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# Electrical Conductivity of Polycrystalline Films of *p*-Sexiphenyl

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**Summary:** In this work the results of DC conductivity measurements of polycrystalline *p*-sexiphenyl thin films are presented. The investigations concerned the effect of temperature, film thickness and electric field on the DC conductivity mechanism. The thickness of the investigated material varied from 0.2 to 2.5 μm. The measurements were carried out for different electrode polarities of the 0 –100 V voltage and at temperatures ranging from 15 to 325 K. Thin films of *p*-sexiphenyl were obtained by controlled vacuum sublimation on BK-7 glass substrate with gold and aluminium electrodes. Analyzing the obtained results we conclude that injection of the charge carrier from electrodes into the investigated material proceeds by thermionic emission and field emission and it is dependent on temperature and external electric field. The charge carrier transport is controlled by localized states (traps) in the forbidden energy gap. The activation energy calculated from formula $\ln I = f(1/kT)$ varied from $kT$ for low temperature up to 1.0 eV.

**Keywords:** DC conductivity; field emission; *p*-sexiphenyl; thin films; tunneling

## Introduction

Polycrystalline thin films contain many structural defects, which perturb the internal potential of crystalline area (grains) so much, that this decides on electric properties of layer. By changing the defects concentration it is possible to obtain a material with hopping or tunneling between neighboring localized states as the dominant mechanism of carrier transport. In disordered materials there is a big number of local energy levels in the forbidden energy gap. In this connection, energetic diagrams of polycrystalline and amorphous structures are very similar. The polycrystalline materials are a convenient object for hopping conductivity investigations in a wide range of temperatures and electric fields. In many cases one can used a variable-range hopping mode [1,2]. There are same difficulties to define the mechanism of the charge carrier phenomena on the basis of $\ln \sigma = f(T^{1/4})$ or $\ln I = f(T^{1/4})$ characteristics only. The following properties of the material determine charge carrier transport and decide whether two- or three-dimensional hopping is observed:

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(1) structural non-homogeneity of the investigated material,

(2) the sample thickness,

(3) energetical distribution of localized states,

(4) the existence of multiphonon processes,

(5) the existence of Coulomb interaction during charge carrier transfer.

At high electric fields ($10^7$ V/m) or in the case when the electrode is not an ideal injecting contact, the current flow through the sample is controlled by contact as well as by bulk phenomena appearing in the material.

The interesting object of the present investigation was *p*-sexiphenyl – a representative of the para-oligophenyl homologous series.

## Experimental

The material under study was *p*-sexiphenyl produced by Aldrich, with structure formula $C_{36}H_{26}$ and molecular mass 458.6194. The *p*-sexiphenyl molecule is constructed from six flat benzene rings spread into two dimensions (Fig. 1). The C-C distance between two benzene rings is $1.48\times10^{-10}$ m and the C-C distance inside benzene rings is $1.42\times10^{-10}$ m.

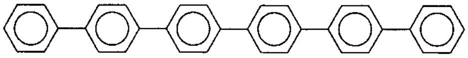


Figure 1. Formula of *p*-sexiphenyl

The *p*-sexiphenyl thin films were obtained by vacuum sublimation on BK-7 glass using thin gold and aluminium electrodes. This process was controlled with respect to:

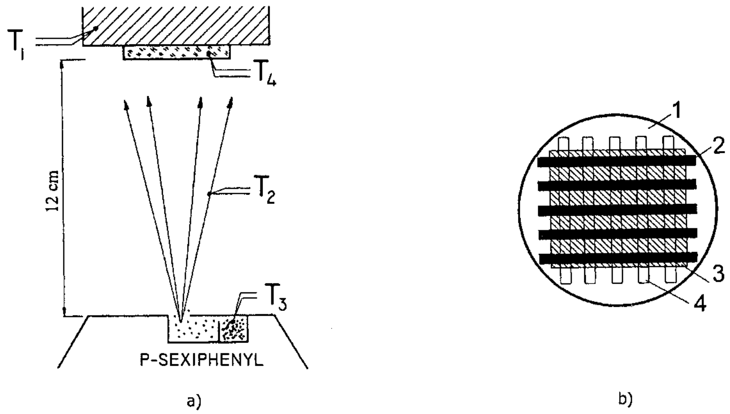
(1) film sublimation rate,

(2) temperature condition of sublimation process ($T_3 = 402$ K),

(3) vacuum condition ($p = 6.7\text{x}10^{-5}$ Pa).

The size of crystalline grains in the obtained films depended on the sublimation rate, temperature and final thickness of the film.

