PLASMA POLYMERIZATION

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Preface

Plasma polymerization is a new material preparation *process* and is not a kind of polymerization. The materials formed by plasma polymerization are vastly different from conventional polymers and constitute a new kind of material. Plasma polymerization has been dealt with, however, as an extension of polymerization from the academic viewpoint and as a new technology to prepare thin films from a practical viewpoint. There seems to be a great conceptual gap between these two approaches, which hampers true understanding of plasma polymerization and thorough utilization of the technology. This book is intended to bridge the gap so that the significance of plasma polymerization in materials science and technology can be recognized and its merit fully utilized in the modern technologies concerned with materials.

Plasma polymerization covers a wide interdisciplinary area of physics, chemistry, interfaces, materials, and so on. Scientists and engineers in different disciplines have contributed to advance the knowledge on plasma polymerization, but without thorough understanding of aspects involved in disciplines other than their own. Consequently, the interpretation of phenomena has been largely dictated by the disciplinary background of the investigator, and the very process of forming polymeric materials has been left more or less as a black box. Although this black box is a major subject of this book, it is also intended to cover fundamental knowledge in different subject areas necessary to grasp plasma polymerization overall. The major topics covered are gas-phase kinetics (Chapter 3), ionization of gases (Chapter 4), fundamentals of polymerization (Chapter 5), mechanism of polymer formation in plasma (Chapter 6), competitive aspects of polymer formation and ablation (Chapter 7), mechanism of polymer deposition (Chapter 8), operational factors of plasma polymerization (Chapter 9), general characteristics of plasma polymers (Chapter 10), and electrical properties of plasma polymers (Chapter 11).

Plasma polymerization is a highly system dependent process. Therefore, without comprehension of this aspect, interpretation of experimental data does not go beyond the boundary of experimental conditions employed in a particular experiment, and the generalization of findings may not be justified or is often

misleading. The interpretations presented in this book are strictly on the basis of the author's view. The chronological citation of literature is intentionally avoided. Instead, the author took the liberty of interpreting all data in a consistent manner in order to avoid accumulating sporadic and noncoherent information.

Plasma polymerization is an ultra-thin-film processing technology and covers very important subject areas that can be recognized as comprising the vacuum deposition of covalently bonded materials. Some of these subject areas have been dealt with under terms such as chemical vapor deposition, plasma-assisted chemical vapor deposition, and so on, in most cases dealing with formation of inorganic materials. Principles described in this book doubtless will be applicable to these relatively new processes. It is the author's view that these new processes and plasma polymerization will emerge as an integrated technology that will penetrate much deeper, over a wider area of materials science, than they would if exploited separately. The author hopes that this book will contribute to the conceptual background for this new group of materials and the processes by which they are prepared.

The author wishes to acknowledge all his colleagues in this subject area for providing valuable information. Special thanks are due to my family, my wife Gerda and my children Ken, Akira, and Lisbeth, for their understanding and sacrifice, which made the preparation of this book possible.

CHAPTER 1

Introduction

Plasma polymerization refers to the formation of polymeric materials under the influence of plasma (partially ionized gas). Because the most practical means of carrying out plasma polymerization involves the use of an electric glow discharge in a vacuum, the term *glow discharge polymerization* has been used, in every practical sense, synonymously with plasma polymerization, although plasma polymerization can be carried out by means other than glow discharge.

It was known for many years that some organic compounds form solid deposits in plasma generated by some kind of electrical discharge (*1–9*). In most cases, however, the deposits were recognized as by-products of phenomena associated with electric discharge; consequently, little attention was paid either to the properties of these materials (undesirable by-products) or to the process as a means of forming useful materials.

At these early stages of discovery, the concept of polymers was not well developed, and obviously these processes had never been considered to be polymerization, that is, plasma polymerization or glow discharge polymerization. Only since the 1960s has the formation of materials in plasma been recognized as a means of synthesizing polymers, and the process, when used to make a special coating on metals, has been referred to as plasma polymerization or glow discharge polymerization (*10–14*).

Following the advancement of polymer science, the formation of organic solids or films in plasma has attracted considerable attention, and the process has been generally recognized as plasma polymerization or glow discharge polymerization. The American Chemical Society has held symposiums (1970, 1974, 1978, and 1982) on this subject.

In these developments (i.e., up to the 1970s), however, the concept of plasma polymerization has been based on the application of the concept of polymerization and/or of polymers developed in preceding decades to the formation of organic material under plasma conditions. In other words, the process has attracted the attention of scientists and engineers as an exotic method of polymerization. Although a great number of research studies have

been published and numerous potential applications and the uniqueness of the polymer formation process have been demonstrated, the subject has not drawn much academic interest as a new subject area of polymer science. This is due largely to the fact that the very unique and advantageous feature (in certain applications) of forming insoluble, infusible polymers has hampered the basic study of the process at the molecular level.

In more recent years, however, the question of whether the concepts of polymers and of polymerization can be applied to plasma-formed materials and to plasma polymerization, respectively, has been reexamined (*15*). The well-recognized concept of polymerization today is based on the molecular processes by which the size of molecules increases. The arrangement of the atoms that constitute the molecules of a monomer is accomplished during the organic synthesis of the monomer. During the polymerization of a monomer, rearrangement of atoms within the molecule seldom occurs.

In contrast to such molecular processes, polymer formation in plasma has been recognized as an atomic (nonmolecular) process (*15*). If one adopted such an atomic process to form materials in which the reaction of new covalent bonds between atoms played a predominant role, one could find numerous new processes and resulting materials that would play vitally important roles in modern technologies. The processes recognized as chemical vapor deposition, plasma chemical vapor deposition, ion-assisted vapor deposition, and sputter coating of polymers all fall into this category.

Plasma polymerization was dealt with in the 1960s and 1970s as a method of polymerization. Although some important differences in polymer formation mechanisms and the properties of resultant polymers were recognized, the underlying concept was an extension of the concepts of polymerization and polymers developed with conventional polymers. Consequently, the underlying concept was represented, for example, by the preparation of a thin layer of polystyrene by the plasma polymerization of styrene or the preparation of a thin layer of polytetrafluoroethylene by the plasma polymerization of tetrafluoroethylene. In other words, plasma polymerization was conceived as a new and exotic method of polymerization.

