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Small signal admittance spectroscopy applied for extraction of charge carrier mobility in thin organic layers

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The work presents new way of extraction of charge carrier mobility from small signal spectra of admittance. It can be a useful method for thin organic layers in a sandwich arrangement. It is better than the version of small signal admittance currently applied for getting charge carrier mobility, since the final result is not charged with uncertainty of geometric capacitance and the upper limit of measurable charge carrier mobility is higher.

Keywords: organic thin films, organic devices, charge carrier mobility, small signal admittance.

1. Introduction

Modelling of organic devices can be successfully performed only if a value of the charge carrier mobility μ is properly assumed. This basic parameter of electric transport is not easy to measure in organic thin films. The direct method such as time of flight technique requires quite thick layers (usually of 1 or more μm). The values of μ obtained in this way are not treated as appropriate for thin layers because we can suspect certain differences in morphology between thick and thin layers. Therefore in order to acquire μ in thin organic layers, several indirect methods are considered. Values of μ extracted with the help of different indirect methods often poorly coincide with each other. Consequently, the discussion on a proper method of estimating μ in thin organic layers is still open. Besides, considering assumptions which have to be fulfilled in a particular indirect method, scientists are also searching for new experimental methods suitable for extraction of μ [1–5].

One of the indirect experimental methods of extracting μ is the method based on small signal admittance (SSA). It attracts recently a great deal of attention as a particularly useful one for thin organic layers in a sandwich arrangement [6–10]. Important advantage of this method is the fact that it can be applied directly to planar organic devices such as organic light emitting diode or photovoltaic cells [11]. Measurements have to be performed on a sample provided with an ohmic contact which has to sustain a flow of space charge limited current (SCLC) [12,13]. Spectral measurements of both parts of complex admittance constitute experimental part of the method. If current flowing in a device is SCLC, characteristic small signal spectra are noticeable [12]. For extraction of μ, only an imaginary part of small signal admittance (i.e. susceptance) is analyzed afterwards [11,14–16]. Additionally, the method requires an exact value of the geometric capacitance C_g. Uncertainty of this quantity contributes to uncertainty of the extracted μ.

In this work, we propose other method of SSA for extraction of charge carrier mobility. It is based on both parts of small signal admittance and it does not require the exact value of C_g. Moreover, the proposed method raises the upper limit of measurable values of μ for thin layers. The comparison between these two methods is presented in this work.

2. Theoretical background

The theory of space charge limited current was elaborated by Mott and Gurney [17]. They considered flow of current through an insulator provided with ohmic electrode, which sustained much higher concentration of charge carriers at the electrode than it was within the bulk of material. The set of equations ruling the flow of SCLC consists of

$$j_c = ep\mu\left(-\frac{dV}{dx}\right), \tag{1}$$

$$-\frac{d^2V}{dx^2} = \frac{e}{\varepsilon_o\varepsilon_r}p, \tag{2}$$

$$\left.\frac{dV}{dx}\right|_{x=0} = 0, \tag{3}$$

$$V(d) - V(0) = -U, \tag{4}$$

$$e\frac{dp}{dt} = -\frac{dj_c}{dx}, \tag{5}$$

where j_c is the conduction current density, e is the elementary charge, p is the concentration of holes, μ is the mobility

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of holes, V is the electric potential, ε_o is the permittivity constant, ε_r is the dielectric constant, d is the thickness of layer, and U is the applied voltage. The above set of equations deals with the hole current. It is positive when it flows in the positive x-direction, and hence anode is located at $x = 0$ while a collecting electrode is located at $x = d$. In small signal measurements, a sample is biased simultaneously by the voltage independent of time U_o and by small voltage harmonically varying in time $[U_1\exp(i\omega t)]$. Total current is then a sum of a term independent of time (direct current) and a term harmonically varying in time. For SCLC case [i.e. for the set of Eqs. (1)–(5)], we obtain the direct current in the form [17,18]

