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Thermal chemical vapor deposition of fluorocarbon polymer thin films in a hot filament reactor

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Abstract

Formation of fluorocarbon polymer films with a linear $(CF_2–CF_2)_n$ molecular structure similar to polytetrafluoroethylene, PTFE is described by a hot filament chemical vapor deposition method. Growth process is analyzed by infrared absorption and C(1s), O(1s) and F(1s) core level electron spectroscopy of films deposited at -5 and $+70$ °C. Absorption doublet at 1220 and 1160 cm^{-1} assigned to C–F_2 asymmetric and symmetric stretches, rock at 518 cm^{-1} and wag at 637 cm^{-1} indicate formation of linearly organized CF_2 groups with minimum hindrance to molecular vibration modes in CVD grown films. Absorption bands at 1660 and 3389 cm^{-1} show O and OH groups in the films which diminish on annealing. The C(1s) components, CF_3, CF and C–CF bonding show branching, cross-liking and defects sites which increase as substrate temperature is increased. The O(1s) line analysis shows O_2 in fluorocarbon films is chemically bonded as C–O and $F_2C{=}O$ with relative ratio depending on the film growth temperature. Both O_2 and OH are the result of additional reaction pathways involving the species generated from fragmentation of $CF_3C(O)F$. Molecular structure of fluorocarbon polymer films involving these species are discussed which are in conformity with the XPS and IR absorption data.

Keywords: Polymer CVD; Fluoropolymer films; XPS

1. Introduction

Thin films of fluorocarbon polymers, in particular polytetrafluoroethylene (PTFE), have important applications in microelectronics as interlayer dielectric [1], bioactive coatings for active agent recognition and response [2,3], biocompatible coating of implants and neural probes [4,5] and engineered surfaces for low adhesion, water repellency [6], etc. Several such applications require conformal fluorocarbon polymer coatings over external surfaces as uniform pinholes free 0.1–1.0 μm thick films without involving corrosive solvents that might affect depositing surfaces. Vapor phase growth methods are preferred in microelectronic device fabrication, as solvents tend to damage devices formed underneath. Since application specific properties are dependent on molecular structure of fluorocarbon films, methods of film deposition that also enable structural control are of much interest. Plasma excited chemical vapor deposition (PECVD) from fluorinated monomers and precursors is a widely studied technique for surface engineering and forming fluorocarbon polymer films. Variety of reactions among species generated by continuous wave inductively coupled r.f. plasma excitation of a number of molecules [7,8], CF_4, C_2F_6–H_2 mixture [9–11] and hexafluoropropylene oxide (C_3F_6O) [12] are used for depositing fluorocarbon polymer films. In the plasma, F-back etch, extraneous ion bombardment and electron generated surface activated sites randomly modify the film structure which results in a lower *F*/*C* ratio, a much smaller CF_2 fraction and a highly cross-linked molecular chains structure [8]. Using the pulsed R.F. plasma technique, periodic excitation of precursors produces less diverse plasma species and fluoropolymer films could be deposited with improved molecular structure [13–15]. Main precursors used in pulsed plasma growth of fluorocarbon films are hexa- and tetra-fluorobenzene C_6F_6 $C_6H_2F_4$ [16], C_3F_6O [13,14], chlorofluorocarbons ($CHClF_2$, Freon 22)

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and hydrofluorocarbons, CH_2F_2 (HFC-32) and $C_2H_2F_4$ (HFC-134) [17].

To deposit fluorocarbon polymer films with minimum bond defects as required for microelectronic devices, a process that facilitates polymerization reactions to proceed in accordance with the established thermodynamic considerations is most preferred. In this context, thermal-chemical vapor deposition (CVD) offers an alternative to the plasma based deposition methods. Here, separation of thermal production of radicals or initiators from the film growth zone allows unhindered bond formations based on chemical interaction between the decomposition species. Absence of energetic interactions by ions and electrons also precludes any damage to the film surface and to the underlying integrated electronic devices. Furthermore, independent control of the precursor pyrolysis temperature, vapor flux and substrate temperature is of distinct advantage and can be used to alter the molecular structure and composition to achieve film properties required for specific applications.

Thermal pyrolysis of precursors or initiators has been used in the past to form polymer films, for example, poly *p*-xylylene films for low κ-dielectrics [18,19], carbon films in diamond like structure [20] and fluorocarbon polymer films in PTFE-like structure [21,22]. Gas phase dissociation is potential step in thermal-CVD of fluorocarbon films for which various approaches such as indirectly heated effusion cells [23] and directly heated filaments [20–22] are described in the literature. In the present work, deposition of fluorocarbon polymer films over Si wafers and Ti/Al film coated Si-substrates by a low-pressure thermal-CVD method from C_3F_6O precursor using a hot filament is described. Changes in the chemical bonding structure of films deposited at different substrate temperatures were observed. Additional process steps affecting the molecular structure and growth of fluorocarbon polymer films from the presence of oxygen containing dissociation species of C_3F_6O have been investigated. This paper describes the results of these studies.

2. Experimental

Thermal CVD process involves (i) exposure of gaseous precursor on to a heated filament, which generates free radicals or excited species by thermal dissociation, (ii) transport of these species towards the substrates held at relatively much lower temperatures and (iii) initiation of polymerization process by free radical association to accomplish growth of the polymer film. C_3F_6O precursor is used since its primary decomposition product is CF_2 radical [21,22,24] which is important to form fluorocarbon polymer films in a PTFE-like structure. Films were deposited in a stainless steel reactor shown schematically in Fig. 1. The substrates were 150 nm thick films of Ti and Al surface coated Si wafers and double side polished (100) Si wafers. A filament consisting of a coiled nichrome wire mounted in a cris-crossing array and electrically heated to about 600 °C was used for flash decomposition of C_3F_6O precursor gas. Undiluted C_3F_6O gas (Aldrich Chemicals Inc. USA) was injected from an inlet port positioned close to the filament assembly and dispersed over heated filament held horizontally such that gas flow is in the perpendicular direction. In this configuration, precursor after activation is directed onto substrates held underneath at ~60 mm distance over a Cu-platform backed by cooling coils for flowing liquid nitrogen (LN_2) or the chilled and heated water in order to maintain the desired temperature. Substrate temperature was monitored and controlled using a type-T thermocouple anchored over a dummy substrate placed alongside the samples and a PID controller model 847 from Eurotherm. A type-R thermocouple embedded in a ceramic sleeve and anchored to the filament similarly monitored filament temperature. Precursor flow metered by a mass flow controller was kept at ~10 standard cubic centimeters per minute (sccm). A throttle valve between the vacuum pump and the deposition chamber was used to maintain the reactor pressure between 100–500 mTorr. The film deposition rates varied typically between 20 and 35 nm/min depending on the filament temperature and the precursor flow rates. In a typical deposition sequence, the system was first evacuated down to 0.1 mTorr and repeatedly flushed by dry N_2 to exclude oxygen from the reactor ambient. Substrates fixed on a copper carrier block held under the filament grid were cooled or heated to the desired temperature. The filament was heated to 600 °C by passing low voltage ac. Earlier in a separate run prior to the actual film deposition, the filament was thoroughly degassed by heating in vacuum and carburized by exposing to C_3F_6O precursor for about 15 min at 600 °C. Film deposition over substrates commences when C_3F_6O precursor gas flow is initiated. To terminate the CVD process after completion of the fluorocarbon polymer film growth, first the precursor gas flow was shutoff and then filament current was switched off. The reactor was pumped down to 0.1 mTorr and all system

