

THEORETICAL ANALYSIS OF A PULSE METHOD FOR MEASURING DRIFT MOBILITIES

JULIUS KREMPASKÝ*, Bratislava

An exact solution of the problem of measuring drift mobilities using the known Shockley-Haynes pulse method is presented. The point, line and plane sources, respectively, of injected electric charges have been taken into account. The analogy with the measuring of thermal diffusivity has been used by the mathematical solution of differential equations. It has been shown that a simple model generally used for the calculation of drift mobilities by the Shockley-Haynes method is valid only in a special case. Many important conditions should be fulfilled if this simple method is to give correct results. It is known that we measure only the so-called "ambipolar" mobility when the conductivity is intrinsic or near intrinsic, respectively. In this paper some methods for the calculation of the proper mobilities of electrons and holes in such a case have been discussed.

I. INTRODUCTION

In the last years direct methods of measuring drift mobilities have often been used, especially in the research of amorphous materials, as the measurement on the basis of the Hall effect cannot be easily interpreted. Various methods for direct measurement of drift mobilities are known [1-4], but the most often used is the famous Haynes-Shockley method [5-7]. By means of it the mobility of charge carriers of many crystalline and amorphous materials were measured [8-12], its principle is based on the generation of a space electric charge in one point of the sample and its transport due to a constant electric field to another point. The time of this transport t is determined by the relation $t = d/E_0\mu$, where d is the distance between these two points, μ the mobility and E_0 the electric field intensity. This relation is valid if the mobility does not depend on the electric field intensity and if the "package" of the electric charge does not disperse during the transport. The disintegration of this package may be caused by recombination or diffuse processes

and by ohmic currents, which are generated by the perturbation of a space electric charge.

These factors have not been analysed in detail, although it is clear that they may have an important influence on the measured quantities. The influence of traps is partially analysed in paper [13].

Some difficulties arise when the method is applied to measure semiconductors with both types of electric conductivity. The question is, what the time delay t between the generation of the excess electric charge and its detection means. It was shown that the measured value of mobility determines the "ambipolar" mobility in the case when the package of electric charge does not disintegrate during its transport. We shall show in this paper that the process of disintegration is characterized by another kind of mobility. When these two mobilities are measured, there is the possibility of calculating the proper mobilities of electrons and holes.

II. BASIC EQUATIONS

For the solution of the problem of the transport of an electric charge perturbation in a sample we use the basic equation of the phenomenological theory of the transport of electric charge carriers, which have the form

$$\frac{\partial n}{\partial t} = G_n - U_n + \frac{1}{e} \operatorname{div} i_n \quad (1)$$

$$\frac{\partial p}{\partial t} = G_p - U_p - \frac{1}{e} \operatorname{div} i_p \quad (2)$$

$$i_n = \sigma_n E + e D_n \operatorname{grad} n \quad (3)$$

$$i_p = \sigma_p E - e D_p \operatorname{grad} p \quad (4)$$

$$\operatorname{div} E = \frac{e}{\epsilon} (p - p_0 + n_0 - n) + \frac{q_r}{\epsilon}, \quad (5)$$

where n , p are the concentrations of electrons and holes; σ_n , σ_p the electron and the hole conductivities, respectively; G_n , G_p the factors of generation of electrons and holes; U_n , U_p the recombination rates of electrons and holes; i_n , i_p the current densities of electrons and holes; D_n , D_p the electrons and holes diffusion coefficients; E the electric field intensity; e the electric charge of the electron; ϵ the dielectric constant and q_r the electric charge on the traps.

During measurement there is always $G_n = G_p = 0$. Further we shall sup-

* Katedra fyziky Elektrotechnickej fakulty SVŠT, BRATISLAVA, Gottwaldovo nám. 2.

pose that the electric charge of the traps is negligible (i. e. $q_r = 0$) and that the surface recombination does not play any role. Supposing that the electrons and holes in the measured materials are not degenerate gases, we can use for the diffusion coefficients the Einstein relations

$$eD_n = u_n kT \quad (6)$$

$$eD_p = u_p kT. \quad (7)$$

We shall solve the system of differential equations (1 — 5) for three important cases: a) The majority charge carriers; b) the minority charge carriers and c) the material near the intrinsic electric conductivity.

