

Radiation-Induced Alteration of the Reflection Spectra of Diazoquinone–Novolac Photoresist Films by Implantation of Ag⁺ Ions

A. A. Kharchenko^a, D. I. Brinkevich^{b, *}, S. D. Brinkevich^{b, c}, and V. S. Prosolovich^b

^a Institute of Nuclear Problems, Belarusian State University, Minsk, 220006 Belarus

^b Belarusian State University, Minsk, 220030 Belarus

^c OOO Moi Meditsinskii Tsentr–Vysokie Tekhnologii, Vsevolozhsk, Leningrad oblast, 188640 Russia

*e-mail: Brinkevich@bsu.by

Received June 11, 2023; revised July 12, 2023; accepted July 14, 2023

Abstract—FP9120 diazoquinone–novolac positive photoresist films 1.5 μm thick implanted with Ag⁺ ions and supported on the surface of KDB-10 (111) silicon wafers by centrifugation have been studied by measuring reflection spectra. It has been shown that ion implantation leads to a decrease in the refractive index of the photoresist due to radiation crosslinking of novolac resin molecules and a decrease in the density ρ and the molecular refraction R_M of the photoresist. It has been established that the reflection coefficient in the opaque region of the photoresistive film increases with the Ag⁺ implantation dose. The changes observed in the optical properties of the films under ion implantation conditions are explained taking into account radiation-chemical processes in the phenol–formaldehyde photoresist.

Keywords: diazoquinone–novolac photoresist, implantation of silver ions, reflection spectrum, refractive index

DOI: 10.1134/S0018143923060061

INTRODUCTION

Diazoquinone–novolac (DQN) resists are the main positive resists used in the submicron lithography process. Ion implantation is widely used in modern semiconductor micro- and nanoelectronics to create doped and insulating layers. The interaction of DCN resists with electromagnetic radiation in the ultraviolet, visible, X-ray, and gamma regions of the spectrum has been studied in sufficient detail [1–3]. However, the effect of ion implantation on the optical properties of these materials has not been sufficiently studied, although the radiation-induced processes occurring in photoresists in the course of ion implantation can have a significant effect on the yield of suitable devices. The purpose of this work was to study the effect of silver ion implantation on the reflection spectra of FP9120 diazoquinone–novolac resist films.

EXPERIMENTAL

Films of FP9120 positive photoresist 1.5 μm thick were deposited on the surface of KDB-10 silicon wafers with the (111) orientation by centrifugation at a rotation speed of 1800 rpm. Before forming a photoresist film, the silicon wafers were subjected to a standard surface cleaning cycle in organic and inorganic

solvents. The centrifuge rotation time was 40 s. After applying the photoresist onto the working side of a plate, drying was carried out for 50–55 min at a temperature of 88°C. The thickness of the photoresist films was controlled on a Dectak profilometer at five fixed points on each plate, while the deviations from the average value for the plate did not exceed 1% in all of the test samples.

Implantation with 30-keV Ag⁺ ions in a fluence range of 5×10^{16} – 1×10^{17} cm⁻² in the constant ion current mode (current density $j = 4 \mu\text{A}/\text{cm}^2$) was carried out at room temperature in a residual vacuum of no worse than 10^{-5} Pa on an ILU-3 implanter. To avoid sample overheating and destruction in the course of implantation, a cassette was used, which ensured an effective drain of the ionic charge from the polymer surface and close contact with the water-cooled metal base.

