Current-Voltage Characteristics of Thin Poly(biphenyl-4-ylphthalide) Films

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Summary: The paper considers the features of the charge transport near to the threshold of the transition of polymer films to the high conductive state, induced by a small uniaxial pressure. The problem has not been solved so far, how the energy structure of a wide-band-gap organic dielectric varies near this threshold. The current-voltage characteristics of poly(biphenyl-4-ylphthalide) films at different uniaxial pressures were measured and analyzed. The interpretation of the obtained results is carried out within the framework of the space charge limited conduction model. The estimation of the injection model of transport parameters such as the charge carrier mobility and concentration, trapping state concentration and others are carried out. The analysis of the obtained results allows to make the following preliminary conclusion. Pressure increase promotes formation of a narrow trap band near the quasi-Fermi level resulting from the increase in the injection. This can give rise to a sharp magnification of the charge carrier mobility and even transition to the metallic state.

Keywords: charge carriers mobility; current-voltage characteristics; high conductive state; poly(biphenyl-4-ylphthalide); Space Charge Limited Conduction

Introduction

In thin electroactive polymer films the transition from a dielectric state to a high-conductive state (HCS), induced by such physical influences as electric field[1], small uniaxial pressure[2], temperature[3], is observed. The feature of this phenomenon is that the temperature dependence of the HCS conductivity is of the metal type and the conductivity can be extremely high (> 10^7 S/m).[4] The initial dielectric state of the polymer can be described in such parameters as the band gap ~ 4.3 eV, the work function of an electron ~ 4.2 eV, the first potential of ionization ~ 6.2 eV.[5] However, so far there has been the unsolved problem how the energy structure of the wide-band-gap organic dielectric varies near the transition into the HCS. In this

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connection, the purpose of the present paper was the study of the laws of the charge transport near the threshold of the transition of polymer films to the HCS, induced by a small uniaxial pressure. For this purpose the current-voltage (*I-V*) characteristics of poly(biphenyl-4-ylphthalide)[6] films of different thickness at different uniaxial pressures were measured and analyzed. The investigations of the *I-V* characteristics of the polymers possessing high conductance are known.[7-11] However, in these papers the data in the vicinity of the transition threshold were not systematic.

Experimental procedure

The choice of poly(diphenylphthalide) (PBP) (Fig. 1) as the object of the investigation was explained by its good film-forming properties on the metal substrates. In paper[12] it was shown that under certain technological conditions the PBP forms continuous homogeneous films of 0.05 - 10 μm thickness. Besides, this polymer has no temperature features in conductivity up to the softenning temperature (360 °C in air). Also PBP is the most investigated polymer from the point of view of HCS inducing.[1,13,14] The quality and homogeneity of the polymer films were checked by optical microscopy methods as described in the paper.[15]

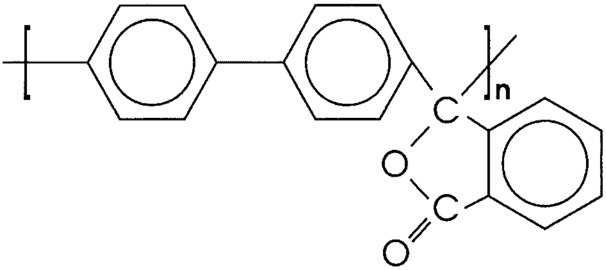

Figure 1. Chemical structure of poly(biphenyl-4-ylphthalide)

The measurements were carried out using the apparatus consisting of a uniaxial pressure device, a pressure sensor and the electrical circuit for the *I-V* characteristics recording. The pressure (*P*) varied up to 900 kPa.

The used samples were of the metal-polymer-metal "sandwich" type. Thin polymer films were prepared by spin coating of the metal electrode surface with a polymer solution. As a solvent, cyclohexanone was used. The metal electrode was deposited on a polished glass plate by the vacuum evaporation method. The other electrode was deposited on the polymer film surface by vacuum evaporation. Various metal films such as Cu, Al and Cr were used for the electrodes. The contacting area was $s \approx 2$ mm^2. The thickness of the films was set by concentration of the solution and checked by the interference method with an MII-4 interferometer; it ranged from 0.8 to 1.5 μm. More than fifty samples were investigated.

Results and discussions

Typical *I-V* characteristics of the 1-μm thick polymer film near the transition to the metal state are shown in a Fig. 2. These dependences are well fitted by the power function of the $I \approx U^n$ type. Under $P = 0$, the *I-V* characteristics can be divided into two regions: the linear with $n = 1$ at small voltages and the quadratic with $n = 2$ at the higher voltages. The transition between these regions occurs at a certain voltage U_1.

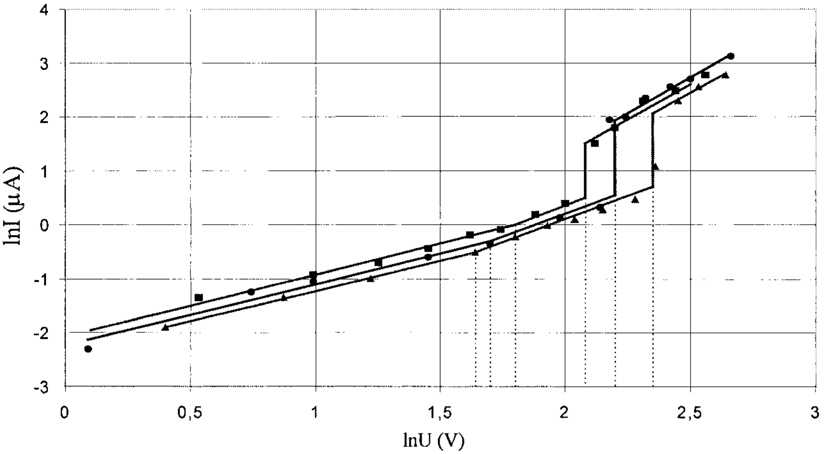

Figure 2. *I-V* characteristics of the polymer films measured at different pressures (above atmospheric): ■-780 kPa; •-820 kPa; ▲-860 kPa . All points are average of 50 measurements. The measurement error is ca. 5 %

