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Optical and electrochromic properties of thin films of ambipolar polyimides with pendant groups based on thioxanthenone derivatives

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The optical and electrochromic properties of thin films obtained by centrifugation from solutions containing ambipolar polyimides with pendant groups based on 9*H*-thioxanthene-9-one and its *S*-dioxide derivative are studied using spectral ellipsometry, spectrophotometry, and spectroelectrochemistry. It is shown that the spectral dependences of the refractive index $n(E)$ and the absorption coefficient $\alpha(E)$ as well as the electrochromic properties of polyimide thin films under electrochemical reduction and oxidation conditions strongly depend on the type of the pendant group. Based on the estimates of the band gap Eg a conclusion is made about the possible promising use of thin films of polyimides as working layers in memristors of a new type.

Keywords: memristors, dielectric films, ambipolar polyimides, ellipsometry, electrochromism.

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Introduction

One of the most promising components for creating a new generation of non-volatile memory is a memristor, whose operation is based on the reversible transition of a dielectric film from a high-resistance state to a low-resistance state when a current pulse flows. Currently, it is generally accepted that the transition to low-resistance state occurs due to the formation of a filament (a thin conducting nanowire with a diameter of 1−5 nm), the small size of which opens up the possibility of developing a terabit resistive memory matrix [1].

The most important parameter of the memristor is the size of the memory window i.e. the difference between the resistance of the memristor in high-resistance and low-resistance states. In the low-resistance state the resistance is set by the conductive filament, while in the high-resistance state it is determined by the conductivity of the dielectric film. The conductivity of the dielectric film depends on the potential barriers for electrons and holes at the metal/insulator interface. The potential barriers for electrons and holes, in turn, depend on the forbidden band gap E_g. The larger E_g is, the greater the barriers for electron and hole injection are, and the lower the dielectric conductivity is, and the larger the memory window of the memristor is [2].

If the conductivity of the dielectric is determined by localized electronic states (traps), the ionization of Coulomb traps in an electric field (the Frenkel effect [3]) can act as the conduction mechanism, while the probability of trap ionization in the Frenkel effect exponentially depends on optical permittivity $\varepsilon_\infty = n^2$, where n is the refraction index [4].

The memristor effect is observed in a wide class of various inorganic materials: perovskite films of $SrTiO_3$ type, dielectric oxides TiO_2, HfO_2, ZrO_2, Ta_2O5, SiO_x, GeO_x, nitrides SiN_x, SiO_xN_y, as well as in some classes of organic films.

The development of memristors based on organic polymers, in particular polyimides (PIs), is also considered as promising direction due to the key properties of PIs: relatively easy variability of their electrical properties, in particular E_g, by changing the structure of the polymer backbone and/or introducing pendant (side) groups of different nature [5,6], high mechanical stability of PI and good flexibility of polyimide films, their compatibility with semiconductor platforms [7,8], high thermal stability [9] and relatively easy production of three-dimensional arrays based on them [5,10,11].

The aim of this paper is to study the dispersion of the refraction index and absorption coefficient, to estimate the forbidden band gap, and study the electrochromic properties of thin films containing ambipolar polyimides with new pendant groups based on 9*H*-thioxanthen-9-one and its S-dioxide derivative for their possible application as working layers in new type memristors. For comparison, the properties of a polyimide without a pendant group and a polyimide with an anthraquinone pendant group described in the literature were also studied [12].