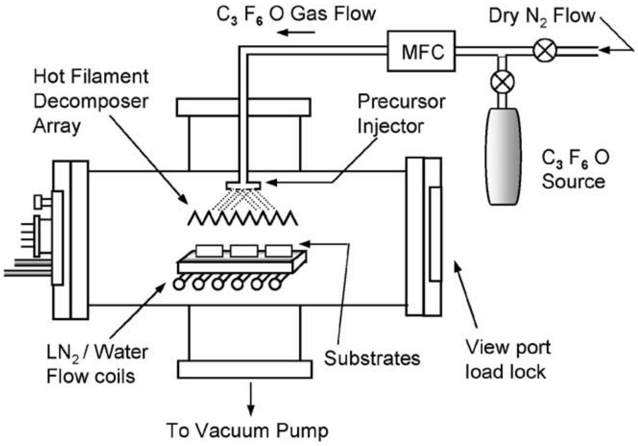


Fig. 1. Schematic of the hot filament chemical vapor deposition reactor for depositing fluorocarbon polymer thin films.

components, substrate, filament and reactor were equalized to room temperature. Films were withdrawn by venting the system with dry N_2 to the atmospheric pressure. In a separate experiment, immediately after removal from the reactor the films were immersed in carbon tetrachloride to exclude the possibility of atmospheric moisture and oxygen from affecting the films. Molecular configuration of films was examined by a Fourier transform infrared (FTIR) spectrometer, Perkin–Elmer model Spectrum 2000 in the transmission mode. Contributions from background, CCl_4 adsorption and Si substrates were subtracted before the final data is used for analysis of characteristic IR absorptions from the deposited polymer films. Bonding structure and chemical composition of films were observed by X-ray photoelectron spectroscopy (XPS) in a Physical Electronics 5100 fixed-lens dual anode photoelectron spectrometer. XPS spectra were recorded at takeoff angles 75° from the film plane with sampling depth of ~ 10 nm. Film morphology was observed by atomic force microscopy, AFM, model Nanoscope IIIa from Digital Instruments in the tapping mode to prevent damage to soft polymer film surface.

3. Results and discussion

3.1. IR spectroscopy

3.1.1. As-deposited films

Fig. 2(a) and (c) show the FTIR spectra of fluorocarbon films of nominal thickness $\sim 0.7 \pm 0.1$ μm deposited by thermal CVD over Si single crystal substrates held at -5 and $+70$ °C, respectively. Main spectral features from C–F_x are seen in the 500–1700 cm^{-1} range. A well-resolved doublet at 1220 and 1160 cm^{-1} assigned to C–F asymmetric and symmetric stretches, respectively associated with CF_2 functionality is seen in both spectra indicating that CF_2 groups in the solid films are organized in an ordered manner through linear attachment. Lower wave number absorption peaks for CF_2 rock at 518 cm^{-1} and wag at 637 cm^{-1} are also observed indicating that linear groupings in the polymeric form encounter minimum hindrance to the molecular vibration modes [25]. An excessively cross-linked or branched network of molecular chains would have reduced mobility and affected observance of these vibrational modes implying that molecular structure of linearly attached $(–CF_2–CF_2–)_n$ polymer chains in CVD grown films is similar to the PTFE-like structure [26,27].

The other two prominent IR absorption peaks seen in both spectra are in the regions, 3380–3400 cm^{-1} and 1655–1665 cm^{-1}. Broad spectral features around, 3389 cm^{-1} are attributed to OH stretch mode [28]. In plasma deposited fluorocarbon polymer films similarly seen OH absorption band is usually assigned to adsorption of atmospheric moisture [9,29]. Dashed curve in Fig. 2(a) and (c), are spectra of films taken immediately after growth and quenching in CCl_4. Still present OH band rules out atmospheric water adsorption as a probable cause in CVD grown films. Intensity of OH absorption band depends on the conditions of film growth. The OH/CF_2 (ν_{asym}) absorption peak ratio decreases from 1.6 to 0.6 as deposition temperature is increased from -5 to $+70$ °C suggesting that OH absorption band is due to bound hydroxyl groups in the molecular structure of the film and forms during the film growth. The 1660 cm^{-1} peak is associated with C=O or COO stretch mode vibrations in particular those with R–(CO)–R′ functional groups [21,28,30,31]. Similar to the OH absorption, C=O/COO to $CF_2(\nu_{asym})$ intensity ratio also decreases as substrate temperature increases.

Reaction of atmospheric oxygen with unterminated $(–CF_2–CF_2–)_n$ chains at chain ends or along the chain has been earlier suggested as a probable mechanism for C=O/COO and OH groups in fluorocarbon polymer films [21]. It was suggested that in absence of a chain termination process in growth of films by :CF_2 association, a reaction with atmospheric O_2 and moisture will form $(–CF_2–CF_2–)_n$–COO and $(–CF_2–CF_2–)_n$–COOH analogous to reactions encountered in γ-ray and electron beam irradiated PTFE material [32,33]. IR results of this study show that reaction with $(–CF_2–CF_2–)_n$ chain during deposition of film rather than on atmospheric exposure are more relevant. A possible internal source of oxygen during CVD growth is trifluoroacetyl fluoride, $CF_3C(O)F$, which is a byproduct of precursor C_3F_6O dissociation. Under certain conditions, $CF_3C(O)F$ can decompose to yield CF_3 and FCO radicals as described by a number of earlier studies on photolytic decomposition of $CF_3C(O)F$ [34–36]. These radicals react with growing $(–CF_2–CF_2–)_n$ polymer chain and due to susceptibility to residual moisture readily form OH bonds [37]. A detailed analysis of the XPS results described in the Section 3.3 shows that oxygen exists in the bound rather than adsorbed state, which supports this conclusion. Reactions involving these radicals are described in the later sections.

3.1.2. Post deposition annealed films

Fluorocarbon polymer films formed at -5 and $+70$ °C were isothermally annealed at 245 °C for 1 h in 100 mTorr vacuum. Post annealed FTIR spectra are shown in Fig. 2(b) and (d). Structural changes were analyzed by comparing the FTIR spectra of the same film in the as-made and post-annealed states. Intensity of both OH and C=O/COO absorptions reduce after annealing. Annealed films are not affected by exposure to moisture or oxygen as their FTIR spectra remain unchanged even after films were left in air for ~ 500 h. Loss of OH group on annealing shows decomposition of chains, which initiates reorganization of the chain structure in order to stabilize the radicals thus formed. Since CF_2 peaks due to rocking, deformation and wagging modes are still seen, linear chain $–(CF_2–CF_2)–$ propagation is indicated during the stabilization process in the annealed films.

