ALUMINUM AND COPPER CHEMICAL VAPOR DEPOSITION ON FLUOROPOLYMER
DIELECTRICS AND SUBSEQUENT INTERFACIAL INTERACTIONS

DISSERTATION

Presented to the Graduate Council of the University of North Texas in Partial Fulfillment of the Requirements For the Degree of DOCTOR OF PHILOSOPHY

By

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December, 1997
Sutcliffe, Ronald, *Aluminum and Copper Chemical Vapor Deposition on Fluoropolymer Dielectrics and Subsequent Interfacial Interactions*. Doctor of Philosophy (Analytical Chemistry), December, 1997, 96 pp, 4 tables, 30 figures, bibliography, 113 titles.

Fluoropolymers have been proposed as a low capacitance replacement for silica glasses currently used in the microelectronics industry as interlevel dielectrics (ILDs). Fluoropolymers are particularly attractive due to their low dielectric constants (2.4 - 1.9) and chemical inertness. However, there are a number of issues that need to be addressed before fluoropolymers can be successfully integrated into microelectronic devices. One such issue is the area of the metallization of fluoropolymers. Problems with adhesion and diffusion at the metal/fluoropolymer interface have thus far limited the use of fluoropolymer ILDs in integrated circuits (ICs).

This study is an investigation of the chemical vapor deposition (CVD) of aluminum and copper on fluoropolymer surfaces and the subsequent interfacial interactions. The fluoropolymers used are known commercially as Teflon-AF (a co-polymer of 2,2-bis(tetrafluoromethyl)-4,5-difluoro-1,3-dioxole and tetrafluoroethylene) and Parylene AF-4 (a homopolymer of α,α,α',α'-tetrafluoro-p-xylene). CVD was accomplished by condensing the organometallic precursors on the polymer surfaces at low temperatures (~115 K) and subsequent annealing to higher temperatures in ultra-high vacuum. The interactions between the deposition species and the polymer substrates were monitored by x-ray photoelectron spectroscopy (XPS).

It was found that a reaction occurs between trimethylaluminum, the polymer surface, and physisorbed water at or below 300 K, producing Al-F, Al-O, and Al-C bonds. The reaction produces a thermally stable aluminum oxide film on the fluoropolymer
surface. A fluoride concentration gradient exists across the aluminum adlayer with increasing fluorination towards the adlayer/polymer interface. Annealing to higher temperature results in further defluorination of the polymer surface and additional Al-F formation. Aluminum CVD on a Parylene AF-4 surface modified by exposure to •OH flux results in increased aluminum uptake by the polymer surface.

Upon deposition on a Teflon-AF surface, it was found that a substantial amount of Cu(I)hexafluoroacetyletacetate-cyclooctadiene loses the neutral cyclooctadiene ligand by 300 K. Annealing to higher temperature results in the reduction of Cu(I) to Cu(0), with some Cu-F formation.
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ACKNOWLEDGMENTS

This work was funded by the Semiconductor Research Corporation, whose generous support is gratefully acknowledged. The author thanks the Semiconductor Research Corporation for an SRC Graduate Fellowship, the National Science Foundation for an NSF Minority Graduate Fellowship, and Texas Instruments for a Summer Internship.

The author also acknowledges the following personnel for their help in supplying materials and expertise that made this study possible: Wei William Lee, Kelly Taylor, Justin Gaynor, Hal Edwards, Rudye McGlothlin (Texas Instruments), and Mary Anne Plano (Novellus Systems). In addition, I thank Sharon Sutcliffe for editing this document.
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CHAPTER I

INTRODUCTION

One of the most important requirements for microelectronic devices is the reduction of the signal interconnection delay time to a small fraction of all the switching delay times.\textsuperscript{1} One method of lowering this delay time is the use of multilayer devices incorporating low capacitance dielectrics, such as fluoropolymers. Before fluoropolymers can be successfully integrated into microelectronic devices, a number of issues need to be addressed such as: metal deposition on fluoropolymer surfaces, metal/polymer interfacial stability and adhesion, and fluorine diffusion from the polymer into the metal. This study is focused on the chemical vapor deposition (CVD) of metals on fluoropolymer surfaces and subsequent interfacial interactions.

\textit{Fluoropolymer Dielectrics for Microelectronic Applications}

The driving force of microelectronics technology is primarily based on the scaling of the devices to smaller dimensions, which gives higher packing densities along with higher operating speeds.\textsuperscript{2} In current generation integrated circuits (ICs), millions of transistors must be interconnected on each chip. In the next generation the number of interconnections will reach into the billions, which will result in an increase in the complexity of interconnect technology. For current advanced logic ICs, interconnection technology is now the limiting factor in packing density and operating speeds. Additionally, long interconnects also have a significant contribution to the power consumption of microelectronic devices.
The capacitance (C) and the resistance (R) of a metal interconnection result in time constant (τ_{RC}) that determines the flow of charge in high-frequency operation. The choice of materials in integrated circuit fabrication is often dictated by the requirement for a low RC time constant.\textsuperscript{2,3} For the fastest microelectronic devices, it is necessary that the RC (or interconnect) delay time be reduced to a small fraction of the sum of all switching delay times.\textsuperscript{2,4} As feature size scales down to the sub-0.5 micron region, the performance of ultra-large scale integration (ULSI) is dominated by the metal interconnect level.\textsuperscript{2,5} The gain in device speed at the metal-oxide semiconductor (MOS) device gate level is offset by the propagation delay at metal interconnects due to the increased RC time constant.\textsuperscript{2,5} For a given feature size, the RC time delay can be reduced by the incorporation of high-conductivity metals and/or the low permittivity dielectric materials. The use of low-k* materials has the additional advantage of reducing inductive cross-talk between neighboring metal lines.

While copper appears to be the only high conductivity metal suitable for integration in microelectronic devices, there are a number of low-k dielectric materials that are possible candidates for integrated circuit fabrication (Table 1). Currently silica glasses are the predominant dielectric materials in microelectronic devices and are expected to remain the predominant dielectric material for 0.25μm technology, with an increased use of fluorinated SiO\textsubscript{2} probable in the near future.\textsuperscript{3,7} Fluoropolymers are one of the materials that have been proposed for use as a low-k replacement for SiO\textsubscript{2}.\textsuperscript{2,8-12} Fluoropolymers have attracted attention for use as low-k dielectrics due to their extremely low dielectric constant and chemical inertness.\textsuperscript{2,8-12} The most well known of these is poly(tetrafluoroethylene) or PTFE. Although PTFE is inert, and has a low dielec-

\* The relative dielectric constant (k) is given by:

\[ k = \varepsilon / \varepsilon_0 \]

where \( \varepsilon \) is the dielectric constant of the material and \( \varepsilon_0 \) is the permittivity of a vacuum.\textsuperscript{6}
Table 1. Projected dielectric materials for future device technologies.\textsuperscript{7}

dielectric constant, and high mechanical strength, its application to the electronic industry has been limited due to poor adhesion and creep associated with its high degree of crystallinity.\textsuperscript{2,5,10,13-23} Alternative fluoropolymers have been developed to improve upon the mechanical properties of PTFE, while maintaining its electrical properties. Two of these alternative fluoropolymers are the basis of this study, known commercially as Teflon-AF and Parylene AF-4.

Teflon-AF is a co-polymer of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole and tetrafluoroethylene (TFE).\textsuperscript{10,11,24,25} The incorporation of oxygen into the structure of Teflon-AF (TAF) imparts amorphous character.\textsuperscript{10,11,24,25} TAF films have been deposited on substrates via laser ablation, thermal deposition, and cast from solution.\textsuperscript{10,11,24,25} Their bulk structure (Fig. 1) has been characterized by infra-red spectroscopy,\textsuperscript{25} atomic force microscopy,\textsuperscript{11} and x-ray diffraction.\textsuperscript{10,11} The typical properties of TAF thin films are given in Table

![Figure 1. Bulk structure of Teflon-AF. Co-polymer ratios (m/n) for commercially available variants: AF 1600: m/n = 1/3, AF 2400: m/n = 1/8.](image-url)
Table 2. Properties of Teflon-AF 1600 and Parylene AF-4 films.

2. Teflon-AF is available commercially in two grades: AF 2400 (87 mol% dioxole) with a $T_g$ of 240°C and AF 1600 (65 mol% dioxole) with a $T_g$ of 160°C. The TAF films used in this study were 65 mol% dioxole (AF 1600).

Parylene AF-4 (PAF) is poly($\alpha$, $\alpha$, $\alpha'$, $\alpha'$-tetrafluoro-p-xylene) with a bulk structure as shown in Figure 2. PAF films are vapor deposited, which is inherently cleaner than a conventional spin-on process. The properties of PAF thin films are given in Table 2. Though PAF has been available in commercial quantities for a relatively short time, it shows promise for use in the microelectronics industry as an interlevel dielectric (ILD). This is primarily due to its excellent thermal stability (m.p. > 500°C) relative to TAF ($T_g = 160°C - 240°C$).

However, there are a number of issues that need to be addressed before fluoropolymers can be successfully integrated into microelectronic devices; one of these is the area of fluoropolymer metallization. Most metallization for microelectronics today is performed by the physical vapor deposition (PVD) processes of evaporation and sputter-

\[
\begin{align*}
\begin{array}{c}
\text{F} \\
\text{C} \\
\text{F} \\
\text{F}
\end{array}
\end{align*}
\begin{align*}
\begin{array}{c}
\text{F} \\
\text{C} \\
\text{F} \\
\text{F}
\end{array}
\end{align*}
\]

Figure 2. Molecular structure of Parylene AF-4.
ing.\textsuperscript{2,25} While there have been a number of reports on the successful PVD metallization of fluoropolymer thin films, PVD processes typically involve high kinetic energies (\( \geq 1 \text{ eV} \)) for the deposition species.\textsuperscript{26} Sputter techniques, for example, can involve the deposition of species at kinetic energies as high as 10 eV.\textsuperscript{26} This is particularly a concern for the metallization of mechanically soft (relative to SiO\textsubscript{2}) materials, such as polymers, where surface roughening can occur due to ablation of the polymer surface by the high kinetic energy bombarding species. To overcome the problems involved with PVD, there has been considerable interest in metallization using chemical vapor deposition.\textsuperscript{26-28}

**Chemical Vapor Deposition of Metals for Microelectronic Applications**

Chemical vapor deposition (CVD) is a process for depositing solid elements and compounds by reactions of gas-phase molecular precursors. CVD processes typically occur at lower kinetic energies (\(< 1 \text{ eV}\)) than sputter techniques (1 - 10 eV). Also, CVD processes are non-directional in that they are dependent upon precursor partial pressure.\textsuperscript{26-28} Shrinking device geometries require metal deposition in high aspect ratio (where vertical dimensions are much greater than horizontal detentions) vias and trenches (Fig. 3). Therefore, given the isotropic nature of CVD processes, they can be used to deposit

![Figure 3. Schematic of step coverage over a high aspect ratio structure. (a) Step coverage = 1, (b) step coverage < 1.](image-url)
highly conformal films on high aspect ratio structures. In contrast, PVD techniques are “line-of-sight” deposition processes, where the substrate to be coated must be placed directly in front of the PVD source. One result of this directionality is that it is difficult to physically deposit films on high aspect ratio structures and maintain good conformality (step coverage), which is defined as the thickness ratio of the deposited film on the structure sidewall to that deposited on the top surface (Fig. 3).

An additional advantage of CVD processes over conventional PVD techniques is that it is possible to deposit material selectively on some substrate materials in the presence of others. This is because deposition via CVD techniques is controlled by the surface chemistry of the precursor/substrate pair. It is therefore possible to chemically

![Figure 4. Schematic for applications of blanket and selective metal CVD for microelectronic applications.](image-url)
deposit material in either a "blanket" mode, where all the surfaces receive material, or a "selective" mode, with material deposition occurring on some regions but not on others. When blanket mode is used, it must be followed by an etchback step as shown in Figure 4.

In the microelectronics industry, CVD processes are used in the deposition of a number of compounds, particularly oxides and nitrides. The only metal currently deposited on an industrial scale using CVD techniques is tungsten for via fill, through the reduction of tungsten hexafluoride. However, the lower resistivities of aluminum (2.71 μΩ-cm) and copper (1.71 μΩ-cm), relative to tungsten (5.39 μΩ-cm), have been the driving force behind research in aluminum and copper CVD.

