Diamond & Related Materials 18 (2009) 1235–1238

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Superhydrophobic carbon nanotube/amorphous carbon nanosphere hybrid film

Maziar Shakerzadeh *, HangTong Edwin Teo, ChongWei Tan, Beng Kang Tay

School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue 50, Singapore 639798, Singapore

ARTICLE INFO

Article history:
Received 5 December 2008
Received in revised form 8 April 2009
Accepted 28 April 2009
Available online 3 May 2009

Keywords:
Carbon nanotube
Amorphous carbon
Superhydrophobic surface

ABSTRACT

Fabrication of superhydrophobic surfaces has been widely investigated due to their wide range of applications. Here, synthesis of self-assembled aligned carbon nanotubes (ACNT)/amorphous carbon (a-C) nanosphere hybrid film is reported. Carbon plasma produced by FCVA was used to deposit a-C nanospheres on the ACNT films fabricated by PECVD. The superhydrophobic properties of the surface was investigated by static contact angle (CA) measurement. It is found that the surface morphology of the film which depends on the size of the a-C nanospheres, has a great influence on the hydrophobic properties of the surface. The hydrodynamic properties of the surface is discussed in terms of both Cassie and Wenzel mechanisms. The microstructure of the films is also investigated by XPS and HRTEM. It is shown that the bombardment of the CNTs with high energy carbon ions will damage the crystalline structure of the CNT walls as well.

1. Introduction

Hydrophobicity and superhydrophobicity (water contact angle (CA) > 150°) of the surface, is the crucial factor for anticontamination [1], self cleaning [2], microfluidic flow channels [3] and many biomedical [4] applications. Beside interfacial energy which is the intrinsic property of the system, surface morphology is another factor which affects the hydrodynamic properties dramatically.

Considerable applications and lack of natural superhydrophobic surfaces attract the researchers to investigate on geometrical parameters which affect the hydrodynamic properties of the surface. According to Wenzel [5], roughening of the hydrophobic and hydrophilic surfaces enhances the hydrophobicity and hydrophilicity respectively. This mechanism has been widely used to fabricate superhydrophobic and superhydrophilic surfaces [6,7]. As it is schematically shown in Fig. 1A, in rough hydrophobic surfaces, the real contact area of the droplet with the surface is higher than the apparent one; therefore the energy balance between the surfaces is satisfied at higher apparent contact angles (CA):

$$\cos\theta' = r\cos\theta \tag{1}$$

Where θ' and θ are the CA of the rough and smooth surfaces respectively and r is the roughness factor.

The other mechanism which has been widely used to fabricate superhydrophobic surfaces [8,9] and is schematically shown in Fig. 1B is based on fabrication of porous structures which was first introduced by Cassie and Baxter [10]. According to this mechanism, the contact of the droplet with a porous structure is the combination of its contact with the actual material, and the air gaps embedded in the surface which will increase the apparent contact angle due to the contact of the liquid with the air gaps in between. The apparent contact angle is then estimated by:

$$\cos\theta_A = -\left(f_2 + f_1\frac{\gamma_{LS} - \gamma_{SA}}{\gamma_{LA}}\right) \tag{2}$$

Where f_1 and f_2 are the total solid/liquid and liquid/air interfaces respectively.

Although the contact angle is high in the structures fabricated according to both Wenzel and Cassie mechanisms, the important practical difference between these two surfaces is that, the droplet will strongly stick on the Wenzel surface due to its high contact area while the Cassie droplet is able to move on the surface with small driving force due to large contact of the droplet with air gaps [1].

Outstanding properties of carbon nanotubes (CNTs) make them highly attractive for different applications [11]; however intrinsic hydrophilic properties of CNTs limits their applications where hydrophobic or superhydrophobic surfaces are required [12]. Different methods such as applying surface roughness through micro/nano patterning of the CNT films [13] and deposition of superhydrophobic polytetrafluoroethylene (PTFE) [14] have been used so far to control the hydrodynamic properties of CNTs and fabricate a CNT base superhydrophobic surface.

In this research, a new structure based on aligned carbon nanotube (ACNT) and amorphous carbon (a-C) is introduced which will combine the Cassie and Wenzel mechanisms to enhance the hydrophobicity. As it is schematically shown in Fig. 1C, a-C nanospheres which will increase

* Corresponding author. Tel.: +65 8118 9089; fax: +65 67933318.
E-mail address: mazi0002@ntu.edu.sg (M. Shakerzadeh).

0925-9635/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2009.04.010

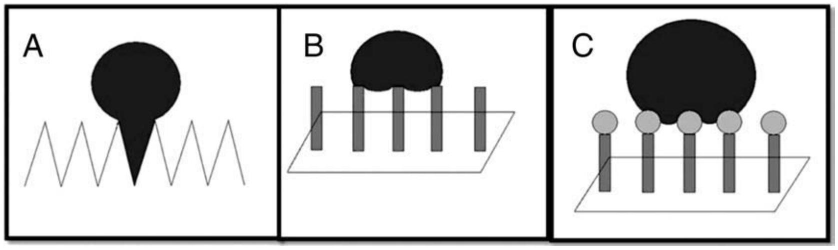

Fig. 1. Schematic representation of (A) Wenzel, (B) Cassie and (C) the new proposed Cassie + Wenzel combined model.

the hydrophobicity according to Wenzel mechanism due to their high curvature, are deposited on ACNT film. The tubular structure of the nanotubes increases the hydrophobicity according to Cassie mechanism. Biocompatibility of both CNTs [15] and a-C [16] promotes the application of this structure in biomedical applications where superhydrophobic surfaces are needed. Besides, self-assembled fabrication of this structure promotes the fabrication of superhydrophobic surfaces in large areas.

