Hydrophobic Metallic Nanorods coated with Teflon Nanopatches by Glancing Angle Deposition

Wisam J. Khudhayer, Rajesh Sharma, and Tansel Karabacak

Department of Applied Science, University of Arkansas at Little Rock, AR, 72204

ABSTRACT

Introducing a hydrophobic property to vertically aligned hydrophilic metallic nanorods was investigated experimentally and theoretically. First, platinum nanorod arrays were deposited on flat silicon substrates using a sputter Glancing Angle Deposition Technique (GLAD). Then a thin layer of Teflon (nanopatches) was partially deposited on the tips of platinum nanorod at a glancing angle of \( \theta = 85^\circ \) as well as at normal incidence (\( \theta = 0^\circ \)) for different deposition times. We show that GLAD technique is capable of depositing ultrathin isolated Teflon nanopatches on selective regions of nanorod arrays due to the shadowing effect during GLAD. Contact angle measurements on Pt/Teflon nano-composite have shown contact angle values as high as 138\(^\circ\), indicating a significant increase in the hydrophobicity of originally hydrophilic Pt nanostructures. Finally, a 2D simplified wetting model utilizing Cassie and Baxter theory of heterogeneous surfaces has been developed to explain the wetting behavior of Pt/Teflon nanocomposite.

INTRODUCTION

Metallic nanostructures have attracted great attention due to their novel properties which are of high interest in many applications such as hydrogen production and storage, surface catalysis, and heat transfer, etc. [1]. Recently, the hydrophilicity of vertically aligned metal nanorods with sharp nanotips was investigated experimentally [1]. It was found that as the surface roughness increases, the contact angle of the metallic nanorods decreases and therefore these nanostructures resulted in hydrophilic surfaces. On the other hand, many studies have focused on utilizing Radio Frequency (RF) sputtering technique to deposit Polytetrafluoroethylene (PTFE), commonly known as Teflon, on rough surfaces to get superhydrophobic surfaces [2-8]. It has been documented that an increase in PTFE film surface roughness increases the contact angle of water and therefore hydrophobicity without altering the surface chemistry [2,3]. In these studies, the resulting Teflon coating was a continuous rough film that enhanced the hydrophobicity.

However, as the micro- and nano-technology based systems emerge, conventional continuous PTFE coatings that completely cover the underlying surface may not be suitable for these applications as they block the desired transfer of photons/atoms/particles from/to the outside environment. Therefore, some applications may require “hydrophobic yet still isolated not-fully-coated nanostructured surfaces”. To the best of our knowledge, there is no reported
study on controlling the hydrophilicity of metallic nanorods with nanoscale roughness, even though there are many important applications for such nanostructures in surface catalysis, hydrogen production/storage, and heat transfer.

In this work, a novel glancing angle deposition (GLAD) technique was used to deposit ultrathin isolated Teflon nanopatches selectively on the tips of platinum (Pt) nanorods. GLAD technique provides a novel capability for growing 3D nanostructure arrays with interesting material properties [9-11]. It is a simple and single-step process unlike the surface roughening and surface modification approaches mentioned above. The GLAD technique uses the “shadowing effect,” which is a “physical self-assembly” process through which obliquely incident atoms/molecules can only deposit to the tops of higher surface points, such as to the tips of a nanostructured array or to the hill-tops of a rough or patterned substrate. We show that the contact angle of the composite structure of Pt nanorods with Teflon nanopatches at the tips dramatically increases from hydrophilic values of uncoated nanorods to the highly hydrophobic values after coating with Teflon tips.

**EXPERIMENT**

In our experiments, a DC magnetron sputtering system was employed for the fabrication of Pt nanorod arrays. The depositions were performed on native oxide p-Si (100) wafer pieces (substrates size $3 \times 3 \text{ cm}^2$), using a 99.99 % pure Pt cathode (diameter about 7.6 cm). The substrates were mounted on a sample holder located at a distance of about 18 cm from the cathode. They were tilted so that the angle between the surface normal of the target and the surface normal of the substrate was $\theta_{\text{dep}} = 85^\circ$. The substrates were rotated around the surface normal with a speed of 30 RPM. The base pressure of about $4 \times 10^{-7}$ Torr was achieved using a turbo-molecular pump backed by a mechanical pump. In all deposition experiments, the power was 200 Watts with an ultra pure Ar working gas pressure of $2.0 \times 10^{-3}$ Torr. The substrate temperature during growth was below ~85 °C. The deposition time was 60 minutes. The deposition rate of the glancing angle depositions of Pt nanorods was measured to be about 10 nm/min from the analysis of cross- sectional SEM images.