Aluminum CVD

There has been considerable interest in aluminum deposition via chemical vapor deposition. Metallic aluminum thin films have been successfully deposited using a variety of organo-aluminum compounds, particularly triisobutylaluminum (TIBA) and trimethylaluminum (TMA). The surface chemistry of aluminum CVD from TIBA, as detailed by Bent and co-workers, goes as:

\[
\begin{align*}
(I) \quad & \text{Al(CH}_2\text{CH(CH}_3\text{)_2})_2 \rightarrow \text{AlH(CH}_2\text{CH(CH}_3\text{)_2})_2 + \text{CH}_2=\text{C(CH}_3\text{)_2} \\
(II) \quad & \text{AlH(CH}_2\text{CH(CH}_3\text{)_2})_2 \rightarrow \text{Al} + \frac{3}{2}\text{H}_2 + \text{CH}_2=\text{C(CH}_3\text{)_2}
\end{align*}
\]

Briefly, the isobutyl ligands of the precursor can readily undergo β-hydride elimination to form isobutylene and hydrogen, which then desorb leaving metallic aluminum. Unfortunately, TIBA decomposition yields relatively low (~0.1 Torr) vapor pressure aluminum alkyl hydride residues, which requires heating of the precursor reservoir and inlet system.
This causes some decomposition of the source to di-isobutyl aluminum hydride, which oligomerizes to a low vapor pressure trimer.28

The dissociation of TMA is dependent upon inter-molecular interactions with reactive surface groups, particularly oxygen-containing moieties.32,33 In a study of the chemisorption of TMA on silica, Rogers and co-workers33 reported that TMA reacts with both surface hydroxyl moieties and siloxane bridges to form aluminum species bound to the silica surface through oxygen bridges and methane. Similarly, White and co-workers32 reported the formation of an aluminum oxy-carbide complex upon the interaction of TMA with a polyvinyl alcohol (PVA) surface, with Al oriented toward the surface (Fig. 5). One drawback to using TMA for the deposition of metallic aluminum is the high carbon content typically found in Al thin films formed from TMA.26,28

In addition to metallic Al films, there have been a number of recent studies on the chemical vapor deposition of aluminum oxide (AlOx) films using TMA.39,40,44 AlOx thin films have been proposed as adhesion promoters and/or diffusion barriers for both aluminum and copper metallic films.5,45,46 CVD AlOx thin films have been deposited using TMA with H2O2, N2O, and H2O as oxidizing agents, using thermal and plasma-assisted CVD techniques.39,61-64

Figure 5. Representation of the formation of aluminum-oxygen-carbon complex upon the interaction of trimethylaluminum with poly(vinylalcohol) surface.32
Copper CVD

The chemical vapor deposition of copper has been an area of rapidly expanding research over the last few years. CVD Copper precursors generally fall into two categories, Cu(II) and Cu(I) compounds. The Cu(II) precursors that have been used with the most success for deposition of copper films are copper(II) β-diketonates in general, and copper(II) bishexafluoroacetylacetone (Cu(II)(hfac)₂) in particular. Studies show the deposition of metallic copper thin films as follows:

\[
\text{(III)} \quad \text{Cu(II)(hfac)}_{2}^{(g)} \rightarrow \text{Cu(I)(hfac)}_{(s)} + \text{hfac}^{(s)}
\]
\[
\text{(IV)} \quad \text{H}_2^{(g)} \rightarrow 2\text{H}^{(s)}
\]
\[
\text{(V)} \quad \text{H}^{(s)} + \text{hfac}^{(s)} \rightarrow \text{hfacH}^{(g)}
\]
\[
\text{(VI)} \quad 2\text{Cu(I)(hfac)}_{(s)} \rightarrow \text{Cu}^{(s)} + \text{Cu(II)(hfac)}_{2}^{(g)}
\]

where Cu(II)(hfac)₂ dissociatively adsorbs on a surface as Cu(I)(hfac)ₙ and hfacₙ (reaction III). The adsorbed Cu(I) species then undergo a disproportionation reaction to form metallic Cu and Cu(II)(hfac)₂, which desorbs (reaction VI). Reaction V must occur or reaction VI will not. However, step V requires step IV, which becomes a limiting step due to the low reaction probability for H₂ on Cu. In the absence of hydrogen, hfac cannot desorb cleanly into the gas phase and will tend to decompose on the surface, resulting in the incorporation of impurities into the growing film. However, the improbability of the dissociation of molecular hydrogen on the growing metallic Cu surface can significantly reduce the rate of film growth. To alleviate this reduction, recent studies indicate that the use of atomic hydrogen can result in substantially increased deposition rates for metallic copper from Cu(II)(hfac)₂.
More recently, the focus has shifted to copper(I) compounds, especially copper(I) β-diketonates. The copper(I) β-diketonates show great promise as copper CVD precursors. These compounds have the general formula $\text{Cu(β-diketonate)L}$, where $L$ is a neutral ligand and the β-diketonate is usually hexafluoroacetylacetonate (hfac). The neutral ligand can be an alkene, trimethylphosphine, or vinyltrimethylsilane (VTMS). Copper thin film deposition using Cu(I) precursors is very similar to deposition using Cu(II)(hfac)$_2$, as shown below.

\[
\begin{align*}
\text{(VII)} & \quad \text{Cu(I)(hfac)}L_{(g)} \rightarrow \text{Cu(I)(hfac)}_{(s)} + \text{L}_{(s)} \\
\text{(VIII)} & \quad \text{L}_{(s)} \rightarrow \text{L}_{(g)} \\
\text{(IX)} & \quad 2\text{Cu(I)(hfac)}_{(s)} \rightarrow \text{Cu}_{(s)} + \text{Cu(II)(hfac)}_{2(g)}
\end{align*}
\]

The Cu(I) precursor dissociatively adsorbs on the surface as Cu(I)(hfac)$_{(s)}$ and L$_{(s)}$ (reaction VII), the latter of which then desorbs. Two adsorbed Cu(I)(hfac) molecules then undergo a disproportionation reaction (step IX) to form metallic copper and Cu(II)(hfac)$_2$. The Cu(II) compound then desorbs leaving a clean metallic film. While similar to Cu deposition from Cu(II)(hfac)$_2$, copper CVD using Cu(I) precursors has an advantage in that the starting material acts as its own reducing agent, obviating the need for an external reducing agent. Copper(I)(hexafluoroacetylacetonate)(1,5-cyclooctadiene) (Cu(I)(hfac)(COD)) has been used to deposit copper without an external reducing agent on both metals and SiO$_2$ at temperatures as low as 130°C, with resistivities as low as 1.9 $\mu\Omega$-cm and at growth rates up to 3750 Å/min. Similar low temperature deposition rates have been achieved for other Cu(I) precursors on a variety of substrates. The achievement of such high deposition rates at relatively surface low temperatures make these molecules attractive as CVD precursors, particularly for deposition on polymers.
**CVD Metallization of Fluoropolymers**

The metallization of fluoropolymers via chemical vapor deposition offers a number of advantages over conventional sputter techniques, particularly in the reduction of possible polymer surface damage caused by the high kinetic energy of the sputtered species. However, the dependence of CVD upon a chemical interaction between the precursor and substrate is the source of a potential problem for the CVD metallization of fluoropolymers. Fluoropolymers are typically non-reactive, low surface energy materials, which accounts for the “non-stick” property popularly associated with Teflon.  

This chemical inertness of the fluoropolymer surface decreases the probability of interaction between the surface and the precursor species necessary for successful precursor decomposition and subsequent metal deposition. Two techniques to increase the interaction between the polymer surface and the CVD precursor are (1) condensation of the precursor at low substrate temperatures (~100 K) and (2) modification of the fluoropolymer surface prior to precursor exposure.

**Precursor Exposure at Low Substrate Temperature**

The surface concentration ($\sigma$, in molecules/cm$^2$) of adsorbed molecules on an initially clean surface is given by the product of the incident flux ($F$) and the residence time ($\tau$):  

$$\sigma = F \tau$$

The residence time of an adsorbed molecule is given by:  

$$\tau = \tau_0 \exp (\Delta H_{\text{ads}}/RT)$$

where $\tau_0$ is a function of the surface atom vibration time (~10$^{-12}$ sec), $T$ is the temperature, and $R$ is the gas constant. Since the residence time of an adsorbed species is exponentially related to the inverse of temperature, decreasing the substrate temperature will result
in substantially increased residence times and surface concentrations. Therefore, CVD precursor exposure to the polymer surface at low temperatures (~100 K) results in condensation of the unreacted precursor on the polymer surface. Condensation of the precursor maintains a large concentration of the precursor in close proximity to the fluoropolymer surface. Thermal energy added to the system will result in a reaction between the condensed species and the polymer surface, provided the activation energy for the reaction is lower than the activation energy for precursor desorption.\(^{38}\)

However, there are a number of drawbacks to precursor deposition at reduced temperatures, particularly for CVD for microelectronics applications. First, should the energy of activation for desorption be lower than the activation energy for reaction, the precursor will simply desorb from the polymer surface unreacted. Second, the thermal cycling would induce large amounts of stress due to the differences in the coefficients of thermal expansion of the layer materials.\(^{59}\) This thermally induced stress could lead to cracking or delamination of the layer materials.\(^{59}\) A third disadvantage of low temperature deposition is condensation of water or other contaminants from the processing chamber ambient along with the CVD precursor. The presence of water is of particular concern with aluminum CVD, as organoaluminum compounds are known to be highly hydrophoric.\(^{36,43}\) Al CVD in the presence of water will form aluminum oxide films instead of metallic aluminum.\(^{36,43}\) Because of these disadvantages, precursor exposure at greatly reduced temperatures is of doubtful industrial viability.

\textit{Fluoropolymer Surface Modification}

An alternate method of increasing the reactivity of fluoropolymer surfaces to CVD precursors is through surface modification by introduction of reactive surface moieties. Such modification may be accomplished by a variety of techniques, including chemical
attack in the presence of ion beams, \textsuperscript{18,19,60,61} electron beams, \textsuperscript{62,63} plasmas, \textsuperscript{11,23,64} direct chemical attack, \textsuperscript{65,66} lasers, \textsuperscript{25,67,68} or uv radiation. \textsuperscript{10} At present, cold plasmas are the most commonly used techniques for polymer surface modification. \textsuperscript{2,11,23,67,68} Plasmas are well known to generate significant quantities of gaseous ionic and free-radical species, which react with and modify the polymer surface. Hydrogen plasmas have been shown to induce substantial defluorination of fluoropolymer surface due to the formation of volatile HF species. \textsuperscript{23} Fluoropolymers also exhibit significant surface modification in the presence of oxygen containing plasmas due to the incorporation of oxygen species on the polymer surface, leading to enhanced metal adhesion upon subsequent metallization. \textsuperscript{14,23} However, in addition to the formation of reactive gaseous species, plasmas also generate significant vacuum ultraviolet radiation (vuv, $\lambda < 175$ nm) of sufficient intensity to break polymer chains and thereby damage the bulk polymer. \textsuperscript{23}

Thermally generated gaseous free radicals have been proposed as a surface modification method with reduced vuv radiation. \textsuperscript{23} It has been shown that gaseous radicals can be generated by flowing a reactant gas over a resistively heated refractory metal filament. \textsuperscript{23,55,69} In a study of the generation of atomic deuterium by passing the molecular gas over a heated tungsten filament heated to $\sim$2000 K, Nuesca et al\textsuperscript{55} reported a D/D$_2$ yield in the range of 30%. Thermally generated atomic hydrogen has been shown to remove surface hydrocarbon contaminants on TiN substrates, leading to enhanced film growth during subsequent CVD metallization. \textsuperscript{53} Sun et al\textsuperscript{23} successfully demonstrated the hydroxylation of a PTFE surface using thermally generated $\cdot$OH free radicals. Fluoropolymers with hydroxylated surfaces have been shown to exhibit increased adhesion and wettability toward metal adlayers. \textsuperscript{14,23} In addition to the formation hydroxyl radicals, the thermal dissociation of H$_2$O on refractory metals is known to lead to the formation of atomic
hydrogen and oxygen species.\textsuperscript{23} Fluoropolymer surfaces exposed to atomic hydrogen and oxygen species have shown enhanced metal adhesion and wettability.\textsuperscript{23}

\textit{Metal/Fluoropolymer Adhesion and Diffusion}

Microelectronics manufacturers use multilayer devices to provide a large number of interconnections in a very small volume. These multilayer devices are composed of alternating layers of metal and insulator, except where via holes permit contact between the different metal layers. The area where the metal contacts the insulator forms an interface. A number of interfacial issues must be addressed before fluoropolymers can be successfully integrated as microelectronic insulators. Among these issues are adhesion of the metal to the fluoropolymer and diffusion across the interface.

Both the polymer and metal films have thermal and hygroscopic expansion coefficients, which may differ between the components by orders of magnitude.\textsuperscript{1,2} The processes involved in IC fabrication induce interfacial stresses, which can cause severe delamination and failure.\textsuperscript{1,2} This destruction is inhibited by strong interfacial adhesion. Therefore, issues concerning interfacial adhesion are critical to device fabrication. Adhesion between two materials occurs from either physical bonding (van der Waal's forces) or chemical bonding across the interface. It is chemical bonding that is strong enough to provide stability when subjected to thermal or mechanical force.\textsuperscript{2} Fluoropolymers are notorious for their chemical inertness to metals. There has been a large amount of research recently to address this problem, with the focus primarily on polymer surface modification to enhance the polymer-metal reactivity.\textsuperscript{2,13,14,17,19,21,23}

A second method of increasing the metal-fluoropolymer adhesion is the use of adhesion promoters. Adhesion promoters are effective because they cause chemical bonding at the promoter-substrate interface and at the promoter-metal interface. They also
have the additional advantage that they may also act as diffusion barriers. Diffusion is a critical interfacial issue for fluoropolymer integration, both as metal diffusion into the polymer and fluorine diffusion into the metal. Copper is known to diffuse into a variety of materials, including SiO$_2$ and polymers. A number of studies have shown metal fluoride formation during fluoropolymer metallization, particularly for aluminum metallization. Therefore, an ideal adhesion promoter should also act as a diffusion barrier. There has been a large amount of work on the application of a variety of metallic systems as diffusion barriers/adhesion promoters. Thus far, however, the focus has been primarily on barriers to metal diffusion into dielectric substrates. Sutcliffe et al. proposed the use of CVD aluminum oxide (AlOx) thin films as barriers to fluorine diffusion. AlOx exhibits a high affinity for fluorine when deposited on fluorocarbon substrates. The AlOx defluorinates the polymer surface, forming a thermally stable fluorinated aluminum oxide (F-AlOx) adlayer. Tabulated bond energy data show the fluorination of aluminum oxide increases bond energies of both the Al-F and the Al-O bonds, relative to pure aluminum fluorides and aluminum oxides respectively. Therefore, F-AlOx acts a thermodynamic “getter” for fluorine, stopping further fluorine diffusion into subsequently deposited metal films, much the same as a native oxide layer prevents the further oxidation of metallic aluminum.

