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The method of synthesizing of superhydrophobic surfaces by PECVD

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Abstract. The aim of this work was to obtain superhydrophobic surfaces in a plasma medium. The experiment was carried out using the PECVD method in two different modes: constant and pulsing. The surface roughness was obtained by applying nanoparticles synthesized in plasma in a mixture of argon and methane. The resulting particles were deposited on the surface of silicon and glass materials. The contact angle increased linearly depending on the number of cycles, until it reached 160° at 150-160th cycles, after that the increase in cycles does not affect the contact angle, since the saturation process is in progress. Also the effect of the working gas composition on the hydrophobicity of the surface was studied. At low concentrations of methane (1%) only particles are synthesized in the working gas, and hydrophobicity is unstable, with an increase in methane concentration (7%) nanofilms are synthesized from nanoclusters, and surface hydrophobicity is relatively stable. In addition, a pulsing plasma mode was used to obtain superhydrophobic surfaces. The hydrophobicity of the sample showed that the strength of the nanofilm was stable in comparison with the sample obtained in the first mode, but the contact angle was lower. The obtained samples were examined using SEM, SPM, optical analysis, and their contact angles were determined.

1. Introduction

As a rule, if a solid surface has $\alpha > 90^\circ$ contact angle (CA) with water, it is considered hydrophobic, and if it has $\alpha < 90^\circ$, then it is hydrophilic. There is also a superhydrophobic surface, that has a contact angle greater than 150° and a superhydrophilic with contact angle less than 10°. The wettability of the surface as a whole depends on two factors: the chemical composition and roughness of the surface. If both parameters are used properly, it is possible to create superhydrophobic surface with contact angle close to 180° (lotus effect) [1]. Hydrophobic or hydrophilic properties of the solid surface are key aspects for creating anti-icing, anti-corrosion, anti-fogging, medicine, water harvesting, oil/water separation, self-cleaning, etc.

At present, many methods have been developed, including physical, chemical and a combination of physical and chemical methods, to produce superhydrophobic surfaces in a simple and environmentally friendly way [2]. Surface modification methods such as plasma treatment, vapor deposition method, electrohydrodynamics/ electrospinning, sol-gel methods, phase separation method, spraying method, one-step method, spin-coating method, ion-assisted deposition method and electrochemical methods are used to create a hydrophobic topography of the surface. This can be a complex multi-step processes. The authors of [3] made tape-like superhydrophobic films by



precipitating fluorocarbons on silicon in the RF glow discharge. Since the rough surface obtained by plasma treatment is easily tuned, this method is unique for obtaining superhydrophobic coatings with good optical properties. For example: in [4] transparent hydrophobic surfaces with a roughness of 20 nm were synthesized. The Khan group in [5] adjusting the LDPE crystallization parameters (crystallization time and growth rate) prepared superhydrophobic surfaces with different structures. The crystallization time and the nucleation rate were increased by evaporation of the solvent at a low temperature, so the contact angle also increased. Then, adding cyclohexane and drying at room temperature, a superhydrophobic surface with a contact angle of 173° was obtained. The polymeric material has a number of advantages, such as relatively inexpensive, transparent, easily manufactured, can be treated with a solvent, etc. Park and others, using a new copolymer, obtained a superhydrophobic surface by spin-coating method [6]. This method can be applied to different substrates with different complexities. After surface damage, the hydrophobicity of such coatings is easily restored by spraying of dispersion. In [7] the authors obtained structured films, consisting of nanoclusters and nanoparticles on a glass substrate, by the sol-gel method. Surface structure can be regulated by controlling the hydrolysis and condensation. The method includes two steps: a sol-gel process for obtaining a surface roughness, after surface modification with fluorides to achieve transparency. Cho and others prepared superhydrophobic surfaces with a contact angle of 160° by the electrochemical reaction of a copper alloy [8]. The non-electric chemical coating of Cu on steel sheets led to microstructures on these surfaces, while nanotubes of copper sulfide on microstructures were obtained by electrochemical reaction of Cu in a sulfur-containing medium at a temperature of 150°C . The LBL method can be combined with others to control surface structures. In [9] the authors obtained a stable superhydrophobic film with a modification by the combination of LBL and electrochemical deposition methods. Miller et al. in [10] obtained superhydrophobic surfaces with a contact angle of $\sim 150^\circ$ using a single-phase PVD. Photolithography is also used to produce a rough surface. In work [11] scientists obtained superhydrophobic surfaces by photolithography. As a result, the obtained surface appears superhydrophobic with low adhesion, and the size of the square bars X-Y is 2 and 32 μm . But when the dimensions of the columns reached 64 and 128 μm , water droplets were fixed to the surface of the substrate.

