# Perfluorooctane Sulfonyl Fluoride as an Initiator in Hot-Filament Chemical Vapor Deposition of Fluorocarbon Thin Films

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We have demonstrated the successful use of an initiator species in hot-filament chemical vapor deposition (HFCVD) of poly(tetrafluoroethylene) thin films from the precursor hexafluoropropylene oxide (HFPO). The introduction of perfluorooctane sulfonyl fluoride (PFOSF) in small concentrations allows the enhancement of deposition rates and increased control over film composition. Endcapping by $CF_3$ groups is possible, which may provide benefits such as enhanced thermal stability and higher hydrophobicity for HFCVD films. Conversion of the PFOSF is high, and HFPO utilization efficiency can be increased significantly. The generation of an initiator radical via the pyrolysis of PFOSF may contribute to enhanced nucleation rates during film growth. Initiation and/or nucleation is rate-limiting at low filament temperatures, and mass transport limitations dominate at higher filament temperatures.

## Introduction

Hot-filament chemical vapor deposition (HFCVD, also known as pyrolytic CVD) offers the ability to tailor the chemistry of films with a polymeric structure.[1−4] In particular, HFCVD allows for more control over precursor fragmentation pathways than conventional plasma-enhanced CVD.[3] HFCVD uses thermal activation in the gas phase to generate reactive species[5] and allows independent control of the substrate temperature to be exercised. The latter characteristic differentiates HFCVD from conventional thermal CVD, in which precursor breakdown temperature and substrate temperature are identical. The control over reaction pathways available via HFCVD makes it possible to produce polymeric fluorocarbon films spectroscopically similar to poly-(tetrafluoroethylene) (PTFE) with the precursor hexafluoropropylene oxide (HFPO, $CF_3CF(O)CF_2$).[3] PTFE has many desirable properties, including a low refractive index and dielectric constant, low coefficient of friction, excellent chemical resistance, and high thermal stability.[6−8] Thin films of PTFE offer advantages for applications as diverse as optical coatings,[9] biopassivation coatings for implantable devices,[10,11] and interlayer dielectrics in integrated circuits.[12,13] However, bulk PTFE's high melt viscosity and poor solubility make it difficult to process into thin, conformal, and uniform films.[8] By contrast, HFCVD is capable of providing good control over film structure and morphology on a wide range of substrates, including those that are thermally sensitive or of complex geometry. HFCVD also has advantages over other thin film deposition techniques such as pulsed-laser deposition (PLD), which is capable of producing PTFE-like films of high crystallinity at comparable deposition rates.[14−16] In PLD, substrates are usually maintained at significantly higher temperatures than in HFCVD,[17] thereby limiting the range of substrates that can be coated. Substrate coverage is also restricted to several square centimeters, whereas HFCVD is capable of producing uniform thin films on 100 mm silicon wafers and can be scaled by increasing chamber size and filament area. Previously, we have reported on the characterization of films produced using this process[2,3] and on progress made in understanding the deposition chemistry of HFPO during HFCVD.[5] In this paper, we report on the effects of adding an initiator species, perfluorooctane sulfonyl fluoride (PFOSF, $CF_3(CF_2)_7$-$SO_2F$), to the HFCVD process. As in conventional polymer chemistry, the use of an initiator allows control over both growth rates and chemical composition of the resulting polymeric film.[18] The use of PFOSF also allows further elucidation of the chemistry of this novel deposition process.

