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Influence of Heterogeneous Physicochemical Processes on the Parameters of Low-Temperature Plasma

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Abstract—The influence of the gaseous products of heterogeneous processes, such as recombination and deactivation of active species on the physical characteristics of plasma and the rates of the processes involving electrons is considered.

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INTRODUCTION

Nonequilibrium plasma is widely used for etching and modification of the surface of polymer materials [1–5]. The reactions of polymers with plasma induce heterogeneous physicochemical processes on the contacting surface, which affect the plasma parameters and, consequently, efficiency of the plasma chemical treatment of the material. These processes depend on the nature and properties of the polymer being treated and the treatment process parameters.

Influence of Plasma-Confining Surface Properties

The so-called loading effect, specifically, dependence of the etching rate of silicon plates on their quantity in a low-pressure plasma reactor is well known in microelectronics [6, 7]. Similar changes in etching rates were also observed in the plasma chemical treatment of polymer materials used in semiconductor manufacturing [8–10]. The explanation of this effect is commonly based on the assumption of a constant rate of generation of plasma reactive species, and account is taken only of changes in their flux toward the plasma-contacting surface. Actually, the probabilities of reaction of the reactive species with different surfaces vary several orders of magnitude (see Table 1), and the apparent polymer etching rate depends on the material of the reactor wall, i.e. on the boundary conditions for reactive species that react with the polymer and deactivate at the wall [1]. The rate constants of heterogeneous recombination decrease from metals to their oxides and polymers. Furthermore, not only the wall material should be taken into account, but also the temperature conditions. As follows from the result of research on the influence of temperature of the reaction kinetics of plasma reactive species with polymers (Table 2), the rates of processes with a high activation energy E_a are quite sensitive to temperature (the fluxes of plasmolysis products into the gas phase may vary several orders of magnitude). Moreover, the fractions of the products of plasma chemical decomposition of polymers may also vary [1].

Influence of Gaseous Products of Plasma Treatment of Polymers

Exposure of polymers to plasma is almost always accompanied by the formation of gaseous products which affect the composition and properties of plasma and, as a consequence, the rate of most physicochemical processes that occur at the plasma–polymer interface. Such a feedback forms a nonlinear system with a complicated dynamic behavior [55].

The effect of gaseous products should be taken into account in designing industrial plasma chemical reactors, where plasma is completely confined by the polymer being treated. The flux of gaseous products in typical plasma chemical reactor compares with the flux of the initial plasma-forming gas [1]. The composition of the reaction of plasma with polymers depend on the nature of the initial plasma-forming gas and on the composition of the polymer (Table 3).

Table 1. Recombination coefficients of oxygen atoms on different surfaces[a]

Material	Recombination probability	Reference	Material	Recombination probability	Reference
			In the plasma zone		
Molybdenum glass	$(0.85–5.6)\times10^{-3}$	[11. 12]	PVC	$(1.5–6.5)\times10^{-3}$	[20]
	$(0.4–4.5)\times10^{-3}$				
	1.9×10^{-4}	[13]	α-Al_2O_3	$(2.9–19.7)\times10^{-2}$	[22]
Pyrex	$2.5\times10^{-3}–4\times10^{-2}$	[14]	α-Al_2O_3 + AlN	$(1.2–11.5)\times10^{-2}$	[22]
Al	$(3.5–6.2)\times10^{-1}$	[15]	$ZrO_2 + Y_2O_3$ $ZrO_2 + CaO$ $ZrO_2 + MgO$	$(0.8 – 2)\times10^{-1}$	[23]
	$(2.5– 8)\times10^{-2}$	[16. 17]	β-cristobalite	2.7×10^{-2}	[24]
	$1\times10^{-2}–4\times10^{-1}$	[18]	β-Quartz	8×10^{-3}	[24]
	$(0.3–3)\times10^{-2}$	[19]			
			In the afterglow zone		
Quartz	$3\times10^{-5} – 3\times10^{-4}$	[25]	Fe	4.1×10^{-1}	[37]
	$1.6\times10^{-4} – 1.4\times10^{-2}$	[26, 27]	Mg	3×10^{-3}	[36]
	$8.6\times10^{-5} – 4\times10^{-4}$	[28]	Mg	$(1.2 – 2.3)\times10^{-3}$	[33]
	$7\times10^{-5} –10^{-4}$	[12]	Nb	9.0×10^{-2}	[37]
	$2\times10^{-5} – 2\times10^{-4}$	[29]	Ni	$8\times10^{-3} – 3\times10^{-2}$	[36, 38]
	$(1.00 – 2.83)\times10^{-5}$	[30]	Ni	2.7×10^{-1}	[37]
Pyrex	$(1.3\pm0.3)\times10^{-4}$	[31, 32]	Pd	$3\times10^{-4}–1.4\times10^{-2}$	[36]
	$(5.6 – 9.2)\times10^{-5}$	[33]	Pt	0.2	[36]
	$(2.4\pm1.1)\times10^{-3}$	[34]	Pt	$(1.6–2.7)\times10^{-3}$	[33]
	3.1×10^{-5}	[35]	Ta	0.3	[36]
	4.5×10^{-5}	[35]	W	$(2–12)\times10^{-2}$	[36]
Ag	0.12–1.00	[36]	Sb	8.2×10^{-4}	[31]
Al	6.8×10^{-3}	[36]	As	4.6×10^{-4}	
	$(2.9 – 4.4)\times10^{-3}$	[33]	Se	1.7×10^{-4}	
Al + Ni	3.6×10^{-3}	[33]	Al_2O_3	$(1.3–1.7)\times10^{-3}$	[33]
Al + teflon	2.0×10^{-3}	[33]		$(1.8–3.4)\times10^{-3}$	[31, 35]
Au	$3\times10^{-4}–3\times10^{-2}$	[36]	B_2O_3	2.8×10^{-4}	2.8×10^{-4}
Au	$(1.9 – 3.2)\times10^{-3}$	[33]		6.3×10^{-5}	6.3×10^{-5}
Co	5×10^{-3}	[36]	CaO	1.6×10^{-3}	1.6×10^{-3}
Cr	$2\times10^{-2} – 1\times10^{-1}$	[36]	CdO	1.6×10^{-3}	1.6×10^{-3}
Cu	$(3–17)\times10^{-2}$	[36]	Co_3O_4	2.5×10^{-3}	2.5×10^{-3}
Cu	$(1.9 – 2.6)\times10^{-2}$	[33]	CoO	4.9×10^{-3}	4.9×10^{-3}
Cu	2.3×10^{-1}	[37]	Cr_2O_3	$(2–2.5)\times10^{-4}$	$(2–2.5)\times10^{-4}$
Fe	$(2–4)\times10^{-2}$	[36]	Cu_2O	1.1×10^{-1}	1.1×10^{-1}

