

Hydrophobic Properties of a Fluoropolymer Film Covering Gold Nanoparticles

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Abstract—Thin fluoropolymer films were deposited on gold nanoparticles with different diameters by the hot-wire chemical-vapor-deposition method. The contact angles of wetting of samples with water and CH₂I₂ were determined using a DSA-100 KRUSS device, and the free surface energy of the coated surface was also determined. The influence of encapsulated gold particles on the hydrophobic properties of the obtained coatings was determined.

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Currently, research on the creation of superhydrophobic materials and coatings for different purposes is being actively carried out. In [1–3], the authors developed a method of deposition of superhydrophobic coatings on various materials for their use in various applications.

Hydrophobicity is determined by the material's characteristics (free surface energy) and by the structure of the subsurface layer and microscale and nanoscale roughness. For example, fluoropolymers have a low surface energy, and, thus, the contact angle in water of such surface is higher than 100° [4]. The influence of inhomogeneities and surface roughness can occur at partial surface wettability (Cassie–Baxter regime) or at complete wettability (Wenzel regime) [5]. As a rule, decreasing the surface energy and nanoscale and microscale roughness of the surface allows to higher values of contact angles to be achieved. For example, the fluoropolymer coatings with different morphologies depending on the deposition conditions were obtained in [6, 7]. It was shown in [6] that the contact angle changes from 120° to 170° depending on the film-deposition regime.

In this article, the influence of gold nanoparticles (NPs) presence under a fluoropolymer film upon its wetting by water was found. Gold nanoparticles with a size of from 10 to 60 nm were synthesized on polished silicon. Then, a fluoropolymer film of 20-nm thickness was deposited on this surface with gold nanoparticles. It was found that the contact angle of these composites changes from 100° to 130° and depends on the presence of gold nanoparticles, which are “hidden” under the fluoropolymer film.

To obtain the samples with gold nanoparticles, thin films of gold with a thickness ranging from 2 to 10 nm were deposited on the surface of the (111) silicon with a 5 × 20-mm area using ion sputtering on a JEOL Auto Fine Coater—JFC-1600 set-up. The process parameters are presented in Table 1. The obtained films were annealed in a vacuum chamber at a temperature of 550°C and pressure of 10⁻¹ Pa for 15 min. During annealing, nanoparticles are formed on the surface of the substrate, the size of which depends, in particular, on the thickness of the initial film and annealing temperature.

Fluoropolymer coatings were deposited on gold nanoparticles by hot-wire chemical-vapor deposition (HWCVD) [8, 9]. The experimental setup was described in [6]. Smooth defect-free fluoropolymer films were obtained using the following conditions: the flow rate of the C₃F₆O precursor gas was 20 sccm, the temperature of the activating mesh was around 680°C, the pressure of the precursor gas was 50 Pa, the distance between the activator and substrate was 50 mm, the deposition time was equal to 7 min, and the substrate temperature was around 30°C.

Table 1. Parameters of samples with gold particles

Sample	Film thickness before annealing, nm	Average size of Au nanoparticles, nm
1	2	12
2	4	22
3	10	55

