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Cheneler, David; Bowen, James; Evans, Stephen D.; Górzny, Marcin; Adams, Michael J. and Ward, Michael C.L. (2011). Characteristics and durability of fluoropolymer thin films. Polymer Degradation and Stability, 96(4) pp. 561–565.

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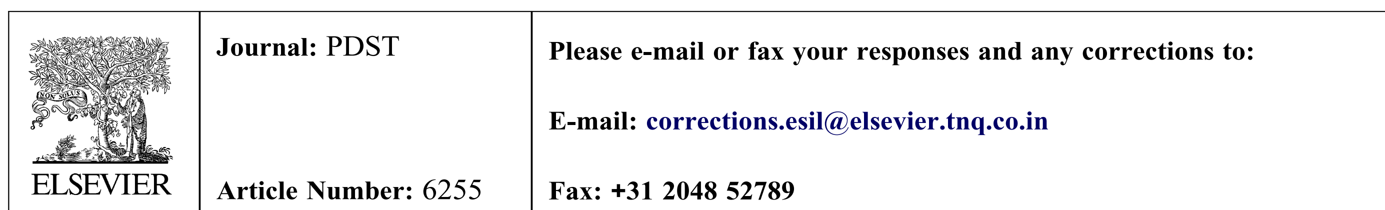

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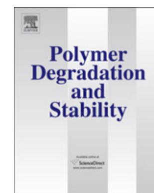

Characteristics and durability of fluoropolymer thin films

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A R T I C L E I N F O

Article history:
Received 21 October 2010
Accepted 29 December 2010
Available online xxx

Keywords:
Fluoropolymer
Ellipsometry
Atomic force microscopy
X-ray photoelectron spectroscopy
Wetting
Solvent
Etchant
Aqueous solution
pH

A B S T R A C T

The use of plasma-polymerised fluoropolymer (CF_xO_y) thin films in the manufacture of micro-electromechanical systems (MEMS) devices is well-established, being employed in the passivation step of the deep reactive ion etching (DRIE) process, for example. This paper presents an investigation of the effect of exposure to organic and aqueous liquid media on plasma-polymerised CF_xO_y thin films. Atomic force microscopy (AFM), scanning electron microscopy (SEM), ellipsometry, X-ray photoelectron spectroscopy (XPS) and dynamic wetting measurements were all employed as characterisation techniques. Highly basic aqueous solutions, including known silicon etchants, were found to cause delamination via degradation of the countersurface below the CF_xO_y thin film. Films were found to be stable in organic solvents, acidic aqueous solutions and slightly basic aqueous solutions.

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1. Introduction

The plasma polymerisation of gaseous fluoropolymers to yield fluoropolymer (CF_xO_y) thin films is frequently used in the manufacture of microelectromechanical systems (MEMS) devices during the deep reactive ion etching (DRIE) process. This process allows deep features and structures with high aspect ratios to be etched into silicon (Si) and consists of a multi-step switched-gas scheme with alternating etching and passivation steps, also known as the Bosch process [1]. The DRIE process, described in full by Wasilik and Chen [2] utilises inductively coupled power (ICP) technology to create a plasma that enhances the etch rate and also improves the passivation of the process. During the passivation step a CF_xO_y thin film is deposited using plasma-enhanced chemical vapour deposition (PECVD), which uses electrical energy to generate the plasma, with gaseous monomer being converted into reactive radicals, ions and neutral molecules. Instead of the plasma colliding and reacting with and etching the substrate surface, the interactions occur in the gas phase resulting in the deposition of polymerised fluoropolymer onto the substrate surface. Under such conditions, film formation occurs at relatively low temperatures whilst providing a conformal film exhibiting strong adhesion, low pinhole density and high surface uniformity.[2] The stoichiometry of the resultant film depends upon the exact reaction conditions, but contains approximately equal amounts of carbon and fluorine, typically 45–50% of each. Previous work where fluoropolymer films have been deposited by e-beam evaporation of PTFE and by spin coating of fluorinated monomer has shown that there will also be a small amount of oxygen present in the film stoichiometry, which is typically less than 10%.[3] The premise that underlies the passivation step is that the fluoropolymer is deposited onto an etched Si surface and consequently the sidewalls of the Si trench are relatively well protected; this allows further etching to occur where the polymer at the base of the trench is removed via the bombardment of the etchant (usually SF_6). As the etchant reacts, high aspect ratio anisotropic features can be etched into the Si substrate.