*Ultra-High Vacuum Techniques*

The majority of surface analytical techniques currently in use are carried out in ultra-high vacuum (UHV). This is done to prevent the contamination of the surface under investigation by contact with gases other than those of interest. UHV is roughly defined as the pressure regime from 10$^{-8}$ Torr to 10$^{-12}$ Torr (10$^{-6}$ Pa to 10$^{-10}$ Pa). Surface science experiments are normally carried out at these pressures to reduce the rate of collision
between gas phase molecules and surface sites, to the point where a cleaned surface will remain clean long enough to complete most experiments. For example, at a pressure of $7.5 \times 10^{-9}$ Torr, an $O_2$ molecule at room temperature will impact each surface site at least once in 43 minutes. For a sticking coefficient of one (where every impact results in adsorption of the gas phase species), this results in a monolayer formation time of 43 minutes. In practice, it is rare that each collision results in a new surface species, particularly in the case of low reactivity substrates such as fluoropolymers. Therefore, the actual monolayer formation time may be many times longer than 43 minutes.

**X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy (XPS) involves the use of photons to eject a core level electron, whose energy is then measured (Fig. 6). Most commercially available systems utilize low energy x-rays (Kα) from a magnesium (1253.6 eV) or aluminum (1486.6 eV) source. The specimen is bombarded with photons of a known frequency ($\nu$), of energy:

$$E = h\nu$$

The kinetic energy of the ejected electron is given by:

$$KE = h\nu - BE - \varphi$$

where $BE$ is the binding energy of the electron and $\varphi$ is the work function of the system. The value of the work function is dependent upon both the sample and the spectrometer, and (to a first approximation) is the difference between the Fermi level of the system and the vacuum level. XPS energies are normally given in electron volts (eV, $1.602 \times 10^{-19}$ J).

The ejection of electrons from an insulator causes the surface to be positively charged. This will cause the photoelectron peaks to move to a lower kinetic energy.
Figure 6. Schematic of the photoemission process.

(higher binding energy), which could result in erroneous chemical state identification. While there are a number of techniques to reduce or eliminate surface charging (such as the use of a low energy electron flood gun or the deposition of a monolayer of a conducting material on the insulator surface), these methods are not always compatible with polymer samples. However since charging shifts all peak energies uniformly, charge referencing can be accomplished using either the difference in the change in the energy of an Auger peak and an equivalent photoelectron peak (Auger parameter), or by referencing an element of known chemical environment, such as the C(1s) peak for hydrocarbon contaminants. For fluoropolymers, charge referencing is normally accomplished by referencing the F(1s) photoelectron peak for the -CF₂⁻ to ~689 eV. This is possible because the extreme electronegativity of fluorine makes it relatively insensitive to secondary chemical shift effects.

By measurement of the photoelectron kinetic energy and knowing the energy of the incident photon, the electron binding energy can be determined. It is the photoelectron binding energy that provides elemental and chemical information from the sample. The
binding energy differs for different orbitals of the same atom and for the same orbital for
different atoms. Further, since electron induction by neighboring atoms changes the
electron density at the emitting atom, there is a slight chemical shift which indicates the
chemical environment of the emitting atom. For reasonably uncomplicated samples,
this permits the quantitative evaluation of the elemental and chemical composition of the
sample.

The mean free path of an emitted photoelectron is dependent upon its kinetic
energy. The mean free path ($\lambda$) is the distance over which the intensity falls to 1/e of
its original value. Therefore, 95% of the intensity is lost by $3\lambda$. This value is the
normally accepted probe depth for XPS in perpendicular (surface normal) mode, giving a
measurement precision of 5%. While mean free path is dependent upon the sample
matrix and kinetic energy of the photoelectron, it is generally accepted to be within the
range of ≤30Å, giving a probe depth of ≤100Å. To reduce this distance, the sample
detector is rotated away from the surface normal toward the horizontal (take-off angle
resolution, Fig. 7). This reduces the sampling depth to $3\lambda \cos \theta$, where $\theta$ is the analyzer
angle measured from the surface normal. X-ray photoelectron spectroscopy in surface
normal mode ($\theta = 0^\circ$) was used in this study to verify surface composition and to monitor
the reactions under study. Take-off angle resolved spectroscopy ($\theta = 60^\circ$) was used to
determine adlayer composition.

Atomic Force Microscopy

A recently developed technique for determining surface morphology is atomic
force microscopy (AFM). AFM is similar to scanning-tunneling microscopy (STM) except
that while STM requires current between the probe and the sample surface, AFM mea-
sures the van der Waals forces between the surface and the probe and can therefore be
Figure 7. Schematic of "take-off angle resolution". The effective escape depth of the emitted photoelectron decreases by $\cos \theta$, where $\theta$ is the angle of the analyzer normal to the sample surface.

used to study insulating surfaces. This is accomplished by bringing a tip of atomic dimensions close to a surface in atomic ranges of 0 - 5Å by piezoelectric ceramics. The piezoelectric ceramics can expand (or contract) by the application of an external voltage on the order of about one angstrom per volt. As the probe tip nears the surface, the tip-surface distance can be stabilized by a force that is equal and opposite to the van der Waals forces operating between the tip and the surface. The opposing force is normally supplied by a spring. The measurement of the stabilization force can be accomplished by a variety of means. In this study, the AFM uses a photodetector to monitor a laser beam reflected from a spring cantilever mounted to the probe tip. The instrument is operated in "tapping mode" where the oscillating probe encounters the surface, which changes the amplitude of the vibration. The probe height is then adjusted to maintain a constant amplitude of oscillation across the surface. By mapping the voltage applied to the piezoelectric used for probe height adjustment as a function of x-y position, a topological map is obtained. AFM was used here to obtain surface roughness data for a
vapor deposited Parylene AF-4 surface. This data was then compared to published surface roughness data for spun-on Teflon-AF surfaces, similar to those used in this study.\textsuperscript{11}

Chapter References


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CHAPTER II

CHARACTERIZATION AND ALUMINUM METALLIZATION

OF A PARYLENE AF-4 SURFACE

Introduction

The study of low dielectric constant materials is an area of rapidly growing interest due to their applications in the microelectronics industry. The application of materials with lower dielectric constants than the materials (silica glasses, $k \approx 3.7 - 4.2$) currently used in microelectronic applications would significantly reduce RC delay and enhance interconnect performance. A number of organic polymers have been investigated for use as interlayer dielectrics,\textsuperscript{1,11} including fluoropolymers and Parylenes ($p$-xylene polymers). Though fluoropolymers generally have low dielectric constants (2.1 to 1.9), their application has thus far been limited by poor metal adhesion.\textsuperscript{1,7,8,12} While the dielectric constants for Parylene variants are slightly higher (2.6 to 2.3), they exhibit better adhesion properties and lower moisture uptake than fluoropolymers.\textsuperscript{9,13}

Parylenes can be vapor deposited, a process which is inherently cleaner than the conventional spin-on process.\textsuperscript{13} A fluorinated version, called Parylene AF-4, has recently become available and has excellent thermal stability (m.p. > 500°C) and a dielectric constant of 2.28.\textsuperscript{13} Parylene AF-4 (also known as AF-4) is poly($\alpha,\alpha,\alpha',\alpha'$-tetrafluoro-$p$-xylene), as shown in Figure 8. In addition to its low dielectric constant, AF-4 exhibits a low dissipation factor (< 0.001) and very low moisture absorption (< 0.1%).\textsuperscript{13}

Metallization by metal-organic chemical vapor deposition (MOCVD) is of particular interest to the microelectronic industry with respect to the use of low dielectric con-
stant polymers. Low dielectric polymers will yield the highest gains in signal processing speeds for architecture dimensions below 0.5 microns.\textsuperscript{14} In addition, the improved step coverage of MOCVD compared to sputtering techniques is of critical importance, particularly if reflow techniques cannot be used due to polymer incompatibility with the required temperatures. Also, sputter deposition of metals on polymer surfaces can result in metal atoms deep with the polymer and surface roughening due to ablation of the polymer surface by the high kinetic energy bombarding species. Whatever method of metal deposition is used, the thermal stability of the metal/polymer interface is a critical requirement.

In this work, atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS) were used in the surface characterization of Parylene AF-4. The AF-4 surface was then exposed to trimethylaluminum (TMA) at reduced temperature and subsequently annealed to higher temperatures. These studies show that TMA will react with the Parylene AF-4 surface and water adsorbed from the ambient at or below 300 K. The reaction forms a thermally stable adlayer on the polymer surface with aluminum-carbide species at the metal/polymer interface, aluminum-oxide on the adlayer surface, and fluorinated aluminum species in between. Annealing to higher temperatures causes further defluorination of the polymer surface and increasing Al-F bond formation. Neither the presence of metallic aluminum nor diffusion of aluminum into the bulk polymer was observed.
Experimental

The Parylene AF-4 films used in this study were vapor-deposited by pyrolitic decomposition of the cyclic dimer in an experimental deposition system by personnel at Novellus Systems using the Gorham process. This process involves vaporizing the solid dimer to a pressure of ~100 mTorr, then allowing the gas to flow down a pressure gradient into a pyrolizer (650 °C) where dimer cracks into the monomer (tetrafluoro-p-xylene). The monomer gas proceeds into the deposition chamber (20 - 40 mTorr) and condenses onto a cold (0 °C) wafer surface where it polymerizes to give the AF-4 film. The AF-4 samples used in this study were deposited at a rate of 150 Å/min to a thickness 5000 Å on 1000 Å SiO₂ on silicon. The refractive index of the as-deposited film was measured using a variable angle, variable wavelength ellipsometer and found to be 1.5584 in-plane and 1.4393 out-of-plane.

Atomic force microscopy was used to determine the surface roughness of the AF-4 sample. The AFM (Digital Instruments) uses a photodetector to monitor a laser beam reflected from a spring cantilever mounted to the probe tip. During image acquisition, the instrument was operated in "tapping mode" where the oscillating probe encounters the surface which changes the amplitude of the vibration. The probe height is then adjusted to maintain a constant amplitude of oscillation across the surface. By mapping the voltage applied to the piezoelectric used for probe height adjustment as a function of x-y position, a topographical map is obtained. Scan areas were 1.00 µm², 25.00 µm², and 100.00 µm².

XPS and CVD experiments were carried out in a UHV surface analysis system. The turbomolecularly pumped UHV system has a base pressure of 5 x 10⁻¹⁰ Torr. The system is equipped with a separate CVD chamber with a base pressure of 1 x 10⁻⁴ Torr. Pressure in both chambers was monitored with nude ion gauges calibrated for N₂, mounted out of direct line of sight to minimize electron damage to the sample. The sample
was mounted on a Ta foil sample holder spot welded to Ta leads. Sample temperature
control was maintained by a combination of resistive heating and liquid nitrogen cooling of
the sample holder. Temperatures were monitored by a chromel-alumel thermocouple spot
welded to the sample holder. The sample was annealed by ramping the sample to the
required temperature and maintaining that temperature for 10 minutes. The sample was
allowed to return to base temperature prior to the taking of spectra.

XPS spectra were obtained using an unmonochromatized MgKα x-ray source
(Phi model 1427) operated at 15 keV and 300 W and a hemispherical analyzer (VG
100AX) operated in the constant pass energy mode (50 eV pass energy). Take-off angle
resolved spectra were obtained by rotating the sample 60° off surface normal, relative to
the analyzer. The analyzer energy scale was calibrated using Au and Cu standards, accord-
ing to established procedure.16 XPS data were analyzed using commercially available
software.17 The full width at half-maximum (FWHM) for the fitted spectra was kept
constant within each atomic species for all spectra of that species. The number of environ-
ments used for deconvolution of a spectral envelope was kept to the minimum number
necessary to obtain an $r^2$ value $> 95\%$. The variation in absolute signal intensity for the
XPS system used in these experiments has been determined experimentally to be $\leq 4\%$.

The exposure of fluoropolymers to x-rays is known to induce defluorination and cross-
linking.6 To minimize x-ray induced damage, exposure of the sample to x-ray flux was
limited to that needed for the acquisition of spectra. The observed binding energies were
affected by sample charging during data acquisition. Therefore the XPS data were refer-
enced to a F(1s) binding energy of 689.1 eV, which is consistent with the published values
for fluorine in a fluorocarbon environment.4,5,8

Semiconductor grade (99.999% pure) trimethylaluminum (TMA) was obtained
from Akzo Nobel Chemicals, Inc. (TMAL-9577) and was introduced directly into the
CVD chamber using a metering valve. The composition of the organometallic precursor was verified by measurements with a quadrapole mass spectrometer. Exposures were performed at elevated (540 K) and reduced (112 K) temperatures. Precursor exposures are reported as a product of background pressure and time of exposure (1 Langmuir (L) = $10^{-6}$ Torr-sec). Exposures have not been corrected for effects of directional dosing or ion gauge sensitivity. The sample was subsequently transferred to the UHV chamber for analysis by XPS. Anneals were carried out in the UHV chamber (in series) with XPS spectra taken after each annealing. To minimize changes in the x-ray flux, the sample was not moved after introduction into the UHV chamber other than rotation to obtain angle resolved spectra.