Reflection spectra of photoresist–silicon structures were recorded in the transparency region of a photoresistive film in the range $\lambda = 210$ – 1100 nm using a PROSKAN MC-122 single-beam spectrophotometer with a resolution of no worse than 1 nm at room temperature. The instrument was calibrated before each measurement. The reflection spectra were recorded at incidence and reflection angles of 20° to

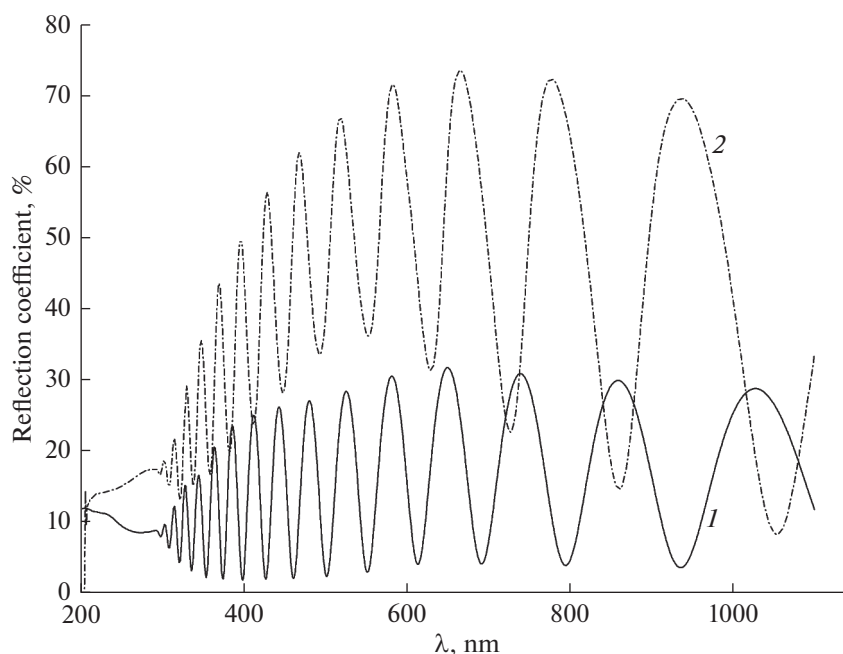


Fig. 1. Spectral dependences of the reflection coefficients of (1) the initial FP9120 photoresist film on silicon and (2) the film implanted with Ag^+ ions at a fluence of $5 \times 10^{16} \text{ cm}^{-2}$.

the normal. Atomic force microscopy measurements showed that the film surface relief was smooth; for the initial and implanted films, the arithmetic mean surface roughness R_a did not exceed 2 nm.

RESULTS AND DISCUSSION

The reflection spectra of unirradiated photoresistive films exhibited interference bands in the transparency region ($\lambda > 300 \text{ nm}$) due to the reflection of light from the photoresist–silicon and photoresist–air interfaces (Fig. 1, curve 1). With an increase in the wavelength in a range of 300–500 nm, the intensity of the interference bands rapidly increased due to an increase in the intensity of a light beam reflected from the photoresist–silicon interface because of a decrease in absorption in the photoresist film.

The interference pattern in the photoresistive films implanted with Ag^+ ions was observed against the background of a wide nonselective reflection band with a maximum near 650 nm (Fig. 1, curve 2). The intensity and position of this reflection band were almost independent of the implantation dose in the studied fluence range of 5×10^{16} – $1 \times 10^{17} \text{ cm}^{-2}$. A broad band with a maximum near 650 nm in the reflection spectra was observed previously upon the implantation of glassy chalcogenide semiconductors, quartz glass, and glassy polymers with Ag^+ ions [4, 5]. The maximum of this band depended on the initial matrix, and it was in a wavelength range of 560–600 nm for the implantation of silver ions into a polymer matrix [5]. Ganeev et al. [4] related this band to

the manifestation of the effect of surface plasmon resonance in metal nanoparticles formed in the matrix upon implantation. This was also confirmed by the calculated spectra of Mie resonances. The surface plasmon resonance was maximal at fluences of $(5\text{--}10) \times 10^{16} \text{ cm}^{-2}$, when nearly spherical silver nanoparticles with sharp boundaries were formed in the matrix [5, 6].

In the opacity region of the photoresistive film ($\lambda < 300 \text{ nm}$), the reflection coefficient increased (Fig. 1, curves 1, 2), and this increase was already observed at an irradiation dose of $5 \times 10^{16} \text{ cm}^{-2}$. With a further increase in the fluence to $1 \times 10^{17} \text{ cm}^{-2}$, the reflection coefficient remained almost unchanged. Previously, a similar effect was observed in the films of polyethylene terephthalate [7] and polyimide [8, 9] under high-energy exposure (γ -irradiation, ion implantation), and it was due to a radiation-stimulated rearrangement of the supramolecular structure of the polymer in the near-surface region and the relaxation of residual mechanical stresses arisen in the process of film production.