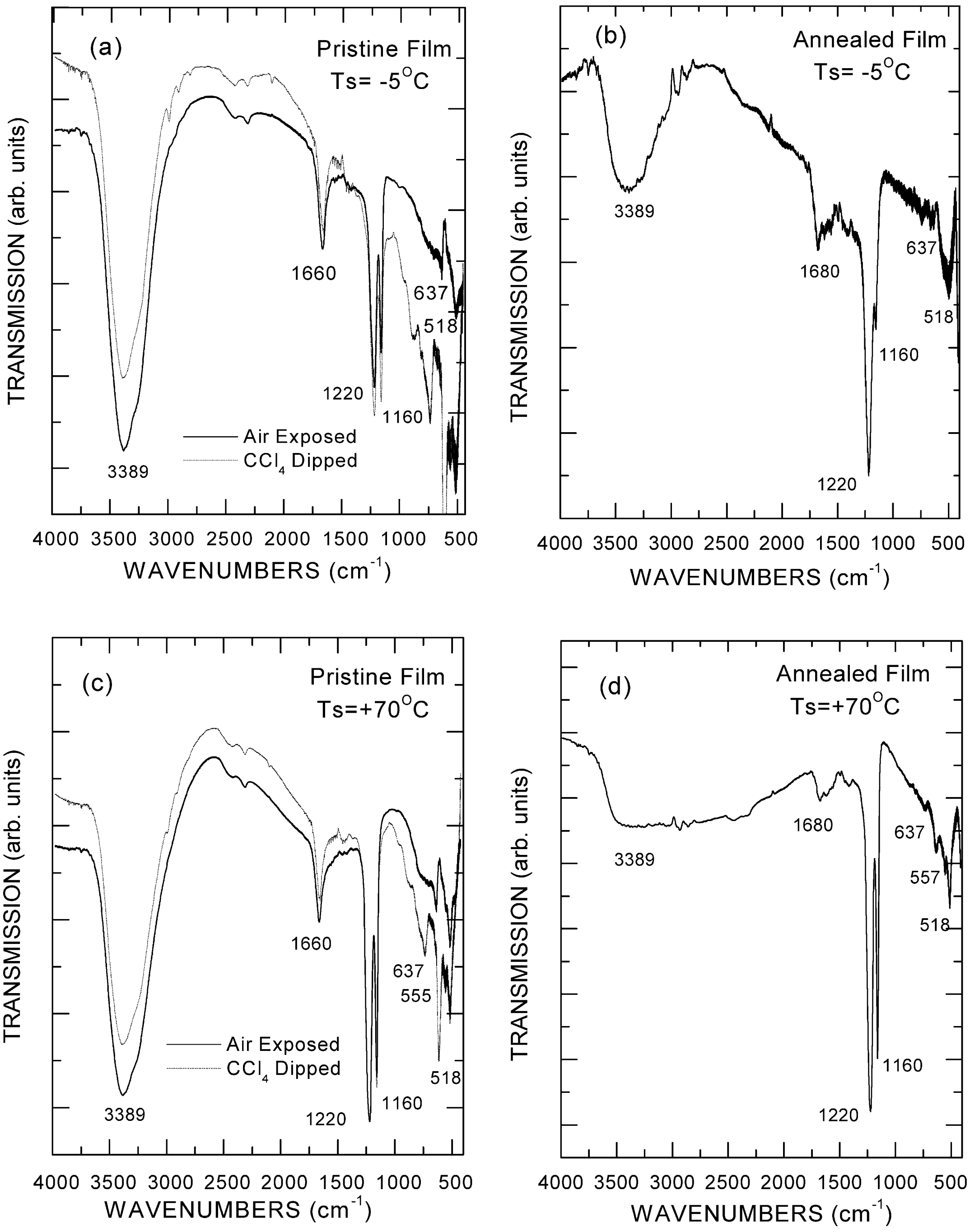


Fig. 2. FTIR spectra of fluorocarbon polymer films (a) deposited at −5 °C, dashed curve is for film quenched in CCl_4, (b) same film after 245 °C for 1 h anneal (c) deposited at +70 °C, dashed curve is for film quenched in CCl_4, (d) same film after 245 °C for 1 h anneal.

Annealing significantly reduces C=O/COO absorption peak. For pristine −5 °C deposited film, the ratio C=O/COO to $CF_2(\nu_{asym})$ is ∼0.55 which reduces to 0.15 after annealing. Similarly, for films deposited at +70 °C, the ratios are 0.46 and 0.20, respectively before and after annealing. This reduction in intensity is also accompanied by a ∼20 cm^{-1} shift in the peak position towards the higher wave numbers for both −5 and +70 °C deposited films. This means that C=O/COO bonds are now attached in a less interactive bonding environment [38]. Decreased intra molecular bonding of C=O/COO bonds could be interpreted as their dissociation from $-(CF_2-CF_2)-$ chains. It is not clear if the loss of C=O/COO bonds are through scission of C–C bonds or due to thermal decomposition.

3.2. Morphology of fluorocarbon films

AFM micrographs in Figs. 3 and 4 show the surface

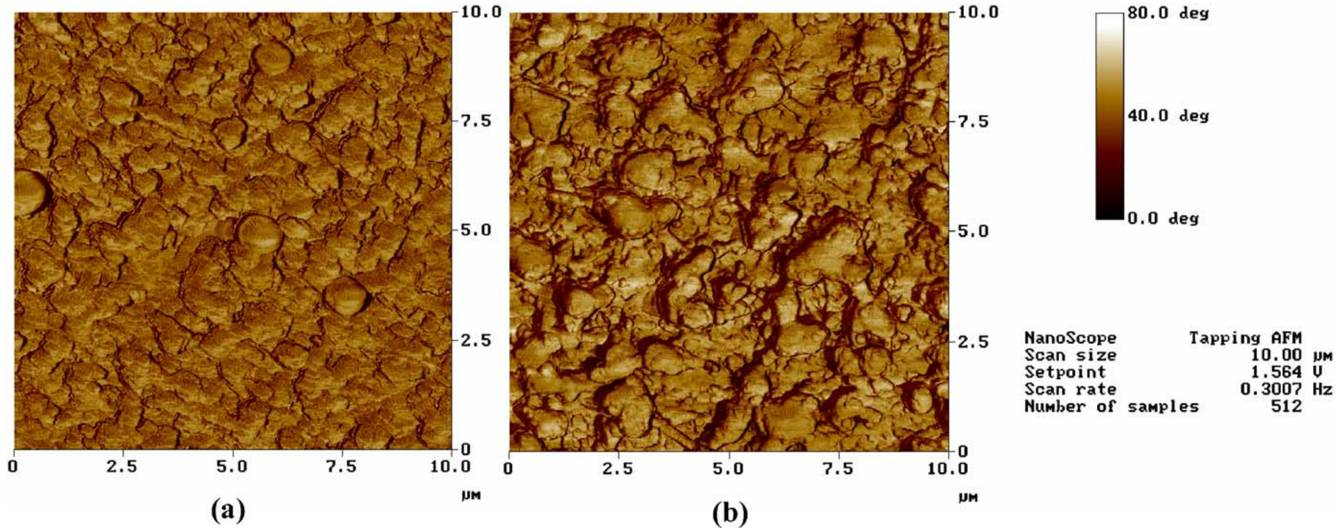


Fig. 3. AFM micrograph showing surface morphology of fluorocarbon polymer films formed at −5 °C substrate temperature. (a) Pristine film and (b) after annealing in vacuum at 245 °C for 1 h.

morphology of fluorocarbon films formed over polished single crystal Si wafers. Films deposited at −5 °C show closely packed and uniformly distributed lamellar like features with average size ∼1.2±0.2 μm (Fig. 3(a)). Surface features in the 70 °C deposited films are of much smaller 0.25–0.6 μm size range. Surface roughness in both cases is ∼50±10 nm. Flat ridge like growth features seen in most lamellae are interpreted as layered growth of polymer films, which form due to folding of long linear –$(CF_2–CF_2)_n$– chain structures. Surface morphology of annealed −5 °C deposited film is affected by break-up of lamellae. Surface features are dominated by non uniform distribution of grains with size between 0.6 and 0.9 μm interceded by much smaller nodular mass of 0.1–0.2 μm size, Fig. 3(b). Annealing causes no significant change in surface morphology of +70 °C film, (Fig. 4(b). Here, lateral dimensions of lamellae have not changed, but disappearance of ridge like structure on several lamellae indicates some coalescence. Microscopy studies are thus supportive of spectroscopic observations.