In addition to being a useful material in the manufacture of MEMS devices, polymerised CF_xO_y thin films exhibit interesting wetting, electrical and thermal insulation properties. Amyot et al. [4] studied the electrical and structural characteristics of plasma-polymerised CF_xO_y thin films up to 8 μm in thickness by investigating the charge storage properties of the films. Vaswani et al. [5] studied the surface modification of paper and cellulose with CF_xO_y

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0141-3910/$ – see front matter © 2011 Published by Elsevier Ltd.
doi:10.1016/j.polymdegradstab.2010.12.022

thin films, for use as a water-proofing agent, whereas Andersson et al. [6] used patches of a CF_xO_y thin film in order to create hydrophobic valves in microfluidic devices. Argyrakis et al. [7] employed CF_xO_y thin films as an anti-adhesion and structure release aide. Grant et al. [8,9] examined the growth and structure of CF_xO_y thin films as a function of the C_4F_8 gas inlet feed position relative to the plasma zone, while Ningel et al. [10] characterised CF_xO_y thin films deposited onto substrates up to 250 mm in length, reporting that the films exhibited excellent surface homogeneity.

In the current paper, a study of the effect of exposure of plasma-polymerised CF_xO_y thin films to organic and aqueous solvents is presented. A number of techniques were employed for the characterisation of the films before and after exposure. Spectroscopic ellipsometry was employed to measure film thickness, the surface topography of the films was assessed using atomic force microscopy (AFM) and scanning electron microscopy (SEM), while the composition of the films was investigated using X-ray photoelectron spectroscopy (XPS). Wetting measurements provided information that may be useful in the fabrication of MEMS devices, particularly microfluidic devices, in which the presence of capillary forces need to be considered to prevent unwanted adhesion between system components. The objective of the research was to determine whether exposure to the liquid media investigated would affect the structure of the films, and their adhesion to the Si countersurface. This is particularly important for two reasons. Firstly, is it possible to use CF_xO_y thin films as a barrier to prevent etching of Si during fabrication processes? Secondly, surfaces present in MEMS devices can be exposed to small amounts of organic and aqueous liquids for prolonged durations, and hence there exists the possibility for degradation of CF_xO_y thin films when submerged or in contact with a liquid for significant time periods. This study aims to build on previous work such as that performed by Elders et al.[3] who reported the chemical resistance of fluoropolymer films to a small number of organic solvents during a 30 min period of exposure, by examining the effect of immersion times up to 24 h in a range of standard laboratory organic solvents, as well as acidic and basic aqueous solutions. Finally, an assessment of the wetting behaviour of a range of organic solvents when in contact with CF_xO_y films may be useful in the design of MEMS devices, particularly those which incorporate microfluidic channels. Capillary forces can dominate and possibly prevent effective functioning of such devices, and therefore understanding the wetting behaviour of a range of solvents may prove beneficial for future designs. It is anticipated that the results presented here will be of practical significance to MEMS researchers and all those researchers who work with fluoropolymer thin films.

2. Experimental details

Plasma-polymerised CF_xO_y films were deposited onto the polished side of single crystal N-type Si (100) wafers (IDB Technologies, UK) using an STS Multiplex ICP DRIE etcher (STS Plc., UK), utilising C_4F_8 gas (Pelchem, South Africa). The C_4F_8 and Ar gas flow rates, deposition time and platen power were varied as listed in Table 1. Wafers were used as received, with any visible dust or debris being removed by sweeping the surface with N_2 gas. Freshly prepared CF_xO_y films were characterised as follows.

Spectroscopic ellipsometry measurements were performed using a UVISEL ellipsometer (Jobin-Yvon/Horiba, UK) over the wavelength range 250–800 nm and at an angle of incidence of 70°. All measurements were made under conditions of ambient temperature, pressure and humidity, and precautions were made to avoid performing measurements on visibly defective locations on the sample. Calculation of the CF_xO_y film thickness was performed for each measurement, based on a four-phase ambient/CF_xO_y film/SiO_2/Si model, in which the CF_xO_y film was assumed to be isotropic.

