ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 3, pp. 642–656. © Pleiades Publishing, Ltd., 2009.
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Vacuum Evaporation-Deposited Polyterafluoroethylene Films: Growth Mechanism, Properties, and Applications

K. P. Gritsenko

Institute of Semiconductor Physics, National Academy of Sciences of Ukraine,
prosp. Nauki 45, Kiev, 03650 Ukraine
e-mail: d_gryts@isp.kiev.ua; d.grytsenko@gmail.com

Received February 1, 2008

Abstract—The method of vacuum evaporation deposition of polyterafluoroethylene films under additional vapor activation with an electron cloud and low temperature plasma was described. The film composition, structure, and properties can be controlled by deposition conditions. Co-evaporation with metals and dyes allowed deposition of various composite films. Gold-filled films were modified with thiol for gas sensor applications.

DOI: 10.1134/S1070363209030463

INTRODUCTION

Since recently, thin polytetrafluoroethylene films have found extensive high-technology application in organic light-emitting diodes, organic field transistors, nanophotonic and nanooptoelectronic systems, and plastic electronic facilities with flexible substrates [1, 2]. A low dielectric permittivity makes polytetrafluoroethylene promising for application in the next-generation microchips [3]. However, thin polytetrafluoroethylene film deposition is a complex task because polytetrafluoroethylene is insoluble in all known solvents. In this connection, it was suggested that oxygen-modified soluble fluoropolymer (Teflon AF etc.) and a polytetrafluoroethylene nanopowder be used for this purpose [4–8]. Al alternative approach implies film deposition from the gas phase: plasma polymerization of perfluormonomers [9–11]; magnetron, synchrotron [12, 13], X-ray [14], or laser [15, 16] sputtering of targets; thermal dissociation of fluorinated compounds [17]; electron beam evaporation [18–20]; and polytetrafluoroethylene evaporation with activation of the products released into the gas phase [21–24]. It should be noted that technologies for polymer film deposition from a gas phase were proposed simultaneously in developed Western countries and in the former UISS (for details, see [24–30]).

A new class of materials is represented by fluoropolymer films filled with nanoclusters. They can be prepared by magnetron sputtering of a gold target in a C_2F_3Cl medium [31, 32], magnetron [33] or ion [34–36] co-sputtering of a metal and polytetrafluoroethylene, and co-evaporation of a metal and polytetrafluoroethylene [37, 38]. Studies into suitability of nanocluster materials for sensor, photonic, plasmonic, waveguide, and other applications are under way now.

Here, we discuss the progress achieved in vacuum deposition of polytetrafluoroethylene films and their high-technological applications.

Physicochemical Principles of Vacuum Deposition of Polytetrafluoroethylene Films

Film deposition from a gas phase produced by heat treatment of polytetrafluoroethylene is underlain by polymer degradation, involving scission of the macromolecular chain in various segments and/or elimination of side groups and atoms. This yields fluorine-containing molecular moieties that specifically form the fluoropolymer film. Depending on the polymer structure, the scission occurs as a random process or as regular depolymerization. Increase in temperature results in a broader spectrum of degradation products and formation of higher-molecular-weight products. The molecular weight of the gaseous moieties is limited by their evaporation. Kuz'mina and Zaev [39] estimated the maximal molecular weight of a moiety able of transition to the gas phase at ~1000 Da. Luff and White [40] and Collins et al. [41] examined thermal degradation of polytetrafluoroethylene and found that the spectrum of

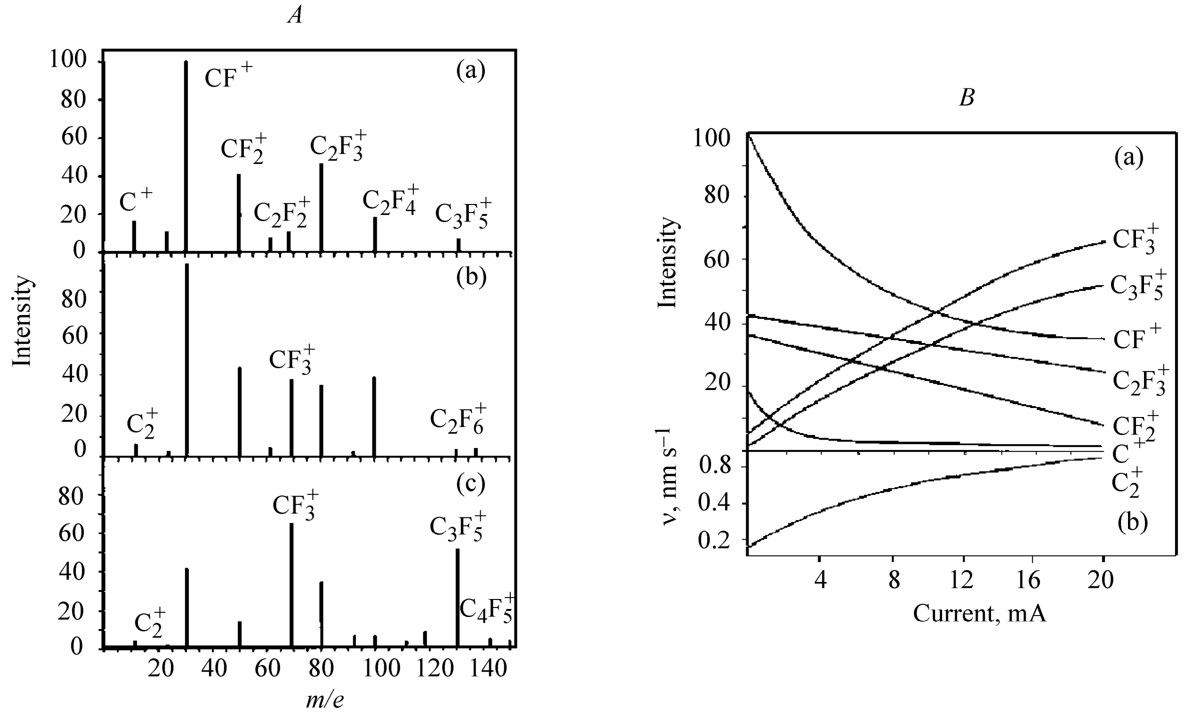

Fig. 1. Measured composition of thermal degradation products of polytetrafluoroethylene and the polymer film growth rate. (*A*) Mass spectra of the degradation products prepared (a) without activation and (b, c) with activation (b) at 3 kV, 30 mA in a quasiclosed crucible and (c) at 3 kV, 20 mA, in an open crucible and (*B*) (a) gas phase composition and (b) film growth rate in relation to the activation current.

the polymer degradation products in an inert gas and in a vacuum differ significantly. Gritsenko [42] obtained an identical mass spectrum of the products of thermal degradation of polytetrafluoroethylene in a vacuum.