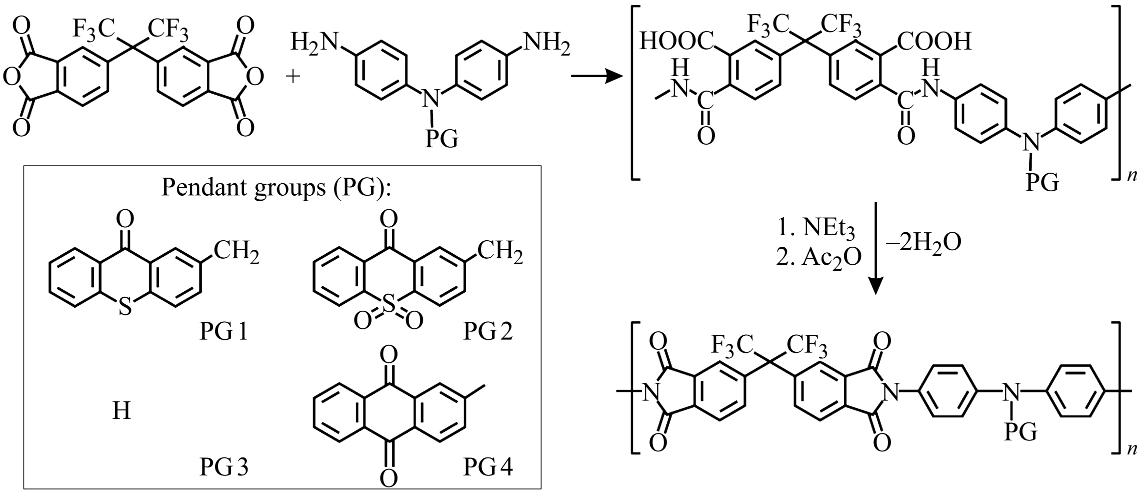

Figure 1. Scheme of synthesis and structure of polyimides (PI 1–4) with pendant groups of the thioxanthene series and anthraquinone.

Experimental part

Synthesis of polyimides

PIs with pendant groups, the structures of which are shown in Fig. 1, were synthesized by a two-stage method, including the synthesis of the corresponding polyamide acids followed by chemical imidization [13]. PI yields, their viscosities, molecular weight characteristics, thermal stability, and electrochemical properties are described in paper [13].

Obtaining PI 1–4 polymer films on silicon wafers

PI 1–4 polymers films were deposited on Si(100) KDB silicon wafers 40 mm in diameter by centrifugation in saturated solvent vapors. For centrifugation a modified MiniSpin centrifuge was used, equipped with a rotor nozzle of own design, which is a round tight chamber with a flat base and thickness of 3 mm, well centered relative to the axis of rotation of the centrifuge rotor. A silicon wafer preliminarily treated with a 10% HF solution was placed and fixed in the central part of the chamber to remove the oxide film. 50 μl 1% solution of PI 1–4 in perfluoroacetone was deposited on the planar side of the plate along its center. Additionally, to create a saturated solvent vapor atmosphere 100 μl of pure solvent was placed in the form of drops along the plate periphery into the space between the plate edge and the chamber wall. The chamber was hermetically covered with a flat polypropylene lid and held for 2 min, which, due to the volatility of perfluoroacetone, was sufficient to create the atmosphere saturated with solvent vapors. Centrifugation was carried out at 800 rpm for 60 s. Further, the sample was held in the closed state for 2 min, then the chamber was opened, and the plate with the applied polymer layer was dried for 30 min in air at room temperature, and then at 120°C in an oven. A sample of film coated silicon wafer compared to a clean silicon wafer is shown in Fig. 2.

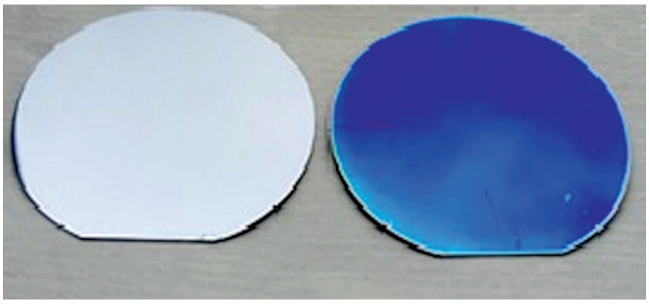

Figure 2. A clean silicon wafer (left) and a PI 4 thin film coated wafer (right).

