

## A growth mechanism for the vacuum deposition of polymeric materials

Hirotsugu K. YASUDA, Y. S. YEH, and S. FUSSELMAN  
Dept. of Chemical Engineering, University of Missouri-  
Columbia  
Columbia, MO 65211 USA

**Abstract-** An overall growth mechanism for the vacuum deposition of polymeric materials is developed from experimental observations for various deposition techniques. The growth mechanism is a rapid step growth process based on the gas phase-surface interactions, as opposed to chain growth for conventional polymerization. The applicability of the proposed mechanism is that it provides a basis for determining how a change in deposition conditions will affect film structure and deposition rate.

### INTRODUCTION

Historically, proposed mechanisms of plasma polymerization have been based on conventional chain growth polymerization, such as free radical or ionic polymerization. In conventional chain growth polymerization, an initiating species reacts with monomer, and this process continues with the subsequent addition of monomer, proceeding until the reaction is terminated by processes such as disproportionation, combination, or transfer of reactive agents to some species separate from the polymer chain.

Chain growth polymerization is a molecular process that can proceed at low (atmospheric) pressure with catalysts, or spontaneously at high pressures without catalysts, or in the liquid phase under a variety of conditions. The resultant polymer has a regular, repeating structure based on the monomer. As will be shown later, vacuum deposition polymerization is an "atomic" process which yields a highly crosslinked product with a random structure, and vacuum conditions make gas phase chain growth a highly improbable growth mechanism due to thermodynamic constraints.

Vacuum deposition processes, such as Parylene polymerization, UVVD and plasma polymerization, occurs due to the dissociation of covalent bonds in gas phase molecules, and subsequent reactions between gas phase species and surfaces result in the deposition of polymeric materials. Dissociation results from interactions between monomer and energetic species, such as ions, electrons, photons, and excited neutrals. In parylene polymerization, bond dissociation is due to thermolysis of monomer. The term monomer is not used in the same sense as in conventional polymerization. In vacuum deposition, the term monomer refers to any compound which can be used to deposit a film of polymeric material. Such compounds include but are not limited to those used in conventional polymerization. For example, plasma polymers can be obtained from methane, benzene, and saturated fluorocarbons.

By an atomic process, it is meant that the species which contribute to growth are not well defined structures. Rather, they are created by fragmentation or rearrangement of the original monomer. Since there is no particular species which exclusively accounts for deposition, much effort has been directed at describing the kinetics of these processes using a "black box" approach. Possible precursor species are identified by analysis of the gas phase and correlated with deposition data, with the growth mechanism itself treated as an unknown, or, a black box. It is important to recognize, however, that no accountable correlation between hypothetical precursor species and material deposition can be established without a proposed growth mechanism.

In this paper, a proposed growth mechanism for the formation of polymeric materials in vacuum is presented, with previous experimental results serving as the bases for this mechanism. The most important aspects of this mechanism is that vacuum deposition polymerization occurs due to the deexcitation of reactive species, that the process is atomic rather than molecular, and that third body collisions are required for polymer formation to occur.

### FORMATION OF REACTIVE SPECIES

The generation of reactive species which take part in the deposition of polymeric films under vacuum can be achieved by the interactions of monomer and energetic species or by thermolysis of monomer. The energetic species can be ions, electrons, photons, or excited

neutrals, and can cause considerable fragmentation of the original monomer. Thermolysis yields reactive species which have a much more predictable structure, as dissociation takes place almost exclusively at a given location in the monomer when the monomer structure is designed to do so.

The reactive species obtained from monomer-energetic species interactions are much less predictable than those obtained from thermolysis of a tailor made molecule, as the former are influenced by steric effects and the random nature in which energetic species approach the monomer. The number of different reactive species resulting from monomer-energetic species interactions is limited only by the energy of the energetic species and the number of ways in which the monomer can dissociate.

### Ions

Low pressure plasmas contain relatively small amounts of ions and electrons. For instance, in a dc magnetron discharge at 1 Torr, the ion density (as well as the electron density) is roughly  $10^8/\text{m}^3$ , and the ratio of ions to neutrals is roughly  $10^{-4}$  (ref. 1). The participation of ions in the deposition of plasma polymers is a matter of considerable debate. In a plasma of monomer only, it seems highly improbable that gas phase ions are capable of causing dissociation of neutrals. At most, the ions might switch charge with neutrals, which can effect the flow of ions in a discharge system by transferring charge from a fast moving ion to a slow moving neutral, or vice versa (ref. 2, p. 33).