2. Experimental

Plasma enhanced chemical vapor deposition (PECVD) was used to grow the ACNT film [17,18]. 10 nm nickel film was deposited on the silicon substrate as the catalyst using magnetron sputtering. The catalyst film was subjected to ammonia etching at 800 °C and 240 scc/m flow rate for 2 min. Nanotubes were grown using C_2H_2 and NH_3 as the feeding gas with flow rates of 60 and 240 scc/m respectively. ACNT films were subjected to carbon plasma using "Double Bend Filtered Cathodic Vacuum Arc" (FCVA) system which is described elsewhere [18,19]. 99.99% cylindrical graphite was used as the cathode where a 60 Ampere arc was held using a graphitic anode. Negative substrate bias of 100 V was applied on the substrate during the deposition.

Morphology of the films was investigated using JSM-5910 LV scanning electron microscopy (SEM) while the microstructure of the films was investigated by Kratos Axis-Ultra XPS and JEOL 2010 transmission electron microscope (TEM). C1s XPS peak was deconvoluted into two peaks located at 284.3 ± 0.1 and 285.2 ± 0.1 eV related to SP^2 and SP^3 carbon bonding hybridization respectively as it is proposed by Diaz et al. [20]. SP^3 fraction of the film was estimated from the area under the respective peak over the total area of the peak.

3. Results and discussion

Fig. 2A shows the SEM image of the CNTs used in this work. As it is shown, by applying the conditions mentioned previously, ACNTs 5 µm in length and 200 nm in diameter were grown. Hydrophobicity of a single CNT was investigated by Dujardin et al. [21] and it was found that 180 mN m^{-1} is the crucial liquid surface energy beyond which the wettability of the CNT is not favorable thermodynamically. Considering the surface tension of water which is 72 mN m^{-1}, it is obvious that as it is also shown in Fig. 2A, the as grown CNTs are hydrophilic. Fig. 2B to E shows the formation of carbon nanospheres on the CNT tips in the samples subjected to carbon plasma using FCVA. As it is shown in Figs. 2B and 4, at initial stages of the growth, spheres with the size of individual nanotubes are formed on the CNT tips. As the deposition time increases, the size of the spheres will also increase and finally, the spheres will coalescence to each other and a uniform film is formed on the CNT film as it is shown in Fig. 2E.

Formation of the spheres on CNT tips, converts the initial hydrophilic state of the CNT films to hydrophobic and superhydrophobic. Fig. 2F shows the top view of the sample which is shown in Fig. 2C. Tubular structure of aligned CNTs fabricates a porous structure which will increase the hydrophobicity according to Cassie

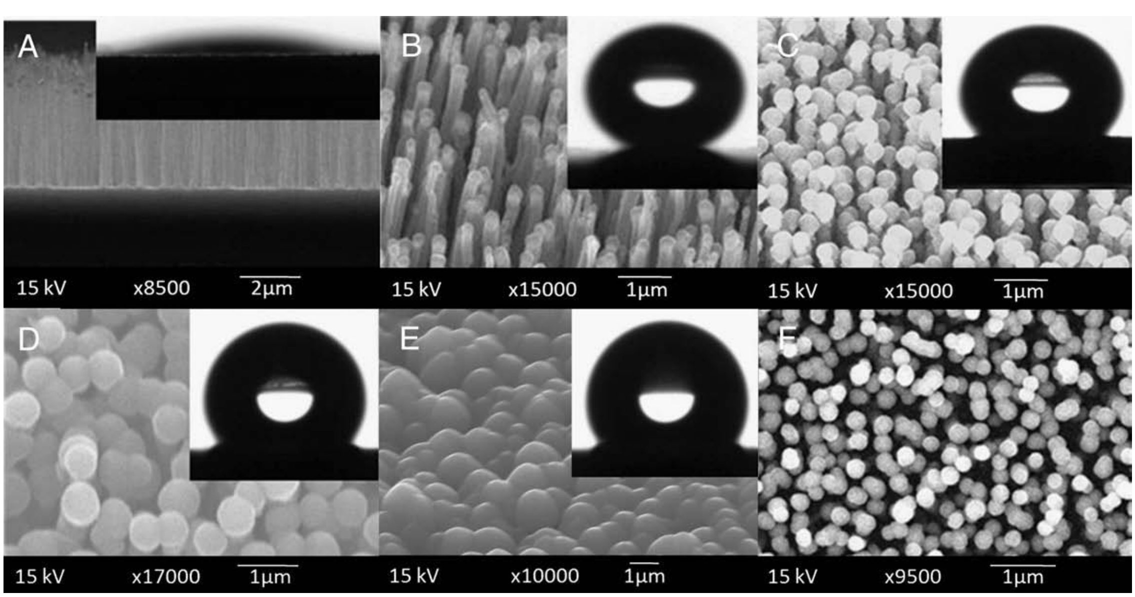

Fig. 2. SEM image of the (A) as grown CNT, and CNT treated with carbon plasma for (B) 2 min, (C) 5 min, (D) 15 min (E) 30 min, and (F) the top view of the sample shown in figure (C).