Spectral ellipsometry

The optical properties of organic films deposited on silicon wafers were studied using a spectral ellipsometer „Ellips-1881SAG“ (ISP SB RAS) in the energy range of light wave quantum $E = 1.13{-}4.96$ eV with a step of 0.01 eV [14]. The spectral dependences of the ellipsometric angles $\Psi(E)$, $\Delta(E)$ were measured at the center of a silicon wafer using a four-zone method with averaging over all zones, while the diameter of the light beam on the surface of the sample under study did not exceed 3 mm. $\Psi(E)$, $\Delta(E)$ spectra were measured at three angles of light beam incidence on the sample — 50°, 60°, 70°. The solution of the inverse problem of ellipsometry and the calculation of the spectral dependences of the refraction index $n(E_i)$, absorption coefficient $\alpha(E_i)$ were carried out in accordance with a simple single-layer model of the reflecting system: medium–film– substrate for each point of spectrum E_i independently using three pairs of values

Table 1. Optical properties of PI 1–4 films deposited by centrifugation on silicon wafers

Sample	d, nm*	n (1.96 eV)	Peaks of absorption, eV		E_g, eV
			1	2	
PI 1	39.2	1.642	–	4.29	3.42
PI 2	44.9	1.663	–	4.31	3.15
PI 3	41.5	1.691	–	4.22	2.49
PI 4	28.5	1.666	2.66	4.39	2.23

Note. * — the thickness was measured at the center of the wafer.

$\Psi(E_i)$, ΔE_i for $\phi_0 = 50°, 60°, 70°$ [15]. The thickness of the films was determined beforehand in the film transparency region ($\alpha = 0$, $E = 1.96$ eV). The method of ellipsometric measurements and calculations is described in detail in paper [16].

Study of electrochromic properties

The electrochromism of PI 1–4 was measured under conditions of electrochemical recovery and oxidation of polyimide films deposited by the solution method on ITO electrode, which served as a working electrode. Electrochromic properties were measured using an electrochemical cell designed on the basis of a standard quartz cuvette for optical measurements with optical path length of 1 cm — similarly to the cell described in the paper [12]. A silver wire and a loop-shaped platinum wire, respectively, served as the reference and auxiliary electrodes. The cell was placed in the cuvette section of a „HP 8453“ UV-VIS-NIR spectrophotometer with a diode array, synchronized with „Elins“ potentiostat (Russia). The measurements were carried out in the stepwise potential sweep mode with a step of 150 mV in the range of negative potentials ($0 > E > 1.85$ V is recovery electrochromism) and separate experiments in the range of positive potentials ($0 < E < 2.1$ V is oxidative electrochromism). In spectroelectrochemical experiments the optical spectra were measured in „differential mode“: $D - D_{\text{blank}}(\lambda)$, where D is absorption density, λ is wavelength, $D_{\text{blank}}(\lambda)$ is spectra of neutral PI 1–4 films taken as a blank ($D(\lambda) = 0$ for the entire range of measured wavelengths before the start of potential scanning). Note that in the „differential “ mode of the electrochromic behavior of films measurement the positive absorption is observed if new optically active particles are formed inside the polymer layer at a certain potential, and „negative“ absorption corresponds to the concentration of neutral polymer fragments decreasing in the original films before the start of the potential scanning. Electrochromic measurements were carried out in acetonitrile, in which PI 1–4 are insoluble, and the films are well retained on the working ITO electrode. 0.1 M solution of Et_4NClO_4 served as the background electrolyte.