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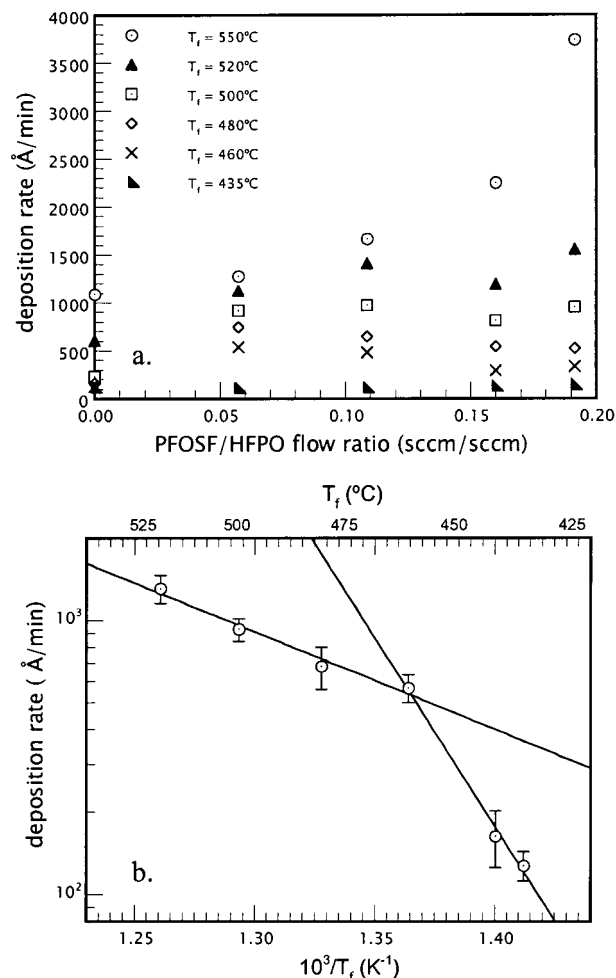
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## Experimental Section

Films were deposited on 100 mm diameter silicon wafer substrates in a custom built vacuum chamber, as described previously.[19] Thermal excitation was accomplished by resistively heating 28 AWG Nichrome wire (80% Ni/20% Cr) strung on a filament holder. The filament holder straddled a cooled stage on which the silicon wafer was placed and was sufficiently large to ensure uniform deposition over the wafer area. The filament to substrate standoff was 1.0 cm. Pressure in the reactor was maintained at 1.0 Torr by a butterfly valve. Undiluted HFPO of 98% purity, donated by DuPont, was metered and controlled by a mass-flow controller. PFOSF was vaporized in a heated vessel and delivered through a needle valve to maintain flow rates ranging from 2 to 11 sccm at different valve settings. Experiments were performed at HFPO flow rates of 35, 78, and 158 sccm to evaluate the effect of the PFOSF/HFPO flow ratio on deposition rate. Measurements of deposition rate as a function of PFOSF flow rate and filament temperature were performed using an HFPO flow rate of 35 sccm and three different PFOSF flow rates of 2, 4, and 7 sccm. Filament temperature was measured using a 2.2 $\mu$m infrared pyrometer. For oxidized Nichrome, a spectral emissivity of 0.85 was estimated from direct contact thermocouple measurements. Temperatures were consistent from run to run, and there was little variation in power requirements for heating the wire. Films were deposited at filament temperatures ranging from 435 to 580 °C. A single filament array was preconditioned for 15 min at 510 °C and used for all runs. Substrate temperature was maintained below 40 °C by backside water cooling. Deposition rates were monitored in situ using interferometry. A cycle thickness of 3300 Å/min was calculated and confirmed by profilometry measurements. NMR experiments were performed on a home-built spectrometer tuned to 254.0 MHz for $^{19}$F detection. A Chemagnetics 3.2 mm double-resonance solids probe was spun at 23–25 kHz to perform high-resolution magic-angle spinning. All spectral chemical shifts were referenced to CFCl$_3$. Other experimental details have been described elsewhere.[20] Atomic force microscopy (AFM) was performed on a Digital Instruments Dimension 3000. Images were taken under tapping mode with a standard etched silicon tip.