X-ray photoelectron spectroscopy (XPS) analysis of CF_xO_y films was performed using an Escalab 250 system (Thermo VG Scientific, UK), and a custom-built instrument. In each instrument an Al Kα X-ray source was used, providing a monochromatic X-ray beam with incident energy of 1486.68 eV, and measurements were made at a pressure of $\sim 1 \times 10^{-8}$ mbar. Samples were immobilised onto stainless steel sample holders using double-sided carbon sticky tape (Shintron tape, Shinto Paint Company, UK). Low resolution survey spectra were obtained using a pass energy of 150 eV over a binding energy range of −10 to 1200 eV with 1 eV increments. High resolution spectra were obtained using a pass energy of 20 eV with 0.1 eV increments.

AFM images were acquired using (i) a Dimension 3100 Nanoscope AFM (Veeco, UK) operating Nanoscope v5.12 software for both real-time analysis and post-capture image processing; and (ii) a NanoWizard II AFM (JPK, UK). Both AFMs were housed on vibration isolation tables and all images were acquired while operating in Tapping Mode (Dimension) and Intermittent Contact Mode (NanoWizard II) under ambient conditions, using rectangular pyramidal-tipped Si cantilevers (RTESP, Veeco, UK) with a nominal tip diameter of 50 nm. The average roughness (R_a) and root-mean-square roughness (R_q) of each film was calculated from an image of dimensions 5 × 5 μm.

SEM images were acquired using an XL30 FEG ESEM (Philips) operating at a pressure of $\sim 10^{-4}$ mbar using a 10 kV electron source, with all images obtained at an angle normal to the sample surface.

Wetting behaviour was assessed using a purpose-built apparatus employing a Charge-Coupled Device (CCD) KP-M1E/K camera (Hitachi, UK) and FTA Video Analysis software v2.0 (First Ten Angstroms, UK). A 25 μL gastight syringe (Hamilton, UK) was used for changing the volume of the droplet, which was released onto the sample surface from a blunt-ended needle of ~0.5 mm inside diameter (Hamilton, UK). All data were collected at room temperature and pressure under ambient humidity conditions.

The fluids used for assessing wetting behaviour are listed in Table 2, and the results obtained were used in the creation of a Zisman plot [11], from which the critical solid surface tension of the CF_xO_y film was estimated. All chemicals were purchased from

Table 1
Deposition conditions and characterisation for CF_xO_y films.

	CF_xO_y film number							
	1	2	3	4	5	6	7	8
Deposition time (s)	60	120	180	240	300	60	60	60
CF_xO_y gas flow rate (sccm)	80	80	80	80	80	80	80	80
Ar gas flow rate (sccm)	0	0	0	0	0	0	10	20
Platen power (W)	600	600	600	600	600	300	600	600
Thickness (nm)	98	210	328	438	558	61	96	99
R_a (nm)	0.44	0.58	0.84	0.90	1.43	0.42	0.43	0.39
R_q (nm)	0.65	0.78	1.10	1.16	1.84	0.73	0.55	0.50
H_2O θ (°)	111 ± 1	111 ± 1	111 ± 1	111 ± 1	111 ± 1	111 ± 1	111 ± 1	111 ± 1

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Table 2
List of liquids to which CF_xO_y films were exposed, liquid pH and surface tension, and contact angle with CF_xO_y film 1.

Liquid	pH	γ (mN/m)	θ (°)
Acetone (SLR grade)	n/a	23.7	33 ± 1
Chloroform (SLR grade)	n/a	27.2	34 ± 1
Ethanol (HPLC grade)	n/a	22.3	35 ± 1
Hexadecane (98+%)	n/a	27.5	47 ± 1
Hexan-1-ol (99+%)	n/a	25.2	41 ± 1
n-Hexane (SLR grade)	n/a	18.4	17 ± 1
Hydrochloric acid solution	2.0	72.8[a]	110 ± 1
MF26a developer	10.4	72.8[a]	110 ± 1
Potassium chloride solution	5.5	72.8[a]	111 ± 1
Potassium hydroxide solution A	10.4	72.8[a]	111 ± 1
Potassium hydroxide solution B	14.0	72.8[a]	110 ± 1
Propan-2-ol (SLR grade)	n/a	21.7	33 ± 1
Sodium chloride solution	5.5	72.8[a]	111 ± 1
Sodium hydroxide solution A	8.4	72.8[a]	111 ± 1
Sodium hydroxide solution B	10.4	72.8[a]	111 ± 1
Sodium hydroxide solution C	14.0	72.8[a]	111 ± 1
Tetrahydrofuran (SLR grade)	n/a	26.4	35 ± 1
Toluene (HPLC grade)	n/a	28.5	48 ± 1
Water (HPLC grade)	5.5	72.8	111 ± 1

