

Paper

Characterization of fluorocarbon thin films deposited by ICP and PP

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(Received: October 4, 2010; Accepted: January 25, 2011)

Fluorine-containing hydrophobic thin films have been treated in this study with a mixture of fluorocarbon precursors like C₂F₆, C₃F₈, and *c*-C₄F₈ and the unsaturated hydrocarbons of C₂H₂ using inductively coupled plasma (ICP) and pulsed plasma (PP) deposition. Process parameters for plasma polymerization such as gas ratio, gas pressure, plasma power, pulse frequency, and processing time were investigated. Surface analytical instruments such as time-of-flight secondary ion mass spectrometry (TOF-SIMS) and x-ray photoelectron spectroscopy (XPS) were used to provide useful information about the surface composition and the chemical structure of the fluorocarbon films. Film thickness and surface morphology were also observed by using FE-SEM and AFM. Water contact angle measurements and FE-SEM results show that the ICP technique provides coarser grained films and more hydrophobic surfaces as well as a higher deposition rate compared to the PP technique. TOF-SIMS and XPS analyses indicate that the ICP technique produced more fluorine-containing functional groups, including CF₂ and CF₃, than the PP technique. From the curve-fitted XPS results, it is clear that fluorocarbon films grown using the ICP technique exhibited less cross-linking and higher CF₂ concentrations than those grown using the PP technique.

1. Introduction

Plasma polymerization is a thin film deposition process [1]. Plasma polymers do not consist of chains with repeating units, but tend to form an irregular three-dimensional cross-linked network. Fluorine-containing plasma polymers have a low dielectric constant, a low friction coefficient and are highly hydrophobic. Plasma polymer films are applied in anticorrosive surfaces, humidity sensors, electrical resistors, scratch resistance coatings, optical filters, membranes, protective coatings, and chemical barrier coatings, etc [2-4].

Plasma sources can be divided into two categories: continuous-wave (CW) plasma and pulsed plasma (PP). Continuous-wave plasmas such as inductively coupled plasma (ICP) and capacitively coupled plasma (CCP) have been examined by many research groups [5-7]. PP has been less studied, and is used to control the plasma deposition environment [8]. In the PP process, RF power is applied for a “pulse-on” time, which is followed by a “pulse-off” time that indicates that

the RF power is turned off. During the pulse-on time, ions and reactive neutrals are produced. The neutrals react with radicals on the surface when the pulse is off. Pulsed plasma is capable of surface tailoring, which is an advantage of PP compared with CW plasma. However, the deposition rate on the substrate of PP is lower than that of CW plasma with identical condition [9].

In this work, fluorocarbon thin films have been deposited from C₂H₂ and a saturated fluorocarbon (C₂F₆, C₃F₈, and *c*-C₄F₈) mixed gas using both ICP and PP. The surface properties and chemical compositions of the fluorocarbon thin films are investigated using water contact angle measurements, field emission-scanning electron microscope (FE-SEM), atomic force microscope (AFM), x-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (TOF-SIMS).

2. Experimental Procedure

2.1. Plasma polymerization process

In-house plasma polymerization equipment was used to deposit the plasma polymers. The reactor was the same as has been described elsewhere [10]. Prior to the deposition process, the Si substrate was surface cleaned in hydrofluoric acid using an ultrasonic process for 30 min. To make the fluorocarbon films, the chamber was filled with one of the working gases at a pressure of 5.33 Pa, i.e., a C_2F_6/C_2H_2 , C_3F_8/C_2H_2 , or $c-C_4F_8/C_2H_2$ mixture gas. The gas ratio of the fluorocarbon precursor/ C_2H_2 was 4:1 v/v percentage. For the ICP process, 13.56 MHz continuous RF was used to generate the plasma with a power of 100 W. In the pulsed-plasma process, the plasma was generated at average RF powers of 100 W with pulse frequencies of 1 kHz, 500 Hz, or 200 Hz and a pulse width of 40 μ s under the same gas ratio conditions used with the ICP process.

2.2. Instrumental evaluation

The differences in the water contact angles of the plasma-polymerized films were monitored. A contact angle goniometer (Ramé-Hart model-100, Netcong, NJ) was used to measure at room temperature using the sessile drop method.

The surface morphologies and cross-section images of the fluorocarbon films were observed by FE-SEM (HITACHI S-4100) at an acceleration voltage of 15 keV.

AFM (PSIA XE-100, Park systems) was used to examine the surface roughness of the plasma-polymerized films. The microscope was operated in non-contact mode.

