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THE PHOTOTHERMOELECTRIC EFFECT

David Emin

Sandia Laboratories

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THE PHOTOTHERMOELECTRIC EFFECT

David Emin
Sandia Laboratories
Albuquerque, New Mexico 87115

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ABSTRACT

With the aim of clarifying the physical origin of the photothermoelectric effect, the emf associated with an illuminated thermocouple is calculated. Some preliminary remarks about possible device applications of this effect are made.

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There has been a longstanding fundamental interest in physical phenomenon via which heat or radiation can be directly utilized to produce an electrical current. In addition, there is a continual and growing desire to exploit such effects to produce energy-conversion devices for a wide variety of applications. In particular, the thermoelectric effect has been exploited in designing devices to convert heat directly into electrical power. The photovoltaic effect is an example of a phenomenon which has been utilized as a basis for devices which produce an emf directly from radiation. Another related, albeit relatively unstudied, effect which involves the in-tandem utilization of heat and radiation in generating an emf is the "photothermoelectric effect." While the demonstration of this effect dates back about twenty years, I am not acquainted with any attempt to employ this effect in the development of an energy-conversion device. Furthermore, I know of only a few examples of this phenomenon being utilized as a tool in solid-state-physics research. It is the purpose of this report simply to describe the essential physics of this phenomenon in a manner which I think is much more transparent than the discussion which presently exists [Jan Tauc, Czech. J. Phys. 5, 528 (1955)]¹.

The physical situation with which we shall be concerned is depicted in Fig. 1. An insulating or semiconducting material, designated as material A, is connected by metallic leads, material B, to a voltmeter. A thermal gradient is imposed over a portion of material A, between T_1 and T_2 , such that the temperature of material A to the left of T_1 is T and to the right of T_2 is $T + \Delta T$. Keeping the voltmeter at temperature T thereby also imposes a temperature gradient over one of the leads to the voltmeter. At this point the circuit is that associated with a simple thermocouple. Now, in addition, radiation producing Δn electron-hole pairs uniformly in material A is assumed to impinge on material A between points L_1 and L_2 . As in the prior study (Tauc), the

boundaries of the illuminated region, L_1 and L_2 , are taken to be sufficiently far from the edges of the semiconductor (material A) which make contact with the metal (material B) at C_1 and C_2 so that the electron-hole pairs recombine before diffusing to these contacts. It is now our task to determine the emf which can be generated in such a situation.

It will henceforth be assumed 1) that only one type of carrier is mobile, its charge being q , 2) that nondegenerate statistics may be applied to carriers in the semiconductor, and 3) that the radiation serves only as a means of generating extra charge carriers (it does not lead to an alteration of the diffusion parameters).

We begin by enumerating the contributions to the open circuit voltage. Starting from the left-hand metal-semiconductor contact one has the "contact voltage" associated with the metal-semiconductor contact at C_1 :

$$V_{C_1} = \frac{1}{q} [\mu_A(T) - \mu_B(T)] \quad (1)$$

where q is the charge of the carrier and $\mu_A(T)$ and $\mu_B(T)$ are the chemical potentials (Fermi levels) associated respectively with materials A and B at a temperature T . In the vicinity of point L_1 the radiation-induced carrier-number differential is associated with a voltage which (assuming no radiation-induced mobility changes) is given by

$$V_{L_1} = -\frac{T}{q} \ln \left[\frac{n_I(T)}{n_0(T)} \right] = \frac{T}{q} [\mu'_I(T) - \mu_A(T)] \quad (2)$$

where $n_I(T)$ is the carrier concentration in the illuminated region (to the right of L_1 in Fig. 1) and $n_0(T)$ is the carrier concentration in the dark region (to the left of L_1); $\mu'_I(T)$ is the "quasi-chemical-potential" (quasi-Fermi level)

associated with the mobile carriers in the illuminated region. The temperature gradient in material A between T_1 and T_2 induces a voltage given by¹

$$\Delta V^A = -S'_A \Delta T + \frac{1}{|q|} [\mu'_A(T + \Delta T) - \mu'_A(T)] , \quad (3)$$

where S'_A is the thermoelectric power of material A under illumination; it is not generally equal to the dark thermoelectric power S_A . In analogy with the situation near L_1 , the carrier-density gradient in the vicinity of the high-temperature edge of the illuminated region near L_2 contributes the voltage:

$$V_{L_2} = \frac{-k}{q} (T + \Delta T) \ln \left[\frac{n_O(T + \Delta T)}{n_I(T + \Delta T)} \right] = \frac{-1}{|q|} \left[\mu'_A(T + \Delta T) - \mu'_A(T + \Delta T) \right] . \quad (4)$$

