Mass Spectrometric Characterization of Pulsed Inductively Coupled Plasmas for Deposition of Thin Polyethylene Glycol-like Polymer Films

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In this work we characterize pulsed inductively coupled rf plasmas of two organic precursor molecules, isopropyl alcohol and 1,4 dioxane using Langmuir probes and in-situ mass spectrometry. We identify the key ionized species diffusing to the substrate and offer an explanation as to how they are generated. We also analyze the deposited films using X-ray Photoelectron Spectroscopy and suggest a correlation between the measured plasma ion mass distributions and chemical bonding character of the deposit. The ultimate goal of this work is to develop predictable models for PECVD processes for thin polymer films with functionalized surfaces.

Key Words: plasma polymerization, PECVD, RF plasmas, plasma mass spectrometry.

1. Introduction

Exciting opportunities are presenting themselves to the thin film community in the form of "designed interfaces" between biological and semiconductor (or polymer) media. New classes of miniaturized biosensors that detect and quantify minute levels of physiologically relevant chemicals for both medicine and chemical/biological warfare are the direct result of successful surface modification and chemical functionalization.[1,2] Miniaturized biosensors often are fabricated using pattern transfer processes including lithography, vacuum evaporation, and plasma processing technologies. The advantages of such technology are that small feature size and multiple arrayed devices allow for extremely low level and simultaneous, multiple species, detection. The performance of these sensors will depend critically upon how well the wet, biological species interact with the dry-processed transducer. Thus, the critical technological challenge in biosensor development is the control of interfacial design between the wet and dry processed components. In addition to its chemical nature, such attributes as substrate adhesion, thickness control, porosity, and mechanical stability will play a crucial role. Within these requirements, plasma polymerization combined with chemical surface functionalization may provide another and potentially superior deposition alternative.[3]

A great deal of focus has been placed recently on surface functionalization strategies using low power glow discharges.[4,5,6] Strategies have included direct deposition of the functional group through PECVD methods, or by activating the surface by creating reactive groups and derivatizing, or grafting molecules in place. Recently, several groups have demonstrated that increased chemical character of the desired polymer functional group is retained if the rf plasma source is pulsed at frequencies in the hertz to kilohertz range.[7,8,9] Models have predicted that pulsing the discharge may be a unique means to controlling the kinetic processes in the plasma.[10] However, the mechanisms that lead to the plasma deposition of high quality functional polymers are still poorly understood. To date, most deposition studies have employed ex-situ film analysis in order to postulate the chemical mechanism.

In the PECVD process, electromagnetic energy is coupled into the precursor gas in order to activate the reactants in the form of electrons, ions, and neutral species. Traditional mechanistic paradigms of plasma chemistry have focussed on electron energy distributions and how their overlap with ionization and bond scission cross sections

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can lead to unique, non-thermal gas phase ion and neutral radical distributions. These species homogeneously react in the gas phase and are transported to the surface where their polymerization chemistry can potentially lead to films with very unique properties. However, one important aspect of plasma chemistry is gas phase, ion-molecule reactions, which often lead to different chemical species than normally anticipated by electron-impact ionization-dissociation or electron recombination-dissociation. Our effort focuses on understanding the fundamental plasma physics and chemistry of a deposition process in sufficient detail as to ultimately yield films with controllable, tailorabl properties. Understanding of such a process would yield a model, which is predictive of the creation and loss of the plasma electrons, ions, and neutral species. We have employed Langmuir probes and in-situ mass spectrometry as our experimental diagnostic method for model development. Finally, we have begun to deposit films and analyze them using X-ray Photoelectron Spectroscopy in order to suggest a correlation between the measured plasma ion mass distributions and chemical bonding character of the deposited polymer.

We have chosen polyethylene glycol, or PEG-like structures as our target PECVD functional group. PEG is well known for its resistance to fouling from biologically active molecules. Therefore, coating non-sensor related surfaces with non-fouling thin films would significantly enhance sensitivity of microfluidic-tranducer modules. PEG has a relatively simple monomer structure \([\text{CH}_2\text{CH}_2\text{O}^-]\), and films of pure PEG have been well characterized via XPS. Several groups have explored plasma depositing of PEG-like structures using organic precursors such as crown ethers and short chain "oligoglymes" followed by XPS or SIMS film analysis as a means to understand the plasma chemistry.