3.3. Photoelectron spectra of fluorocarbon polymer films

3.3.1. As-deposited films

Carbon 1s (C1s) XPS spectra for −5 and +70 °C deposited films are shown in Fig. 5(a) and (b). Contributions from CF_3, CF_2, CF and C–CF bonding structures from features at 294, 292, 289.6 and 287.5 eV, respectively were determined by deconvolution of the C(1s) spectra. A peak at 285 eV is assigned to carbon with β-substituted fluorine [39]

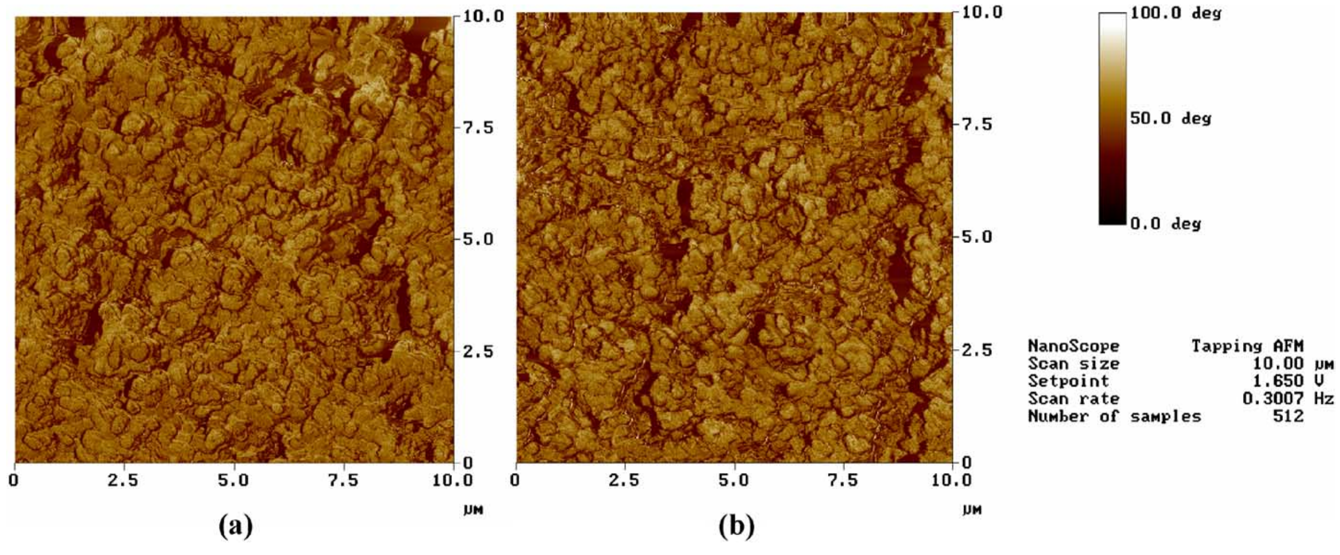


Fig. 4. AFM micrograph showing surface morphology of fluorocarbon polymer films formed at +70 °C substrate temperature. (a) Pristine film and (b) after annealing in vacuum at 245 °C for 1 h.

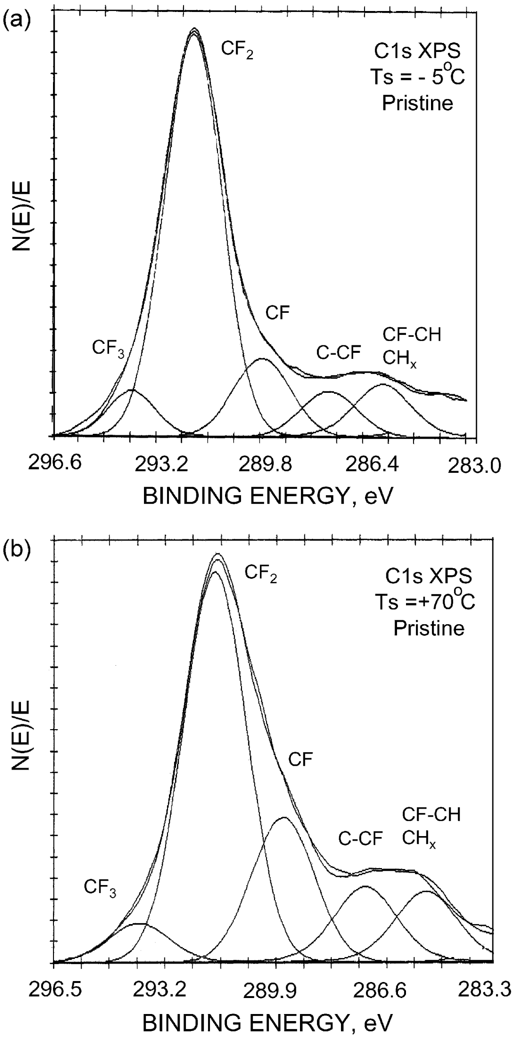


Fig. 5. C(1s) electron spectra of PTFE-like fluorocarbon polymer films in the as-deposited state. Films formed at (a) −5 °C and (b) +70 °C substrate temperature.

but might also include contributions from adventitious hydrocarbon on the film surface. Results of XPS analysis are shown in Table 1. A dominant CF_2 growth fraction is seen in all thermal-CVD deposited fluorocarbon films, typical values are ~65% for −5 °C and ~53% for +70 °C deposited films. The %CF and %C–CF concentration is higher in +70 °C formed films, typically 11–20% compared to 7–12% in films deposited at −5 °C. A CF_3 bond structure with concentration ~5.8±0.5 at% is observed in all films irrespective of the deposition temperature. Computed stoichiometry of the −5 and +70 °C deposited films determined from the ratio of integrated C(1s) to F(1s) spectral peaks are $C_1F_{1.66}$ and $C_1F_{1.49}$, respectively. Improved stoichiometry of the −5 °C deposited films is due to increased F incorporation in the polymer chains. Relative concentration of CF and C–CF bonding, which are the branching and linking sites in molecular chain structure determines the degree of cross-linking according to the expression,

$$\text{Cross-linking\%} = [\text{Pk(CF)\%} + \text{Pk(C} - \text{CF)\%}]/\ \text{Total } 100\%.$$

Films deposited at −5 °C are cross-linked to a lesser degree ~19.7% as compared to +70 °C films which show cross-linking to an extent of ~29%.