$$j_o = \frac{9}{8}\varepsilon_o\varepsilon_r\mu\frac{U_o^2}{d^3}, \tag{6}$$

and the following relation between small signal current $[j_1\exp(i\omega t)]$ and small signal voltage $[U_1\exp(i\omega t)]$ [12,19]

$$j_1 = \frac{(1/6)g_o(i\omega\tau)^3}{1 - i\omega\tau + 1/2(i\omega\tau)^2 - \exp(-i\omega\tau)}U_1, \tag{7}$$

where

$$g_o = \frac{dj_o}{dU_o} = \frac{9}{4}\varepsilon_o\varepsilon_r\mu\frac{U_o}{d^3} \tag{8}$$

and

$$\tau = \int_0^d \frac{dx}{\mu F_o} = \frac{4}{3}\frac{d^2}{\mu U_o} \tag{9}$$

According to Eqs. (8) and (9), g_o is called the differential conductance, while τ is called the time of flight.

Small signal response can be presented as the complex admittance

$$Y = Y' + iY'', \tag{10}$$

with

$$Y' = S\,\mathrm{Re}(j_1/U_1)$$
$$= \frac{1/6\,Sg_o(\omega\tau)^3[\omega\tau - \sin(\omega\tau)]}{2 - 2\omega\tau\sin(\omega\tau) + [(\omega\tau)^2 - 2]\cos(\omega\tau) + 1/4(\omega\tau)^4}, \tag{11}$$

and

$$Y'' = S\,\mathrm{Im}(j_1/U_1)$$
$$= \frac{1/6\,Sg_o(\omega\tau)^3\left[\cos(\omega\tau) - 1 + 1/2(\omega\tau)^2\right]}{2 - 2\omega\tau\sin(\omega\tau) + [(\omega\tau)^2 - 2]\cos(\omega\tau) + 1/4(\omega\tau)^4}, \tag{12}$$

where S is the active area of electrodes. Equations (6)–(9) were obtained on the base of Eqs. (1)–(5) at charge carrier mobility independent of electric field strength and of frequency.

Figure 1 shows simulation of both parts of complex admittance for three selected values of U_o. Curves have been computed for $d = 100$ nm, $\varepsilon_r = 4$, $S = 10$ mm^2, and $\mu = 1\times10^{-4}$ cm^2/(Vs).

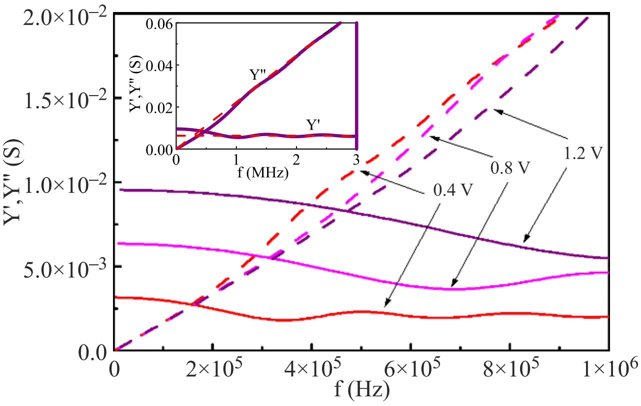

Fig. 1. Real (solid lines) and imaginary (dash lines) parts of admittance *vs.* frequency at the following values of steady voltage: 0.4 V, 0.8 V, 1.2 V. Inset presents real and imaginary parts of admittance (both curves are solid) and lines of $Y' = 2Sg_o/3$, $Y'' = \omega C_o$ (red dash lines) at $U_o = 1.2$ V.

3. Extraction of μ from $-\Delta B$

As it is seen in the inset of Fig. 1, both parts of complex admittance are modulated by oscillations whose amplitude decreases with increasing frequency. Time of flight, defined by Eq. (9), determines numbers of oscillations per interval of frequency.

