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Design and engineering of sculptured nano-structures for application in hydrophobicity

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ABSTRACT

The design and engineering of suitable structures for enhancement of the hydrophobic property of a surface is one of the most challenging problems. In order to achieve a superhydrophobic structure we have designed and fabricated Mn nano-sculptured thin films with different shapes and dimensions, namely helical squares and helical pentagons on glass substrates. The contact angle (CA) of three liquids; α–bromonaphtalene (apolar), water and formamide (polar) to these surfaces was measured and the surface free energy was calculated. Changes to the geometry of the structure produced results ranging from hydrophilic (CA = 51°) to superhydrophobic (CA = 152°). The superhydrophobic structure is a helical square shaped structure with high porosity (deposited at 83°) which also shows the rose petal effect with the additional property of high adhesion. The resemblance of this structure to that of gecko feet, which shows both high adhesion forces and superhydrophobic property is discussed. All structures investigated in this work showed negative spreading coefficients with highest values for the largest contact angle for each type/shape of structure. The superhydrophobic sample also acts as a sticky surface which is confirmed by hysteresis of the contact angle obtained from advancing and receding contact angles measurements. The influence of the volume of liquid drop and different surface morphologies on the wetting transition from Cassie–Baxter to Wenzel states is also reported.

Introduction

Glancing angle deposition (GLAD) (deposition angle >85°) or oblique angle deposition (OAD) (deposition angle <85°) techniques are physical vapor deposition methods in which sculptured thin films can be engineered under controlled conditions. The rotation of the substrate about two axes provides the facility to produce three dimensional anisotropic nano-structures with different morphologies and high porosity. These structures are formed of columns with 1–100 nm diameter. The intriguing point in these sculptured structures is their controllable geometry and the potential use of vast number of materials for deposition which has led many researchers to investigate their different applications [1–5]. One of these applications is their use as hydrophobic or superhydrophobic surfaces, because of their controllable morphology. Recent investigations have shown that structures with low surface energy and high surface roughness usually lead to superhydrophobic phenomenon [6]. Both of these characteristics can be controlled in the process of GLAD/OAD sculptured thin films. Hence, in this work we investigate the applicability of this deposition method in the field of hydrophobicity by design and engineering of different shapes and morphologies.

Wettability of a surface is usually defined by the size of the contact angle between the water/liquid drop and the solid surface. According to the size of this angle, surfaces are classified in three categories, namely hydrophilic (0°–90°), hydrophobic (90°–150°) and superhydrophobic (150°–180°) [7–9]. Hydrophobic surfaces are usually formed either from materials with low surface energy or are produced using a two stage process; in the first stage, structures with micro/nano scale (hierarchical micro/nano-scale binary structures) features are formed and in the second stage some refinements/corrections are carried out to their surface using materials with low surface energy [10–12]. An alternative to the low surface energy approach utilizes contamination due to

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energetically favorable hydrocarbon adsorption, particularly on noble metals (Au and Ag) [13]. Recently Preston et al. [14] studied the effect of hydrocarbon adsorption on the wettability of rare earth oxide ceramics (i.e., holmia (Ho_2O_3) and ceria (CeO_2)) both experimentally and theoretically and reported that the hydrophobicity on the surface of these oxides occurs due to the same hydrocarbon adsorption mechanism seen on noble metals.

In this work, unlike the published literature, we have used only one stage vapor deposition method without using material with inherent low surface energy (i.e., Mn is deposited using OAD technique together with the suitable process for production of predesigned nano-structure). Mn is a hard silver–gray and brittle metal [15] whose properties are given in detail in a review paper by Demangeat and Parlebas [16]. Owing to the unique properties of Mn many research works have been devoted to this metal in recent years [17–19].

The aim of this work is to produce sculptured nano-structures of different shapes and morphologies using the oblique angle deposition technique (OAD) together with selected rotation of substrate about its surface normal and to investigate the influence of various geometrical parameters on the hydrophobicity, free surface energy and adhesion. To the best of our knowledge at the time of submission of this manuscript this investigation on this topic concerning sculptured thin films is the first of its kind being reported. It is worthwhile to mention that the use of Mn should not restrict our work to this material as the geometry of the structure is the main feature influencing the results.