3.3.2. F(1s) XPS spectra

F(1s) XPS lines were analyzed to probe chemical groups bound to F in CVD formed fluorocarbon films and the results are presented in Table 2. F1(s) line shape in both −5 and +70 °C deposited films is symmetrical and consistent with the single line features with full width at half maximum (FWHM) ~2.9–3.0 eV. For −5 °C deposited films, F(1s) line manifests at binding energy ~690.6 eV and for +70 °C deposited films at 689.4 eV implying a chemical shift of ~1.2 eV under the same instrumental conditions. As the F(1s) binding energy for fluorine covalently bonded to carbon is ~689 eV [40], the broad (FWHM ~3 eV) higher binding energy F(1s) line observed here indicates formation of fluoropolymer films with high degree of fluorination. A chemical shift in F(1s) binding energy shows that −5 °C deposited films are closer to the linear $–CF_2–CF_2–$ polymeric form [41]. Further, CVD grown fluorocarbon polymer films do not have fluorine in the ionic state as low binding energy ~685–687 eV peak is not seen in the XPS spectra.

3.3.3. O(1s) XPS spectra

XPS survey spectra of thermal-CVD grown fluorocarbon polymer films (not shown here) show O1(s) peak confirming the presence of oxygen. Films deposited at −5 °C show ~2.0 at% oxygen compared to 3.8 at% for +70 °C deposited films. Most previous studies attribute this to moisture adsorption or oxygen permeation [21,32,33]. Fluorocarbon films formed by plasma show a greater tendency to oxidize, which explains oxygen detected in such films [42,43]. We have examined the bonding environment of oxygen in $–(CF_2–CF_2)_n–$ fluorocarbon polymer films in order to understand its role in the film growth by CVD.

The O(1s) electron spectra of −5 °C and +70 °C deposited fluorocarbon polymer films are shown in Fig. 6(a) and (b), respectively, and line parameters are given in Table 2. The O(1s) spectra is deconvoluted by fitting Gaussian line profile which shows two distinct lines indicating that oxygen in the films is attached in two different bonding configurations. For −5 °C deposited films, binding energies of the two O(1s) lines are 535.3 and 533.6 eV and for +70 °C deposited films, 534.7 and 533.0 eV. Typically, oxygen associated with various functional groups, *for example*, carboxyls and ketones, exhibit O(1s) binding energy around 532 eV [44]. A higher O(1s) binding energy 534.7 and 535.3 eV in CVD formed films suggests that oxygen is bonded to carbon atoms that are also bonded with fluorine. Highly electronegative fluorine in fluorocarbon groups such as $CF_3–O–CF_2$ draws out

Table 1
XPS C(1s) data and elemental composition for fluorocarbon polymer films deposited over Si wafer substrates

Film deposition temperature		C1s contribution (%)					Elemental composition (%)				F/C
		CF_3	CF_2	CF	C-CF	CF-CH	F	C	O	Si	
−5 °C	As-deposited	6.3	64.7	12.3	7.4	9.3	61.1	36.9	2.0	–	1.66
		3.7	46.1	17.4	14.9	17.9	58.0	36.5	5.5	–	1.58
+70 °C	As-deposited	5.4	53.2	19.7	11.2	10.5	57.5	38.7	3.8	–	1.49
	Annealed	4.7	49.2	18.4	10.5	17.2	58.3	36.0	5.7	–	1.62

Table 2
XPS parameters of O1s and F1s spectra of fluorocarbon polymer films

Film deposition temperature		O1s Binding energy (eV) [ratio]			O1s FWHM (eV)	Intensity (C/s)	F1s B.E. (eV)	F1s FWHM (eV)	Intensity (C/s)	F/O intesity ratio
−5 °C	As-deposited	532.8 [1.0]	535.3 [1.9]		2.5	5372	690.6	2.9	24505	4.6
	Annealed	532.7 [1.0]	534.4 [2.1]	530.8	3.7	11437	689.3	2.8	46614	4.1
+70 °C	As-deposited	533.0 [1.0]	534.7 [0.9]		2.3	7334	689.4	3.0	28625	3.9
	Annealed	533.0 [1.0]	534.1 [1.0]	531.4	3.2	9394	689.6	2.9	30137	3.2

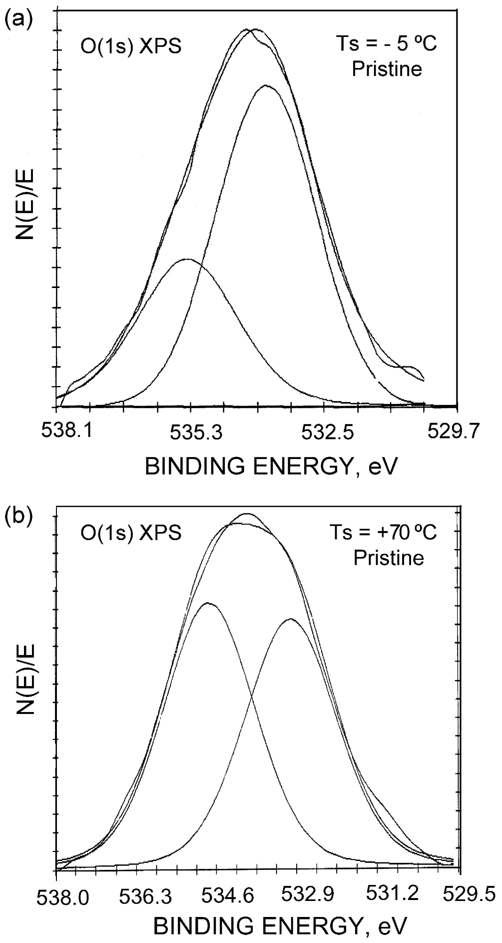


Fig. 6. O(1s) electron spectra of PTFE-like fluorocarbon polymer films in the as-deposited state. Films formed at substrate temperature (a) −5 °C and (b) +70 °C.

electrons increasing the binding energy of oxygen atom. The lower binding energy O(1s) line suggests the presence of oxygen functionalities involving heteroatoms. In a number of other polymers which contain C and O in various functional groups such as aliphatic C–O–C, O–C–O, O–C–C and C–OH, the O(1s) binding energy relative to saturated hydrocarbon occurs between 532.7 and 533.5 eV [43,45]. By analogy, it is suggested that part of oxygen present in fluorocarbon polymer films exists in the singly bonded state with carbon. Integrated intensity analysis of the two O(1s) XPS lines show that films deposited at −5 °C have a higher ratio 1.9:1 of oxygen bonded to fluorine containing carbon groups such as $F_3C–O–CF_2$, F_2 C=O. A similar analysis for the +70 °C deposited film show that oxygen bonded with –C–O– like and CF_x containing groups is nearly equal in proportion, typical ratio being 0.9:1.

It is notable that singly bonded oxygen to carbon as in alcohol gives C(1s) XPS line between 286.5 and 286.8 eV. For carbonyl bonds, C(1s) line appears at 289.5 eV [42]. The binding energy of carbon shifts further towards higher energy if it is also bonded to fluorine or fluorocarbon groups. In interpreting the C(1s) spectra, of Fig. 5(a) and (b), peaks around 287–287.5 eV were attributed to *C*F and at 289.7–289.9 eV to *C*–CF bonds. Presence of bonded oxygen in fluorocarbon polymer film indicates that these lines could be composite lines having additional contributions from carbon singly bonded to oxygen and fluorine and carbonyl carbon with carbon containing one fluorine [40,43]. An inference from the O(1s) XPS analysis is that rather than physiosorbed, oxygen incorporates by reaction in the fluorocarbon polymer films during growth. This is consistent with the FTIR study. Internal source of oxygen in the CVD reactor is derived from $CF_3C(O)F$ and radicals CFO and CFOH formed from its decomposition which interfere with the CF_2 radical polymerization. Reaction of these radicals can lead to oxygen bound in two different environments in fluorocarbon polymer films as discussed later.