Plasma polymerization today is gaining recognition as an important process for the formation of entirely new kinds of materials. The materials obtained by plasma polymerization are significantly different from conventional polymers and are also different from most inorganic materials. Thus, plasma polymers lie somewhere between organic polymers and inorganic materials. Plasma polymerization should be considered a method of forming such new types of materials rather than a method of preparing conventional polymers. Consequently, the term *plasma polymerization* should not be limited to the formation of organic materials but should cover a wider area that includes metallic or inorganic elements, although the major portion of studies

covered in this volume involve the formation of polymeric materials from organic compounds.

To take full advantage of the new kinds of materials recognized as plasma polymers and of the process by which they are made, it is important to recognize that we are not dealing with conventional polymers and polymerization in the strict sense, although these terms are used. Therefore, considerable effort is spent comparing plasma polymerization with conventional polymerization.

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CHAPTER 2

Scope of Polymer Formation by Plasma Polymerization

2.1 Preferred Form of Plasma Polymers

Historically, polymers formed under plasma conditions were recognized as an insoluble deposit that provided nothing but difficulty in cleaning the apparatus. This undesirable deposit, however, had extremely important characteristics that are sought after in the modern technology of coatings, that is, (1) excellent adhesion to substrate materials and (2) strong resistance to most chemicals.

Awareness of the fact that such material could be utilized as an excellent coating led to the exploitation of the technical method recognized today as plasma polymerization. The undesirable deposit formed in certain electric discharge processes was essentially converted to an excellent coating by controlling the deposition such that it occurred on an appropriate substrate in plasma polymerization. This situation provides an excellent illustration of the uniqueness of the preferred form of plasma polymers.

To appreciate the uniqueness of plasma polymerization, it is useful to compare the steps necessary to obtain a good coating by a conventional coating process and by plasma polymerization. If one wants to coat a certain substrate with a conventional polymer, at least several steps are required: (1) synthesis of a monomer, (2) polymerization of the monomer to form a polymer or intermediate polymer to be further processed in a succeeding step, (3) preparation of coating solution, (4) cleaning and/or conditioning of the substrate surface by application of primer or coupling agent, (5) application of the coating, (6) drying of the coating, and (7) curing of the coating.

In coating by plasma polymerization, in contrast, all these functional steps are replaced by an essentially one-step process starting from a relatively simple gas that often is not considered a monomer for polymerization.

Polymers formed by plasma polymerization aimed at such a coating are in most cases highly branched and highly cross-linked. Such polymers are characteristically formed during plasma polymerization, although low molec-

ular weight materials that are soluble in various solvents and noncohesive powders can also be formed (*1*).

Chemical reactions that occur under plasma conditions are generally very complex (*2–4*) and consequently are nonspecific in nature. Such reactions are of merit when special excited states of molecules are required as intermediate states and cannot be achieved, or can be achieved only with great difficulty, by conventional chemical reactions. Thus, plasma polymerization should be recognized as a special means of preparing unique polymers that cannot be made by other methods rather than as a special way of polymerizing monomers.

In this context, the most important forms of plasma polymers are ultrathin films. The characteristics of ultrathin films require special attention. Many bulk properties of a polymer film, such as permeability, electric volume resistivity, and dielectric constant, may be considered material constants. In all characteristic material constants, a thickness factor is included, and therefore these parameters do not change as the thickness of the film varies. This is true for a film as long as its thickness is above a certain critical value, that is, 0.05–0.1 μm, depending on parameters under consideration. As the thickness of the film decreases below the critical value, the constancy of such parameters is no longer observed, probably due to the increased contribution of flaws to the total film, which progressively increases as the thickness of the film decreases.

From the technical point of view, it is very difficult to prepare a flawless film with thickness below the critical value. With certain polymers that have exceptionally good film-forming characteristics, such as cellulose acetate, ultrathin films of such thickness as "monolayer" can be prepared by special techniques such as the spreading of a dilute solution of polymer on a water surface. However, it is extremely difficult to utilize such an ultrathin film in a practical manner, and the technique cannot be applied to any kind of polymer; that is, the method is highly dependent on the film-forming characteristics of polymers.

Thus, the capability of plasma polymerization to form an ultrathin film containing a minimal amount of flaws, if not completely flawless, is unique and is a valuable asset. Many important and useful chemical reactions that occur under plasma conditions but do not yield plasma polymers in this preferred form are not major subjects of this book. Discussions of such reactions can be found in general plasma chemistry texts.

2.2 Plasma-State Polymerization versus Plasma-Induced Polymerization

Plasma, which contains ions, excited molecules, and energetic photons, can be utilized in the general polymerization of organic monomers in a number of ways. In the polymerization of a monomer plasma can be considered a kind of

"radiation" source. However, in such applications plasma contacts monomer in either the solid or the liquid phase directly, and consequently the transfer of some excited species from the plasma phase to either the liquid or the solid monomer phase takes place. This is a significant difference from ordinary radiation polymerization, in which only energy is transferred to a monomer phase to create reactive species, such as ions or free radical of the monomer.

An important aspect of plasma initiation of monomer liquid or solid is that the formation of polymerization chain-carrying species (e.g., free radicals, cations, or anions) and the propagation of polymer chains take place in the different phases, whereas in most radiation polymerization, these two reactions occur in the same phase.

The principles of plasma-initiated polymerization have been applied to the polymerization of liquid and solid monomers by the insertion of a sealed ampule between a pair of parallel-plate electrodes connected to a 13.56-MHz radio frequency power source (*5–9*). Polymers with extremely high molecular weight have been formed from some monomers. The formation of polymer film at the interface of monomer and vapor in a sealed ampule was observed when a leak detector (Tesla coil) was used to check for pinholes in the seal (*10*, *11*). In this case, plasma created in the vapor phase in the sealed reaction tube by the Tesla coil initiated the polymerization to yield the film at the interface.

Free radicals formed on the surface of polymers and other solid materials exposed to plasma can be utilized to initiate graft polymerization in a manner that is similar to preirradiation grafting (*12*, *13*). Free radicals formed on polyethylene and polypropylene by plasma were utilized to obtain grafts of vinyl polymers by (1) the direct addition of degassed monomer in a vacuum and (2) the formation of peroxide followed by heating in the presence of degassed monomer.