The implantation of Ag^+ ions also led to a shift in the interference maximums and a change in the distance between them (Fig. 1, curves 1, 2). Interference maximums are observed when the optical path difference of beams reflected from the air/photoresist and photoresist/silicon interfaces is equal to an integer number of wavelengths:

$$2dn = m\lambda_m, \quad (1)$$

where n is the refractive index of the photoresistive film; d is the distance traveled by a light beam in the photopolymer; m is the maximum number in the reflection spectra; and λ_m is the wavelength corresponding to the m th maximum.

The experimental data indicated that a change in the value of dn was observed upon the implantation of Ag^+ ions. The value of d is determined by the geometric thickness of a polymer film. Measurements made mechanically on a Dectak profilometer showed that there was no significant shrinkage of the photoresist upon implantation. The film thickness varied within the limits of a measurement error of ~ 10 nm at all studied implantation doses up to a maximum of $1 \times 10^{17} \text{ cm}^{-2}$. These experimental results correlate with the data obtained by Kharchenko et al. [10] using atomic force microscopy upon the implantation of a thin polyimide film with a narrow ion beam. Kharchenko et al. [10] found that shrinkage of a polyimide film was observed only at ion fluences above $1 \times 10^{17} \text{ cm}^{-2}$, and the shrinkage was lower than 80 nm, which is smaller than 4.5% of the film thickness, even at $\Phi = 1 \times 10^{18} \text{ cm}^{-2}$. The same result was also observed with a photoresist polymer film [11, 12]. Because the geometric film thickness did not change significantly in the course of implantation, the optical path difference $2dn$ reflected changes in the refractive index n of the photoresistive film upon implantation.

Based on the reflection spectra, the dependences of the optical path difference $2dn$ on the wavelength λ were calculated based on the numbers and positions of the maximums/minimums according to formula (1); Figure 2 shows these dependences. The function $2dn(\lambda)$ for the initial photoresist samples looks like the normal dispersion $dn/d\lambda < 0$. In the initial films, the refractive index n increased from 1.68 at $\lambda = 1000$ nm to 1.9 at 300 nm.

A decrease in the refractive index was observed after ion implantation with a fluence of $5 \times 10^{16} \text{ cm}^{-2}$ (Fig. 2). Thus, at $\lambda = 930$ nm, the value of n decreased by $\sim 7\%$, from 1.68 in the initial film to 1.56 in the implanted one.

As the fluence was further increased to $1 \times 10^{17} \text{ cm}^{-2}$, an opposite effect was observed—the refractive index of the photoresist film n increased to 1.63 at $\lambda = 930$ nm (Fig. 2, curve 3). In our opinion, the observed increase in the refractive index was due to the formation of a silver-doped continuous carbonized layer at fluences of $\sim 1 \times 10^{17} \text{ cm}^{-2}$. Amorphized carbon can have a value of n up to 3.0 [13], which is significantly higher than the refractive index of the photoresist. As is well known [9], the implanted layer thickness was ≈ 45 nm upon the introduction of 30-keV Ag^+ ions. Estimates showed that, at such a thickness of the carbonized layer, its refractive index should be ~ 2.5 for consistency with the experimental results. This value is comparable with the values of n observed earlier by