Table 1. (Contd.)

Material	Recombination probability	Reference	Material	Recombination probability	Reference
In the afterglow zone					
B_2O_3	2.8×10^{-4}	[31]	PbO	$(5.8–6.3)\times10^{-3}$	[27, 35]
	6.3×10^{-5}	[35]	SiO_2	7.1×10^{-4}	[31]
CaO	1.6×10^{-3}	[35]	SnO_2	1×10^{-3}	[35]
CdO	1.6×10^{-3}	[26]	V_2O_5	4.8×10^{-4}	[35]
Co_3O_4	2.5×10^{-3}	[26]	WO_3	1.7×10^{-2}	[35]
CoO	4.9×10^{-3}	[35]	ZnO	$(4.4–5.9)\times10^{-4}$	[26, 35]
Cr_2O_3	$(2–2.5)\times10^{-4}$	[26, 35]	PVC	$(5.0–6.0)\times10^{-4}$	[39]
Cu_2O	1.1×10^{-1}	[26]	PAA	$(5.0–6.0)\times10^{-5}$	[39]
CuO	$(2–4.5)\times10^{-2}$	[26, 31, 35]	PIB	$(1.0–2.0)\times10^{-4}$	[39]
Fe_2O_3	$(5.2–8.5)\times10^{-3}$	[26, 31, 35]	PVA	$(2.0–3.0)\times10^{-4}$	[39]
Ga_2O_3	1.3×10^{-4}	[35]	PI	1.0×10^{-4}	[40]
GeO_2	1.3×10^{-4}	[35]	PP	1.0×10^{-4}	[40]
MoO_3	1×10^{-3}	[35]	PE	1.2×10^{-4}	
	$(1.1–2.5)\times10^{-2}$	[26, 35]	PETP	2.0×10^{-4}	
Mn_2O_3	2×10^{-3}	[26]	PTFE	$(6.4 – 7.3)\times10^{-5}$	[33. 35]
	1.3×10^{-2}	[35]		$(4.4–4.8)\times10^{-5}$	[39]
NiO	$(1.5–8.9)\times10^{-3}$	[26, 27, 35]			

[a] (PVC) Polyvinyl chloride; (PETP) polyethylene terephthalate; (PVA) polyvinyl alcohol; (PTFE) polytetrafluoroethylene; (PAA) polyacrylic acid; (PIB) polyisobutylene; (PI) polyimide; (PP) polypropylene; and (PE) polyethylene.

Treatment of polyolefins with an inert gas plasma results in a release of hydrogen and small amount of methane, and, therewith, the yield of methane increases with increasing branching of the polymer chain. In the case of an oxidative plasma, the main gaseous products are CO_2, CO, H_2O, and H_2. The relative rates of release of these products depend not only on the composition and structure of the polymer, but also on the discharge parameters (pressure, discharge current or power, plasma-forming gas flow rate) [56], as well as duration of plasma treatment.

Research on the kinetics of the formation of gaseous products in an oxygen or air plasma at the initial, nonsteady-state stage of the process [57, 58, 65, 70] showed that the plasma-induced oxidative polymer degradation begins with hydrogen abstraction of the macromolecule. The time dependences of the rate of hydrogen release pass peak at characteristic times of 0.2–0.5 s. Upon long-term exposure of polymers to plasma generated in an oxygen flow, the rate of release of molecular hydrogen is generally very low. Within the first few seconds of plasma treatment the rate of consumption of oxygen from the gas phase is higher than the rate of its release in the composition of gaseous products. This fact suggests formation of an oxidized modified film on the surface of the material being treated. However, if plasma treatment is prolonged to minutes or tens of minutes, the rates of oxygen release with products and oxygen consumption almost equalize (within experimental error), implying equal rates of degradation and restoration of the oxidized film. Consequently, the properties of plasma (electrophysical parameters) in the first few seconds of treatment may radically differ from those in the steady state [1].

The composition of gaseous products is enriched, if the macromolecule contains functional groups. Thus, the plasma oxidative degradation of polyvinyl chloride involves HCl release at a rate close to the rates of formation of oxygen-containing molecules. One of the products of the oxidative degradation of polyimide in a low-pressure oxygen plasma is NO (a product of imide ring cleavage in the macromolecule).