XPS was performed to examine the chemical structure on the surface of the fluorocarbon films using a PHI-5800 instrument (Physical Electronics, Eden Prairie, MN). The XPS analysis was conducted with monochromatic Al $K\alpha$ radiation (1486.6 eV) at a power of 250 W.

For the TOF-SIMS measurements, an ION-TOF instrument (model TOF-SIMS⁵) was used with a Bi ion gun operating at 25 keV at an ion current of 1 pA.

3. Results and Discussion

3.1. Hydrophobic properties and surface morphology of thin films

The water contact angles of the plasma-polymerized films are shown in Table 1. The table shows contact angles measured immediately after polymerization, and the value is the average value of three measurements. Table 1 shows the water contact angles of the fluorocarbon thin films made using the ICP and PP techniques, where the pulse

frequency varied under the same pressure (5.33 Pa), deposition time (30 min) and gas ratio (4:1 v/v percentage) conditions. The water contact angle of the film produced by the ICP technique was from 101° to 112°. The film produced by this technique showed higher water contact angle than that produced by the PP technique. The contact angle for PP decreased as the pulse frequency decreased. The contact angle of C_2H_2/C_2F_6 for both 500 Hz and 1 kHz was the highest.

Table 1. Water contact angles of plasma polymers.

	Water Contact Angle (deg)		
	C_2F_6	C_3F_8	$c-C_4F_8$
PP (1kHz)	108.3 ± 0.2	104.4 ± 0.5	98.8 ± 0.3
PP (500 Hz)	106.0 ± 1.0	101.5 ± 0.5	96.0 ± 0.1
PP (200 Hz)	74.5 ± 1.5	78.5 ± 0.5	81.5 ± 0.5
ICP	102.0 ± 0.2	101.0 ± 0.5	112.0 ± 0.5

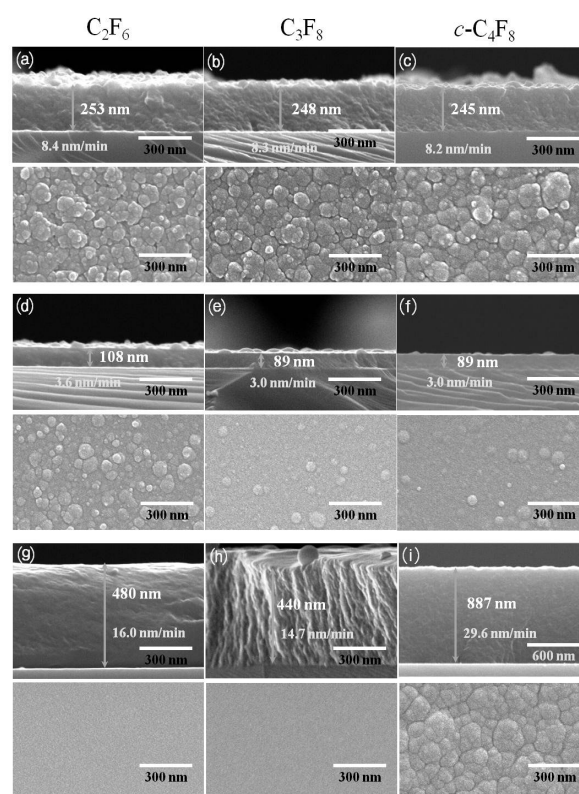


Fig. 1. FE-SEM images of cross section and surface: (a-c) PP at the pulse frequency of 1 kHz and (d-f) PP at 200 Hz and (g-i) ICP technique.

Fig. 1 shows FE-SEM cross-section and surface images of the deposited fluorocarbon films. The upper (a-f) and lower images (g-i), which correspond to the PP and ICP techniques, respectively, show the thickness and the surface morphology. The average deposition rate of the fluorocarbon film was calculated by dividing the thickness by the total deposition time. As shown in Fig. 1, the ICP technique produced a thicker

film and a higher deposition rate than the PP technique. This result is due to the formation of the plasma polymer during the pulse-on time. Labelle *et al.* reported that pulsed-plasma deposition rates can be attributed almost entirely to the pulse-on time. They also found, however, that there is a slight dependence on the pulse-off time [9].

The surface roughness of the plasma polymers was obtained by AFM. Surface roughness may influence the water contact angle of the sample surface. Fig. 2 shows the surface morphology for both the ICP and PP techniques. The root mean square roughness (R_{rms}) values for the PP-deposited films are higher than those for the ICP-deposited films. However, the influence of the roughness on the contact angle can be ignored if the roughness is below $0.1 \mu\text{m}$.