## Results and Discussion

**Deposition Rate.** The addition of small quantities of PFOSF to the HFCVD process increases deposition rates significantly, as indicated in Figure 1a. The data indicate that upon the addition of PFOSF, the deposition rate is approximately zero order in PFOSF for filament temperatures from 435 to 520 °C. Because the conversion of HFPO is low over this temperature range (~2% for the highest deposition rate reported at 520 °C), the deposition rate is proportional to the overall rate constant for this system. Deposition rate as a function of filament temperature can thus be plotted in Arrhenius form, as shown in Figure 1b. This is a technique widely used in the vapor deposition literature to estimate apparent activation energy.[21,22] Two kinetic regimes are observed in Figure 1b, with the transition point occurring at a filament temperature of about 460 °C. Such behavior is a common feature of many reactor systems and is often an indication that mass transport effects must be considered.[22] Below 460 °C, the deposition rate depends strongly on filament temperature, and an apparent activation energy of 263 kJ/mol is estimated. Above this temperature, the deposition rate is significantly less sensitive to temperature, and the apparent activation energy is low at 68 kJ/mol.
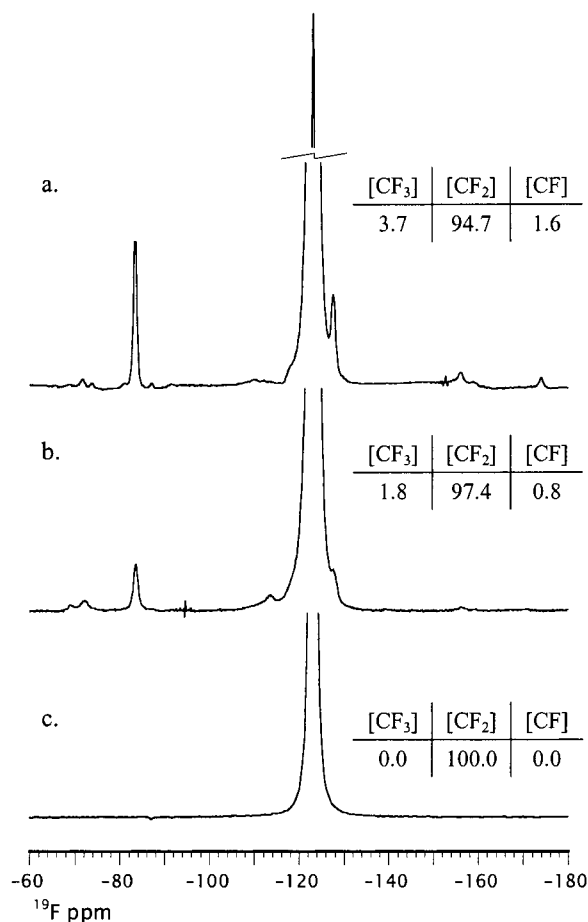
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**Figure 1.** Deposition rates of HFCVD fluorocarbon films from PFOSF and HFPO, showing the effect of (a) adding PFOSF and (b) changing filament temperature. Panel b shows deposition rates plotted in Arrhenius form, with standard deviations indicated by error bars. Regression fits illustrate kinetic regimes above and below 460 °C.

**NMR Spectroscopy.** To elucidate differences in composition between films produced with and without PFOSF, solid-state $^{19}$F NMR spectroscopy was performed on the films (Figure 2a,b). Assignments are made from the literature.[20] As in bulk PTFE (Figure 2c), both films show a primary peak at −123 ppm assigned to CF$_2$CF$_2$*CF$_2$. The HFCVD films, however, show a shift at −84 ppm, which is associated with the endgroup CF$_3$*CF$_2$CF$_2$, and a corresponding shift at −128 ppm from CF$_3$CF$_2$*CF$_2$. The HFCVD films also show evidence of CF* near −156 ppm. No spectroscopic evidence was found indicating retention of the SO$_2$ group from PFOSF. Other peaks of low concentration are also observed but could not be conclusively identified. A summary of possible assignments for these shifts appears elsewhere.[20] The concentrations of each of the moieties of CF, CF$_2$, and CF$_3$ have been tabulated in Figure 2a−c. The concentration of CF$_3$ in bulk PTFE is typically on the order of 0.01 mol %, below NMR sensitivity.[6] Films deposited from HFPO with the addition of PFOSF have a higher CF$_3$ concentration than both bulk PTFE and films deposited from HFPO alone.

