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Enhancing hydrophobic properties of ZnO structures using gold coatings

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The effect of enhancement the hydrophobic properties of the ensemble of micro- and nanostructures ZnO as a result of coating with gold was discovered. For the first time, it has been shown that coating the ensemble with a micro- and nanoparticle ZnO layer of gold leads to a sharp increase in the wetting edge angle from 145 to 168° (water drop volume 5 mm3) and a decrease in the hydrophobicity/hydrophilicity transition time under ultraviolet irradiation. Keywords: ZnO, gold, superhydrophobic.

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The interest in superhydrophobic coatings stems primarily from their high resistance to water and resistance to corrosion, icing, biofouling, and various types of contamination. This makes it all the more important to introduce superhydrophobic materials into modern nanoelectronics. Unfortunately, materials traditionally used in nanoelectronics do not feature hydrophobic properties and often require special surface treatment. For example, metal-assisted etching [1] is used in silicon technology to form porous surfaces with high values of the contact angle of wetting. Another example is the use of surfaces with multimodal roughness. A superhydrophobic state with a contact angle of 151° was achieved in [2] for ZnO samples with multimodal surface roughness. Another problem is the necessity of forming gold contacts to different elements of an electronic platform, which may serve as additional water adsorption sites. Debates on hydrophilic and hydrophobic properties of gold have actually been going on for quite some time. According to the data from [3], a clean gold surface is hydrophilic. However, if the surface of gold is contaminated, its wetting quality decreases considerably. The results of microstructuring and subsequent coating of a gold surface with thiol performed in order to make the surface hydrophobic were reported in [4]. We have found no published papers focused on the effect of gold coating on the hydrophobic properties of materials (specifically, zinc oxide). At the same time, the Au−ZnO is used in electronic devices; therefore, its performance characteristics are subject to stringent requirements. Gold stands out for its nonpolar crystal structure and fine adhesion to ZnO. This may be a prerequisite to enhancement of the hydrophobicity of ZnO coated with gold. In the present study, the hydrophobic properties (contact angle of wetting, slip angle, hydrophobicity/hydrophilicity switching) of a clean ZnO surface and a surface with a gold coating with various morphologies are compared.

The ZnO sample with a well-developed surface microstructure on a sapphire substrate (type I sample) was formed by self-catalyzed gas-phase synthesis. ZnO deposition was performed in the growth zone from zinc vapor and a gas mixture of argon and oxygen. The reactor was evacuated in advance to a pressure of 10 Pa. The temperature in the zinc evaporation zone was reduced at the end growth stage to form a distinct ZnO micromorphology.

The deposition of gold on a part of the ZnO sample (type II sample) was performed using a VN-2000 thermal evaporation setup. The vacuum was no worse than 10^{-6} Pa. The gold layer thickness was monitored with a KIT-1 quartz thickness gage. The type II sample was annealed in ambient conditions at a temperature of 650°C in a tube-type furnace to investigate the effect of the gold coating micromorphology on the hydrophobic properties.

A solid gold film on sapphire was synthesized additionally for comparison.

Microscopic studies were carried out using a Jeol Neoscope 2 (JCM-6000) scanning electron microscope (SEM) fitted with an energy-dispersive X-ray microanalyzer. The hydrophobicity/hydrophilicity of microstructured clean and gold-coated surfaces of zinc oxide was analyzed in accordance with the „sitting drop"method. A distilled water droplet with a volume on the order of 5 mm^3 was introduced with a syringe onto the horizontal sample surface. A digital camera was used for optical imaging of the droplet on the surface. The contact angle was determined in accordance with the procedure outlined in [5]. Optical studies were performed using a Levenhuk optical microscope. The process of hydrophobicity/hydrophilicity switching was examined with an ultraviolet light-emitting diode (with its emission maximum at 375 nm).