This paper presents some experimental results on the production of superhydrophobic and superhydrophilic surfaces by the PECVD method in the RFCD plasma.

2. Experimental study

Carbon nanoparticles were synthesized in RFC discharge plasma in gas mixtures of argon and methane. The main part of the experimental installation is an electrode system, which consists of plane-parallel discs with a diameter of 10 cm. Interelectrode distance is 3 cm. The upper electrode is connected to the RF generator and the lower electrode is grounded. The experimental setup is presented and described in [12,13]. The gas flow was observed and controlled via MFC Bronkhorst. The experiment was performed at different plasma parameters (discharge power, gas pressure, the percentage of the mixture gas flow and maintain the plasma, etc.).

3. Results and discussion

At ignition of plasma at certain parameters nanoparticles are synthesized due to the carbon-containing gas. When plasma is excluded, depending on time a certain number of these nanoparticles is deposited on the surface of the substrate that is located on the lower electrode. This process is carried out cyclically. Thus, the amount of particles on the substrate can be regulated by the number of cycles used to produce a surface with different roughness. With increasing numbers of cycles increases the density of particles on the substrate, which leads to an increase in contact angle. This effect for different cycles of deposition of nanoparticles on the surface of a glass substrate is shown in Figure 1.

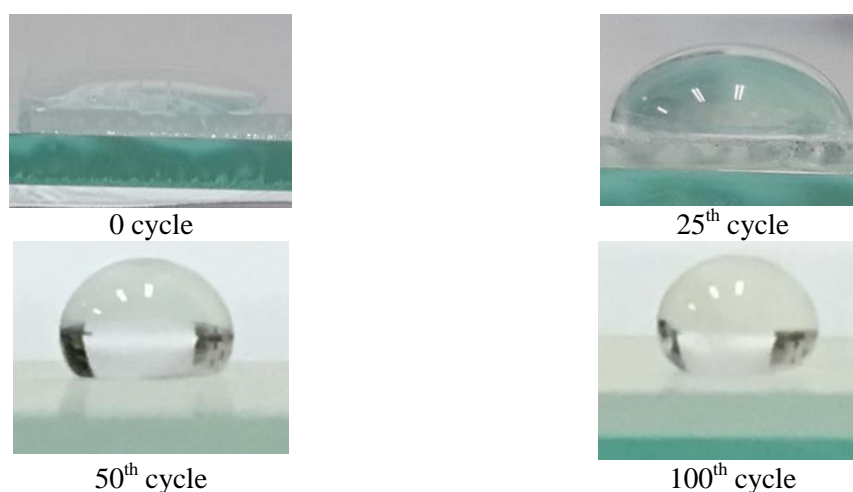


Fig. 1 – Photographs of obtained hydrophobic surfaces at different cycles of deposition of nanoparticles

Using the obtained experimental data the dependence of the contact angle on the deposition of nanoparticles was found, it is shown in Figure 2. As it can be seen from the graph the contact angle increases linearly depending on the number of cycles, until it reaches a value of about 160° at 150 cycles. After this an increase in cycles does not affect the contact angle, since saturation is reached. The graph also shows the curves for different cycle times, which directly affects the contact angle of the surface. This effect can be explained by the fact that at the same plasma parameters depending on time nanoparticles with specific sizes are synthesized, for example, in 10 seconds nanoparticles with diameter of $\sim 70\text{-}90$ nm are synthesized, in 15 seconds nanoparticles with diameter of $\sim 120\text{-}170$ nm are synthesized. Depending on the size of the precipitated nanoparticles the surface roughness changes affecting the contact angle.

