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Hydrophibicity of Well-Ordered Glancing Angle Deposition Molybdenum Nanorod Arrays Coated with Teflon

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Inspired by water-repellent behavior of micro and nanostructured plants and insects surfaces, the hydrophobic property of well-ordered, peroidic, vertically aligned molybdenum (Mo) nanorods coated with Teflon has been studied experimentally. In order to investigate the effect of nanorods separation and surface roughness on water contact angle (WCA), Mo nanorods were sputter deposited on various topograpies including flat silicon (Si) substrate, single layer hexagonal closely packed Polystyrene (PS) nanospheres deposited on Si wafers, and periodic silver nanoseeds fabricated on Si substrate by glancing angle deposition (GLAD) technique. The PS nanospheres were deposited on Si wafers utilizing modified nanospheres lithography (m-NSL) technique. A combination of m-NSL and thermal evaporation techniques was used to fabricate the periodic silver nanoseeds on the Si substrates. GLAD Mo nanorods growth was followed by normal incidence Teflon sputter deposition to introduce a hydrophobic layer. An increase in the contact angle was observed with increasing the nanorods separation and enhancing the surface roughness, which is attributed to the decreased area fraction of solid-liquid interface.

Keywords: Metallic Nanorods, Hydrophobicity, Modified Nanosphere Lithography (m-NSL), Glancing Angle Deposition (GLAD), Molybdenum, Teflon.

1. INTRODUCTION

From wings of flies to plant leafs, hydrophobic surfaces are quite common in nature. Self-cleaning lotus leaf is a well known superhydrophobic surface in nature which is composed of micrometer- and nanometer-scaled patches coated with a 1 nm thick hydrophobic layer. The roughness of the patches enables trapping of air below the water droplet, thus helping the rolling of water droplets easily, resulting in a well designed superhydrophobic surface.[1] The increase in hydrophobicity with increasing surface roughness is described by Wenzel and Cassie based on full and partial wetting of the surface, respectively.[2] 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.[3–6] These surfaces have potential applications including self-cleaning materials, surface catalysis, hydrogen production/storage, heat transfer, prevention of snow accumulation on out-door antennas and windows.[4–8] Thus, controlling the wettability of these surfaces is an important issue relevant to many area of technology.

Here, we report a facile approach to fabricate well ordered peroidic metallic nanorods utilizing glancing angle deposition (GLAD) technique on flat silicon (Si) substrates, single layer hexagonal closely packed Polystyrene (PS) nanospheres deposited on Si wafers, and periodic silver nanoseeds fabricated on Si substrate. The GLAD technique provides a novel capability for growing room-temperature nanostructured arrays with interesting material properties.[9,10] It offers a simple, single-step, low-temperature, cost- and time-efficient method to fabricate nanostructured arrays of various elemental materials as well as alloys and oxides. The GLAD technique uses the "shadowing effect," which is a "physical self-assembly"

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†Dr. Wisam J. Khudhayer was employed at UALR while performing the experimental part.

process through which obliquely incident atoms/molecules can only deposit on the tops of higher surface points, such as to the tips of a nanostructured array or on the highest points of a rough or patterned substrate.

In this work, PS nanospheres were deposited on Si wafers utilizing modified nanospheres lithography (m-NSL) technique.[7] For patterened substrates of periodic silver (Ag) nanoseeds, m-NSL was used to introduce a PS nanosphere layer as the shadow mask, which is followed by normal incidence thermal evaporation of Ag. Having a patterned layer on the substrate leads to a controlled condensation of the atoms onto the seeds (e.g., PS spheres or Ag islands), which in turn results in highly ordered nanostructures. The NSL has been successfully applied to pattern the substrates,[11] which can be used to fabricate nano-patterned metallic surfaces. These surfaces have received increasing attention in nanotechnology due to their potential applications such as surface catalysis,[12] sensors,[13] capacitors,[14] and solar cells. NSL is a low cost and simple technique for growing two-dimensional (2D) periodic nano-particles arrays. It is based on self-assembly of PS or silica nanospheres onto a substrate to form a closely packed monolayer or bi-layer, which is employed as a deposition mask.[11] In addition to the above advantages of low cost and simplicity, NSL offers precise control over surface pattern at the nanometer scale simply by using spheres of different diameters. Finally, GLAD nanostrcutres were coated with normal incidence sputter deposited Teflon thin film in order to introduce a low surface energy layer. We have shown that the nanorod-to-nanorod separation and surface rougness factors have positive effects on tunning the wettability property of the surfaces.