3.3.4. XPS analysis of annealed films

C(1s) XPS spectra of −5 and +70 °C films after 245 °C, 1 h anneal are shown in Fig. 7(a) and (b). Molecular arrangement in +70 °C formed films is relatively stable against thermal effects as XPS peak intensities for CF_3, CF and C–CF relative to CF_2 are unchanged on annealing (Table 2). F(1s) analysis shows no loss of film stoichiometry as F/C ratio after annealing is nearly the same. For −5 °C deposited films, annealing has altered the distribution of CF_n ($n=1,2,3$) functionality. As shown in Table 2, increase in relative intensities of C–CF (287.5 eV) and CF, (289.8 eV) XPS lines and a decrease in main CF_2 peak at 292 eV indicate considerable reorganization. In an extraneous rise of $-CH_x$ at 285.4 eV also seen in the −5 °C films, hydrocarbon surface contamination from vacuum annealing is suspected. Fig. 8(a) and (b) show O(1s) line spectra of annealed films deconvoluted into three distinct line features at binding energies shown in Table 2. High binding energy O(1s) line shifts towards the lower energy side of pristine value after annealing; the shift for −5 °C deposited film is ~1 eV and for +70 °C deposited film ~0.6 eV. These observations suggest a loss of oxygen bound to fluorinated carbon sites on annealing. Thus O-linking sites in fluorocarbon polymer chains are the weak links, which tend to dissociate on annealing and induce a process of chain dissociation and regrouping.

3.4. Fluorocarbon polymer film growth process

Thermal decomposition of C_3F_6O, follows a unimolecular reaction producing gaseous difluorocarbene (CF_2) radicals and $CF_3C(O)F$ products as shown below [21,24],

$$CF_3CFOCF_2 \rightarrow$$

$$:CF_2 + CF_3C(O)F \text{ (trifluoroacetyl fluoride gas)} \qquad (1)$$

Addition reaction among the: CF_2 free radicals results in the formation of fluorocarbon polymer film similar to a PTFE structure [24]. Although vapor state formation of double bonded perfluoroalkanes, $CF_2{=}CF_2$ or $CF_3CF{=}CF_2$ has a

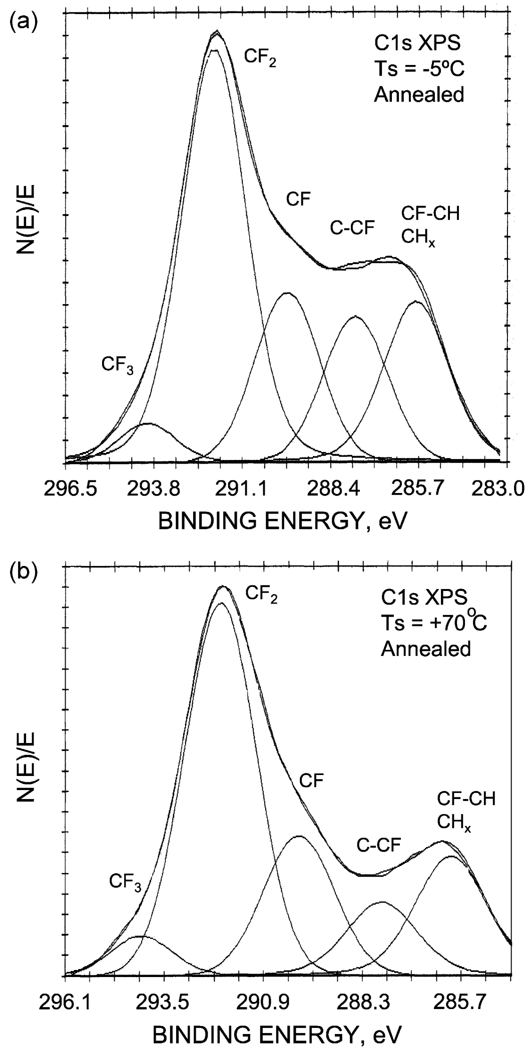


Fig. 7. C(1s) electron spectra of PTFE-like fluorocarbon polymer films after annealing at 245 °C for 1 h, in vacuum. Films formed at substrate temperature (a) −5 °C and (b) +70 °C.

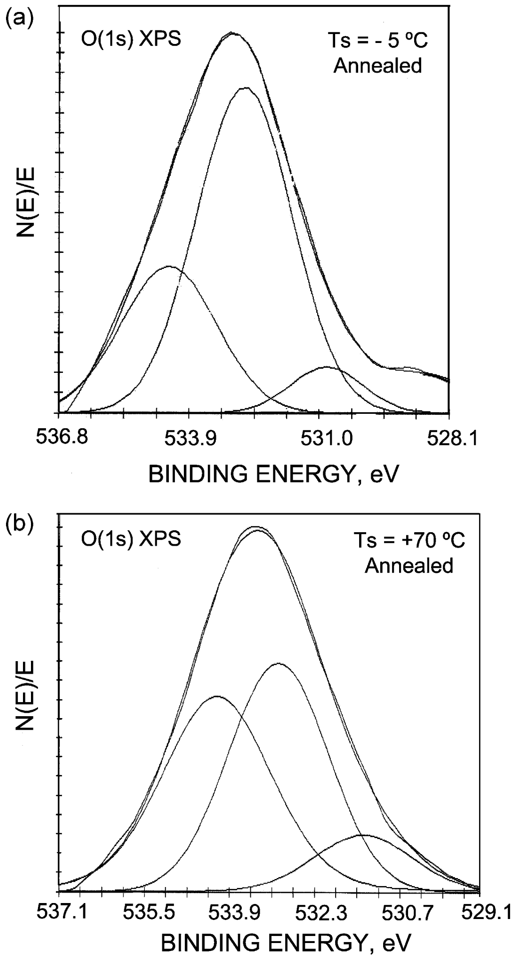


Fig. 8. O(1s) electron spectra of PTFE-like fluorocarbon polymer films after annealing in vacuum at 245 °C for 1 h. Films formed at substrate temperature (a) −5 °C and (b) +70 °C.

finite probability but due to highly negative enthalpy of formation, attachment of singlet CF_2 to such species is improbable beyond three-carbon chain [46] and cannot account for formation of fluorocarbon polymer films unless CVD conditions favor thermal decomposition of tetrafluoroethylene, $CF_2{=}CF_2$ [47]. Polymerization reaction is therefore through combining singlet CF_2 to the singly bonded CF_2 chain [46]. This polymerization step occurs in the vapor phase as well as on the substrate surface. The primary process generating CF_2 radicals takes place in the vapor state and as the abundance of these radicals depends on the system pressure, precursor flow rate and filament temperature, it determines the film deposition rate [48]. Substrate processes are more relevant in determining the molecular structure and morphology of the deposited films [48]. A high percentage of CF_2 in CVD grown fluorocarbon polymer films indicates primary reaction pathway for polymer film growth is through association of a large number of CF_2 radicals. Differences in %CF and %C–CF C(1s) components, and bonding structure and $\%O_2$ in the films deposited at low −5 °C and high +70 °C substrate temperatures show that polymerization process is also activated at the substrate surface. Sticking coefficient of CF_2 radical is high due to enhanced tendency to condense over the substrates held at low −5 °C compared to high +70 °C temperature. This translates in a higher CF_2 fraction bound as $-(CF_2-CF_2)-$ linear chains in polymer films formed at −5 °C. This is consistent with IR absorption and XPS data. Over all reactions for linear chain attachment of CF_2 radicals through preexisting singly bonded molecules or a molecular chain in the vapor and at a substrate site, [S] are as shown below,