Table 2. Apparent activation energies of reactions of plasma and polymers

Polymer	Plasma-forming gas	E_a, kJ/mol	Reference
Polyimide	$[O_2] : [CF_4] : [Ar] = 75 : 20 : 5$	12.5±3	[41]
	H_2	37.7	[42]
	O_2	11.7	[42]
		20±6, 43±6	[43]
		48±6 to 7±3	[44]
	$O_2 + CF_4$	20.2	[8]
		7±3	[45]
Polyethylene	O_2	0	[46]
		0.38.8±8.8	[47]
	O_2 afterglow	0.41.9±13.3	[47]
Polyvinyl alcohol	O_2	12.5	[39]
Polyacrylic acid	O_2	12.5	[48]
Polyvinyl chloride	O_2	83.5,20	[39]
		7.94±0.5, 6.9±0.4	[47]
	O_2 afterglow	104±29, 27.2±7.5	[49]
		104±26, 27.2±3.5	[47]
Poly(2,3-dichloro-1-propyl acrylate)	O_2	13.4	[50]
Poly(*N*-vinylcarbazole)	O_2	2	[50]
Poly(methyl methacrylate)	CF_4+O_2	13–27	[50]
	CF_4	113	[50]
	O_2	40.5	[50]
		76±19, 4 5±11	[47]
	O_2 afterglow	105±23	[47]
Phenol-formaldehyde resin	O_2	61.3, 43.5	[51]
Polyethylene terephthalate	O_2 afterglow	41±3	[52]
	O_2	18±3, 35±2	[53]
Polytetrafluoroethylene	O_2	15	[54]

As a rule, gaseous products are formed by several routes dependent on different reactive plasma components [59]. At the same time, the fact that the products have equal apparent activation energies of formation point to a nonlinear relationship between the product formation routes. Unfortunately, no deeper insight into these interrelationships is possible because of the scarcity of available published evidence.

The impact of gaseous products on the electrophysical parameters of plasma is the stronger, the larger is the difference in the effective total electron scattering cross sections (especially in the low-energy range) for the initial plasma-forming gas and the mixture of gaseous polymer plasmolysis products.

At a fixed reduced electric field intensity, increasing content of etching products in an oxygen/air plasma (CO_2, CO, H_2O, H_2) slows down high-threshold plasmolysis processes because of the decreasing fraction of energetic electrons in the plasma (Fig. 1). The effect of each concrete product depends not only on its mole fraction, but also on the threshold energy of the elementary processes under consideration and on the reduced electric field intensity (E/N). The most essential changes in the kinetic characteristics of electrons take place at low E/N values (high pressures), and the effect is the stronger, the higher threshold energies (E_n) are characteristic of the specific elementary process (Fig. 2). It is also noteworthy that similar processes involving an

Table 3. Gaseous reaction products of nonequilibrium plasma with polymers

Polymer	Plasma-forming gas	Products	Reference
Polyethylene	He, Ar, Kr	H_2	[60, 61]
Docosane, polypropylene, polyisobutylene	Ar	H_2, CH_4	[62]
Polyvinyl alcohol	Ar	H_2, H_2O, CO	[39]
Polyacrylic acid	Ar	H_2, H_2O, CO, O_2	[39]
Polytetrafluoroethylene	He	CF_4, C_2F_4, C_2F_6, C_3F_6, C_3F_8,	[63]
	He, He + O_2	COF_2, C_2F_4, CF_4, C_2F_6, C_3F_6,C_3F_8, CO_2, CO	
Docosane, polyethylene, polypropylene, polyisobutylene, polyvinyl alcohol, polyacrylic acid, polyethylene terephthalate	O_2 O_2+Ar Air	CO_2, CO, H_2O, H_2	[64–67, 58] [68] [69–72]
	O_2+N_2	CO_2, CO, H_2O, H_2, NH_3	[73, 74]
Polyvinyl chloride	O_2	CO_2, CO, H_2O, H_2, HCl	[75, 76]
Polychlorodiphenyl	O_2	CO_2, CO, H_2O, H_2, HCl, Cl_2, ClO_2	[64]
	H_2	HCl, butane, ethane, propane, isobutane, pent-1-ene	[64]
Isoprene photoresist	O_2	CO_2, CO, H_2O	[77]
Kapton-H polyimide	O_2, SF_6, O_2+SF_6	CO, CO_2, H_2O, CF_4, HF, COF_2,	[92]
	O_2	CO_2, CO, H_2O, H_2, NO	[57, 67, 78, 79]
	O_2 + CF_4	CO_2, CO, H_2O, COF_2, COF, HF	[44]

admixture (for example, its ionization or dissociation), as well as changes in the conductivity of plasma and the attendant changes in electron concentration at a given E/N value cannot compensate for the slowdown of the process involving the initial plasma-forming gas.