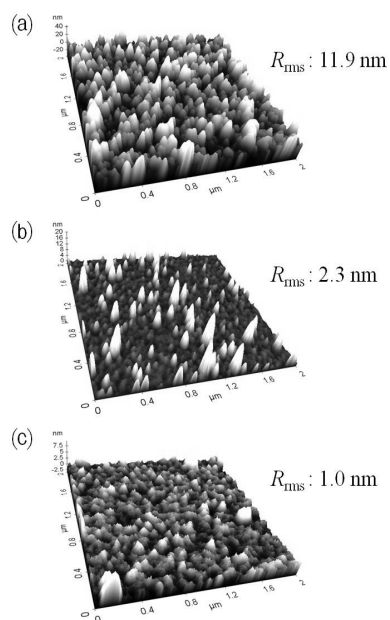


Fig.2. AFM images of plasma polymer films produced by $\text{C}_3\text{F}_8/\text{C}_2\text{H}_2$ mixture gas: (a) PP at the pulse frequency of 1 kHz, (b) PP at 200 Hz, and (c) the ICP technique.

3.2. Chemical characterization of deposited thin film surfaces

The chemical compositions of the plasma polymer surface were determined from the XPS C 1s core level spectra. To offset the surface charging phenomena, all binding energies in the C 1s core level spectra were referenced to the C–C peak centered at 284.8 eV. Fig. 3 shows the C 1s spectra of the fluorocarbon thin film surfaces prepared by (a) PP at the pulse frequency of 1 kHz, (b) PP at 200 Hz, and (c) the ICP technique, fed with the C_2F_6 working gas at an RF power of 100 W and a gas ratio of 4:1 v/v percentage. As shown in Fig. 3,

six main peaks were observed: C–C, C– CF_n , CF, CF-CF_n , CF_2 , and CF_3 , for the C 1s region in the figure. In Fig. 3, the XPS spectra show some differences between the films produced by the ICP and PP techniques. The ICP technique shows more fluorine-containing functional groups, as indicated by the height and area of the peaks, especially for CF-CF_n , CF_2 , and CF_3 , and a relative decrease in the C–C groups compared to the PP technique. On the other hand, the PP technique shows relatively more carbon species of the C–C, C– CF_n , and CF groups. Table 2 gives the percentage of each carbon functional group obtained by deconvolution and the F/C ratio measured in the spectra. This data clearly reveals that the relative peak area ratios of the sum of the CF_2 and CF_3 groups to the total C 1s components

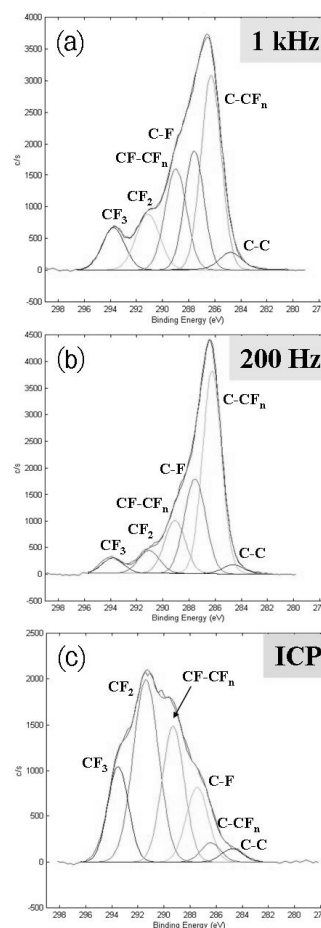


Fig.3. XPS C 1s spectra of plasma polymer films produced by $\text{C}_2\text{F}_6/\text{C}_2\text{H}_2$ mixture gas: (a) PP at the pulse frequency of 1 kHz and (b) PP at the 200 Hz and (c) ICP technique.

are 55.6%, 47.8%, and 45.7% for the cases of C_2F_6 , C_3F_8 , and *c*- C_4F_8 , respectively, using the ICP technique. Meanwhile, these values of the PP technique are 20.4%, 21.8%, and 23.9%, respectively, at a pulse frequency of 1 kHz. On the other hand, the relative peak area ratios of the C–C

and C–CF_n groups for the PP technique are more than triple that of the ICP technique. Similarly, the F/C ratios in the ICP technique are 1.67, 1.51, and 1.50, and those of the PP technique are 0.90, 0.90, and 0.92, respectively. The F/C ratio was calculated from the curve-fitted C 1s spectra using the following relationship [11]:

$$F/C = [(3 \times \%CF_3) + (2 \times \%CF_2) + (1 \times \%CF-CF_n) + (1 \times \%CF)]/100.$$

These results indicate that the higher hydrophobicity of the ICP polymer surface is caused by the greater amount of fluorine containing groups, especially CF₂, and CF₃.