After fabricating Pt nanorods, Teflon was deposited on top of Pt nanorods by utilizing an RF sputter deposition at a glancing angle of $\theta_{\text{dep}} = 83.7^\circ$ (GLAD) for different deposition times of 1, 5, 15, and 30 minutes. For the normal incidence ($\theta_{\text{dep}} = 0^\circ$), the deposition times were 20 seconds and 5 minutes. GLAD allows coating Teflon only to the tips of the Pt nanorods resulting in a bi-layer structure nanorod structure (Pt base and Teflon tip) while normal incidence results in a continuous Teflon thin film coating. A custom-made Teflon (Applied Plastics Technology, Inc.) disk was used as the sputtering target. The target was 0.3175 cm thick and 5.08 cm in diameter. The substrates (arrays of Pt nanorods on silicon wafer piece) were rotated around the surface normal with a speed of 1 RPM. The deposition was performed under a base pressure of about $4 \times 10^{-7}$ Torr. During Teflon deposition experiments, the power was 150 Watts with an ultra pure Ar working gas pressure of $3.2 \times 10^{-3}$ Torr. Finally, our composite (Pt/Teflon) structures were analyzed using scanning electron microscopy (SEM) and the hydrophobic behaviour was investigated by contact angle measurements using a VCA optima surface analysis system (AST Products, Inc., MA). In addition, elemental chemical analysis on sample surface was made using an energy dispersive x-ray analysis (EDAX) system attached to the SEM unit.
RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM) was used to study the morphology of our multifunctional composite (Pt/Teflon) nanostructures. Figure 1 shows the SEM images of pure Pt nanorods and the composite structure of Pt nanorods with Teflon tips which are deposited using RF sputtering technique at a glancing angle as well as at normal incidence for different deposition times. It was challenging to get clear SEM images of Pt/Teflon composites due to the charging of Teflon surface. However, this charging helped us to locate the Teflon coated regions on the Pt nanorods, which was visualized as a whitish coating in cross sectional SEM images.

Based on SEM images analysis, it was found that GLAD technique was able to deposit Teflon selectively on the tips of Pt nanorods, which results in isolated arrays of composite nanostructures. On the other hand, conventional normal incidence deposition of Teflon on Pt nanorods resulted in a continuous Teflon capping thin film layer lying mainly at the tips of Pt nanorods. We also observed that as the deposition time increases, Teflon islands tend to coalesce with other Teflon islands on neighboring nanorods in both normal incidence and GLAD depositions, which results in a smoother Teflon surface at the top and a decrease in the contact angle values. In general, for normal angle deposition, coalescence of Teflon islands is more pronounced, film quickly gets smoother, and therefore contact angle values decreases faster compared to the GLAD Teflon as shown in Table 1.

![Figure 1: Top and cross-section views of (a) bare glancing angle deposition (GLAD) Pt nanorods, (b) Pt nanorods with GLAD-Teflon nanopatches at the tips are shown (ultrathin Teflon deposition was made for 1 minute).](image)

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Sputtering Mode</th>
<th>Deposition time</th>
<th>Teflon Thickness (nm)</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Normal Incidence (capping)</td>
<td>20 s</td>
<td>4.26</td>
<td>130°</td>
</tr>
<tr>
<td>2</td>
<td>Normal Incidence (capping)</td>
<td>5 minutes</td>
<td>64</td>
<td>122°</td>
</tr>
<tr>
<td>3</td>
<td>GLAD nanopatches</td>
<td>1 minute</td>
<td>4.27</td>
<td>138°</td>
</tr>
<tr>
<td>4</td>
<td>GLAD nanopatches</td>
<td>5 minutes</td>
<td>21.35</td>
<td>135°</td>
</tr>
<tr>
<td>5</td>
<td>GLAD nanopatches</td>
<td>15 minutes</td>
<td>64</td>
<td>133°</td>
</tr>
<tr>
<td>6</td>
<td>GLAD nanopatches</td>
<td>30 minutes</td>
<td>128</td>
<td>132°</td>
</tr>
</tbody>
</table>

Energy Dispersive X-ray Analysis (EDAX) was also utilized for elemental analysis and mapping of Pt/Teflon composites (samples 2 and 4 in Table 1). EDAX analysis (not shown)
reveals that the elements present in our composite samples are carbon, fluorine, Pt, and silicon. True carbon to fluorine ratio for a chemical composition analysis of Teflon layer cannot be determined from EDAX plots due to the carbon contamination in EDAX chamber. In addition, we also analyzed the spatial EDAX distribution of fluorine atoms (not shown) mapped for GLAD and normal incidence deposited Teflon on Pt nanorods. In this analysis, although the fluorine atoms boundaries were not well defined due to the size of EDAX beam, which is about 100 nm, it could be seen that the density of fluorine at the tips of Pt nanorods is higher than that are at the gaps. This indicates that Teflon is concentrated on the tips of Pt nanorods when it is deposited by GLAD. This result further supports our SEM image analysis and shows that GLAD is capable of producing isolated composite nanostructures. On the other hand, for normal incidence deposition of Teflon, the distribution of fluorine atoms was relatively more uniform on the Pt nanorods and in the gaps compared to the GLAD Teflon nanopatches.

