Superhydrophobic Coating Using Metallic Nanorods For Aerospace Applications

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ABSTRACT

Ice formation on the body of airplanes poses several problems like increasing drag and decreasing lift. It can also cause engine stoppage due to its accumulation on carburetor/fuel nozzles and the engine’s air source. A superhydrophobic coating that has a high ice adhesion redactor factor can be a solution to avoid ice formation. In this paper, we are presenting a modified technique to generate Al nanorods followed by Teflon coating to obtain the contact angle of 155° with water droplet. A combination of anodization and glancing angle sputtering deposition (GLAD) technique was used to fabricate nanorods of Al. To our knowledge this is the first time GLAD sputtering technique was coupled with aluminum lattice templates obtained by the anodization for the growth of nanorods. The nominal size of the nanorods was 30-80 nm in diameter. A conformal coating of teflon was applied using RF sputtering. The water droplets bounced off from the surface indicating possible applications in anti-icing coating for aerospace.

Keywords: Anti-icing coating, superhydrophobic surface, Al nanorods, glancing angle deposition technique (GLAD), aluminum lattice membrane.

1. INTRODUCTION

Mimicking naturally occurring superhydrophobic behavior in some of the plant leaves such as in lotus, on a metallic surface has been a great challenge for researchers. If a metallic surface can be successfully tailored to exhibit superhydrophobicity, that can find applications in various fields such as aerospace, power transmission lines, wind turbines, etc. There are several reports of metallic surface, with a surface modification, showing fairly high contact angle with a water droplet [1-3]. However, it is a great challenge to develop a super hydrophobic coating for aerospace applications as the coating must be strong enough to sustain rugged conditions like abrasion from impacting water droplets in rain in flight. As well, such coatings should be suitable to operate effectively with other chemicals common in the aerospace environment.

Glancing angle deposition technique has been effectively used to generate nanorods of metals with various size and shape [4-8]. Although, GLAD can be used with various thin film deposition techniques such as e-beam evaporation, thermal evaporation, the use of GLAD with sputtering deposition technique gives a new dimension to the fabrication of the nanorods. The size, shape, spacing and distribution of nanorods can be tailored by controlling a partial pressure of Ar during sputtering deposition that are not possible with the other methods of thin film deposition techniques. Instead of GLAD sputtering technique, some researchers used normal sputtering to generate nanorods using aluminum lattice templates [9]. The anodization of aluminum surface along with subsequent chemical etching leaves aluminum lattice templates that act as nucleation center for the growth of the nanorods.

In this paper we are presenting a combination of two techniques, aluminum lattice template and GLAD sputtering, to generate a nano surface roughness in aluminum. An ultrathin coating of Teflon on aluminum nanorod surface was used to reduce the surface energy. While aluminum lattice template had been extensively used for the generation of metallic nanorods, to our knowledge it is the first time the GLAD technique was coupled with aluminum lattice templates to generate metallic nanorods. The variation of contact angle of
water droplet with aluminum surface at different stages of surface modification has been discussed.

2. EXPERIMENTAL PROCEDURE

2.1 Fabrication of aluminum lattice template

Aluminum sheet (99.99% pure) of 1 mm thick, obtained from Alfa Aesar, was annealed at 500°C for 4 hours. The annealed sheet of aluminum was then cleaned and electro-polished to get a smooth shining surface. Anodization was carried out in 0.3M/L oxalic acid solution at a constant cell potential of 40V for 45 min. at 278 K. The anodized aluminum surface was subjected to chemical etching for 20 min. in a mixture of phosphoric acid and chromic acid. The resulted aluminum lattice template surface is shown in Fig. 1.

![Image of aluminum lattice template](image1.jpg)

Figure 1: SEM image of the aluminum lattice template.

2.2 Generation of aluminum nanorods

Aluminum nanorods were grown on aluminum lattice templates using a DC magnetron sputtering GLAD technique as shown in Fig. 2. As seen in the schematic diagram, the substrate normal was making 85° angle with the target normal. The chamber was pumped down to a base pressure of 5x10⁻⁷ torr. The plasma was generated using Ar gas at 2.5 mTorr pressure. The sample-substrate distance was 6”. The nanorods were deposited at power density of 3.5 W/cm². The substrate was rotated at 10 rpm using a DC stepper motor. To reduce the surface energy of the nanorods, a thin coating of Teflon was deposited using a RF magnetron sputtering source. The substrate-target distance for this deposition was 2” and the deposition was carried out in a normal deposition mode with power density of 6W/cm². The thickness of Teflon coating was less than 10 nm.

![Image of in-house built RF/DC magnetron sputtering deposition system](image2.jpg)

Figure 2: In-house built RF/DC magnetron sputtering deposition system along with a schematic of glancing angle deposition technique.

2.3 Morphology and contact angle measurement

Surface morphology of aluminum lattice template and aluminum nanorods were studied using scanning electron microscope (JEOL700). The static contact angle of water with Teflon coated nanorod aluminum surface was measured using sessile drop method (VCA Optima).