Influence of Processes at the Discharge–Solution Interface in Plasma–Solution Systems

One of the characteristic examples of the influence of the heterogeneous physicochemical processes that

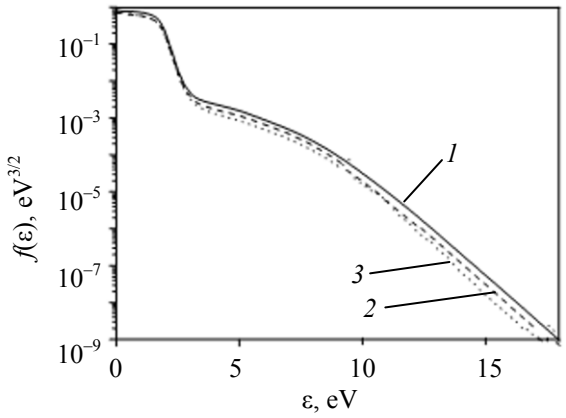

Fig. 1. Energy distribution of electrons in an air plasma: (*1*) without polymer and in the presence of a polypropylene film with the total molar fractions of products (CO_2, CO, H_2O, H_2) of (*2*) 0.076 and (*3*) 0.115. $E/N = 4.59 \times 10^{-16}$ V/cm^2.

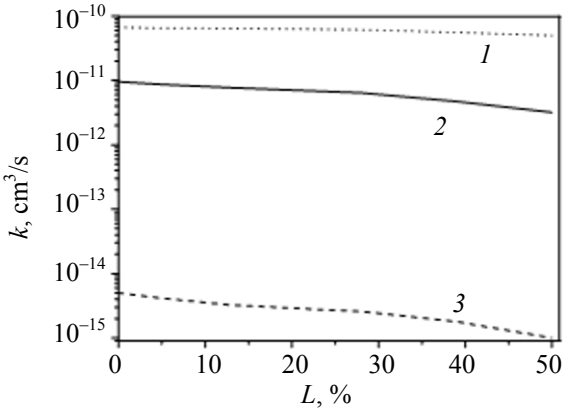

Fig. 2. Dependence of the rate constants of (*1*) $O_2(a^1D_g)$ excitation by direct electron impact (E_n = 0.982 eV), (*2*) O_2 dissociation (E_n = 6.1 eV), and (*3*) O_2 ionization (E_n = 12.08 eV) on the reactor loading with polypropylene film. Air plasma, $E/N = 4.59 \times 10^{-16}$ V/cm^2.

occur at the discharge–electrolyte solution (cathode) on the electrophysical parameters of low-temperature plasma is provided by transfer of liquid cathode particles in plasma–solution systems. Liquid cathode discharge glowing suggests emission of electrons from the electrolyte solution. Measurement of electrolyte cathode potentials and evaluation of electron g-emission coefficients in terms of the classical theory of cathode voltage drop showed that the emission coefficients for such cathodes lower by an order of magnitude compared to the respective values for metal cathodes under low-pressure glow discharge conditions [80–83]; however, ion bombardment of the surface of an electrolyte cathode gives rise to cathode sputtering, a process involving nonequilibrium transfer of solution components to the plasma zone. The transfer coefficients of solvents and solutes from aqueous salt solutions are reported in [83–85].

The transfer of water molecules from a liquid water cathode into plasma increases the electric field intensity compared with an atmospheric pressure discharge between metal electrodes (other plasma ignition conditions being equal) [86, 87]. This is explained by the fact that electrons more frequently «stick» to water molecules, thereby affecting the balance of changed species (accelerated decay of electrons requires that the ionization rate be higher to maintain the desired discharge current), as well as by higher rates of pulse transfer to H_2O molecules in the low-energy range, which prevents energy transfer to electrons from the field, slows down reactions involving electrons, and their mean energies and drift rates. This effect is especially characteristic of discharges with low E/N values [88]. Since the temperatures in the gas phase of a liquid-cathode glow discharge are also higher, the reduced electric field intensity in this case is double as high as in atmospheric-pressure microdischarges between metal electrodes [86]. Note that the apparent vibrational temperatures in both types of discharge coincide within measurement error, whereas the current densities (and, consequently, scattered power density) in the positive plasma column are quite different because of the cathode spot dimensions. As a result, the electron mean energies and concentrations in the two types of discharge in focus differ essentially.

When solutions of salts of metals with low ionization potentials are used as liquid cathodes, the transfer of atoms to the discharge zone and considerable increase of ionization rate affect the balance of charged species, electric field intensity, and energy distribution of electrons in the plasma, but, therewith, the plasma composition does not change considerably (the molar fraction of atoms is not higher than 0.001). As a rule, the field intensity increases with increasing concentration of salt solutions used as a liquid cathode, and this change is the greater, the lower is the ionization potential of the metal in the salt. The presence of threshold currents that induce emission of metal atoms in the plasma can be explained as follows. If the power scattered on the electrolyte cathode is lower of a critical (threshold) value, we deal primarily with molecular transfer of the solvent to gas phase. At higher powers, clusters comprising hydrated solute species start to appear in the flux from the cathode surface. The presence of coarse clusters is evidenced by high water transfer coefficients (the number of molecules transferred to the plasma per one ion transferred to the solution) which equal 5×10^2–10^3 for dilute solutions of alkali metal halides [87].

Influence of Reactor Loading

A number of publications are available in the literature that report the results of research on the influence of the degree of reactor loading with polymer materials on the electrophysical parameters of low-pressure glow discharge, such as the intensity of electric field in the plasma [40, 89–91], temperature of the neutral components of the plasma [40, 89], and concentration of certain plasma components [40, 89, 92, 97].

Turban and Papeaux [92] established in their study on the etching of polyimide and epoxide resin in radiofrequency O_2/CF_4 and O_2/SF_6 plasmas that the relative concentrations of some gaseous etching products change with increasing surface area of the material being treated. The way in which the etching rate varies with increasing sample surface area depends on process conditions and polymer properties.