The basis for excluding monomer ions as a major contributor to the formation of reactive species is presented as follows: At a pressure of 10 mTorr and approximate temperature of 300 K, the mean free path in a methane plasma is roughly  $1.2 \times 10^{-3}$  m for ionized monomer. In order for the ion to accumulate sufficient energy to cause dissociation ( $> 4$  eV), it must travel through an electric field of roughly 30 V/cm. In the positive column of a glow discharge, the electric field is typically on the order of 1 V/cm (ref. 3). Therefore, it is highly unlikely that ions play any important role in gas phase dissociation when a single gas is present. However, ion impact at a biased surface can be of sufficient energy, as the field strength can become quite large in the vicinity of a surface. It is well known that when a substrate is negatively biased, the deposition rate on the substrate increases as the bias voltage becomes more negative. Westwood (ref. 4) found that the deposition rate at a biased auxiliary electrode in a dc bell jar system increased linearly as the bias voltage decreased from +80 V to -80 V. Westwood concluded that deposition was brought on by positive ions impinging on surface adsorbed monomer. It is contended here that ions are not necessary at the substrate for deposition to occur, but that the deposition rate can be enhanced when ions of sufficient energy cause bond dissociation at the surface, which leads to greater concentration of reactive species at the surface. Furthermore, it is most unlikely that surface adsorption of monomer occurs at low pressures and ambient temperature unless the monomer has a very high molecular weight.

For a mixture of gases, such as argon and tetrafluoroethylene (TFE), there is a large enough difference in the ionization potentials (15.8 eV and 10.1 eV, respectively) that a collision resulting in electron transfer from TFE to argon would have sufficient excess energy to result in dissociation as well as ionization of TFE. Therefore, in a gas mixture, it is possible for ion-neutral collisions to create polymerizable reactive species.

### Electrons

Electrons are believed to play a much more important role in gas phase bond dissociation than ions. For electrons, the mean free path,  $\lambda_e$ , is given by the expression

$$\lambda_e = 4/\pi n d^2 \quad (1)$$

where  $n$  is the number of molecules per unit volume and  $\pi d^2/4$  is the collision cross section for the molecule. For the same conditions as the ion energies calculated previously with methane, the electron mean free path is  $6.8 \times 10^{-3}$  m. The equation for estimating electron energy is (ref. 2, p. 39)

$$kT_e \text{ (eV)} = 0.30(m_m/m_e)E\lambda_e \quad (2)$$

where  $E$  is the field strength,  $m_m$  is the mass of the monomer molecule, and  $m_e$  is the electron mass. For an electron to accumulate 4 eV of energy, the field strength would need to be roughly 0.2 V/cm. Therefore, the field strength in the positive column of a low pressure discharge should be more than sufficient to induce both bond dissociation and ionization of monomer. At pressures above roughly 100 mTorr, the electron energy in the positive column becomes too low to account for any appreciable formation of reactive species. However, at the cathode the field is much higher, and the electrons should still be able to acquire enough energy to cause dissociation and ionization. It should be noted that if the field strength in the region of the cathode is insufficient to cause ionization, then a plasma will not be formed.

Electrons are responsible for electron excitation of monomers or carrier gases, as well as bond dissociation and ionization. Electron excitation can result in either photon emission, which occurs shortly after excitation ( $\sim 10^{-6}$  s), or in some instances metastable species which do not return to the ground state until they collide with a surface or another gas phase species.

### Excited neutral species

The photons emitted by glow discharges are due to the deexcitation of electrons orbiting a nucleus that devolve to a less energetic state, typically the ground state unless the molecule is multiply excited. The energy lost by the electron is emitted as a photon, and is often sufficient to cause bond dissociation in monomer if the photon-monomer collision is direct. Therefore, if monomer collides with an excited neutral before emission occurs, then bond dissociation can take place. The collision frequency should be greater than roughly  $10^6$  s<sup>-1</sup> in order for collisions to occur before the excited neutral emits a photon. Since the glow discharge plasmas are typically of low intensity and the gas phase is optically thin, then photon-monomer collisions are not considered a significant contributor to the creation of reactive species in the gas phase under typical conditions. However, photopolymerization is a viable route for vacuum deposition of polymeric materials under appropriate conditions, as will be discussed later.

The other type of electronically excited species to be considered is the neutral in the metastable state. When in a metastable state, the electron occupies an energy level from which it cannot spontaneously return to the ground state without violating transition rules. Therefore, it remains excited until it undergoes a collision in which the excess energy can be removed. Metastable energies are usually greater than the ionization potential for most organic materials, and are more than sufficient to cause bond dissociation. Only the inert gases (i.e. He, Ne and Ar) form metastable species, so this consideration applies only to plasma polymerization with carrier gases.

### Photons

Photon-induced vacuum deposition of polymeric materials is a viable process, but the deposition rate is typically an order of magnitude less than for plasma polymerization. Photon-monomer collisions resulting in bond dissociation are infrequent relative to electron-monomer or excited neutral-monomer collisions, therefore surface photopolymerization requires a large flux of energetic photons and monomer concentrations greater than those for plasma polymerization.