[a] Surface tension of water prior to dissolution of material.

Fisher Scientific (UK) and Sigma-Aldrich (UK) with the exception of MF26a developer (Shipley Europe, UK).

Freshly prepared CF_xO_y films were subsequently immersed in the liquids presented in Table 2 for 24 h in order to assess if any macroscopic degradation of the films or degradation of the Si countersurface occurred. Aqueous solutions at pH 2, pH 8.4 and pH 10.4 were prepared by diluting hydrochloric acid (Fisher Scientific, UK) and dissolving sodium hydroxide pellets (Fisher Scientific, UK) in HPLC grade water. Similarly, aqueous solutions of potassium chloride (Fisher Scientific, UK) and potassium hydroxide (Fisher Scientific, UK) were prepared by dissolving the materials in HPLC water. It should be noted that HPLC water was found to have a pH of 5.5 due to the presence of dissolved carbon dioxide, while MF26a was found to have a pH of 10.4. pH measurements were performed using an IQ150 pH meter (IQ Scientific Instruments, UK).

A CF_xO_y film of ~100 nm thickness was also deposited onto tipless rectangular Si AFM cantilevers (CSC12, MikroMasch, Estonia) of 250 μm and 350 μm length. The static deflection and curvature of the beams was assessed before and after deposition using a Scantron MicroXAM interferometer (OmniScan, UK) operating a white light source. Scanning Probe Image Processor software (Image Metrology, Denmark) was employed for the analysis of acquired images.

3. Results and discussion

3.1. Characterisation of films 1–8

Table 1 lists the measured thickness, roughness and water contact angle behaviour of CF_xO_y films 1–8. The film thickness was found to increase approximately linearly with increasing deposition time (films 1–5) at a mean rate of 110 nm/min, with film surface roughness increasing slightly as a function of thickness. Reducing the platen power during film deposition (film 6) reduced the film thickness, whilst the roughness and water contact angle behaviour remained approximately constant. Similarly, adding Ar gas into the deposition chamber was not found to have a significant effect on roughness or water contact angle behaviour. In all cases the water contact angle was found to be 111°, which is in good agreement with previously reported results [10]. Upon production of a Zisman plot, the critical solid surface tension of the CF_xO_y films was estimated as 9.3 mN/m, and it was generally found that the higher the surface tension of the liquid investigated, the higher the contact angle with the CF_xO_y film; although interestingly, polar molecules such as ethanol (35°) and propan-2-ol (33°) display remarkably low contact angles. Such a result suggests that the nature of the interaction between the solvents and the CF_xO_y film may be quite complex, perhaps as a result of the variety of chemical bonds present at the film surface.

Table 3
Calculation of residual stress following CF_xO_y film deposition.

Liquid	Beam 1	Beam 2
Length (μm)	350	250
Curvature in beam before deposition (m^{-1})	1.143	1.300
Curvature in beam after deposition (m^{-1})	23.821	28.703
Stress in beam before deposition (Pa)	0.0335	0.0381
Stress in beam after deposition (Pa)	0.698	0.841

The percentage composition of the CF_xO_y films as determined by XPS was found to be approximately 50% carbon and 50% fluorine, with a small amount of oxygen detected, generally between 2 and 5%. This amount of oxygen present in the film is in-keeping with the findings of Elders et al. [3], who typically found that a plasma deposited fluoropolymer film contains somewhere in the region of 1–10% oxygen. The shape of the C 1s photoelectron spectra resembles those published by Amyot et al. [4], Jiang et al. [12] and Grant et al. [9], with the principal peaks in the C 1s photoelectron spectra for all CF_xO_y films attributed to photoelectrons from the C–F and C–F_2 bonds in the films. The remainder of the spectra consists of photoelectrons from the C–F_3, C–CF and C–C bonds. Small O 1s photoelectron peaks were observed for all CF_xO_y films, suggesting that C 1s photoelectrons from C–O–C and C=O bonds also contribute to the C 1s photoelectron spectra [4,13].

