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Deposition of transparent Al_2O_3 coatings with extreme wetting properties by nanosecond laser ablation of aluminum in background oxygen

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Transparent aluminum oxide nanostructures with extreme wetting properties were synthesized by nanosecond laser deposition in background oxygen. The transparency and morphology of the samples were analyzed. Non-monotonic behavior of the transmittance coefficient was observed with varying background oxygen pressure in the range of 20 to 140 Pa, attributed to differences in the kinetics of ablation product dispersion. The evolution of the contact angle was studied, ranging from ~ 5 to $\sim 120^\circ$, during the storage of coatings in air under normal conditions.

Keywords: pulsed laser deposition, thin films, aluminum oxide, laser ablation in the background gas.

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The interest in the controlled variation of wettability properties has increased significantly over the last 20 years, especially in the obtaining of superhydrophilic and superhydrophobic coatings [1]. Such coatings have a wide range of applications: enhancement of the water harvest efficiency [2], anti-fogging [3], control of surface biofouling [4], and engineering biomedical applications, such as the production of low-friction catheters, eye lenses, etc. [5]. Special attention is given to superhydrophobic or superhydrophilic coatings with high transparency. Transparency may expand their range of application in solar power engineering, „smart" window technologies, camera lenses, optoelectronic devices, etc. [6]. Specifically, it has been reported that the durability of optical instruments increases (with the transparency remaining intact) as a result of laser deposition of alumina nanostructures onto their surface [7].

According to the Wenzel equation [8], the morphology and surface energy specify the wetting properties of coatings:

$$\cos\theta_{rough} = r\cos\theta,$$

where θ_{rough} is the contact angle, r is the roughness parameter, and θ is the equilibrium contact angle of a clean surface. Angle θ depends strongly on the surface composition, restricting the choice of initial materials. The method of pulsed laser ablation is universal with respect to material types and has a number of fundamental advantages: high locality and purity of obtained films and flexibility with respect to the composition of background radiation. Laser synthesis in a gas medium provides an opportunity to adjust the porosity of deposited nanostructures. This, in turn, enables control over the wetting properties of coatings [9], as nanoporous structures can bind –OH groups, resulting in the surface becoming superhydrophilic [10].

Transparency and roughness are normally mutually exclusive, since an increase in roughness may lead to an enhancement of light scattering. The present study is focused on the determination of optimum characteristics of laser deposition for the production of transparent nanostructures (with aluminum oxide structures used as an example) with extreme wetting properties. The effect of the background gas pressure on the transparency, morphology, and wetting properties of aluminum oxide nanostructures is investigated.

Al_2O_3 nanostructures were synthesized by nanosecond laser ablation of aluminum in a background oxygen atmosphere. The oxygen pressure (20–140 Pa) and the number of laser pulses (20 000–60 000) were varied in experiments. The obtained nanostructures were analyzed with a JEOL JSM-6700F scanning election microscope (SEM) and an SF-2000 spectrophotometer. The vacuum chamber was evacuated to $P \sim 10^{-4}$ Pa (a Meradat-VIT-19IT (-VIT19IT2) vacuum gauge was used) by an oil-free system featuring forevacuum (ANEST IWATA Corporation ISP-500C) and turbomolecular (KYKY FF-200/1300E) pumps. The chamber design allowed for controlled injection of the background gas (a UFPGS-2 dual-channel gas flow regulator was used). The angle between the target and the laser beam was 45°. Targets were irradiated with second-harmonic radiation of an Nd:YAG laser (the pulse width was 8 ns). The laser beam was scanned over the target surface in order to prevent cratering. The beam was focused by a lens with a focal distance of 300 mm to a spot 0.1 mm^2 in area. with a focal distance of 300 mm to a spot 0.1 mm^2 in area. The chamber design allowed for controlled injection of the background gas (a UFPGS-2 dual-channel gas flow regulator was used). The spot size was determined based on the $1/e^2$ criterion using a beam profiler BEAMAGE-3.0-