## VACUUM DEPOSITION POLYMERIZATION PROCESSES

### Thermodynamic constraints on recombination

For a chemical reaction to proceed, the Gibbs free energy,  $\Delta G$ , must be negative.  $\Delta G$  is given by

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

where  $\Delta H$  and  $\Delta S$  are the enthalpy and entropy of reaction, both of which are negative for a recombination process.

From a thermodynamic analysis of the activation complex theory for a bimolecular gas phase reaction (ref. 5), with

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (4)$$

and the rate coefficient,  $k_2$ , is defined as

$$k_2 = \kappa(kT/h)(RT/p)\exp(-\Delta G^\ddagger/RT) \quad (5)$$

where  $\kappa$  is defined as the transmission coefficient.

Also, the enthalpy term is defined as

$$\Delta H^\ddagger = E_a - 2RT \quad (6)$$

where  $E_a$  is the activation energy. By substitution for  $\Delta G^\ddagger$  in the equation for  $k_2$ , and substituting for  $\Delta H^\ddagger$ , then

$$k_2 = (\kappa Te^2/h)(RT/p)\exp(\Delta S^\ddagger/R)\exp(-E_a/RT) \quad (7)$$

where  $\kappa$  is taken into the entropy term. The expression for the entropy term obtained by rearrangement is

$$\Delta S^\ddagger = R \ln(hAp/L(ekT)^2) \quad (8)$$

where A is the preexponential term in the rate constant and L is Avogadro's number. For  $\Delta G^\ddagger = 0$ , the point at which the reaction will no longer proceed, then by substitution for  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$ , the following is obtained

$$p = (L(kT)^2/hA)\exp(E_a/RT) \quad (9)$$

Since we are considering a recombination of free radicals, then no activation energy is required ( $E_a = 0$ ) and

$$p = L(kT)^2/hA \quad (10)$$

The meaning of this equation is that at a given pressure, p, the maximum temperature at which the reaction can proceed is

$$T_{\max} = (pAh/Lk^2)^{1/2} \quad (11)$$

The coefficient A is dependent on temperature (see for example, the data in ref. 6) 1989), and for free radical combination processes

$$A = aT^{-n} \quad (12)$$

where

$$0.5 < n < 3.0 \quad (13)$$

and so the actual temperature dependence is

$$T_{\max} = (pah/Lk^2)^{1/(2+n)} \quad (14)$$

As an example, using data from reference 6 for the reaction



for which  $n = 3.0$  and  $a = 8.0 \times 10^{26} \text{ mole}^3 \cdot \text{s} / \text{K}^3 \cdot \text{cm}^3$ , then at atmospheric pressure the maximum temperature at which the reaction will proceed is 860 K. At 1 Torr, the maximum temperature is 230 K. Note that in the reaction expression a third body, M, is required to remove energy released by recombination, as otherwise the reaction product would fly apart soon after formation (ref. 5). However, it does seem feasible that large molecules, such as the para-xylylenes to be discussed in the next section, might on rare occasions be capable of dispersing the energy released by recombination among the numerous vibrational modes available in the molecule.

Although this is not a precise treatment of the thermodynamic behavior of recombination, it does sufficiently illustrate that gas phase recombination is not a viable growth mechanism at the low pressures required for plasma polymerization.

### Parylene polymerization

The effects of process parameters on the deposition rate of poly-(p-xylylenes) were studied using the method reported by Gorham (ref. 7), in which di-para-xylylene (Parylene N) and di-chloro-para-xylylene (Parylene C) are subjected to vacuum pyrolysis. At pressures below 1 Torr, p-xylylene and chloro-p-xylylene spontaneously polymerize on surfaces with temperatures below 30°C and 90°C, respectively. The conversion to polymeric film is almost 100% for both monomers. The following is a summary of the findings (ref. 8, 9 and 10).

#### Effect of inert gas on deposition rate

Inert gases at room temperature were introduced to the vacuum chamber to study the effect of cold third bodies in the gas phase on the deposition rate in the deposition chamber (the chamber immediately preceding the cold trap chamber).

The effect of inert gas pressure on the local deposition rate in the substrate chamber was monitored with all other variables held constant. Without argon, 70% of the Parylene C and 23% of the Parylene N was deposited in the substrate chamber. For Parylene N, the film thickness increased linearly with argon pressure up to 70 mTorr, the maximum argon pressure employed. However, for Parylene C the film thickness reaches a maximum at an argon pressure of 10 mTorr. An apparent explanation is that the increasing argon pressure shifts the point of maximum deposition further upstream for Parylene C. In other words, as argon pressure increases above 10 mTorr, the gas phase at the substrate position becomes depleted of monomer due to deposition on upstream surfaces. For Parylene N, the point of maximum deposition remains downstream in the pressure range studied. If it is assumed that the rate of deposition depends on both monomer temperature and monomer concentration, then it can be

understood qualitatively why there would be a maximum in the deposition rate at some downstream position, and that this position would move upstream as the argon pressure increases due to the increased rate of energy loss by monomer.