Films prepared by heat treatment of polytetrafluoroethylene grow at a low rate. To accelerate this process, Gritsenko et al. [21, 22] suggested that the polytetrafluoroethylene degradation products be activated with accelerated electrons, which causes the film growth rate to increase fivefold.

Activation with electron cloud causes a number of transformations in the gas phase (Fig. 1). The concentrations of the CF_3 and C_3F_5 moieties correlate with the film growth rate, for which reason it was presumed that these moieties are specifically responsible for the film growth [22, 42]. The spectrum of the degradation products yielded by evaporation in a quasiclosed crucible differs from that in the case of an open crucible. Also, in the former case the products are not activated with electrons.

Wijesundara et al. [43] examined modification of the polystyrene surface with CF_3^+ and $C_3F_5^+$ ions having 25–100 eV energies. The structure of the deposits (according to X-ray photoelectron spec-troscopic data) is identical to that of the per-fluorpolymer prepared by plasma polymerization. An increase in the ion energy causes an increase in the concentration of CF_n groups different from CF_3. The maximal concentration of the CF_2 groups was achieved by exposure to 50-eV ions. According to Wijesundara et al. [43], the polymer film grows more rapidly from $C_3F_5^+$ than from CF_3^+ ions. This validates the film growth mechanism proposed by Gritsenko [42], who also presumed that the polymer chain scission in a vacuum yields products different from the monomer, which, unlike the latter, can be activated with fast electrons This concept was further developed by E.M. Tolstopyatov from the Institute of Mechanics of Metal-Polymer Systems, National Academy of Sciences of Belarus, who showed that the primary degradation product of polytetrafluoroethylene macromolecules is highly reactive difluorocarbene :CF_2. Secondary gas-phase reactions yield the monomer, as well as other compounds, depending on the parameters of the process. Reactions of reactive compounds with the polymer molecules yield new molecular groups in their chains [44].

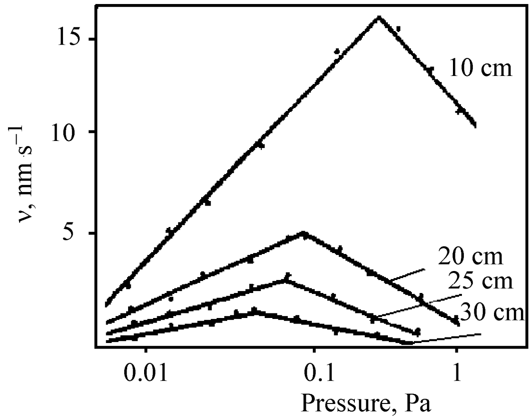

Fig. 2. Polytetrafluoroethylene film growth rate vs. gaseous products pressure at different evaporator–substrate distances.

Film growth examinations showed that, after a certain limiting pressure is attained in the chamber, further increase in pressure causes the film growth to decelerate, despite an increase in temperature (Fig. 2). This limiting pressure is the higher, the smaller the distance separating the evaporator and the substrate. The reason is that, with increasing pressure, the free path length of the molecular moieties gets smaller than the evaporator–substrate distance, which causes the moieties to react together in the gas phase and lose their reactivity. Gritsenko [42] estimated the mass of the reactive moieties at 50–150 amu. This lends support to the film growth mechanism via secondary polymerization from small moieties. Unexpected results were obtained in experiments with evaporation of polytetrafluoroethylene upon exposure to ^{60}Co γ-rays [45] or to CO$_2$ laser radiation [44]. The relief of the resulting film is shown in Fig. 3. It was found that the films deposited from a pretreated material have a more uniform relief and a tenfold lower birefringence.

The film grows the faster, the profounder the degradation of the polymer before evaporation. This fact is in line with the known data on nonstationary kinetics of polytetrafluoroethylene degradation: The degradation is accelerated with increasing process time. Gritsenko [46] examined film deposition by vacuum evaporation and found that the film growth rate is somewhat higher in the case of repeated evaporation of the vacuum-deposited polytetrafluoroethylene films and that the gas phase contains a larger amount of C_3F_5 moieties.

Influence of the Deposition Parameters on the Film Structure and Properties

Gritsenko et al. [46, 47] found that the most uniform surface relief of the polytetrafluoroethylene films deposited from a gas phase is achieved at the film thickness ranging from 30 nm to 10 μm [46, 47].The structure and properties of the films are affected by the pressure of gaseous degradation products and electron activation current and voltage. The table lists selected properties of the films deposited under different conditions.

In all the IR transmission spectra (Fig. 4) the bands at 526, 555, 640, 729, 1151, and 1213 cm^{-1} correspond to the structure of the 15_7 polytetrafluoroethylene macromolecule [48, 49]; the band at 980 cm^{-1} is associated with the CF$_3$ groups, and that at 1352 cm^{-1}, with the C=C groups. The most intense bands are those associated with the stretching vibrations of the CF$_2$ groups. An increase in the electron activation power causes the intensity of the bands at 980 and 1352 cm^{-1} to increase, which suggests an increase in the concentrations of the CF$_3$ and C=C groups, respectively. At the same time, the bands at 555, 625, 777, and 1150 cm^{-1} tend to decrease in relative intensity.

As follows from the corresponding diffraction patterns (accelerated electron diffraction), the film deposited without activation has a crystalline structure, while those in the case of activation contain an

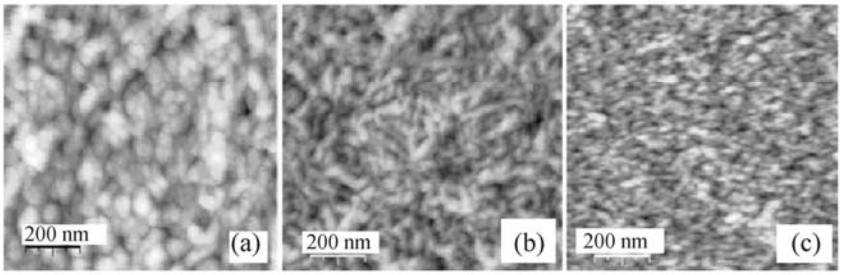

Fig. 3. Surface relief of the films prepared by polytetrafluoroethylene evaporation (a) without and (b, c) with treatment using (b) γ-rays and (c) CO$_2$ laser radiation.

amorphous phase in the amount proportional to the activation current. The intensities of the IR bands at 980 and 1352 cm^{-1} suggest a small number of side chains and cross links. The films consist predominantly of linear macromolecules, by contrast to the films deposited by plasma polymerization, as well as by magnetron or ion sputtering. All this allowed qualification of the films deposited from the gas phase as specifically polytetrafluoroethylene films.

Variation of the pressure of the polytetrafluoroethylene evaporation products from 4×10^{-3} to 2×10^{-4} mm Hg induced a change in the refractive index of the films from 1.15 to 1.38. The corresponding ellipsometric data suggest that the film material contains pores oriented perpendicular to the substrate surface. The highest density and uniformity are characteristic of the films deposited at a low pressure and a high activation current of accelerated electrons.