In this initial study, we have chosen two organic precursors, isopropyl alcohol and 1,4 dioxane, a cyclic version of the di-ethylene glycol structure. The reason for the choice is not because they give rise to films of superior quality as those reported above but because they give rise to simple and relatively easily interpreted mass spectra. Therefore, an initial study of the behavior of these molecules will represent a stepping stone for interpretation of the much more complex precursor structures currently being attempted by other groups. Furthermore, the precursors are inexpensive, readily available, and have very high vapor pressures. High vapor pressure precursors are advantageous as a starting material not only because of their ease in introducing them into the gas phase discharge, but also that the surface coverage during deposition will be low because of the high desorption rate. The films therefore do not contain a large component of entrained precursors in the polymer matrix, which eventually solubilizes and leaves voids and exfoliated regions.

We deduce from the ion fragment mass distributions found in an isopropyl alcohol/Ar discharges that two distinct chemical pathways are present. One reaction, a direct electron dissociation-ionization reaction, yields the fragment \(\text{CH}_3\text{CHOH}^+\) \((m/z=45)\). Another process, an ion molecule protonation reaction followed by unimolecular dehydrogenation reaction, produces the fragment \(\text{CH}_3\text{CHCH}_3^+\) \((m/z=43)\). If we tacitly assume that our desire is to introduce the functionality, \(\text{CH}_2\text{CHOH}\), into a film, then plasma conditions must be sought where dissociation-ionization dominates. We show this to be consistent with our results. Conversely, using 1,4 dioxane as a precursor, we show that ion-molecule chemistry must dominate in order for the incident ion mass distribution to contain the desired chemical character.

2. Experimental Apparatus

2.1 Plasma Chamber and Gas Handling

![Figure 2: Schematic representation of apparatus.](image-url)
commercially available double-walled, 8-in. diameter, 6-way conflat cross attached to an additional tee (MDC Inc.). The tee supports a 450 l/sec turbomolecular pump. Pressure control is achieved through a variable conductance iris valve (RJ Munns Inc.). The base pressure of the system is 3 X 10^-8 Torr. Both non-reactive gases and reactive gases are introduced into the system through independently bakeable manifolds where they are mixed just prior to the inlet into the plasma chamber. Non reactive gases such as Ar and O2 are all ultra high purity pure (Spectra Gases). Both isopropyl alcohol and 1,4 dioxane are purchased as ultra-pure, transferred in a glove box under dry, inert conditions and followed by three freeze-pump-thaw cycles. Discharges could be easily maintained with pressures between 5 and 100 mTorr and flow rates of 50 sccm without exceeding the pumping limits of the system.

2.2 Plasma Source

The plasma source is a commercial 13.56 MHz generator (RF Power Products Model 30 PWT) which can be pulsed between 1 to 100 kHz. The results presented in this work explored variations in pressure and power, the pulse characteristics were held constant at 100µs period (10 kHz) and 20% duty factor (plasma "on" time = 20 µs). The generator is attached to an auto-matching network (RFPP Model AM-20). The inductively coupled plasma source antenna is a 4 in. diameter, 6-turn, planar coil made of copper tubing (3/8 in. OD) that couples to the plasma through a quartz window. Plasma was easily generated with as low as 4 W of power. For all data reported in this work, the source is held fixed at 7.5 cm above the surface.

2.3 Langmuir Probe

Estimates of the plasma temperature and density in the vicinity of the mass spectrometer entrance aperture were obtained using an emissive Langmuir probe, positioned 1-cm above the aperture. The probe comprised a 0.6-cm-long, 0.013-cm-diam thoriated-tungsten filament driven by a floating power supply. The connection to the measurement circuit was located at the filament midpoint to minimize distortion of the measurements by the filament voltage drop. [16]

The plasma potential must be known in order to interpret probe I-V traces. While in principle it can be determined from the traces, in practice this is difficult and a direct measurement is preferred. Here, the time-varying plasma potential is equated to the probe floating potential measured under conditions of strong emission (where the probe temperature is increased to the point that the emitted current reaches a plateau). This simple technique has inherent sources of error.[17] However, here we are concerned with large swings in the potential and the 1-2 V accuracy of this method is tolerable. Previous measurements here have shown reasonable (~1 eV) agreement between this method and a more accurate comparison of hot and cold probe I-V traces. The probe was connected directly to a 1-MΩ scope input and the resulting floating potential recorded over the 100-µs pulse period. The time response was limited by stray capacitance to a few µs, which is sufficient for this work.