In order to extract μ, only the imaginary part of SSA is taken into account. First, the function of ΔB, defined as

$$\Delta B = Y'' - \omega C_g, \tag{13}$$

is computed within the whole investigated range of frequency. Calculating ΔB, the exact value of geometric capacitance is required. This quantity can be obtained from active area of electrodes, thickness and dielectric constant of organic layer, since

$$C_g = \varepsilon_r\varepsilon_o\,S/d. \tag{14}$$

Next, the obtained values of ΔB are presented in a graph of $-\Delta B$ *vs.* frequency. Here, the series of several maxima should be obtained (Fig. 2). The first maximum is the biggest one and it occurs at

$$\omega\tau = 4.55. \tag{15}$$

If we note the frequency at which the first maximum of $-\Delta B$ occurs by f_{max} then, according to Eqs. (15) and (9) we can write down the following relation

$$f_{\max} = 0.543\frac{\mu U_o}{d^2}. \tag{16}$$

As it can be seen, f_{max} is proportional to steady voltage and the proportional coefficient depends only on charge carrier mobility and layer thickness. Values of f_{max} can be extracted from experimental results for various values of U_o and next they can be put into a graph of f_{max} *vs.* U_o (upper series of points in Fig. 3). If the points align with a straight line with an intercept close to 0, a slope of the line can be

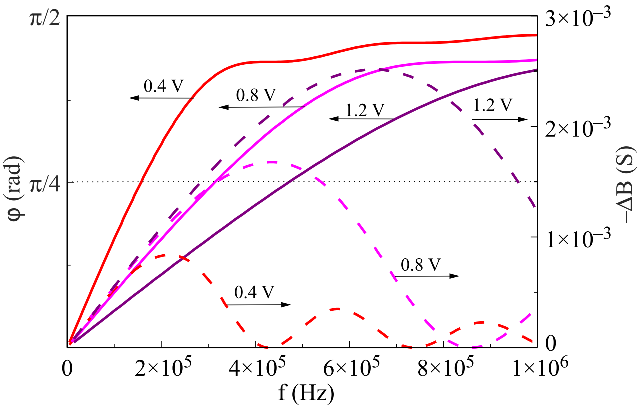

Fig. 2. Phase of admittance (solid lines) and $-\Delta B$ (dash lines) *vs.* frequency at the following values of steady voltage: 0.4 V, 0.8 V, 1.2 V.

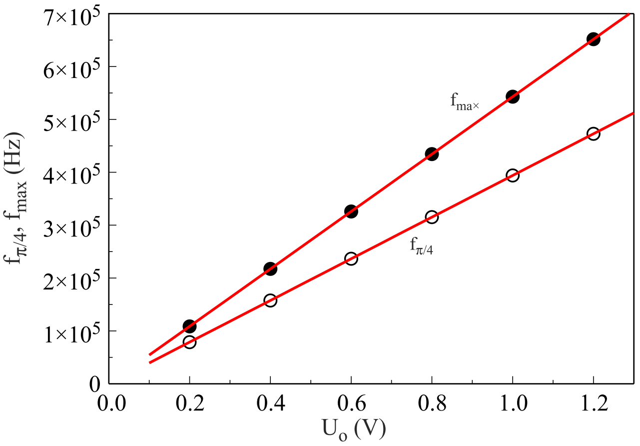

Fig. 3. Dependence of f_{max} (solid circles) and $f_{\pi/4}$ (open circles) *vs.* steady voltage.

used to estimate μ. To acquire μ, we need the value of layer thickness. This method will be hereinafter called the f_{max} method.

Scientists using this method usually take only two significant figures of the coefficient in Eq. (16) and therefore they consider 0.54 [7–9,11,13,15]. Only Tsang *et al.* [14] and Tsung *et al.* [6] report 0.56. This small difference between 0.54 and 0.56 may result from different numbers of significant figures in values taken into calculation of the coefficient in Eq. (16).

