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DC-ELECTRICAL CONDUCTIVITY OF THE POLYCRYSTALLINE FILMS OF *P*-TERPHENYL

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In this paper the results of DC conductivity investigation carried out for the polycrystalline *p*-terphenyl thin films, including temperature influence on the formation of the films, are presented. The conductivity measurements were done for the samples 1,7–12,5 μm thick with the polarizing voltages in the range 0–200 V at temperature varying from 15 to 325 K. The investigated thin films were supplied with gold and aluminium electrodes. The obtained results and their analysis indicate that the injection of charge from the electrodes into the area of the investigated material proceeds by field- and thermo-emission dependently on the temperature and electric field values. The charge transport through the material's bulk is controlled by traps present in the energy gap area (hopping mechanism and Poole-Frenkel phenomenon). The determined values of the activation energy are in the range of thermal energy (kT), which is equivalent to the none-activating hopping energy, close to 0,06 eV in the range of 15–200 K. In that temperature range conductivity of doping character is observed. In temperature varying from 200 to 325 K conductivity is metallic-like and the activation energy value is about 0,6 eV.

Key words: p-terphenyl, DC conductivity, organic semiconductors.

Polycrystalline films are characterized with many structural defects, which parturbate the material's internal potential so much that it influences its electrical conductivity. Changing the defects concentration it is possible to obtain samples with different electrical properties.

In the low ordered structures, instead of well defined energy gap, an area characterized with high density of traps exists. The Fermi level is placed near the center of the area and charge density wave functions overlap in a small degree. Therefore, energy diagrams of well compensated crystalline and polycrystalline semiconductors and amorfic materials are very similar. Polycrystalline materials are convenient objects for hopping conductivity investigations in a wide range of temperatures and electric fields. Deviations from the classical transport of thermally activated electrons that were observed in the low-ordered materials became a base for the hopping model with a variable range proposed by N.F. Mott in 1968 [1, 2, 6]. There are some problems with the determination of charge transport mechanism through such material's bulk going only on the $\ln\sigma = f(T^{-1/4})$ characteristics.

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Even assuming that the traps distribution in the sample's bulk is homogenous and their activation energy changes linearly does not simplify the problem.

The physical properties of the investigated materials are crucial for the observed conductivity mechanism. Two- or three-dimensional hopping is observed dependently on:

1) how density of trap states changes with temperature,
2) what is dimensionality of the investigated sample, especially its thickness,
3) inhomogenities of the sample's bulk,
4) the existence of multiphoton processes,
5) the existence of Coulomb interaction during charge carriers transport (the influence of bulk on the value of current conducted in the material).

In high electric fields or in the case when the system electron-material is not an ideal injecting contact the current flowing through the sample is controlled by contact as well as bulk phenomena appearing in the material.

The subject of investigation reported here was p-terphenyl being one of the *p*-phenyl homologue row.

The material under investigation was scintillationally clean p-terphenyl, produced by FLUKA, of $C_{18}H_{14}$ stochiometry and molecular mass equal to 230,3101. The p-terphenyl molecule is flat and consists of three benzene rings lying in a straight line (fig. 1, *a*). The C-C bond length in benzene ring and between the rings is about $1{,}42\cdot10^{-10}$ and $1{,}48\cdot10^{-10}$ m, respectively. The *p*-terpehnyl crystal unit cell is monoclinic with the following crystallographic parameters: $a = 8{,}08\cdot10^{-10}$ m, $b = 5{,}6\cdot10^{-10}$ m, $c = 13{,}5\cdot10^{-10}$ m, $\beta = 91^{o}55'$ (fig. 1, *b*) [3–5].

The *p*-terphenyl samples used in the DC conductivity measurements was obtained as polycrystalline thin films. The samples were obtained through vacuum sublimation process on either BK–7 glass or gold substrate supplied with the gold electrodes. The sublimation process was controlled in regard of:

1) the rate of the layers growth;
2) the deposition process temperature
3) he pressure inside the chamber.

