Polymer Nanocoatings by Initiated Chemical Vapor Deposition (iCVD)

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ABSTRACT

Initiated chemical vapor deposition (iCVD) is a novel process capable of producing a range of polymeric and multifunctional nanocoatings. The process utilizes hot filaments to drive gas phase chemistry which enables the deposition of true linear polymers rather than the highly crosslinked organic networks often associated with plasma enhanced CVD. Importantly, the object to be coated remains at room temperature, which means that nanothin coatings can be prepared on materials ranging from plastics to metals. The process is also conformal, which means it provides uniform coverage on objects which have small, complex, 3D geometries.

Keywords: chemical vapor deposition, polymer, surface modification, polytetrafluoroethylene

1 INTRODUCTION

For iCVD of polymeric films (Fig. 1), the resistively heated filament serves to drive the decomposition of

- a precursor gas, forming a polymerizing monomeric species, and/or
- an initiator, forming a reactive radical promoting polymerization.

The resulting pyrolysis products adsorb onto a substrate which is generally maintained at room temperature by backside water cooling and react to form a film [1-6]. Since the growth of many polymeric films are subject to absorption limitations, cool substrates are essential to rapid film growth. The filament to substrate stand-off is typically between 1 and 4 cm.

The iCVD method is a nanocoating process in the sense that it can be used (1) to encapsulate objects containing nano-sized features, and (2) produce surfaces with thicknesses in the nanometer range. It is particularly valuable for its ability to create ultrathin layers of insoluble polymers. The combination of chemical flexibility and generic substrate requirements opens up new markets for polymer nanocoating technology.

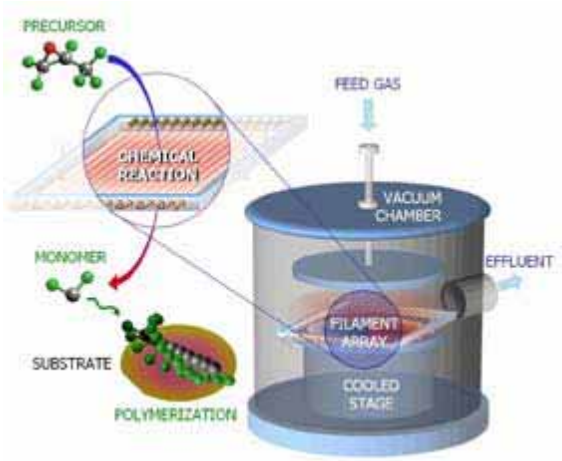

Figure 1. Process schematic for Initiated Chemical Vapor Deposition (iCVD).

2 POLY(TETRAFLUOROETHYLENE) (PTFE)

PTFE is one of the most useful and ubiquitous polymers. It is renowned for its excellent chemical and thermal resistance, biostability, low friction characteristics, and dielectric performance. However, PTFE's stability means that conventional coatings must be prepared from aqueous powder dispersion and cured at high temperatures (300°C+). This limits the nature of substrates which can be coated to those able to withstand curing, and limits the minimum feature sizes which can be used. In contrast, iCVD can be utilized to grow PTFE nanoncoatings directly on the surface of devices. Both porous and dense coatings can be prepared, and these coatings share all of the properties of conventional PTFE surfaces. The process is economical and capable of coating materials at high rates and efficiencies.

The iCVD of PTFE [7,8] has recently been used to create ultrathin (<100 nm) coatings which conformally coat carbon nanotubes (Fig. 2) [9]. In contrast, conventional coating methods result in PTFE coating thicknesses of > 10 μm. Hydrophobic nanocoatings can be deposited on nearly any object, as the substrate remains at ambient temperature during the PTFE iCVD process.

For the iCVD of PTFE, an array of stainless steel filaments, resistively heated to 500 °C, thermally decomposes hexafluoropropylene oxide (HFPO). The filament segments form a parallel array suspended above the deposition surface. Difluorocarbene (CF_2) forms and

polymerizes into PTFE on a substrate that is held at room temperature using backside water cooling. The filament to substrate distance was 1.5 cm.

An initiator, perfluorobutane-1-sulfonyl fluoride, promotes the polymerization. The HFPO and the initiator have flow rates of 23 and 6 sccm, respectively, into a chamber held at 0.5 Torr. Fourier transform infrared (FTIR) spectroscopy of the iCVD PTFE coating on the nanotubes shows strong symmetric and asymmetric CF_2 stretches in the 1250-1150 cm^{-1} region, the same signature as for bulk PTFE [10].

Because of its extremely low surface energy (18 mN/m), smooth PTFE surfaces exhibit a high contact angle with water, 108°[11]. The advancing and receding contact angles of the PTFE iCVD treated carbon nanotube forest are even greater: 170º and 160º, respectively, resulting in nearly spherical water droplets on a macroscopic level when water is deposited on the surface, as shown in Figure 3. This superhydrophobicity is most likely a consequence of secondary roughness produced by the variation in heights between nanotubes [9].

