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Preparation of super-hydrophobic films using pulsed hexafluorobenzene plasma

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ABSTRACT

In this study, super-hydrophobic films were deposited in a one-step simple process by pulsed RF C_6F_6 plasma, and the influence of the duty-cycle (DC) on the surface structure and chemical characteristics of depositing fluorocarbon films was examined. The deposited coatings were analyzed by X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectrometry (FTIR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Contact Angle Analyzer. It was found that by decreasing the DC from 1 to 0.1, the rough structure of the film with a lot of particles was obtained. In addition, the super-hydrophobic property was obtained on this composite fluorocarbon film. Finally, the adhesion of fluorocarbon films could be increased by deposited on the cotton fiber substrates instead of Si wafer.

1. Introduction

A super-hydrophobic surface has a high water contact angle of over 150° and very low contact angle hysteresis [1]. On this surface, water droplets do not wet the surface at all and easily roll off to remove dirt and debris. This self-cleaning property of a super-hydrophobic surface is called the "lotus effect" [2]. The solid surface with the lotus effect is governed by two factors — low surface energy and the roughness of the surface. The incorporation of fluorine atoms, which have a small atomic radius and high electro-negativity, could achieve low surface energy [3]. In another research, a smooth surface was covered with regularly aligned and closely packed fluorine atoms, and the greater water contact angle of the smooth surface with very low surface energy such as PTFE films was established at about 120° [4]. With increasing the roughness of these surfaces, the contact angle of these increase. Therefore, water droplets remain on these highly rough hydrophobic surfaces and do not fill into the crevices of these surfaces. Surface modification methods such as plasma etching [5], plasma deposition [6], laser treatment [7], sol–gel processing [8], anodic oxidation of aluminum [9], and chemical etching [10] have used to fabricate super-hydrophobic surface topography. These might involve complicated multistage processes. Several studies regarding plasma deposition have discussed the retention of the chemical structure and functional group on the surfaces. It is generally noted a decrease of power supply reduces the destruction of the functional group in the plasma polymerization. The pulsed plasma polymerization with the control of the variable duty cycle (DC) especially has a great effect on the chemical structure of plasma polymers [11,12]. Moreover, an unusual 'ribbon-like' micrometric morphology has been found for the coatings deposited at low DC [13].

Fluorinated amorphous carbon (a-C:F) films has high chemical stability, low surface energy, low refractive index, and good thermal stability [14]. When fluorocarbon film is properly deposited on different substrates (cotton, metal, polymer … etc.), these materials may be used in many fields such as textiles, packaging, biomaterials, and micro-electronics [13].

On the other hand, the preparation of super-hydrophobic films needs high roughness and low surface energy, and usually needs a complicated process when these two attributes are present simultaneously. In this study, a pulsed plasma polymerization was used to prepare fluorocarbon super-hydrophobic film in a one-step process. Moreover, the adhesion property between fluorocarbon film and cotton was also discussed. The deposited coatings were analyzed using XPS, FTIR, SEM, TEM, and the hydrophobic behavior is confirmed by contact angle meter.

2. Experimental

The Si wafer and cotton was chosen as the substrate to deposit the fluorocarbon film. All experiments were carried out using pulsed plasma equipment with a 13.56 MHz pulsed RF and an electrode attached externally to the reactor. The power was generated from a CESAR® 1310 RF GENERATOR in this experiment, and the reflected wave was set to zero and the power was set to 50 W. The generator was only worked during power on time,

$$DC = t_{on}/t_{on} + t_{off}$$

where t_{on} and t_{off} are the plasma on and off time. Hence, different DCs have different dissociation times to deposit the film. The pulsed

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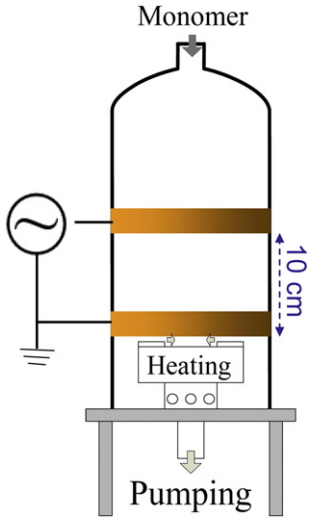

Fig. 1. Deposition reactor sketched.

plasma polymerization provided film chemistry controllability during film formation. A schematic diagram of the deposition system is shown in Fig. 1. The equipment had a quartz bell jar reactor (30 cm outer diameter, 50 cm length) and the outer electrodes were separated at a distance of 10 cm. All runs were first purged with argon and pumped down to a base pressure of about 40 mTorr. The hexafluorobenzane (C_6F_6) as the deposition monomer (Aldrich, 97% purity) was introduced into the reactor and maintained for 1 min or until it reached a stable state. The flow rate of C_6F_6 was kept at 6 sccm using a needle valve. The applied power, pulse frequency, pressure and deposition time were set at 50 W, 100 Hz, 500 mTorr and 5 min, respectively.

