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Surface analytical studies of Ar-plasma etching of thin heptadecafluoro-1-decene plasma polymer films

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Abstract

An audio-frequency plasma polymerization set-up with a planar plasma source was used to deposit thin heptadecafluoro-1-decene (HDFD) plasma polymer films. The morphology and chemical structure of the films after deposition were compared with the state of the film after a subsequent Ar-plasma treatment by means of in situ Fourier transform infrared reflection absorbance spectroscopy (FT-IRRAS), X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and atomic force microscopy (AFM) as well as contact angle measurements. The results revealed the correlation of wettability of the model Teflon-like films with change of surface chemistry and surface topography as a result of Ar-plasma treatment.

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Keywords: Plasma polymer; Plasma etching; Teflon-like films; Morphology; Surface

1. Introduction

Teflon-like thin films are of high interest for microelectronic and optical applications but are also considered as long-term stable corrosion resistant and aesthetic thin films for their low dielectric constant, high hydrophobicity, high chemical inertness and low friction coefficient [1–3]. At the same time, increasing interest has been devoted to the modification of the fluoropolymer surface characteristics to obtain improved adhesion, wettability and other functionalities [4–6].

Yet, little has been published on the detailed structure of thin Teflon-like plasma polymer films and their behaviour etched in inert plasmas [7,8]. The latter treatment can be used to tailor the chemical structure as well as the surface roughness of the functional films and thereby optical and mechanical properties as well as wettability. Heptadecafluoro-1-decene (HDFD) was used as monomer to deposit thin Teflon-like plasma polymer films in an audio-frequency discharge. The chemical structure and surface morphology were studied after thin film deposition and after an additional argon plasma treatment. The change in the chemical structure and morphology of the thin plasma polymer films during argon plasma treatment was measured by combining in situ FT-IRRAS, XPS, ToF-SIMS and AFM. The surface chemistry and surface morphology were correlated with the surface energy as calculated by contact angle measurements.

2. Experimental

2.1. Materials

Argon 99.998%, oxygen 99.995% and nitrogen 99.99% (Messer Griesheim GmbH Germany) were used as gases in the plasma processes, and heptadecafluoro-1-decen (HDFD, $CF_3(CF_2)_7CHCH_2$, purity >97%, Fluka) was used as liquid monomer without further purification for the deposition of plasma polymer films. Polished Si (1 0 0) wafers (Si-Mat Germany) and gold coated quartz crystals were used as substrates.

2.2. Plasma deposition

A bell-jar type reactor with internal parallel capacitive electrodes was used to carry out plasma etching and polymer deposition. The substrates and a gold coated quartz crystal of

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Table 1
Process parameters of HDFD plasma polymerization and the following Ar-plasma etching of thin HDFD plasma polymer films

Condition	Overall flow rate (1.5 sccm)				
	P_{Ar} (mbar)	P_{HDFD} (mbar)	Voltage (V_{eff})	Current (mA)	Frequency (kHz)
Plasma polymerization	0.2	0.1	≈400	1	4
Ar-plasma etching	0.3		≈400	1	1

20 mm diameter used for in situ quartz crystal microbalance measurements were fixed in the grounded electrode. The details of this set-up were described elsewhere by Grundmeier and Stratmann [9]. The exact plasma polymerization and plasma etching conditions are given in Table 1. The Ar-plasma etching was performed directly after the plasma polymerization in different gas atmospheres (see Table 1). Prior to the deposition of the plasma polymer, all substrates were cleaned in an oxygen plasma for 5 min to remove any kind of organic contamination layers.

