Mechanistic reaction pathway for hexafluoropropylene oxide pulsed plasma deposition of PTFE-like films

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Abstract

The pulsed plasma deposition of PTFE-like thin films using hexafluoropropylene oxide (HFPO) precursor has been investigated by time-resolved in situ mass spectrometry. Electron-impact and electron-attachment ionisation modes have been employed to monitor neutral plasma species; whilst electrical discharge negative and positive ions have been detected by switching-off the mass spectrometer electron-impact ionisation source. The relative concentrations of neutral versus ionic plasma species were found to rise for shorter pulse duty cycles. Mechanistically, HFPO molecules underwent pulsed plasma-initiated decomposition to form difluorocarbene (CF₂) radical species, and these can combine to form tetrafluoroethylene (CF₂ = CF₂) molecules, which subsequently polymerise leading to the growth of PTFE-like ([-CF₂]ₙ) perfluoroalkyl chains. Shorter pulsed plasma duty cycles enhance the growth of linear PTFE-like perfluoroalkyl chains.

1. Introduction

Hexafluoropropylene oxide (HFPO) is a stable fluorine-containing cyclic molecule [1, 2]. Thermal or pulsed plasma excitation of HFPO is employed for the deposition of PTFE-like ([-CF₂]ₙ) thin films for a variety of technological applications; these include liquid repellency, low dielectric constant electronic materials, encapsulation barrier layers, and biologically implantable devices [3–5]. The HFPO pyrolysis mechanism is understood to proceed via the formation of either fluoro(trifluoromethyl) carbene (II) and carbonyl difluoride (III), or difluorocarbene (VI) and trifluoroacetyl fluoride (VII) species, scheme 1 [6–11]. Under these conditions, it is the polymerisation of difluorocarbene (CF₂) radicals which is postulated to give rise to the growth of PTFE-like films [12–15]. Whilst in the case of pulsed plasma excitation of HFPO gas, such intermediate difluorocarbene species, have been detected by time-resolved ultraviolet absorption spectroscopy within the duty cycle on-period (t_on); followed by recombination processes predominating during each subsequent off-period (t_off) [13]. However, the direct growth of perfluorocarbon chains within the electrical discharge has not previously been validated. Rather, x-ray photoelectron spectroscopy (XPS) and infrared analysis of the pulsed plasma deposited films have shown an enhancement in [-CF₂]ₙ group content with decreasing pulsed plasma duty cycle (i.e. greater structural retention to form PTFE-like films) [4, 16]. In this article, the pulsed plasma polymerisation mechanism for HFPO precursor is investigated by time-resolved in situ mass spectrometry, with a particular emphasis on the role played by difluorocarbene species during the growth of PTFE-like perfluoroalkyl chains ([-CF₂]ₙ).

2. Materials and methods

In situ mass spectrometry analysis was undertaken during pulsed plasma polymerisation inside a cylindrical glass reactor (8.5 cm diameter and 2943 cm³ volume), figure 1. This chamber was pumped down to a base pressure of 8 × 10⁻³ mbar, via a liquid nitrogen cold trap attached to a turbomolecular drag pump (model TPD 022, Pfeiffer Vacuum Technology AG) backed by a diaphragm pump (model N813.4 ANE, KNF Neuberger GmbH). A copper coil (7 mm diameter, 4 turns, spanning 10.5 cm) wrapped around the glass chamber was connected to
a 13.56 MHz radio frequency (RF) power supply (model RFG 600SE, Coaxial Power Systems Ltd) in conjunction with a LC circuit matching unit (to minimise reflected power). A pulse signal generator (model TG503 5 MHz pulse, Thurlby Thandar Instruments Ltd) was used to trigger the RF power supply and monitored using an oscilloscope (model OX 530 20 MHz, Metrix Ltd). For pulsed plasmas, a fixed 500 ms off-period ($t_{\text{off}}$) and variable on-periods ($t_{\text{on}}$) of 10, 5 and 2 ms (corresponding to duty cycles of 2, 1 and 0.4% approximately) were employed in conjunction with 50 W power input during the on-period ($P_{\text{on}}$).