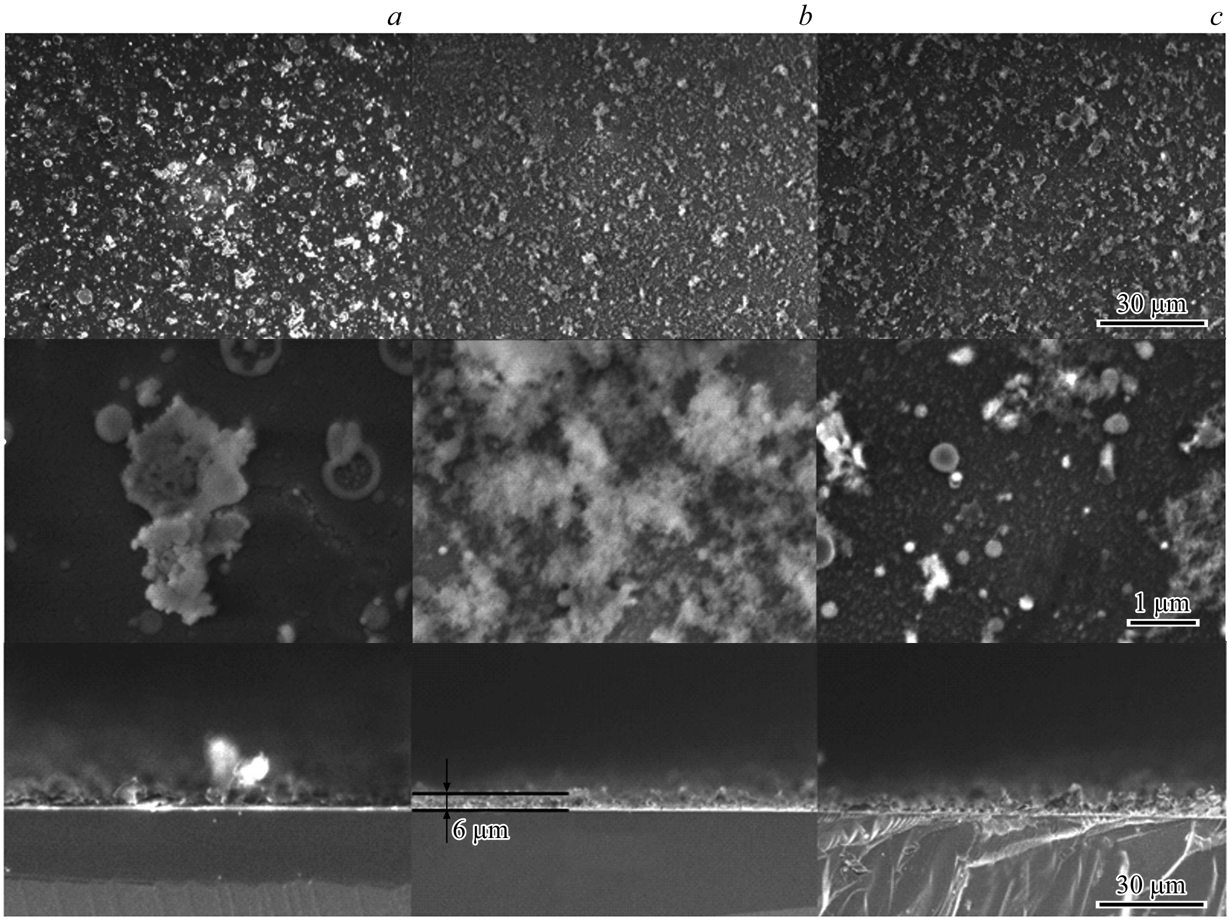

Figure 1. SEM images of the surface and cross section of coatings synthesized under a background pressure of 20 (*a*), 80 (*b*), and 140 Pa (*c*). SEM images of cleaved faces of samples are presented in the bottom row.

Gentec-EO. The mean laser fluence was 12.5 J/cm^2 (with a mean threshold fluence of the target being 0.6 J/cm^2), which allowed us to reduce the number of microdroplets on the substrate surface; the pulse repetition rate was 8 Hz. Prior to experiments, all materials were subjected to ultrasonic cleaning in surface-active substances, isopropyl alcohol, and distilled water. Targets were mounted normally to the substrate at a distance of 20 mm from its surface. Aluminum (99.9% pure) was the target material, and single-crystal silicon (Si (100)) and quartz plates 18×12 mm in size served as substrates. Deposition on quartz and silicon substrates was carried out simultaneously; based on the results of the study [11], it can be assumed that the substrate material will not affect the morphology of the coatings. Synthesis was carried out at room temperature.

Figure 1 presents the SEM images of deposited nanostructures. All coatings have a granular structure. The changes in morphology are induced by two competing processes. On the one hand, increasing the background pressure of oxygen leads to the formation of shock waves in the laser plume [12], resulting in increased pressure and temperature at the wave front. This may increase the material's porosity by enhancing the number of chemical oxidation reactions during the plume expansion, as it is known that preferential oxidation occurs precisely during the expansion stage [13].