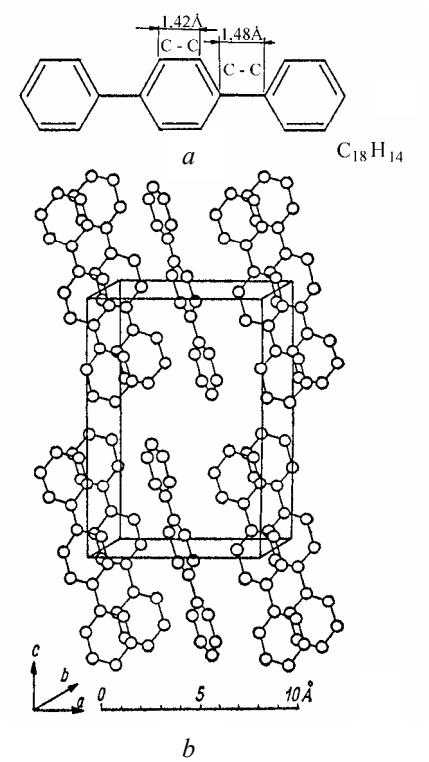


Fig. 1. *p*-terphenyl (*p*-twophenylonbenzene): *a* – single molecule, *b* – crystal unit cel. Monoclinic cell $a = 8{,}08 \cdot 10^{-10}$ m; $b = 5{,}6 \cdot 10^{-10}$ m; $c = 13{,}5 \cdot 10^{-10}$ m; $\beta = 91°55'$; $z = 2$

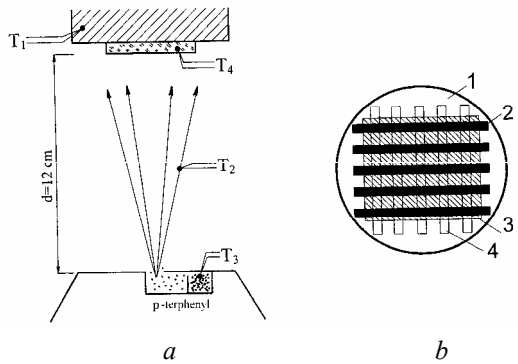


Fig. 2. *a* – Schematic arrangement for the production of *p*-terphenyl thin films T_1, T_2, T_3, T_4 – copper – constantan thermocouples measuring temperatures of substrate, sublimation chamber, evaporator and sample, respectively; *b* – sample arrangement: *1* – substrate (BK–7 glass); *2* – upper electrode (aluminium); *3* – p-terphenyl film; *4* – bottom electrode (gold)

Fig. 2, *a* presents a scheme of the thin films sublimation process together with the temperature check points. In fig. 2, *b* the system of electrodes and the way of giving the proper shape to the investigated material deposited on the glass substrate (BK–7) are presented.

The crystalline grains size present in the obtained thin films depended on sublimation process conditions, such as: the process temperature (in various part of sublimation chamber), the rate of *p*-terphenyl deposition and the type of substrate [5].
In fig. 3 and 4 the pictures of p-terphenyl thin films deposited on glass and gold substrate are presented. It is obvious that the size of crystalline grains of a thin film deposited on glass substrate depends on the *p*-terphenyl film thickness.

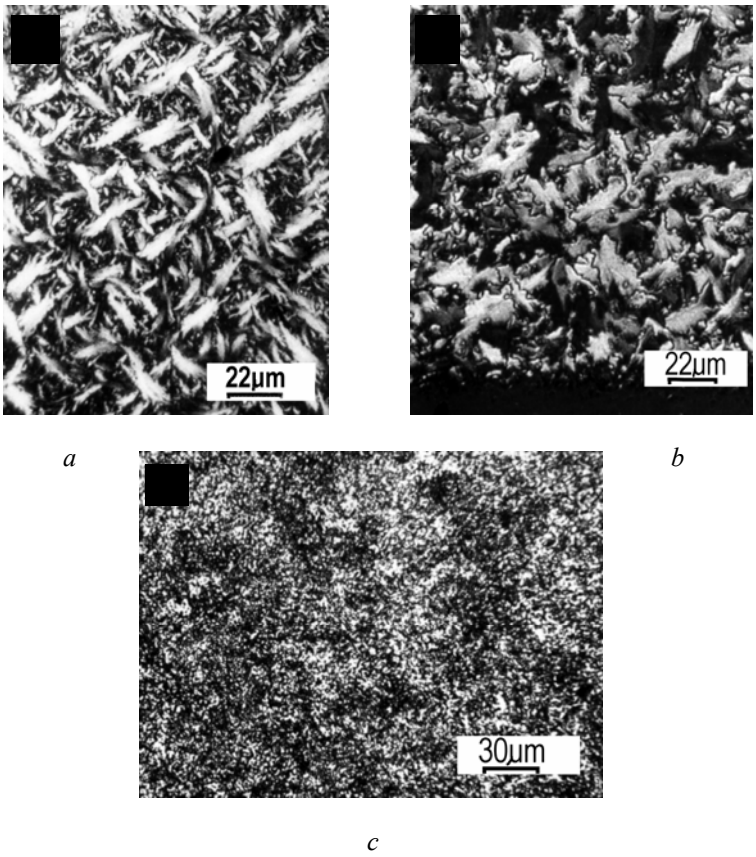
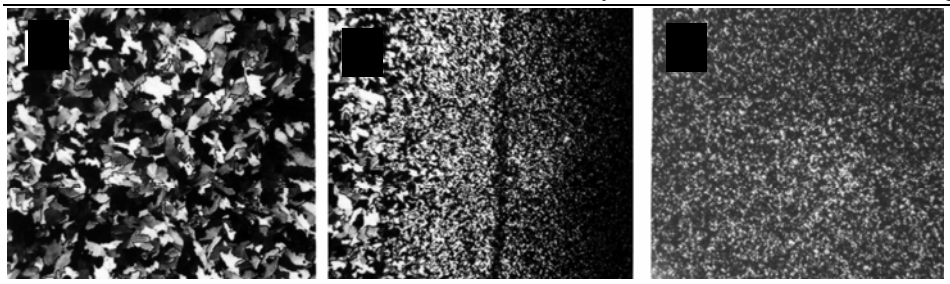


