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OPTICAL PROPERTIES IN UV WAVELENGTH RANGE OF AMORPHOUS PERFLUORINATED POLYMERS BASED ON DIOXOLS AND VINYL ETHERS AND THEIR APPLICATION FOR FORMATION OF ULTRATHIN PROTECTIVE PELLICLES

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Abstract: "Free-standing" ultrathin films (pellicles) have been fabricated from amorphous perfluorinated copolymers of dioxols and vinyl ethers, the polymers, which are the analogues of Teflon AF and Cytop. It is shown that the pellicles with the thicknesses of 250 – 800 nm possess high optical transparency in the UV wavelength range of 190 – 250 nm and are promising for protecting photomasks and reticles used in microelectronics.
Keywords: Amorphous perfluorinated polymers, dioxols, vinyl ethers, ultrathin free-standing films, protective pellicles.

Introduction

Amorphous perfluorinated polymers possess high optical transparency, low refractive index *n*, low material dispersion $dn/d\lambda$ in the "telecommunication" wavelength regions near λ = 850, 1300, 1550 nm, thus the polymers are used for the fabrication of light-guiding fibers and integrated-optical waveguides for high-throughput transmitting of optical signals [1 - 4]. Additionally, these polymers possess low dielectric permittivity, low tangent of dielectric losses and high breakdown voltage making them promising for the application in microelectronics [5 - 7]. Amorphous perfluorinated polymers find one more region of application, the formation of so called "pellicles" – ultrathin free-standing films for protecting photomasks and reticles used in microelectronic lithography devices [8 - 11]. These pellicles should have high optical transparency in the UV spectral range and good mechanical properties (high toughness, resistance to stretching, bending, etc.). Currently the variety of commercially available amorphous perfluorinated polymers is quite limited, thus Teflon AF (developed by DuPont company) and Cytop (developed by Asachi Glass) are usually exploited for the formation of protective pellicles [11]. Therefore, the synthesis of new amorphous perfluorinated polymer materials which have the complex of attractive properties and suit for the fabrication of ultrathin pellicles represents an up-to-date problem.

Earlier we reported on the synthesis by the help of ultrahigh pressure method of the amorphous perfluorinated copolymers of dioxols and vinyl ethers [12, 13]. The fabrication of free-standing films (pellicles) from these polymers with the thickness of 250 – 800 nm is reported in the present paper. It is shown that the pellicles possess high optical transparency in the UV spectral range of 190 – 250 nm and can be used for protecting photomasks and reticles.

Ultrahigh pressure synthesis of amorphous perfluorinated polymers

Produced by “P&M Invest” company the perfluoro-(2,2-dimethyl-1,3-dioxol) (D1) and perfluoro-(nonyl-vinyl) ether (E6) monomers representing transparent colorless liquids have been used for obtaining copolymers. Before the synthesis D1 monomer has been purified from stabilizer by distillation. The synthesis of copolymers has been conducted by the ultrahigh pressure method without the use of any initiators. The synthesis details are presented in papers [12, 13]. Fig. 1 demonstrates the fragment of the structure of the copolymer synthesized by us from D1 dioxol and E6 ether.

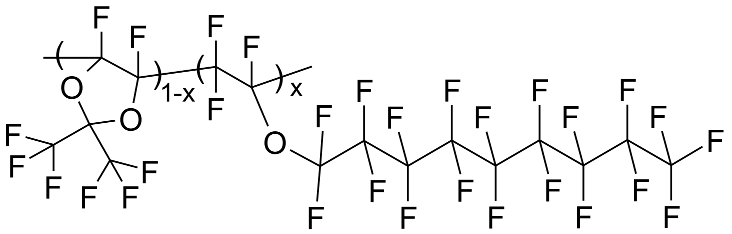

Figure 1. *The fragment of the structure of the copolymer of perfluoro-(2,2-dimethyl-1,3-dioxol) (D1) and perfluoro-(nonyl-vinyl) ether (E6). x is the molar concentration of the ether units in the macromolecule of* $D1_{1-x}E6_x$ *copolymer.*

$D1_{1-x}E6_x$ copolymers obtained are amorphous and have low refractive index n = 1.305 - 1.325 (depending on the molar concentration x of the ether units in the macromolecule). They dissolve at room temperature in perfluorinated solvents: perfluorohexane, perfluorooctane, hexafluorobenzene, etc. This permits to fabricate thin films of the given copolymers on various substrates by the spin-coating method.

Fabrication of ultrathin polymer pellicles

Free-standing films of $D1_{1-x}E6_x$ copolymers with the thickness of 250 – 800 nm have been fabricated on silicon wafers by the technique which is described in paper [14]. The solutions of the copolymers in perfluorooctane with the weight concentration of 1.5 – 5% have been used for this purpose. Transmittance spectrum for the pellicle fabricated from $D1_{1-x}E6_x$ copolymer with x = 0.3 and the thickness of $H_f \approx$ 700 nm is depicted in Fig. 2. The characteristic oscillations in $T(\lambda)$ transmission coefficient are caused by light interference in the pellicle. As follows from Fig. 2, the pellicle is transparent in UV spectral region (its transmission coefficient is T = 91.1% near λ = 248 nm and T = 90% near λ = 193 nm). Therefore, fabricated free-standing films of D1E6 amorphous perfluorinated copolymers synthesized without the use of initiators by the ultrahigh pressure method can be promising for protecting reticles and photomasks in lithography processes with the wavelengths of 193 nm (ArF laser) and 248 nm (KrF laser).

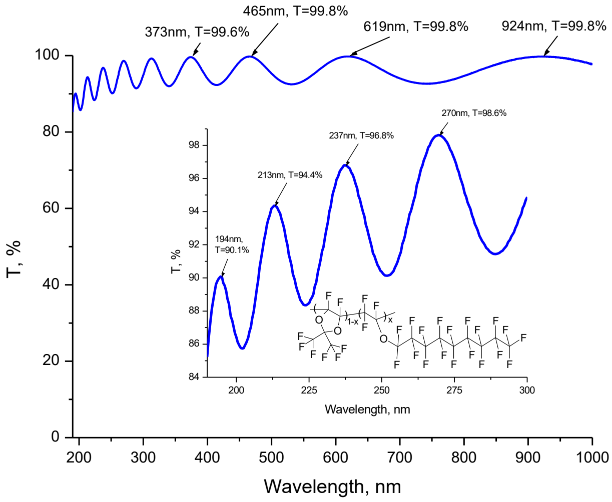

Figure 2. *Transmittance spectrum $T(\lambda)$ of the polymer pellicle fabricated from $D1_{1-x}E6_x$ amorphous perfluorinated copolymer with x = 0.3 and the thickness of $H_f \approx$ 700 nm.*

Conclusions

The amorphous perfluorinated polymers, which are the analogues of Teflon AF and Cytop, have been synthesized on the basis of dioxols and vinyl ethers without the use of radical polymerization initiators by the ultrahigh pressure method. "Free-standing" films with the thicknesses of 250 – 800 nm have been fabricated from these copolymers. It is shown that the films possess high optical transparency in the UV wavelength range (their transmission coefficient is T = 96.8% at λ = 237 nm and T = 89.6% at λ = 193 nm) and are promising for the formation of the pellicles protecting photomasks and reticles used in microelectronics.

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