The DC conductivity measurement was performed by measuring the current flow through the film (material bulk) between gold and aluminium electrodes. The measurements were carried out in the temperature range from 15 K up to 325 K. Such extensive range of temperature for *p*-sexiphenyl was used for the first time. The DC current conductivity measurement equipment is described in Ref. [3]



a) b)

Figure 2. Schematic arrangement of the production of *p*-sexiphenyl thin films

a) $T_1$, $T_2$, $T_3$, $T_4$ – copper-constantan thermocouples measuring temperatures of substrate, sublimation chamber, evaporator and sample, respectively

b) 1 – substrate (glass – BK-7)
2 – upper electrode (aluminium)
3 – *p*-sexiphenyl film
4 – bottom electrode (gold)

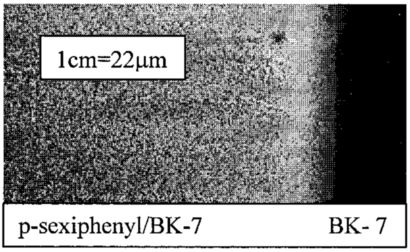


Figure 3. Polarizing microscope pictures taken for transmitting light with crossed polarizer and analyzer. *p*-Sexiphenyl sample thickness of – $d$ = 1.376 μm, magnification 440, $T_1$ = 301.6 K, $T_2$ = 305 K, $T_3$ = 402 K, $T_4$ = 302 K

## Results and discussion

Analysis of the obtained results forthe DC conductivity of *p*-sexiphenyl polycrystalline thin films suggests that the charge carrier transfer through the material bulk may be described by many different conductivity mechanisms. The shape of the current-voltage characteristics $I=f(U)$ presented in Fig. 4 confirms that non-Ohmic conductivity exists. Analyzing these characteristics we can see that for different *p*-sexiphenyl thicknesses 0.73 μm film thickness in Fig. 4a and 2 μm in Fig. 4b), the shape of curves is the same. The shape of current-voltage characteristics for *p*-sexiphenyl is similar for semiconductor diodes. The charge carrier transport in the conductance direction exists for (+) polarity of Au electrode and the charge carrier transfer in reverse direction exists for (-) polarity of this electrode. This phenomenon is observed for the temperature range from 15 K up to 325 K.

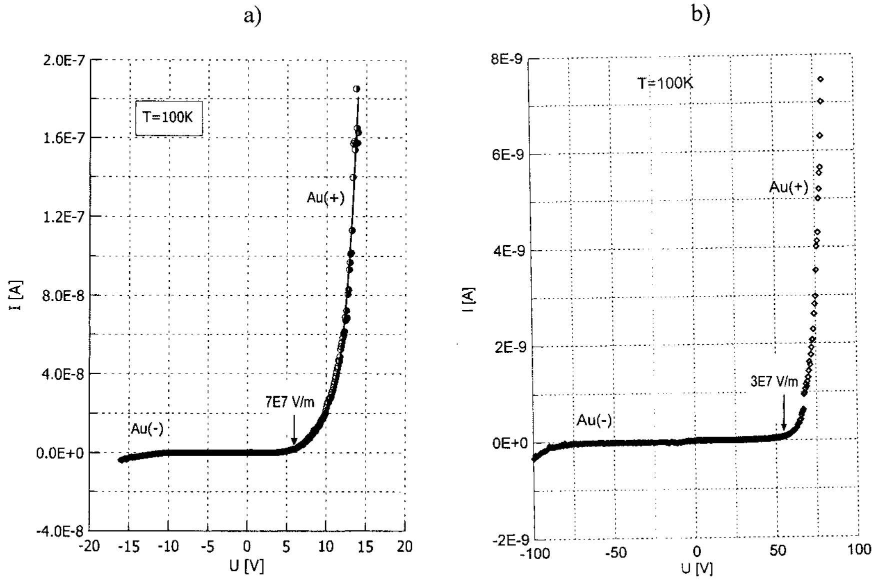


Figure 4. Current-voltage dependence for polycrystalline films of *p*-sexiphenyl equipped with Au-Al electrodes with various electrode polarities. *p*-Sexiphenyl film thickness and sample temperature: a) $d$=0.73 μm, $T$=100 K; b) $d$=2.033 μm, $T$=100 K

By analysis of the $\ln I = f(1/kT)$ relation, where $k$ is the Boltzman constant, $T$ temperature, $I$ current intensity, the activation energy of DC conductivity was determined for various polarizing voltages. Plotting the dependences $\ln I = f(1/kT)$, one can identify some rectilinear regions with different slopes. The $E_3$ region (Fig. 5) relates to non-activated hopping conductivity. The $E_2$ region gives energy about $kT$ and higher and relates to thermal-activated hopping conductivity with participation of the Poole-Frenkel effect. The $E_1$ region relates to spontaneous conductivity of *p*-sexiphenyl with activation energy from 0.25 eV up to 0.98 eV (Table 1).