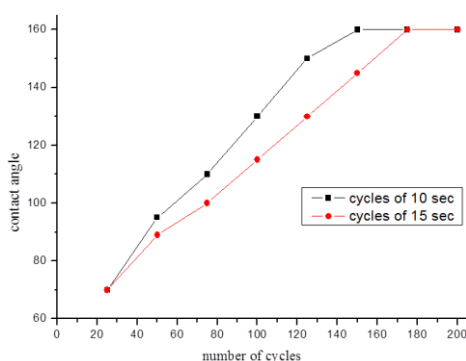


Fig. 2 – Dependence of the contact angle on the deposition cycle of nanoparticles

In addition, the dependence of the hydrophobicity of the surface on the composition of the working gas was investigated. At low concentrations of methane (1%) only nanoparticles are synthesized in the working gas, and with increasing methane concentration (7%) simultaneously with the nanoparticles nanofilm is synthesized. It is shown by the SEM, optical images and photos of the obtained samples shown in Figure 3 and Figure 4. When only nanoparticles are deposited on the surface, they interact with water, which leads to the destruction of hydrophobicity. When surface of substrate with nanoparticles and nanofilm is obtained, the hydrophobicity during contact with water is not destroyed due to the fact that the nanofilm is the connecting element between nanoparticles, due to which surface roughness appears.

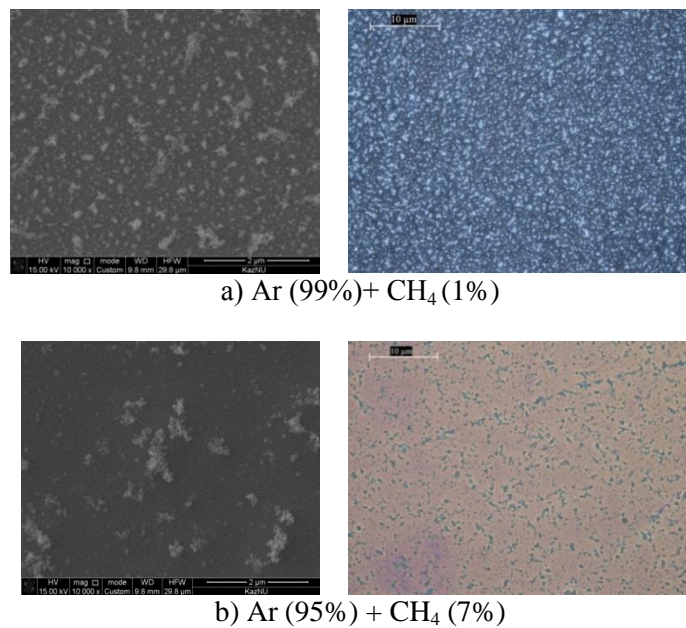


Fig.3 – SEM and optical images of the samples obtained at different gas compositions



Fig.4 – Photos of the samples obtained at different gas compositions

To obtain stable hydrophobic surface, consisting of nanoparticles and nanofilms, plasma pulse mode can also be used. In this mode hydrophobic surfaces with small contact angles in comparison to the previous method results were obtained. In this method of obtaining hydrophobicity plasma confinement time is significantly low, therefore nanoparticles with diameter of about 4-10 nm and nanofilms that affect surface roughness are synthesized. The obtained sample was investigated with SZM, which indicates that the surface is rough and has an ordered structure. Figure 5 shows the results of the SZM analysis.