1. Majority charge carriers

For the sake of simplicity let us suppose that a sample is of the p -type conductivity, i. e. $n = 0$. In this case we have $U_n = U_p = 0$ and equation (2) gets the form of the known continuity equation

$$\text{div } i_p + \frac{\partial \rho}{\partial t} = 0. \quad (8)$$

With respect to expression (4) we can write $\text{div } i_p$ in the form

$$\text{div } i_p = \sigma_p \text{div } E + (E_n + E_t) \cdot \text{grad } \sigma_p - eD_p \Delta p, \quad (9)$$

where $E_n = U_n/d$ is the external field intensity, E_t the internal electric field intensity, Δ the Laplace operator. Considering only a small perturbation in the concentration of majority charge carriers we can deal with the electric conductivity in the first term of the right-hand side of equation (9) as a constant. Thus this term becomes linear. In the second term there remains, however, a nonlinearity due to the electric field intensity E_t . This nonlinearity can be removed by the supposition that the external electric field intensity is much greater than the internal field intensity E_t , i. e.

$$E_n \gg E_t. \quad (10)$$

This important condition will be elaborated later into a more detailed expression. When considering the space electric charge determined by the relation $\rho = e(p - p_0)$, one obtains from equation (8) with regard to relation (9) the equation

$$\rho \frac{\sigma_p}{e} + E_n \sigma_p \cdot \text{grad } \rho - D_p \Delta \rho + \frac{\partial \rho}{\partial t} = 0. \quad (11)$$

It can be easily found that the solution of this equation can be written in the form

$$\rho(r', t) = e^{-t/\tau} f(|r' - r_p| E_p t), \quad (12)$$

where $\tau = \epsilon/\sigma$ and the function $f(r', t)$ satisfies the differential equation

$$\Delta f = \frac{1}{D_p} \frac{\partial f}{\partial t}. \quad (13)$$

These results can be interpreted as follows: The influence of an external electric field can be considered by the transformation $r' = r - r_p E_p t$ and the influence of the ohmic part of electric current upon the package of electric charges by the factor $\exp[-t/\tau]$, where $\tau = \epsilon/\sigma$ is a relaxation constant. In well conductive materials ($\sigma > 1 \text{ ohm}^{-1} \text{ m}^{-1}$) $\tau < 10^{-10} \text{ sec}$, and the equilibrium arises after a very short time delay. In the amorphous materials with $\sigma < 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ there is $\tau > 10^{-6} \text{ sec}$ and therefore the detection of signals is easier. That is one of the arguments for using this method when measuring amorphous semiconductors.

Equation (13) is analogous to the differential equation characterizing a heat transport. Regarding the similarity of the method of generation of the excess charge carriers to the pulse method of measuring the thermal diffusivity we can easily find the corresponding solution. The following functions are valid for point, line and plane sources, respectively, on the bulk material or a point and line sources, respectively, on a thin film ($r' = r - E_p w t$)

$$f_b(r', t) = \frac{Q_b}{(4\pi D_p t)^{3/2}} \exp \left[-\frac{r'^2}{4D_p t} \right], \quad (14)$$

$$f_l(r', t) = \frac{Q_l}{4\pi D_p t} \exp \left[-\frac{r'^2}{4D_p t} \right], \quad (15)$$

$$f_p(r', t) = \frac{Q_p}{(4\pi D_p t)^{1/2}} \exp \left[-\frac{r'^2}{4D_p t} \right], \quad (16)$$

$$f_{ab}(r', t) = \frac{Q_b}{(4\pi D_p t)^{3/2}} \exp \left[-\frac{r'^2}{4D_p t} \right] \left[\frac{(\pi D_p t)^{1/2}}{h} - 1 \right], \quad (17)$$