Contact angle measurements were performed for characterization of bare Pt nanorods, conventional flat Teflon thin film, Pt nanorods coated with normal incidence deposited Teflon film, and Pt-nanorods with ultrathin GLAD Teflon tips (nanopatches) using a VCA optima surface analysis system. In the literature, the term “ultrathin” films mean that the thickness of the films is less than about 5 nm [3]. Measured contact angle values of Pt nanorods, Teflon thin film, and Pt-nanorods-coated with Teflon tips are listed in table 1. It was found that the average contact angle of Pt nanorods was about 52° indicating a hydrophilic surface. Similarly, for the normal angle deposited flat Teflon thin film, the average contact angle was about 108° which indicates a hydrophobic surface, and it is in close agreement with the previously reported values of the contact angle of Teflon films [5]. As can be seen in Table 1, higher contact angle values of composite (Pt/Teflon) have been measured indicating a significant increase in the hydrophobicity of originally hydrophilic Pt nanostructures. This newly imparted hydrophobicity of nanorods may be attributed to the presence of low surface energy Teflon nanopatches with large surface area as can be observed in the SEM images shown in Fig.1.

In order to better understand the wetting of composite nanorods, a simplified two dimensional model has been developed utilizing Cassie and Baxter theory [12] of partial wetting of rough surfaces that leads to a heterogeneous interface formed by contacts of solid and vapor (air) with the liquid. In our model illustrated in Fig. 2a, \(d\) represents the water depth measured from the tip of the nanorods, \(a\) is the diameter of the nanorods, \(b\) is the gaps among the nanorods, \(t\) is the portion of Teflon at the side walls of the nanorods starting from the base line of the nanorods tips, and \(\alpha\) is the tilt angle of the facets of the nanotips measured from the line parallel to the bottom plane. The average diameter of the nanorods is around 150 nm which measured from the SEM images. Under the Cassie and Baxter assumption, the fluid forms a composite surface with the solid where the water droplet sits upon a composite surface of the solid tops and the air gaps. Therefore, the Wenzel's model, which assumes that the fluid completely wets the solid structure, was modified by introducing the fractions \(f_s\) and \(f_a\) which correspond to the area in contact with the liquid and the area in contact with the trapped air beneath the drop, respectively [1,12]:

\[
\cos \theta_{CB} = f_s \cos \theta_Y + f_a - 1
\]  

(1)

where, \(\theta_Y\) is the contact angle that a liquid drop makes with an ideally flat surface (Young's theory) and \(f_s\) is the area fraction of the solid-fluid interface. As can be seen from Eq. (1) that if \(f_s\) tends to zero, the contact angle approaches 180° and as \(f_s\) tends to one, the expression tends to
the Wenzel’s equation. In our model, the nanostructured surface is flattened so that the water droplet sits upon a composite surface of the solid tops and the air gaps. This approximation is especially valid since the water droplet size is much bigger than the feature size of nanostructured surface as in the case of our experiments. Therefore, the Cassie and Baxter equation can be applied with two assumptions: first, assuming the shape of nanorods to be a cylinder with pyramidal tips; second, the average contact angle of a flat surface composed of Teflon and Pt portions, where the water completely wets (i.e. no air gaps) is given by:

\[
\cos \theta_{\text{Pt-Teflon}} = f_t \cos \theta_t + f_{\text{Pt}} \cos \theta_{\text{Pt}}
\]  

(2)

where, \(f_t\) and \(f_{\text{Pt}}\) are the area fractions of both Teflon and Pt in touch with water and \(\theta_t\) and \(\theta_{\text{Pt}}\) are the contact angles of flat Teflon and flat Pt surfaces, respectively.