Table 2. Relative concentrations of C 1s components and F/C ratio of fluorocarbon films using PP and ICP techniques.

Peak Intensities (%)				
	(B.E., eV)	C ₂ F ₆	C ₃ F ₈	c-C ₄ F ₈
PP (1 kHz)	C-C (284.8)	3.8	4.0	3.8
	C-CF _n (286.5)	35.4	38.0	37.6
	CF (288.2)	21.0	18.7	17.0
	CF-CF _n (289)	19.4	17.5	17.6
	CF ₂ (291)	11.9	11.5	14.9
	CF ₃ (293)	8.5	10.3	9.0
	F/C ratio	0.90	0.90	0.92
PP (200 Hz)	C-C (284.8)	2.6	5.0	6.3
	C-CF _n (286.5)	48.7	43.3	42.5
	CF (288.2)	25.0	27.2	20.5
	CF-CF _n (289)	13.7	11.9	13.4
	CF ₂ (291)	6.0	6.2	12.8
	CF ₃ (293)	4.0	6.5	4.6
	F/C ratio	0.63	0.71	0.73
ICP	C-C (284.8)	2.3	4.4	5.0
	C-CF _n (286.5)	3.3	8.9	3.2
	CF (288.2)	13.7	14.8	16.3
	CF-CF _n (289)	25.1	24.0	29.9
	CF ₂ (291)	39.0	30.9	33.5
	CF ₃ (293)	16.6	16.9	12.2
	F/C ratio	1.67	1.51	1.50

The TOF-SIMS analysis provides information on the molecular structure and composition of the polymer surfaces. Its spectra show specific fragment ions including carbon group and fluorine containing functional groups such as F⁺ (*m/z* of 19), CF⁺ (*m/z* of 31), CF₂⁺ (*m/z* of 50), and CF₃⁺ (*m/z* of 69) (spectra not shown). The peak intensity ratios of the specific fragment ions showed considerable differences between the ICP and PP techniques. The TOF-SIMS intensity ratios for each plasma polymerization technique are listed in Table 3. In order to normalize the fluorine containing ion peaks with the carbon peak (matrix), the peak intensity ratios of the fluorine containing groups to the carbon ions were obtained by intersecting the peak areas of the two fragment ions. As shown in Table 3, the peak ratios of the fluorine-containing ions to the carbon

ions for the fluorocarbon films using ICP are larger than for those using the PP technique. Notably, the value of the PP technique at a pulse frequency of 200 Hz was sharply lower than the others. This result indicates that the ICP technique produced more hydrophobic species such as CF₂ and CF₃ groups on the surface of the fluorocarbon films than did the PP technique.

Table 3. TOF-SIMS peak intensity ratios of fluorocarbon thin films using the PP and ICP techniques.

Peak Intensity Ratios				
		C ₂ F ₆	C ₃ F ₈	c-C ₄ F ₈
PP (1 kHz)	F ⁺ /C ⁺	0.09	0.08	0.09
	CF ⁺ /C ⁺	1.97	1.81	2.02
	CF ₂ ⁺ /C ⁺	0.24	0.19	0.21
	CF ₃ ⁺ /C ⁺	1.71	1.35	1.48
PP (200 Hz)	F ⁺ /C ⁺	0.12	0.11	0.09
	CF ⁺ /C ⁺	1.29	1.20	1.37
	CF ₂ ⁺ /C ⁺	0.15	0.13	0.13
	CF ₃ ⁺ /C ⁺	0.96	0.85	0.67
ICP	F ⁺ /C ⁺	0.06	0.06	0.07
	CF ⁺ /C ⁺	1.39	1.68	2.06
	CF ₂ ⁺ /C ⁺	0.52	0.50	0.54
	CF ₃ ⁺ /C ⁺	1.32	1.61	2.98

4. Conclusion

Plasma-polymerized fluorocarbon films were produced using the ICP and PP deposition techniques. The hydrophobic properties, surface morphologies, and chemical compositions were studied through water contact angle, FE-SEM, AFM, XPS, and TOF-SIMS. The water contact angle results showed that the ICP technique produced a plasma polymer film with a more hydrophobic surface than that produced using the PP technique. In addition, the pulse frequency of 200 Hz showed the lowest water contact angle for all types of fluorocarbon precursors. Surface analysis results indicated that the ICP technique generated more fluorine-related functional groups such as CF–CF_n, CF₂ and CF₃. CF₂ and CF₃ functional groups contribute greatly to the hydrophobic properties of plasma polymer films. Therefore, the ICP technique is a more useful means of producing hydrophobic surfaces than the PP technique.

5. References

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