An electrostatic quadrupole mass spectrometer probe (model HAL EQP 2500 Hiden Analytical Ltd), with a grounded 50 $\mu$m orifice was positioned inside the plasma chamber along the central axis (this acted as an earthed substrate), figure 1. The instrument comprised an ion extractor, electron-impact ionisation source, a 45° sector field energy filter, and a triple-filter quadrupole mass filter with secondary electron multiplier detection. The mass spectrometer analyser was pumped by a turbomolecular pump (model TMU 260, Pfeiffer Vacuum Technology AG) backed by a rotary vane pump (model DUO 2.5, Pfeiffer Vacuum Technology AG) to give a mass spectrometer base pressure of better than $2 \times 10^{-9}$ mbar. The electron-impact/attachment ionisation source of the mass spectrometer was operated at 70 eV to allow for the detection of neutral and radical plasma species. Ionised gaseous species (plasma ions) were sampled directly from the electrical discharge through the 50 $\mu$m end cap orifice with the mass spectrometer ionisation filament switched off. For time-resolved pulsed plasma measurements, signal gating of the mass spectrometer detector allowed for any specified time window ($t_{\text{on}}$ or $t_{\text{off}}$) to be monitored. This was achieved by using an additional pulse signal generator (model TGP110

Scheme 1. Mechanistic reaction pathways for the fragmentation of hexafluoropropylene oxide (HFPO) and subsequent difluorocarbene polymerisation. The initial fragmentation steps (Route A and Route B) are analogous to reported HFPO thermal decomposition mechanisms [6, 8, 9].

Figure 1. Plasma system: (a) reactor configuration; and (b) pulsed plasma duty cycle time period.
10 MHz, Thurlby Thandar Instruments Ltd) connected to the mass spectrometer interface unit through a transistor–transistor logic (TTL) level acquisition input. One pulse signal generator triggered both the plasma duty cycle ignition and the other pulse signal generator; where the latter was set to trigger the mass spectrometer ion counting detector during the whole duty cycle, or either the \( t_{on} \) or \( t_{off} \) (afterglow) time windows. Therefore, the mass spectra scans sampled the whole duty cycle, or either the \( t_{on} \) or \( t_{off} \) (afterglow) time frames, and were averaged over multiple pulse cycles to improve signal-to-noise (typically 2 min total scan time for 0–400 m/z range).

Prior to each experiment, the chamber was cleaned with a 50 W oxygen plasma (0.2 mbar pressure) and then purged with HFPO gas precursor (HFPO, +98%, Aldrich Chemical Company Inc.) at a pressure of 0.2 mbar via a fine control needle valve (model 145–217–4P4PC, Meggitt Avionics Ltd) for 20 min, prior to electrical discharge ignition. A range of standard perfluorocarbon molecules were also analysed in the gas phase (no plasma) using the same instrument in order to provide reference electron-impact ionisation mass fragmentation patterns and cross-checked against the American NIST database [17, 18]. These included perfluoro-n-pentane (+99%, Fluorochem Ltd) and perfluoro(methylcyclohexane) (+90%, Fluorochem Ltd).