In all of these examples, polymers are formed by *plasma-induced polymerization*, and the essential chemical reaction is believed to be the conventional molecular polymerization that occurs without the influence of plasma. Although plasma is utilized in these polymerizations, they are distinguished from *plasma-state polymerizations*, which occur only under plasma conditions, that is, vapor phase in the plasma state.

Whereas plasma-state polymerization is limited to the vapor phase and the interface in contact with plasma, plasma-induced polymerization is not limited to liquid- or solid-phase polymerization. When conventional monomers such as vinyl compounds are used in plasma polymerization, both plasma-state and plasma-induced polymerizations can occur simultaneously. The extent to which each mechanism occurs is dependent on the conditions of the plasma polymerization. The details of this aspect are discussed in Chapter 6, dealing with mechanisms of polymer formation.

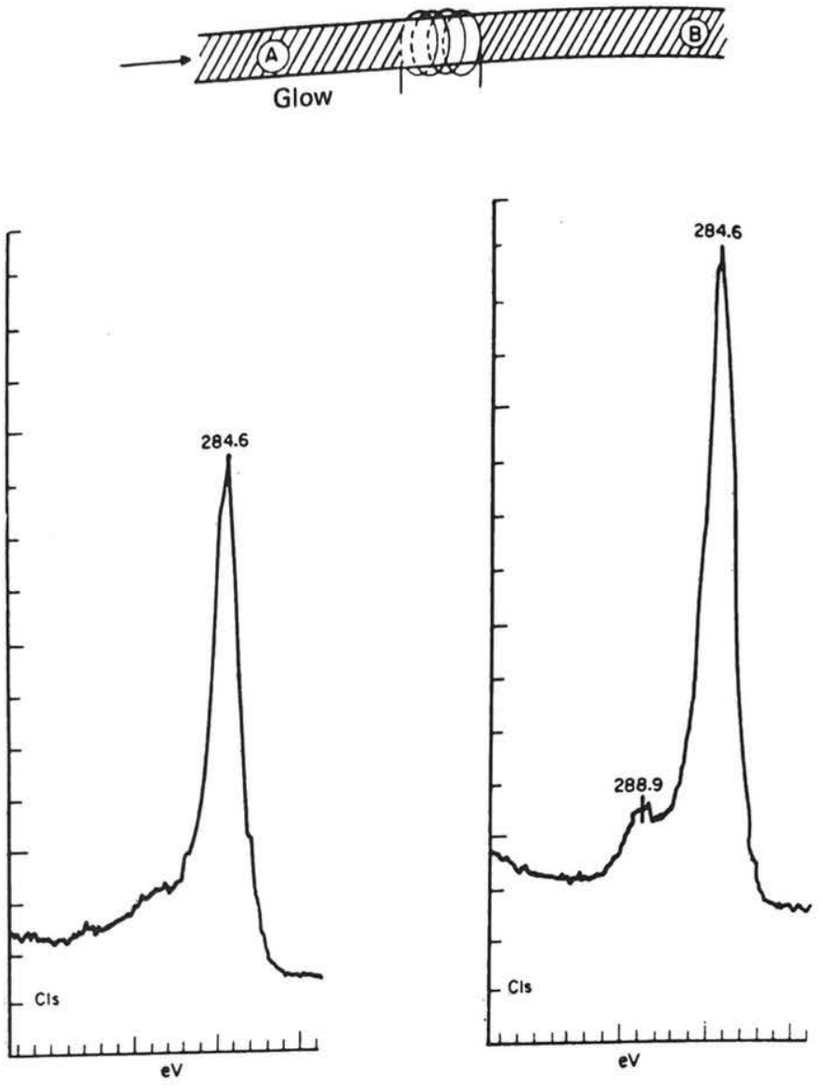

Fig. 6.42 ESCA C_{1s} peaks of glow discharge polymers of tetrafluoroethylene in the same reactor shown in Fig. 6.41, but at the higher discharge power level of 7.7×10^8 J/kg. Adapted from Yasuda (*33*).

6.8 Atomic (Nonmolecular) Nature of Plasma Polymerization

The plasma polymerization so far discussed is characterized by (1) the extensive fragmentation and/or rearrangement of a structural moiety or atoms in the starting material and (2) simultaneously occuring reactions involving many kinds of chemical species.

These phenomena are seldom found in conventional polymerizations, which can be recognized as molecular reactions. In other words, in conventional polymerizations, molecules of monomers are linked together with a minimum alteration of chemical structure of the monomer, and the structure of a polymer can be well predicted from the structure of the monomer. In