3.2. Interfacial stress due to CF_xO_y film deposition

Upon deposition of a 100 nm CF_xO_y film on the upper side of the cantilevers only, each cantilever was found to exhibit a significant deflection, whereas prior to film deposition they did not. If this deflection was due to the added mass of the CF_xO_y film, the deflection would have the form [14]:

$$y(x) = \frac{Wx^2}{24EI}\left(6L^2 - 4Lx + x^2\right) \qquad (1)$$

Table 4
Damage map for CF_xO_y films. Q2

Liquid	CF_xO_y film number							
	1	2	3	4	5	6	7	8
Acetone	N	N	N	N	N	N	N	N
Chloroform	N	N	N	N	N	N	N	N
Ethanol	N	N	N	N	N	N	N	N
Hexadecane	N	N	N	N	N	N	N	N
Hexan-1-ol	N	N	N	N	N	N	N	N
Hexane	N	N	N	N	N	N	N	N
Hydrochloric acid solution	N	N	N	N	N	N	N	N
MF26a developer pH 10.4	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**
Potassium chloride solution	N	N	N	N	N	N	N	N
Potassium hydroxide solution pH 10.4	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**
Potassium hydroxide solution pH 14.0	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**
Propan-2-ol	N	N	N	N	N	N	N	N
Sodium chloride solution	N	N	N	N	N	N	N	N
Sodium hydroxide solution pH 8.4	N	N	N	N	N	N	N	N
Sodium hydroxide solution pH 10.4	N	N	N	N	N	N	N	N
Sodium hydroxide solution pH 14.0	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**
Tetrahydrofuran	N	N	N	N	N	N	N	N
Toluene	N	N	N	N	N	N	N	N
Water	N	N	N	N	N	N	N	N

N = no damage to film; Y = delamination of film.

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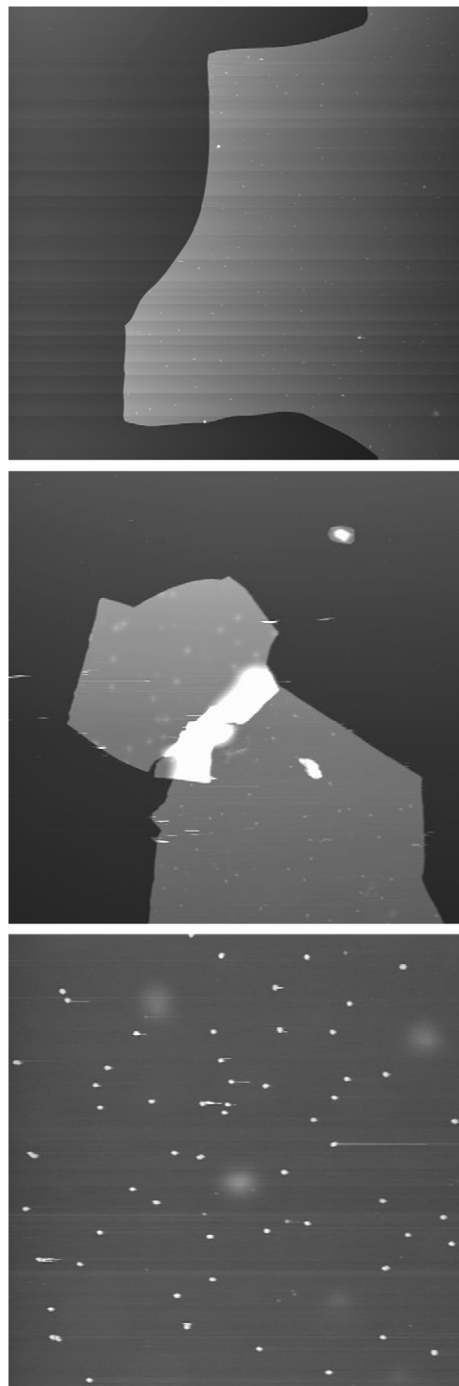

Fig. 1. Surface topography of fractured CF_xO_y film 1 as determined by AFM following 1 min immersion in MF26a. (a) Region 1. Image dimensions are 40 μm × 40 μm. Height scale is 100 nm. (b) Region 2. Image dimensions are 20 μm × 20 μm. Height scale is 100 nm. (c) Region 3. Image dimensions are 5 μm × 5 μm. Height scale is 100 nm.