### 3. Results and discussion

#### 3.1. Time-averaged mode detection of plasma species

The parent fragment ion (molecular mass of HFPO = 166 amu), was absent during mass spectrometric analysis of the precursor molecule (\( t_{on} = 0 \) ms, i.e. no plasma), with \( \text{CO}^+ \) (28 m/z), \( \text{CF}_2^+ \) (31 m/z), and \( \text{CF}_3^+ \) (69 m/z) being the predominant peaks, figure 2 [19]. Plasma ignition leads to an order of magnitude increase in concentration of neutral species together with the appearance of ionic fragments. In time-averaged mass spectrometry detection mode, the relative concentration of neutral species is several orders of magnitude greater than positive ions, and was found to rise dramatically as the \( t_{on} \) period was shortened. Conversely, the number of positive plasma ions detected increased for longer \( t_{on} \) values, figure 2. The most intense peaks for electron-impact of neutral plasma species were \( \text{CO}^+ \) (28 m/z), and \( \text{CF}_3^+ \) (69 m/z); whilst the most intense peak for positive plasma ions was \( \text{CF}_2^+ \) (69 m/z). At longer \( t_{on} \) values, the mass spectra approached those observed for continuous wave (non-pulsed) HFPO plasmas [20]. Whilst for decreasing \( t_{on} \) values, the electron-impact of neutral plasma species \( \text{CO}^+ \) (28 m/z) : \( \text{CF}_3^+ \) (69 m/z) ratio approaches that observed for the HFPO precursor molecule (\( t_{on} = 0 \) ms).

In the absence of electron-impact/attachment ionisation, no negative ion species (including \( \text{F}^- \) ions) were detected. Whilst for electron-attachment negative-mode mass spectrometry detection of plasma species, only fluorine atoms (19 m/z) were measured in all time frames (time-averaged, resolved on-period and resolved off-period), figure 3.

#### 3.2. Time-resolved electron-impact ionisation positive-mode mass spectrometry of neutral plasma species

In the case of reference mass spectra taken for standard linear \( \text{C}_n\text{F}_{n+2} \) perfluoroalkanes, the \( \text{CF}_2^+ / \text{CF}_3^+ \) ion signal ratio remains fairly constant for \( n > 3 \). This \( \text{CF}_2^+ / \text{CF}_3^+ \) ion ratio was also found to be steady for the analysis of HFPO pulsed plasma neutral species, which therefore supports the growth of linear \( \text{C}_n\text{F}_{n+2} \) perfluoroalkyl chains (species XII) in scheme 1, figure 4. Other evidence for the formation of neutral linear chain perfluorocarbon species included the detection of mass spectrometric electron-impact ionisation mass fragments: \( \text{C}_2\text{F}_4^+ \) (100 m/z), \( \text{C}_3\text{F}_6^+ \) (119 m/z), \( \text{C}_4\text{F}_8^+ \) (150 m/z), \( \text{C}_5\text{F}_9^+ \) (169 m/z), \( \text{C}_6\text{F}_{10}^+ \) (181 m/z), \( \text{C}_7\text{F}_{11}^+ \) (219 m/z) and \( \text{C}_8\text{F}_{12}^+ \) (269 m/z), figure 4. The signal intensity of these perfluoroalkyl chain fragments was found to increase by an order of magnitude (in both the \( t_{on} \) and \( t_{off} \) windows) with decreasing \( t_{on} \) period, which supports there being less plasma-induced fragmentation of growing polymer chains for shorter \( t_{on} \) values [21].

On the other hand, electrical discharge generated fragments arising from HFPO decomposition byproducts become relatively more predominant at longer \( t_{on} \) values; for instance the \( \text{CO}^+ \) (28 m/z) signal is greater compared to the \( \text{CF}_2^+ \) (69 m/z) intensity at \( t_{on} = 10 \) ms and lower for \( t_{on} = 2 \) ms. These observations are also consistent with the aforementioned attenuation of extended plasma-induced HFPO molecule breakdown at shorter \( t_{on} \) periods (less CO by-product formation).

The relative signal intensity of neutral species measured during the \( t_{off} \) window was greater compared to either time-averaged or \( t_{on} \) period detection modes; which indicates that radical concentrations are highest during the \( t_{off} \) window (a prerequisite for polymer chain propagation mechanism involving either difluorocarbene (VI) or tetrafluoroethylene (V) intermediate species, scheme 1), figures 2 and 4.

#### 3.3. Time-resolved positive-mode mass spectrometry of positive ion plasma species

In contrast to 70 eV electron-impact mass spectrometry of the HFPO precursor molecule (\( t_{on} = 0 \) ms, figure 4), the HFPO parent molecular positive ion (166 m/z) was detected in the pulsed plasmas suggesting that the HFPO
molecule undergoes much more gentle ionisation within the electrical discharge due to lower energy plasma electron-impact collisions, allowing the formed HFPO molecule positive ion to remain intact.