Fig. 3. Polarizing microscope pictures taken for transmitting light with crossed polarizer and analyzer (*d* – thickness layer of *p*-terphenyl, *p* – magnification): *a* – *p*-terphenyl on the BK–7 glass substrate: d = 2,45 μm; p = 440; T_1 = 301,4 K; T_2 = 306,7 K; T_3 = 403 K; T_4 = 303 K, *b* – *p*-terphenyl on the BK–7 glass substrate: d = 12,5μm; p = 460; T_1 = 301,4 K; T_2 = 307 K; T_3 = 402,3 K; T_4 = 303 K, (visible layers edges and glass BK–7), *c* – *p*-terphenyl on the gold substrate: d = 12,5 μm; p = 328; T_1 = 301,1 K; T_2 = 308 K; T_3 = 383 K; T_4 = 304 K



a *b* *c*

Fig. 4. The pictures *p*-terphenyl thin films deposited on a glass or gold substrate: *a* – *p*-terphenyl on glass substrate (PT/BK–7); *b* – left side: *p*-terphenyl on PT/BK–7 glass substrate, right side: *p*-terphenyl on PT/Au substrate; *c* – *p*-terphenyl on gold substrate (PT/Au)

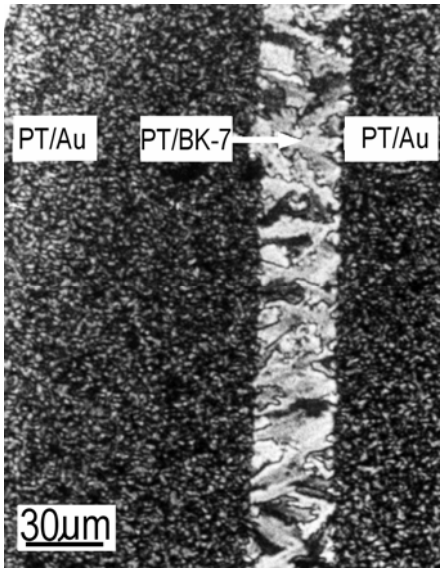


Fig. 5. The pictures of the *p*-terphenyl thin films deposited on a glass or gold substrate taken with the use of polarise microscope in passer-by light with crossed analyzer and polarizer. Left and right side: PT/Au – small crystallitesCentral part of the picture: PT/BK–7 – large crystallites T_1 = 301,4 K; T_2 = 306,7 K; T_3 = 402,3 K; T_4 = 302,6 K

In fig. 3, *c*, 4, *c* and 5 it is seen that the size of crystalline areas is rather small and those samples might be considered as nanocrystals. This was caused by the rate of heat offtake from the "hot" *p*-terphenyl molecules which crystallized on gold substrate. Fig. 5 is an evidence that the substrate type has significant influence on the *p*-terphenyl polycrystal grains size. The width of the glass substrate in that case was about 35 μm.

The thickness of the investigated *p*-terphenyl polycrystalline films was in the range 1,5–15 μm. Measurements were consisted in evaluation of current flowing through the sample bulk between the gold and aluminium electrodes. The measurements were

carried out for different electrodes polarities in the voltage range from 0 to 200 V in several temperatures changing from 15 to 325 K. Such wide range of temperatures was, to our knowledge, for the first time used in investigations of p-terphenyl thin films. The equipment used in the DC conductivity experiment was described in Ref. [5]. At the moment the equipment is fully computer controlled.