The experiments on additional modification of the growing films with a low-temperature plasma (a 40.68-MHz discharge) [46, 50, 51] showed that the rate of the film growth on a high-frequency electrode decreases proportionally to the increase in the discharge power (from 30 W); at 70 W the film growth is terminated. Therefore, the film deposited onto an electrode is thinner than that deposited in the discharge space within identical period.

All the IR spectra contain the main peaks characteristic for vacuum-deposited polytetrafluoroethylene. An increase in the high-frequency discharge power causes the bands at 980 and 1352 cm^{-1} to significantly grow in intensity, which suggests increases in the concentrations of the CF_3 and C=C groups, respectively. The peaks associated with the stretching vibrations of the CF_2 groups abruptly decrease in intensity. The corresponding electron diffraction patterns showed that the films deposited without plasma treatment contain a certain amount of the crystalline phase, while the plasma-deposited films are totally amorphous.

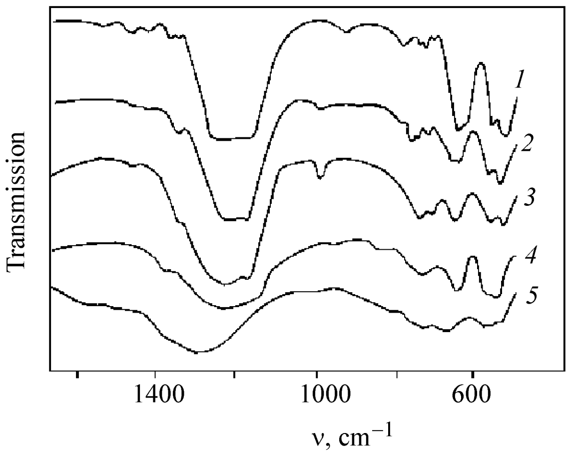

Fig. 4. IR transmission spectra of polytetrafluoroethylene films deposited from the gas phase by (*1*) thermal evaporation; (*2, 3*) with electron activation at the current of (*2*) 10 and (3) 20 mA; and (*4, 5*) with electron activation and plasma treatment at the activation current of (*4*) 20 mA and 30-W high-frequency discharge and (*5*) 20 mA and 70-W high-frequency discharge.

Figure 5 presents the X-ray photoelectron spectroscopic (XPS) data for the films. It is seen that the films grown in the electrode gap at the discharge power of 40 W are characterized by the main C1s peak at 293.2 eV, associated with the CF_2–CF_2 groups. Also, the spectrum contains low-intensity peaks corresponding to terminal groups and cross links. The oxygen content in the films is under 1%. Based on the chemical composition, the films can be qualified as polytetrafluoroethylene films. The C1s spectrum of the film deposited onto a high-frequency electrode exhibits a maximum at 288.52 eV, associated with unsaturated C=CF bonds. The maxima at 285.8, 284, and 282 eV were assigned to the C–CF and C–C bonds in the fluorinated medium and to hydrocarbons. The IR and

Refraction index and structure of polytetrafluoroethylene films

Activation current, mA	Film thickness, nm	Refraction index		Film structure	
		before annealing	after annealing	before annealing	after annealing
0	31.9	1.36	1.42	Crystalline	Crystalline
10	26.4	1.33	1.39	Amorphous	The same
20	26.7	1.32	1.37	The same	″
20 + 30 W H-F	28.3	1.38	1.38	″	Amorphous

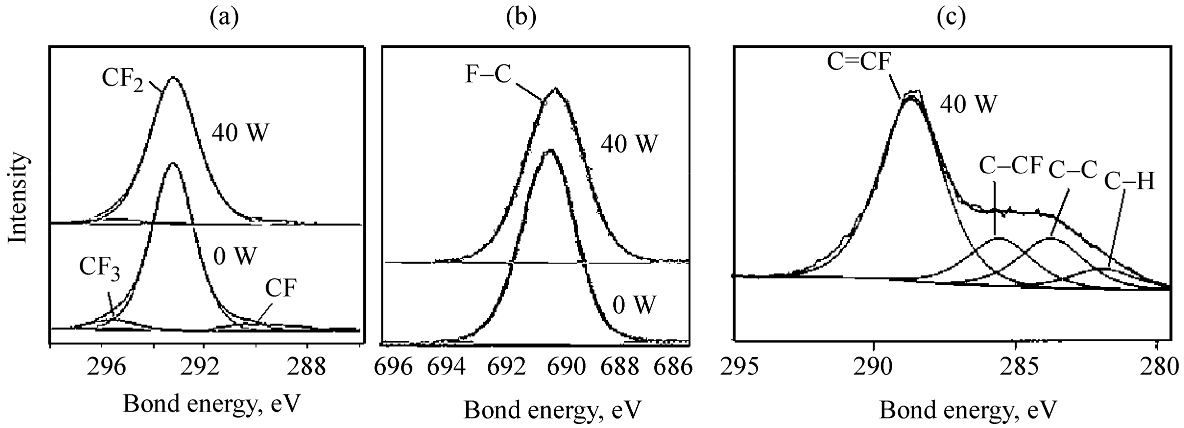

Fig. 5. C1*s* and F1*s* maxima in the X-ray photoelectron spectra of the polytetrafluoroethylene films: (a, b) Films deposited in the electrode space without and with a 40-W discharge and (c) film deposited on a high-frequency electrode.

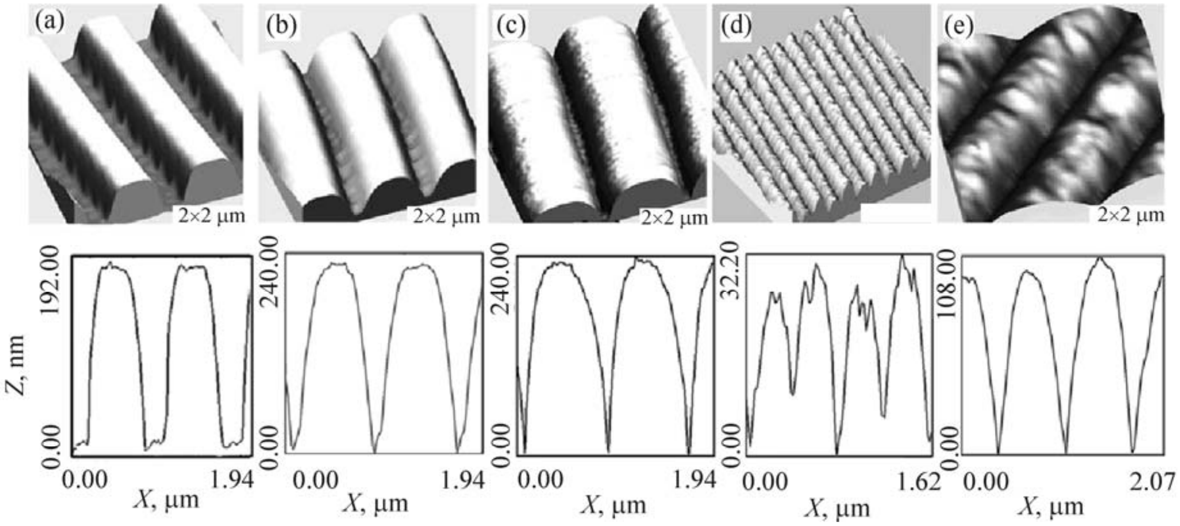

Fig. 6. Surface relief of the polytetrafluoroethylene films on a DVD substrate: (a) neat DVD substrate; (b) film deposited without plasma treatment onto a gold-coated DVD substrate; (c) film deposited from plasma onto neat DVD substrate; (d) film deposited without plasma treatment onto neat DVD substrate; (e) poly(*p*-xylylene) film deposited onto OLED (a multilayer structure with polymeric and metal layers).