Next, probe I-V traces were obtained. The probe was operated under warm conditions, below the temperature threshold for emission. The probe bias was stepped in 0.2-V increments from -35 to 35 Volts. At each voltage, the probe current was measured over the pulse period. Transposing these data yields the I-V traces at different times. Floating the probe sense resistor, scope, and controlling PC at the probe bias voltage minimized the effects of parasitic reactances.[18] The remnant stray capacitance of the probe connection limits the time response to better than 1 µs.

2.4 Quadrupole Mass Spectrometer

The quadrupole mass spectrometer (QMS) has been described previously.[19] The plasma ion flux mass distributions are measured with a 1-1000 amu Extranuclear ELQ400 quadrupole mass spectrometer. The mass spectrometer is housed in a separate vacuum chamber, pumped by a 350 l/sec turbomolecular pump, and easily achieves a base pressure of 10^-8 Torr. The sampling aperture is part of a custom designed front cap which has two components: a copper plate (5.6 in. diam. X 3/16 in. thick and a stainless steel front plate (5.25 in diam. X 1/16 in. thick) which are clamped together. The sampling aperture is a hole, 0.8 mm in diameter, which has been carefully aligned with the axis of the mass spectrometer's ion optics. Across this hole we have secured a grid of 30µm diameter holes, spaced 90µm apart, laser drilled through a 0.002-in. thick stainless steel shim. The hole diameter and spacing are designed to be less than the Debye length of the plasma, thus minimizing perturbations of the sheath fields.[20] The number of holes (~ 100) is to ensure the gas dynamics is sufficient to minimize subsequent collisions in the ionizer, yet maintain sufficient signal levels. Typical pressures in the mass spectrometer were between 5 X 10^-7 -8 X 10^-6 Torr. To measure the mass distribution of the ion flux, the ionizer was turned off and the output of the electron multiplier passed through a current sensitive amplifier (Kiethly). Typical gains varied between 10^5-10^6. The amplified signal is digitized on an oscilloscope and stored on PC. Typically 100 sweeps of 100 amu were averaged.
Typical experiments were as follows. After setting gas flow and pressure conditions, a discharge was initiated and conditions were allowed to achieve a stable, steady state. This usually took no longer than 2-5 minutes and the system remained unchanged for several hours. Mass spectra and probe data were obtained in this period. Finally at the completion of a data acquisition session, a high power (400-500 W) \( \text{O}_2 \) discharge was sustained in order to etch the chamber and substrate back to the initial state. Cleanliness was carefully monitored by using the mass spectrometer as a residual gas analyzer while monitoring oxidation products such as \( \text{CO} \) and \( \text{CO}_2 \).

2.5 X-ray Photoelectron Spectroscopy

Films were deposited on 1 cm\(^2\) stainless steel chips while the plasma was simultaneously sampled by the mass spectrometer. Prior to deposition, the reactor and substrates were subjected to a cleaning procedure consisting of a high density (500W) continuous wave (CW) oxygen plasma for 45 minutes. Pulsed plasma deposition times were between 3-6 hours. The XPS spectra were acquired \textit{ex situ}, with the samples having been stored in a dry atmosphere for several weeks. However, before the spectra were obtained, the samples were placed in the vacuum chamber load-lock and allowed to out-gas for 72 hours at a pressure of less than 10\(^{-7}\) Torr.

Survey and high resolution spectra were acquired using a Fisons (220IXL) X-ray Photoelectron Spectrometer with a take-off angle of 45°. Al K\(\alpha\) radiation was used, with photon energy of 1486.6 eV. High-resolution scans of the C 1s and O 1s core electron regions were taken with a pass energy of 20 eV. Spectra were analyzed by fitting Gaussian peaks using a least-squares fitting routine. The peaks were chosen to be pure Gaussians, as opposed to the standard Gaussian with 20% Lorentzian, as will be discussed in the next section.

The samples were not ion-sputter cleaned in the XPS chamber, as the effects of ion bombardment on the film composition and morphology were judged to be too severe. Generally, ion-sputter cleaning is problematic in that certain elements in the film will likely be preferentially etched, causing changes in the surface composition. Ion bombardment can also change the morphology of carbon samples. It has been shown to, for example, create amorphous layers on crystalline graphite and diamond surfaces.[21] Polymeric films are particularly susceptible to damage caused by keV ions impinging on the surface, with effects such as induced crosslinking.