**Film Morphology.** The morphology of films produced with the addition of PFOSF was investigated using AFM. Figure 3 shows the effect of filament temperature on films produced using a PFOSF/HFPO ratio of 0.145. Anisotropic, rodlike grain morphologies are observed in the film deposited at a filament temperature of 435 °C (Figure

a.

| [CF$_3$] | [CF$_2$] | [CF] |
|----------|----------|------|
| 3.7 | 94.7 | 1.6 |

b.

| [CF$_3$] | [CF$_2$] | [CF] |
|----------|----------|------|
| 1.8 | 97.4 | 0.8 |

c.

| [CF$_3$] | [CF$_2$] | [CF] |
|----------|----------|------|
| 0.0 | 100.0 | 0.0 |

-60   -80   -100   -120   -140   -160   -180
$^{19}$F ppm

**Figure 2.** NMR spectra of (a) HFCVD film from the precursors HFPO and PFOSF deposited at a PFOSF/HFPO ratio of 0.145 and a filament temperature of 500 °C, (b) HFCVD film from the precursor HFPO with no PFOSF deposited at a filament temperature of 500 °C, and (c) bulk PTFE. Concentrations of CF$_3$, CF$_2$, and CF are shown in mol %.

3a), and a root mean square (rms) roughness of 47 nm is calculated. The film deposited at a filament temperature of 580 °C (Figure 3c) shows nodular morphology and is much smoother with an rms roughness of 6 nm. A roughness of 15 nm was measured for the film deposited at 510 °C (Figure 3b). By comparison, the underlying silicon wafer substrate has an rms roughness of 0.5 nm.[23] Previous work[24] has shown that films grown from HFPO at low deposition rates possess high-aspect ratio grain structures similar to those observed in Figure 3c. Nodular structures comparable to those observed in Figure 3a were observed at higher deposition rates. Changes in morphology were attributed to competition between the rates of nucleation and propagation during the HFCVD process.[24] By this reasoning, growth of films from PFOSF and HFPO at filament temperatures below 510 °C must be dominated by nucleation and/or initiation pathways rather than propagation events.

**Reaction Chemistry.** The pyrolysis of PFOSF has been investigated by other workers over a temperature range of 460–550 °C, comparable to the range of filament temperatures used in our work.[25,26] No activation energy

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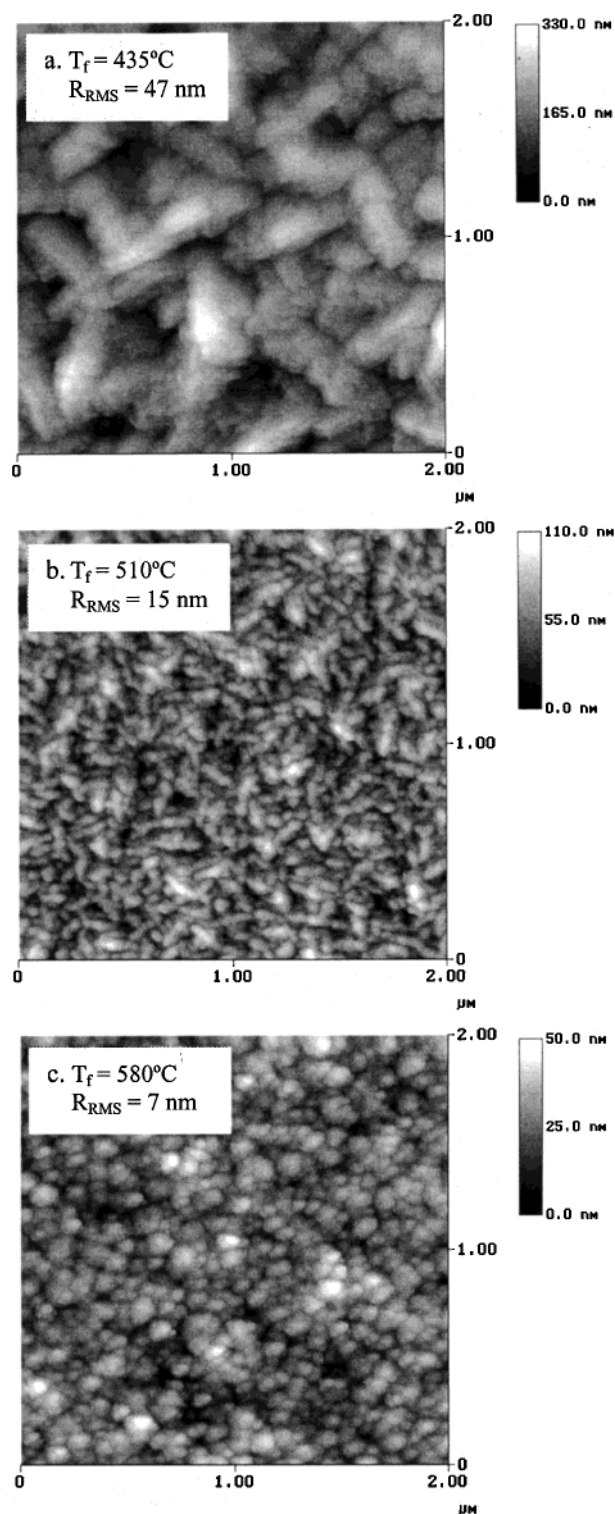