As shown in [78], as the surface area of the polyimide film treated in a dc oxygen plasma is increased, the etching rate not only does not decrease, but also it becomes less sensitive to discharge parameters (current and pressure). According to mass spectral measurements, with increasing surface area of a polymer sample, a decrease the rates of oxygen consumption and formation of oxygen-containing products is observed; with hydrogen, an inverse dependence takes place.

The results of field intensity measurements in an oxygen plasma confined by different materials (glass, polyethylene, polyimides) [90] showed that the appearance of reacting species in the plasma not only the field intensity, but also its dependence on the discharge current and the plasma-forming gas flux.

In [89] we studied the influence of the loading of the laboratory reactor with a polyethylene terephthalate fabric on the parameters of a dc discharge plasma in air. The portion of the reactor wall, covered by the polymer material, was as large as 50%. The rate of weight loss of the sample, the electric field intensity, and the emission line intensities of the second positive system of molecular nitrogen ($C^3\Pi_u \rightarrow B^3\Pi_g$ transition) and atomic oxygen were measured. The composition of stable products in the gas phase was determined by mass spectrometry. The gas temperature, apparent vibrational temperature of N_2 molecules, and concentration of oxygen atoms were found from spectral measurements.

Study of the dependence of the weight loss of a polyethylene terephthalate fabric and the plasma concentration of atomic oxygen on the surface area of the material being treated [40] showed that already at a low fabric loading (covers only a ~10% portion of the wall) the plasma concentration of atomic oxygen considerably decreases. As a result, the concentration of NO molecules formed in an air plasma decreases with reactor loading almost 8-fold. The UV flux intensity also decreases due to deactivation of excited NO molecules. The presence of polymer in the plasma strongly decreases the apparent vibrational temperature of N_2 molecules.

The experiments also revealed a 10% increase in field intensity in the case of treatment of samples with a large surface area and an almost the same decrease in gas temperature along the reactor axis. As a result, at fixed discharge current and total pressure, the reduced electric field intensity varies only slightly [40]. Similar results were obtained in an oxygen plasma.

The influence of the surface area of polymer films on their surface composition on treatment in oxygen [93], oxygen/nitrogen [94], and nitrogen plasmas [95] was studied by Fourier transform IR spectroscopy. It was found that the functional groups formed by plasma treatment are nonuniformly distributed in the thin surface polymer layer. Similar studies on polyethylene terephthalate fabrics in oxygen [96] and air plasmas [97] showed that the oxygen plasma, all other conditions (pressure, discharge current, plasma-forming gas flow rate) being equal, is less sensitive to the loading effect than the air plasma: The rates of all processes decrease slower and the contributions of degradation channels remains invariable. This results is most likely explained by the fact that nonequilibrium oxygen plasma is a less complicated system having less feedback channels between plasma parameters and rates of heterogeneous physicochemical processes, and the composition of the gas phase in the oxygen plasma is less sensitive to the reagent than in the air plasma. It can be suggested that the accumulation of degradation products in the gas phase, while slowing down the generation rates and decreasing the flux of reactive species toward the surface, does not affect the relative contributions of the fluxes. If the plasma –sample contact time is shorter that the characteristic times of chemical reactions, the rates of heterogeneous processes are controlled by contact times. The mutual effect of heterogeneous and bulk processes becomes appreciable even if the plasma –sample contact times are longer than the characteristic times of chemical reactions.

CONCLUSIONS

Nonequilibrium plasma is a unique tool for modifying the properties of its contacting materials and products. To design and optimize the main physicochemical and technological processes involving plasma treatment, one should construct models based on the solution of the Bolzmann equation and vibrational and chemical kinetics equations with account for the interrelationship between the physical parameters of plasma and the rates of heterogeneous processes that occur at the plasma-confining surface.

REFERENCES

1. Kutepov, A.M., Zakharov, A.G., and Maksimov, A.I., *Vakuumno-plazmennoe i plazmenno-rastvornoe modifitsirovanie polimernykh materialov* (Vacuum Plasma and Plasma Solution Modification of Polymer Materials), Moscow: Nauka, 2004.
2. *Entsiklopediya nizkotemperaturnoi plazmy* (Encyclopedia of Low-Temperature Plasma), Lebedev, Yu.A., Plate, N.A., and Fortov, V.E., Eds., Moscow: Yanus-K, 2006, special issue XI–5.
3. *Entsiklopediya nizkotemperaturnoi plazmy* (Encyclopedia of Low-Temperature Plasma), Fortov, V.E., Ed., Moscow: Nauka, 2000, introductory vol. 4, p. 386
4. *Entsiklopediya nizkotemperaturnoi plazmy* (Encyclo-

pedia of Low-Temperature Plasma), Fortov, V.E., Ed., Moscow: Nauka, 2000, introductory vol. 4, p. 399.