3. Results and Discussion

3.1 Langmuir Probe

Inferred plasma potentials are shown as the solid curves in Figure 3. The potential changes rapidly in response to the RF power pulse. At the onset of the power pulse, the potential exhibits an overshoot, particularly in the low-power case where the potential jumps to greater than 40 V. This overshoot is much less pronounced with pure \( \text{Ar} \) plasmas. We speculate that the overshoot arises from a temporary imbalance between electron heating from the RF and cooling by ionization. The plasma potential represents a moment of the electron velocity distribution and is thus a useful indication of the electron temperature. For example, in a pure, Maxwellian argon plasma the plasma and floating potentials will differ by a voltage slightly more than five times the electron temperature in eV.

Electron temperatures are estimated from the slope of the I-V traces in the region between the floating and plasma potentials. These are quite consistent with the inferred plasma potentials, as shown in Figure 3. The two quantities exhibit the expected ratio of about five (the floating potential, not shown, was negligible compared to the plasma potential).

Electron densities were estimated by equating the probe current at the plasma potential to the electron saturation current. Densities so obtained are shown in Figure 4. While the density also follows the RF power pulse, it responds more slowly than the electron temperature and shows less modulation. Both the temperature and density response to the RF power are qualitatively

![Figure 3. Plasma potential (V\(\text{p}\)) and electron temperature (T\(\text{e}\)) for two discharge conditions: 50 % \text{ipOH} in \text{Ar}. a) 80W power, 5 mTorr pressure b) 50W, 100 mTorr pressure](image-url)
consistent with previous studies of pulsed plasmas.[22]

Single, bare probes are known to provide less accurate (–factor of 2-3 in density) measurements in RF plasmas than compensated or double probes.[23] We intend to perform more refined probe measurements in the future. The present measurements still provide a good estimate of the plasma Debye length. Proper interpretation of the mass spectrometer results requires that the sheath thickness at the aperture, which will be on the order of a few Debye lengths, be large compared to the aperture diameter. In our case this length is smallest during the time the RF is off. Based on the probe measurements, this length is a minimum of roughly 100 microns for the low-pressure case and 400 microns for the high-pressure case. Therefore, we do not believe that the aperture used here represents a significant perturbation.

3.2 Ion Mass Distributions

Figure 5 compares an electron-impact ionization mass spectrum (EI-MS), reproduced from a table of standards, to a plasma-generated ion mass spectrum (PI-MS) for isopropyl alcohol.[24] The EI-MS is dominated by the 45 amu fragment and shows no “parent” ion of 60 amu. The fragment corresponding to 45 amu results from a direct electron dissociation-ionization reaction:

$$(\text{CH}_3\text{CH}_2\text{CHOH} + e^- \rightarrow \text{CH}_3\text{CH}_2\text{CHO}^+ + \text{H}_2\text{O}^- \text{)} \quad \text{(1)}$$

However, when considering the plasma-generated ion mass spectrum it is clear there are alternative ionization channels in the discharge which yield ion fluxes impinging on the surface with masses of 43, 59, and 61 amu in addition to mass 45. We explain these results by invoking the following ion-molecule protonation chemistry:

$$(\text{CH}_3\text{CH}_2\text{CHOH} + \text{MH}^+ \rightarrow (\text{CH}_3\text{CH}_2\text{CHOH})^+ + \text{M} \text{)} \quad \text{(2)}$$

where M is Ar, or H₂. This reaction is followed by the rapid unimolecular decomposition which eliminates water and the isopropyl cation (m/z=43 amu):

$$(\text{CH}_3\text{CH}_2\text{CHOH})^+ \rightarrow (\text{CH}_3\text{CH}^+ + \text{H}_2\text{O}^- \text{)} \quad \text{(3)}$$

A competing reaction occurs when the protonated radical cation (m/z=61) formed in reaction (2) eliminates H₂:

$$(\text{CH}_3\text{CH}_2\text{CHOH})^+ \rightarrow (\text{CH}_3\text{CH}_2\text{CHO})^+ + \text{H}_2 \quad \text{(4)}$$