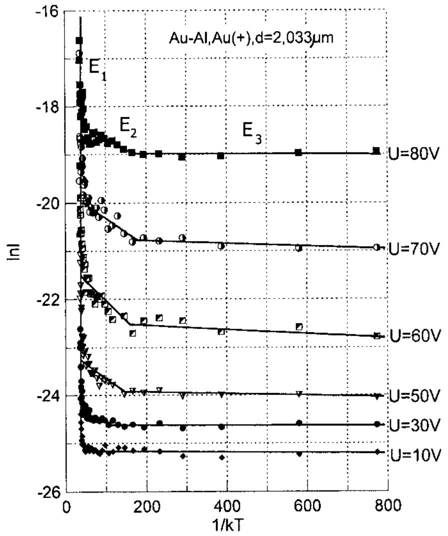


Figure 5. The dependence ln $I$=$f$(1/$kT$) for $p$-sexiphenyl films - sample thickness 2.033 μm, Au-Al, Au (+)

Table 1. The influence of the voltage on activation energy

| $U$[V] | 20 | 30 | 40 | 50 | 60 | 70 | 80 |
|---|---|---|---|---|---|---|---|
| $E_1$[eV] | 0.415 | 0.563 | 0.375 | 0.250 | 0.420 | 0.620 | 0.800 |
| $E_2$[eV] | 0.042 | 0.043 | 0.016 | 0.050 | 0.117 | 0.097 | 0.053 |

The charge carrier transport at low temperatures takes place through hopping between localized states over the potential barriers that are lowered due to the electric field according to the Poole-Frenkel effect. The hopping is confirmed by straight-line characteristics of $\ln I = f(T^{1/3})$ and $\ln I = f(T^{1/4})$. As it is seen from the characteristics (Fig. 6), non-active three-dimensional hopping exists for film thicknesses $d$ > 2 μm for a low temperature and low voltage. The thermal-activated three-dimensional hopping exists at temperatures above 60 K. The two-dimensional hopping exists for thin films of $p$-sexiphenyl (Fig. 7) for a low-polarity voltage. The polymer – electrodes contact phenomena play an important role at high voltages. The height of the barriers lowered due to the increase in the electric field shows that the material bulk plays an important role in charge carrier transport between electrodes (Poole-Frenkel effect). The straight-line part of the $\ln I = f(U^{1/2})$ characteristics (Fig. 8) shows that the Poole-Frenkel effect exists in charge carrier transport through the material bulk.

The injection of the charge carrier from Au electrode (Au electronic work function 5.2 eV, Al electronic work function 4.3 eV) [3] into the investigated material proceeds by thermionic emission and field emission. The injection of the charge carrier from electrodes into *p*-sexiphenyl proceeds by field emission for low voltages. In Fig. 10 we can see the influence of the Schotky effect on the charge carrier injection from electrodes into investigated material, which confirms the interface effect. The influence of the photoemission effect is observed at low electric fields (the charge carriers are thermoactivated in the material bulk). The dependence shown in Fig. 9 is called the Fowler-Nordheim curve and shows participation of the influence of the surface and interface polymer – electrode on the current value in the investigated material [4]. The negative gradient of the straight-line part of the characteristic suggests a field emission process from electrode into the *p*-sexiphenyl area.

The number of free-charge carriers injected from electrode into the investigated material and the current-voltage characteristic are dependent on properties of the material bulk in the same region of the electric field. capacity, the electric field inside the material bulk generates a current-voltage dependence described by formula:

$$\frac{I}{d}=\frac{A}{d}\left[\exp Bd^{1/2}\left(\frac{U}{d^{2}}\right)^{1/2}\right]$$

where $A$ and $B$ are constants.

The influence of the electrode on the current versus voltage dependence is shown in Fig. 10.