The results of the study of polycrystalline *p*-terphenyls thin films DC conductivity let us conclude that charge transport through the material's bulk is caused by various conductivity mechanisms. Character of the conductivity depends on the electric field value, temperature and electrodes polarities. The I–V characteristics shown in fig. 6 inform us about other than ohmic character of conductivity in the investigated material. Fig. 6, *a* and 6, *b* shows that switching of electrodes polarity does not change the shape of the I–V characteristics, i.e. does not influence the conductivity character. We can conclude that for the sample of 1,73 μm thick in a wide range of temperatures the sample behaves as a varistor and the conductivity is a bulk process (fig. 6, *a* and 6, *b*). Another sample, 6 μm thick, in a wide range of temperatures (16–260 K) the conductivity character does not depend on the electrodes polarity – the I–V characteristics are symmetrical – but the influence of the sample olarity is slightly seen. In the case of p-terphenyl 8,5 μm thick the conductivity character is like in semiconducting diode (fig. 6, *d*). When polarity is Au(-) we observe current flowing in conductivity direction while with polarity Au(+) the direction is damming. Such effect is observed in a wide range of temperatures (16–325 K).

Using the lnI=f(1/kT) relation (k- Boltzmann constant, T- temperature, I - current) we determined the DC conductivity energy for various sample polarizing voltages for the samples of different thickness. Typical lnI=f(1/kT) characteristics are shown in figure 7 [5, 6].

In each of lnI=f(1/kT) p-terphenyl characteristics it is possible to separate three areas with different slope. The slope magnitude is the measure of the activation energy for conductivity.

For example E_3 area in Fig. 7, *a* or E_2 in Fig. 7, *b* correspond to the energy of hopping conductivity through the localized states in the area of structural defects (lub barier jakichstam). The value of the activation energy for those mechanisms is of kT magnitude and was not shown in tables 1–5. The E_2 area seen in fig. 7, *b* characterises with the activation energy 0,01–0,06 eV in the temperature range 100–220 K. In this area the investigated material works like a semiconductor. The activation energy values greater tthan 0,1 eV but less than 0,7 eV correspond to metal-like conductivity. In fig. 8 the dependence of resistivity (R) of p-terphenyl thin film in respect to room temperature (R_t) was shown, T = 295 K. It is seen from the figure that the investigated material had semiconductor features below 80 K, while in temperature over 80 K behaved as metal.

