Features of the charge carriers transport in the semiconductor−polymer−metal structure

© A.N. Lachinov [1,2], D.D. Karamov [1,2], A.F. Galiev [1,2], S.N. Salazkin [1,3], V.V. Shaposhnikova [1,3], T.N. Kost [1], A.B. Chebotareva [1]

[1] Moscow State University, Moscow, Russia
[2] Institute of Molecule and Crystal Physics, Ufa Federal Research Centre, Russian Academy of Sciences, Ufa, Russia
[3] A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow, Russia
E-mail: AChebotareva@mics.msu.su

The mechanism of charge carrier transport in the tin doped indium oxide (ITO)/polymer/Cu structure was studied for the first time, where thin films of poly(arylene ether ketone), which has the properties of electronic switching from the insulating to the highly conductive state, were used. The system under study can be considered as a model of a current-collecting contact system in a solar cell with ITO top layer.

New approaches to the formation of current-collecting contacts to solar cells (SCs) with a top layer made of transparent conducting oxides (TCOs) are being developed rapidly in current photovoltaics [1]. These approaches are based on efficient low-temperature processes that minimize the use of silver. One promising method of the formation of such kind of contact involves the use of cardo poly(arylene ether ketones) (PAEKs) with fluorene side groups, which are unique thermoplastic polymer materials. PAEKs are used as adhesives for securing a metal grid to TCOs and forming an electrical contact with a low resistivity (lower than $1 \, m\Omega \cdot cm^2$) [2]. These polymers switch spontaneously from a dielectric state to a highly conductive one in the course of low-temperature lamination (below $220°C$) under a slight pressure excess (up to 1 atm). However, a TCO/PAEK/metal contact system has a drawback that the contact resistivity increases with time. In order to uncover the reasons behind this degradation and design a stable contact, one needs first to examine the mechanisms of carrier transport in the TCO/PAEK/metal system.

The aim of the present study is to investigate the mechanisms of carrier transport in the TCO/PAEK/metal system with indium tin oxide (ITO) and copper serving as TCO and metal, respectively. ITO is the most widely used top-electrode material in solar cells. The thickness range of polymer films (up to $2 \, \mu m$) corresponded to the distances between metal wire contacts and the SC surface after lamination.

The sample has a multilayer Si/ITO/PAEK/Cu structure (Fig. 1, *b*). An ITO layer with a thickness of approximately 100 nm and a resistivity of $0.5 \, m\Omega \cdot cm$ was formed by ultrasonic spray pyrolysis on the surface of polished silicon [3]. The Si/ITO structure imitated an SC surface.

Random copolymer PAEK was synthesized through polycondensation using nucleophilic substitution for an activated halogen in an aryl halide, by reacting 4,4'difluorobenzophenone with dipotassium bisphenolates of a mixture of bisphenol A (90 mol.%) and 9,9-bis(4-hydroxyphenyl)fluorene (10 mol.%). The process was similar to the preparation of homopolymers previously reported in [4]. The PAEK synthesis procedure was described in detail elsewhere[5]. Synthesized PAEK dissolved readily in a wide range of solvents (chloroform, cyclohexanone, tricresol, etc.); as a result of solution casting, the polymer forms strong transparent films (with a tensile strength from $77 to 87$ MPa). Its glass transition temperature is $164°C$. The structural formula of PAEK is presented in Fig. 1, *a*.

A polymer film was deposited onto the ITO layer surface by spin coating from a solution of PAEK in cyclohexanone at 1500 rpm within 1 min. The thickness of polymer films was set by varying the concentration of solutions within the range from 1.25 to 15 wt.%.

Following this deposition, the sample was dried in two stages: 60 min under normal conditions and 60 min at a temperature of $150°C$. A copper electrode 6×6 mm in size with a thickness of $2 \, \mu m$ was formed by thermal diffusion deposition in vacuum.

The surface morphology and the thickness of polymer films were determined using an atomic force microscope. The thickness varied with solution concentration within the range from 50 nm to $2.1 \, \mu m$. As polymer films grew thicker, their root-mean-square roughness R_q decreased from 1.4 to 1.0 nm. Since the ITO layer is granular in nature ($R_q \sim 5.0$ nm), it is fair to state that PAEK fills all substrate surface irregularities in the process of fabrication. The estimates obtained indicate a low degree of roughness of polymer films and their high film-forming properties.
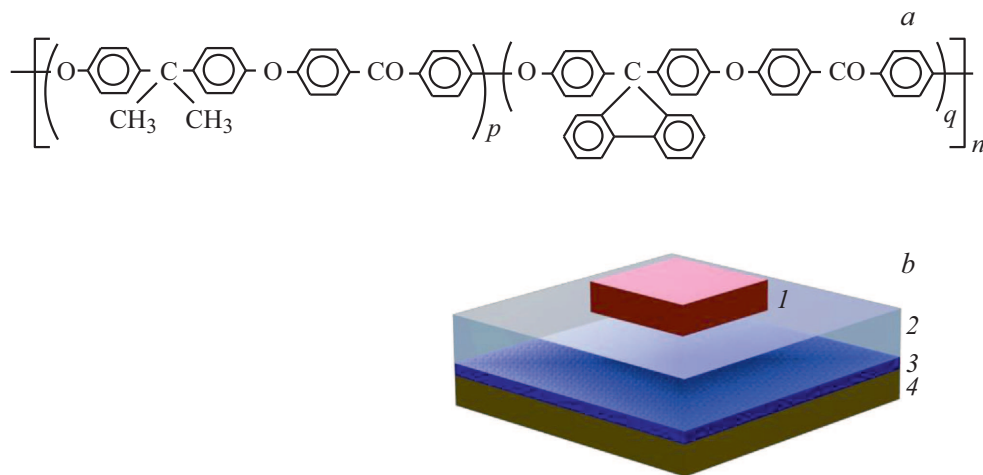
Figure 1. *a* — Structural formula of PAEK, $p/q = 0.90/0.10$; *b* — Schematic diagram of the sample: *1* — Cu, *2* — PAEK, *3* — ITO, *4* — Si.
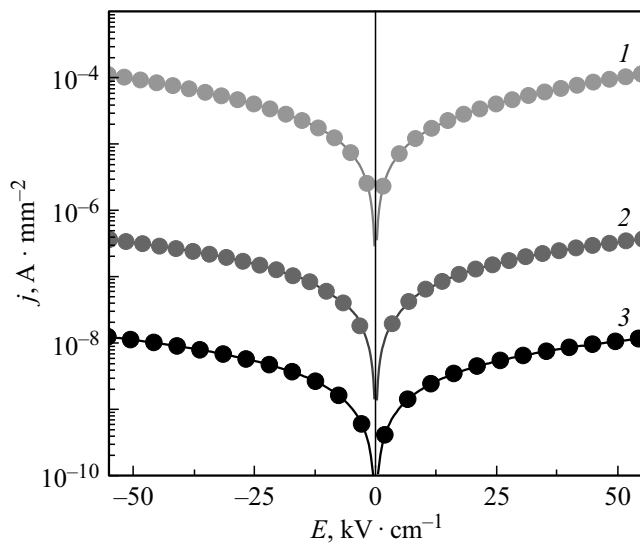

