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Charge transport mechanism and trap origin in methyl methacrylate copolymer with thioxanthenone side groups

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ABSTRACT

The transverse charge transport mechanism in a specially synthesized novel methyl methacrylate copolymer containing 2 % electron-accepting 9*H*-thioxanthene-9-one side groups (poly(MMA-*co*-ThS)) has been studied experimentally and theoretically. These side groups are shown to be deep electron traps. The charge transport in poly(MMA-*co*-ThS) is governed by the model of phonon-assisted tunneling between traps. The optical ionization trap energy ($W_{opt} = 1.8$ eV), independently determined by a reduction spectroelectrochemical method, confirms the validity of the phonon-assisted tunneling model used to describe charge transport in organic dielectrics with high content of electron traps.

1. Introduction

Unlike inorganic materials, the electrical properties of organic polymers can be varied relatively easily by synthesizing polymer structures with different chain blocks and/or side (pendant) groups [1,2]. In this context, the use of organic polymer thin films as working layers in memristors is considered as a promising alternative to inorganic dielectrics. Recently, a non-volatile memristor memory based on organic polymer films has been developed [3,4]. Such memory is promising for next-generation flash memory and neuromorphic artificial intelligence devices. In organic field-effect transistors and organic memristors, it is important to understand the mechanisms of charge transport in the transverse direction to the organic film. If the trap origin is determined, then it is not only possible to predict the parameters and properties of the studied films, but also, by changing the trap concentration, it is possible to control the leakage currents in such films, which will reduce the power consumption of devices based on these films.

Polymethyl methacrylate and its copolymers are considered as promising materials for memristor memory [5,6]. Meanwhile, 9*H*-thioxanthen-9-ones (thioxanthenones) were found to be strong electron acceptors capable of forming long-lived radical anions [7]. This suggests that thioxanthenones are deep one-electron traps. Thioxanthenones have also found application in the elaboration of ambipolar polyimides with thioxanthenone-based pendant (side) groups [8]. These modified polyimides are characterized by high thermal stability, low redox potentials and a band gap (E_g) of 3.15 – 3.42 eV [9]. Metal-insulator-semiconductor (MIS) type memory devices based on these polyimides have demonstrated WORM (write-once-read-many-times) nonvolatile behavior [10].

The idea of our work was to introduce electron traps with high electron affinity as structural units into a polymer with a rather high energy gap, e.g. methyl methacrylate, whose E_g is 4.5 eV [11]. This can lead to the appearance of long-lived spin doublet electronic states “inside” the E_g of the polymer when electrons are injected into the polymer film, which can contribute to charge transport. Thus, the aim of this work is to study the charge transport mechanism and to verify the origin of the trap in the methyl methacrylate copolymer containing 2 % electron-withdrawing side groups of thioxanthenone type (poly(MMA-*co*-ThS)). To determine the value of the trap ionization energy responsible for the charge transport in the poly(MMA-*co*-ThS) films, we compared the experimental current density-electrical field (*j*-*F*) characteristics measured at different temperatures in poly(MMA-*co*-ThS) films with different theoretical models. In addition, to independently establish the origin of the traps, optical transition energies of electrochemically reduced poly(MMA-*co*-ThS) and its side group precursors were obtained using optical spectroelectrochemistry in the reduction

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range of potentials.

2. Materials and methods

Poly(MMA-*co*-ThS) (Fig. 1) was synthesized by radical polymerization as described in our recent work [12] (see Electronic Supplementary Information (ESI) for details). This copolymer is a novel methyl methacrylate-type material in which thioxanthenone side groups were introduced for the first time. The copolymer has good molecular weight characteristics (ESI, Table S1) to form homogeneous thin films on silicon wafers.

Poly(MMA-*co*-ThS) polymer film was deposited on Si(1 0 0) p-type silicon wafers with the resistance of 10 Ohm*cm by centrifugation. Spin-coater “spin NXG-P1AC” was used for centrifugation. Before applying the active layer, the Si substrate was pretreated with a 10 % HF solution to remove the oxide film. The 1 % solution of poly(MMA-*co*-ThS) in chloroform was applied to the planar side of the silicon wafer. The array of top Al electrodes was thermally sputtered through a shadow mask. The area of an Al electrode of the array was 0.5 mm^2. The thickness and refractive index of poly(MMA-*co*-ThS) at the quantum energy of 1.13 eV were measured on the Ellips-1881 SAG spectral ellipsometer and were found to be 52.5 nm and 1.51, respectively (ESI, Table S2). The *j-F* characteristics of the metal–insulator-semiconductor structure were measured using a Keithley 2400 at different temperatures.