Continuing around the circuit, one finds a voltage contribution from the high-temperature semiconductor-metal contact which is

$$V_{C_2} = \frac{1}{|q|} [\mu_B(T + \Delta T) - \mu_A(T + \Delta T)] . \quad (5)$$

Finally, returning to the voltmeter one has the temperature-gradient induced voltage in material B:

$$\Delta V^B = S_B \Delta T + \frac{1}{|q|} [\mu_B(T) - \mu_B(T + \Delta T)] , \quad (6)$$

where S_B is the thermoelectric power of material B and μ_B is its chemical potential.

Proceeding to sum the contributions of Eqs. (1) - (6), one finds the voltage drop over the open circuit is given simply by

$$V = (-S'_A + S_B)\Delta T \quad . \quad (7)$$

Assuming, as before, that while the radiation creates extra charge carriers it does not alter the diffusion constant, one finds that the thermoelectric power associated with the illuminated semiconducting material A, S'_A , is simply related to the nonirradiated thermoelectric power, S_A , via the relation

$$S'_A = S_A + \frac{1}{|q|T} [\psi'_A(T) - \psi_A(T)] \quad . \quad (8)$$

The radiation-induced term on the right-hand side of Eq. (8) may be rewritten with the aid of Eq. (2) to yield

$$\Delta S_A = \frac{1}{|q|T} [\psi'_A(T) - \psi_A(T)] = \frac{-k}{T} \ln \left[\frac{n_I(T)}{n_0(T)} \right] \quad . \quad (9)$$

$$n_I(T) = n_0(T) + \Delta n, \quad (10)$$

one finds that the emf, $-V$, of the circuit is

$$\text{emf} = \left[S_A - S_B - \frac{k}{q} \ln \left(1 + \frac{\Delta n}{n_0} \right) \right] \Delta T \quad . \quad (11)$$

The emf associated with the semiconductor is then

$$(\text{emf})_A = \left[S_A - \frac{k}{q} \ln \left(1 + \frac{\Delta n}{n_0} \right) \right] \Delta T \quad . \quad (12)$$

For a nondegenerate semiconductor devoid of radiatively-induced carriers²

$$S_A = \frac{k}{q} \left\{ -\ln[n_0/N(T)] + A \right\} \quad , \quad (13)$$

where $N(T)$ is the density of thermally available states near the appropriate band edge and A is the "heat of transport" constant (typically ~ 2). Thus the emf associated with the irradiated semiconductor may be written as

$$(\text{emf}) = \frac{k}{q} \left\{ -\ln \left[\frac{n_0 + \Delta n}{N(T)} \right] + A \right\} \Delta T \quad (14)$$

In the absence of illumination the argument of the logarithm is much less than unity, $n_0 \ll N(T)$, and hence the logarithm is itself negative. With an increase in Δn the argument increases and the magnitude of the logarithmic term decreases. Nominally when $n_0 + \Delta n = N(T)$ the logarithm is zero. However, it must be cautioned that when Δn becomes comparable to $N(T)$ the use of non-degenerate statistics will no longer be strictly applicable.

The magnitude of the photothermoelectric effect, ΔS_A , depends on the ratio of the number of photo-induced carriers to the equilibrium number of carriers, $\Delta n/n_0$. This ratio is determined by the temperature, the quantum efficiency and the frequency distribution of the incident radiation. It can in principle be quite large. Even for "low illumination" at room temperature in germanium crystals, Tauc (1955) estimates $\Delta n/n_0$ to be ~ 0.1 .

The herein-discussed photothermoelectric effect may be thought of as simply being a manifestation of the shifting of the "quasi-Fermi level" as the sample is illuminated. In particular, in the above example, with an increase in illumination the "quasi-Fermi level" is brought closer to a band edge; this is associated with an increase in the carrier number and a decrease in the magnitude of the thermoelectric power.