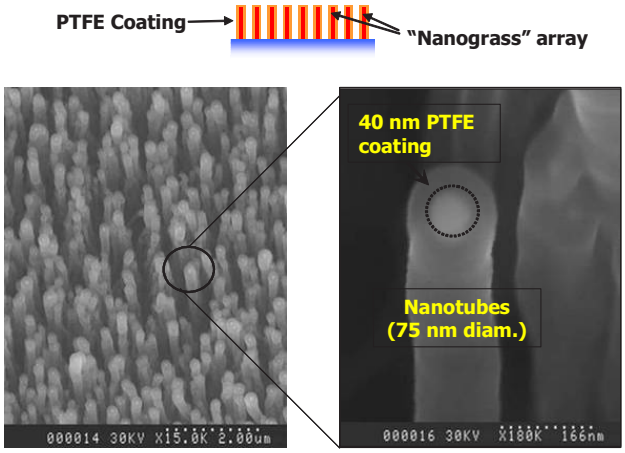

Figure 2. Conformal PTFE coating on an array of carbon nanotubes. Nanotubes have been individually "shrink-wrapped" to provide chemical resistance and hydrophobicity.

Figure. 3 A nearly spherical water droplet resting on a forest of iCVD coated carbon nanotubes.

3 POLY(GLYCIDYL METHACRYLATE) (PGMA)

PGMA contains a pendant epoxy group which can be converted into different kinds of functionalities through ring-opening reactions. In particular, the crosslinking reaction of the epoxy group in PGMA under electron-beam exposure creates the potential for a high-sensitivity negative tone electron-beam resist [12].

iCVD PGMA thin films is a dry processing alternative to the conventional spin casting of resists from solution, representing a potential reduction in volatile organic compounds (VOC) emissions. Using an initiator resulted a low energy vapor deposition process which selectively drives the polymerization of GMA while retaining both its irradiation-sensitive pendent epoxy groups and the linear, uncrosslinked, polymeric structure [4].

PGMA films were deposited on silicon wafers resting on a stage maintained at 25°C using a parallel array of Nichrome filaments (80% Ni/20% Cr) at temperatures between 180°C and 250°C. The power required was less than 3 W. The distance between the filament and the stage was 2.2 cm. Pressure in the vacuum chamber was maintained at 0.5 torr using a butterfly valve. The flow rate of glycidyl methacrylate (GMA) precursor was 2 sccm, while the flow rate of tert-butyl peroxide (TBP) was varied between 0 and 1.7 sccm. The presence of the TBP initiator was found to be essentially for rapid growth at low filament temperatures. Decomposition of the TBP initiator begins at temperatures as low as 150 °C. The formation of tert-butyl radicals initializes the polymerization of GMA, which greatly enhances the film growth rate.

Solution state ^1H NMR confirmed the retention of pendent epoxide groups and the linear polymeric structure in the iCVD PGMA films. The ability to completely dissolve the iCVD film in $CDCl_3$ provides strong evidence of the lack of crosslinking. The chemical shifts and the relative areas of these peaks are almost identical to conventionally synthesized PGMA chemical structure [13]. The intensity differences at around 2 ppm are due to differences in tacticity.

Additionally, the number-average molecular weight (M_n) of PGMA films can be systematically varied from 3,000 g/mol to over 33,000 g/mol by adjusting the filament temperature, the flow ratio of initiator to precursor, and the configuration of the reactor. The ability to control film molecular weight in-situ allows optimization of the tradeoff between the sensitivity improvement and the resolution loss due to the swelling problem in negative-tone resists [12]. The electron-beam sensitivity of iCVD PGMA film (27 $\mu C/cm^2$) was similar to that of PGMA (30 $\mu C/cm^2$) prepared from solution polymerization with approximately the same molecular weight (M_n~11,000 g/mol) [14]. As film molecular weight decreases, the electron-beam sensitivity decreases, but the resolution is greatly improved. The smallest feature obtained for PGMA with M_n 11,000 is

500 nm, while the PGMA film with M_n 4,700 g/mol resolved 80 nm features.

4 ADDITIONAL POLYMERS

Deposition of organosilicon iCVD films onto room temperature substrates from the precursors hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4) occurs at high rates (>1 micron/min) and permits systematic control over the incorporation of cyclic and linear siloxane structures [15]. Filament temperatures ranged from 800 to 1200 °C.

iCVD has also successfully produced copolymer thin films consisting of fluorocarbon and organosilicon groups, where the presence of covalent bonds between the fluorocarbon and organosilicon moieties in the thin films has been confirmed by FTIR, X-ray photoelectron spectroscopy (XPS) and solid-state NMR [16]. Employing an initiator allowed deposition at relatively low filament temperatures (370 °C), and under these conditions, chemical characterization showed that polymerization occurs across the vinyl bonds of V_3D_3, a D3 analog with a vinyl group replacing a methyl group on each Si The resulting films consisted of polymer chains with carbon backbones and siloxane rings as pendant moieties [3]. Additionally, fluoroorganosilicon iCVD copolymer films can be modified to facilitate the surface attachment of peptides such as poly-L-lysine and the arginine-glycine-aspartic acid (RGD) tripeptide [17].

iCVD has also been demonstrated as a novel method for making thin sacrificial layers of polyoxymethylene (POM) [18]. Trioxane, a cyclic trimer of formaldehyde, decomposes cleanly into three molecules of formaldehyde with no side reactions and the kinetics of this reaction is well-known [19]. The decomposition of trioxane is driven by the hot filaments and polymerization onto the cool substrate can be enhanced by a variety of initiators.

4 ACKNOWLEDGEMENTS

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