Since poly(MMA-*co*-ThS) is well soluble in all solvents used in electrochemistry [12], the UV–Vis-NIR spectroelectrochemical measurements were performed using a solution of poly(MMA-*co*-ThS) (5 mg in 6 mL of acetonitrile) at 295 K. A TSC spectroelectrochemical cell (RHD instruments, Germany) equipped with a platinum mesh working electrode was used for the measurements. The reduction potentials were quoted with reference to an Ag/AgCl pseudo reference electrode. The cell was connected to a PGSTAT 101 potentiostat (Metrohm Autolab) via a three-electrode circuit and to a UV–Vis-NIR spectrophotometer (AvaSpec-ULS2048CL-EVO Avantes) via a fiber-optic line. All cell manipulations were performed in a nitrogen-filled glove box. The optical absorption spectra (EAS) of the poly(MMA-*co*-ThS) solution (ESI, Fig. S 4*a*) were obtained in potentiostatic mode at a potential of − 1.7 V (vs Ag/AgCl) corresponding to the one-electron transfer to the thioxanthenone side groups or its precursors [13]. Optical absorption measurements for the neutral poly(MMA-co-ThS) solution were also performed for comparison (ESI, Fig. S3).

3. Results and discussion

The experimental *j-F* characteristics of poly(MMA-*co*-ThS) measured at different temperatures and the their comparison with the Frenkel model are shown in Fig. 2 [14–16].

The current density *j* through a dielectric containing traps is described by the expression [17,18]:

$$j = \frac{e}{a^2}P = eN^{2/3}P \tag{1}$$

here $N = a^{-3}$ – trap concentration, *a* – average distance between traps, *P* – trap ionization probability.

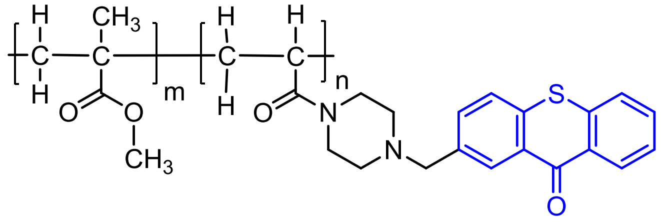

Fig. 1. Chemical structure of poly(MMA-*co*-ThS). The thioxanthenone side group is shown in blue. The m:n monomer ratio is 98:2.

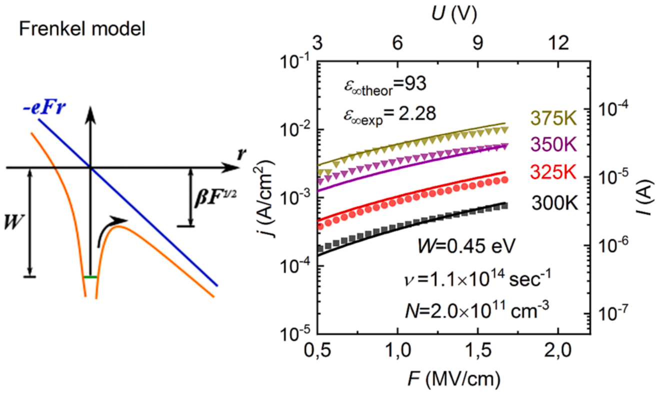

Fig. 2. The diagram of the potential of the Coulomb trap in an electric field *F* in the Frenkel model (left) and the *j-F* characteristics of Si(1 0 0) p/poly(MMA-*co*-ThS)/Al devices at different temperatures (markers) together with their simulations (solid curves) with the Frenkel model (right). For the corresponding fitting parameters and X^2 values, see ESI, Tab. S3.

$$P = \nu \exp\left(-\frac{W - \left(\frac{e^3}{\pi\varepsilon_\infty\varepsilon_o}\right)^{1/2}\sqrt{F}}{kT}\right) \tag{2}$$

here $\upsilon = W/h$ – attempt to escape factor, *W* – trap ionization energy, *h* – Planck’s constant, *e* – electron charge, $\varepsilon_\infty = n^2$ – high frequency permittivity, *n* – refractive index, ε_0 – dielectric constant, *F* – electric field, *k* – Boltzmann’s constant, *T* – temperature.