Table 2. Characteristic absorption bands of neutral PI 1–4 films and under the conditions of their electrochemical recovery and oxidation on the ITO electrode

Polyimide film	λ_1, nm (E, eV)[a]	λ_2, nm (E, eV)	λ_3, nm (E, eV)
Neutral state			
PI 1	297 (4.17)	323 (3.84)	—
PI 2	294 (4.22)	336 (3.69)	—
PI 3	297 (4.17)	320 (3.87)	—
PI 4	309 (4.01)	353 (3.51)	460 (2.70)
Electrochemical recovery			
PI 1	363 (3.42)	409 (3.03)	683 (1.82)
PI 2	355 (3.49)		644 (1.93)
PI 3	354 (3.50)	467[b] (2.65)	—
PI 4	344 (3.60)	386 (3.21)	566 (2.19)
Electrochemical oxidation			
PI 1	378 (3.28)	446 (2.78)	754 (1.64)
PI 2	378 (3.28)	488 (2.54)	772 (1.61)
PI 3	376 (3.30)	443 (2.80), 478 (2.59)	766 (1.62)
PI 4	395 (3.14)	463 (2.68)	780 (1.59)

Note. a — the corresponding quantum energy is given in parentheses, b — low-intensity absorption bands.

Results and discussion

The optical properties of four samples with PI 1–4 films deposited on silicon wafers are given in Table 1. The Table data show that the films on all samples have a thickness in the range of 28–45 nm and a rather high for organic coatings refraction index value: $n = 1.642-1.691$ ($E = 1.96$ eV). The spectral dependences of the refraction index n and the absorption coefficient α obtained by solving the inverse problem of ellipsometry are shown in Fig. 3, *a, b*. As can be seen from the data in Fig. 3, *b*, all the films studied in this paper have strong absorption of light in the visible region of the spectrum, mainly in the short-wavelength part. The shape of the $n(E)$ and $\alpha(E)$ spectra strongly depends on the type of the pendant group (Fig. 1, Table 1): thus, the appearance and further enhancement of absorption occurs in different parts of the spectra, to a large extent affecting the E_g value. The main absorption peaks lie in the range 4.22–4.39 eV with components at 3.81–4.09 eV. Moreover, the PI 4 film has an absorption maximum in the longer wavelength region at $E \sim 2.66$ eV.

PI 1–4 have a pronounced electrochromic behavior. Under conditions of electrochemical recovery, in the optical spectra of PI 1–4 polyimide films, absorption bands appear in the near ultraviolet and visible regions, the intensity of which depends on the applied potential (Fig. 4, *a, b*, Fig. 5, *a, b*). The appearance of bands in the visible region (PI 1, 2, 4) is observed when the applied potential reaches the recovery potential of pendant groups (−1.63,

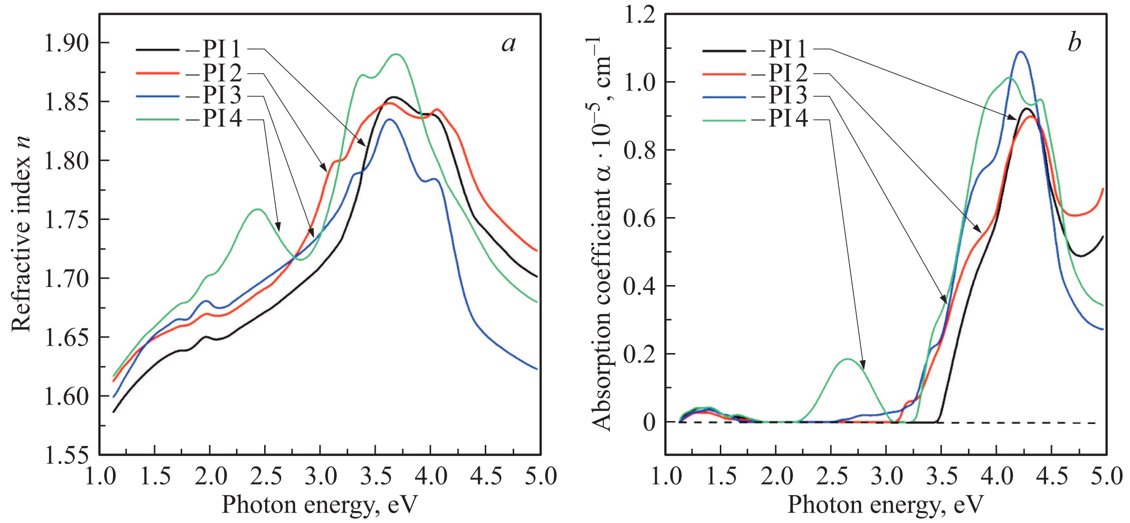

Figure 3. Spectral dependences of PI 1–4 films: *a* — refraction index, *b* — absorption coefficient.