$$f_{al}(r', t) = \frac{Q_l}{4\pi D_p t} \Phi \left[\frac{b}{4(D_p t)^{1/2}} \right] \exp \left[-\frac{r'^2}{4D_p t} \right] \left[\frac{(\pi D_p t)^{1/2}}{h} - 1 \right], \quad (18)$$

where Q_b is the electric charge injected into the sample by a point source, Q_l the electric charge injected from a unit length of the line source, Q_p the electric charge injected from a unit area of the plane source, Φ the error

function, b the length of the line source, h the thickness of a plate (film). In all cases mentioned above it was supposed that $h/(D_p t)^{1/2} < 1$.

2. Minority charge carriers

Let us consider a semiconductor of the n -type conductivity, i. e. when the minority charge carriers are holes. In this case the recombination rate U_p is expressed by the formula

$$U_p = \frac{p - p_0}{\tau_p}, \quad (19)$$

where τ_p is the lifetime of holes. Then, fulfilling the condition (10) and the condition $p_0 < e/\epsilon\tau_p u_p$, we can get a differential equation in the form

$$\frac{\rho}{\tau_p} + u_p E_0 \cdot \text{grad } \rho - D_p \Delta \rho + \frac{\partial \rho}{\partial t} = 0. \quad (20)$$

This equation is identical with the equation (11), if the lifetime τ_p is substituted by the term e/σ_p . Then the solution is determined by the function (12) and the functions (14–18), if we put $\tau \rightarrow \tau_p$.

3. Semiconductors near the intrinsic electric conductivity

After two limit cases $p_0 \gg n_0$ and $p_0 \ll n_0$ we shall now consider the case $n_0 \approx p_0$. Subtracting equation (1) from equation (2) we can derive with regard to equations (3–5) and the inequality (10) the following differential equation

$$\begin{aligned} \frac{\partial(p - n)}{\partial t} &= U_n - U_p - \frac{\sigma}{e}(p - p_0 - n + n_0) - \\ &- E_0(u_n \text{ grad } n + u_p \text{ grad } p) + kT(u_n \Delta p - u_n \Delta n), \end{aligned} \quad (21)$$

where $\sigma = \sigma_n + \sigma_p$ is the total electric conductivity.

The mobilities of electrons and holes generally differ, therefore it is not possible to reduce equation (21) to the form (11) or (20), respectively. However, we can take into account the fact that only a small perturbation in the electric charge equilibrium realizes during the measurement. Using the Maxwell-Boltzmann statistics we can express the concentrations of electrons and holes in this case by the relations

$$p(r) = p_0 \exp [eV(r)/kT], \quad (22)$$

$$n(r) = n_0 \exp [-eV(r)/kT], \quad (23)$$

where $V(r)$ is the potential; n_0 and p_0 are the concentrations of electrons and holes in the place characterized by a zero potential level. For small values of this potential (smaller than 30 mV at room temperature) the exponential functions in the relations (22) and (23) can be approximated by the two first terms of the Taylor series. Then, e. g., the relation between the space electric charge ρ and the potential V will have the form

$$\rho = e(p - p_0 - n + n_0) \approx \frac{e^2}{kT}(n_0 + p_0)V. \quad (24)$$

By this relation the changes in the space electric charge are proportional to the changes of the potential.

Substituting the relations (22) and (23) into the relation (21) and supposing (similarly as in the previous cases) that $E_i \ll E_0$ and further $|eV/kT| < 1$, we get the equation

$$\frac{\sigma}{e} \rho + u_p E_0 \cdot \text{grad } \rho - \frac{kT}{e} u_d \Delta \rho + \frac{\partial \rho}{\partial t} = e(U_n - U_p), \quad (25)$$

where

$$u_i = \frac{u_p p_0 - u_n n_0}{n_0 + p_0}, \quad (26)$$

$$u_d = \frac{u_p p_0 + u_n n_0}{n_0 + p_0}. \quad (27)$$

If the recombination process has a bimolecular character, then $U_n = U_p$ and equation (25) is identical to equation (11), after substituting $u_p \rightarrow u_i$ and $eD_p \rightarrow kT u_d$. The transformation $r' = r - E_0 u_p t$ has now the form $r' = r - E_0 u_d t$.

