

Rapid communication

From super-hydrophilic to super-hydrophobic surfaces using plasma polymerization combined with gas aggregation source of nanoparticles



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ABSTRACT

Control of surface wettability is of great importance in a wide range of technological applications. In this study we report on the possibility to cover the full range of surface wetting characters from super-hydrophilic to super-hydrophobic one using plasma polymerization (plasma enhanced chemical vapor deposition) performed with different mixtures of hexamethyldisiloxane/oxygen and in combination with nanoparticle deposition.

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Plasma processing of solid objects is a well-established technique for many applications because of its ability to modify surface properties of treated objects without affecting their bulk properties. Plasma based techniques furthermore offer several advantages when compared to other methods: plasma treatment is a dry and typically low temperature process, which limits the necessity to use solvents or potentially toxic substance and allows the processing of heat-sensitive materials. In addition, plasma processing of materials is very flexible and versatile and can be used for etching, texturing or chemical modification of surfaces as well as for deposition of thin functional coatings. Related to the latter, increasing attention is devoted to the plasma based fabrication of coatings with adjustable wettability including the possibility to produce super-hydrophilic or super-hydrophobic surfaces (e.g. Refs. [1–4]). The interest in tailoring surface wettability is given by the fact that this surface characteristic is one of the key parameters that govern interaction of solid objects with their surrounding environment.

It is now well established that wetting behavior is influenced by surface chemistry and topography: whereas the chemical

composition determines surface free-energy, the surface roughness enhances the hydrophilic or hydrophobic nature of the surface. The latter may be explained either by a larger area of contact between the surface and water droplet (Wenzel's model of wetting [5]) or by entrapping air in the protrusions beneath the water droplet (Cassie-Baxter's model of wetting [6]). In other words, in order to control wettability of a surface both surface roughness and its chemical composition have to be properly adjusted. Different strategies have been proposed using non-equilibrium plasmas that meet this requirement, such as for instance a combination of various lithographic methods or plasma etching with plasma enhanced chemical vapor deposition (PE-CVD) (e.g. review article [7]). In this study we report on an alternative, fully vacuum based process that allows us to cover the full range of surface wettability from super-hydrophilic to super-hydrophobic one. This process is based on a combination of plasma enhanced chemical vapor deposition of thin films with variable chemical composition and gas aggregation source of nanoparticles that can be utilized for control of surface nano-roughness.

In order to demonstrate applicability of this strategy, first experiments were focused on the possibility to tailor surface wettability by alteration of chemical composition of coatings prepared by PE-CVD from hexamethyldisiloxane (HMDSO, $C_6H_{18}OSi_2$) and HMDSO/oxygen mixtures. Used plasma reactor consisted of a

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stainless steel vacuum chamber equipped with 3-inch, planar, water cooled electrode, which was capacitively coupled through a matchbox to an RF generator working at a frequency of 13.56 MHz. During depositions, RF power was fixed at 40 W. The precursor HMDSO used as obtained from Sigma was thermally stabilized and vaporized outside the apparatus. The HMDSO flow rate was 0.25 sccm in all experiments. When using oxygen, the O₂ was mixed with HMDSO and fed into the plasma chamber. O₂ flow was varied from 0 sccm up to 15 sccm, which corresponds to HMDSO/O₂ ratios up to 1:60. Pressure during depositions was 4 Pa.

In the second step, coatings with different values of surface roughness were produced. As recently shown in case of fluorocarbons [8], plasma sputtered nylon or plasma polymerized n-hexane [9], this may be achieved by deposition of an underlying film of nanoparticles that are subsequently overcoated by either hydrophobic or hydrophilic thin film. In this study plasma polymerized C:H nanoparticles (110 nm in diameter) were used for tailoring the roughness of deposited coatings. A gas aggregation source that was described in more detail in a previous publication [10] was used for deposition of C:H nanoparticles. It is based on a 2-inch, water cooled, planar RF magnetron mounted into a cylindrical aggregation chamber. The aggregation chamber, which was 11 cm long and 6 cm in diameter, was separated from a high vacuum deposition chamber by conically shaped lid ending in an orifice 1.5 mm in diameter. The deposition chamber was pumped by rotary and diffusion pumps. The polymeric particles were produced using a gas mixture of argon and hexane (hexane flow 0.8 sccm, argon flow 10.7 sccm). The pressure inside the aggregation chamber was 160 Pa, power input to the RF magnetron was 120 W and deposition time was up to 20 min.