which accounts for mass 59. These ionization schemes have been studied at length by mass spectrometrists under the name “chemical ionization” mass spectrometry (CI-MS) and the technique continues to be exploited as a means of minimizing the level of fragmentation in very large organic molecules. [25, 26] Consequently, we have a wealth of kinetic data [27] to draw upon in order to construct plasma chemistry models, and this work is currently in progress. Furthermore, in support of this chemical scheme, we have confirmed, using downstream residual gas analysis, that significant partial pressures of H₂ are produced by the discharge, which will promote the protonation/dehydrogenation chemistry mechanism steps 2-4. It is fortuitous that, by simply monitoring the intensities of two neighboring ions, m/z 43 and 45, we have the ability to monitor two general classes of plasma ion formation chemistry: electron driven and ion driven, and to seek conditions where we can exacerbate one over the
other. Mapping the conditions where we favor one chemical pathway is the beginning of gaining control of the fluxes to a substrate. Understanding and ultimately predicting this level of control in plasma chemistry can potentially make great strides in understanding organic thin film PECVD and surface functionalization.

Figure 6 demonstrates the conditions under which electron versus ion-molecule process can be tuned. The three panels correspond to ion flux mass distributions as a function of pressure and, to a lesser extent, power. Both the gas inflow composition and the pulse duty factor were held constant. Probe measurements of \( V_p \), \( T_e \), and \( N_e \) correspond to the first and third panel’s plasma conditions. When probe and MS data are together, we can begin to hypothesize regarding the nature of the plasma electron environment and the subsequent atomic and molecular chemistry. At 5 mTorr, 80W, the peak electron density is six times greater than the 100 mTorr case. Furthermore the plasma is roughly twenty times less collisional. Therefore electron dissociation-ionization will dominate over ion-molecule processes and this is clearly observed in the mass flux ratio of 45/43 \( \approx 3 \). At low pressure, we measure a 50-fold increase in Ar ions impinging on the substrate. This suggests that the rates of both ion recombination and Ar ion charge exchange with \( \text{H}_2 \) are slow with respect to ambipolar diffusion to surfaces. Consequently, these results suggest that the Ar ions have had insufficient opportunity to react with \( \text{H}_2 \) to convert into the powerful protonating agent \( \text{ArH}^+ \). Conversely, in the 100-mTorr case, we observe the relative 45/43 mass flux intensity ratio to reach 0.5 indicating a highly collisional, ion molecule reaction-dominated environment. The center panel shows a flux ratio of unity, which we display to demonstrate that the plasma conditions do not correspond to specific “asymptotic” states, and can be varied smoothly.

Furthermore, we see evidence of higher mass fluxes at 88 amu. At this point in our research effort, we cannot definitively ascertain whether this is ion-pair formation or true gas phase polymerization. Furthermore, we know that 88 amu is in the range of a dimer of the basic (C-C-O) unit, and the growth of the peak is correlated to both \( m/z=45 \) and possibly \( m/z=40 \). We have also seen evidence that, under very high power, the neutral molecule is apparent. However, under most plasma conditions investigated in this study, the corresponding neutral species flux is very low.

Figure 7. Ion Mass Distributions for three different discharges. Inflow gas: 50% 1,4 dioxane in Ar. Plasma 100µs period, 20% duty factor. Panels a) 100 mTorr, 20W, b) 100 mTorr, 100W, c) 2.5 mTorr, 100W

As a complement to the isopropyl alcohol case, Figure 7 displays the ion flux mass distributions for the molecule 1,4 dioxane. In the low pressure (2.5 mTorr), high power (100W) case (electron dissociation-ionization promoting conditions), we observe a mass spectrum which is highly fragmented, dominated by low molecular weight ions such as ethylene, \( \text{C}_2\text{H}_4 \) (m/z=28). As in the case of isopropyl alcohol, the plasma ion flux mass distribution is very reminiscent of a standard El
mass spectrum. However in this case the fragment at 43 amu emanates from a CH-O-CH₂ species which occurs when the ring is symmetrically cleaved across the C-C bonds by electron dissociative ionization. The fragment at 45 amu stems primarily from the ring being cleaved symmetrically across the C-O bonds to form a CH₂CH₂OH from a protonation-ring opening reaction and is generally very weak in El-MS. As we increase the pressure to 100 mTorr and maintain 100W power, we observe an inversion of the 43/45 flux intensity ratio. This suggests that the ion molecule protonation rate is increasing to be commensurate to the electron dissociative ionization channel. In the 100 mTorr, 20W discharge, the flux distribution simplifies considerably, with the dominant flux corresponding from the precursor molecule, and the principal fragment is -CH₂CH₂OH. These results suggest that the electron density in the 20W discharge is not large enough to provide suitable competition for the protonation rates.