The results mentioned above can be interpreted as follows: The electric charge package moves in a semiconductor with a conductivity near the intrinsic one by a „transport“ ambipolar mobility u_i (26), while the disintegration of this package is characterized by another „diffuse“ ambipolar mobility u_d (27). Both relations (26, 27) have already been deduced (see, e. g., [15–17]). If it is possible to measure both ambipolar mobilities u_i and u_d , one could calculate the proper mobilities of electrons and holes using the relations

$$u_p = \left(1 + \frac{n_0}{p_0}\right) \frac{u_i + u_d}{2}, \quad (28)$$

$$u_n = \left(1 + \frac{p_0}{n_0} \right) \frac{|u_i - u_d|}{2}. \quad (29)$$

In p -type semiconductors, there is $p_0 \gg n_0$ and therefore $u_i \approx u_d \approx u_p$; in an intrinsic semiconductor ($n_0 = p_0$) there is, however, $u_i = \frac{1}{2}(u_p - u_n)$ and $u_d = \frac{1}{2}(u_p + u_n)$. As it will be seen, the transport ambipolar mobility is that value, which is always measured by the Shockley-Haynes method, therefore the value $\frac{1}{2}(u_n - u_p)$ is determined in the intrinsic semiconductor.

III. CALCULATION OF MOBILITIES

In the Shockley-Haynes arrangement the time delay between the generation of the electric charge pulse (various methods of realizing such pulses are described in papers [17-20]) and its detection at another point of the sample is measured. By neglecting all the influences which cause the disintegration of the electric charge package (ohmic currents, recombination and diffusion) we can calculate this time delay from the transformation $r' = r - E_v u_i$. By this relation the maximum of a pulse moves with the velocity $v = E_v u_i$ and therefore the time delay is given by the expression

$$t = \frac{d}{E_v u_i} = \frac{d^2}{U_v u_i}, \quad (30)$$

where d is the distance between the generator and the detector, U_v the constant external voltage. This relation determines the mobility u . However, the time of the maximum of the electric charge density is, in general, defined by the condition $\partial q/\partial t = 0$. It is possible to solve this condition for all the cases mentioned above simultaneously. We denote the relation time as τ and the mobilities as u_i and u_d . For special cases it is necessary to substitute the symbols according to Table 1.

Table 1

	Majority carriers		Minority carriers		Intrinsic conductivity (near intrinsic)
	$p_0 \gg n_0$	$n_0 \gg p_0$	Electrons	Holes	
τ	$\frac{\epsilon}{\sigma}$	$\frac{\epsilon}{\sigma}$	τ_n	τ_p	
u_i	u_p	u_n	u_n	u_p	$\frac{u_p p_0 - u_n n_0}{n_0 + p_0}$
u_p	u_p	u_n	u_n	u_p	$\frac{u_p p_0 + u_n n_0}{n_0 + p_0}$

Let us consider the arrangement with a plane source, which is used most frequently. With regard to the supposition that the surface recombination is negligible, the problem becomes one-dimensional. According to relations (12) and (13) the general function characterizing the space charge is of the form

$$q(x, t) = \text{const. } t^{-1/2} \exp \left[-\frac{e}{kT} \frac{(x - E_v u_i t)^2}{4u_i t} - \frac{t}{\tau} \right]. \quad (31)$$

The time of the maximum of this function is determined by the relation

$$t_m = \frac{1}{2q} \left[-\frac{1}{2} + \left(\frac{1}{4} + \frac{e q x^2}{u_i kT} \right)^{1/2} \right], \quad (32)$$

where

$$q = \frac{e}{kT} \frac{u_i^2 E_v^2}{4u_i d} + \frac{1}{\tau}.$$

Expression (32) is very complicated for the calculation of the mobility (it does not allow this calculation in the case of intrinsic conductivity, because it contains two unknown quantities: u_i and u_d). We shall take into account, therefore, only two special cases defined by the conditions, which can be easily fulfilled by measuring.