If this was the case, the curvature would be increasing along the length of the beam, becoming infinite at the end. However the curvature of the beam before and after deposition was essentially constant along its length, although the curvature increased after film deposition, suggesting that the deflection is due to a tensile stress on the surface of the beam. Initially this would be due to the stress in the native oxide on the beam becoming unbalanced during fabrication. As the CF_xO_y layer is typically 5% or less of the beam thickness, the stress, σ, needed to bend the beam to a given curvature, k, can be given by Stoney's formula [15]:

$$\sigma = \frac{kEt^2}{6} \tag{2}$$

where t is the beam thickness and E is the effective Young's modulus of the beam. As can be seen in Table 3, the curvature and associated stress in the two beams increased significantly upon deposition of the CF_xO_y film, and therefore the deposited CF_xO_y films are under tensile stress, on the order of 0.7–0.85 Pa.

3.3. Effect of immersion in organic solvents

In this study, films were immersed for 24 h in both organic and aqueous solvents. Table 4 lists the results of the immersion of CF_xO_y films 1–8 in the organic and aqueous solvents listed in Table 2. Films 1–8 were resistant to immersion in the organic solvents acetone, chloroform, ethanol, hexadecane, hexan-1-ol, n-hexane, propan-2-ol, tetrahydrofuran and toluene. These results complement and improve upon those of Elders et al. [3], who reported that fluoropolymer films were resistant to 30 min immersion in amyl acetate, chlorobenzene, cyclohexene, ethanol, glycerol, 1,1,1,3,3,3-hexamethyldisilazane, n-hexane, methanol, propan-2-ol and trichloroethane.

3.4. Effect of immersion in aqueous solutions

As listed in Table 4, CF_xO_y films did not degrade or delaminate upon immersion in water and aqueous solutions of HCl (pH 2.0), NaCl (pH 5.5), KCl (pH 5.5), and NaOH at pH 8.4 and pH 10.4. Delamination of the CF_xO_y film from the Si countersurface was found to occur upon immersion in three aqueous solutions, namely MF26a developer (pH 10.4) and aqueous solutions of KOH (pH 14.0) and NaOH (pH 14.0). For these three solutions, macroscopic degradation of the Si countersurface was observed, accompanied by the delamination of the CF_xO_y film. Countersurface degradation usually occurred after an immersion time of 1 h or more, whilst the CF_xO_y films could delaminate in only a matter of minutes. Delamination of films which were immersed in the MF26a developer was

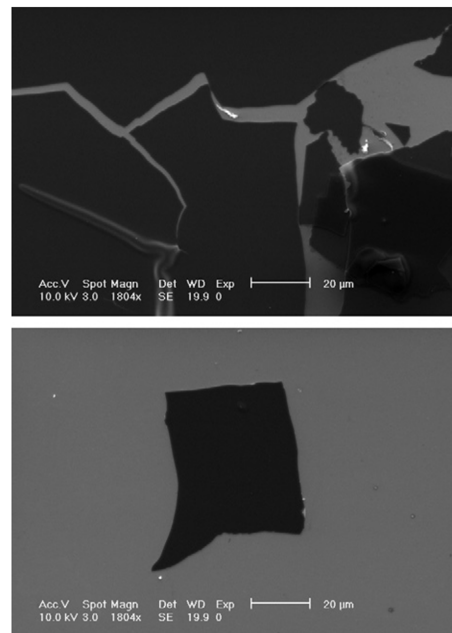

Fig. 2. Fragmentation of the CF_xO_y film as seen by SEM following 1 min immersion in MF26a. (a) Region 1. Image dimensions are 160 μm × 108 μm. (b) Region 2. Image dimensions are 160 μm × 108 μm.

