# *СЕКЦИЯ 3*
# *МОДИФИКАЦИЯ СВОЙСТВ МАТЕРИАЛОВ*

# *SECTION 3*
# *MODIFICATION OF MATERIAL PROPERTIES*

## INFLUENCE OF SWIFT HEAVY IONS IRRADIATION ON CARRIER TRANSPORT OF POLYIMIDE FILMS

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In the present paper we report results concerning the influence of Swift Heavy Ions (SHI) irradiation on the mechanisms of electron transport in 22 μm thick polyimide (PI) films. The PI films were subjected to SHI irradiation with fluences $1\times10^8$ ions/cm$^2$. The following etching of latent tracks with the 13% NaOCl solution resulted in the formation porous PI membranes (PPI). It is shown that the formation of carboxyl (COOH) moieties on the internal surfaces of the formed pores results in creation of highly-conductive layers along the pores. Experimental and modelling studies of transversal I – V characteristics in Cu/PI/Cu and Cu/PPI/Cu structures in the temperature range 240 - 300 K have shown that the low-temperature carrier transport is due to the formation of space charge limited current and described by the improved Mott-Gurney law developed in Mark-Helfrich model.

***Keywords:*** polyimide; carrier transport; porous membranes; swift heavy ion irradiation.

### Introduction

Polyimides (PI) of the Kapton type are among the most frequently used modern polymer materials. PIs have high thermal stability, good mechanical, electric and dielectric characteristics, as well as compatibility with the human body. Therefore, they attract considerable attention for use in various applied fields (in biomedicine [1], electronics and electrical engineering [2-6], etc.). In addition, PI films have a good ability to planarize the surface, low values of mechanical stresses and high fields of electrical breakdown [6], which creates prospects for the use porous PI membranes (PPI) as substrates for flexible electronics. including in the form of with artificially formed vertical channels (pores) formed by etching latent tracks arising from irradiation with Swift Heavy Ions (SHI) [7].

The aim of this work is to study in detail the mechanisms of electron transport in Cu/PI/Cu (Fig. 1*a*, *c*) and Cu/PPI/Cu (Fig. 1*b*, *d*) structures.

### Experimental techniques

The paper compares the dependences of the current density $j$ on the electric field $E$ in the pristine PI film and porous PI membranes (PPI) in the temperature range 240-300 K at $E < 5\cdot10^5$ V/m. An average diameter of pores was about 1 μm. The electric field was applied perpendicular to the surface of the structure and directed along pores. In addition, to determine the dielectric constant in Cu / PI / Cu and Cu / PPI / Cu structures, the low-frequency dependences of the impedance were measured at 300 K.

The membranes were made from PI film of Kapton-H type (DuPont, USA) in two stages: (a) irradiation with SHI of PI foil and (b) its subsequent chemical etching. PI films were irradiated by Xe ions with an energy of 1 MeV/nucleon and a fluence of $(2\text{-}4)\cdot10^8$ ion/cm$^2$ using the U-300 cyclotron in the

Flerov Laboratory of Nuclear Reactions (JINR, Dubna) [7].

At the second stage of membrane formation, chemical etching of PI film in a 13% solution of sodium hypochlorite (NaOCl) 40–55 °C was used [8, 9]. At this stage, in the irradiated Kapton 22 μm thick film, the latent tracks were removed transforming into hollow channels. After the manufacture of the porous membrane, copper layers with a thickness of d = 80 nm were deposited on both sides of it. As follows from optical microscopy (Fig. 1c, d), the density of pores was about 15.5%, and their average diameter