In another experiment, the effect of the size of inert gas atoms on the deposition rate at the substrate was measured. It was reported by Cravath (ref. 11) that the energy loss for a particle of mass  $m$  at a temperature  $T_m$  moving through particles of mass  $M$  at temperature  $T_M$  is given by

$$f = (8mM/3(m+M)^2)(1-T_M/T_m) \quad (16)$$

where  $f$  is the average energy lost per collision by particles of mass  $m$  as a fraction of the average energy of these particles. This equation predicts that as the mass of the inert gas approaches that of the monomer, then  $f$  will increase. Since monomer mass  $m$  is greater than that of the inert gases considered, an increase in inert gas mass results in an increase in  $f$ .

Using Parylene N as the monomer, it was found that the deposition rate at the substrate increased with inert gas pressure, and that the film thickness increased as the inert gas was changed from helium to neon to argon. This would be expected if decreasing monomer energy leads to higher deposition rate.

When the slopes of the thickness vs. inert gas pressure lines were plotted vs. product of the collision frequency and average fraction of energy loss terms for different inert gases, a linear fit was obtained. This is taken as further evidence that cold third bodies in the gas phase enhance deposition of reactive gas phase species by removing energy from monomer.

**Heat effects during parylene polymerization** In these experiments, a "cold finger" is inserted into the cold trap chamber, with either a thermocouple arrangement to measure the temperature change between the coolant inlet and coolant outlet streams, or a rotameter to measure the amount of liquid nitrogen evaporated.

For both Parylene C and Parylene N, two heat effects were observed. The first was a continuous temperature difference between the inlet and outlet coolant streams indicating a continuous exothermic reaction at the surface. The second was a large exothermic spike, which is attributed to a sudden polymerization reaction. The spikes only occurred below a certain temperature, occurring with greater frequency at low temperatures and early in the reaction.

The monomer, after undergoing pyrolysis, is either in the singlet (quinonoid) or the triplet (diradical) state. At the pyrolysis temperature virtually all monomer is in the triplet state, and at room temperature virtually all monomer is in the singlet state. Therefore, almost all monomer at the surface is in the singlet state. The energy released by the transition from the triplet to singlet state is 12 kcal/mol, and the reaction is essentially irreversible at room temperature or lower. However, if monomer in the triplet state combine to form a diradical dimer, then it is trapped in the triplet state for as long as it remains in the gas phase. The polymerization step takes place when initiated by the diradical dimer. However, the overwhelming fraction of monomer is in the quinonoid (singlet) state. Although the quinonoid form is highly reactive, it is also highly unlikely that two quinonoid monomer will react to form the diradical dimer. Therefore, continuous polymerization occurs when the rate of adsorption of quinonoid monomer is slower than the reaction rate. As the temperature of the surface decreases, the rate of adsorption outpaces the reaction rate and an excess of quinonoid monomer is adsorbed at the surface. When an initiating species reacts with the excess quinonoid monomer, a solid-state polymerization occurs instantaneously and an exothermic spike evolves.

Based on these results, it is evident that deposition and polymerization are not necessarily simultaneous processes. For species that are readily adsorbable, such as para-xylylenes, monomer can accumulate at the surface without undergoing reaction for relatively long periods of time. When sufficient concentrations of initiating species are present at the surface, the deposition and polymerization proceed simultaneously. In other words, the rate of polymerization exceeds the rate of adsorption. This observation for parylene polymerization is a special case for vacuum deposition, as the monomer is of sufficient mass and the temperature of the substrate is low enough that the monomer can be readily adsorbed at the substrate even under vacuum conditions. For most vacuum deposition processes, the substrate temperatures and the monomers employed are not conducive to adsorption at the surface, and the condensed species are not necessarily difunctional, as the quinonoid monomer from parylenes are. Therefore, even if adsorption at the surface does occur, it is unlikely that it is a necessary or even contributory process to film growth.

### Vacuum deposition of TFE

One of the greatest virtues of plasma polymerization is versatility. Plasmas can be generated by various types of power supplies (dc, ac, af, rf, and mw), several types of flow configurations can be used, the selection of monomer is limited only by the quality that it can

be introduced to the gas phase, operational parameters (monomer flow, pressure, input power, etc) can be freely manipulated, and virtually any type of substrate can be coated, with several options regarding the environment to which the substrate is subjected (bias voltage, position relative to plasma, coolant temperature, etc).

The number of ways in which plasma polymer films can be obtained presents considerable challenge in developing a model which encompasses all methods. Many mechanisms have been proposed which consider only the method being employed in a particular set of experiments

Regardless of the confusion engendered by the numerous options, they do present an advantage in identifying a general growth mechanism by allowing us to identify aspects common to all deposition methods, and to remove from consideration those aspects that are unique to a particular system. What follows is a summary of results obtained for different vacuum deposition polymerization processes, and through comparison the common aspects will be considered in the reaction mechanism, while aspects particular to a given system will not.