According to SEM data, the type I sample was an ensemble of hexagonal ZnO microrods with a diameter up to 1 μm that had pointed ZnO nanorods extending from their end faces. The length and the diameter of these nanorods were 3−4 μm and 100−150 nm, respectively. The surface micromorphology of the type II ZnO sample remained almost unchanged after the deposition of a gold

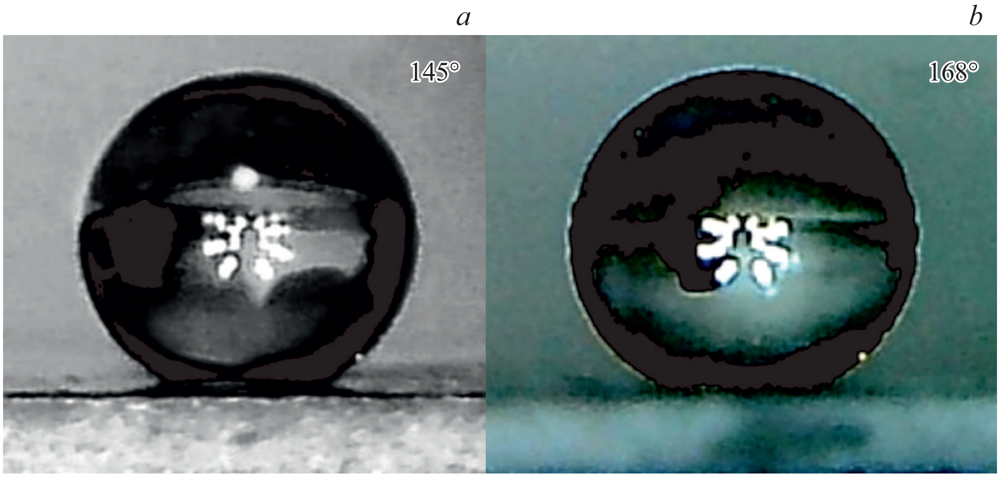

Figure 1. Photographic images of water droplets on the surface of ZnO samples with the contact angles indicated. *a* — type I, *b* — type II.

coating layer with a thickness on the order of 60 nm. The presence of gold (~ 2 at.%) was detectable only in the energy-dispersive X-ray microanalysis spectra.

The formation of a distinct ZnO microstructure in the conditions of our experiment is quite predictable. At the initial stage, hexagonal ZnO microrods form in accordance with the vapor–liquid–solid mechanism. Liquid Zn islets on the substrate catalyze their growth. Oxygen molecules diffuse through zinc pairs to the substrate and react with zinc there, thus forming zinc oxide. With the oxygen concentration being low, one may easily control the diameter of growing ZnO structures by adjusting the temperature in the zinc evaporation zone. The diameter of ZnO rods may be reduced by reducing the temperature in the zinc evaporation zone at the end stage of synthesis. The growth of a ZnO nanorod from a smaller zinc droplet on the end face of the parent microrod is initiated. The ZnO nanorod growth is inhibited later on by reducing gradually the concentration of zinc in the gas phase, and a pointed end of the nanorod is shaped.

At the next stage, the hydrophobic properties of the surface of samples were studied. A water droplet with a volume of $5\,\mathrm{mm}^3$ was deposited. Judging by the shape of this droplet and the value of contact angle $\theta = 145^\circ$ (Fig. 1, *a*), the Cassie–Baxter state was established on the sample surface [5]. An array of ZnO micro- and nanorods forms a surface with a complex morphology and allows one to implement the „lotus effect“ [6]. An ideally smooth ZnO surface is highly hydrophilic, and, according to [7], the contact angle of wetting is no more than 5°. The contact between a water droplet and ZnO is minimized, and the region of contact between the droplet and the air layer, which fills micropores in the bulk of ZnO, forms the primary phase interface. Considering that the wetting angle of the gas phase with liquid is 180°, the area fraction of the ZnO–liquid interaction estimated in accordance with the Cassie–Baxter model [5] for the type I sample is 0.18.