1. Small disintegration of the electric charge package

Let us assume that the following conditions are fulfilled

$$\frac{e}{kT} \frac{q x^2}{u_i} \gg \frac{1}{4}, \quad (33)$$

$$\frac{e}{kT} \frac{u_i^2 E_v^2}{4u_i d} \gg \frac{1}{\tau}. \quad (34)$$

Then the relation (32) reduces to the form

$$t_m = \frac{x}{E_v u_i}, \quad (35)$$

which is identical to the basic relation of the Shockley-Haynes method. For this reason we can take conditions (33) and (34) together with condition (10) as criteria for the possibility of using the above mentioned method. We shall give them a more detailed form.

According to relation (34) the external electric field must fulfil the inequality

$$E_0 > \frac{2}{u_i} \left(\frac{kT u_i}{e} \right)^{1/2} \quad (36)$$

which transforms into the form

$$E_0 > 2 \frac{kT}{e \tau_p u_p} \quad (37)$$

for minority carriers and into the form

$$E_0 > 2 \frac{kT p_0}{e} \quad (38)$$

for a semiconductor with one type of conductivity. This last inequality gives $E_0 > 10^{-5} p_0^{1/2}$ (V/cm) for room temperature. It is a rather exacting condition, as, e. g. for semiconductors with $p_0 = (10^{16} - 10^{18}) \text{ cm}^{-3}$ there must be $E_0 > (10^4 - 10^5) \text{ V/cm}$.

If condition (34) is fulfilled, the inequality (37) has the form

$$E_0 > \frac{kT}{e} \frac{u_i}{x u_i} \quad (39)$$

This condition applied to the case of a semiconductor with only one type of conductivity or the case of minority carriers, respectively ($u_i = u_n$), gives

$$E_0 > n \frac{kT}{e} \frac{1}{x}, \quad (40)$$

where $n = 1, 2, 3$ for plane, line and point charge sources, respectively.

By a numerical calculation of condition (40) we shall find that by fulfilling condition (33) inequality (40) is fulfilled too.

A more detailed analysis of condition (10) can be found, e. g., in the book [20]. We shall present here only a more simple consideration of this assumption. The electric space charge is given by the expression $\rho = e(p - p_0 + n_0 - n)$. For the sake of simplicity let us suppose the electric charge of one sign, e. g., positive. The most critical is the case, which arises immediately after the generation of excess carriers, because later on, the internal electric field will be diminished due to the various internal processes. The integration of the equation $dE/dx = e(p - p_0)$ gives for this critical time the relation

$$E(0) - E(d) = \frac{1}{e} \int_0^d e(p - p_0) dx = \frac{eN_0}{e}, \quad (41)$$

where N_0 is the number of all holes injected into the semiconductor. If the contact at $x = d$ is sufficiently far from the point of injection, we can put $E(d) = 0$. The critical value of the internal field intensity is $E_c(0)$. Then, if we wish $E_0 \gg E_c$, the following inequality must be fulfilled

$$N_0 < \frac{e}{e} E_0. \quad (42)$$

It means that the critical number of the injected holes must be $N_0 < 10^{15}$ for the critical field intensity $E = 10^4 \text{ V/cm}$ mentioned above. Evidently this condition is not limiting excessively the choice of the intensity of the perturbation.

2. Strong disintegration of the electric charge package

Let us suppose that the condition reverse to condition (33) is valid, i. e.

$$\frac{e}{kT} \frac{q x^2}{u_i} \ll \frac{1}{4}. \quad (43)$$

Condition (34) need not be fulfilled in this case. It can be easily shown that the time of the maximum of the electric charge function is given by the relation

$$t_m = \frac{1}{2n} \frac{e}{kT} \frac{x^2}{u_i}, \quad (44)$$

where $n = 1, 2, 3$ for point, line and plane sources, respectively.