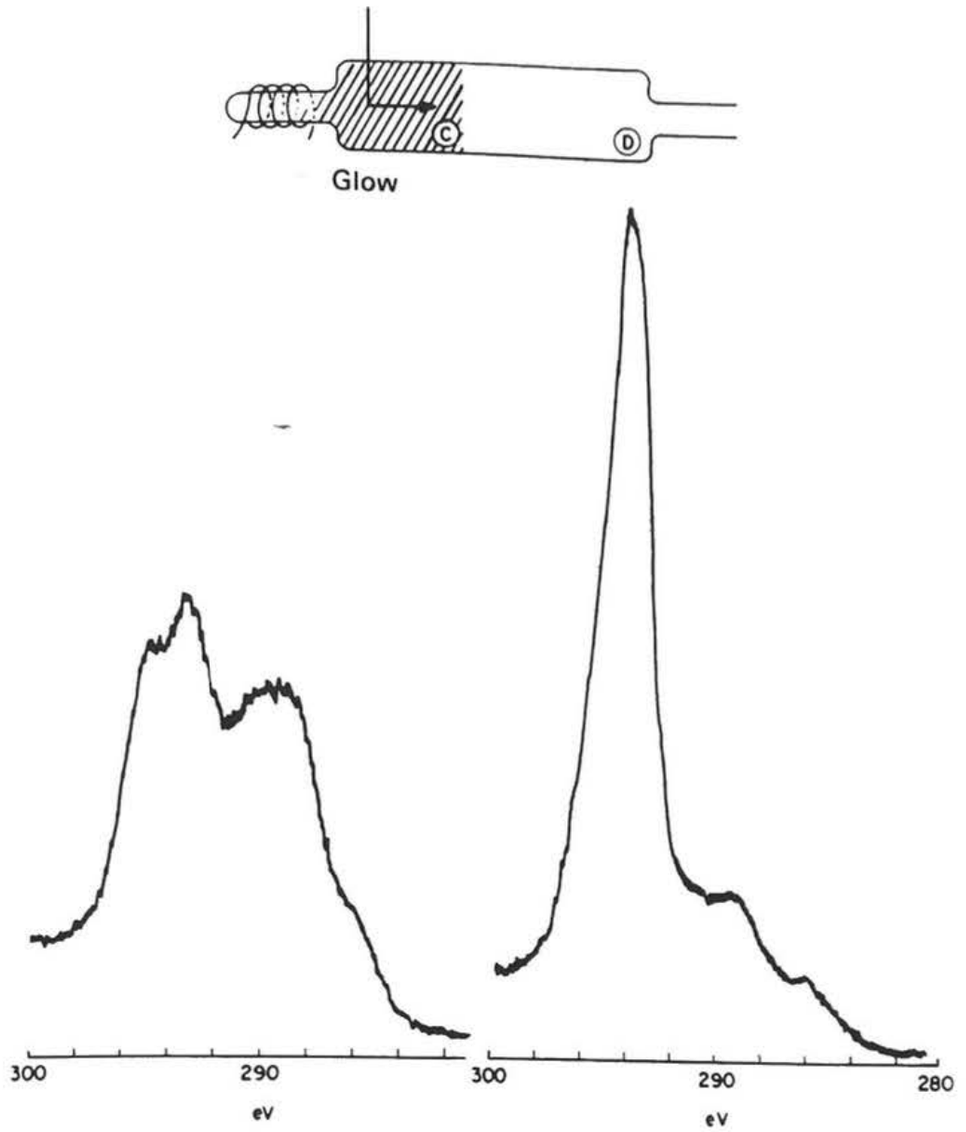

Fig. 6.43 ESCA C_{1s} peaks of glow discharge polymers of tetrafluoroethylene prepared in a reactor shown in the inset: (C) at the end of the glow region; (D) at the end of the tube in the nonglow region. Adapted from Yasuda (*33*).

contrast, the structure of a polymer formed by plasma polymerization cannot be predicted in this way. Perhaps the only sure prediction one could make would concern the elements constituting the polymer and, to a lesser extent, the elemental ratios.

This situation becomes clearer once we recognize the fact that plasma polymerization is not a regular "molecular polymerization." Such a "non-molecular polymerization" can be expressed by the term *atomic polymerization*. The word *atomic* might be misleading in a general sense; however, insofar as we are discussing the growth mechanisms of polymer formation, perhaps *atomic polymerization* is the most adequate and accurate expression of what is occurring in plasma polymerization.

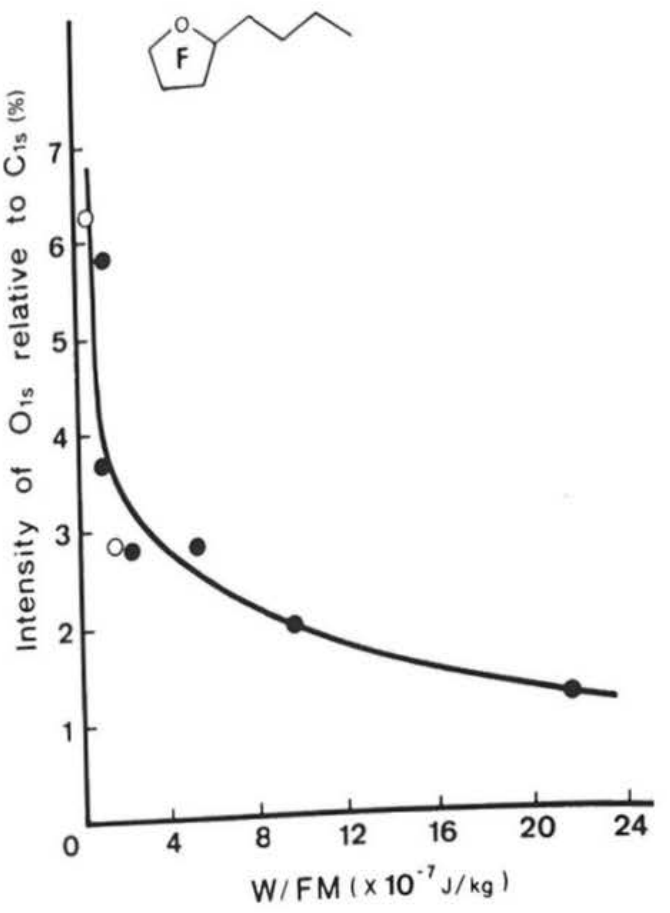

Fig. 6.44 Dependence of oxygen content in the plasma polymer of perfluoro-2-butyltetrahydrofuran on W/FM. Key: ○, reactor B; ●, reactor C. Adapted from Clark and Abraham (*34*).

In a molecular polymerization, the arrangement of atoms to form a special molecule of monomer is carried out in the organic synthesis of the monomer, and the rearrangement of atoms and chemical ligands seldom occurs during the process of polymerization. Therefore, the two independent chemical reactions—the synthesis of monomer structure and the polymerization—can be clearly distinguished. In "atomic" polymerization, the structures prepared during monomer synthesis may be largely destroyed: on the other hand, polymers may be formed from simple molecules such as CH_4 and CS_2 that are not the monomers of conventional polymerizations.

"Atomic" polymerization does not imply that the deposition of atoms is a process of plasma polymer formation similar to the formation of a film of metal in the sputter-coating process. It simply means that the building blocks are no longer molecules. After all, one of the most important aspects of plasma polymerization in comparison with other film deposition processes is the formation of covalently bonded materials. In the process of forming covalently bonded materials, conventional (molecular) polymerization uses molecules as the building blocks, but in plasma polymerization this is not the case. In this way, graphitic or diamondlike carbon films can be prepared from benzene by "atomic" polymerization.

The atomic aspect of plasma polymerization is evident in the incorporation of nonpolymerizable gases such as CO, H_2O, and N_2 discussed in Section 6.5. Namely, these gases are incorporated into the polymer structure not as molecules, but as atoms (from a gas). The ionization characteristics of a gas determine its plasma copolymerization characteristics. The important aspect is that active species created by the ionization of a gas do participate in the polymer-forming reactions.