#### UV vacuum deposition (UVVD) of TFE

UVVD of polymeric films (ref. 12) was carried out by subjecting tetrafluoroethylene, at room temperature and pressures between 10 and 70 Torr, to photon flux from a low pressure hydrogen plasma with photon wavelengths between 130 nm and 215 nm. At these wavelengths, photon energies are lower than the ionization potential for TFE, so gas phase dissociation due to photon-monomer collisions must be the process by which reactive species are formed. It was found that when the substrate was positioned parallel to the photon flux, the deposition rate was roughly 40% of that for a substrate perpendicular to the photon flux. Therefore, it is considered unlikely that film growth is due exclusively to interactions between photons and monomer in the vicinity of the substrate surface, as no deposition on the parallel substrate would be expected if this were the case. However, it does appear that photon-surface collisions do enhance deposition. It is most likely that photon impingement at the substrate creates reactive surface sites, increasing the probability that reactive gas phase molecules will be able to react at the surface.

#### RF glow discharge system

A tubular rf glow discharge system (ref. 12) was used to study the effects of carrier gas and monomer inlet position on plasma polymerization of TFE. The reactor was very similar to that used in the UVVD experiments, with the exception that the plasma generated in the upper chamber was admitted to the deposition chamber via a glass tube. Three flow configurations were investigated: I) Monomer admitted directly through the electrode region, II) Monomer admitted to the deposition chamber and diffuses to the electrode zone, and III) Carrier gas (argon) admitted through electrode region with monomer admitted to the deposition chamber.

A general observation for all three flow configurations is that the deposition rate drops off drastically as the substrate is removed from the tail flame, with maximum deposition occurring at the point where the tip of the tail flame just touches the surface. Yeh attributes this to extremely low electron densities outside of the tail flame, which results in a marked decrease in the rate of monomer-electron collisions leading to reactive gas phase species, and fewer electron-surface collisions generating surface reactive sites.

In flow configurations I and II, monomer is ionized as it is the only gas present in the system. Therefore, ionized monomer cannot be ruled out as the dominant reactive species. In flow configuration III, argon is admitted through the electrode zone, but due to the low pressure and the small linear velocity of argon entering the deposition chamber, an appreciable amount of monomer can still diffuse into the electrode zone.

In order to approximate the extent of monomer diffusion, it was approximated that the flow is at steady state, the concentration profile is invariant with respect to time, and that perfect mixing at the plasma inlet to the deposition chamber occurs. Therefore, assuming that the pressure is constant throughout the chamber, then

$$y(z) = y_0 \exp\{-v_z z / D_{AB}\} \quad (17)$$

where  $y$  is the mole fraction of monomer at a distance  $z$  from the plasma inlet,  $v_z$  is the linear velocity of argon in the tube leading to the deposition chamber, and  $D_{AB}$  is the diffusion coefficient for an argon-TFE mixture, which was estimated for ordinary diffusion in gases at low density (ref. 13).

At 300 K and for flow rates of 5.0 sccm argon and 3.0 sccm TFE, the chamber pressure is 0.74 Torr. The estimated diffusion coefficient at these conditions is roughly  $94 \text{ cm}^2/\text{s}$ . For perfect mixing,  $y_0 = 0.375$  at  $z = 0$ . At  $z = 10 \text{ cm}$ , the distance from the plasma inlet to the electrode zone, the mole fraction of TFE is roughly 0.056. Therefore, the presence of monomer in the electrode zone is not negligible relative to that in the deposition chamber, and appreciable ionization of monomer can still occur even though a carrier gas is being employed. Since most plasma polymerization reactors operate at low pressures and low flow rates, which implies high diffusion coefficients and low gas velocities, it is usually impossible to exclude monomer from ionization processes in the electrode region, and subsequently impossible to separate ionization processes from bond dissociation processes.

**DC cascade arc system** In this system, a dc arc discharge is created in a narrow diameter (4mm) column at high carrier gas flow rates ( $\approx 2000$  sccm argon). The plasma jet enters the deposition chamber, where it reacts with monomer. The argon pressure in the cascade arc column was estimated from the Paschen curve for argon, and the estimated column pressure was found to increase linearly with argon flow rate. Therefore, the gas velocity in the column is roughly constant, being estimated at roughly  $1.75 \times 10^6$  cm/s. Using the same assumptions as for the tubular glow discharge reactor, and for 2000 sccm argon with 10 sccm TFE, it was estimated that the mole fraction of TFE dropped to  $1 \times 10^{-9}$  at 0.001 cm into the anode disk from  $4 \times 10^{-3}$  at the end of the anode disk. Therefore, penetration of monomer into the plasma source is negligible, so that plasma formation (ionization) and bond dissociation are essentially discrete processes. The deposition rate for the cascade arc is somewhat greater than for the rf glow discharge discussed earlier, even though the input power per unit mass is one or two orders of magnitude less for the cascade arc.