On the other hand, the expansion of the laser plume decreases by almost 2 times with an increase in the pressure from 20 to 140 Pa [14]. Consequently, the reaction zone decreases, resulting in a reduction in the number of occurring reactions and particles reaching the target.

Transparent coatings with a well-developed surface morphology are of greatest interest that contributes to achieving critical values of contact angles. The static contact angle was measured using the sessile drop method to qualitatively assess the influence of depositing modes on the wetting properties of surfaces [15]. The dependence of the evolution of the contact angle on the storage time of samples in the air was obtained (Fig. 2, *a*). The initial contact angle of substrates was 90°. The samples became superhydrophilic with a static contact angle of $< 5^\circ$ after deposition, and all samples acquired hydrophobic properties with a wetting angle $> 100^\circ$ after 30 days of storage in the air. This is attributable to the absorption of organic compounds from the surrounding atmosphere. Note that the surface obtained at 20 Pa pressure is initially less hydrophilic and less prone

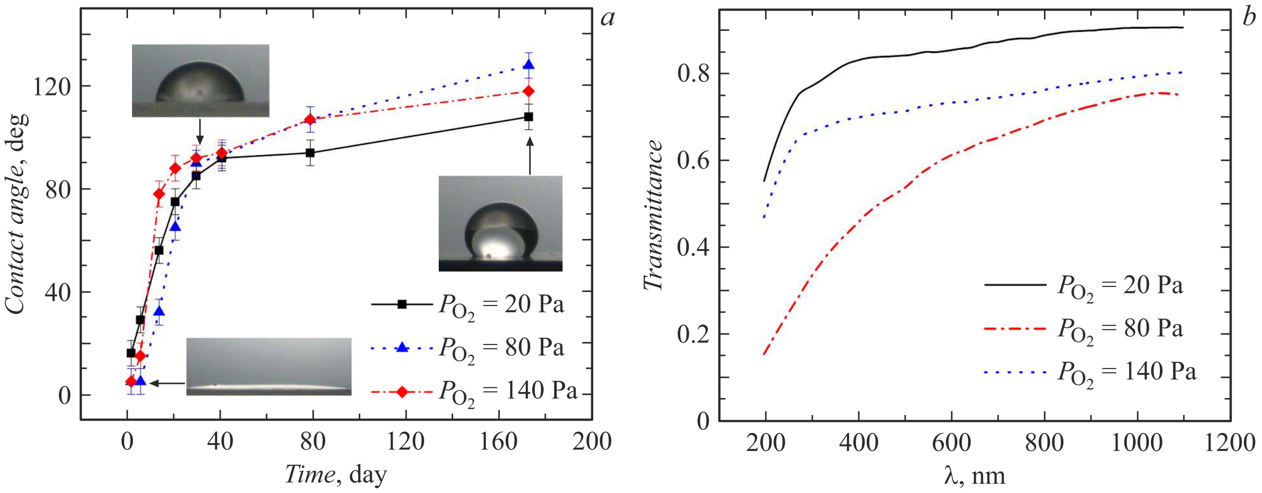

Figure 2. Temporal evolution of the contact wetting angle (*a*) and wavelength dependence of the transmittance of samples (*b*) under different background oxygen pressure levels. Number of ablation events $N = 40\,000$.

to hydrophobization, this is due to its less developed morphology.

All coatings have a high transmittance. Figure 2, *b* presents the wavelength dependence of the transmittance of samples under different levels of background oxygen pressure P_{O_2}. Optical spectra were recorded immediately after the deposition of coatings. Non-monotonic behavior of transmittance was found with increasing background oxygen pressure. The minimum was observed at an oxygen of $P_{O_2} = 80\,\text{Pa}$, which is attributed to a more developed surface morphology ($R_a = 21\,\mu\text{m}$, $R_q = 4\,\mu\text{m}$). The transmittance decreased with increasing number of laser ablation events, since the deposited coatings became thicker in the process.

According to the EDX analysis of the sample at $P_{O_2} = 80\,\text{Pa}$, the atomic ratio O/Al ≈ 3; the elevated oxygen content was attributed to the absorption of water molecules. However, an analysis of literature [16] as well as previous studies by the authors [13] allows us to conclude that under these conditions, aluminum oxide was synthesized.

Transparent Al_2O_3 nanostructures with extreme wetting properties were fabricated. Their morphology and transparency were analyzed. A non-monotonic behavior of the transmittance coefficient of the synthesized nanostructures was observed with varying background oxygen pressure, attributed to changes in surface morphology. The dependence of the contact angle of Al_2O_3 nanostructures on the storage time in the air was obtained.

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Conflict of interest

The authors declare that they have no conflict of interest.

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