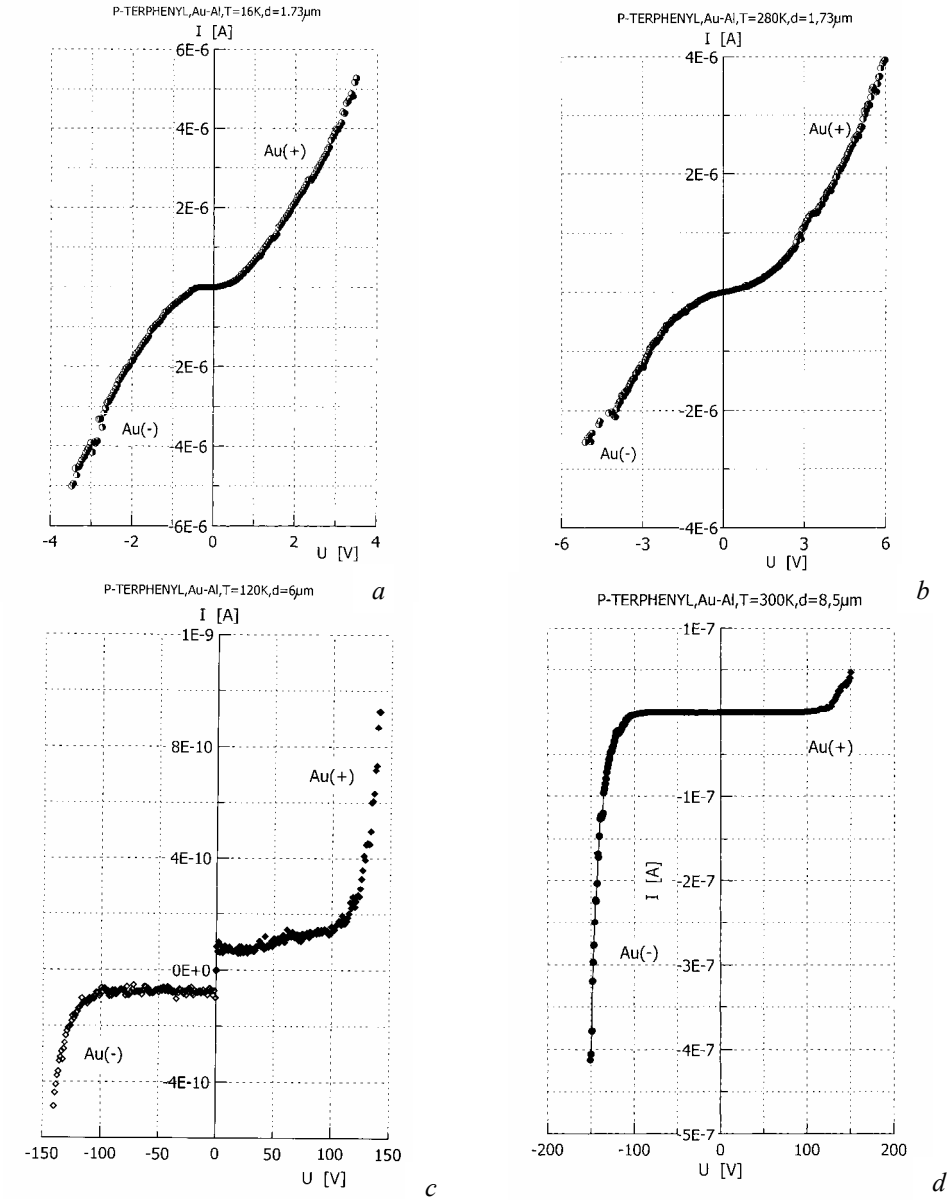
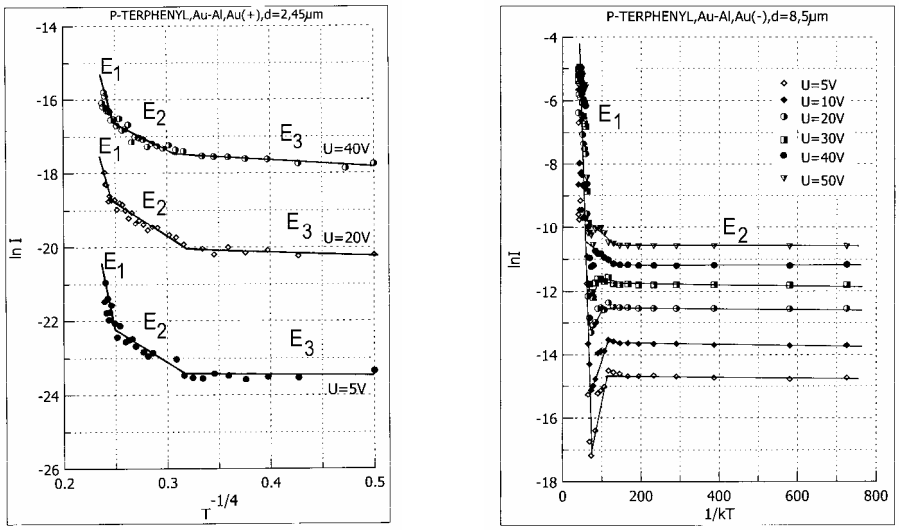


Fig. 6. Current – voltage dependences for polycrystalline films of *p*-terphenyl supplied with Au-Al electrodes with various electrodes polarities. PT film thickness and sample temperature, respectively: *a* – 1,73 μm, 16 K; *b* – 1,73 μm, 280 K; *c* – 6 μm, 120 K; *d* – 8,5 μm, 300 K



a *b*

Fig. 7. The dependence lnI=f(1/kT) for *p*-terphenyl films: *a* – sample thickness 2,45 μm, Au-Al; Au(-); *b* – hickness 8,5 μm, Au-Al; Au(-)

Table 1

Activation energy values determined form lnI=f(1/kT) dependence for polycrystalline *p*-terphenyl 2,45 μm thick (Au-Al electrodes) at different voltages polarizing the sample *d* = 2,45 μm, Au-Al

U[V]	E_a[eV]			
	E_2 Au(+)	E_1	E_2 Au(-)	E_1
5	0,003	0,08	0,005	0,046
10	0,008	0,06	0,008	0,066
15	0,005	0,05	0,009	0,053
20	0,005	0,04	0,007	0,043
25	0,005	0,03	0,006	0,032
30	0,004	0,03	0,005	0,032
35	0,005	0,04	0,004	0,037
40	0,004	0,05	0,004	0,035
45	0,004	0,05	0,003	0,042

Table 2

Activation energy values determined form lnI=f(1/kT) dependence for polycrystalline *p*-terphenyl 6 μm thick (Au-Al electrodes) at different voltages polarizing the sample

U[V]	E_a[eV]	
	E_1 Au(+)	E_1 Au(-)
5	0,006	0,008
15	0,010	0,018
25	0,011	0,019
35	0,006	0,016
45	0,011	0,026
55	0,019	0,033
65	0,021	0,040
75	0,192	0,075
85	0,013	0,065
95	0,019	0,080
105	0,023	0,088
115	0,058	0,100
125	0,065	0,123
135	0,092	0,172