**Figure 3.** Atomic force micrographs showing the effect of filament temperature on the morphology of HFCVD films from HFPO and PFOSF. Films were deposited at a PFOSF/HFPO ratio of 0.145 and filament temperatures of (a) 435, (b) 510, and (c) 580 °C. The rms roughnesses are also shown.
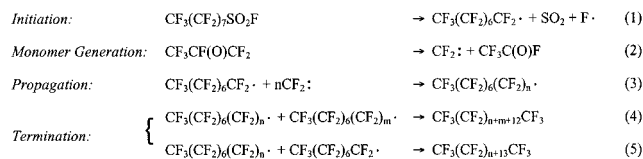
was reported. Conversion of the PFOSF was found to increase with temperature, and conversions of greater than 90% were reported above 490 °C at all PFOSF flow rates considered.[25] Observed products were perfluorinated straight chain molecules from C$_8$ to C$_{16}$. A free radical mechanism was postulated to account for the formation of these products, with CF$_3$(CF$_2$)$_6$CF$_2$· as the primary reactive species. Similar pyrolysis chemistry is expected

*Initiation:*    $CF_3(CF_2)_7SO_2F$        $\rightarrow CF_3(CF_2)_6CF_2\cdot + SO_2 + F\cdot$    (1)

*Monomer Generation:*    $CF_3CF(O)CF_2$        $\rightarrow CF_2\colon + CF_3C(O)F$    (2)

*Propagation:*    $CF_3(CF_2)_6CF_2\cdot + nCF_2\colon$        $\rightarrow CF_3(CF_2)_6(CF_2)_n\cdot$    (3)

*Termination:* $\begin{cases} CF_3(CF_2)_6(CF_2)_n\cdot + CF_3(CF_2)_6(CF_2)_m\cdot \rightarrow CF_3(CF_2)_{n+m+l2}CF_3 & (4) \\ CF_3(CF_2)_6(CF_2)_n\cdot + CF_3(CF_2)_6CF_2\cdot \rightarrow CF_3(CF_2)_{n+l3}CF_3 & (5) \end{cases}$

**Figure 4.** Proposed polymerization mechanism for HFCVD using HFPO and PFOSF.

to occur in our HFCVD system, and the formation of this radical species may constitute an initiation event analogous to that described in classical polymer chemistry. The diradical species, $CF_2$ (difluorocarbene), generated from the pyrolysis of HFPO would then constitute the propagating species. The proposed polymerization scheme is illustrated in Figure 4. Reaction 1 describes initiation via the pyrolysis of PFOSF. Reaction 2 describes the generation of polymerizable species from the pyrolysis of HFPO,[5,27−29] and reaction 3 is the propagation step. Termination can occur via reaction with an oligomeric fragment or the initiator species, as illustrated in reactions 4 and 5.