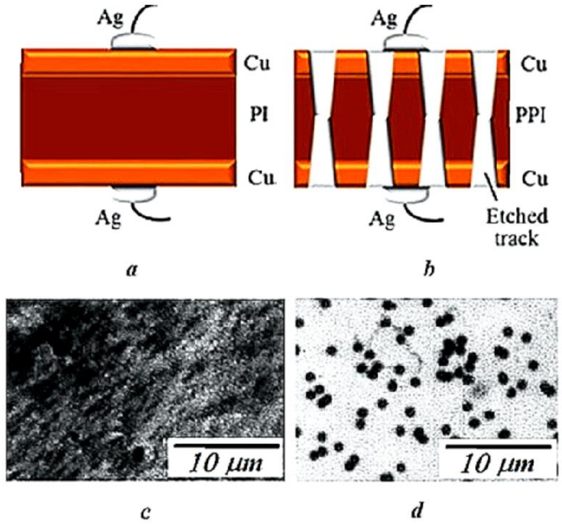


Fig. 1. Schematic cross-sectional view (a, b) and optical micrographs (c, d) of the studied samples of Cu / PI / Cu (a, c) and Cu / PPI / Cu (b, d) structures

was about 1.0 μm. As seen from Fig. 1c and 1d, the pores were retained on the copper electrodes.

The impedance and transversal current-voltage (I-V) characteristics were measured on samples 2x3 mm$^2$ in size. When measuring the dielectric constant in the frequency range 1-1000 kHz, an Agilent LCR meter was used. To measure the *j*(*E*) dependences and the impedance of the PI and PPI, copper wires 0.1 mm in diameter were attached to the electrical copper contacts on both their sides with silver paste (Fig. 1a, b). Then the wires were soldered with indium to the gold-plated electrical contacts of a special measuring cell. The cell with the sample was connected either to an impedance meter or inserted into a special measuring probe, which was placed in a cryostat Cryogenics Ltd (London) based on a closed-cycle refrigerator and connected to the measuring circuit. Details of these experiments were described earlier in [10].

## Results & Discussion

The experimental dependences *j*(*E*) for the Cu / PI / Cu and Cu / PPI / Cu structures are shown in Fig. 2. To understand the mechanisms of charge carrier transport in the samples under study at different temperatures, the *j*(*E*) curves were plotted on different scales, corresponding to different models of electrical transport. These *j*(*E*) rearrangements were preliminary checked for models describing the mechanisms of trap-enhanced tunneling through the PI layer (Poole-Frenkel model) or emission of charge carriers from a metal electrode into a polymer (Schottky-Richardson model) [5, 8, 11-19]. Such rearrangements did not give a physically substantiated result for these models, since, according to the literature data, these models in pol yimides are valid only at temperatures much

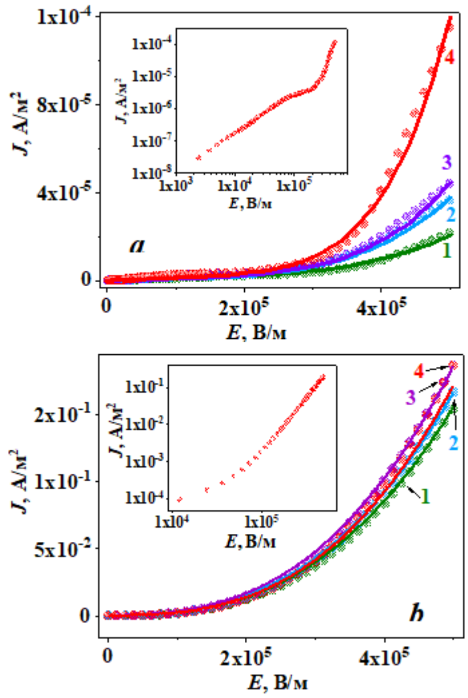


Fig. 2. Experimental (points) and calculated (solid lines) dependences of the current density *J* on the field strength *E* in linear coordinates for samples of the initial PI film (a) and porous membrane (b) at temperatures T, K: 1 -240, 2-260, 3-280, 4-300. The inset shows *J*(*E*) dependences in a logarithmic scale

higher than room temperature [5, 13-15].