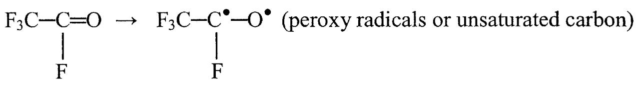
Vapor State

$$\begin{aligned}&-(CF_2-CF_2)- + 2n(:CF_2) \rightarrow -(CF_2-CF_2)_{n+1}-[\text{vapor}]\\&-(CF_2-CF_2)_{n+1}-(\text{vapor}) + [S] \rightarrow (CF_2-CF_2)_{n+1}[\text{film}]\end{aligned} \tag{2}$$

Substrate

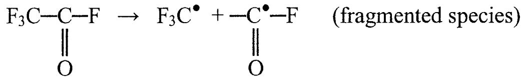
$$\begin{aligned}&2n(:\mathrm{CF_2}) + [\mathrm{S}] \rightarrow \text{–}(\mathrm{CF_2\text{–}CF_2})_n[\text{film}]\\ &\text{–}(\mathrm{CF_2\text{–}CF_2})_n\text{–} + 2m(:\mathrm{CF_2}) + [\mathrm{S}] \rightarrow \text{–}(\mathrm{CF_2\text{–}CF_2})_{n+m}\text{–}[\text{film}]\\ &\quad\text{–}(\mathrm{CF_2\text{–}CF_2})_p\text{–}[\text{substrate}] + \text{–}(\mathrm{CF_2\text{–}CF_2})_q\text{–}[\text{substrate}]\\ &\quad+[\mathrm{S}] \rightarrow \text{–}(\mathrm{CF_2\text{–}CF_2})_{p+q}\text{–}[\text{film}] \qquad (3)\end{aligned}$$

Existence of CF_3, CF and C–CF bonding structures in films as shown by XPS cannot be understood based on C_3F_6O decomposition Reaction-1. Further, this reaction also does not provide any viable chain termination process. To reconcile these aspects and also understand the bonded oxygen in the films, a more active role is considered for the other reaction product $CF_3C(O)F$ of precursor C_3F_6O decomposition. Decomposition of C_3F_6O at 500 °C is earlier shown to produce stable $CF_3C(O)F$ product [21], but under plasma, species from $CF_3C(O)F$ fragmentation such as COF_2, CO, C_2F_4 and C_3F_6 are readily seen [49]. Dissociation of $CF_3C(O)F$ by photolytic processes is widely studied [34–37,50] according to which molecular decomposition at the initial stages produces excited $CF_3C^{\cdot}(O)F$, peroxyradicals, CF_3 and C(O)F radicals [35]. Extending these concepts to the CVD growth process, flash thermal dissociation of $CF_3C(O)F$ is possible by a direct strike at the heated (600 °C) filament according to the following,



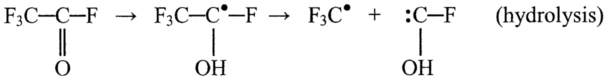
$$F_3C{-}\underset{\overset{|}{F}}{C}{=}O \rightarrow F_3C{-}\underset{\overset{|}{F}}{C^\bullet}{-}O^\bullet \ \text{(peroxy radicals or unsaturated carbon)}$$

(Reaction A)



$$F_3C{-}\underset{\overset{\|}{O}}{C}{-}F \rightarrow F_3C^\bullet + {-}\underset{\overset{\|}{O}}{C^\bullet}{-}F \quad \text{(fragmented species)}$$

(Reaction B)



$$F_3C{-}\underset{\overset{\|}{O}}{C}{-}F \rightarrow F_3C{-}\underset{\overset{|}{OH}}{C^\bullet}{-}F \rightarrow F_3C^\bullet + :\underset{\overset{|}{OH}}{C}{-}F \quad \text{(hydrolysis)}$$

(Reaction C)

These short lived decomposition species readily react with the growing linear –(CF_2–CF_2)– molecular chain and modify the structure of the deposited films. Other possible reactions are among the radicals themselves and with the initial molecule that convert into stable products or regenerate precursor molecule, as shown below [35],

$$^{\cdot}\mathrm{CF_3} + {}^{\cdot}\mathrm{CF_3} \rightarrow \mathrm{C_2F_6} \qquad (4a)$$

$$^{\cdot}\mathrm{COF} + {}^{\cdot}\mathrm{COF} \rightarrow \mathrm{COF_2}\ [\text{gas}] + \mathrm{CO}\ [\text{gas}] \qquad (4b)$$

These products exit from the CVD reactor without interacting with the depositing film as previously seen [21]. Due to dynamic conditions prevalent during CVD growth, a finite fraction of radicals produced by the Reactions A–C participate in the formation of fluorocarbon polymer films through additional reaction pathways. Fig. 9(a) and (b) show possible reactions, which yield molecular structural forms of fluorocarbon polymer chains that are consistent with the XPS and FTIR results and with the overall stoichiometry of the films formed at different substrate temperatures. These reactions are inclusive and cannot be unambiguously described, as interaction of these radicals may be more complex and involvement of one or a combination of reactions is possible. Reaction of $^{\cdot}CF_3$ with –(CF_2–CF_2)– chain provides for a chain termination process. Reactions (a)–(c) of growing –(CF_2–CF_2)– chains with oxygen-containing radicals are consistent with O1(s) XPS results showing 3–5% bonded oxygen in films and also reflect C–F and C–CF branching and crosslinking sites. Reactions (b) is the chain elongation that do not affect the concentration of linear –(CF_2–CF_2)– polymer chains in the film. Reactions (a) and (c) link CF_2 linear