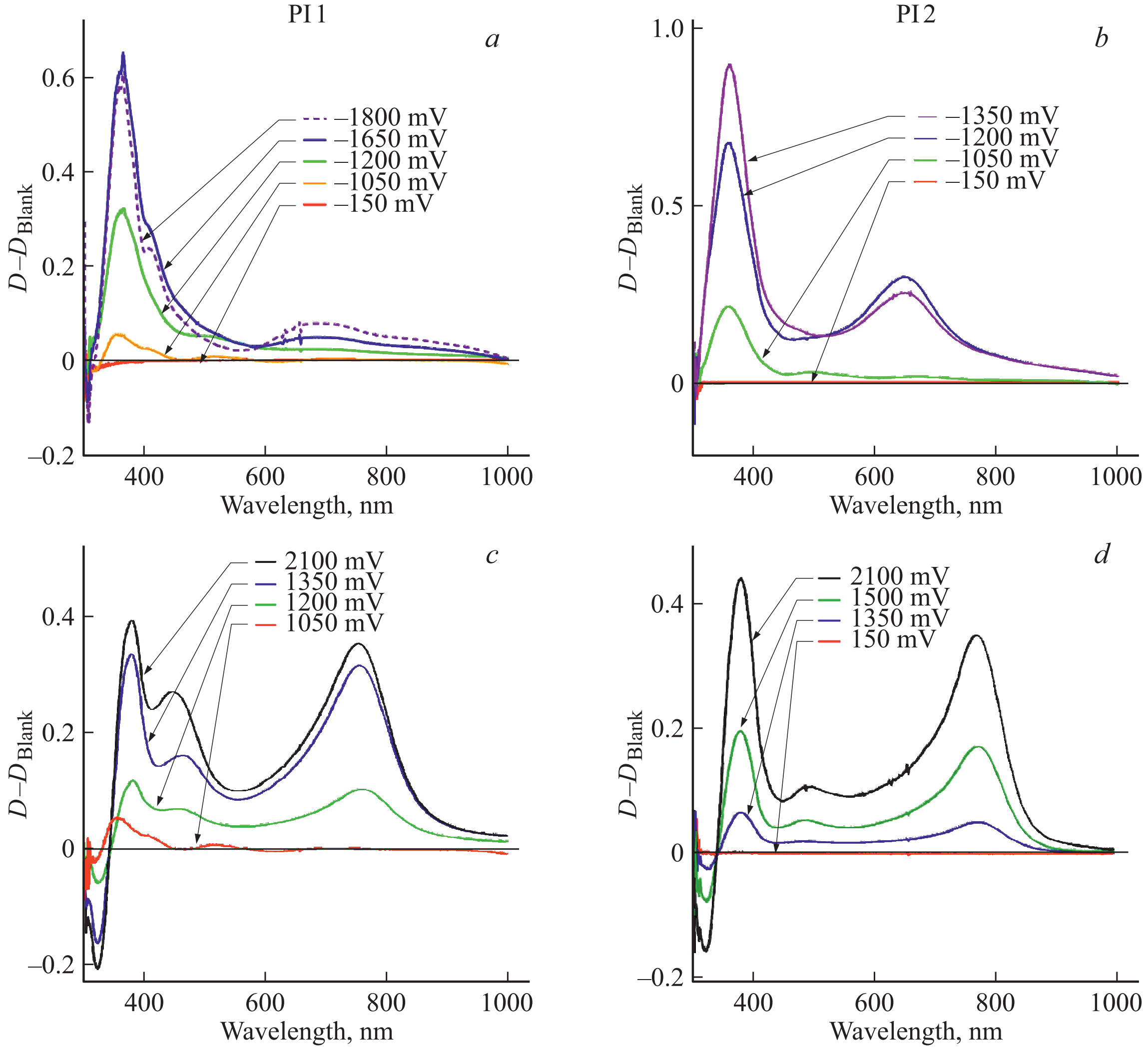

Figure 4. Electrochromism of polyimide films PI 1, PI 2 in recovery (a, b) and oxidizing (c, d) areas of potentials.

