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Generation of functional sub-µm sphere patterns on quartz substrates using fs-laser

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Abstract

In recent years, the formation of laser-induced periodic surface structures (LIPSS) has attracted many researches in the field of laser microprocessing. The formation of LIPSS can be observed for a big variety of materials where e.g. silicon is prone to form more distinctive structures than e.g. glasses. Moreover, LIPSS usually appear in form of sinusoidal parallel structures. Spherical shaped patterns, especially with undercut, could enable several new surface functionalities and applications.

In this work we utilize LIPSS formation to generate sub-micron-size quartz spheres, distributed in a specific pattern and fixed on a quartz surface. As a first step, a thin layer of amorphous silicon (a-Si) was selectively structured on a quartz substrate. Due to the crystallinity of the material and the limited layer thickness small silicon droplets form instead of the usually observed parallel LIPSS structures. This pattern can now be transferred into SiO_2 by a thermal oxidation step. The final device is all quartz with a functional surface showing a pattern of spheres with undercut where the appearance can be controlled by the laser process parameters. The surface exhibits water contact angles of up to 163° and a contact angle hysteresis of up to 151° ($\theta a = 163°$, $\theta r = 12°$). Additional, the transparency show values close to 80 %.

Keywords: femtosecond laser, functional surface, wetting properties, contact angle ;

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1. Introduction

Ultrashort pulsed laser ablation as a structuring method for functional surfaces is very popular due to the high process flexibility. The nonlinear absorption in combination with “cold” ablation allows structuring of nearly any material with high precision. Therefore many works can be found in literature on the generation of functional surfaces on a big variety of material classes (Kam et al., 2012; Vorobyev and Guo, 2015). The hierarchical surface roughness, which is required for extreme wetting properties, is obtained by the spontaneous formation of laser induced periodic surface structures (LIPSS) in combination with micron sized structures generated by the ablation procedure (Bonse et al., 2012; Zhang et al., 2010).

2. Material & Methods

The functional surface is generated by a process chain based on the conversion of a fs-laser structured a-Si layer into quartz by a thermal oxidation step. This leads to an all quartz device. The substrate used is a four-inch fused quartz wafer with a thickness of 0.5 mm. As a first step an a-Si layer was deposited in a PVD process using an Evatec® LLS EVO sputter coating system. The a-Si layer was selectively structured by a femtosecond laser (Spirit®, Spectra Physics) with a pulse duration of 400 fs and a pulse repetition rate of 200 kHz. The laser was operated at its second harmonic with a wavelength of 520 nm and was focused by a 100 mm telecentric objective onto the sample surface. After laser structuring the sample was thermally (wet) oxidized at 1100° until the a-Si layer was fully converted to SiO_2.The water contact angle (CA) of the quartz wafer was measured to be 40°. Therefore an assistant layer was applied to shift the contact angle of the material to a value higher than 90°. For this purpose a 50 nm thick layer of Teflon-like polymer ($(CF_2)_n$) was deposited onto the oxidized SiO_2 surface. This was done by applying only the passivation step of a standard BOSCH® DRIE plasma etching process. The complete process chain is shown in Fig. 1. In the image on the right panel the final surface is shown after the oxidation step. Due to the selective ablation process the 564 nm thick a-Si layer is completely removed along the scanning lines with the maximum laser fluence. The residual structures show a distinctive formation of spheres with diameters in the range of 1-2 µm.

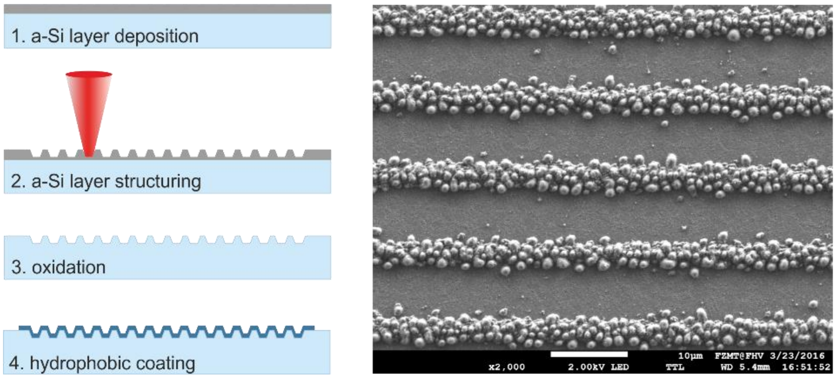

Fig. 1. Process steps (1. to 4.) for the generation of a functional surface showing high adhesion superhydrophobic behavior. An SEM image of the surface after the oxidation step is shown on the right panel.