The trap energy $W = 0.45$ eV is determined from the current temperature dependence. The attempt to escape factor is determined by the formula$\nu = W/h = 1.1 \times 10^{14}\ sec^{-1}$ for the found trap ionization energy *W*. In the Frenkel model, the high-frequency dielectric constant value is determined from the experimental is equal to ε_∞=93. From ellipsometric measurements, the refractive index is $n = 1.51$ (ESI, Table S2), the high frequency dielectric constant is determined from the squared refractive index and is equal to $\varepsilon_\infty = n^2 = (1.51)^2 = 2.28$. As we can see from the comparison of the theoretical high-frequency dielectric constant value and the experimental value, the Frenkel effect does not describe the charge transport mechanism in the poly(MMA-*co*-ThS) film. In addition, when the experimental *j-F* characteristics are simulated by the Frenkel effect, an anomalously low trap concentration is obtained ($N = 2.0 \times 10^{11}$ cm^{-3}). The trap concentration in inorganic dielectrics is in the range of 10^{18}-10^{21} cm^{-3} [16].

The phonon-assisted tunneling to a neighboring trap model of Nasyrov and Gritsenko describes the charge transport mechanism of multiphonon trap ionization for the case of high trap concentration, where due to the small distance between traps it is more advantageous for an electron to tunnel to a neighboring trap rather than into the conduction band [19] (Fig. 3).

4.

The trap ionization probability in the Nasyrov and Gritsenko model has the form [19]:

$$\begin{aligned} P = {} & \frac{2\sqrt{\pi}\hbar W_t}{m^* a^2\sqrt{2kT\left(W_{opt} - W_t\right)}}\exp\left(-\frac{W_{opt} - W_t}{kT}\right)\exp\Bigg(\\ & -\frac{2a\sqrt{2m^* W_t}}{\hbar}\Bigg)\sinh\left(\frac{eFa}{2kT}\right) \end{aligned} \tag{3}$$

here *P* – trap ionization probability, ħ – reduced Planck constant, W_t – thermal trap ionization energy, m^* – effective mass, *a* – average distance between traps, *k* – Boltzmann’s constant, *T* – temperature, W_{opt} – optical

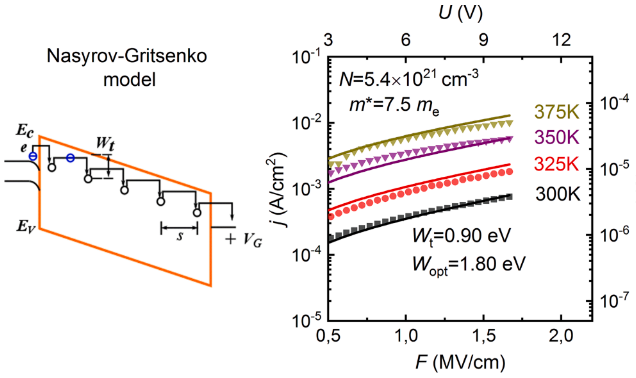

Fig. 3. Diagram showing electron excitation from a trap and subsequent tunneling to a neighboring trap (left); *j-F* characteristics of Si(100) p/poly (MMA-*co*-ThS)/Al devices at different temperatures (markers) and comparison with the phonon-assisted tunneling to a neighboring trap model of Nasyrov and Gritsenko (solid curves) (right). For the corresponding fitting parameters and X^2 values, see ESI, Tab. S3.

trap ionization energy, *e* – electron charge, *F* – electric field.

In the Nasyrov and Gritsenko model, the trap ionization probability depends exponentially on the distance between neighboring traps ($a = N^{-1/3}$); therefore, it also depends exponentially on the trap concentration *N*. Thus, the trap concentration can be determined from the experimental *j-F* characteristic (Fig. 3). The experimental analysis gives the trap concentration value $N = 5.4 \times 10^{21}$ cm^{-3}, the thermal trap ionization energy value $W_t = 0.9$ eV, the optical trap ionization energy value $W_{opt} = 1.8$ eV and the effective mass value $m^*=7.5\ m_e$. In our opinion, the overestimated electron tunneling mass value is due to the high trap concentration value $N = 5.4 \times 10^{21}$ cm^{-3}. At such a high trap concentration, we should take into account the presence of space charge in the dielectric, which leads to the local electric field dependence on the normal coordinate *F(z)* [20]. In this work, we used a simplified model that does not take into account the presence of space charge.

The trap configuration diagram is shown in Fig. 4a. In the trap, the electron passes from the ground state (black) to the excited state (red). W_t is equal to the minimum distance between the minima of the ground state and the excited state of the trap, W_{opt} is equal to the energy required for a direct transition from the ground state to the excited state. The Nasyrov and Gritsenko phonon-assisted tunneling to a neighboring trap model can determine the ionization energy value of the trap from the current temperature dependence, but cannot reveal the trap origin from the charge transport mechanism.