X-ray photoelectron spectra suggest the presence of cross links between the macrochains and a branched structure of the macromolecules. The cross links and branches tend to increase in number both with increasing electron activation current and plasma discharge power.

The hardness (load to the print area ratio) of the films was measured with a nanoindenter. At the 13-μN load the hardness was estimated at 237 и 260 MPa for films deposited without and with plasma treatment, respectively.

The above-said suggests the following. The structure of the films deposited onto an electrode in high-frequency plasma is similar to that of the films deposited by plasma polymerization of the monomers; the macromolecules in the films deposited in the electrode space at a low power of the high-frequency discharge have a linear structure with a minimal content of double bonds and branches. These are amorphous films, distinguished from vacuum evaporation-deposited crystalline films by enhanced uniformity and stability.

Figure 6 shows the surface relief of the polytetrafluoroethylene films deposited onto the surface of a standard DVD polycarbonate substrate (with stamped tracks and without recording layer). Without plasma treatment of the fluorine-containing gas phase, the microsteps of the film on the gold-coated substrate preserve a rectangular shape, although the film thickness on the top exceeds that in indentations. On a polycarbonate substrate, the film forms a roll inside indentation, which suggests that it is nonwettable. Plasma treatment of the polytetrafluoroethylene vapor yields a nearly conform film (a coating that replicates the surface relief of any shape and having a thickness, identical for all segments within the tolerance set) on the polycarbonate as well. The degree of conformity varies with the deposition parameters. Figure 6e shows, for comparison, the relief of a poly(p-xylylene) film grown from the gas phase without plasma treatment. The polytetrafluoroethylene film grown at a low power of high-frequency discharge exhibits excellent covering power with a uniform thickness on a plastic material, which is characteristic of poly(p-xylylene) films.

Codeposition of Polytetrafluoroethylene with Organic and Inorganic Materials

Preparation of composite films on a polytetrafluoroethylene matrix has long attracted researchers' attention. Such films should combine valuable properties inherent in the matrix with those of the filler. Films filled with inorganic materials were prepared by magnetron or ion sputtering. Attempted filling of the polymer with a dye by plasma polymerization of fluoromonomers resulted in degradation of the dye molecule [52]. The only way to prepare dye-filled films is via thermal evaporation of polytetrafluoroethylene with simultaneous evaporation of a dye.

Codeposition of Polytetrafluoroethylene with Inorganic Materials

Petrov et al. [38] examined films prepared by co-evaporation of polytetrafluoroethylene with Au, Te, and As-Se-Te alloys and found that the Au films deposited onto potassium bromide are more uniform than those deposited onto KBr precoated with a polymer film. This effect was associated with diminished nucleation sites for Au clusters on the films with a low surface energy. The Au-polytetrafluoroethylene composite films prepared by co-evaporation of polytetrafluoroethylene and gold are more uniform than the Au film. The metal clusters in the film grow in size with increasing their concentration. The amorphous clusters of the As–Se–Te alloy are smaller than neat Te clusters [46].

Gritsenko et al. [53–56] applied new techniques to examine the film growth in situ. Figure 7A presents several series of optical absorption spectra of Au-polytetrafluoroethylene films, recorded during film growth with and without high-frequency plasma treatment. In the film growth onset period, the spectra exhibit a plasmon peak near 480 nm associated with the Au clusters, which is shifted to 520 nm with increasing film thickness (10% Au). The peak grows in intensity with increasing film thickness. The optical density at 420–430 nm is higher for the films deposited with plasma treatment. The plasmon peak of the film containing 20% Au in the growth onset period is observed near 480 nm and shifted to 560 nm with film thickness increasing to 15 nm, whereupon its position remains unaffected by further film growth. Possibly, in the growth onset period, small gold clusters are formed which subsequently grow in size until a certain thickness of the matrix is achieved, whereupon the growth is terminated.

Figure 7B presents the XPS data for the Au-polytetrafluoroethylene films. They suggest that the Au clusters are incorporated into the polymer matrix, which complicates their quantitative description. The concentration of the CF и C–CF groups for Au-polytetrafluoroethylene films is higher than that for neat polytetrafluoroethylene, with the highest concentration of these groups observed in the films deposited under plasma treatment. This suggests that the composite films comprise more profoundly branched polytetrafluoroethylene precluding the growth of Au clusters, which, however, affect, in turn, the secondary polymerization. The effects exerted by plasma treatment and Au clusters on the polymer structure in the films are summed. The occurrence of a band at 286.5 eV in the spectra of all the films is hard to explain. For the film prepared by codeposition of gold and polytetrafluoroethylene, this band has a 10 times lower intensity. This is presumably associated with the presence of hydrocarbons adsorbed on the surface of Au nanoclusters from the atmosphere.

Figure 8 shows the electron-microscopic images of Au-filled polytetrafluoroethylene films. The size of the Au clusters was estimated at 4–8 and 2–13 nm in the films deposited without and with plasma treatment, respectively. The optical properties of the Au clusters were simulated with the use of ellipsometric data in terms of the isotropic and uniaxial-anisotropic models. The anisotropic model provides a closer correspondence between the simulated and experimental data. The films exhibit certain birefringence. A quasiclassical approximation was applied for assessing