The comparative analysis of the *I-V* characteristics, introduced in Fig. 2, showed, that increase in pressure leads to the reduction of the voltage U_1. When the voltage exceeds a value of $U_2 >$

U_1, practically vertical growth of the current is observed. The increase in the pressure leads to the shift of U_2 towards higher voltages. After the vertical region at U_2, a quadratic region is observed on the *I-V* characteristics again. A further increase in pressure gives rise to electronic switching of the polymer sample to the HCS.

For interpretation of the obtained *I-V* characteristics the space charge limited conduction (SCLC) model was used[16] , which allowed to characterize local states in the polymer band gap and explain the shape of the *I-V* dependence. Before passing to the obtained results, it is necessary to note that within the framework of the problem given in this paper, we use the limit of monochromatic traps. The results of the investigation show that even in this limit we can trace the effect of external influences on the injection model parameters.

The model predicts the Ohmic behavior up to a voltage U_1, at which the concentration of the thermally generated equilibrium charge becomes comparable to that of the injected charge:

$$J \approx e n_0 \mu \frac{U}{L}, \tag{1}$$

where e is the charge of an electron, n_0 the concentration of the equilibrium free charge, μ the electron mobility and L the film thickness.

Further increase in voltage gives rise to the trapping quadratic dependence:

$$J \approx \theta \varepsilon \varepsilon_0 \mu \frac{U^2}{L^3}, \tag{2}$$

where ε is the relative permittivity, ε_0 the permittivity of vacuum and θ the value defining the trap-filling degree.

A practically vertical region follows the quadratic region. It is interpreted as the voltage ($U_2 = U_{\mathrm{TFL}}$) of limiting trap-filling. The mode of limiting trap filling is a consequence of the crossing by the quasi-Fermi level of the range of trapping states in the polymer band gap. As a result, the quantity of the injected charge carriers in the polymer sharply increases, which gives rise to a considerable increase in the current. At higher voltages, the *I-V* characteristic is normally described by the square-law (Fig. 2):

$$J \approx \varepsilon \varepsilon_0 \mu \frac{U^2}{L^3}. \tag{3}$$

The thickness dependence of a current was measured. It was revealed that $I = f(L^{-3})$. Such dependence is in a good correspondence with the equations of injection model.

Table 1 shows the values of voltages U_l, U_TFL and basic parameters of the SCLC model: μ - the electron mobility, n_0 – the concentration of the thermally generated equilibrium electrons, $p_{\mathrm{t},0}$ – the concentration of the empty trapping states (this concentration is proportional to their total concentration N_t, which depends on the applied uniaxial pressure). For the estimations, the following relations were used[16,17] :

$$n_0 \approx \frac{\theta\varepsilon\varepsilon_0 U_\mathrm{l}}{eL^2}\ ;\ \mu = \frac{JL^3}{\theta\varepsilon\varepsilon_0 U_\mathrm{l}^2}\ ;\ p_{\mathrm{t},0} = \frac{\varepsilon\varepsilon_0 U_\mathrm{TFL}}{eL^2} \qquad (4)$$

Table 1. Influence of uniaxial pressure on some parameters of the injection model.

P kPa	$\mu\cdot10^{-9}$ $\mathrm{m^2/V\cdot s}$	$n_0\cdot10^{20}$ $\mathrm{m^{-3}}$	U_l V	U_TFL V	$p_{\mathrm{t},0}\cdot10^{21}$ $\mathrm{m^{-3}}$	θ
780	1.4	3.8	6.1	8.1	1.4	0,36
820	1.6	2.4	5.5	9.1	1.5	0,26
860	1.8	2.2	5.2	10.6	1.8	0,25

It is necessary to note that the conductivity σ in the linear region of the *I-V* characteristic calculated from the current and voltage values coincides within an order of magnitude with the value σ, calculated from the formula

$$\sigma = en_0\mu$$

From the data shown in the table follows that the increase in pressure leads to the following changes in the parameters of the charge transport: the concentration of the equilibrium charge carriers diminishes, which apparently results from the change of the quasi-Fermi level. The decrease in U_l value with increasing pressure confirms our suggestion that the deep trapping states begin to play the basic role and their concentration grows. Growth of the charge carrier mobility is observed, which can be explained most likely by an increase in the concentration of the trapping states and decrease in the trap filling degree.

Conclusions

The analysis of the obtained results allows us to make the following preliminary conclusions. An increase in pressure leads to a change in the charge carrier injection into the polymer film. Probably, this results from the destruction of the relevant surface electronic states.[18] The excess charge in the polymer can create deep trapping states by the mechanism described in the paper.[19] It is possible to assume, that an increase in pressure will lead to a growth of electronic states concentration in a band gap and will cause transition of a localization-delocalization type, for example, by the Mott mechanism. Such state in polymer we term, as HCS. As a result of this process in the polymer band gap near the quasi- Fermi level, a narrow trap band can be formed, which underlies the charge carrier transport and gives rise to an increase in their mobility.

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