4. Extraction of μ from Y''/Y'

Properties of SSA spectra obtained under SCLC and expressed by Eqs. (11) and (12) enable us to propose a simpler method for extraction of μ than the f_{max} method. First, it is worth noticing that imaginary and real parts of admittance are equal to each other at the particular value of $\omega\tau$. So, the subject of our analysis will be a phase of the admittance φ defined as

$$\varphi = arctg\left(\frac{Y''}{Y'}\right). \tag{17}$$

Curves of φ *vs.* ω, for the same as in Fig. 1 three selected values of U_o, are presented in Fig. 2. When the imaginary part of admittance equals the real one $\varphi = \pi/4$ and this case occurs at

$$\omega\tau = 3.30. \tag{18}$$

If we note the value of frequency at which $\varphi = \pi/4$ by $f_{\pi/4}$ then, according to Eqs. (18) and (9) we can come to the conclusion that

$$f_{\pi/4} = 0.394\frac{\mu U_o}{d^2}. \tag{19}$$

Similarly as in the case of f_{max}, also the value of $f_{\pi/4}$ is proportional to steady voltage and the proportional coefficient depends only on μ and layer thickness. We can now analogically perform extraction of μ. First, we should present experimental results in a graph of admittance phase *vs.* frequency for various values of U_o (Fig. 2). From the graph, we read $f_{\pi/4}$ and make a plot of $f_{\pi/4}$ against U_o (lower series of points in Fig. 3). Next, we approximate experimental points with a straight line. Finally, the charge carrier mobility is extracted from the slope of the line.

5. Discussion and conclusions

As it was emphasized in the Introduction, the f_{max} method attracts a great deal of attention as a method particularly useful for extraction of μ in thin organic layers provided with planar electrodes. The method has been applied both for polymer layers [10,11,15] and for layers of small organic molecules [6,14,16]. In Ref. 13, Hoping *et al.* has shown that hole mobility extracted in 628 nm-thick BCP layer with the f_{max} method correlated quite well with the hole mobility obtained with time of flight technique. Tsang *et al.* has obtained similar agreement for 3.5–µm-thick layer of m-MTDATA [14].

On the other hand, the f_{max} method has some natural limitations. First of all, we must notice that the maximum of $-\Delta B$ has to occur within the investigated range of frequency. Let us assume we work with LCR bridge with the upper limit of frequency equal to 3 MHz. In such case applying 1 V of steady bias to a 100–nm-thick sample we will not measure charge carrier mobility if it is greater than 5.5×10^{-4} cm^2/Vs. This upper range of measurable μ can be raised a little if we use $f_{\pi/4}$ instead of f_{max}. It results from the fact that $f_{\pi/4} \approx 0.73 \cdot f_{max}$ at the same value of steady voltage.

The other problem in the f_{max} method is the need of exact value of geometric capacitance. It can be calculated from a thickness of organic layer, its dielectric constant and area of an active part of electrodes. Uncertainties of all these three quantities contribute to uncertainty of C_g and this affects accuracy of ΔB function. Obviously, this is not the only way for getting C_g. This value can be straightly measured either within lower range of frequency for reverse bias or within the higher range of frequency for forward bias. Both attitudes, however, have to meet certain requirements.

The former case can be applied if there is strong rectification of current (i.e. the case of SCLC diode) and then small signal spectra for reverse bias are entirely determined by C_g within lower range of frequency. The latter method of measuring C_g can be theoretically always applied under SCLC condition since according to Eq. (11)

$$\lim_{\omega \to \infty} (Y''/\omega) = C_g. \qquad (20)$$

However, small signal responses of real sandwich organic devices are quite often affected by resistance of electrodes within frequency range higher than about 100 kHz [16,20–22]. The accuracy of C_g measured in such cases can be unsatisfactory.

It is worth noticing here that the $f_{\pi/4}$ method does not refer to geometric capacitance. It is based on both parts of small signal admittance instead. For extraction of μ we need only the thickness of an organic layer, since $f_{\pi/4}$ [Eq. (19)] similarly as f_{max} [Eq. (16)] depends on d.

With the respect to all above points, we come to conclusion that the proposed method can be better for extraction of μ than f_{max}. The final result is not charged with uncertainty of C_g and the upper limit of measurable charge carrier mobility is higher.

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