Table 3

Activation energy values determined form lnI=f(1/kT) dependence for polycrystalline *p*-terphenyl 6,5 μm thick (Au-Al electrodes) at different voltages polarizing the sample.
E_1 – T ∈ (180–320 K), E_2 – T ∈ (100–180 K)

U[V]	Au(+)		Au(-)	
	E_1[eV]	E_2[eV]	E_1[eV]	E_2[eV]
10	0,113	0,007	0,100	0,038
20	0,108	0,009	0,098	0,010
30	0,122	0,032	0,110	0,051
40	0,001	0,054	0,114	0,067
50	0,125	0,054	0,083	0,062
60	0,113	0,067	0,179	0,065
70	0,091	0,057	0,254	0,054
80	0,154	0,052	0,240	0,054
90	0,236	0,445	0,263	0,059
100	0,025	0,038	0,281	0,061
110	0,373	0,025	0,272	0,065
120	0,530	0,024	0,307	0,067
130	0,537	0,024	0,345	0,066
140	0,544	0,025	0,485	0,058
150	0,407	0,025	0,735	0,026
160	0,368	0,017	0,501	0,026
170	0,338	0,009	0,403	0,025
180	0,183	0,009	0,308	0,023

Table 4

Activation energy values determined form lnI=f(1/kT) dependence for polycrystalline *p*-terphenyl 8,5 μm thick (Au-Al electrodes) at different voltages polarizing the sample

d = 8,5 μm, Au-Al

U[V]	E_a[eV]	
	E_1 Au(+)	E_1 Au(-)
10	0,011	0,011
20	0,011	0,011
30	0,003	0,011
40	0,002	0,003
50	0,001	0,008
60	0,020	0,017
70	0,017	0,520
80	0,041	0,109
90	0,073	0,155
100	0,089	0,204
110	0,180	0,196
120	0,169	0,200
130	0,164	0,197
140	0,166	0,198
150	0,168	0,205

Table 5

Activation energy values determined form lnI=f(1/kT) dependence for polycrystalline *p*-terphenyl 12,5 μm thick (Au-Al electrodes) at different voltages polarizing the sample

U[V]	E_a[eV]	
	E_1 Au(+)	E_1 Au(-)
5	0,034	0,094
10	0,030	0,030
15	0,024	0,071
20	0,073	0,083
25	0,076	0,023
30	0,019	0,085
35	0,730	0,750
40	0,131	0,164
45	0,305	0,222
50	0,434	0,344
55	0,483	0,399
60	0,559	0,403
65	0,626	0,531
70	0,655	0,482
75	0,637	0,448
80	0,625	0,457
85	0,558	0,394
90	0,437	0,337
95	0,406	0,257
100	0,463	0,208

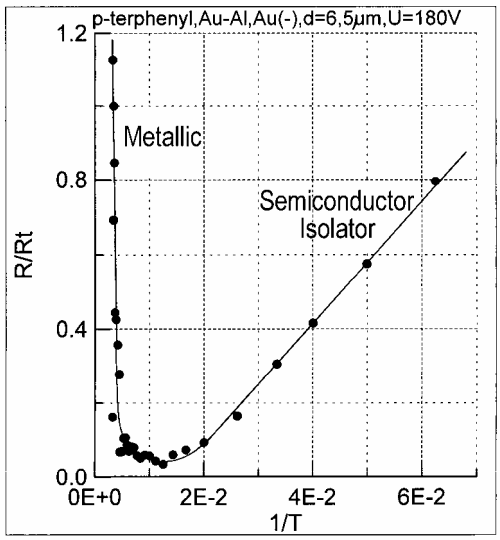
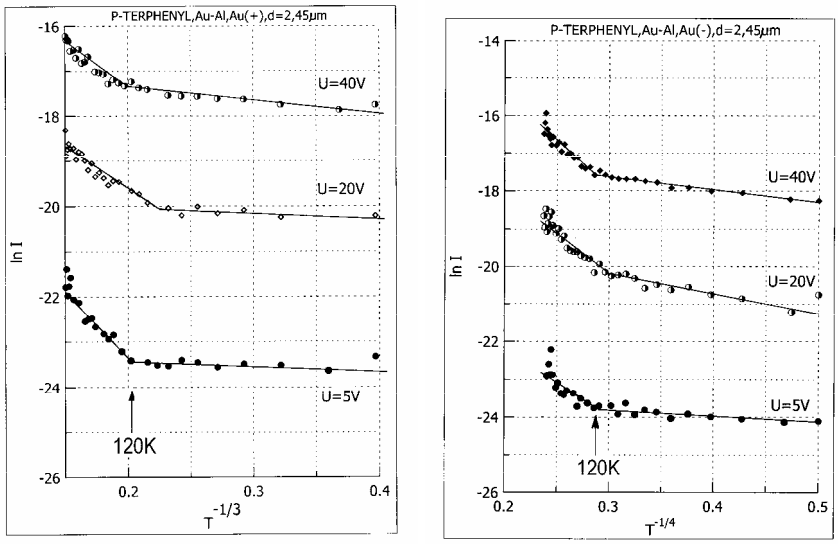