The wetting behavior of the laser-generated structures was studied by contact angle measurements. We used a drop-shape analyser (DSA25, Kruess) with a fully automated dosing unit. Static contact angles as well as the contact angle hysteresis (CAH) were determined. The hysteresis measurements were carried out using the volume changing method where the contact angle is measured during wetting (advancing angle θ_a) and dewetting (receding angle θ_r); the maximum difference between the two CA values is the CA hysteresis.

Additionally, the relative transmission of the device for different wavelengths was measured for visible light by integrating a spectrometer (USB4000, Ocean optics) into the trinocular port of an optical microscope working in transmission mode.

3. Results & Discussion

For line as well as cross hatch patterns static contact angles of up to 163° can be measured. To achieve such high values, a number of laser passes of at least 10 was necessary where the distinctive formation of the microspheres occurs. After one pass the surface is just slightly roughened for all values of laser power, which leads to a shift of the contact angle from 110°, which is the contact angle of an untreated area with (CF2)n coating, to values of about 130°.

A parameter window was found where all surfaces show static contact angles in the superhydrophobic regime and high CAH values of up to 131° with minor influence of the laser output power on the results. Such high values lead to a remarkable high adherence of the droplets on the surface which ensures an anchorage of the droplets although the contact area of water and surface is very small. The high adherence is demonstrated by the hanging water droplets shown in the image on the right panel of fig. 2. The high static contact angle is demonstrated in the image on the left panel. Here, the drop shape analysis of a surface processed with a 10 µm line hatch and a laser output power of 72 mW shows a high CA value of 163°. The highest value of CA hysteresis for the line hatch pattern was measured for $P = 100$ mW and $N=50$ with a value of 135°. Using a cross hatch pattern further increases the CAH value of up to 151° ($\theta a = 163°$, $\theta r = 12°$). To additionally obtain a high transparency of the surface, higher power values result in a relative transmission of up to 80%.

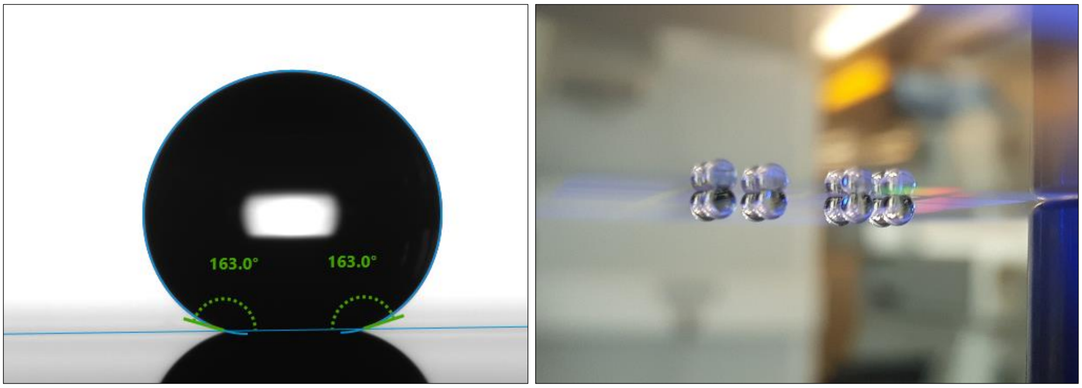

Fig. 2. In the image on the left panel a contact angle measurement of a surface processed with a 10 µm line hatch pattern is shown. A contact angle of 163° was measured using a Laplace fit. The image on the right panel shows hanging droplets on the functional surface demonstrating the high adherence in combination with a high contact angle value.

4. Conclusion

We demonstrate a fabrication process for the generation of quartz surfaces showing both high transparency and superhydrophobic behaviour. With this process chain it is possible to generate a functional surface with a water contact angle of up to 163° together with high transparency close to 80%. Additional measurements of the CA hysteresis show that surfaces generated by the Si-ablation/oxidation process exhibit extremely high values of up to 151°. The high static contact angle and a contact angle hysteresis of 151° represents a parameter combination which has, to our knowledge, not been reported in literature up to now. It leads to a remarkable high adherence of the water on the surface although the contact area is very small. This surface property, together with the high transparency, makes the surface a candidate for biological applications, e.g. the hanging drop technique. In our surfaces, a large amount of hanging droplets can be placed on a transparent specimen slide with minimized contact of the liquid to the substrate.

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