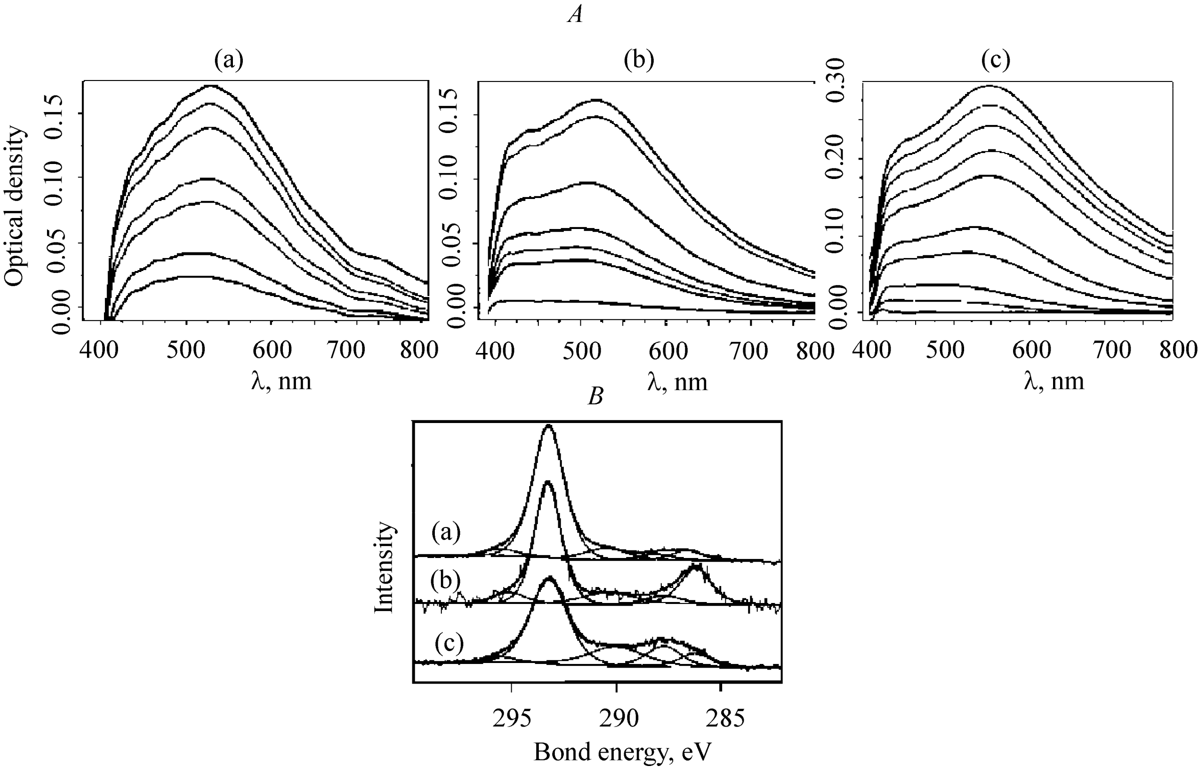

Fig. 7. (*A*) Absorption spectra of Au + polytetrafluoroethylene films during growth and (*B*) C1*s* X-ray photoelectron spectra of the films. (*A*): Films deposited (a, c) without plasma treatment, with (a) Au_{12} and (c) Au_{42} clusters and (b) films deposited with plasma treatment, with Au_{18} clusters. (*B*): (a, b, c) films with (a) Au_{42}, (b) Au_{12}, and (c) Au_{18} clusters.

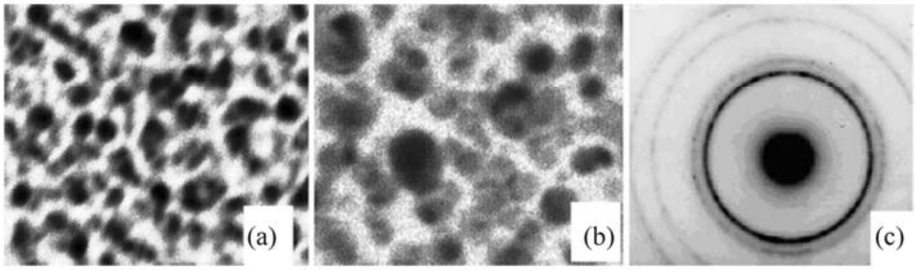

Fig. 8. Structures of Au-filled polytetrafluoroethylene (PTFE) films: (a, b) electron microscopic images of (a) Au_{12}-PTFE and (b) Au_{18}-PTFE films (×500000 magnification) and (c) electron diffraction pattern of Au_{12}-PTFE film.

the dielectric permittivity as a function of the Au cluster size. The calculated diameter of the Au clusters in the films deposited without plasma treatment is close to the average measured value (electron microscopy), while for plasma-deposited films the calculated diameter is close to the minimal measured value. This validates aggregation of clusters in plasma-deposited films.

The optical properties of the nanocomposites were simulated with the use of the modified Maxwell-Harnett theory which takes into account the shape distribution of nanolcusters [51, 56]. Comparison of the experimental and calculated spectra showed that the films contain spherical and cylindrical gold clusters in a ratio varying with the film growth conditions. The absorption spectra were also calculated for the films with nonuniform distribution of the clusters over the film thickness.

Gritsenko et al. [53] examined aluminum-filled polytetrafluoroethylene films and found that they absorbed light but got transparent because of oxidation with air supplied to the chamber. Manikowski et al.

[57] examined fullerene-filled films by optical spectroscopic and ESR methods and reported that the optical absorption spectra were broadened and blue-shifted relative to the spectra of neat fullerene films. When in high concentrations, fullerene is aggregated in films; with decreasing concentration the aggregates disappear, but the resulting spectrum differs from that of the monomer fullerene. In the spectra of the composite, the relative intensity of the absorption bands varies with decreasing fullerene concentration because of formation of new products. The band at 22200 cm^{-1} is associated with polymeric fullerene.

The relevant ESR spectra are indicative of a charge transfer in the fullerene-polytetrafluoroethylene composite films.

Codeposition of Polytetrafluoroethylene with Organic Molecules

Yang et al. [58] prepared composite films from polytetrafluoroethylene and a stilbene derivative by evaporation from the same evaporator. The stilbene concentration in the film is by 10% lower than that in the weighed portion being evaporated. Fujii et al. [59] reported on laser evaporation-deposited films of perfluorinated cyclooxyaliphatic polymer with a stilbene derivative. The films containing < 25% stilbene are amorphous, and at higher concentrations they comprise crystallites. The XPS spectra showed that there is no covalent bonding between the stilbene derivative and polytetrafluoroethylene, which suggests that the film has a composite structure.

Gritesnko et al. [25, 46, 60–62] examined polytetrafluoroethylene films filled with phthalocyanines (Pc): H_2Pc, VOPc, ZnPc, CoPc, and CuPc. Electron-microscopic examinations show that the dye forms an individual phase with 5–30-nm nanocrystallites, depending on the dye concentration. The optical spectra of phthalocyanines exhibit a two-component structure of the *Q* peak. A short-wave band suggests the presence of aggregates, and a long-wave band, of a less ordered structure. The spectrum of the H_2Pc-polytetrafluoroethylene film contains a broad peak at 610 nm. The dye molecules react together more actively than with the matrix, for which reason they form aggregates randomly spread over the matrix. The annealing of the film at 473 K caused minor changes, as follows from the corresponding spectrum.

Optical spectra of the H_2Pc-polytetrafluoroethylene films (Fig. 9) show that, at a high dye concentration, aggregates are formed, and at a low concentration, the dye molecules are "immobilized" by the matrix at their adsorption sites. The kinetic factor is responsible for formation of a nonequilibrium structure comprising individual dye molecules.

