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Cu surfaces with controlled structures: From intrinsically hydrophilic to apparently superhydrophobic

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ABSTRACT

A series of Cu films with different surface structures were fabricated by an improved electric brush-plating technique. In the absence of surface chemical modification, the Cu films exhibited hydrophobic and even superhydrophobic behaviors due to their three-level hierarchical structures. Based on the classical Wenzel and Cassie models, the effects of two dimensionless geometrical parameters (the aspect ratio and the spacing factor of micro-scale structure) on the wetting behaviors of the Cu films were investigated. It was demonstrated that to obtain the stable Cassie superhydrophobic state, the aspect ratio and the water contact angle on the basal surface should be as large as possible and the spacing factor should be limited within a specific range for given aspect ratio and water contact angle on the basal surface.

1. Introduction

Wettability with a liquid is one of important properties of solid surfaces. It has been known that wettability evaluated by water contact angle (WCA) is governed mainly by both surface geometrical structures and chemical compositions [1]. An extreme case of wettability, namely superhydrophobicity with WCA larger than 150°, has aroused considerable interest due to its great significance in both fundamental researches and practical applications in various fields, such as liquid transmission, oil–water separation and corrosion resistance, etc. [2–4]. Biologically inspired design for fabricating artificial superhydrophobic surfaces is derived originally from surfaces of some plants and animals in nature, such as lotus leaves [5,6], water-strider legs [7] and butterfly wings [8], which show a dual-level surface roughness along with a waxy coating. Conventionally, artificial superhydrophobic surfaces have been produced mainly by two ways: creating roughness on hydrophobic surfaces and modifying roughed hydrophilic surfaces by low surface energy materials. Two classical models, developed independently by Wenzel [9] and Cassie and Baxter [10], are commonly used to explain the effect of surface roughness on the wetting behavior of solid surfaces. The enhancement of surface hydrophobicity can be produced by either increasing surface roughness of solid surfaces based on the Wenzel model or reducing solid–liquid contact area based on the Cassie model. The former calls for an increase in the effective surface area of solid surfaces, whereas the latter calls for a sufficiently high aspect ratio of surface structures where the liquid cannot penetrate [11]. Surface roughening provides an opportunity to alter the relative contribution of the two wetting regimes involved in the solid–liquid contact system to the enhancement of surface hydrophobicity. It has been suggested that for a hydrophobic surface, increasing surface roughness usually leads to an initial Wenzel-type enhancement of the surface hydrophobicity followed by a sharp wetting transition to a Cassie-type superhydrophobicity in the presence of a sufficiently high aspect ratio of surface structures [12].

Metals are important and irreplaceable engineering materials widely used in many industrial and daily life fields. Metallic surfaces with high surface free energy are intrinsically hydrophilic. Nearly all liquids tend to wet the metallic surfaces. Up to now, many efforts have been made to fabricate superhydrophobic surfaces on metal substrates generally by creating surface roughness in conjunction with surface chemical modification due to their potential applications in many fields, such as self-cleaning materials, corrosion resistance and microfluidic system, etc. [11,13–18]. However, the chemically modified layers on metals are commonly fragile and not eco-friendly and might affect some intrinsic properties of metals, e.g. electrical conductivity. From this point of view, it is of both theoretical and practical significance to fabricate metallic superhydrophobic surfaces without surface chemical modification. But, success has been demonstrated only for a few cases and most of them are generally subjected to certain limitations, e.g. complicated processes and small sizes [19–22]. Therefore, the fabrication of superhydrophobic surfaces on bare metals still remains a great challenge due to the fundamental limit of the high surface free energy of metals and the technique limit of existing fabricating

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methods, e.g. electroless galvanic deposition [14,19], electrochemical deposition [11,13,17,18,20–22] and chemical etching [15], etc. to create desirable surface structures with sufficiently large surface roughness and high aspect ratio.

We recently proposed a facile and promising technique for fabricating various metallic films and coatings on different substrates, namely electric brush-plating technique [23]. Compared with other electroplating techniques, the electric brush-plating technique has the advantages of simple device, easy operation, and high deposition rate as well as low cost and high throughput. Moreover, the electric brush-plating technique is more flexible and effective in controlling the surface structures with dimensions of features ranging from micro- to nano-scale and can break through the limitation in fabricating films and coatings with sizes scaled up to an industrial level. In this paper, a series of Cu films with controlled surface geometrical structures and surface roughness were fabricated on smooth Cu substrates by using an improved electric brush-plating technique under different plating voltages. The wettability of the Cu films without surface chemical modification changed from hydrophobicity to superhydrophobicity. The effect of the surface geometrical structures on the wetting behaviors of the Cu films was investigated based on the classical Wenzel and Cassie models.

2. Experimental

The Cu films were deposited on smooth Cu sheets by an improved electric brush-plating technique using the plating solution mainly containing copper sulfate pentahydrate (260 g/l), ammonium nitrate (30 g/l), citric acid monohydrate (3 g/l) and cationic-type surfactants (5 g/l). All the chemicals were dissolved with deionized water. Two electrodes were employed in the plating system. The cathode (substrate) is a polycrystalline Cu sheet, and the anode (stylus) is a stainless steel wrapped with absorbent materials with proper thickness to hold the plating solution. The plating voltage between two electrodes varies from 3 V to 4.8 V. The shifting speed and pressure of the anode on the surface of the cathode were controlled manually. The plating was carried out at room temperature. After plating, the Cu films were degreased with ethanol and washed with deionized water, followed by drying in a stream of pure N_2.