3.3 X-ray Photoelectron Spectroscopy of Deposited Films

Figure 8: High resolution C 1s XP Spectrum of film deposited with isopropyl alcohol under conditions depicted in PIMS Figure 6c. Best-fit convolution of known carbon oxidation states are indicated by arrows.

Figure 8 is the high resolution C 1s spectrum for a thin film deposited in an iPrOH/Ar plasma corresponding to the PIMS displayed in Figure 6c. Four peaks were fitted to the spectrum. In pure PEG, each carbon is bound to another carbon atom, one oxygen atom and two hydrogen atoms, i.e. (CH₃CH₂O)ₙ. Thus, the C 1s spectrum would have only one peak at 286.5 eV [13]. The variety of peaks indicates that the structure of these films is quite complex. It is characteristic of thin films deposited by plasma polymerization to have several peaks in the XPS spectrum.[7, 28] Each peak represents one or more chemical structures that exist in the film. The multitude of structures is due to the nature of a plasma discharge. As we have observed in the measured plasma ion mass spectra, electron and ion driven gas phase chemistry will generate a distribution of chemical radical ion and neutral species, and many of these species will be incorporated into the film.[29] The resulting film has polymeric chains composed of statistically incorporated reactive species. Using in situ PIMS, and varying the plasma process parameters we directly measure the relative weighting of the distribution for the ion incident flux. The relative intensity of the ideal XPS peak is then used as a measure of the degree to which the desired structure has been incorporated into the film.

The largest peak in Figure 8 is located at approximately 284.8 eV. There are several carbon configurations that can contribute to the intensity of this peak. One is hydrocarbon contamination from the exposure of the film to atmosphere. It is expected that a significant contribution to this peak area is from carbon incorporated into ethylene chains, i.e. (CH₂-CH₂-CH₂)ₙ. There are several other bonding configurations that will cause the C 1s electrons to have a binding energy within the range 284.8 ± 0.3 eV. If one includes the very real possibility that carbon-carbon double or triple bonds exist, there are 11 possible core electron states that could be a part of this peak. The binding energy for each of these configurations will be subject to perturbations due to variations in the next-nearest neighbors of the carbon atom. Given that the peak at 284.8 eV could be due to several different peaks within a small range of binding energy, the decision was made to fit the peaks as pure Gaussians, instead of the standard Gaussian with a 20% Lorentzian structure.

In spite of the limited ability of XPS to determine thin film structures, XPS does reveal the nature in which the carbon atoms are bound to oxygen. The second peak in Figure 8 is due to carbon atoms with one bond to an oxygen atom. As stated before, in a high-quality PEG sample these carbon atoms will be arranged as O-CH₂-C. However, there are most likely other bond C-O configurations present, such as C-COH-C (286.44 eV) and O-CH₃ (286.7 eV) [30].

At approximately 288.0 eV, there is intensity that is a convolution of peaks with two carbon oxygen bonds, i.e. O-CH₂-O and C-C=O, and their isomers. Also, there is a peak at approximately 289.2 eV. This is due to a ester or carboxylic acid group, or -O-C=O bonding.
Figure 9 displays the C 1s spectrum of a film deposited with 1,4 dioxane as the precursor under PIMS conditions depicted in Figure 7a. As with the isopropanol samples, the largest peak is due to carbon atoms bound exclusively to hydrogen and other carbon atoms. However, the C-O peak area is 65% of the aliphatic peak area. This is much more than in any of the films deposited with isopropanol. The best film deposited with iPrOH had a C-O/C-C peak ratio of 0.25. These results, while giving limited information about the structure of the films, do show that the 1,4 dioxane precursor results in films much closer in structure to bulk PEG.

![Figure 9: High resolution C 1s XP Spectrum of film deposited using dioxane under conditions depicted in PIMS Figure 7a. Best fit convolution of known carbon oxidation states are indicated by arrows.](image)

The O 1s region of the XPS spectra revealed limited information about the structure of the films. This is because the peaks due to the possible oxygen bonding configurations are too close in binding energy to distinguish. For example, C-O-C and C-OH both have binding energies of 532.7 eV, and O=C has a binding energy of 532.4 eV.[30] 

We now seek to relate the in situ measurements of the ion flux mass distributions to the film composition as revealed by the XPS results. Simple peak intensity ratios were used to quantify changes in the iPrOH mass spectra and XPS results. As has been discussed earlier, the iPrOH ion spectra have prominent peaks at 43 and 45 amu. The species at mass 45 amu is CH₃CH⁺OH and is believed to be beneficial for the formation of -(C-C-O)- chemical character in the deposited film. The species at mass 43 amu is the CH₃CH⁺CH₃ ion that will incorporate aliphatic carbon into the film. The ion flux ratio of the peak intensities (45/43 amu) was used to characterize the plasma. The greater the ratio, the greater the flux of the desired ions to the surface.