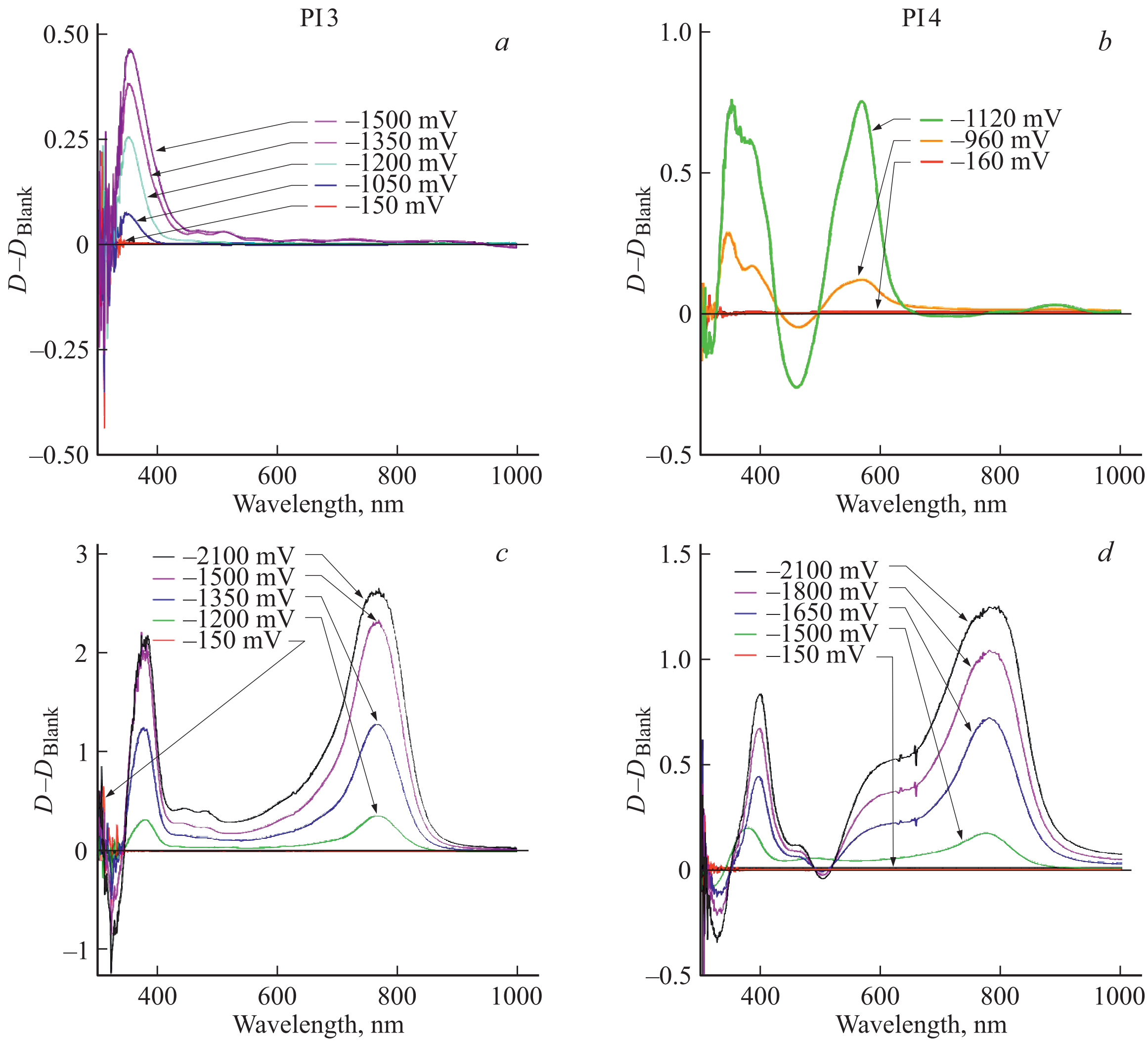

Figure 5. Electrochromism of polyimide films PI 3, PI 4 in recovery (a, b) and oxidizing (c, d) areas of potentials.

-1.03, -0.95 V respectively for 9*H*-thioxanthen-9-one, its S-dioxide and anthraquinone). For PI 3, which does not contain a pendant group, no noticeable electrochromism is observed in the visible region of the spectrum (400-750 nm), except for bands of very weak intensity (Fig. 5, *a*, Table 2). The electrochromic behavior of polyimide films can be explained by the formation of rather long-lived negatively charged states of pendant groups (radical anion states), which fully corresponds to the first stage of the mechanism of electrochemical recovery of the corresponding precursors, namely, reversible one-electron transfer [17]. Note also, that the occurrence of absorption bands in the ultraviolet region for all PI 1–4 films is most likely associated with the formation of anionic states of the diimide fragment of the polyimide chain (Fig. 1), since the electrochemical recovery of polyimides without pendant groups is a two-electron process [18].

Electrochromic behavior of PI 1–4 in the region of positive potentials — oxidative electrochromism (Fig. 4, *c, d*, Fig. 5, *c, d*) has the same tendency as the electrochromic behavior of PI 1–4 in the region of recovery potentials, and corresponds to the results obtained earlier for polyimides [12]. Under electrochemical oxidation conditions all PI 1–4 polyimides exhibit intense absorption bands in the visible and near-IR spectral regions, which are characterized by a noticeable bathochromic shift compared to absorptions in the recovery region of potentials (Fig. 4, 5).

