Hydrophobicity of Teflon Coated Well-Ordered Silver Nanorod Arrays

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Hydrophobicity of Teflon Coated Well-Ordered Silver Nanorod Arrays

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ABSTRACT

From wings of flies to plant leaves, hydrophobic surfaces are well-common in nature. Many of these surfaces have micro and nano hierarchical structures coated with low surface energy layer. In this work, we mimicked similar structure by fabricating Teflon coated periodic and well-ordered silver nanorod arrays and investigated the effect of nanorod separation on water contact angle (WCA). The silver nanorod arrays were deposited on patterned and flat silicon substrates using glancing angle deposition (GLAD) technique. Then a thin layer of Teflon was deposited on the silver nanorods by small angle deposition (SAD) technique. A systematic increase in water contact angle was observed with increasing nanorod separation which is attributed to the decreased area fraction of solid-liquid interface.

INTRODUCTION

From wings of flies to plant leaves, hydrophobic surfaces can be observed at many animals and plants in nature. The well-known example is the lotus flower which grows in swamps and shallow waters but stays totally clean. The secret of lotus and many others is their micro and/or nano scale textured surfaces coated with a thin layer of low surface energy material. The increase in hydrophobicity with increasing surface roughness is described by Wenzel and Cassie based on full and partial wetting of the surface, respectively. Inspiring from the design of lotus flower; many researchers investigated the effect of feature shape and periodicity of the underlying substrates on the hydrophobic property. These studies addressed the potential application of superhydrophobic surfaces in various industry products including self-cleaning surfaces, anti-icing coatings, water-repellent textiles and microfluidic devices.

In this study, we prepared well-ordered periodic and nonperiodic silver nanorod arrays using glancing angle deposition on patterned and flat silicon substrates, respectively, and coated with low surface energy Teflon thin film by small angle deposition technique. The patterned substrates were prepared utilizing nanosphere lithography (NSL) technique. The NSL involves three principles steps. First, mono- or double- layers of nanospheres are formed on a substrate via a self-assembly process. Second, the voids between the spheres act as a shadow mask during thin film deposition. Finally, the spheres are removed to leave behind nanostructured patterns, such as nanolands, on the substrate. NSL offers precise control over surface pattern at the nanometer scale simply by using spheres of different diameters. Since nanorods are directly grown on these nanoislands, changing the size of spheres results in a systematic increase in water contact angle as the nanorods separation increases which is attributed to the reduction in the area fraction of the solid-liquid interface.
Prior to silver deposition by GLAD system (Excel Instruments), (100) oriented single crystal p-type silicon wafers with native oxide were patterned using NSL technique. For substrate preparation, the silicon substrates were sonicated in acetone for 10 minutes, then thoroughly cleaned with standard RCA I process, that is, a treatment with 1:1:5 solution of NH₄OH (25%) : H₂O₂(30%) : H₂O at 80°C for 15 minutes. This treatment removes organic impurities and increases surface hydrophilicity which is a very important step for the nanosphere assembly process. Then the substrates were rinsed with deionized water and dried with nitrogen gas.

The polystyrene (PS) nanospheres (Bangs Laboratories, Inc.) with 490 and 1010 nm in diameter were assembled onto cleaned silicon wafers in single layer hexagonal closely packed (hcp) form by a convectional self-assembly method. In order to fill the gaps among the PS nanospheres effectively by normal evaporated silver, the nanospheres were etched under oxygen plasma. To that end, the samples were loaded in a vacuum chamber and pumped down to 20 x 10⁻³ mbar using mechanical pump. Next, high purity oxygen gas was introduced to the chamber and working gas pressure was set to 500 x 10⁻³ mbar. Oxygen plasma was generated by applying 50 W RF power between parallel plate electrodes. The 490 nm and 1010 nm diameter polystyrene nanospheres were etched for 1 min and 3 min, respectively.

Silver was deposited by thermal evaporation in the voids between the spheres at normal angle of θ=0º in a vacuum deposition chamber. The base pressure of 3 x 10⁻⁶ mbar was achieved using a turbo-molecular pump backed by a mechanical pump. The deposition rate of the thermal deposited silver was measured utilizing a quartz-crystal microbalance attachment (Inficon). The thickness of the deposited silver was measured to be 150 nm. After silver deposition, PS spheres were removed from the substrate by dissolving them in toluene for 45 minutes. Finally, the samples were rinsed with DI-water, leaving behind a honeycomb pattern of silver nanoslands. The topography of the silver nanoislands was investigated using Veeco Dimension 3100 atomic force microscope (AFM).