2. EXPERIMENTAL WORK

First, (100) oriented single crystal *p*-type silicon wafers with native oxide were cleaned by RCA-I procedure. In summary, samples were dipped into $NH_4OH(30\%):H_2O_2(30\%):H_2O = 1:1:5$ solution at 80 °C for 15 minutes, rinsed with deionized water, and dried with nitrogen gas. This cleaning process not only removes organic contamination on the surface of samples, it also increases the surface hydrophilicity which is very important for the nanosphere assembly process. Next, PS nanospheres of 250 nm in diameter were assembled onto silicon wafers in single layer hexagonal closely packed (hcp) form using m-NSL technique.[7] The PS nanospheres were used as shadow mask for the following silver thin film deposition. The silver was deposited by thermal evaporation in the voids among the PS nanospheres at normal angle ($\theta = 0°$) in a vacuum deposition chamber with a base pressure of 1.5×10^{-6} mbar. The substrates were also rotated azimuthally around the surface normal with a speed of 2 rpm. The silver deposition time was 25 minnutes. Then, the PS nanospheres were removed from the substrate by dissolving them in toluene with the aid of sonication for 45 minutes. Finally, the samples were rinsed with milli-Q water to remove/liftoff the PS nanospheres completely from the substrate, leaving behind a honeycomb pattern of Ag seeds.

Following the fabrication of well-ordered periodic silver nano-islands, Mo nanorods were directly grown on these islands as well as on PS nanospheres deposited on Si wafers and flat Si substrates by GLAD technique. These substrates were loaded into the deposition chamber which was pumped down to 3×10^{-6} mbar. Samples were tilted at a deposition angle $\theta = 87°$ with respect to incoming Mo flux and rotated at 2 rpm around the substrate normal axis. We used a Mo sputter target (i.e., source) of 7.6 diameter and source to substrate distance was 18 cm. During Mo deposition, the DC sputter power was 200 W with an ultra pure argon (Ar) working gas pressure of 3.5×10^{-3} mbar. The deposition time was 45 min. After GLAD Mo nanorods growth, they were conformally coated with ~50 to 75 nm normally deposited ($\theta = 0°$) Teflon thin film in the same chamber. Teflon target was 7.6 cm in diameter and source to substrate distance was 18 cm. High purity Ar gas was introduced to the chamber and working gas pressure was set to 3×10^{-3} mbar. The plasma was generated by applying 150 W RF power to the sputter target.

The morphology of Mo nanorods before and after Teflon coating was analyzed by JEOL 7000F scanning electron microscope (SEM). Hydrophobicity of Teflon coated Mo nanorods was investigated utilizing contact angle measurements (VCA optima surface analysis system, AST Products, Inc., MA). It should be noted that reference samples (Mo thin film, Teflon thin film, GLAD Mo nanorods) were also prepared for comparison.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the top view SEM image for a monolayer of 250 nm in diameter PS nanospheres, which were deposited on Si substrate by the m-NSL technique. The monolayer is regular hexagonal shape in structure and looks sufficiently uniform and closely packed. It should be noted that uniform hcp structure was obtained on a substrate area of ~1 cm^2. This result shows that under proper conditions, it is possible to form large area, uniform, and closely packed PS monolayer using our recently developed m-NSL setup. After deposition of silver seeds and lifting PS nanoparticles off using toluene, periodically arranged silver dots in honeycomb-like were obtained, as shown in top and cross-sectional SEM images of Figures 1(b) and (c), respectively, which were used as the nucleation seeds for the subsequent GLAD growth of the Mo nanorods.

