Experimental study of the wettability of silicon substrates coated with vertically oriented carbon nanotubes

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Abstract. The experimental study of the wettability of silicon substrates coated with vertically oriented carbon nanotubes is conducted. It is found that carbon nanotube coatings are superhydrophobic and have small hysteresis. Heat treatment of the carbon nanotube coatings significantly reduces the receding contact angle and virtually doesn’t change the advancing contact angle. It should be noted that the thickness of the carbon nanotube coatings doesn’t significantly affect the substrate wettability.

1. Introduction

Wettability of the surface plays an important role in many physical processes. Various coatings that change the surface wettability are used in industry to create anti-icing surfaces, self-cleaning surfaces, water-repellent surfaces, etc.

Surface wettability also affects heat transfer processes. Wetting properties of a surface have shown significant influence on pool boiling heat transfer [1, 2]. Paper [3] presents results of an experimental study of the effect of hydrophobic fluoropolymer coating on the multiscale characteristics of heat transfer at water boiling. Experimental observations of dropwise condensation of water vapor on a chemically textured surface of glass and its detailed computer simulation are presented in [4]. In [5], the rupture of thin liquid films sprayed on solid surfaces with different wettability is studied. The effect of the equilibrium contact angle of wetting on the dynamics of the dry spot propagation and on the critical heat flux upon the breakdown of a horizontal water film heated locally from the substrate side is studied experimentally in [6]. In [7] different working liquids and coatings of the working surface are used in the experiments to investigate the effect of the wetting angle on the nonisothermal breakdown of the falling liquid film. In [8, 9], the effect of the wettability on the structure of a two-phase flow in a channel is investigated. Papers [10-13] show that substrate wetting properties play an important role in the process of the drop evaporation. Evaporation of microliter water droplets on a hot copper substrate coated with single-walled carbon nanotubes is performed in [14].

2. Experimental equipment and methods

Square silicon wafers with the thickness of 0.5 mm and 10 mm side coated with vertically oriented carbon nanotubes were used as test substrates. The substrates were made at the Nikolaev Institute of
Inorganic Chemistry. The thickness of the nanotube coatings varied from 100 to 400 μm and was determined from the images (figure 1) obtained using a scanning electron microscope. Three types of substrates with different thermal treatment were used: 1) substrates annealed at a temperature of 200°C in the atmosphere; 2) substrates annealed at a temperature of 450°C in vacuum; and 3) those without heat treatment.

![Figure 1. SEM images of nanotube coatings with a thickness of about 100 μm. Top view (left image) and side view (right image).](image1.jpg)

Surface wettability is characterized by the contact angle formed between the tangent drawn to the surface of the liquid-gas interface and a solid surface with the vertex located at the point of contact of the three phases, and conventionally measured through the liquid phase. In order to characterize the substrate wettability more completely, the advancing and receding contact angles are usually measured when the liquid drop moves linearly on the surface during liquid injection and removal, respectively. Studies of the wettability of silicon substrates coated with carbon nanotubes are performed using the DSA100 system for drop shape analysis produced by KRUSS (figure 2).

![Figure 2. DSA100 drop shape analysis system.](image2.jpg)

The procedure for measuring the contact angle was as follows: the nanotube-coated substrate was mounted on the three-axis positioning system; using a high-precision dosing system (with the dosing
step of 0.1 μl), the liquid (ultrapure Milli-Q water) was injected onto the substrate through a needle with a diameter of 0.52 mm at a rate of 0.05 ml/min to realize the advancing contact angle (the maximum drop volume varied from 20 to 80 ml), then the liquid was withdrawn through the needle at a rate of 0.05 ml/min to realize the receding contact angle; contact angle measurements were performed using the DSA100 software, that automatically processed shadow images of the drop. The images were captured at 2 fps by an optical shadow system including the 50 W light source and a CCD camera with a resolution of 780х580 pixels (viewing field from 3.7х2.7 mm to 23.2х17.2 mm).

The temperature and relative humidity of the ambient air during the experiments was 22-24 °C and 20-30 %, respectively.

3. Experimental results and discussion
It is found that nanotube coated substrates without heat treatment are superhydrophobic (figure 3) and have a small hysteresis (practically the same advancing and receding contact angles). The thickness of the nanotube coating in the studied range (100-400 μm) does not significantly affect the substrate wettability (figure 4). However, it should be noted that thicker coatings (about 300-400 μm) are less stable and can be peeled off from the substrate even at a short contact with the liquid, so correct measurement of the receding contact angle is impossible.

![Figure 3](image-url)

**Figure 3.** Shadow images of the drop on the substrate coated with carbon nanotubes, without heat treatment. Advancing contact angle (left image), receding contact angle (right image).

![Figure 4](image-url)

**Figure 4.** Changes in wettability of the substrate coated with carbon nanotubes (without heat treatment) vs nanotube coating thickness.

Annealing of substrates coated with carbon nanotubes under various conditions (in a vacuum at a temperature of 450°C; in air at a temperature of 200°C) for 4 hours doesn’t affect the advancing contact angle. However, it radically changes the receding contact angle, which virtually becomes equal
to zero (figure 5). Unfortunately, it is not possible to accurately measure the small receding contact angle, since the DSA100 KRUSS software cannot reliably measure contact angles below 10°. Annealing changes the chemical properties of the coating; as a result, the contact line is pinned (when pumping liquid from the drop, the contact area with the surface is constant). The nanotube coating thickness for annealed substrates does not significantly affect the substrate wettability either (figure 6).

**Figure 5.** Shadow images of the drop on the substrate coated with carbon nanotubes and annealed in air at a temperature of 200°C for 4 hours. Advancing contact angle (left image), receding contact angle (right image).

**Figure 6.** Changes in wettability of the substrate coated with carbon nanotubes and annealed for 4 hours vs. nanotube coating thickness. Substrates annealed at a temperature of 200°C in the atmosphere (left image), substrates annealed at a temperature of 450°C in vacuum (right image).

**Conclusions**
Substrates coated with vertically oriented carbon nanotubes are superhydrophobic and have small hysteresis. Annealing of the substrates for 4 hours a) in air at a temperature of 200°C; b) in vacuum at a temperature of 450°C significantly changes the receding contact angle and virtually doesn’t change the advancing contact angle. The thickness of the carbon nanotube coatings doesn’t significantly affect the substrate wettability; however, thicker coatings are less stable.

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