5. *Entsiklopediya nizkotemperaturnoi plazmy* (Encyclopedia of Low-Temperature Plasma), Fortov, V.E., Ed., Moscow: Nauka, 2000, introductory vol. 3, p. 576.
6. *Plasma Processing for VLSI*, Einspruch, N.G. and Brown, D.M., New York: Academic, 1985, 1st ed.
7. *Semiconductor Lithography: Principles, Practices, and Materials*, Moreau, W.M., Ed., New York: Plenum, 1990, part 2.
8. Lamontagne, B., Wrobel, A.M., Jelbert, G., and Wertheimer, M.P., *J. Phys. D: Appl. Phys*., 1987, vol. 20, no. 7, pp. 844–850.
9. Economau, D., Aydit, E.S., and Barno, G., *Solid State Technol*., 1991, vol. 34, no. 4, pp. 107–111.
10. Lerner, N.R. and Wydeven, T., *J. Electrochem. Soc*., 1989, vol. 136, no. 5, pp. 1426–1430.
11. Brovikova, I.N., Kholodkova, N.V., and Kholodkov, I.V., *Surf. Eng. Appl. Electrochem*., 2011, vol. 47, no. 2, pp. 167–169.
12. Kholodkova, N.V., Kholodkov, I.V., and Brovikova, I.N., *Teplofiz. Vys. Temp*., 2009, vol. 47, no. 3, pp. 473–480.
13. Hest, M.F.A.M. van, Haartsen, J.R., Weert, M.H.M. van, Schram, D.C., and Sanden, M.C.M. van, *Plasma Sources Sci. Technol*., 2003, vol. 12, no. 4, pp. 539–553.
14. Pagnon, D., Amorim, J., Nahorny, J., Touzeau, M., and Vialle, M., *J. Phys. D: Appl. Phys.,* 1995, vol. 28, pp. 1856–1868.
15. Kurunczi, P.F., Guha, J., and Donnelly, V.M., *J. Phys. Chem. B*., 2005, vol. 109, pp. 20989–20998.
16. Guha, J., Kurunczi, P., Stafford, L., Donnelly, V.M., Yi-Kang, Pu, *J. Phys. Chem. B*., 2008, vol. 112, pp. 8963–8968.
17. Stafford, L., Guha, J., Khare, R., Mattei, S., Boudreault, O., Clain, B., and Donelly, V.M., *Pure Appl. Chem*., 2010, vol. 82, no. 6, pp. 1301–1315.
18. Gomez, S., Steen, P. G., and Graham, W.G., *Appl. Phys. Lett*., 2002, vol. 81, pp. 19–21.
19. Kholodkova, N.V., Kholodkov, I.V., and Abramov, A.V., *Surf. Eng. Appl. Electrochem*., 2013, vol. 49, no. 2, pp. 107–110.
20. Aleksandrova, S.N., Grinevich, V.I., and Chesnokova, T.A., *Zh. Prikl. Spektrosk*., 1993, vol. 59, nos. 5–6, pp. 473–477.
21. Aleksandrova, S.N., Grinevich, V.I., and Chesnokova, T.A., Abstracts of Papers, *2 Mezhdunarodnyi simpozium po teoreticheskoi i prikladnoi plazmokhimii* [2nd Int. Symp. On Theoretical and Applied Plasma Chemistry (ISTAPC-91)], Ivanovo, 1995, pp. 320–322.
22. Balat-Pichelin, M., Bedra, L., Gerasimova, O., and Boubert, P., *Chem. Physics*, 2007, vol. 340, pp. 217–226.
23. Balat-Pichelin, M., Passarelli, M., and Vesel, A., *Mater. Chem. Phys*., 2010, vol. 123, pp. 40–46.
24. Bedra, L., Rutigliano, M., Balat-Pichelin, M., and Cacciatore, M., *Langmuir*, 2006, vol. 22, pp. 7208–7216.
25. Polak, L.S., Slovetskii, D.I., and Todesaite, R.D., *Khim. Vys. Energ*., 1975, vol. 9, no. 2, pp. 142–148.
26. Dickens, P.G. and Sutcliffe, M.B., *Trans. Faraday Soc*., 1964, vol. 60, pp. 1272–1285.
27. Greaves, J.C. and Linnet, J.W., *Trans. Faraday Soc*., 1959, vol. 55, pp. 1355–1361.
28. Carty, G., Magne, L., and Cernogora, G., *J. Phys. D.: Appl. Phys*., 1999, vol. 32, pp. L53–L56.
29. Brovikova, I.N., *Teplofiz. Vys. Temp*., 2004, vol. 42, no. 6, pp. 869–872.
30. Brovikova, I.N., *Cand. Sci. (Chem.) Dissertation*, Ivanovo, 1980.
31. Greaves, J.C. and Linnet, J.W., *Trans. Faraday Soc*., 1958, vol. 54, pp. 1323–1330.
32. Melin, G.A. and Madix, R., *Trans. Faraday Soc*., 1971, vol. 67, pp. 198–211.
33. Wickramanayaka, S., Meikle, S., Kobayashi, T., Hosokawa, N., and Hatanaka, Y., *J. Vac. Sci. Technol. A*., 1991, vol. 9, no. 6, pp. 2999–3002.
34. Magne, L., Coitout, H., Cernogora, G., and Cousset, G., *J. Phys. III France*, 1993, vol. 3, no. 9, pp. 1871–1889.
35. Greaves, J.C. and Linnet, J.W. *Trans. Faraday Soc*., 1959, vol. 55, pp. 1346–1354.
36. Kislyuk, M.U., *Khim. Fiz*., 1989, vol. 8, no. 1, pp. 59–72.
37. Mozetic, M. and Gvelbar, U., *Int. J. Nanosci*., 2007, vol. 6, no. 2, pp. 121–124.
38. Yabłoński, A., *J. Chem. Soc., Faraday Trans. 1*, 1977, vol. 73, pp. 111–120.
39. Menagarishvili, V.M., *Cand. Sci. (Chem.) Dissertation*, Ivanovo, 1990.
40. Smirnov, S.A., Titov, V.A., and Rybkin, V.V., *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol*., 2012, vol. 55, no. 4, pp. 12–20.
41. Vucanovic, V., Takacs, G.A., Matuszak, E.A., et al., *J. Vac. Sci. Technol*., 1986, vol. A4, no. 3, pp. 698–699.
42. Robb, F.Y., *J. Electrochem. Soc*., 1984, vol. 131, no. 7, pp. 1670–1674.
43. Kuvaldina, E.V., Lyubimov, V.K., and Rybkin, V.V., *Khim. Vys. Energ*., 1992, vol. 26, no. 5, pp. 471–474.
44. Kuvaldina, E.V., Lyubimov, V.K., Maksimov, A.I., and Rybkin, V.V., *Khim. Vys. Energ*., 1990, vol. 24, no. 5, pp. 471–475.
45. Rybkin, V.V., Kuvaldina, E.V., and Lyubimov, V.K., *Khim. Vys. Energ*., 1993, vol. 27, no. 1, pp. 83–87.
46. Ershova, E.S., Maksimov, A.I., Menagarishvili, S.D., and Menagarishvili, V.M., *Khim. Vys. Energ*., 1983, vol. 17, no. 4, pp. 378–380.