A scanning electronic microscope (SEM) (JSM-5310, JEOL, Japan) and a field emission scanning electron microscopy (FESEM) (JSM-6700F, JEOL, Japan) were employed to investigate the surface structures of the Cu films. A laser scanning confocal microscope (LSCM) (LEXT OLS3000, OLYPUS, Japan) was used to investigate the surface roughness of the Cu films, accompanied by the production of three-dimensional images of the surfaces of the Cu films. The crystalline structures and grain sizes of the Cu films were measured by using the X-ray diffraction (XRD) (D/max-2500PC, Rigaku, Japan) with Cu Kα radiation ($\lambda = 0.154056$ nm), recorded at a scanning rate of 0.02°/s with the 2θ range from 35° to 100°. The surface chemical compositions of the Cu films were analyzed by the energy dispersive X-ray spectrometer (EDS) (X-Max, Oxford, Germany). The wettability of the Cu films was evaluated by the WCA measurement on an optical contact angle meter (OCA20, Dataphysics, Germany) at ambient temperature and humidity. One deionized water droplet with the volume of about 5 μl was drop carefully onto the surfaces of the Cu films. The reported values of WCAs were the average of ten measurements at different areas of the same sample.

3. Results and discussion

Texturization of materials surfaces is a very active field in materials science. Solid surfaces with certain textures exhibit interesting physical/chemical properties [24]. Electroplating has been recognized as an effective method to create textured surfaces on metal substrates by rigid control of current density, plating solution compositions and substrate roughness, etc. Conventional electroplating technique produces disorderly rough surfaces usually with large cauliflower-like structures [25]. The metallic films fabricated by an improved electric brush-plating technique exhibit uniformly rough surfaces with fine micro- and nanostructures owing to the cooperation of special electrochemical effect of complexing agent and surfactant in the plating solution and unique physical disturbance between stylus and substrate during brush-plating. In the case of given plating solution compositions, the surface roughness and surface structures of the brush-plated metallic films depend strongly on the plating voltage applied between anode and cathode. Under low plating voltage, metal ions deposit preferentially on the top of protrusions on substrate surface, resulting in a rough surface owing to the top-discharge effect and diffuse-limited condition [20,26,27]. On the contrary, under high plating voltage, current density distributes uniformly on the cathode surface and then metal ions in the plating solution under diffuse-free condition deposit uniformly on the substrate surface, thus leading to a smooth surface.

Fig. 1(a) shows the SEM image of the Cu film with plating voltage of 3 V (which is called as Cu film I for convenience). It can be seen that plenty of micro-protrusions with sizes of 1–3 μm form uniformly on the Cu film. Some of the micro-protrusions with pyramid-like shape are found on the Cu film. The corresponding enlarged SEM image of the Cu film shown in Fig. 1(b) reveals clearly that the micro-protrusions are built up of many submicro-bumps with sizes of 200–500 nm, which pile up in layer following the special deposition type of electric brush-plating. Besides, the submicro-bumps are also found on the lower surface of the Cu film. The corresponding LSCM image shown in Fig. 1(c) presents the uniform Cu film at larger length scale with a surface roughness (arithmetical mean deviation of the profile SR_a) of 0.62 μm. The surface geometrical parameters, i.e. diameter D, height H and pitch P, of the micro-protrusions were statistically analyzed based on the SEM and LSCM images of the Cu film. The microstructure statistical distributions of ~200 micro-protrusions show that the statistical values of D, H and P of the micro-protrusions are 1.34 μm, 1.78 μm and 2.48 μm, respectively (Fig. 1(c)). The Cu film exhibits a typical diffraction peak characteristic of a pure face center cubic (FCC) Cu and an average grain size of ~46 nm according to the XRD pattern (Fig. 1(d)). The Cu film was oxidized a little in air as revealed by the EDS analysis (Fig. 1(e)).

Fig. 2 shows the SEM and LSCM images and the microstructure statistical distributions of the Cu films with plating voltages of 3.5 V, 4 V and 4.5 V (which are called as Cu film II, Cu film III and Cu film IV, respectively, for convenience). It is clear that the evolution of the surface structures of the Cu films depends strongly on the plating voltage. When the plating voltage increases from 3 V to 3.5 V, the surface structures of Cu film II become disordered and the surface roughness SR_a decreases obviously, as indicated by the decrease in D and H and the increase in P of the micro-protrusions of Cu film II (Fig. 2(a) and (b)). When the plating voltage further increases to 4 V and 4.5 V, the micro-protrusions grow along with the direction of brush shifting in a long-range and become flat on the surfaces of Cu film III and Cu film IV (Fig. 2(c)–(f)). The corresponding enlarged SEM images of these Cu films, which are not shown here, indicate that the micro-protrusions are also composed of many submicro-bumps similar to that found on Cu film I. Based on the corresponding SEM and LSCM images and microstructure statistical distributions of these Cu films, the statistical values of the surface geometrical parameters including D, H, and P were determined and are listed in Table 1. The surface roughness SR_a measured by the LSCM was plotted in Fig. 3 as a function of the plating voltage.

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