Because of the atomic nature of the growth mechanism of polymer formation, plasma polymerization is highly system dependent. The fragmentation of molecules of a starting material or the rearrangment of molecular structure as visualized by diagnostic data based on the fragmentation products depends on the structure of the starting material and the conditions of plasma polymerization. Therefore, the selection of a monomer for an expected polymer requires a knowledge of the plasma polymerization conditions and of the atomic nature of the process under the conditions. This situation can be illustrated by the plasma polymerization of tetrafluoroethylene versus that of hexafluoroethane in the presence of H_2 gas. The details of this comparison are presented in Chapter 7, where ablation in plasma and the competitive nature of ablation and polymer formation are discussed.

As far as the importance of the atomic nature of plasma polymerization and its significance in the selection of monomer are concerned, the fact that essentially the same polymer can be formed from tetrafluoroethylene and from hexafluoroethane under certain conditions of plasma polymerization should be recognized. There is a significant difference in the costs of these monomers. Under certain conditions, however, the precious structure, C=C, contributes little to the overall polymer formation mechanism and the results of IR and ESCA indicate that the polymers are almost identical.

The extent of "atomic" polymerization that takes place in a particular set of plasma polymerizations is dependent on parameters specific to the reactor; perhaps the most important factor is the energy input level manifested by W/FM, that is, energy input per mass of monomer given in joules per kilogram. Because of the difficulty of determining the effective flow rate in a reactor, the value of W/FM contains some degree of uncertainty; within a given reactor, however, the value of W/FM can be used as the major parameter of plasma polymerization.

It is important to note that plasma polymerization manifested by polymer deposition rates for various kinds of monomers (carried out in the same reactor) can be reduced to the master relationship (*35*) shown in Fig. 6.45, where the deposition rate is expressed by polymer deposition rate divided by monomer mass flow rate, and the energy input is expressed by W/FM. In the figure, 16 different monomers from four different groups (each group

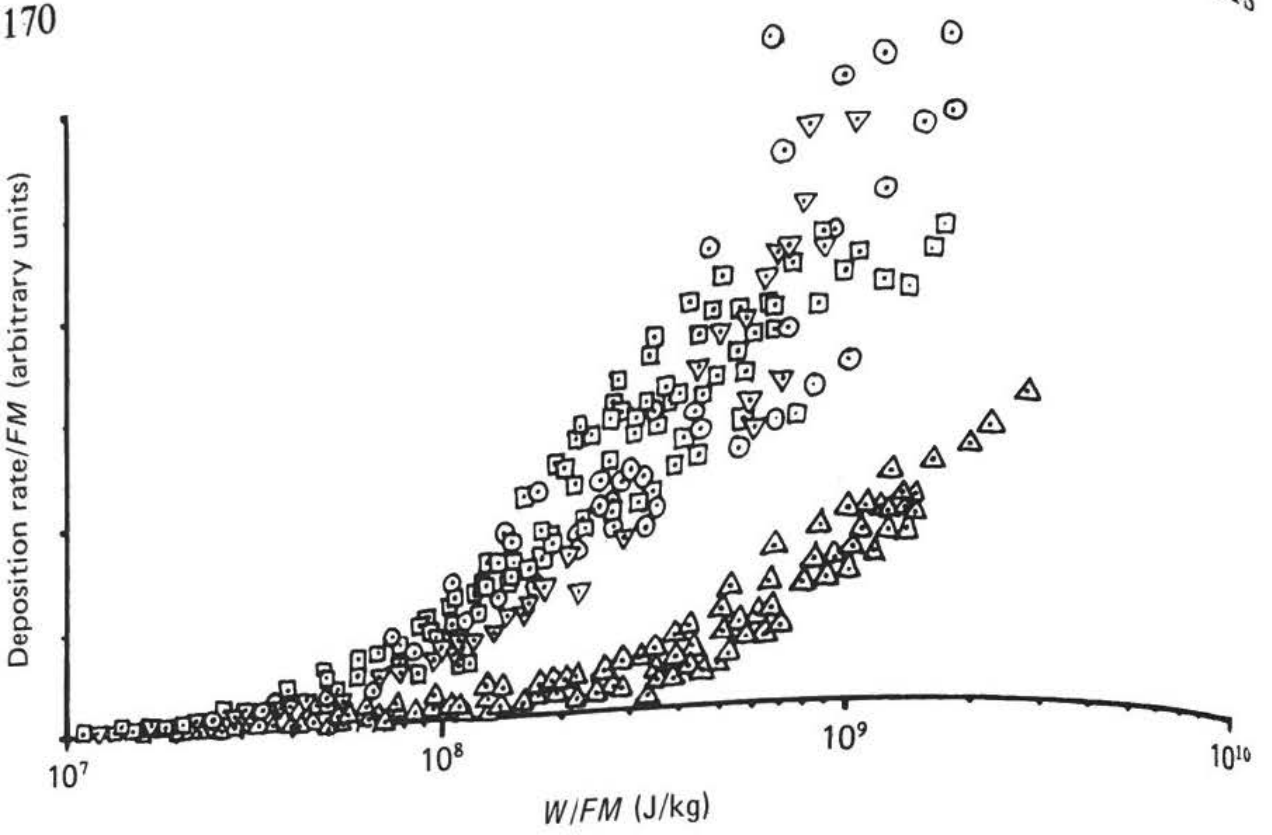

Fig. 6.45 Deposition rate/FM (deposition yield) relationships versus W/FM for four groups of monomers studied. Key: ⊙, sulfur-containing compounds; ⊡, organosilicones; ▽, fluorocarbons; △, hydrocarbons. Adapted from Gazicki and Yasuda (*35*).

containing different atoms, e.g., carbon, sulfur, fluorine, and silicon are compared. The deposition rate/mass flow rate represents the value proportional to the conversion yield of monomer to polymer in the system. The following aspects are important, as far as the growth mechanism is concerned, for the contribution of "atomic" polymerization:

1. Despite orders of magnitude differences among deposition rates of monomers at various discharge conditions, the data plotted in this manner show rather small differences among monomers, indicating that all monomers polymerize, by and large, in a similar fashion.
2. There is a clear difference between hydrocarbons and other types of monomers investigated, indicating that the type of atoms contained in the monomer structure plays an important role in plasma polymerization.
3. The differences among monomers within a group, such as hydrocarbons, are greater at a lower energy input level (W/FM), but these differences tend to diminish as the value of W/FM increases, and at very high W/FM regions, all monomers polymerize in an almost identical manner. (This aspect is not clearly seen in Fig. 6.45 due to the compressed scale of the plot.)