When the water is partially wetting the Pt/Teflon nanorods and there exists air gaps at the bottom between the nanorods, then Pt/Teflon portion that is in contact with the water will contribute the solid fraction term \(f_s\) in Eq. (1). And, the term \(\theta_t\) will be replaced by the final average contact angle of the wetted portion of the Pt/Teflon surface. Therefore, using Eq. (1) and (2), modified Cassie and Baxter equation for our composite nanorods become:

\[
\cos \theta_{\text{CB Composite}} = f_{\text{Composite}} \cos \theta_{\text{Pt-Teflon}} + f_s - 1
\]  

(3)

where, \(f_{\text{Composite}}\) is the area fraction of solid-liquid (Pt/Teflon portion in contact with water) interfaces. Equation (1) can be used when the water is wetting Teflon only. On the other hand, when the water is wetting both Pt and Teflon, the Equation (3) can be applied. The fraction of solid-water interface can also be represented in terms of water depth \(d\) (Fig. 2a) penetrating into the gaps of nanorods as measured from their tips (e.g. no wetting when water depth is zero and complete wetting when it is equal to nanorods length):

\[
f_s = \frac{2d / \sin \alpha}{[(2d / \sin \alpha) + ((a \tan \alpha - 2d) / \sin \alpha) + b]}
\]  

(4)

\[
f_{\text{Composite}} = \frac{[(2 \times (a / 2) \times \tan \alpha) / \sin \alpha + d - ((a / 2) \times \tan \alpha)]}{[(2 \times (a / 2) \times \tan \alpha) / \sin \alpha + d - ((a / 2) \times \tan \alpha) + b]}
\]  

(5)

\[
f_{\text{Composite}} = \frac{[(2 \times (a / 2) \times \tan \alpha) / \sin \alpha + (d - t - ((a / 2) \times \tan \alpha))]}{[(2 \times (a / 2) \times \tan \alpha) / \sin \alpha + (d - t - ((a / 2) \times \tan \alpha) + b]}
\]  

(6)

In our model, the water depth \(d\) has been changed in a wide range of values in order to predict the contact angle of Pt/Teflon composite at different values of \(d\). Hence, different scenarios can be considered: first, Teflon is only at the pyramidal tips of the nanorods and water is partially wetting Teflon only. Therefore, Eq. (4) can be applied followed by Eq. (1) to determine the contact angle. In the second case, water is completely wetting Teflon tips and also partially in contact with Pt base. Hence, after calculating the \(f_{\text{composite}}\) value from Eq. (5), the contact angle of Pt/Teflon composite can be calculated using Eq. (3). And finally, the third scenario assumes that the Teflon, which completely covers the tips of Pt nanorods, is also assumed to partially coat the upper portion of the Pt side walls at bottom of tips due to the flux.
angular distribution effect explained above. Similarly, the contact angle in this case can be calculated from Eq. (3) in which the $f_{\text{composite}}$ value can be extracted from Eq. (6).

Since there is a possibility that an unknown amount of Teflon might have been deposited at the side walls of Pt nanorods due to the angular distribution in the sputter flux in our experiments, we also studied the effect of Teflon side wall coating portion ($t$ in Fig. 2a) on the contact angle of Pt/Teflon nano-composite. For this we changed the parameter $t$ in Eq. (6) for nanorods with tip angle $\alpha = 45^\circ$, nanorod diameter $a = 150$ nm, nanorod gap $b = 50$ nm, plotted predicted contact angle values in Fig. 2b. The result in Fig. 2b shows that as Teflon side wall portion increases, the contact angle increase for a given water depth. This is due to fact that water is in contact with more Teflon for large value of $t$ compared to the case where Teflon just coated the tips of Pt nanorods. As presented above, our experimental contact angle of Pt/Teflon composite is about 138° for nanorod coated with GLAD-Teflon. Therefore, according to the result of our model plotted in Fig. 2b, it is predicted that solid-liquid interface is expected to be mainly at Teflon tips when the composite nanorods are in contact with water.

![Figure 2](image)

**Figure 2:** (a) Cross section of the simplified wetting model on Pt/Teflon nanocomposite. The composite surface is flattened so that the Cassie and Baxter theory can be applied to predict the composite contact angle and (b) Contact angle values as a function of water penetration depth, as predicted by our wetting model for various values of the Teflon portion at the Pt nanorods side walls $t$ (apart from the Teflon at the tips).

**CONCLUSIONS**

The wetting of water on a composite nanostructured surface formed by arrays of Pt with Teflon nanopatches has been investigated experimentally and theoretically. A sputter glancing angle deposition (GLAD) technique was used to fabricate nano-composite Pt/Teflon surface. We demonstrated that the hydrophilic Pt nanostructured surfaces can be turned into highly hydrophobic surfaces by adding a little amount of Teflon at the tips of Pt nanorods. The contact angle measurements on this composite have shown contact angle values as high as 138°, indicating a significant increase in the hydrophobicity as compared to the originally hydrophilic Pt nanostructures with contact angle value about 52°. In addition, a 2D simplified wetting model utilizing Cassie-Baxter theory of heterogeneous surfaces has been developed to explain the wetting behavior of Pt/Teflon nanocomposite.

**ACKNOWLEDGMENTS**
The authors would like to thank to the UALR Nanotechnology Center staff Dr. Fumiya Watanabe for his valuable support and discussions during SEM measurements.

REFERENCES