Fig. 8. The dependence $R/R_t=f(T^{-1})$ for polycrystalline *p*-terphenyl layers; the sample thickness: 6,5 μm, U=180 V; Au-Al; Au(-); R_t – layer resistivity at 295 K



a *b*

Fig. 9. The $\ln I=f(T^{-1/3})$ (*a*) and $\ln I=f(T^{-1/4})$ (*b*) curves obtained for polycrystalline *p*-terphenyl layers 2,45 μm thick; Au-Al electrodes

In low temperatures the transport of charge carriers, which concentration found from the $I = f(U^2/d^3)$ dependence was equal to $n = 0{,}4–0{,}5\cdot10^{22}$ m^{-3}, takes place through the hopping between localized states (the boundaries of crystalline grains) over the potential barriers separating the areas. An external electric field generated by the electrodes voltage lowers the barriers height, according to Poole – Frenkel low. In this case the hopping model is supported by rectilinear characteristics $\ln\sigma = f(T^{-1/3})$ and $\ln\sigma = f(T^{-1/4})$. It is evident (fig. 9) that we can consider two- and three- dimensional hopping [5–6]. Hopping mechanism is dominant in temperature below 120 K (fig. 9, *a*, 9, *b*).

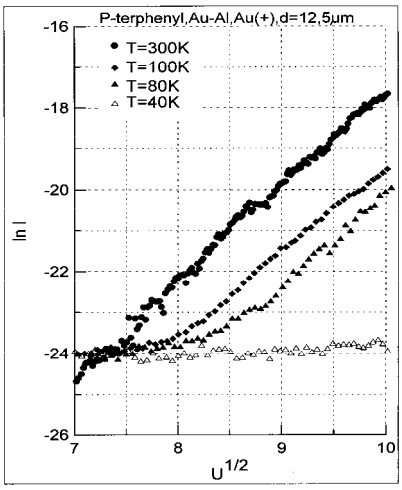


Fig. 10. $\ln I = f(U^{1/2})$ dependence for – terphenyl layers 12,5 μm thick at ifferent temperatures; Au-Al electrodes, Au(+)

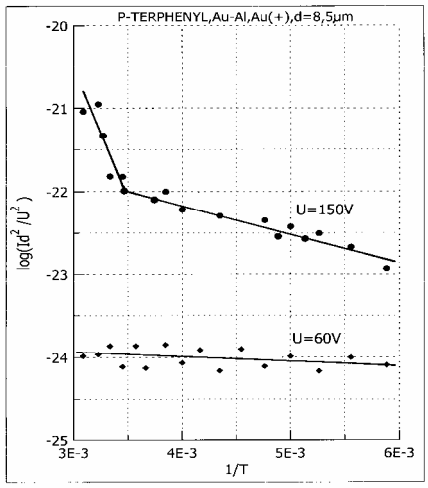


Fig. 11. $\log(Id^2/U^2)=f(1/T)$ ependence for p-terphenyl 8,5μm tthick Au-Al electrodes, Au(+)

While the external electric field increases the height of potential barrier near traps decreases (Poole-Frenkel effect) which makes the material's bulk involved into charge transport through the bulk. The Poole-Frenkel phenomenon is seen in via typical shape of $\ln I = f(U^{1/2})$ curve and lowering activation energy while supplied voltage increases (fig. 10). The presence of the phenomenon is also confirmed by the shape of the $\log(Id^2/U^2) = f(1/T)$ characteristics – fig. 11. The rectilinear section of the curves suggests that electric charge tunnels between bouded with structural defects trap states [5–6].

The injection of charge carriers from the electrodes to the investigated material bulk proceeds through thermo- and field emission. Figure 12 shows that high voltage determines injection of charge from an electrode to the p-terphenyl bulk in field emission (tunnelling) process and this phenomenon is dominant. This is a contact phenomenon confirmed additionally in fig. 13. It is seen that in the case of high electric field (U>60 V) Schottky phenomenon occurs as dominant. In the case of lower electric fields thermo-emission of charge from the electrodes to the sample's bulk is also important (fig. 12). The dependence shown in fig. 12 (Fowler-Nordheim curve)

illustrates contribution of the investigated material's surface and contact with the metal electrodes in the charge transport into the bulk [5].