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found to begin after an immersion time of only 1 min, with the loss of fragments of the CF_xO_y film resolved by AFM and SEM analysis of the surface. After a 5 min immersion time there was additional delamination of CF_xO_y film fragments and evidence of a secondary process taking place underneath the CF_xO_y film, evidenced in the form of raised patches of film, resembling blisters. Figs. 1 and 2 show AFM and SEM images taken from samples immersed in MF26a developer for 5 min. After a 10 min immersion time only a small amount of the CF_xO_y film had not delaminated, and that which did remain exhibited further blistering underneath the film. Interestingly, the fragmentation of the CF_xO_y film often appeared to follow approximately rectangular geometries, which may correspond to the crystal structure of the underlying Si(100), and AFM images showed that the film always fractured in a unit of the full thickness of the deposited film. MF26a developer is an aqueous solution of pH 10.4 containing tetramethylammonium hydroxide (TMAH) at a molarity of 0.26 M [16]. TMAH is often used for the etching of Si [17,18] and the results presented here indicate that a CF_xO_y thin film does not act as a significant diffusion barrier to aqueous solutions of TMAH, and hence the etching of Si in the presence of TMAH can proceed. The blistering of the CF_xO_y film observed by AFM is thought to be a result of the etching of Si underneath the CF_xO_y film. When the adhesion between the CF_xO_y film and the Si countersurface is no longer present, the tensile stress in the CF_xO_y film is released, causing the film to rise away from the Si countersurface. As the area over which this process occurs increases, total film delamination follows within a matter of minutes.

The effect of aqueous solution pH on the delamination or survival of the CF_xO_y film was investigated using aqueous NaOH solutions of pH 8.4 (NaOH solution A), 10.4 (NaOH solution B) and 14.0 (NaOH solution C), and aqueous KOH solutions of pH 10.4 (KOH solution A) and pH 14.0 (KOH solution B). Exposure of CF_xO_y films to aqueous NaOH solutions at pH 10.4 and below did not cause any film delamination or countersurface degradation, which suggests that when films 1–8 are immersed in MF26a developer, it is the TMAH present within the MF26a developer solution which damages the countersurface and leads to film delamination. In contrast, the delamination of CF_xO_y films and macroscopic degradation of the Si countersurface when immersed in aqueous NaOH solution at pH 14.0, and aqueous KOH solutions at pH 10.4 and pH 14.0 is attributed to the dissolution of the underlying SiO_2 layer, native to the Si surface, which has previously been documented to occur rapidly when SiO_2 is in contact with highly basic solutions [19]. Upon removal of the native SiO_2 layer, the CF_xO_y film delaminates from the Si countersurface, a result which suggests that the CF_xO_y film does not present a significant barrier to the diffusion of known aqueous etchants of Si.

4. Conclusions

The effect of exposing plasma-polymerised CF_xO_y films deposited on Si wafers to a variety of organic solvents and aqueous solutions has been investigated. The films, which were hydrophobic in nature, were found to be stable in a range of organic solvents and were also stable when immersed in water, acidic aqueous solutions and basic aqueous solutions up to pH 10.4. Delamination occurred within minutes when substrates were exposed to MF26a developer, an etchant for Si. Aqueous solutions of NaOH at pH 14 and KOH at pH 10.4 and pH 14 all promoted dissolution of the underlying native SiO_2 layer, leading to delamination of the CF_xO_y film. Therefore the CF_xO_y film is not effective as a diffusion barrier. In contrast, delamination did not occur after 24 h immersion in aqueous solutions of NaOH at pH 10.4 and below.

Acknowledgements

The University of Birmingham and Unilever Research & Development are acknowledged for financial support for JB and DC. The atomic force microscope and interferometer used in this research were obtained through Birmingham Science City: Innovative Uses for Advanced Materials in the Modern World (West Midlands Centre for Advanced Materials Project 2), with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF). We acknowledge the assistance provided with the XPS and ellipsometry measurements by Mr. Stuart Arkless. We also acknowledge the assistance provided with CF_xO_y film deposition by Dr. Carl Anthony.

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Please cite this article in press as: Cheneler D, et al., Characteristics and durability of fluoropolymer thin films, Polymer Degradation and Stability (2011), doi:10.1016/j.polymdegradstab.2010.12.022