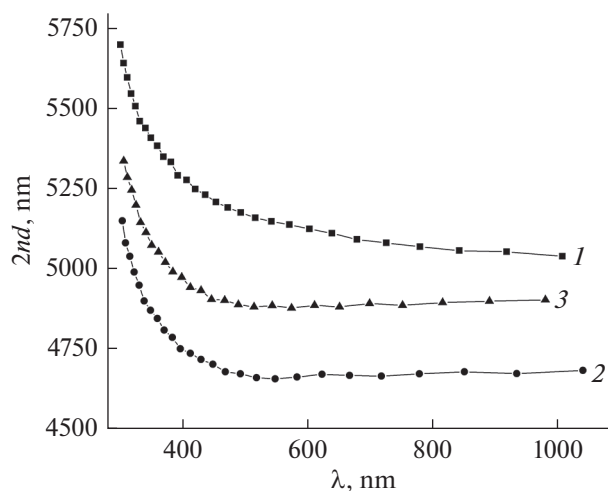
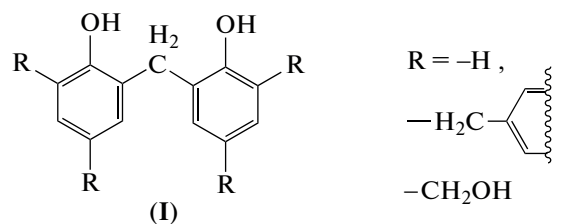


Fig. 2. Spectral dependences of the optical path differences $2dn$ in (1) the initial photoresist film and the films implanted with Ag^+ ions at fluences of (2) 5×10^{16} and (3) $1 \times 10^{17} \text{ cm}^{-2}$.

Bumai et al. [14] in the modified layers of polyimide films implanted with nickel ions ($n = 2.3$).

Phenol–formaldehyde resins are among the oldest representatives of network polymers. They are obtained by the condensation of phenol and formaldehyde, as a rule, in the presence of special functional additives that regulate the molecular weight, the degree of crosslinking of the network, or individual physicochemical properties of the polymer compound. In addition, the composition and structure of the polymer strongly depend on the reaction conditions of polymer synthesis and curing and on curing processes. Taking into account the irregular structure, we can represent the main structural fragment of phenol–formaldehyde resin (I) in the following generalized form:



According to the Lorentz–Lorentz formula [15], the refractive index n of polymers with the molar mass M of the repeating unit, the substance density ρ , and the molecular refraction R_M can be determined from the expression

$$n^2 = \frac{M + 2R_M\rho}{M - R_M\rho} \quad (1)$$

The molecular refraction R_M is an additive quantity, and it consists of refractions R_i of individual atoms and

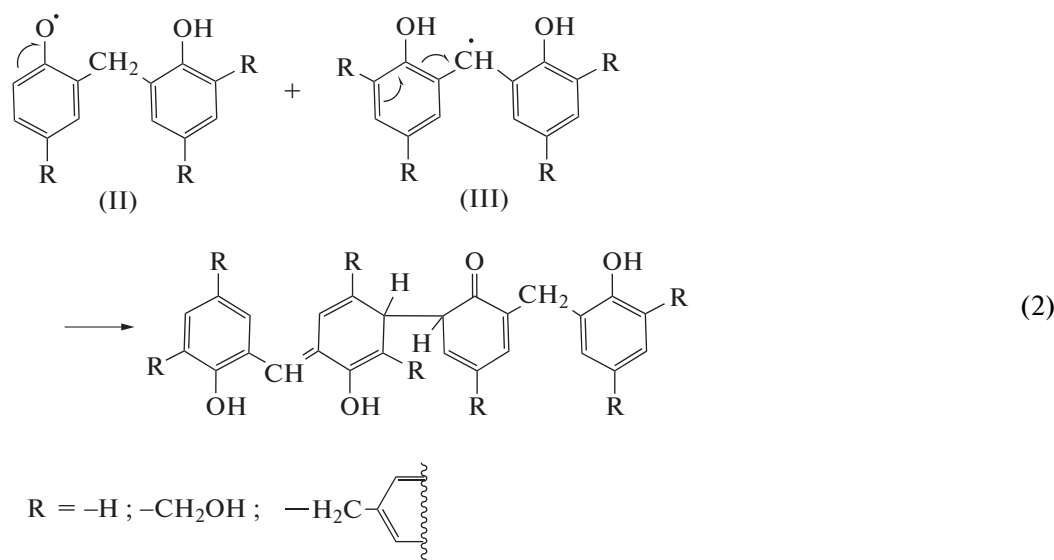
increments for the types of chemical bonds (double, triple).