It should be noted from Eq. (7) that the illuminated region may be expanded to include the entire semiconductor without altering our result. Thus the restricted illumination region assumed in the prior analysis by Tauc is, in

principle, unnecessary. In a real material, however, illuminating the regions in the vicinity of the metal-semiconductor contacts may produce spurious photovoltaic voltages.

As an analytical tool the incremental thermopower associated with illumination produces (in sufficiently simple situations) a means of relating the carrier density in the dark to the number of carriers produced by radiation. Thus, used in conjunction with photoconductivity measurements, photothermoelectric power measurements may be useful in analysis.

As far as relevance to an energy conversion device is concerned, it is noted that the light-induced alterations of both the thermopower and the conductivity are similar to the effects produced by the doping of semiconductors with shallow dopants. However, when one carrier-type (the electrons, for example) does not dominate both the conductivity and thermoelectric power, the situation can become somewhat more involved (see Appendix A). Nonetheless, the photo-thermoelectric effect may be useful as the basis of a thin-film device which would be free of the problems which are associated with the high doping levels characteristic of traditional thermoelectric devices. In addition, one may consider devices in which the incident light will not only serve to generate extra carriers but also provide the temperature gradient required by the device. Detailed consideration of the nature and practicality of any such device is however beyond the scope of this note.

Appendix A

The preceding analysis may be readily generalized to include the case of an intrinsic semiconductor in which both electrons and holes are mobile. In particular, Eqs. (2)-(4) are then modified to yield the following expressions.

$$V_{L_1} = \frac{1}{|q|} \left[\left(\frac{b}{b+1} \right) \eta'_{A,e}(T) + \left(\frac{1}{b+1} \right) \eta'_{A,h}(T) - \eta_A(T) \right] , \quad (A.1)$$

$$\begin{aligned} \Delta V^A = & -S'_A \Delta T + \frac{1}{|q|} \left\{ \left(\frac{b}{b+1} \right) \left[\eta'_{A,e}(T+\Delta T) - \eta'_{A,e}(T) \right] \right. \\ & \left. + \left(\frac{1}{b+1} \right) \left[\eta'_{A,h}(T+\Delta T) - \eta'_{A,h}(T) \right] \right\} , \end{aligned} \quad (A.2)$$

$$V_{L_2} = - \frac{1}{|q|} \left[\left(\frac{b}{b+1} \right) \eta'_{A,e}(T+\Delta T) + \left(\frac{1}{b+1} \right) \eta'_{A,h}(T+\Delta T) - \eta_A(T+\Delta T) \right] , \quad (A.3)$$

where $\eta'_{A,e}$ and $\eta'_{A,h}$ are the electron and hole quasi-Fermi levels and b is the ratio of the electron and hole mobilities at temperature T . With these replacements one once again obtains Eq. (7). The expression for the thermoelectric power, Eq. (8), is however altered to

$$S'_A = S_A + \frac{1}{|q|T} \left\{ \left(\frac{b}{b+1} \right) \left[\eta'_{A,e}(T) - \eta_A(T) \right] + \left(\frac{1}{b+1} \right) \left[\eta'_{A,h}(T) - \eta_A(T) \right] \right\} .$$

The radiation-induced contribution to the above expression may be rewritten in terms of the number of radiation-induced electron-hole pairs, Δn , and the equilibrium number of pairs $n_o(T)$ to read

$$S'_A = S_A + \frac{k}{|q|} \left(\frac{b-1}{b+1} \right) \ln \left[1 + \frac{\Delta n}{n_o(T)} \right] .$$

In the limit of only one type of carrier being mobile ($b \rightarrow \infty$, for electrons or $b \rightarrow 0$, for holes) the previous expression for $\Delta S_A = S'_A - S_A$, Eq. (9), is regained.

References

1. See Eq. (12) of "A General Derivation of the Seebeck Effect Formula"
by this author: Sandia Laboratories Report SAND75-0045.
2. See Eq. (13) of the above reference.

FIG. 1. A PHOTOTHERMOELECTRIC EFFECT CIRCUIT

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