It follows from the data in Table 2 that under the conditions of electrochemical recovery, the λ_1 absorption band with a noticeable bathochromic shift relative to the corresponding λ_1 band of the neutral film can be attributed to electronic transitions of particles, formed as a result of one-electron transfer to the polymer chain, since it is observed for all PIs, including PI 3, which does not contain the pendant group. The λ_2 bands are possibly of mixed nature, while the λ_3 bands (see also Fig. 4, *a, b*, Fig. 5, *b*) refer to the optical absorption of one-electron recovered pendant groups, since for PI 3 no absorption is observed in this region in the entire studied potential range (Fig. 5, *a*).

Conclusion

Thus, in this paper we studied the optical properties of thin polyimide films obtained by centrifugation from solutions of ambipolar polyimides, including those containing electrochemically active pendant groups based on 9*H*-thioxanthen-9-one, its S-dioxide derivative, and anthraquinone. It is shown that the optical properties of the films, in particular the forbidden band gap, depend on the nature of the pendant groups. According to ellipsometry data, when pendant groups of the thioxanthenone series are introduced into the polyimide structure, the forbidden band gap increases on average by 0.93 eV compared to polyimide without the pendant group and polyimide containing the anthraquinone pendant group. Since it is known that the memory window of the memristor increases with increasing of the forbidden band gap, ambipolar polyimides with pendant groups of the thioxanthenone series, which have higher E_g values among the entire range of studied polyimides, are of interest for creating memristors based on them. Note that a model resistive memory device based on PI 4 with the anthraquinone pendant group and implemented on the ITO platform demonstrated WORM behavior [12].

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Conflict of interest

The authors declare that they have no conflict of interest.

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