47. Rybkin, V.V. and Menagarishvili, S.D., *Khim. Vys. Energ*., 1993, vol. 27, no. 6, pp. 71–73.
48. Clark, D.T. and Dilks, A., *J. Polym. Sci.: Polym. Chem. Ed*., 1979, vol. 17, no. 4, pp. 957–976.
49. Brovikova, I.N., Menagarishvili, S.D., and Rybkin, V.V., *Khim. Vys. Energ*., 1992, vol. 26, no. 4, pp. 381–382.
50. Taylor, G.N. and Wolf, T.M., *Polym. Eng. Sci*., 1980, vol. 20, no. 16, pp. 1087–1092.
51. Cook, J.M. and Benson, B.W., *J. Electrochem. Soc*., 1983, vol. 130, no. 12, pp. 2459–2464.
52. Kuvaldina, E.V., Rybkin, V.V., Terekhina, E.A., and Titov, V.A., *Khim. Vys. Energ*., 1994, vol. 28, no. 4, pp. 359–360.
53. Kuvaldina, E.V., Rybkin, V.V., Terekhina, E.A., and Titov, V.A., *Khim. Vys. Energ*., 1994, vol. 28, no. 5, pp. 422–425.
54. Wydeven, T., Golub, M.A., and Narcinda, R., *J. Appl. Polym. Sci*., 1989, vol. 37. no. 12, pp. 3343–3355.
55. Kutepov, A.M. and Maksimov, A.I., *Teor. Osnovy Khim. Tekhnol*., 1998, vol. 32, no. 4, pp. 411–421.
56. Kuvaldina, E.V., Rybkin, V.V., Titov, V.A., and Ivanov, A.N., *Khim. Vys. Energ*., 2000, vol. 34, no. 6, pp. 456–459.
57. Rybkin, V.V., Kuvaldina, E.V., Smirnov, S.A., Titov, V.A., and Ivanov, A.N., *Khim. Vys. Energ*., 1999, vol. 33, no. 6, pp. 463–466.
58. Rybkin, V.V., Kuvaldina, E.V., Smirnov, S.A., Ivanov, A.N., and Titov, V.A., *Khim. Vys. Energ*., 2001, vol. 35, no. 1, pp. 42–45.
59. *Entsiklopediya nizkotemperaturnoi plazmy* (Encyclopedia of Low-Temperature Plasma), Lebedev, Yu.A., Plate, N.A., and Fortov, V.E., Eds., Moscow: Yanus-K, 2005, special issue VIII – 1, pp. 130–170.
60. Hansen, R.H. and Schonhorn, H., *J. Polym. Sci*., 1966, vol. B4, no. 3, pp. 223–229.
61. Vasilets, V.N., Tikhomirov, L.A., and Ponomarev, A.N., *Khim. Vys. Energ*., 1979, vol. 13, no. 2, pp. 171–177.
62. Grinevich, V.I. and Maksimov, A.I., *Primenenie nizkotemperaturnoi plazmy v khimii* (Application of Low-Temperature Plasma in Chemistry), Polak, L.S., Moscow: Nauka, 1981, pp. 135–169.
63. Mathias, E. and Miller, G.Y., *J. Phys. Chem*., 1967, vol. 71, no. 8, pp. 2671–2675.
64. Grinevich, V.I. and Maksimov, A.I., *Khim. Vys. Energ*., 1982, vol. 16, no. 1, pp. 76–79.
65. Grinevich, V.I., Maksimov, A.I., and Rybkin, V.V., *Khim. Vys. Energ*., 1982, vol. 16, no. 6, pp. 547–550.
66. Titov, V.A., Shikova, T.G., Rybkin, V.V., and Ivanov, A.N., *Khim. Vys. Energ*., 2003, vol. 37, no. 2, pp. 140–142.
67. Titov, V.A., Shikova, T.G., Kuvaldina, E.V., and Rybkin, V.V., *Khim. Vys. Energ*., 2002, vol. 36, no. 5, pp. 391–394.
68. Kuvaldina, E.V., Shikova, T.G., Smirnov, C.A., and Rybkin, V.V., *Khim. Vys. Energ*., 2007, vol. 41, no. 4, pp. 330–333.
69. Titov, V.A., Kuvaldina, E.V., Smirnov, S.A., Ivanov, A.N., and Rybkin, V.V., *Khim. Vys. Energ*., 2002, vol. 36, no. 2, pp. 148–152.
70. Rybkin, V.V., Titov, V.A., Kuvaldina, E.V., Serova, N.Yu., and Smirnov, S.A., *Khim. Vys. Energ*., 1996, vol. 30, no. 3, pp. 219–223.
71. Titov, V.A., Rybkin, V.V., Kuvaldina, E.V., and Ivanov, A.N., *Khim. Vys. Energ*., 2003, vol. 37, no. 3, pp. 223–226.
72. Rybkin, V.V., Titov, V.A., Kuvaldina, E.V., and Smirnov, S.A., *Khim. Vys. Energ*., 1997, vol. 31, no. 6, pp. 449–452.
73. Kuvaldina, E.V., Shutov, D.A., Rybkin, V.V., and Smirnov, S.A., *Khim. Vys. Energ*., 2004, vol. 38, no. 3, pp. 231–233.
74. Kuvaldina, E.V., Rybkin, V.V., Titov, V.A., and Shutov, D.A., *Khim. Vys. Energ*., 2005, vol. 39, no. 5, pp. 392–395.
75. Menagarishvili, S.D. and Rybkin, V.V., *Khim. Vys. Energ*., 1994, vol. 28, no. 2, pp. 187–188.
76. Ponomarev, A.N., Maksimov, A.I., Vasilets, V.N., and Menagarishvili, V.M., *Khim. Vys. Energ*., 1989, vol. 23, no. 3, pp. 286–287.
77. Lin, T.H., Belser, M., and Tzeng, Y., *IEEE Trans. Plasma Sci*., 1988, vol. 16, no. 6, pp. 631–637.
78. Maksimov, A.I., Rybkin, V.V., and Kuvaldina, E.V., *Khim. Vys. Energ*., 1995, vol. 29, no. 1, pp. 60–62.
79. Rybkin, V.V., Kuvaldina, E.V., and Titov, V.A., *Khim. Vys. Energ*., 1998, vol. 32, no. 6, pp. 465–469.
80. Khlyustova, A.V. and Maksimov, A.I., *Elektron. Obrab. Mater*., 2002, no. 5, pp. 35–40.
81. Titov, V.A., Rybkin, V.V., Smirnov, S.A., and Kulentsan, A.L., *High Temp. Mater. Process*, 2007, vol. 11, no. 4, pp. 515–526.
82. Konovalov, A.S., Golubev, S.N., Ivanov, A.N., Shutov, D.A., Smirnov, S.A., and Rybkin, V.V., *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol*. , 2012, vol. 55, no. 12, pp. 55–58.
83. Maximov, A.I. an Khlustova, A.V., *High Temp. Mater. Process*, 2007, vol. 11, no. 4, pp. 527–535.
84. Maksimov, A.I., Titov, V.A., and Khlyustova, A.V., *Khim. Vys. Energ*., 2004, vol. 38, no. 3, pp. 227–230.
85. Zakharov, A.G., Maksimov, A.I., and Titova, Yu.V., *Russ. Chem. Rev*., 2007, vol. 76, no. 3, p. 235.
86. Petrov, A.E., Kalbenin, D.A., Titov, V.A., Kulentsan, A.L., and Smirnov, S.A., *Gorenie Plazmokhim*., 2011, vol. 9, no. 3, pp. 160–168.
87. Maksimov, A.I., *Entsiklopediya nizkotemperaturnoi plazmy* (Encyclopedia of Low-Temperature Plasma), Lebedev, Yu.A., Plate, N.A., and Fortov, V.E., Eds., Moscow: Yanus-K, 2006, special issue XI – 5, pp. 263–309.