Following the well-ordered periodic silver nanoisland fabrication, silver nanorods were directly grown on these nanoislands by using glancing angle thermal evaporation technique. The silver nanorods were deposited at a glancing angle of θ = 85º (with respect to substrate normal) with a substrate rotation rate of 5 rpm on flat and patterned Si substrates. The base and operating pressures of silver deposition were 3 x 10⁻⁶ and 3 x 10⁻³ mbar, respectively. Successively, the silver nanorods were conformally coated with 20 nm Teflon thin film by small angle magnetron sputter deposition in the same chamber. High purity argon gas was introduced to the chamber and working gas pressure was set to 3 x 10⁻³ mbar. Argon plasma is generated by applying 150 W RF power to the cathode (Teflon target). Samples were tilted at a deposition angle θ = 30º with respect to incoming Teflon flux and rotated at 5 rpm. Silver nanowires’ morphology before and after Teflon coating was analyzed using JEOL 7000F scanning electron microscope (SEM). Hydrophobicity of Teflon coated silver nanowires was investigated by contact angle measurements using a VCA optima surface analysis system (AST Products, Inc., MA).

Fig. 1a shows top view SEM image of hexagonally closed packed single layer 490 nm diameter PS nanospheres. In order to increase the gaps between the nanospheres, they were
etched in oxygen plasma and their diameter was decreased as shown in Fig. 1b. Etched nanospheres were used as a shadow mask for 150 nm thin film silver deposition. Depositing the silver layer on top of nanospheres filled the gaps, and after nanosphere lift-off, hexagonal patterned well-ordered silver nanoislands were obtained as shown in Fig. 1c. Same procedure was followed for the 1010 nm diameter PS nanospheres. AFM analysis of the nanoislands reveals that nanoisland height is 120 nm and their morphology is pretty uniform as shown in Fig. 1d.

![Figure 1](image)

**Figure 1** Top view SEM images of polystyrene nanospheres before (a) and after (b) oxygen plasma etching. AFM image of silver nanoislands (c) and corresponding section analysis (d).

Silver nanorods were grown on patterned and flat samples by directing a flux of evaporated silver atoms at a deposition angle of $\theta = 85^\circ$ with substrate rotation rate 5 rpm. At high deposition angles with respect to substrate normal, incoming atoms selectively deposit on nanoislands due to “shadowing effect”, where incident atoms may not reach certain points on the substrate due to the taller structures. Hence, well-ordered silver nanorods were grown directly on nanoisland at the patterned samples as shown in Fig. 2b and c. On the other hand, during the nanorod growth on flat samples, nanorods grow randomly and some of them grow faster capturing more incident flux. As the deposition progress, taller nanorods start to shadow shorter ones and this competitive growth process leads to nonperiodic nanorod growth as shown in Fig. 2a. Scanning electron microscopy images show nanorods deposited on flat samples are very dense with respect to patterned samples and nanorod separation can be controlled by changing nanosphere size. Especially, samples patterned with 1010 nm PS spheres show well-ordered and separated silver nanorods. Next, silver nanorods were coated with 20 nm Teflon thin film by using small angle magnetron sputter deposition by tilting the sample at a deposition angle $\theta = 30^\circ$.  

with respect to incoming Teflon flux and rotating the substrate at 5 rpm. As shown in Fig. 2d and e, silver nanorods were conformally coated with thin film of Teflon.

Hydrophobicity of Teflon coated silver nanowires fabricated on both flat and patterned samples were investigated by water contact angle measurements. Water contact angle values were measured as 134°, 138°, 142° with a 1° error for nanowires deposited on flat sample, 490 nm and 1010 nm diameter PS spheres patterned samples, respectively. It was found that as the gap among the nanorods increases, the contact angle also increases. This increase in the contact angle is attributed to the enhanced area fraction of the air beneath the water droplet for the nanorods of larger separation. This is consistent with the Cassie and Baxter theory which states that increasing the area fraction of the trapped beneath the water droplet (reducing the area fraction of the solid-liquid interface) results in an increase in the contact angle. On the other hand, it has been reported that an increase in surface roughness increases the contact angle of water and therefore hydrophobicity without altering the surface chemistry.

Figure 1: Top-view SEM images of silver nanorods grown on flat substrate (a), patterned substrate by using NSL with 490 nm in diameter PS spheres (b), and patterned substrate by using NSL with 1010 nm in diameter nm PS sphere (c) before Teflon coating. Top (d) and cross-section (e) SEM images of silver nanorods deposited on patterned substrate by using NSL with 1010 nm in diameter PS spheres after Teflon coating and corresponding water contact angle measurement (f).

CONCLUSIONS

In summary, we have fabricated well-ordered silver nanorods coated with Teflon thin film by using glancing angle and small angle deposition techniques, respectively. We showed that the nanorod separation can be controlled by surface patterning and affects the water wettability of low surface energy material coated nanorods. Our systematic study shows that an increase in nanorod separation results in a decrease in the area fraction of the solid-liquid interface, leading to higher water contact angle. In addition, the enhanced hydrophobicity of silver nanorods coated Teflon thin film might be attributed to the enhanced roughness of an
underlying, individual silver nanorod due to surface patterning compared to silver nanorods grown on flat substrates. More detailed experimental work for enhancing the hydrophobicity towards superhydrophobicity of these nanostructures is currently under investigation.

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