**Results**

A. *Surface Analysis of Parylene AF-4*

The atomic force micrograph for the 5.00x5.00 μm scan is shown in Figure 9 and surface roughness data for all AFM scans are given in Table 3. The average root-mean-square (rms) of the AF-4 surface profile (5.54 nm) compares favorably with that of spin-
Table 3. AFM surface roughness data for vapor deposited Parylene AF-4 coated Teflon AF (6.27 nm). Water contact angle measurements show a contact angle of 97°. This indicates the AF-4 surface to be hydrophobic, though somewhat less so than amorphous Teflon (118°).

The x-ray photoelectron spectra for the virgin Parylene AF-4 surface are given in Figure 10. The observed binding energies were affected by sample charging during the acquisition of spectra. Published charge compensation studies of fluoropolymers report F(1s) binding energies for fluorine in a -CF$_2$- environment 689.1 - 689.0 eV. We
therefore assign the single feature seen in the F(1s) spectrum to a binding energy of 689.1 eV. The O(1s) spectrum for the neat polymer at room temperature (not shown) contained no observable features.

The C(1s) spectrum of the neat Parylene AF-4 surface (Fig. 10) shows two well resolved features at 291.8 eV and 286.6 eV. The published C(1s) binding energies for poly(tetrafluoroethylene) are 290 eV (-CF2-) and 285 eV (aromatic). While the C(1s) peak-to-peak spacing observed in this study (5.2 eV) is identical to the published values, the entire C(1s) spectrum of this study is 1.7 eV higher in binding energy than previously reported values. Differences in charge referencing is one possible explanation for this discrepancy. However, in neither published study is the method of charge compensation given. Also, comparison of the F(1s) to C(1s)[-CF2-] peak spacing for this study with the literature values is impossible because the F(1s) binding energy is not given for either published study. Assignment of the high binding energy C(1s) peak seen in this study (291.4 eV) to the difluoride linkages (-CF2-) gives an F(1s) to C(1s)[-CF2-] peak spacing of 397.3 eV. Published XPS studies of non-oxygenated fluoropolymers report F(1s) to C(1s)[-CF2-] peak spacing in the range 397.0 to 396.8 eV, lower than that seen here (397.3 eV). An increase in the F(1s) to C(1s)[-CF2-] peak spacing is indicative of a decrease in the electronegativity of the carbon environment as shown by the F(1s) to C(1s)[-CF2-] peak spacing for poly(1,1-difluoroethylene) (398.8 eV), poly(1,2-difluoroethylene) (400.9 eV), and poly(monofluoroethylene) (401.3 eV). Therefore, an increase in the F(1s) to C(1s)[-CF2-] peak spacing for Parylene AF-4, with respect to PTFE, is not unreasonable. Also, C(1s) shifts to higher binding energy due to secondary fluorine effects have been well documented for both aliphatic and aromatic carbon. Therefore, the feature seen at 286.6 eV is assigned to the aromatic ring of the xylene parent compound. The integrated intensity ratio of the 291.8 eV and 286.6 eV peaks is 3.0
± 0.3, which agrees well with the theoretical structure of Parylene AF-4 (3.0). The asymmetry seen on the low binding energy side of the 286.6 eV feature is attributed to presence of x-ray satellites from the high binding energy C-F peak.\textsuperscript{18} The asymmetry observed on the high binding energy side of the fitted peak at 291.8 eV is a shake-up satellite due to the aromatic $\pi \rightarrow \pi^*$ transition.\textsuperscript{18,26}

B. Exposure to TMA at 112K

XPS spectra for the sample after exposure at low temperature (112 K) to trimethylaluminum are shown in Figure 11. The F(1s) signal (not shown) exhibits total signal attenuation due to the condensed TMA overlayer. The C(1s) spectrum also shows a large, asymmetric peak with a maximum at 284 eV. The asymmetry is indicative of the presence of more than one carbon environment. Using a FWHM of 1.8 eV (as determined from the C(1s) spectrum for the neat polymer surface), the feature is well fit by two environments: 284.9 eV and 283.9 eV. The low binding energy feature (283.9 eV) is
assigned to carbon in the methyl ligands of the TMA precursor. The high binding energy component peak (284.9 eV) agrees well with the accepted value for hydrocarbons (285.0 eV). Previous experience with the chamber used in these experiments has shown that some decomposition of the organometallic precursor invariably occurs prior to deposition on the sample. We therefore assign the feature at 284.9 eV to adsorbed hydrocarbon from the partially decomposed precursor.

The Al(2p) spectrum shows a large single feature at 73.8 eV, 0.4 eV higher than the published binding energy for trimethylaluminum (73.4 eV). However, the Al(2p) to C(1s) peak spacing of TMA observed in this study (210.1 eV) is in excellent agreement with that of Akhter and co-workers (210.0 eV). Therefore, differences in observed binding energies may be attributed to the different methods of charge referencing: F(1s)[-CF$_2$] for this study versus C(1s)[-CH$_2$] for that of Akhter and co-workers. We therefore tentatively assign the Al(2p) feature at 73.8 eV to the TMA precursor.

After precursor deposition, a large feature appears in the O(1s) spectrum at 532.7 eV (Fig. 4), which is within the range of published values for adsorbed water (533.3 eV - 532.6 eV). Given a base pressure for the CVD chamber of $1 \times 10^{-8}$ Torr and the low deposition temperature used in these experiments, the physisorption of ambient water is unavoidable. Therefore, we assign the O(1s) feature at 532.7 eV to be that of adsorbed water (H$_2$O$_a$).

C. Effects of Annealing

1. Annealing to 300 K

Figures 12 and 13 show the changes in the XPS spectra upon annealing of the TMA-dosed Parylene AF-4 sample in UHV. The F(1s) spectrum (Fig. 12a) exhibits a single, asymmetric feature with the centroid assigned to 689.1 eV. The asymmetric broad-
Figure 12. XPS spectra of TMA on Parylene AF-4 annealed to 300 K and 550 K. (a) F(1s) and C(1s). (b) Al(2p) and O(1s).

ening is indicative of multiple fluorine environments. Using a fixed FWHM of 2.0 eV (as determined from the neat polymer spectrum) the spectrum is well fit by two environments, 689.1 eV and 687.7 eV. The former (689.1 eV) is attributed to the polymer substrate. Published studies show the F(1s) binding energy for carbon-bound fluorine to be insensitive to changes in the local chemical environment. In a study of radiation-induced crosslinking of PTFE, the F(1s) envelope exhibited negligible changes upon exposure to x-radiation for extended periods. It is therefore unlikely that the low binding energy fitted feature can be due to monofluoro-carbon species resulting from polymer defluorination. Also, the presence of a monofluoro-carbon species should give rise to a C(1s) feature with a binding energy ~3.0 eV lower than that of the -CF$_2$- species. No such feature is observed in the C(1s) spectrum for the TMA dosed and annealed AF-4 sample (Fig. 12a).

The formation of aluminum fluorides has been observed during the evaporative deposition
of aluminum on fluoropolymers\textsuperscript{8,32} and during the interactions of clean, metallic aluminum with perfluoroalkyl ethers, acyl fluorides, and fluorocarbon lubricants\textsuperscript{31} The low binding energy fitted feature seen here (687.7 eV) is in good agreement with published binding energies for aluminum fluorides\textsuperscript{8,21-33}

After annealing to 300K, the C(1s) spectrum (Fig. 12a) exhibits a \(-1.5\) eV shift to higher binding energy and \(-1.0\) eV increase in FWHM of the main feature, relative to the spectrum taken at 112 K (Fig. 11). There is also a small additional feature at 292.0 eV, attributable to C-F species from the polymer substrate. These changes are indicative of the desorption and decomposition of the TMA precursor and subsequent reaction with the polymer surface. The overlayer thickness on the polymer at 300 K can be calculated from the attenuation of the fluorocarbon C(1s) signal using the formula:

$$d_A = \lambda_A (E_B) \ln(I_{F} / I_{B})$$

where $I_{F} / I_{B}$ is the ratio of the unattenuated signal of the substrate to the attenuated signal.
and $\lambda_{\alpha}(E_p)$ is the mean free path of the substrate photoelectron of interest in the adlayer matrix.\textsuperscript{26} Using a mean free path of 11 - 30 Å for a C(1s) photoelectron in an alumina matrix gives an adlayer thickness of 17 - 47 Å after annealing to 300 K.\textsuperscript{26} There is also a 52% decrease in the total signal intensity of the C(1s) spectrum upon annealing to 300 K, which is consistent with desorption of methyl ligands from the decomposed precursor. The increase in the FWHM of the main C(1s) feature is indicative of an increase in the number of carbon environments. Because of the reappearance of the high binding energy feature (292.0 eV) attributable to the fluoride species of the polymer substrate, a corresponding signal from the aromatic carbon from the polymer (at $\sim$286.5 eV) can be inferred, with a signal intensity approximately three times that of the fluoride signal. Other possible environments include hydrocarbons from the decomposition products, metal-carbides from either unreacted precursor or metal/polymer interactions, and carboxy species from interactions with the co-adsorbed water. However, the published C(1s) binding energies for carbon species in oxygenated environment are 286.5 eV (alcohols and ethers) or higher.\textsuperscript{19} After compensation for the aromatic carbon of the polymer substrate, there is no spectral evidence for additional carbon species in the low binding energy feature with binding energies above $\sim$285.5 eV. The large feature at low binding energy is well fit by three environments: 286.6 eV, 285.2 eV, and 284.1 eV. The fitted peak at 286.6 eV is assigned to the aromatic carbon of the polymer substrate. The feature at 284.1 eV is within the range of published values for metal carbides.\textsuperscript{1,27,31-33} The most probable sources of a carbide signal under the experimental conditions extant are unreacted precursor in the adlayer or interactions between the aluminum and carbon in the polymer substrate. Differentiation between these environments using C(1s) data alone would be highly subjective. However, the Al(2p) spectrum for the TMA dosed surface (Fig. 12b) shows substantial changes upon annealing to 300 K (see below). The changes observed in the Al(2p) and
C(1s) spectra indicate near complete decomposition of the TMA precursor upon annealing to 300 K. The formation of aluminum-carbon bonds has been observed in a number of studies involving the interactions of aluminum with fluorocarbons. We therefore tentatively assign the fitted feature at 284.1 eV to aluminum bound to the polymer surface through Al-C bonds. The fitted feature at 285.2 eV is tentatively assigned to the remaining hydrocarbon species arising from the decomposition of the TMA precursor.

The Al(2p) spectrum (Fig. 12b) exhibits significant broadening and a shift to higher binding energy upon annealing to 300 K. There is also very slight increase in total signal intensity. Using a fixed FWHM of 1.9 eV (as determined from the condensed precursor at 112 K), the spectrum is well fit by three environments: 76.8 eV, 75.6 eV, and 74.2 eV. In a study of the interaction between thermally deposited aluminum and fluoropolymers, Du and Gardella reported binding energies for aluminum fluorides (76.4 eV to 76.8 eV), aluminum oxides (75.4 eV), and aluminum carbides (74.3 eV to 74.5 eV), which are very close to the binding energies of the fitted Al(2p) features in this study. Other studies have reported similar assignments for the interaction between aluminum and fluorocarbons. Therefore, for reasons mentioned previously, we assign the fitted peaks in the annealed Al(2p) spectrum as follows: Al-F (76.8 eV), Al-O (75.6 eV), and Al-C (74.2 eV).

Upon annealing to 300 K, the O(1s) spectrum (Fig. 12b) exhibits a shift to lower binding energy and the appearance of an asymmetry on the high binding energy side of the main feature. This decrease in binding energy and asymmetric broadening is indicative of the formation of one or more additional oxygen environments. Curve fitting using a fixed FWHM (2.2 eV, as determined from the low temperature O(1s) spectrum) gives a good fit with two environments: a large peak centered at 531.7 eV and a smaller peak at 533.3 eV. While the former (531.7 eV) is well within the range of published values for aluminum oxides, previous studies involving the interaction of aluminum with adsorbed water indi-
cate some hydroxide formation at low temperature.\textsuperscript{5,35-36} The published O(1s) binding energy for a mixed phase aluminum-oxide/hydroxide (Al-O/OH) is 532.5 eV, relative to a bulk AlO\textsubscript{x} signal of 531.5 eV.\textsuperscript{34,35} Annealing to higher temperature reportedly causes a shift to lower binding energy in the O(1s) spectra as the mixed phase Al-O/OH converted to a bulk AlO\textsubscript{x}.\textsuperscript{34-36} In this study, no shift in the O(1s) binding energy is observed upon annealing to temperatures above 300 K (see below). We therefore assign the fitted feature at 531.7 eV to a AlO\textsubscript{x}. The smaller feature at 533.3 eV is assigned to the re-adsorption of water from the ambient upon returning the sample to 112 K after annealing.

2. \textit{Annealing above 300 K}

Figures 12 and 13 show the changes in the XPS spectra upon annealing to higher temperature in UHV. The total fluorine signal intensity increases as a function of temperature. The F(1s) spectra of the sample show increasing asymmetry upon annealing to above 300 K (Figs. 12a & 13a), which indicates increasing aluminum-fluorine bond formation with respect to temperature. This increase in Al-F formation is represented graphically by the increase in the fitted feature attributed to Al-F (687.6 eV), as a function of temperature.