An anomalously high hydrophobicity (the contact angle of wetting increases to 168°) is observed (Fig. 1, *b*) in the part of the ZnO structure coated with gold (type II). It should be noted that such high values of the contact angle of wetting have been reported earlier only for „coral-like“ ZnO structures with a polymer coating [8]. The measured contact angle of wetting for the surface of a solid gold film ($\sim 63^\circ$) is indicative of its low wettability. Another factor possibly contributing to the enhancement of hydrophobicity of the type II sample is a probable increase in roughness (or a change in its structure) in the process of coating the surface with gold. SEM data reveal no noticeable changes in the morphology of ZnO structures after the deposition of a gold layer. It is unlikely that the increase in contact angle of wetting is associated in this case with an increase in roughness of the lateral surfaces of ZnO micro- and nanorods after the deposition of gold. Assuming that the area fraction of the ZnO–liquid interaction remains unchanged following the deposition of gold on the type I sample, the overall enhancement of its hydrophobicity is attributable to a reduction in wettability (enhancement of the hydrophobic component) in each contact region. An intriguing result was obtained in experiments with tilted samples (the tilt time was 5 s). Samples type I and II with water droplets were tilted by 90° in the vertical plane (i.e., to a vertical position). The obtained results (Fig. 2) for the type I sample demonstrate that the area of contact between a droplet and the sample surface remained almost unchanged, while the droplet itself tilted under the influence of gravity. A drastic reduction in contact angle and an enlargement of the area of contact between a droplet and the sample surface was observed for the type II sample. It should be noted that water droplets did not slide down the surface of samples even when they were tilted by 90°.

The presence of polar and nonpolar directions is a distinctive feature of the wurtzite structure of ZnO. The pointed part of nanorods is aligned with polar axis *c* and

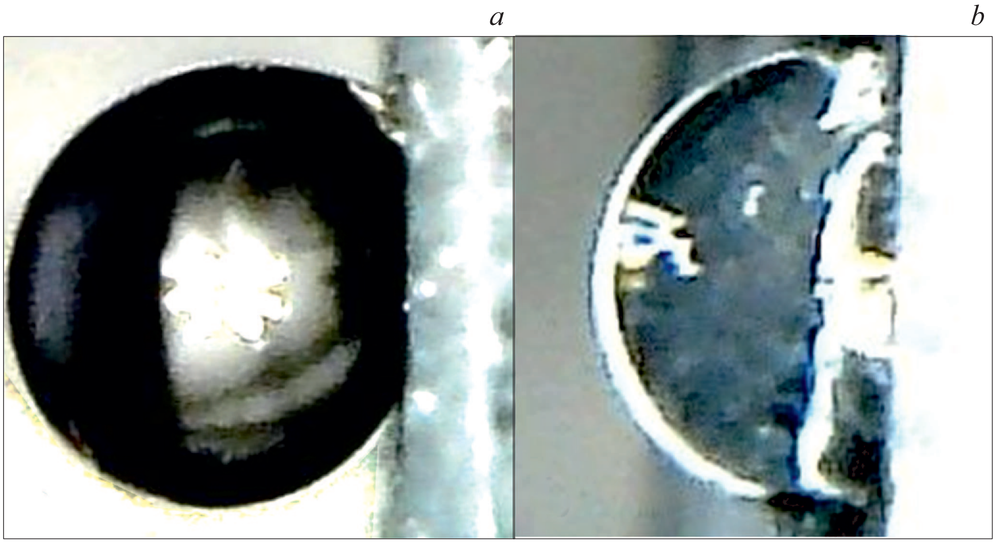

Figure 2. Photographic images of water droplets on the surface of ZnO samples tilted at an angle of $\sim 90^\circ$. *a* — type I, *b* — type II.