The fact that we can make such a master diagram for plasma polymerization has several important implications for the growth mechanism of polymer

formation in plasma. First, if plasma polymerization occurred mainly by true molecular polymerization, which depends on the chemical reactivity, condensability, adsorption, and other characteristics of the monomer, such a master diagram would be beyond the realm of scientific expectation. Second, even in the region where plasma polymerization is considered least atomic or most molecular, the polymer deposition rate is determined largely by the mass of monomer, which indicates that the characteristic rate by which monomer molecules are linked together (to form a polymer) is almost independent of the chemical properties of monomer.

Another "atomic" feature of plasma polymerization is evident from the plasma codeposition of more than one monomer. In conventional molecular polymerization, copolymerization is governed by the monomer reactivity ratio, and a mixture of monomer A and monomer B in a 1:1 ratio does not produce a 1:1 copolymer of A and B, except in the special case of *azeotropic copolymerization*. This is due to the facts that the reactivities of two monomers differ depending on the chemical structures and that polymerization is very specific to the monomer structure and to the chain-carrying species. In contrast, the plasma polymerization of a mixture of two monomers nearly always yields polymers corresponding to azeotropic copolymerization, indicating the absence of specificity of monomers toward plasma polymerization. Because of this, plasma codeposition rather than plasma copolymerization was used to describe the plasma polymerization of more than one monomer when the plasma copolymerization of nonpolymerizable gases was discussed earlier (Section 6.5).

As the extent of the atomic nature of polymerization increases, the extent of fragmentation of the starting material becomes greater, and this straightforward dependence on the mass is less evident. However, in the extreme case of maximum atomic polymerization (in the context discussed in this chapter), the deposition of material is governed by the feed-in rate of atoms that form the backbone or constituent network of material (deposit), and the generalized relationship becomes evident again.

Thus, one cannot discuss plasma polymerization, particularly the polymerization mechanism, in general terms without specifying the domain of plasma polymerization conditions which is discussed in detail in Chapter 9. In conjunction with the major domains of plasma polymerization conditions, we must also pay attention to the location of the polymer deposition. Because there is a very important factor involved in plasma polymerization that cannot be separated from the deposition aspect, detailed discussions of the deposition mechanisms are presented in Chapter 8. In this section, only an important aspect relevant to the growth mechanism is pointed out.

The polymer formation that takes place at or near the electrode surface can be significantly different from that in the rest of the glow. An example of this

aspect can be seen in a comparison of a polymer deposited on the electrode surface and one deposited on a substrate suspended in the plasma phase. ESCA C_{1s} spectra of polymers obtained by the plasma polymerization of tetrafluoroethylene (*36*) are compared in Fig. 6.46. From the figure, it is quite evident that the polymer formation at the electrode surface and that in the plasma phase could be significantly different. The important point here is that these differences (i.e., the properties of polymers deposited onto substrates at different locations within a reactor and/or onto the electrode surface, etc.) are due to the deposition mechanism rather than the growth mechanism of polymerization. Therefore, it is premature to draw a conclusive picture of plasma polymerization based on a limited case of experimental conditions. Apparently, contradictory findings reported in the literature could often be attributed to this point.

The atomic nature of plasma polymerization can also be seen in a comparison of the properties of plasma polymers of tetrafluoroethylene and of hexafluoroethane. With a double bond in the monomer, $F_2C{=}CF_2$, the formation of a new C—C bond without the detachment of fluorine (molecular polymerization) is possible, whereas plasma polymerization of hexafluoroethane cannot proceed without the detachment of fluorine atoms

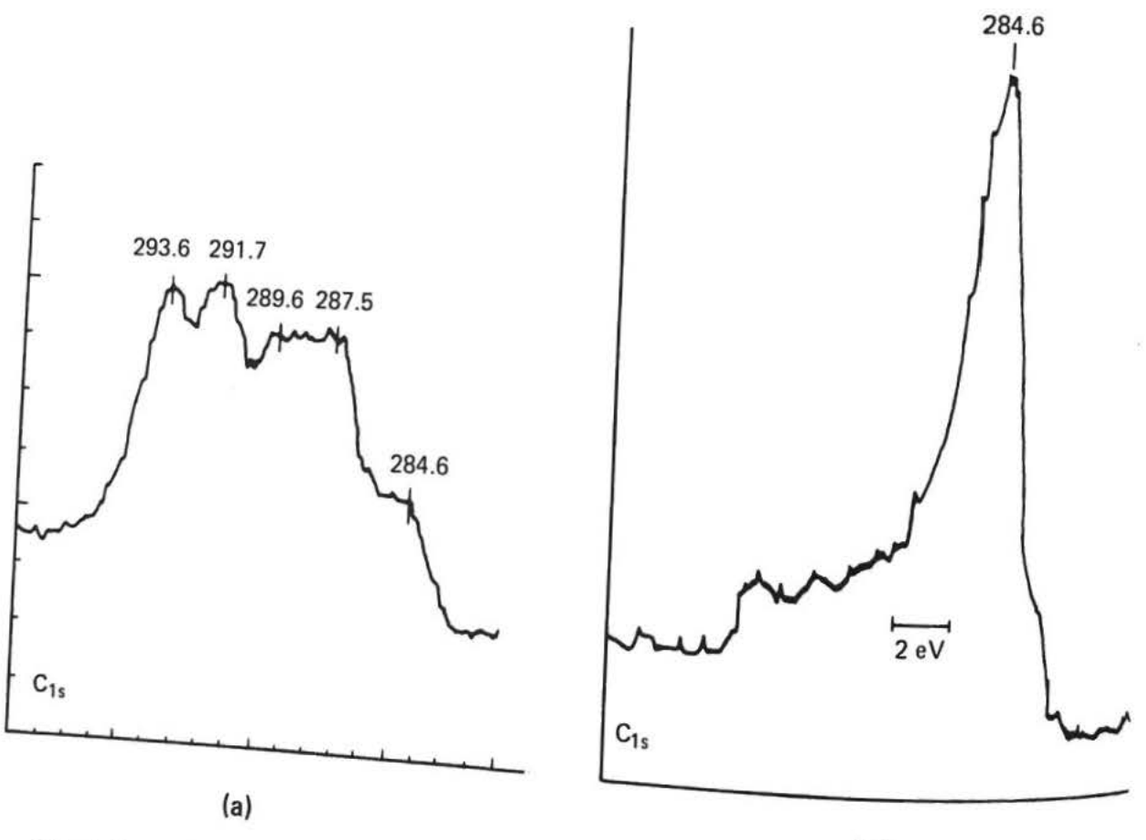

Fig. 6.46 ESCA C_{1s} spectra of plasma polymers of tetrafluoroethylene. (a) Polymer deposited on the electrode surface; (b) polymer deposited on a substrate suspended in plasma. Adapted from Morosoff *et al.* (*36*).