### Structural characteristics of vacuum deposited TFE films

ESCA is particularly useful in characterizing polymeric films obtained from fluorocarbons, as the attachment of highly electronegative fluorine atoms to carbon creates a shift in the spectra of carbon so that the presence of  $CF_3$ ,  $CF_2$ ,  $CF$  and  $C$  species can be estimated by curve fitting the  $C_{1s}$  spectra. These estimates can be checked by comparison with the  $F_{1s}/C_{1s}$  area ratios.

In this section, ESCA results for TFE films obtained from the UVVD, rf glow discharge, and dc cascade arc systems are compared. For conventional polymers of TFE, such as Gore-Tex or Teflon, F/C ratios obtained from the  $F_{1s}$  and  $C_{1s}$  areas range from 1.93 to 1.98. By comparison, typical films from TFE for UVVD, rf glow discharge, and dc cascade arc have F/C ratios of 1.7, 1.4-1.8, and 1.3-1.5, respectively. The range of atomic percentages for  $CF_3$ ,  $CF_2$ ,  $CF$  and  $C$  in conventional TFE polymers and vacuum deposition TFE films are as follows: PTFE - 5, 88, 3 and 4 atomic percent, respectively; UVVD - 10-11, 69-72, 6-7 and 12-13; RF glow - 13-20, 28-59, 14-41, and 10-24; and DC cascade arc - 11-21, 21-32, 35-46 and 11-25.

The UVVD films most resemble PTFE, with roughly 70% of the carbon species being  $CF_2$ . However, UVVD films possess  $CF_3$ ,  $CF$  and  $C$  in much greater quantities than PTFE. Consequently, a considerable amount of dissociation and/or restructuring of TFE occurs in UVVD. In this respect, UVVD is similar to the plasma polymerized films. The high percentage of  $CF_3$ ,  $CF$  and  $C$  in plasma polymerized films is taken as an indication of greater monomer fragmentation in the gas phase, due to monomer-excited species collisions of greater energy and frequency.

This is also born out by the higher deposition rate for plasma polymerization vs. UVVD. The larger degree of "cross-linking" sites ( $CF$  and  $C$ ) would imply a greater concentration of reactive sites at the surface and/or gas phase species with more free radicals, either of which should increase the deposition rate.

### Deposition rate and structural dependence on substrate temperature

Yasuda and Wang (ref. 14) compared the deposition rate dependence on substrate temperature for the monomers TFE, perfluoro-2-butyltetrahydrofuran (PFBTHF), ethylene and styrene. The boiling points for these monomers are -76, 107, -104 and 145°C, respectively. One of the purposes of this study was to determine whether or not the "condensability" of monomer would effect the deposition rate. Deposition rate data for PFBTHF and TFE at several temperatures and at similar W/FM showed little difference between specific deposition rates (A/kg) for these monomers, which indicates that the extent to which a monomer may adsorb on the substrate has no noticeable impact on its deposition rate in plasma polymerization.

From the deposition rate data at various substrate temperatures, it was found that the specific deposition rate ( $k_0$ ) obeyed the equation

$$k_0 = A \exp(-bT) \quad (18)$$

where  $A$  represents the extrapolated specific deposition rate at  $T=0$  K. Although we have not been able to elucidate the physical significance of this relationship, it was found to be valid for all four monomers over a wide temperature range (210 K to 350 K). Furthermore, it was found that the coefficient  $b$  was independent of discharge conditions ( $W$  and  $F$ ), and was constant for a given monomer. The experimentally obtained values for  $b(K^{-1})$  for ethylene, styrene, TFE and PFBTHF were 0.0045, 0.0060, 0.0112 and 0.0143, respectively. It is apparent that  $b$  is more sensitive to the composition of the monomer (i.e., hydrocarbon vs. fluorocarbon) than to the volatility of the monomer. This further reinforces the contention that surface adsorption is not a major consideration in plasma polymerization.

One last major finding was the structural dependence on substrate temperature. If surface adsorption of monomer and subsequent polymerization brought on by impinging gas phase species were the major path to film growth, then it would be reasonable to expect that substrate temperature would have a negligible effect on structure. However, ESCA results for

PFBTHF films show a noticeable increase in the percentage of CF<sub>3</sub> and CF<sub>2</sub> groups as the substrate temperature was decreased from 75°C to -25°C, with concomittant decreases in CF and C. This indicates that film structure is dependent not only on the plasma conditions, but also on the extent to which substrate temperature allows incorporation of gas phase species and/or gas-surface reactions leading to ablation to take place. At higher substrate temperatures, the ability of the surface sites to dissipate the energy released by bond formation is impaired and will reduce to some extent the incorporation of specific gas phase species. Higher substrate temperatures also increase the probability that a gas-surface reaction will result in bond dissociation at the surface leading to ablation of deposited material. For example, the reaction



becomes more probable as the substrate temperature is increased.