The chemical structures of the a-C:F films deposited on Si wafers were characterized using a Fourier Transform Infrared spectrometer (FTIR, LX20000G). Each spectrum was obtained from an average of 16 scans in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1}. The surface composition of the a-C:F film was investigated using X-ray Photoelectron Spectroscope (XPS, VG Scientific Microtab 310F) with Mg Kα source (1253.6 eV). The surface morphology and structure of the a-C:F films were noted using Scanning Electron Microscope (SEM, JEOL JSM 6500-F) and Transmission Electron Microscopy (TEM, Hitachi S-800), respectively. The hydrophilic and hydrophobic characteristics of the fluorocarbon films were measured using a contact angle analyzer (First Ten Angstroms FTA125) based on the sessile water drop measured method.

3. Results and discussion

In the present study, the power of plasma was not below 50 W because there was no significant deposition on the surface. Therefore, the film was prepared by continue plasma above 50 W (50–200 W) and had a smooth surface with a contact angle between 90 and 110°. As mentioned above, the DC of the plasma could have played an important role in achieving the roughness of the surface because homogenous species reaction occurred while controlling plasma off in a short period. Therefore, the effect of DC in pulsed plasma polymerization on the surface and chemical composition and physical morphology of the surface films are discussed. In addition, a simple deposition mechanism of super-hydrophobic fluorocarbon film was also proposed by the experimental data.

3.1. Chemical structure

The effect of DC on the contact angle and composition of the film are shown in Table 1. It was found that the contact angles did not change (about 110°) when the DC was above 0.15. On the other hand, the water contact angle significantly increased over 160° and a superhydrophobic surface was obtained as the DC was 0.1. The XPS analysis of the films are shown in Table 1 which also provides a quantitative value for the F/C ratio incorporation in the plasma-generated polymers approaching the limiting stoichiometric value of 1:1 present in the C_6F_6 starting monomer. This indicates that the composition of the surface was the same as the monomer because the monomer deposited on the surface with little dissociation or the C_6F_6 molecule was dissociated to a small molecule and polymerized. The F/C ratio incorporation in the plasma generated polymers decreased under the continuous-wave conditions. It was considered that the monomer C_6F_6 was dissociated to a small molecule and deposited on the surface or this small molecule such as F_2 was pumped out.

Table 1
Deposition conditions and results of fluorocarbon films

Run no.	DC[a]	Contact angle (°)	F/C ratio[b]
A	0.1	>160	0.95
B	0.15	111	0.97
C	0.2	105	1.01
D	1 (Continue-wave)	108	0.79

[a] $DC = t_{on}/(t_{on}+t_{off})$.
[b] F/C ratio: XPS atomic concentration ratio.

The deconvolution of C_{1s} XPS spectra and relative abundance of various CF_x groups in a-C:F film are shown in Fig. 2. The deconvolution procedure employed and the corresponding peak assignments were in accordance with the recommendations derived from the literature for fluorocarbon film. The peaks at 284.6, 286.4, 287.9, 289.2, 291.2, 293.2

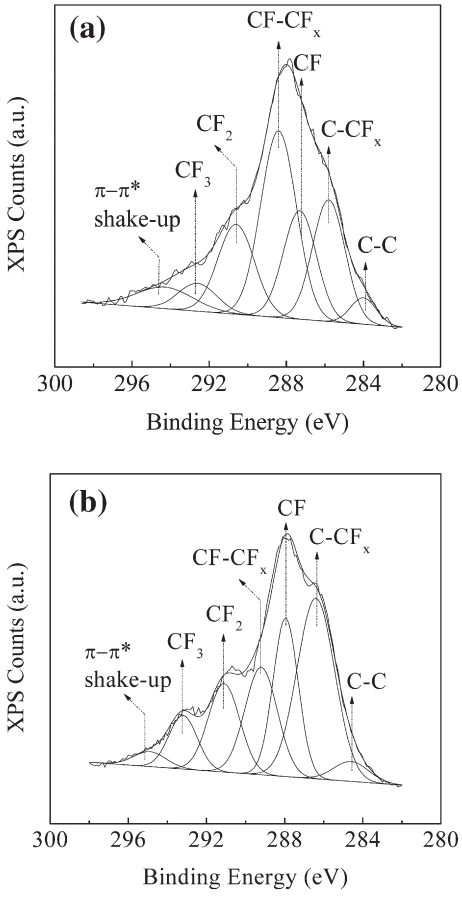

Fig. 2. The C_{1s} XPS spectra deconvolution of the fluorocarbon films under various DC. (a) 0.1; (b) 1.