While the total carbon signal intensity decreases with respect to temperature, the intensity of the high binding energy (292.1 eV) component of the C(1s) spectra (assigned to C-F) increases. In addition, the low binding energy component narrows with temperature and shifts to higher binding energy (286.5 eV) by 550 K. These changes are indicative of further desorption of the hydrocarbon decomposition products produced in the initial reaction between the TMA precursor and the AF-4 surface.

The total Al(2p) signal intensity shows a slight increase upon annealing (Figs. 12a & 13a), which can be attributed to the desorption of the hydrocarbon decomposition
products upon exposure of the sample to higher temperatures. The overall shape and position of the Al(2p) envelope remains constant upon annealing to temperatures above 300 K.

The O(1s) spectra (Figs. 12b & 13b) exhibit a steady increase in total signal intensity and decrease in the high binding energy asymmetry upon annealing. This can be attributed to the desorption of the hydrocarbon decomposition products from the aluminum adlayer (see above) and further reaction between the aluminum and water re-absorbed on the adlayer surface upon cooling between anneals.

3. Angle Resolved Spectra

Take-off angle resolved spectra (taken at 60° off surface normal) for the sample annealed to 600 K are shown in Figures 13a & 13b. The F(1s) spectrum (Fig. 13a) experiences significant broadening to lower binding energy in the angle resolved spectrum. This is indicative of an increase in the relative contribution of the spectral component attributed to aluminum fluorides (687.5 eV), when compared to the surface normal spectrum. Also, the C(1s) spectrum (Fig. 13a) shows a general decrease in the spectral features attributable to the C-F species of the underlying polymer (291.8 eV). The low binding energy peak shows signal broadening and a shift in the centroid to lower binding energy. These spectral changes indicate that the XPS sampling region is inhomogeneous over a range of ~30 Å. The relative concentrations of unfluorinated carbon and metal-carbide species are greater toward the outer border (vacuum/solid interface) of the sampling region.

The Al(2p) spectrum (Fig. 13b) shows a small (~0.3 eV) shift to lower binding energy and a decrease in asymmetry on the low binding energy side at shallow angle (surface sensitive) geometry. The slight shift of the spectral maxima to lower binding energy is indicative of an increase in the signal attributed to the oxide species (75.7 eV)
and the decrease in asymmetry indicates a decrease in the signal attributed to Al-C species (74.1 eV). These changes suggest the aluminum oxide to be at the adlayer/vacuum interface, the Al-C species to be at the adlayer/polymer interface, and the aluminum fluoride species (76.9 eV) to lie between. The angle resolved O(1s) spectrum (Fig. 13b) shows a slight increase in the high binding energy asymmetry, indicating adsorbed water (H$_2$O) at the adlayer surface.

**Discussion**

Trimethylaluminum reacts with the Parylene AF-4 surface to yield aluminum bonded to oxygen, fluorine, and carbon species, with no metallic Al species evident. The aluminum containing adlayer is stable even upon annealing to temperatures as high as 600 K, as shown by the Al/Al(112 K) ratio in Figure 14. Previous experiments with the XPS system used in this study have shown a variation in absolute signal intensity of ≤4% for elemental spectra. The total aluminum signal remains relatively constant upon annealing to higher temperature, with a slight increase attributable to a decrease in signal attenuation because of temperature induced desorption of hydrocarbon species formed from the decomposition of the TMA. Further evidence for hydrocarbon desorption is seen in Figure 14, as the decrease in the ratio of non-polymeric carbon to aluminum (C(non-polymer)/Al) with increasing temperature.

The presence of oxygen in the Al adlayer suggests the possibility of oxyfluoride (-OF) formation upon annealing. We are unaware of any published values for unambiguously assigned XPS binding energies for oxyfluoride species. However, published bond energy data (Table 4) show the Al-F bond energy to be approximately three times that of the O-F bond (664 kJ/mol vs. 222 kJ/mol). In addition, the fluorination of an aluminum oxide (AlOx → F-AlOx) increases the energy of both the Al-F bond (by 97 kJ/mol vs.
Figure 14. Variations in Al/Al(112 K), F/Al, and non-polymeric C/Al signal ratios as a function of annealing temperature.

\[ \text{AlF}_x \) and the Al-O bond (by 70 kJ/mol vs. AlOx).\(^{37}\) Therefore, the changes in total enthalpy (H) for aluminum oxyfluoride and fluorinated aluminum oxide formation are:

1. \[ \text{F} + \text{AlO}_x \rightarrow \text{Al-O-F} \quad \Delta H = +490 \text{ kJ/mol} \]
2. \[ \text{F} + \text{AlO}_x \rightarrow \text{F-AlO}_x \quad \Delta H = -319 \text{ kJ/mol} \]

Thus, under the experimental conditions extant, a fluorinated aluminum oxide (F-AlOx) phase is thermodynamically more likely to form than either a Al(OF)\(_x\) phase or a separate AlF\(_x\) phase. We therefore assign the low binding energy F(1s) feature (687.7 eV) to Al-F in a fluorinated aluminum oxide.
Table 4. Published bond energies for selected aluminum compounds.  

<table>
<thead>
<tr>
<th>Bond Energies (kJ mol⁻¹)</th>
<th>Al-Al</th>
<th>186</th>
<th>Al-C</th>
<th>255</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-O</td>
<td>512</td>
<td></td>
<td>FAl-O</td>
<td>582</td>
</tr>
<tr>
<td>Al-F</td>
<td>664</td>
<td></td>
<td>OAl-F</td>
<td>761</td>
</tr>
</tbody>
</table>

Annealing also results in increased aluminum-fluoride formation, as shown by the increasing fitted features in both the F(1s) spectra (687.7 eV) and Al(2p) spectra (76.9 eV) (Figs. 12 & 13). It is well known that x-rays have the potential to defluorinate fluoropolymers, which should be manifested in a steadily decreasing F(1s) total signal intensity. Figure 14 shows the F/Al ratio to be increasing much more rapidly than the total Al(2p) signal as a function of annealing. This indicates the fluorine concentration of the aluminum adlayer to increase upon annealing to increasing temperature. It has been shown that fluorine diffuses into aluminum films evaporated on to modified fluoropolymers. A similar situation is seen here, with fluorine diffusing into the aluminum adlayer. Angle resolved spectra reveal the fluoride concentration to be decreasing toward the adlayer/vacuum interface, with a non-fluorinated aluminum oxide species concentrated near the surface. This indicates the presence of a fluorine concentration gradient consistent with fluorine diffusion into the aluminum adlayer. Du and Gardella reported a decrease in fluorine diffusion for aluminum/fluoropolymer systems containing oxygen. The angle resolved Al(2p) spectrum (Fig. 13b) show aluminum carbide species to be present at the Al/polymer interface. The composition of the aluminum adlayer is shown graphically in Figure 15.

Summary and Conclusions

XPS was used to study the interaction between trimethylaluminum and Parylene AF-4. The data demonstrate that aluminum compounds deposited on unmodified AF-4 by
low temperature CVD is stable to elevated temperatures. At low temperature, the TMA precursor and ambient water condenses on the polymer surface. Upon annealing to 300 K, the precursor decomposes and reacts with both carbon and fluorine from the polymer surface, as well as oxygen from the adsorbed water. The precursor/fluoropolymer/water reaction forms a thermally stable aluminum oxide film bonded to the polymer surface through aluminum-carbon bonds. A fluorine concentration gradient exists across the adlayer with decreasing fluorination toward the adlayer/vacuum interface (Fig. 15). The aluminum defluorinates the polymer at all temperatures studied, with fluorine diffusion into the aluminum film. No metallic aluminum is observed at any time.

Chapter References


CHAPTER III

MO-CVD OF ALUMINUM AND COPPER ON TEFILON-AF

Introduction

The metallization of materials with low-dielectric constants is an area of rapidly growing interest because of applications to the multilevel metallization of integrated circuits. A lower dielectric constant material results in reduced capacitive coupling between metal lines and improved signal processing times. Polytetrafluoroethylene (Teflon or PTFE) has an extremely low dielectric constant with good mechanical strength as well as chemical and thermal stability. However, problems with creep associated with the high degree of crystallinity in PTFE have led to the introduction of amorphous fluoropolymers (AF), which incorporate groups designed to eliminate crystallinity. One such species is known commercially as Teflon-AF 1600, which is a co-polymer of 33 mol% PTFE and 66 mol% 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3 dioxole. Such films have been deposited on substrates via spin-coating, plasma deposition, thermal deposition and laser ablation. Their bulk structure (Fig. 16) has been characterized by infra-red spectroscopy, scanning electron microscopy, and x-ray diffraction. For applications involving the deposition and adhesion of metal films, surface composition and resulting surface-metal interactions play a critical role.

In this work, x-ray photoelectron spectroscopy (XPS) was used to characterize a Teflon-AF surface and subsequent interactions with two organo-metallic precursors: trimethylaluminum (TMA) and copper(I)hexafluoroactylacetate-cyclooctadiene (Cu(I)hfac(COD)). The neat polymer surface was exposed to the precursor at reduced
temperature and subsequently annealed to higher temperature. These studies show that TMA will react with the Teflon-AF surface and water adsorbed from the ambient, at or below 300 K, to form a thermally stable, fluorinated aluminum-oxide adlayer with aluminum-carbide species at the adlayer/polymer interface. Annealing to higher temperature causes further polymer defluorination and increasing Al-F formation. Studies of the interaction between the neat Teflon-AF surface and Cu(I)hfac(COD) show the loss of the neutral ligand (COD) by the copper precursor at or below room temperature. Upon annealing to higher temperature, the Cu(I) adsorbate undergoes a disproportionation reaction on the polymer surface resulting in the formation of a Cu(0) adlayer. Some Cu-F formation is also indicated.

**Experimental**

Thin films (~3 - 5 μm) of Teflon-AF were formed by spin coating from a Teflon-AF 1601 S-6 (Dupont) solvent on Si(100) wafers with a native oxide. The films were then annealed in a nitrogen environment for five minutes at 300°C. This procedure has been found to produce adherent films of consistent composition, comparable to those obtained by laser ablation and other methods.
Experiments were carried out within a stainless steel, turbomolecularly pumped surface analysis system with a base pressure of $6 \times 10^{-10}$ Torr. The system is equipped with a separate CVD chamber with a base pressure of $1 \times 10^{-8}$ Torr. The analysis chamber was equipped with a dual anode x-ray source, hemispherical analyzer and quadrupole mass spectrometer for residual gas analysis. Pressure in both chambers was monitored using a nude ion gauge calibrated for dinitrogen. The ion gauge was mounted out of direct line of sight of the sample, in order to minimize electron damage of the sample. The sample was heated by a combination of resistive heating and liquid nitrogen cooling of the sample holder. Sample temperatures were monitored by a chromel-alumel thermocouple. Annealing was carried out by ramping the sample to the required temperature for 30 minutes. The sample was allowed to return to base pressure prior to the acquisition of spectra.

XPS spectra were obtained using an unmonochromatized MgKα x-ray source operated at 15 keV and 300 W, and a commercial hemispherical analyzer operated in the constant pass energy mode (50 eV pass energy). Take-off angle resolved spectra were obtained by rotating the sample 60° off surface normal. The analyzer was calibrated using Au and Cu standards, according to established procedure. XPS data were analyzed using a commercially available software package. The exposure of fluoropolymers to x-ray flux is known to induce defluorination and cross-linking. Therefore, x-ray exposure was limited to that needed for spectral acquisition. XPS binding energies were affected by sample charging during data acquisition. Therefore, the data were referenced to a F(1s) binding energy of 689.1 eV, which is consistent with the published values for fluorine in a C-F environment. The full width at half-maximum (FWHM) for the fitted spectra was kept constant with each atomic species for all spectra of that species. Differentiation between Cu(I) and Cu(0) oxidation states was accomplished using published methods. Briefly, copper oxidation state determination is accomplished by a combination of Cu(L3,VV) line shape analysis and
by calculation of the modified Auger parameter. For a Cu(0) oxidation state, the Cu(LVV) spectrum shows a narrow feature with a large asymmetry on the high binding energy side, whereas Cu(I) gives a broader, more symmetric peak. The modified Auger parameter is determined by the distance (in eV) between the Cu(2p_{3/2}) feature and the maximum of the Cu(LVV) feature, added to the x-ray photon energy. This parameter is then compared to tabulated parameters to determine the copper oxidation state.

Metal-organic chemical vapor deposition was carried out using trimethylaluminum (TMA) and Cu(I)hexafluoroacetylacetate-cyclooctadiene (Cu(I)hfac(COD)) obtained from commercial sources. The precursors were introduced directly into the CVD chamber using a metering valve. Compositions of the organometallic precursors were verified by measurements with a quadrapole mass spectrometer. The sticking coefficients of the precursors to the polymer were maximized by performing the exposures at reduced temperatures (< 115 K). Exposures are reported in Langmuirs (1 Langmuir (L) = 10^-6 Torr-sec), and have not been corrected for directional dosing effects or ion-gauge sensitivity. The samples were then transferred to the analysis chamber for XPS analysis. Anneals were carried out in UHV (in series) with spectra taken after each annealing. To minimize changes in x-ray flux, the sample was not moved after introduction into the UHV chamber, other than rotation to obtain angle resolved spectra.