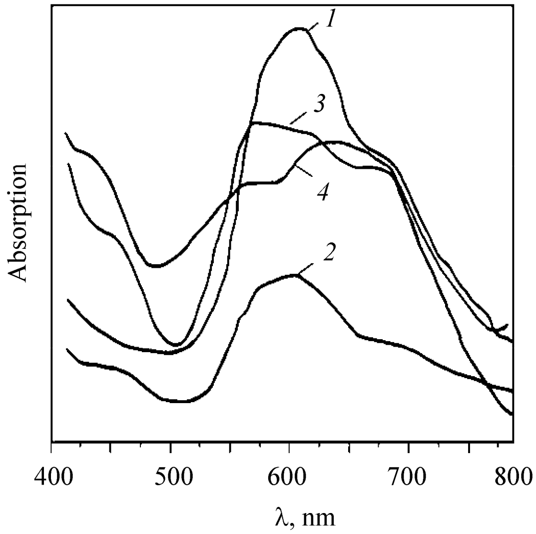

Fig. 9. Absorption spectra of annealed H_2Pc-polytetrafluoroethylene films. Annealing conditions: 200°C, 4 h. Curves (*1–4*) correspond to films with decreasing dye concentrations.

The absorption spectra of the VOPc-polytetrafluoroethylene films, both freshly deposited and annealed (Fig. 10), suggest the following. With increasing polymer content in the film the peak at 720 nm decreases in intensity more profoundly than that at 655 nm. A 0.5-h annealing is sufficient for the phase transition to occur in a neat dye film, while in the polytetrafluoroethylene matrix it is not complete even within 10 h. The peak intensity at 825 nm decreases proportionally to the polytetrafluoroethylene concentration. Film annealing results in enhanced ordering of the dye molecules inside the clusters, and not in the growth of the dye aggregates, since migration of the dye molecules, as well as the growth and phase transition from the low- to the high-temperature phase are suppressed by the polymer matrix.

Figure 11 shows the optical spectra of substituted squaraine dye deposited onto various substrates and of that incorporated into a polytetrafluoroethylene matrix. The difference in the spectra of the dye in the polymer matrix and on glass is due to the difference in the nucleation conditions. When in low concentrations in the matrix, the dye molecules occur in the monomeric form, like in the case of H_2Pc. A number of

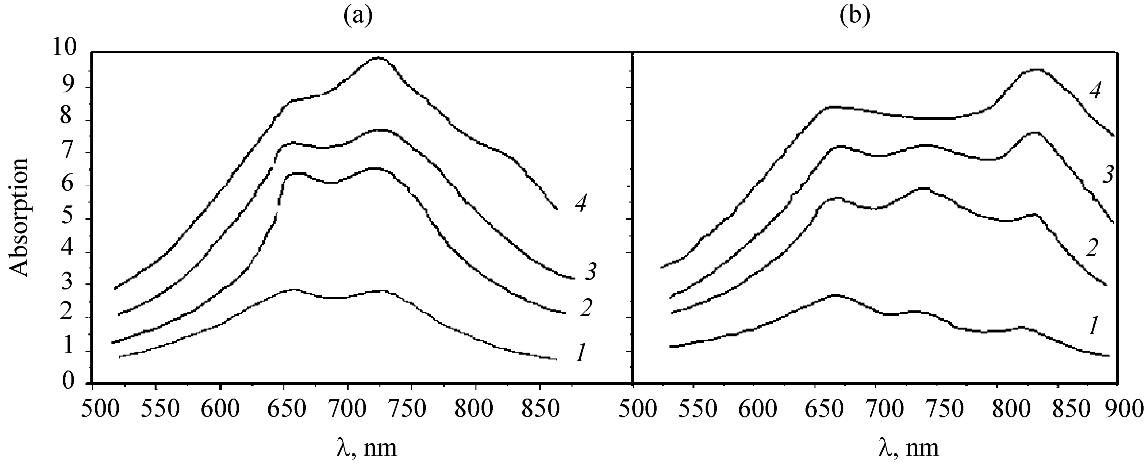

Fig. 10. Absorption spectra of (a) freshly deposited and (b) annealed VOPc-polytetrafluoroethylene films. Curves (*1*–*4*) correspond to films with increasing dye concentrations.

polymethine dyes form composites in a polytetrafluoroethylene matrix, and this is not accompanied by noticeable aggregation [55]. The use of dyes containing bulky side groups which are not aggregated even when in high concentrations allows preparation of more uniform composites.

Also, films were prepared by co-evaporation of polytetrafluoroethylene and poly(p-phenylenesulfide). It was found that, in the presence of even trace amounts of polytetrafluoroethylene, more uniform composite films are formed, able of light scattering. The refractive index of poly(p-phenylenesulfide) is 1.6–1.7, and its codeposition with polytetrafluoroethylene allows preparation of films whose refractive index can be controlled within 1.1–1.7 [51].

Multicomponent Films in a Polytetrafluoroethylene Matrix

The latest developments, in particular, those intended for sensor applications, utilize materials containing gold nanoclusters. These materials are mostly prepared from the liquid phase by the vacuum technology. The latter is very flexible as regards the selection of the formulations and substrates because of the lack of limitations associated with the wettability of the substrate and the film. There exist two methods for preparation of Au-polytetrafluoroethylene films modified with organic molecules [54, 55, 63, 64]: three-components co-evaporation in situ and immersion of an Au-polytetrafluoroethylene film into a thiol solution ex situ.

Dye-Au-Polytetrafluoroethylene Films

Figure 12 shows the absorption spectra of a CoPc-Au-polytetrafluoroethylene film, recorded during its growth, as the film thickness was increasing. The composition of the film is Au:CoPc:polytetrafluoroethylene = 6:44:50 vol % [54, 55]. The spectra of the film are superimpositions of the plasmon peak of Au (520 nm) and the bands corresponding to CoPc

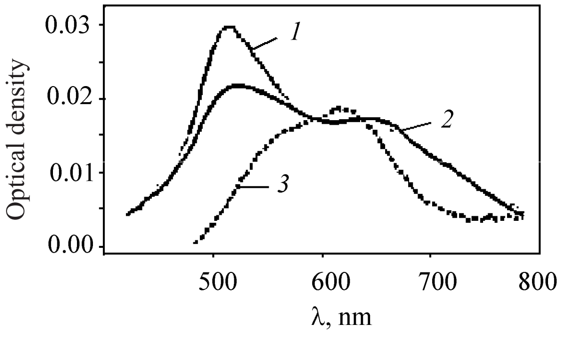

Fig. 11. Absorption spectra of hydroxyphenyl squaraine dye (*1, 2*) deposited onto (*1*) polytetrafluoroethylene sublayer and (*2*) glass and (*3*) incorporated into a polytetrafluoroethylene matrix.