### PROPOSED GROWTH MECHANISM FOR VACUUM DEPOSITION POLYMERIZATION

From previous discussion, we have concluded the following:

i) Reactive, polymerizable species can be generated by collisions with excited species (ions, electrons, excited neutrals, and photons) as well as by thermolysis of monomer. However, the occurrence of deposition does not require the presence of any particular excited species. Therefore, the general growth mechanism is independent of the method used to generate reactive, polymerizable species.

ii) Thermodynamic constraints rule out gas phase chain growth and gas phase recombination of reactive species as significant contributors to the growth process. The growth process occurs almost exclusively at surfaces, including on powders suspended in the gas phase such as aerosol or airborne powders.

iii) Deposition and polymerization do not necessarily occur simultaneously, Deposition is dependent on the rate of transfer of polymerizable species to the surface and polymerization is dependent on the number of reactive species at the surface. When polymerization proceeds faster than deposition, the two processes occur simultaneously and continuously. In an extreme case, when the polymerization rate is much greater than the deposition rate, the formation of airborne powders occurs. Once the suspended surface is created, it becomes the predominant site of deposition under such conditions. In the extreme case where the deposition rate exceeds the polymerization rate, as witnessed from Parylene polymerization, the polymerization reaction can occur as an instantaneous solid state polymerization via rapid step-growth with difunctional species.

iv) The vacuum deposition of TFE involves considerable dissociation/rearrangement of monomer. In light of this, and the fact that substances which are "non-polymerizable" in a conventional manner form films in vacuum deposition, it is concluded that vacuum deposition is an atomic rather than a molecular process, implying that the building block of the deposited material is often smaller than the molecule used as monomer.

The irregular structure of the deposited film and thermodynamic constraints rule out chain growth polymerization



as the growth mechanism in vacuum deposition. Instead, the most likely growth process is a rapid step-growth polymerization



where N represents the number of repetitions of similar reactions.

The species participating in the rapid step growth polymerization can be mono- or multifunctional (radical, cation, cation-radical, diradical, etc.). Figure 1 shows the excitation processes, the possible reactive species created, and the reaction paths available for gas phase and surface species. In reaction (1), a gas phase reactive species abstracts a fragment from the surface, leading to the formation of a non-reactive gas phase species and a reactive surface site. Although this step represents a loss of deposited material, it can be part of a process in which the deposition rate is increased. For example, in a hydrocarbon plasma, hydrogen atoms may abstract hydrogen from the surface, which creates reactive sites for the attachment of reactive hydrocarbon fragments.

Reactions (2) and (8) are rapid step growth processes in which free radicals initiate the solid state polymerization of surface adsorbed (as opposed to surface bound) monomer. Reac-