Results and Discussion

A. XPS of the Neat Polymer Surface

The XPS spectra of the unmodified polymer are displayed in Figure 17. Spectra for the neat polymer show a single feature in the F(1s) spectrum. Charge compensated studies of bulk and thin film show the F(1s) peak to be at 689.1 eV, which is in good agreement with fluorine in a fluorocarbon environment. We therefore assign the F(1s)
feature seen here to a binding energy of 689.1 eV, which is then used as an internal reference for all subsequent elemental spectra. The O(1s) spectrum also shows a single feature at 534.9 eV and is assigned to oxygen in the dioxole ring.\textsuperscript{39} The C(1s) XPS spectrum (Fig. 17) shows a large, unresolved doublet, with environments at approximately 293 and 291 eV. These C(1s) binding energies are in good agreement with published values for Teflon-AF 1600 and 2400 (67% and 82% dioxole ring segment, respectively).\textsuperscript{39}

B. \textit{TMA on Teflon-AF}

1. \textit{Exposure at 112 K}

C(1s) and Al(2p) XPS spectra for the polymer exposed to 30 L TMA at 112 K and subsequently annealed to temperatures up to 550 K are displayed in Figure 18. The corresponding F(1s) and O(1s) spectra are shown in Figure 19. In addition to the high binding energy doublet characteristic of the polymer, the C(1s) spectrum (Fig. 18) shows

![Graph showing XPS spectra of F(1s), O(1s), and C(1s)]

Figure 17. F(1s), O(1s), and C(1s) XPS spectra of neat Teflon-AF surface referenced to F(1s) binding energy of 689.0 eV.
a large feature at low binding energy (283.5 eV). The published C(1s) binding energy for the Al-C bonds in TMA is 283.4 eV, which is in good agreement with the feature seen here. We therefore assign the low binding energy feature (283.5 eV) to the methyl ligands of the unreacted precursor. A small peak centered at ~282.5 eV was added to the calculated spectrum (Fig. 18) to compensate for the MgKα x-ray satellites from the C(1s) features of the polymer substrate. The Al(2p) spectrum (Fig. 18) shows a single feature at 73.7 eV, which is in good agreement with the published value for condensed TMA (73.4 eV).

The F(1s) spectrum at 112 K (Fig. 19) shows the large feature of the polymer substrate referenced to 689.1 eV. The low temperature O(1s) spectrum (Fig. 19) exhibits significant broadening and the appearance of an asymmetry on the high binding energy side. The broadening of the O(1s) feature upon exposure to TMA indicates the presence of oxygen environments, in addition to that of the polymer. Using a FWHM of 2.5 eV for

Figure 18. C(1s) and Al(2p) spectra of Teflon-AF surface exposed to 30 L TMA at 112 K and subsequently annealed to 300 K and 550 K (in series) in UHV.
Figure 19. O(1s) and F(1s) spectra of Teflon-AF surface exposed to 30 L TMA at 112 K and subsequently annealed to 300 K and 550 K (in series) in UHV.

Each component of the fitted O(1s) spectrum, as determined from the spectrum of the neat polymer (Fig. 17), the exposed O(1s) spectrum is well fit by two environments: 534.7 eV (attributed to the polymer substrate) and 533.8 eV. Experiments involving the low temperature exposure of non-oxygenated fluoropolymers to the environment of the deposition chamber also show an O(1s) feature at ~533.5 eV, which is in the range of published binding energies for adsorbed water.\textsuperscript{17,18} Given the relatively high working pressure of the deposition chamber (~5 x 10\textsuperscript{-7} Torr) and the low deposition temperature (112 K) used in these experiments, the physisorption of water on the polymer substrate is not unreasonable. Therefore, we assign O(1s) the feature at 533.8 eV to be that of adsorbed water (H\textsubscript{2}O\textsubscript{2}).
2. Effects of Annealing

a. Annealing to 300 K

The C(1s) spectrum of the TMA exposed polymer surface annealed to 300 K (Fig. 18) shows a 54.6% decrease in relative signal intensity and a shift to higher binding energy (~1.0 eV) for the feature attributed to Al-C bonds (284.4 eV). These changes indicate the decomposition of the precursor and a reaction between the aluminum and carbon in the polymer surface. In a study of the adhesion strength between metals and fluoropolymers, Chang and co-workers found a correlation between the adhesion strength and the concentration of carbide species formed at the metal/polymer surface. Also, there is an intensity increase in the doublet attributed to the polymer substrate. This indicates substantial desorption of the methyl ligands from the decomposed precursor, with a corresponding lowering in the signal attenuation of the polymer substrate.

The Al(2p) spectrum (Fig. 18) displays a shift to higher binding energy and significant broadening upon annealing to 300 K. The spectrum is well fit by three peaks: 76.1 eV, 74.9 eV, and 73.8 eV; assigned to Al-F, Al-O, and Al-C, respectively. In a study of the interaction between thermally deposited aluminum and fluoropolymers, Du and Gardella reported binding energies for aluminum fluorides (76.4 eV to 76.8 eV), aluminum oxides (75.4 eV) and aluminum carbides (74.3 eV to 74.5 eV), which are approximately 0.5 eV higher than the values seen here. These discrepancies are likely due to differences in methods of charge referencing; i.e. using the C(1s) signal for hydrocarbon contaminants (Du and Gardella) and the F(1s) of the polymer substrate (this study). Other studies have reported similar assignments for the interaction between aluminum and fluorocarbons.

The F(1s) spectrum for the TMA dosed surface, annealed to 300 K, is shown in Figure 19. The total F(1s) signal intensity experiences a marked increase due to the lessening of the signal attenuation from the desorption of the precursor decomposition products.
Figure 19 also shows the appearance of asymmetric broadening on the low binding energy side of the F(1s) spectrum. The low binding energy asymmetry is in the region of the XPS spectrum where the F(1s) signal for metal-fluoride bonds are commonly found. A good fit (Fig. 19) is obtained using a feature with a binding energy of 687.0 eV, which is in good agreement with published binding energies for aluminum fluorides. The formation of aluminum fluorides has been observed during the evaporative deposition of aluminum on fluoropolymers and during the interactions of clean, metallic aluminum with perfluoroalkyl ethers, acyl fluorides, and fluorocarbon lubricants. The presence of oxygen both in the polymer and on the surface presents the possibility of oxyfluoride (-OF) formation upon annealing. We are unaware of published binding energies unambiguously assigned to oxyfluoride species. However, published bond energy data (Table 4) show the Al-F bond energy to be approximately three times the that of O-F (664 kJ/mol vs. 222 kJ/mol). In addition, aluminum oxide fluorination increases the bond energy of both the Al-F bonds (by 97 kJ/mol vs. AlF3) and Al-O bonds (by 70 kJ/mol vs AlOx). Thus, a fluorinated aluminum oxide (F-AlOx) is thermodynamically more likely to form than an aluminum oxyfluoride (Al(OF)n). We therefore tentatively assign the low binding energy F(1s) feature (687.0 eV) to Al-F in a fluorinated aluminum oxide.

Upon annealing to 300 K, the O(1s) spectrum (Fig. 19) exhibits significant broadening to lower binding energy and a ~2.0 eV shift in the peak maximum to lower binding energy. Additionally, the spectrum shows a shoulder on the high binding energy side. The shift to lower binding energy is indicative of metal-oxide formation. A good fit is obtained using three oxygen environments: 534.6 eV, 533.8 eV, and 532.2 eV. The fitted feature at 534.6 eV can be attributed to the dioxole oxygen of the underlying polymer. Also, since the sample was allowed to return to low temperature prior to the taking of spectra, the fitted feature at 533.8 eV is reasonable for readsorbed water. Given the reactivity of organo-aluminum compounds with water and the experimental conditions extant here, aluminum oxide and/
or hydroxide formation can be reasonably expected. In a study of the interaction between a clean aluminum surface and D$_2$O, Rogers reported an O(1s) binding energy for aluminum oxide/hydroxide mixed phase (Al-O/OH) to be 532.5 eV, slightly higher than that of a pure bulk oxide (531.5 eV). We therefore assign the fitted feature at 532.2 eV to be from a mixed phase Al-O/OH.

b. Annealing to 550 K

Figures 18 & 19 also show the changes in the XPS spectra upon annealing to 550 K in UHV. The C(1s) spectrum shows a continued decrease (51.9%) in the relative signal intensity of the low binding energy feature (285.0 eV) and a corresponding increase in the high binding energy doublet of the Teflon-AF substrate, indicating further desorption of the methyl ligands from the precursor.

The Al(2p) spectrum of the aluminum/polymer system annealed to 550 K is also shown in Figure 18. The overall signal intensity of the Al(2p) feature remains constant upon annealing to 550 K. The Al(2p) signal maxima has experienced a 0.7 eV shift to higher binding energy, indicating an increase in the formation of Al-F bonds. Also, the Al(2p) feature displays an overall narrowing, with an asymmetry on the lower binding energy side. This suggests a decrease in the low binding energy Al-C signal. These changes suggest increasing fluorination of the Al adlayer with Al-F species forming over the Al-C species and attenuating signal intensity, which is shown graphically by curve fitting. The fitted feature attributed to Al-F (75.9 eV) shows an increase as a percentage of the total Al(2p) signal, from 22.8% to 40.5%, while the feature attributed to Al-C (73.6 eV) displays a corresponding decrease from 28.4% to 10.4%. The fitted peak attributed to Al-O (75.1 eV) remains constant (48.7% to 49.1%) upon annealing to 550 K.
Upon annealing to 500 K, the O(1s) spectral maximum exhibits an ~0.5 eV shift to lower binding energy (Fig. 19). Also, the high binding energy shoulder has become more fully resolved. The spectrum is well fit by three environments: 534.6 eV, 533.8 eV, and 531.8 eV. Binding energies of 534.6 eV and 533.8 are attributable to the polymer substrate and adsorbed water (H₂O), respectively, for reasons mentioned previously. The shift to lower binding energy of the spectral maximum (and accompanying shift of the low binding energy fitted feature) indicate a change from a mixed phase Al-O(H) to a bulk oxide (AlOx). A similar phenomena was reported for the interaction of methanol with a clean aluminum surface, where methanol was condensed on aluminum at low temperature and subsequently annealed.²⁴⁻²⁵ By room temperature, the methanol partially decomposes to a chemisorbed methoxy species which forms a bulk aluminum oxide at higher temperatures (500 K).²⁴⁻²⁵ Here, the aluminum oxide/hydroxide mixed phase loses hydrogen to form AlOx by 550 K. We therefore assign the fitted feature to AlOx.

The F(1s) spectrum shows a large increase in total signal intensity upon annealing to 550 K. Also, the contribution of the fitted peak attributed to Al-F (686.8 eV) shows a small increase as percentage of total F(1s) signal intensity (5.16% to 6.57%). This increase in the Al-F contribution in the F(1s) spectrum, combined with the increase in the Al(2p) spectrum, indicates increasing defluorination of the polymer substrate by the aluminum adlayer as a function of temperature.

3. Take-off Angle Resolved Measurements

XPS take-off angle resolution provides a non-destructive means of depth profiling using XPS.²⁶ Given that XPS depth resolution is a function of the inelastic mean free path of the photoelectrons, changing the sample/analyzer angle (relative to surface normal) will decrease the effective electron escape depth by cosine θ.²⁶ The 60° take-off angle resolved Al(2p) spectrum for the TMA dosed and annealed polymer is displayed in Figure 20. At the more surface sensitive geometry, the Al(2p) feature exhibits significant broadening towards lower binding
energy, indicating an increase in the relative contribution of one or more of the low binding energy environments. Curve fitting shows a marked increase in the relative intensity of the component attributed to Al-O (75.1 eV), while the fitted peak attributed to Al-C (73.6 eV) experiences a corresponding decrease. These changes indicate the Al adlayer to be an fluorinated aluminum oxide (F-AlOx), bound to the polymer surface through aluminum carbide bonds. The fluorination in the adlayer exists as a concentration gradient increasing toward the polymer/adlayer interface (Fig. 21).

C. Cu(I)hfac(COD) on Teflon-AF

1. Exposure at 105 K

The XPS spectra for the neat Teflon-AF surface exposed to Cu(I)hfac(COD) are given in Figures 22 (C(1s), F(1s) and O(1s)) & 23 (Cu(2p) and Cu(L_3VV)). CVD studies using

![Figure 20. Surface normal and 60° take-off angle resolved Al(2p) spectra of TMA dosed and annealed Teflon-AF surface.](image-url)
Cu(I) β-diketonate precursors typically involve dissociative chemisorption, where the organo-copper precursor loses the neutral ligand upon bond formation with the substrate. The C(1s), O(1s), and F(1s) spectra (Fig. 22) for the dosed surface at 112 K show spectra characteristic of the hexafluoroacetylacetate (hfac) and cyclooctadiene (COD) ligands. This indicates complete attenuation of the photoelectron signal of the underlying polymer. The low temperature Cu(2p) and

![Figure 21. Composition diagram of aluminum adlayer on Teflon-AF](image)

![Figure 22. C(1s), O(1s), and F(1s) spectra of Cu(I)hfac(COD) on Teflon-AF at 105 K, 300 K, and 600 K.](image)
Cu(L3VV) spectra (not shown) are featureless. Previous experience with the CVD system used in these experiments has shown substantial precursor decomposition in the introduction lines, which releases free ligands (primarily COD) into the CVD chamber. Due to the reduced temperature used during exposure, the free ligands are then co-adsorbed on the sample surface along with the precursor. The physisorption of the additional ligands causes total attenuation of the Cu photoelectron signal.