from the monomer. However, because of simultaneous "atomic" polymerization, which occurs in the plasma polymerization of tetrafluoroethylene and increases with increasing energy input, the contribution of the olefinic double bond is relatively small, as evidenced by the IR spectra of the polymers (*37*, *38*). Infrared and ESCA spectra of the plasma polymers of hexafluoroethane prepared in the presence of H_2 ($H_2/C_2F_6 = 1.0$) are essentially identical to those of the plasma polymer of tetrafluoroethylene polymerized under conditions of low W/FM (see Figs. 6.47 and 6.48). Furthermore, IR and ESCA data for the plasma polymer of tetrafluoroethylene polymerized under conditions of high W/FM, in which "atomic" polymerization dominates, are again virtually identical to those for the plasma polymerization of hexafluoroethane (without H_2).

Acetylene has been considered a main precursor of plasma polymerization by many investigators because of its relatively high rate of polymer deposition and its abundant presence in plasma of hydrocarbons based on plasma diagnostic data. (The precursor concept of the first category discussed in Section 6.6 relies on the intuitive assumption that plasma polymerization proceeds via the chain-growth polymerization of the double or triple bond.) If we recognize the difference in the mass of the starting materials and the

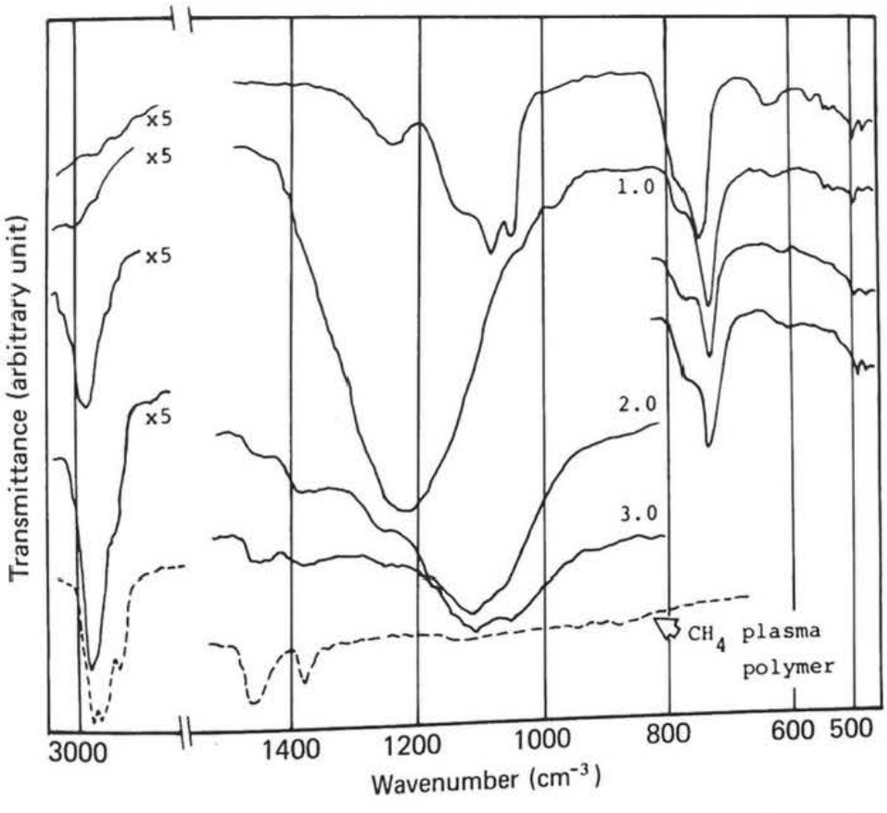

Fig. 6.47 Infrared spectra of various plasma polymers prepared under various H_2/C_2F_6 ratio conditions and also from CH_4 plasma polymerization for reference: 30 W; $F(C_2F_6) = 0.93$ cm^3/min; $H_2/C_2F_6 = 0$. Adapted from Masuoka and Yasuda (*37*).