Figure 2. Room-temperature I-V curves of ITO/PAEK/Cu structures for different PAEK thicknesses: *1* — 50 nm, *2* — 850 nm, *3* — 2.1 μm.

Figure 3. Temperature dependences of current in the ITO/PAEK/Cu structure in Arrhenius coordinates for different PAEK thicknesses: *1* — 50 nm, *2* — 850 nm, *3* — 2.1 μm. The magnitude of the applied electric field is $E = 10$ kV/cm.

The conductivity of the experimental structure was examined by measuring its current–voltage curves (I-V curves) using a B2902A sourcemeter and an MPI ETS50 probe station within the temperature range of $25-125°$C. Contacts to ITO and Cu for I-V measurements were formed with the use of indium to ensure soft grip. The temperature interval was chosen taking into account the operating conditions of solar cells.

The measured I-V curves revealed a near-linear dependence for different thicknesses of polymer films at two polarities of the applied voltage; while the strength of the applied electric field varied within ± 60 kV/cm. The 50-nm-thick film was an exception: the sample with it had a I-V characteristic with a slightly nonlinear section. In this case, the I-V curves of all samples were symmetric (Fig. 2).
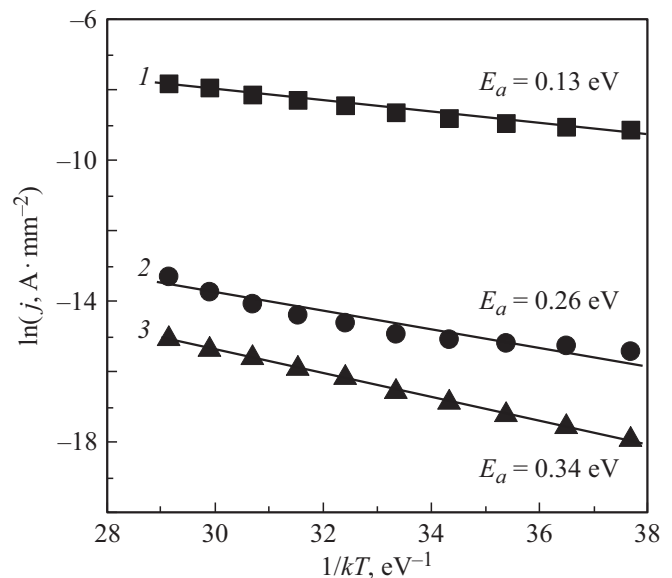
As the thickness goes down from 2.1 μm to 50 nm, the resistivity of polymer films decreases by a factor of 10^4.

The applicability of several models of carrier transport in a semiconductor/polymer/metal structure (specifically, the Poole−Frenkel model [6], Fowler−Nordheim thermionic emission [7], Schottky over-barrier emission [6], and space-charge-limited injection [8]) was evaluated. The last of the mentioned models is often applied to metal/polymer/metal structures. It was found that space-charge-limited injection is the most probable mechanism in the present case. If the obtained data are analyzed in the context of the injection mechanism, the lack of a superlinear section implies that either we operate in the region of transport of intrinsic

carriers within the given voltage interval, or the formalism is inapplicable in this specific case.

The temperature dependences of current replotted in Arrhenius coordinates (Fig. 3) allowed us to estimate the energy of activation of electron states over which carriers are transported. As the thickness of polymer films decreases, the activation energy goes down from 0.34 to 0.13 eV, and this is manifested in a reduction of resistance of films.

The symmetry of I-V characteristics implies that the relative positions of injection levels of ITO and Cu are close in energy. This is quite conceivable, since ITO is distinguished by a wide spectrum of electron states in the bandgap (the near-midgap region included [9,10]).

Thus, it was established that carrier transport in the ITO/PAEK/Cu structure is driven by tunneling in the domain of electron states in a polymer film. The energy of activation of these states decreases with decreasing thickness of polymer films. Given that electron states located near the midgap are involved in transport in such structures, the symmetry of I-V curves relative to voltage is enabled by the presence of electron states of the corresponding energy in the ITO bandgap.

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Conflict of interest

The authors declare that they have no conflict of interest.

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