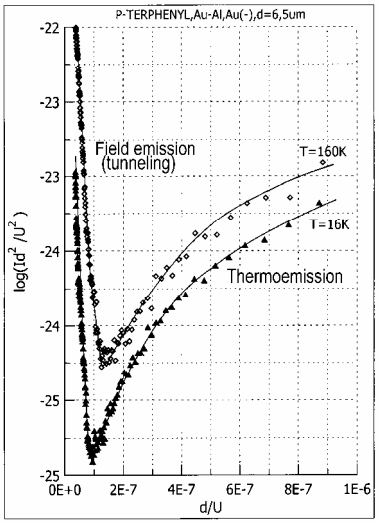


Fig. 12. Fowler-Nordheim plot $\ln(I/U^2)=f(1/U)$ for *p*-terphenyl layers 2,45 μm thick; Au-Al, Au(+)

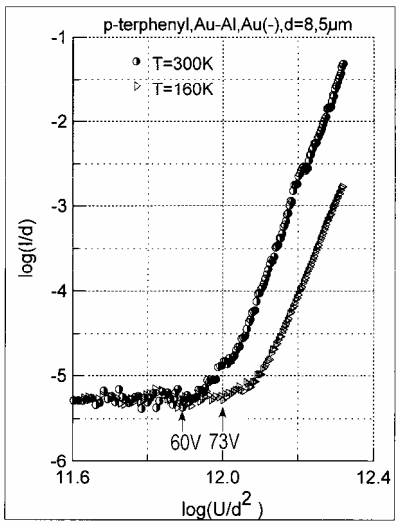


Fig. 13. $\log(I/d)=f[\log(U/d^2)]$ curve characteristic for Schottky phenomenon (rectilinear segments of the curves corresponding to higher voltage) taken at different temperatures.

1. There is more than one mechanism of conductivity in polycrystalline *p*-terphenyl films investigated in a wide range of temperatures and electric fields.
2. Electric charge injection from a metal electrode into the area of the investigated material occurs through the field emission (tunneling).
3. In high electric fields contribution of surface (metal electrode – *p*-terphenyl contact) is noticeable in charge transport through the sample bulk – Schottky phenomenon.
4. In high electric fields the Poole-Frenkel effect influences charge transport through the *p*-terphenyl bulk.
5. In low electric fields while temperature is less than 200 K the charge transport occurs through non-activated hopping (two- and three-dimensional), which is confirmed with small value of activation energy.

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ЕЛЕКТРИЧНА ПРОВІДНІСТЬ ЗА ПОСТІЙНИМ СТРУМОМ ПОЛІКРИСТАЛІЧНИХ ПЛІВОК *P*-ТЕРФЕНИЛУ

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Запропоновано результати дослідження провідності за постійним струмом полікристалічних тонких плівок *p*-терфенилу та вплив температури на їх утворення. Вимірювання провідності проводили на зразках завтовшки 1,7–12,5 мкм з напругою поляризації 0–200 В при зміні температури від 15 до 325 К. Для досліджуваних тонких плівок використовувалися золоті та срібні електроди. Отримані результати засвідчують, що інжекційні зміни від електродів у ділянці досліджуваного матеріалу відбуваються завдяки авто- і термоемісії. Показано, що значення енергії активації є в межах теплової енергії, яка еквівалентна до неактиваційної енергії захоплення, близької до 0,06 еВ в області 15–200 К. За температури від 200 до 325 К енергія активації становить 0,6 еВ.

Ключові слова: *p*-терфенил, провідність за постійним струмом, органічні напівпровідники.

ЭЛЕКТРИЧЕСКАЯ ПРОВОДИМОСТЬ ПО ПОСТОЯННОМУ ТОКУ ПОЛИКРИСТАЛЛИЧЕСКИХ ПЛЕНОК *P*-ТЕРФЕНИЛА

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Предложены результаты исследования проводимости по постоянному току поликристаллических тонких пленок *p*-терфенила и влияние температуры на их образование. Измерения проводимости проводились на образцах толщиной 1,7–

12,5 мкм с напряжением поляризации 0–200 В при изменении температуры от 15 до 325 К. Для исследуемых тонких пленок использовались золотые и серебряные электроды. Полученные результаты удостоверяют, что инжекционные изменения от электродов в участке исследуемого материала происходят благодаря авто- и термоэмиссии. Показано, что значение энергии активации находится в пределах тепловой энергии, которая эквивалентна неактивационной энергии захвата, близкой к 0,06 еВ в области 15–200 К. При температуре от 200 до 325 К энергия активации составляет 0,6 еВ.

Ключевые слова: *p*-терфенил, проводимость по постоянному току, органические полупроводники.

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