The GLAD Mo nanorods grown on flat Si, PS nanospheres deposited on Si wafers, and silver nanoseeds deposited on Si wafers are shown in Figures 2(a), (c), and (e), respectively. It should be noted that during the

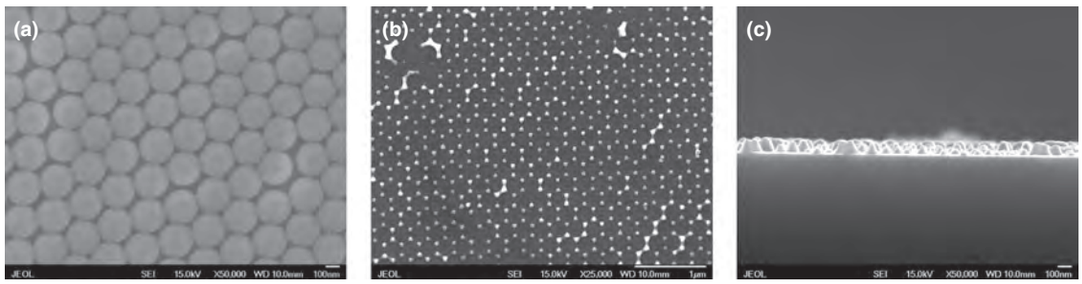

Figure 1. (a) Top view SEM image for PS nanospheres deposited on Si substrate by m-NSL technique, (b) and (c) are top and cross-sectional SEM images for silver nanoislands fabricated by m-NSL technique with the assistance of thermal evaporation.

nanorods growth on flat Si subsrate, nanorods grow randomly and some of them grow faster capturing more incident flux. As a results, the taller nanorods start to shadow shorter ones. The compeitive growth process leads to non-periodic nanorods growth as shown in Figure 2(a). On the other hand, Mo nanorods replicate the hexagonal closely packed morphology of PS nanospheres and the honeycomb dot pattern of silver nanoseeds as shown in Figures (c) and (e). Despite tha fact that we used the same depsoition rate of Mo nanorods, the Mo nanorods on patterened substrates are shorter and bigger in diameter than those grown on flat subsrates. This is due to the presence of PS nanospheres and silver nanoseeds on which Mo nanorods were grown. In addition to that, it should be noted that the increase in film thickness does not only lead to an increase in the structure diameter, but also to the development of of a triangle cross-section of the growing nanostrutures as shown in Figures 2(c) and (e).

Next, Mo nanorods were coated with Teflon, which was deposited at a normal angle ($\theta = 0°$) with rotating