88. Bobkova, E.S., Khodor, Ya.V., and Rybkin, V.V., *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol*., 2012, vol. 55, no. 12, pp. 59–62.
89. Kuvaldina, E.V., Rybkin, V.V., Smirnov, S.A., and Titov, V.A., Abstracts of Papers, *X Vserossiiskaya konferentsiya po fizike gazovogo razryada (FGR-X)* [X Russian Conf. on Gas Discharge Chemistry (FGR-X)], Ryazan: Ryazan. Gos. Radiotekh. Inst., 2000, pp. 99–101, part 1.
90. Kutepov, A.M., Maksimov, A.I., Nikiforov, A.Yu., and Titov, V.A., *Teor. Osnovy Khim. Tekhnol*., 2003, vol. 37, no. 4, pp. 365–373.
91. Titov, V.A., Rybkin, V.V., and Smirnov, S.A., *Khim. Vys. Energ*., 2009, vol. 43, no. 3, pp. 218– 226.
92. Turban, G. and Papeaux, M., *J. Electrochem. Soc*., 1983, vol. 130, no. 11, pp. 2231–2236.
93. Kuvaldina, E.V. and Rybkin, V.V., *Khim. Vys. Energ*., 2007, vol. 41, no. 2, pp. 155–158.
94. Kuvaldina, E.V., *Surf. Eng. Appl. Electrochem*., 2010, vol. 46, no. 2, pp. 138–143.
95. Kuvaldina, E.V., *Surf. Eng. Appl. Electrochem*., 2011, vol. 47, no. 3, pp. 256–262.
96. Kuvaldina, E.V., *Surf. Eng. Appl. Electrochem*., 2009, vol. 45, no. 1, pp. 42–46.
97. Kuvaldina, E.V., *Surf. Eng. Appl. Electrochem*., 2008, vol. 44, no. 2, pp. 127–132.