The logarithmic rearrangement of the Experimental curves Lg (*j*) - Lg (*E*) for the studied structures gave two linear sections with different slopes (see insets to Figure 2). It turned out that the slope of linear sections in the region of weak fields $E < 2{\cdot}10^4$ is close to 1 in accordance with the Mott-Gurney model for the space charge limited current (SCLC) [17, 20]. In higher fields, according to this model, there should be a transition from the linear law *j*(*E*) to the quadratic one. This transition occurs when the concentration of charge carriers injected from the metal electrode under the action of an electric field begins to exceed the concentration of equilibrium free charge carriers generated by thermal vibrations of the lattice. However, according to our experiments, the high-field contribution to the *j*(*E*) really has a power-law character $j(E) \sim E^m$, where m is much higher than 2. This can be described by the Mark-Helfrich SCLC model [16, 20]:

$$J(E) = en(T)\cdot\mu(T)\cdot E + \\ + e\mu N_C\left[\frac{\varepsilon\varepsilon_o m}{eN_t(m+1)}\right]\left[\frac{2m+1}{m+1}\right]\frac{E^m}{d^{2m}} \cdot \quad (1)$$

In model (1), localized states with a density $N_t$ are characterized by an exponential rather than a Gaussian energy distribution of electron traps. In this model, the exponent *m* determines the energy width $E_{th} = 2mkT$ of the "tail" of localized states, which can be seen in the inset to Fig. 3a (*k* is the Boltzmann constant). In this case, the occupied states (below the Fermi level) are negative, while the empty ones (above the Fermi level) are neutral. The values of concentration *n* and mobility $\mu$ of free carriers obtained by fitting the dependences *j*(*E*, *T*) according to model (1) are shown in Fig. 3. According to the simulation results, the values of other fitting parameters are in the ranges $2 < m < 4.5$, $56 < E_{th} < 140$ meV and $3.4{\cdot}10^{20} < N_t < 1.3{\cdot}10^{22}$ $м^{-3}$.

The above estimates of the fitting parameters (including those presented in Fig. 3) do not contradict the Mark-Helfrick model (1)

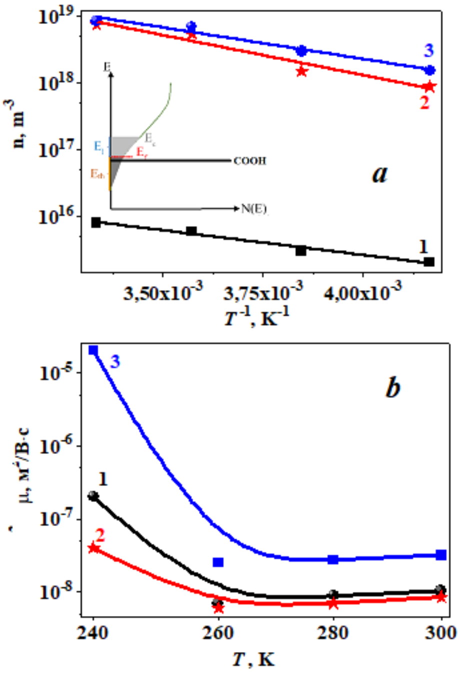


Fig. 3. Experimental (points) and approximated (solid lines) temperature dependences of the concentrations of free charge carriers n in Arrhenius coordinates (a), as well as their mobilities μ (b) on a logarithmic scale for the investigated Cu/PI/ Cu (1) and Cu/PPI/Cu (2) structures

and for all studied structures in the temperature range of 240-300 K as a whole lead to a satisfactory agreement between the calculated and experimental curves *j*(*E*) both in the region of weak fields (ohmic contribution) and in strong fields (power-law contribution to relation (1) with exponent $m \geq 2$). In addition, we note that in the range of room temperatures for the initial Cu/PI/Cu structure, they are quite consistent with the known literature data for Kapton [2-5, 20-24]. Nevertheless, attention is drawn to a number of significant differences in the behavior of *j*(*E*, *T*) curves (and conductivity) and, accordingly, fitting parameters in different types of the studied structures.

The first feature follows from a comparison of the experimental curves *j*(*E*) in Fig. 2. It can be seen that the etching of pores in PI film leads to a sharp (by about 3-4 orders of magnitude) increase in the transverse current density, i.e. an increase in the conductivity of the membrane in comparison with the initial PI film. However, it turns out that in porous membranes *j*(*E*) curves themselves begin to depend on temperature much weaker (Fig.