ends with Zn^+ ions. Polar water molecules are deposited easily on these ions. The lateral faces of hexagonal ZnO rods are formed by nonpolar *m*-planes [9]. Calculated data [10] demonstrate that water molecules aggregate and dissociate on *m*-planes of ZnO, thus maintaining a stable hydrophilic surface state. Thus, a smooth ZnO surface is highly hydrophilic (the contact angle of wetting is below 5°), which is confirmed by the results presented in [7]. This is the reason why a water droplet does not slide down the clean ZnO sample (type I) and no slipping of the bottom edge is observed. The fact that a droplet spreads out on the tilted ZnO sample coated with gold (type II sample) may be attributed to the tendency to reduce the droplet–ZnO/Au interfacial energy and to the fulfillment of condition $\sigma_{sl} \ll \sigma_{sv}$ (surface energies at the solid–liquid and solid–gas interfaces, respectively) between the specific free energies of the surfaces involved. Taken together, the observed effects may be associated with the complex nature of interaction between water molecules and the surface of gold [11]. The contact angle of wetting even for a smooth sold surface varies within a wide range of 30–80° (according to the data from review [3]). Presumably, the Au–H hydrogen bond plays a leading part in the interaction between water molecules and the surface of gold [12]. Unfortunately, the energy of this bond is not known. However [3], even insignificant contamination (less than a monolayer of carbon) reduces the wettability of a gold coating. Since the contact angle of wetting for a solid gold film is $\sim 63^\circ$, the surface should be contaminated. The inhomogeneity of the gold coating of the ZnO structure with a complex micro- and nanorelief is another probable contributing factor. The type II sample was annealed to reveal the influence of micromorphology of the gold coating. The gold coating coagulated in the process of annealing, but this had no significant effect on the hydrophobicity of the type II sample (Fig. 3, sample ZnO/Au). The contact angle variation was within the limit of error. It was found that the hydrophobicity/hydrophilicity transition time decreased to 10 min under ultraviolet irradiation. Note for comparison that the contact angle and the size of a water droplet decreased within the same time interval on a clean ZnO surface.

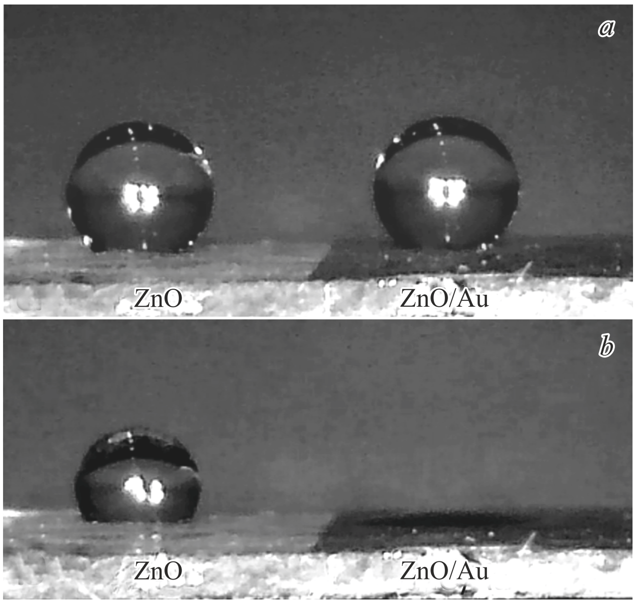

Figure 3. Investigation of the hydrophobicity/hydrophilicity switching process for annealed ZnO samples (type I and II) under ultraviolet irradiation. *a* — prior to irradiation, *b* — 10 min after irradiation.

Thus, the effect of enhancement of superhydrophobic properties of an ensemble of ZnO micro- and nanostructures induced by coating them with gold has been observed for the first time. An ensemble of hexagonal ZnO microrods with a diameter up to $1\,\mu$m and pointed ZnO nanorods extending from their end faces was prepared in a specialized deposition regime. This regime ensured the formation of complex surface topography with multimodal roughness. When this ensemble of ZnO micro- and nanostructures was coated with a layer of gold with a thickness on the order of 60 nm, their superhydrophobic properties were enhanced considerably. The contact angle of wetting increased from 145 to 168° (the water droplet volume was $5\,\text{mm}^3$). It was also found that the hydrophobicity/hydrophilicity transition time decreased under ultraviolet irradiation. The above results may be of interest in the context of application of the Au–ZnO system in electronic devices and improvement of their performance characteristics.

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Conflict of interest

The authors declare that they have no conflict of interest.

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