The refractive index of polymers can be decreased on high-energy irradiation by various mechanisms. As follows from formula (1), an increase in the molar mass of the polymer M leads to a decrease in the value of n . Indeed, when phenol–formaldehyde resins were irradiated, crosslinking reactions dominated over destruction due to the structure peculiarities of the polymer [16].

Gas (mainly hydrogen and its compounds) evolution from the implanted layer also caused a decrease in the value of n upon ion implantation. This led to a decrease in the density of the substance ρ because the film thickness of the photoresist did not change significantly, but its weight decreased. In addition, gas evolution also led to a decrease in the molecular refraction R_M due to a decrease in the contribution of the refractions R_i of hydrogen atoms. In accordance with expression (2), a decrease in the values of ρ and R_M should decrease the value of n . A combination of these circumstances is responsible for a decrease in the refractive index n of the photoresist in the course of ion implantation.

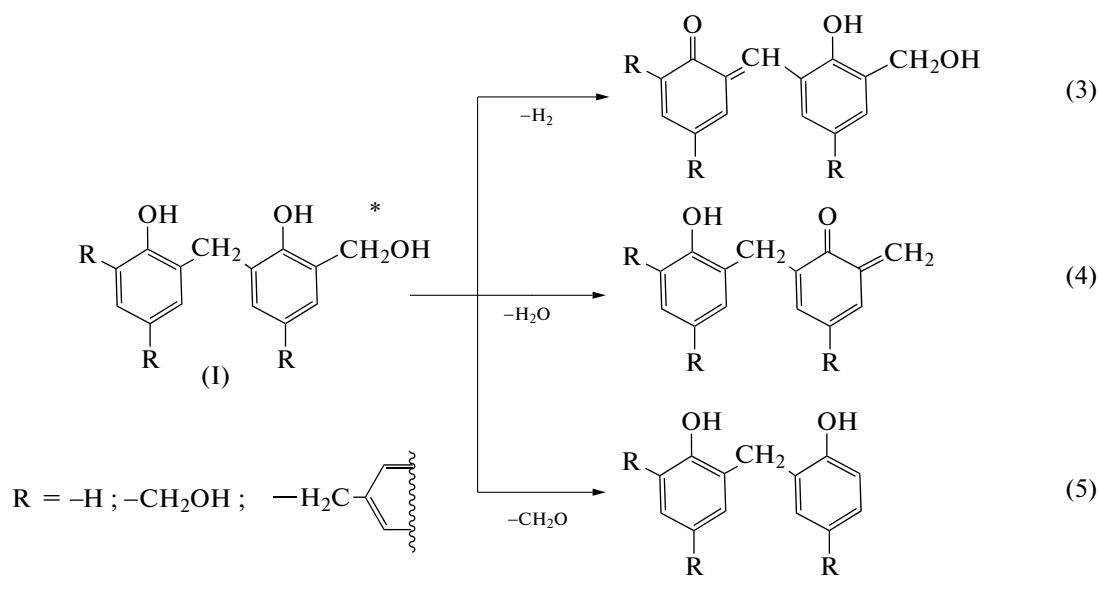
Previously, the mechanisms of radiation-induced transformations of phenol–formaldehyde photoresists both under the conditions of implantation with ions [17–19] and under irradiation with low linear energy transfer particles such as electrons and photons [2, 3, 20] were considered in detail. Therefore, in this work, we will only schematically present the key reactions responsible for the observed changes in the optical properties of films under ion implantation conditions.

The increase in the molecular weight of phenol–formaldehyde photoresists observed upon ion implantation mainly resulted from the recombination of various oxygen-centered (II) and carbon-centered (III) radicals, for example, according to reaction (2). The addition of radicals to macromolecules is the second possible process leading to the formation of new carbon–carbon bonds and an increase in the average molecular weight of the polymer. However, the high values of the linear energy transfer of silver ions and the dose rates created by an industrial accelerator on implantation create very high concentrations of radicals in tracks. Therefore, the contribution of radical–molecule processes to the increase in molecular weight is negligible compared to that of biradical recombination reactions according to reaction (2) and similar ones.