2.3. Surface analysis

The chemical compositions of the plasma polymer films were investigated by means of XPS (Quantum 2000, Physical Electronics, USA). Spectra were measured using a monochromated Al Kα source and at pass energy of 23.5 eV. Calibration of the spectra was performed by using the F 1s peak (binding energy, BE = 689 eV) as internal reference. During the fitting procedure, the line width (full width at half-maximum, FWHM) for the peaks was kept constant for all components of the respective element spectrum in a particular spectrum. In situ FT-IRRAS spectra were measured using a Digilab FTS 3000 spectrometer with a liquid N_2 cooled MCT detector by means of an in situ plasma cell. The corresponding set-up and method for the in situ FT-IRRAS measurement were recently described by Raacke, Giza and Grundmeier [10]. The set-up consists of a vacuum chamber with moveable sample holder inside, so that the sample can be moved with defined velocities between 0.1 and 30 mm/s through the plasma region to the diagnostic position. The infrared beam of spectrometer is transmitted through ZnSe windows and is reflected on the sample at an incidence angle of 80°. The absorbance spectra in parallel and vertical polarization were measured as A_p and A_s, and then the ratio of A_p to A_s was calculated to eliminate the influence of the ambient medium on the spectra. The mass spectrometry measurements were performed using a ToF-SIMS TRIFT II System (Physical Electronics). The primary Ga^+ ion beam was accelerated by a 15 kV voltage and had an intensity of 600 pA.

AFM measurements were carried out using a dimension 3100 from Digital Instruments in tapping mode with tetrahedral

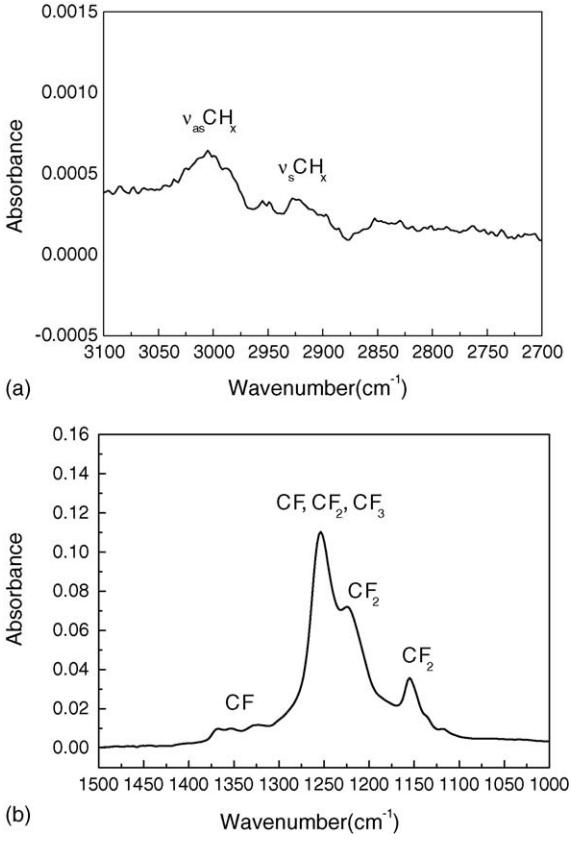

Fig. 1. (a, b) FT-IRRAS-spectra of HDFD plasma polymers.

AFM measurements were carried out using a dimension 3100 from Digital Instruments in tapping mode with tetrahedral

Table 2
Atomic composition of the HDFD plasma polymer films and after Ar-plasma etching treatment (condition I: HDFD plasma polymer films; II, III: HDFD plasma polymer films after Ar-plasma treatment for 30 and 60 s, respectively)

Element	At. conc. (%)		
	I	II	III
F 1s	53.2	42.7	38.3
C 1s	46.8	54.2	58.7
O 1s	0	3.1	3.0

Table 3
Fitting data of C 1s spectra from XPS analysis (condition I: HDFD plasma polymer films; II, III: HDFD plasma polymer films after Ar-plasma treatment for 30 and 60 s, respectively)

Element	Binding energy (eV)	Assignment	Percentage (%)		
			I	II	III
F 1s	689	$–CF_2–$	100	100	100
C 1s	286.0 ± 0.2	$–\boldsymbol{C}H_2–CFH–$	9.1	15.3	16.8
	288.0 ± 0.2	$–CH_2–\boldsymbol{C}FH–$	17.3	27.1	32.4
	290.6 ± 0.3	$–CH_2–\boldsymbol{C}F_2–$	26.8	22.4	22.6
	292.7 ± 0.3	$–CF_2–\boldsymbol{C}F_2–CF_2–$	41.3	30.9	25.3
	295.1 ± 0.2	$–\boldsymbol{C}F_3$	5.5	4.3	2.9
O 1s	534.5 ± 0.2	–CO–	0	100	100