3b) than was observed in the initial Cu/PI/Cu structure (Fig. 3a). This behavior correlates with the detected increased (by 3-4 orders of magnitude) concentration of electrons in porous membranes in comparison with the initial (unirradiated and unetched) PI film. We attribute this fact to the formation of carboxyl groups (COOH) on the pore walls during etching of PI films with sodium hypochlorite NaClO after SHI irradiation [25]. A small drop in the mobility of charge carriers observed in Fig. 3b for the porous membrane is apparently due to their additional scattering due to an increase in the concentration of carboxyl traps (see the sharp narrow peak of the density of states in the inset in Fig. 3a).

As a second feature, we note the largest observed deviations of the model $j(E)$ dependences from the experimental ones in the range of intermediate values of the electric fields in the samples under study. This is clearly seen in the inset to Fig. 2a, where room temperature $j(E)$ curves are shown in a logarithmic scale. In the literature, this fact is most often associated with the transition to the regime of the so-called limiting filling of traps in this range of electric field and temperature [26].

Basing on $j(E)$ dependences, we have estimated numerically the thick of a highly conductive layer (its other characteristic as well) that appears at the internal surfaces of pores as a result of latent tracks etching. These estimates are made on the assumption that this highly conductive layer consists of carboxyl groups (COOH), which create additional trapping states, along which can drift additional electrons injected by copper electrodes into the polyimide film.

According to the literature [27], the carboxyl groups COOH are practically flat and look like a trapezoid. The estimation of the thickness of the carboxyl groups layer on the internal surface of pores has gavev a value of 0.42 nm, which is close to the diameter of the atoms included in the COOH. The estimated packing density of carboxyl groups on the inner surfaces of the pores allowed to calculate the number of additional surface states along the carboxyl groups layer. Taking into account the known shape and size of each carboxyl group, this calculation gave the number of states per pore of the order of $7.5 \cdot 10^8$ m$^{-2}$. Hence it follows that the bulk concentration of excess injected electrons that should drift through the highly conductive layer under impact of applied electric bias field for all pores is about of $1 \cdot 10^{25}$ м$^{-3}$.

## Resume

In the present paper we have studied the influence of SHI irradiation on the mechanisms of electron transport polyimide films. We observed the formation of highly-conductive layers along the pores in PI films after their subjection by SHI irradiation with fluences $1\times10^8$ ions/cm$^2$ and following etching of latent tracks with the 13% NaOCl solution. It is shown that the formed layer is due to creation of carboxyl (COOH) moieties in the internal surface of pores. Experimental and modelling studies of transversal I – V characteristics in Cu/PI/Cu and Cu/PPI/Cu structures in the temperature range 240 - 300 K have shown that the low-temperature carrier transport is mainly due to space charge limited currents describing by the Mark-Helfrich model.

## References

1. Sun Y., Lacour S.P., Brooks R.A., Rushton N., Fawcett J., Cameron R.E. *J. of Biomed. Mater.* 2009; 90 (3): 648-655.
2. Dupont Kapton. Summary of properties. Bulletin “Kapton® Polyimide Film— Products of Decomposition” (H-16512).
3. Ghosh M.K., Mittal K.L. Polyimides: Fundamentals and Application. New York, Marcel Dekker, 1996. 891 p.
4. Muruganand S., Narayandass S.K., Mangalaraj D. and Vijayan M. Dielectric and conduction properties of pure polyimide films. *Polymer Int.* 2001; (50): 1080-1084.
5. Blythe A.R. Electrical properties of polymers. Cambridge University Press, New York, 1979. 475 p.
6. Volksen W., Miller R.D. and Dubois G. Low Dielectric Constant Materials. *Chem. Rev.* 2010; 110 (1): 56-110.
7. Flerov G.N., Apel P.Yu., Didyk A.Yu, Kuznetsov V.I., Oganessian R.Ts. *Atomic Energy* (*USSR*) 1989; 67: 274-279. (In Russian).