The optical ionization energy of the trap in a thin poly(MMA-*co*-ThS) film, $W_{\text{opt}} = 1.8$ eV, calculated using the Nasyrov and Gritsenko model, proved to be in a good agreement with the maximum at 1.85 eV observed in the optical absorption spectrum of the electrochemically reduced poly(MMA-*co*-ThS) in acetonitrile solution (Fig. 4 b, ESI, Fig. S4*b,d*). Solvation has a minimal effect on the maxima positions of the optical absorption bands of electrochemically reduced polymer films with pendant groups in the polymer structure compared to the spectra of its reduced solution or the electrochemically reduced solution of pendant group precursors [8,13]. Thus, transitions in the visible photon energy region obtained by spectroelectrochemistry (Fig. 4 b) were clearly interpreted as optical transitions associated with *radical anion states* of the thioxanthenone side groups, which are actually the “filled” traps (ESI, Fig. S4*b, d*). Note that TD-DFT calculations of the optical transitions of a precursor of the side groups, 2-methyl-9*H*-thioxanthen-9-one radical anion, in the same photon energy region, also showed an optical transition close to W_{opt} [13] (ESI, Fig. S4 *d*). This fact, together with the observed experimental data confirms the nature of the traps in the poly(MMA-*co*-ThS) film as side groups. To our knowledge, this is the first example where the nature of the traps has been directly determined based on a comparison of the optical transition energies observed for long-lived radical anion states of side groups in a polymeric insulator and the optical ionization energy of the traps obtained by analyzing the current–voltage characteristics of the MIS structure based on this insulator.

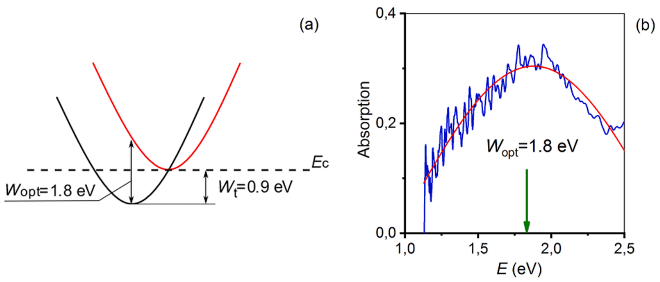

Fig. 4. (a) Trap configuration diagram of the ground state (black curve) and excited state (red curve); (b) optical absorption spectrum of electrochemically reduced 1 % poly(MMA-*co*-ThS) acetonitrile solution in the visible region of photon energies after 1000 s of electrolysis (blue curve) together with its Gaussian fit approximation (red curve) and the position of the optical ionization energy of the trap found with the Nasyrov and Gritsenko model (green arrow).

5. Conclusion

In conclusion, the charge transport mechanism in a methyl methacrylate copolymer containing 2 % electron-accepting thioxanthenone side groups (poly(MMA-*co*-ThS)) is well described by the Nasyrov-Gritsenko model of phonon-assisted tunneling between traps. Using this model, the thermal ($W_{\text{t}} = 0.9$ eV) and optical ($W_{\text{opt}} = 1.8$ eV) ionization energies of the traps and their concentration ($N = 5.4 \times 10^{21}$ cm^{-3}) in the film were determined. The value of the optical trap ionization energy obtained by modeling the current density-electrical field characteristics of p-Si/poly(MMA-*co*-ThS)/Al devices coincides with the observed electron transition energy of 1.85 eV in the electronic absorption spectrum of the electrochemically reduced poly(MMA-*co*-ThS). The latter value is associated with the first optical transition of radical anion states of the side groups. Thus, using two independent experimental methods, spectroelectrochemistry and electrophysics, we establish the origin of electron traps in the poly(MMA-*co*-ThS)-based devices as thioxanthenone side groups of the copolymer. Overall, the described result is the first example where the Nasyrov and Gritsenko model of phonon-assisted tunneling between neighboring traps has been successfully applied to describe charge transport in organic copolymers.

CRediT authorship contribution statement

Andrei A. Gismatulin: Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Danila S. Odintsov:** Validation, Resources, Methodology, Investigation, Formal analysis, Data curation. **Inna K. Shundrina:** Resources, Methodology, Investigation, Formal analysis. **Irina A. Os’kina:** Resources, Methodology, Investigation, Formal analysis. **Ivan A. Azarov:** Visualization, Methodology, Investigation, Formal analysis, Data curation. **Leonid A. Shundrin:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization. **Vladimir A. Gritsenko:** Writing – review & editing, Writing – original draft, Validation, Supervision, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cplett.2024.141140.

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