3. RESULTS AND DISCUSSION

The aluminum nanorods grown on aluminum lattice templates using GLAD sputtering technique are shown in Fig. 3. As shown in the figure, the aluminum nanorods of the size in the range, 30-80 nm are distributed uniformly over the substrate. It is interesting to note that the size and shape of the nanorods show a large deviation from the size and shape of aluminum lattice templates. The aluminum lattice templates show mostly hexagonal structures as seen in Fig. 1, in agreement with the reports on aluminum lattice templates [10]. The aluminum nanorods grown on aluminum lattice templates exhibit mostly near-circular structures. Moreover, each aluminum nanorod looks like a bunch of agglomerated smaller nanorods as evident from the multiple facets on each nanorod.
The growth of nanorods on aluminum lattice templates using normal sputtering deposition technique has been discussed by many researchers [9]. In such a case, the shape and size of the nanorods closely follow the shape and size of aluminum lattice templates. The template pits generally serve as nucleation centers for the nanorod growth. The separation of nanorods in such a scenario is mostly governed by the width of the template wall. The width of the template wall depends on the cell potential and temperature during anodization process [11]. However, the growth of nanorods on aluminum lattice templates using GLAD has not been discussed so far in the literature. Form the preliminary results that we have presented here, the growth of the nanorods are mostly governed by the height of the template wall. During GLAD, the substrate normal was tilted at an angle of 85° with the target normal as shown in Fig. 2. As the growth of nanorods on a normal surface during GLAD mainly governed by the shadowing effect of the material that is deposited in the beginning [12], in the present scenario hypothetically the template walls provide nucleation centers for the growth rather than template pits. In other words, the template walls shadow the template pits. In addition, the junction of different hexagonal structures (marked by red circles in Fig. 2) has larger area than the rest of the template walls. Hence, it can be assumed that these junctions are preferred for the growth of nanorods over the rest of the template walls. These preferred centers coupled with the substrate rotation during the deposition, facilitate a near-circular structure of the aluminum nanorods.

Figs. 4(a)-(d) show the variation of contact angle of water droplet on aluminum surface at different stages of surface modification. The as-received aluminum surface shows contact angle of ~51° with water droplet. This is in agreement with the value reported in the literature [13]. The aluminum lattice templates, obtained by anodization and subsequent etching, show about 6-10° contact angle with water droplet. The formation of aluminum lattice templates increased the surface roughness and hence the roughness factor r (the ratio of actual over apparent surface area). This in turn reduced the contact angle according to the Wenzel’s law of wettability [14]. In Fig. 4(C), the shape and contact

Figure 3: SEM image of Aluminum nanorods generated on the nano-templates using glancing angle sputtering technique.

Figure 4: The contact angle of water droplet with, (a) as-received aluminum surface, (b) aluminum lattice templates, (c) aluminum nanorods, coated with Teflon, grown on as-received aluminum surface, (d) aluminum nanorods, coated with Teflon, grown on aluminum lattice templates.

Figure 5: Shape of water droplets on modified aluminum surface (the surface corresponding to Fig. 4(d)). The central circular groove is the modified surface.
angle of water droplet on aluminum nanorods, coated with the thin layer of Teflon, on as-received aluminum surface. The observed contact angle of 139° is in agreement with our previously reported work [15]. Finally, Fig. 4(d) shows a near spherical shape of water droplet on the aluminum nanorods, coated with a thin layer of Teflon, grown on aluminum lattice templates. The measured contact angle was ~155°, the highest among all the other surfaces discussed above.

Fig. 5 shows lotus like behavior of aluminum nanorod surface (corresponding to the surface that is discussed in Fig. 4(d) above). These water droplets are larger than that of the water droplets shown in Figs. 4(a)-(d). It was observed that a small tilt to the substrate, bounced off all the water droplets shown in Fig. 5 confirming the superhydrophobic behavior of the sample. From the Cassie theory [16] of superhydrophobicity, it is understood that a superhydrophobic surface needs to have a low surface energy rough surface and trapped air in the gap of rough structures. While the generation of the nanorods increased surface roughness, the coating of thin layer of Teflon on the nanorod surface reduced the surface energy. The reduction in the surface energy ensured the repulsion of the water drops and the air trapped in the gap of the nanorods ensured floating of water droplets and thereby preventing the water from sliding inside the gap. The generation of nanorods on aluminum lattice membrane created a two-stage roughness. The first stage roughness was provided by the pits of templates and the second stage roughness was provided by the gap between aluminum nanorods. This may be the reason for a significant improvement in the observed contact angle of 155° (Fig. 4(d)) with water droplet as opposed to 139° that was observed on Teflon coated aluminum nanorods on the as-received aluminum surface (Fig. 4(c)).

4. CONCLUSIONS

The observation of superhydrophobic behavior on nanorod aluminum surface grown on aluminum template is highly promising for anti-icing applications in various fields such as aerospace. The combination of anodization and GLAD technique for the growth of nanorods has shown a potential of generating a two-stage roughness that is required for obtaining very high contact angle with water. With further investigation, it is possible to modify aluminum like aerospace compatible lightweight materials to exhibit a very high ice adhesion reduction factor.

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