2. Effects of Annealing

a. Annealing to 300 K

Upon annealing to 300 K, the C(1s) spectrum (Fig. 22) displays significant broadening of the low binding energy feature and an increase in the relative intensity of the high binding energy feature. These changes in the C(1s) spectrum indicate substantial desorption of COD ligands. Both the F(1s) and O(1s) spectra remain constant upon annealing to 300 K.

The Cu(2p) and Cu(L3VV) spectra for the annealed surface are shown in Figure 23. After annealing to 300 K, the Cu(2p) spectrum shows two well resolved peaks at 951.8 eV and 932.2 eV, corresponding to Cu(2p1/2) and Cu(2p3/2) respectively. The Cu(L3VV) shows a single, broad peak at 338.5 eV (KE = 915.1 eV). The overall shape to the Cu(L3VV) spectrum indicates the copper to be in the form Cu(I). Further evidence for a Cu(I) is given by the modified Auger parameter of 1847.3, which is within range normally seen for Cu(I) (1847 eV- 1849 eV).

b. Annealing to 600 K

Annealing to 600 K causes substantial changes in the C(1s) spectrum (Fig. 22). The low binding energy portion of the spectrum (attributed to the hfâc/COD ligands of the precursor)
experiences a large decrease in relative signal intensity, which indicates further desorption of the precursor ligands. Corroboration of this is seen in the re-emergence of the high binding energy features attributed to the underlying polymer. Additionally, the O(1s) spectrum shows the signal to have split into a partially resolved doublet. Curve fitting shows the O(1s) signal to be a combination of the underlying polymer (534.9 eV) and the hfac ligand (531.3 eV).

The copper XPS spectrum of the dosed and annealed surface are shown in Figure 23. The Cu(2p) spectrum shows a 0.8 eV shift to lower binding energy (931.0 eV). The Cu(L$_3$VV) spectrum shows narrowing and a shift to lower binding energy of 3.7 eV, to 334.8 eV. The change in overall line shape of the Cu(L$_3$VV) spectrum indicates reduction to Cu(0). Copper reduction is corroborated by the change in the modified Auger parameter to 1849.8, which is within the range expected for Cu(0)\(^{14,15,30}\). Studies involving MOCVD of copper using Cu(I) or Cu(II) \(\beta\)-diketonate precursors on TiN and other surfaces indicate Cu(0) formation through disproportionation, which involves a 50% loss in total copper on the surface\(^{15,27-30}\). In this study, this loss of copper would be manifest as a 50% reduction in the total Cu signal intensity. However, due to
signal attenuation effects of the adsorbed ligands, determination of total copper in this study is
difficult. Total Cu determination is further complicated by the similarity in chemical composition of
the Teflon-AF substrate and the hexafluoroacetylacetate ligand, which obviates the calculation of
signal attenuation using an internal standard. Therefore, it is unclear whether Cu(0) formation is
through disproportionation. Further studies are necessary to determine how metallic copper
formation is taking place.

The F(1s) spectrum (Fig. 23) shows the presence of an asymmetry on the low binding
energy side. Curve fitting reveals a new environment at 686.3 eV, which is within the range ex-
pected for metal-fluorides. This indicates that, like aluminum, copper also defluorinates
the Teflon-AF surface.

**Summary and Conclusions**

XPS was used to study the interaction between trimethylaluminum and Teflon-AF. The
data demonstrate that aluminum deposited on unmodified Teflon-AF by low temperature CVD is
stable to elevated temperatures. At low temperature, the TMA precursor and ambient water
condenses on the polymer surface. Upon annealing to 300 K, the precursor decomposes and
reacts with both carbon and fluorine from the polymer surface, in addition to oxygen from the
adsorbed water. The TMA/polymer/water reaction forms a thermally stable aluminum oxide film
bonded to the polymer surface through aluminum-carbon bonds. A fluorine concentration gradient
exists across the adlayer with decreasing fluorination toward the adlayer/vacuum interface (Fig.
21). Upon annealing to higher temperature (550 K), aluminum reacts preferentially with fluorine at
the expense of carbon. The aluminum defluorinates the polymer at all temperatures studied, with
fluorine diffusion into the adlayer film.

The interaction between Cu(I)hfac(COD) and a neat Teflon-AF surface was also studied
using x-ray photoelectron spectroscopy. The data show that low temperature CVD results in
Cu(0) on the fluoropolymer surface by 600 K, with some metal fluoride formation. The Cu(I) precursor condenses on the Teflon-AF surface at low temperature and reacts with the polymer by 300 K, with the resulting loss of the neutral cyclooctadiene ligand. Annealing to 600 K results in some Cu(I) to Cu(0) reduction and the desorption of substantial amounts of the hexafluoroacetylactaite ligands. The F(1s) spectra of the annealed surface indicates some metal fluoride formation by 600 K.

Chapter References


CHAPTER IV

MODIFICATION OF A PARYLENE AF-4 SURFACE BY EXPOSURE TO •OH FLUX AND SUBSEQUENT INTERACTIONS WITH TRIMETHYLANLUMINUM

Introduction

The scaling of devices to sub-0.5 micron dimensions has resulted in integrated circuits with performance constrained by interconnect RC delay. This interconnect delay can be reduced by replacing aluminum with a lower resistivity metal and/or replacing SiO$_2$ with a lower dielectric constant material. Fluoropolymers’ low dielectric constants (2.4 - 1.9), low moisture absorption, and high resistivity to chemical attack make them attractive candidates as a low-k replacement for SiO$_2$. Copper, with a resistivity of 1.7 $\mu$Ω•cm, has been proposed as an alternative to aluminum. Combining these materials would significantly reduce the device interconnect delay, allowing higher frequency operations.

However, the extreme chemical inertness of fluoropolymers makes metallization very difficult, and direct deposition of metals on fluoropolymer surfaces yields unsatisfactory adhesion. To address this problem, several methods have been developed to modify fluoropolymer surfaces to improve metal adhesion. The most promising techniques involve the incorporation of reactive functionalities, particularly oxygen-containing moieties, on the polymer surface. The most common techniques employ plasma treatment. However, in addition to the formation of reactive gaseous species, plasmas also generate significant vacuum ultraviolet radiation (vuv, $\lambda < 175$ nm) of sufficient intensity to break polymer chains and thereby damage the bulk polymer.
As an alternative to plasma modification, Sun et al.\textsuperscript{23} have developed a process using thermally generated gaseous free radicals to incorporate oxygen functionalities on polymer surfaces. This technique involves flowing water vapor over a resistively heated (~2000 K) refractory metal filament, generating hydroxide free radicals, and atomic hydrogen and oxygen species.\textsuperscript{23} These species then react with the polymer surface resulting in oxygen incorporation in the surface.\textsuperscript{23} Several studies have shown increased metal/fluoropolymer adhesion for oxygen-containing polymers.\textsuperscript{2,4,5,31,32}

However, in addition to problems with adhesion, there are a number of other issues that need to be addressed before copper and fluoropolymers can be successfully integrated into microelectronic devices. It is well known that Cu can diffuse through a variety of materials at relatively low temperatures (<200°C), including polymers.\textsuperscript{33,34} This is of particular concern to microelectronic fabrication as copper diffusion in an integrated circuit can cause serious device deterioration.\textsuperscript{33,34} Therefore, a diffusion barrier is necessary before copper can be used as an interconnect metal in IC fabrication. A wide variety of metals and compounds have been studied as potential diffusion barrier materials for copper, with the best results obtained for high melting point materials.\textsuperscript{35-40}

There is the additional problem of fluorine diffusion in a system containing fluoropolymers. Metal-fluoride formation has been observed for the interactions of a variety of metals with fluoropolymers.\textsuperscript{4,5,32} Therefore, the ideal diffusion barrier for a copper/fluoropolymer system would be a material that limits the diffusion of both copper and fluorine, while also having strong adhesion to copper and fluoropolymers. Recent studies in our laboratory indicate that CVD aluminum oxide (AlOx) thin films exhibit a high affinity for fluorine on fluoropolymers.\textsuperscript{41} Published thermodynamic data indicates that the fluorination of aluminum oxide increases both the Al-F and Al-O bond energies,
relative to pure aluminum fluoride and oxide respectively.\textsuperscript{42} Therefore, aluminum oxide may act as a "getter" for fluorine, effectively limiting fluorine diffusion.

Aluminum oxide thin films are typically deposited via plasma-enhanced chemical vapor deposition (PE-CVD), using organo-aluminum precursors with either $N_2O$ or $H_2O$ as an oxidizing agent.\textsuperscript{43-46} Also, recent studies show that aluminum oxide thin films can be formed on fluoropolymers by the interaction of trimethylaluminum (TMA) and water coadsorbed on the polymer surface.\textsuperscript{41} However, AlOx formation by this technique involves extremely low temperatures (~100 K) during the initial condensation of the reactants on the fluoropolymer surface. A number of studies on the deposition of metallic aluminum thin films of fluoropolymer surfaces report enhanced metal adhesion on fluoropolymers that contain oxygen, versus similar non-oxygenated polymers.\textsuperscript{2,4,5,31,32} The enhanced metal adhesion is attributed to anchoring of the aluminum adlayer through higher energy Al-O bonds versus Al-C bonds.\textsuperscript{4} Therefore, the incorporation of oxygen containing surface functionalities on a fluoropolymer surface, and subsequent interaction with organo-aluminum precursors, could result in thin AlOx films bound to the polymer surface through oxide bridges. Films formed by this method could then be used as a fluorine and/or copper diffusion barrier, in addition to an adhesion promoter for subsequent metallization.

We report on the modification of a Parylene AF-4 (PAF) surface by exposure to a thermally generated flux of gaseous hydroxide free radicals and the interaction of a modified PAF surface with trimethylaluminum. Parylene AF-4 is poly($\alpha,\alpha,\alpha',\alpha'$-tetrafluoro-$p$-xylene), with the XPS spectra of the neat surface are given in Figure 24. PAF has been proposed as a low-k replacement for $SiO_2$ due to its low dielectric constant ($k = 2.28$). While the dielectric constant of PAF is slightly higher than that of amorphous Teflon (Teflon-AF, $k = 1.9$), the greater thermal stability of PAF (m.p. > 500°C) versus Teflon-AF
Figure 24. F(1s) and C(1s) XPS spectra of neat Parylene AF-4 surface.

\( T_g = 160 - 240^\circ C \) decreases potential problems with subsequent processing steps.\(^{47,48}\)

However, condensation of the precursor on the polymer surface at low temperature (~112 K) and subsequent annealing results in the formation of a thermally stable fluorinated aluminum oxide adlayer.\(^{41}\)

In part A, we report on the modification of the PAF surface by repeated exposure to thermally generated \( \cdot OH \). XPS spectra indicate that Parylene AF-4 exhibits increasing oxygen uptake as a function of exposure to \( \cdot OH \) flux. O(1s) spectra indicate at least two oxygen environments present on the polymer surface. In part B, we report on the interaction of trimethylaluminum with a Parylene AF-4 surface modified by exposure to gaseous hydroxide flux. Trimethylaluminum reacts with the modified polymer surface at room
temperature to form an aluminum oxide thin film on the polymer surface. The presence of both Al-C and Al-F bonds is also indicated.

**Experimental**

The Parylene AF-4 films used in this study were vapor-deposited by pyrolytic decomposition of the cyclic dimer in an experimental deposition system at Novellus Systems using the Gorham process. The AF-4 samples used in this study were deposited to a thickness of 5000 Å on 1000 Å SiO₂ on silicon. The refractive index of the as-deposited film was measured using a variable angle, variable wavelength ellipsometer and found to be 1.5584 in-plane and 1.4393 out-of-plane.

XPS, surface modification, and CVD experiments were carried out in a UHV surface analysis system. The turbomolecularly pumped analysis system has a base pressure of 5 \times 10^{-10} \text{Torr}. The system is equipped with a separate CVD chamber with a base pressure of 1 \times 10^{-4} \text{Torr}. Pressure in both chambers was monitored with nude ion gauges calibrated for N₂, mounted out of direct line of sight to minimize electron damage to the sample. The sample was mounted on a Ta foil sample holder spot welded to Ta leads. Temperatures were monitored by a chromel-alumel thermocouple spot welded to the sample holder.

XPS spectra were obtained using an unmonochromatized MgKα x-ray source (PHI model 1427) operated at 15 keV and 300 W and a hemispherical analyzer (VG 100AX) operated in the constant pass energy mode (50 eV pass energy). The analyzer energy scale was calibrated using Au and Cu standards, according to established procedure. XPS data were analyzed using commercially available software. Calculated intensities were derived using atomic sensitivity factors supplied by the analyzer manufacturer. The exposure of fluoropolymers to x-rays is known to induce defluorination and
cross-linking. To minimize x-ray induced damage, exposure of the sample to x-ray flux was limited to that needed for the acquisition of spectra. The observed binding energies were affected by sample charging during data acquisition. Therefore the XPS data were referenced to a F(1s) binding energy of 689.1 eV, which is consistent with the published values for fluorine in a fluorocarbon environment. The full width at half-maximum (FWHM) for the fitted spectra was kept constant within each atomic species for all spectra of that species.