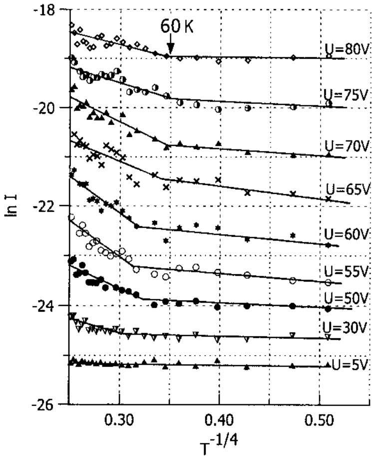


Figure 6. The ln $I=f(T^{-1/4})$ curves obtained for polycrystalline *p*-sexiphenyl layers 2.033 μm thick, Au (-), Au-Al electrodes, at different polarizing voltages

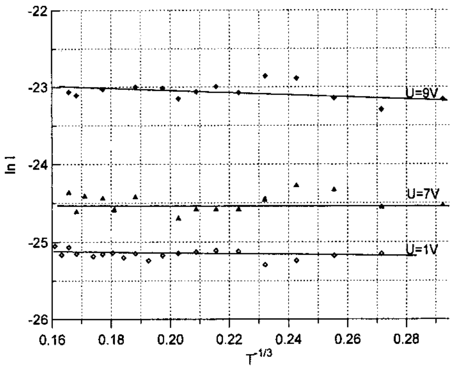


Figure7. The ln $I=f(T^{-1/3})$ curves obtained for polycrystalline *p*-sexiphenyl layers 0.73 μm thick, Au (-), Au-Al electrodes, at different polarizing voltages

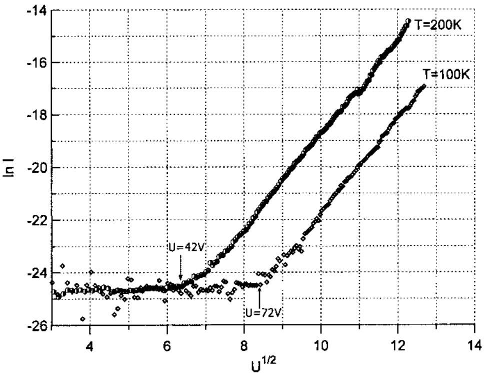


Figure 8. The dependence ln $I=f(U^{1/2})$ for *p*-sexiphenyl films, sample thickness 2.033 μm at different temperatures; Au-Al electrodes, Au (-)

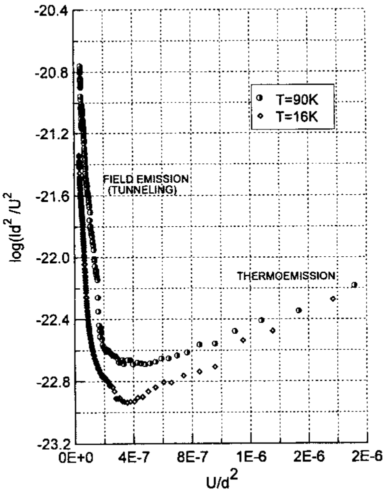


Figure 9. Fowler-Nordheim plot $\log(Id^2/U^2)=f(d/U)$ for *p*-sexiphenyl layers 0.23 μm thick, Au-Al electrodes, Au(-) at 16 K and 90 K

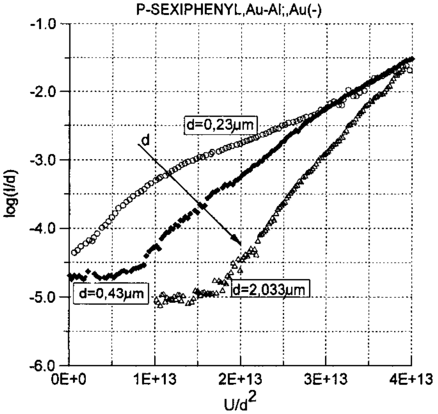


Figure 10. Influence the Schottky effect on space charge limited currents [5]

The current passed through the material is lower than the current which can flow when the electric field increases. A similar effect exists when the interface material-electrode is not ideal injecting. P.N. Murgatroyd [5] has shown that, around the electrode with limited emission.

## Conclusions

- The Schottky effect exists on the electrodes (Au, Al) and *p*-sexiphenyl interface [6].
- The current-voltage characteristics are asymmetric. The reverse current transfer and conduction current transfer exist for the *p*-sexiphenyl-electrodes interface.
- The injection of the charge current into the *p*-sexiphenyl area proceeds by field emission[4]
- The charge current transfer proceeds between localized states (traps) in the forbidden energy gap (two- and three-dimensional hopping).
- The Poole-Frenkel phenomenon influences the *p*-sexiphenyl film conduction process to high electric fields.

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