Polymeric Fluorocarbon Films via Hot-Filament Chemical Vapor Deposition

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Hot Filament Chemical Vapor Deposition (HFCVD) offers the ability to tailor the chemistry of films with polymeric structure. In particular, HFCVD allows for more control over precursor fragmentation pathways than conventional plasma-enhanced CVD (PECVD). HFCVD uses thermal activation in the gas phase to generate reactive species, 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 make it possible to produce polymeric fluorocarbon films spectroscopically similar to poly(tetrafluoroethylene) (PTFE) with the precursor hexafluoropropylene oxide (HFPO; $CF_3CF(O)CF_2$). PTFE has many desirable properties, including a low refractive index and dielectric constant, low coefficient of friction, excellent chemical resistance, and high thermal stability. Thin films of PTFE offer advantages for applications as diverse as optical coatings, biopassivation coatings for implantable devices, and InterLayer Dielectrics (ILDs) in integrated circuits. However, bulk PTFE's high melt viscosity and poor solubility make it difficult to process into thin, conformal, and uniform films. 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.

In conventional polymer chemistry, the use of an initiator allows control over both growth rates and chemical composition of the resulting polymeric film. This understanding has been applied to the HFCVD process. For HFCVD of Poly(tetrafluoroethylene) (PTFE) thin films, the propagation step involves the production of difluorocarbene (CF_2) from the precursor hexafluoropropylene oxide (HFPO). The introduction of perfluorooctane sulfonyl fluoride (PFOSF) in small concentrations produces an initiator radical. This enhances enhances deposition rates and increases control over film composition. Endcapping by CF_3 groups is possible, which enhances thermal stability and results in 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.