Chemical composition of prepared coatings was determined by X-ray photoelectron spectroscopy (XPS, Specs Phoibos 100). The XPS spectra were acquired in the energy range 0–900 eV and recorded using 40 eV pass energy (step 0.5 eV, dwell time 0.1 s). No sputter cleaning of samples was performed prior to XPS measurements. CasaXPS software was used for the determination of atomic elemental composition using manufacturer set of relative sensitivity factors. It was found that thin (40 nm, measured by a variable angle spectroscopic ellipsometer Woolam M-2000DI) and smooth (root-mean-square roughness below 1 nm) films deposited using pure HMDSO have a structure typical for plasma polymerized organic films with high atomic concentration of carbon (57%) and relatively low O and Si atomic concentrations (16% and 27%, respectively). In agreement with previous studies (e.g. Refs. [11,12]), addition of oxygen to HMDSO causes a dramatic decrease of carbon, which is accompanied by a substantial increase of atomic concentration of oxygen and slight increase of Si. As can be seen in Fig. 1, the increase of atomic concentration of oxygen and Si takes place with rising O₂:HMDSO ratio up to 20. Above this value further increase of oxygen fraction in the working gas mixture has no significant impact on the chemical composition of deposited coatings that retain a structure close to stoichiometric SiO₂ with O to Si ratio close to 2.

The changes in chemical composition described above largely influence surface energy of the deposited coatings that was determined on a goniometer of custom construction from the contact angles of deionized water and diiodomethane (Sigma Aldrich) according to Fowkes' theory [13]. As can be seen in Fig. 2, the surface energy and consequently also the wettability of the deposited thin films gradually increases with increasing fraction of oxygen in O₂:HMDSO working gas mixture. This may be explained by lowering of hydrocarbon content in coatings and increasing their silica-like character with increasing fraction of oxygen in the working gas mixture: whereas water molecules are not able to form hydrogen bonds with the non-polar hydrocarbons and thus films

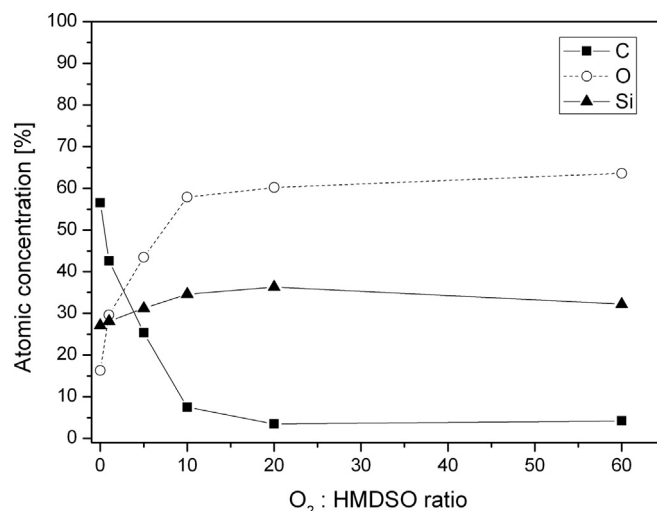


Fig. 1. Chemical composition of coatings as dependent on the O₂:HMDSO ratio.

with high fraction of hydrocarbons are hydrophobic, silica-like films form hydrogen bonds with the water molecules, which results in lowering of value of water contact angle with increasing of silica-like character of coatings.

Moreover, it can be seen that the variations of wettability are given predominantly by the increase of the polar component of surface energy, which is consistent with the formation of polar oxygen-containing functional groups in oxygen rich plasmas. In conclusion it can be stated that wettability range from about 15° to 100° can be covered solely by the variation of working gas mixture used for film deposition (see upper row of Fig. 3).

In order to further enhance the hydrophobic or hydrophilic character of deposited coatings, their roughness has to be increased, which was achieved by deposition of an underlying film of C:H nanoparticles. Morphology of the samples with and without underlying film of C:H nanoparticles was evaluated by atomic force microscopy (AFM, Quesant Q-scope 350) in the semi-contact mode in dry state. Each reported value of surface root-mean-square (RMS) roughness represents an average of three 5 μm × 5 μm scans at randomly selected positions on the samples.

As can be seen in Fig. 4, where sections of AFM scans of plasma polymerized HMDSO coatings (100 nm thick) deposited over C:H

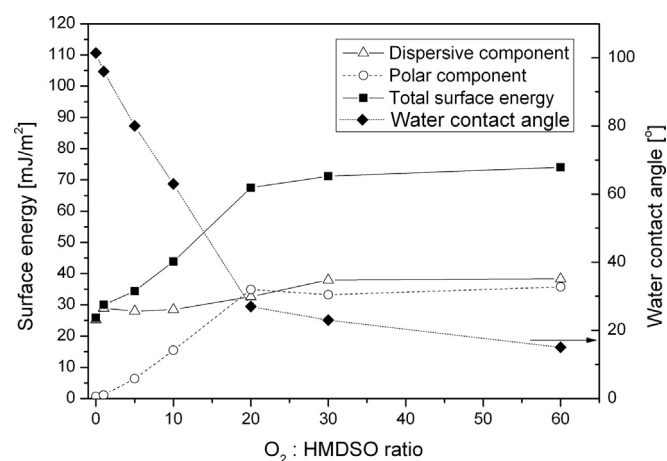


Fig. 2. Surface energy and water contact angles of coatings prepared in different O₂:HMDSO mixtures.

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