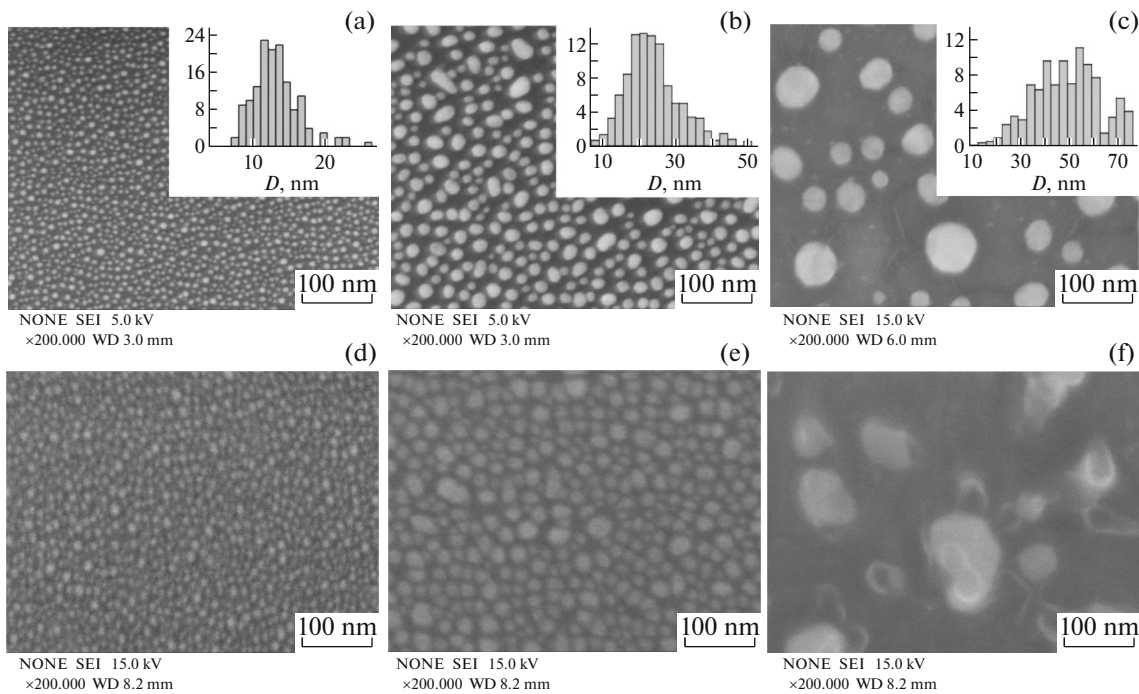


Fig. 1. Micrographs of the surface with gold nanoparticles (a–c) before and (d–f) after deposition of fluoropolymer film with 20-nm thickness. Average size of particles: (a, d) 12, (b, e) 22, and (c, f) 55 nm; the distributions of particle sizes are shown in the inserts.

Micrographs obtained by a JEOL JSM-6700F scanning electron microscope of gold nanoparticles (a–c) and composite coatings (d–f) obtained in the experiment are presented in Fig. 1. Using a BSE (backscattered electron) detector, it was determined that the form and shape of gold nanoparticles do not exhibit any change upon deposition of a fluoropolymer coating. Thus, metal–polymer composites with controlled geometry were obtained.

To determine the degree of roughness, measurements of surface profiles of the sample were carried

out using a Solver P47H (NT MDT, Zelenograd) atomic-force microscope. The ratio of profile line length to the length of its projection was determined on the basis of these measurements (Table 2). The average roughness amplitude was 1.4 nm for sample 1, 3 nm for sample 2, and 50 nm for sample 3.

The influence of the geometric characteristics of the surfaces on the contact angle was determined by the Wenzel formula [5]:

$$\cos(\alpha_c) = y \cos(\alpha),$$

where α_c is the contact angle of the rough surface, α is the contact angle of the smooth surface, and y is the ratio value of the profile line length to the length of its projection. Angle $\alpha = 166^\circ$ corresponds to our measurements of the wettability of fluoropolymer coating by water on polished silicon [6] (sample 4 in Table 3). The value of angle α_c for the investigated samples are given in Table 2.

It follows from the results of calculation that the roughness of samples 1 and 2 almost does not change the contact angle, while for sample 3, $|\cos \alpha_c| > 1$, which indicates the inapplicability of this formula to the case of incomplete wetting of a surface.

The measurements of contact angle and free energy of sample surface F were performed using the DSA-100 KRUSS device (Table 3). These measurements were carried out for two liquids, water (polar liquid) and diiodomethane CH_2I_2 (nonpolar liquid). According to [4], the contact angle for water on Teflon surface

Table 2. Values of y and α_c calculated by Wenzel's equation

Parameter	Sample 1	Sample 2	Sample 3
y	1.00076	1.0028	1.127
α_c	166.1°	166.5°	–

Table 3. Results of measurements of contact-angle and surface energy in polar (H_2O) and nonpolar (CH_2I_2) liquids

Sample	Contact angle in H_2O , deg	Contact angle in CH_2I_2 , deg	Free surface energy F , mN/m
1	105	77	25.5
2	101	73	27.3
3	134	79	20.4
4	166	118	4.7

(thick film of fluoropolymer) is $\sim 105^\circ$ and that for diiodomethane (CH_2I_2) is 85° . Apparently, the difference is linked with the size effects manifesting in the film of a fluoropolymer with a nanoscale surface structure.

The measured water contact angles for the obtained samples (Table 3) differ from the calculated values shown in Table 2. The results of calculations indicate the weak influence of the surface roughness on a contact angle due to the low value of parameter γ . Consequently, for these samples, the value of the contact angle is determined mainly by free surface energy F . From the results of measurements, it was determined that introduction of gold nanoparticles into fluoropolymer films leads to a considerable change of F . Thus, the presence of gold nanoparticles in a fluoropolymer films leads to a change of the free surface energy of a fluoropolymer and, correspondingly, a change of contact angle.

The procedure of surface-energy determination was realized by means of Owens, Wendt, Rabel and Kaelble method, in which it was assumed that the surface energy of the solid body has two components: disperse and polar [10]. The disperse component includes van der Waals forces and other nonspecific interactions, and the polar component includes the strong interactions and hydrogen bonds. Van der Waals forces can act at a distance of around 100 nm [11]. It is clear that, at a fluoropolymer-film thickness of 20 nm, the liquid can “sense” the presence of encapsulated gold nanoparticles. Usually, the metal has a higher free surface energy than the fluoropolymer. Consequently, the presence of gold nanoparticles will increase the surface energy.

Composite coatings consisting of gold nanoparticles and a thin film of fluoropolymer deposited on the top were obtained. It was found that the presence of encapsulated gold nanoparticles influences the hydrophobic properties of a thin fluoropolymer film. The direct dependence of the change of the hydrophobic properties of the sample surface on the presence and size of encapsulated gold nanoparticles was shown.

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