Theory

The surface free energy can be calculated by Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta_Y \quad (1)$$

where θ_Y is the Young contact angle between the liquid and the solid surface and γ_{lv} and γ_{sl} are liquid–vapor and solid–liquid tensions, respectively. In this equation γ_{sl} cannot be measured directly, hence calculation of γ_{sv} is subject to some complications. A few methods have been suggested for calculation of γ_{sv}, by Kwok and Neumann [20], Fowkes [21–23], Owens and Wendt [24], Wu [25,26] and Fox and Zinsman [27,28] but in this work we have used the acid-base method which is also known as the Van Oss–Chaudhry–Good method [29,30]. In this method the total interfacial tension is calculated by summation of polar and apolar component values [29,30] as:

$$\gamma_l^{tot}(1+\cos\theta) = 2\sqrt{\gamma_s^{LW}+\gamma_l^{LW}} + 2\sqrt{\gamma_s^- + \gamma_l^+} + 2\sqrt{\gamma_s^+ + \gamma_l^-} \quad (2)$$

where γ_l^{tot} is the total interfacial tension of the liquid drop, γ^{LW} is the interfacial tension due to Lifshitz-Van der Waals forces [29,30],γ^+ is the interfacial tension due to electron acceptor component and γ^- is the interfacial tension due to electron donor component from acid-base elements. θ is the contact angle and s and l define solid and liquid, respectively. There are three unknown quantities in this equation, namely γ^{LW}, γ^+ and γ^-. In order to obtain their values we need to have the contact angles of three liquids with different polarities and known surface tensions, such as α–bromonaphtalene (apolar), water and formamide (polar) (Table 1). Once, the values of these parameters are obtained, then by using Eqs. (3) and (4) we can calculate the total surface tension:

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^+\gamma_s^-} \quad (3)$$

$$\gamma_s^{tot} = \gamma_s^{LW} + \gamma_s^{AB} \quad (4)$$

where $\gamma_s^{AB}$is the polar component of Lewis acid-base interaction [29,30].

Sun et al. [31] in their work pointed out the role of surface roughness on the surface free energy by means of atomic force microscope (AFM) measurement of surface roughness and give a relationship between these two parameters as;

$$\gamma_s^{tot} = W = \frac{1}{N}\sum_i^N \vec{r_i}\cdot\left(\vec{F_i} - \frac{1}{N}\vec{F_c}\cdot\sum_i^N \vec{F_i}\right) - \vec{F_c}R_{rms} \quad (5)$$

where, F_c is the constant adhesion force, R_{rms} is the root mean square surface roughness, W is the average work done by the adhesion force vector on the surface as the tip of the AFM moves the displacement vector $\vec{r_i}$. $\vec{F_i}$ is the adhesion force which can be obtained from the spring constant of the AFM tip. N is the number of samples. According to this equation the surface energy increases with increasing surface roughness.

Table 1
Components of surface tension at room temperature (mJm^{-2}) [28].

Liquid	γ^{tot}	γ^{LW}	γ^+	γ^-
α–Bromonaphtalene (apolar)	44.4	44.4	0	0
Water (polar)	72.8	21.8	25.5	25.5
Formamide (polar)	58	39	2.28	39.6

Experimental details

Nano-sculptured manganese thin films with different shapes and morphologies were deposited on glass (microscope slide; 3 × 2 cm; Thermo Scientific Menzel-Glaser, Soda lime glass) substrates by electron beam evaporation from a graphite crucible of 6 mm diameter at room temperature. The purity of Mn was 99.99% (Goodfellow metals Cambridge Ltd., UK). An Edwards (Edwards E19 A3) coating plant with a base pressure of 2×10^{-7} mbar was used. Apart from one sample deposited at surface normal deposition angle and a helical square sculptured thin film deposited at 83° deposition angle, the rest of the samples examined in this work were deposited at 80°.

The samples were produced by deposition of Mn on fixed substrates for a preset time with the deposition rate of 1.0 $Å s^{-1}$ and then the substrate was rotated by an angle (i.e., azimuthal angle: 90° for square and 72° for the pentagon structure). After a preset deposition time the rotation of the substrate through these angles was repeated until the helical nano-structure with the required thickness and number of pitches was obtained. The length of each arm (L) of the nano-structure is consistent with the deposition time and the deposition rate used.

The substrate holder system is controlled by two stepping motors which can rotate the substrate holder by two angles, the vapor incident angle (α) and rotation of the substrate about its surface normal (φ), with 0.01°/step accuracy and with controlled speed. The movement of the stepper motor for rotation of substrate about its surface normal (φ), its speed of revolution and the facility for dividing each revolution into different sectors are controlled through interface to a computer in which the related software (in the LABVIEW format) is written and installed. All these are domestic made. The substrate holder was a stainless steel disc of 12 cm diameter. The substrates were fixed along two orthogonal diameters of this disc. Hence, in each run four sets of three samples were produced for use in different analyses and to serve as a reproducibility check of the samples. A schematic of deposition setup is given in Fig. 1.

In oblique angle deposition the angle between the axis of columns and the normal to the substrate surface "β" when the

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