Figure 2. Time-averaged positive-mode mass spectra for electron-impact of neutral plasma species and positive plasma ions as a function of duty cycle for HFPO pulsed plasma ($t_{off} = 500$ ms, $P_{on} = 50$ W, and 0.2 mbar).

The greater visibility of higher mass range fragments in positive-ion detection mode relative to fragments at lower masses is again due to the lower energy plasma electron-impact

Figure 5 Linear $C_{n}F_{n+2}$ perfluorocarbon chain positive ion plasma fragments were also detected ($C_{2}F^{+}_{4}$ (100 m/z), $C_{3}F^{+}_{3}$ (119 m/z), $C_{3}F^{+}_{4}$ (150 m/z), $C_{3}F^{+}_{5}$ (169 m/z), $C_{4}F^{+}_{6}$ (181 m/z), $C_{4}F^{+}_{7}$ (200 m/z), $C_{4}F^{+}_{9}$ (219 m/z), $C_{5}F^{+}_{8}$ (231 m/z), $C_{5}F^{+}_{11}$ (269 m/z)). The greater visibility of higher mass range fragments in positive-ion detection mode relative to fragments at lower masses is again due to the lower energy plasma electron-impact.
ionisation process (compared to the higher 70 eV energy electron-impact ionisation employed for neutral species detection mode, figure 4) [22]. The relative intensity of these perfluoroalkyl chain positive ion fragments rises with decreasing \( t_{\text{on}} \) period, which supports there being less plasma-induced fragmentation/damage of growing polymer chains at shorter \( t_{\text{on}} \) values. Interactions between ions and HFPO is observed with the exchange of an \( \text{F}^+ \) ion with an \( \text{O}^2^- \) ion derived from HFPO giving rise to an intense \( \text{C}_3\text{F}_7^- \) peak, figure 5 [23].

The previously described enhancement of neutral plasma species concentration during the \( t_{\text{off}} \) period at shorter \( t_{\text{on}} \) values detected in mass spectrometry electron-impact ionisation mode (figure 4) is mirrored by a corresponding drop in intensity of positive-ion plasma species detected during the \( t_{\text{off}} \) period. Furthermore, the positive-ion signal intensities are several orders of magnitude greater during the \( t_{\text{on}} \) period (electrical discharge) compared to the \( t_{\text{off}} \) period, figure 5.

### 3.4. Mechanism

The detection of perfluoroalkyl chain fragments (\( \text{C}_2\text{F}_4^+ (100 \text{ m/z}), \text{C}_2\text{F}_5^+ (119 \text{ m/z}), \text{C}_3\text{F}_7^+ (150 \text{ m/z}), \text{C}_4\text{F}_9^+ (169 \text{ m/z}), \text{C}_4\text{F}_8^+ (181 \text{ m/z}), \text{C}_4\text{F}_9^+ (200 \text{ m/z}), \text{C}_5\text{F}_{10}^+ (219 \text{ m/z}), \text{C}_5\text{F}_{11}^+ (231 \text{ m/z}), \text{C}_5\text{F}_{11}^+ (269 \text{ m/z}) \)) is consistent with reaction pathway B (scheme 1) along with the formation of trifluoroacetyl fluoride (VII) by-product. The HFPO decomposition difluorocarbene (VI) product species (observed by time-resolved ultraviolet absorption spectroscopy [13]) exists in gas phase equilibrium with tetrafluoroethylene (V); where the balance between tetrafluoroethylene (\( \text{C}_2\text{F}_2 = \text{CF}_2 \)) and difluorocarbene (\( \text{CF}_2 \)) radicals lies towards \( \text{CF}_2 = \text{CF}_2 \) (\( -\log K_{\text{eq}} \) ranges between 4.28 and 5.33) [24, 25]. A concurrent equilibrium with perfluorocyclopropane (IV) species is consistent with the detection of \( \text{C}_4\text{F}_8^+ (150 \text{ m/z}) \) signal, scheme 1, figures 4 and 5 [8, 9]. The rearrangement of perfluorocyclopropane (IV) to perfluoropropane followed by polymerisation can be ruled out due to the lack of expected –\( \text{CF}_3 \) groups detected by XPS in the deposited PTFE-like films [4].