Gaseous *OH was produced directly within the UHV analysis chamber by passing H$_2$O over a heated tungsten filament (~2000 K) mounted within the chamber. The total H$_2$O pressure was controlled by a manual leak valve. Previous atomic deuterium studies using mass spectrometry measurements have shown this method produces a mixed flux of atomic and molecular species, with a dissociation ratio of about 30%. Exposures are reported as a product of background pressure and time of exposure (1 Langmuir (L) = 10$^{-6}$ Torr-sec). Exposures have not been corrected for effects of directional dosing or ion gauge sensitivity. Exposures to this mixed flux were carried out without sample temperature control. The proximity to the heated filament (about 10 cm) produced a rise in sample temperature of (typically) 30 K, for a maximum sample temperature near 340 K during the dosing process. XPS studies detected no damage attributable directly to thermal heating of the sample. Surface modification experiments were performed by repeated exposure of the polymer surface to 3000 L (1 x 10$^{-5}$ Torr, 5 min) of flux obtained from H$_2$O cracking, to a maximum of 15,000 L (15 kL). XPS analysis was performed between each exposure. For experiments involving polymer surface modification prior to aluminum deposition, the Parylene AF-4 surface was exposed to 3000 L (1 x 10$^{-5}$ Torr, 5 min), with modification verified by XPS, prior to exposure to aluminum MO-CVD precursor.
Semiconductor grade (99.999% pure) trimethylaluminum (TMA) was obtained from Akzo Nobel Chemicals, Inc. (TMAL-9577) and was introduced directly into the CVD chamber using a metering valve. The composition of the organometallic precursor was verified by measurements with a quadrapole mass spectrometer. Precursor exposures are reported in Langmuirs, without correction for directional dosing or ion gauge sensitivity. The polymer surface was modified by exposure to •OH flux prior to aluminum deposition (see above). TMA exposures were performed at ambient (~300 K) temperatures. The sample was subsequently transferred to the UHV chamber for analysis by XPS. XPS spectra were obtained between each exposure.

**Results and Discussion**

A. *Parylene AF-4 Surface Modification by Exposure to •OH*

F(1s), O(1s), and C(1s) XPS spectra for a Parylene AF-4 surface exposed to 15,000 L •OH (5 exposures, 3 kL each) are given in Figure 25. Upon exposure to •OH flux, a large feature appears in the O(1s) spectrum, centered at approximately 534.5 eV. The total oxygen XPS signal increases with exposure to •OH flux, with a gradual shift in the centroid of the O(1s) feature to lower binding energy (Fig. 26). The O(1s) feature also becomes increasingly asymmetric to the high binding energy side with increasing exposure to •OH flux. Curve fitting with a fixed FWHM of 2.2 eV results in a good fit for two oxygen environments. Previous experience with the hardware and software used in these studies shows this FWHM to be reasonable for oxygen in either a fluoropolymer or AlOx environment. Fitting to two oxygen environments gives binding energies of 535.7 eV and 533.9 eV. A binding energy of 535.7 eV is in good agreement with an oxygen environment such as those found in oxygenated fluorocarbons. We therefore assign the high binding energy O(1s) fitted feature (535.7 eV) to FC-O.
For the experimental conditions extant, other possible oxygen environments include carbonyls, esters, and aromatic alcohols. However, the published O(1s) binding energy range for polymer carbonyls is 531.25 eV to 532.37 eV, which is too low to account for an O(1s) signal of 533.9 eV.\textsuperscript{53} The published O(1s) binding energy range for a bridging oxygen in polymeric esters (533.24 eV to 533.86 eV) is very close in energy to the low binding energy fitted feature observed here (533.9 eV).\textsuperscript{53} However, the insertion of a bridging oxygen into the polymer chain would involve near simultaneous defluorination and oxygenation of two carbon atoms by an oxygen diradical, which is a low probability event. It is unlikely that oxygen insertion into the polymer chain could account for a signal as large as the low binding energy fitted feature (533.9 eV) observed here.

Figure 25. F(1s), O(1s) and C(1s) XPS spectra of +OH modified Parylene AF-4 surface.
The published binding energy for a hydroxide moiety on an aromatic ring is 533.63 eV. This value is ~0.3 eV lower than the low binding energy O(1s) feature in this study. This difference is likely due to secondary fluoride effects of the fluorocarbon linkages in Parylene AF-4. We therefore assign the low binding energy fitted feature (533.9 eV) to hydroxyl attachment to the aromatic ring.

The relatively high binding energy of the centroid of the O(1s) feature at 3 kL exposure strongly suggests hydroxylation to occur preferentially at the –CF$_2$– groups on the polymer chain (Fig. 26). However, cracking H$_2$O on tungsten generates atomic hydro-
gen in addition to gaseous •OH. It has been shown that atomic hydrogen can modify fluoropolymer surfaces by defluorinating the polymer surface. It is not unreasonable to assume that atomic hydrogen will also exchange with hydrogen on the aromatic ring, which would be undetectable by XPS. Therefore, at least initially when the aromatic hydroxide concentration is small, modification at carbon difluoride surface sites is statistically more likely to appear in the XPS spectrum. Upon further exposure to the modification flux the concentration of aromatic hydroxide will increase, relative to that of the fluorocarbon, due to the decreasing probability of a hydrogen exchange on the aromatic ring. This effect is manifest in the O(1s) XPS spectra by a shift in the centroid of the O(1s) feature upon subsequent exposure to the modification flux (Fig. 26). The O/C and O/F ratios (Fig. 27) exhibit an increase as a function of exposure to •OH flux. This is consistent with an increasing oxygen uptake of the polymer surface as a function of hydroxide exposure. The O/C ratio exhibits a higher rate of increase due to increasing aromatic hydroxylation at higher exposures.

Upon exposure to gaseous •OH, the C(1s) spectrum exhibits increased intensities at binding energies between the two peaks attributable to the bulk polymer (Fig. 25). Therefore, some surface modification is clearly indicated. While the spectrum is well fit by the addition of two additional environments at 289.3 eV and 287.7 eV, given the broad envelope and relatively small contribution of these moieties, the exact number and placement of these new features would be highly subjective. Further study is necessary before unambiguous assignment of these peaks can be attempted.

The overall line shape of the F(1s) spectrum exhibits little change upon exposure of the polymer surface to •OH flux. However, the total fluorine to carbon ratio exhibits a decrease as a function of exposure to the modification flux (Fig. 27). This decrease in F(1s) signal intensity is indicative of defluorination of the polymer surface by the modifica-
tion flux. Atomic hydrogen has been shown to defluorinate fluoropolymers by reaction with surface fluorine forming volatile HF species, which desorb\textsuperscript{23}. This is manifest in the decrease in the F/C ratio in Figure 27.

B. Interaction of TMA with a Modified Parylene AF-4 Surface at \textendash310 K

A Parylene AF-4 surface was modified by exposure to 3 kL (1 \times 10^{-5} Torr, 5 min.) \textbullet OH flux and subsequently exposed to 12000 L (four 3 kL exposures) of trimethylaluminum near room temperature \textendash310 K. The F(1s), O(1s), and C(1s) spectra of the polymer surface before and after TMA exposure are displayed in Figure 28. Upon exposure to TMA, the F(1s) spectrum exhibits the appearance of a low binding energy asymmetry, indicative of metal fluoride formation. The formation of aluminum fluoride
Figure 28. F(1s), O(1s), and C(1s) spectra of OH modified Parylene AF-4 surface: (a) before and (b) after exposure to 12 kL trimethylaluminum.

upon the interaction of TMA with fluoropolymer surfaces has been observed in previous studies, with a binding energy of 687.0 eV. Curve fitting of the asymmetry gives a fitted peak at 687.1 eV, which is in good agreement with the binding energy for aluminum fluorides formed upon the interaction of aluminum with fluoropolymer surfaces. The O(1s) spectra exhibit a slight decrease in the binding energy of the centroid of the main feature. The formation of a fluorinated aluminum oxide (F-AlOx) has been proposed for the interaction of trimethylaluminum with fluoropolymer surfaces in the presence of oxygen containing species. The O(1s) binding energy assigned to this compound is 532.4 eV. While the shift to lower binding energy of the O(1s) centroid is indica-
tive of the presence of a low binding energy species, the lack of feature broadening and the number of possible environments makes curve fitting highly subjective. We therefore leave exact determination of the oxygen environments extant for future study.

The C(1s) spectra exhibit the appearance of an asymmetry on the low binding energy side of the feature attributed to the aromatic carbon of the bulk polymer (286.4 eV). Curve fitting gives a good fit for a fitted peak at 284.9 eV, attributable to adsorbed hydrocarbon species from the decomposition of the TMA precursor. A previous study of the interaction of TMA with Parylene AF-4 reported the formation of aluminum carbide bonds between the aluminum adlayer and the polymer surface. The reported binding energy for these Al-C bonds was 284.1 eV, 0.8 eV lower than the C(1s) fitted feature observed here. However, the Al(2p) spectrum of the 12 kL dosed surface (Fig.

![Figure 29](image)

Figure 29. Al(2p) spectra of a modified Parylene AF-4 surface exposed to trimethylaluminum. (a) Fitted spectrum of surface exposed to 12 kL TMA at 300 K. (b) Changes in the Al(2p) spectra as a function of exposure.
indicates the presence of carbidic species. Using atomic sensitivity factors supplied by
the analyzer manufacturer, the total Al uptake upon exposure to 12 kLTMA is
-5 atomic%, with 1.6 atomic% attributable to aluminum carbide. A binding energy of
284.1 eV is very close to the binding energy of the Kα3 x-ray satellite (283.6 eV) from the
high binding energy –CF2– feature (291.6 eV). Given the relatively small amount of
carbidic species indicated, this feature could easily be obscured by the combined signals
from fitted feature at 284.9 eV and that of the Kα3 satellite.

The Al(2p) spectrum for the modified PAF surface exposed to 12000 L of TMA is
given in Figure 29a. The spectrum exhibits a single feature centered at -75 eV, with a
large asymmetry on the low binding energy side and a smaller asymmetry to high binding
energy. The feature is well fit by three environments: 77.0 eV, 75.6 eV, and 74.0 eV. These
binding energies are very close to those observed for the interaction of aluminum (both
PVD and CVD) with a variety of fluoropolymer substrates.45,52,41 A binding energy of
75.6 eV has been previously reported for aluminum oxides and a binding energy 74.0 eV is
very close to the published value for aluminum carbides (74.2 eV).45,54 We therefore assign
the features at 75.6 eV and 74.0 eV to Al-O and Al-C, respectively. The formation of a
fluorinated aluminum oxide species has been reported previously for the interaction of
TMA with fluoropolymer substrates.41 The reported binding energy for this species is 76.8
eV, very close to the high binding energy fitted feature (77.0 eV) observed here.41 A
binding energy of 77.0 eV has also been observed upon the evaporative deposition of Al
on fluoropolymer substrates and for tribological studies of metallic aluminum with fluoro-
carbon lubricants.5,34 We therefore assign the fitted feature at 77.0 eV to F-AlOx.

Changes in the Al(2p) spectra with respect to TMA exposure are given in Figure
29b. The Al(2p) feature exhibits a gradual shift to higher binding energy in the feature
centroid (from -74 eV to -75.6 eV), upon increasing exposure to the organometallic
precursor. This shift to higher binding energy is indicative of an increase in aluminum oxide formation and fluoride formation. The changes in the fitted Al(2p) spectra are summarized in Figure 30. The total Al(2p) signal intensity increases upon subsequent exposure to the TMA precursor, indicating increasing aluminum uptake on the polymer surface. The relative contributions of each of the fitted components are also given. The relative contributions of the fitted components attributed to Al-C and Al-O bonds exhibit an inverse relationship, with carbide bonds decreasing with exposure and oxide bonds increasing. Metallic Al films formed from TMA typically exhibit substantial carbon contamination. The results shown in Figure 30 show that carbide formation is substantially reduced by the presence of oxygen moieties on the polymer surface. This is likely due to
the thermodynamic favorability of Al-O bond formation over Al-C bonds. Fluoride formation increases initially, then remains relatively constant at higher exposures.

**Summary and Conclusions**

Exposure of a neat Parylene AF-4 surface to •OH flux results in modification of the polymer surface by defluorination and oxygenation. Oxygen uptake by the polymer surface increases with increasing exposure to the modification flux. At low exposures, the oxygenation of the polymer surface as observed by XPS appears to occur preferentially at the -CF₂-linkages, forming FC-O environments. Higher exposures result in increasing hydroxylation of the polymer aromatic rings.

Exposure of the •OH modified Parylene AF-4 surface to trimethylaluminum at room temperature (~310 K) results in the formation of an aluminum adlayer on the polymer surface. Studies involving the exposure of a neat Parylene AF-4 surface to trimethylaluminum (up to 50 kL) at both room temperature (312 K) and elevated temperature (525 K) resulted in no detectable aluminum on the polymer surface. Therefore, modification by exposure to •OH flux results in a significant increase in the reactivity of the Parylene AF-4 surface to the organo-aluminum precursor. XPS data indicate the aluminum adlayer on the modified polymer surface to be in the form of a fluorinated oxide, which has been observed in previous studies involving the interaction of aluminum with fluoropolymer substrates. Subsequent exposures to TMA exhibit increasing aluminum uptake on the adlayer surface, with aluminum-oxygen bonds forming at the expense of aluminum-carbon bonds. Fluoride formation increases during initial exposure, then reaches a maximum, whereupon it remains constant. This indicates the existence of a fluorine diffusion limit in the oxide adlayer.
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