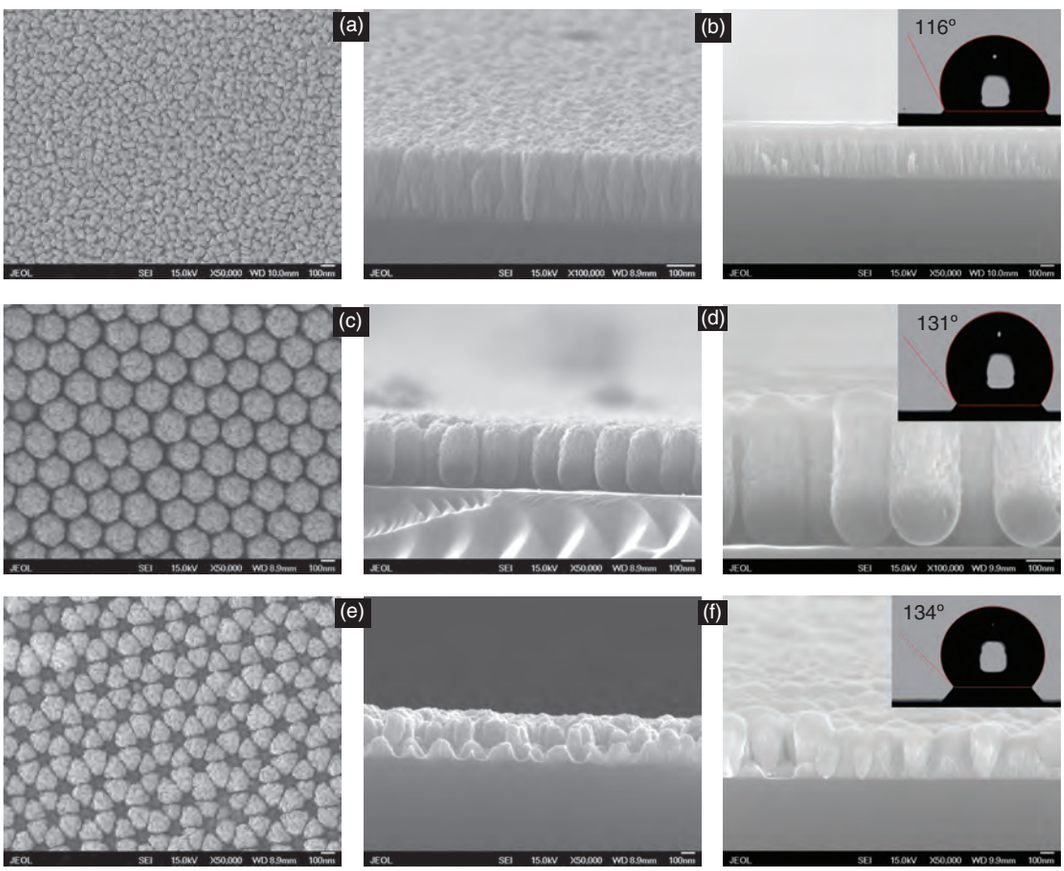

Figure 2. Top and cross-sectional SEM images for Mo nanorods grown on (a) flat Si substrates, (c) on PS nanospheres, which were deposited on Si wafers by m-NSL technique, and (e) on silver nanoseeds which were formed on Si by the combination of m-NSL technique and thermal evaporation technique. Cross-sectional SEM images of Mo nanorods coated with Teflon (b), (d), and (f), and the corresponding contact angle values were reported at the top right corner in the insert figures.

the subsrate at a rate of 2 rpm as shown in Figures (b), (d), and (f). The average water contact angle were measured to be 116°, 131°, and 134° with error of 1° for Mo nanorods grown on flat Si substrate, PS nanospheres, and silver nanoseeds, respetively. 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. It has been also reported that an increase in surface roughness increases the contact angle of water and therefore hydrophobicity without altering the surface chemistry.[6] We have also observed that the slight enhancement in contact angle of Mo nanorods deposited on silver nanoseeds compared to that of Mo nanorods deposited on PS nanospheres can be due to the enhanced nanorod separation as shown in Figure 2.

It should be noted that higher water contact angle values were expected for Mo nanorods grown on PS nanospheres and silver nanoseeds due to the expected enhanced separation and surface roughness. This is caused by depositing higher amount of Teflon than required on the Mo nanorods. Since a high amount of Teflon is deposited on Mo nanorods, the Teflon islands tend to coalesce with other Teflon islands on neighboring nanorods, which results in a smoother Teflon surface at the top and a decrease in the contact angle values as observed in the SEM images in Figures 2(b), (d), and (f). Thus, our study reveals the need of more detailed experimental and modeling studies for describing the hydrophobicity behavior of composite nanostructures. These studies would help to optimize the following factors:

(1) the amount of Teflon to be deposited on the nanostructures, which can be controlled by adjusting the deposition time,

(2) the separation/gaps among the nanorods, and

(3) the surface roughness. It has also been shown that the last two factors can be controlled by surface pattering.

4. CONCLUSION

The Mo nanorods were grown on flat Si, PS nanospheres, and silver nanoseeds substrates utilizing GLAD technique. The patterned substrates (silver nanoseeds and PS nanospheres) were fabricated on Si wafers by m-NSL. The aim of depositing Mo nanorods on substrates with different morphology is to investigate the effect of separation/gaps among the nanostructures, which is induced by the surface pattering, on the water wettability of nanorods coated with a low surface energy material. It has been shown that as the nanorods separation increases, the wettability decreases (higher water contact angle) due to a decrease in the area fraction of the solid-liquid interface. More detailed experimental work for enhancing the hydrophobicity towards superhydrophobicity of these nanostructures is currently under investigation.

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