The postulated mechanism provides an explanation for the results observed in our work. The enhanced deposition rate of the films from HFPO and PFOSF is consistent with a mechanism in which PFOSF contributes to initiation. The sensitivity of deposition rate to filament temperature shown in Figure 1b indicates that there exists two kinetic regimes over the range of temperatures studied. Below about 460 °C, initiation via the pyrolysis of PFOSF is the rate-controlling step. Indeed, the apparent activation energy of 263 kJ/mol for this region is close to the reported C−S bond energy of 272 kJ/mol.[30] Above 460 °C, the kinetics is dominated by mass transfer limitations, and deposition rate is relatively insensitive to filament temperature.[31] In previous work, the conversion of PFOSF at 460 °C has been reported as greater than 90% for low flow rates.[25,26] The conversion was observed to reach a maximum of about 97% at 530 °C and was almost independent of flow rate above 550 °C.[25] This suggests that above 460 °C, initiation via reaction 1 is no longer limiting.

Initiation by pyrolysis of PFOSF is also evidenced by the higher $CF_3$ concentrations observed in films deposited from both PFOSF and HFPO. These $CF_3$ moieties originate from the initiator radical produced by reaction 1 and are incorporated into PTFE chains as end groups during propagation and termination. When HFPO is used without PFOSF, initiation and termination by $CF_3$ groups is less likely, and films reveal the presence of OH and CO/COO moieties due to the reaction of unterminated $CF_2$ chain radicals with oxygen and moisture.[19] Carboxyl end groups are observed in fluoropolymers produced using bulk processing methods and are generally considered deleterious and unstable.[32−34] $CF_3$ end groups can impart

properties desirable for many applications, including thermal stability and hydrophobicity.[33,35] The presence of the PFOSF initiator radical thus provides a means for selectively endcapping the PTFE chains.

The morphological effect induced by filament temperature suggests that initiation and nucleation may be related in our system. In previous work with only HFPO, it was proposed that nucleation was rate-limiting at low deposition rates, and propagation was rate-limiting at higher deposition rates.[19] In our system, the initiation step is found to be rate-limiting at low temperatures, and a rodlike morphology consistent with nucleation-limited film growth is observed. Conversely, at high temperatures when initiation is no longer limiting, nodular morphology is observed analogous to that observed for propagation-limited film growth. The pyrolysis of PFOSF may thus constitute both an initiation and a nucleation event. This may be due to a higher sticking coefficient for the PFOSF initiator radical than for $CF_2$. Indeed, the sticking coefficient for higher molecular weight fluorocarbon radicals is expected to be higher than that for $CF_2$,[36] which is typically on the order of $10^{-4}-10^{-3}$ in the absence of low-energy ion bombardment.[37,38] The PFOSF initiator species may thus adsorb preferentially to the substrate surface and enable film growth. It is significant that morphological control that was previously available primarily by variation of filament condition and residence time can now be implemented by adding a secondary nucleating species.

## Conclusions

We have demonstrated the successful use of an initiator species in HFCVD of fluorocarbon thin films. The introduction of PFOSF in small concentrations allows the enhancement of deposition rates, increased control over film composition, and control over film morphology. Endcapping by $CF_3$ groups is possible, which may provide benefits such as enhanced thermal stability and higher hydrophobicity for HFCVD films. Conversion of the PFOSF is high, and HFPO utilization efficiency can be increased significantly. The generation of an initiator radical via the pyrolysis of PFOSF may contribute to enhanced nucleation rates during film growth. Initiation and/or nucleation is rate-limiting at low filament temperatures, and mass transport limitations dominate at higher filament temperatures. The demonstration of PFOSF as an initiator species validates the argument that many techniques relevant to classical polymer chemistry may be applied to HFCVD.

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