The formation of low-molecular-weight compounds (hydrogen, water, and formaldehyde) occurs due to the decomposition of excited macromolecules according to reactions (3)–(5) presented below. These low-molecular-weight compounds are easily removed from the film under ion implantation conditions: a deep vacuum and slight heating. Neverthe-

less, previously, Brinkevich et al. [20] detected formaldehyde among the products of radiation-induced transformations of the photoresist using ATR Fourier transform IR spectrometry. The release of methane is also possible because small amounts of xylene, a molecular weight regulator, are introduced into the resin.



Note that radiation-induced modification mainly occurs at the side substituents of aromatic rings. As a result of the decay of excited particles, the hydrogen content of the polymer decreases and various quinoid structures accumulate; these structures are more stable under radiolysis conditions than the initial polymer due to the presence of a system of conjugated multiple bonds. The final result of the accumulation of quinoid structures upon ion implantation is the graphitization of the phenol–formaldehyde photoresist in the thermalization region of heavy Ag ions. The resulting metal–carbon composite has a high refractive index close to that of diamond (2.42 [21]).

CONCLUSIONS

This work showed that implantation with Ag⁺ ions at a fluence of up to $5 \times 10^{16} \text{ cm}^{-2}$ led to a decrease in the refractive index of the photoresist due to radiation crosslinking of the novolac resin and a decrease in the density ρ and the molecular refraction R_M of the photoresist because of the release of low-molecular-weight compounds upon the decay of excited macromolecules. With an increase in the dose to $1 \times 10^{17} \text{ cm}^{-2}$, an increase in the optical length $2dn$ of the photoresistive layer was observed. In our opinion, it was caused by the formation of a carbonized layer with the refractive index $n \sim 2.5$, which significantly exceeds the refractive index of the photoresist, in the path of the silver ions. Upon the implantation of Ag⁺, an increase in the reflection coefficient of the photoresistive film in the opacity region ($\lambda = 200\text{--}300 \text{ nm}$) was observed.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- Moreau, W.M., *Semiconductor Lithography. Principles, Practices and Materials*, New York: Plenum, 1988.
- Brinkevich, S.D., Brinkevich, D.I., Prosolovich, V.S., and Sverdlov, R.L., *High Energy Chem.*, 2021, vol. 55, no. 1, p. 65.
- Vabishchevich, S.A., Brinkevich, S.D., Vabishchevich, N.V., Brinkevich, D.I., and Prosolovich, V.S., *High Energy Chem.*, 2021, vol. 55, no. 6, p. 495. <https://doi.org/10.1134/S0018143921060151>
- Ganeev, R.A., Rvasnyansky, A.I., Stepanov, A.L., and Usmanov, T., *Phys. Status Solidi B*, 2003, vol. 238, no. 2, p. R5.
- Galyautdinov, M.F., Nuzhdin, V.I., Fattakhov, Ya.V., Farrakhov, B.F., Valeev, V.F., Osin, Yu.N., and Stepanov, A.L., *Tech. Phys. Lett.*, 2016, vol. 42, no. 2, p. 182.
- Golovchuk, V.I., Kharchenko, A.A., Brinkevich, D.I., Lukashevich, M.G., Vabishchevich, S.A., and Vabishchevich, N.V., *Vestn. PGU, Ser. C: Fundam. Nauki*, 2017, no. 2, p. 42.
- Bumai, Yu.A., Brinkevich, D.I., Volobuev, V.S., Dolgikh, N.I., Karpovich, I.A., and Lukashevich, M.G., *Vestn. BGU, Ser. 1: Fiz. Math. Inform.*, 2012, no. 3, p. 41.
- Kharchenko, A.A., Brinkevich, D.I., Brinkevich, S.D., Lukashevich, M.G., and Odzhaev, V.B., *J. Surf. Invest.: X-ray, Synchrotron Neutron Tech.*, 2015, vol. 9, no. 1, p. 87. <https://doi.org/10.1134/S1027451015010103>
- Brinkevich, D.I., Kharchenko, A.A., Brinkevich, S.D., Lukashevich, M.G., Odzhaev, V.B., Valeev, V.F., Nuzhdin, V.I., and Khaibullin, R.I., *J. Surf. Invest.: X-ray, Synchrotron Neutron Tech.*, 2017, vol. 11, no. 4, p. 801. <https://doi.org/10.1134/S1027451017040188>
- Kharchenko, A.A., Shvarkov, S.D., Kolesnik, E.A., and Lukashevich, M.G., *Vestn. BGU, Ser. 1: Fiz. Math. Inform.*, 2012, no. 2, p. 29.
- Kharchenko, A.A., Brinkevich, D.I., Prosolovich, V.S., Brinkevich, S.D., Odzhaev, V.B., and Yankovski, Yu.N.,