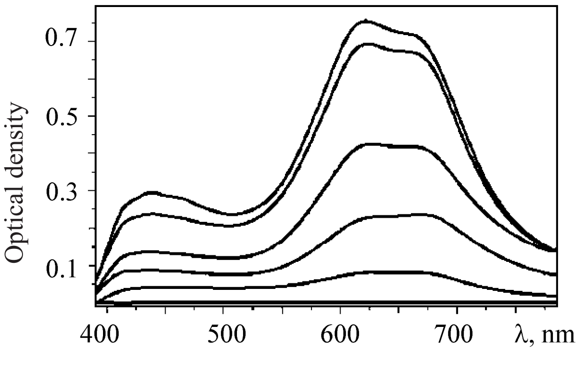

Fig. 12. Absorption spectra of CoP–Au-polytetrafluoroethylene film, recorded during the film growth.

(430, 610, and 670 nm). The band at 430 nm, associated with neat CoPc, is shifted in the spectrum of the film to 420 nm; the intensity of the band at 610 nm is lower than that at 670 nm. The former effect can be attributed to the occurrence of small Au clusters, and the latter, to active suppression of CoPc aggregation by Au clusters. The film contains 3–7-nm gold clusters, most of which are shaped as perfect spheres. The electron diffraction pattern exhibits point reflexes, which suggests formation of crystallites with a predominant orientation. Such multicomponent films can contain newly identified structures having novel properties. Also, films of different metal phthalocyanines and polymethine dyes were prepared on a polytetrafluoroethylene matrix with gold clusters. The relationships in formation of the structure of this film are identical to those described above, as expected for all the films in which the components do not enter into chemical reactions.

The absorption spectra of an azo dye-Al-polytetrafluoroethylene film are superimpositions of those of the dye and aluminum. The absorption of the films decreases because of oxidation of aluminum nanolusters in air. Some dyes in such systems are also oxidized [51], by contrast to the system with a neat polytetrafluoroethylene matrix. Aluminum nanoclusters exhibit certain catalytic activity.

Thiol Modification of Au-Polytetrafluoroethylene Films

Gritsenko et al. [54] carried out experiments with keeping Au-polytetrafluoroethylene films in solutions of various thiols and examined their sensor properties with respect to organic vapors. Figure 13 shows the absorption spectra of the Au-polytetrafluoroethylene film deposited onto a quartz substrate before and after keeping in a dodecanethiol solution. The absorption spectrum of this film has two specific features: a decrease in the optical density with increasing wavelength and the occurrence of a plasmon resonance peak near 530 nm. The plasmon peak intensity varies with the Au cluster size, the distance between them, and the ambient characteristics. Upon thiol modification of the film, the plasmon peak is blue-shifted; its intensity and the absorption in the red region are enhanced. The reaction between the sulfur and Au atoms results in thiol adsorption from solution onto the gold cluster surface.

The electron-donating sulfur atoms cause the electron density of the clusters to increase. The C1*s* and S2*p* peaks in the X-ray photoelectron spectrum suggest an increase in the hydrocarbon content and the occurrence of the Au–S bond in all the modified films. However, the spectral line intensities vary with the kind of thiol and the film preparation procedure employed. The film deposited under plasma treatment is characterized by a lower concentration of dodecanethiol.

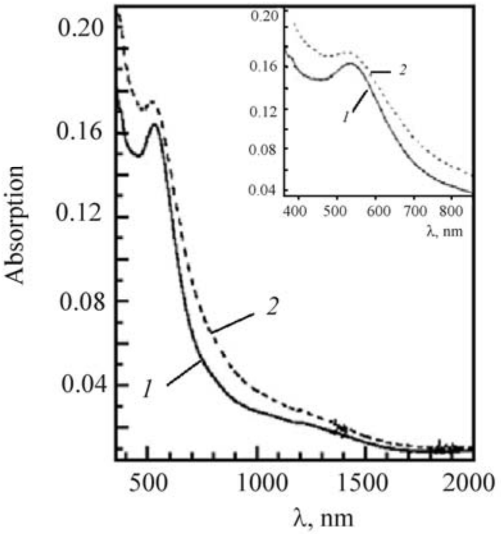

Fig. 13. Absorption spectra of Au-polytetrafluoroethylene film (*1*) before and (*2*) after modification with dodecanethiol.

Examination of the sensor properties of the films involved recording their reflection spectra in a spectrometer with a hermetically sealed cell through which pentane vapor was passed (Fig. 14). The maximum and minimum in the spectrum are shifted to long waves, which suggests film thickening. The spectra were analyzed by standard numerical matrix

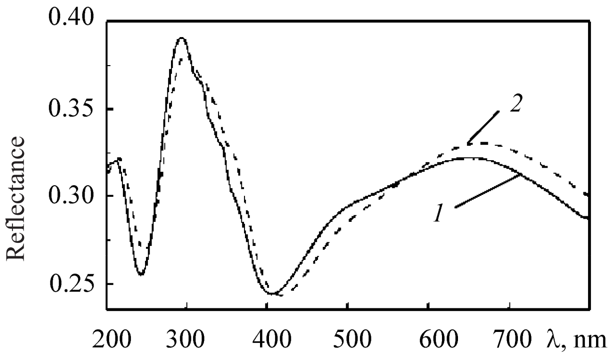

Fig. 14. Reflection spectra of Au-polytetrafluoroethylene film modified with dodecanethiol (*1*) before and (*2*) after

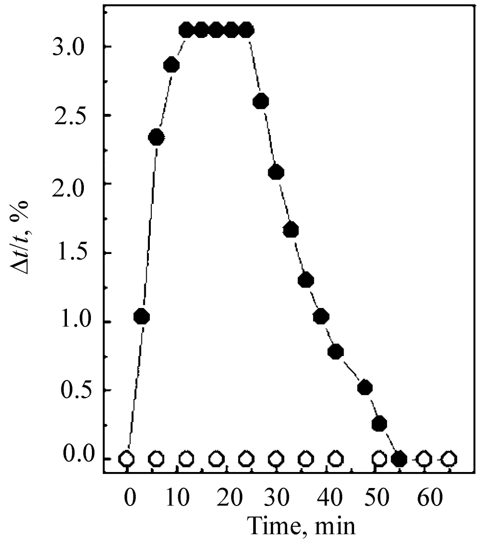

Fig. 15. Response from Au–polytetrafluoroethylene films before and after functionalization to pentane vapor: (○) initial film and (●) dodecanethiol-modified film.

method. The film thickness gradient (Δt/t) served as the sensor response. Figure 15 shows how the sensor response in the initial and modified films varies with the time of keeping in pentane vapor. The functionalized film exhibits the inverse sensor response (signal growth time ~8 min; restoration time 20 min). The initial film is insensitive to pentane vapor. Those experiments also involved examination of the sensitivity to acetone for the films modified with various thiols. The results suggest that the modified Au-polytetrafluoroethylene films are suitable as chemical sensors.