8. Boyd G.H. Desalination with Charged Nanopores, PhD thesis. University of California, Irvine, 2018.
9. Siwy Z., Apel P., Baur D., Dobrev D., Korchev Y., Nuemann R., et al. Preparation of Synethetic Nanopores with Transport Analogous to Biological Channels. *Surface Science* 2003; 532: 1061-1066.
10. Fedotov A.K., Prischepa S.L., Fedotova J.A., Bayev V.G., Ronassi A.A., Komissarov I.V., et al. Electrical conductivity and magnetoresistance in twisted graphene electrochemically decorated with Co particles. *Physica E: Low-dimensional Systems and Nanostructures* 2020; 117: 113790-1-9.
11. Bellucci F., Khamis I., Senturia, S.D., Latanision R.M. Moisture effects on the electrical conductivity of kapton polyimide. *Journal of the Electrochemical Society*, 2006; 137: 1778-1784.
12. Kim T.Y., Kim W.J., Lee T.H., Kim J.E. Electrical conduction of polyimide films prepared from polyamic acid (PAA) and preimidized polyimide (PI) solution. *eXPRESS Polymer Letters* 2007; 1(7): 427–432.
13. Nevin J.H. and Summe G.L. Conduction mechanisms in thin polyimide films. *Microelectron Reliab.* 1981; 21 (5): 699-705.
14. Ansari A.A. and Al-Marzouki F.M. Electrical conduction in polyimide films. *Indian J. Phys.* 1999; 73A (6): 789-792.
15. Sessler G.M., Hahn B., and Yoon D.Y. Electrical conduction in polyimide films. *J. Appl. Phys*. 1986; 60 (1): 318-326.
16. Mark P. and Helfrich W. Space-Charge-Limited Currents in Organic Crystals. *J. of Applied Physics* 1962; 33(1): 205-215.
17. Mott N.F., Gurney R.W. Electronic Processes in Ionic Crystals. Clarendon Press, Oxford 1940; 209 p.
18. Sze S.M. Physics of Semiconductor Devices, New York: Wiley, 3rd ed., 2006; 842 p.
19. Lampert M.A. and Mark P. Current Injection in Solids. New York: Academic Press 1970; 351 p.
20. Rohr J.A. Measurements and Modelling of Space-Charge-Limited Current Transport in Organic Single-Carrier Devices. PhD thesis. Imperial College, London, 2018.
21. Lamb D. R. Electrical Conduction Mechanisms in Thin Insulating Films. London, Methuen, 1967. 130 p.
22. Liang T., Makita Y., Kimura S. Effect of film thickness on the electrical properties of polyimide thin films. *Polymer* 2001; 42: 4867-4882.
23. Chisca S., Sava I., Musteata V., Bruma M. Dielectric and conduction properties of polyimide films. *Annual Report Conference on Electrical Insulation Dielectric Phenomena.* 2011; 253-256.
24. Deligoez H., Yalcinyuva T., Ozguemus S., Yildirim S. Electrical Properties of Conventional Polyimide Films. *Journal of Applied Polymer Science*. 2006; 100: 810-818.
25. Siwy Z., Dobrev D., Neumann R., Trautmann C., Voss K. Electro-responsive asymmetric nanopores in polyimide with stable ion-current signal. *Applied Physics a-Materials Science & Processing* 2003**;** 76 (5), 781-785.
26. Il'yasov V.Kh., Lachinov A.N., Moshelev A.V., Ponomarev A.F. Estimation of the Parameters of Charge Carriers in Polymers in the Vicinity of the Threshold of Thermally Stimulated Switching *Physics of Solid State* 2008; 50(3): 568-572
27. Dence C.W. Determination of Carboxyl Groups. In: Lin S.Y., Dence C.W. (eds) Methods in Lignin Chemistry. Springer Series in Wood Science. Springer, Berlin, Heidelberg. 1992: 33-61.