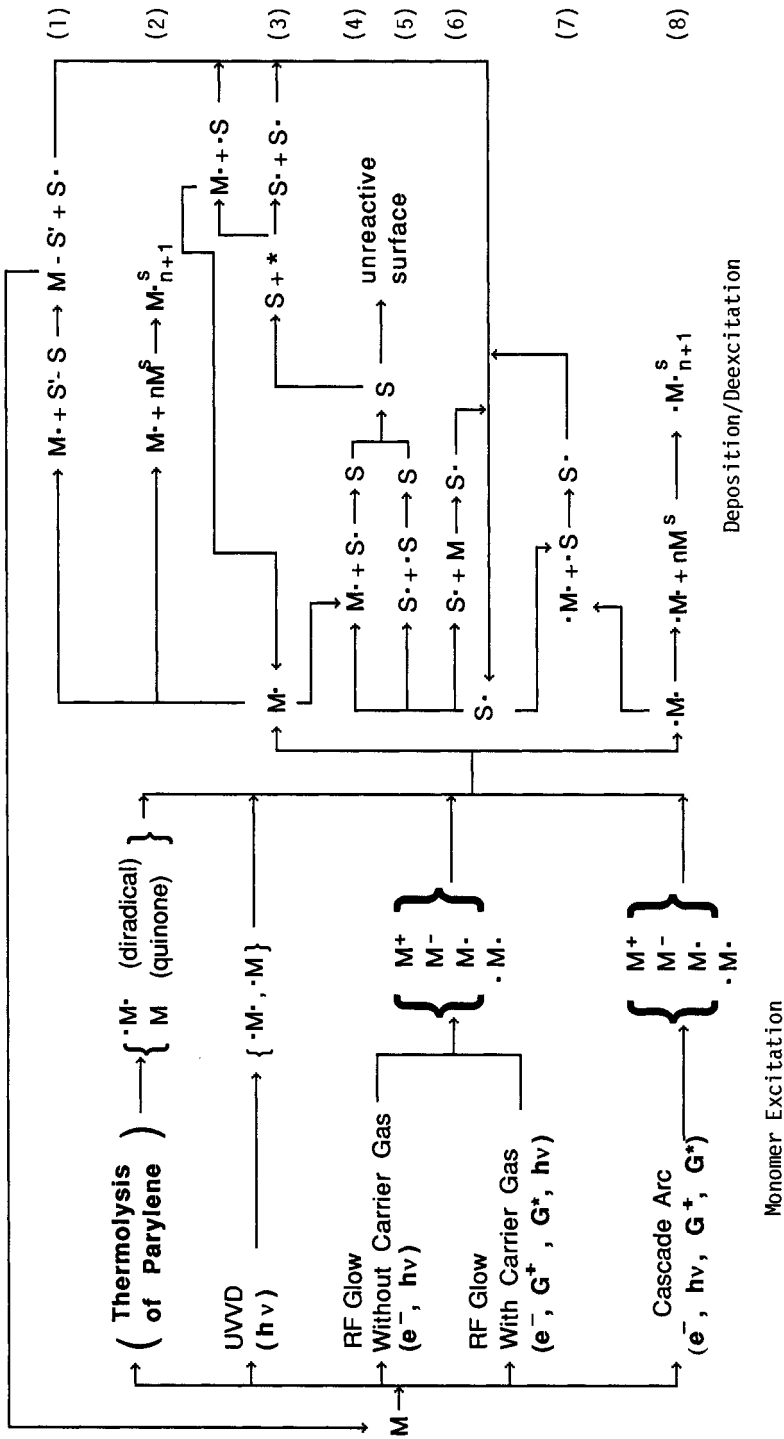


Fig. 1. Overall reaction mechanism for vacuum deposition of polymeric materials. The \* in (3) refers to any energetic species in the plasma. M• and •M• in the deposition (deexcitation step refer to any mono- or multifunctional monomer fragments.

tion (8) is the growth process for Parylene polymerization. The surface adsorbed monomer must be difunctional, such as the quinonoid form of para-xylylene, in order for reactions (2) and (8) to proceed. These two paths are not considered to be major factors in plasma polymerization processes.

Reaction (3) occurs when a surface site reacts with an energetic or reactive species from the gas phase, with subsequent bond dissociation. This yields either a single reactive surface site and a single reactive gas phase species, or two reactive surface sites.

Reactions (4) and (5) lead to the formation of unreactive surface sites. In (4), a gas phase species passivates a surface site. This is the step by which polymer surfaces are fluorinated using a  $CF_4$  plasma. This step is also the most likely cause for the decrease in deposition rate when the substrate is moved further from the tail flame, as the reactivation step (3) becomes less likely. (5) is a crosslinking reaction, the step which is responsible for the high degree of crosslinking in plasma polymer and plasma treated films.

Reaction (6) is a propagation reaction at the surface, which can only occur if the monomer has an appropriate structure. This is not a true chain growth mechanism, as the surface site is probably not constructed of repeating monomer units.

Reaction (7) is the process by which film growth progresses most rapidly. When multifunctional groups bind to reactive surface site, a new reactive surface site (or sites) is created, so that the total number of reactive surface sites remains the same or increases. If the gas phase species being bound at the surface is in a quartet state or higher, then there is a net gain in reactive surface sites which can subsequently crosslink or remain in the film as trapped free radicals.

Although the overall reaction mechanism is complicated, there are conditions at which only a few of the given reactions dominate. When a polymer is treated with a nonreactive plasma, such as argon, reactions (3) and (5) dominate, with reactive surface sites being created by impinging energetic species and then forming surface-surface crosslinks. When a polymer is treated with a chemically reactive but non-polymerizable plasma, reactions (1) and (4) can dominate. An example is etching with a  $CF_4$  plasma, where (1) is the major process. When a  $CF_4$  plasma is used to fluorinate polymer surfaces with  $CF_3$  groups, (1) and (3) create reactive sites which are subsequently passivated by  $CF_3$  via reaction (4).

In plasma polymerization, any of the reactions, with the exceptions of (2) and (8), can contribute to the overall mechanism. The extent to which a reaction contributes is determined by plasma parameters, the nature of the monomer, and conditions at the substrate. The net results in a deposition system can range from ablation, to fast deposition of highly crosslinked films, to slow deposition of films with a relatively low degree of crosslinking, with the deposition behavior dependent on the position of the substrate in the system.

The usefulness of the general reaction mechanism in Fig. 1 is that it provides a basis for interpreting data from vacuum deposition processes for polymeric materials. Consequently, a basis is provided for anticipating how a change in experimental conditions will affect film properties and the rate of material deposition.

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