Deposition of fluorocarbon film with 1,1,1,2-tetrafluoroethane pulsed plasma polymerization

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ABSTRACT

The fluorocarbon films were synthesized by radio frequency pulsed 1, 1, 1, 2-tetrafluoroethane plasma polymerization using various duty cycles. The deposition rates and water contact angles were examined for radio frequency pulsed plasma polymerized fluorocarbon films. The film surface properties were also determined by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy. For varying duty cycle from 100% to 10% in pulsed plasma process, the plasma polymerized film drastically changed the surface property. Specifically, it has been observed that modulated plasmas with the proper duty cycle of 10% lead to the formation of the super-hydrophobic film by static water contact angle value of 150°. The surface properties of fluorocarbon films were determined as the Cassie state. In the transmittance, UV–VIS transmission spectra showed that these radio frequency pulsed plasma polymerized coatings were transparent in visible light region. By adjusting duty cycles in relation to radio frequency pulsed plasma polymerization, the hydrophobicity of the resulting thin fluorocarbon films could be tuned.

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1. Introduction

The fluorocarbon thin films have been well known to obtain the hydrophobicity, low refractive index, chemical stability, and good thermal insulation which rely on the nature of the fluorine-containing moiety and its fluorine content [1]. The unique properties of fluorocarbon thin film make it applicable as dielectric material, stain-repellent coating, micromechanics, and gas separation membranes etc [2,3]. Plasma polymerization is one of the mainly manufactory techniques for forming fluorocarbon thin films with the constructive benefits included in single-step fabrication and dry process. However, plasma polymerization also unfortunately results in the poor control of film deposition. In particular, the functional groups of original monomers are extremely dissociated and few can be retained in the deposited/polymerized film in the traditional continuous wave (CW) plasma polymerization. For this reason, it is desirable for the flexile mode to control surface structures of plasma polymerized films. The pulsed plasma polymerization with the variable duty cycles (DC) has been paid many attentions in research field in recent years [4–6]. It is a flexible method in surface structure tailoring of plasma deposited/polymerized film, and allows a high-degree of control on the ion bombardment and on the production of active species [7,8]. Moreover, the super-hydrophobic film surface has been found for the coatings deposited at low DC [9]. Among many studies of the pulsed plasma polymerization, there is a need to examine

pulsed fluorocarbon plasma polymerization that is capable to coat super-hydrophobic film on heat-sensitive polymeric materials.

The goal of this work is to study the use of radio frequency (RF) pulsed plasma polymerization to retain carbon–fluorine/super-hydrophobic characteristics in the plasma polymerized film. Only a handful of studies dealing with the hydrophobic fluorinated carbon thin films from 1,1,1,2-tetrafluoroethane ($C_2H_2F_4$) plasma polymerization have been published to date. Hence, $C_2H_2F_4$ was chosen as the monomer of RF pulsed plasma polymerization in this study. Moreover, the effect of duty cycles on plasma polymerized fluorocarbon thin film was also discussed. In this study, we reported that fluorocarbon films with super-hydrophobic characteristics can be achieved by RF $C_2H_2F_4$ pulsed plasma polymerization, and their surface characteristics were discussed on the results of Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) analyses.

2. Experimental details

2.1. Low-pressure plasma deposition system

The monomer used for plasma polymerization of fluorocarbon film was 1,1,1,2-tetrafluoroethane ($C_2H_2F_4$, 99.99% purity). The plasma reactor system used in this study was a bell jar-type reactor, with dimension of 44.5 cm in height and 19.0 cm in diameter as shown in Fig. 1. An electrode assembly was connected with a 13.56 MHz RF power supply (CESAR 133 RF300W, U.S.A.). The ring-shaped copper electrodes (3 cm in width) were wrapped around the glass bell jar with 8 cm distance between power and ground. A stainless steel plate (7 cm in

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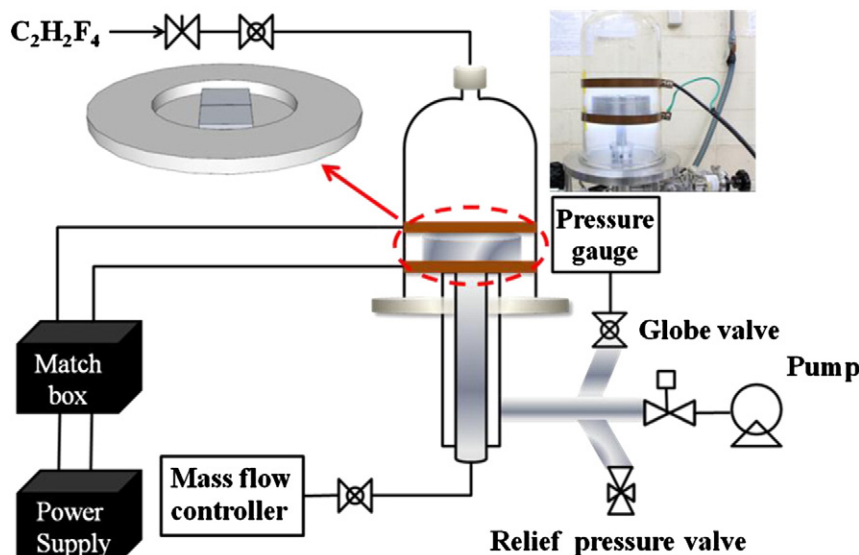E-mail address: chunhuang@saturn.yzu.edu.tw (C. Huang).