- J. Surf. Invest.: X-ray, Synchrotron Neutron Tech.*, 2020, vol. 14, no. 3, p. 558.
<https://doi.org/10.1134/S1027451020030283>
12. Brinkevich, D.I., Kharchenko, A.A., Prosolovich, V.S., Odzhaev, V.B., Brinkevich S.D., and Yankovski, Yu.N., *Russ. Microelectron.*, 2019, vol. 48, no. 3, p. 197.
<https://doi.org/10.1134/S1063739719020021>
 13. Konshina, E.A., *Amorfnyi gidrogenizirovannyi uglerod i primeneniye ego v opticheskikh ustroystvakh* (Amorphous Hydrogenized Carbon and its Application in Optical Devices), St. Petersburg: SPbGU ITMO, 2010.
 14. Bumai, Yu.A., Dolgikh, N.I., Kharchenko, A.A., Valeev, V.F., Nuzhdin, V.I., Khaibullin, R.I., Nagim, F.A., Lukashevich, and M.G., Odzhaev, V.B., *J. Appl. Spectrosc.*, 2014, vol. 81, no. 2, p. 188.
<https://doi.org/10.1007/s10812-014-9908-7>
 15. Askadskii, A.A. and Kondrashenko, V.I., *Komp'yuternoe materialovedeniye polimerov. Tom 1. Atomno-molekulyarnyi uroven'* (Computer Materials Science of Polymers, vol. 1: Atomic-Molecular Level), Moscow: Nauchnyi Mir, 1999.
 16. Grassie, N. and Scott, G., *Polymer Degradation and Stabilisation*, Cambridge: Cambridge Univ. Press, 1985.
 17. Brinkevich, D.I., Brinkevich, S.D., Oleshkevich, A.N., Prosolovich, V.S., and Odzhaev, V.B., *High Energy Chem.*, 2020, vol. 54, no. 2, p. 115.
<https://doi.org/10.1134/S0018143920020046>
 18. Brinkevich, S.D., Grinyuk, E.V., Brinkevich, D.I., and Prosolovich, V.S., *High Energy Chem.*, 2020, vol. 54, no. 5, p. 342.
<https://doi.org/10.1134/S0018143920050045>
 19. Brinkevich, D.I., Brinkevich, S.D., and Prosolovich, V.S., *High Energy Chem.*, 2022, vol. 56, no. 4, p. 270.
<https://doi.org/10.1134/S0018143922040051>
 20. Brinkevich, S.D., Brinkevich, D.I., Prosolovich, V.S., Lastovskii, S.B., and Pyatlitski, A.N., *J. Appl. Spectrosc.*, 2021, vol. 87, no. 6, p. 1072.
<https://doi.org/10.1007/s10812-021-01111-9>
 21. *Fiziko-khimicheskie svoystva poluprovodnikovyykh veshchestv. Spravochnik* (A Handbook on Physicochemical Properties of Semiconductor Materials), Moscow: Nauka, 1979.

Translated by V. Makhlyarchuk

SPELL: 1. OK