_M$ the factor in the square brackets is equal to $t^2/2\tau_M^2$ and $V(t)$ is independent of τ_M. At $t \gg \tau_M$ the factor in the square brackets is equal to t/τ_M and $V(t)$ is decreased by a factor τ_M/t compared with the case $t \ll \tau_M$. At times longer than Γ^{-1}, the photo-emf is determined by the diffusion process. Solving Eq. (4), we find that

$$\Phi(|k|,t,z)=\frac{b}{2(\pi D)^{1/2}}\int_0^t \frac{d\tau}{\tau^{1/2}}\exp(-z^2/4D\tau), \tag{7}$$

and the photo-emf is in this case

$$V(t)=\frac{4}{\sqrt{\pi}}\lambda_I\tau_M^{1/2}(D_e^{1/2}-D_h^{1/2})\,t\exp\left(-\frac{t}{\tau_M}\right)Y'(x)|_{x=(t/\tau_M)^{1/2}}. \tag{8}$$

Here $Y(x)$ is given by the following integral:

$$Y(x)=\frac{1}{x}\int_0^x e^{z^2}dz; \quad Y'(x)=\frac{x}{3} \quad (x\to 0);$$
$$Y'(x)=\frac{e^{x^2}}{2x} \quad (x\to\infty). \tag{9}$$

In the diffusion regime $V(t)\propto t^{3/2}$ at $t \ll \tau_M$ and $V(t)\propto t^{1/2}$ at $t \gg \tau_M$.

We consider now the kinetics of the photo-emf for the case of a thin film $L \ll l_n$. Since the resultant formulas are cumbersome, we present the answer only for the limiting cases $\tau_M \gg (\ll) t,\ t_0$ for one type of carrier. The question of the value of the stationary photo-emf will be discussed only qualitatively. For a film with a thermalizing the rear boundary (see Fig. 2a), by calculating the current on the basis of (5) and substituting it in (1), we obtain the following expression for $V(t)$:

$$V(t)=\frac{\lambda_I L t_0}{2}\begin{cases}\dfrac{t^2}{t_0^2}\theta(t_0-t)+\left(4\dfrac{t}{t_0}-3-2\ln\dfrac{t}{t_0}\right)\theta(t-t_0); & t,t_0\ll\tau_M,\\ \dfrac{2t\tau_M}{t_0^2}\theta(t_0-t)+\dfrac{2(2t-t_0)\tau_M}{tt_0}\theta(t-t_0); & t,t_0\gg\tau_M.\end{cases} \tag{10}$$

It follows from (10) that at the initial instant of time $t \ll t_0$ the photo-emf increases, and then, at $t \gg t_0$, τ_M it assumes a constant value $2\lambda_I L\tau_M$ which is independent of the velocity and mass of the carriers. If the lifetimes of the electrons and holes $l_{t,e,h}$ greatly exceed the stationary value of L, the photo-emf is of the characteristic order of magnitude $\lambda_I L^2\tau_M\times(l_{te}^{-1}-l_{th}^{-1})$.

If the hole mass greatly exceeds the electron mass, the double inequality $l_{ne} \gg L \gg l_{th}$ can set in, and the jetlike photo-emf $\lambda_I L\tau_M$ determines the characteristic order of the stationary photo-emf. The calculation of the jetlike photo-emf in the case of a film with two dielectric boundaries (see Fig. 2b) is more complicated and can be carried out by taking the Fourier transform with respect to time in Eq. (1) and (3). The resultant integrals are evaluated by using the residue theorem, and the infinite sums are calculated by the formulas given in Ref. 12. The final expressions for $V(t)$ are

$$V(t)=\lambda_I L\tau_M\left[\frac{t}{t_0}\theta(t_0-t)+\theta(t-t_0)\left[1+\frac{t_0}{6t}\left[\eta_3\left(\frac{t}{t_0}\right)-\eta_1\left(\frac{t}{t_0}\right)-\eta_3\left(\frac{t-t_0}{t_0}\right)+\eta_1\left(\frac{t-t_0}{t_0}\right)\right]\right]\right] \quad \text{at} \quad \tau_M\ll t,t_0,$$
$$V(t)=\tau_M^{-1}\int_0^t V(\tau)|_{\tau_M\ll\tau,t_0}d\tau \quad \text{at} \quad \tau_M\gg t,t_0. \tag{11}$$

Here $\eta_n(x)$ is a periodic function of the argument x with period 2, and is equal to x^n on the segment $(-1,1)$. $V(t)$ increases like t^2 or like t at $t<t_0$, and τ_M assumes a constant value $\lambda_I L\tau_M$ at $t>t_0$. The most interesting aspect is the fact that the approach to the stationary value is oscillatory, and the amplitude of the oscillations decreases like t^{-1}. The question of the stationary value of the photo-emf must be solved on the basis of the arguments advanced above.

In conclusion, the authors thank B. S. Ryvkin and A. S. Terekhov for stimulating discussions.

[1)] The structure shown in Fig. 3 is obtained when the electrodes are made of identical metals, the electron affinity is less a wide-band than in a narrow-band semiconductor, and the screening radius in the semiconductor structure does not exceed substantially the thickness of the latter.

[2)] Obviously, by specially choosing $\hbar\omega$ we can generate directly electrons and holes with kinetic energy lower than the energy of the optical phonon.

[3)] In the case of the diffusion process, these lengths are customarily called diffusion lengths.

[4)] We assume that the conductivity σ is determined mainly by the thermalized carriers, and that the time between the collisions of the thermalized carriers is shorter than the other characteristic times τ_M, t, t_0 of the problem.

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