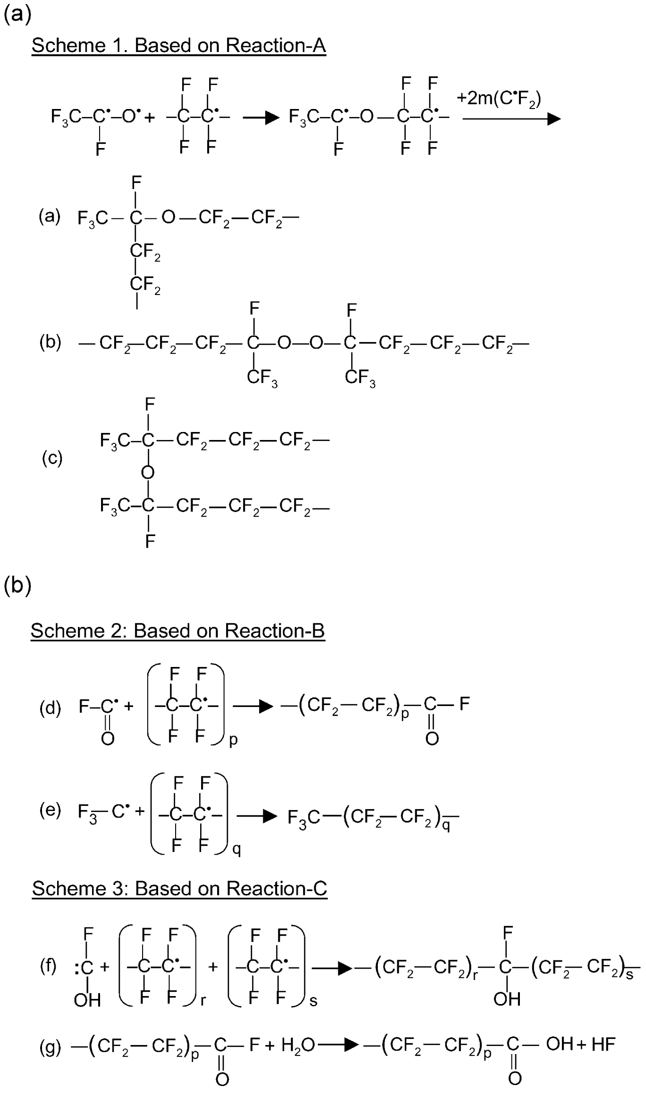


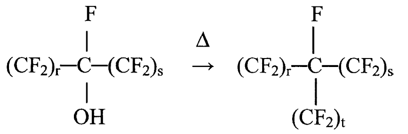
Fig. 9. Reactions leading to modified molecular structure of fluorocarbon polymer films due to involvement of $CF_3C(O)F$ fragmentation species (a) based on Reaction A and (b) based on Reactions B and C.

chains at O-sites and (d) and (e) are chain termination reactions. Similar reactions are discussed in the literature dealing with the oxidation of tetrafluoroethylene, which involve polymerization with simultaneous decomposition of growing radicals across O–O and C–C bonds [51]. Structures (a) and (b) show carbon in the ≡C–O and C–CF bonding configuration, which is responsible for contributing to the C1(s) XPS peak at 287.5 eV [43]. Structure (d) has a linear $–(CF_2–CF_2)–$ chain configuration terminated through $^{\cdot}CFO$ radicals. This bonding structure also contributes to C(1s) XPS peak consistent with >CF– bonds which occur at 289.9 eV [43].

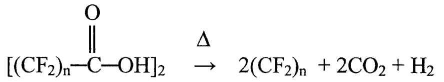
It is seen that annealing induces chain scission and regrouping to form a more stable molecular association. Structures described in Fig. 9(a) and (b) facilitate emergence of new bonding structures from dissociation of CF_3–C–F– junction links between two linear chains in a way that do not result in the loss of entire linear $–(CF_2–CF_2)_n–$ structure. On annealing, molecular chain structure stabilizes by repositioning at substituted carbon sites as evidenced from increased CF and C–CF XPS peak intensity and therefore in increased degree of cross-linking to 32% from a pristine film value ∼19.7%. Post annealed FTIR spectra still show doublet character for CF_2 stretch suggesting basically CF_2 linear chain structure is intact but diminished.

FTIR data also support chain scission at C–O bonding sites as inferred from reduced intensity and shift of C=O/COO IR peak towards lower wavenumber (Fig. 2(b) and (d)). Regrouping of molecular chains promotes cross-linked structure and loss of linear chain attachments. For +70 °C deposited films, degree of cross-linking ∼29%, is not changed since a preexisting cross-linked structure imparts stability to molecular bonds. In annealed films, concentration of fluorine relative to carbon has not decreased much. Since increase in cross-linked structure is generally associated with reduction in fluorine, it is inferred that molecular structure of annealed fluorocarbon polymer film is still determined by large linear $–(CF_2–CF_2)_n–$ chain segments which are linked.

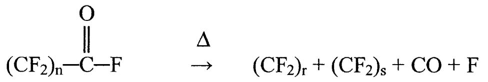
Understanding of OH bonds in the film is based on the reaction of CFOH radicals with $–(CF_2–CF_2)–$ chains as shown in Fig. 9(b) reaction (f). CFOH radicals are derived from CF_3CFOH as in Reaction C [52]. The other possible way OH can be included in the film is by hydrolysis of $(CF_2)_{2n}$–C(O)F (Fig. 9(b) reaction (e)), to produce $(CF_2)_{2n}$–C(O)OH and HF during the film growth as shown by reaction (g) in Fig. 9(b) [50,53]. A substantial decrease in OH IR absorption is seen after anneal which remain unaffected after exposure of annealed films to atmospheric moisture. This irreversibility suggests break-up and regrouping of molecular chain in a way that renders it less susceptible to moisture. Possible decomposition reactions that breakup C–OH and C=O bonds and diminish IR absorption due to OH and O in the films are,



$$(CF_2)_r\text{–}\overset{\overset{F}{|}}{\underset{\underset{OH}{|}}{C}}\text{–}(CF_2)_s \xrightarrow{\Delta} (CF_2)_r\text{–}\overset{\overset{F}{|}}{\underset{\underset{(CF_2)_t}{|}}{C}}\text{–}(CF_2)_s \tag{5a}$$



$$[(CF_2)_n\text{–}\overset{\overset{O}{\|}}{C}\text{–}OH]_2 \xrightarrow{\Delta} 2(CF_2)_n + 2CO_2 + H_2 \tag{5b}$$



$$(CF_2)_n\text{–}\overset{\overset{O}{\|}}{C}\text{–}F \xrightarrow{\Delta} (CF_2)_r + (CF_2)_s + CO + F \tag{6}$$

Reaction (5a) shows breakup of C–OH bonds that leads to reorganization of $–(CF_2–CF_2)–$ chains by reaction with other linear chains producing a crosslinked structure. Breakup of CF_2 chains by Reaction (5b) takes place with the evolution of CO_2 in case OH bond are involved in chain termination as shown in Fig. 9(b)-reaction (g). Reaction (6) depicts decomposition of CF_2 chains and release of CO. Such reactions have been previously described in Refs. [7, 53]. These reaction pathways reduce CO and OH bonding, increase crosslinked structure and do not cause extensive breakup of linear CF_2 chains, which is consistent with the XPS and IR absorption results.

4. Conclusions

Formation of fluorocarbon polymer films by thermal CVD from gaseous C_3F_6O precursor in a heated filament reactor is described. Structure of films is analyzed by a combined study of C(1s), O(1s) and F(1s) core level electron binding energies and FTIR spectra. Fluorocarbon polymer films grow by attachment of:CF_2 radicals to singly bonded CF_2 chains under high radical concentration in a molecular structure similar to that of PTFE. Substrate temperature affects morphology and molecular structure due to varied sticking coefficients for the adsorbed free radicals and other species. Radicals emerging from fragmentation of trifluoroacetyl fluoride, $CF_3C(O)F$ increase the tendency to form cross-linked polymeric structure, inclusion of CF, C–CF bond defects, C=O/COO and OH bond formation and provides a viable chain termination process. This study shows that rapid elimination of $CF_3C(O)F$ or depressing its decomposition reactions within the CVD reactor are important to minimize the oxygen related defects and produce thermally stable PTFE-like fluorocarbon polymer films at relatively lower substrate temperatures. Reducing temperature of heated filament is one possible method although it adversely affects film growth rates.

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