Fig. 1. Schematic diagram of low-pressure RF pulsed $C_2H_2F_4$ plasma system.

diameter) inside the bell jar was used as a substrate holder to receive plasma deposition. This power supply obtained the pulsed plasma mode. For pulsed plasma deposition, a 10/100 ms pulse sequence, where the plasma was on for 10 ms and off for 90 ms was kept constant for pulsed experiments. The 10/100 ms pulse sequence corresponds to a duty cycle of 10% (defined as the ratio of pulse on time to the total cycle time).

2.2. Film characterization and surface analysis

The thickness of RF pulsed plasma-polymerized fluorocarbon films was measured using the optical thin-film thickness detector (MFS-630 Hong-Ming Technology, Inc., Taiwan). UV–VIS transmission detection was carried out using a GBC Cintra 202 UV spectrophotometer to determine the transmittance of RF pulsed plasma-polymerized films. The chemical structure of RF pulsed plasma-polymerized films was characterized using the attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometer (PerkinElmer Spectrum 100). The ATR-FTIR crystal was ZnSe, and its incidence angle was 45°. Each spectrum was obtained from an average of 256 scans in the range of 650–4000 cm^{-1} at a resolution of 4 cm. The surface morphology of the RF pulsed plasma-polymerized fluorocarbon carbon thin film was observed by scanning electron microscopy (SEM) with a JEOL model JSM-5600 apparatus. A tungsten filament was used as the electron source. A 20-kV

accelerator voltage was used for scanning RF pulsed plasma-polymerized film surfaces. X-ray photoelectron spectroscopy (XPS) measurements are carried out on a VG Scientific Microlab 310F system, using nonmonochromatic Mg Kα-radiation (hυ = 1253.6 eV) and Al Ka-radiation (hυ = 1486.6 eV) operated at 25 kV. Spectra were acquired with the angle between the direction of the emitted photoelectrons and the surface equal to takeoff analysis angle 60°.

The static contact angles of RF pulsed plasma polymerized films were measured by projecting an image of an automatic sessile droplet resting on a coating surface with a Magic Droplet Model 100SB Video Contact Angle System (Sindatek Instrument Corporation, Taipei, Taiwan). In order to understand the nature of the surface change of RF pulsed plasma polymerized films, the dispersion and polar interaction contributions to the surface energy of the materials were calculated using the Owens–Wendt model [10]:

$$\gamma_{LV}(1 + \cos\theta) = 2\left(\gamma_L^d \cdot \gamma_S^d\right)^{1/2} + 2\left(\gamma_L^p \cdot \gamma_S^p\right)^{1/2}. \tag{1}$$

The liquids used for calculating the surface energies of RF pulsed plasma polymerized films were water and di-iodomethane of known γ^p (polar component) and γ^d (disperse component). The surface energy of a solid (γ^s) has two components, namely, a polar component and a disperse component. Both components contribute to the total surface energy. The polar and disperse components are responsible for the hydrophilic and hydrophobic properties. Cassie equation [11] proposed the mathematical model, it can be energetically favorable for a liquid to bridge across the tops of surface features so that the droplet rests upon a composite surface of flat solid tops and flat air gaps between them, as described by the Cassie–Baxter relationship. The contact
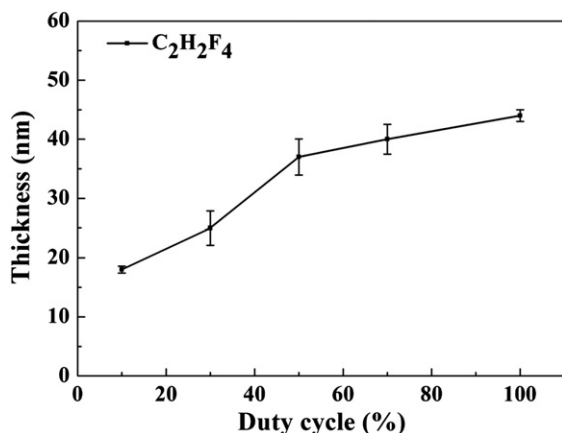

Fig. 2. The average thickness of RF pulsed $C_2H_2F_4$ plasma deposited films with various duty cycles (DC) of pulse plasma. Plasma condition: RF 20 W, 7 sccm, 133.3 Pa at 10 min.

Table 1
Static contact angle values of two suitable liquids for the surface energy measurement of RF continuous wave (CW)/pulsed $C_2H_2F_4$ plasma polymerized films. Plasma condition: RF 20 W, 7 sccm, 133.3 Pa at 10 min.

Duty cycle (%)	Contact angle (degree)		Surface free energy (mJ/m^2)		
	Water	Diiodomethane	Polar	Dispersive	Total
100 (CW)	106	88	1.64	13.6	15.24
70 (pulse)	104	87	1.99	14.06	16.06
50 (pulse)	110	86	0.74	14.53	15.28
30 (pulse)	127	92	0.05	11.83	11.83
10 (pulse)	150	118	0.52	3.57	4.09