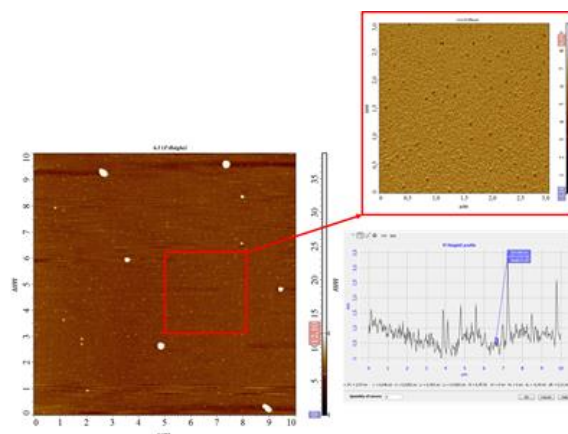


Fig.5 – SZM analysis of the obtaining samples in pulse mode

When superhydrophobic surface is treated with a buffer plasma (argon or nitrogen), the hydrophobicity is destroyed and the surface acquires superhydrophilic properties. Figure 6 shows the transformation from superhydrophobicity to superhydrophilicity. It should also be noted that the contact angle decreases with increasing plasma processing time.

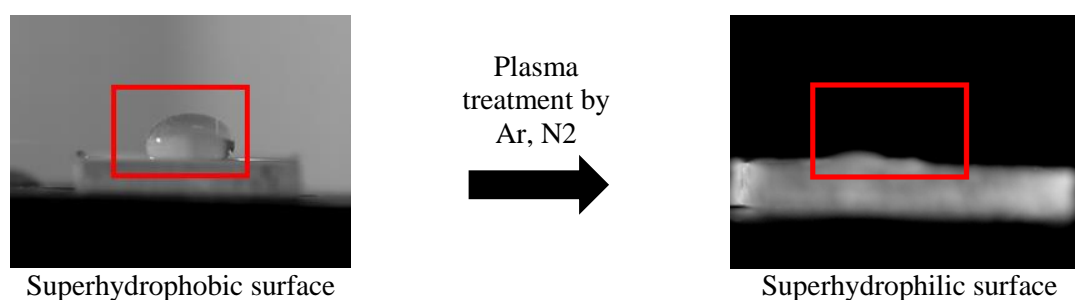


Fig.6 – Transformation from superhydrophobicity to superhydrophilicity

In this work, firstly, we got superhydrophobic surfaces using a simple one-step process, based on polymerizing carbonaceous nanoparticles in plasma and deposition on silicon wafer. Nanoparticles arising in plasma polymerization process are typical example of plasma polymers, i.e. materials, which in difference to conventional structured polymers, do not consist of repeating units. In addition, we researched how wetting characteristics were changing when processed in different plasma environments. We focused on the process of growth of nanoparticles and their subsequent deposition. Specific feature of this process is the negative charge of the nanoparticles. Once the particles reach a size of several nanometers, they quickly collect a negative charge (due to the high mobility of the electrons in the plasma). As a result, the particles are held in positive plasma potential, i.e. they are levitating in the discharge, where they continue to grow due to the accumulation of neutral radicals and positive ions. After the plasma turns off, particles lose the negative charge and fall down to the lower electrode. Every time plasma is turned off a certain amount of nanoparticles will fall onto the substrate, which is located on the lower electrode.

The SEM image shows that the synthesized materials have a rough surface with contact angles of from 100° to 165° , depending on the plasma parameters. Experimentally it has been found, that the number of particles on a silicon substrate depends on the number of cycles, i.e. the film's hydrophobic feature (contact angle) increases with the number of cycles.

4. Conclusion

In this paper, as a result of the conducted experiments, superhydrophobic and superhydrophilic surfaces were obtained. The obtained samples were examined by SEM, photos and optical microscopy, the results of which indicate surface roughness. It was found that the hydrophobicity of the surface varies depending on the nanoparticles application cycle, the cycle time and the resulting surface structure.

5. Acknowledgments

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