Application of Thin Polytetrafluoroethylene Films

Polytetrafluoroethylene films are suitable as protective, antifriction, and dielectric layers [19–30]. In sensors, fluorpolymers serve as substrates in selective deposition of reactive materials [65], layers with controlled permeability by gases [66, 67], and matrices for immobilization of reactive material nanoparticles [34–38, 68, 69].

It was found that a thin polytetrafluoroethylene layer deposited by the friction transfer in one direction at 300°C is capable of orienting other substances when deposited both from liquid [70] and gas [71, 72] phases. This method was extensively used for preparation of oriented films of various materials. More recently it was found that vacuum-deposited polytetrafluoroethylene films that were subsequently rubbed with a cloth in one direction acquire the orienting power as well [73–75]. The polarized absorption spectra of a film of substituted squaraineund showed that it contains H- (530 nm) and J- (780 nm) aggregates, with the concentration of the latter increasing with film thickening. However, Gritesenko et al. [75] found that the dichroism better correlates with absorption near the monomer peak and presumed that formation of the J-aggregates is associated with the geometric action of the sublayer, and formation of H-aggregates, with intermolecular interactions. Figure 16 shows the relief of the substituted squaraine films deposited onto a polytetrafluoroethylene sublayer.

On a sublayer deposited by the hot slip method, fairly large individual squaraine crystals are grown. The sublayer prepared by vacuum evaporation and not rubbed with a cloth contains medium-sized disoriented crystals. On the rubbed sublayer, the smallest crystals are grown, in which all the molecules are regularly oriented. The orientation is governed by the ratio of the energies of interaction of the dye molecules with one another and with polytetrafluoroethylene. Each subsequent dye layer grows only under the action of the dye proper. In the case of a vacuum evaporation-

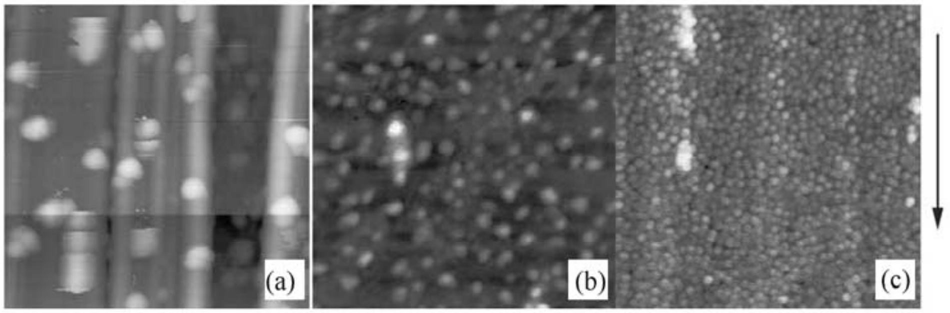

Fig. 16. Relief of substituted squaraine films on polytetrafluoroethylene sublayers, deposited by various procedures: (a) hot slip under pressure; (b) vacuum evaporation, and (c) vacuum evaporation followed by film rubbing with a cloth.

deposited polytetrafluoroethylene sublayer rubbed with a cloth, a much more uniform dye film is formed, which suggests a higher energy of its interaction with the dye.

The latest studies of the orientation action in relation to the polymer sublayer thickness, as well as to the structure of squaraine series dyes and pentacene [76–80], showed that the optimal thickness of the polytetrafluoroethylene film lies within 50–70 nm. The orienting action of the film is manifested for a series of compounds, through fairly limited one. Among squaraines, dialkylaminohydroxyaryl compounds are oriented solely. On this basis, the following mechanisms of the orientation action of the polytetrafluoroethylene film were proposed: geometric matching of the dye and polytetrafluoroethylene lattices; topographic ordering; and intermolecular interaction. Our experiments support the last-named mechanism, but they also revealed the influence exerted by the surface topography. Possibly, each of the three mechanisms makes a contribution, whose size varies with the properties of the growing film and the orienting sublayer, as well as with the deposition regime.

Also, bilayer films were prepared from squaraines with methyl (Me-OHSQ) and ethyl (Et-OHSQ) terminal groups. In both cases the deposition of the second layer causes the dichroism of the film to enhance. The second harmonics signal increases only in the system comprising Me-OHSQ dye as the first layer [79, 80]. Both systems have a crystalline structure; their unit cells are characterized by parameters sufficiently close for providing the layer epitaxy and at the same time sufficiently different for generation of the second harmonics in the system characterized by the Me-OHSQ unit cell even with symmetrical molecules. However, the situation with the cell parameters and the generation of the second harmonics still remains to be elucidated.

Also, the development of planar fluoropolymer waveguides for integrated optical facilities is under way [8, 51]. A broad transparency range stretching from ultraviolet to near infrared region makes polytetrafluoroethylene highly promising for optical applications. Depending in the film deposition mode, films with amorphous structure and the refractive index within 1.1–1.42 can be prepared [51, 81]. This allows deposition of waveguides from the same polytetrafluoroethylene sample by varying the formation mode: a sublayer with the refractive index of 1.1–1.2, and a core with the refractive index of 1.25–1.35. The optical loss in such waveguides with a thickness of 0.5 μm does not exceed 1dB cm^{-1}, which is acceptable for application in integrated optical facilities. Waveguides can be doped with reactive compounds to develop elements for controlling optical radiation, sensors, etc.

Polytetrafluoroethylene films with micro zones serve as a basis for development of polymer microlenses [82]. Polytetrafluoroethylene films filled with silver and gold nanoclusters are applied as antimicrobial coatings [83]. Also, nanostructured films [84] and nanotubes [85] were prepared from polytetrafluoroethylene by gas-phase deposition methods.

CONCLUSIONS

Heating polytetrafluoroethylene in a vacuum with activation of the evaporation products constitutes a flexible technology for preparation of neat and composite nanostructured films. The film properties can be controlled by deposition parameters. Polytetrafluoroethylene films filled with metal and organic nanoclusters hold promise for photonic, optoelectronic, medical, and biological applications as waveguides, sensors, etc.

ACKNOWLEDGMENTS

The author is grateful to all the participants of the studies presented, including colleagues from the Institute of Information Recording Problems; Institute of Organic Chemistry; Institute of Materials Science Problems; Institute of Semiconductor Physics. National Academy of Sciences of Ukraine; Institute of Metal-Polymer System Mechanics, National Academy of Sciences of Belarus; Poznan University of Technology, Poland; Federal Institute for Materials Research and Testing, University of Potsdam (Germany); University of Applied Sciences, Wildau (Germany); Institute of Nanostructured Materials, Italy; and Institute Charles Sadron, France. Also, the author is grateful to Academician Yu. M. Pleskachevskii; Corresponding Member of the Russian Academy of Sciences O. E. Belyaev; Dr. V. A. Barachevskii; Prof. R. A. Lessard; and Prof. L. Bremer for their personal contribution to promoting this scientific direction.

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