Using these relations one can calculate the value of diffuse ambipolar mobility. In the case of one type conductivity or in the case of the minority carriers this does not bring anything new in relation to the previous case, but in the case of intrinsic conductivity relation (44) can be of great importance. If conditions (10), (33) and (34) are fulfilled (the measurement in a „strong“ electric field), one can determine the value u_i . By fulfilling conditions (10) and (43) (the measurement in a rather „small“ electric field) we obtain the value u_n . Then using relations (28) and (29) we can find the values of proper mobilities of electrons and holes.

It is possible to find also another method for the determination of the quantity u_n . According to relation (31) the ratio of two maximums of electric space charge functions corresponding to two different points x_1 and x_2 at the same time ($t = x/E_0 u_i$) is given by the relation

$$\frac{\rho(x_1)}{\rho(x_2)} \approx \frac{V(x_1)}{V(x_2)} = \exp \left[\frac{e}{kT} \frac{x_2^2 - x_1^2}{4u_i t} \right].$$

Then

$$\mu_d = \frac{kT}{e} \frac{x_2^2 - x_1^2}{4t \ln [V(x_2)/V(x_1)]}. \quad (45)$$

IV. CONCLUSION

A theoretical analysis of the problem of measurement of drift mobilities by the pulse method has been presented in this paper. The processes causing a disintegration of the electric charge package have been taken into account. It has been found that some important conditions must be fulfilled to obtain good results by the Shockley-Haynes method of measurement. It is necessary to distinguish between the "transport" and "diffuse" ambipolar mobility, when semiconductor samples near the intrinsic type of conductivity are measured. Methods for measuring both these mobilities are suggested. By means of such a measurement one can calculate the values of proper mobilities of electrons and holes.

REFERENCES

- [1] Grove R. W., Journ. Appl. Phys. 27 (1956), 156.
- [2] Kepler R. G., Phys. Rev. 119 (1960), 1226.
- [3] Le Blanc O. H., Journ. Chem. Phys. 33 (1960), 626.
- [4] Brown F. C., Dart F. E., Phys. Rev. 108 (1957), 281.
- [5] Shockley W., *Electrons and holes in semiconductors*. Princeton 1950.
- [6] Haynes J. R., Shockley W., Phys. Rev. 75 (1949), 691.
- [7] Prince M., Phys. Rev. 92 (1953), 681.
- [8] Many A., Harnik E., Gerlich D., Journ. Chem. Soc. 23 (1955), 1733.
- [9] Le Blanc O. H., Journ. Chem. Phys. 35 (1961), 1276.
- [10] Le Blanc O. H., Journ. Chem. Phys. 33 (1961), 626.
- [11] Kearns D. R., Calvin M., Journ. Chem. Phys. 34 (1961), 2022.
- [12] Gutman F., Lyons L. E., *Organic Semiconductors*. J. Wiley and Sons, Inc., New York - London - Sydney 1967.
- [13] Spear W. E., Noncryst. Solids 1 (1969), 197.
- [14] Krempaský J., *Meranie termofyzikálních veličin*. Vydavatelstvo SAV, Bratislava 1969.
- [15] Jonscher A. K., *Principles of Semiconductor Device Operation*. A. Bell and sons, London 1959.
- [16] Sze S. M., *Physics of Semiconductor Devices*. J. Wiley and sons, New York - London - Sydney - Toronto 1969.
- [17] Frank H., Šnejdar V., *Halbleiter Bauelemente*, Band 1. Akademie Verlag, Berlin 1964.
- [18] Shockley W., Pearson G. L., Haynes J. R., Bell Syst. Tech. J. 28 (1949), 344.
- [19] Spear W. E., Proc. Phys. Soc. B 70 (1957), 1139.
- [20] Smith R. A., *Semiconductors*. University Press, Cambridge 1959.

Received February 24th, 1971