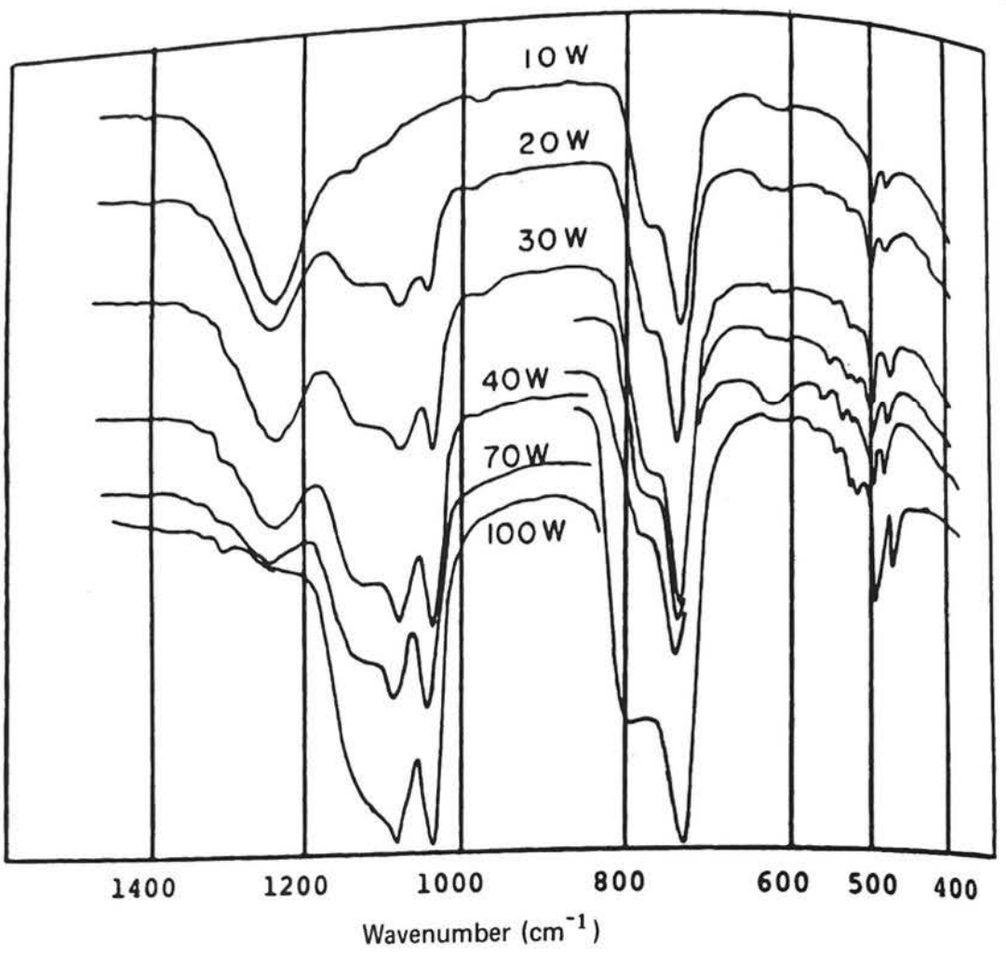

Fig. 6.48 Infrared spectra of plasma-treated sodium chloride powder under various wattage conditions ($F = 0.155$ cm^3/min). Adapted from Masuoka and Yasuda (*38*).

difference in the mode of polymer collection, however, the specific rates by which polymers deposit are not so different.

Most studies that utilize polymer deposition onto the electrode surface are carried out under conditions of relatively high flow rate and low discharge wattage. Thus, the domain of the plasma polymerization conditions is, in most cases, in the power-deficient region, where the atomic nature of the polymerization is less pronounced. In contrast, Inagaki and Yasuda's data (*39*) obtained by collecting polymer onto substrates located between electrodes in the monomer-deficient, or the energy-saturated, region obtained by a magnetron glow discharge powered by 10 kHz show very little difference among the deposition rates of polymer from acetylene, ethylene, and methane (Fig. 6.49). If we consider the difference in the mass of the monomers, we come to a different conclusion, namely, that the specific rates by which methane and acetylene polymerize in plasma are very close under these conditions. If one argues that the plasma polymerizations of acetylene in these cases are different, then the entire subject of plasma polymerization becomes meaningless. The growth mechanism with which we are dealing in this chapter is a basic

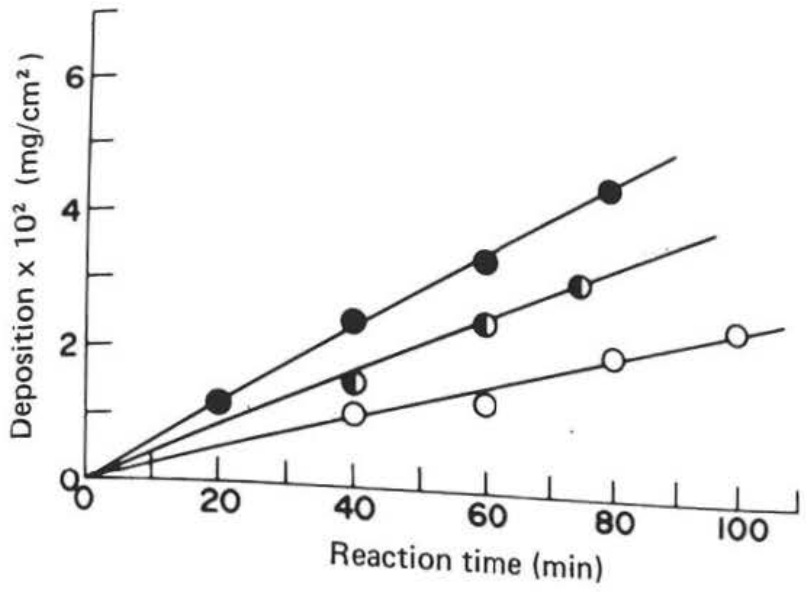

Fig. 6.49 Deposition rate as a function of used gas. Deposition rates (mg/cm²·hr) are as follows: ○ (CH_4), 1.6×10^{-2}; ◐ (CH_2CH_2), 2.5; ● (CHCH), 3.6. Adapted from Inagaki and Yasuda (*39*).

mechanism that can be applied to all cases. As discussed in more detail in Chapter 8, this problem cannot be thoroughly understood unless the growth mechanism and the polymer deposition mechanism are separated conceptually.

Thus, "atomic" polymerization, in the context described in this section, is a very important aspect of plasma polymerization. Although the degree to which plasma polymerization is atomic in nature is dependent on the chemical structure of the monomers, the ionization characteristics, and the conditions of plasma polymerization, the complete elimination of "atomic" polymerization from plasma polymerization by manipulating the conditions and the structure of the monomers seems to be nearly impossible. If one could succeed in completely eliminating the contribution of "atomic" polymerization, all advantageous features of plasma polymerization would be lost.

In summary, the most important aspects of the growth mechanism of plasma polymerization are as follows:

1. The chain-growth mechanism does not play a significant role in the vapor depositions of polymers in a vacuum. Addition reactions to the multiple bonds can and would occur in a vacuum; however, the kinetic chain length is too short to be recognized as polymerization in the conventional sense.
2. The major growth mechanism is the rapid step-growth mechanism in which the reactions between the activated species (in contrast to an activated species and a molecule) predominate. Such a reaction might be termed *polyrecombination*, that is, the consecutive recombination of the activated species. The mechanism shown in Fig. 6.1, however, contains reactions that are not polyrecombination.

3. Consequently, any single species or a certain number of dominating species cannot be responsible for the plasma polymerization of a monomer. Furthermore, the nature and number of activated species formed from a monomer are dependent on the conditions of plasma polymerization.

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