The C 1s XPS results were used to quantify the quality of the films. The C-O and O-C=O peak areas were referenced to the aliphatic peak area. The C-O/C-C and O-C=O/C-C ratios were calculated and compared to the mass spectral results. The ratio of the C-O to aliphatic peak areas (C-O/C-C) is a measure of the desired incorporation of oxygen into the film. In contrast, the O-C=O/C-C peak area ratio is a measure of the undesired incorporation of oxygen into the film. In Figure 10, both of the XPS ratios are plotted against the PIMS flux ratio (45/43 amu). Two clear trends are apparent. As the 45/43 amu peak intensity ratio increases, the C-O/C-C ratio increases monotonically. However, the O-C=O/C-C ratio decreases with increasing ion flux ratio.

![Figure 10: Relationship between deposited film's bonding character and PIMS 45/43 amu flux ratio.](image)

The results are encouraging for the use of in-situ ion mass spectrometry in relating the molecular ionic flux impinging on a surface to the concentration of a functional group incorporated into a film. In Figure 10, we observe that a six-fold increase in the mass flux of the CH₃CHOH⁺ radical ion (45amu) over the isopropyl radical ion (CH₃CHCH₃⁺: 43amu) results in a two-fold increase in the C-O character of the film. In order to appreciate why there is not a greater slope to the curve, we must consider the neutral radical flux as well. As we observed in reaction (1), for every CH₃CH⁺OH radical ion produced by dissociation-ionization of the isopropyl alcohol precursor molecule, a neutral methyl radical is produced as well. Therefore, some fraction of this gas phase radical density will incorporate into the film and contribute aliphatic character.
The decrease in C=O bond character with increasing 45/43 flux ratio is not as directly explained. The reaction that produces the isopropyl molecular ion also produces a water molecule. We postulate that when the 45/43 flux ratio is low, production of 1120 is elevated, and there is a concomitant increase in species such as H2O, OH, O, and H impinging on the surface. The hydroxyl radical, for example, serves as a powerful oxidant, which, if it attacks a surface carbonyl, will convert it to a carboxylic acid. In addition, both OH, and H atoms are equally powerful abstraction agents for saturated hydrocarbons, and will equally activate surface sites by producing H2O and H2 respectively. These open sites are then subject to oxidation or cross linking by subsequent collisions with the impinging molecular and atomic flux. Clearly more study of the chemical character of the neutral species is warranted.

4. Summary

In this work we have presented preliminary Langmuir probe and in-situ mass spectrometry as a means of characterizing pulsed inductively coupled glow discharges of organic precursor molecules in Ar. We have explored a variety of plasma conditions and have found large variations in the plasma ion flux distributions. We then offer a tentative hypothesis which qualitatively explains our findings. The results embodied in Figures 6 and 7 suggest that, in the designing of a PECVD process, where the goal is to terminate the surface with chemical moieties of a given functional group (e.g. -C-C-O-), it is critical to understand the specific plasma chemistry which gives rise to the incident reactive mass flux distributions. To the extent that the ion mass distributions reflect the global chemistry (electrons, ions, and neutrals) different combinations of plasma conditions such as power, pressure, and duty factor, will favor different chemical pathways, such as electron and ion generated production branches. In examining the behavior of the simple molecules employed in this work, we demonstrated that very different conditions must be employed in order to obtain fluxes of similar composition.

The results from our XPS studies suggest that there is a direct correlation between the mass spectra and the resulting film properties. Although the plasma parameters used to achieve these results cover a wide range of plasma conditions, the resulting in situ mass spectra have a very simple relationship with the film quality. This enables a better method of parameter optimization than a simple plasma parameter/film property study. The ability to tune plasma parameters and receive immediate feedback on film quality from the mass spectra measurements will enable the time-effective determination of optimum plasma parameters for film deposition.

Our current work is focussed on characterizing the neutral mass flux, and performing bio-adhesion studies to determine their non-fouling viability.

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5. References