On this basis, the proposed mechanism entails HFPO molecules undergoing plasma-induced fragmentation during the \( t_{\text{on}} \) period to form difluorocarbene (\( \text{CF}_2 \)) species, and these then readily undergo polymerisation via \( \text{CF}_2 \) or intermediate tetrafluoroethylene (\( \text{CF}_2 = \text{CF}_2 \)) species to form growing perfluoroalkyl chains (\( \text{[–CF}_2\text{–]}_n \)), scheme 1. Shorter \( t_{\text{on}} \) values (less amount of energetic plasma-induced fragmentation) lead to the formation of longer perfluoroalkyl chains—which correlates to the high levels of –\( \text{CF}_2\text{–} \) content found in HFPO pulsed plasma deposited PTFE-like films at low duty cycles (up to 70% measured by XPS [4, 14, 16]).

### 4. Conclusions

Pulsed plasma polymerisation of HFPO proceeds via electrical discharge initiated decomposition of precursor molecules to yield difluorocarbene (\( \text{CF}_2 \)) radicals during the pulse \( t_{\text{on}} \) period. These then readily combine to form tetrafluoroethylene (\( \text{CF}_2 = \text{CF}_2 \)) intermediate species, which are able to subsequently undergo polymerisation to create PTFE-like perfluoroalkyl chains. Shorter pulsed plasma duty cycles (\( t_{\text{on}} \)) give rise to a greater concentration of neutral species (including polymerisable tetrafluoroethylene (\( \text{CF}_2 = \text{CF}_2 \)) molecules), in conjunction with an attenuation of plasma ion concentrations—leading to the growth of longer perfluoroalkyl PTFE-like chains.
Figure 4. Time-resolved electron-impact ionisation positive-mode mass spectra of HFPO pulsed plasma neutral species as a function of duty cycle $t_{on}$ period ($t_{off} = 500$ ms, $P_{on} = 50$ W, and 0.2 mbar). The detector was triggered for the whole duration of $t_{on}$ and $t_{off}$ time windows respectively. C$_n$F$_{2n+1}^+$ fragments are labelled as: C$_2$ = C$_2$F$_5^+$ (119 m/z), C$_3$ = C$_3$F$_7^+$ (169 m/z), C$_4$ = C$_4$F$_9^+$ (219 m/z), and C$_5$ = C$_5$F$_{11}^+$ (269 m/z). $t_{on} = 0$ ms corresponds to the fragmentation pattern of HFPO precursor molecule (absence of plasma ignition).
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Author contributions

JPSB and AC devised the experiments. AC performed the experiments. The manuscript was jointly drafted by JPSB and AC. Both authors gave final approval for publication.

Data accessibility

Supporting data can be accessed at http://collections.durham.ac.uk

Conflicts of interest

There are no conflicts of interest to declare.

Figure 5. Time-resolved positive-mode mass spectra of HFPO pulsed plasma positive ions species as a function of duty cycle $t_{on}$ period ($t_{off} = 500$ ms, $P_{on} = 50$ W, and 0.2 mbar). For each duty cycle, the detector was triggered for the whole duration of $t_{on}$ and $t_{off}$ time windows respectively. $C_{n}F_{2n+1}$ fragments are labelled as: $C_2 = C_2F_3^+$ (119 m/z), $C_3 = C_3F_7^+$ (169 m/z), $C_4 = C_4F_{11}^+$ (219 m/z), and $C_5 = C_5F_{15}^+$ (269 m/z).
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